

Modification of Anaerobic Digestion Model No. 1 for Accumulation and Biomass Recycling

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Abstract. In this paper, modification of Anaerobic Digestion Model No. 1 (ADM1), developed by the International Water Association (IWA) Task Group, to accommodate effects of accumulation of waste in the digester is explained. The modification includes incorporation of a physically-based methodology to ADM1 to account for an unsteady state. The methodology is used to estimate the decrease in the operating volume and the increase in retention time consecutively due to biomass recycling in the reactor caused by the accumulation of particulate matter and operational variations. The methodology considers both the reduction in the operating volume, and the increase in retention time due to the accumulation, and accompanied biomass recycling. By the evaluation of The Modified Model outputs and comparison with the Original Model outputs, the methodology, developed in the research, is found to be necessary and suitable for simulation of the anaerobic digestion in a Colorado Pork anaerobic digester.

1. Introduction

The anaerobic digestion (AD) process includes series and parallel interrelated reactions. The organic waste goes through different biochemical processes as depolymerization, acidogenesis, acetogenesis, and methanogenesis and other than these, physico-chemical, thermal processes as well take place during the digestion. Many approaches have been developed for AD process modeling such as mass-balance and knowledge models. Each of these models has their advantages and disadvantages. Their applicability is limited by time, expertise (i.e., knowledge of the process structure), and available data. Generic dynamic model development based on the process dynamics, application and extension of the models for different cases, such as different reactor types, environmental conditions, organic waste types, operating conditions for the AD process are needed (Chynoweth et al., 1998; Batstone et al., 2002b).

Anaerobic Digestion Model No. 1 (ADM1) was developed by Batstone et al. (2002b), is a generic dynamic model, which is based on the works of Siegrist et al. and other researchers. The model includes the main relevant processes of AD to make it simple and widely applicable. The model is suitable for extension to specific cases through its open structure and common nomenclature.

In this paper, the modification of ADM1 by incorporating a physically-based methodology to account for accumulation in the reactor and accompanying biomass recycling has been explained. The modification allows estimation of both decrease in the reactor volume due to the solids accumulation and increase in retention time due to biomass recycling. The Modified Model successfully characterized the performance of a full-scale anaerobic reactor validating the necessity and applicability of the methodology developed.

2. The Anaerobic Digestion Model No. 1

In ADM1, biochemical reactions, and physico-chemical reactions are modeled as number of sequential and parallel steps (Batstone et al., 2002b). The process and component inclusion in the model is determined considering the maximization of the applicability while maintaining a simple model structure. The model includes the three overall biological (cellular) steps, (i.e. acidogenesis, acetogenesis and methanogenesis) as well as an extracellular disintegration (partly non-biological) and depolymerization step (Figure 1).

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 and Droste 2000; Batstone et al. 2002b). Physico-chemical 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. The overall process reactions including acid-base equilibriums are given in Appendix A and nomenclature is given in Appendix B.

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 and 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. All biochemical extracellular steps are assumed to be first order, which is a simplification based on empiricism, reflecting the cumulative effect of a multi-step process (Masse and Droste, 2000; Batstone et al., 2002b). 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. First order biomass decay was assumed.

In the Modified Model, a methodology to account for solids accumulation and biomass recycling due to the accumulation is incorporated into the Original Model. The schema of the Modified Model is given Figure 2.

The Original Model processes and relevant equations are briefly reviewed in the following paragraphs. Further details regarding the Original Model could be found in Batstone et al. (2002b).

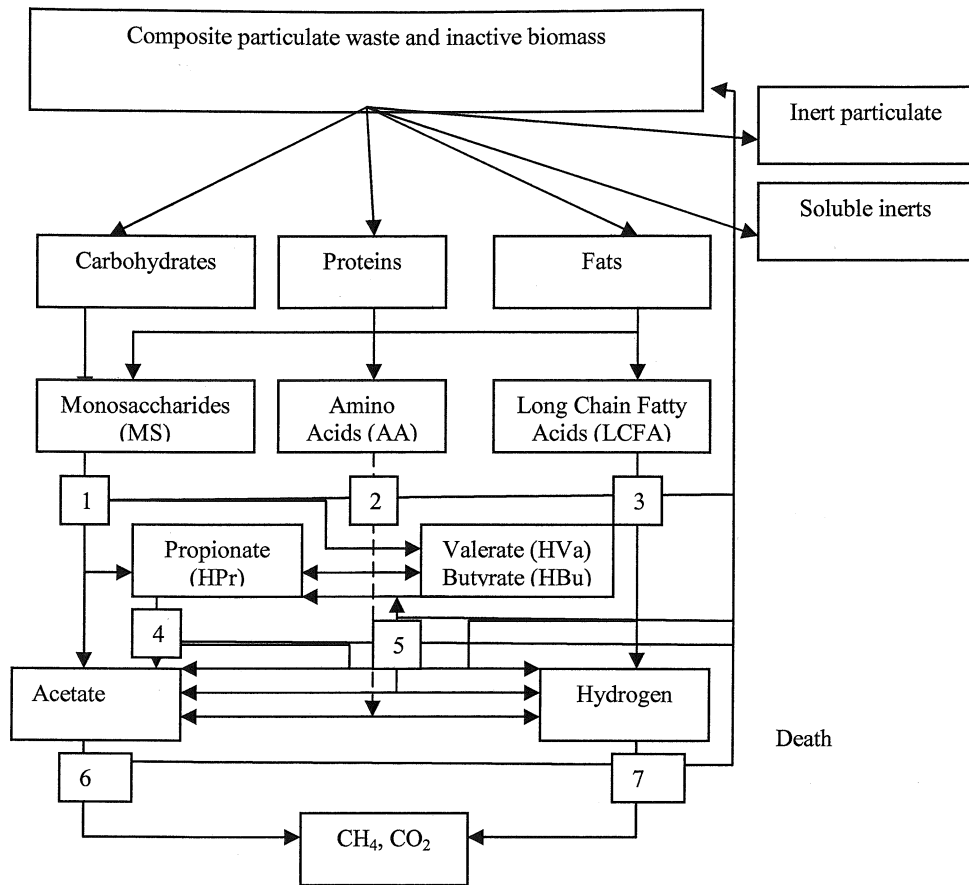


Figure 1. The Anaerobic Digestion Model No. 1 as implemented including biochemical processes: 1. acidogenesis from sugars (MS); 2. acidogenesis from amino acids (AA); 3. acetogenesis from long chain fatty acids (LCFA); 4. acetogenesis from propionate; 5. acetogenesis from butyrate and valerate; 6. acetoclastic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

Note: In the Original Model:

Digester volume changes (i.e., decrease) and biomass recycling are not considered in mass balance equations.

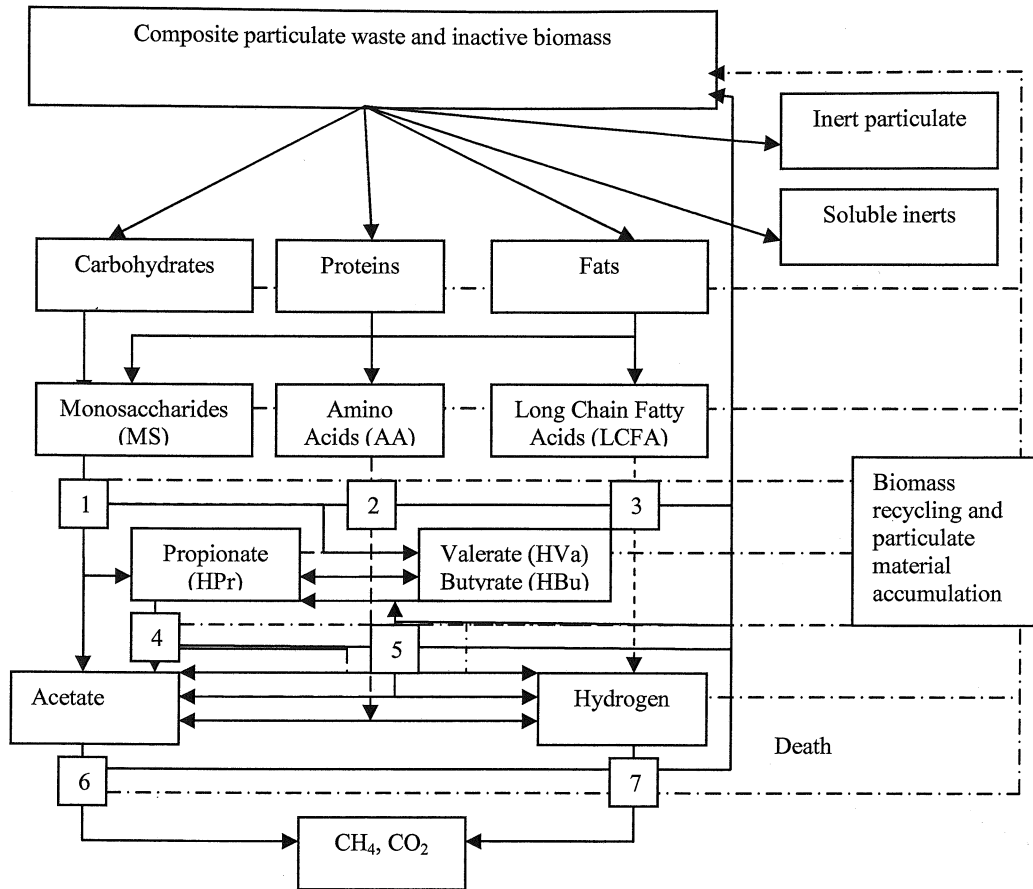


Figure 2. The Modified Model for Anaerobic Digestion as implemented, including biochemical processes: 1. acidogenesis from sugars (MS); 2. acidogenesis from amino acids (AA); 3. acetogenesis from long chain fatty acids (LCFA); 4. acetogenesis from propionate; 5. acetogenesis from butyrate and valerate;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

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

$$[\text{Accumulation of mass}] = [\text{Input}] - [\text{Output}] + [\text{Production}](1)$$

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

$$\frac{dVS_{li,i}}{dt} = q_{in}S_{in,i} - q_{out}S_{liq,i} + V \sum_{j=1-19} \rho_j v_{i,j} \quad (2)$$

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

$$\frac{dS_{li,i}}{dt} = \frac{q_i S_{in,i}}{V_{liq}} - \frac{q S_{liq,i}}{V_{liq}} + \sum_{j=1-19} \rho_j v_{i,j} \quad (3)$$

, and for varying retention time:

$$\frac{dVX_{li,i}}{dt} = \frac{q_i X_{in,i}}{V_{liq}} - \frac{q X_{liq,i}}{V_{liq} + t_{res,x} q} + \sum_{j=1-19} \rho_j v_{i,j} \quad (4)$$

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

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:

$$\frac{dS_{gas,i}}{dt} = -\frac{q_{gas} S_{gas,i}}{V_{gas}} + \rho_{T,i} \frac{V_{liq}}{V_{gas}} \quad (5)$$

where $S_{gas,i}$ is the gas volume specific concentration variable, q_{gas} is the overall dry gas flow (water corrected), V_{gas} is the headspace volume, V_{liq} is the bulk reactor volume, and $\rho_{T,i}$ = Liquid volume specific gas transfer rate, and i stands for one of the three gas components (i.e., carbon dioxide, hydrogen and methane).

The liquid-gas transfer rate equation is given below:

$$\rho_{T,i} = k_L a (S_{liq,i} - K_{H,i} p_{gas,i}) \quad (6)$$

where $\rho_{T,i}$ is the specific mass transfer rate of gas i, $k_L a$ is the overall mass transfer coefficient, $S_{liq,i}$ is the concentration of gas component i in the bulk, $K_{H,i}$ is the Henry's law coefficient for gas i, $p_{gas,i}$ is the 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 is calculated using ideal gas law and corrected for water vapor.

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

$$\rho_{A/B,i} = k_{A/B,i} (S_{liq,i-} (K_{a,i} + S_{H+}) - K_{a,i} S_{liq,i}) \quad (7)$$

where $\rho_{A/B,i}$ is the production rate of acid from the base, $k_{A/B,i}$ is the acid-base kinetic constant, $S_{liq,i}$ is the total concentration of free form of an organic acid, dissolved carbon dioxide or ammonium, $S_{liq,i-}$, concentration of ionic form, $S_{liq,H+}$ is the concentration of hydrogen ions in the bulk, $K_{a,i}$ is the acid-base equilibrium coefficient. Free ammonia and hydrogen inhibition, pH inhibition and Nitrogen limitation are assumed in the model.

3. Modification Methodology for Accumulation in the Reactor and Biomass Recycling

Increase in the solids retention time (SRT), and decrease in reactor volume due to accumulation and accompanying biomass recycling 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. In the derivation of the settling methodology in the reactor, discrete particles, equal distribution of flow in horizontal and vertical directions, no turbulence in the reactor, movement of the particles horizontally at the same velocity as the organic waste are assumed.

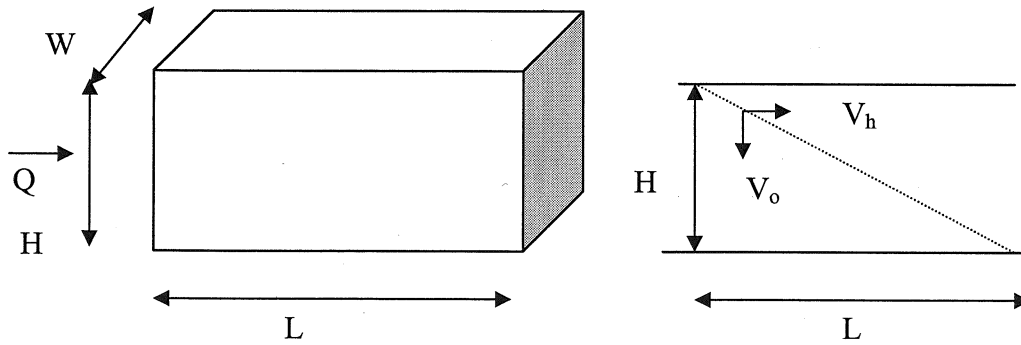


Figure 3. Schematic of settling in the reactor

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:

$$HRT = \frac{V}{Q} = \frac{HLW}{Q} \quad (8)$$

where HRT is the hydraulic retention time, H is the height of the reactor, L is the length of the reactor, and W is the width of reactor

$$HRT = \frac{H}{V_o} = \frac{L}{V_h} \quad (9)$$

where V_h is the horizontal component of velocity, V_o is the critical particle settling velocity.

, and solving V_o :

$$V_o = \frac{Q}{A_s} \quad (10)$$

where A_s is the 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:

$$F_g - F_D - F_n = m \frac{dV}{dt} = 0 \quad (11)$$

where F_g is the weight of particle, F_D is the drag force, and F_n is the 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:

$$R_{ep} = \frac{d_p V_s \rho_f}{\mu} \quad (12)$$

where d_p is the particle diameter, V_s is the fall velocity of the particle, ρ_f is the fluid density, and μ is the fluid viscosity.

The drag force can be computed as:

$$F_D = \frac{1}{2} C_D \rho_f V_s^2 A \quad (13)$$

where A is the projected frontal area of particle, C_D is the 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 and solving for V_s :

$$V_s = \frac{g(\rho_p - \rho_f)d_p^2}{18\mu} \quad (14)$$

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):

$$SR = \frac{\partial}{\partial t} \iiint_{CV} C dV = \iint_{CS} C n \cdot \mathbf{V}_s dA \quad (15)$$

where SR is the sedimentation rate, dV = Change in the volume of the CV, $\mathbf{n} \cdot \mathbf{V}_s$ is the component of velocity normal to the sludge layer, and A is the area of sludge under the CV.

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

$$SR = -C \frac{dV}{dt} = CA \overline{V}_s \quad (16)$$

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 μ m diameter quartz silt and for 200 μ m 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:

$$-\frac{dV}{dt} = A \overline{V}_s \quad (17)$$

The increase in retention time for each quarterly period, Δt , may be estimated as (Cesur 2004):

$$tres_{,x} = \frac{HRT_{\Delta t}(i) dV_{in,i}}{q_{out}(i+1)_{liq}} = \frac{HRT_{\Delta t}(i) A \overline{V}_s}{q_{out}(i+1)} \quad (18)$$

Where: $HRT_{\Delta t}(i)$ = hydraulic retention time (i.e., number of days waste stays in the reactor 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 reactor operating volume can be calculated using mass balance of suspended solids, fixed solids, total phosphorous, copper and zinc for Colorado Pork reactor (Martin, 2003).

4. The Original 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 Original Model is implemented and the model parameters are estimated using the experimental data. In the second phase, the Original Model is modified for accumulation. The Modified Model is implemented as Dynamic Equation (DE) system since this implementation in MATLAB is less sensitive than the Dynamic and Algebraic Equation (DAE) system implementation. Single stage DE implementation schema is shown in Figure 4. There are 32 dynamic state variables, 19 biochemical process rates and 3 liquid-gas transfer

processes in DE system. The DE system contains 6 more dynamic state variables due to the acid-base dissociation in the system. The Modified Model is applied for simulation of the anaerobic digestion process taking place at Colorado Pork, LLC, reactor.

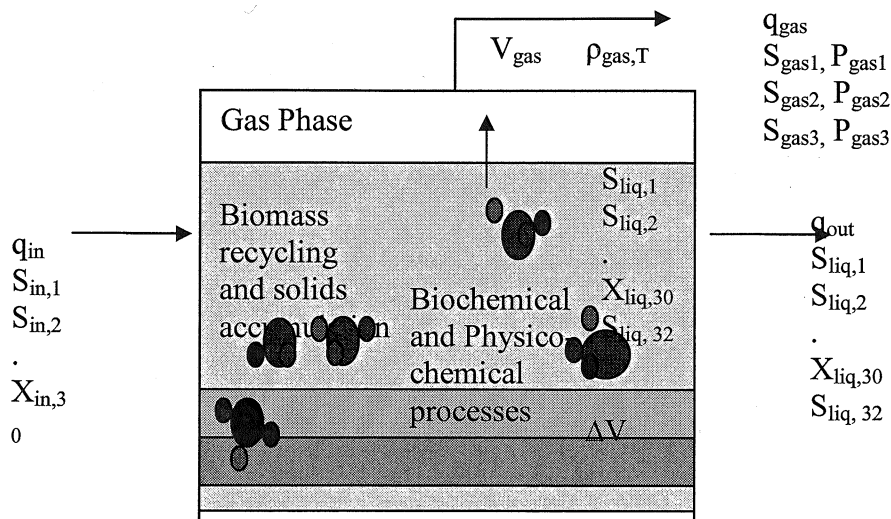


Figure 4. Schematic of a typical single tank reactor with solids accumulation and biomass recycling (q_{in} = flow into the reactor, m^3/day ; q_{out} =flow out of reactor, m^3/day ; q_{gas} = gas flow, m^3/day ; $\rho_{gas, T}$ = Liquid-gas transfer rate, M/day ; V = volume (variable), m^3 , ΔV = change in volume; $S_{in,i}$ = Concentration of liquid components, $kgCOD/m^3$; $X_{in, i}$ = Concentration of particulate components, $kgCOD/m^3$) (Modified from Batstone et al., 2002a)

In the first phase, most of the kinetic parameters are assumed to be fixed due to their low variability (Batstone et al., 2002b). 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 and Droste 1997; Masse and 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 et al., 1990). Stoichiometric coefficients were also taken from the IWA task group report. Carbon and nitrogen contents were recalculated by implementing the balance terms in the rate equation matrix. Physicochemical parameters were taken from the report and other resources (Stumm and 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. (2002b).

Parameters with high sensitivity and high variability are estimated using experimental data of researchers and the nonlinear constrained optimization method was implemented using MATLAB 6.5 optimization toolbox and the two-parameter optimizations around optimum using secant

method was implemented using Aquasim 2.1d version. (Masse et al., 1996; Masse et al., 1997; Masse and Droste, 1997; Masse and Droste, 2002; Siegrist et al. 2002). The initial values of the parameters to be estimated were taken from the scientific and the report of IWA task group, research of Masse and Droste, and Chynoweth et al. (Chynoweth et al., 1998a; Batstone et al., 2002b; Masse et al. 1996; Masse et al. 1997a; Masse and Droste, 1997b; Masse and Droste, 2000). Estimation methods were applied for the disintegration constant, k_{dis} , maximum uptake rates for acetate and propionate utilizers, $k_{m,ac}$, $k_{m,pro}$, half saturation constants for acetate, propionate and hydrogen utilizers, $K_{S,ac}$, $K_{S,pro}$, K_{S,H_2} .

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 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 2.

Table 2. 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) | $kgCODAc. m^{-3}$ |
| $K_{S,pro}$ | Half saturation constant for propionate utilizers | 0.20 (0.1-10) | $kgCODPro. m^{-3}$ |
| K_{SH_2} | Half saturation constant for H_2 utilizers | 7.10^{-6} (7.10^{-6} -0.5) | $kgCODH_2. m^{-3}$ |

5. The Modified Model Implementation

Colorado Pork, LLC (CP), AD reactor data set was used to verify the Modified Model. The Modified Model output was compared with the measured data.

Colorado Pork, LLC, Anaerobic Digester is a mesophilic, intermittently mixed anaerobic digester used for swine manure stabilization and biogas production at Lamar, Colorado. The facility houses 5000 sow breed sows to weaner pigs. Manure from the facility has low (deviation < 5

percent as percentage of averages) pH, CO₂, and CH₄ variability. 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 m³ (V_{total}) operating volume of 1892.59 m³ (V_{liquid}). This gives the volume of headspace as 168.88 m³ (V_{gas}). The digester is heated to maintain a temperature of approximately 39 °C. 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 m³ per day to 41.64 m³ per day and averaged 52.41 m³ per day (i.e., 6.07·10⁻⁴ m³/sec). Design hydraulic retention time was estimated to be 40 days (Martin, 2003). The AD system achieved 65.00 percent volatile solid (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.

Swine waste is characterized by little above the neutral pH, 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).

Sampling data collected for each of the reporting quarters approximately two-week time intervals at 26 sampling points during 364 days period between April 2000 and April 2001 (Mattocks et al., 2002; Martin, 2003). Gas samples were collected from gas line in the pipe chase and were sent for analysis. 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. The digestion system operation data is given in Table 3, influent constituent averages by quarter is given in Table 4, and effluent constituent averages are given Table 5.

Table 3. Digestion system operation information (Mattocks et al. 2002).

| | | 1st Q 4/24-7/24 | | | 2nd Q 8/14-10/24 | | |
|-------------------------------|-------------------------------|-----------------|--------|--------------|------------------|--------|--------------|
| | | Av | Av | AvDev% Av | Av | AvDev | AvDev %Av |
| 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/m³, 3-MPN/g, 4-kg/m³, 5-kg CaCO₃/m³, 6-m³/m³/hr,
 Av = Average, AvDev: Average deviation, AvDev%Av: Average deviation percentage of Average

Table 3. Digestion system operation information (Continued) (Mattocks et al. 2002).

| | | 3rd Q 11/6-1/23 | | | 4th Q 2/5-4/16 | | |
|-------------------------------|-------------------------------|-----------------|----------|-----------|----------------|--------|-----------|
| | | Av | AvDev | AvDev %Av | Av | AvDev | AvDev %Av |
| 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/m³, 3-MPN/g, 4-kg/m³, 5-kg CaCO₃/m³, 6-m³/m³/hr

Av = Average, AvDev: Average deviation, AvDev%Av: Average deviation percentage of Average

Table 4. Influent constituent averages by quarter (Mattocks et al. 2002).

| | 1st Q 4/24-7/24 | | | 2nd Q 8/14-10/24 | | |
|--|-----------------|---------|--------------|------------------|---------|--------------|
| | Av | AvDev | AvDev% Av | Av | AvDev | AvDev %Av |
| M ³ /day | 63.88 | 7.10 | 11 | 51.37 | 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 ⁺ , % | 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/m³, 3-MPN/g. 4-kg/m³, 5-kg CaCO₃/m³, 6-m³/m³/hr

Av = Average, AvDev: Average deviation, AvDev%Av: Average deviation percentage of Average

Table 4. Influent constituent averages by quarter (Continued) (Mattocks et al. 2002).

| | 3rd Q 11/6-1/23 | | | 4th Q 2/5-4/16 | | |
|--------------------------------------|-----------------|---------|-----------|----------------|---------|-----------|
| | Av | AvDev | AvDev %Av | Av | AvDev | AvDev %Av |
| 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 , | 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 ⁺ , % | 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 ² | 654,000 | 212,800 | 33 | 1,033,33 | 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/m³, 3-MPN/g. 4-kg/m³, 5-kg CaCO₃/m³, 6-m³/m³/hr

Av = Average, AvDev: Average deviation, AvDev%Av: Average deviation percentage of Average

Table 5. Effluent constituent averages by quarter (Mattocks et al. 2002).

| | 1st Q 4/24-7/24 | | | 2nd Q 8/14-10/24 | | |
|--------------------------------------|-----------------|-------|--------------|------------------|-------|--------------|
| | Av | AvDev | AvDev %Av | Av | AvDev | AvDev %Av |
| 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 ⁺ , % | 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 Solids ⁴ Sus | 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/m³, 3-MPN/g, 4-kg/m³, 5-kg CaCO₃/m³, 6- m³/m³/hr

Av = Average, AvDev: Average deviation, AvDev%Av: Average deviation percentage of Average

Table 5. Effluent constituent averages by quarter (Continued) (Mattocks et al. 2002)

| | 3rd Q 11/6-1/23 | | | 4th Q 2/5-4/16 | | |
|--|-----------------|-------|-----------|----------------|-------|-----------|
| | Av | AvDev | AvDev %Av | Av | AvDev | AvDev %Av |
| 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 |
| P ₂ O ₅ ¹ , % | 0.21 | 0.05 | 25 | 0.23 | 0.06 | 26 |
| K ₂ O 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 |
| NH ₄ ⁺ , % | 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 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/m³, 3-MPN/g. 4-kg/m³, 5-kg CaCO₃/m³, 6- m³/m³/hr

Av = Average, AvDev: Average deviation, AvDev%Av: Average deviation percentage of Average

6. Results and Discussion

The Modified 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 model input is based on feed analysis which was performed during the sampling period. The characteristic percentages for the influent constituents were given in Table 6. 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. (1997b), Chynoweth et al. (1998b), and Batstone et al. (2003). Volatile fatty acids are split into acetate, propionate, butyrate and valerate components. Simulations were carried out using the original model as well to compare the original model outputs with the Modified Model outputs (Table 7, Figure 5).

Table 6. 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 |

The comparison of the measured, the Modified Model and the Original Model simulated biogas production data shows that the model represents the digestion process quite well (Table 7, Figure 5). The absolute error of the Modified Model was 83 m³/day, the relative error was 10.34 percent, the RMSE was 29.77 m³/day, coefficient of variation was 0.040, and the correlation coefficient was 0.66. The original model absolute error was 109.49 m³/day, relative error was 15.60 percent, RMSE was 41.23 m³/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 7, Figure 5). The discrepancies observed could be attributed to the changes in waste characteristics between periods, characterization errors (i.e., errors in proportioning the waste

constituents) due to the lack of data on waste stream before the sampling period, changes in operating conditions, and model representation limitations. Additionally, at the beginning of the sampling period digester operation appears to be less stable than the later periods.

The variation in biogas is due to the varying influent waste characteristics and operating conditions. Biogas generated by the digester had a stable gas composition of 66 percent methane, 32 percent carbon dioxide, 0.6 percent oxygen and 1.5 percent nitrogen. 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.

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.

Table 7. Comparison of the measured, Original and Modified Model simulated biogas production

| Months | Biogas measured (m ³ /day) | Biogas simulated the Original Model (m ³ /day) | Biogas simulated the 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 |

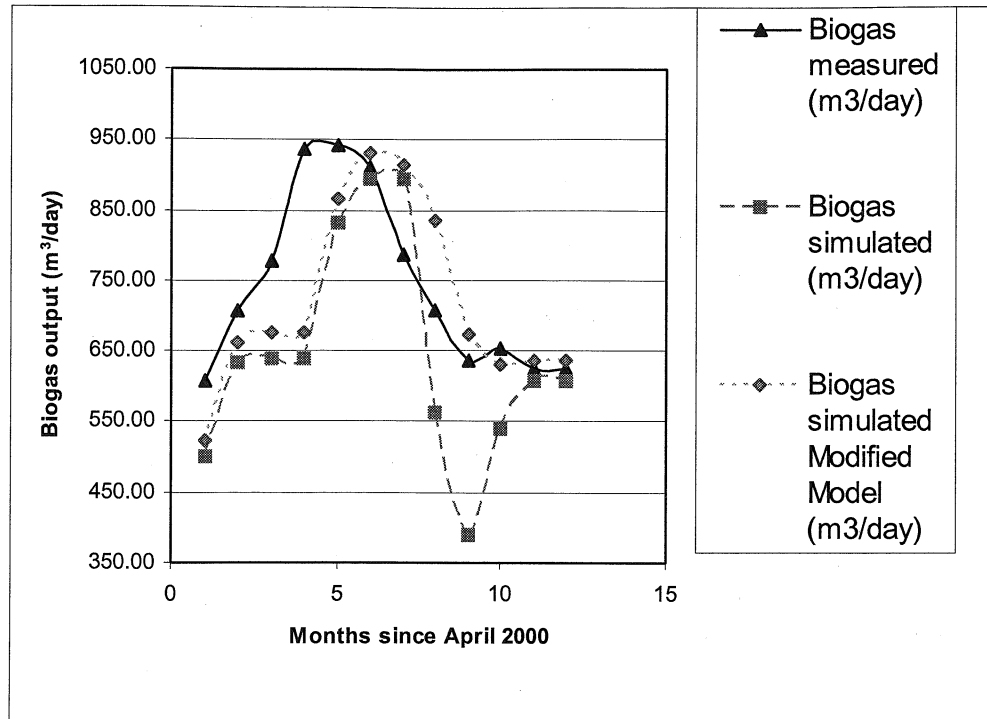


Figure 5. Comparison of measured and the original model simulated biogas production

7. Conclusions

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 by the developed methodology. 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 an unsteady state operation.

A physically-based 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. The comparative results of the Original Model and the Modified Model given in Table 7, and Figure 5, prove the suitability and the necessity of the modification of the model for simulation of the Colorado Pork anaerobic digester.

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Appendix A. The Modified Model Differential Equation System

Process rates

Biochemical process rates

$$\rho_1 = k_{dis} \cdot X_c \quad (1)$$

$$\rho_2 = k_{hyd,ch} \cdot X_{ch} \quad (2)$$

$$\rho_3 = k_{hyd,pr} \cdot X_{pr} \quad (3)$$

$$\rho_4 = k_{hyd,li} \cdot X_{li} \quad (4)$$

$$\rho_5 = k_{m,su} \cdot \frac{S_{su}}{K_{S,su} + S_{su}} X_{su} \cdot I_5 \quad (5)$$

$$\rho_6 = k_{m,su} \cdot \frac{S_{aa}}{K_{S,aa} + S_{aa}} X_{aa} \cdot I_6 \quad (6)$$

$$\rho_7 = k_{m,fa} \cdot \frac{S_{fa}}{K_{S,fa} + S_{fa}} X_{fa} \cdot I_7 \quad (7)$$

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

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

$$\rho_{10} = k_{m,pr} \cdot \frac{S_{pro}}{K_{S,pro} + S_{pro}} X_{pro} \cdot I_{10} \quad (10)$$

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

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

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

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

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

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

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

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

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

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})

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

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

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

Process inhibition

Inhibition:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

, and

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

Water phase equations

Differential equations 44-47, soluble matter:

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

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

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

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

Differential equations 48-51, soluble matter

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

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

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

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

Differential equations 52-55, soluble matter:

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

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

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

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

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:

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

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

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

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

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

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

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

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

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

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

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

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

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

Differential equations 70-73 particulate matter:

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

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

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

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

Differential equations 74-77, particulate matter:

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

$$\frac{dX_{aa}}{dt} = \frac{(X_{aa,in} - X_{aa})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{aa,xc} \rho_6 - \rho_{14} \quad (75)$$

$$\frac{dX_{fa}}{dt} = \frac{(X_{fa,in} - X_{fa})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{fa} \rho_7 - \rho_{15} \quad (76)$$

$$\frac{dX_{c4}}{dt} = \frac{(X_{c4,in} - X_{fa})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{c4} \rho_8 + Y_{c4} \rho_9 - \rho_{16} \quad (77)$$

Differential equations 78-81, particulate matter:

$$\frac{dX_{pro}}{dt} = \frac{(X_{pro,in} - X_{pro})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{pro} \rho_{10} - \rho_{17} \quad (78)$$

$$\frac{dX_{aa}}{dt} = \frac{(X_{ac,in} - X_{ac})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{ac} \rho_{11} - \rho_{18} \quad (79)$$

$$\frac{dX_{h2}}{dt} = \frac{(X_{h2,in} - X_{h2})}{\frac{V_{liq}}{q_{in}} + t_{res}} + Y_{su} \rho_{12} - \rho_{19} \quad (80)$$

$$\frac{dX_I}{dt} = \frac{(X_{I,in} - X_I)}{\frac{V_{liq}}{q_{in}} + t_{res}} + f_{xl,xc}\rho_1 \quad (81)$$

Differential equations 82-83, cations and anions:

$$\frac{dS_{cat^+}}{dt} = \frac{q_{in}}{V_{liq}} (S_{cat^+,in} - S_{cat^+}) \quad (82)$$

$$\frac{dS_{an^-}}{dt} = \frac{q_{in}}{V_{liq}} (S_{an^-,in} - S_{an^-}) \quad (83)$$

Differential equations 83-88, ion states:

$$\frac{dS_{va^-}}{dt} = -\rho_{A,4} \quad (84)$$

$$\frac{dS_{bu^-}}{dt} = -\rho_{A,5} \quad (85)$$

$$\frac{dS_{pro^-}}{dt} = -\rho_{A,6} \quad (86)$$

$$\frac{dS_{ac^-}}{dt} = -\rho_{A,7} \quad (87)$$

$$\frac{dS_{hco3^-}}{dt} = -\rho_{A,10} \quad (88)$$

$$\frac{dS_{nh3}}{dt} = -\rho_{A,11} \quad (89)$$

Algebraic equation:

$$S_{H^+} = -\frac{\theta}{2} + \frac{1}{2}\sqrt{\theta^2 + 4K_w} \quad (90)$$

$$\theta = S_{cat^+} + S_{nh4^+} - S_{hco3^-} - \frac{Sac}{64} - \frac{Spr}{112} - \frac{Sbu}{160} - \frac{Sva}{208} - S_{an^-} \quad (91)$$

$$S_{nh4} = S_{IN} - S_{nh3} \quad (92)$$

$$S_{nh4} = S_{IC} - S_{hco3^-} \quad (93)$$

Gas phase equations:

For hydrogen:

$$\frac{dS_{gas,h2}}{dt} = -\frac{q_{gas}S_{gas,h2}}{V_{gas}} + \rho_{T,8}\frac{V_{liq}}{V_{gas}} \quad (94)$$

For methane:

$$\frac{dS_{gas,ch4}}{dt} = -\frac{q_{gas}S_{gas,ch4}}{V_{gas}} + \rho_{T,9}\frac{V_{liq}}{V_{gas}} \quad (95)$$

For carbon dioxide:

$$\frac{dS_{gas,co2}}{dt} = -\frac{q_{gas}S_{gas,co2}}{V_{gas}} + \rho_{T,10} \frac{V_{liq}}{V_{gas}} \quad (96)$$

$$p_{gas,,h2} = S_{gas,h2} \frac{RT_{op}}{16} \quad (97)$$

$$p_{gas,,ch4} = S_{gas,ch4} \frac{RT_{op}}{64} \quad (98)$$

$$p_{gas,co2} = S_{gas,co2} \frac{RT_{op}}{16} \quad (99)$$

$$q_{gas} = \frac{RT}{p_{atm} - p_{gas,H_2O}} V_{liq} \left(\frac{\rho_{T,8}}{16} + \frac{\rho_{T,9}}{64} + \rho_{T,10} \right) \quad (100)$$

Appendix B. Nomenclature

| | |
|------------------------------------|---|
| Symbol | Description |
| 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 |
| $F_{\text{product, substrate}}$ | Yield (catabolism only) of product in substrate, kg COD/kg COD |
| $Y_{\text{substrate}}$ | Yield of biomass on substrate, kg COD/kg COD |
| H_{gas} | Gas law constant (equal to K_H^{-1}), bar/M |
| $K_{a,\text{acid}}$ | Acid-base equilibrium constant, $M=\text{kmole}/\text{m}^3$ |
| K_H | Henry's law coefficient, M/bar |
| R | Gas law constant (8.314×10^{-2}), $\text{bar} \cdot \text{M}^{-1} \cdot \text{K}^{-1}$ |
| pH | $-\log_{10}[\text{H}^+]$, (2) |
| $P_{\text{gas},i}$ | Partial pressure of gas i, bar |
| $K_{A/Bi}$ | Acid-base kinetic constant, d^{-1} |
| $k_{\text{dec,acid}}$ | First order decay rate, d^{-1} |
| $I_{\text{inhibitor, process}}$ | Inhibition function |
| k_{process} | First order constant, normally for hydrolysis, d^{-1} |
| $k_L a$ | Gas-liquid transfer coefficient, d^{-1} |
| $K_{I, \text{inhibit, substrate}}$ | 50% inhibitory concentration, kgCOD/m^3 |
| $k_m, \text{process}$ | Monod maximum specific uptake rate, $\text{kgCOD S}/\text{kgCODX}^{-1} \cdot \text{d}^{-1}$ |
| $K_s, \text{process}$ | Half saturation constant, $\text{kgCOD S}/\text{m}^3$ |
| ρ_j | Generalized rate of process j |
| Symbol | Description |
| $\text{p}K_a$ | $-\log_{10}[K_a]$ |
| $K_{A/Bi}$ | Acid-base kinetic constant, d^{-1} |
| $k_{\text{dec,acid}}$ | First order decay rate, d^{-1} |
| $I_{\text{inhibitor, process}}$ | Inhibition function, |
| k_{process} | First order constant, normally for d^{-1} hydrolysis, |
| $k_L a$ | Gas-liquid transfer coefficient, d^{-1} |
| $K_{I, \text{inhibit, substrate}}$ | 50% inhibitory concentration, kgCOD/m^3 |
| $k_m, \text{process}$ | Maximum uptake rate, $\text{kgCOD}_S \cdot \text{kgCOD}_X^{-1} \cdot \text{d}^{-1}$ |
| $K_s, \text{process}$ | Half saturation constant, $\text{kgCOD}_S/\text{m}^3$ |
| ρ_j | Generalized rate of process j |
| μ_{max} | Monod maximum specific growth rate, d^{-1} |