Acknowledgements

Assigned under the subject F4203, the individual graduation project had been carried out during the 4th semester of the two years study. This thesis is the description and outcome of the experiments and analysis.

Transient response to shock loads in biogas processes is the focus of the project. This is studied by feeding a biogas batch reactor intermittently with different load volume and time interval. Through parameters measurements, the shock loads were determined and the responses to the shock loads were observed and analyzed. The ADM1 (Batstone et al., 2002) was used as the model to simulate the loads and the responses through AQUASIM 2.1f.

During this period, all the help I got promoted the project proceeding smoothly. I would like to express my heartfelt thanks to professor Rune Bakke for his great guidance, and to Mr. P.G. Rathnasiri for his valuable advices, also to Hildegunn Hegna Haugen, Jo-Ela Johansen, Carlos Dinamarca-Røed, Deshai Botheju, Trine Eilefsen, Eivind Fjelddalen and He Zhao for their kind help.

Porsgrunn, Jul. 2006

Abstract

Active culture which is in a semi steady state was extracted from an anaerobic digestion reactor, transferred to a continuously stirred batch reactor with rather small head space. 35±1ºC was controlled for the reactor to run at mesophilic condition, synthetic substrate was used to feed intermittently. The transient response to the intermittent load was monitored through the measurements of biogas production, biogas composition and pH in the culture. By changing the feed volume and the feeding interval, the measurements of biogas production in terms of specific production rate show a distribution of different inhibition extent, which is the result of the correlation between the load and the biomass concentration, and as the ratio of load/biomass concentration increase, the extent of inhibition increase. Small head space made it possible to get the data of biogas composition at different time points, the measurements show methane composition decrease as the inhibition increase. pH measurements also show the pH drop increase as the inhibition increase. The inhibition indicates a perturbation of the steady state, the intermittent load which result in this inhibition is thus called a shock load.

ADM1 (Anaerobic Digestion Model No.1) (Batstone et al., 2002) was used as the model to simulate this process through the software AQUASIM 2.1f. The simulations fit the experimental data well for the specific production rate by starting with a suitable biomass concentration, as well for the biogas composition for the case without obvious inhibition, but not for the pH.

Key word: anaerobic digestion, head space, intermittent load, specific production rate, inhibition, shock load, shock extent

CONTENTS

1 INTRODUCTION

Biogas is generated when bacteria degrade organic matter in the absence of oxygen, in a process known as anaerobic digestion. The process is successfully used for the treatment of municipal sludge, animal manure, industrial sludge, and industrial and municipal wastewater (Wilkie, 2005). Since biogas is a mixture of methane and carbon dioxide, it has similar properties to natural gas and is by far the most cost effective renewable fuel (Schmersahl and Scholz, 2005). Biogas can be used for heating, electricity generating from Combined Heat and Power engines, integration in natural gas pipelines, fuel for vehicles and fuel for fuel cells, etc. Its energy content is defined by the methane concentration. If the biogas burns, the methane content is at least 45%[(1)] . Therefore not only the biogas production but also the biogas quality is concerned, especially for the high grade biogas needing field, such as pipeline gas, fuel for vehicles and fuel for fuel cells. The stable biogas process is expected since the variation of production and gas composition may cause difficulties in controlling of the application processes. In the fuel cell, the power output varies with methane content, with maximum power production occurring at 45% methane (staniforth and Ormerod, 2002).

From time to time most biogas plants have experienced substantial declines in the gas production due to interruptions of the biological process. Often a more effective control of the process will prevent such incidents and thereby improve the economy of the plants. (Nielsen et al., 2006). The stability of the biogas process is affected by many factors: temperature, organic load, alkalinity and pH, biomass concentration, etc. Through some parameters, the stability of the process can be monitored, and the process can be controlled. These parameters are called control parameters. Four parameters are of particular interest: the methane production, the concentration of hydrogen, pH and the concentration of volatile fatty acids (VFA) (Nielsen et al., 2006).

Digesters operating in industry are likely to be fed either continuously, daily, weekly, or at some intermediate time interval. Since the process is relatively stable by continuous feed, it is important to know how the process fluctuates by feeding intermittently. In this project, the purpose is to study how the process response to the intermittent load by monitoring the biogas production, biogas composition and pH, and find out in which condition the load is a shock load, which gives the process inhibition, thereby provide useful information for the process optimization.

(1) Waste digester Design. University of Florida Civil Engineering.

2 THEORY

2.1 Anaerobic Digestion

Anaerobic digestion is the breakdown of organic material by a microbial population that lives in an oxygen free environment (Burke, 2001). Three basic steps are involved in the overall anaerobic oxidation (Tchobanoglous et al., 2003):

The first step is hydrolysis, in which particulate material is converted to soluble compounds, then hydrolyzed further to simple monomers.

The second step is acidogenesis (fermentation), where amino acids, sugars and some fatty acids are degraded further, the principal products are acetate, hydrogen, CO_2 and propionate and butyrate. The propionate and butyrate are fermented further to also produce hydrogen, CO_2, and acetate. Thus, the final products of fermentation are acetate, hydrogen, and CO_2. The free energy change associated with the conversion of propionate and butyrate to acetate and hydrogen requires that hydrogen be at low concentrations in the system ($H_2 < 10^{-4}$ atm), or the reaction will not proceed (McCarty and Smith, 1986).

The third step is methanogenesis. Two groups of methanogenic organisms are involved in methane production. One group, termed aceticlastic methanogens, split acetate into methane and carbon dioxide. The second group, termed hydrogen-utilizing methanogens, use hydrogen as the electron donor and CO_2 as the electron acceptor to produce methane.

Schematic of the anaerobic digestion process is show in Figure 1.

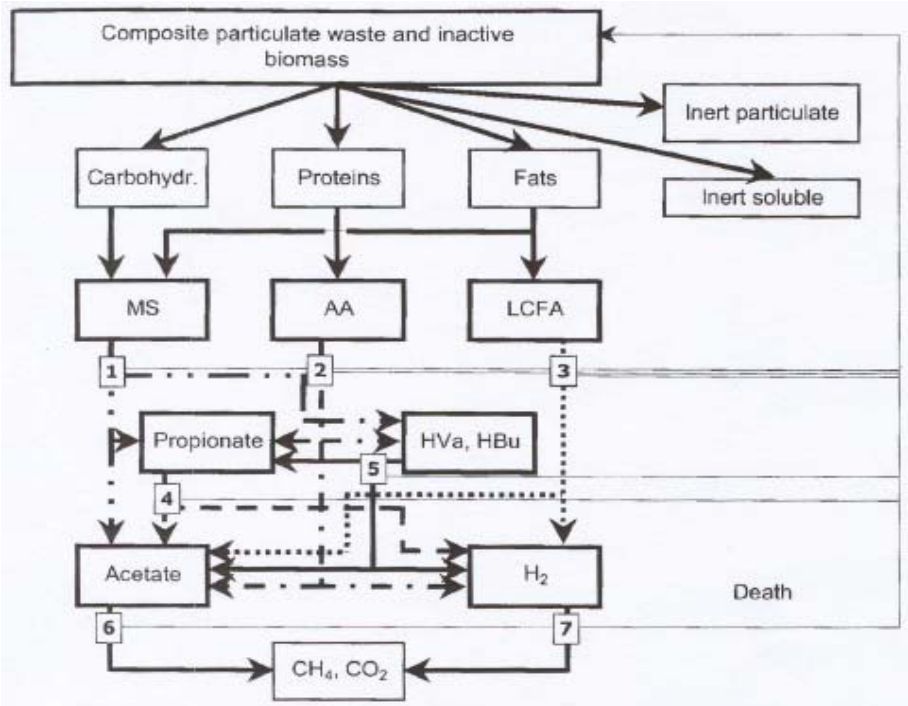

Figure 1. Schematic of anaerobic digestion (Batstone et al., 2002). The numbers represent the following processes: (1) acidogenesis from sugars; (2) acidogenesis from amino acids; (3) acetogenesis from LCFA; (4) acetogenesis from propionate; (5) acetogenesis from butyrate and valerate; (6) aceticlastic methanogenesis; (7) hydrogenotrophic methanogenesis.

2.2 Steady State and Shock Condition

The methanogens and the acidogens form a syntrophic (mutually beneficial) relationship in which the methanogens convert fermentation end products such as hydrogen, formate, and acetate to methane and carbon dioxide. Because the methanogens are able to maintain an extremely low partial pressure of H_2, the fermentation reactions is shifted toward the formation of more oxidized end products (e.g., formate and acetate). The utilization of the hydrogen produced by the acidogens and other anaerobes by the methanogens is termed interspecies hydrogen transfer. In effect, the methanogenic organisms serve as a hydrogen sink that allows the fermentation reactions to proceed. If process upsets occur and the methanogenic organisms do not utilize the hydrogen produced fast enough, the propionate and butyrate fermentation will be slowed with the accumulation of volatile fatty acids in the anaerobic reactor and a possible reduction in pH (Tchobanoglous et al., 2003).

Under the steady state of the anaerobic digestion process, the speed of the acidogenesis is in equilibrium with the speed of methanogenesis. There is no excess of volatile fatty acids and the methane production rate is relative high. Since methanogens grow much slower than acidogens and are extremely pH-sensitive (pH 6.8-7.4 optimum) (Fulhage et al., 2005), they usually act as the limiting factor in the digestion process. If an excess of organic material is fed to a digester, the acidogens will grow rapidly, and produce an excess of volatile acids. This can lead to increase concentrations of these acids since the methanogens can not keep up with this change and degrade these acids as fast as they are generated by the acidogens. The accumulated acids will lower the pH, inhibiting the methanogens (Fulhage et al., 2005) and the digester will fall out of balance and produce less than optimal results. This chain reaction inhibiting the methane production in the process is defined as a shock condition and is the main focus of the present study. The different growth rates of the acidogens and the methanogens is claimed to be the main reason for the described shock condition (Zhou et al., 2003), a claim that is further evaluated in this study. In this evaluation it is also necessary to define what is meant by “excess organic load”, as it is relative to the biomass concentration in the reactor.

3 MATERIALS AND METHODS

3.1 Experimental Setup

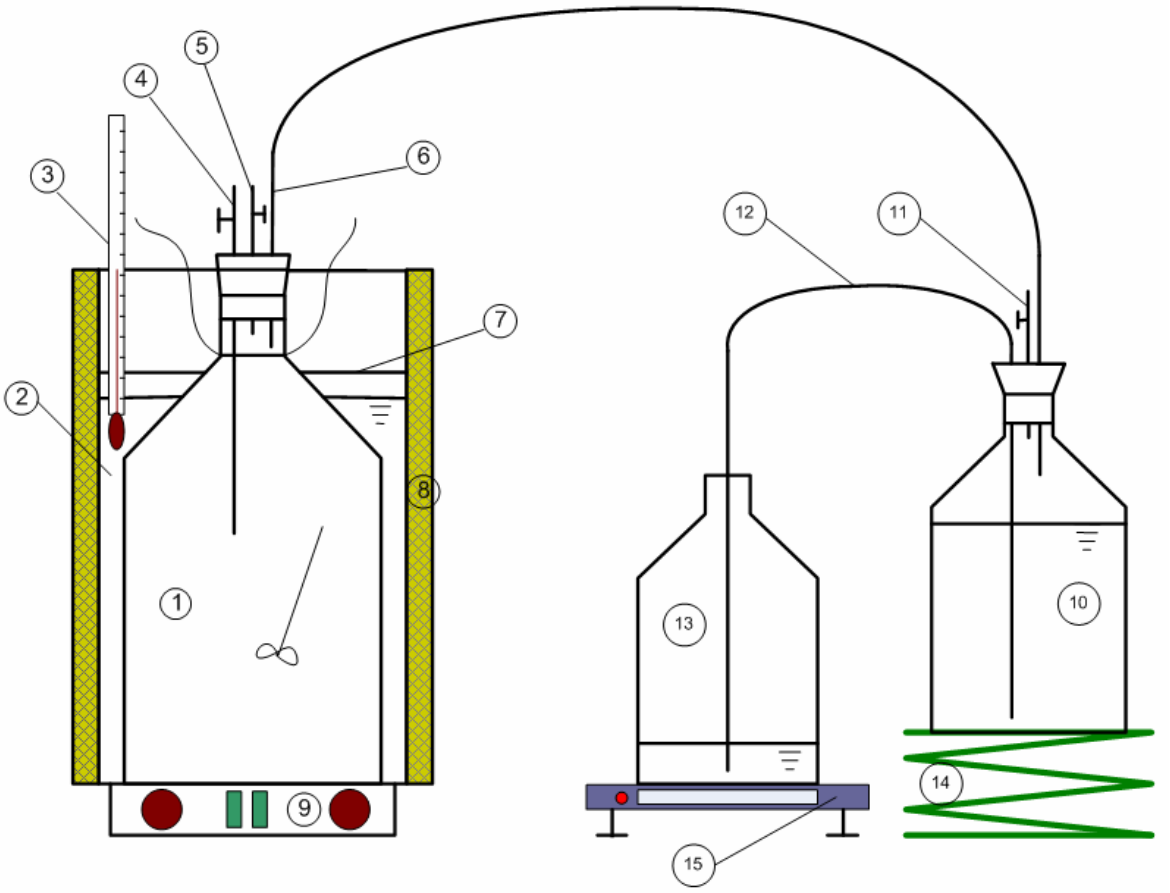

Figure 3.1 Schematic of the experimental setup. (1) anaerobic digester (2) water bath (3) thermal meter (4) liquid inlet / outlet (5) gas sample outlet (6) teflon tube for gas flow outlet (7) cover (8) insulation layer (9) magnetic stirrer and heater (10) gas collection bottle with NaCl + Citric acid solution (11) gas release valve (12) liquid transmission tube (13) liquid collection bottle (14) supporter (15) electronic scale

The experimental setup is presented in Figure 3.1. A batch reactor with 1092ml active culture was purged with nitrogen to create the anaerobic environment, sealed with a rubber stopper with one liquid inlet / outlet, one gas sample outlet, and one gas flow outlet. The space between the liquid and the stopper is called the head space. In this reactor, the head space is approximately 20ml. The reactor was put into a water bath with insulation layer and cover to keep 35±1ºC by manually regulating the heating. The magnetic stirrer (Typ: RCT) was used for both heating and stirring the reactor.

A teflon tube connected the reactor and the gas collection bottle for the biogas flow because teflon tubes are less gas permeable than others. With the internal diameter of 5mm, and length of 1000mm, 12.5ml gas can be stored inside the teflon tube. In this way, the gas samples from different time are distinguishable since it is not mixed with the gas inside the gas collection bottle.

NaCl + Citric acid solution was filled in the gas collection bottle to avoid CO_2 dissolving into the water. A gas release valve is opened when refilling the solution to the gas collection bottle.

A Tygon tube connected the gas collection bottle and the liquid collection bottle to transfer the liquid between them when produced biogas push liquid out of the gas collection bottle. The electronic scale (CP 6201) performed the online measuring for the varying liquid weight as a measurement of biogas production.

3.2 Chemicals Used

3.2.1 For substrate:

The ingredients of the substrate used as feed for the biogas producing culture, is shown in Table 3.1.

Ingredient	Dosage (g/2L)
Peptone	6.0208
Starch	7.7982
Yeast extract	7.1620
K_2HPO_4	0.5714
KH_2PO_4	0.5806

Table 3.1 The ingredients of the substrate.

3.2.2 For NaCl + Citric acid solution:

The ingredients of the NaCl + Citric acid solution in the gas collection bottle is shown in Table 3.2.

Ingredient	Dosage (g/L)
NaCl	200
Citric acid	5

Table 3.2 The ingredients of the NaCl + Citric acid solution.

3.3 Experimental Procedure

3.3.1 Substrate and NaCl + Citric acid solution preparation

The substrate and the NaCl + Citric acid solutions are prepared according to the Table 3.1 and Table 3.2. The substrate is sterilized by pressure cooking in an autoclave (Hiclave HV-50) for 40 minutes at 121ºC before use to kill living organisms and prevent the substrate from being contaminated within a short time.

3.3.2 Setting the system ready for biogas production measurements

After filling in the NaCl + Citric acid solution, the gas collection bottle with the rubber stopper as shown in Figure 3.1 is sealed. The gas release valve is opened and the liquid transmission tube is filled by the solution, by a syringe to form a liquid flow from the gas collection bottle to the liquid collection bottle. Then the gas release valve is closed. The pressures on both ends of the transmission tube are balanced until the biogas produced from the reactor is released to the gas collection bottle and the same volume of the liquid will be pushed to the liquid collection bottle. The electronic scale display show the weight of the liquid pushed through the transmission tube by the produced biogas, thereby showing changes in the reactor dynamically. The equivalence of the liquid weight to the volume of the gas is calibrated as 1.12 g liquid /ml gas.

3.3.3 Loading to the reactor

From the liquid inlet / outlet of the reactor, a certain volume of the reactor bulk liquid must be taken out (by a syringe) before the same volume of the substrate is loaded to the reactor in order to keep a constant volume inside the reactor. The substrate is injected to the reactor from the same liquid inlet / outlet. The volumes thus fed are 20ml, 40ml, 60ml and 80ml, and 1 to 8 days feeding intervals are chosen in the experiments.

3.3.4 Biogas production measuring

The biogas production is measured by means of the increment of the weight of the liquid inside the liquid collection bottle. The number displayed on the electronic scale is recorded manually every 30 minutes at the highest frequency. Typically 24 hours' data after loading and 1 hour's data before loading are collected except some hours during the night.

3.3.5 Biogas sampling and composition analyzing

The biogas sample is taken out through the gas outlet by a syringe through a syringe valve. 10ml gas is required for one sample to be analyzed by the Portable Gas Chromatograph (GC P200H). The time interval of the sampling depends on the gas production rate. When the production rate is high, it takes relatively shorter time to get enough gas for sampling, and vice versa. One sample before loading and several samples after loading within 24 hours are collected except some hours during the night.

The gas samples are analyzed by the GC according to the instruction. The biogas composition is measured in terms of relative amounts of CH_4, CO_2, O_2, and N_2.

3.3.6 pH measuring

The pH of the bulk liquid is measured by a pH meter (Φ390): one point before loading and several points after loading within 24 hours, except some hours during the night. To keep constant liquid volumes inside the reactor, the liquid which is taken out for pH measuring is injected back into the reactor.

3.4 Data Analysis

3.4.1 Specific Biogas Production Rate

Biogas volume increment (m^3) = liquid weight increment / density of the liquid

Specific production rate ($m^3 \cdot d^{-1} \cdot kgCOD^{-1}$) = Biogas volume increment /(Time · COD load)

For substrate shown in Table 3.1, the soluble COD is 10.5 kg/m^3, include 60% proteins (6.3 kg/m^3) and 40% carbohydrates (4.2 kg/m^3) (Botheju, 2006), and these numbers are used for the values of variables in the simulations.

3.4.2 The relationship among the specific biogas production rate, COD load and the condition before loading

The COD load and the feeding interval result in a certain condition before next loading since other conditions are fixed. This certain condition can be reflected by the production rate. The three dimensional relationship of the specific biogas production rate after loading, as functions of COD load and the production rate before loading, is studied by plotting production rates as functions of these variables in 3-D graphs.

3.5 Simulation

The ADM1 (Batstone et al., 2002) is used as the model to simulate the specific biogas production rate, CH_4 and CO_2 composition and pH through AQUASIM 2.1f.

One day response after loading is simulated. The main simulation steps for a typical case include:

1. Set values which match the experimental setup.
2. Continuous feed (150-200 days) to a steady state.
3. Run a time interval (days) without feeding to a pre-loading condition. The length of the time interval is chosen by trial and error.
4. Feed with a short time duration to simulate the intermittent load.
5. Run “one day” without feeding.
6. Present the result and compare with the experimental data.

4 RESULTS

Experimental results and simulations of the experiments are presented in this chapter, divided into sub-chapters for the parameters measured.

4.1 Results from Experiments

4.1.1 Specific Biogas Production Rate

The experimental results of loading with 20ml, 40ml, 60ml and 80ml substrate on different time interval (1 to 8 days) are presented in Figure 4.1 in terms of specific biogas production rate.

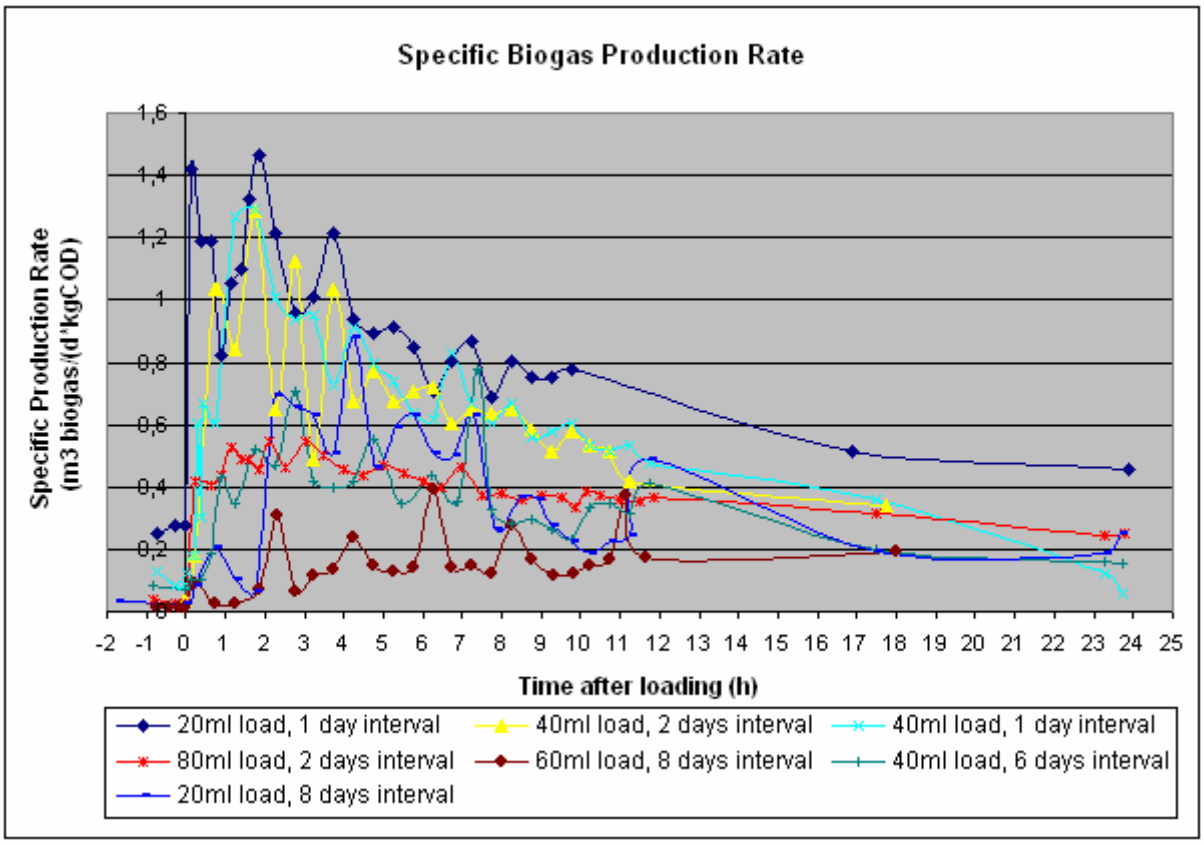

Figure 4.1 Specific biogas production rates for different loading volumes and time intervals.

All curves in Figure 4.1 show similar trend but with different peak values and different positions of the peak values along the Time coordinate. The highest specific biogas production rate happens when the load is the least and the time interval is the shortest, and it

takes the shortest time to reach the peak value. The lowest specific biogas production rate happens when the load is the most and the time interval is the longest, and it takes the longest time to reach the peak value. The other cases are distributed between these two cases by different extents. The curves have different specific production rates before the loading point, which are the result of the loading volume from last time and the time interval. The relationship among the specific production rate after loading, the production rate before loading and the loading volume is shown in Figure 4.2. The average specific production rate for the first 7 hours after loading is used as an indication of how well the culture handles the various loads for various pre-loading conditions.

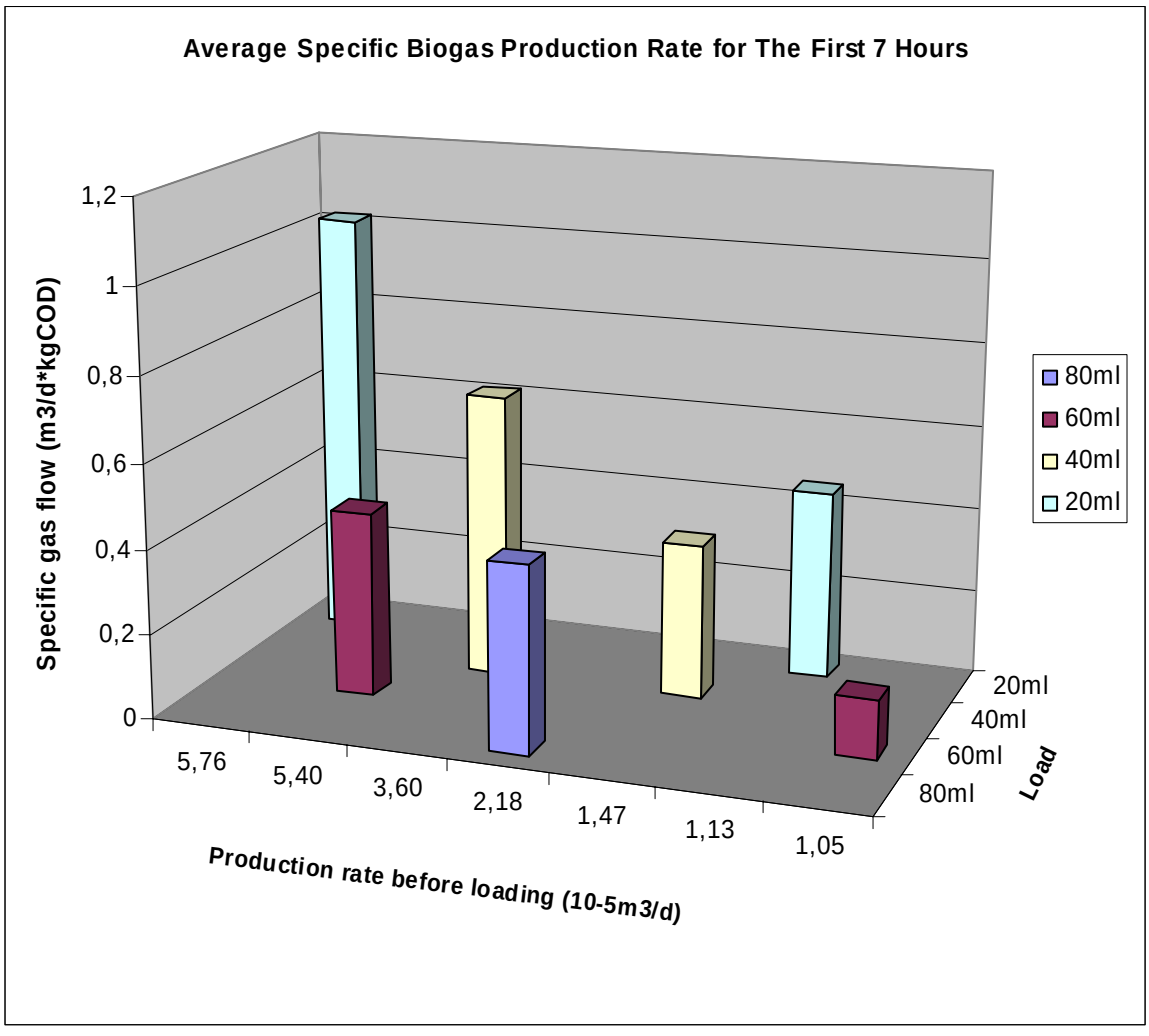

Figure 4.2 Relationship among the average specific production rate, loading volume and the production rate before loading.

The highest specific production rate happens when the load is the least and the production rate before loading is the highest for the conditions tested here (Figure 4.2). This is, therefore,

the loading case that the culture handles best in terms of efficiently converting the feed into biogas. The lowest specific production rate happens when the load is the most and the production rate before loading is the lowest. This is, therefore, the loading case that most problems for the culture in terms of efficiently converting the feed into biogas, and is defined as the strongest shock load. The other cases are distributed in a relatively flat plain between these two cases, and follow the trend that the specific production rate decrease as the production rate before loading decrease and as the load increase.

4.1.2 Biogas composition and ratio of CH_4 / CO_2

With different loading volume and time interval, two typical cases show the biogas composition change with time in Figure 4.3. Only CH_4 and CO_2 are considered and presented here, even though both nitrogen and oxygen were found in the biogas. N_2 and O_2 levels were assumed irrelevant for this analysis. They were, not on purpose, introduced with the feed.

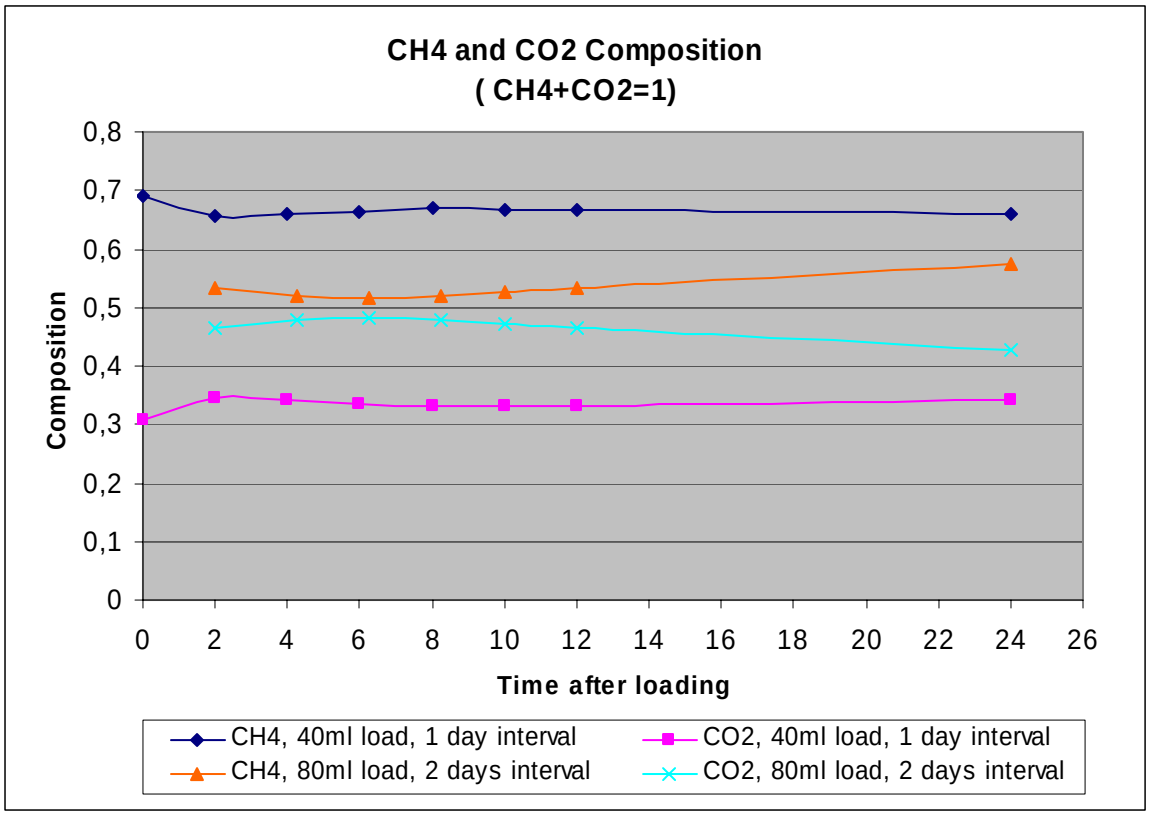

Figure 4.3 CH_4 and CO_2 Composition change with time for different loading volumes and time intervals.

Figure 4.3 indicates that after loading, CH_4 composition first decrease, then increase gradually to a stable level. CO_2 composition first increase, then decrease gradually to a stable level. For the case of more load and longer time interval, the fluctuation of the composition is

much more than the case of less load and shorter time interval, and the deviation from the typical biogas composition CH_4 65% and CO_2 35% (Henham and Makkar, 1998) is much more obvious.

The ratio of CH_4 / CO_2 changes with time for several experiments with different loading volume and time interval is presented in Figure 4.4.

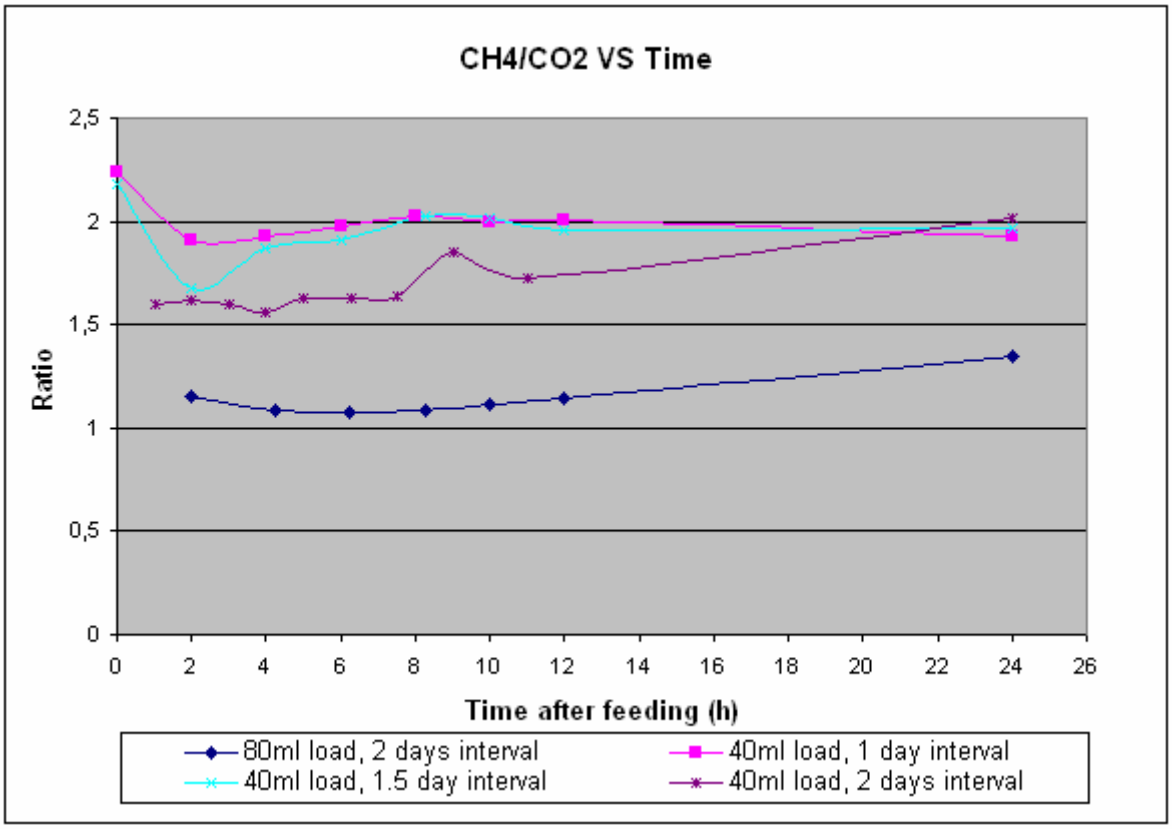

Figure 4.4 Ratio of CH_4 / CO_2 changes with time for different loading volumes and time intervals.

All the curves in Figure 4.4 show that the ratio of CH_4 / CO_2 decrease first after loading and then increase, but the extents of fluctuation are different. For the case of less load and shorter time interval, the fluctuation is less and it takes shorter time to reach a stable value, which is the typical ratio of CH_4 / CO_2 in biogas (approximately equal to 2). For the case of more load and longer time interval, such as 80ml load with 2 days interval, the ratio of CH_4 / CO_2 keeps much lower levels for a long time after loading, then gradually increase towards the typical value of CH_4 / CO_2. And the minimum CH_4 / CO_2 ratio occurs earlier in the lower loading cases compare to the higher loading cases.

4.1.3 pH in the bulk liquid

The pH measurements for cases with different loading volumes and time intervals are presented in Figure 4.5.

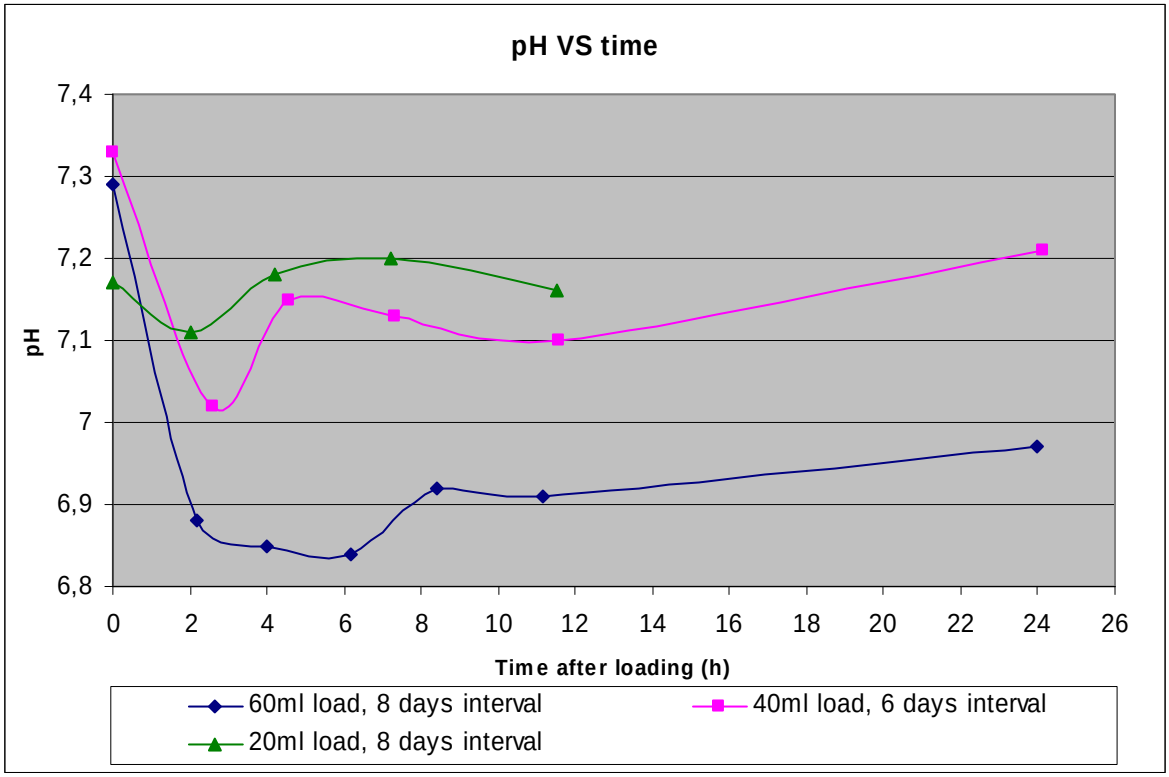

Figure 4.5 pH changes with time for different loading volumes and time intervals.

For each case in Figure 4.5, pH drops after loading and then increase gradually towards the value before loading. The fluctuation is the most significant for the case with the most load and the longest time interval.

4.2 Results from Simulations

4.2.1 Simulation for specific biogas production rate

The simulation results for three typical cases are presented in Figure 4.6, Figure 4.7, and Figure 4.8 respectively, together with the data from the experiments for comparison. Note that the model used is the ADM1 (Batstone et al., 2002) with no parameter adjustments for curve fitting, except that the time interval with no feed before loading is different from the real case, for reasons discussed later.

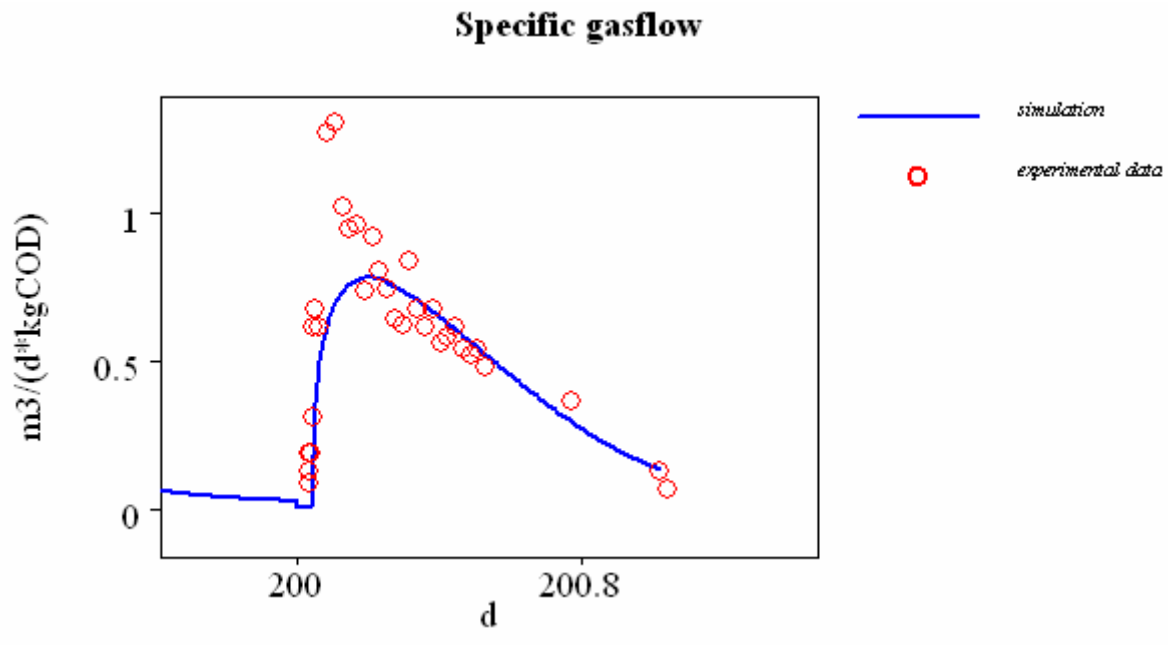

Figure 4.6 Specific biogas production rate for the case of 40ml load and 1 day interval (1 day interval from the steady state in the simulation).

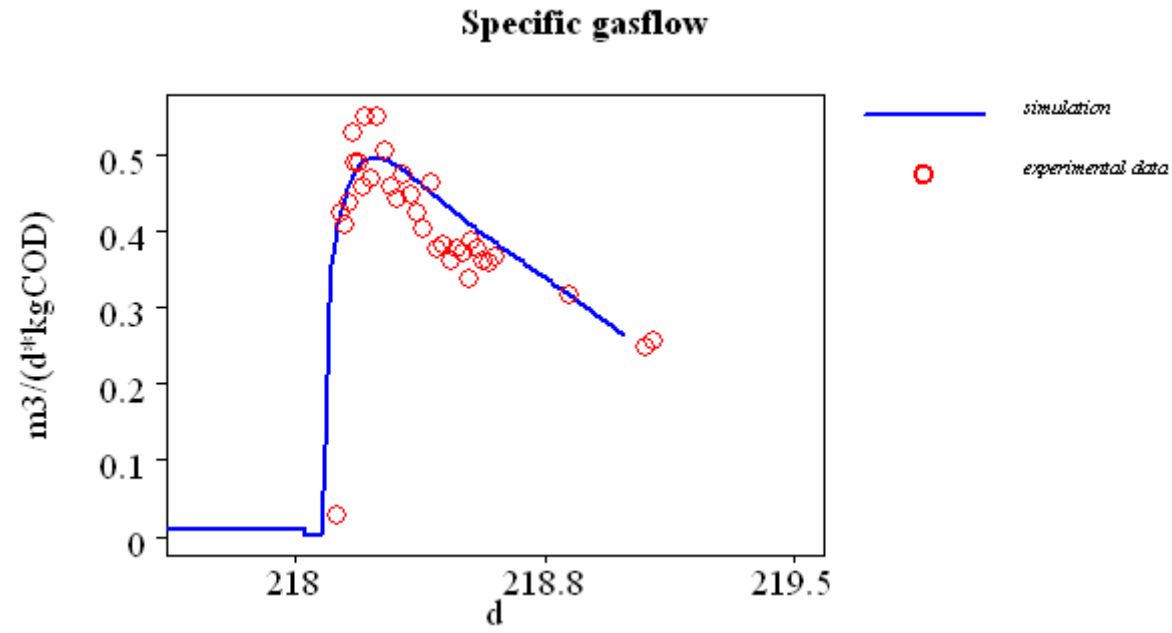

Figure 4.7 Specific biogas production rate for the case of 80ml load and 2 days interval (20 days interval from the steady state in the simulation).

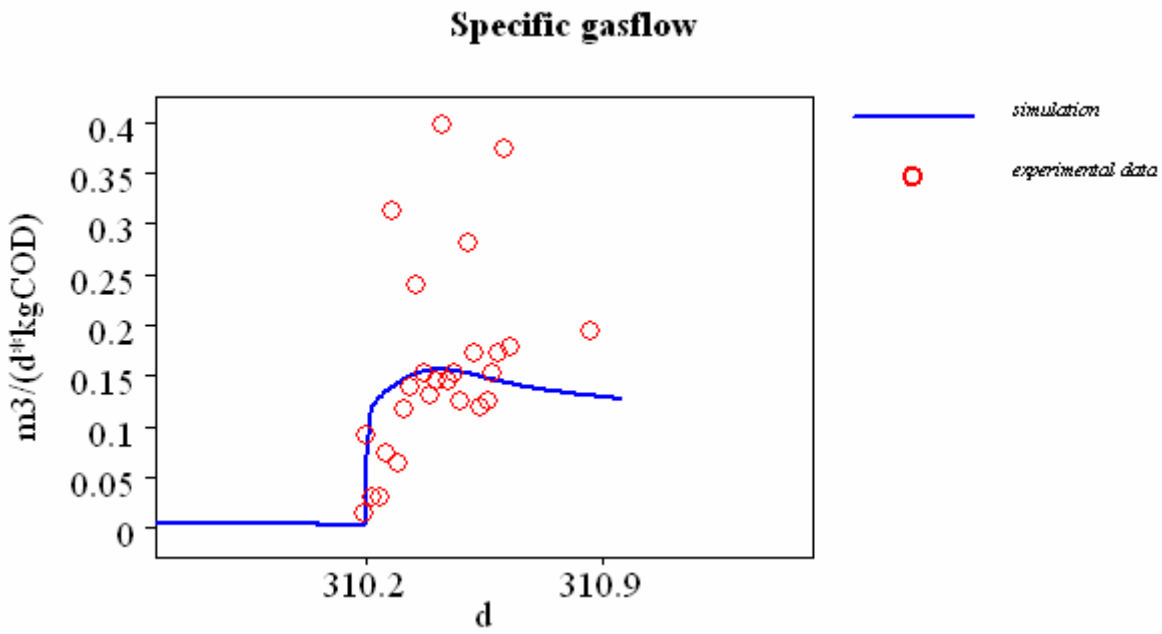

Figure 4.8 Specific biogas production rate for the case of 60ml load and 8 days interval (110 days interval from the steady state in the simulation).

All the three figures show that the simulation results fit the experimental results reasonably well, but the time intervals from the steady state in the simulations are much longer than the real time intervals in the experiments when the time intervals of the experiments are relatively longer.

4.2.2 Biogas composition

The simulation results for two typical cases are presented in Figure 4.9 and Figure 4.10, together with the data from the experiments for comparison.

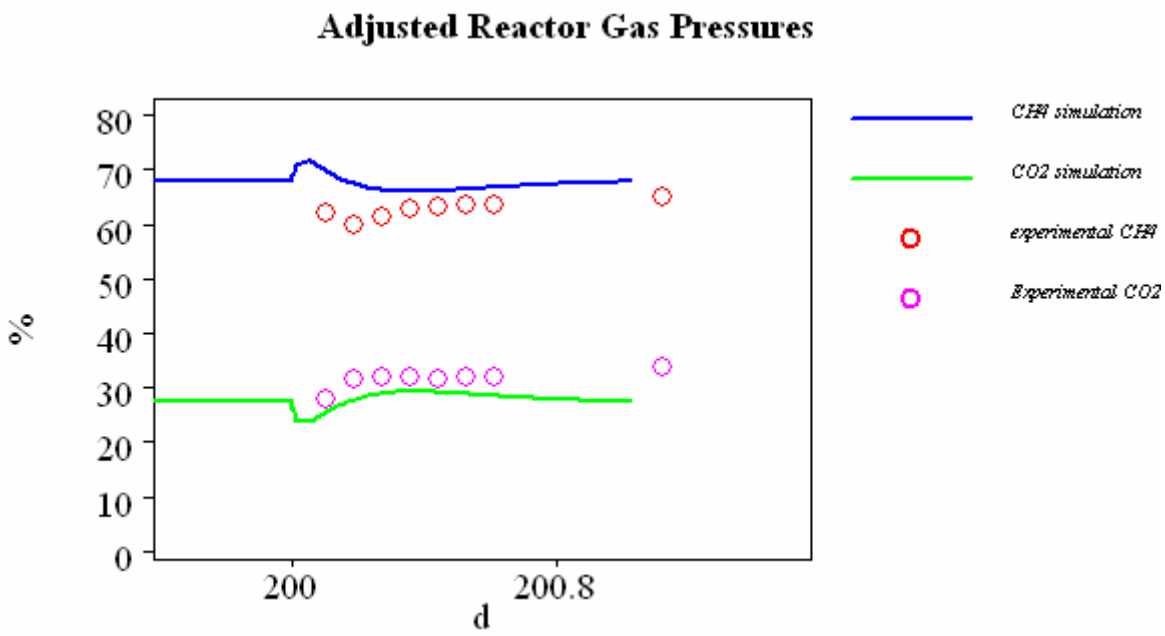

Figure 4.9 Composition of CH_4 and CO_2 for the case of 40ml load and 1 day interval (1 day interval from the steady state in the simulation).

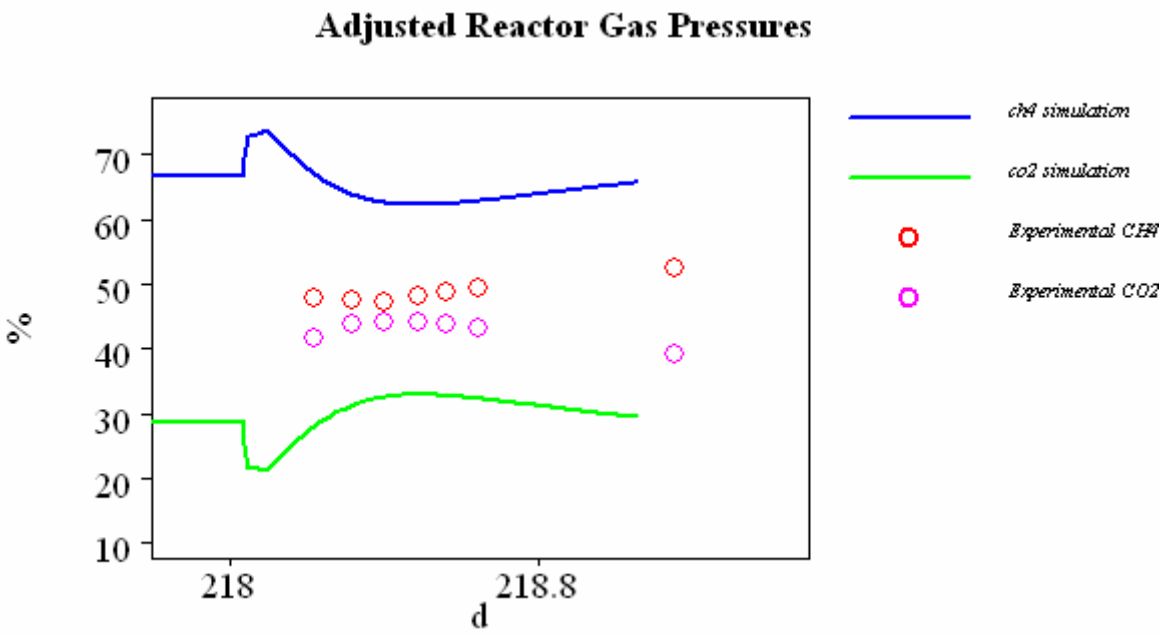

Figure 4.10 Composition of CH_4 and CO_2 in biogas for the case of 80ml load and 2 days interval (20 days interval from the steady state in the simulation).

Figure 4.9 and 4.10 show that the simulation result fits the experimental result for the case of less load and shorter time interval (Figure 4.9), but not for the case with more load and longer time interval (Figure 4.10). Possible explanations are discussed in 5.7.

4.2.3 pH in the bulk liquid

The simulation result for the case of 60ml load and 8 days interval is presented in Figure 4.11, together with the data from the experiment for comparison.

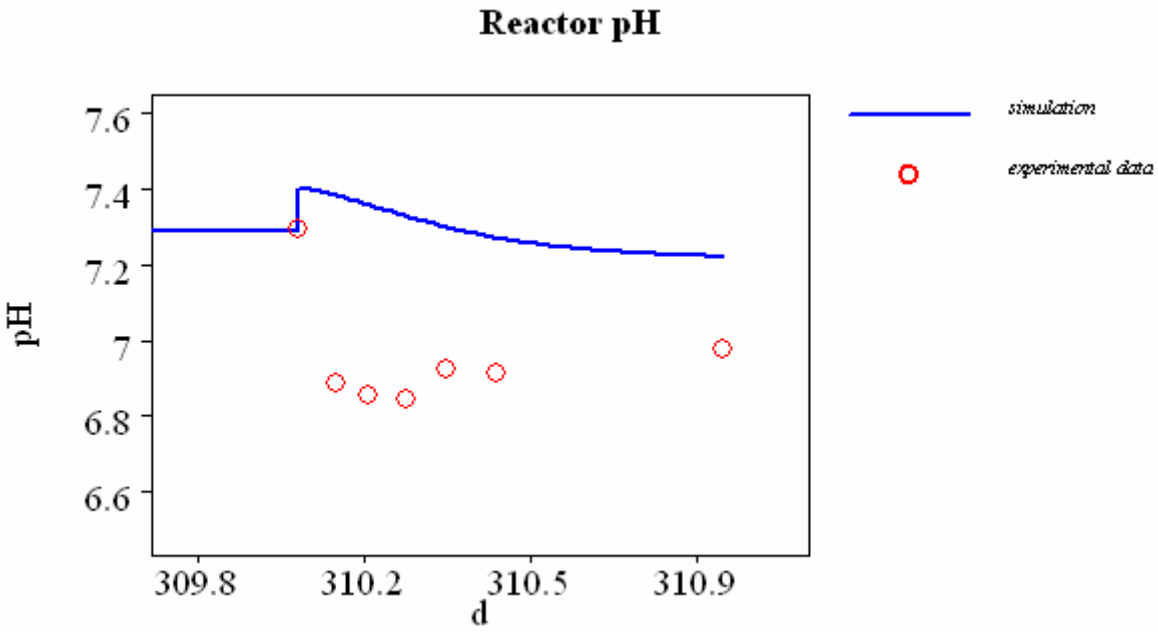

Figure 4.11 pH in the bulk liquid for the case of 60ml load and 8 days interval (110 days interval from the steady state in the simulation).

Figure 4.11 and Figure 4.8 are the simulations of the same experimental case. The simulation for the specific production rate fits the experimental result, while the pH from simulation and experiment do not match.

5 DISCUSSION

The transient response to the intermittent loads and the possible reasons are discussed in this chapter on the basis of the results from the experiments and simulations and the literature oppinions.

5.1 Pre-loading Condition

The pre-loading condition is mainly influenced by the load given the reactor the previous time and the time interval since this loading was given, and this result in a certain concentration of biomass and remaining feed COD before loading. Since the biomass decay according to

$r_d = k_d X$ (Tchobanoglous et al., 2003)

Where, r_d = biomass decay rate, g VSS/(m^3·d)

k_d = endogenous decay codfficient, g VSS/(g VSS·d)

X = biomass concentration, g/m^3

the longer time interval, the lower the biomass concentration should be.

5.2 Shock Condition and Shock Load

According to the Monod equation:

$$\mu = \frac{\mu_{max} S}{K_s + S}$$ (Tchobanoglous et al., 2003)

Where μ = Specific biomass growth rate

μ_{max} = Maximum specific bacterial growth rate

S = growth-limiting substrate concentration in solution

K_s = half-velocity constant

When feed COD suddenly increase in the reactor, the acidogens start to grow rapidly since the substrate concentration is relatively high at the beginning. When methanogens are not able to consume the volatile fatty acids as fast as they are produced, they are accumulated. This causes pH drop, which inhibit the activity of the methanogens, leading to even more VFA accumulation. The specific biogas production rate is therefore reduced. This condition is defined as a shock condition and the load is a shock load.

5.3 The Shock Extent and The Correlation between the Load and the Biomass Concentration

The shock conditions have different extents from slight to serious as the experimental results shown in Figure 4.1 and 4.2. The same volume of load can be a slight or a serious shock load by different pre-loading condition, such as the case of 20ml load with 1 day interval and the case of 20ml load with 8 days interval. Therefore, the correlation between the load and the pre-loading condition is the key factor of the shock extent.

Since usually the COD concentration under the pre-loading condition is very low, compare to the load, its effect is negligible, so the effect of the biomass concentration is dominant in the effect of pre-loading condition. The load amount and the biomass concentration at the loading time are therefore the key factors determining the severity of the shock or the shock extent. The longer time interval and the lower production rate before loading represent a lower biomass concentration, and thereby potentially more severe shock conditions. This is consistent to Burke's opinion: At a given temperature, the bacterial consortia can only consume a limited amount of food each day. In order to consume the required number of pounds of waste one must supply the proper number of pounds of bacteria. The food to microorganism ratio is the controlling factor in all biological treatment processes. A lower the ratio will result in a greater percentage of the waste being converted to gas (Burke, 2001).

From Figure 4.1, we find that as the product of load volume · time interval increase, the shock extent increase. Since the biomass concentration is inversely proportional to the time interval, it implies that the shock extent increase as the ratio of load volume / biomass concentration increase. From Figure 4.2, we find that as the ratio of load volume / production rate before loading increase, the shock extent increase in the same way as for the ratio of load volume / biomass concentration. Figures 4.1 and 4.2 show the effect of the correlation between the load and the biomass concentration to the shock extent consistently, and the mechanism of the effect can be explained by the 'Excess of organic load' stated in item 5.4.

5.4 Excess of Organic Load

The excess of organic load is the amount of organic matter that can not be converted to biogas by the methanogens at a certain time point. It is relative to both the load and the methanogens biomass concentration.

Since the methanogens grow much slower than the acidogens, and they are usually the limiting factor, the excess of the organic load exist when methanogens can not convert the products of acidogenesis as fast as they are generated by the acidogens. When the biomass concentration is low, even a relatively low organic load can be excessive, and as the ratio of load / biomass concentration increases, the excess of organic load increases. More excess of

the organic load results in more volatile fatty acids accumulation, causes more pH drop, and the activity of the methanogens will be more inhibited.

When the load is low enough or the biomass concentration is high enough that makes the substrate become the limiting factor, there is no excess of organic load, and no inhibition happens.

5.5 Position of Points of Inflection in The Charts of Specific Biogas Production Rate, CH_4/CO_2, and pH

In Figure 4.1, the peak of the specific biogas production rate occurs earlier for the less inhibited cases compare to the stronger inhibited cases; In Figure 4.4, the minimum CH_4/CO_2 ratio occurs earlier for the less inhibited cases compare to the stronger inhibited cases; In Figure 4.5, the lowest pH value occurs earlier for the less inhibited cases compare to the stronger inhibited cases. All these can be explained by the same mechanism: The less inhibited cases have less relative excess of organic load, and the activity of methanogens are less inhibited than the stronger inhibited cases, it takes shorter time to convert the accumulated volatile fatty acids to biogas, and decrease the substrate concentration to a level which makes the substrate become the limiting factor. The points of inflection of the curves occur at this time. That is why for the same case, the point of inflection of the specific production rate, the CH_4/CO_2 ratio and the pH occurs at almost the same time point in each figure (some deviations can be the measuring error and / or the sampling point problem).

5.6 Simulation of The Specific Biogas Production Rate

Three typical cases are simulated for the specific biogas production rate: A case with slight inhibition, a case with medium inhibition and a case with serious inhibition/shock conditions (Figures 4.6, 4.7 and 4.8). The simulations fit the experimental data reasonably well, but the difference between measured and simulated biogas production increase with increasing shock conditions, if the initial biomass concentration is as simulated for steady state (not shown). The fit between the simulated and measured biogas production in the cases with medium inhibition and serious inhibition are better when the initial biomass concentration at the loading time is significantly lower than the simulated steady state biomass concentrations (Figures 4.6, 4.7 and 4.8). This is obtained in the simulations by allowing longer time for decay, by simulating longer time interval from the steady state than in the real case (from last loading) to reach a suitable pre-loading condition. Two main reasons why the amount of methanogens are lower than that predicted are considered:

1. The activity of methanogens is inhibited under low pH, and the activity decrease as the pH decrease. In Figure 4.11, the pH drop from experiment is much deeper than

that from the simulation. Since the model does not simulate the pH drop correctly, the inhibition of the activity of methanogens is underestimated, and the specific biogas production rate is overestimated.

2. The biomass concentration in the reactor is lower than that in the steady state simulated, because:

- Since the model can not simulate the pH drop correctly, the biomass concentration in the simulation is over estimated compare to the real case since the growth rate of biomass is higher under a better pH condition.
- In the simulation, the time interval starts from the simulated steady state by continuous feeding. In the experiment, starting point of the time interval is a condition after many days' intermittent feeding. Two example figures Figure 5.1 and Figure 5.2 make a comparison of the biomass concentration change by these two kinds of feeding and the numbers of relative difference after 60 days are presented in Table 5.1 (only examples, numbers are not related to this project).

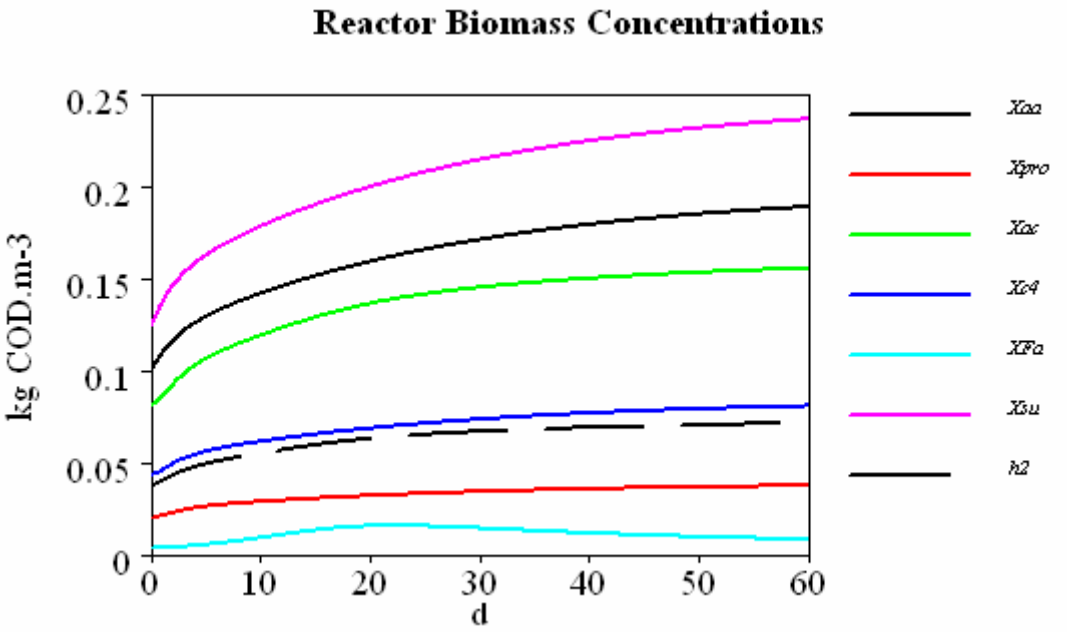

Figure 5.1 Biomass concentration change by continuous feeding.

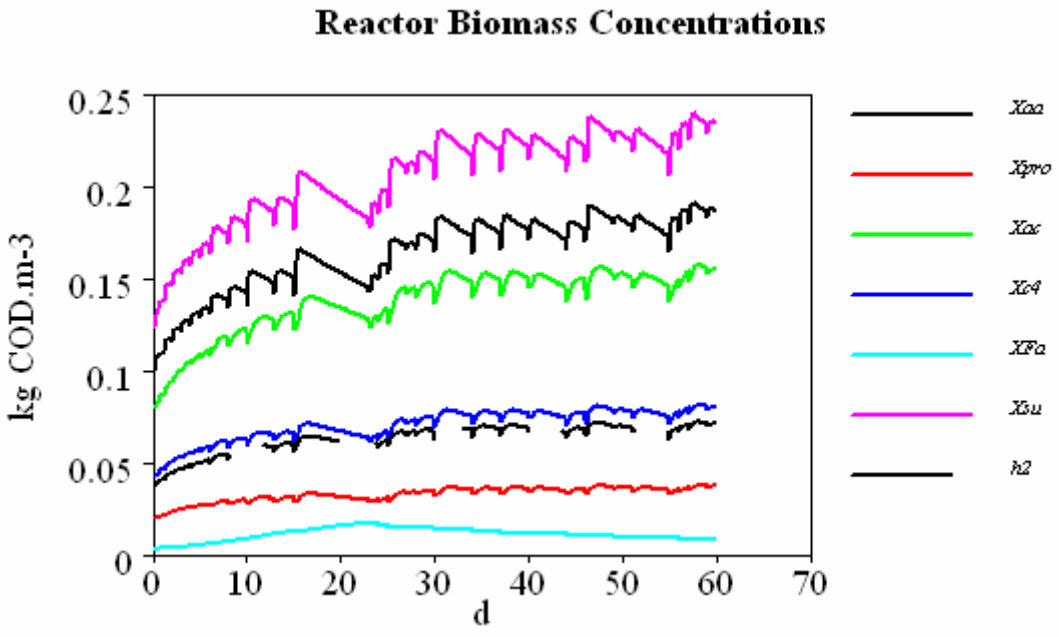

Figure 5.2 Biomass concentration change by intermittent feeding with the same total substrate feed as Figure 5.1.

Bacteria	Biomass concentration after feeding 60 days ($kgCODm^{-3}$)		
	Continuous feed with 20ml/d	Intermittent feed with the same total volume as continuous feed	Relative difference (%)
Xsu	0,239	0,2357	1,38
Xaa	0,1905	0,1876	1,52
Xac	0,1575	0,1565	0,63
Xc4	0,08305	0,08254	0,61
Xh	0,07439	0,07216	3,00
Xpro	0,03974	0,03972	0,05
Xfa	0,01029	0,009874	4,04
Average relative difference (%)			1,60

Table 1. Comparison of biomass concentration between continuous feeding and intermittent feeding (with the same total feeding volume).

Figure 5.1, 5.2 and Table 1 indicate that after 60 days' growth by feeding intermittently, the biomass concentration is by average 1.60% lower than that by feeding continuously when the total feeding volumes are the same. Given that the pH is not adequately simulated, the actual difference between intermittently and continuously fed systems is expected to be even larger.

note also that Xh (hydrogen consuming organisms) and Xfa (fatty acids consuming organisms) are more negatively influenced by intermittent feeding than the other organisms.

Figure 5.3 and Table 5.2 give another example to show when the total feeding volume is 3.3% less in the intermittent feeding than in the continuous feeding, how much difference should be, because in actual the total feeding volume could be less than strict continuous feeding.

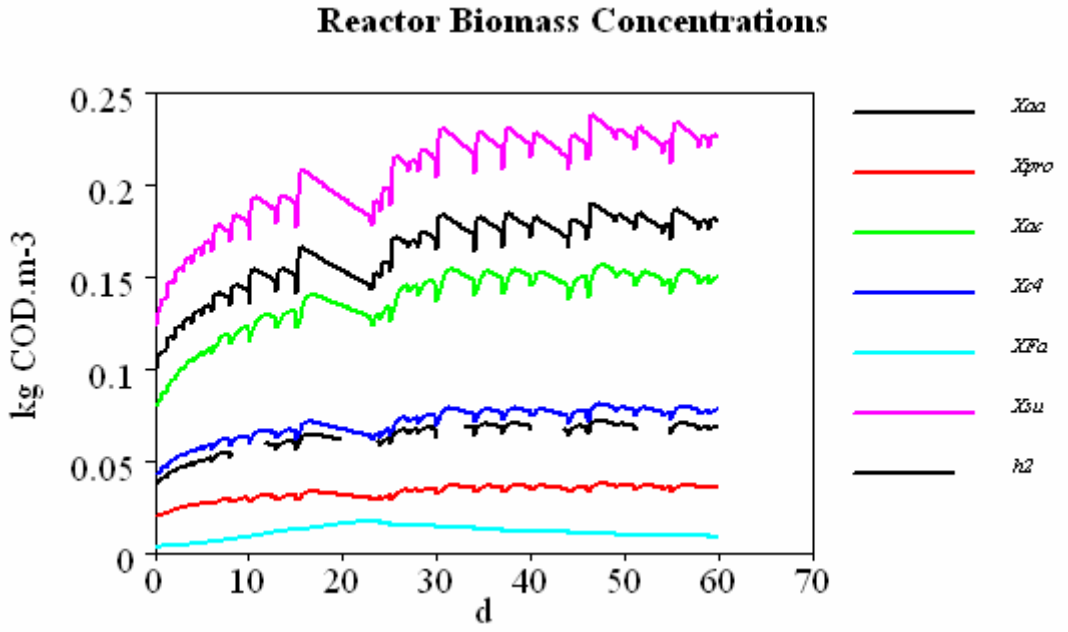

Figure 5.3 Biomass concentration change by intermittent feeding with total substrate 3.3% (40ml) less than Figure 5.1.

Bacteria	Continuous feed with 20ml/d	Intermittent feed with 40ml less than total volume of continuous feed	Relative difference (%)
Xsu	0,239	0,2278	4,69
Xaa	0,1905	0,1821	4,41
Xac	0,1575	0,1526	3,11
Xc4	0,08305	0,07884	5,07
Xh	0,07439	0,06999	5,91
Xpro	0,03974	0,03754	5,54
Xfa	0,01029	0,01099	-6,80
Average relative difference (%)			3,13

Table 5.2 Comparison of biomass concentration between continuous feeding and intermittent feeding (3.3% (40ml) less total feeding volume in the intermittent feeding).

Figure 5.3 and Table 5.2 indicate that after 60 days' growth by feeding intermittently with 3.3% less total feeding volume than continuous feeding, the biomass concentration is by average 3.13% lower than that by feeding continuously.

Note that the intermittent feeding causes pH drop, and since the model can not simulate the pH drop well, the biomass growth by intermittent feeding can be over estimated in the simulation, the actual difference should be bigger, so the biomass concentration difference between the real condition and the simulated steady state is considerable.

For the case in Figure 4.6, which is a slightly inhibited case, the time interval in the simulation is not longer than the real experiment. That is because the pH drop is slight and the activity of the methanogens is not much reduced. Also, the real biomass concentration is not much lower than that in the simulation because no long feeding time intervals or inhibited cases happen before this experiment.

For the case in Figure 4.7 and 4.8 which are medium and serious inhibited cases, the above mentioned reasons for reduced biomass and methanogenic activity should be considered.

5.7 Simulation of The Biogas Composition

In Figure 4.9 and 4.10, the experimental data used is the composition of CH_4 and CO_2 in the biogas mixture ($CH_4\,\% + CO_2\,\% < 100$ in both simulations and experiments).

The simulations show an initial CH_4 increase and CO_2 decrease for a short time. This might be a numerical diffusion error in dynamic calculation since we can not conclude this from the theory and the experiments. A slight minimum CH_4 and maximum CO_2 occurs after a few hours both in the experiments and in the simulations, as discussed earlier.

The case in Figure 4.10 is a stronger inhibited case than the one in Figure 4.9. The simulation in Figure 4.10 does not fit the experimental data well, while the simulation in Figure 4.9 fits the experimental data reasonably well. This can be explained also through the problems with the pH simulation:

The model can not simulate the pH drop as deep as the experimental data (Figure 4.11). The growth rate and activity of methanogens are, therefore, over estimated, and this result in more CH_4 produced in the simulations than in the real case, and visa versa for CO_2. The long no feeding interval is used in the simulation to reduce the biomass concentration before loading, but this only can reduce the over estimation of the specific production rate, not the composition.

6 CONCLUSIONS

- Intermittent feeding of biogas processes can cause shock effects leading to reduced biogas production and reduced biogas methane content.
- The intermittent loading shock effects appear to be rather consistent and predictable when the pre-loading conditions are well known and the feed amount added is known.
- The shock extent is a function of load / biomass concentration, and as the ratio increase, the shock extent increase.
- As the shock extent increase;
    - the specific biogas production rate decrease,
    - the ratio of CH_4 / CO_2 decrease,
    - the pH drop in the bulk liquid increase,
    - the time for recovering increase.
- The ADM1 (Batstone et al., 2002) with the kinetic and stoichiometric parameters recommended, is an applicable model for simulating the intermittently fed process investigated, but the correlations between the simulations and the experimental results deteriorate as the shock load increase, apparently due to limitations regarding pH predictions.
- It appears that shock effects on both the reactor biomass composition and on more direct pH effects on methane production must be accounted for in order to predict and understand the consequences of intermittent feeding on biogas processes.

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APPENDIX

- Data of specific biogas production rate
- Data of biogas composition analysis
- Data of simulations

Appendix is provided by an electronic copy (CD).