DISSERTATION

EXTENSION OF ANAEROBIC DIGESTION MODEL NO. 1 AND ITS IMPLEMENTATION

Submitted by

Durmus Cesur

The Department of Civil Engineering

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY DURMUS CESUR ENTITLED EXTENSION OF ANAEROBIC DIGESTION MODEL NO. 1 AND ITS IMPLEMENTATION BE ACCEPTED AS FULLFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Committee on Graduate Work

M. M. Sildqui

Adviser

Department Head

ABSTRACT OF DISSERTATION

EXTENSION OF ANAEROBIC DIGESTION MODEL NO. 1 AND ITS IMPLEMENTATION

The Anaerobic Digestion Model No. 1 (ADM1) from the IWA Task Group is modified to accommodate accumulation of swine manure in the digester.

The Modified Model offers a physically-based methodology to solve for an unsteady state (i.e., variation in hydraulic retention time, HRT). The methodology is used to estimate the decrease in operating volume and the increase in retention time due to biomass recycling in the reactor caused by the accumulation of particulate matter and operational variations. The methodology is unique in that it considers both the reduction in the operating volume and the increase in retention time simultaneously. The methodology developed and incorporated into the Original Model is one of the first attempts to generalize the anaerobic digestion (AD) process modeling to account for unsteady state operation which is generally the observed case for full-scale reactors. Generalization for unsteady state is especially important for the reactor start-up period, which is a very critical time frame that determines the future operation of the reactor.

The Modified Model has been verified and used for the optimization of the anaerobic digestion in a Colorado Pork (CP) waste reactor. The Modified Model simulation has a 10 % relative error, which is a lower error than the 15.6 % relative error

of the Original Model simulation. The Modified Model outputs are evaluated and compared with the original model outputs. The conclusions that are drawn are as follows:

a. The physically-based modification methodology, developed in the research, is suitable and necessary for simulation of the anaerobic digestion in a Colorado Pork anaerobic digester.

b. The Modified Model is suitable for use in optimization studies. The Modified Model can be used to test the outputs of various digester management practices.

The comparison of the Modified Model results with the Original Model results has clearly shown that the modification is necessary to simulate the effects of accumulation on the AD process.

Durmus Cesur

Civil Engineering Department

Colorado State University

Fort Collins, CO 80523

Fall 2004

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CHAPTER 1: INTRODUCTION

Anaerobic Digestion (AD) is a highly promising, and environmentally friendly technology for the beneficial use of organic waste. Controlled AD of organic wastes has many advantages with respect to the sustainable waste management. AD is faster than a similar process taking place in common landfills. Nearly all biomass may be digested by AD with the provision of enough retention time and other favorable operational conditions for producing methane that can be used for energy production and stabilized sludge that can be used as a soil conditioner and fertilizer. AD is the only process, which achieves both exergy (i.e., work potential of a system) utilization and stabilization. It is the most favorable process considering energy balance, nutrient recycling and global warming (Reeh & Moller, 2001).

AD has some disadvantages as far as its operation is concerned. The process sometimes fails due to overloading accompanied with process instability, and in the short-term, it is a more expensive option (Ecke & Lagerkvist, 2000). Some low cost approaches of AD could be applied at different scales, and for different types of wastes. However, these processes are generally underutilized due to the lack of detailed knowledge and understanding of the process biology, physics, thermodynamics and their interactions. It is necessary to understand the fundamentals of the process to realize the enormous potential of AD as a sustainable waste treatment technology and to apply it to variety of specialized cases (Varon-Pena, 2002).

The anaerobic pond technology is now emerging as one of the low cost approaches for AD. This technology can be designed to meet the effluent standards, can treat the variety of organic wastes, and can be applied at different scales ranging from local agricultural reactors to regional industrial waste treatment facilities. Anaerobic pond technology is simple, economical option that requires moderate management, and can treat concentrated wastes and while withstanding waste inflow variation (Oswald, Green, & Lundquist, 1994). It is also flexible as far the storage duration is concerned, and effluent could be reused in flushing systems. It has disadvantages of nutrient loss, and sludge and salt accumulation. Additionally, it could cause pollution of the groundwater resources and objectionable odor levels.

In order to develop operationally stable, efficient and yet simple and inexpensive technologies and methods, modeling and optimization of existing technologies is necessary. This will allow AD to be applied to its fullest potential for disposal and constructive utilization of organic wastes (i.e., organic waste management). This includes the production of methane, which is itself a major source of clean energy and is a basic material for the production of hydrogen, plastics, pharmaceuticals and other products. Additionally, knowledge and integration of the process chemical, biological and thermal factors for modeling are important to understand and to improve the process (Batstone et al., 2002b).

1.1 Background

AD process is one of the oldest biological processes used by humans starting with food and beverage production (Batstone et al., 2002b). Biogas was used in Assyria and Persia during the 10^{th} and 16^{th} centuries BC. In 17^{th} century, Jan Baptista Van Helmont

established that flammable gases evolved from decaying organic matter (Verma, 2002). Alessandro Volta showed that there is a relationship between the amount of decaying organic matter and amount of the gas. In 1808, Humphry Davy showed the production of methane by anaerobic digestion of cattle manure.

The industrialization of the AD began in 1859 with the first plant in Bombay, India. In England biogas produced from a sewage treatment facility was used as a fuel for street lights in Exeter. Buswell and others identified the anaerobic bacteria and the conditions that promote methane production in 1930 (Verma, 2002). Until the 1920's, most of the AD reactors were ponds. Closed tanks and stirring, heating equipment were used in AD facilities starting in the 1920s. Waste stabilization by AD led to its use in the treatment of municipal sludge. However, methane production by AD was not favored due to the low cost of coal and petroleum until WWII. During WWII due to the energy shortages, the interest and use of the AD technology reemerged.

In developing countries such as India and China, use of AD systems for energy generation and sanitation gradually increased during the years after WWII. The interest in the development of simple AD systems to produce biogas renewed in the developed countries due to the energy crisis of 1973 and 1979. During that time in Europe, North America and Soviet Union AD research for methane production from animal manure increased. In China, India and Southeast Asia, the number of small scale AD reactors increased remarkably. In the US, renewable energy programs were established with an emphasis on energy production from biomass.

However, failure rates of the AD reactors increased as the AD applications increased and diversified, ranging from small scale farm digesters to industrial, and

municipal digestion units. In US, the failures of farm digesters approached 80%. In China, India, and Thailand, 50% failure rates were reported (Verma, 2002). The stable AD reactor designs furthered the interest in research and development of AD technologies. AD technology found wider acceptance due to nutrient recovery, reduction of biological oxygen demand and toxic and pathogenic agents, and sludge treatment. Farm based reactors became a dominant application of the AD. Currently, around six to eight million low technology digesters have been reported to provide biogas energy with varying degrees of success and problems (Verma, 2002).

Due to the higher energy prices and more stringent environmental regulations, Europe came under pressure to explore the AD technology as a sustainable and a viable option. Many nations have implemented or are considering implementing AD as an option to reduce the environmental impacts of the waste disposal and management. The incentives are well established in some European Countries to promote the AD technology and its use.

In Europe application of AD technology for treating the waste from a variety of sources such as agricultural, industrial, and municipal wastes has been well established. Some of European AD facilities have been operation for decades. In Europe, more than 600 simple-design farm digesters are operated and large centralized AD systems are as well established. In Europe and South America, more than 35 industries including chemicals, pharmaceuticals, fiber, food, dairy, poultry, meat, and textiles have been reported to use AD to treat the industrial wastes (Verma, 2002). AD technology is generally employed as a pretreatment step to lower sludge disposal cost and odor. AD is an energy producing technology as compared to classical aerobic treatment technologies.

In the last 30 years, application of AD technology has been modified to various waste systems, full scale implementations have been developed, new application areas for the technology have been explored such as sulfur removal, and understanding of the fundamentals of the AD process has improved. However, the process still appears to be "black box" (Kalyuzhnyi, 2001). The generalization of accumulated knowledge and experience in the form of mathematical dynamic generic models is necessary to correct the erroneous image of the AD process as a poorly understood process. The generalization will lead to underpinning and optimization of the process control, and will facilitate education, teaching, and public awareness. Many different models of AD have been developed. However, their use by engineers and process technology providers and operators (i.e., AD industry), has limited. This is due to the models being either too specific, too complex, too empirical, low identifiable, or having weak predictive capability (Kalyuzhnyi, 2001).

The AD process includes series and parallel interrelated reactions. The organic waste goes through different biochemical processes including depolymerization, acidogenesis, acetogenesis, and methanogenesis. Physico-chemical, and thermal processes also take place during the digestion. To extend the application of AD to different cases it is necessary to understand the fundamentals of the process, including the biochemisty, physico-chemistry, thermodynamics, process kinetics and effects of environmental factors on AD and include these in the modeling (Kalyuzhnyi, 2001; Masse & Droste, 2000; Varon-Pena, 2002; Batstone et al., 2002b). Several approaches have been developed for AD modeling. These include mass-balance approaches and knowledge models among many others. Each of these models has advantages and

disadvantages. Their applicability is limited by time, expertise (knowledge of the process structure), and available data. The models developed are generally applicable for specific cases. The black box type models do not explain the processes and lack the robustness to model the complex digestion process properly. Generic dynamic model development based on the process dynamics and application and extension of the models for different cases, such as different reactor types, environmental conditions, and organic waste types for the AD process are needed (Chynoweth et al., 1998a; Chynoweth et al., 1998b, Batstone et al. 2002b).

The first dynamic model was developed by Andrews in 1969 (Azeiterio et al., 2001). In this model, constant pH is assumed. This limitation is later on removed by Andrews and Graef by considering the liquid, gas and biological phase physicochemical interactions (Masse & Droste, 2000). However, in this model only a single bacterial group is included due to the assumption of methanogenesis as the rate limiting step. Hill and Barth (1977) added the second bacterial group for acid formation and incorporated hydrolysis. They also added the carbonate equilibria, nitrogen balance, cation exchange and inhibition of the methane formation by ammonia-N and volatile fatty acids (VFA) to the model (Hill & Barth, 1977). An AD Model developed by Mosey (1983) included four different bacterial groups and the role of hydrogen gas in the formation of acetic, butyric, and propionic acids as well as the conversion of propionic and butyric acids to acetic acid (Masse & Droste, 2000). Thermodynamics of the AD reactions were investigated by Thauer et al. (1977), Harper and Pohland (1986), McInerney et al. (1988). Modified versions of the model of Mosey are developed by Merlini (1983), Rozzi et al. (1985), Jones and Hall (1992) and Costello (1991a, 1991b). Simeonov et al. (1996)

developed a non-linear model of the continuous process in stirred tank reactors considering the time-variation of the model parameters based on the reaction schema of the model of Hill and Barth (Simeonov, Momchev, & Grancharov, 1996). Masse and Droste (2000) developed a generic dynamic model for sequential batch reactor (SBR). The model is based on models of Merlini (1983), Rozzi et al. (1985), and Costello et al (1991a, 1991b), with revised assumptions supported by the experimental data (Masse & Droste, 2000).

Siegrist et al. developed a model based on six different conversion processes as hydrolysis, anaerobic oxidation, fermentation, acetotroph and hydrogenotroph, five additional processes to account for the decay of the five distinct microbial groups, and two more processes for pH calculation (Siegrist, et al., 1993). Lokshina and Vavilin developed multi-component and multi-species model called as METHANE that takes the complex processes in the gaseous and liquid phases into account (Lokshina & Vavilin, 1999). The model uses the system of differential equations for three group of variables as suspended organic matter (bacteria, suspended solids), soluble components, and gaseous phase components. It also considers the four basic stages of the AD as hydrolysis, acidogenesis, acetogenesis and methanogenesis together with lysis and hydrolysis of cell biomass. Additionally, substrate limitation and inhibition functions are taken into account in the model. Modified versions of METHANE model for psychrophilic conditions were developed (Lokshina & Vavilin, 1999; Vavilin et al., 2001). Batstone et al. (2002b) developed a generic dynamic model based on the works of Siegrist et al. and other researchers. The model considers the main relevant processes of AD to make it simple and widely applicable. The model is applied for continuously stirred tank reactor

(Batstone et al., 2002b). The model needs to be modified and extended to applications for specific cases. This is possible through the open structure and common nomenclature used by the model.

1.2 Purpose and Objectives of the Research

In this research, modeling of the AD process using Anaerobic Digestion Model No. 1 (ADM1) for intermittently mixed, quasi-steady mesophilic anaerobic digester of Colorado Pork, LLC. (CP), will be investigated. The original ADM1 model was developed by the International Water Association (IWA) Task Group for Mathematical Modeling of Anaerobic Digestion Processes. In this research, the model is modified to account for the effects of accumulation in the reactor on the AD process. **The aims** of the research are as follows:

1. **To modify the ADM1 model to simulate the AD process taking place at Colorado Pork anaerobic digester with less than 15% error.** The extension will include the development of a methodology to account for the effects of the accumulation and incorporation of this to ADM1 model to simulate the AD process at Colorado Pork Reactor. The model performance will be evaluated using statistical error estimates indicating the suitability of the extension (i.e., methodology developed and incorporated to the original model) for accumulation..
2. **To optimize the hydraulic retention time for the reactor using the Modified Model.**

Accuracy of the ADM1 in the modeling of the Colorado Pork reactor process will be evaluated. The error statistics will be computed and evaluated. The reasons for the differences between the modeled and the observed values will be explained.

The **objectives** of the research will be:

1. **To modify the model to account for accumulation and its effects.** The major model extension for ADM1 will include the development of a physically-based method and its incorporation into the model to account for a quasi steady-state condition, and an estimation of the increased retention time due to recycling of the microorganisms as a result of settling and operational variations. This method and its incorporation into the model is presented in Chapter 3.
2. **To assess the applicability of the Modified Model, for the Colorado Pork reactor.** This includes identification and estimation of the model parameters. Two methodologies to be used to estimate the unknown parameters are presented in Chapter 4.
3. **To test the Modified Model using Colorado Pork reactor data and to evaluate model performance and limitations.**
4. **To optimize the hydraulic retention time (HRT) for the Colorado Pork reactor.**

CHAPTER 2: LITERATURE REVIEW AND THEORY

Anaerobic digestion is a versatile biotechnology capable of converting almost all types of organic polymeric materials into methane, carbon dioxide and stabilized sludge (Chynoweth & Pullammanappallil, 1996). During this conversion a variety of microorganisms including fermentative acidogens; hydrogen-producing, acetate-forming acetogens; and methane-producing methanogens harmoniously grow and produce reduced end-products (Zinder 1992; Miyamoto, 1997). Anaerobic digestion reduces the pollution and recovers fuel gas from industrial and agricultural wastes (Chynoweth & Pullammanappallil, 1996; Henze et al., 1997; Chynoweth et al., 1998a).

Different groups of microorganisms are responsible for the conversion of organic carbon into its most reduced form (methane) and its most oxidized form (carbon dioxide) (Leisinger, 1993; Ecke & Lagerkvist, 2000). Anaerobic microorganisms are usually classified as either facultative or obligate anaerobes, depending on their sensitivity to oxygen. The facultative anaerobes can grow either in the presence or absence of oxygen and the obligate microorganisms cannot grow in the presence of oxygen. Organisms that are killed by oxygen are called strict anaerobes (Gottschalk, 1986). In AD, mixed microbial populations of these groups work together to degrade organic waste into the major products of methane and carbon dioxide and stabilized sludge (Oswald et al., 1994; Varon-Pena, 2002; Verma, 2002).

Anaerobic digestion is the consequence of a series of metabolic interactions among various groups of microorganisms (biochemical processes) and as well as physico-chemical processes (Batstone et al., 2002b). Biochemical processes are catalyzed by intra-cellular or extracellular enzymes. Disintegration and depolymerization of the waste are extracellular processes, and subsequent digestion of the soluble materials by the microbial consortia are intracellular processes resulting in the growth and decay of the organisms (Baltstone et al., 2002b). In the depolymerization stage, a particular group of microorganisms secretes enzymes which convert polymeric materials to monomers such as glucose and amino acids (Verma, 2002). In the acidogenesis stage, the products of depolymerization are converted to higher volatile fatty acids, hydrogen and acetic acid. In the acetogenesis stage, hydrogen-producing acetogenic bacteria convert the higher volatile fatty acids (i.e., long chain fatty acids) to hydrogen, carbon dioxide, and acetic acid (Verma, 2002). In the final stage, methanogenic bacteria convert H_2, CO_2, and acetate, to CH_4 and CO_2.

The physico-chemical processes of AD are not biologically mediated and include the ion association, dissociation, gas-liquid transfer, mixing pattern and some other processes (Siegrist et al., 1993; Merkel et al., 1999; Lokshina & Vavilin, 1999; Vavilin et al., 2000; Vavilin et al., 2001; Masse & Droste 2000; Alex & Ogurek, 2001; Kalyuzhnyi 2001; Batstone et al., 2002a, Batstone et al., 2002b). In the following sections, the biochemistry and microbiology of the anaerobic breakdown of polymeric materials to methane and other end-products and the roles of the various microorganisms involved will be explained.

2.1 Biochemical Processes

Biochemical processes are catalyzed by intracellular or extracellular enzymes that act on the pool of biologically available organic material. Disintegration of composites (such as dead biomass) to particulate constituents and the subsequent enzymatic depolymerization of these to monomers are extracellular processes (Kalyuzhnyi, 2001; Batstone et al., 2002b). Further degradation of soluble materials is mediated by organisms intracellularly, resulting in biomass growth and subsequent decay (Varon-Pena, 2002).

2.1.1 Disintegration and Depolymerization

Disintegration and depolymerization processes include the breakdown and the solubilization of the complex organic materials to soluble substrates (i.e., smaller molecules, monomers) by depolymerizing enzymes, such as lipases, proteases, cellulases, amylases, lyases, etc. (Chynoweth & Pullammanappallil, 1996; Chynoweth et al., 1998a). Polymeric materials such as lipids, proteins, and carbohydrates are primarily depolymerized by extracellular enzymes secreted by microorganisms. The products of depolymerization are soluble smaller molecules and hence, this step is also known as solubilization (Chynoweth & Pullammanappallil, 1996). Other products of this step include inert particulate and inert soluble material. Depolymerization of the substrates converts them into a form which can be assimilated into the microbial cell and can be metabolized. A distinct physiological population of bacteria is responsible for depolymerization of the organic polymers.

Depolymerization can be mediated either by hydrolases or lyases (Chynoweth & Pullammanappallil, 1996). Hydrolysis reactions are carried out by extracellular enzymes called hydrolases which catalyze reactions that could be formulated as follows:

$$A\text{-}X + H_2O \Leftrightarrow X\text{-}OH + HA \qquad (2.1)$$

Depending on the bond catalyzed these hydrolases can be esterases (enzymes that hydrolyze ester bonds), glycosidases (enzymes that hydrolyse glycosidic bonds) or peptases (enzymes that hydrolyse peptide bonds).

Lipases convert lipids to long-chain fatty acids secreted by Clostridia and the micrococci. Proteins are depolymerized to amino acids by proteases, secreted by *Bacteroides, Butyrivibrio, Clostridium, Fusobacterium, Selenomonas*, and *Streptococcus*. Glycosidases hydrolyze the polysaccharide component of plant cell walls and phosphodiesterases hydrolyze the ester bonds of some extended polysaccharides (Ecke & Lagerkvist, 2000). Polysaccharides such as cellulose, starch, and pectin are hydrolyzed by cellulases, amylases, and pectinases. These enzymes act synergistically on cellulose effectively hydrolyzing its crystal structure, to produce glucose. Microbial hydrolysis of raw starch to glucose requires amylolytic activity. Pectins are degraded by pectinases, including pectinesterases and depolymerases. Lyases catalyze the non-hydrolytic (with no water) removal of substrates from organic waste (Chynoweth & Pullammanappallil, 1996). For example, pectate lyases depolymerize the pectate component of plant cell wall.

In anaerobic digestion of waste containing high concentrations of organic polymers, the depolymerization activity relevant to each polymer is important, in that

polymer degradation may become a rate-limiting step for the production of simpler bacterial substrates to be used in subsequent degradation steps (Verma, 2002).

2.1.2 Acidogenesis

In acidogenesis, sugars, amino acids, and fatty acids produced by microbial degradation of biopolymers are metabolized to fermentation end products such as lactate, propionate, acetate, and ethanol by other enzymatic activities which vary with microbial consortia. Acidogenesis is an energy yielding process. It can be performed in the absence of oxygen. Organic compounds serve as both electron donors and electron acceptors. The process results in products that are more, and others that are less oxidized than the original substrate (Batstone et al., 2002b). Several fermentation pathways are known. They are named according to the main fermentation products, such as alcohol, lactate, propionate, formate, butyrate and butanol-acetone fermentation (Miyamoto, 1997; Kalyuzhnyi, 2001; Batstone et al., 2002b). Substrates of depolymerization; sugars, amino acids and fatty acids are converted to volatile fatty acids such as acetic, propionic, butyric, isobutyric, valeric and caproic acid as well as carbon dioxide and hydrogen by acidogenesis. In AD, alcohol fermentation is generally negligible. Additionally, acidogenesis of amino acids results in ammonia, carbon dioxide, hydrogen and sulfide aside from volatile fatty acids.

2.1.3 Acetogenesis

Some acetate and hydrogen are directly produced by acidogenic fermentation of sugars, and amino acids, however, both products are primarily derived from the acetogenesis and dehydrogenation of higher volatile fatty acids by microorganisms such as *Syntrophobacter wolinii*, a propionate decomposer and *Sytrophomonos wolfei*, a

butyrate decomposer (Siegrist et al., 1993; Kalyuzhnyi, 2001; Alex & Ogurek, 2001; Batstone et al., 2002b). Obligate H_2-producing acetogenic bacteria are capable of producing acetate and H_2 from higher fatty acids. Acetogenesis is the link between three-carbon or long chain fatty acids and acetate (Ecke & Lagerkvist, 2000). Carbon-carbon bonds are broken up by obligate proton-reducing acetogens until the major end-products acetate and hydrogen are produced. H_2 production by acetogens is generally energetically unfavorable due to high free energy requirements (i.e., free energy change, $\Delta G^{o'} > 0$) (Ecke & Lagerkvist, 2000). In other words, under standard conditions (298°K, $1.013 \cdot 10^5$ Pa) these reactions are only exergonic ($\Delta G° < 0$) if hydrogen is removed and its partial pressure is kept at a low level between 6 to 400 Pa (Chynoweth & Pullammanappallil, 1996; Ecke & Lagerkvist, 2000). However, this involves the growth of obligate proton-reducing bacteria at the expense of the above reactions and critically depends on the consumption of hydrogen by other microorganisms. The combination of H_2-consuming bacteria, co-culture systems provide favorable conditions for the decomposition of fatty acids to acetate and CH_4 or H_2S ($\Delta G^{o'} < 0$). This syntrophic relationship is called interspecies hydrogen transfer (Chynoweth & Pullammanappallil, 1996; Ecke & Lagerkvist, 2000; Batstone et al., 2002b).

There are three hydrogenotrophic groups of microorganisms supporting the interspecies hydrogen transfer. The first are homoacetogens, either growing on carbon dioxide and hydrogen or on multicarbon compounds where carbon dioxide is consumed in an intermediate step. The two other groups are non-acetogenic hydrogen-consuming organisms, such as sulfate reducing bacteria and methanogens.

In addition to the decomposition of long-chain fatty acids, ethanol and lactate are also converted to acetate and H_2 by an acetogen and *Clostridium formicoaceticum*, respectively (Miyamoto, 1997; Verma, 2002; Batstone et al. 2002b).

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \quad (2.2)$$

2.1.4 Methanogenesis

Methanogenesis is a process that carried out by the group of bacteria within archaea (Ecke and Lagerkvist, 2000). They can not degrade complex compounds. They are entirely dependent on the previous work of other microorganisms. Only one-carbon substrates such as carbon dioxide, carbon monoxide, methanol, formate, and ethylamines and acetate as the only two-carbon substrate are utilized by methanogens.

In this phase of the AD, acetate, carbon dioxide and hydrogen are the main substrates. The products are water and biogas consisting of methane and carbon dioxide. H_2/CO_2-consuming methanogens reduce CO_2 as an electron acceptor via the formyl, methenyl, and methyl levels through association with unusual coenzymes, to finally produce CH_4. The main reactions in this phase are (Varon-Pena, 2002; Verma, 2002; Batstone et al., 2002b):

$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ (Aceticlastic methanogenesis)} \quad (2.3)$$

$$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \quad (2.4)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ (Homoacetogenesis)} \quad (2.5)$$

The composition of the biogas depends on the mean oxidation state of the carbon. As carbon becomes more reduced, the ratio of methane to carbon dioxide becomes higher (Ecke & Lagerkvist, 2000). AD of carbohydrates yields an equimolar quantity of methane

and carbon dioxide. Protein and lipid decomposition result in up to 65 and 75 percent methane by volume, respectively.

If the chemical composition of the substrate is known and total anaerobic mineralization is assumed, the amount and composition of the biogas can be estimated using (Ecke & Lagerkvist, 2000):

$$C_aH_bO_cN_d + (a-1/4b-1/2c+ 3/4d)\ H_2O \rightarrow (1/2a+1/8b -1/4c-3/8c)CH_4$$

$$+ (1/2a-1/8b +1/4c+ 3/8c)\ CO_2 + dNH_3 \qquad (2.6)$$

For substrates characterized in COD (Chemical Oxygen Demand in gram O2 /gram of organic waste) and TOC (Total Organic Carbon in gram C per gram of organic waste), the molar CH4:CO2 ratio for the gas generated can be estimated by Equation (2.7) (Ecke & Lagerkvist, 2000). For instance, glucose results in a CH4:CO2 ratio of 1.0 mol/mol.

$$CH_4/CO_2 = 8/ (8 -1.5*COD/TOC) - 1 \qquad (2.7)$$

Biodegradation is limited by intramolecular cleavage and by its redox potential. Methane is the most reduced organic compound; therefore, no energy can be yielded from further decomposition (Varon-Pena, 2002). Hence methanogenesis is the terminal link of the anaerobic nutrient chain.

Methanogens include several groups of obligately anaerobic bacteria and are defined as microorganisms capable of methane production. Anaerobic digestion is completely dependent on the physiological capabilities of methanogens. Although acetate and H_2/CO_2 are the main substrates available in the natural environment, formate, methanol, methylamines, and CO_2 are also converted to CH_4 (Ecke & Lagerkvist, 2002).

Methanogens can be divided into two groups: H_2/CO_2- and acetate-consumers (Verma S. 2002). Although some of the H_2/CO_2-consumers are capable of utilizing formate, acetate is consumed by a limited number of strains, such as *Methanosarcina* spp. and *Methanothrix* spp. (i.e., *Methanosaeta*), which are incapable of using formate. Since a large quantity of acetate is produced in the natural environment, *Methanosarcina* and *Methanothrix* play an important role in completion of anaerobic digestion and in accumulating H_2, which inhibits acetogens and methanogens. H_2-consuming methanogens are also important in maintaining low levels of hydrogen (Chynoweth & Pullammanappallil, 1996; Miyamoto, 1997).

2.1.5 Thermodynamics

Microorganisms catalyze redox reactions. Only reactions that are thermodynamically possible are carried out, i.e. the free-energy change, ΔG has to be negative. In order to make the comparison between ΔG of different reactions possible, their free-energy change is given at standard conditions ($\Delta G°$), i.e. T = 298 K, p = 1.013×105 Pa and activity a_i = 1 mol/l. For biological reactions, the standard conditions are usually extended ($\Delta G\ °'$) (Ecke & Lagerkvist, 2000). The apostrophe indicates that the proton activity has been adjusted to pH 7 to better reflect conditions at which biological reactions occur. The $\Delta G\ °'$ values for some important substrates of AD is given in Table 2.1

The relationship between $\Delta G\ °'$ and $\Delta G\ °$ is:

$$\Delta G\ °' = \Delta G\ ° + m\ \Delta G_f'\{H+\} \qquad (2.8)$$

Where: m = Molar amount of protons formed or removed.

$\Delta G_f'\{H+\}$ is the molar free-energy change for protons. At pH 7 it becomes:

$$\Delta G_f'\{H+\} = 2.3xRTlog(10^{-7}) = 39.89 \text{ kJ/mol} \quad (2.9)$$

Where: R = Gas constant (8.315 J/ mol/K)

T = Absolute temperature (298 ^oK)

Table 2.1 $\Delta G^{o'}$ values for some important substrates of AD (Ecke & Lagerkvist, 2000)

Phase	Substrate -> Products	$\Delta G^{o'}$ kJ
Fermentation	$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO_3^- + 4H^+ + 4H_2$	-207
	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3(CH_2)_2COO^- + 2HCO_3 + 3H^+ + 2H_2$	-135
	$3C_6H_{12}O_6 \rightarrow 4CH_3CH_2COOH + 2CH_3COOH + 2CO_2 + 2H_2O$	-922
Acetogenesis	$CH_3CH_2OH + H_2O \rightarrow 2CH_3COO^- + 3H^+ + 2H_2$	+10
	$CH_3CH_2COO^- + 3H_2O \rightarrow 2CH_3COO^- + H^+ + 3H_2 + HCO_3^-$	+76
	$CH_3(CH_2)_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	+48
	$HCO_3^- + 4H_2 + H^+ \rightarrow CH_3COO^- + 4H_2O$	-105
Methanogenesis	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-130
	$4HCOO + 4H+ \rightarrow CH_4 + 3CO_2 + 2H_2O$	-120
	$CH_3COO + H^+ \rightarrow CH_4 + CO_2$	-33
	$4\ CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$	-309
	$4(CH_3)_3NH^+ + 6\ H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_4$	-666
	$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$	-186
Denitrification	$12NO3 + C_6H_{12}O_6 \rightarrow 12NO_2 + 6CO_2 + 6\ H_2O$	-1946
	$8NO_2 + C_6H_{12}O_6 \rightarrow 4N_2O + 6CO_2 + 6\ H_2O$	-632
	$12N2O + C_6H_{12}O_6 \rightarrow 12N_2 + 6CO_2 + 6\ H_2O$	-134
Sulfate reduction	$4H_2 + SO_4^{2-} + H \rightarrow 4H_2O + HS-$	-152
	$CH_3COO + SO_4^{2-} \rightarrow 2HCO_3 + HS^-$	-48
	$4CH_3CH_2COO- + 3SO_4^{2-} \rightarrow 4CH_3COO- + 4HCO_3^- + H+$	-151

Acetogenic reactions are not carried out automatically at extended standard conditions (pH 7) because $\Delta G^{\circ\prime} \geq 0$. However, interspecies hydrogen transfer lowers the hydrogen partial pressure, {H2}, and thereby the actual $\Delta G'$ becomes negative. The relationship between $\Delta G'$ and $\{H_2\}$ is described by the Nernst equation (Zinder, 1992; Batstone et al., 2002b):

$$\Delta G' = \Delta G^{0\prime} + RT\ln\Pi\{\text{product i}\}^{ni}/\Pi\{\text{educt j}\}^{nj} \qquad (2.10)$$

Where: ni and nj = The stoichiometric constants of products and educts, respectively.

Free energy exchange, $\Delta G'$ increases with decreasing hydrogen partial pressure. The interspecies hydrogen transfer is only possible within a defined range of hydrogen partial pressure (Veeken et al., 2000; Yu & Fang, 2003; Batstone et al., 2002b). If either hydrogen-production or hydrogen-consumption reactions become endergonic, interspecies hydrogen transfer stops (i.e., anaerobic nutrient chain is interrupted).

2.1.6 Inhibition and Toxicity

AD process is restricted by the toxicity and inhibition. The toxicity is defined as an adverse effect on bacterial metabolism, and inhibition is defined as an impairment of bacterial function (Speece, 1996). These mechanisms are alternatively defined as biocidial inhibition (i.e., toxicity) which is reactive toxicity, and normally irreversible and biostatic inhibition (i.e., inhibition) which is non-reactive toxicity and normally reversible. The biocidial inhibition caused by low carbon fatty acids, detergents, aldehydes, nitro compounds, and biostatic inhibition caused by pH, cations etc. (Leighton & Foster, 1997; Lin & Chen, 1999; Mosche & Jordening, 1999; Yu & Fang, 2003).

The inhibitory concentration depends upon different variables, including pH, hydraulic retention time (HRT), temperature, and the ratio of the toxic substance concentration to the bacterial mass concentration (Marek & Jordening, 1999; Mosche & Jordening, 1999). The toxic effect of an inhibitory compound depends upon its concentration and the ability of the bacteria to acclimate to its effects (Liu, Chan, & Fang, 2002; Merkel et al., 1999; Munoz, Sanchez, Rodriguez-Maroto, Borrego, & Morinigo, 1997).

Toxicity and inhibition in anaerobic digesters is reflected by accumulation of volatile acids (related to overloading or toxic feed components), high ammonia levels (related to nitrogenous feeds), or toxic feed components, and decrease in yield (Chynoweth et al., 1998a). The imbalance starts when the concentration of total volatile organic acids is in the range of 2,000 mg/L or higher. Digesters can acclimate to concentrations as high as 10,000 mg/L. This tolerance is related to alkalinity levels which are influenced by ammonia and bicarbonate.

High nitrogen content of swine wastes result in high ammonia concentrations during anaerobic digestion. Concentrations in the range of 3,000 mg/L or higher can be inhibitory to anaerobic digestion (Chynoweth & Pullammanappallil, 1996; Chynoweth et al., 1998a). This level could get higher through acclimation.

2.1.7 Temperature Effects

AD has been reported at temperatures ranging from 2°C to over 100°C (Chynoweth & Pullammanappallil, 1996). Temperature could affect the biochemical reactions of AD in five main ways as increase in reaction rates (around optimum), decrease in reaction rates (above optimum), decrease in yields due to the turnover and

maintenance energy with increased temperature, shifts in yields due to thermodynamic yield, microbial population changes and increase in death rate (Batstone et al., 2002b).

AD reactors have been operated under either psychrophilic (4°C to 15°C), mesophilic (20 °C to 40°C), or thermophilic (45 °C to 60°C) temperatures. In general, the overall process kinetics double for every 10°C increase in operating temperature up to some critical temperature above which a rapid drop-off in microbial activity occurs (Chynoweth & Pullammanappallil, 1996). The temperature dependence of microorganism consortia can be described by Arrhenius equation up to an optimum temperature. This equation is given below (Mahmoud, 2002, Yu & Fang, 2003):

$$r = A \exp\left(-\frac{E_a}{RT}\right) \qquad (2.11)$$

Where: r = Reaction rate (d^{-1})

A = Arrhenius constant (d^{-1})

E_a = Apparent activation energy ($kJ.mole^{-1}$)

R = Ideal gas constant ($J.mole^{-1}.{}^{o}K$)

T = Absolute temperature (^{o}K)

Optimal temperatures are around 35 °C and 55 °C for mesophilic and thermophilic ranges respectively. Above these ranges, the process may become unstable and could fail (Henze, Harremoes, Jansen, & Arvin, 1997). Digestion processes at low temperatures, require longer retention times, and a low-temperature inoculum for effective startup.

2.1.8 Physico-chemical processes

These reactions are non-biologically mediated reactions that are critical to express inhibition processes, and dependency of performance variables on them. They could be

grouped as; liquid-liquid processes, liquid-gas processes, and liquid-solid processes. In general, liquid-gas, and liquid-liquid processes are addressed in AD modeling.

When modeling anaerobic systems, the physico-chemical processes are critical to express biological inhibition factors (eg., pH, free acids and bases), to determine the performance variables (e.g., gas flow and carbonate alkalinity), and to calculate control set point pH.

2.1.9 Liquid-liquid processes

These processes include ion association, dissociation with hydrogen and hydroxide ions. Some compounds have pKa values around the pH values of AD systems such as CO_2/HCO^{-3} pair with pKa value of 6.35. These compounds play an important role in ion association/dissociation processes of AD. The processes are very rapid and generally referred to as the equilibrium processes (Batstone et al., 2002b).

Acid base processes could be modeled using differential equations or implicit set of algebraic equations and could be solved using charge balance or tableau methods (Batstone et al., 2002b). Charge balance is the generally preferred method since it is easy to understand and gives insight into the process. Charge balance method is expressed as:

$$\sum S_{c^+} - \sum S_{a^-} = 0 \qquad (2.12)$$

Where: S_{c_+} = The cationic equivalent concentration in the solution

S_{a^-} = The anionic equivalent concentration in the solution.

In the equation, equivalent concentration is calculated by multiplying the valance of an ion by its molar concentration.

2.1.10 Liquid-Gas Transfer

In the AD processes, the main gas components are:

a. H_2 (relatively low solubility)

b. CH_4 (relatively low solubility)

c. CO_2 (relatively high solubility)

Hydrogen sulfide (H_2S) and ammonia (NH_3) could also be included depending on the process. The liquid-gas transfer is formulized by transfer equations.

a. Liquid-gas transfer equations

Gas and liquid phases in contact reach equilibrium. When the liquid phase is dilute, Henry's gas law could be used to express the equilibrium. This law, indicating the dependency of the concentration in the liquid phase on the gas phase partial pressure, is given below (Masse & Droste, 2000; Batstone et al., 2002b):

$$K_H p_{gas,i,,ss} - S_{liq,i,ss} = 0 \qquad (2.13)$$

Where: K_H = Henry's law constant (M/bar)

$p_{gas,i,,ss}$ = Steady-state, gas partial pressure of component i (in bar)

$S_{liq,i,ss}$ = Steady-state, liquid phase concentration of the component i (M)

Dynamic gas transfer equations are used to describe the liquid-gas transfer since the resistance to transfer of relatively insoluble gases of concern in the liquid phase causes the gases to be supersaturated in relation to the effluent and total COD balance. The dynamic gas transfer equation derived from the two-film theory of Whitman is given below (Masse & Droste, 2000; Batstone et al., 2002b):

$$\rho_{Ti} = k_L a(S_{liq,i} - K_H p_{gas,i}) \qquad (2.14)$$

Where: $k_L a$ = Overall transfer coefficient multiplied by specific transfer area (d^{-1})

ρ_{Ti} = Specific mass transfer rate of gas i, (M/day)

$S_{liq,i}$ = Liquid phase concentration for component i (M)

K_H is corrected with the relevant factors for each component, to account for the COD basis of the $S_{liq,i}$ as compared to the molar basis of K_H. Since transfer of all the gases are liquid film controlled and diffusivities are similar, they have K_La values of similar order of magnitude. Therefore, even k_La varies with temperature, mixing and liquid properties, k_La can be approximated to be the same for all three gases for modeling purposes.

2.1.11 Variation of physico-chemical parameters with temperature

As temperature changes equilibrium coefficients change. This change is generally more pronounced than the changes in physico-chemical parameters. The Integrated Van't Hoff equation could be used to describe these changes. The equation is given below for the case where heat of reaction is assumed to be independent of temperature (Batstone et al., 2002b):

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (2.15)$$

Where: ΔH^o = Heat of reaction at standard pressure and temperature

R= Gas law constant, 8.324 J $mole^{-1}K^{-1}$

K_1 = Known equilibrium coefficient at reference temperature T_1

K_2 = Unknown equilibrium coefficient at temperature T_2

Assuming $T_1 x T_2 \approx T_1^2$ and $\theta = \frac{\Delta H^o}{RT_1^2}$, this equation becomes:

$$K_2 = K_1 e^{\theta(T_2 - T_1)} \qquad (2.16)$$

This equation is effective for all equilibrium coefficients except organic acids for temperatures ranging from 0 °C to 60 °C. K_a values could be assumed to be constant for organic acids, due to the very small variation of K_a in this temperature range.

2.2 Anaerobic Digestion Modeling

There are many approaches that are applied to model the microbial populations, and their interactions with the physical and chemical environment in AD (Chynoweth & Pullammanappallil, 1996). Their application for AD processes varies depending on various factors such as availability of quality data, priori knowledge, expertise, complexity of the process and difficulty in identification of relevant parameters, and many others. These approaches could be classified as follows (Harmand, Pons, & Dagot, 2002):

a. The mass balance approach

b. The fuzzy approach

c. The statistical and artificial neural network (ANN) approach

d. The knowledge model approach

2.2.1 Mass Balance Approach

These models are based on mass-balance equations, and use mathematical expressions to describe the interactions in the process, including rates of substrate utilization, microbial growth, product formation, and physico-chemical equilibrium relationships (Alex & Ogurek, 2001). These models are generally simplified for process design, optimization, operation, and process control. The models incorporate depolymerization, acidogenesis, acetogenesis, methanogenesis phases, and inhibition.

As an example of these models, a mass-balance model using Contois equation to describe reaction kinetics is given below (Chynoweth et al., 1998a):

$$B = B_o\left(1 - \frac{K}{\mu_m\theta - 1 + K}\right) \tag{2.17}$$

$$\lambda v = B_o L\left(1 - \frac{K}{\mu_m\theta - 1 + K}\right) \tag{2.18}$$

Where: B = Methane yield, m^3/kg VS

B_o = Ultimate methane yield at infinite retention time, m^3/kg VS

K = Kinetic parameter

μ_m = Maximum specific growth rate, d^{-1}

λ_v = Volumetric methane production rate, m^3 CH_4/ m^3 digester volume per day

L = Volumetric loading rate, kg VS/m^3 digester volume per day.

Ultimate anaerobic biodegradability (B_o) of swine manure in the range of 0.32 - 0.48 m^3 CH_4/kg VS has been reported by Chynoweth et al. (1998a). The model applications are generally limited to continuously stirred tank reactor (CSTR) digesters and to accommodate other designs such as batch, attached-film digesters these models should be extended. They have the following advantages and disadvantages listed below.

Advantages of this modeling approach are:

a. They are highly informative (highly structured).

b. They use well known estimation and control techniques.

Disadvantages are:

a. Applying the model is tedious.

b. The parameters for the model are difficult to identify.

2.2.2 Fuzzy Approach

In this approach, a discrete fuzzy model is developed to describe the AD process (Punal et al., 2002). Fuzzy model schema is shown in Figure 2.1. In this model, COD is known in each step and this COD is used as a tuning parameter in inference rule database.

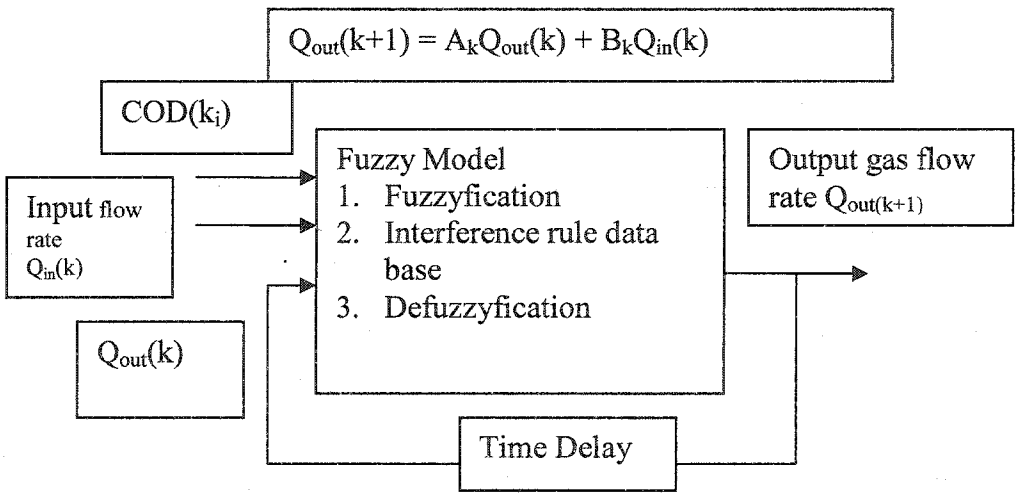

Figure 2.1 Fuzzy model (Harmand et al., 2001)

Advantages of fuzzy modeling approach listed below:

a. They could incorporate the linguistic knowledge from experts and/or from operators of the process into the model

b. They are rapid and efficient (fast modeling to get satisfactory results), if the number of variables is limited.

Disadvantages of these models are:

a. They are not appropriate to understand and/or explain phenomena.

b. They perform poorly (i.e., less accurate) when used for prediction.

2.2.3. The Statistical and Artificial Neural Network (ANN) Approach

Statistical or artificial neural networks based on statistical functions or neurons having certain activation functions that form a regression model or a network together with inputs and outputs (Alcaraz-Gonzalez et al., 1999; Harmand et al., 2001). The artificial network schema is shown in Figure 2.2.

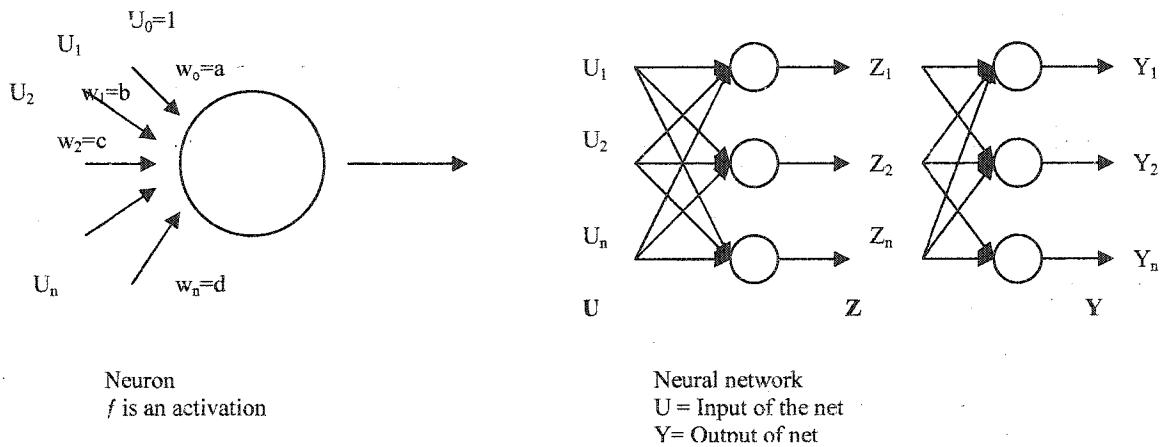

Figure 2.2 ANN Model (Harmand et al., 2001).

Advantages of the ANN model include:

a. No a priori knowledge is required (the modeling is only based on data).

b. Rapid and efficient (fast modeling to get satisfactory results) even if the number of variables is large.

Disadvantages include:

a. This approach is not appropriate to understand and/or explain phenomena.

b. Large amount of data are needed for this approach.

2.2.4 Knowledge Model Approach

This approach considers generic conceptual schema (i.e., digestion pathways) to start with and applies mass-balance, stoichiometry, and kinetics equations accordingly.

The knowledge model has been developed by going through the following steps (Siegrist et al., 1993; Harmand et al. 2001; Masse & Droste 2000; Batstone et al., 2002b):

a. Identification of the parameters by experiments,

b. Conceptual modeling (i.e., description of knowledge in abstract terms),

c. Validation of global model for different AD processes,

d. Real-case simulation.

2.2.5 Model Selection

The selected model for simulation is highly dependent on the modeling objective. The following could be considered as selection criteria (Harmand et al., 2001; Batstone et al., 2002b):

1. Knowledge model building is time consuming, therefore, for the cases where time is not a limiting factor, knowledge model can be built.

2. In the case where expertise is limited either to state the structure of the model or to design a rule based system, but sufficient data is available, data based approaches (black box) such as statistical methods or artificial neural networks could be used for modeling.

3. A knowledge or a mass or energy balance model can be developed, in the case where the most important parameters are monitored using a significant set of actuators and sensors implemented on the process and there is enough expertise to state the general process mass or energy balance.

4. If there is a large experience of the operators (expertise) with very little data available (almost no sensors), a heuristic approach could be used to model the process such as fuzzy models, expert systems and rule based approaches.

2.3 Summary

In this chapter, the AD processes are described. The AD modeling approaches are explained. In this research, the ADM1 model, which is classified as a knowledge model, is selected since the model comprehensively includes the main relevant series and parallel processes of the AD. In the model selection, consideration of various operational cases such as unsteady state, different waste streams, different reactor configurations etc. through the open structure and nomenclature of the model, is taken into account. The selected model, the ADM1, is modified to accommodate the quasi-steady state caused by the solids accumulation and the operational changes. The modification methodology is described in the following chapter.

CHAPTER 3: ANAEROBIC DIGESTION MODEL NO. 1

In this chapter, the Anaerobic Digestion Model No. 1 (ADM1) concept, parameters, implementation specifics, and modification are explained. The modification methodology specifics are given.

The ADM1 is a structured knowledge model which takes biochemical, physicochemical and thermal processes of the AD into account. Additionally, it includes regulatory inhibition functions to estimate the adverse effects of low pH, free ammonia and hydrogen and others. In the following sections, the AD process modeling by the ADM1 is explained.

3.1 Model Parameters and State Variables

In the model, state concentration variables are expressed in $kgCOD/m^3$. For the components that have no COD content, molar basis, M ($kmole/m^3$) is used. The overall units used throughout the modeling are given in Table 3.1. The units applied are given in Tables 3.2-3.5. Model parameters include: stoichiometric coefficients, equilibrium coefficients and constants, kinetic constants and rates and dynamic state variables and algebraic variables.

The ADM1 is implemented as a differential equation (DE) system. The implementation specific variables are given in Appendix A. The stoichiometric coefficients, equilibrium coefficients and constants, kinetic parameters, rates, and inhibition functions used in the model are given in Appendix B.

Table 3.1 Units used in the model

Description	Units
Concentration	$kgCOD.m^{-3}$
Concentration (carbon non-COD)	$kmole\ C.m^{-3}$
Concentration (nitrogen non-COD)	$kmoleN.m^{-3}$
Concentration (cations and anions)	$kmole\ .m^{-3}$
Pressure	bar
Temperature	^{o}K
Volume	m^3
Time	d

Table 3.2 Nomenclature, description of stoichiometric coefficients

Symbol	Description	Units
C_i	Carbon content of component i	kmole C/kg COD
N_i	Nitrogen content of component i	kmole N/kg COD
v_{ij}	Rate coefficients for component i on process j	$kg\ COD/m^3$
$F_{product,\ substrate}$	Yield (catabolism only) of product in substrate	kg COD/kg COD
Ysubstrate	Yield of biomass on substrate	kg COD/kg COD

Table 3.3 Nomenclature, description of equilibrium coefficients and constants

Symbol	Description	Units
H_{gas}	Gas law constant (equal to K_H^{-1})	Bar/M
$K_{a,acid}$	Acid-base equilibrium constant	$M\ (kmole/\ m^3)$
K_H	Henry's law coefficient	M/bar
pK_a	$-\log10[K_a]$	
R	Gas law constant ($8.314x10^{-2}$)	$bar.M^{-1}K^{-1}$

Table 3.4 Nomenclature, description of kinetic constants and rates

Symbol	Description	Units
$K_{A/Bi}$	Acid-base kinetic constant	d^{-1}
$k_{dec,acid}$	First order decay rate	d^{-1}
$I_{inhibitor,\ process}$	Inhibition function	-
$k_{process}$	First order constant, normally for hydrolysis	d^{-1}
k_La	Gas-liquid transfer coefficient	d^{-1}
$K_{I,\ inhibit,\ substrate}$	50% inhibitory concentration	$kgCOD/m^3$
$k_{m,\ process}$	Monod maximum specific uptake rate	kgCOD_S.kgCOD_
$K_{s,\ process}$	Half saturation constant	$kgCOD\_S/m^3$
ρj	Generalized rate of process j	
μ_{max}	Monod maximum specific growth rate	d^{-1}

Table 3.5 Nomenclature, description of dynamic state variables (1), algebraic variables (2) and physical reactor parameters (3).

Symbol	Description	Units
pH	-log10[H+], (2)	_
$P_{gas,i}$	Partial pressure of gas i, (2)	Bar
P_{gas}	Total gas pressure (1.013 bar), (3)	Bar
S_i	Soluble component i, (1)	$kgCODm^{-3}$
T	Temperature, (3)	^oK
V	Volume (3)	m^3
X_i	Particulate component i, (1)	d^{-1}

3.2 Anaerobic Digestion Model No. 1 Development

The ADM1 was developed by the IWA Task Group for Mathematical Modeling of Anaerobic Digestion Processes (Batstone et al., 2002a). It has the following benefits:

a. Model application for full-scale plant design, operation and optimization.

b. Process optimization and control, aimed at direct implementation in full-scale plants as a further development work.

c. Forming the common basis for further model development and validation studies to make outcomes more comparable and compatible.

d. Technology transfer from research to industry.

Many anaerobic models have been developed. However, their use has been very limited, due to the wide variety of models available and their very specific nature.

3.3 Reaction System

In the ADM1 model two main type reactions are modeled as number of sequential and parallel steps (Batstone et al., 2002b). These are:

a. Biochemical reactions.

b. Physicochemical reactions.

The process and component inclusion in the model is determined considering the maximization of the applicability while maintaining a simple model structure. The Original Model includes three overall biological intracellular steps, (i.e. acidogenesis, acetogenesis and methanogenesis) as well as an extracellular disintegration (partly non-biological) and depolymerization step (Figure 3.1). The Modified Model (implemented in this research) schema is given Figure 3.2. In the Modified Model, solids accumulation and biomass recycling are incorporated into the Original Model.

In the biochemical processes, available degradable substrate and total input COD are separated, since a considerable fraction of the input COD may not be anaerobically biodegradable (Masse & Droste, 2000; Batstone et al., 2002b). Physicochemical conversions aside from the biochemical equations are included in the model to describe the physico-chemical state effects, such as effects of pH and gas concentration, on biochemical reactions.

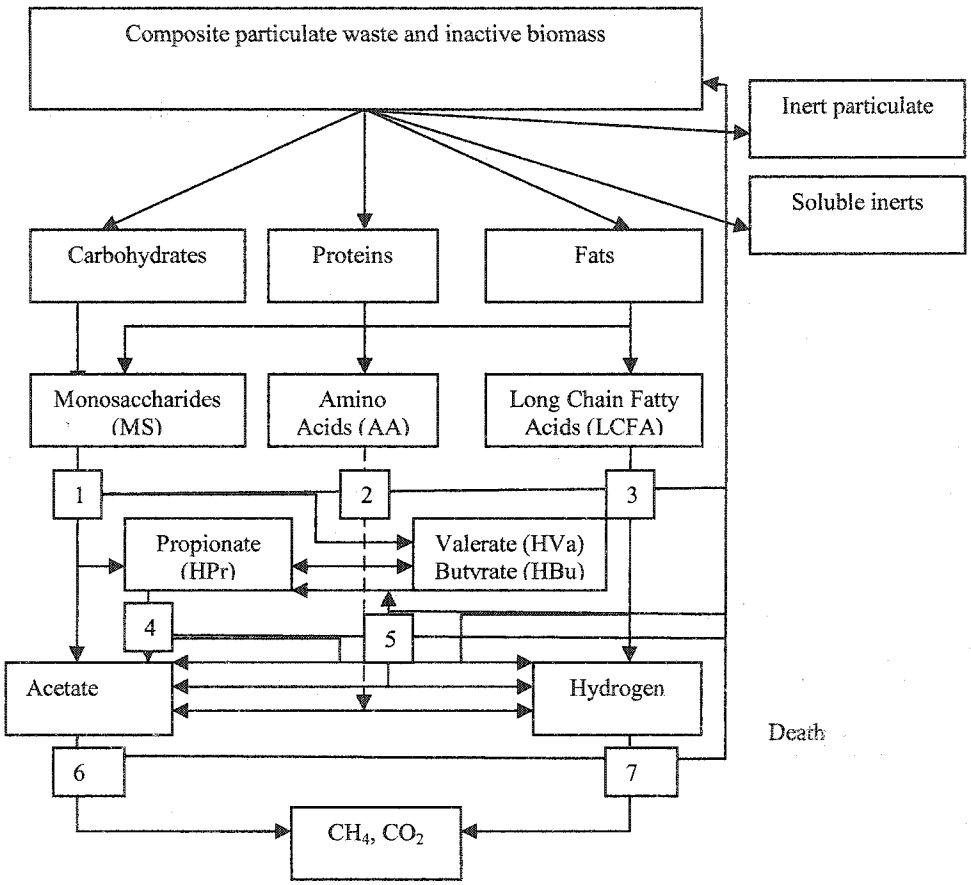

Figure 3.1 The Anaerobic Digestion Model No. 1 as implemented including biochemical processes: 1. acidogenesis from sugars (MS); 2. acidogenesis from amino acids (AA); 3. acetogenesis from long chain fatty acids (LCFA); 4. acetogenesis from propionate; 5. acetogenesis from butyrate and valerate; 6. aceticlastic methanogenesis; and 7. hydrogenotrophic methanogenesis (Batstone, Torrijos, Ruiz, & Schmidt, 2004).

Note: In the Original Model: Digester volume changes (i.e., decrease) and biomass recycling are not considered in mass balance equations.

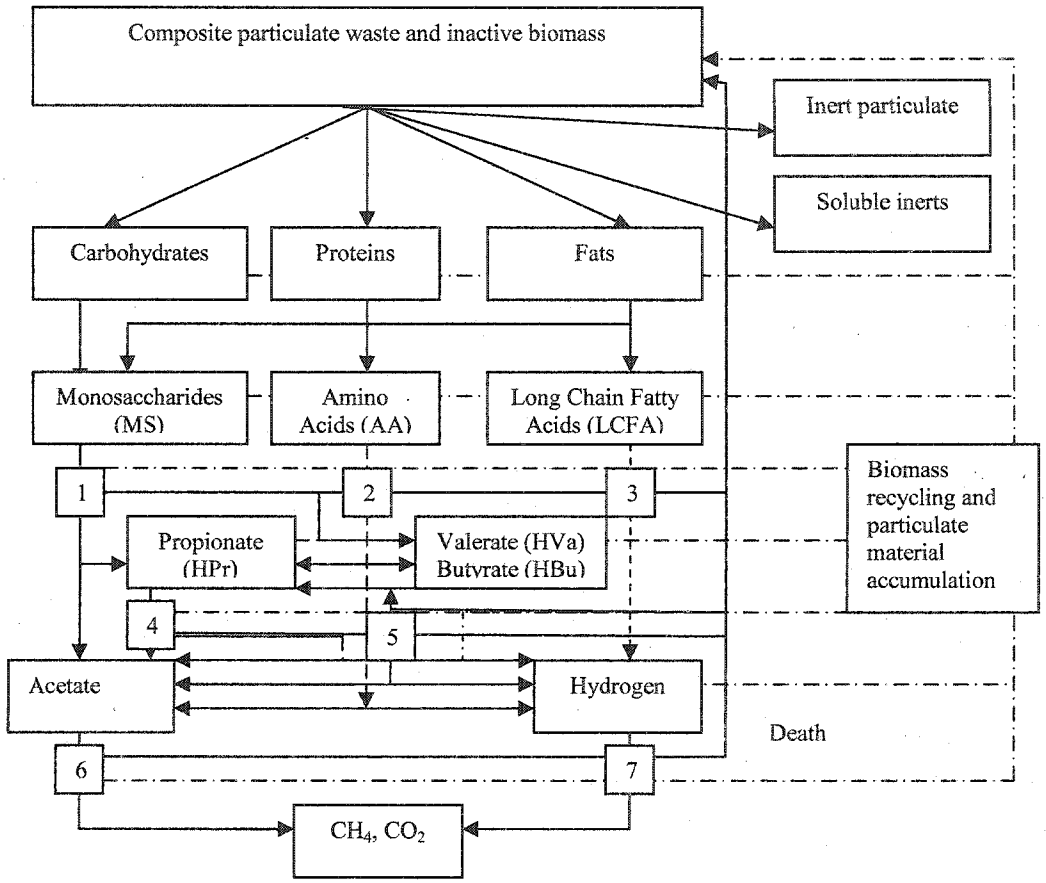

Figure 3.2 The Modified Model for Anaerobic Digestion as implemented, including biochemical processes: 1. acidogenesis from sugars (MS); 2. acidogenesis from amino acids (AA); 3. acetogenesis from long chain fatty acids (LCFA); 4. acetogenesis from propionate; 5. acetogenesis from butyrate and valerate; 6. aceticlastic methanogenesis; and 7. hydrogenotrophic methanogenesis.

Notes: In the Modified Model:

a. Digester volume changes (i.e., decrease in operating volume) for each simulation period due to the accumulation of solids in the reactor. The decrease is calculated using the mass balance for fixed solids by the method proposed in the research based on settling theory.
b. Biomass is recycled due to the accumulation in the reactor. The effect of the biomass recycling has been included in the Modified Model using the increase in retention time, t_r as a variable, calculated by a method proposed for the Modified Model. The mass balance for particulate components include this term in the Modified Model.

In the Original Model, disintegration of homogeneous complex particulate waste first to carbohydrate, protein and lipid particulate substrate, as well as particulate and soluble inert material, is assumed. The disintegration occurs before the depolymerization, since the primary substrate is represented by lumped kinetic and biodegradability parameters (Siegrist et al., 1993; Masse & Droste, 2000; Batstone et al., 2002b; Varon-Pena, 2002). The complex particulate waste pool is also used as a pre-lysis repository of decayed biomass. The disintegration step includes lysis, non-enzymatic decay, phase separation, and physical breakdown and some other processes.

All biochemical extracellular steps were assumed to be first order, which is a simplification based on empiricism, reflecting the cumulative effect of a multi-step process (Masse & Droste, 2000; Batstone et al., 2002b). The cellular processes were defined by uptake, growth, and decay expressions. Substrate uptake is chosen as a key rate equation to decouple the growth from uptake and to allow variable yields. The uptake is based on Monod-type kinetics. The substrate uptake includes the biomass growth implicitly. First order biomass decay as was assumed.

The process rate and stoichiometry matrix for biochemical reactions are given in Appendix A, together with the physico-chemical rate equations. Suggested parameters and qualitative sensitivity and variability are given in Tables 3.6 and 3.7.

3.4 ADM1 Model Implementation and Its Extension

Anaerobic digestion could be implemented as a Dynamic Equation (DE) System; a set of ordinary differential equations or Dynamic and Algebraic Equation (DAE) System; a set of ordinary differential equations and algebraic equations. The system formulation depends on whether the acid-base reactions are implemented as an implicit

algebraic equation (i.e., DAE implementation) or a number of additional kinetic rate and differential equations (i.e., DE implementation) (Batstone et al., 2002b; Rosen & Jeppsson, 2002). The DE system is selected since its implementation in MATLAB is less sensitive than the DAE implementation. Single stage DE implementation schema is shown in Figure 3.3.

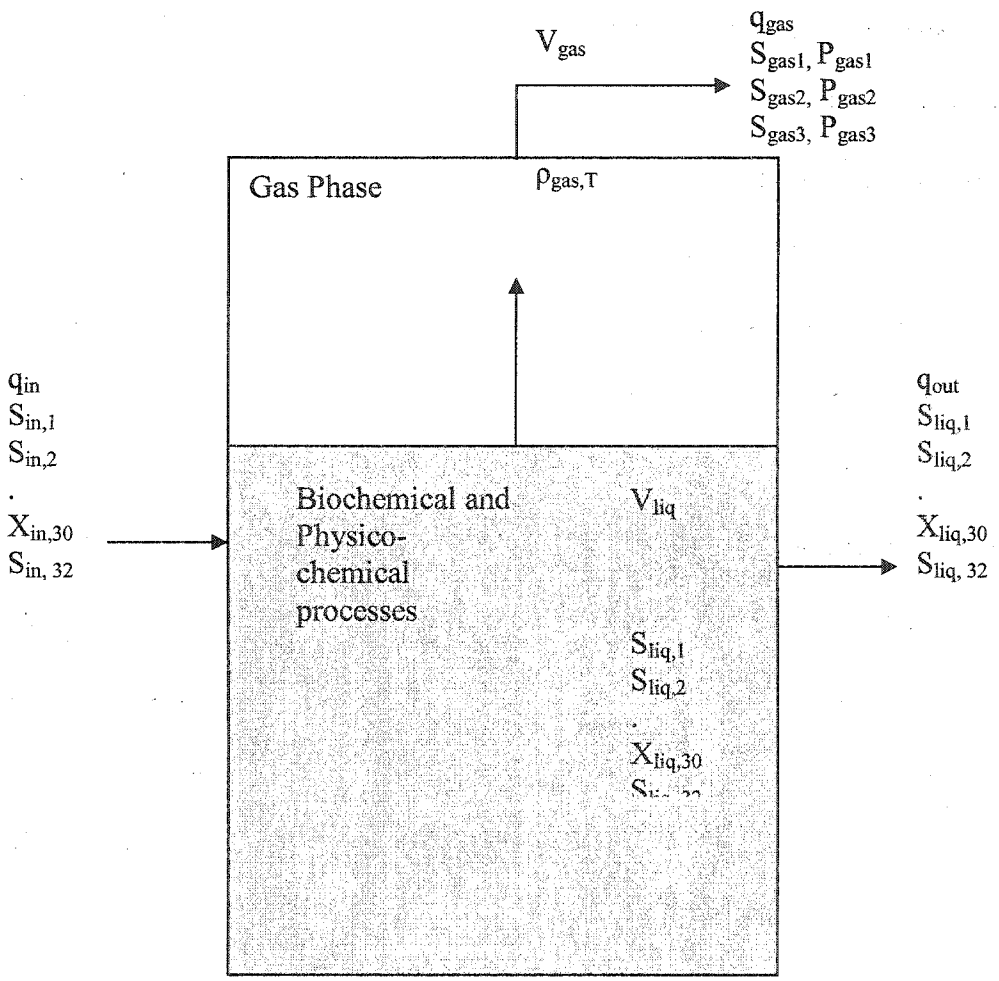

Figure 3.3 Schematic of a typical single tank reactor (q_{in} = flow into the reactor, m^3/day; q_{out}=flow out of reactor, m^3/day; q_{gas} = gas flow, m^3/day; $\rho_{gas,T}$ = Liquid-gas transfer rate, M/day;V = volume, m^3, $S_{in,i}$ = Concentration of liquid components, kgCOD/m^3; $X_{in,i}$ = Concentration of particulate components, kgCOD/m^3) (Batstone et al., 2002a)

Table 3.6 Suggested stoichiometric parameters and qualitative sensitivity and variability (Batstone et al., 2002b)

Parameter (dimensionless)	Description	Value	Var	Notes
$f_{si,xc}$	Soluble inerts from composites	0.1	2	1
$f_{xi,xc}$	Particulate inerts from composites	0.25	2	1
$f_{ch,xc}$	Carbohydrates from composites	0.20	2	1
$f_{pr,xc}$	Proteins from composites	0.20	2	1
$f_{li,xc}$	Lipids from composites	0.25	2	1
$N_{xc,}N_i$	Nitrogen content of composites and inerts	0.002	2	1
$f_{fa,li}$	Fatty acids from lipids	0.95	1	2
$f_{h2,su}$	Hydrogen from sugars	0.19	3	3
$f_{bu,su}$	Butyrate from sugars	0.13	3	3
$f_{pro,su}$	Propionate from sugars	0.27	3	3
$f_{ac,su}$	Acetate from sugars	0.41	3	3
$f_{h2,aa}$	Hydrogen from amino acids	0.06	2	3
N_{aa}	Nitrogen in amino acids and proteins	0.007	2	3
$f_{va,aa}$	Valerate from amino acids	0.23	2	3
$f_{bu,aa}$	Butyrate from amino acids	0.26	2	3
$f_{pro,aa}$	Propionate from amino acids	0.05	2	3
$f_{ac,aa}$	Acetate from amino acids	0.40	2	3

Var= Variability of parameter, 1= varies very little between processes; 2= varies between processes and substrates; 3= varies dynamically within process.
Notes:

1. Varies widely
2. Based on palmitate triglyceride
3. Calculated from sugar and amino acid values

Table 3.7 Suggested parameter values and qualitative sensitivity and variability for mesophilic digestion (Batstone et al., 2002b)

Parameter	Mesophilic high-rate (nom. 35 °C)	Mesophilic solids (nom .35 °C)	S	Var	Notes
k_{dis} (d^{-1})	0.40	0.50	3	3	1
k_{hyd_CH} (d^{-1})	0.25	10	3	2	2
k_{hyd_PR} (d^{-1})	0.2	10	2	3	2
k_{hyd_LI} (d^{-1})	0.1	10	2	3	2
$t_{res,\ x}$ (d)	40	0	3	2	
K_{dec_all} (d^{-1})	0.02	0.02	2	2	3
$K_{S\_NH3\_all}$ (d^{-1})	$1x10^{-4}$	$1x10^{-4}$	1	1	
pH_{UL} acet/acid	5.5	5.5	1	2	4
pH_{LL} acet/acid	4	4	1	2	4
k_{m_su} ($CODCODd^{-1}$)	30	30	1	2	
k_{S_su} ($kgCODm^{-3}$)	0.50	0.50	1	2	
Y_{su} ($CODCOD^{-1}$)	0.10	0.10	1	1	
k_{m_aa} ($CODCODd^{-1}$)	50	50	1	2	
k_{S_aa} ($kgCODm^{-3}$)	0.30	0.30	1	1	
Y_{aa} ($CODCOD^{-1}$)	0.08	0.08	1	1	
k_{m_fa} ($CODCODd^{-1}$)	6	6	1	3	
k_{S_fa} ($kgCODm^{-3}$)	0.40	0.40	1	3	
Y_{fa} ($CODCOD^{-1}$)	0.06	0.06	1	1	
$K_{I,H2\_fa}$ ($kgCODm^{-3}$)	$5x10^{-6}$	$5x10^{-6}$	1	1	
k_{m_c4+}($CODCODd^{-1}$)	20	20	1	2	
k_{S_c4+} ($kgCODm^{-3}$)	0.30	0.20	1	3	
Y_{c4+} ($CODCOD^{-1}$)	0.06	0.06	1	1	
$K_{I,H2\_c4+}$ ($kgCODm^{-3}$)	1x10-5	1x10-5	1	1	
k_{m_pro}($CODCODd^{-1}$)	13	13	2	2	
k_{S_pro} ($kgCODm^{-3}$)	0.30	0.10	2	2	
Y_{pro}($CODCOD^{-1}$)	0.04	0.04	1	1	
$K_{I,H2\_pro}$ ($kgCODm^{-3}$)	3.5x10-5	3.5x10-5	2	1	
k_{m_ac} ($CODCODd^{-1}$)	8	8	3	2	

Table 3.7 Suggested parameter values and qualitative sensitivity and variability for mesophilic digestion (Continued) (Batstone et al., 2002b)

Parameter	Mesophilic high-rate (nom 35 oC)	Mesophilic solids (nom 35 oC)	S	Var	Notes
k_{S_ac} ($kgCODm^{-3}$)	0.15	0.15	3	2	
Y_{ac}($CODCOD^{-1}$)	0.05	0.05	1	1	
$pH_{UL\ ac}$	7	7	3	1	5
$pH_{LL\ ac}$	6	6	2	1	5
k_{m_h2} ($CODCODd^{-1}$)	35	35	1	2	
k_{S_h2} ($kgCODm^{-3}$)	$2.5x10^{-5}$	$7x10^{-6}$	2	2	
Y_{h2}($CODCOD^{-1}$)	0.06	0.06	1	1	
$pH_{UL\ ac}$	6	6	2	2	5

S= Sensitivity of important output to parameter at average parameter values.
1 = low or no sensitivity of all outputs to parameter
2 = some sensitivity or significant sensitivity under dynamic conditions
3 = Significant sensitivity under steady-state conditions and critical sensitivity under dynamic conditions.

Var = Variability of parameter
1= varies within 30%
2= varies within factor of 100%;
3= varies within factor of 300%.

Notes:
1. Mainly of importance in solids digester
2. Mainly of importance for pure or semi-separated solid substrates (such as slaughterhouse or starch). When used with activated sludge digesters, k_{dis} is rate limiting.
3. Decay rates can be set equal as a first guess. In many cases, a k_{dec} double the given values can be used for certain groups, such as acidogens and aceticlastic methanogens.
4. $pH_{acet/acid}$ inhibition factors for all acidogenic and acetogenic bacteria. Form 2 is used here (i.e., only low pH inhibition)
5. Notes as for (4) except values are methanogen specific.

3.5 Ordinary Differential Equation Solutions

MATLAB/Simulink system provides ordinary dynamic equation solver systems. Some of these are explained below (The MathWorks, 2002a; Copp et al., 2002; Rosen & Jeppsson, 2002):

Ode23: This solver is an implementation of an explicit Runge-Kutta (2,3) pair of Bogacki and Shampine. It is a one-step solver. It could be more efficient than ode45 in cases of crude tolerances and moderate stiffness.

Ode45: This solver is based on an explicit Runge-Kutta (4,5) formula, the Dormand-Prince pair. It is a one-step solver. It could be considered as the best function to apply as a "first try" for most problems.

Ode15s: This solver is a variable order solver based on the numerical differentiation formulas (NDFs). Optionally, it uses the backward differentiation formulas (BDFs, also known as Gear's method) that are usually less efficient. Its is a multistep solver. It is considered to be good for stiff problems, or when solving a differential-algebraic problem.

Ode23s: This solver is based on an extended Rosenbrock formula of order 2. It is a one-step solver, therefore, could be more efficient than ode15s at crude tolerances and is used for the solution of specific type of stiff problems where Ode15s are not efficient.

3.6 Dynamic State Variables

There are 32 dynamic state variables, 19 biochemical process rates and 3 liquid-gas transfer processes in DE system. Additionally, six acid-base kinetic processes exist. The DE system contains 6 more dynamic state variables due to the acid-base dissociation in the system. In other words, additional components have been taken into the account for

VFA, inorganic carbon, IC, inorganic nitrogen, IN. For VFA, ionic and free forms (i.e., 4 additional variables), for IC, dissolved carbon dioxide and bicarbonate, and for IN, ammonium, and ammonia are considered in the DE system. The DE system variables for soluble and particulate components are given Table 3.8 and Table 3.9 respectively.

Table 3.8 Soluble components of DE system dynamic state variables

State Number	Name	Variable used	Description	Units
1	S_{su}	S_su	Sugars	kgCOD.m^{-3}
2	S_{aa}	S_aa	Amino acids	kgCOD.m^{-3}
3	S_{fa}	S_fa	Long chain fatty acids	kgCOD.m^{-3}
4	S_{hva}	S_hva	Valeric acid	kgCOD.m^{-3}
5	S_{va-}	S_va	Valerate	kgCOD.m^{-3}
6	S_{hbu}	S_hbu	Butyric acid	kgCOD.m^{-3}
7	S_{bu-}	S_bu	Butyrate	kgCOD.m^{-3}
8	S_{hpro}	S_hpro	Propionic acid	kgCOD.m^{-3}
9	S_{pro-}	S_pro	Propionate	kgCOD.m^{-3}
10	S_{hac}	S_hac	Acetic acid	kgCOD.m^{-3}
11	S_{ac}	S_ac	Acetate	kgCOD.m^{-3}
12	S_{h2}	S_h2	Dissolved hydrogen	kgCOD.m^{-3}
13	S_{CH4}	S_ch4	Dissolved methane	kgCOD.m^{-3}
14	S_{CO2}	S_co2	Dissolved carbon dioxide	kgCOD.m^{-3}
15	S_{HCO3-}	S_hco3	Dissolved bicarbonate	kgCOD.m^{-3}
16	S_{NH4+}	S_nh4	Ammonium	kgCOD.m^{-3}
17	S_{NH3}	S_nh3	Ammonia	kgCOD.m^{-3}
18	S_I	S_i	Soluble inerts	kgCOD.m^{-3}
31	S_{cat}	S_cat	Cations	kmole.m^{-3}
32	S_{an}	S_an	Anions	kmole.m^{-3}

Table 3.9 Particulate components of DE system dynamic state variables

State Number	Name	Variable used	Description	Units
19	X_c	X_xc	Composites	$kgCOD.m^{-3}$
20	X_{ch}	X_ch	Carbohydrates	$kgCOD.m^{-3}$
21	X_{pr}	X_pr	Proteins	$kgCOD.m^{-3}$
22	X_{li}	X_li	Lipids	$kgCOD.m^{-3}$
23	X_{su}	X_su	Sugar degraders	$kgCOD.m^{-3}$
24	X_{aa}	X_aa	Amino acid degraders	$kgCOD.m^{-3}$
25	X_{fa}	X_fa	LCFA degraders	$kgCOD.m^{-3}$
26	X_{C4}	X_c4	C4 degraders	$kgCOD.m^{-3}$
27	X_{pro}	X_pro	Propionate degraders	$kgCOD.m^{-3}$
28	X_{ac}	X_ac	Acetate degraders	$kgCOD.m^{-3}$
29	X_{h2}	X_h2	Hydrogen degraders	$kgCOD.m^{-3}$
30	X_I	X_i	Particulate inerts	$kgCOD.m^{-3}$

3.7 Rate Equation Matrix

Physicochemical equations are included to express the effect of the physico-chemical states on biochemical reactions. The overall process reactions including acid-base equilibria are given in Appendix A.

3.8 Liquid Phase Equations

The general mass balance equation neglecting the diffusional terms and interface transfer for CSTR reactor is given below (Chynoweth & Pullammanappallil, 1996):

[Accumulation of mass] = [Input] – [Output] + [Production] (3.1)

For each state component this equation can be written as (Batstone et al. 2002b):

$$\frac{dVS_{li,i}}{dt} = q_{in}S_{in,i} - q_{out}S_{liq,i} + V\sum_{j=1-19}\rho_j \nu_{i,j} \quad (3.2)$$

Where: $\sum \rho_j \nu_{i,j}$ is the summation of the specific kinetic rates for process j multiplied by rate coefficient, ν_{ij}. Assuming constant volume, $q=q_{in}=q_{out,}$, equation further be refined as:

$$\frac{dS_{li,i}}{dt} = \frac{q_i S_{in,i}}{V_{liq}} - \frac{q\ S_{liq,i}}{V_{liq}} + \sum_{j=1-19}\rho_j \nu_{i,j} \quad (3.3)$$

, and for varying retention time:

$$\frac{dVX_{li,i}}{dt} = \frac{q_i X_{in,i}}{V_{liq}} - \frac{q\ X_{liq,i}}{t_{res,x} + \frac{V_{liq}}{q}} + \sum_{j=1-19}\rho_j \nu_{i,j} \quad (3.4)$$

Where: $t_{res,x}$= Retention time of solids components above hydraulic retention time used to simulate the separate solids retention.

3.8.1 Accumulation and Retention Time

Increase in the solids retention time (SRT), and decrease in reactor volume due to accumulation in the reactor could be estimated by determining vertical and horizontal components of the settling velocity. Procedure for the determination of velocity components and volume of the waste settled in the tank is explained below. The relevant settling schema is given in Figure 3.4.

For the settling in the reactor, the following is assumed:

a. Discrete particles (i.e., particles do not interact with each other, no floc formed)

b. Equal distribution of flow in horizontal and vertical directions

c. No turbulence in the reactor

d. Particles move horizontally at the same velocity as the organic waste

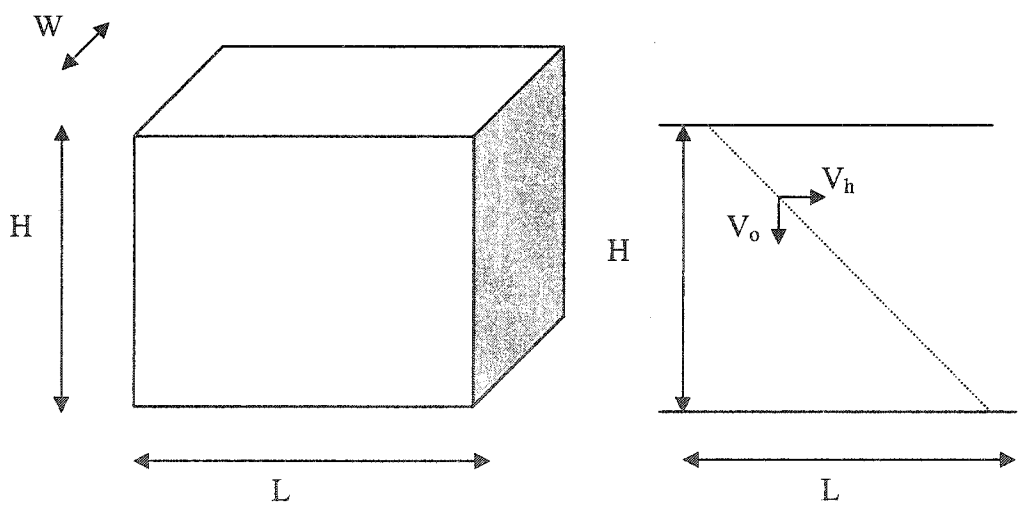

Figure 3.4 Schematic of settling in the reactor

Assuming a particle whose terminal velocity, V_o enters at the upper left corner of the tank. This particle is defined as a "critical particle" as any other faster particle will be removed from the tank regardless of the point of entry:

$$HRT = \frac{V}{Q} = \frac{HLW}{Q} \tag{3.5}$$

Where: HRT = Hydraulic retention time

H = Height of reactor

L= Length of reactor

W = Width of reactor

$$HRT = \frac{H}{V_o} = \frac{L}{V_h} \tag{3.6}$$

Where: V_h= Horizontal component of velocity

V_o= Critical particle settling velocity.

$$V_h = \frac{Q}{A} = \frac{Q}{HW} \tag{3.7}$$

, and

$$V_o = V_h \frac{H}{L} = \frac{Q}{HW} \cdot \frac{H}{L} = \frac{Q}{WL} \tag{3.8}$$

, and solving V_o:

$$V_o = \frac{Q}{A_s} \tag{3.9}$$

Where A_s: Surface area of the reactor.

The particle settling velocity may be computed from fluid mechanics equations. The downward mass flux due to sedimentation depended on the downward velocity of waste particles. The downward velocity resulted from the net value of the buoyancy force

(assuming the density of the particle was different from that of water), the drag force (acting upward) and the weight (acting downward).

Assuming steady state, drag, buoyancy and weight are related as:

$$F_g - F_D - F_n = m\frac{dV}{dt} = 0 \qquad (3.10)$$

Where: F_g = Weight of particle.

F_D = Drag force.

, and F_n = Buoyancy force.

Considering a particle of waste material as a sphere, the drag force is a function of the particle Reynolds number, R_{ep}, which is defined as:

$$R_{ep} = \frac{dVs\rho_f}{\mu} \qquad (3.11)$$

Where: d = Particle diameter.

V_s = Fall velocity of the particle.

ρ_f = Fluid density.

μ = Fluid viscosity.

The drag force can be computed as:

$$F_D = \frac{1}{2}C_D\rho_f V_s^2 A \qquad (3.12)$$

Where: A = Projected frontal area of particle

C_D = Drag coefficient that can be calculated from experimental correlations.

The weight and buoyancy forces are function of the size of the particle, the particle density, and the fluid density. Combining these into the force balance equation gives:

$$V_s = \sqrt{\left[\frac{2g(\rho_p - \rho_f)}{C_D \rho_f}\right]\left[\frac{V_p}{A_p}\right]} \tag{3.13}$$

Assuming spherical particle, volume of particle, V_p:

$$V_p = \frac{\pi d_p^{\,3}}{6} \tag{3.14}$$

Area of the particle, A_p is:

$$A_p = \frac{\pi d_p^{\,2}}{4} \tag{3.15}$$

For $R_{ep} < 0.1$

$$C_D = \frac{24}{\mathrm{Re}_p} = \frac{24\mu}{\rho V_s d_p} \tag{3.16}$$

This gives:

$$V_s = \frac{g(\rho_p - \rho_f) d_p^{\,2}}{18\mu} \tag{3.17}$$

This equation can be generalized for the whole process by estimating the average settling velocity for the settling particles. The average settling velocity and sedimentation rate can be determined from the settling velocity by analyzing a control volume, CV, with the bottom surface in contact with the sludge layer. If the concentration of particles, C, is assumed to be spatially uniform and the top boundary moved downward at Stokes velocity, the rate of particle accumulation could be found as (Fleming, 2002):

$$SR = \frac{\partial}{\partial t}\iiint_{CV} C dV = \iint_{CS} C n.V_s dA \qquad (3.18)$$

Where: SR = Sedimentation rate

dV = Change in the volume of the CV

$\mathbf{n.V_s}$ = Component of velocity normal to the sludge layer

A= Area of sludge under the CV.

Assuming the concentration within the CV is steady (C is a constant), the sedimentation rate is:

$$SR = -C\frac{dV}{dt} = C\overline{AV_s} \qquad (3.19)$$

A starting point for the average settling velocity (representative value for the settling particles), $\overline{V_s}$, can be taken from the literature values (Knowles, 1999). Particle settling velocities ranging between 0.02 mm/s and 0.5 mm/s for 5 μm diameter quartz silt and for 200 μm aggregates of the silt particles respectively are given in the literature (Knowles, 1999; Fleming, 2002). These values can be considered as an upper and lower bounds of $\overline{V_s}$. Change in volume of the reactor due to settling can be calculated as:

$$-\frac{dV}{dt} = \overline{AV_S} \quad , \qquad (3.20)$$

and the increase in retention time for each quarterly period, Δt, may be estimated as:

$$tres, x = \frac{HRT_{\Delta t}(i)dV_{in,i}}{q_{out}(i+1)_{liq}} = \frac{HRT_{\Delta t}(i)\overline{AV_s}}{q_{out}(i+1)} \qquad (3.21)$$

Where: $HRT_{\Delta t}(i)$ = hydraulic retention time (i.e., number of days waste stays in the reactor for CSTR with no recycling, this is equal to solid retention time, SRT) for a

quarterly period over which AD process is steady. The initial estimate of settling and associated increase in retention time and decrease in rector operating volume can be calculated using mass balance of fixed solids, total phosphorous, copper and zinc for Colorado Pork reactor (Martin, 2003).

3.9 Gas Phase Equations

Assuming constant reactor volume, and integrating the gas state variables into the system of dynamic state variables, the gas phase differential equations can be stated as follows:

$$\frac{dS_{gas,i}}{dt} = -\frac{q_{gas}, S_{gas,i}}{V_{gas}} + \rho_{T,i}\frac{V_{liq}}{V_{gas}} \qquad (3.22)$$

Where $S_{gas,I}$= Gas volume specific concentration variable

q_{gas} = Overall dry gas flow (water corrected)

V_{gas}= Headspace volume

V_{liq}= Bulk reactor volume,

$\rho_{T,i}$ = Liquid volume specific gas transfer rate, and i stands for one of the three gas components.

Table 3.10 Gas components

State Number	Name	Abbreviation	Description	Unit
33	H_2	H2	Hydrogen	$kgCOD^{m-3}$ or bar
34	CH_4	CH4	Methane	$kgCOD^{m-3}$ or bar
35	CO_2	CO2	Carbon Dioxide	$kgCOD^{m-3}$ or bar

3.9.1 Liquid-Gas Transfer

The liquid-gas transfer rate equation is given below:

$$\rho_{T,i} = k_L a(S_{liq,i} - K_{H,i} p_{gas,i}) \quad (3.23)$$

Where $\rho_{T,i}$ = Specific mass transfer rate of gas i

$k_L a$ = Overall mass transfer coefficient

$S_{liq,i}$ = Concentration of gas component i in the bulk

$K_{H,i}$ = Henry's law coefficient for gas i

$p_{gas,i}$ = Partial pressure of gas i in the headspace

To account for the COD basis of $S_{liq,i}$ as compared to molar basis of K_H is corrected by a factor of 16 and 64. Partial gas pressure, p_{gas} for each gas component can be calculated using ideal gas law pressure as:

$$P_{gas,i} = S_{gas,i} RT_{op} \quad (3.24)$$

Where $S_{gas,i}$ = Gas volume specific concentration of gas i

R = Universal gas constant (0.08134 bar.M^{-1}.K^{-1})

T= Operating temperature in ^{o}K

$S_{gas,i}$ is divided by 16 and 64 for hydrogen and methane respectively to account for the COD equivalents of the gases.

The overall gas flow corrected for water vapor is found as:

$$q_{gas} = \frac{RT}{p_{gas} - p_{gas,H_2O}} V_{liq} \left(\frac{\rho_{T,H_2}}{16} + \frac{\rho_{T,CH_4}}{64} + \rho_{T,CO_2} \right) \quad (3.25)$$

Where p_{gas}= Total gas pressure generally could be fixed to 1.013 bar

$p_{gas,H20}$ = Gas pressure of water at headspace corrected for operating temperature T_{op} using the following formula :

$$p_{gas,H_2O} = 0.0313 \exp\left(5290\left(\frac{1}{298} - \frac{1}{T_{op}}\right)\right) \quad (3.26)$$

The total head pressure of 1.013 bar could be assumed for the case where the gas volume is frequently exchanged with the environment and direct connection to normal pressure conditions in the environment is provided.

3.10 Acid-Base Equilibria

Six more state variables are required for DE solution to represent the acid-base equilibria (Rosen & Jeppson, 2002). Acid-base equilibrium equation is given below:

$$\rho_{A/B,i} = k_{A/Bi}(S_{liq,i-}(K_{a,i} + S_{H+}) - K_{a,i}S_{liq,i}) \quad (3.27)$$

Where $\rho_{A/B,i}$ = Production rate of acid from the base.

$k_{A/Bi}$= Acid-base kinetic constant

$S_{liq,\ i}$ = Total concentration of free form of an organic acid, dissolved carbon dioxide or ammonium

$S_{liq,i\ -}$ = Concentration of ionic form

$S_{liq,H+}$ = Concentration of hydrogen ions in the bulk

$K_{a,i}$ = Acid-base equilibrium coefficient

Acid-base kinetic constant, $k_{A/Bi}$, is generally set to one order of magnitude higher than the highest biochemical rate since physicochemical reactions run faster than the biochemical ones. $k_{A/Bi}$ of 10^8 is applied for all acid-base equilibria and 10^{12} applied to the IN and IC (CO_2) results in model performance with best numerical stability. Acid-base rates for VFA and IC is applied as follows (Rosen & Jeppsson, 2002):

$$\frac{dS_{liq,i}}{dt} = \frac{qS_{i,in}}{V_{liq}} - \frac{qS_{liq,i}}{V_{liq}} \quad (3.28)$$

Where $S_{i,in}$ = Total concentration of organic acid in incoming waste

$S_{i,liq}$= Total concentration of organic acid in outgoing waste,

and for ionic components:

$$\frac{dS_{i-}}{dt} = -\rho_{A/B,i} \tag{3.29}$$

Where i is the total concentration and i- is the ionic concentration form of the organic acids.

3.11 Determination of pH

The pH is computed using the following equation:

$$\sum S_{C+} - \sum S_{A-} = 0 \tag{3.30}$$

Where S_{C+} = The cationic equivalent concentrations

S_{A-} =is anionic equivalent concentrations

Charge balance equation as implemented in ADM1 is given below:

$$S_{Cat^+} + S_{NH4^+} + S_{H^+} - S_{HCO_3^-} - \frac{S_{Ac^-}}{64} - \frac{S_{pr^-}}{112} - \frac{S_{Bu^-}}{160} - \frac{S_{va^-}}{208} - S_{OH-} - S_{An-} = 0 \tag{3.31}$$

For S_{OH^-}:

$$S_{OH^-} = \frac{K_w}{S_{H^+}} \tag{3.32}$$

The S_{H+} is computed from the quadratic equation (algebraic equation) by substituting equation 3.31 into the equation 4.30 (Stumm & Morgan, 1996; Rosen & Jeppsson, 2002): The equation obtained by this substitution is given below:

$$S_{H+} = -\frac{v + \sqrt{(-v)^2 + 4K_w}}{2} \tag{3.33}$$

Where:

$$v = S_{Cat^+} S_{NH4^+} - S_{HCO_3^-} - \frac{S_{Ac^-}}{64} - \frac{S_{pr^-}}{112} - \frac{S_{Bu^-}}{160} - \frac{S_{va^-}}{208} - S_{An^-} \qquad (3.34)$$

Where: K_W = Ion product of water corrected for particular operating temperature. This equation gives only one physical solution and the pH value is obtained from the following:

$$pH = -\log(S_{H+}) \qquad (3.35)$$

3.12 Inhibition

The following inhibition forms are assumed in the implementation:

1. Free ammonia and hydrogen inhibition: Inhibition due to the free ammonia is applied for the group of aceticlastic methanogens. Inhibition due to the high hydrogen levels is applied to long chain fatty acids, C4 (butyrate, valerate) and propionate degrading bacteria. The inhibition is expressed as a non-competitive function:

$$I = \frac{1}{1 + S_I / K_I} \qquad (3.36)$$

2. pH inhibition: This inhibition is applied to all degrading bacteria with specific limits for aceticlastic methanogens and hydrogen-utilizing methanogens. No inhibition is assumed above a pH of 7 (i.e., $I_n = 1$).

$$I = \exp\left(-3 \left(\frac{pH - pH_{UL}}{pH_{UL} - pH_{LL}} \right)^2 \right) \qquad (3.37)$$

3. Nitrogen limitation: This is included as a growth limitation due to the lack of nitrogen, using the following term:

$$I = \frac{1}{1 + K_I / S_I} \tag{3.38}$$

3.13 Summary

In this chapter, AD process modeling using the ADM1 was explained. The concepts, parameters, implementation details for the ADM1 were given. The modification which was made in this research to accommodate the accumulation was described in detail. The method developed and incorporated into the Original Model provides estimates for both the amount of settling solids in the reactor and the residence time for biomass recycling caused by the solids accumulation.

CHAPTER 4: MODEL IMPLEMENTATION AND PARAMETER ESTIMATION

In the implementation of the ADM1, MATLAB and Simulink are used together with a package for optimization. In the first phase, the ADM1 model is implemented and the model parameters are estimated using experimental data. In the second phase, the Original Model is modified for accumulation. The Modified Model is implemented for simulation of the anaerobic digestion process taking place at Colorado Pork LLC reactor. Then the Model is optimized for hydraulic retention time (HRT).

4.1 Modeling Software Package

MATLAB ™ is an application in which computation, visualization and programming are integrated in a common environment. MATLAB includes toolboxes for a particular class of problems such as optimization toolbox. Simulink® is an add-on software package for modeling, simulating, and analyzing dynamic systems (The Mathworks, 2002a; Copp et al., 2002). Simulink provides a graphical user interface (GUI) for building and integrating models as block diagrams. It provides a comprehensive library for building customized blocks using already existing ones or S-functions. The simulation results can be transferred to MATLAB workspace for post-processing, storage and visualization. The simulation results can also be displayed using scopes while the model is running. The model developed in this study is implemented using MATLAB version 6.5, release 13, and Simulink 5 (The Mathworks, 2002b).

4.2 Model Implementation

The model implementation is accomplished using Simulink model block diagrams. The model consists of model blocks and connectors integrated on the Simulink platform. In the first phase of the model implementation, single-stage steady flow case is implemented, and later on unsteady state methodology developed is integrated into the model. Simulink model block for a single-stage steady process is shown in Figure 4.1. Time block is inserted to keep track of the time passed respectively.

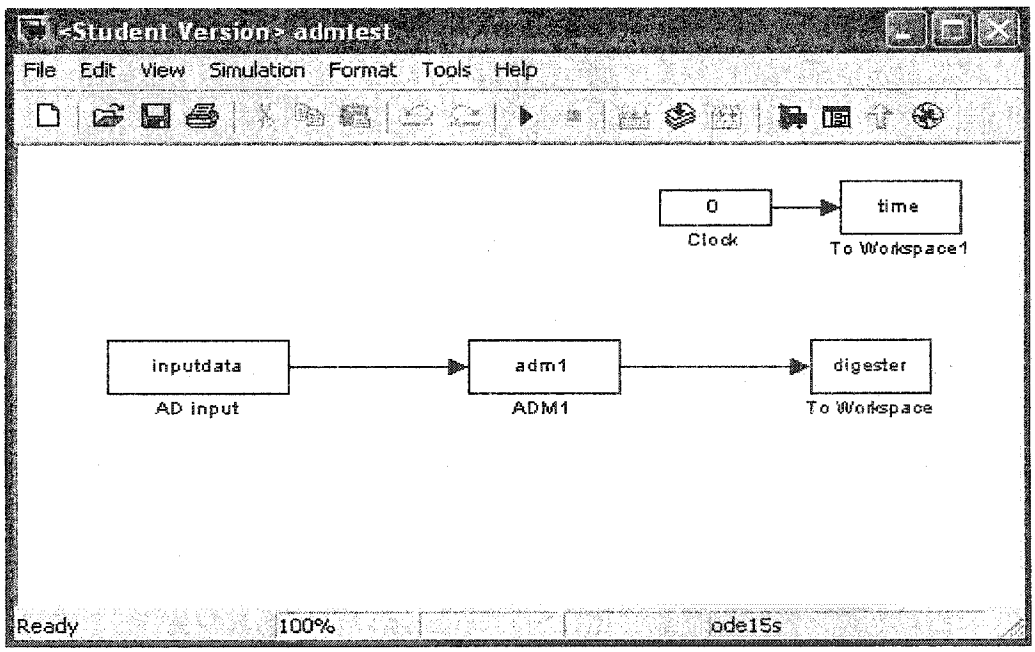

Figure 4.1 Simulink model block for a single-stage process

S-Function: The main component of the model is S-Function which is the Simulink block, written in C language. S function in the model dynamically computes the ODEs given in the rate equation matrix. The function evaluates model inputs, calculates the variables derived from the dynamic states (e.g., pH, gas flow), and specifies the output.

Simulation parameters: The simulation parameter window in the simulation menu is used to specify the simulation time, type of solver used, step size, tolerance, and output produced (Figure 4.2).

Figure 4.2 Simulation parameters form

In this implementation, ODE 15s solver is used since there was no significant benefit observed using higher order solvers such as ODE 23, or ODE 23s, ODE 45 etc.). ODE 15s is a multi-step variable order solver based on the numerical differentiation formulas (NDFs). In case of a stiff problem instead of higher order solutions ODE 15s with variable time step can be used (The Mathworks, 2002a). In the solution, absolute and relative tolerance of 1e-6 is used. The relative tolerance of 1e-6 means that the computed state is accurate to within 0.0001 percent.

Simulation Outputs: Model outputs could be saved as M files in MATLAB workspace or exported to other software for further analysis, data visualization, and

model performance evaluation. Evaluation procedures and model output visualizations are implemented in Excel.

4.3 Model Structure

In the model implementation, in the first phase, single stage steady state is realized. In the second phase, the model is modified to simulate unsteady state caused by reactor operating schedule and accumulation in the reactor. Initially, the model is built using simple block diagrams for the calculation of a few processes (scaled-down model) for single-stage process. Then, the rest of the components of the model have been added.

The single stage steady state model implementation consists of:

a. Model block diagram

b. Input vector for storage of inflow characteristics

c. Output matrix

d. S-function (for dynamic simulation of ODEs for steady state)

e. Set of parameters for single-stage mesophilic reactor

In the second phase, accumulation is implemented with the outlined methodology, is and incorporated to the model. The final model includes the following components:

a. Model block diagram

b. Input vector for storage of inflow characteristics

c. Output matrix

d. S-function (for dynamic computation of the ODEs modified for accumulation)

e. Set of parameters for mesophilic reactor

The model implementation for steady state operation and its extension for quasi-steady state are included in the following steps:

1. Model verification: This step included the testing of the model implementation (process developed). The step included testing the model procedure with the other implementations of the same model using the same parameter sets (comparison of Aquasim 2.1d and MATLAB implementations outputs).

2. Parameter estimation: In this step, some of the model parameters are estimated using the procedures outlined. Model calibration has been carried out for a single stage implementation.

3. The Modified Model verification and optimization: In this step, the Modified Model is used to simulate the AD process at the Colorado Pork LLC (i.e., the Modified Model verification is carried out). Reactor. Additionally, the model optimization has been carried out for HRT.

The Modified Model developed in this research is applied for a full-scale AD farm digester. The use of the model for other cases requires a comprehensive understanding of the anaerobic digestion process as applied to the process in consideration and expertise in modeling platform (i.e., MATLAB, Simulink). Further developments can include modifications to custom-made import/export functionalities, automatic parameter estimation using other estimation procedures and incorporation of these into the Simulink platform, implementation of control functions, and further customization of the application and the interface.

4.4 ADM1 Model Verification

For the model verification, mass balance checks have been applied for COD, carbon and nitrogen. The balance checks are listed below:

a. COD Balance: This is implicit in the rate equation matrix. Coefficients of the model were recalculated for the changes in stoichiometric parameters.

b. Carbon Balance: The carbon balance term is originally applied to uptake of sugars, amino acids, propionate, acetate, and hydrogen. This application is due to the fact that in these cases inorganic carbon is the source or the product of anabolism or catabolism. DE implementation also requires the term to be applied for the expanded dynamic state variables as:

$$v_{IC,j} = -\sum_{i=1-19,11-24} C_i v_{i,j} \qquad (4.1)$$

Where: C_i = Carbon content (kmole C/kg COD) of the component i

$v_{i,j}$ = Inorganic carbon stoichiometric coefficient for the process j. Inorganic carbon balance term is introduced for the decay terms (Blumensaat, 2002).

c. Nitrogen balance: Inorganic nitrogen balance is introduced for decay processes. Assuming decaying biomass is retained in the system, the nitrogen balance cycle should close. Due to the difference in nitrogen content of the biomass (N_{bac}= 0.00625 kmole C/kg COD) and the particulate composites (N_c=0.002 kmole C/kg COD) the following term is included:

$$v_{i,j} = -\sum_i N_i v_{i,j} \qquad (4.2)$$

Where N_i is the nitrogen content (kmole N/kg COD) of the component i and $v_{16,j}$ is the inorganic nitrogen stoichiometric coefficient for the process j.

4.5 Parameter Estimation

The goal of the estimation is to determine a realistic parameter set from a given number of inputs that minimizes some objective function measuring the differences

between measured and computed values assuming that the structure of the model is explicitly known (Pohjanpalo, 1982; Dochain & Vanrolleghem, 2001). Parameter estimation is carried out to generate a realistic set of parameters from a number of given dynamic inputs (Blumensaat, 2002). Parameter values are adjusted to match the model and experimental data. Estimated parameters are validated using the same parameter set for the different data sets obtained from experiments or full-scale applications.

The knowledge models including ADM1 are complex and require estimation of large number of parameters (Batstone et al., 2002a; Noykova, Muller, Gyllennberg, & Timmer, 2002). Some of the parameters can be taken from the literature of the similar type of studies or could be determined experimentally. Methods for the parameter estimation for AD models is one of the areas for which very limited literature exists (Batstone et al., 2002b). The following strategy can be applied for the estimation of parameters:

a. Parameters with low sensitivity and variability can be taken from the literature values.

b. More variable parameters with limited sensitivity can be taken from studies with similar reactor design and feed matrix.

c. Parameters can be reduced through numerical analysis of sensitivity, identifiability and correlation (Batstone et al., 2002b; Dochain & Vanrolleghem, 2002). The remaining parameters can be estimated by optimization using experimental data or by performing system tests upon single parameter (Batstone et al., 2002a; Blumensaat, 2002; Noykova et al., 2002a; Noykova, 2002b)

There are several approaches to determine identifiability of the model, and to estimate parameters. These approaches range from local state Isomorphism Theorem to Taylor series expansion approach (Pohjanpalo, 1982; Chappell & Godfrey, 1990; Noykova, 2002; Noykova et al., 2002). In the case of estimation of the model parameters using experimental data, model outputs and experimental data are compared and output curves are fitted using numerical methods such as least squares of quadratic estimation methods or heuristic method using human judgment and a "best fit" quantification method (Dochain & Vanrolleghem, 2001). In the numerical estimation, objective function defining the model's fit is optimized by manipulating the parameters. In other words, the difference between model outputs and measured data is minimized by adjusting the parameters. This estimation method is limited by the dependency of the model parameters on each other, and the occurrence of local optima. For models with a large number of parameters, the heuristic method by which reasonable parameter set is selected by assessing the curve fit can be used. In the case of parameter estimation using system tests, the parameter of concern is isolated in a single test. This method is time consuming, and may not be applied for all the parameters of the model. In the dissertation, numerical parameter estimation methods optimizing predefined objective function are used.

4.6 Model Parameter Identifiability

Two different numerical parameter estimation methods were used to estimate the parameters of the model with high variability and sensitivity. These were described below.

Structural (theoretical) and practical identifiability of the parameters needs to be checked to continue with the estimation. For the determination of structural identifiability, the unknown subset of the model parameters, $\mathbf{p}_2$ is tested using structural identifiability methods. The possibility of determination of every unknown parameter in $\mathbf{p}_2$ using precise and noiseless experimental data is evaluated by using structural identifiability methods. For this evaluation, the Taylor series expansion method can be used. In this method, the AD model can be represented as follows:

$$Mp_2\left\{\begin{array}{c}\dot{x}(t,\mathbf{p}) = f(x(t,\mathbf{p}),t,\mathbf{p}) \\ y(t,\mathbf{p}) = g(x(t,\mathbf{p}),t,\mathbf{p}) \\ x_0 = x(t_0,\mathbf{p})\end{array}\right\} \tag{4.3}$$

Where the parameter vector, $\mathbf{p}$ is:

$$\mathbf{p} = [\mathbf{p}_1, \mathbf{p}_2]^T \tag{4.4}$$

, and vector of known parameters, $\mathbf{p}_1$ is:

$$\mathbf{p}_1 = [\mathbf{C_{so}(0)}, \mathbf{C_{x1}(0)}, \mathbf{C_{s1}(0)}, \mathbf{C_{x2}(0)}\ldots, \mathbf{k_{S1}}, \ldots. \mathbf{K_i}\ldots. \mathbf{Y_b}, \ldots \mathbf{Y_g}] \tag{4.5}$$

, and vector of unknown parameters, $\mathbf{p}_2$ is:

$$\mathbf{p}_2 = [\mu, \mathbf{k_S2}, \mathbf{Y_3}\ldots.], \tag{4.6}$$

and f and g are nonlinear vector functions defining the known coupling parameterized by the parameter vector $\mathbf{p}$.

In the Taylor series approach, measurable output y(t), and its successive time derivatives, are evaluated in terms of the unknown model parameters $\mathbf{p}_2$ at a particular time, generally t =0, as:

$$y(t,p_2) = y(0,p_2) + y^{(1)}(0,p_2)t + y^{(2)}(0,p_2)\frac{t^2}{2} .. + y^{(i)}(0,p_2)\frac{t^i}{i!} \tag{4.7}$$

Where $y^{(i)}$ is:

$$y^{(i)}(0,\mathbf{p}_2)=\frac{d^i y}{dt^i}(0,\mathbf{p}_2)) \tag{4.8}$$

All the derivatives of the measurement vector are unique since the measurement vector itself is unique. Then, the problem of showing the identifiability of parameters $\mathbf{p}_2$ reduces to determination of the number of solutions for $\mathbf{p}_2$ for a set of algebraic equations as:

$$g^{(k)}(0,\mathbf{p})=y^{(k)}(0,\mathbf{p}_2) \quad k=0,.....,\infty \tag{4.9}$$

Where: $g^{(k)}$ =The k^{th} derivative of the vector function g.

If the set of solutions is uncountable, the parameter $\mathbf{p}_2$ is unidentifiable. If the set of solutions are countable, the parameter $\mathbf{p}_2$ is locally identifiable. If there is a unique solution, $\mathbf{p}_2$ is globally identifiable (Chappell & Godfrey, 1990; Noykova et al., 2002).

Practical identifiability of the parameters depends on the quality of the data and their informational value (Dochain & Vanrolleghem, 2001; Noykova, 2002; Noykova et al., 2002). The practical identifiability can be assessed using sensitivity analysis (Reichert, 1994; Dochain & Vanrolleghem, 2001; Noykova, 2002; Noykova et al., 2002). In the sensitivity analysis, the effects of a small deviation in the parameter set on the fit of the model data is investigated using sensitivity functions (Noykova et al.; 2002; Dochain & Vanrolleghem, 2001). Relative sensitivity or logarithmic sensitivity functions are generally used for sensitivity analysis since they are non-dimensional and allow comparison of results for different parameters and variables. The logarithmic sensitivity function is defined as follows:

$$T_{Q_i} = \frac{\partial \ln Q}{\partial \ln p_i} \qquad i=1,2,..n \qquad (4.10)$$

Where Q = Output measurable parameter

p_i = Parameter for which sensitivity is evaluated

If the sensitivity functions are linearly dependent, the model is not practically identifiable (Noykova et al., 2002).

4.7 Modeling Error and Relevant Statistics

The average error of modeling could be found by:

$$E_a = \frac{1}{N} \sum_{i=1}^{N} (O_i - S_i) \qquad (4.11)$$

Where: N = Number of observations.

O_i = Observation value i.

S_i = Simulated value corresponding to O_i.

The unit of the average error is the same unit as the observed and simulated values. The relative error can be found by:

$$E_a = \frac{\sum_{i=1}^{N} |O_i - S_i|}{N} x100\% \qquad (4.12)$$

The relative error is calculated by normalizing the magnitude of the error by the magnitude of the observations. These two error estimates indicate whether or not the model consistently over predicted or under predicted the observed data. Therefore, large positive errors could balance out large negative errors and yield small error estimates.

Root-mean-square error (RMSE) can be used to avoid this case. The RMSE is found by:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(O_i - S_i)^2}{N}} \tag{4.13}$$

The RMSE has the same units as the original observations. A low value of RMSE indicates high precision. RMSE of zero indicates perfect precision. Normalizing the RMSE to the average observed value, O_a gives the dimensionless coefficient of variation, C_V, as:

$$C_V = \frac{RMSE}{O_a} \tag{4.14}$$

The correlation coefficient, r, and the coefficient of determination, r^2, describe the degree of correlation between simulated and observed data. The correlation coefficient equation is given below:

$$r = \frac{N\sum_{i=1}^{N} O_i S_i - \sum_{i=1}^{N} O_i \sum_{i=1}^{N} S_i}{\sqrt{\left[N\sum_{i=1}^{N} O_i^2 - (\sum_{i=1}^{N} O_i)^2\right]\left[N\sum_{i=1}^{N} S_i^2 - (\sum_{i=1}^{N} S_i)^2\right]}} \tag{4.15}$$

The correlation coefficient, r approaches unity when the simulated data set is perfectly correlated with the experimental data set. The coefficient approaches zero when the data sets were completely uncorrelated. The coefficient of determination of 0.8, for example, indicates that the model explained 80 percent of the variability in the observed data.

4.8 Model Parameter Estimation Methods

The model parameter estimation is carried out using two different methods. These methods were the nonlinear constrained optimization method and the secant method. These two methods are explained in the following paragraphs.

a. Nonlinear constrained optimization:

The parameters of the high sensitivity and variability can be estimated using the optimization toolbox of MATLAB and non-linear constrained optimization method, if information about the boundaries of the parameters is available. The optimization criterion is selected as:

$$\text{CRIT}(\mathbf{p}_2) = \text{CRIT}_1(\mathbf{p}_2) + \text{CRIT}_2(\mathbf{p}_2), \tag{4.16}$$

and

$$CRIT(\mathbf{p2}) = \sum_{i=0}^{N} wi(Q^i(p2) - Q^i{}_{\exp})^2, j = 1,..,3 \tag{4.17}$$

Where: $w_i = \dfrac{1}{error_i}$ = The weighting coefficient

$\mathbf{p}_2$ = Parameter vector to be estimated

N = Number of the data points

b. Two-parameter optimizations around optimum using the secant method: Two-parameter optimizations around optimum using the secant method was implemented by Reichert (1994). The nonlinear parameter and uncertainty estimation procedure, minimizing the objective function, J, is used for the estimation of the model parameters. If the residuals are normally distributed, a critical value, J_{crit}, that defines the surface of

the parameter uncertainty region, can be defined using the F distribution (Batstone, 2003):

$$J_{crit} = Jopt\left(1 + \frac{p}{N_{data} - p} F_{\alpha, p, N data - p}\right) \quad (4.18)$$

Where: J_{crit} = Critical value

N_{data} = Number of data points measured

P = Number of parameters

$F_{\alpha, p, N data - p}$ = The value of F distribution for α, p, and N_{data-p}. α = 0.05, $F_{0.05, 2, \infty}$ = 2.996 has been used to estimate 95 percent confidence regions. The parameters defining the 95 percent confidence space are found using the gradient search technique, with the initial estimate based on the linear parameter uncertainty. The base objective function used was:

$$J = RSS = \sum (y - \bar{y})^2 \quad (4.19)$$

Where: J = Objective function

Y= Measured value

$\bar{y}$ = Simulated value

For log normally distributed data the following can be used

$$J = RSS = \sum (\ln(y) - \ln(\bar{y}))^2 \quad (4.20)$$

This formulation allows the normal distribution of the residuals. Therefore, the formulation yields F distribution in J.

4.9 Model Parameter Estimation

Many of the biochemical, physicochemical and physical parameters were taken from the scientific and technical report of the International Water Association (IWA) task group, research of Masse & Droste, and Chynoweth et al. (Chynoweth et al., 1998a; Batstone et al., 2002b; Masse et al., 1996; Masse et al., 1997; Masse & Droste, 1997; Masse & Droste, 2000). These values were used as an initial estimate of the parameters. Stochiometric coefficients were also taken from the same report. Carbon and nitrogen contents were recalculated by implementing the balance terms in the rate equation matrix. Physicochemical parameters are taken from the report and other resources (Stumm & Morgan, 1996; Batstone et al. 2002b). The mass balance has been checked for COD, carbon and nitrogen contents using the Excel spreadsheet developed by Batstone et al. (2002). Most of the kinetic parameters are assumed to be fixed due to their low variability (Batstone et al., 2002b). Sensitivity analysis results obtained by the IWA task group during the development of ADM1 were used to reduce the number of the parameters to be estimated. Parameters with low sensitivity and variability were taken from the literature (Batstone et al. 2002b). Parameters with high variability and limited sensitivity were taken from the research on similar processes (Masse et al., 1996; Masse et al., 1997; Chynoweth et al., 1998a; Masse & Droste, 1997; Masse & Droste, 2002). Physical parameters such as overall mass transfer coefficient, k_La or total gas pressure, p_T in the headspace are set to a fixed value, since they are dependent on the reactor configuration used (Pauss, Andre, Perrier, & Guiot, 1990). The overall model parameters, variables, and coefficients are given in Appendix B.

Parameters with high sensitivity and high variability are estimated using experimental data of Siegrist et al., 2002; Masse et al., 1996; Masse et al. 1997; Masse & Droste, 2002; and the selected optimization methods (Masse et al., 1996; Masse et al. ,1997; Masse & Droste,1997, Masse & Droste, 2002; Siegrist et al., 2002). The nonlinear constrained optimization method was implemented using MATLAB 6.5 optimization toolbox. The two-parameter optimization around optimum using the secant method is implemented using Aquasim 2.1d version. Estimation procedures were applied for the following parameters:

a. The disintegration constant, k_{dis}.

b. Maximum uptake rates for acetate and propionate utilizers, $k_{m,ac}$, $k_{m,pro}$.

c. Half saturation constants for acetate, propionate and hydrogen utilizers, $K_{S,ac}$, $K_{S,pro}$, $K_{S,\,H2}$.

The parameter estimation started with the parameter affecting the entire process, disintegration constant, k_{dis}. The experimental data details are explained in the following paragraphs.

One of the data sets used for optimization was generated by Siegrist et al. by laboratory experiments (Siegrist et al., 2002). The experimental set-up, included a laboratory scale plant with two reactors in series, a thermophilic reactor and a mesophilic reactor. Total gas pressure in the reactor was 0.95 bar. The following parameters were measured:

d. Inflow

e. Operating temperature

f. Total chemical oxygen demand, TCOD

g. Soluble chemical oxygen demand, SCOD

h. pH

i. Biogas flow and CH_4, CO_2, and H_2 content of the biogas

j. Acetate

k. Propionate

l. Ammonium

m. Bicarbonate

The raw sludge used was a mixture of primary, secondary and tertiary sludge from a municipal treatment plant with chemical phosphate precipitation. The sludge was added in 30-60 minutes time intervals, and one batch of sludge was used for 2-3 months. The average composition of the sludge used in the experiments was 40 g total COD/l, 4.5 gr soluble COD/l, 1.5 gr of acetate/l, 0.7 gr of propionate/l, 0.4 gr of NH_4-N/l, 1.6 gr N_{tot}/l, and pH was 6.8 (Siegrist et al. 2002). The total COD measured was divided into the following components: 40% soluble inerts, 30% particulate degradable and 30% hydrolysis products (Siegrist et al. 2002). The hydrolysis products are divided into 6% sugars, 9% proteins, 15% LCFA, and 1.5% percent inert soluble COD.

The second data set was generated from the experiments of Masse (1995). The experiments were carried out using 42 liter plexiglass sequencing batch reactors. The manure slurry was obtained from storage gutters under a partially slatted floor in a growing-finishing barn at a commercial swine operation (Masse 1995, Masse & Droste, 1996). The reactors were fed swine manure slurry. The slurry was collected on three occasions and frozen. It was thawed and fed to the reactor. The C, H, O and N content of particulate organics in the slurry was $C_{1.0}H_{1.9}O_{1.0}N_{0.1}$. Particulate COD was ranging

from 43 percent to 53 percent of the total COD. The sludge C, H, O, N contents were calculated on three separate occasions These calculations yielded formulas $C_{5.0}H_{8.7}O_{1.8}N_{0.76}$, $C_{5.0}H_{9.0}O_{1.68}N_{0.70}$, and $C_{5.0}H_{9.4}O_{0.67}N_{1.8}$. The mixing was provided by the evolution of the gas from metabolism. Long cycle times were allowed to obtain good treatment. Sludge composition of $C_5H_7O_2N$ was used. The following parameters were measured:

a. Inflow
b. Operating temperature (20°C fixed operating temperature)
c. Total chemical oxygen demand, TCOD
d. Soluble chemical oxygen demand, SCOD
e. pH
f. Biogas production and its composition (i.e., CH_4, CO_2, and H_2 content)
g. Total Kjeldahl Nitrogen, TKN (i.e, organic nitrogen and ammonia)
h. Alkalinity (measured as gr $CaCO_3$/l)
i. Total solids
j. Volatile solids
k. Volatile acids (i.e., acetic, propionic, butyric acids)

The physical reactor parameters were taken from the experimental set-ups for both datasets and applied to the model. The operating temperatures were 35°C and 20°C for experiments of Siegrist (2002) and for experiments of Masse (1995) respectively. All simulations were run to steady-state using a constant input including a constant flow rate that was given through the initial conditions of the dynamic experiments, to avoid numerical problems that could occur when starting a simulation with dynamic input. The

prior simulations were run over an integration period of 200 days to find the effective steady state. Generally it is recommended to run the steady-state simulation for at least five times the hydraulic retention times to reach the sufficiently accurate steady state (Siegrist et al., 2002). In the experimental data used, the HRT is 20 days for the mesophilic set of experiments of Siegrist et al. (2002) and 28 days for the experiments of Masse et al. (1995). The overall estimation procedure is shown in Figure 4.3.

4.10 Parameter Estimation Results

Initial and optimized parameters are shown and discussed briefly in this section. The results of the parameter estimation indicate a good fit between the model and the measured data. Parameters with low sensitivity and low variability have not been optimized after carrying out sensitivity analysis using Aquasim 2.1d software, and evaluating prior research results for the similar cases. These are taken directly from the literature since there are a large number of parameters for the model (i.e., 37 model parameters), and the effect of these parameters on the model outcomes is quite limited (Batstone et al., 2002a).

Optimization of the low sensitivity parameters has not been carried out since further tuning of these parameters requires highly accurate experimental data, and changes in the model outputs would be relatively small as compared to errors in the data. The parameters selected for the optimization in the research are typical (i.e., similar to the ones generally selected for the optimization).

In the estimation procedure, the disintegration constant was first estimated by matching the model output with measured outputs for biogas flow. Then the outputs for acetate and propionate concentrations were changed by changing the half saturation

constants and maximum uptake rates for the acetate and the propionate degrading processes respectively. The K_m, K_S parameters for acetate and propionate utilizers were optimized together since they have the lowest correlation and the highest relevance (Batstone et al., 2003). The value ranges and optimum values for the parameters are given in Table 4.1.

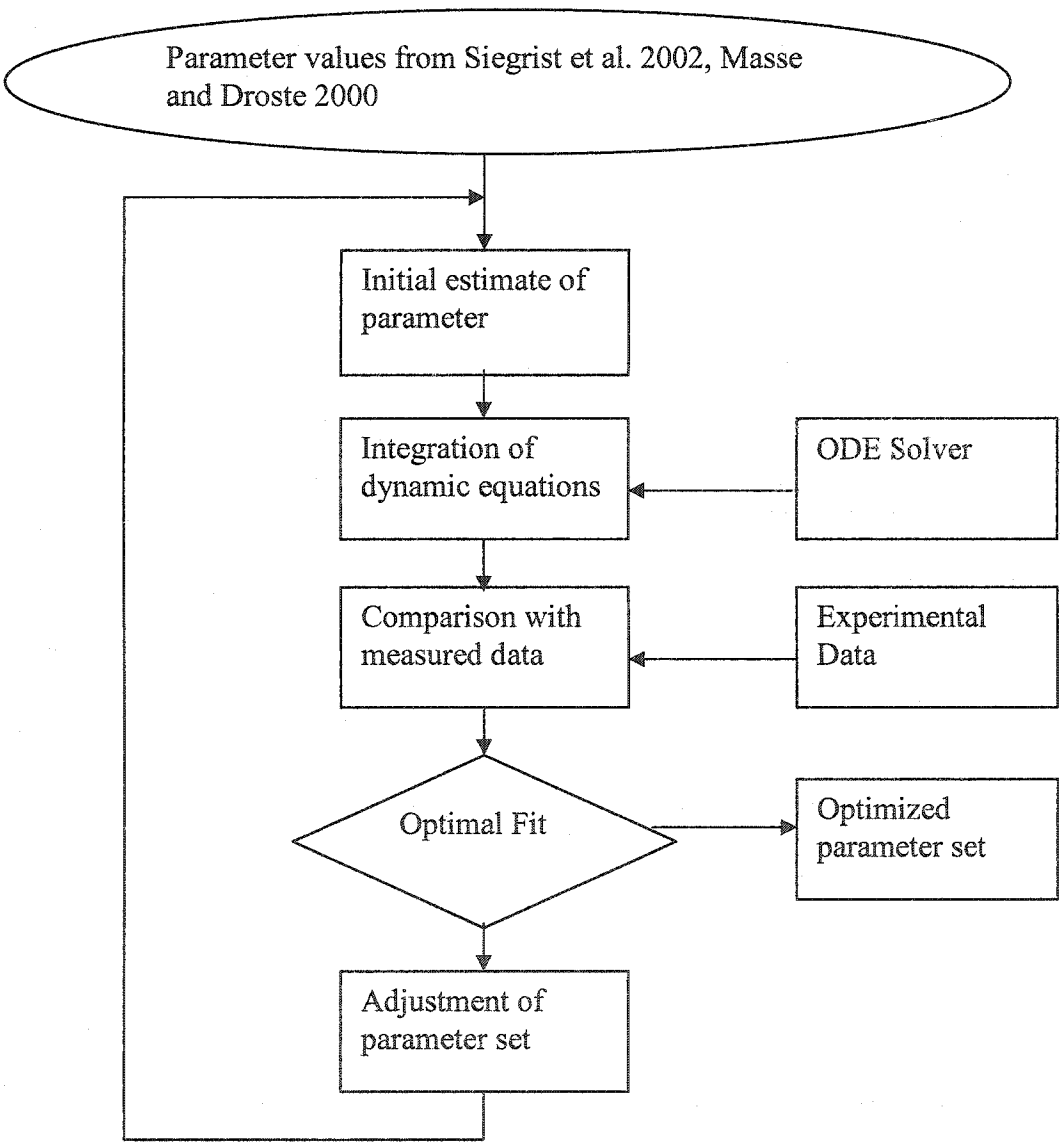

Figure 4.3 Overall estimation procedure

Table 4.1 Parameter estimation results

Name	Description	Optimum Value (Range)	Unit
k_{dis}	Disintegration constant	0.75 (0.5-1.0)	d^{-1}
$K_{m,ac}$	Max uptake rate of acetate	9 (8-20)	kgCODS.kgCODX.d^{-1}
$K_{m,pro}$	Max uptake rate of propionate	9 (13-100)	kgCODS.kgCODX.d^{-1}
$K_{S,ac}$	Half saturation constant for acetate utilizers	0.15 (0.15-10)	kgCODAc. m^{-3}
K_{Spro}	Half saturation constant for propionate utilizers	0.20 (0.1-10)	kgCODPro. m^{-3}
K_{SH2}	Half saturation constant for H_2 utilizers	7.10^{-6} (7.10^{-6}-0.5)	kgCODH_2. m^{-3}

4.11 Summary

The parameter estimation step is a preliminary step for the modeling. At this step, parameters that are to be used in the modeling, are identified and estimated. In this chapter, general outline for the parameter estimation, theoretical and practical parameter identifiability, and the numerical methods used for the estimation of the parameters with high sensitivity and variability are explained. The experimental data sets used for the parameter estimation are described. The numerical methods have found to be a viable alternative for the estimation of parameters of the ADM1 with high sensitivity and high variability. The estimated parameter values were found within the limits cited in the literature for the Canadian waste stream (i.e., The parameters estimated using the numerical approaches are a realistic set) (Masse & Droste, 2000).

CHAPTER 5: THE MODIFIED MODEL VERIFICATION AND OPTIMIZATION

Colorado Pork LLC (CP) AD reactor data set was used to test the Modified Model. The Modified Model output was compared with the measured data. The reactor information, waste characteristics, validation and optimization results are summarized in the following sections.

5.1 Colorado Pork Reactor

Colorado Pork, LLC, Anaerobic Digester is a mesophilic, intermittently mixed anaerobic digester used for swine manure stabilization and biogas production near Lamar, Colorado. Data collection covers a period between April 2000 and April 2001 (Mattocks et al., 2002; Martin, 2003).

The facility houses 5000 sow breed saws to weaner pigs. Manure from the facility has low (deviation < 5 percent as percentage of averages) pH, CO_2, and CH_4 variability. Nearly 35 percent of farm needs were met by biogas, and 430.46 m^3 gas was burned per day on average. Over 130 tons of methane was destroyed during the project time.

The anaerobic digester is an in-ground concrete tank, 19.81 meters in width, 24.38 meters in length, and 4.27 meters in depth, and has a total volume of 2061.47 m^3 (V_{total}) operating volume of 1892.59 m^3 (V_{liquid}). This gives the volume of headspace as 168.88 m^3 (V_{gas}).

The digester is heated to maintain a temperature of approximately 39 °C (102 °F) using cooling system heat from an 80 kW engine-generator set which is used to generate

electricity from the biogas (Mattocks et al., 2002). Temperature fluctuation in the system is shown in Table 5.1 and Figure 5.1. Digester effluent is discharged to a storage and evaporation pond of approximately 45424.80 m^3 in volume (Martin, 2003).

The digester is operated as a fill and draw reactor on a 24-hour cycle with two 30 to 45 minute mixing episodes in one day. Influent flow through the digester decreased over the 12 months of data collection from 64.35 m^3 per day to 41.64 m^3 per day and averaged 52.41 m^3 per day (i.e., $6.07.10^{-4}$ m^3/sec) (Tables 5.2-5.4, Figures 5.2-5.4). During the first quarter, influent volume was 63.87 m^3/day. It decreased during the second quarter to 51.37 m^3/day and then further to 43.91 m^3/day during the third quarter. In the final quarter of the 12-month period of data collection, influent volume was 45.43 m^3/day. The decrease in digester hydraulic loading rate over time was the result of a trial and error process to reduce water use to a level that would generate a constant 47.32 m^3/day of digester influent flow. Design hydraulic retention time was estimated to be 40 days (Martin, 2003).

The AD system achieved 65.00 (Are you sure about these decimal places?) percent volatile solids (VS) reduction, 89.00 percent VFA reduction, 71.00 percent chemical oxygen demand (COD), 82.00 percent biochemical oxygen demand (BOD) reduction and 99.90 percent fecal coliform reduction (Tables 5.5, 5.6, Figures 5.5, 5.6). Large quantities of hydrogen sulfide (H_2S) was burned in the engine set.

Table 5.1 Temperature variation (Mattocks et al., 2002)

Months	Effluent (°C)	Mix Pit (°C)	Lagoon (°C)	Ambient (°C)
1	38.33	21.67	17.78	16.39
2	38.89	22.50	20.00	22.78
3	39.44	22.50	20.00	23.89
4	39.72	21.94	17.50	22.78
5	39.44	21.39	15.56	18.89
6	38.89	20.00	12.22	14.44
7	38.61	19.17	9.44	10.00
8	38.61	17.78	6.11	4.44
9	38.33	16.67	3.33	0.00
10	38.33	16.11	1.94	-3.89
11	38.89	15.56	1.67	-4.44
12	39.44	16.67	3.33	-2.78
13	40.00	17.50	6.94	3.33
Average	39.00	19.18	10.45	9.68

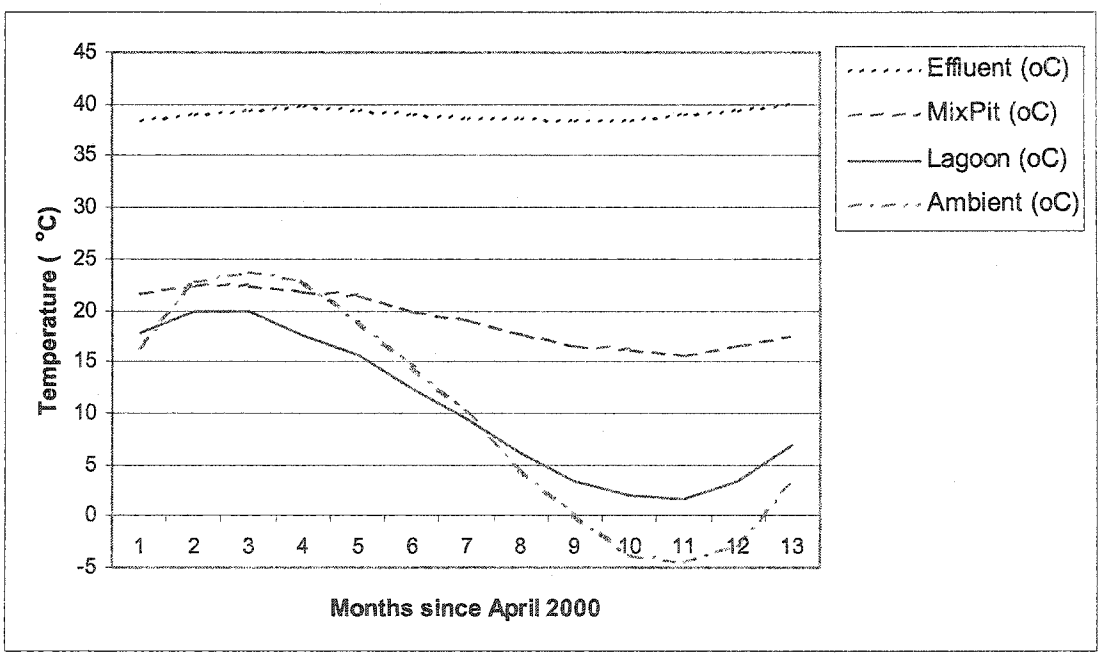

Figure 5.1 Temperature variation (Mattocks et al., 2002)

Table 5.2 Quarterly operations summary (Mattocks et al., 2002)

Month	Influent TS (kg/Day)	Influent VS (kg/Day)	Influent (m^3/day)	Biogas (m^3/day)	kWhr Sample Period	Flare Observed (%)	Engine operating time
1	3674.16	2268.00	64.35	702.36	11000	55	80
2	2993.76	1814.40	60.57	814.74	10000	30	88
3	2494.80	1587.60	58.67	899.02	10300	12	94.1
4	2268.00	1360.80	54.89	935.55	11200	10	97
5	2170.00	1360.80	53.00	941.16	12000	17	99
6	2041.20	1360.80	51.10	910.26	13000	32	99
7	2041.20	1360.80	48.45	842.83	13500	46	99
8	2100.00	1360.80	45.42	758.55	13800	59	97
9	2268.00	1360.80	44.29	682.70	14000	69	95
10	2268.00	1460.00	43.15	646.17	14000	78	93.6
11	2268.00	1530.00	43.53	618.08	14000	83	92.6
12	2268.00	1550.00	45.42	618.08	13500	78	92
13	2041.20	1360.80	47.32	632.13	13000	65	92

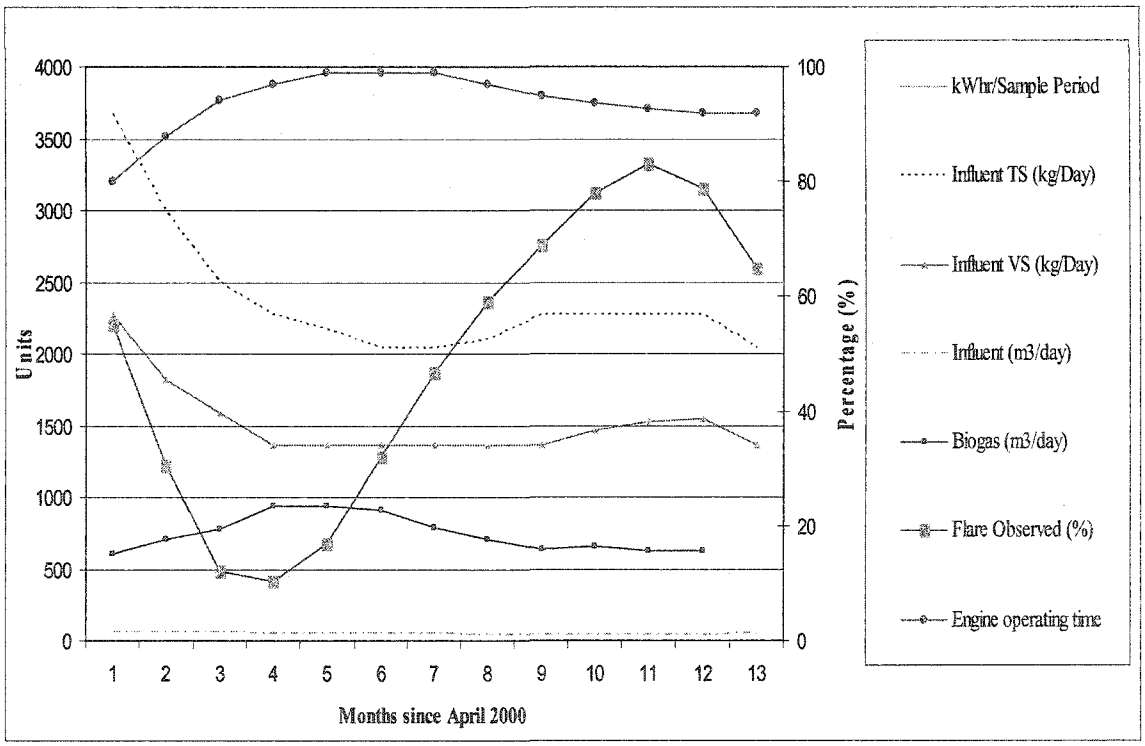

Figure 5.2 Quarterly operations summary (Mattocks et al., 2002)

Table 5.3 Water usage and feed rate (Mattocks et al., 2002)

Months	Manure Fed (m^3/day)	Water Usage (m^3/day)
1	64.35	87.06
2	62.46	83.28
3	59.43	77.60
4	55.65	71.92
5	51.86	64.35
6	48.83	54.89
7	46.18	46.18
8	45.05	41.26
9	43.91	38.61
10	43.15	37.85
11	43.15	38.23
12	43.53	40.50
13	44.67	44.29

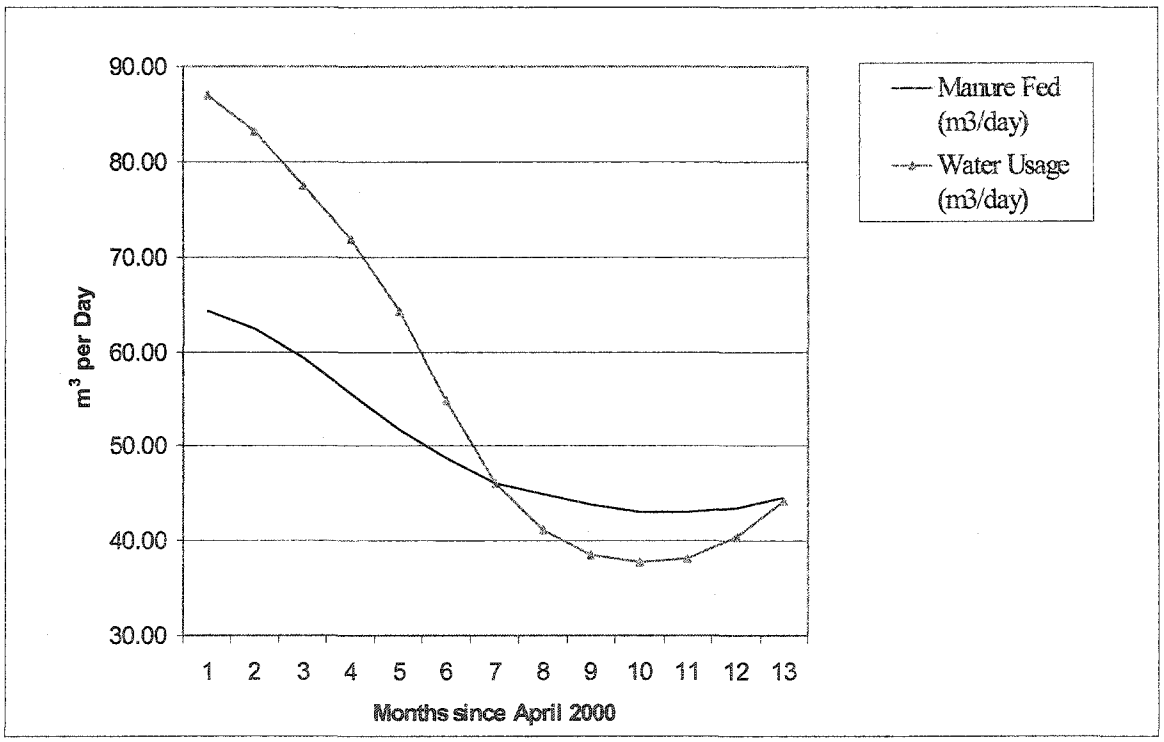

Figure 5.3 Water usage and feed rate (Mattocks et al., 2002)

Table 5.4 Energy sources (Mattocks et al., 2002)

Month	VFA (kg/day)	BOD (kg/day)	VS (kg/day)	COD (kg/day)
1	453.60	1496.88	2177.28	5443.20
2	453.60	1315.44	1814.40	4944.24
3	430.92	1224.72	1542.24	4395.38
4	408.24	1224.72	1406.16	3991.68
5	362.88	1242.86	1338.12	3515.40
6	317.52	1315.44	1292.76	3129.84
7	272.16	1360.80	1315.44	2789.64
8	249.48	1451.52	1315.44	2617.27
9	226.80	1496.88	1360.80	2449.44
10	226.80	1496.88	1406.16	2358.72
11	226.80	1440.18	1428.84	2268.00
12	226.80	1297.30	1428.84	2268.00
13	272.16	952.56	1406.16	2313.36

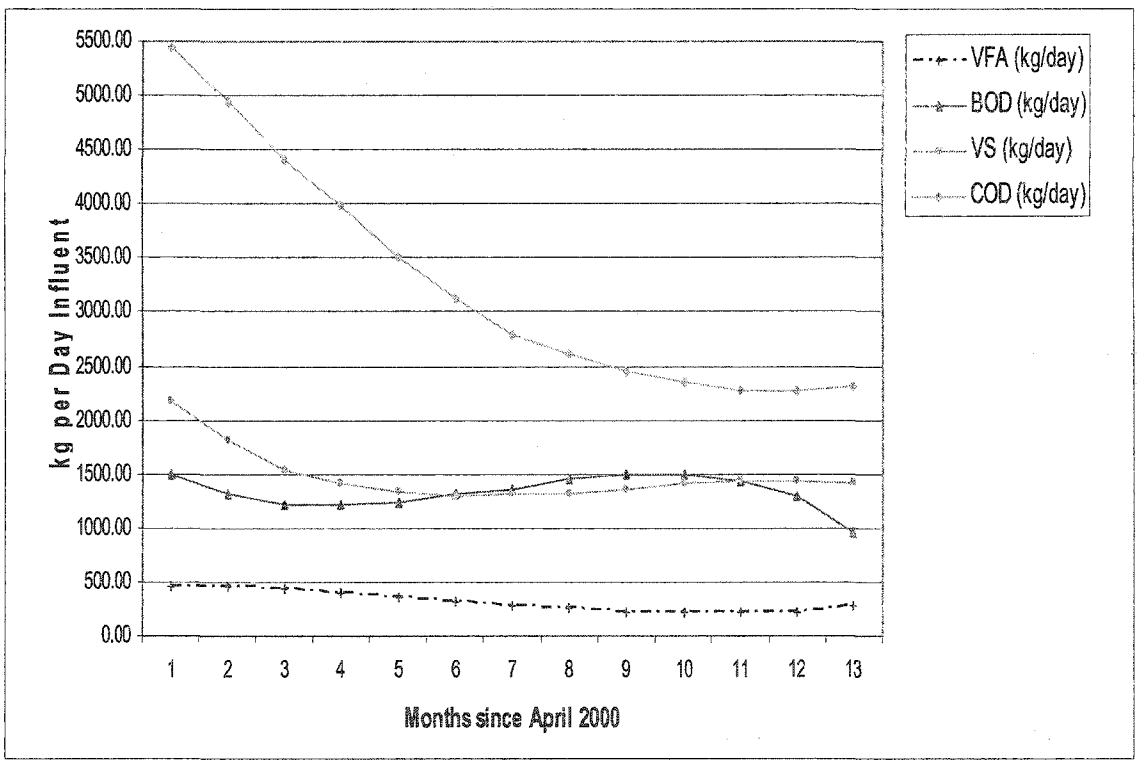

Figure 5.4 Energy sources (Mattocks et al., 2002)

Table 5.5 Contaminate reductions (Mattocks et al., 2002)

Months	Fecal Coliform	HRT (days)	VFA (%)	BOD (%)	COD (%)	VS (%)	TS (%)
1	100.00	32.50	89.00	84.00	75.00	66.00	58.00
2	100.00	35.00	91.00	82.50	73.80	65.00	57.00
3	100.00	37.00	93.00	82.00	72.50	64.00	56.00
4	100.00	39.30	94.00	81.50	71.40	63.50	55.00
5	100.00	41.10	95.00	81.00	70.40	63.50	54.60
6	100.00	42.90	95.00	81.00	69.30	63.50	54.00
7	100.00	43.80	95.00	81.00	68.50	63.50	54.00
8	100.00	44.60	94.00	81.00	67.50	64.00	54.00
9	100.00	45.00	92.30	81.50	67.00	64.00	54.50
10	100.00	45.00	90.00	82.00	66.50	64.50	55.00
11	100.00	45.00	87.20	82.50	66.00	65.00	55.50
12	100.00	44.50	84.00	83.00	65.80	65.50	56.40
13	100.00	44.00	80.00	83.50	65.70	66.00	57.50

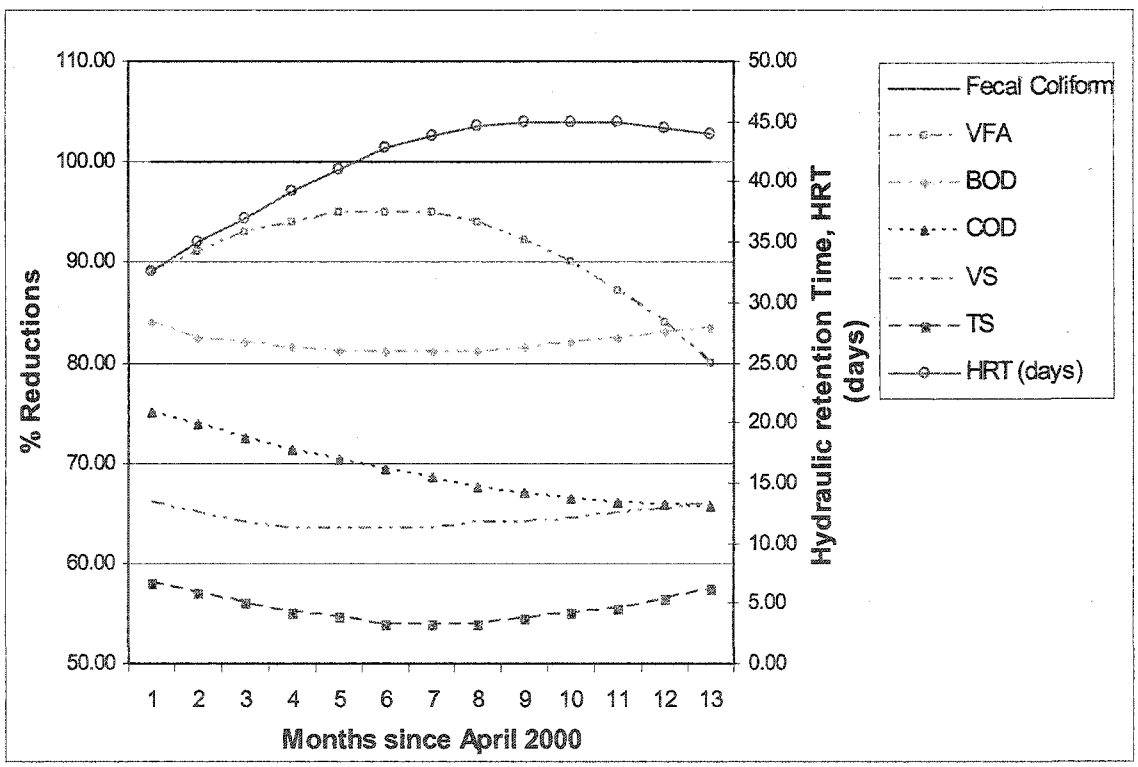

Figure 5.5 Contaminate reductions (Mattocks et al., 2002)

Table 5.6 Coliform counts (Mattocks et al., 2002)

Sampling Time	Coliform Influent (colonies/3.8 m^3)	Coliform Effluent (colonies/3.8 m^3)	Percent Reduction in Coliforms
1	2.95E+10	1.05E+08	99.65
2	2.29E+10	9.12E+07	99.60
3	1.70E+10	9.12E+07	99.46
4	1.51E+10	8.00E+07	99.47
5	1.26E+10	7.50E+07	99.40
6	1.17E+10	6.50E+07	99.45
7	1.12E+10	6.00E+07	99.47
8	1.12E+10	5.13E+07	99.54
9	1.15E+10	4.17E+07	99.64
10	1.32E+10	3.31E+07	99.75
11	1.51E+10	2.40E+07	99.84
12	1.66E+10	1.86E+07	99.89
13	2.04E+10	1.41E+07	99.93
14	2.45E+10	1.20E+07	99.95
15	2.75E+10	1.00E+07	99.96
16	3.24E+10	9.00E+06	99.97
17	3.89E+10	8.00E+06	99.98
18	4.57E+10	7.50E+06	99.98
19	4.90E+10	7.00E+06	99.99
20	5.25E+10	7.00E+06	99.99
21	5.37E+10	8.00E+06	99.99
22	5.13E+10	1.00E+07	99.98
23	4.90E+10	1.26E+07	99.97
24	4.68E+10	1.74E+07	99.96
25	4.47E+10	2.34E+07	99.95
26	4.47E+10	2.75E+07	99.94

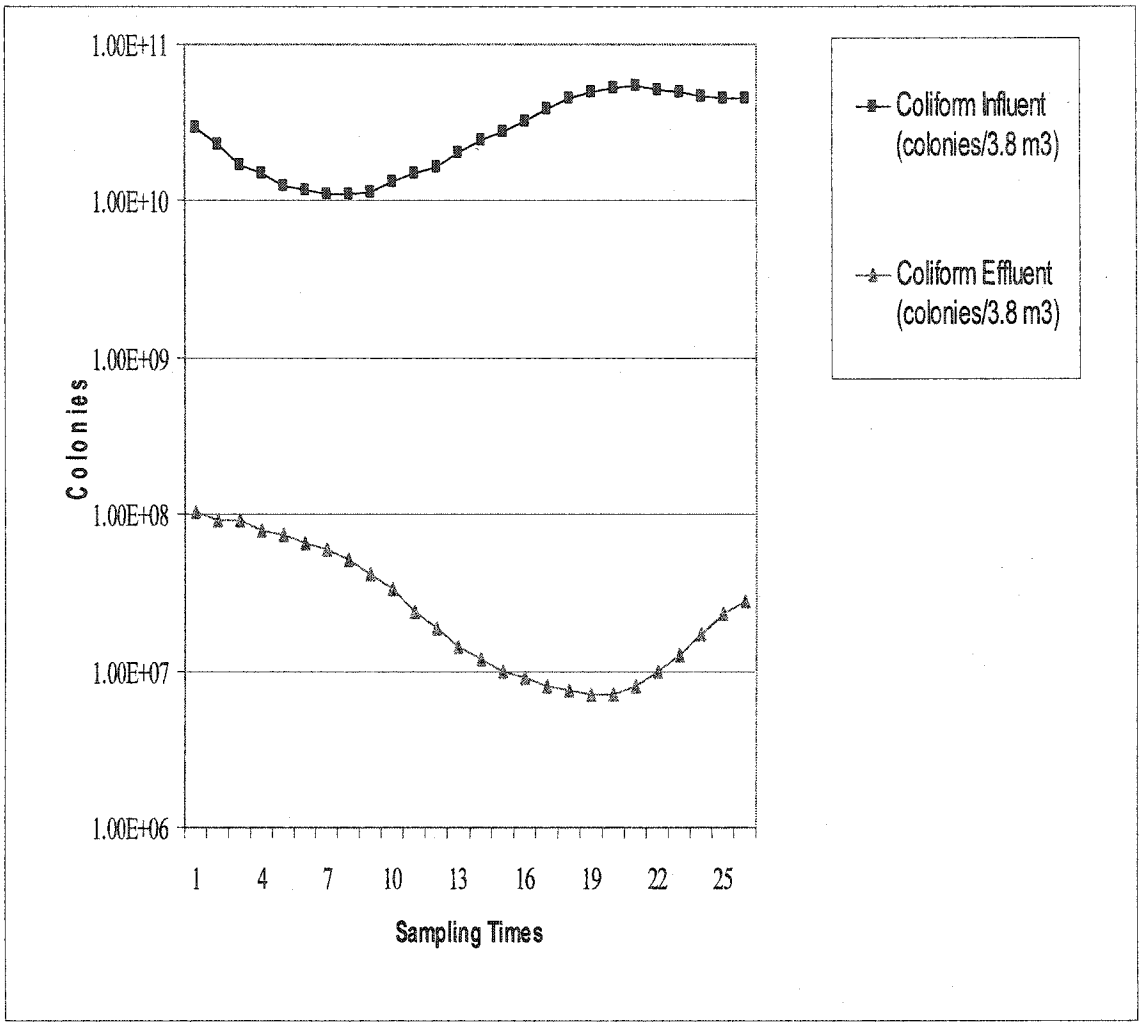

Figure 5.6 Coliform counts (Mattocks et al., 2002)

5.2 Organic Waste Characteristics

Characteristics of piggery waste are summarized in Tables 5.7-5.11. Swine waste is characterized by a pH slightly above neutral, high and sometimes toxic levels of ammonia, significant levels of volatile solids, COD, phosphorus, ortho-phosphorus, pathogens and coliform bacteria indicative of the fecal pollution (Chynoweth et al., 1998a; Chynoweth et al., 1998b).

Table 5.7 Body mass, waste production, and other characteristics per 1000 kg of swine (Chynoweth et al., 1998a)

Characteristic	Mean	Standard Deviation
Live Weight, kg	61.00	--
Total manure, kg	84.00	24.00
Urine, kg	39.00	4.80
Density, kg/m^3	990.00	24.00
Total Solids, kg	11.00	6.30
Volatile Solids, kg	8.50	0.66
COD, kg	8.40	3.70
BOD_5, kg	3.10	0.72
pH	7.50	0.57
Total Kjeldahl nitrogen, TKN kg *	0.52	0.21
Ammonia-N, kg *	0.29	0.10
Total P, kg	0.18	0.10
Ortho-P, kg	0.12	--

Notes: * Measure of organic nitrogen (N) and ammonia (NH_3) (reduced forms)

Table 5.8 Production and characteristics of fresh manure by pigs (Chynoweth et al., 1998a)

Characteristic	Nursery	Growing	Finishing	Gestation Sow	Sow and Litter	Boar
Live Weight, kg	15.9	29.5	68.1	125	170	159
Manure kg/day	1	1.9	4.4	4	14.9	5
Total Solids, kg/day	0.0091	0.18	0.41	0.36	1.36	0.45
Volatile Solids, kg/day	0.0077	0.14	0.33	0.30	1.09	0.420
BOD_5	0.032	0.059	0.14	0.12	0.45	0.16
N kg/day	0.007	0.013	0.031	0.028	0.10	0.035
P_2O_5 kg/day	0.005	0.010	0.023	0.022	0.078	0.027
K_2O kg/day	0.005	0.11	0.024	0.022	0.082	0.028

Table 5.9 Swine waste characteristics from storage tanks under slats (Chynoweth et al., 1998a)

Characteristic	Farrow	Nursery	Finish	Breeding
Moisture, kg	96.5	96	91	97
Total Solids, % w.b.	3.5	4.00	9.00	3.00
Volatile Solids, % w.b.	2.28	2.79	6.74	1.80
FS, % w.b.	1.22	1.71	2.26	1.20
N g/L	3.6	4.8	6.3	3.00
NH_4-N g/L	2.8	4.0	--	--
P, g/L	1.8	1.6	2.7	1.20
K, g/L	2.8	1.6	2.2	2.10
C:N ratio	4	3	6	3

Table 5.10 Swine waste characteristics from storage/treatment facilities (Chynoweth et al., 1998a)

	Anaerobic Lagoon	Feedlot		
Characteristic	Sludge	Supernatant	Settled Sludge	Runoff
Moisture, kg	92.4	99.8	88.8	98.5
Total Solids, % w.b.	7.60	0.25	11.2	1.5
Volatile Solids, %	4.68	0.12	90.7**	--
FS, % w.b.	2.92	0.13	21.3**	--
BOD5 g/L	--	0.40	--	--
COD g/L	64.6	1.2	--	--
N, g/L	3.0	0.35	5.6**	2.0**
NH4-N g/L	0.76	0.22	4.5**	1.2**
P, g/L	2.7	0.13	2.2**	0.38**
K, g/L	7.6	0.38	10.0**	1.10**
C:N Ratio	8	2	--	--

Notes: * Semi-humid climate, ** kg/d/1000kg of animal weight

Table 5.11 Digestibility of organic matter during anaerobic digestion of piggery wastes (Finishing hogs fed 14% protein ration with corn or milo; mesophilic digester with retention time of 15 days) (Chynoweth et al., 1998a)

Component	Influent	% Destroyed
TS, %	6.9	52
VS, %TS	82.6	60
COD, g/L	73.8	58
total N, g/L	3.9	--
Protein, %TS	19.3	47
hemicellulose, %TS	20.1	65
cellulose, %TS	12.4	64
lipids	14.8	69
starch	1.6	94
lignin	4.4	3

5.3. Data Collection and Details

Gary Swanson of Colorado Pork LLC. was responsible for onsite data collection. Monte Torres of Southeast Land and Environment was responsible for overall execution of the project. Richard Mattocks of Environomics was responsible for technical guidance for project planning, implementation, consolidation of data for review, and reporting (Mattocks et al., 2002).

Daily and periodic data samples were collected during 364 days period between April 2000 and April 2001. Sampling data collected for each of the reporting quarters approximately two-week time intervals at 26 sampling points. Sample collection details are noted in a sample day log sheet. Two samples were collected; one for freezing and one for shipment to Midwest Labs for analysis. Before sample collection from raw manure collection tank, the tank was mixed. Digester effluent samples were collected at the discharge point to the effluent storage structure. Samples were collected approximately at the same point in manure collection lagoon. At the same time gas

samples were collected from gas line in the pipe chase and were sent to Empact Analytical Systems for analysis. At one point in the project samples were further analyzed for viscosity, particle size distribution, heat value and density (Table 5.12 and Figure 5.7). Standard analytical procedures were used for sample testing

Daily manure and cogeneration system parameters were recorded. The daily data included gas metering, energy generation, temperature, flare activity and other operational measurements. Manure samples were collected at the influent collection and mixing tank (digester influent), at the effluent collection chamber (digester effluent), and at the effluent storage structure sequentially on the same day.

Table 5.12 Particle size distribution (Mattocks et al., 2002)

Sieve Number	Opening, mm	Digester Feed (passed % weight)	Digester Effluent (passed % weight)	Lagoon (passed % weight)
8	2.38	100	100	100
28	0.638	60	91	99
65	0.23	46	89	98
100	0.149	43	88	98
200	0.074	37	84	97
325	0.044	32	81	97
pan	--	0	0	0

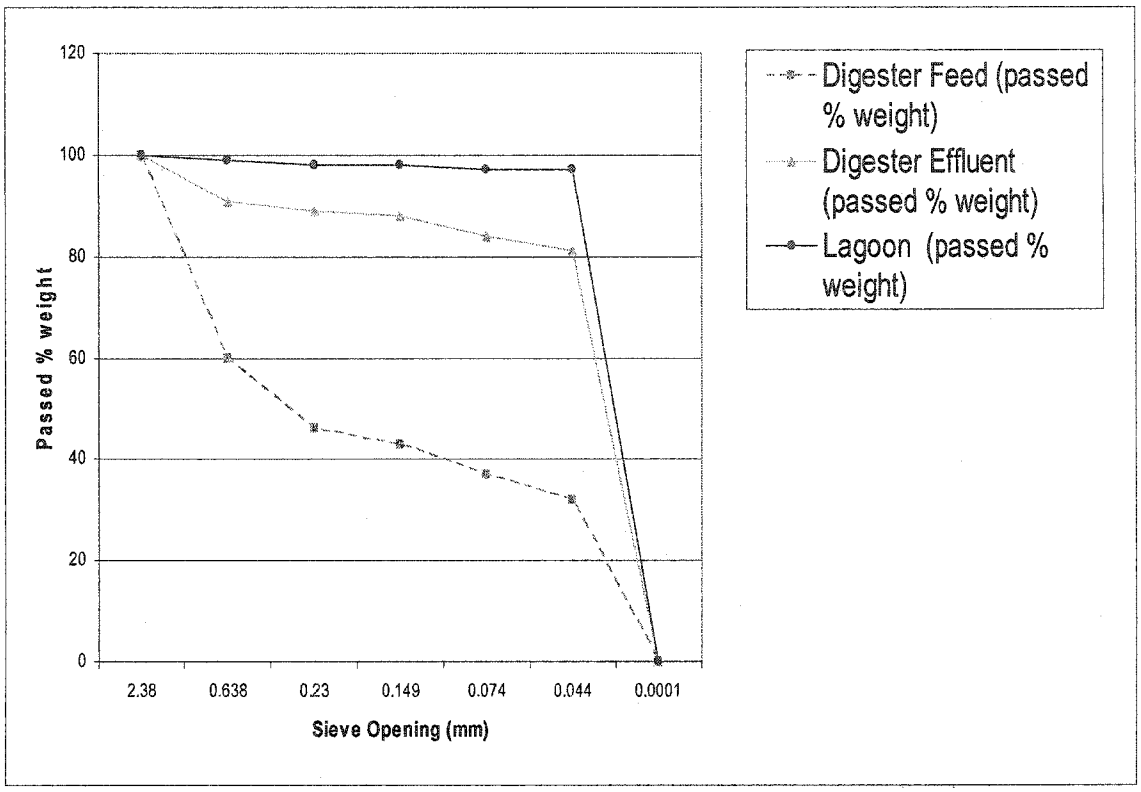

Figure 5.7 Particle size distribution (Mattocks et al, 2002)

Samples collected from the influent collection and the mixing tank were grab samples following the flushing of one of the pull-plug pits and after 30 minutes of mixing. Sampling depth was 0.31 m below the liquid surface. Samples of the digester effluent were collected from the effluent collection chamber, as influent was being pumped into the digester. The point of sample collection was at the point of discharge to the effluent storage structure. Four plastic sample containers (one 1 liter, two 250 ml, and one 125 ml) were filled during each sampling episode. Each container was filled from a composite of a minimum of three sub samples.

Samples of effluent storage structure contents were collected at three locations at the north end of the sediment trap, which is approximately 182.88 m from the point of digester effluent discharge. Each sampling location was 1.82 m from the end and at least

6.1 m from the sides of the storage structure. Four plastic sample containers (one 1 liter, two 250 ml, and one 125 ml) were filled during each sampling episode. Each container was filled from a composite of three sub samples from the three sample collection locations. All samples were collected at a depth of 0.31 m below the liquid surface when digested effluent was being discharged from the effluent collection chamber.

The one liter and 250 ml samples were received by the laboratory performing the physical and chemical analyses on the second day after sampling. The 125 ml samples are received by the same laboratory for microbial density determinations on the day following sample collection.

Biogas samples were taken from the pipeline delivering biogas to the engine-generator set. One liter Tedlar gas collection bags were used for sampling. All biogas samples were received by the laboratory performing the gas analyses, Empact Analytical Systems, Inc., Brighton, Colorado, on the day following the sample collection. Biogas sampling conducted on the same days as manure sampling.

Averages, standard deviations, and standard errors were provided for system operations, influent, effluent samples in Tables 5.13-5.15. There were 8, 7, 5, 6 sample dates with 12.3, 13.1, 18.2, and 13.8 days between sample dates for the first, second, third and fourth quarters respectively (Mattocks et al., 2002). More variation was observed in the early days than in the later days of sampling.

Digester HRT increased from 31.6 days in the first quarter to mid 40s in the last two quarters. Incoming manure average deviation was greater than the effluent and the lagoon average deviation. Fate of mass and total solids indicated accumulation in the digester (Tables 5.16 -5.20 and Figures 5.8-5.12).

The greatest deviations were observed for the micronutrients. In general, these nutrients are very low in concentration, and often approximate the lower sensitivities of the analytical equipment.

A comparison of the constituents entering the digester with those leaving the digester is given in Tables 5.21-5.23. Laboratory concentrations were multiplied by flow rates and liquid densities to determine the weight of constituents entering and leaving the system.

Mass, water, nitrogen and potassium entering the system closely approximated that leaving the digester. Total solids, volatile solids, volatile acids, COD and BOD are reduced as they are converted to biogas. Most of the nutrients exiting the digester were lower than the quantity entering. Both the Fate of Mass and Fate of Total Solids measurements indicated accumulation in the digester.

Gas characteristics were found to be similar throughout the project and summarized in Tables 5.24-5.29 and in Figure 5.13. Major constituents in the biogas were methane (CH_4), hydrogen sulfide (H_2S) and carbon dioxide (CO_2) (Figure 5.13). Variation of hydrogen sulfide (H_2S) with temperature is given in Table 5.27 and Figure 5.14. Small quantities of other gases were observed. Apparent viscosities of digested manure were 30-50 percent lower than the raw manure (Table 5.28).

Table 5.13 Digestion system operation information (Mattocks et al., 2002)

		1st Q 4/24-7/24			2nd Q 8/14-10/24		
		Average	AveDev	AvgDev %Avg	Average	AveDev	AvgDev %Avg
Days in Sample Period		12.3	3.9	32.10	13.1	3.3	24.80
Samples, Total		8			7		
Eng. Hours, %up		80	10.50	13.10	99	1.40	1.40
KWh/d	per day avg	873	374	42.80	1077	84	7.80
	kW avg	44.7	14.7	32.90	45.4	3.1	6.80
Facility kWh		1743	154	8.90	1510	199	13.20
Cogen meter, hr.		571	23	4.00	993	79	8.00
Total Farm Use, kWh/d		2314	131	5.70	2503	201	8.00
Farm from Cogen		25	2	9.70	0.4	0.04	9.60
Labor	Man hr/d	0.81	0.24	29.60	0.66	0.11	16.00
Down due to utility (hr)					4	0	0.00
perday avg,%					0.60	0.60	100.00
Facility water (m^3/day)		87	5	6.20	64	17	27.10
Gas moisture (kg/m^3)		0.010	0.003	32.90	0.039	0.013	33.60%
Gas meter (m^3/d)							
Biogas/day		698	229	32.90	930	141	15.10
M^3/kwh		0.95	0.32	33.60	0.86	0.11	13.00
Temperatures (°C)							
Ambient		16.56	-11.94	17.00	19.83	-9.33	22.40
Mix pit		21.61	3.50	4.90	21.50	19.50	4.40
Effluent		38.33	1.00	1.00	39.11	-17.22	0.90
Lagoon		18.06	5.10	7.90	15.89	-12.39	16.00
Influent/day, m^3		64	7.10	11.10	51	8.50	16.50

Notes: All on an "as delivered" basis: 1- on an "as delivered" basis; 2 kg/m^3, 3-MPN/g, 4-kg/m^3, 5-kg $CaCO_3/m^3$, 6-m^3/m^3/hr

Table 5.13 Digestion system operation information (Continued) (Mattocks et al., 2002)

		3rd Q 11/6-1/23			4th Q 2/5-4/16		
		Average	AveDev	AvgDev %Avg	Average	AveDev	AvgDev %Avg
Days in Sample Period		18.2	3.4	18.50	13.8	1.4	10.40
Samples, Total		5			6		
Eng. Hours, %up		97	2.80	2.90	93	8.80	9.40
kWh/d	per day avg	894	75	8.40	1056	108	10.20
	kW avg	38.4	2.9	7.60	47	1.4	3.00
Facility kWh		1597	98	6.10	1545	149	9.70
Cogen meter, hr.		837	66	7.90	995	134	13.50
Total Farm Use, kWh/d		2,434	47.22	1.90	2540	181	7.10
Farm from Cogen		34	3	8.90	39	3	7.60
Labor	Man hours/d	0.69	0.04	5.50	0.74	0.25	34.60
Down due to utility (hr)		11.2	10.64	95.00	0	0	
per day avg, %		2.30	2.10	89.40	0.00	0.00	
Facility water (m^3/day)		41	3.104028	7.60	44	6	14.20
Gas moisture (kg/m^3)		0.030	0.005	16.70			
Gas meter (m^3/d)							
Biogas/day		711	111,488	12.60	633	207	32.80
m^3/kwh		0.80	0.09	11.30	0.60	0.15	25.10
Temperatures (°C)							
Ambient		-0.44	-16.56	6.90	3.44	-14.89	13.70
Mix pit		16.78	-16.94	2.40	17.61	1.40	2.20
Effluent		38.56	-16.89	1.60	40.17	1.10	1.00
Lagoon		3.50	-15.44	10.90	7.06	5.00	11.10
Influent/day, m^3		43.91	2.00	5.50	45	0.00	0.00

Notes: All on an "as delivered" basis: 1- on an "as delivered" basis; 2 kg/m^3, 3-MPN/g, 4-kg/m^3, 5-kg $CaCO_3/m^3$, 6-m^3/m^3/hr

Table 5.14 Influent constituent averages by quarter (Mattocks et al., 2002)

	1st Q 4/24-7/24			2nd Q 8/14-10/24		
	Average	AveDev	AvgDev %Avg	Average	AveDev	AvgDev %Avg
m^3/day	63.88	7.10	11	51.3716 634	8.50	17
HRT (days)	31.6	3.4	11	39.9	5.6	14
Density[1] (kg/m^3)	1030.53	0	0	1030.53	0	0
Moisture[1]	94.70	2.10	2	95.90	1.20	1
T. Solids[1],%	5.30	2.10	40	4.10	1.20	30
V. Sol[1], %TS	68.50	15.70	23	63.20	4.80	8
N[1], % total	0.43	0.07	17	0.42	0.06	15
P2O5[1], %	0.31	0.06	20	0.47	0.14	29
K2O[1], %	0.20	0.03	14	0.25	0.04	16
S[1], %	0.03	0.02	75	0.05	0.01	23
Mg[1], %	0.03	0.02	85	0.07	0.02	36
Ca[1], %	0.09	0.07	81	0.20	0.07	33
Na[1], %	0.04	0.03	75	0.08	0.01	13
Fe[1], ppm	158.4	42.9	27	209.7	45.1	22
Al[1], ppm	47.2	13.4	28	60.4	16.2	27
Mn[1], ppm	19	6	32	24.4	7.1	29
Cu[1], ppm	8.4	2.1	25	10.7	2.6	24
Zn[1], ppm	72.6	11.9	16	98.3	24.2	25
Ash[1], %	2.10	1.20	57	1.50	0.33	22
pH[1]	7.72	2.87	37	8	0.2	3
NH4+[1], %	0.31	0.06	18	0.31	0.03	9
%avail	71	5.90	8	74.90	4.60	6
COD[1], kg/m^3	88.38	36.11	41	69.03	17.04	25
BOD[1], kg/m^3	24.73	4.74	19	25,39	8.25	33
Vol. Acids kg/m^3	7.73	1.67	22	7,35	1.28	17
Fecal Colif[3]	245,125	168,719	69	461,429	262,041	57
Total Sus Solids (kg/m^3)	63.750	-	0	-	-	0
Alkalinity[5]	11.26	1.81	16	13.74	2.066	15
Settle Solids[6]	0.483	0.194	40	0.193	0.154	80

Notes: All on an "as delivered" basis: 1- on an "as delivered" basis; 2 kg/m^3, 3-MPN/g. 4-kg/m^3, 5-kg $CaCO_3/m^3$, 6-$m^3/m^3/hr$

Table 5.14 Influent constituent averages by quarter (Continued) (Mattocks et al., 2002)

	3rd Q 11/6-1/23			4th Q 2/5-4/16		
	Average	AveDev	AvgDev %Avg	Average	AveDev	AvgDev %Avg
m^3/day	43.91	2.43	6	45.42	0	0
HRT (days)	45.5	2.8	6	43.8	0	0
Density[1]	1018.54	0.1	1	1018.54	0.07	1
Moisture[1]	95.30	1.40	1	95.80	1.40	1
T. Solids[1],%	4.70	1.40	30	4.20	1.40	32
V. Sol[1], %TS	61.20	6.70	11	70.70	8.00	11
N[1], % total	0.51	0.03	7	0.42	0.03	8
P2O5[1], %	0.50	0.12	25	0.40	0.25	63
K2O[1], %	0.28	0.02	6	0.25	0.02	7
S[1], %	0.06	0.01	15	0.05	0.01	27
Mg[1], %	0.06	0.03	47	0.05	0.05	93
Ca[1], %	0.24	0.07	30	0.18	0.14	76
Na[1], %	0.06	0.01	14	0.05	0.00	8
Fe[1], ppm	211	49.6	24	166	106.3	64
Al[1], ppm	58	14.4	25	39.2	26.6	68
Mn[1], ppm	26.6	7.4	28	20.8	16.1	77
Cu[1], ppm	12.6	3	24	10	6	60
Zn[1], ppm	104.6	25.4	24	75.7	51.6	68
Ash[1], %	1.70	0.28	16	1.20	0.35	30
pH[1]	8.16	0.07	1	8.3	0.1	1
NH4+[1], %	0.36	0.02	7	0.33	0.02	6
%avail	71.40	3.80	5	78.30	5.30	7
COD[1], kg/m^3	54.57	19.31	35	52.09	13.57	26
BOD[1], kg/m^3	34.40	17.47	51	21.73	4.252	20
Vol Acids	6.49	2.13	33	6,47	1.25	16
Fecal Colif[3]	654,000	212,800	33	1,033,333	377,778	37
Total Sus	-	-	0	-	-	0
Alkalinity[5]	14.50	0.83	6	14.54	-	0
Settle Solids[6]	0.177	0.145	82	0.9	0	0

Notes: All on an "as delivered" basis: 1- on an "as delivered" basis; 2 kg/m^3, 3-MPN/g. 4-kg/m^3, 5-kg $CaCO_3/m^3$, 6-$m^3/m^3/hr$

Table 5.15 Effluent constituent averages by quarter (Mattocks et al., 2002)

	1st Q 4/24-7/24			2nd Q 8/14-10/24		
	Average	AveDev	AvgDev %Avg	Average	AveDev	AvgDev %Avg
m^3/day	61.99	7.10	11	49.48	8.50	17
Density[1]	1006.56	0	0	1006.56	0	0
Moisture[1]	97.70	0	0	97.90	0.25	0
T. Solids[1],%	2.30	0	17	2.10	0.25	12
V. Sol[1], %TS	53.20	6	11	50.30	2.84	6
N[1], % total	0.45	0.05	11	0.39	0.01	2
P2O5[1], %	0.21	0.06	29	0.27	0.04	15
K2O[1], %	0.24	0.03	12	0.28	0.08	30
S[1], %	0.04	0.01	24	0.04	0.01	14
Mg[1], %	0.02	0.01	60	0.03	0.02	44
Ca[1], %	0.07	0.03	43	0.09	0.02	16
Na[1], %	0.07	0.01	19	0.09	0.03	30
Fe[1], ppm	122.2	38.3	31	145.6	16.5	11
Al[1], ppm	25	8.8	35	37.7	5.1	14
Mn[1], ppm	11.8	5.3	45	14.4	2.7	18
Cu[1], ppm	6.2	1.5	25	7.3	0.9	12
Zn[1], ppm	51.4	17	33	62.9	8.7	14
Ash[1], %	1.10	0.26	24	1.00	0.19	18
pH[1]	8.3	2.02	24	8.5	0.07	1
NH4+[1], %	0.37	0.04	11	0.30	0.01	3
%avail	81.60	2.45	3	77.40	2.28	3
COD[1], kg/m^3	21.53	3.69	17	22.04	2.07	9
BOD[1], kg/m^3	4	1	25	5	3	55
Vol Acids[2]	0.845	0.362	43	0.457	0.081	18
Fecal Colif[3]	1,066	900	84	421	565	134
Total Sus Solids[4]	16	-	0	-	-	0
Alkalinity[5]	15.29	0.44	3	14.40	0.44	3
Settle Solids[6]	0.056	0.053	94	0.014	0.012	86

Notes: All on an "as delivered" basis: 1- on an "as delivered" basis; 2- kg/m^3, 3-MPN/g , 4-kg/m^3, 5-kg $CaCO_3/m^3$, 6- $m^3/m^3/hr$

Table 5.15 Effluent constituent averages by quarter (Continued) (Mattocks et al., 2002)

	3rd Q 11/6-1/23			4th Q 2/5-4/16		
	Average	AveDev	AvgDev %Avg	Average	AveDev	AvgDev %Avg
m^3/day	42.02	2.42	6	43.53	0	0
Density[1]	1006.56	1.19	0	1006.56	8.38	1
Moisture[1]	97.90%	0.08	0	98.00%	0.28	0
T. Solids[1],%	2.10	0.08	4	2.00	0.28	14
V. Sol[1], %TS	52.90	3.13	6	55.90	2.18	4
N[1], % total	0.42	0.02	4	0.44	0.02	3
P2O5[1], %	0.21	0.05	25	0.23	0.06	26
K2O[1], %	0.24	0.02	7	0.27	0.00	1
S[1], %	0.03	0.01	14	0.04	0.00	0
Mg[1], %	0.01	0.01	63	0.02	0.02	109
Ca[1], %	0.07	0.02	28	0.08	0.02	31
Na[1], %	0.07	0.01	7	0.06	0.00	0
Fe[1], ppm	117.2	25.8	22	124.7	26.2	21
Al[1], ppm	27	7.6	28	25.5	7	27
Mn[1], ppm	9.8	3	30	10.7	3.9	36
Cu[1], ppm	7.2	1.8	26	7.3	1.8	24
Zn[1], ppm	52.2	11.4	22	55.3	9.8	18
Ash[1], %	1.00	0.10	10	0.90	0.16	18
pH[1]	8.5	0.14	2	8.5	0.16	2
NH4+[1], %	0.34	0.02	6	0.37	0.02	5
%avail	80.50	1.20	1	84.50	5.02	6
COD[1], kg/m^3	17.59	1.91	11	18.87	2.55	14
BOD[1], kg/m^3	7	2	24	4	0.535	14
Vol Acids[2]	0.461	0.116	25	1	1	100
Fecal Colif[3]	71	83	118	407	664	163
Total Sus. Solids[4]	-	-	0	-	-	0
Alkalinity[5]	14.92	0.691	5	-	-	0
Settle Solids[6]	0.056	0.051	91	-	-	0

Notes: All on an "as delivered" basis: 1- on an "as delivered" basis; 2- kg/m^3, 3-MPN/g. 4-kg/m^3, 5-kg $CaCO_3/m^3$, 6- $m^3/m^3/hr$

Table 5.16 Influent nutrients by period (Mattocks et al., 2002)

Months	TS *	VS *	VFA*	NH3-N*	P *	N *	K *	Ca *
1	5443.2	4082.4	453.6	317.5	226.8	360.3	186.0	99.8
2	4309.2	3175.2	499.0	249.5	214.1	294.2	172.4	95.3
3	3402.0	2721.6	499.0	204.1	205.9	249.5	163.3	95.3
4	3265.9	2585.5	453.6	181.4	205.9	225.8	149.7	104.3
5	3265.9	2585.5	430.9	172.4	205.9	205.9	140.6	113.4
6	3402.0	2585.5	408.2	158.8	205.9	191.7	131.5	117.9
7	3628.8	2585.5	373.8	158.8	205.9	199.8	131.5	117.9
8	3628.8	2630.9	340.2	158.8	205.9	195.7	131.5	117.9
9	3628.8	2630.9	317.5	158.8	205.9	199.8	131.5	117.9
10	3402.0	2630.9	308.4	158.8	193.9	193.9	131.5	113.4
11	3175.2	2608.2	308.4	149.7	190.0	190.0	127.0	104.3
12	3039.1	2585.5	340.2	149.7	179.3	188.2	127.0	95.3
13	2721.6	2585.5	362.9	158.8	172.1	184.4	136.1	81.6
Months	S *	Na *	Mg*	Fe *	Zn*	Al *	Mn*	Cu *
1	55.5	40.8	17.1	9.9	4.4	3.3	1.4	0.4
2	40.8	41.7	19.3	11.9	4.5	3.3	1.4	0.4
3	36.3	43.1	23.7	12.6	4.6	3.4	1.4	0.5
4	32.1	45.4	27.3	12.9	4.9	3.4	1.4	0.5
5	28.4	45.4	31.5	13.4	5.0	3.4	1.4	0.5
6	27.8	45.4	32.8	12.9	5.0	3.4	1.4	0.5
7	29.0	43.1	36.6	12.4	5.0	3.3	1.4	0.5
8	29.6	38.6	38.6	12.4	5.0	3.2	1.4	0.5
9	31.5	36.3	36.3	11.9	4.9	3.0	1.4	0.5
10	36.3	31.8	34.0	11.6	4.4	2.9	1.4	0.5
11	36.3	29.5	27.2	10.1	4.2	2.7	1.4	0.5
12	31.8	31.8	29.0	9.5	4.1	2.6	1.4	0.4
13	27.2	36.3	36.3	7.7	3.9	2.4	1.2	0.4

Notes: * kg/day

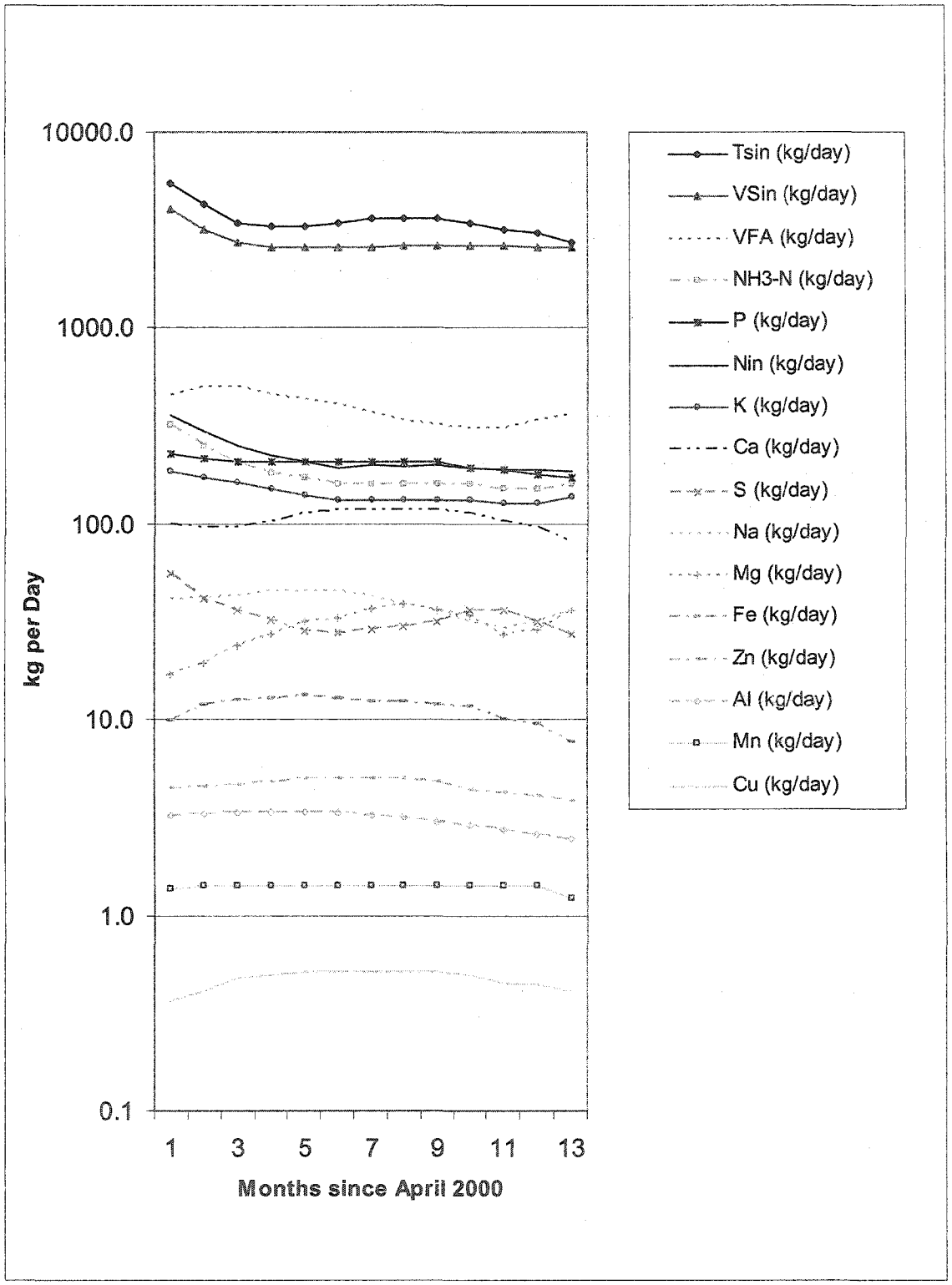

Figure 5.8 Influent nutrients by period (Mattocks et al., 2002)

Table 5.17 Solids influent versus effluent (Mattocks et al., 2002)

Months	TS_{in} (kg/day)	TS_{out} (kg/day)	VS_{in} (kg/day)	VS_{out} (kg/day)	Ash_{in} (kg/day)	Ash_{out} (kg/day)
1	3538.08	1428.84	2222.64	771.12	1451.52	657.72
2	2925.72	1315.44	1859.76	635.04	1179.36	612.36
3	2517.48	1202.04	1610.28	589.68	952.56	589.68
4	2222.64	1088.64	1428.84	544.32	816.48	544.32
5	2086.56	1020.6	1338.12	498.96	725.76	498.96
6	2041.20	952.56	1315.44	476.28	703.08	476.28
7	2063.88	929.88	1315.44	453.6	703.08	453.60
8	2109.24	907.20	1338.12	462.67	725.76	430.92
9	2154.60	907.20	1360.80	462.67	793.80	417.31
10	2199.96	884.52	1406.16	462.67	793.80	408.24
11	2199.96	861.84	1428.84	462.67	793.80	394.63
12	2131.92	861.84	1406.16	476.28	725.76	385.56
13	2018.52	861.84	1383.48	476.28	635.04	385.56

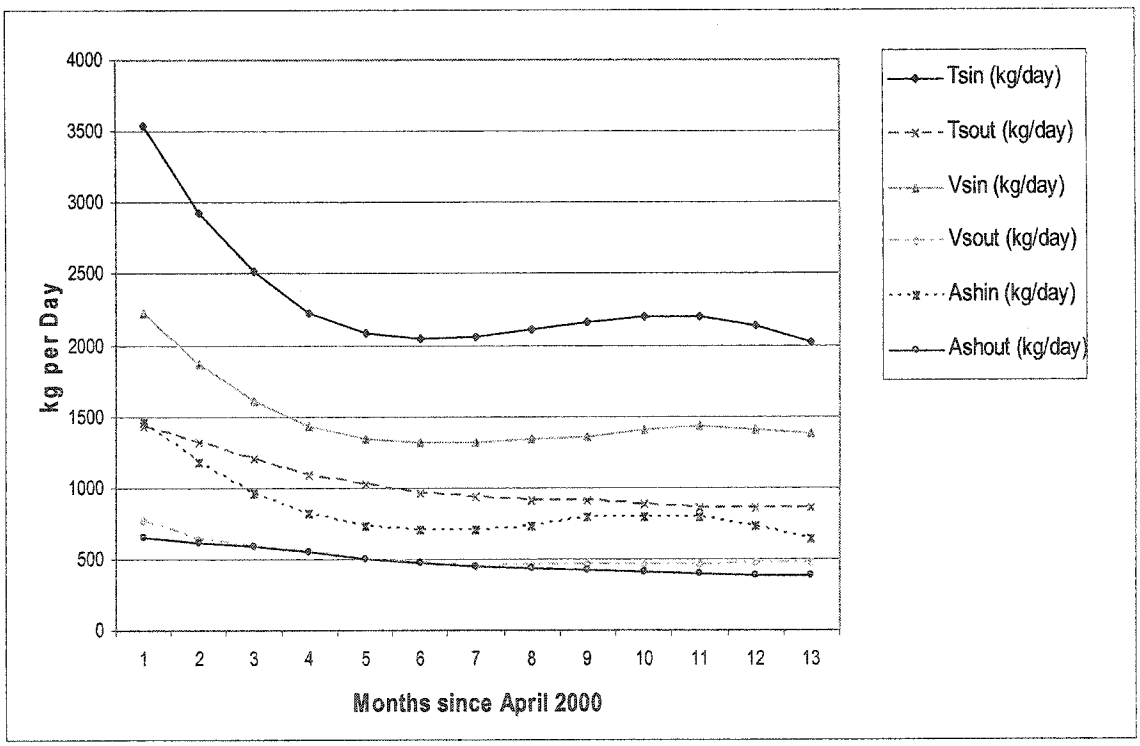

Figure 5.9 Solids influent versus effluent (Mattocks et al., 2002)

Table 5.18 Macronutrients, N, P, K influent versus effluent (Mattocks et al., 2002)

Months	K_{in} (kg/day)	K_{out} (kg/day)	P_{in} (kg/day)	P_{out} (kg/day)	N_{in} (kg/day)	N_{out} (kg/day)
1	129.28	145.15	195.05	122.47	285.77	285.77
2	127.01	154.22	215.46	138.35	251.75	249.48
3	124.74	157.40	226.80	142.88	231.34	222.26
4	124.74	151.96	233.60	140.62	220.00	204.12
5	124.74	147.87	235.87	133.81	215.46	192.78
6	124.74	138.35	235.87	122.47	216.37	183.71
7	124.74	127.01	233.60	111.13	217.73	179.17
8	122.47	117.94	231.34	102.06	222.26	176.90
9	122.47	106.60	226.80	90.72	226.80	176.90
10	120.20	102.06	217.73	81.65	226.80	181.44
11	117.94	97.52	208.66	79.38	222.26	185.98
12	115.67	104.33	197.32	86.18	208.66	190.51
13	113.40	113.40	185.98	102.06	192.78	185.98

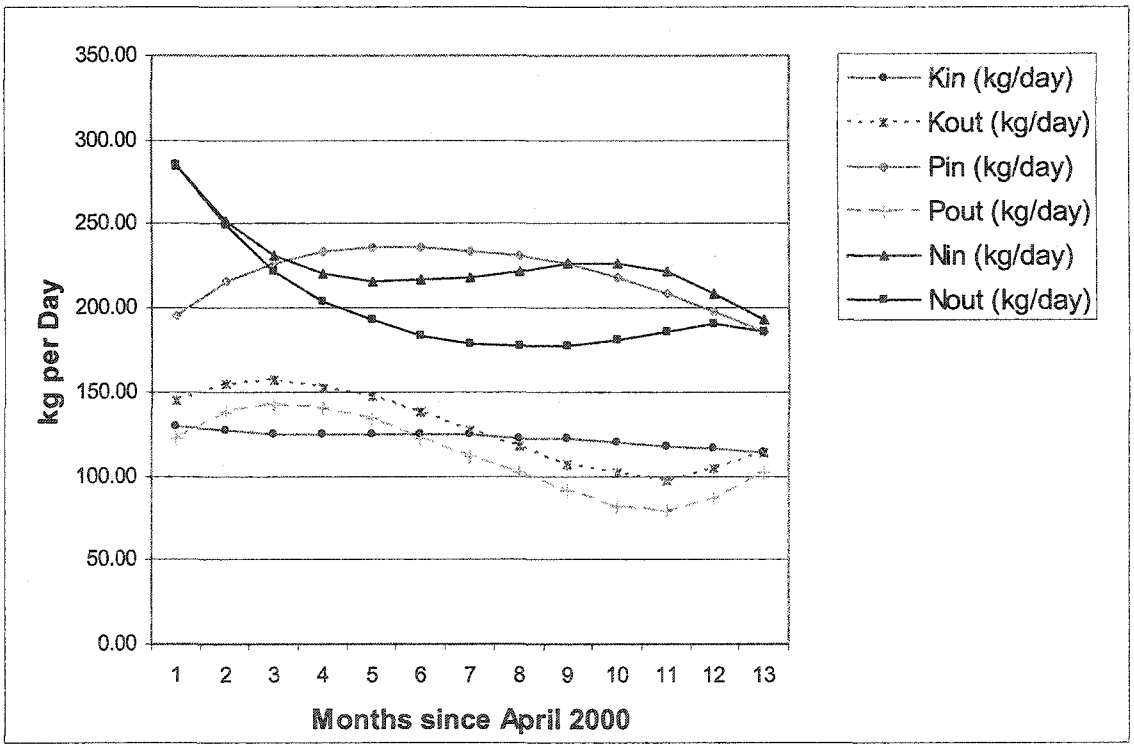

Figure 5.10 Macronutrients, N, P, K influent versus effluent (Mattocks et al., 2002)

Table 5.19 Micronutrients Ca, Mg, S influent versus effluent (Mattocks et al., 2002)

Months	Mg_{in} (kg/day)	Mg_{out} (kg/day)	Ca_{in} (kg/day)	Ca_{out} (kg/day)	S_{in} (kg/day)	S_{out} (kg/day)
1	54.43	40.82	15.88	14.52	18.14	20.41
2	72.58	47.63	24.95	16.78	21.32	18.14
3	84.82	52.16	29.48	18.14	19.50	17.69
4	97.52	49.90	31.75	18.14	27.22	17.24
5	102.06	47.63	32.66	16.78	28.58	14.97
6	106.60	40.82	32.66	15.88	29.03	14.52
7	108.86	38.56	31.75	11.34	29.48	14.06
8	108.86	34.02	29.48	9.07	29.48	13.61
9	106.60	31.75	28.12	6.80	29.03	13.61
10	102.06	29.48	24.95	4.54	27.67	14.52
11	99.79	29.48	23.59	4.54	27.22	14.97
12	88.45	31.75	22.68	5.44	24.95	15.88
13	81.65	34.02	22.68	9.07	23.59	16.78

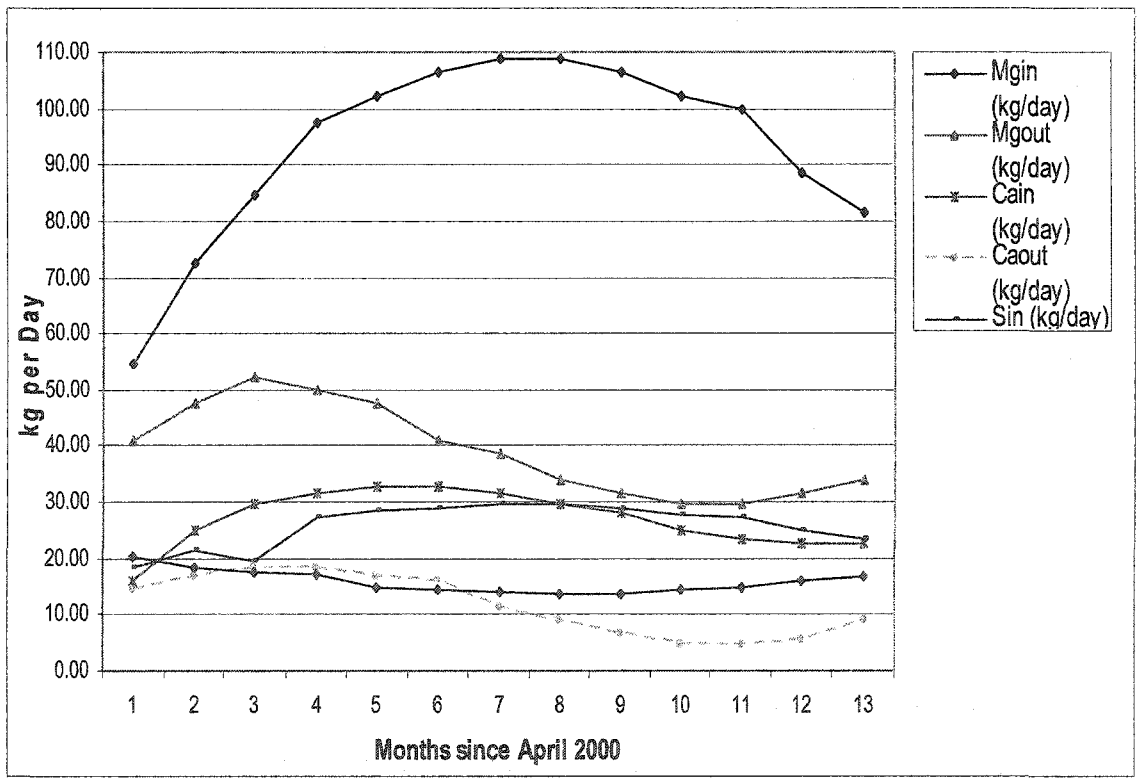

Figure 5.11 Micronutrients Ca, Mg, S influent versus effluent (Mattocks et al., 2002)

Table 5.20 Micronutrients Na, Fe, Al, Mn, Cu, Zn influent versus effluent (Mattocks et al., 2002)

Mo.	Mn_{in} (kg/d)	Mn_{out} (kg/d)	Al_{in} (kg/d)	Al_{out} (kg/d)	Zn_{in} (kg/d)	Zn_{out} (kg/d)	Fe_{in} (kg/d)	Fe_{out} (kg/d)	Na_{in} (kg/d)	Na_{out} (kg/d)
1	1.36	0.73	3.27	1.95	4.45	3.40	9.92	6.80	31.75	43.09
2	1.41	0.82	3.31	2.45	4.54	3.63	10.39	7.71	36.29	49.74
3	1.41	0.84	3.36	2.72	4.63	3.72	11.39	8.16	42.18	52.16
4	1.41	0.84	3.40	2.81	4.85	3.72	11.66	8.39	46.27	52.16
5	1.41	0.77	3.40	2.72	5.00	3.58	11.66	7.71	45.36	49.90
6	1.41	0.69	3.36	2.36	5.00	3.49	11.66	7.26	43.09	45.36
7	1.41	0.57	3.27	2.00	5.00	3.04	11.66	6.35	40.82	41.73
8	1.41	0.45	3.18	1.68	5.00	2.72	11.66	5.44	39.01	38.56
9	1.41	0.00	3.04	1.45	4.85	2.59	11.66	4.54	36.74	35.83
10	1.41	0.00	2.90	1.36	4.40	2.36	11.13	4.54	32.66	31.75
11	1.41	0.00	2.72	1.27	4.22	2.31	10.63	4.54	32.21	31.75
12	1.41	0.00	2.59	1.27	4.08	2.49	10.39	4.99	33.11	33.11
13	1.22	0.00	2.45	1.36	3.86	2.68	10.43	5.90	33.11	32.21

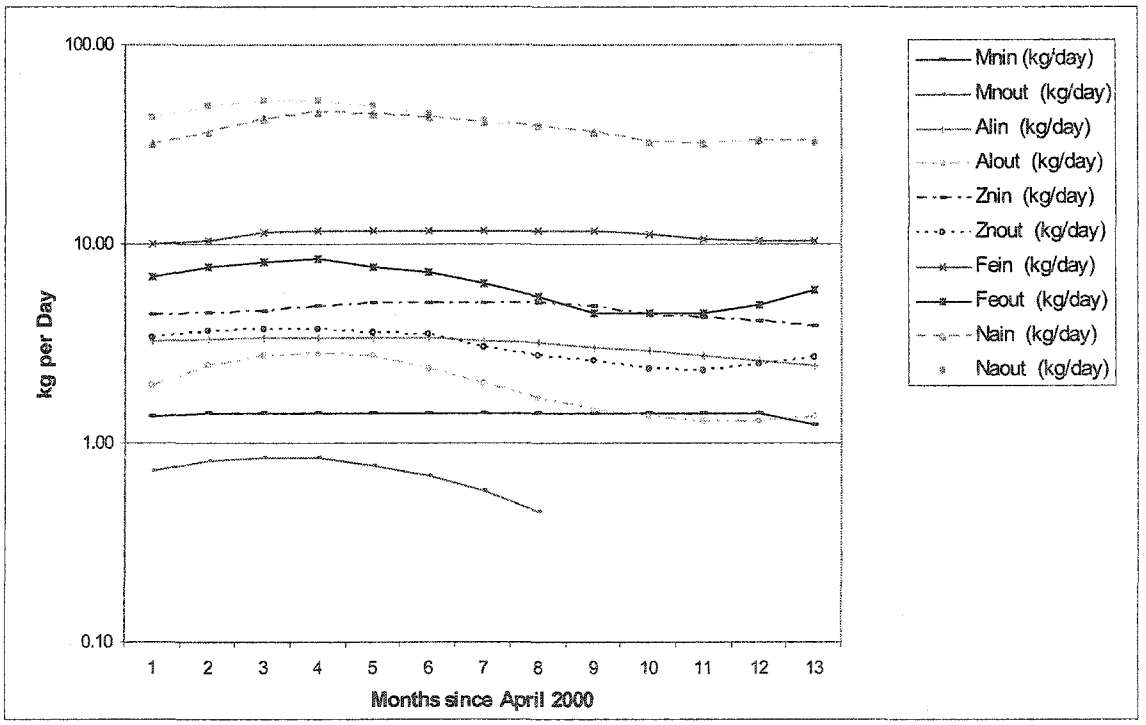

Figure 5.12 Micronutrients Na, Fe, Al, Mn, Cu, Zn influent versus effluent (Mattocks et al., 2002)

Table 5.21 Mass balance average values (Mattocks et al., 2002)

	Influent	Effluent	Difference	% Change
m^3	52	51	1.8927	4%
Density (kg/m^3)	1078.46	958.63	--	--
Mass	53,553	50,798	2,755	-5%
Water	51,057	49,711	1,346	-3%
TS	2,496	1,086	1,409	-56%
VS	1,628	570	1,057	-65%
ASH	1,991	1,138	853	-43%
N	515	479	36	-7%
NH4	378	388	9.7	3%
AVAIL	74%	81%	7.10%	10%
P2O5	465	254	-211.6	-45%
K2O	276	289	13.2	5%
S	53	39	-14.5	-27%
Mg	54	24	-30.1	-56%
Ca	186	86	-100.5	-54
Na	68	81	13.6	20
Fe	21	14	-7.1	-34
Al	6	3	-2.6	-45
Mn	3	1	-1.3	-50
Cu	1	1	-0.4	-35
Zn	10	6	-3.8	-39
pH	7.4	8.1	0.7	9
Alkalinity	13.197	14.927	1.730	13
Vol. Acids	7	0.784	-6	-89
COD	8	2	-6	-71
BOD	3	0.523	-2	-82
Fecal Colif	563,885	549	-563,336	-99.90
Total Sus Solids	63.750	8.200	-55.550	-87
Settle Solids	0.308	0.039	-0.269	-87

Table 5.22 Fate of mass and total solids (Mattocks et al., 2002)

Biogas	1.4%
CH4	0.6%
CO2	0.8%
Grit	1.5%
Filtrate	94.9%
	99.2%

Table 5.23 Fate of total solids (Mattocks et al., 2002)

Biogas	24.6%
Grit	31.8%
Filtrate	43.5%
Total	100.0%

Table 5.24 Gas analysis summary (Mattocks et al., 2002)

Component	Units	Average	AverageDev	AvgDev%Avg
H	%	0.0005	0.00076	153
O	%	0.57	0.22	39
N	%	1.76	0.62	35
CO2	%	31.37	1.42	5
CH4	%	66.29	1.36	2
CH4/CO2		2.12	0.13	6
BTU @ 60 F wet		661.4	13.7	2
Density	sg air	0.869	0.012	1
H_2S	ppm	5912	1063	18
MeSH	ppm	1.0	0.4	43
CS2	ppm	0.4	0.6	152
EtSH	ppm	0.1	0.1	184
DMS	ppm	0.1	0.2	168
I-PrSH	ppm	1.3	0.8	66
n-PrSH	ppm	0.2	0.4	160
s-BuSH	ppm	0.2	0.4	160

Table 5.25 Gas analysis by quarter (Mattocks et al. 2002)

Component	Unit	1st Quarter Average	2nd Quarter Average	3rd Quarter Average	4th Quarter Average
H		0	0	0	0
O	%	0.57	0.63	0.7	0.38
N	%	1.76	1.91	2.03	1.26
CO2	%	31.37	31.46	30.08	32.13
CH4	%	66.29	65.98	67.18	66.24
CH4/CO2		2.1	2.1	2.2	2.1
BTU @ 60 F wet		661	658	670	661
Density	sg air	0.87	0.87	0.86	0.87
H_2S	ppm	5912	6085	4773	6060
MeSH	ppm	1	1.1	1.1	0.6
CS_2	ppm	0.4	0.7	0.5	0
EtSH	ppm	0.1	0.1	0.1	0
DMS	ppm	0.1	0.1	0.3	0
I-PrSH	ppm	1.3	2.3	1.6	0.6
n-PrSH	ppm	0.2	0.2	0	0.8
s-BuSH	ppm	0.2	0.7	0	0

Table 5.26 Major biogas constituents (Mattocks et al., 2002)

Months	CH_4	CO_2	O_2	N
1	66.5	32	0.65	1.8
2	66.5	31	0.7	2.1
3	67	30	0.73	2.25
4	67	30	0.7	2.2
5	67	30	0.65	2.03
6	67	31	0.59	1.8
7	67	32	0.53	1.62
8	66.75	32.5	0.46	1.4
9	66.5	33	0.35	1.25
10	66.5	33	0.3	1.2
11	66	33.5	0.3	1.2
12	65.5	33	0.4	1.35
13	65	33	0.5	1.7

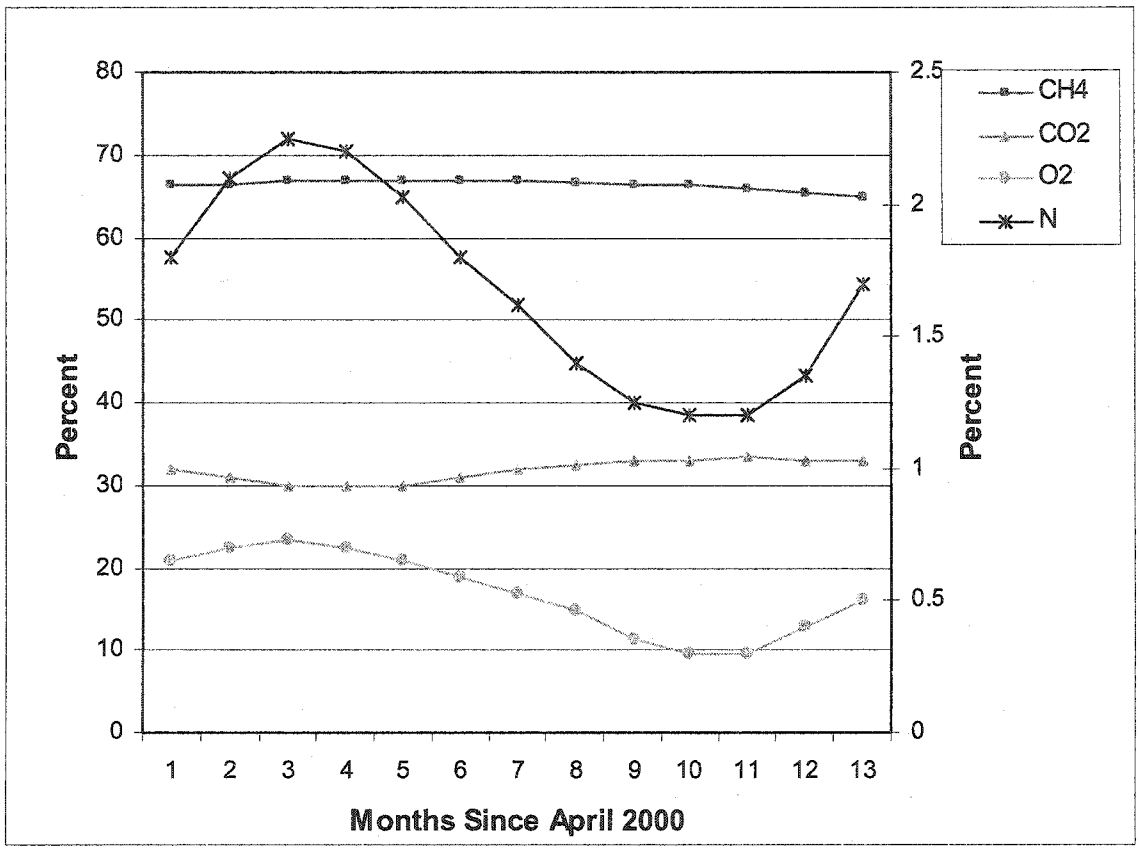

Figure 5.13 Major biogas constituents (Mattocks et al., 2002)

Table 5.27 Temperature biogas H_2S comparison (Mattocks et al., 2002)

Months	Temperature (°F)	Temperature (°C)	H_2S (PPM)
1	71.50	21.94	6100.00
2	72.50	22.50	5300.00
3	73.00	22.78	4850.00
4	72.50	22.50	4800.00
5	71.50	21.94	4800.00
6	69.26	20.70	4900.00
7	67.00	19.44	5200.00
8	64.00	17.78	5600.00
9	62.50	16.94	5900.00
10	61.50	16.39	6250.00
11	61.00	16.11	6600.00
12	62.00	16.67	6900.00
13	64.00	17.78	6950.00

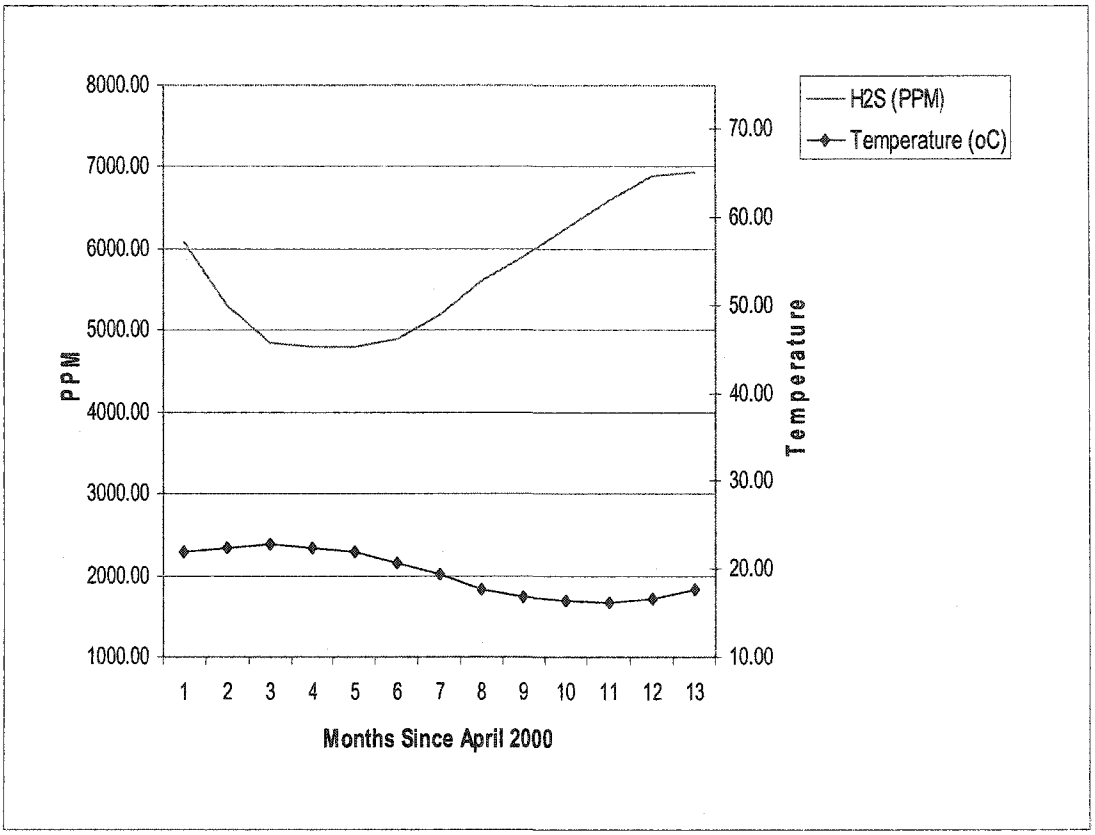

Figure 5.14 Hydrogen sulfide (H_2S) variation with temperature (Mattocks et al., 2002)

Table 5.28 Brookfield viscometer results (Mattocks et al., 2002)

	Influent	Effluent	Lagoon
Description	Heterogeneous	Near	Near
	Settling	homogeneous	Homogeneous
	Some fiber	Fine solids	Fine solids
Analysis Temp, °C	4.44	4.44	4.44
Apparent Viscosity, cps			
@ 60 rpm	12.9	8.5	12.4
@ 30 rpm	13.2	7	12.6
@ 12 rpm	15.5	7	11.5
@ 6 rpm	19	7	17
@ 3 rpm	22	8	20

5.4 Data Analysis Summary

The digester mean influent and effluent concentrations for the period between 24 April 2000 and 3 April 2001 is given in Table 5.29. Mass reductions and biogas characteristics are given in Tables 5.30, 5.31 respectively. Digester effluent, storage and evaporation pond characteristics are given in Table 5.32.

All data sets were approximately normally distributed with the exception of bacterial densities. Linear regression analysis was used to determine if digester influent or effluent total volatile solids (TVS) concentrations, and other characteristics by inference, or biogas utilization varied with time in response to variation in daily digester influent volume (Martin, 2003).

The evaluation of the performance of the CP anaerobic digester was based on the average influent flow rate of 52.41 m^3/day over 12 months of data collection. Because of the variation in the hydraulic loading rate with time, the assessment of the system performance should be considered as an assessment under quasi steady-state conditions.

There was a significant variation of physical and chemical characteristics of the influent to the Colorado Pork digester during the 12-month collection time. The source of the variation was attributed to the difficulties in obtaining representative samples. The variation in the digester effluent was found to be low for a given design HRT of 40 days.

Anaerobic digester of Colorado Pork was found to produce substantial reductions in TS, TVS, BOD_5, COD, VA, S, and FC during the 12 month sampling period. TP, Cu and Zn reductions in the digester indicated settling of particulate matter in the digester. The settlement in the digester was obvious from the measured fixed solids (FS), and bacteria reductions. Additionally, some accumulation of TVS and COD was found to be

taking place in the digester. The settlement rate per year was estimated to be around 2.5 percent of the digester operating volume using FS accumulation rate. Actual loss in digester operating volume was estimated to be substantially higher than 2.5 percent per year. The reduction in organic matter concentrations of influent was due to the accumulation in the reactor and conversion to methane, carbon dioxide, and sulfur gases.

The average rate of biogas utilization at the Colorado Pork reactor was found to be 775.03 m^3/day. The Average methane content of the biogas was found to be 67.9 percent. This translated to an average rate of methane utilization of 526.24 m^3/day. The theoretical rate of 69 percent of 2174.56 kg COD was calculated to be converted to biogas assuming 0.16 m^3 of methane per 0.45 kg of COD (Metcalf & Eddy, 1991). This theoretical calculation suggested that as much as 332.04 kg per day total volatile solids (TVS) reduction. Assuming TVS density of 997.37 kg/m^3, approximately 6.4 percent accumulation rate was estimated on moisture free basis. The accumulation in the reactor is observed to be mitigated by the increase in solid retention time (SRT). This is due to the fact that the accumulating TVS is essentially 100 percent biodegradable and a fraction of the accumulating TVS remaining decrease with time as further microbial biodegradation occurs. It is estimated that with the accumulation in the reactor, eventually HRT will reduce to below the critical value for process stability. Consequently, influent stabilization will approach to zero. Removal of FS and TVS is necessary before the critical HRT was reached.

Biogas utilization averaged 775.03 m^3 per day which translated to 56.57 m^3 per sow-year for 5000 sows. Biogas characteristics were summarized in Table 5.31. Percentage of methane and carbon dioxide is corrected for nominal contamination in the

biogas samples, as indicated by the presence of minimal percentages of oxygen, argon and nitrogen (Martin, 2003). Average moisture content of the biogas was found to be 0.35 m^3 per 283.17 m^3 of biogas produced. Average sulfur content of the biogas found to be 0.58 percent and of the total sulfur present, 99.99 percent or more was found to be hydrogen sulfide. Average biogas sulfur content is found to be 0.25 kg per 28.31 m^3.

Table 5.29 Comparison of the Colorado Pork Anaerobic Digester mean influent and effluent concentrations for the period 24 April 2000 through 3 April 2001*(Martin, 2003)

Parameter	Average Digester influent	Average Digester effluent	Reduction, %
Total solids, kg/m^3	47.181[a]	21.161[b]	55.1
Total volatile solids, kg/m^3	30.858[a]	11.114[b]	64.0
Fixed solids, kg/m^3	16.460[a]	10.111[b]	38.6
Biochemical oxygen demand, 5-day, kg/m^3	24.620[a]	4,459[b]	81.9
Chemical oxygen demand, kg/m^3	61.404[a]	19.920[b]	67.6
Volatile acids, kg/m^3	7.055[a]	0.599[b]	91.5
Total Kjeldahl nitrogen, kg/m^3	4.504[a]	4.276[a]	nsd
Ammonia nitrogen, kg/m^3	3.244[a]	3.423[a]	nsd
Organic nitrogen, kg/m^3	1.260[a]	0.853[b]	32.3

Table 5.29 Comparison of the Colorado Pork Anaerobic Digester mean influent and effluent concentrations for the period 24 April 2000 through 3 April 2001*(Continued) (Martin, 2003)

Parameter	Digester influent	Digester effluent	Reduction, %
Total phosphorus, kg/m^3	1.00[a]	0.526[a]	47.5
Copper, kg/m^3	0.011[a]	0.007[b]	36.3
Zinc, kg/m^3	0.095[a]	0.056[b]	41.0
Sulfur, kg/m^3	0.579[a]	0.363[b]	37.3
Fecal coliforms, log10 CFU/g†	5.610[a]	1.780[b]	99.9
pH	8.000[a]	8.400[b]	n/a

Notes: *Means with a common superscript are not significantly different ($P<0.01$).

†Log_{10} colony-forming units per g.

Table 5.30 Colorado Pork anaerobic digester mass reductions (Martin, 2003)

Parameter	Reduction, kg/day
Total solids	1363.98
Total volatile solids	1034.66
Fixed solids	329.31
Biochemical oxygen demand, 5-day, BOD_5	1056.43
Chemical oxygen demand, COD	2174.56
Volatile acids	338.39
Total phosphorus	24.95
Copper	0.21
Zinc	2.05
Sulfur	11.29

Table 5.31 Colorado Pork Anaerobic Digester biogas characteristics (Martin, 2003)

Parameter	Mean ± standard deviation
Methane, %	67.90±1.79
Carbon dioxide, %	32.10±1.79
Higher heating value, Btu/ft^3	673.5±17.9
Lower heating value, Btu/ft^3	661.8±17.6
Total sulfur, µL/L (ppm)	5,786.0±1,243.5

Table 5.32 Comparison of the characteristics of the digester effluent and storage and evaporation pond contents* (Martin, 2003)

Parameter	Digester effluent	Storage and evaporation pond contents
Total solids, kg/m^3	$21.161^{a}\pm4.049$	$32.775^{b}\pm9.670$
Total volatile solids, kg/m^3	$11.114^{a}\pm1.956$	$17.697^{b}\pm6.661$
Fixed solids, kg/m^3	$10.111^{a}\pm14.874$	$14.874^{b}\pm3.570$
BOD_5, kg/m^3	$4.459^{a}\pm1.831$	$17.001^{b}\pm6.887$
COD, kg/m^3	$19.920^{a}\pm3.714$	$42.102^{b}\pm10.640$
Volatile acids, kg/m^3	$0.599^{a}\pm0.331$	$6.984^{b}\pm2.584$
Total nitrogen, kg/m^3	$4.276^{a}\pm0.448$	$3.708^{b}\pm0.332$
Ammonia nitrogen, kg/m^3	$3.423^{a}\pm0.421$	$2.639^{b}\pm0.379$
Organic nitrogen, kg/m^3	$0.853^{a}\pm0.164$	$1.069^{b}\pm0.256$
Total phosphorus, kg/m^3	$0.526^{a}\pm0.169$	$0.593^{a}\pm0.120$
Copper, kg/m^3	$0.007^{a}\pm0.002$	$0.008^{a}\pm0.002$
Zinc, kg/m^3	$0.056^{a}\pm0.016$	$0.057^{a}\pm0.016$
Sulfur, kg/m^3	$0.363^{a}\pm0.068$	$0.317^{a}\pm0.079$
Fecal coliforms, log_{10} CFU/g†	$1.78^{a}\pm1.240$	$1.87^{a}\pm0.950$
pH	8.4a±0.2	8.4a±0.2

Notes: * Means with a common superscript are not significantly different ($P<0.01$).
† Log_{10} colony-forming units per g.

5.5 The Modified Model Verification and Optimization Results

Model validation is conducted by considering four separate periods due to the distinct variation in the process in these periods (indicated by variation in HRT, influent flow rates). The characterization of the model input is based on feed analysis which was performed during the period of 24 April 2000 through 3 April 2001. The characteristic percentages for the influent constituents were given in Table 5.33. Constituent percentages were determined using the feed sludge characteristics given in Mattocks et al. (2002), and representative values given in Masse et al. (1996), Masse et al. (1997), Chynoweth et al. (1998), and Batstone et al. (2003). Volatile fatty acids are split into acetate, propionate, butyrate and valerate components.

Table 5.33 Characteristic influent constituents

Major Constituents	Percentage (%)
Inert particulate	54.00
Particulate carbohydrate	28.00
Volatile Acids	16.00
Acetic Acid (% of Volatile Acid)	50.00
Butyric Acid (% of Volatile Acid)	20.00
Propionic Acid (% of Volatile Acid)	23.00
Valeric Acid (% of Volatile Acid)	7.00
Ammonia	0. 30
Others	1.70

Feed sludge characteristics were varied for each period due to the change in influent composition as revealed by the measurements. For a quarterly period constant

feed flow rate and constant temperature were assumed. Model input for a period is defined with a constant inflow rate and influent characteristics. Ammonium concentration and alkalinity are based on experimental values measured.

5.5.1 Modeling Results

The modeling results for the process taking place at CP Digester are given and discussed in this section. The initial estimates of the reduction in digester volume is calculated using mass balance for fixed solids, and the increase in retention time is estimated using mass balance for macronutrients such as nitrogen, potassium and phosphorus and suspended solids. The methodology outlined in Section 3.8.1 was employed to adjust and fine tune the estimates. Outputs of the simulations are compared with the CP Digester outputs. The quality of the measurements used for the model validation should be considered as one of the factors adversely affecting the model performance. The Modified Model predicts the trends in the observations and periodic fluctuations. Model predicts the hike in the second quarterly period due to the addition of high counts of microorganisms, favorable operating and environmental conditions for the microbial activity, addition of low pH, mostly decomposed waste influent, and very high retention times for biomass for this period.

In the Modified Model verification phase, model parameters remained unchanged. However, this has its limitations, since model calibration data was from fully controlled experimental scale set-ups with different waste characteristics, and operating conditions. The comparison of observed and simulated biogas production data shows that the model represents the digestion process quite well (Table 5.34, Figure 5.15). The discrepancies observed could be attributed to the changes in waste characteristics between periods,

characterization errors (i.e., errors in proportioning the waste constituents) and changes in operating conditions. Specifically, lack of data on waste stream, operational and environmental conditions before the assessment period caused poor characterization of initial conditions for the digestion process and the relevant lesser quality simulations specifically in the first quarterly period.

Table 5.34 Comparison of measured and the Modified Model simulated biogas production

Months	Biogas observed (m^3/day)	Biogas simulated (m^3/day)
1	608.72	524.22
2	706.11	663.10
3	779.16	675.48
4	936.56	675.83
5	942.19	867.13
6	911.25	930.54
7	787.08	912.63
8	708.38	835.36
9	637.53	672.09
10	651.90	630.77
11	623.55	637.34
12	623.55	637.12

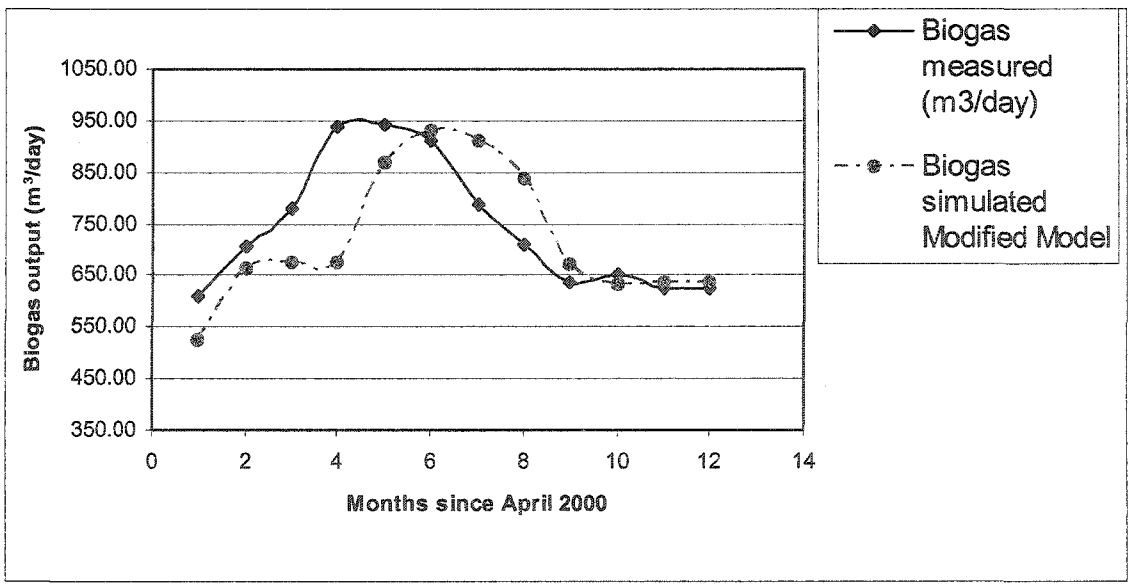

Figure 5.15 Comparison of measured and the Modified Model simulated biogas production

Additionally, at the beginning of the assessment period digester operation appears to be less stable than the later periods. This less stable operating condition could be understood from the moderate level of variation of the measured parameters in the first quarterly period.

The variation in biogas is due to the varying influent waste characteristics and operating conditions. As feed composition and operating conditions change, amount and composition of the biogas as well changes. Methane yield is fixed for sugar, amino acids and LCFA (i.e., soluble substrate). Biogas generated by the digester had a stable gas composition of 66 percent methane, 32 percent carbon dioxide, 0.5 percent oxygen and 1.0 percent nitrogen, and 0.50 percent hydrogen sulfide. However, the model predictions of biogas composition are found not to be very accurate because of the limitations of defining the alkalinity levels in particular. Additionally, lack of actual biogas measurements on days with flare activity should be considered as another factor making it difficult to compare and asses the model performance for the simulation of biogas composition.

Temperature of the system throughout the sampling period was around 39 °C. This stable operating temperature has been maintained by recirculation of the hot water recovered from the engine cooling process (Martin, 2002). Therefore, system operating conditions could be considered as mesophilic.

The changes in ammonium concentration correspond to the changes in measured feed contents. Possible changes in feed protein contents, and subsequent degradation products could be considered as the main reasons for the observed ammonium content changes. Discrepancy between model predicted and measured pH values (i.e., model

predicts lower values) indicates limitation of both the Original Model and the Modified in predicting the VFA degradation. Accumulation in the reactor, variations in operating conditions and feed composition, and possible measurement quality issues (i.e., gaps, sample storage conditions etc.) could explain the discrepancies observed. In summary, the model predicts COD and total biogas production reasonably well. The model is found to be limited in prediction of pH and VFA.

Simulations were carried out using the original model as well to compare the original model outputs with the Modified Model outputs (Table 5.36, Figure 5.17). The comparison clearly indicates better performance of the Modified Model as compared to the original model. The Modified Model simulated biogas outputs were found to be better fit to the measured biogas outputs. The comparative results prove the necessity and the suitability of the extension for the Colorado Pork anaerobic digestion process. As could be seen from Table 5.36 and Figure 5.17 the original model always simulates lower biogas production than the Modified Model. Especially, for winter period, the Modified Model outperforms the original model. For example, for the month of december while original model simulates biogas production of 389.55 m^3/day, the Modified Model simulates biogas production of 672.09 m^3/day, and the measured biogas production is 637.54. This translates to 61% difference between original model simulated biogas production and the measured biogas production. The biogas production peak (summer time) in the original model appears to be more shifted than the Modified Model as well.

Table 5.35 Comparison of measured and the original model simulated biogas production

Months	Biogas Measured (m^3/day)	Biogas Simulated Original Model (m^3/day)
1	608.72	499.22
2	706.12	633.20
3	779.16	640.35
4	936.56	640.28
5	942.19	831.92
6	911.25	895.16
7	787.08	895.16
8	708.38	561.79
9	637.54	389.55
10	651.90	538.81
11	623.55	607.47
12	623.55	607.47

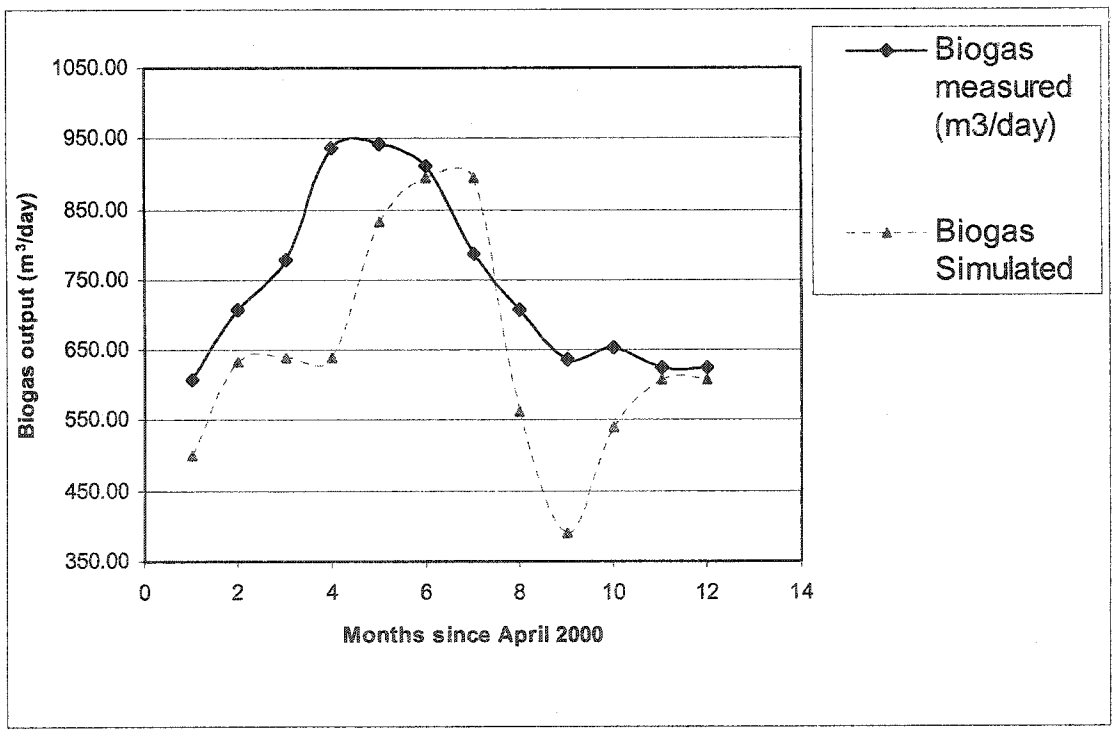

Figure 5.16 Comparison of measured and the Original Model simulated biogas production

Table 5.36 Comparison of the Original Model, the Modified Model simulated, and the measured biogas production

Months	Biogas Measured (m^3/day)	Biogas Simulated Original Model (m^3/day)	Biogas Simulated Modified Model (m^3/day)
1	608.72	499.22	524.22
2	706.12	633.20	663.10
3	779.16	640.35	675.48
4	936.56	640.28	675.84
5	942.19	831.92	867.13
6	911.25	895.16	930.54
7	787.08	895.16	912.64
8	708.38	561.79	835.36
9	637.54	389.55	672.09
10	651.90	538.81	630.78
11	623.55	607.47	637.34
12	623.55	607.47	637.12

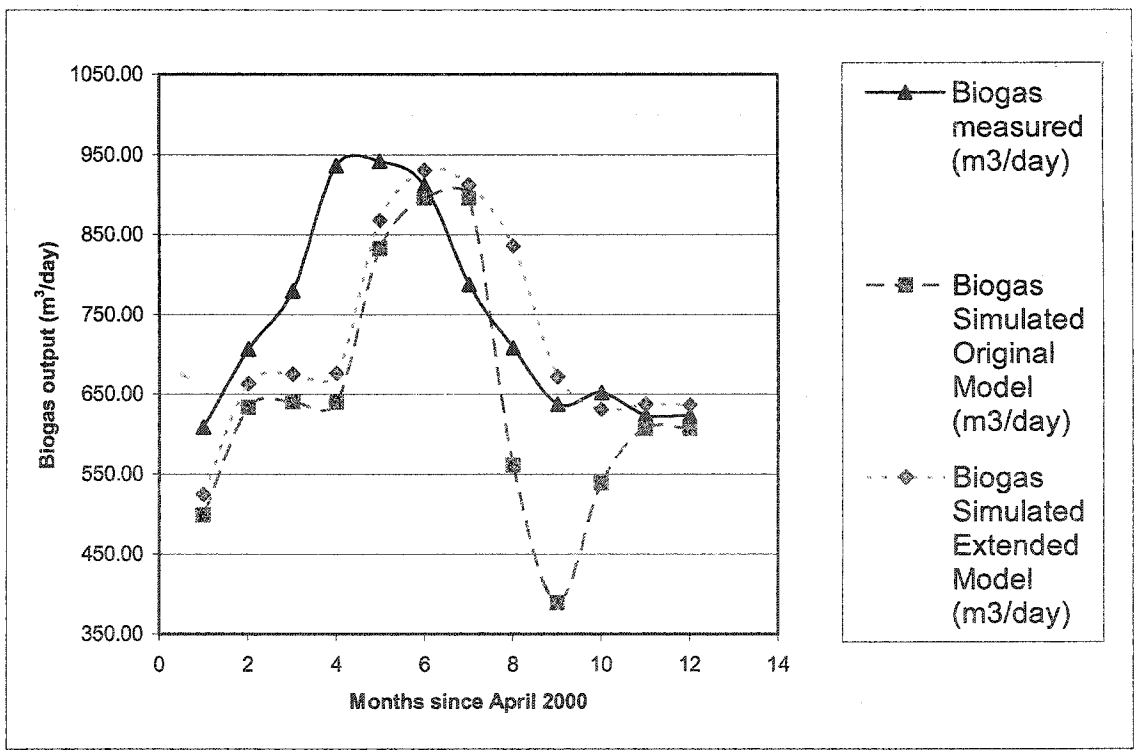

Figure 5.17 Comparison of the Original Model, the Modified Model simulated, and the measured biogas production

5.5.2 Optimization Results

After the Modified Model was calibrated, it was used to evaluate the effect of the changes in HRT and to optimize this parameter for the system. A second series of model runs were conducted with varying HRT values. In these runs, other operating and waste stream parameters remained unchanged. The Modified Model simulations were conducted with varying flow rates to observe the model sensitivity to HRT and to find the optimum for this parameter. The optimum HRT was found to be at 40 days (Table 5.37, Figure 5.18).

Table 5.37 Optimization of HRT

Days since the start of operation	Gas production HRT=28 (m^3/day)	Gas production HRT=32 (m^3/day)	Gas production HRT=36 (m^3/day)	Gas production HRT=40 (m^3/day)	Gas production HRT=45 (m^3/day)
294.6	446.13	500.49	552.62	708.57	616.44
326.2	445.97	500.88	555.76	712.47	624.31
353	442.57	497.15	551.69	707.70	619.77
392.9	753.95	847.80	941.64	1209.53	1058.85
432.8	752.61	846.21	939.94	1207.35	1056.96
443	746.20	838.89	931.56	1196.14	1047.34
488.5	744.18	836.89	929.58	1194.26	1045.40
533	254.71	286.27	317.81	407.81	615.44
576.8	576.49	648.32	720.13	637.83	811.85
620.6	574.87	646.50	718.12	922.64	808.17
623	416.76	480.41	545.92	738.21	631.38
Total	6154.45	6929.82	7704.77	9642.52	8935.92

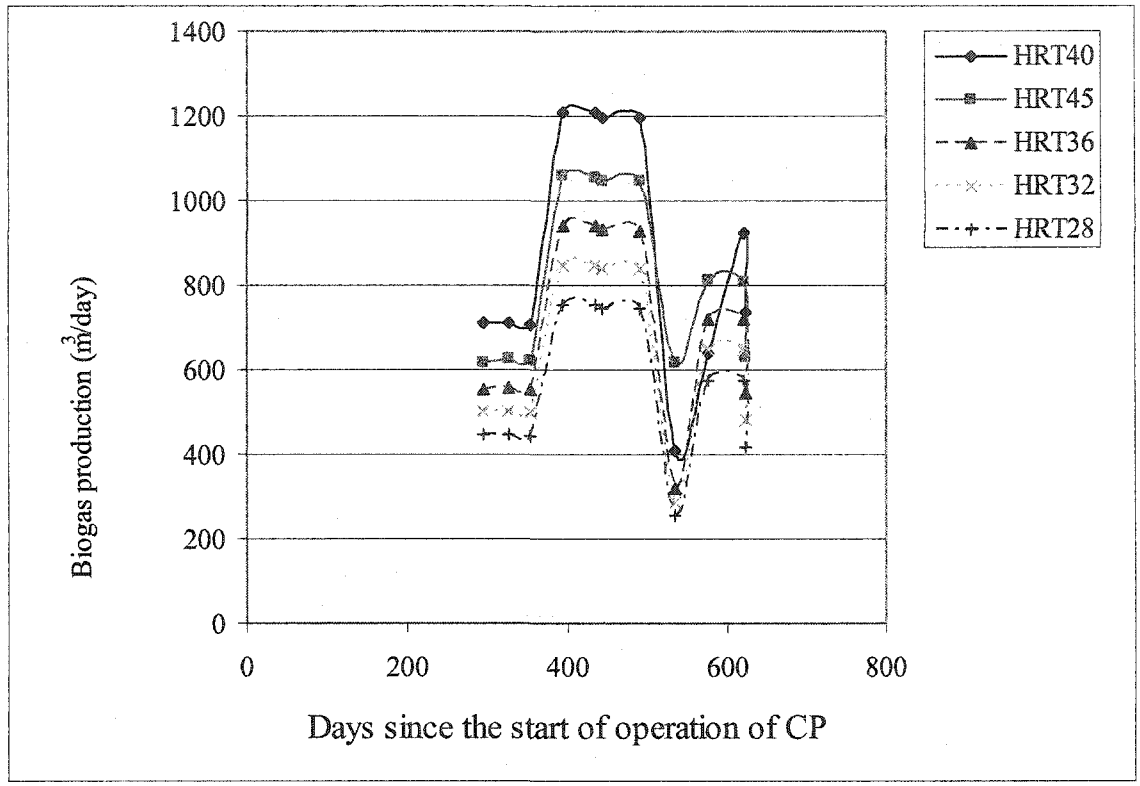

Figure 5.18 Optimization of HRT

5.6 Summary

In this chapter, the simulation results for the Original Model and the Modified Model are given. The Modified Model results are compared with the Original Model simulation results. It has been found that the Modified Model is successful in modeling quasi-steady state caused by the accumulation and the operational variations. Additionally, the Modified Model is found to be performing better than the original model. This finding proved the necessity and the suitability of the extension for the AD process at the Colorado Pork reactor. The optimization was carried out for HRT. The optimum for HRT is found to be 40 days.

CHAPTER 6: SUMMARY OF THE RESULTS

A summary of the results is given in this chapter. The summary includes the results for the parameter estimation and other preliminary steps of the modeling, model implementation and optimization.

6.1 Summary of the Parameter Estimation Results

The parameter estimation is carried out using two distinct numerical parameter estimation techniques for the selected limited set of parameters with high sensitivities. The methods used for the parameter estimation with the Original Model were the secant method and nonlinear constrained optimization. The numerical estimated techniques used were the secant method and constrained optimization. The estimated parameters of the model were the disintegration constant (k_{dis}), the maximum uptake rates for acetate and propionate utilizers, $k_{m,ac}$, $k_{m,pro}$, and the half saturation constants for acetate, propionate and hydrogen utilizers ($K_{S,ac}$, $K_{S,pro}$, $K_{S,H2}$). The disintegration constant was found to be 0.75 d^{-1}, the maximum uptake rate of acetate was found to be 9 kg COD Ac.kg CODX.d^{-1}, the maximum uptake rate of propionate was found to be 9 kg COD Pro.kg CODX.d^{-1}, the half saturation constant for acetate utilitizers was found to be 0.15 kg COD Ac/m^3, the half saturation constant for propionate utilizers was found to be 0.20 kg COD Pro/m^3, and the half saturation constant for H_2 utilizers was found to be 7.10^{-6} kg COD H_2/m^3. The estimated parameter values are found within the limits cited in the literature for a

Canadian piggery waste stream (Masse & Droste, 2000). These parameters were used in the Modified Model.

The Modified Model was used to simulate the AD process taking place at Colorado Pork, LLC, anaerobic digester. The Modified Model estimates total biogas production well (i.e., with less than 15% error). The absolute error of the Modified Model was 83 m^3/day, the relative error was 10.34 percent, the RMSE was 29.77 m^3/day, coefficient of variation was 0.040, and the correlation coefficient was 0.66. The original model absolute error was 109.49 m^3/day, relative error was 15.60 percent, RMSE was 41.23 m^3/day, and the coefficient of variation was 0.055. This clearly indicates the simulations with the Modified Model yield better estimates of biogas production than the original model (Table 5.36 and Figure 5.17). In the research, the modeling of the farm (agricultural) anaerobic covered tank type anaerobic reactor using the Modified Model is accomplished successfully. The modification offers a unique approach for the further generalization of the anaerobic digestion model for unsteady-state operation of the reactor.

The Modified Model simulated the biogas production at Colorado Pork reactor with very small error which clearly indicates good simulation considering the complexity of the modeling of the full-scale anaerobic digestion process. The model is found to be limited in prediction of pH (i.e., model predictions of pH were lower than the observed values), VFA and biogas composition. Model predictions of pH are found to be lower than the measured values, possibly due to the difficulty in representing the alkalinity of the waste stream and the limitation of the model in predicting the volatile fatty acids degradation. In general, the discrepancies between modeling outputs and the

measurements could be attributed to variations in operating conditions, feed composition changes, waste characterization errors and the measurement quality issues (i.e., data measurement gaps due to the operational problems, sample storage and delivery conditions, delay between sampling and testing times etc.).

6.2 Summary of the Modified Model Optimization Results

The Modified Model is used to test the outputs of one possible digester management practice; the effects of change in HRT on biogas production. The HRT, has been optimized. The optimum HRT for the system was found to be 40 days. For the other parameters optimization has not been carried out. However, due to the natural variations observed in the anaerobic digestion process variables (i.e., temperature, pH) in consideration given in Tables 5.13-5.15, it can be stated that temperature increase causes increase in biogas production up to a certain optimum (this value is around 37°C for mesophilic range which is the case in the research), and decrease in biogas production after the optimum from the results obtained in this research as shown in Table 5.36, Figure 5.17. Additionally, similar results can be drawn for pH. In other words, pH increase causes increase in biogas production up to a certain optimum (this pH value is approximately 7). Due to the scope constraints defined in the research proposal, and time limitations, optimization for the other parameters of the digestion process has not been carried out. However, due to the natural variations observed in the anaerobic digestion process variables (i.e., temperature, pH) in consideration given in Tables 5.13-5.15.

CHAPTER 7: CONCLUSIONS

In this dissertation, the questions related to ADM1 for the simulation of Colorado Pork, LLC, reactor have been investigated. One major research outcome was the modification of the model to simulate the anaerobic digestion process taking place in the Colorado Pork, LLC, reactor by using physically based methodology. Additionally, the optimum for the HRT was found for the reactor. Conclusions drawn from this research are given in this chapter.

7.1 Goals

The **goals** of the research as described in Chapter 1 and how these are met in the research described below:

1. **To modify the ADM1 model to simulate the AD process taking place at Colorado Pork anaerobic digester with less than 15% error.**

A methodology was developed (i.e., derived using settling theory) and incorporated into the model to account for the effects of accumulation on the anaerobic digestion process with solids accumulation. The developed methodology computes both the increase in retention time due to the recycling of the biomass and the loss of operating volume simultaneously. It is physically-based and the derivation is given in Section 3.8.1.

The comparative results of the Original Model and the Modified Model given in Table 5.36, and Figure 5.17, prove the suitability and the necessity of the modification of the model for simulation of the Colorado Pork anaerobic digester.

By the developed methodology, the AD process modeling using ADM1 is successfully modified and implemented to account for unsteady state operation which is generally the case for full-scale reactors. This is a major modification and improvement of the Original Model structure, considering the fact that the steady state operation is a special case of unsteady-state operation.

The model implementation is the first modification and implementation of the ADM1 model for agricultural waste (i.e., piggery waste), and for the anaerobic covered tank type reactor with a quasi-steady state operation. Previous applications of the Original Model include only industrial scale or experimental scale continuously stirred, batch or other types of municipal waste treatment plants or reactors with almost full control of the waste inputs, compositions, and other factors. The reactor configuration and waste stream properties for the Colorado Pork reactor are completely different than the previous cases where the Original Model is used for simulations. **These facts make this research accomplishment more valuable and distinct.**

2. **To optimize the hydraulic retention time for the reactor using the Modified Model.**

The Modified Model is found to be suitable for use in optimization studies. The Modified Model can be used to test the outputs of various digester management practices such as variation of HRT, temperature, pH etc. In the research, one of the major parameters of the digestion process, HRT, has been optimized. The optimum HRT for the system was found to be 40 days.

7.2 Objectives

The **objectives** of the research and how these are met in the research are described below:

1. **To modify the model to account for accumulation and its effects.**

The Original Model is modified by developing a physically based method and incorporating it into the Original Model to account for an unsteady state caused by the solids accumulation in the reactor and the variation in the operating conditions. The developed method considers both the increase in retention time, due to the recycling of the biomass, and the loss of operating volume. It is physically based and the derivation is given in Section 3.8.1.

2. **To assess the applicability of the Modified Model, for the Colorado Pork reactor.**

The assessment of the applicability of the Modified Model included the parameter estimation using numerical methods. The use of numerical methods for the anaerobic digestion with the Original Model is found to produce a realistic set of parameters. In other words, the estimated parameter values are found within the limits cited in the literature for the waste stream and reactor configuration under consideration (Masse & Droste, 2000; Batstone, 2002b). Therefore, it can be stated that use of numerical methods for parameter estimation is a viable technique for describing the anaerobic digestion processes.

3. **To test the Modified Model using the Colorado Pork reactor data and to evaluate model performance and limitations.**

The Modified Model was tested by using it to simulate the anaerobic digestion process at Colorado Pork, LLC, anaerobic digester. The rate of biogas production was simulated with less than 15% error using the Modified Model. The comparative simulation results of the anaerobic digestion process using the Original and the Modified Model, given in Table 5.36, and Figure 5.17, proves the necessity and the suitability of the modification of the Original Model by incorporating the method described in Section 3.8.1.

4. **To optimize the hydraulic retention time (HRT) for the Colorado Pork reactor.**

In the research, the effects of HRT on biogas production is investigated, and this parameter is optimized. In the research, the optimum HRT for the system using the Modified Model was found to be 40 days. **The Modified Model is found to be suitable for use in optimization studies to test various possible management practices for an anaerobic digester.**

In summary, the Modified Model is capable of simulating the full-scale anaerobic digestion process taking place in the Colorado Pork, LLC, reactor. The Modified Model estimations are far better than the Original Model estimations (Table 5.36 and Figure 5.17). This proves the necessity and the suitability of the modification made to account for the effects of the accumulation on the anaerobic digestion process. Additionally, the Modified Model can be used to estimate the changes in gas production and effluent output for differing environmental and operating conditions, and to optimize the operating and environmental variables for optimal biogas yield.

CHAPTER 8: RECOMMENDATIONS

In this research, a Modified Model is developed to account for accumulation in the reactor and incorporated into the ADM1. This Modified Model was then applied to simulate the process taking place at the Colorado Pork, LLC, anaerobic reactor. The modification included a physically based methodology to estimate the effects of the accumulation in the reactor.

The modification was found to be necessary for simulation of the quasi steady-state operation of Colorado Pork LLC anaerobic reactor with better accuracy. However, other alternatives to account for the recycling of the biomass and the reduction of operating volume caused by the accumulation need to be investigated. These alternatives could include accommodation of the regulation factor to account for accumulation similar to the case proposed by Mosey (1983) to account for the regulatory effect of hydrogen. Additionally, time variation of parameters and development of generic methodology to account for this, could as well be proposed as a further future improvement for the model specifically for the processes with limited or no control and therefore, periodically fluctuating depending on the waste stream, operational conditions and environmental conditions. Existence of a seasonal variation in the process can be understood from the observations for the Colorado Pork, LLC, digester. An approach developed by Simeonov et al. (1996) to account for time-variation of kinetic parameters could be incorporated to the model. Improved characterization of the waste influent stream is expected to yield

better simulation results (Gralapp et al., 2002). Simulations with further time refinement can yield better outputs.

Incorporation of global optimization methods such as branch and bound and evolutionary algorithms to avoid the limitations of numerical optimization methods such as termination at the local minima or maxima is recommended as a future step for parameter estimation. For the full-scale Colorado Pork digester, the parameter set found by optimization using the mesophilic lab-scale experimental data set could be considered as partially applicable due to the differences in waste characteristics and operating conditions. The key parameters found using the optimization techniques need further refinement using data obtained from lab-scale or full-scale implementations with similar waste characteristics and operation conditions. It is expected that using data from experimental set-ups with similar waste characteristics and operating conditions would yield more accurate parameters and better simulations. In the case of using lab scale data, possible limitations in the parameter estimation should as well be considered. However, finding the experimental or full-scale comprehensive high quality data sets with the similar waste and operating conditions is difficult. As the anaerobic digestion model matures, and more tests are carried out by researchers, the high quality data are expected to become available for different waste streams and different operating conditions.

For the practical applicability of the model for full-scale plant design, operation and optimization, further refinement (i.e., reduction) of the number of the components of the model to include only the typical major processes involved for the waste and operating conditions should be investigated. Extensive research with varying waste

streams and operating conditions using experimental and full-scale set-ups is needed to realize the further refinement of the model for practical operational applications.

Further automation of the input data feed (i.e., pre-processing of the data for model entry) and output data processing (i.e., post-processing of the data for further assessment and visualization) are recommended from the point of view of model construction and implementation. Additionally, improving the program code to facilitate automatic inter-application data transfers (i.e., data transfers between Excel, MATLAB, and Simulink) would expedite and streamline the simulations. Implementing a certain data model with a time series component for the input and output data could streamline the simulation process and could yield more structured and more efficient model verification and validation. Further enhancements that are recommended in this dissertation are expected to make the model more applicable for practical, operational use, and yield a more robust and complete model structure.

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APPENDIX A. THE MODIFIED MODEL DIFFERENTIAL EQUATION SYSTEM

Process rates

Biochemical process rates

$$\rho_1 = k_{dis}.X_c \tag{1}$$

$$\rho_2 = k_{hyd,ch}.X_{ch} \tag{2}$$

$$\rho_3 = k_{hyd,pr}.X_{pr} \tag{3}$$

$$\rho_4 = k_{hyd,li}.X_{li} \tag{4}$$

$$\rho_5 = k_{m,su}.\frac{S_{su}}{K_{S,su}+S_{su}}X_{su}.I_5 \tag{5}$$

$$\rho_6 = k_{m,su}.\frac{S_{aa}}{K_{S,aa}+S_{aa}}X_{aa}.I_6 \tag{6}$$

$$\rho_7 = k_{m,fa}.\frac{S_{fa}}{K_{S,fa}+S_{fa}}X_{fa}.I_7 \tag{7}$$

$$\rho_8 = k_{m,c4}.\frac{S_{fa}}{K_{S,c4}+S_{va}}X_{c4}.\frac{S_{va}}{S_{bu}+S_{va}+1e-6}I_8 \tag{8}$$

$$\rho_9 = k_{m,c4}.\frac{S_{va}}{K_{S,c4}+S_{va}}X_{c4}.\frac{S_{va}}{S_{bu}+S_{bu}+1e-6}I_9 \tag{9}$$

$$\rho_{10} = k_{m,pr}.\frac{S_{pro}}{K_{S,pro}+S_{pro}}X_{pro}.I_{10} \tag{10}$$

$$\rho_{11} = k_{m,ac} \cdot \frac{S_{ac}}{K_{S,ac} + S_{ac}} X_{pro} \cdot I_{11} \quad (11)$$

$$\rho_{12} = k_{m,h2} \cdot \frac{S_{h2}}{K_{S,h2} + S_{h2}} X_{pro} \cdot I_{12} \quad (12)$$

$$\rho_{13} = k_{dec,Xsu} \cdot X_{su} \quad (13)$$

$$\rho_{14} = k_{dec,Xaa} \cdot X_{aa} \quad (14)$$

$$\rho_{15} = k_{dec,Xfa} \cdot X_{fa} \quad (15)$$

$$\rho_{16} = k_{dec,Xc4} \cdot X_{c4} \quad (16)$$

$$\rho_{17} = k_{dec,Xpro} \cdot X_{pro} \quad (17)$$

$$\rho_{18} = k_{dec,Xac} \cdot X_{ac} \quad (18)$$

$$\rho_{19} = k_{dec,Xh2} \cdot X_{h2} \quad (19)$$

Acid-base rates

$$\rho_{A,4} = k_{A,Bva}(S_{va} - (K_{a,va} + S_{H+}) - K_{a,va} \cdot S_{va}) \quad (20)$$

$$\rho_{A,5} = k_{A,Bbu}(S_{va} - (K_{a,bu} + S_{H+}) - K_{a,bu} \cdot S_{bu}) \quad (21)$$

$$\rho_{A,6} = k_{A,Bpro}(S_{pro} - (K_{a,pro} + S_{H+}) - K_{a,pro} \cdot S_{pro}) \quad (22)$$

$$\rho_{A,7} = k_{A,Bac}(S_{ac} - (K_{a,ca} + S_{H+}) - K_{a,ac} \cdot S_{ac}) \quad (23)$$

$$\rho_{A,10} = k_{A,BCO2}(S_{HCO3} - (K_{a,CO2} + S_{H+}) - K_{a,CO2} \cdot S_{IC}) \quad (24)$$

$$\rho_{A,11} = k_{A,BIN}(S_{NH3} - (K_{a,IN} + S_{H+}) - K_{a,IN} \cdot S_{IN}) \quad (25)$$

Gas transfer rates (Note that S_{CO2} is used in expression for $\rho_{T,10}$ not S_{IC})

$$\rho_{T,8} = k_L a(S_{h2} - 16K_{H,h2}p_{gas,h2}) \quad (26)$$

$$\rho_{T,9} = k_L a(S_{ch4} - 64K_{H,ch4}p_{gas,,ch4}) \quad (27)$$

$$\rho_{T,10} = k_L a(S_{co2} - K_{H,co2}P_{gas,,co2}) \quad (28)$$

Process inhibition

Inhibition:

$I_{5,8} = I_{pH,aa} \cdot I_{IN,\,lim}$ (29)

$I_2 = I_{pH,\,aa}\, I_{IN,\,lim}\, I_{h2,\,fa}$ (30)

$I_{8,9} = I_{pH,\,aa}\, I_{IN,\,lim}\, I_{h2,\,c4}$ (31)

$I_{10} = I_{pH,\,ac}\, I_{IN,\,lim}\, I_{h2,\,pro}$ (32)

$I_{11} = I_{pH,\,ac}\, I_{IN,\,lim}\, I_{nh3}$ (33)

$I_{12} = I_{pH,\,h2}\, I_{IN,\,lim}$ (34)

$$I_{pH,aa} = \begin{cases} \exp\left(-3\left(\dfrac{pH - pH_{UL,aa}}{pH_{UL,aa} - pH_{LL,aa}}\right)^2\right) : & pH < pH_{UL,aa} \\ 1 & pH > pH_{UL,aa} \end{cases} \quad (35)$$

$$I_{pH,ac} = \begin{cases} \exp\left(-3\left(\dfrac{pH - pH_{UL,ac}}{pH_{UL,ac} - pH_{LL,ac}}\right)^2\right) : & pH < pH_{UL,ac} \\ 1 & pH > pH_{UL,ac} \end{cases} \quad (36)$$

$$I_{pH,h2} = \begin{cases} \exp\left(-3\left(\dfrac{pH - pH_{UL,h2}}{pH_{UL,h2} - pH_{LL,h2}}\right)^2\right) : & pH < pH_{UL,h2} \\ 1 & pH > pH_{UL,h2} \end{cases} \quad (37)$$

$$I_{IN,\lim} = \frac{1}{1 + K_{S,IN} / S_{IN}} \tag{38}$$

$$I_{h2,fa} = \frac{1}{1 + S_{h2} / K_{I,h2,fa}} \tag{39}$$

$$I_{h2,c4} = \frac{1}{1 + S_{h2} / K_{I,h2,c4}} \tag{40}$$

$$I_{h2,pro} = \frac{1}{1 + S_{h2} / K_{I,h2,pro}} \tag{41}$$

$$I_{nh3} = \frac{1}{1 + S_{nh3} / K_{I,nh3}} \tag{42}$$

, and

$$pH = -\log_{10}(S_{H+}) \tag{43}$$

Water phase equations

Differential equations 44-47, soluble matter:

$$\frac{dS_{su}}{dt} = \frac{q_{in}}{V_{liq}}(S_{su,in} - S_{su}) + \rho_2 + (1 - f_{fa,li})\rho_4 - \rho_5 \tag{44}$$

$$\frac{dS_{aa}}{dt} = \frac{q_{in}}{V_{liq}}(S_{aa,in} - S_{aa}) + \rho_3 - \rho_6 \tag{45}$$

$$\frac{dS_{fa}}{dt} = \frac{q_{in}}{V_{liq}}(S_{fa,in} - S_{fa}) + f_{fa,li}\rho_4 - \rho_7 \tag{46}$$

$$\frac{dS_{va}}{dt} = \frac{q_{in}}{V_{liq}}(S_{va,in} - S_{va}) + (1 - Y_{aa})f_{va,aa}\rho_6 - \rho_8 \tag{47}$$

Differential equations 48-51, soluble matter

$$\frac{dS_{bu}}{dt} = \frac{q_{in}}{V_{liq}}(S_{bu,in} - S_{va}) + (1 - Y_{su})f_{bu,su}\rho_5 + (1 - Y_{aa})f_{bu,aa}\rho_6 - \rho_9 \quad (48)$$

$$\frac{dS_{pro}}{dt} = \frac{q_{in}}{V_{liq}}(S_{pro,in} - S_{pro}) + (1 - Y_{su})f_{pro,su}\rho_5 + (1 - Y_{aa})f_{pro,aa}\rho_6 - (1 - Y_{c4})0.54\rho_8 - \rho_{10} \quad (49)$$

$$\frac{dS_{ac}}{dt} = \frac{q_{in}}{V_{liq}}(S_{ac,in} - S_{ac}) + (1 - Y_{su})f_{ac,su}\rho_5 + (1 - Y_{aa})f_{ac,aa}\rho_6 - (1 - Y_{fa})0.7\rho_7 + (1 - Y_{c4})0.31\rho_8 + (1 - Y_{c4})0.8\rho_9 + (1 - Y_{pro})0.57\rho_{10} - \rho_{11} \quad (50)$$

$$\frac{dS_{h2}}{dt} = \frac{q_{in}}{V_{liq}}(S_{h2,in} - S_{h2}) + (1 - Y_{su})f_{h2,su}\rho_5 + (1 - Y_{aa})f_{h2,aa}\rho_6 - (1 - Y_{fa})0.3\rho_7 + (1 - Y_{fa})0.31\rho_7 + (1 - Y_{c4})0.15\rho_8 + (1 - Y_{c4})0.2\rho_9 + (1 - Y_{su})0.43\rho_{10} - \rho_{12} - \rho_{T,8} \quad (51)$$

Differential equations 52-55, soluble matter:

$$\frac{dS_{ch4}}{dt} = \frac{q_{in}}{V_{liq}}(S_{ch4,in} - S_{ch4}) + (1 - Y_{ac})\rho_{11} + (1 - Y_{aa})\rho_{12} - \rho_{T,9} \quad (52)$$

$$\frac{dS_{IC}}{dt} = \frac{q_{in}}{V_{liq}}(S_{IC,in} - S_{IC}) + \sum_{j=1}^{19}\left(\sum_{i=1-9,11-24} C_i v_{ij}\rho_j\right) - \rho_{T,10} \quad (53)$$

$$\frac{dS_{IN}}{dt} = \frac{q_{in}}{V_{liq}}(S_{IN,in} - S_{IN}) + Y_{su}N_{bac}\rho_5 + (N_{aa} - Y_{aa}N_{bac})\rho_6 - Y_{fa}N_{bac}\rho_7 - Y_{c4}N_{bac}\rho_8 - Y_{c4}N_{bac}\rho_9 - Y_{pro}N_{bac}\rho_{10} - Y_{c4}N_{bac}\rho_{11} - Y_{h2}N_{bac}\rho_{12} + (N_{bac} - N_{xc})\sum_{i=13}^{19}\rho_i + (Nxc - f_{xI,xc}N_I - f_{sI,xc}N_I - f_{pr,xc}N_{aa})\rho_1 \quad (54)$$

$$\frac{dS_I}{dt} = \frac{q_{in}}{V_{liq}}(S_{I,in} - S_I) + f_{sI,xc}\rho_1 \quad (55)$$

The sum of equation 53 is computed as:

$$\sum_{j=1}^{19}\left(\sum_{i=1-9,11-24} C_i v_{i,j}\rho_j\right) = \sum_{k=1}^{12} s_k\rho_k + s_{13}(\rho_{14} + \rho_{15} + \rho_{16} + \rho_{17} + \rho_{18} + \rho_{13} + \rho_{19} \quad (56)$$

Where:

$$s_1 = -C_{xc} + f_{sI,xc}C_{sI} + f_{ch,xc}C_{ch} + f_{pr,xc}C_{pr} + f_{li,xc}C_{li} + f_{xI,xc}C_{xI} \quad (57)$$

$$s_2 = -C_{ch} + C_{su} \quad (58)$$

$$s_3 = -C_{pr} + C_{aa} \quad (59)$$

$$s_4 = -C_{li} + (1 - f_{fa,li})C_{su} + f_{fa,li}C_{fa} \quad (60)$$

$$s_5 = -C_{su} + (1 - Y_{su})(f_{bu,su}C_{bu} + f_{pro,su}C_{pro} + f_{ac,su}C_{ac}) + Y_{su}C_{bac} \quad (61)$$

$$s_6 = -C_{aa} + (1 - Y_{aa})(f_{va,aa}C_{va} + f_{bu,aa}C_{bu} + f_{pro,aa}C_{pro} + f_{ac,aa}C_{ac}) + Y_{aa}C_{bac} \quad (62)$$

$$s_7 = -C_{fa} + (1 - Y_{fa})0.7C_{ac} + Y_{fa}C_{bac} \quad (63)$$

$$s_8 = -C_{va} + (1 - Y_{c4})0.54C_{pro} + (1 - Y_{c4})0.31C_{ac} + Y_{c4}C_{bac} \quad (64)$$

$$s_9 = -C_{bu} + (1 - Y_{c4})0.8C_{ac} + Y_{c4}C_{bac} \quad (65)$$

$$s_{10} = -C_{pro} + (1 - Y_{c4})0.57C_{ac} + Y_{pro}C_{bac} \quad (66)$$

$$s_{11} = -C_{ac} + (1 - Y_{ac})C_{ch4} + Y_{ac}C_{bac} \quad (67)$$

$$s_{12} = (1 - Y_{h2})C_{ch4} + Y_{h2}C_{bac} \quad (68)$$

$$s_{13} = -C_{bac} + C_{xc} \quad (69)$$

Differential equations 70-74 particulate matter:

$$\frac{dX_c}{dt} = \frac{(X_{c,in} - X_c)}{\frac{V_{liq}}{q_{in}} + t_{res}} - \rho_1 + \sum_{j=1}^{19} \rho_i \tag{70}$$

$$\frac{dX_{ch}}{dt} = \frac{(X_{ch,in} - X_{ch})}{\frac{V_{liq}}{q_{in}} + t_{res}} + f_{ch,xc}\rho_1 - \rho_2 \tag{71}$$

$$\frac{dX_{ch}}{dt} = \frac{(X_{pr,in} - X_{pr})}{\frac{V_{liq}}{q_{in}} + t_{res}} + f_{pr,xc}\rho_1 - \rho_3 \tag{72}$$

$$\frac{dX_{li}}{dt} = \frac{(X_{li,in} - X_{li})}{\frac{V_{liq}}{q_{in}} + t_{res}} + f_{li,xc}\rho_1 - \rho_4 \tag{73}$$

Differential equations 74-76, particulate matter:

$$\frac{dX_{su}}{dt} = \frac{(X_{su,in} - X_{su})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{su}\rho_5 - \rho_{13} \tag{74}$$

$$\frac{dX_{aa}}{dt} = \frac{(X_{aa,in} - X_{aa})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{aa,xc}\rho_6 - \rho_{14}$$

$$\frac{dX_{fa}}{dt} = \frac{(X_{fa,in} - X_{fa})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{fa}\rho_7 - \rho_{15} \tag{75}$$

$$\frac{dX_{c4}}{dt} = \frac{(X_{c4,in} - X_{fa})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{c4}\rho_8 + Y_{c4}\rho_9 - \rho_{16} \tag{76}$$

Differential equations 77-80, particulate matter:

$$\frac{dX_{pro}}{dt} = \frac{(X_{pro,in} - X_{pro})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{pro}\rho_{10} - \rho_{17} \tag{77}$$

$$\frac{dX_{aa}}{dt} = \frac{(X_{ac,in} - X_{ac})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{ac}\rho_{11} - \rho_{18} \tag{78}$$

$$\frac{dX_{h2}}{dt} = \frac{(X_{h2,in} - X_{h2})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{su}\rho_{12} - \rho_{19} \tag{79}$$

$$\frac{dX_I}{dt} = \frac{(X_{I,in} - X_I)}{\frac{V_{liq}}{q_{in}} + t_{res}} + f_{xI,xc}\rho_1 \tag{80}$$

Differential equations 81-82, cations and anions:

$$\frac{dS_{cat^+}}{dt} = \frac{q_{in}}{V_{liq}}(S_{cat^+,in} - S_{cat^+}) \tag{81}$$

$$\frac{dS_{an^-}}{dt} = \frac{q_{in}}{V_{liq}}(S_{an^-,in} - S_{an^-}) \tag{82}$$

Differential equations 83-88, ion states:

$$\frac{dS_{va^-}}{dt} = -\rho_{A,4} \tag{83}$$

$$\frac{dS_{bu^-}}{dt} = -\rho_{A,5} \tag{84}$$

$$\frac{dS_{pro^-}}{dt} = -\rho_{A,6} \tag{85}$$

$$\frac{dS_{ac^-}}{dt} = -\rho_{A,7} \tag{86}$$

$$\frac{dS_{hco3^-}}{dt} = -\rho_{A,10} \tag{87}$$

$$\frac{dS_{nh3}}{dt} = -\rho_{A,11} \tag{88}$$

Algebraic equation:

(89)

$$S_{H+} = -\frac{\theta}{2} + \frac{1}{2}\sqrt{\theta^2 + 4K_w}$$

$$\theta = S_{cat+} + S_{nh4+} - S_{hco3-} - \frac{Sac}{64} - \frac{Spr}{112} - \frac{Sbu}{160} - \frac{Sva}{208} - S_{an-} \tag{90}$$

$$S_{nh4} = S_{IN} - S_{nh3} \tag{91}$$

$$S_{nh4} = S_{IC} - S_{hco3-} \tag{92}$$

Gas phase equations:

For hydrogen:

$$\frac{dS_{gas,h2}}{dt} = -\frac{q_{gas}S_{gas,h2}}{V_{gas}} + \rho_{T,8}\frac{V_{liq}}{V_{gas}} \tag{93}$$

For methane:

$$\frac{dS_{gas,ch4}}{dt} = -\frac{q_{gas}S_{gas,ch4}}{V_{gas}} + \rho_{T,9}\frac{V_{liq}}{V_{gas}} \tag{94}$$

For carbon dioxide:

$$\frac{dS_{gas,co2}}{dt} = -\frac{q_{gas}S_{gas,co2}}{V_{gas}} + \rho_{T,10}\frac{V_{liq}}{V_{gas}} \tag{95}$$

$$p_{gas,,h2} = S_{gas,h2}\frac{RT_{op}}{16} \tag{96}$$

$$p_{gas,,ch4} = S_{gas,ch4}\frac{RT_{op}}{64} \tag{97}$$

$$p_{gas,co2} = S_{gas,co2}\frac{RT_{op}}{16} \tag{98}$$

$$q_{gas} = \frac{RT}{p_{atm} - p_{gas,H_2O}} V_{liq}\left(\frac{\rho_{T,8}}{16} + \frac{\rho_{T,9}}{64} + \rho_{T,10}\right) \tag{99}$$

APPENDIX B. ADM1 MODEL PARAMETERS, VARIABLES, COEFFICIENTS

Table B.1 Yield of catabolism

Name	Variable used	Description	Value	Units
$f_{si,xc}$	f_si_xc	Soluble inerts from composites	0.1	-
$f_{xl,xc}$	f_xi_xc	Particulate inerts from composites	0.2	-
$f_{ch,xc}$	f_ch_xc	Carbohydrates from composites	0.35	-
$f_{pr,,xc}$	F_pr_xc	Proteins from composites	0.2	-
$f_{li,xc}$	f_li_xc	Lipids from composites	0.15	-
$f_{fa,li}$	f_fa_li	Fatty acids from lipids	0.95	-
$f_{h2,su}$	f_h2_su	Hydrogen from sugars	0.19	-
$f_{bu,su}$	f_bu_su	Butyrate from sugars	0.13	-
$f_{pro,su}$	f_pro_su	Propionate from sugars	0.27	-
$f_{ac,su}$	f_ac_su	Acetate from sugars	0.41	-
$f_{h2,aa}$	f_h2_aa	Hydrogen from amino acids	0.06	-
$f_{va,aa}$	f_va_aa	Valerate from amino acids	0.23	-
$f_{bu,aa}$	f_bu_aa	Butyrate from amino acids	0.26	-
$f_{pro,aa}$	f_pro_aa	Propionate from amino acids	0.05	-
$f_{ac,aa}$	f_ac_aa	Acetate from amino acids	0.4	-

Table B.2 Nitrogen contents after adjustment according to the continuity check

Name	Variable used	Description	Value	Units
N_{aa}	N_aa	Nitrogen in amino acids	0.007	kmole N kg COD^{-1}
N_{bac}	N_bac	Nitrogen in biomass	0.00625	kmole N kg COD^{-1}
N_i	N_si	Nitrogen in soluble inerts	0.004286	kmole N kg COD^{-1}
N_{xc}	N_xc	Nitrogen in composites	0.002	kmole N kg COD^{-1}

Table B.3 Carbon contents after adjustment according to the continuity check

Name	Variable used	Description	Value	Units
C_{bac}	C_bac	Carbon in biomass	0.3125	kmole C kg COD^{-1}
C_{xc}	C_xc	Carbon in composites	0.03	kmole C kg COD^{-1}
C_{ch}	C_ch	Carbon in carbohydrates	0.0313	kmole C kg COD^{-1}
C_{pr}	C_pr	Carbon in proteins	0.03	kmole C kg COD^{-1}
C_{li}	C_li	Carbon in lipids	0.022	kmole C kg COD^{-1}
C_{si}	C_si	Carbon in soluble inerts	0.03	kmole C kg COD^{-1}
C_{xI}	C_xi	Carbon in particulate inerts	0.03	kmole C kg COD^{-1}
C_{su}	C_su	Carbon in sugars	0.0313	kmole C kg COD^{-1}
C_{aa}	C_aa	Carbon in amino acids	0.03	kmole C kg COD^{-1}
C_{lcfa}	C_fa	Carbon in long chain fatty acids	0.0217	kmole C kg COD^{-1}
C_{va}	C_va	Carbon in valerate	0.024	kmole C kg COD^{-1}
C_{bu}	C_bu	Carbon in butyrate	0.025	kmole C kg COD^{-1}
C_{pro}	C_pro	Carbon in propionate	0.0268	kmole C kg COD^{-1}
C_{ac}	C_ac	Carbon in acetate	0.0313	kmole C kg COD^{-1}
C_{ch4}	C_ch4	Carbon in methane	0.0156	kmole C kg COD^{-1}

Table B.4 Henry's law coefficients

Name	Variable used	Description	Value	Units
$K_{H, H2}$	K_H_h2	Henry's law coefficient for Hydrogen at 308 ^{o} K	0.000721	$M.bar^{-1}$
$K_{H, CH4}$	K_H_ch4	Henry's law coefficient for Methane at 308 ^{o} K	0.00107	$M.bar^{-1}$
$K_{H, CO2}$	K_H_co2	Henry's law coefficient for CO_2 at 308 ^{o} K	0.0243	$M.bar^{-1}$

Table B.5 Enthalphies

Name	Variable used	Description	Value	Units
ΔH^{0}_{IN}	D_H0_IN	Enthalpy of reaction $NH_4 \leftrightarrow NH_3$	51965	$J.mole^{-1}$
ΔH^{0}_{IC}	D_H0_co2	Enthalpy of reaction $CO2 \leftrightarrow HCO_3$	7646	$J. mole^{-1}$
ΔH^{0}_{H20}	D_H0_h2o	Enthalpy of reaction $H2O \leftrightarrow OH+H^{+}$	55900	$J. mole^{-1}$
ΔH^{0}_{H2}	D_H0_KH_h2	Enthalpy of reaction $H_{2gas} \leftrightarrow H_{2\ liquid}$	-4180	$J. mole^{-1}$
ΔH^{0}_{CH4}	D_H0_KH_ch4	Enthalpy of reaction $CO_{2gas} \leftrightarrow CO_{2liquid}$	-19410	$J. mole^{-1}$
ΔH^{0}_{CO2}	D_H0_KH_co2	Enthalpy of reaction $CH_{4gas} \leftrightarrow CH_{4liquid}$	-14240	$J. mole^{-1}$

Table B.6 Acid-Base equilibrium coefficients

Name	Variable used	Description	Value	Units
$K_{a, va}$	K_a_va	A/B equilibrium coefficient of reaction Hva ↔ Va-	$1.38.10^{-5}$	$kmole.m^{-3}$
$K_{a, bu}$	K_a_bu	A/B equilibrium coefficient of reaction Hbu ↔ Bu- (m)	$1.51.10^{-5}$	$kmole.m^{-3}$
$K_{a, pro}$	K_a_pro	A/B equilibrium coefficient of reaction Hpro- ↔Pro- (m)	$1.32.10^{-5}$	$kmole.m^{-3}$
$K_{a, ac}$	K_a_ac	A/B equilibrium coefficient of reaction Hac ↔ Ac- (m)	$1.74.10^{-5}$	$kmole.m^{-3}$
$K_{a, co2}$	Ka_co2	A/B equilibrium coefficient of reaction CO2↔ HCO3- (298 °K)	$4.94.10^{-7}$	$kmole.m^{-3}$
$K_{a, in}$	Ka_IN	A/B equilibrium coefficient of reaction NH4 ↔ NH3- (298 °K)	$1.11.10^{-9}$	$kmole.m^{-3}$
K_w	Kw_d	A/B equilibrium coefficient of reaction H20 ↔ OH- + H+ (298 °K)	$2.08.10^{-14}$	$kmole.m^{-3}$

Table B.7 Constants and standard values

Name	Variable used	Description	Value	Units
T_{base}	T_base	Base temperature for conversions	298.15	°K
T_{op}	T_op	Operating temperature	312.15	°K
R	R	Gas law constant	$8.314.10^{-2}$	$bar.M^{-1}K^{-1}$

Table B.8. Half saturation constants (HSC)

Name	Variable used	Description	Value	Units
$K_{S, su}$	K_S_su	HSC for sugars	0.50	$Kg\ COD\_SU.m^{-3}$
$K_{S, aa}$	K_S_aa	HSC for amino acids (mesophilic)	0.30	$Kg\ COD\_AA.m^{-3}$
$K_{S, fa}$	K_S_fa	HSC for fatty acids	0.4	$Kg\ COD\_FA.m^{-3}$
$K_{S, c4}$	K_S_c4	HSC for C4+ acids	0.2	$Kg\ COD\_C4.m^{-3}$
$K_{S, pro}$	K_S_pro	HSC for propionate	0.2	$Kg\ COD\_PRO.m^{-3}$
$K_{S, ac}$	K_S_ac	HSC for acetate	0.15	$Kg\ COD\_Ac.m^{-3}$
$K_{S, h2}$	K_S_h2	HSC for hydrogen	7.10^{-6}	$Kg\ COD\_H^2.m^{-3}$
$K_{S, IN}$	K_S_IN	HSC for inorganic nitrogen	1.10^{-1}	$kmoleIN.m^{-3}$

Table B.9 Yields of anabolism

Name	Variable used	Description	Value	Units
Y_{sugars}	Y_su	Yield for sugars	0.10	kg COD_X. kg COD su^{-1}
$Y_{amino\ acids}$	Y_aa	Yield for amino acids	0.08	kg COD_X. kg COD aa^{-1}
$Y_{fatty\ acids}$	Y_fa	Yield for fatty acids	0.06	kg COD_X. kg COD fa^{-1}
Y_{C4}	Y_c4	Yield for C4+ acids	0.06	kg COD_X. kg COD $c4^{-1}$
$Y_{propionate}$	Y_pro	Yield for propionate	0.04	kg COD_X. kg COD pro^{-1}
$Y_{acetate}$	Y_ac	Yield for acetate	0.05	kg COD_X. kg COD_ac^{-1}
$Y_{hydrogen}$	Y_h2	Yield for hydrogen	0.06	kg COD_X. kg COD_$h2^{-1}$

Table B.10 First order decay rates, coefficients

Name	Variable used	Description	Value	Units
$k_{dec,Xsu}$	K_dec_Xsu	Decay rate for sugar degraders	0.02	d^{-1}
$k_{dec,\ Xaa}$	K_dec_X	Decay rate for amino acid degraders	0.02	d^{-1}
$k_{dec,Xfa}$	k_dec_Xfa	Decay rate for fatty acid degraders	0.02	d^{-1}
$k_{dec,Xc4}$	k_dec_Xc4	Decay rate for c4 degraders	0.02	d^{-1}
$k_{dec,Xpro}$	k_dec_Xpro	decay rate for propionate degraders	0.02	d^{-1}
$k_{dec,Xac}$	k_dec_Xac	decay rate for acetate degraders	0.02	d^{-1}
$k_{dec,Xh2}$	k_dec_Xh2	decay rate for h2 degraders	0.02	d^{-1}
$k_{A/Bi}$	kA_B	Rate coefficient for the acid/base reaction	1.10^{8}	d^{-1}
$k_{A/B,\ IN}$	k_A_B_IN	Rate coefficient for the acid/base reaction	1.10^{12}	d^{-1}
$k_{A/B,\ IC}$	k_A_B_co2	Rate coefficient for the acid/base reaction	1.10^{12}	d^{-1}
k_La_{H2}	kLa_h2	Gas-liquid transfer coefficient for hydrogen	200	d^{-1}
k_La_{CH4}	kLa_ch4	Gas-liquid transfer coefficient for methane	200	d^{-1}
k_La_{CO2}	kLa_co2	Gas-liquid transfer coefficient for carbon dioxide	200	d^{-1}

Table B.11 First order constants for disintegration and hydrolysis

Name	Variable used	Description	Value	Units
k_{dis}	K_dis	Distintegration	0.75	d^{-1}
$K_{hyd,ch}$	K_hyd_ch	Hydrolysis of Carbohydrates	10	d^{-1}
$K_{hyd,\ pr}$	K_hyd_pr	Hydrolysis of proteins	10	d^{-1}
$K_{hyd,\ li}$	K_hyd_li	Hydrolysis of lipids	10	d^{-1}

Table B.12 Monod maximum specific uptake rate

Name	Variable used	Description	Value	Units
$K_{m, su}$	Km_su	Uptake rate for sugars	30	kg COD_su/(kgCOD_X.d)
$K_{m, aa}$	Km_aa	Uptake rate for amino acids (mesophilic)	50	kg COD_aa/(kgCOD_X.d)
$K_{m, fa}$	Km_fa	Uptake rate for fatty acids	6	kg COD_fa/(kgCOD_X.d)
$K_{m, c4}$	Km_c4	Uptake rate for C4+ acids	20	kg COD_c4/(kgCOD_X.d)
$K_{m, pro}$	Km_pro	Uptake rate for propionate	9	kg COD_pro/(kgCOD_X.d)
$K_{m, ac}$	Km_ac	Uptake rate for acetate	9	kg COD_Ac/(kgCOD_X.d)
$K_{m, h2}$	Km_h2	Uptake rate for hydrogen	35	kg COD_h^2/(kgCOD_X.d)

Table B.13 pH limits for pH inhibition

Name	Variable used	Description	Value	Units
pH_{UL}	pH_UL_bac	pH level where no inhibition for the bacteria	5.5	-
pH_{LL}	pH_LL_bac	pH level where full inhibition for the bacteria occurs	4	-
pH_{ULac}	pH_LL_ac	pH level where no inhibition for the Ac degraders	7	-
PH_{LLac}	pH_LL_ac	pH level where full inhibition for the Ac degraders	6	-
pH_{UL_h2}	pH_UL_h2	pH level where no inhibition for H2 degraders	6	-
PH_{LL_h2}	pH_LL_h2	pH level where full inhibition for H2 degraders	5	-

Table B.14 Gas components as additional algebraic variables

State Number	Name	Variable used	Description	Units
33	H_2	h2	Hydrogen	kgCOD.m^{-3} gas/bar
34	CH_4	ch4	Methane	kgCOD.m^{-3} gas/bar
35	CO_2	co2	Carbon dioxide	kgCOD.m^{-3} gas/bar

Table B.15 Inhibition factors implied in inhibition functions

Name	Variable used	Description	Value	Units
$K_{I,H2\text{-}fa}$	K_Ih2fa	Inhibitory hydrogen concentration for LCFA degraders	5.10^{-6}	$kgCODm^{-3}$
$K_{I,H2\text{-}C4+}$	K_Ih2c4	Inhibitory hydrogen concentration for C4 degraders	1.10^{-5}	$kgCODm^{-3}$
$K_{I,H2\text{-}pro}$	K_Ih2pro	Inhibitory hydrogen concentration for propionate degraders	$3.5.10^{-5}$	$kgCODm^{-3}$
$K_{I,NH3}$	K_Inh3	Inhibitory free ammonia concentration for Ac degraders	0.0011	$kmoleNm^{-3}$
$K_{I,IN}$	K_INLIM	Inorganic nitrogen concentration at which growth stops	1.10^{-4}	$kmoleNm^{-3}$

Table B.16 Inhibition functions

Name	Variable used	Description	Units
$I_{ph,bac}$	I_PHbac	pH inhibition for all acidogens and acetogens	-
$I_{ph,Xac}$	I_PHXac	pH inhibition for acetate degraders	-
$I_{ph,Xh2}$	I_PHXh2	pH inhibition for hydrogen degraders	-
$I_{IN,lim}$	I_INLIM	Inhibition function to limit growth due to lack of inorganic nitrogen	-
$I_{NH3,Xac}$	I_nh3Xac	Free ammonia inhibition for acetate degraders	-
$I_{H2,LCFA}$	I_h2FA	Hydrogen inhibition function for LCFA degraders	-
$I_{H2,C4}$	I_h2c4	Hydrogen inhibition function for C4 degraders	-
$I_{H2,pro}$	I_H2pro	Hydrogen inhibition function for propionate degraders	-
I_1	I1	Inhibition function for process 5,6 (I_PHBAC.I_INLIM)	-
$I_{2,LCFA}$	I2_fa	Inhibition function for process 7 (I_PHBAC.I_INLIM.I_H2FA)	-
$I_{2,C4}$	I2_c4	Inhibition function for process 8,9 (I_PHBAC.I_INLIM.I_H2C4)	-
$I_{2,pro}$	I2_pro	Inhibition function for process 10 (I_PHBAC.I_INLIM.I_H2PRO)	-
I_3	I3	Inhibition function for process 11 (I_PHXAC.I_INLIM.I_NH3XAC)	-
I_4	I4	Inhibition function for process 12 (I_PHX2.I_INLIM)	-

Table B.17 Reactor, operation specific inputs and process temperature

Name	Variable used	Description	Average Value	Units
Q	Q	Flow rate	62.93	m^3/day
V_{liq}	V_liq	Liquid bulk volume	1892.59	m^3
V_{gas}	V_gas	Headspace volume	183.75	m^3
T_{op}	T_op	Operating process temperature (311.50 °K)	312.15	°K
T_{base}	T_base	Base temperature (298.15 °K)	298.15	°K

Table B.18 Constants

Name	Variable used	Description	Value	Units
P_{tot}	P_gas	Total gas pressure	1.013	bar
P_{atm}	P_atm	Atmospheric pressure	1.013	bar