PSYCHROPHILIC ANAEROBIC DIGESTION OF SWINE MANURE SLURRY IN INTERMITTENTLY FED SEQUENCING BATCH REACTOR

BY

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ABSTRACT

Animal manure management practices, principally in regions where there is a surplus of manure are often detrimental to the environment and also represent a potential hazard to human and animal health.

The primary objective of this study was to evaluate the feasibility of psychrophilic anaerobic digestion (PAD) in sequencing batch reactors (SBR) as a low cost and easy to operate process to: a) reduce the pollution potential of swine manure slurry; b) recover energy; and c) reduce odours of swine manure slurry.

Experiments were carried out in 12 40-Litre SBRs operated under different conditions. Experimental results indicated that PAD of swine manure slurry at 20°C in intermittently fed SBR: 1) reduced the pollution potential of swine manure slurry by removing 85 to 95% of the soluble chemical oxygen demand (SCOD); 2) produced biogas at rates from 0.48 to 0.66 L of CH_4 per gram of volatile solids (VS) fed; and 3) successfully reduced odours.

In all experimental runs, the PAD of swine manure slurry in SBR was found very stable. Other interesting findings were that PAD in SBR process does not require mixing and can be intermittently fed only once and three times a week without affecting the SBR stability and performance.

The second objective of this study was to model PAD of swine manure slurry in SBR in order to: 1) increase knowledge of PAD in SBR; and 2) predict process performance.

Existing mathematical models of anaerobic digestion formed the basis for the two models proposed in this study for PAD in SBR. These two models were: 1) a simple model that considered only two populations of bacteria as well as particulate solubilization rate; and 2) an advanced model that considered six populations of bacteria as well as the interaction between the biological, liquid (physico-chemical) and gas phases.

The simple model predicted reasonably well the trend in VA, SCOD accumulation as well as methane production. The advanced model which made use of a large number of kinetic constants also predicted reasonably well the methane production as well as the trend in accumulation in acetic, propionic and butyric acids, dissolved and gaseous hydrogen and SCOD.

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a	constant in modified Monod kinetics, mmol/d
A	anions concentration, mM
A_c	acetic acid, mM
A_c^-	acetate, mM
A_{cT}	total concentration of acetic acid, mM
B_u	butyric acid, mM
B_u^-	butyrate, mM
B_{uT}	total concentrations of butyric acid, mM
CO_{2o}	dissolved concentration of CO_2 in influent, mM
CO_2	dissolved concentration of CO_2 in SBR, mM
Ca	cations concentration, mM
C	concentration of soluble carbohydrates in SBR, mM
Co	concentration of soluble carbohydrates in influent, mM
COD	chemical oxygen demand
CNB	non-biodegradable organic in SBR, mM
CNBo	non-biodegradable organic in influent, mM
CO_{2s}	saturation concentration of dissolved carbon dioxide, mM
EE	error of estimate
F	COD equivalent of VSS
F_d	biodegradable fraction of microorganisms
H_{2g}	hydrogen concentration in gas phase, mM
H_{2L}	hydrogen concentration in liquid phase, mM
H_{2s}	saturation concentration of dissolved hydrogen, mM
$[HCO_3^-]$	bicarbonate concentration in SBR, mM
$[HCO_{3o}^-]$	bicarbonate concentration in influent, mM

$[H^+]$	hydrogen ions concentration, mM
HRT	hydraulic residence time, d
i	number of days in EE calculation
K_{a1}	dissociation constant for HCO_3^-/H_2CO_3
K_{a2}	dissociation constant for HCO_3^-/CO_3^{2-}
K_{NH4}	dissociation constant for NH_4^+/NH_3
K_{da}	decay rate of acid formers, d^{-1}
K_{dBu}	decay rate of acetogens butyric, d^{-1}
K_{dPr}	decay rate of acetogens propionic, d^{-1}
K_{dAc1}	decay rate of *Methanosaeta*, d^{-1}
K_{dAc2}	decay rate of *Methanosarcina*, d^{-1}
K_{dH2}	decay rate of hydrogen utilizer methanogens, d^{-1}
KH_{CO2}	Henry's constant for carbon dioxide, mM/atm
KH_{H2}	Henry's constant for hydrogen, mM/atm
KH_{NH3}	Henry's constant for ammonia, mM/atm
Ka_{Ac}	dissociation constant for A_c^-/A_c
Ka_{Pr}	dissociation constant for P_r^-/P_r
Ka_{Bu}	dissociation constant for B_u^-/B_u
Kla_{CO2}	mass transfer coefficient for carbon dioxide, d^{-1}
Kla_{H2}	mass transfer coefficient for hydrogen, d^{-1}
Kla_{NH3}	mass transfer coefficient for ammonia, d^{-1}
K_p	first order stabilization rate constant, d^{-1}
K_{sc}	saturation constant for acetogens, mM
K_{H2}	maximum specific dissolved hydrogen uptake rate, mmol/mg-d
K_c	maximum specific carbohydrate utilization rate, mmol/mg-d

K_{Bu}	maximum specific butyric acid utilization rate, mmol/mg-d
K_{Pr}	maximum specific propionic acid utilization rate, mmol/mg-d
K_{ac1}	maximum specific acetic acid utilization by *Methanosaeta*, mmol/mg-d
K_{ac2}	maximum specific acetic acid utilization by *Methanosarcina*, mmol/mg-d
K_{H2}	maximum specific hydrogen utilization by hydrogen utilizers, mmol/mg-d
Ks_{Pr}	saturation constant for acetogenic propionic, mM
Ks_{Bu}	saturation constant for acetogenic butyric, mM
Ks_{Ac1}	saturation constant for *Methanosaeta*, mM
Ks_{Ac2}	saturation constant for *Methanosarcina*, mM
Ks_{H2}	saturation constant for hydrogen utilizer methanogens, mM
n	number of moles of gas
N	number of estimates in EE calculation
NAD	nicotinamine adenine dinucleotide (electron carrier)
NH_3-N	ammonia nitrogen, mM
NH_4^+	ammonium ions concentration in SBR, mM
NH_{3s}	saturation concentration of ammonia nitrogen, mM
P_T	digester total gas pressure, atm
P_{CO2}	partial pressure of carbon dioxide, atm
P_{H2}	partial pressure of hydrogen, atm
P_{NH3}	partial pressure of ammonia, atm
P_r	propionic acid, mM
P_r^-	propionate, mM
P_{H2O}	partial pressure of water, atm

P_{rT}	total concentration of propionic acid, mM
Q	influent flow rate, d^{-1}
Q_{CH4}	methane flow rate, d^{-1}
Q_g	biogas flow rate, d^{-1}
Q_T	biogas flow rate
P	particulate concentration in SBR, mg COD/L or mM
Po	influent particulate concentration, mg COD/L or mM
PEE	percent error of estimate
R	universal gas constant
r	ratio of reduced to oxidized electron carrier molecule
r_p	solubilization rate of particulate, mg COD/L-d
rC	unregulated soluble carbohydrate utilization rate, mM/d
R_{Ac}	regulation factor for acetic acid production
R_{Bu}	regulation factor for butyric acid production
R_{Pr}	regulation factor for propionic acid production
R_{BBu}	regulation factor for butyric acid utilization
R_{PPr}	regulation factor for propionic acid utilization
rs_{Bu}	unregulated butyric acid utilization rate, mM/d
rs_{Pr}	unregulated propionic acid utilization rate, mM/d
rs_{Ac1}	acetic acid utilization rate by *Methanosaeta*, mM/d
rs_{Ac2}	acetic acid utilization rate by *Methanosarcina*, mM/d
rs_{H2}	dissolved hydrogen utilization rate, mM/d
S	SBR soluble COD concentration, mg/L
So	influent soluble COD concentration, mg/L
SBR	sequencing batch reactor

SCOD	soluble chemical oxygen demand, mg/L
TCOD	total chemical oxygen demand, mg/L
TKN	total Kjeldahl nitrogen, mg/L
TS	total solids, mg/L
TSS	total suspended solids, mg/L
T	temperature, °K
Tr	gas transfer rate, mM/d
t_f	length of fill period, d
VSS	volatile suspended solids, mg/L
VA	total volatile acids in SBR, mg COD/L
VAo	total volatile acids in influent, mg COD/L
V_{Lo}	initial liquid phase volume, L
V_L	liquid phase volume, L
V_{go}	initial gas phase volume, L
V_g	gas phase volume, L
$Vmax_a$	maximum specific SCOD uptake rate, mg COD/mg-d
$Vmax_m$	maximum specific VA uptake rate, mg VA COD/mg-d
V_{TP}	volume of 1 m mole of gas at 1 atm and 20°C L/mmol
X_a	acid formers concentration, mg/L
X_m	methane formers, mg/L
X_{Bu}	concentration of acetogenic butyric bacteria, mg/L
X_{Pr}	concentration of acetogenic propionic bacteria, mg/L
X_{Ac1}	concentration of *Methanosaeta* bacteria, mg/L
X_{Ac2}	concentration of *Methanosarcina* bacteria, mg/L
X_{H2}	concentration of hydrogen utilizing bacteria, mg/L
Y_a	acetogen yield

Y_m	methane formers yield
Y_c	amount of carbohydrate use in the formation of 1 g of acid formers, mM/mg
Y_{Ac}	microorganism yield, mg X_a/mg carbohydrate to A_c
Y_{Pr}	microorganism yield, mg X_a/mg carbohydrate to P_r
Y_{Bu}	microorganism yield, mg X_a/mg carbohydrate to B_u
Y_{bb}	yield factor for acetogenic butyric, mg X_{Bu}/mmol B_u
Y_B	amount of butyric acid use for the formation of 1 gr of X_{Bu}
Y_{pp}	yield factor for acetogenic propionic, mg X_{Pr}/mmol P_r
Y_p	amount of propionic acid use for the formation of 1 gr of X_{Pr}
Y_{a1}	amount of acetic acid in synthesis of 1 g of *Methanosaeta*, mmol/mg
Y_{a2}	amount of acetic acid in synthesis of 1 g of *Methanosarcinas*, mmol/mg
Y_{aa1}	*Methanosaeta* yield, mg X_{ac1}/mmol
Y_{aa2}	*Methanosarcinas* yield, mg X_{ac2}/mmol
Y_{hh2}	hydrogen utilizing bacteria yield, mg X_{H2}/mmol
Y_{PrCO2}	amount of CO_2 use for the formation of 1 gr X_{Pr}, mmol/mg
Y_{BuCO2}	amount of CO_2 use for the formation of 1 gr X_{Bu}, mmol/mg
Y_{H2CO2}	amount of CO_2 use for the formation of 1 gr X_{H2}, mmol/mg
Y_{PN}	ammonium ions yield from particulate solubilization, mmol/mmol
Y_N	ammonium ions uptake from bacteria synthesis, mmol/mg
Z	net cations concentration in SBR, mM
Zo	net cations concentration in influent, mM

CHAPTER 1

INTRODUCTION

Over the last 30 years or so, agriculture has changed from being subsistent to being very specialized and intensive. As a result, many agricultural practices have experienced major changes. Farms are now more specialized and concentrated with larger animal populations. A large portion of producers purchase their feed and do not have an adequate land-base for proper land application of animal manure. These changes took place in order to increase the animal production but unfortunately not enough effort was made to develop adequate practices for sound animal manure management.

Animal manure management practices in regions where there is a surplus of manure are often detrimental to the environment and also represent a potential hazard to human and animal health. Occasionally in areas of Canada, the drinking water source is polluted and water bodies cannot be used for recreational purposes due to manure contamination. The affected communities are expecting changes in manure management from the farm industry. If these changes do not take place in the near future, these communities will put pressure on governments to impose legislation on the farm

industry. The legislation may not be reasonable and could possibly penalize the farm industry and greatly reduce the farmers' income. The National Workshop on Land Application of Animal Manure, CARC (1991), recommended innovative research that would allow farmers to adopt sustainable and environmentally sound agricultural practices where animal manure is integrated into the overall production systems. It was further recommended that processes to stabilize, deodorize and add value to animal manure be developed.

Anaerobic treatment is a natural process that has several ecological benefits and great potential to treat animal manure. Conventional anaerobic digestion of animal manure in farm scale digesters was tried in several locations across Canada during 1975-1985. It was not successful for several reasons (Van Die, 1987):

- the treatment objectives were to produce proteins and recover energy. Little consideration was given to odour reduction, manure stabilization and increased fertilizer value;
- anaerobic digesters were not cost-effective because their capital costs were too high and their control and maintenance were labour intensive;
- continuous flow digesters required expensive liquid pumps that necessitated frequent calibration;
- digesters were designed to operate at mesophilic and

thermophilic temperatures. Because of prolonged sub-freezing winter temperatures in most of Canada, digesters operating at these temperatures during the winter not only used most of the gas they produced but sometimes required supplementary heating to maintain the digester temperature;

- digesters were difficult to control, they required skilled operators and had poor stability because they were pushed to the limit to achieve maximum gas production.

The farm industry will be interested in animal manure treatment only if the process can be achieved at low cost, is very stable, easy to operate, requires minimum skill and does not interfere with regular farm operations. In this study it is proposed to evaluate PAD in intermittently fed SBR to reduce the pollution potential of swine manure slurry and to recover a significant quantity of energy. Anaerobic digestion of animal manure slurries at low temperatures would be more appropriate for Canadian farm conditions because: 1) it might not necessitate the heating of manure slurry prior to it being fed to the digester; and 2) the digesters should contain a larger variety of bacteria at psychrophilic than at mesophilic and thermophilic temperatures and as a result the anaerobic process should be more stable. The intermittent feeding of the SBRs should allow the utilization of the existing manure

handling equipment and storage facilities. It should also minimize the interference of the SBR operation with regular farm activities. Therefore PAD in SBR represents a promising process to treat swine manure slurry on small and large farm operations.

1.1 Research Objectives

The objectives of this research are:

1) to determine the feasibility of using PAD at 20°C in intermittently fed SBRs to: a) reduce the pollution potential; b) recover energy; and c) reduce odours of swine manure slurry on both small and large farm operations;
2) to study the effect of environmental and operational factors such as inoculum type, organic loading rates, fill and react period length, mixing intensity, feeding frequency, and sludge age on the performance of PAD in SBR;
3) to develop mathematical models based on the experimental data to: a) extend knowledge on the interaction of micro-organisms in anaerobic digestion; b) predict process performance.

CHAPTER 2

REVIEW OF THE LITERATURE

2.1 Feasibility of Psychrophilic Anaerobic Digestion

A limited number of studies have been carried out on psychrophilic anaerobic digestion (PAD) of municipal waste water and animal manures. Most of the studies concentrated on biogas production while little consideration was given to odour reduction, waste stabilization or increases in availability of plant nutrients.

2.1.1. Past Experience with PAD

Garber (1977) stated that for anaerobic digestion at temperatures below the thermophilic range, the microorganisms are less affected by temperature fluctuation. In this study only thermophilic (40-60°C) and mesophilic (25-40°C) anaerobic digestion were compared. Therefore there is a good possibility that PAD at 5 to 25°C will be more stable than anaerobic digestion at mesophilic and thermophilic temperatures.

O'Rourke (1968), found that cellulose and nitrogenous material from municipal wastewater can be degraded at temperatures

lower than 20°C. For a hydraulic residence time (HRT) of 60 days, when the temperature was decreased from 20°C to 15°C methane was still produced, but its production was substantially reduced from 360 to 120 mL/g COD. The volatile solids (VS) were reduced by 80 and 50% at temperatures of 20 and 15°C, respectively.

At 20°C and a HRT of 15 days, the chemical oxygen demand (COD) reduction was 90% of the reduction achieved at a mesophilic temperature of 35°C. Therefore, anaerobic digestion in the upper range of psychrophilic temperature compared well with mesophilic anaerobic digestion.

Wellinger and Kaufmann (1982) found that at a temperature between 15 and 21°C the start-up phase was a long process. The biomass adapted very slowly at these temperatures; it took up to 6 months before the digester became stable.

Chandler and Hermes (1983) successfully used PAD in a lagoon containing swine manure. The slurry temperature varied between 11 and 20°C without affecting the digester stability. The biogas produced at 11°C was 0.13 m^3/m^2-day which represented 42% of the biogas production at 20°C. The start-up phase took a month. No information was given concerning the start-up procedure. Because they used existing manure

storage facilities and the maintenance costs were low, they claimed that the payback period was less than 3 years.

Cullimore et al. (1985) studied the influence of temperature between 4 and 40°C on biogas production from swine manure stored in a lagoon. They found that the biogas production decreased linearly to zero when the temperature decreased from 26°C to somewhere between 0 and 8°C. Their most interesting finding was that the minimum temperature at which biogas was produced was 8.5°C the first year, and decreased to 4.6°C the second year. This clearly indicates that the psychrophilic biomass adaptation to low temperature conditions was a very slow process.

Maly and Fadrus (1971) found that the ultimate methane yield (L of CH_4 per g of VS added) was temperature independent over the temperature range of 10 to 50°C. Therefore PAD will produce the same amount of energy as mesophilic and thermophilic anaerobic digestion provided that longer HRTs are provided.

Lo and Liao (1986) studied the PAD of screened manure in a 4 L fixed film digester. They found that the fixed film digester could survive a sudden change in temperature without ceasing gas production. The temperature was decreased suddenly from 22 to 12°C. Initially the biogas production at

12°C was 0.09 L CH_4/L-d but it continuously increased to a steady rate of 0.3 L CH_4/L-d. A HRT of one day and a loading rate of 28.7 g VS/L-day was used in their study. They also found that the fixed film reactor operated at 22°C produced more energy than the continuous-flow stirred-tank reactor (CSTR) operated at 22, 36 and 55°C.

Sutter and Wellinger (1987) studied methane production from cow manure at psychrophilic temperatures. They carried out laboratory tests in two litre cylinders filled with 50% fresh manure and 50% inoculum at temperatures ranging from 5 to 20°C. Two types of inoculum were investigated. They consisted of psychrophilic and mesophilic adapted cultures. Biogas was produced at all temperatures in the sample inoculated with the psychrophilic adapted culture. At 5°C the gas yield was 0.005 L/g VS added which represents about 2.5% of the gas produced at 20°C. Figure 2.1 compares the test results of samples seeded with the inoculums. Samples seeded with the psychrophilic inoculum produced more gas than the sample seeded with mesophilic adapted inoculums. At 15°C the gas yield was 0.120 L/g VS for samples with psychrophilic inoculum compared to only 0.025 L/g VS for samples seeded with mesophilic inoculum. Therefore it is very important that the biomass be acclimatized to low temperature either by using a well-adapted inoculum or by allowing enough time to obtain good digester performance and stability.

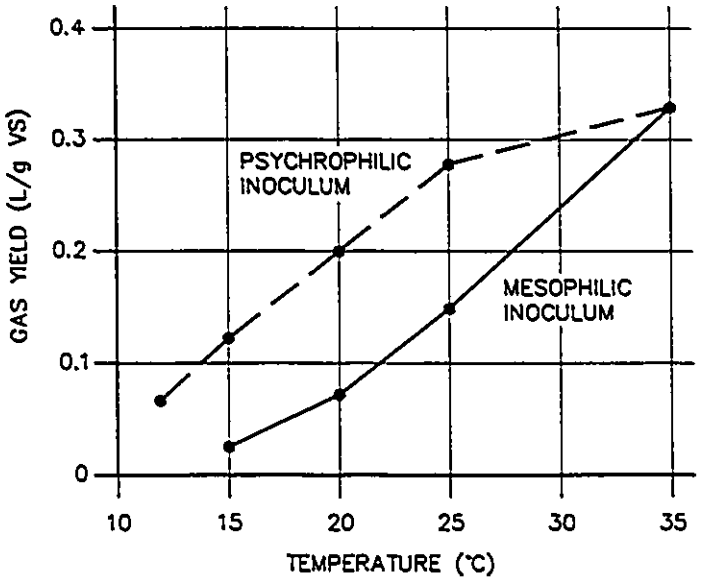


Fig. 2.1 Gas yield from dairy cattle manure versus temperature after 30 days of batch digestion. (Sutter and Wellinger, 1987)

2.1.2. Discussion

This literature review shows that PAD has the potential to be used successfully as a low cost process to produce methane from animal manure. The literature shows a large variation in PAD process performance. There is not enough information provided in the literature to find explanations for the large variation in process performance. The energy or fibre content of the diet, or the presence of antibiotics or food additives are not indicated. Also several reports did not provide any information on the age of the manure or its characteristics. Additional research is therefore necessary to evaluate precisely the feasibility of PAD in SBR.

2.2. Description of SBR System

An SBR has simple operating conditions as shown in Fig. 2.2. It consists of a tank where the following five consecutive time periods take place: 1) Fill; 2) React; 3) Settle; 4) Draw; and 5) Idle. During the fill period the organic waste is loaded to the SBR. When the SBR is full the react period starts. The length of react period should be long enough to meet the treatment objectives. The settle period immediately follows the react period. During this period no mixing is provided and quiescent settling conditions prevail. This period allows the treated liquid to be separated from the solids as well as the retention of bacteria in the system. During the draw period the treated liquid is removed and

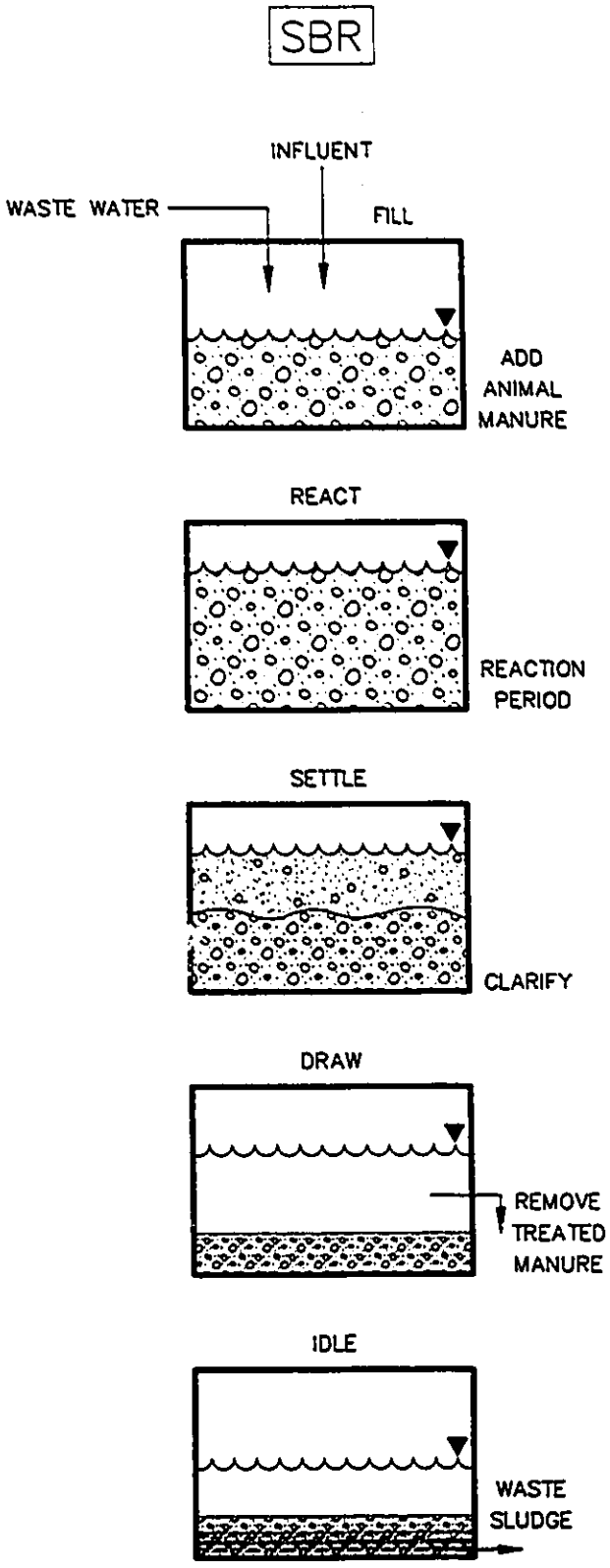


Fig. 2.2 Typical operation for a SBR during a complete cycle. (Metcalf and Eddy, 1991)

finally the idle period offers the flexibility of coordinating the simultaneous operation of two or more SBRs.

2.2.1 Potential Benefits of SBR to Carry Out PAD of Animal Manures

The microbial activities and ecosystem of anaerobic digestion are affected by the digester design as well as by the environmental and operational conditions (Harper and Suidan, 1991). The SBR is highly suitable for the treatment of animal manure at ambient temperatures because it offers optimum conditions to retain a high concentration of slow growing microorganisms in the tank. Dague et al. (1992) noted that with anaerobic SBR the food to microorganism (F/M) ratio is high after the fill period and low just prior to the settling period. They indicated that the above operating conditions resulted in efficient bioflocculation and solids separation. Dague et al. (1992) also indicated that with SBR the partial pressure of CO_2 is maintained in the reactor during the settling period. As a result no significant quantity of CO_2 is transferred to the head space. Therefore this reduces the suspension of particulates in the supernatant that occurs when CO_2 is transferred from the liquid to the gas phase. The long biomass retention time in the SBR may allow PAD to adapt to environmental changes such as temperature variations, changes in organic loading rate, and presence of inhibitory elements.

Another very important feature of a SBR is that it might not require continuous feeding. As a result PAD in SBR should not interfere with regular farm operations as previous systems did. It can be loaded during normal manure removal operations and the farmer will not have to deal daily with digester effluent. At the farm the SBR effluent will need to be handled once every one or two months, depending on the operating conditions. Because of intermittent feeding the SBR will make use of existing manure handling equipment at the farm and also because SBR will not interfere with farm operation, it has the potential to increase interest in anaerobic digestion to treat animal manure on small and large farm operations.

The main disadvantage of an SBR is that it is more difficult to plan a biogas-use strategy because the biogas production is not uniform during the fill and react periods. Other disadvantages are that no control strategies and few experimental data are available for PAD of animal manure in SBR.

2.3 Modelling of PAD in SBR

Anaerobic digestion of a complex waste such as animal manure is an interrelated multistage microbial process of serial and parallel reactions (Colleran et al., 1991; Gujer and Zehnder, 1983 and Zinder et al., 1984). In order to be able to develop

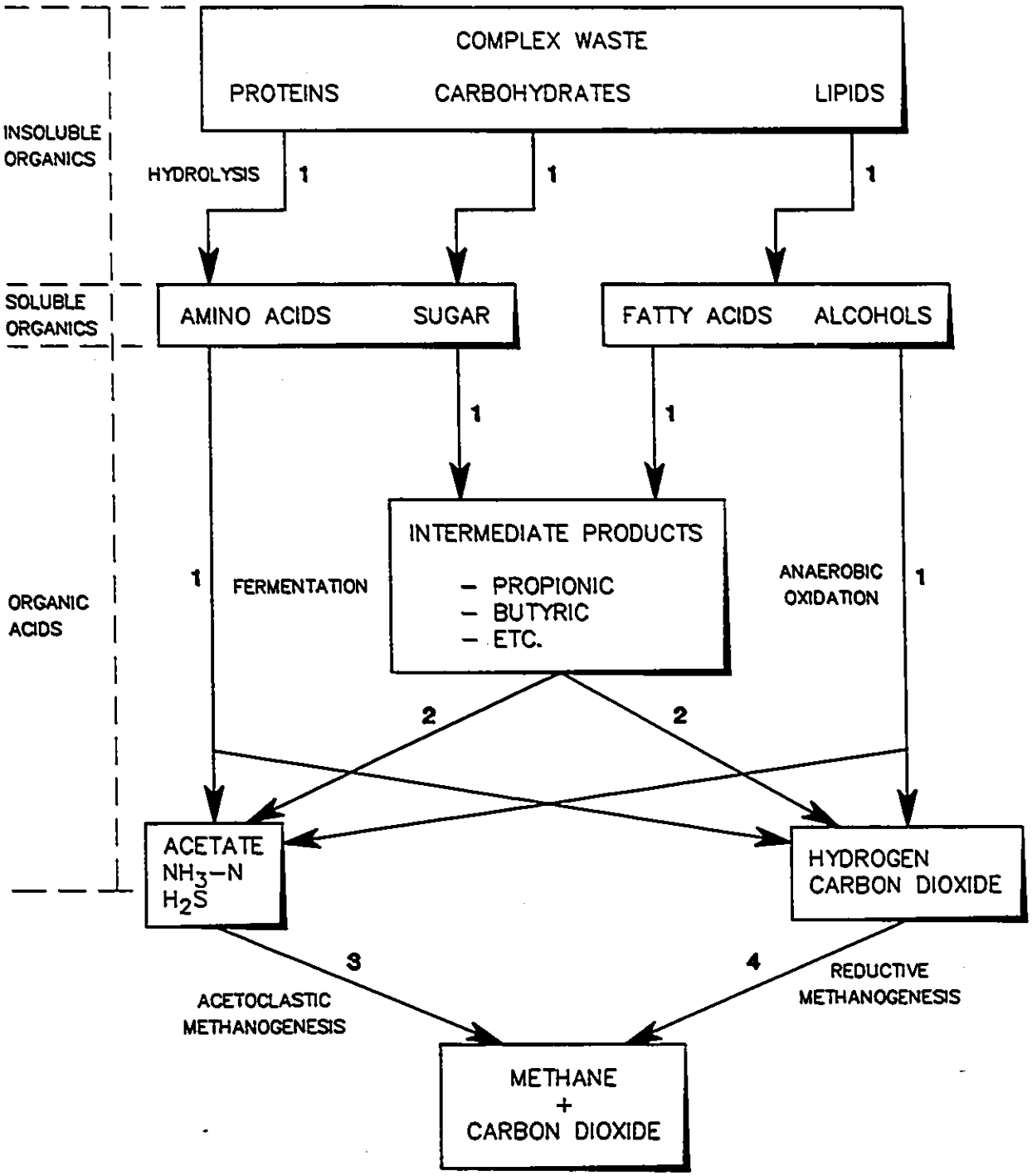
a realistic kinetic model, the metabolic pathways and basic reactions involved in anaerobic digestion should be known, as well as the microbiology involved in the process.

2.3.1 Steps Involved in Anaerobic Digestion

Fig. 2.3 shows the most probable reaction scheme for the anaerobic digestion of organic waste such as animal manure (Pavlosthathis and Giraldo-Gomez, 1991 and Kouzeli-Katsiri and Kartsonas, 1986). The chemical composition of the manure has an effect on the path followed during anaerobic digestion. Each component of the manure (carbohydrate, proteins and lipids) goes through three stages: hydrolysis; fermentation; and methane production. These stages are made possible by the action of the following bacteria: 1) fermentative or acid forming bacteria; 2) hydrogen-producing acetogenic bacteria; 3) acetoclastic methanogens; and 4) carbon dioxide-reducing methanogenic bacteria.

2.3.2 Microbiology

Gaudy and Gaudy (1980) indicated that the fermentative or acid forming bacteria produce extra-cellular enzymes which break down the carbohydrates, proteins and lipids to produce soluble sugars, amino acids and fatty acids respectively. These soluble materials pass through the fermentative bacteria cell membrane and are used as a source of energy for normal metabolic functions. The acid producing bacteria transform



1 FERMENTATIVE BACTERIA – CHEMOHETEROTROPH NONMETHANOGENS ACID FORMING BACTERIA

2 HYDROGEN – PRODUCING ACETOGENIC BACTERIA

3 ACETOCLASTIC METHANOGENS

4 CARBON DIOXIDE – REDUCING METHANOGENS

Fig. 2.3 Reaction scheme for the anaerobic digestion of animal manure adaptation from Pavlostathis and Giraldo–Gomez, (1991) and Kouzeli–Katsiri and Kartsonas, (1986).

these nutrients into acetic, propionic and butyric acids and other intermediate products such as higher molecular weight VAs, hydrogen and CO_2. The metabolic pathways used by the fermentative bacteria to convert proteins and lipids to VAs and micro-organisms involved are not well known (McInnerney, 1988). Only the metabolic pathways for the degradation of carbohydrate to VAs is well understood. The following chemical reactions describe the stoichiometry of break down of glucose into acetic, propionic and butyric acids via the Embden-Meyerhof Pathway (Mosey, 1983).

Acetic Acid

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 + 4ATP \qquad (2.1)$$

Propionic Acid

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O + 2\ ATP \qquad (2.2)$$

Butyric Acid

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 + 2\ ATP \qquad (2.3)$$

The second group of bacteria is the hydrogen-producing acetogenic bacteria. This group of bacteria oxidize fatty acids longer than acetic acid (Zinder, 1984) to produce acetic acid, hydrogen and carbon dioxide.

Conversion of propionic into acetic acid

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 + 1\ ATP \quad (2.4)$$

Conversion of butyric into acetic acid

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2 + 2\ ATP \quad (2.5)$$

The third group of bacteria are the acetoclastic methanogens (*Methanothrix* and *Methanosarcina*). This group transforms acetic acid to methane and carbon dioxide.

$$CH_3COOH \rightarrow CH_4 + CO_2 + 0.25\ ATP \quad (2.6)$$

About 75% of the methane produced during anaerobic digestion comes from the conversion of acetic acid (Mah et al., 1980). *Methanothrix* and *Methanosarcina* have different morphology and growth kinetics (McCarty and Mosey, 1989). *Methanosarcina* grows faster than *Methanothrix* but they have less affinity for the substrate. This is clearly indicated in Fig. 2.4. Therefore the *Methanothrix* will outcompete the *Methanosarcina* in a continuous flow digester where the acetic acid concentration is low. The reverse will occur when a high concentration of acetic acid is present in the digesters. In an SBR both populations should be present because acetic acid concentration is very low at the beginning of the fill period, high at the end of the fill period and low again at the end of the react period.

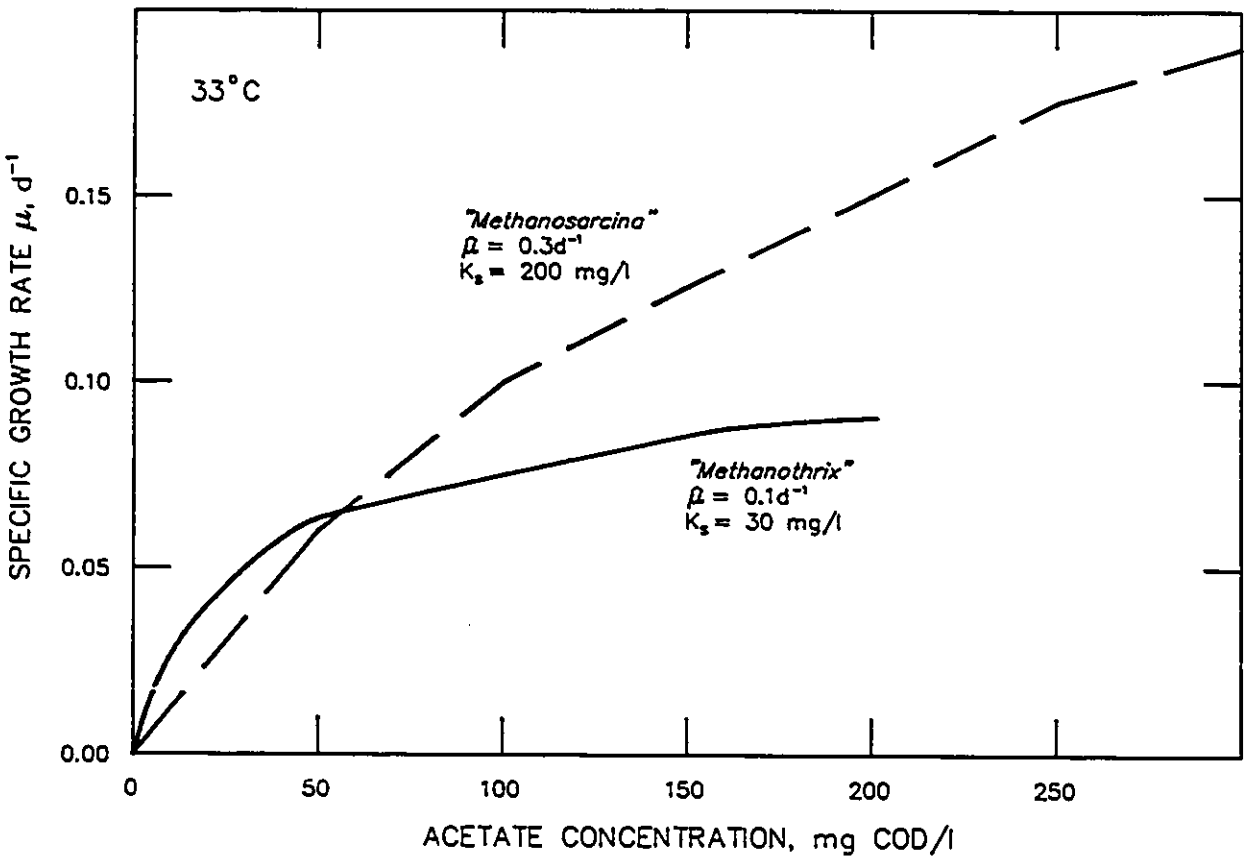


Fig. 2.4 Comparison of typical growth kinetics for acetate cleaving methanogens (Gujer and Zehnder, 1983)

Jetten et al. (1990) found that the lowest concentration of acetic acid reached during its removal by *Methanosarcina* ranged between 12 and 72 mg/L and for the *Methanotrix* it ranged between 0.4 and 4 mg/L. Methanothrix has been renamed *Methanosaeta* by Patel (1990). The latter name will be used from now on in the manuscript.

The last group of bacteria is the H_2 utilizing methanogens. Several species of hydrogen utilizer have been found to reduce carbon dioxide to methane: *Methanobacterium omelianski*, *M.formicium*, *Methanococcus vannielli* and *Methanasarcina barkerii*. These bacteria are responsible for about 25% of the CH_4 production (Mah et al., 1980; Jeris and McCarty, 1965).

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_20 + 1\ ATP \qquad (2.7)$$

These bacteria have a very important role in anaerobic digestion. Their role will be discussed in more detail below.

In anaerobic digestion not all the substrates are converted to final products such as CH_4 and CO_2. A small fraction is used for synthesis and maintenance of bacteria. The following expressions give the synthesis stoichiometry for the different groups of bacteria involved in an anaerobic process. In this study it is assumed that the composition of bacteria is similar to the one used by Christensen and McCarty (1975). They assumed that the bacteria composition was $C_5H_7NO_2$.

1) Acid Formers Synthesis

$$5C_6H_{12}O_6 + 6NH_3 \rightarrow 6C_5H_7NO_2 + 18H_2O \quad (2.8)$$

2) Acetogenic Bacteria Synthesis

a) *Syntrophobacter wolini*

$$3CH_3CH_2COOH + CO_2 + 2NH_3 \rightarrow 2C_5H_7NO_2 + 4H_2O + H_2 \quad (2.9)$$

b) *Syntrophomonas wolfei*

$$CH_3CH_2CH_2COOH + CO_2 + NH_3 \rightarrow C_5H_7NO_2 + 2\,H_2O \quad (2.10)$$

3) Acetoclastic Bacteria Synthesis

Methanosaeta and *Methanosarcina*

$$5\,CH_3COOH + 2NH_3 \rightarrow 2C_5H_7NO_2 + 6H_2O \quad (2.11)$$

4) Hydrogen Utilizers Synthesis

$$5CO_2 + 10H_2 + NH_3 \rightarrow C_5H_7NO_2 + 8H_2O \quad (2.12)$$

2.3.3 Regulatory Role of Hydrogen in Anaerobic Digestion

The interrelationships between the bacteria have a direct impact on the substrate utilization pattern and on the relative concentration of intermediate products in the anaerobic digester. Harper and Pohland (1986) and Mosey (1983) indicated that hydrogen concentration in the digester controls the course of utilization of the substrate. A well functioning digester has a very low dissolved hydrogen concentration and converts most of the substrate to acetic

acid. In digesters experiencing transient conditions the H_2 concentration is more important and some of the substrate is converted to propionic and butyric acid.

McInerney and Bryant (1981), Zehnder et al. (1980) and Harper and Pohland (1986) have considered the thermodynamics of reactions occurring in anaerobic digestions to determine the effect of dissolved hydrogen gas on the production of acetic, propionic and butyric acids. This thermodynamics relationship is shown in Fig. 2.5. This figure indicates that the conversion of acetate to CH_4 and CO_2 is independent of H_2 partial pressure. The conversion of propionic and butyric acids to acetic acid occurs only when P_{H2} is less 10^{-4} and 10^{-3} atm respectively. Harper and Pohland (1986) also indicated that when pH_2 is larger than 10^{-4} atm the Gibbs free energy change is larger for the CO_2 reduction than for the acetate cleavage. Therefore methane producers such as *Methanosarcina* that can use both substrates will favour the reduction of CO_2 over acetate cleavage. This step is very important because it reduces the concentration of H_2 to a level low enough to favour the conversion of acetic acid to methane.

Mosey (1983) investigated the regulatory role of hydrogen by considering the metabolic pathways of the substrate within the acid formers. He developed a comprehensive mathematical model for the utilization of glucose via the Embden-Meyerhof pathway

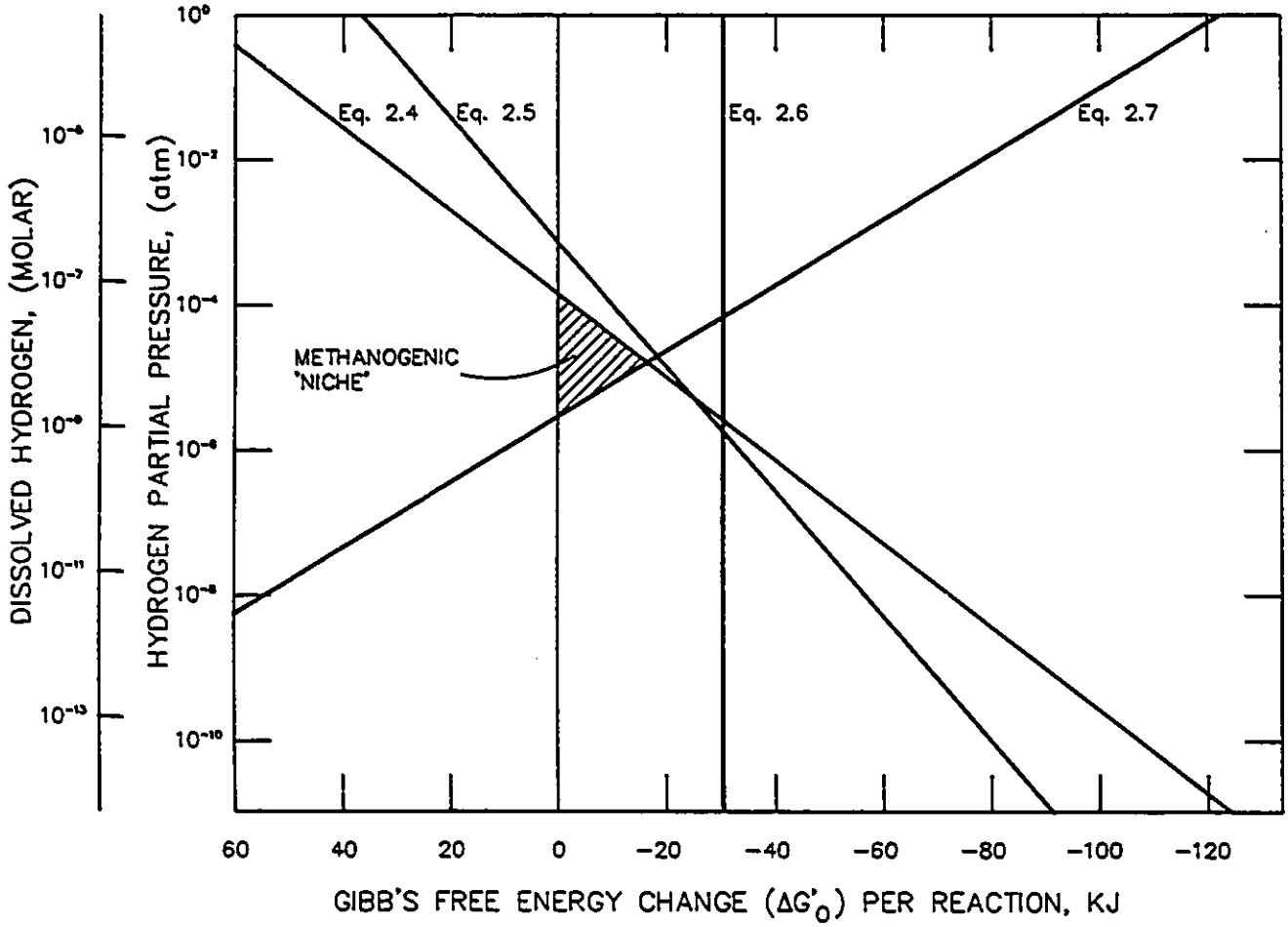


Fig. 2.5 Thermodynamic favorability of the hydrogen–dependent reactions (Harper and Pohland 1986); acetic acid, 25mM; propionic, butyric, bicarbonate, 20 mM; methane, 0.7 atm

(Fig. 2.6). Mosey (1983) assumed that the relative availability of the hydrogen carrier molecule NAD^+ and NADH, controlled the relative production of acetic, propionic and butyric acids from the degradation of glucose. For example, at sites A and B on Fig. 2.6 the hydrogen atom is taken up by NAD^+ to form NADH + H^+. Assuming that the total concentration of NAD^+ and NADH is constant, implies that reaction at sites A and B will continue only if NADH is reconverted to NAD^+ per Eq. (2.13).

$$NADH + H^+ \rightleftharpoons NAD^+ + H_2 \qquad (2.13)$$

The hydrogen gas released by the reaction above must be used in order to keep the partial pressure of H_2 below 10^{-4} atm. Mosey (1983) indicated that the acid formers will use H_2 by producing propionic acid (Eq. 2.2) and also by producing butyric acids (Eq. 2.3) instead of acetic acid (Eq. 2.1). The production of propionic acid requires H_2 as substrate and production of butyric acid instead of acetic acid reduced hydrogen production by 50%.

In order to develop mathematical expressions that will predict the relative production of acetic, propionic and butyric acids from the utilization of glucose, Mosey (1983) related the relative availability of NAD^+ and NADH to the hydrogen partial pressure in the gas phase. But this development necessitated the following assumptions: 1) bacteria maintain a constant

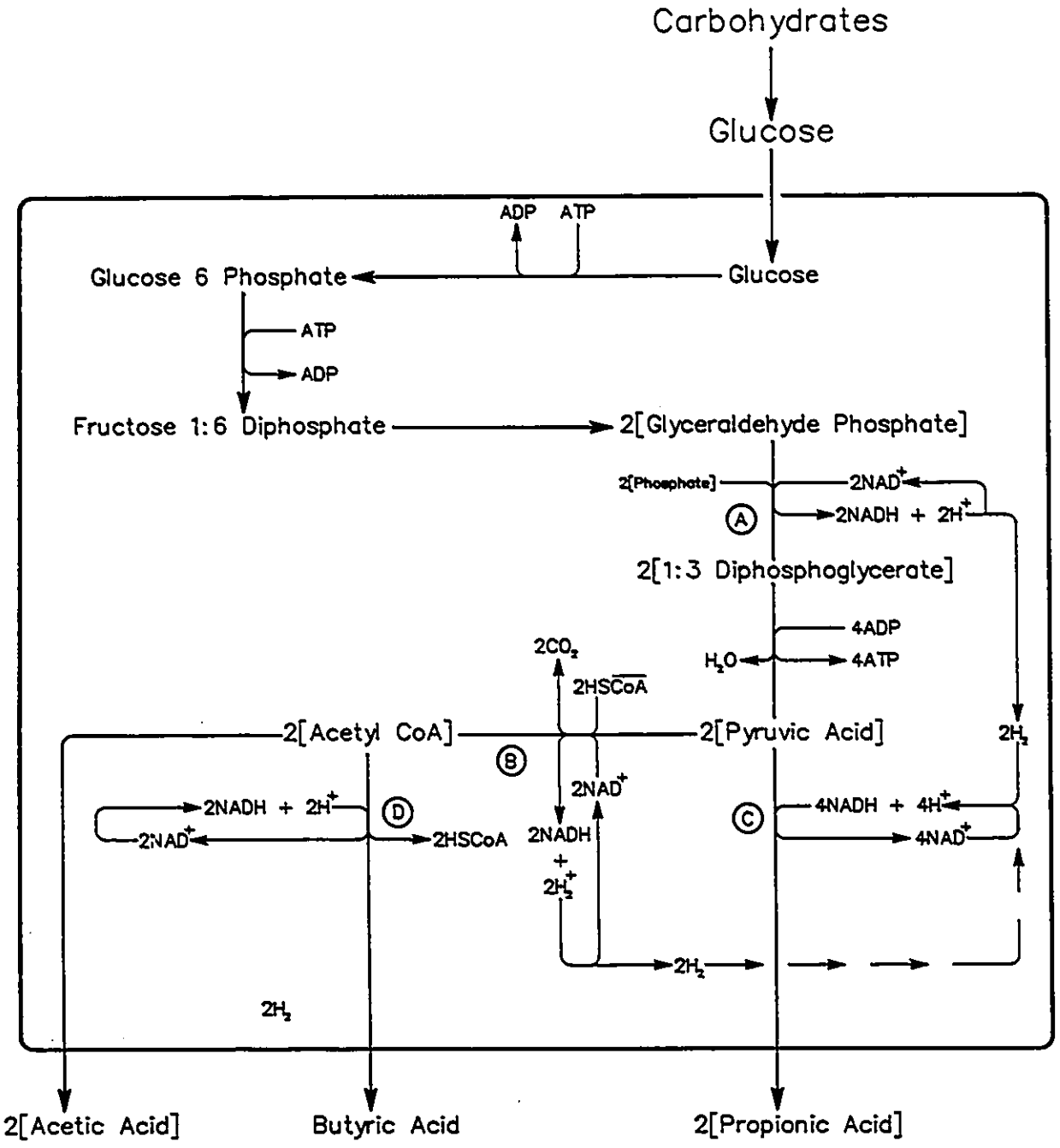


Fig. 2.6 Metabolic pathways for glucose inside acid–forming bacteria (Mosey 1983)

internal pH value of 7.0; and 2) the hydrogen partial pressure in the bacteria is the same as the partial pressure of hydrogen in the digester gas. Based on the above assumptions, Mosey (1983) related the oxidation state of the NAD carrier molecule to the concentration of hydrogen in the digester gas phase.

$$r = \frac{[NADH]}{[NAD^+]} = 1500 P_{H_2} \qquad (2.14)$$

where:

r = ratio of reduced to oxidized carrier molecule

P_{H2} = partial pressure of hydrogen gas, ppm

NADH = concentration of reduced carrier molecule

NAD^+ = concentration of oxidized carrier molecule

Mosey (1983) considered the stoichiometry of the reactions at sites A, B, C and D on Figure 2.6 to determine the regulation factor for each individual volatile acid produced from the biodegradation of carbohydrates as well as for the utilization of butyric and propionic acids. These regulation factors are listed below.

$$R_{A_c} = \frac{1}{(1+r)^3} \qquad (2.15)$$

$$R_{Pr} = \frac{r}{(1 + r)^2} \quad (2.16)$$

$$R_{Bu} = \frac{r}{(1 + r)^3} \quad (2.17)$$

$$R_{BBu} = \frac{1}{(1 + r)} \quad (2.18)$$

$$R_{PPr} = \frac{1}{(1 + r)} \quad (2.19)$$

where:

R_{Ac} = regulation factor for conversion of soluble carbohydrate to acetic acid

R_{Pr} = regulation factor for conversion of soluble carbohydrate to propionic acid

R_{Bu} = regulation factor for conversion of soluble carbohydrate to butyric acid

R_{BBu} = regulation factor for conversion of butyric to acetic acid

R_{PPr} = regulation factor for conversion of propionic to acetic acid

2.3.4 Simple Model Development

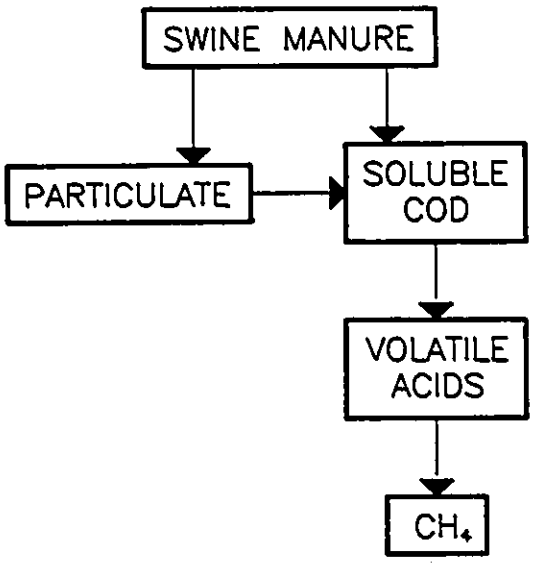
A simple model that simulates accurately the PAD in SBR would be very useful to size a SBR, determine the substrate utilization rate under different operating conditions and recommend design specifications and operation scenarios for a full scale plant.

Simple models are easy to use because they make use of only a small number of kinetic parameters and material mass balances. Several simple models have been developed previously by Chen and Hashimoto (1978), Hill (1983), Hill and Nordstedt (1980) and Droste and Kennedy (1988). The simplified scheme of PAD in SBR used in this study to develop the simple model is illustrated in Figure 2.7. It includes only two microbial groups: 1) the fast growing acid formers and slow growing methane formers. The proposed model will be used to simulate the biological phase only. The parameters considered are SCOD, VA and methane production. VS and total COD are not considered because in a non-mixed SBR their accumulation can not be modelled accurately because their removal is also largely due to settling. The model proposed for the simplified scheme is based on the following assumptions:

2.3.4.1 Model Assumptions

1. The model considers the hydraulic regimes of a SBR.
2. Swine manure contains both particulates and soluble substrates.
3. Particulates are converted to soluble COD.
4. Any reduction in soluble COD is converted to VA and acid formers.
5. VA are converted to methane and methane formers.

a.



b.

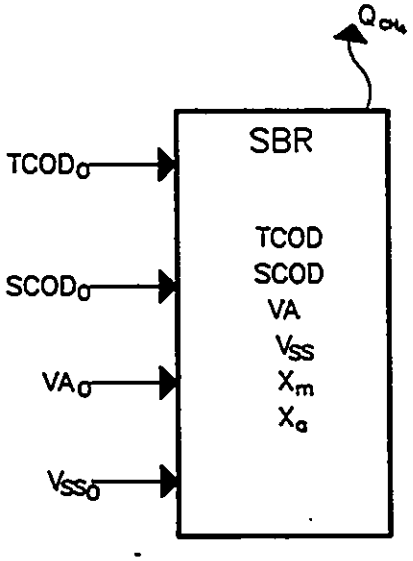


Fig. 2.7 a. Simplified scheme for anaerobic digestion
b. Parameter considered in simple model development

6. pH, VA and NH_3-N concentrations do not have an effect on process kinetics.
7. Soluble substrate utilization follow Monod kinetics.
8. Both acid former and methane former populations change during the simulation.
9. Methane solubility in the liquid phase is assumed negligible. The SBR has no effluent therefore the methane leaving the SBR with the biogas is assumed to be equal to the methane produced by the methane formers.
10. Only one population of acetoclastic methanogens is present in the digesters.
11. Psychrophilic conditions (T=20°C) are maintained in SBR.

Some of the above assumptions will be modified if they are not supported by the experimental results.

2.3.4.2 Material Mass Balance

The following general material mass balance was used with each substrate, intermediate product and final product.

Accumulation = Input - Output + Production - Utilization

Particulate Organics

$$\frac{d(PV_L)}{dt} = QPo - r_p V_L \qquad (2.20)$$

where:

Po = particulate COD concentrations in influent, mg/L

P = particulate COD concentrations in SBR, mg/L

Q = influent flow rate, L/d

V_L = SBR liquid phase volume, L

r_p = solubilization rate of particulates, mg COD/L-d

In a SBR during the fill period, both the particulates concentration and liquid phase volume are functions of time.

$$\frac{d(PV_L)}{dt} = P\frac{dV_L}{dt} + V_L\frac{dP}{dt} \qquad (2.21)$$

It is known that:

$$\frac{dV_L}{dt} = Q \qquad (2.22)$$

Substituting Eq. (2.22) into Eq. (2.21) gives:

$$\frac{d(PV_L)}{dt} = PQ + V_L\frac{dP}{dt} \qquad (2.23)$$

Substituting Eq. (2.23) into Eq. (2.20) and simplifying further yields:

$$\frac{dP}{dt} = \frac{Q(Po-P)}{V_L} - r_P \qquad (2.24)$$

where:

$r_p = K_pP$, mg COD/L-d

K_p = first order solubilization rate, d^{-1}

Gujer and Zehnder (1983), indicated that a first-order hydrolysis rate for particulate solubilization may be the most appropriate for complex wastes and was therefore used in this study.

The mass balance for a SBR during the fill period is identical to the mass balance for a CSTR. The term PQ in the above expression (Eq. 2.24) does not represent the effluent output. It rather represents the reduction in concentration due to dilution caused by the increase in SBR liquid phase volume.

Similar mass balances for the fill period were also developed for soluble COD, volatile acids COD, acid and methane formers as well as methane production. These mass balances are listed in Table 2.1. The mass balances for the react period are similar to the ones listed in Table 2.1. The only difference is that the influent flow rate term is equal to zero.

Table 2.1 Simple model material mass balances for the fill period.

Particulates COD

$$\frac{dP}{dt} = \frac{Q\ (Po - P)}{V_L} - K_p\ P \qquad (2.24)$$

Soluble COD

$$\frac{dS}{dt} = \frac{Q\ (So - S)}{V_L} + K_p\ P - \frac{Vmax_a\ X_a\ S}{K_{sa} + S} + (K_{da}\ X_a + K_{dm}\ X_m)\ F \qquad (2.25)$$

VA COD

$$\frac{dVA}{dt} = \frac{Q(VAo - VA)}{V_L} + Y_A\left(\frac{Vmax_a\ X_a\ S}{K_{sa} + S}\right) - \left(\frac{Vmax_m\ X_m\ VA}{K_{sm} + VA}\right) \qquad (2.26)$$

Acid Formers

$$\frac{dX_a}{dt} = -\frac{Q\ X_a}{V_L} + Y_a\left(\frac{Vmax_a\ X_a\ S}{K_{sa} + S}\right) - K_{da}\ X_a \qquad (2.27)$$

Methane Formers

$$\frac{dX_m}{dt} = -\frac{Q\ X_m}{V_L} + Y_m\left(\frac{Vmax_m\ X_m\ VA}{K_{sm} + VA}\right) - K_{dm}\ X_m \qquad (2.28)$$

Methane Production

$$Q_{CH_4} = \left[\left(\frac{Vmax_m\ X_m\ VA}{K_{sm} + VA}\right) - F * Y_m\left(\frac{Vmax_m\ X_m\ VA}{K_{sm} + VA}\right)\right] * V_L \qquad (2.29)$$

Note: Mass balances are similar for the react period except that the influent flow rate Q = 0.

where:

So = influent SCOD concentration, mg COD/L

S = SBR SCOD concentration, mg COD/L

VAo = influent volatile acid COD concentration, mg COD/L

VA = SBR volatile acid COD concentration, mg COD/L

$Vmax_a$ = maximum specific SCOD uptake rate, mg COD/mg X_a-d

X_a = acid formers concentration, mg/L

K_{da} = decay rate constant for acid formers, d^{-1}

K_{dm} = decay rate constant for methane formers, d^{-1}

F = theoretical COD equivalent of VSS, mg COD/mg VSS

Y_A = true yield of volatile acid COD from substrate

K_{sa} = saturation constant mg SCOD/L

K_{sm} = saturation constant mg VA COD/L

$Vmax_m$ = maximum specific VA uptake rate, mg VA COD/mg X_m-d

Y_a = acid formers yield factor

Y_m = methane formers yield factor

Q_{CH4} = methane production rate, g COD/d

X_m = methane formers concentration, mg/L

The liquid zone volume changes with time during the fill period. Therefore in the expressions (Eqs. 2.24 to 2.29) the liquid phase volume is determined as follows:

$$V_L = V_o + \int Q \, dt \qquad (2.30)$$

where:

V_o = SBR initial volume, L

The major limitation of a simple model like this, is its incapacity to assess the process stability. This is mainly because it is based on simplified assumptions and also the parameters considered in the simple model are not the most appropriate to evaluate the stability of an SBR. The simple model predicts the accumulation of VA but gives no information on the relative accumulation of individual VAs. Accumulation of VA in a SBR does not necessarily indicate digester instability but a significant increase in propionic and butyric acids could indicate imminent of process failure.

2.3.5 Advanced Model Development

Andrews and Graef (1971) stated that there is no single parameter that will indicate the eminence of an anaerobic process failure. They indicated that process stability can be assessed by considering several parameters simultaneously (pH, alkalinity, gas production, gas composition and VA concentration). Mosey (1983), Gujer and Zehnder (1983) and Harper and Pohland (1986) indicated that process stability could be assessed by monitoring only the partial pressure of hydrogen in the gas phase. A more advanced and comprehensive model is necessary in order to consider all these parameters and their interaction.

Andrews (1969) developed the first dynamic model that could simulate anaerobic process under steady state and transient

conditions. The major limitation of his model was that the pH was assumed constant. Andrews and Graef (1971) removed this limitation by considering the interaction between the liquid, gas and biological phases. They used modified Monod kinetics to consider inhibition of methane formers by unionized VAs. Andrews and Graef (1971) assumed that the utilization of acetic acid by methane formers was the rate limiting step in the process. Therefore their model included only one group of bacteria. The work by Andrews and Graef (1971) has been the foundation for the development of several advanced models. Hill and Barth (1977) considered Andrews and Graef (1971) work to develop a model to simulate the anaerobic digestion of animal waste. They added a second bacterial population to the model in order to consider VAs production by acid formers and VAs utilization by methane formers. They also considered the particulates hydrolysis rate in their model. Hill and Barth (1977) modified further the Monod expression to include inhibition of methane formers by both ammonia nitrogen and VAs. Hill and Barth's (1977) model only predicted the general trend of anaerobic digestion of animal manure.

Mosey (1983) developed a model that considered the biological phase of anaerobic digestion of glucose. Two important advancements in that model were: 1) consideration of four populations of bacteria; and 2) consideration of the role of hydrogen gas on the formation of intermediate products such as

acetic, propionic and butyric acid, and on the conversion of intermediate products such as propionic and butyric acids into acetic acid. A number of researchers (Merlini, 1983; Rozzi et al. 1985; Costello, 1991, and Jones, 1992) have developed advanced models based: 1) on the four bacteria population model developed by Mosey (1983) for the biological phase; and 2) the model by Andrew and Graef (1971) for the physico-chemical system. These advanced models predicted the change of individual VA species, pH, partial pressure of hydrogen and biogas production and composition as a function of time.

Costello et al. (1991) compared the prediction of their model with previously reported experimental data and Jones (1992) operated a pilot scale anaerobic digester to validate his model. In both cases, the advanced model only predicted the trends for substrate utilization, intermediate products accumulation and biogas production. These models were not therefore appropriate for process control or to predict eminence of process failure.

The model proposed in this study has similarities with models developed by Merlini (1983), Rozzi et. al (1985), Costello (1991) and Jones (1992) but it is based on new assumptions that are supported by the recent literature. Previous models that incorporated hydrogen dynamics assumed that the gas and liquid phases were in equilibrium. As a result the hydrogen

gas partial pressure was assumed to be directly proportional to the dissolved concentration of hydrogen. They used Henry's law to relate the partial pressure of hydrogen to the dissolved concentration of hydrogen. Research work by Pauss et al. (1989, 1990) suggested that there is a hydrogen transfer limitation from the liquid to the gas phase in an anaerobic digester. The hydrogen gas transfer resistance should be more important in a non-mixed or intermittently mixed SBR. Therefore the proposed advanced model will incorporate a mass transfer coefficient for hydrogen. Interpretation of the work by Jetten et al. (1990) and McCarty and Mosey (1991) suggests that two populations of acetoclastic methanogens (*Methanosaeta* and *Methanosarcina*) could be present in a SBR.

2.3.5.1 Advanced Model Assumptions

1. Digester is operated as a SBR.
2. Swine manure contains both soluble and particulate organics.
3. Soluble COD of swine manure is mainly composed of carbohydrates. This assumption is necessary because the metabolic pathways for proteins and lipids are not well understood. Also data presented later indicate that carbohydrates are the main compound of the swine manure slurry.
4. Soluble carbohydrates are converted tc acetic,

propionic and butyric acids via the Embden-Meyerhof pathway.

5. The rates of formation of the individual VA from the degradation of carbohydrates and the utilization rate of butyric and propionic are regulated by the partial pressure of hydrogen in the gas phase.
6. Propionic and butyric acids are converted to acetic acid, H_2 and CO_2 by the acetogenic bacteria.
7. Acetic acid is converted to methane by the acetoclastic methanogens (*Methanosarcina* and *Methanosaeta*).
8. Methane is also produced from the reduction of CO_2 by the hydrogen utilizers (*Methanobacterium omelianski*, *M.formicium*, *Methanococcus vannielli* and *Methanasarcina barkerii*).
9. Gases are ideal.
10. Effect of ionic strength is neglected.
11. pH effect on microorganisms kinetic is assumed negligible.
12. Soluble substrate utilization follows Monod kinetics and the particulates substrate utilization follow first order kinetics.
13. Bacteria concentrations change during the simulation.
14. Fraction of substrates converted to microorganisms are considered.

15. Nitrogen requirement for microorganisms synthesis is considered.
16. Gas and liquid phases are not in equilibrium. There is a mass transfer limitation for hydrogen, carbon dioxide and ammonia nitrogen gas.
17. Methane solubility in the liquid phase is negligible. With a SBR, there is no effluent during the fill and react periods. Therefore all the methane produced during these periods is discharged with the biogas.
18. Psychrophilic conditions prevail, T = 20°C.
19. A fraction of the CO_2 produced accumulates in the SBRs liquid phase.
20. The model considers the difference in the total concentrations of cations and anions.
21. It is also assumed that the growth rates of microorganisms are not affected by high concentrations of VAs and ammonia nitrogen.
22. Transient conditions exist in SBR.

Some of the above assumptions will be changed if they are not supported by this study's experimental results. Any changes to any of these assumptions will be discussed in detail in chapter 5.

2.3.5.2 Material Mass Balance for the Fill Period

The following general material balance equation was used with each substrate, intermediate compound and product to predict its accumulation in the SBR.

Accumulation = Input - Output + Production - Utilization

Particulate Organics

$$\frac{dP}{dt} = \frac{Q}{V_L}(P_o - P) - K_p P \qquad (2.31)$$

where:

P_o = particulate concentration in influent, mM

P = particulate concentration in SBR, mM

Q = influent flow rate, L/d

V_L = SBR liquid phase volume, L

K_p = first order solubilization rate, d^{-1}

Recall that:

$$V_L = V_o + \int Q\, dt \qquad (2.30)$$

Carbohydrates

Soluble organic (carbohydrates) are produced from particulates solubilization and used by the acid forming bacteria to produce VAs according to Eqs. (2.1), (2.2) and (2.3).

$$\frac{dC}{dt} = \frac{Q}{V_L}(C_o - C) + K_p P - \left(\frac{dC}{dt}\right)_{A_c} - \left(\frac{dC}{dt}\right)_{P_r} - \left(\frac{dC}{dt}\right)_{B_u} - \left(\frac{dX_a}{dt}\right) Y_c \quad (2.32)$$

where:

C_o - influent concentration of soluble carbohydrate, mM

C - SBR soluble carbohydrate concentration, mM

$\left(\frac{dC}{dt}\right)_{A_c}$ - carbohydrate degradation into acetic acid, mM/d

$\left(\frac{dC}{dt}\right)_{P_r}$ - carbohydrate degradation into propionic acid, mM/d

$\left(\frac{dC}{dt}\right)_{B_u}$ - carbohydrate degradation into butyric acid, mM/d

$\left(\frac{dX_a}{dt}\right)$ - concentration change of acid formers, mg/L-d

Y_c - carbohydrate used for synthesis of X_a, mmol/mg

The transformation of carbohydrate to VA is obtained from the following expressions:

$$\left(\frac{dc}{dt}\right)_{A_c} = rC * R_{A_c} \quad (2.33)$$

$$\left(\frac{dc}{dt}\right)_{P_r} = rC * R_{P_r} \qquad (2.34)$$

$$\left(\frac{dc}{dt}\right)_{B_u} = rC * R_{B_u} \qquad (2.35)$$

where:

rC = unregulated soluble carbohydrate utilization rate, mM/d

R_{Ac} = regulation factor for conversation of soluble carbohydrate to acetic acid

R_{Pr} = regulation factor for conversion of soluble carbohydrate to propionic acid

R_{Bu} = regulation factor for conversion of soluble carbohydrate to butyric acid

The unregulated soluble carbohydrate conversion rate to VAs follows Monod kinetics as indicated in the following expression.

$$rC = \frac{K_c\, C\, X_a}{K_{sc} + C} \qquad (2.36)$$

where:

K_c = maximum specific carbohydrates utilization rate, mmol/mg-d

K_{sc} = saturation constant, mM

X_a = concentration of acid formers, mg/L

The term that represents the change in concentration of acid formers in Eq. (2.32) is determined as follow:

$$\left(\frac{dx_a}{dt}\right) = Y_{Ac}\left(\frac{dc}{dt}\right)_{Ac} + Y_{Pr}\left(\frac{dc}{dt}\right)_{Pr} + Y_{Bu}\left(\frac{dc}{dt}\right)_{Bu} - K_{da}\,X_a \qquad (2.37)$$

where:

Y_{Ac} = microorganisms yield, mg X_a/mmol carbohydrate to A_c

Y_{Pr} = microorganisms yield, mg X_a/mmol carbohydrate to P_r

Y_{Bu} = microorganisms yield, mg X_a/mmol carbohydrate to B_u

K_{da} = decay rate of acid formers, d^{-1}

The constant Y_c in Eq. (2.32) is determined from the stoichiometry of carbohydrate conversions to microorganisms Eq. (2.8). This stoichiometry expression indicates that 7.374 x 10^{-3} mmol of soluble carbohydrate are required to produce 1 mg of microorganisms. Therefore $Y_c = 7.374 * 10^{-3}$ mmol/mg.

The yield factors, Y_{Ac}, Y_{Pr} and Y_{Bu} in Eq. (2.37) were determined by Mosey (1983). He assumed that 10 g of microorganisms are formed per mole of ATP produced. Using the ATP yield from reactions in Eqs. (2.1) to (2.3) gives the following values for:

Y_{Ac} = 40 mg X_a/mmol carbohydrate to acetic acid

Y_{Pr} = 20 mg X_a/mmol carbohydrate to propionic acid

Y_{Bu} = 20 mg X_a/mmol carbohydrate to butyric acid

Non Biodegradable organics

$$\left(\frac{dc}{dt}\right)_{NB} = \frac{Q}{V_L}\,(CNB_o - CNB) \qquad (2.38)$$

where:

CNB_o = nonbiodegradable organics in influent, mM

CNB = nonbiodegradable organics in SBR, mM

Butyric Acid

Butyric acid is produced from the biodegradation of soluble carbohydrates according to Eq. (2.3). It is converted to acetic acid and acetogenic butyric microorganisms according to Eqs. (2.5) and (2.10) respectively. The variation in butyric acid concentration is determined with the following mass balance.

$$\left(\frac{dB_u}{dt}\right) = \frac{Q}{V_L}\,(B_{uo} - B_u) + \left(\frac{dC}{dt}\right)_{B_u} - rs_{B_u}\,R_{BB_u} - Y_B\,rs_{B_u}\,Y_{bb} \qquad (2.39)$$

where:

B_{uo} = concentration of butyric acid in influent, mM

B_u = concentration of butyric acid in SBR, mM

rs_{Bu} = unregulated butyric acid utilization rate, mM/d

R_{BBu} = regulation factor for conversion of butyric to acetic acid

Y_B = amount of butyric acid used for the formation of 1 g of acetogenic bacteria, mmol/mg of X_{Bu}

Y_{bb} = microorganisms yield, mg X_{Bu}/mmol butyric converted to Ac

Based on Mosey's (1983) assumption, the ATP yield in Eq. (2.5) indicates that Y_{bb} is equal to 20 mg of X_{Bu} per mmol of butyric acid used. Value of the constant Y_B was determined from Eq. (2.10) and was found equal to 8.849×10^{-3} mmol/mg.

The unregulated butyric acid utilization rate was assumed to follow Monod kinetics.

$$rs_{B_u} = \frac{K_{B_u} X_{B_u} B_u}{K_{sB_u} + B_u} \qquad (2.40)$$

where:

K_{Bu} = maximum butyric acid specific utilization rate, mmol/mg-d

K_{sBu} = saturation constants, mM

X_{Bu} = concentration of acetogenic butyric bacteria, mg/L

Propionic Acid

Propionic acid is produced from the degradation of soluble carbohydrate (Eq. 2.2). It is consumed when: 1) converted to acetic acid as per Eq. (2.4); and 2) used in the synthesis of acetogenic propionic microorganisms as indicated in Eq. (2.9). Equations similar to those developed for butyric acid are also used for propionic acid. They are listed below.

$$\left(\frac{dP_r}{dt}\right) = \frac{Q}{V_L}(P_{ro} - P_r) + 2\left(\frac{dC}{dt}\right)_{P_r} - rs_{P_r} R_{PP_r} - Y_P\, rs_{P_r} Y_{pp} \qquad (2.41)$$

$$rs_{P_r} = \frac{K_{p_r} X_{p_r} P_r}{K_{sP_r} + P_r} \qquad (2.42)$$

where:

P_{ro} = influent propionic acid concentration, mM

P_r = propionic acid concentration in SBR, mM

R_{ppr} = regulation factor for conversion of propionic to acetic acid

Y_p = amount of propionic acid used for the synthesis of 1 g of acetogenic propionic bacteria, mmol/mg of X_{pr}

Y_{pp} = microorganism yield per mM of propionic acid converted to acetic acid, mg X_{pr}/mmol

rs_{pr} = unregulated propionic acid utilization rate, mM/d

K_{pr} = max. propionic acid specific utilization rate, mmol/mg-d

K_{spr} = saturation constant, mM

X_{pr} = concentration of acetogenic propionic bacteria, mg/L

Eqs. (2.9) and (2.4) were used to determine the values of constants Y_{pp} and Y_p.

Y_p = 13.27 x 10^{-3} mmol P_r/mg X_{pr}

Y_{pp} = 10 mg X_{pr}/mmol Pr

Acetic Acid

In this study it is assumed that two populations of acetoclastic bacteria (*Methanosaeta* and *Methanosarcina*) are present in the SBRs (assumption 7). These bacteria convert the acetic acid produced from the degradation of soluble carbohydrate (Eq. 2.1), propionic (Eq. 2.4) and butyric acids (Eq. 2.5) into methane, carbon dioxide and new biomass (Eq. 2.11). The variation in acetic acid concentration is determined with the following material balance.

$$\frac{dA_c}{dt} = \frac{Q}{V_L}(A_{co} - A_c) + 2\left(\frac{dC}{dt}\right)_{A_c} + 2\left(\frac{dB_u}{dt}\right)_{A_c} + \left(\frac{dP_r}{dt}\right)_{A_c}$$

$$- rs_{A_{c1}} - rs_{A_{c2}} - Y_{A1}\, rs_{A_{c1}}\, Y_{aa1} - Y_{A2}\, rs_{A_{c2}}\, Y_{aa2} \qquad (2.43)$$

$$rs_{A_{c1}} = \frac{K_{A_{c1}}\, X_{A_{c1}}\, A_c}{(K_{sA_{c1}} + A_c)} \qquad (2.44)$$

$$rs_{A_{c2}} = \frac{K_{A_{c2}}\, X_{A_{c2}}\, A_c}{(K_{sA_{c2}} + A_c)} \qquad (2.45)$$

where:

A_{co} = influent concentration of acetic acid, mM

A_c = concentration of acetic acid in SBR, mM

rs_{Ac1} = acetic acid specific utilization rate by *Methanosaeta*, mM/d

rs_{Ac2} = acetic acid specific utilization rate by *Methanosarcina*, mM/d

Y_{aa1} = *Methanosaeta* yield per mmol of acetic acid converted to methane, mg/mmol

Y_{aa2} = *Methanosarcina* yield per mmol of acetic acid converted to methane, mg/mmol

Y_{A1} = amount of acetic acid used for synthesis of 1 g of *Methanosaeta*, mmol/mg

Y_{A2} = amount of acetic acid used for synthesis of 1 g of *Methanosarcina*, mmol/mg

K_{Ac1} = maximum acetic acid utilization rate by *Methanosaeta*, mmol/mg-d

K_{Ac2} = maximum acetic acid utilization rate by *Methanosarcina*, mmol/mg-d

K_{sAc1} = saturation constant (*Methanosaeta*), mM

K_{sAc2} = saturation constant (*Methanosarcina*), mM

X_{Ac1} = concentration of *Methanosaeta*, mg/L

X_{Ac2} = concentration of *Methanosarcina*, mg/L

Eqs. (2.6) and (2.11) were used to evaluate the following constants:

$$Y_{A1} = Y_{A2} = 22.12 \times 10^{-3} \text{ mmol/mg}$$

$$Y_{aa1} = Y_{aa2} = 2.5 \text{ mg/mmol}$$

The material mass balances for each group of microorganisms in the SBR are given below:

Acidogens

$$\frac{dX_a}{dt} = -\frac{Q}{V_L}X_a + Y_{Ac}\left(\frac{dc}{dt}\right)_{Ac} + Y_{Pr}\left(\frac{dc}{dt}\right)_{Pr} + Y_{Bu}\left(\frac{dc}{dt}\right)_{Bu} - K_{da}X_a \quad (2.46)$$

Acetogenic Propionic

$$\frac{dX_{Pr}}{dt} = -\frac{Q}{V_L}X_{Pr} + Y_{pp}\,rs_{Pr}\,R_{pp_r} - K_{dPr}X_{Pr} \quad (2.47)$$

where:

K_{dPr} = decay rate of acetogenic propionic bacteria, d^{-1}

Acetogenic Butyric

$$\frac{dX_{Bu}}{dt} = -\frac{Q}{V_L}X_{Bu} + Y_{bb}\,rs_{Bu}\,R_{BB_u} - K_{dBu}X_{Bu} \quad (2.48)$$

where:

K_{dBu} = decay rate of acetogenic Butyric bacteria, d^{-1}

Methane Formers

1) *Methanosaeta*

$$\frac{dX_{Ac1}}{dt} = -\frac{Q}{V_L}X_{Ac1} + Y_{aa1}\,rs_{Ac1} - K_{dAc1}X_{Ac1} \quad (2.49)$$

where:

K_{dAc1} = decay rate of *Methanosaeta*, d^{-1}

2) *Methanosarcina*

$$\frac{dX_{Ac2}}{dt} = -\frac{Q}{V_L}X_{Ac2} + Y_{aa2}\,rs_{Ac2} - K_{dAc2}\,X_{Ac2} \qquad (2.50)$$

where:

K_{dAc2} = decay rate of *Methanosarcina*, d^{-1}

H_2 Utilizing Methanogens

$$\frac{dX_{H_2}}{dt} = -\frac{Q}{V_L}X_{H_2} + Y_{hh2}\left(\frac{dH_2}{dt}\right)_M - K_{dH_2}\,X_{H_2} \qquad (2.51)$$

where:

Y_{hh2} = microorganism yield, mg/mmol

K_{dH2} = decay rate, d^{-1}

X_{H2} = concentration of hydrogen utilizing bacteria, mg/L

Eq. 2.12 yielded a value of Y_{hh2} = 2.5 mg/mmol of H_2.

Methane Production

The methane flow rate out of the SBR is equal to methane production rate in the liquid phase (assumption 17).

$$\left(\frac{dCH_4}{dt}\right)_{Bio} = rs_{Ac1} + rs_{Ac2} + \frac{1}{4}\left(\frac{dH_2}{dt}\right)_M \qquad (2.52)$$

where:

$\left(\frac{dCH_4}{dt}\right)_{Bio}$ = Biological production of CH_4, mM/d

$\left(\frac{dH_2}{dt}\right)_M$ - Biological utilization of H_2, mM H_2/d

It was assumed that biological removal by the hydrogen utilizing bacteria followed Monod kinetics as indicated in the expression below.

$$\left(\frac{dH_2}{dt}\right)_M = \frac{K_{H_2} X_{H_2} H_2}{K_{sH_2} + H_2} \qquad (2.53)$$

where:

K_{H2} = maximum specific dissolved hydrogen uptake rate, mmol/mg-d

K_{sH2} = saturation constant, mM

H_2 = dissolved concentration of H_2, mM

In order to determine the methane production rate of the hydrogen utilizing methanogens, the actual concentration of H_2 must be known. H_2 can be determined by using a mass balance for hydrogen gas in both the liquid and gas phases.

Mass Balance for Dissolved Hydrogen

$$\left(\frac{dH_2}{dt}\right) = -\frac{Q}{V_L} H_2 + \left(\frac{dH_2}{dt}\right)_{Bio} - \left(\frac{dH_2}{dt}\right)_{Tr} \qquad (2.54)$$

where:

$\left(\frac{dH_2}{dt}\right)_{Bio}$ - H_2 variation caused by biological activity, mM/d

$\left(\frac{dH_2}{dt}\right)_{Tr}$ - H_2 variation caused by gas transfer, mM/d

The biological production and utilization of H_2 is determined by the following expression.

$$\left(\frac{dH_2}{dt}\right)_{Bio} - 4\left(\frac{dC}{dt}\right)_{A_c} + 2\left(\frac{dC}{dt}\right)_{B_u} - 2\left(\frac{dC}{dt}\right)_{P_r} + 2\left(\frac{dB_u}{dt}\right)_{A_c}$$

$$+ 3\left(\frac{dP_r}{dt}\right)_{A_c} - \left(\frac{dH_2}{dt}\right)_{M} - Y_{H_2}\left(\frac{dH_2}{dt}\right)_{M} Y_{hh2} \qquad (2.55)$$

where:

Y_{H2} = amount of hydrogen used for the synthesis of 1 mg of X_{H2}, mmol/mg

Eq. 2.7 yielded a value of Y_{H2} = 0.0884 mmol/mg X_{H2}.

For the transfer rate of hydrogen from the liquid to gas phase, a mass balance for H_2 in the gas phase is necessary. In the development of the following material balance, it was assumed that the gas flow rate due to the decrease in gas phase volume during the fill period was negligible compared to the biogas production.

moles in - moles out = change in moles

$$V_L\left(\frac{dH_2}{dt}\right)_{Tr} - Q_g H_{2_g} - V_g\left(\frac{dH_{2_g}}{dt}\right) \qquad (2.56)$$

where:

Q_g = biogas flow rate, L/d

H_{2g} = hydrogen concentration in gas phase, mM

V_g = gas phase volume, L

In a SBR the gas phase volume changes with time during the fill period. The volume at any time is obtained from the following expression:

$$V_g - V_{go} - \int Q\, dt \qquad (2.57)$$

where:

V_{go} = initial gas phase volume, L

The ideal gas law states that:

$$P_T V_{TP} - n R T \qquad (2.58)$$

Therefore:

$$H_{2_g} - \frac{n_{H_2}}{V_g} - \frac{P_{H_2}}{RT} \qquad (2.59)$$

where:

P_{H2} = partial pressure of H_2 in gas phase, atm

P_T = total biogas pressure, atm

One mole of gas at a specific temperature has a volume equal to:

$$V_{TP} = \frac{R\,T}{P_T} \tag{2.60}$$

Substituting Eqs. (2.59) to (2.60) into (2.58) and rearranging yields the following expression to determine the change in hydrogen partial pressure in the gas phase.

$$\left(\frac{dP_{H_2}}{dt}\right)_g = V_{TP}\,P_T\left(\frac{V_L}{V_g}\right)\left(\frac{dH_2}{dt}\right)_{Tr} - \left(\frac{Q_g}{V_g}\right)P_{H_2} \tag{2.61}$$

where:

$\left(\frac{dP_{H_2}}{dt}\right)$ - rate of change of H_2 gas phase pressure, atm/d

Assumption 16, indicates that the present model must include an expression for hydrogen mass transfer. Based on the two film theory the following expression allows the determination of the rate of transfer of hydrogen at the liquid-gas interface.

$$\left(\frac{dH_2}{dt}\right)_{Tr} = Kla_{H_2}\,[H_2 - H_{2s}] \tag{2.62}$$

where:

H_{2S} = concentration of hydrogen in liquid phase when in equilibrium with the gas phase, mM

$H_{2s} = KH_{H_2}\,P_{H_2}$

Kla_{H2} = hydrogen gas transfer coefficient, d^{-1}

KH_{H2} = Henry's constant for hydrogen, mM/atm

Substituting results of Eqs. (2.55), (2.61) and (2.62) into Eq. (2.54) allows the determination of the rate of change in dissolved concentration of H_2 in the liquid phase and substituting Eq. (2.54) and Eq. (2.53) into Eq. (2.52) yields the molar methane flow rate.

Methane Volumetric Flow Rate

The molar methane production rate can be converted to an equivalent volumetric production rate as follow.

$$Q_{CH_4} = V_{TP}\, V_L \left(\frac{dCH_4}{dt}\right)_{Bio} \tag{2.63}$$

where:

Q_{CH4} = volumetric methane flow rate, L/d

Biogas Flow Rate

Based on Dalton's law the total pressure of the gas mixture in a SBR is equal to:

$$P_T = P_{CH_4} + P_{CO_2} + P_{NH_3} + P_{H_2O} + P_{H_2} + P_{H_2S} \tag{2.64}$$

where:

P_i = partial pressure of individual gas, atm

Combining the ideal gas law (Eq. 2.58) and Dalton's law (Eq. 2.64) gives the following expressions:

$$\frac{P_{CH_4}}{P_T} = \frac{n_{CH_4}}{n_T} = \frac{Q_{CH_4}}{Q_T} \tag{2.65}$$

$$n_T = \frac{n_{CH_4} P_T}{P_{CH_4}} \tag{2.66}$$

Assuming that P_T = 1 atm, yields the following expression to determine the biogas flow rate.

$$Q_g = \frac{Q_{CH_4}}{P_{CH_4}} = \frac{Q_{CH_4}}{1 - P_{CO_2} - P_{NH_3} - P_{H_2S} - P_{H_2} - P_{H_2O}} \tag{2.67}$$

The partial pressures of NH_3, H_2S and H_2 were assumed negligible when compared to partial pressures of CO_2 and H_2O. Therefore the expression for biogas flow rate (Eq. 2.67) is simplified further:

$$Q_g = \frac{Q_{CH_4}}{1 - P_{CO_2} - P_{H_2O}} \tag{2.68}$$

where:

Q_g = biogas flow rate, L/d

Q_{CH4} = methane flow rate, L/d

P_{CO2} = partial pressure of carbon dioxide, atm.

P_{H2O} = partial pressure of water at 20°C, atm.

In order to determine the biogas flow rate with Eq. (2.68), the partial pressure of carbon dioxide must be determined first. The determination procedure for the P_{CO2} is given in the following section. It requires a material balance for CO_2 in both liquid and gas phases.

Carbon Dioxide Mass Balance (Liquid Phase)

A mass balance similar to one used by Andrews and Graef (1971) and Hill and Barth (1977) is used here.

$$\left(\frac{dCO_2}{dt}\right) = \frac{Q}{V_L}(CO_{20} - CO_2) + \left(\frac{dCO_2}{dt}\right)_{Bio} + \left(\frac{dCO_2}{dt}\right)_{Chem} - \left(\frac{dCO_2}{dt}\right)_{Tr} \quad (2.69)$$

where:

CO_{20} = dissolved CO_2 concentration in influent, mM

CO_2 = dissolved CO_2 concentration in SBR, mM

$\left(\frac{dCO_2}{dt}\right)_{Bio}$ = rate of change caused by biological activity, mM/d

$\left(\frac{dCO_2}{dt}\right)_{Chem}$ = rate of change caused by chemical reactions, mM/d

$\left(\frac{dCO_2}{dt}\right)_{Tr}$ = rate of change caused by gas transfer, mM/d

Biological Production and Utilization of CO_2

$$\left(\frac{dCO_2}{dt}\right)_{Bio} - 2\left(\frac{dC}{dt}\right)_{A_c} + 2\left(\frac{dC}{dt}\right)_{B_u} - Y_{BuCO_2}\left(\frac{dBu}{dt}\right)Y_{bb} - Y_{PrCO_2}\left(\frac{dP_r}{dt}\right)Y_{pp}$$

$$+\left(\frac{dA_c}{dt}\right) - \frac{1}{4}\left(\frac{dH_2}{dt}\right)_M + \left(\frac{dP_r}{dt}\right)_{A_c} - Y_{H_2CO_2}\left(\frac{dH_2}{dt}\right)_M Y_{bb_2} \qquad (2.70)$$

where:

Y_{PrCO2} = 4.42 x 10^{-3}, mM CO_2/mg X_{Pr}

Y_{BuCO2} = 8.84 x 10^{-3}, mM CO_2/mg X_{Bu}

Y_{H2CO2} = 44.2 x 10^{-3}, mM CO_2/mg X_{H2}

The above stoichiometric coefficients for CO_2 utilization in microorganism synthesis were determined from Eqs. (2.9), (2.10) and (2.12).

Transfer of CO_2 to Gas Phase

The mass balance for CO_2 in the gas phase is very similar to the balance developed for hydrogen (Eq. 2.61).

$$\left(\frac{dP_{CO_2}}{dt}\right)_g - V_{TP}\,P_T\,\frac{V_L}{V_g}\left(\frac{dCO_2}{dt}\right)_{Tr} - \left(\frac{Q_g}{V_g}\right)P_{CO_2} \qquad (2.71)$$

where:

$\left(\frac{dP_{CO_2}}{dt}\right)_g$ - rate of gas phase P_{CO_2} change, atm/d

Andrews (1971) indicated that the transfer rate of CO_2 is slow when compared with its ionic reaction rates. The transfer rate of CO_2 is determined by the following expression.

$$\left(\frac{dCO_2}{dt}\right)_{Tr} = KLa_{CO_2}[CO_2 - CO_{2s}] \qquad (2.72)$$

where:

$$CO_{2s} = KH_{CO_2} P_{CO_2}$$

Kla_{CO2} = carbon dioxide transfer coefficient, d^{-1}

CO_{2s} = concentration of carbon dioxide in liquid phase when in equilibrium with the gas phase, mM

KH_{CO2} = Henry's constant for CO_2, mM/atm

P_{CO2} = partial pressure of CO_2, atm

Chemical Reaction of CO_2

$$\left(\frac{dCO_2}{dt}\right)_{chem} = \frac{Q}{V_L}(HCO_{3o} - HCO_3) + \left(\frac{dCO_2}{dt}\right)_{A_c} + \left(\frac{dCO_2}{dt}\right)_{P_r} + \left(\frac{dCO_2}{dt}\right)_{B_u}$$

$$- \left(\frac{dCO_2}{dt}\right)_{Z} - \left(\frac{dCO_2}{dt}\right)_{NH_4} \qquad (2.73)$$

where:

HCO_{3o} = bicarbonate concentration in influent, mM

HCO_3 = bicarbonate concentration in SBR, mM

$\left(\frac{dCO_2}{dt}\right)_{A_c, P_r, B_u}$ = CO_2 production, mM/d; HCO_3^- reaction with A_c, P_r, B_u

$\left(\frac{dCO_2}{dt}\right)_Z$ - CO_2 production,mM/d; HCO_3^- reaction with cations

$\left(\frac{dCO_2}{dt}\right)_{NH_4^+}$ - CO_2 production,mM/d; HCO_3^- reaction with NH_4^+

The terms in Eq. (2.73) are determined by the following expressions:

$$\left(\frac{dCO_2}{dt}\right)_{A_c} - \left(\frac{dA_c}{dt}\right) \tag{2.74}$$

$$\left(\frac{dCO_2}{dt}\right)_{P_r} - \left(\frac{dP_r}{dt}\right) \tag{2.75}$$

$$\left(\frac{dCO_2}{dt}\right)_{B_u} - \left(\frac{dB_u}{dt}\right) \tag{2.76}$$

$$\left(\frac{dCo_2}{dt}\right)_{z} - \left(\frac{dZ}{dt}\right) \tag{2.77}$$

$$\left(\frac{dCO_2}{dt}\right)_{NH_4^+} - \left(\frac{dNH_4^+}{dt}\right) \tag{2.78}$$

Equations (2.77) and (2.78) above require additional mass balances for ammonium ion and net cation concentrations to determine their rate of change in the liquid phase.

Ammonium Ion Mass Balance

The mass balance for ammonium ions is shown in Eq. (2.79).

$$\left(\frac{dNH_4^+}{dt}\right) - \frac{Q}{V_L}\left(NH_{4o}^+ - NH_4^+\right) + \left(\frac{dNH_4^+}{dt}\right)_{Bio} - \left(\frac{dNH_3}{dt}\right)_{Tr} \qquad (2.79)$$

where:

NH_{4o} = Concentration of ammonium ion in influent, mM

NH_4^+ = Concentration of ammonium ion in SBR, mM

$\left(\frac{dNH_4^+}{dt}\right)_{Bio}$ - rate of change caused by biological activity, mM/d

$\left(\frac{dNH_3}{dt}\right)_{Tr}$ - rate of change caused by gas transfer, mM/d

Biological Production and Utilization of NH_4^+

$$\left(\frac{dNH_4^+}{dt}\right)_{Bio} - Y_{PN}\,K_p\,P - Y_N \sum \frac{dX_i}{dt} \qquad (2.80)$$

where:

Y_{PN} = NH_4^+ yield from particulates solubilization, mmol/mmol

Y_N = concentration of NH_4^+ in bacteria, mmol/mg

Ammonia Transfer Rate

The determination of ammonia transfer rate requires a mass balance for ammonia in the liquid and gas phases because the transfer rate depends on relative concentrations of ammonia in liquid and gas phases. Eq. (2.81) gives the mass balance for

ammonia gas. This mass balance is similar to those for hydrogen and carbon dioxide.

$$\left(\frac{dP_{NH_3}}{dt}\right)_g = V_{TP}\, P_T\, \frac{V_L}{V_g} \left(\frac{dNH_3}{dt}\right)_{Tr} - \left(\frac{Q_g}{V_g}\right) P_{NH_3} \qquad (2.81)$$

where:

$\left(\frac{dP_{NH_3}}{dt}\right)_g$ - rate of change of ammonia gas phase pressure, atm/d

Hill and Barth (1977) assumed that gas phase NH_3 was not in equilibrium with the liquid phase. Using this assumption, the actual transfer rate can be determined by Eq. (2.82)

$$\left(\frac{dNH_3}{dt}\right)_{Tr} = Kla_{NH_3} (NH_3 - NH_{3s}) \qquad (2.82)$$

Recall that:

a) $NH_{3s} = KH_{NH_3}\, P_{NH_3}$

b) $NH_3 = \frac{NH_4^+\ K_{NH_4}}{H^+}$

where:

Kla_{NH3} = mass transfer coefficient for ammonia, d^{-1}

NH_{3S} = dissolved concentration of ammonia when in equilibrium with ammonia in gas phase, mM

NH_3 = dissolved ammonia nitrogen, mM

KH_{NH3} = Henry's constant for ammonia nitrogen, mM/atm

P_{NH3} = gas phase partial pressure of ammonia nitrogen, atm

H^+ = hydrogen ion concentration, mM

K_{NH4} = dissociation constant for ammonia/ammonium ion

The determination of ammonia nitrogen required the determination of hydrogen ion concentration in SBR. Determination of pH will be discussed in detail below.

Mass Balance on Net Cations

The mass balance equation for net cations other than nitrogen and hydrogen ions is represented by

$$\frac{dZ}{dt} = \frac{Q}{V_L}(Zo-Z) \qquad (2.83)$$

where:

Zo = Co - Ao, net cation concentration in influent, mM

Z = C - A, net cation concentration in SBR, mM

C_o, C = cations concentrations, mM

A_o, A = anions concentration, mM

The determination of Zo and Z can be obtained from a charge balance of cations and anions.

$$Z = HCO_3^- - NH_4^+ + A_C^- + P_I^- + B_U^- \qquad (2.84)$$

The experimental values of Zo and Z were determined from measured pH, alkalinity, A_c^-, P_r^-, B_u^- and NH_4^+ concentrations.

pH DETERMINATION

pH can be determined from the carbonate equilibria in the SBR liquid phase as follows:

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-, \quad K_{a1} = 10^{-6.33} \tag{2.85}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}, \quad K_{a2} = 10^{-10.34} \tag{2.86}$$

Combining Eqs. (2.85) and (2.86) and assuming that:

$$H_2CO_3^* = CO_2$$

yields the following expression for hydrogen ion determination:

$$H^+ = \frac{K_{a1}\, CO_2}{HCO_3^-} \tag{2.87}$$

Eq. (2.87) contains two unknowns, H^+ and HCO_3^-. Another relationship is necessary for their determination. A charge balance provided this additional relationship.

$$H^+ + Z + NH_4^+ = HCO_3^- + 2CO_3^{2-} + A_c^- + P_r^- + B_u^- + OH^- \tag{2.88}$$

The pH in SBRs should be around 7.0. Therefore it can be assumed that $H^+ = OH^-$ and CO_3^{2-} concentration is negligible.

The simplified and rearranged mass balance becomes:

$$HCO_3^- = Z + NH_4^+ - A_c^- - P_r^- - B_u^- \quad (2.89)$$

The pH can be now calculated by substituting Eq. (2.89) in Eq. (2.87). The predicted pH is used to determine the concentration of the ionized VAs as follows:

$$A_c^- = \frac{K_{Ac}\, A_{cT}}{H^+ + Ka_{Ac}} \quad (2.90)$$

$$P_r^- = \frac{K_{Pr}\, P_{rT}}{H^+ + Ka_{Pr}} \quad (2.91)$$

$$B_u^- = \frac{K_{Bu}\, B_{uT}}{H^+ + Ka_{Bu}} \quad (2.92)$$

where:

A_c^-, P_r^-, B_u^- = ionized concentration of A_c, P_r and B_u, mM

A_{cT}, P_{rT}, B_{uT} = total concentration of A_c, P_r and B_u, mM

Ka_{Ac}, Ka_{Pr}, Ka_{Bu} = VA ionization constants

The mass balances for the react period are identical to those for the fill period except that the influent flow rate term "Q" is equal to zero.

The solution of the non-linear differential equations for both the simple and advanced models will be carried out numerically with a fourth-order Runge Kutta method. The basic format of a fortran computer programme developed by Droste and Kennedy (1988) to simulate the biological phase of a fixed film reactor was used in this study to develop coded program for the simple and advanced models. The source codes for these programs are given in Appendices A and B.

2.4 Determination of H_2 and CO_2 Mass Transfer Coefficients

The mass transfer coefficients for hydrogen and carbon dioxide required by the advanced model will be determined experimentally in this study. The following procedures will be used to calculate these constants from experimental data.

2.4.1 Mass Transfer Coefficient for H_2 Gas

The hydrogen mass transfer coefficient can be determined by using a mass balance for hydrogen gas in the gas phase of a SBR. In the following development it was assumed that the gas flow rate due to the decrease in gas phase volume during the fill period was negligible compared to the biogas production.

IN - OUT = ACCUMULATION

$$V_L \left(\frac{dH_{2L}}{dt}\right)_{Tr} - Q_g H_{2g} - V_g \left(\frac{dH_{2g}}{dt}\right) \qquad (2.93)$$

where:

V_L = volume of liquid phase, L

V_g = volume of gas phase, L

H_{2g} = gas phase concentration of H_2, mM

$(dH_2/dt)_{Tr}$ = transfer rate of H_2, mM/d

(dH_{2g}/dt) = rate of change in H_2 concentration, mM/d

The ideal gas law states that:

$$P_{H2}\ V_g = n_{H2}\ R\ T \tag{2.94}$$

where:

P_{H2} = partial pressure of hydrogen, atm

n_{H2} = number of mmol of H_2

R = gas constant

T = temperature, °K

Substituting Eq.(2.94) into Eq.(2.93) gives

$$V_L\left(\frac{dH_2}{dt}\right)_{Tr} - Q_g\ \frac{P_{H_2}}{RT} - \frac{V_g}{RT}\left(\frac{dP_{H_2}}{dt}\right) \tag{2.95}$$

Rearranging Eq. 2.95 yields:

$$\frac{dP_{H_2}}{dt} - \left(\frac{V_L}{V_g}\right) RT\left(\frac{dH_2}{dt}\right)_{Tr} - Q_g\ \frac{P_{H_2}}{V_g} \tag{2.96}$$

From the two-film theory, the transfer of a gas at the gas-liquid interface is determined by the following expression:

$$\left(\frac{dH_2}{dt}\right)_{Tr} - Kla_{H2}\left[H_2 - KH_{H2}\ P_{H_2}\right] \tag{2.97}$$

where:

KH_{H2} = Henry's constant for H_2 at 20°C

Substituting Eq.(2.97) into Eq.(2.96) and rearranging yields:

$$Kla_{H_2} = \left(\frac{\frac{dP_{H_2}}{dt} + \frac{Q_g P_{H_2}}{V_g}}{P_T \; V_{TP} \frac{V_L}{V_g}} \right) + \left(H_2 - KH_{H2} P_{H_2}\right) \qquad (2.98)$$

where:

P_T = SBR total gas pressure, atm

V_{TP} = volume of one mole of gas at 20°C

The gas phase and liquid zone volumes change with time during the fill period. Therefore in the above expression (Eq. 2.98) the gas and liquid phase volumes are determined as follows:

$$V_g = V_{go} - \int Q \, dt \qquad (2.99)$$

$$V_L = V_{Lo} + \int Q \, dt \qquad (2.100)$$

where:

V_{go} = initial gas phase Volume, L

V_{Lo} = initial liquid phase Volume, L

Q = influent flow rate, L/d

t = time, day

2.4.2 Mass Transfer Coefficient for CO_2 Gas

The carbon dioxide mass transfer coefficient can be determined by using an equation similar to Eq. (2.98). The partial pressure of CO_2 can be determined with a gas chromatograph. The dissolved concentration of carbon dioxide can be calculated from known concentrations of hydrogen ions and alkalinity. This methodology is presented in detail in several textbooks on water chemistry. The concentration of dissolved carbon dioxide calculated this way also includes the concentration of carbonic acid. Snoeyink and Jenkins (1980) indicated that the carbonic acid represents only 0.16% of dissolved CO_2 in water at 25°C. Therefore in this study the concentration of carbonic acid will not be subtracted from the calculated dissolved CO_2 value.

CHAPTER 3

EXPERIMENTAL PROCEDURE

Experiments were carried out in laboratory scale digesters located in a controlled temperature room. All the tests were carried out at a temperature of 20°C.

3.1 Experimental Design

For results to be applicable to farm conditions, laboratory tests should simulate as closely as possible the actual farm operation. At a typical farm, manure is generally removed from the barn one to three times a week. Therefore the SBR should be intermittently fed one to three times a week. The fill cycle should not be longer than a month in order to limit the volume of the SBR. The react period should be long enough to produce almost odourless effluent with reduced pollution potential and increased fertilizer value. For the PAD in SBR to be cost effective, it is very important that the operational cost is kept very low. The operation of SBR at ambient temperatures and the reduction or elimination of mechanical mixing would substantially reduce the energy input and increase the energy efficiency of the SBR because all the energy produced will be available for on-farm utilization.

Experimental runs no. 1, 2 and 3 were carried out to test the reliability of the experimental hardware. The following problems occurred during these initial experimental runs: 1) mechanical pump failures caused by the abrasiveness of the sludge; 2) conduits plugging; and 3) all the SBRs lost their gas-tightness because the glue used in their assembly reacted with both digester mixed liquor and biogas. The loss in gas tightness and presence of toxic compounds resulted in SBRs failure. Therefore the experimental data from these test runs were not considered in this study.

These technical problems were overcome by using: 1) biogas recirculation to mix the SBRs; 2) larger conduits and fittings; and 3) glueless SBRs. Experimental test runs 4, 5, 6 and 7 were carried out without any technical problems. Table 3.1 gives the operating conditions that were used in these test runs. In this study several operating parameters were varied to: 1) simulate the different pig manure slurry managements at the farm; 2) to provide the most efficient and stable process design and control and 3) to minimize the interference of the SBR operation with regular farm activities. Test run no. 4, which was the start-up run, had the lowest organic loading rate. In this run, the effect of inoculum type and loading rate on process start-up were investigated. Test runs No. 5, 6, and 7 investigated the effect of higher loading rates, mixing intensity, fill-react

Table 3.1 SBR Operating Conditions

RUN NO.	DIGESTER NO.	LOADING RATE		FEEDING FREQUENCY (#/WEEK)	MIXING**	FILL PERIOD (WEEK)	REACT PERIOD (WEEK)	NO. CYCLE	SLUDGE*** TYPE
		g COD/feed	g COD*/L-d						
4	1-2	12.6	0.72	3	No	4	4	1	A
	3-4	12.6	0.72	3	No	4	4	1	B
	5-6	21.0	1.20	3	No	4	4	1	A
	7-8	21.0	1.20	3	No	4	4	1	B
5	1-2	14.25	0.81	3	No	4	4	1	B
	3-4	14.25	0.81	3	Yes	4	4	1	B
	5-6	21.40	1.22	3	No	4	4	1	B
	7-8	21.40	1.22	3	Yes	4	4	1	B
	9-10	28.50	1.63	3	No	4	4	1	B
	11-12	28.50	1.63	3	Yes	4	4	1	B
6	1-2	28.50	1.63	3	No	4	4	1	B
	3-4	85.50	1.63	1	No	4	4	1	B
	5-6	28.50	1.63	3	No	2	2	2	B
	7-8	85.50	1.63	1	No	2	2	2	B
	9-10	28.50	1.63	3	No	1	1	4	B
	11-12	85.50	1.63	1	No	1	1	4	B
7	9-10	66.00	1.26	1	No	1	1	4	B
	11-12	66.00	1.26	1	No	2	2	2	B

* Equivalent loading rate if the swine manure would have been fed continuously.

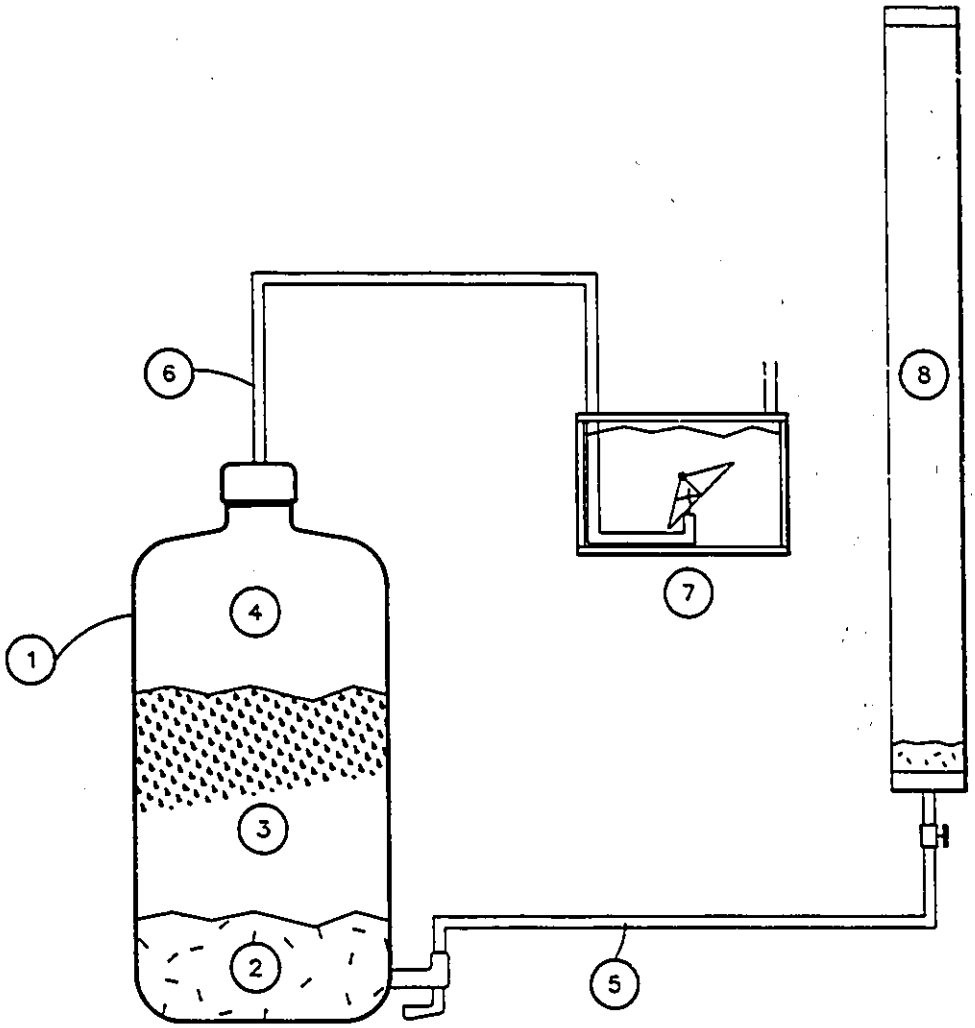
** SBR was intermittently mixed by biogas recirculation. Mixing lasted 10 minutes every thirty minutes.

*** A - Agropur Sludge
B - Mixture of Agropur and Municipal Sludge

period length, feeding frequency and sludge age on the performance of PAD of swine manure slurry in SBR.

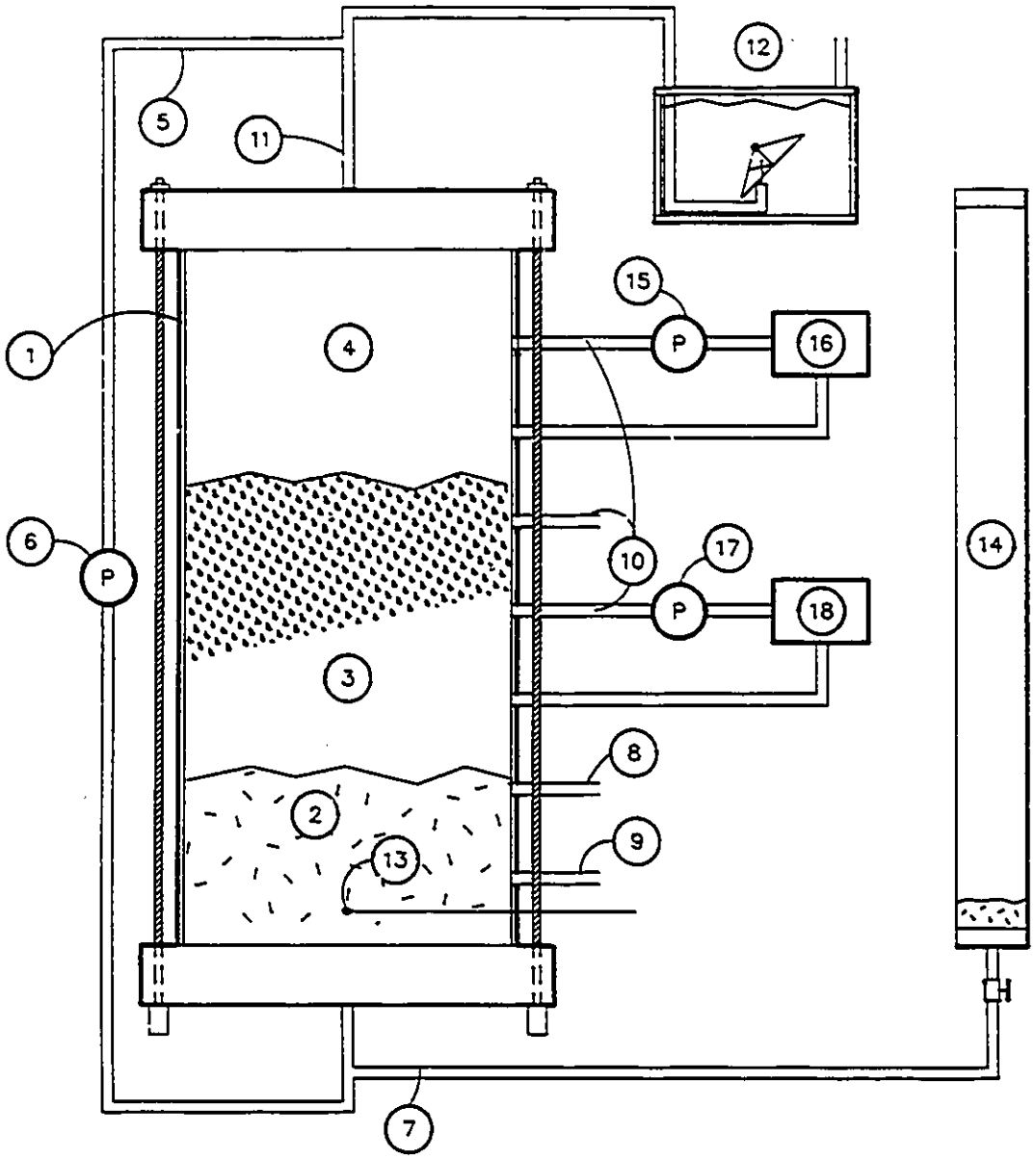
3.2 Experimental Equipment

Figures 3.1. and 3.2. are schematic diagrams of the bench scale SBRs and feeding system used in this study. Eight 25-L nalgene bottles (Fig. 3.1.) were used in the start-up run and 12, 42 L plexiglass digesters (Fig. 3.2) were fabricated and used in subsequent experimental runs. The plexiglass digesters offered the flexibility to remove mixed liquor samples during experimental runs as well as supernatant and sludge samples at the end of the react period. The nalgene bottle SBRs were operated without mixing. The plexiglass SBRs had the flexibility to provide mixing by recirculating the biogas. Intermittent mixing periods of 10 minutes every 30 minutes were provided by recirculating the biogas produced through an inlet located at the bottom of the digesters. One plexiglass digester had hydrogen gas monitors connected to the gas and liquid zones to measure the hydrogen gas concentrations in both gas and liquid phases. Wet cup gas meters were used to measure the daily biogas production. The feeding procedure consisted of adding fresh swine manure slurry to the feeders. Thereafter nitrogen gas was used to pressurize the individual feeder to transfer the manure slurry to the SBR. This feeding method worked very well and took less than one minute per SBR. The treated manure in the



1	25L NALGENE DIGESTER	5	INFLUENT LINE
2	SLUDGE BED ZONE, 7.5 L	6	GAS OUTLET
3	VARIABLE VOLUME ZONE, 12.0 L	7	GAS METER
4	HEAD SPACE ZONE, 5.5 L	8	FEEDER TUBE

Fig. 3.1 Schematic of laboratory scale SBRs used for the start up run. (test run no. 4)



1 300 mm DIAMETER PLEXIGLASS DIGESTER
2 SLUDGE BED ZONE, 7.5 L
3 VARIABLE VOLUME ZONE, 28.0 L
4 HEAD SPACE ZONE, 6.5 L
5 GAS RECIRCULATION LINE
6 BIOGAS RECIRCULATION PUMP
7 INFLUENT LINE
8 EFFLUENT LINE
9 SLUDGE SAMPLING PORT, ALSO USE FOR SLUDGE WASTAGE
10 MIXED LIQUOR OR SUPERNATENT SAMPLING PORT
11 GAS OUTLET
12 GAS METER
13 THERMOCOUPLE
14 FEEDER TUBE
15 GAS PUMP
16 HYDROGEN GAS MONITOR
17 LIQUID PUMP
18 DISSOLVED HYDROGEN GAS MONITOR

Fig. 3.2 Schematic of laboratory scale SBRs used for test runs 5, 6 and 7.

plexiglass SBR was removed from an outlet located just above the sludge bed zone. For the nalgene SBRs this operation was more cumbersome. The lid had to be removed and the treated manure was pumped out.

3.3 Swine Manure Slurry Collection and Storage

Manure slurry was obtained from gutters under a partially slatted floor in a growing-finishing barn at a commercial swine operation. The manure was up to four days old at the time of collection. It was screened to remove particles larger than 3.5 mm to prepare feed samples. These large particles tend to create operational problems with small scale laboratory digesters. Also in order to reduce experimental variation, a volume of manure large enough to carry out a test run was collected, screened and mixed to prepare uniform feed samples. The feed samples were stored in a freezer at -15°C to prevent biological activity. Manure feed samples were heated to the digester operating design temperature (20°C) prior to feeding.

3.4 Sample Collection

A mixed liquor sample of 100 ml was withdrawn from each SBR at the beginning of the experiment and once a week during the experimental run. The non-mixed SBRs in test runs 5, 6 and 7 were mixed by biogas recirculation for 15 minutes just prior samples collection in order to obtain representative samples. At the end of the test, after the sedimentation period,

additional 100 ml samples were withdrawn from the supernatant and settled sludge bed zones. Sludge sampling was sometimes difficult because the supernatant above the sludge zone made its way to the sludge sampling port. As a result the sludge sample was very diluted and not representative. Swine manure slurry was sampled just before it was fed to the SBRs. The samples were analyzed for pH, redox potential, alkalinity, solids, volatile acids (VA), total Kjeldahl nitrogen (TKN), ammonia nitrogen, total COD and soluble COD. Some of the samples were further analyzed to determine concentration of C, H, N and other elements. The concentration of hydrogen gas in gas phase and liquid phase were monitored continuously in one SBR. The biogas production was monitored daily and its composition analyzed weekly. Gas samples were withdrawn through septums located in digester gas lines with 10 ml syringes.

3.5 Analytical Techniques

Soluble COD was determined by analyzing the supernatant of centrifuged slurry. The SCOD was determined according to the method developed by Knechtel (1978). The pH, redox potential, alkalinity, TS, TSS, VS, VSS, TKN were determined using standard methods (APHA, 1992). TKN and ammonia nitrogen were determined using a kjeltec auto-analyzer model TECATOR 1030. The VA concentrations were determined by a Perkin Elmer gas chromatograph model 8310, that had a DB-FFAP high resolution column. The biogas composition was determined by using a

Carle 400 AGC gas chromatograph. Metal concentrations (K, Ca, Mg, Cu, Zn, Hg, Ba, Cd, Cr, Co, Mn, Mb, Ni, Pb, Sr, V) were determined by the inductively coupled plasma (ICP) method (APHA, 1992). The ICP operating conditions are given in Appendix C. The C, H and N were determined using a carbon, hydrogen and nitrogen analyzer model LECO CHN 600.

The hydrogen gas concentration in the biogas was determined with a GMI exhaled H_2 Monitor. This equipment makes use of three electrode electrochemical cells to measure hydrogen accurately in parts per million. The dissolved concentration of hydrogen in the SBR was measured by using a hydrogen/air fuel cell (SYPROTEC HYDRAN 202N). A procedure similar to the one utilized by Pauss et al. (1989) was used for the calibration of this cell.

3.6 Start-up of SBR

For experimental test run no. 4, all eight digesters were initially started using 7.5 L of granulated anaerobic sludge obtained from the Agropur dairy wastewater treatment plant at Notre-Dame du Bon Conseil. Digesters 3, 4, 7 and 8 received an additional 2 L of anaerobic non-granulated sludge obtained from the Robert O. Pickard, Environmental Centre, Ottawa, Ontario. The Agropur sludge substrate consisted mainly of fats and proteins. The anaerobic municipal sludge substrate comes from both the primary and secondary clarifiers. The addition of municipal sludge that is already acclimatized to

compounds such as cellulose, hemicellulose and lignin should increase the treatment efficiency. Compositions of the Agropur and municipal anaerobic sludge are given in the results section. The swine manure was fed from the bottom of the SBR and no mixing was provided.

3.7 Experimental Determination of VA Utilization Kinetics

Batch experiments were carried out to determine the utilization rate of individual VAs. The batch reactors were made of three 3-litre nalgene bottles similar in geometry to the one shown in Figure 3.1. Each batch reactor received 1 L of acclimatized sludge collected from the plexiglass SBRs. The volatile suspended solids (VSS) of the inoculum sludge was 20000 mg/L. These batch tests focused on the VAs utilization rather than growth rate of bacteria. Acetic, propionic and butyric acids were fed to separate batch reactors to obtain respective initial concentrations of 2500, 2000 and 2000 mg/L respectively. Mixed liquor samples of 5 ml were collected daily for VAs determination. A batch test was considered complete when the VA fed to the bottle was all consumed. These kinetic tests were carried out at a temperature of 20°C. Utilization of the experimental data in the determination of acetic, butyric and propionic acids utilization kinetics is discussed in detail in chapter 4.

CHAPTER 4

EXPERIMENTAL RESULTS

The anaerobic SBRs were operated at 20°C for a period of 8 months between June 14, 1993 and June 1, 1994 without any sign of breakdown or process instability. During that period the SBRs were idle for a period of 4 months. Extra time was required between test runs to: 1) replace the nalgene SBRs with the plexiglass SBRs; 2) test SBRs for gas tightness; 3) calibrate gas meters; 4) install feeders; and 5) repair analytical equipment. Results of analytical tests are given in the following sections and Appendix D.

4.1 Composition of Swine Manure Slurry

Table 4.1 gives the composition of the swine manure used in the experimental runs. Values in Table 4.1 represent the average of 5 replicates. Three batches of manure were collected at a commercial farm at different times over the year. The first batch was used in the test run No. 4, the second batch in test runs 5 and 6 and the third batch in test run 7. This table indicates that the composition of fresh

swine manure slurry at the farm is highly variable with time. For this particular swine operation the total solids content of the manure slurry was high. It ranged from 2.9 to 4.8% (weight basis). The fresh manure had a neutral pH and very high concentrations of TCOD, SCOD, TKN, NH_3-N, VAs and alkalinity. The concentrations of inorganic elements such as calcium, magnesium, potassium, sodium, zinc and copper were also quite high. Phosphorus was not measured in this study. Loehr (1980) reported that the phosphorus concentration in swine manure slurry ranged between 250 and 4600 mg/L.

Based on the concentrations of C, N and H given in Table 4.1, the composition of the insoluble organic fraction of the fresh swine manure slurry was $[C_{1.0}H_{1.9}O_{1.0}N_{0.1}]_{3.2}$. This composition was similar to the formula for carbohydrates $[CH_2O]_n$.

4.2 Composition of Inoculum Sludge

Table 4.2 gives the characteristics of the Agropur and municipal anaerobic sludge used to inoculate the digester in the start-up run. Values in Table 4.2 represent the average of 5 replicates. The main characteristics of the Agropur granulated sludge were that it had very high solids, TCOD, SCOD, TKN and calcium content. The municipal sludge was less concentrated than the granulated Agropur sludge but it had a higher fibre content on a dry weight basis and also had a lower alkalinity. Both of these sludges came from digesters operated at 35°C.

TABLE 4.1 COMPOSITION OF SWINE MANURE

CONSTITUENT	TEST NO.		
	4	5 AND 6	7
Total Solids, %	4.8	4.1	2.9
Total Suspended Solids, %	3.6	3.1	2.2
Volatile Solids, %	3.0	2.7	1.8
Volatile Suspended Solids, %	2.6	2.1	1.5
Soluble COD, g/L	39	28	25
Total COD, g/L	84	57	44
TKN, g/L	7.5	6.8	4.8
NH4-N, g/L	5.8	5.0	4.2
pH	7.4	7.3	7.4
Alkalinity, g $CaCO_3$/L	19.0	13.5	11.6
Acetic Acid, g/L	6.3	5.3	4.2
Propionic Acid, g/L	1.9	1.7	1.4
Butyric Acid, g/L	2.5	2.2	1.5
Cellulose, % TS	2.43	NA*	NA
Hemicellulose, % TS	4.15	NA	NA
Lignin, % TS	1.31	NA	NA
Carbon, % VS	38.18	NA	NA
Nitrogen, % VS	4.69	NA	NA
Hydrogen, % VS	6.10	NA	NA
Oxygen, % VS	51.00**	NA	NA
Barium, mg/kg TS	31	NA	NA
Cadmium, mg/kg TS	7	NA	NA
Calcium, mg/kg TS	54790	NA	NA
Chromium, mg/kg TS	31	NA	NA
Copper, mg/kg TS	957	NA	NA
Magnesium, mg/kg TS	8643	NA	NA

* not available

TABLE 4.1 Continued.

CONSTITUENT	TEST NO.		
	4	5 AND 6	7
Manganese, mg/kg TS	127	NA*	NA
Molybdenum, mg/kg TS	23	NA	NA
Nickel, mg/kg TS	23	NA	NA
Lead, mg/kg TS	96	NA	NA
Potassium, mg/kg TS	42760	NA	NA
Sodium, mg/kg TS	13900	NA	NA
Strontium, mg/kg TS	71	NA	NA
Vanadium, mg/kg TS	58	NA	NA
Zinc, mg/kg TS	4470	NA	NA

* not available
** % Oxygen = 100 % - (% Carbon + % Nitrogen + % Hydrogen)

TABLE 4.2 INOCULA CHARACTERISTICS

CONSTITUENT	AGROPUR SLUDGE	MUNICIPAL SLUDGE
Total Solids, %	11	2.6
Total Suspended Solids, %	10.7	2.3
Volatile Solids, %	5.6	1.26
Volatile Suspended Solids, %	5.4	1.17
Carbon, % VS	48.41	55.9
Nitrogen, % VS	9.64	8.40
Hydrogen, % VS	7.54	10.6
Oxygen, % VS	34.41**	25.10**
Soluble COD, g/L	10	3
Total COD, g/L	73	8.2
NH4-N, g/L	1.3	1.0
TKN, g/L	7.9	1.8
Cellulose, % TS	0.70	0.84
Hemicellulose, % TS	0.73	3.98

TABLE 4.2 continued.

CONSTITUENT	AGROPUR SLUDGE	MUNICIPAL SLUDGE
Lignin, % TS	1.56	2.88
pH	7.6	7.3
Alkalinity, $gCaCO_3/L$	16	6
Operating Temp., °C	35	35
Sludge Residence Time, week	26	2
Barium, mg/kg TS	108	450
Cadmium, mg/kg TS	2	4.1
Calcium, mg/kg TS	84720	46800
Chromium, mg/kg TS	29	84
Cobalt, mg/kg TS	2.2	3.0
Copper, mg/kg TS	78	629
Magnesium, mg/kg TS	1772	2600
Manganese, mg/kg TS	28.5	1453
Mercury, mg/kg TS	N/A	2422
Molybdenum, mg/kg TS	14	13
Nickel, mg/kg TS	38	14
Sodium, mg/kg TS	7058	400
Lead, mg/kg TS	59	100
Potassium, mg/kg TS	6162	10000
Strontium, mg/kg TS	176	504
Vanadium, mg/kg TS	26.6	21
Zinc, mg/kg TS	1236	608

** % Oxygen = 100 % - (% Carbon + % Nitrogen + % Hydrogen)

The concentrations of carbon, hydrogen and nitrogen of the organic fraction of Agropur and municipal sludges given in Table 4.2 yield the following stoichiometric formulations for the volatile solids composition:

Municipal sludge: $C_5 H_{11.5} N_{0.66} O_{1.8}$

Agropur sludge: $C_5 H_{9.25} N_{0.84} O_{2.7}$

The anaerobic sludge in digesters 1, 5 and 12 was reanalysed for C,H,and N contents after 8 months of operation. Table 4.3 gives the concentration of these elements as well as the composition of the organic fraction.

TABLE 4.3 Composition of organic fraction of anaerobic sludge

Digester No.	C % VS	H % VS	N % VS	Composition of Volatile Suspended Solids
1	55.8	8.1	10.0	$C_5 H_{8.7} N_{0.76} O_{1.8}$
5	57.7	8.7	9.1	$C_5 H_{9.0} N_{0.70} O_{1.6}$
12	55.8	8.7	8.8	$C_5 H_{9.4} N_{0.67} O_{1.8}$

The composition of the organic fraction (particulates and bacteria) in the digester sludge slightly changed with time. After 8 months of operation, the organic fraction composition was similar to the composition of bacteria assumed by Christensen and McCarty (1975), $C_5 H_7 N O_2$. Therefore the assumed composition of bacteria in the advanced model development is supported by the experimental results.

4.3 Start-up Run Results

Figures 4.1 and 4.2 gives the cumulative biogas production as a function of time, loading rate and inoculum type. The shapes of cumulative biogas production curves are similar for the four treatments considered. The rate of gas production

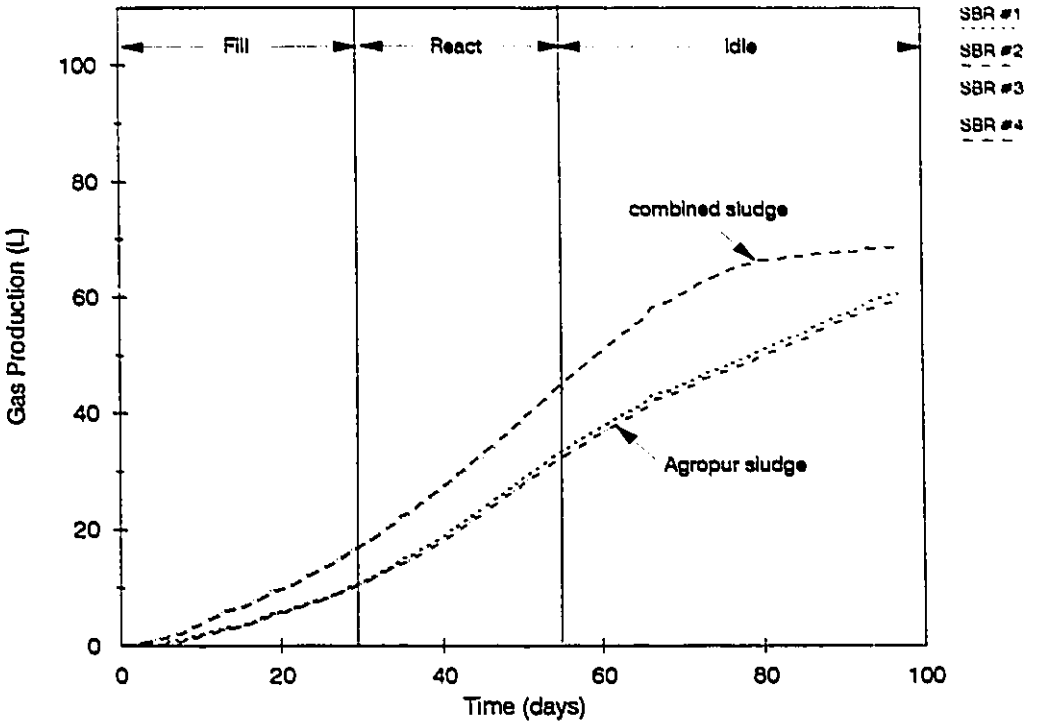


FIG. 4.1 Cumulative biogas production as a function of time for SBRs with an organic loading rate of 0.72g COD/L-d, (test run 4).

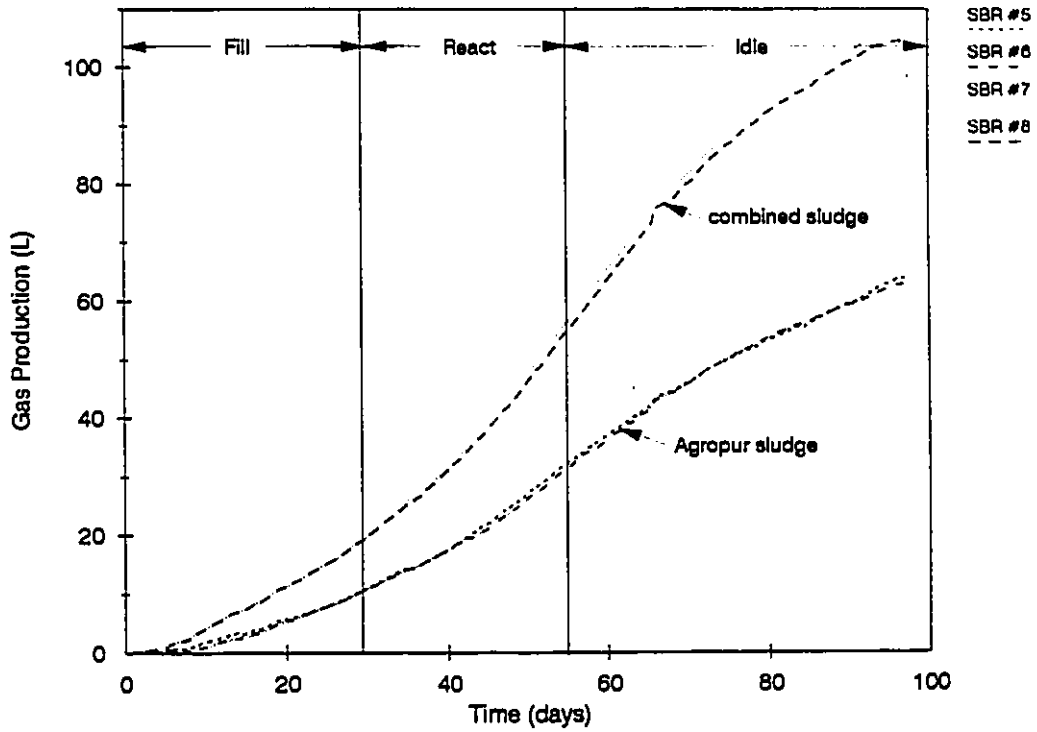


FIG. 4.2 Cumulative biogas production as a function of time for SBRs with an organic loading rate of 1.20g COD/L-d, (test run 4).

was low during the fill period and increased during the react period. The lag phase in biogas production lasted about 40 days. It was probably due to the acclimatization of microorganisms to the decrease in operating temperature from 35 to 20°C and to the new substrate (swine manure). During the react period the biogas production rate increased exponentially, until the end of the react period when it started to decline as the availability of substrate became the limiting factor. Figures 4.1 and 4.2 also show that substantial amounts of biogas were produced beyond the react period. This is an indication that the treatment of the manure slurry fed during the startup run is not complete at the end of react period. Therefore during the startup run the organic loading rate should be reduced or the react period extended.

The digesters with combined sludge produced the highest amount of biogas. The cumulative biogas production was 30 and 70% higher in these digesters at organic loading rates of 0.72 and 1.20 g COD/L-d, respectively. The higher biogas production may have been caused by an increased hydrolysis rate. The combined sludge contained anaerobic sludge from municipal wastewater treatment plants. This sludge is already acclimatized to compounds such as cellulose, hemicellulose and lignin. The Agropur sludge was only acclimatized to proteins and fats which are the major constituents of dairy wastewater.

Another possible reason for the higher biogas production could be that the activity of the municipal sludge was higher than the activity of the Agropur sludge. Actual sludge activities were not measured in this study.

During the first 60 days, an increase in loading rate had no significant effect on biogas production for the digesters with the Agropur sludge. But for the digester with combined sludge there was an increase in biogas production of 40% when the organic loading rate increased from 0.72 to 1.20 g COD/L-d.

Figures 4.3 and 4.4 gives the average (of two replicates) methane concentration in the biogas as a function of time. For the four treatments tested, the methane fraction in the biogas was not constant. It continuously increased with time. At the start of the fill period the methane concentration ranged from 47 to 63%. At the end of the react period the methane concentration was about the same for all treatments. It ranged from 77 to 80%.

Figures 4.5 to 4.10 illustrate the acetic, propionic and butyric acid concentrations as a function of time respectively. They also indicate the cumulative feeding concentration of each individual VA. Figures 4.5 and 4.6 indicate that acetic acid accumulated rapidly from 0 to 5500 mg/L during the fill period. This accumulation is about five

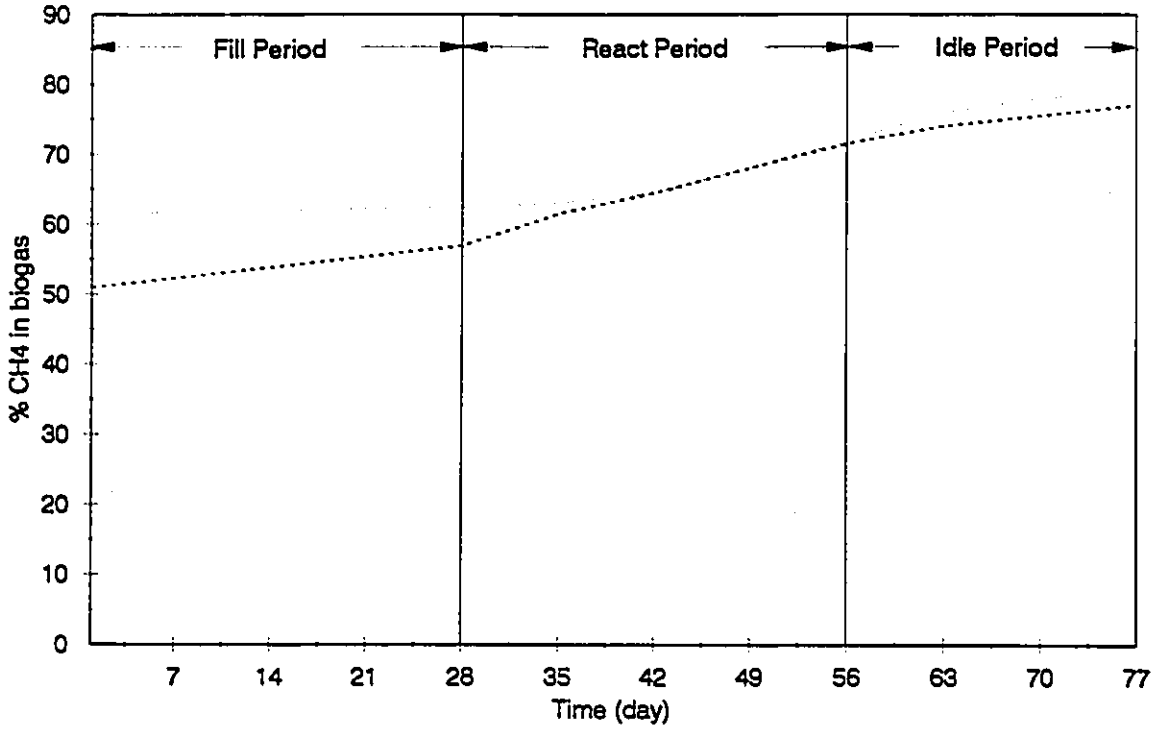


Fig. 4.3 Methane content in biogas as a function of time for SBRs with a loading rate of 0.72g COD/L-d, (test run 4), ------- average of SBRs 1 - 2, ... average of SBRs 3 - 4.

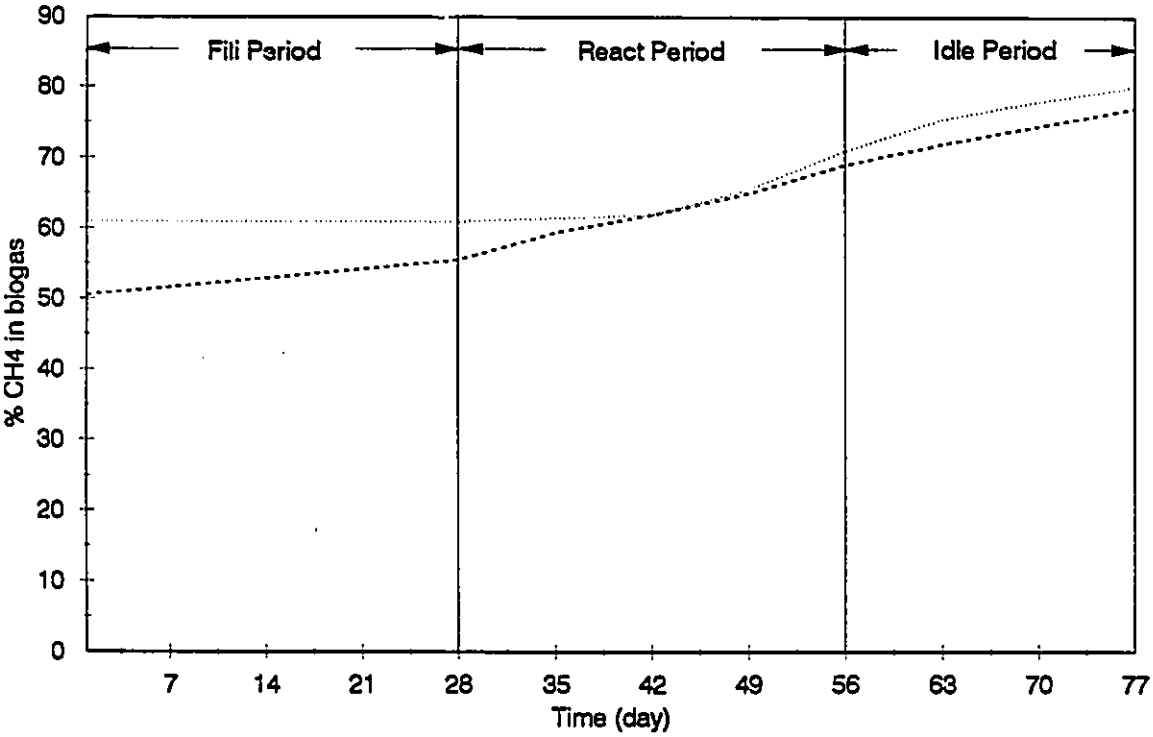


Fig. 4.4 Methane content in biogas as a function of time for SBRs with a loading rate of 1.2g COD/L-d, (test run 4), ------ average of SBRs 5 - 6, ... average of SBRs 7 - 8.

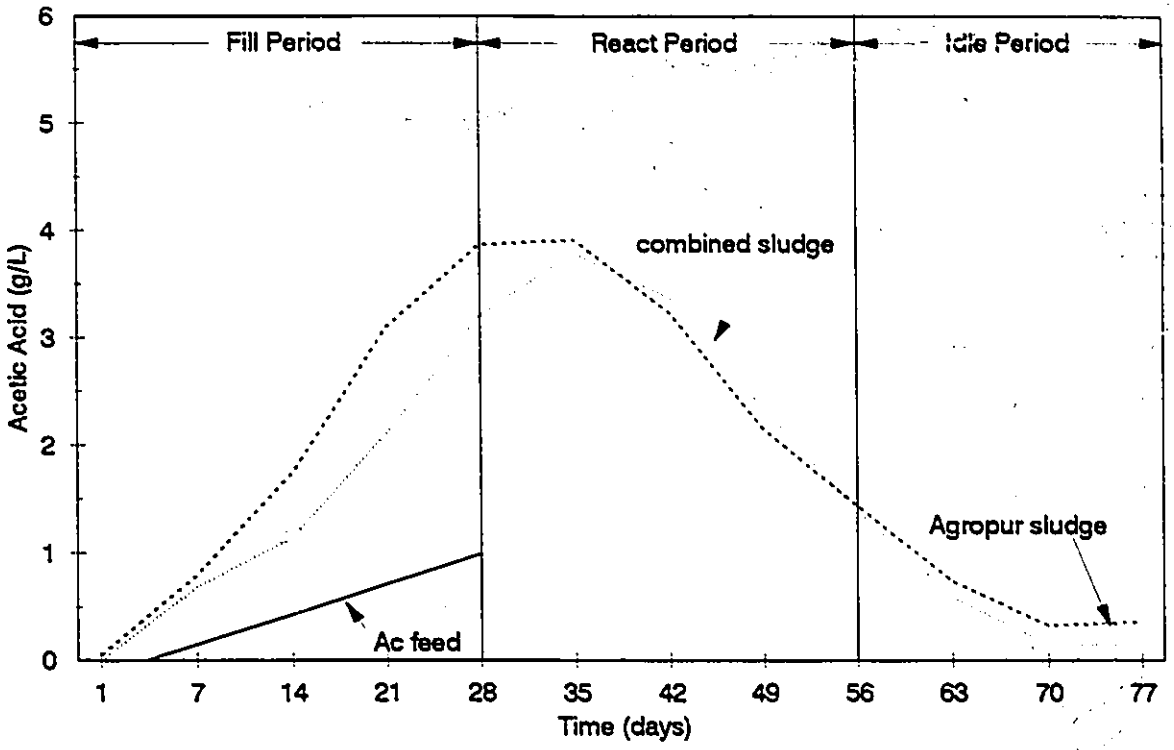


Fig 4.5 Average acetic acid concentration as a function of time for SBRs with a loading rate of 0.7g COD/L-d, (test run 4). ····· average of SBRs 1 - 2, ------ average of SBRs 3 - 4.

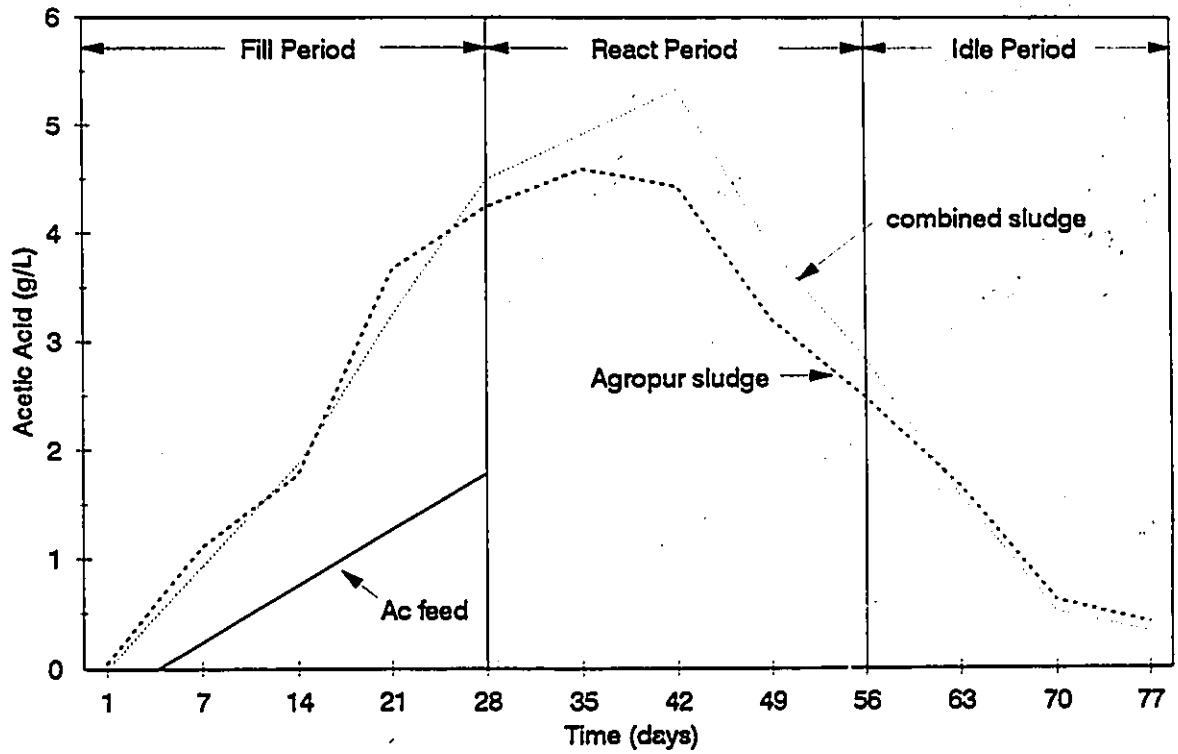


Fig 4.6 Average acetic acid concentration as a function of time for SBRs with a loading rate of 1.2g COD/L-d, (test run 4). ····· average of SBRs 5 - 6, ------ average of SBRs 7 - 8.

times larger than the amount of acetic acid fed to the digesters. Figures 4.7 and 4.8 show that propionic acid was accumulating faster in digesters with the Agropur sludge than in digesters with combined sludge during the fill period. Explanations for the increase in propionic acid are given later. For digesters with combined sludge the propionic acid accumulations were equal to the cumulative concentration fed. Figures 4.9 and 4.10 show that butyric acid was not accumulating during the fill period, but rather was consumed because the concentrations of butyric acid in the digesters were substantially lower than the cumulative concentration fed.

The rapid increase in acetic acid concentration during the fill period shows that hydrolysis and acidification were occurring. It also indicates that during the fill period the utilization of acetic acid by the methane formers was the rate limiting step.

The rapid increase in acetic acid is usually due to the faster growth rate of acid formers or inhibition of methane formers by an increase in concentration of VAs or other compounds. By comparing Figures 4.1 and 4.2 with Figures 4.5 and 4.6 it is obvious that methane formers were not inhibited by the increase in VAs concentration. These figures indicate that during the period of increased VA concentration the methane production rate is also increased. Therefore the increase in

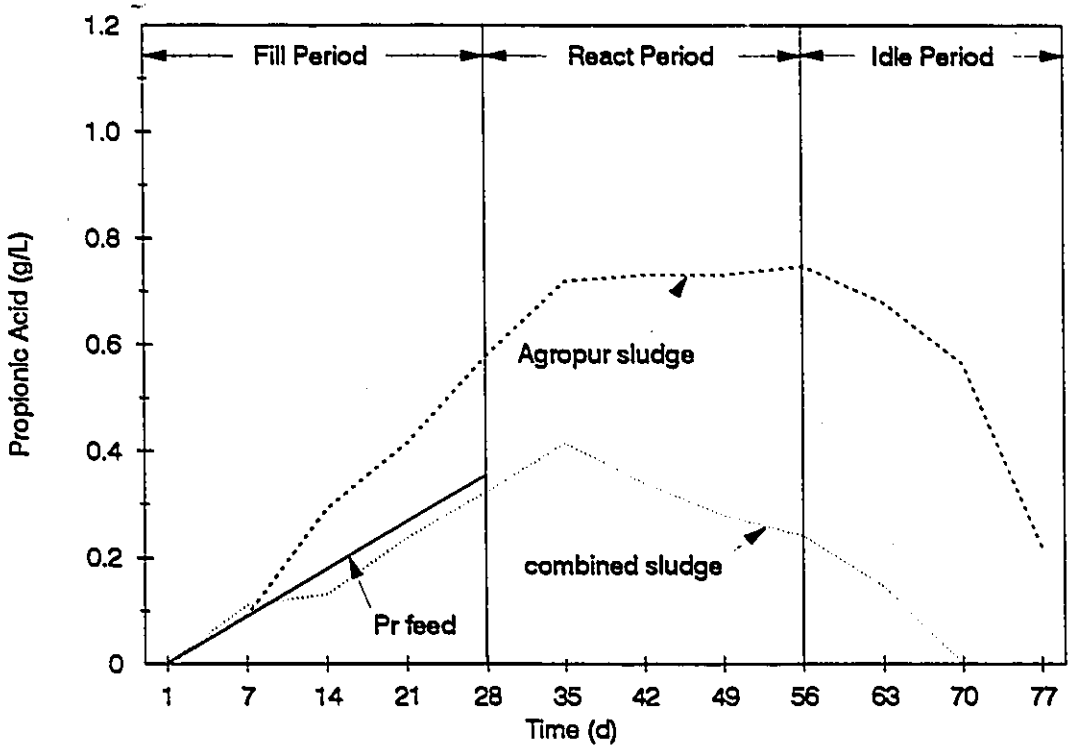


Fig 4.7 Average propionic acid concentration as a function of time for SBRs with a loading rate of 0.7g COD/L-d, (test run 4). ------ average of SBRs 1 - 2, ... average of SBRs 3 - 4.

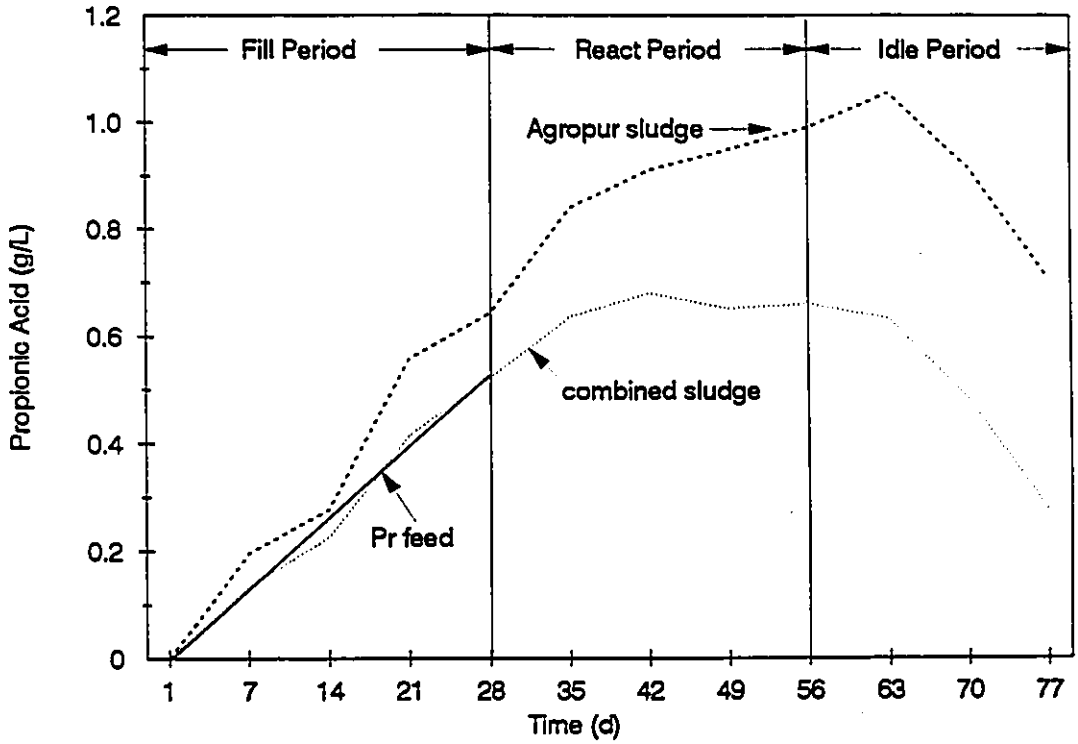


Fig 4.8 Average propionic acid concentration as a function of time for SBRs with a loading rate of 1.2g COD/L-d, (test run 4). ------ average of SBRs 5 - 6, ... average of SBRs 7 - 8.

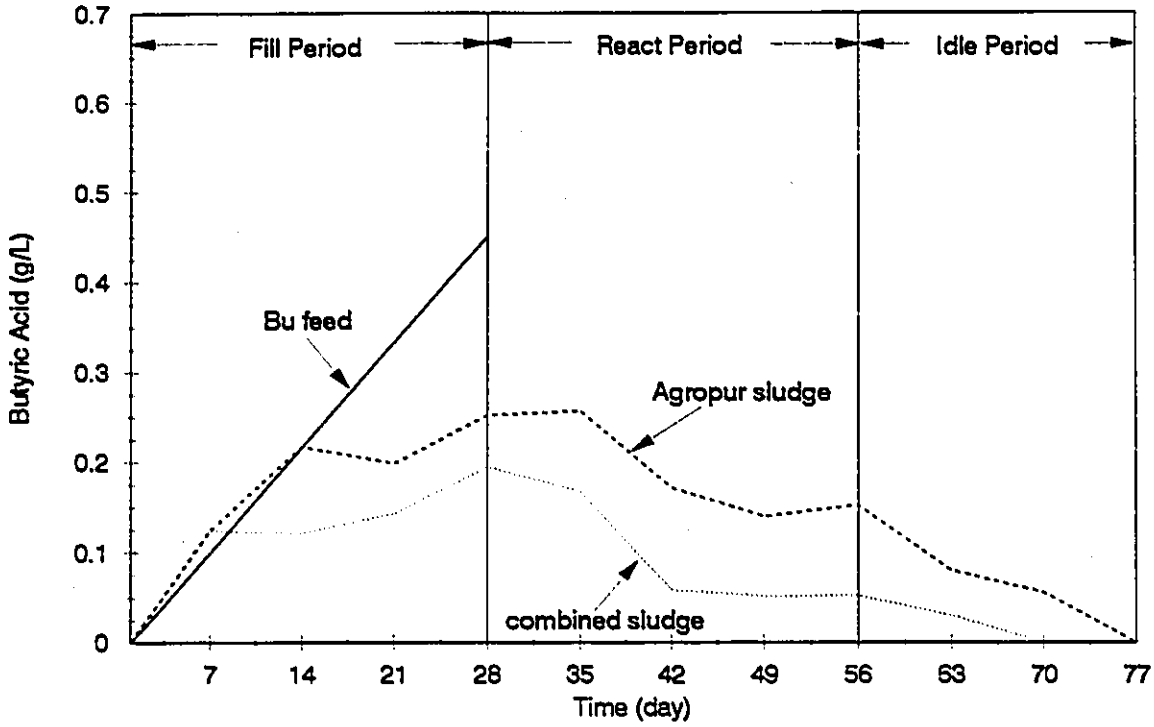


Fig. 4.9 Average butyric acid concentration as a function of time for SBRs with a loading rate of 0.7g COD/L-d, (test run 4), ------ average of SBRs 1 - 2, ... average of SBRs 3 - 4.

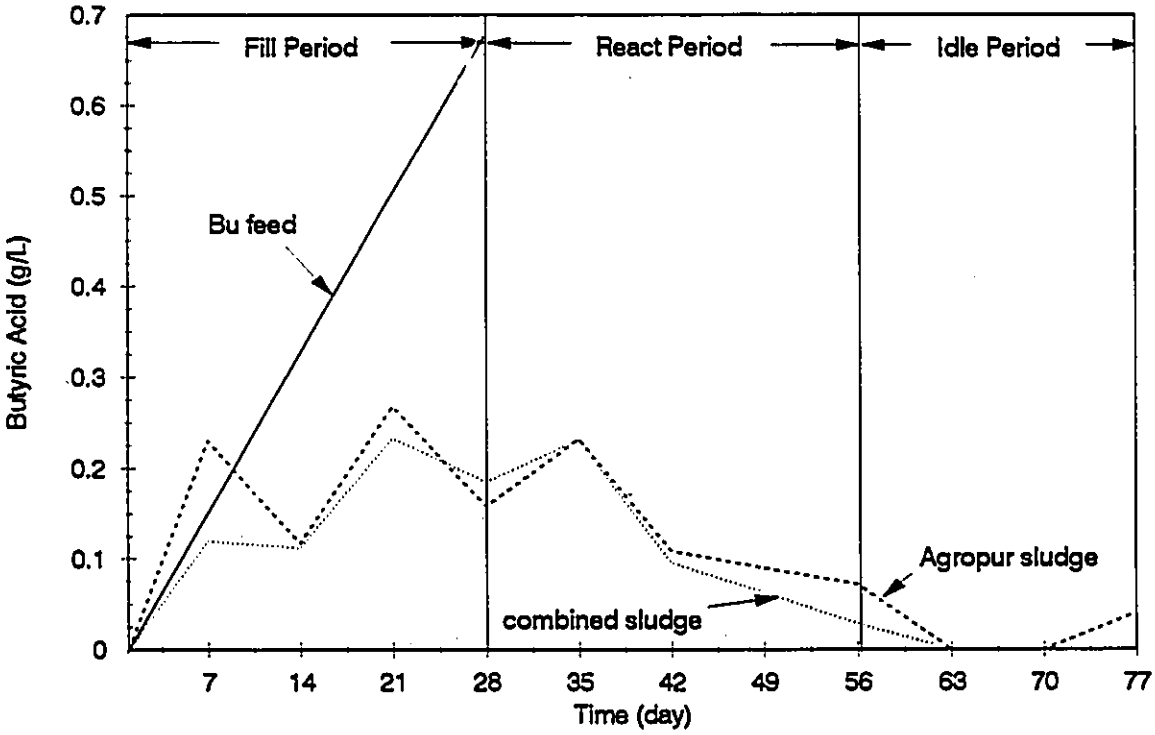


Fig. 4.10 Average butyric acid concentation as a function of time for SBRs with a loading rate of 1.2g COD/L-d, (test run 4), ------ average of SBRs 5 - 6, ... average of SBRs 7 - 8.

VAs is more probably due to the faster growth rate of acid formers. The large increase in VAs did not affect the process stability. This was because; 1) the alkalinity in the SBRs was very high (16000 mg $CaCO_3$/L) (the large increase in VAs caused only a small drop in pH); and 2) the pH was maintained between 7.5 and 7.8 (the unionized volatile acids concentration was always low (unionized VAs $\leq$ 6 mg/L)). This information is very important in kinetic model development. Several existing models assume that growth rate of methane formers is affected by the VAs concentration. Based on the preliminary results of this work, this theory does not apply up to concentrations of 6000 mg/L acetic acid in anaerobic digestion of swine manure at 20°C in SBR. Figure 4.5, 4.6, 4.9 and 4.10 show that during the react period there was rapid utilization of acetic and butyric acids. The decrease in acetic and butyric acid concentrations indicate that hydrolysis and acidification were the rate limiting processes during the react period.

Figures 4.5 to 4.10 show that when the organic loading rate increased from 0.72 to 1.20 g COD/L-d, the maximum acetic, propionic and butyric acid concentrations in the SBR increased by 25, 13 and 33%, respectively.

The inoculum type did not have much effect on acetic acid concentrations in SBR. The SBR digesters with the combined

sludge inoculum had higher CH_4 production and lower propionic and butyric acid concentrations at any time. This indicates that SBRs were more stable with combined sludge than with Agropur sludge. For this reason all subsequent experimental runs were carried out with the combined sludge inoculum.

Figure 4.11 shows the total and individual VA concentrations as a function of time for each treatment. This figure shows that propionic acid is the only VA that increased during the react period. A mass balance on propionic acid would show that it was being utilized during the fill period also but at a rate lower than the feed and production rate. The increase in propionic acid might be due to the increase in dissolved hydrogen gas concentration (Mosey, 1983). Fukazaki et al. (1990) stated that fermentation of propionic acid to CH_4 and CO_2 is inhibited by dissolved hydrogen and acetic acid. Results for SBRs 3-4 in Figure 4.11 indicate that propionic acid was utilized even when the concentration of acetic acid was high. Therefore the propionic acid accumulation in this study is likely due to the effect of dissolved hydrogen in the SBRs. Another possibility for the increase in propionic acid is inhibition of the hydrogenotrophic methanogens. Figure 4.11 also confirmed that the manure slurry was partly treated at the end of the react period. This figure also indicates that if the react period for the startup run would be increased by 20 days all the VAs would be completely used.

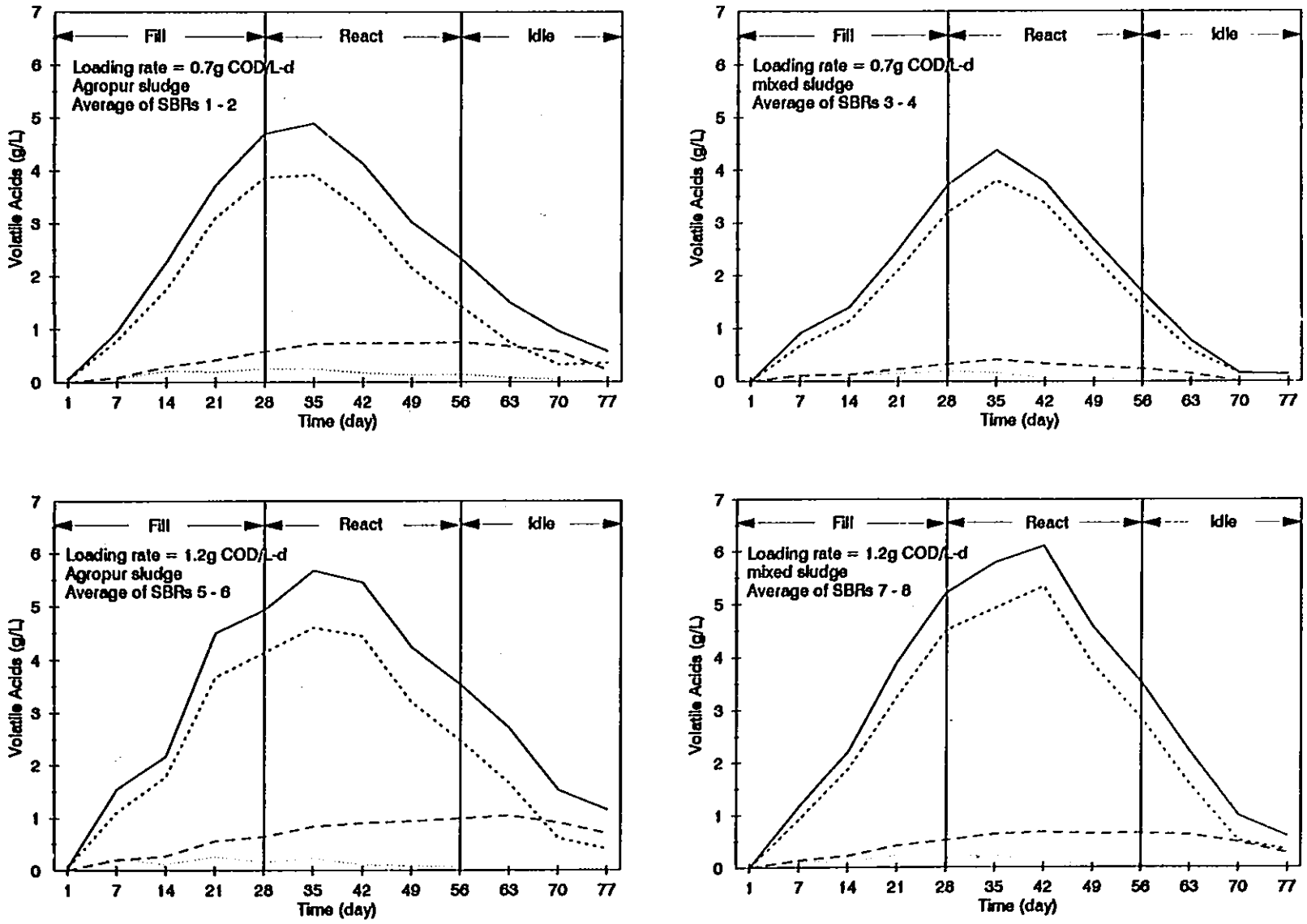


Fig. 4.11 Total and individual volatile acids concentration as a function of time. (test run 4). (—— total volatile acids, ····· acetic acid, ····· butyric acid, - - - propionic acid).

For the startup run of a full scale SBR the organic loading rate should be reduced by 50% or the react period extended by 20 days.

Figures 4.12 to 4.14 give the pH level, alkalinity and ammonia concentrations respectively as a function of time for the SBR with an organic loading rate of 1.2 g COD/L-d. Similar curves were obtained at the lower organic loading rate of 0.7 g COD/L-d. The pH ranged from 7.4 to 7.8. The higher concentration of VAs during the react period did not affect the microorganisms because of the high initial alkalinity in the SBR. The increase in VAs slightly reduced the pH and alkalinity during the fill periods. During the react period both the alkalinity and pH started to increase mainly due to VAs utilization. The contribution of ammonia nitrogen to the pH and alkalinity increase during the react period was negligible because there was no increase of ammonia nitrogen during this period as indicated in Figure 4.14.

The high concentration of ammonia nitrogen did not inhibit the methane formers in the SBR, because both the methane production and the ammonia-nitrogen concentration increased concomitantly. Kroecker et al. (1979) found that ammonia is inhibitory to the methanogenic bacteria when its concentration exceeds 2000 mg/L. Melbinger and Donnellon (1971) found that ammonia is toxic only when its concentration exceeds the

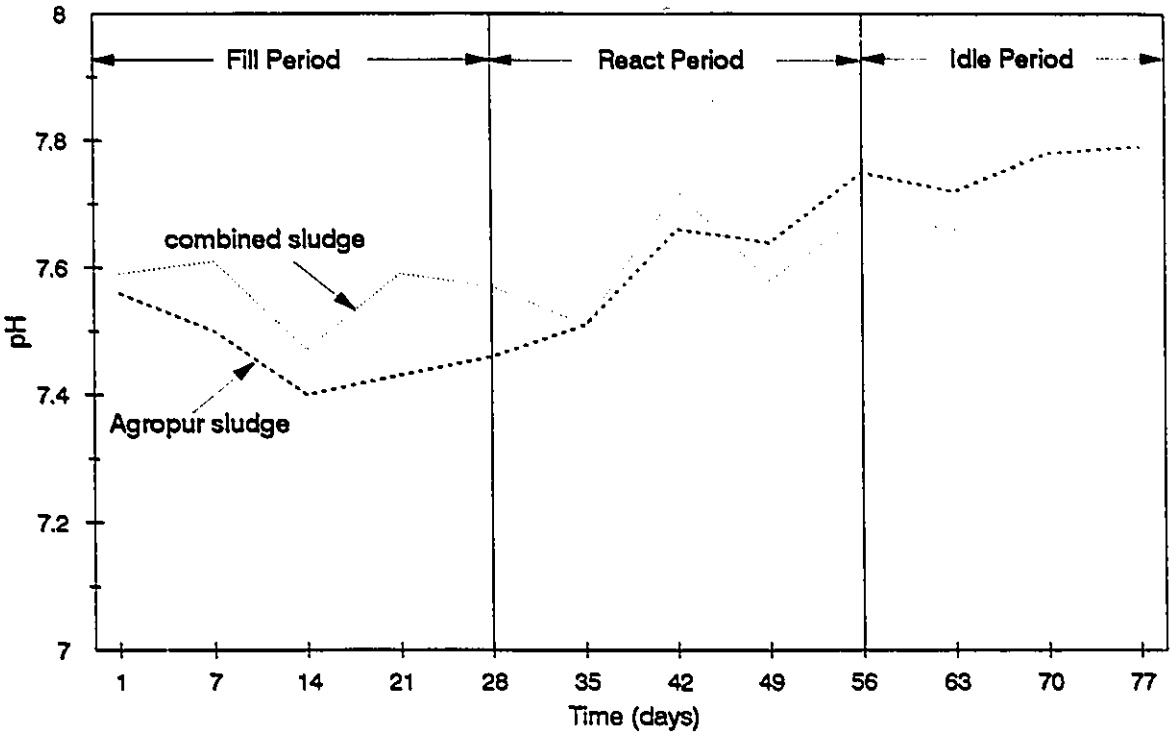


Fig 4.12 pH as a function of time for SBRs with a loading rate of 1.2g COD/L-d, (test run 4), ------- average of SBRs 7 - 8, ... average of SBRs 5 - 6.

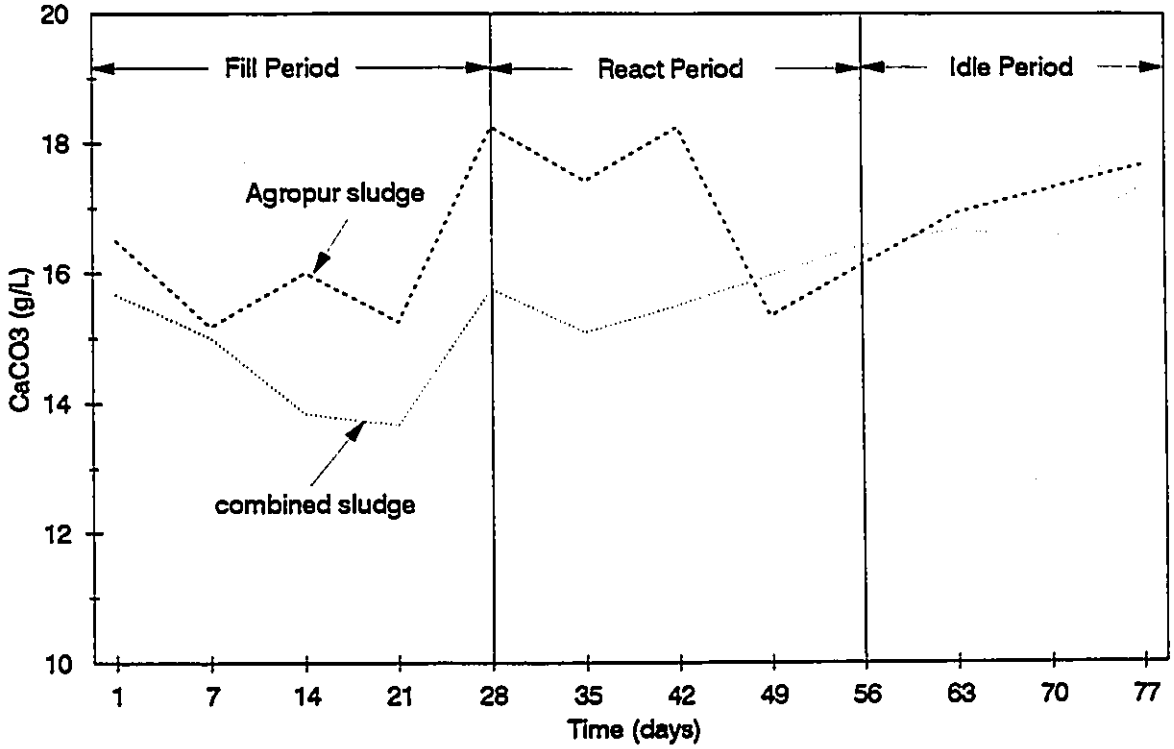


Fig 4.13 Alkalinity concentration (g CaCO3/L) as a function of time for SBRs with a loading rate of 1.2g COD/L-d, (test run 4), ------- average of SBRs 7 - 8, ... average of SBRs 5 - 6.

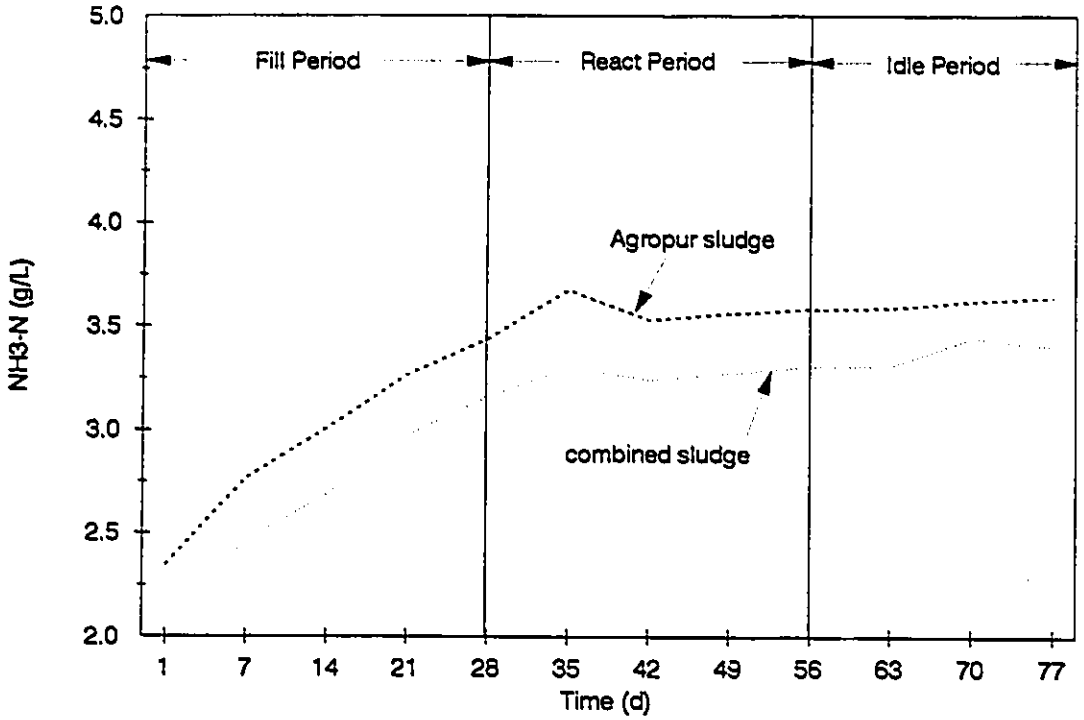


Fig 4.14 NH3-N concentration as a function of time for SBRs with a loading rate of 1.2g COD/L-d, (test run 4), ---- average of SBRs 5 - 6, ···· average of SBRs 7 - 8.

threshold limit of 1700 to 1800 mg/L and is increasing faster than the acclimatization of the methanogenic bacteria. McCarty (1964) indicated that an ammonia nitrogen concentration exceeding 3000 mg/L is toxic to the anaerobic bacteria regardless of pH. Henze (1983) indicated that dissolved ammonia gas is substantially more toxic than ammonium ions to anaerobic bacteria. He indicated that a dissolved ammonia gas concentration ranging between 100 and 200 mg/L should have an inhibitory effect on the anaerobic process. In this test, the total ammonia nitrogen concentration (3700 mg/l) represents the sum of ammonium ions (3550 mg NH_4^+/L) and dissolved ammonia gas (150 mg NH_3/L). Inhibition by ammonia-nitrogen was not observed in this work. It is likely due to the long hydraulic and solids residence times provided in this test, this should allowed the microorganisms to increase their tolerance to high concentrations of ammonia-nitrogen. PAD in SBR appears to be suitable to treat wastewaters with high nitrogen content.

4.4 SBR Operating Parameters Investigated

In this study several operating parameters were varied to: 1) simulate the different pig manure slurry managements at the farm; and 2) to provide the most efficient and stable process design and control.

4.4.1 Effect of Loading Rate

Figure 4.15 shows the typical response of the intermittently mixed SBRs, fed three times a week, with different organic loading rates. Organic loading rates of 0.81, 1.22 and 1.63 g COD/L-d were considered in this test. In this study, the specific organic loading rate was not determined. Because of sampling difficulties, it was not possible to measure accurately the VSS concentration in the SBRs. As well the swine manure slurry fed to the SBRs had a high concentration of organic particulates and therefore it was not possible to determine precisely the fraction of VSS that represented the active microorganisms. During the four-week fill period the cumulative biogas production was the same for the three organic loading rates. A possible reason for this might be that the three sets of digesters had about the same population of methane formers at the start of the test and the methane production rate was not limited by the substrate availability. During the subsequent four-week react period the digesters with the lowest organic loading rate (0.81 g COD/l-d) stopped producing methane. This should be because most of the soluble COD and VAs were consumed during the fill period. The digester with the intermediate organic loading rate (1.22 g COD/l-d) stopped producing gas midway through the react period for similar reasons.

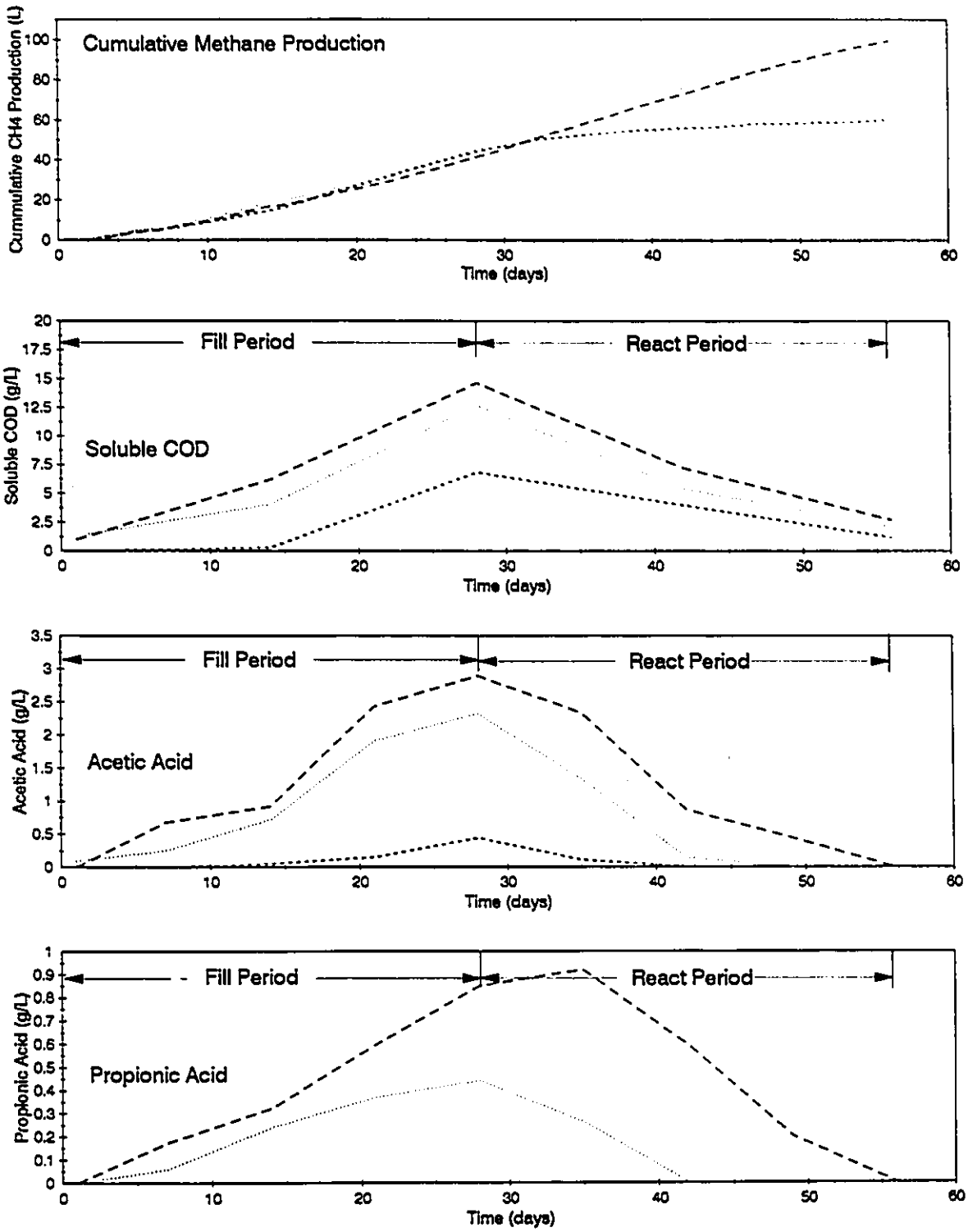


Fig. 4.15 Comparison of operating performance of intermittently mixed SBRs, in test run 5, for different organic loading rates (OLR), fed three times a week.

------- SBRs 3 - 4, OLR = 0.81g COD/L-d

..... SBRs 7 - 8, OLR = 1.22g COD/L-d

- - - - SBRs 11 - 12, OLR = 1.63g COD/L-d

Figure 4.15 also indicates as expected that the concentration of VAs in the SBR increased with an increase in organic loading rate. For the lowest loading rate (0.81 g COD/L-d) there was no propionic acid accumulation in the SBR while acetic acid concentration stayed below 500 mg/L. For the SBRs with the highest loading rate (1.63 g COD/L-d) acetic and propionic acids were both present and their respective concentrations reached maximum values of 3000 and 900 mg/L at the end of the fill period. For each loading rate the VAs were completely utilized at the end of the react period. From these results it can be concluded that the SBRs were very stable at these loading rates. The lowest loading rate should not be recommended because no treatment occurs during the react period. A loading rate of 1.63 g COD/L-d should be recommended. As shown in Figure 4.15 at this loading rate the react period is utilized to its maximum. Complete utilization of both VAs and soluble COD occurred at the end of this period.

4.4.2 Effect of Mixing

Figures 4.16 and 4.17 compare the SBR performance for different intensities of mixing. Digesters 7, 8, 11 and 12 were intermittently mixed 10 minutes every half hour.

Figure 4.16 shows that intermittent mixing of SBR with an organic loading rate of 1.22 g COD/L-d increased the production of methane by 13% and the utilization rate

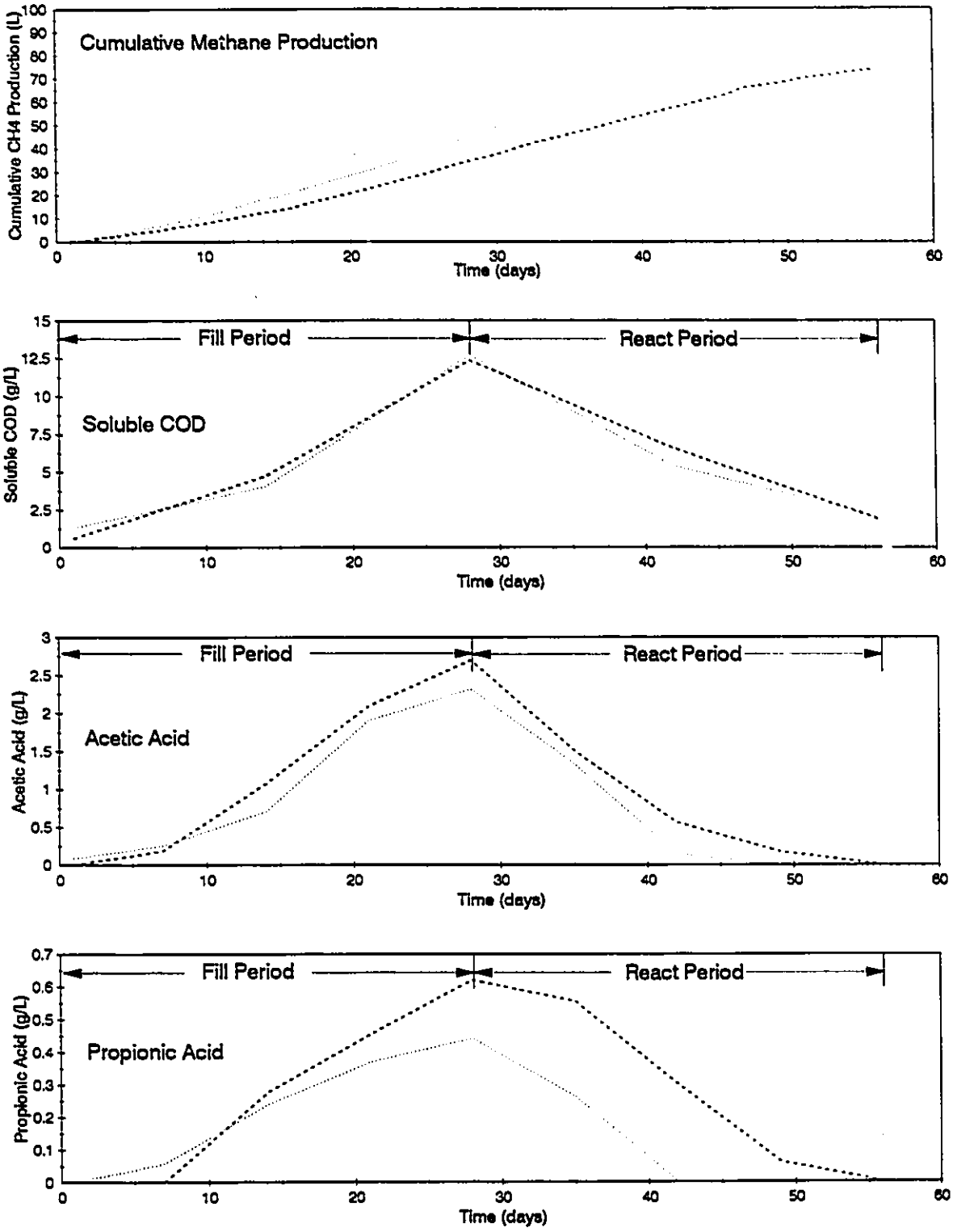


Fig. 4.16 Comparison of SBRs operating performance in test run 5, for different levels of mixing, with an organic loading rate = 1.22g COD/L-d, SBRs fed three times a week.
..... SBRs 5 - 6, no mixing, ... SBRs 7 - 8, mixed for 10 minutes each half hour.

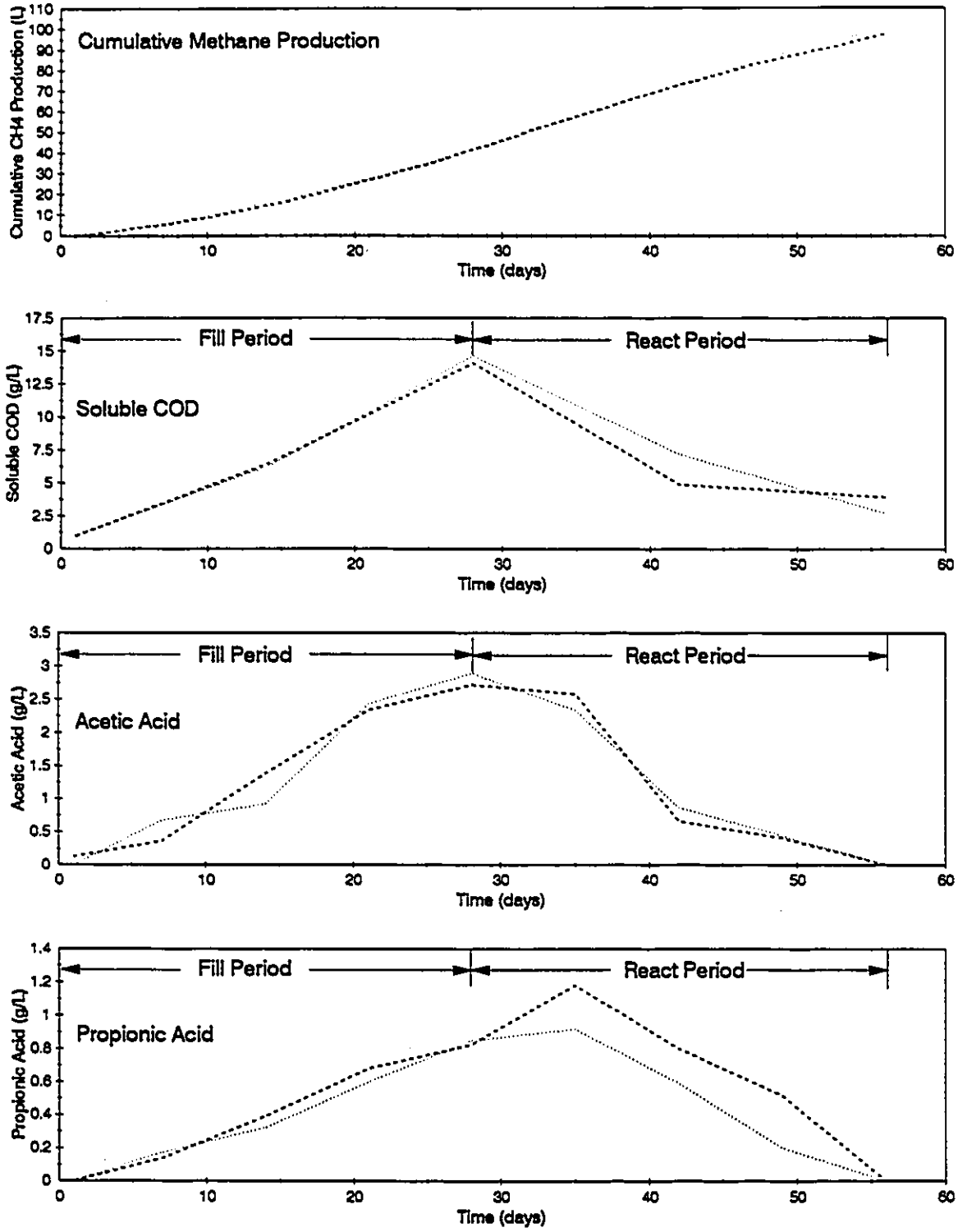


Fig. 4.17 Comparison of SBRs operating performance in test run 5, for different levels of mixing. Organic Load Rate = 1.63g COD/L-d, SBRs fed three times a week.
----- SBRs 9 - 10, no mixing, ... SBRs 11 - 12, mixed for 10 minutes each half hour.

of VAs, but did not seem to have an effect on soluble COD accumulation.

Figures 4.17 shows that for digesters fed at a higher organic loading rate (1.63 g COD/L-d), the methane production, SCOD and VAs accumulation were similar for the intermittently mixed and non-mixed digesters. Mixing of a full scale digester consumes large amounts of energy and based on these experimental results, SBR mixing may not be necessary for full scale farm digesters. However, it would be preferable to provide a minimum level of mixing to reduce potential for compaction of solids at the bottom of the SBRs as well as for separation and floating of light organic material. The level of mixing used in this test was arbitrary selected and if it would have improved the process performance, other mixing strategies would have been investigated.

4.4.3 Effect of Feeding Frequency

At a typical swine operation, the pig manure slurry is either removed from the barn daily, three times a week or once a week. For most swine operations evacuation of manure occurs once a week. Test run No. 6 was used to investigate the feeding frequency of SBR that correspond to the evacuation frequency of manure from the livestock buildings.

Figures 4.18 and 4.19 compare the typical response of SBR to feeding frequency of 1 to 3 times a week with the same total

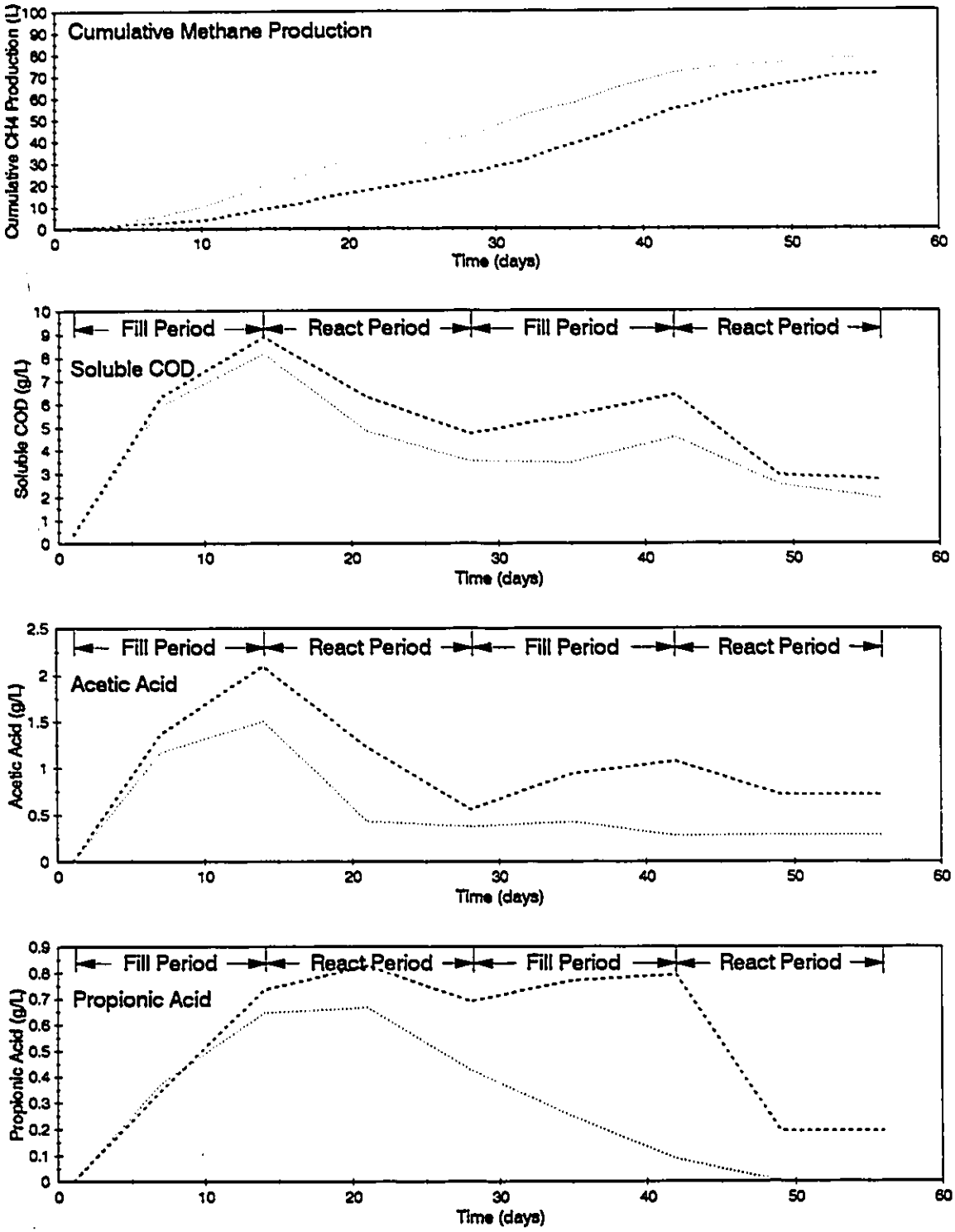


Fig. 4.18 Comparison of SBRs operating performance in test run 6, for different feeding frequencies, with a cycle length of 28 days. ----- SBRs 5 - 6 fed 28.5g COD three times a week, ... SBRs 7 - 8 fed 85.5g COD once a week.

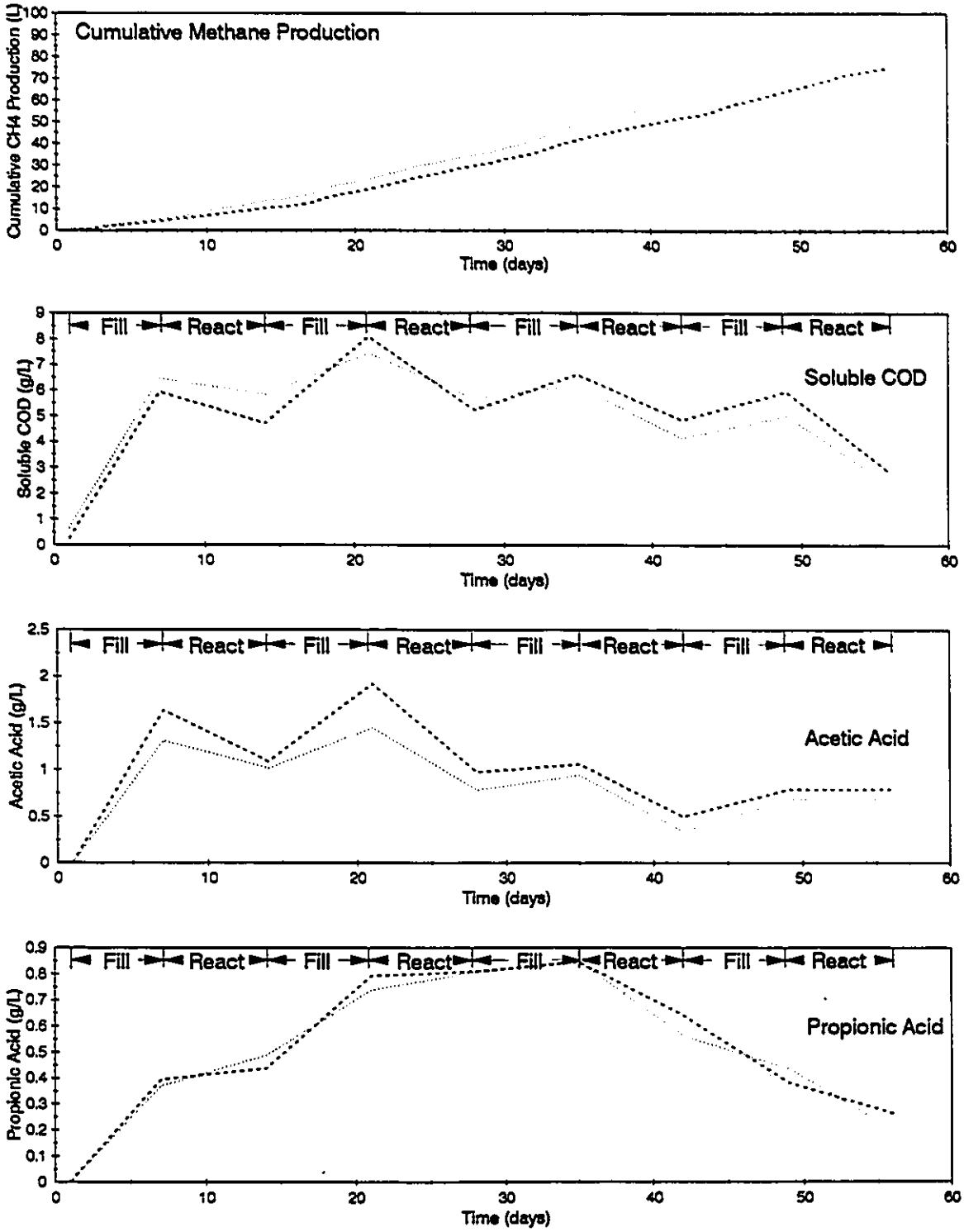


Fig. 4.19 Comparison of SBRs operating performance in test run 6, for different feeding frequencies. Cycle length of 14 days. ----- SBRs 9 - 10 fed 28.5g COD three times a week, ... SBRs 11 - 12 fed 85.5g COD once a week.

weekly organic loading (66 g COD/week) for all SBRs. Figure 4.18 shows that the SBRs fed once a week produced 13% more gas and had about the same effluent soluble COD concentration as reactors fed 3 times per week. The higher biogas production for the SBRs fed once a week was likely due to the longer residence time of the swine manure slurry in these digesters. These results indicate that the SBRs fed once a week were also very stable.

For the SBRs with a cycle length of 14 days the feeding frequency had no effect on SCOD, acetic and propionic acids accumulation. Only the cumulative methane production was 14% higher. These experimental results indicate that both one and three times a week feeding frequency may be acceptable for farm scale SBRs.

4.4.4 Effect of Cycle Length

Cycle length is an important parameter in the design of SBR because it controls the size of the digester, the treatment efficiency as well as the frequency that the farmer has to deal with SBR effluent removal. In this test, cycle lengths of 14 and 28 days were used over a period of 56 days.

Figures 4.20 and 4.21 show that the cycle length had an effect on the SCOD and acetic acid accumulation pattern during the process. The SBRs with the shorter feed-react period (14

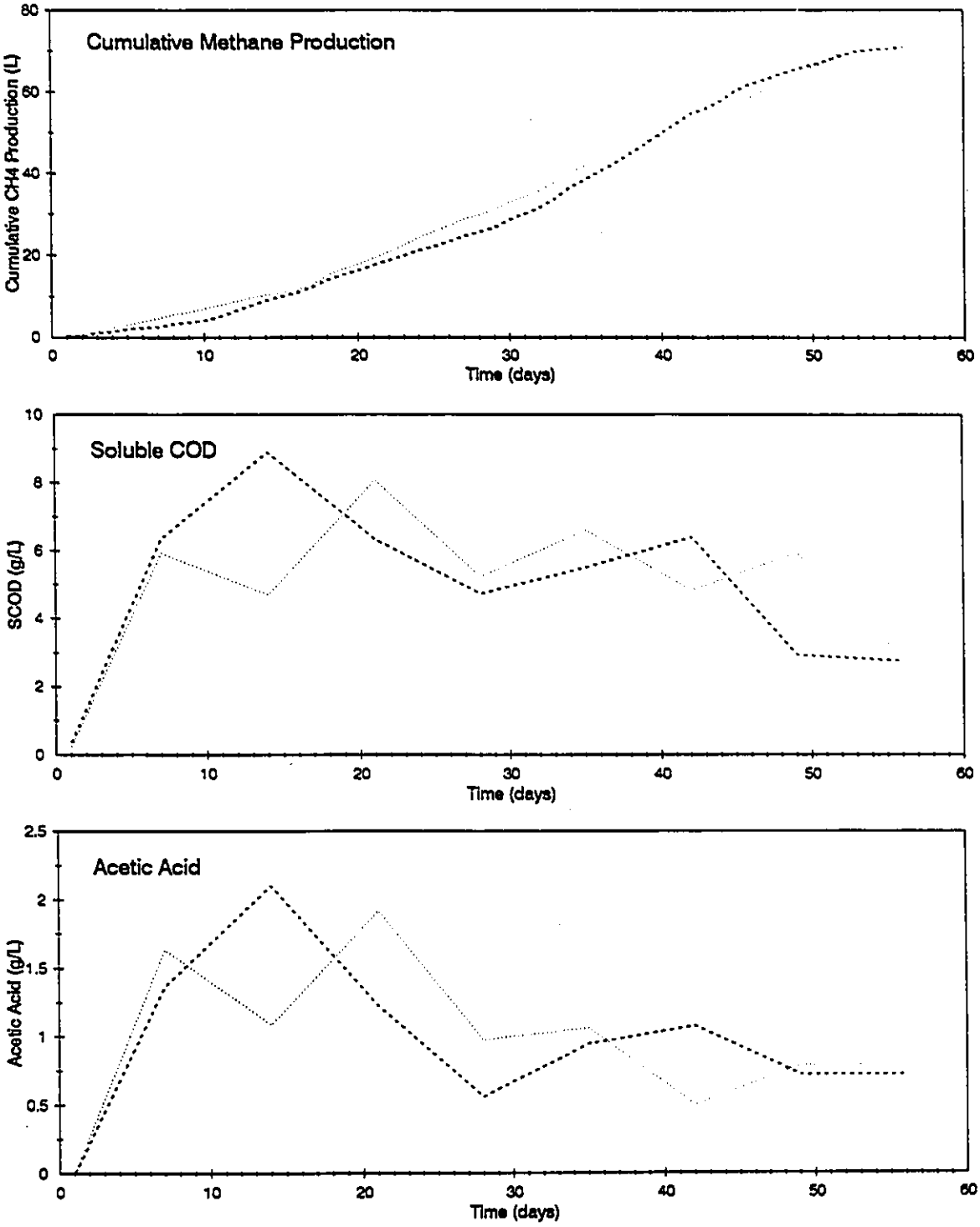


Fig. 4.20 Comparison of SBRs operating performance in test run 6 for different cycle lengths.
SBRs were fed three times a week, OLR = 1.63g COD/L-d,
----- SBRs 5 - 6, cycle length 28 days, ... SBRs 9 - 10, cycle length 14 days.

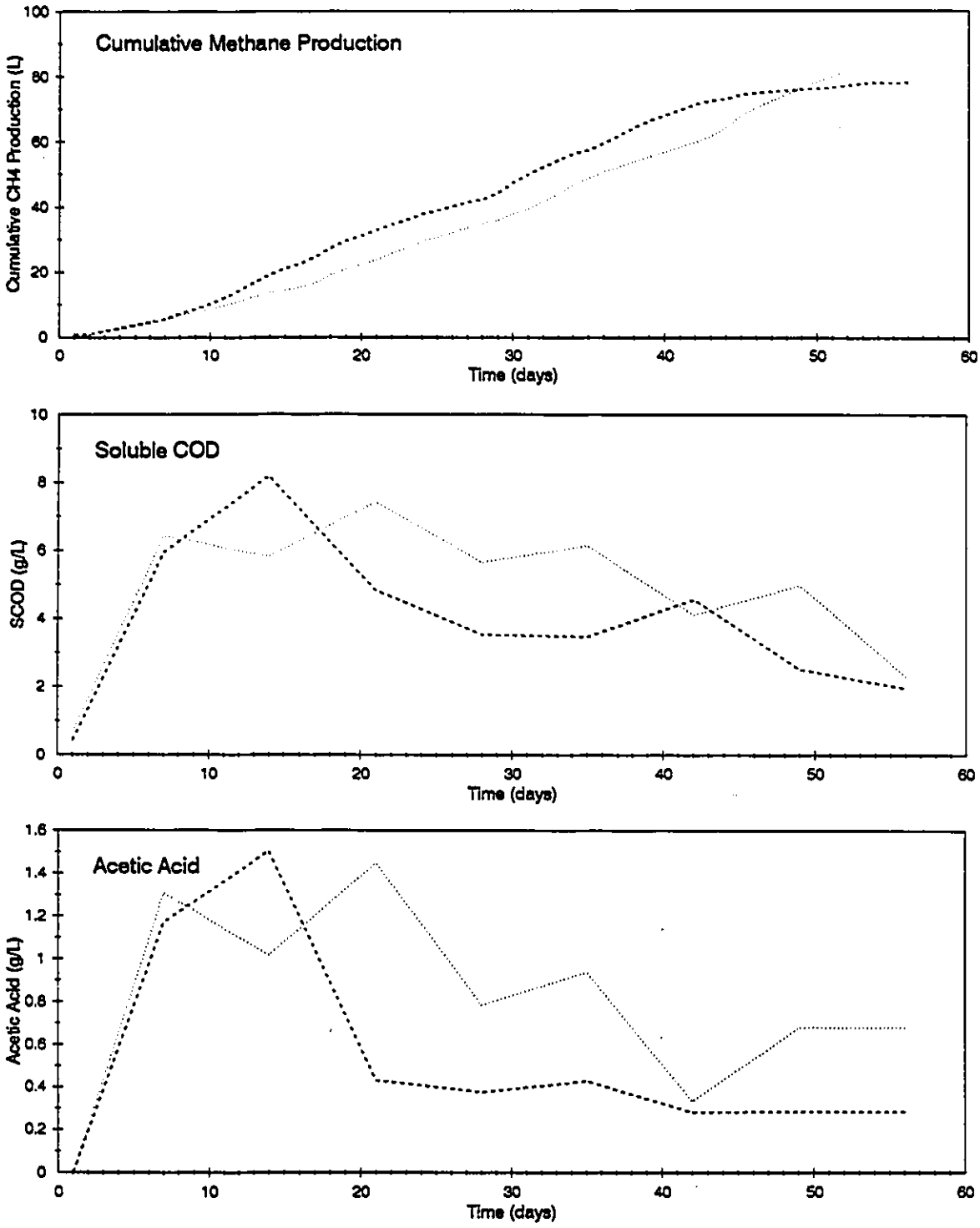


Fig. 4.21 Comparison of SBRs operating performance in test run 6 for different cycle lengths. SBRs were fed once a week, OLR = 1.63g COD/L-d,
------ SBRs 7 - 8, cycle length 28 days, ... SBRs 11 - 12 cycle length 14 days.

days) had twice the number of cycles compared to the longer feed-react period (28 days) over the 56 days of operation. As a result, the SBRs with the shorter feed-react period had more fluctuations in weekly accumulation of SCOD and acetic acid. Figures 4.20 and 4.21 also show that the increase in cycle length from 14 to 28 days had no major effect on process performance. Final concentrations of SCOD and acetic acid were the same after 56 days of SBR operation using either the two-week or four-week cycle.

Figures 4.22 and 4.23 show the effect of cycle length on cumulative and daily methane production. For both cycle lengths (14 and 28 days) the maximum daily methane production occurred at the end of the fill period and the minimum at the end of the react period. As expected the SBRs with the shorter cycle length (14 days) showed more variation in weekly methane production.

Figure 4.22 shows that the total cumulative methane production after 56 days was the same for both cycle lengths. Therefore the total amount of energy recovered by PAD in SBR was not affected by the cycle length investigated in this study.

At the farm a steady and constant production of methane gas would be preferable in order to develop an adequate biogas utilization strategy. A minimum of two SBRs would be required

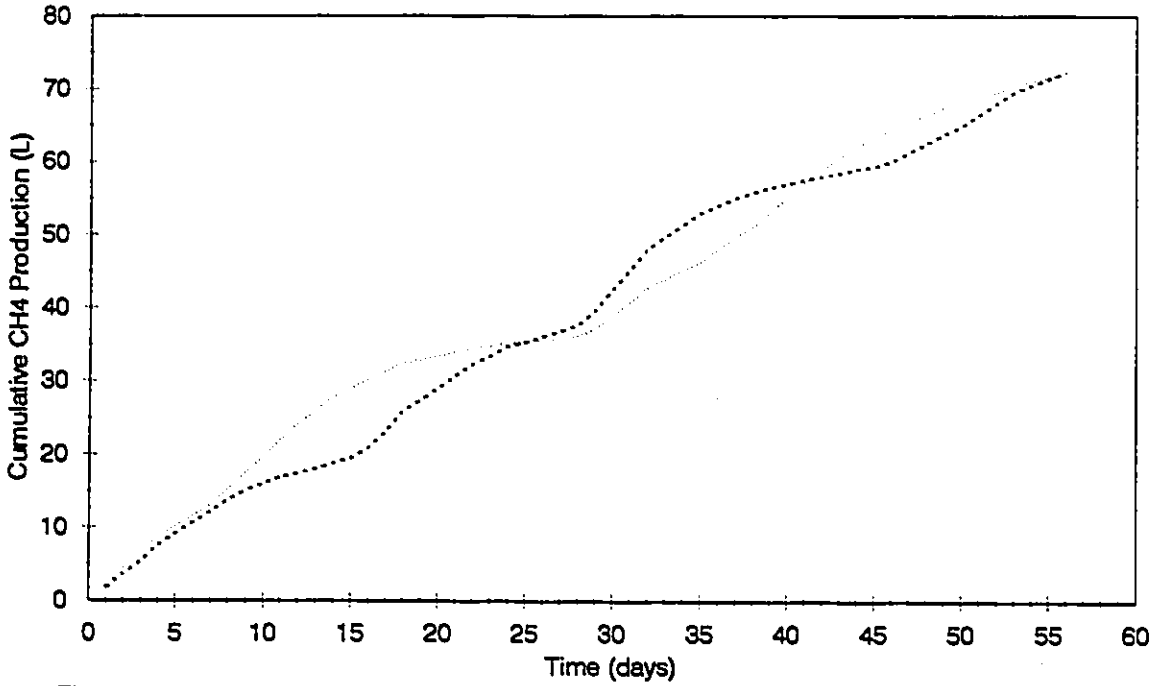


Fig. 4.22 Effect of cycle length on cumulative methane production. SBRs fed once a week, (test run 7), OLR = 1.63g COD/L-d, ------- SBRs 9-10, cycle length 14 days, ... SBRs 11-12, cycle length 28 days.

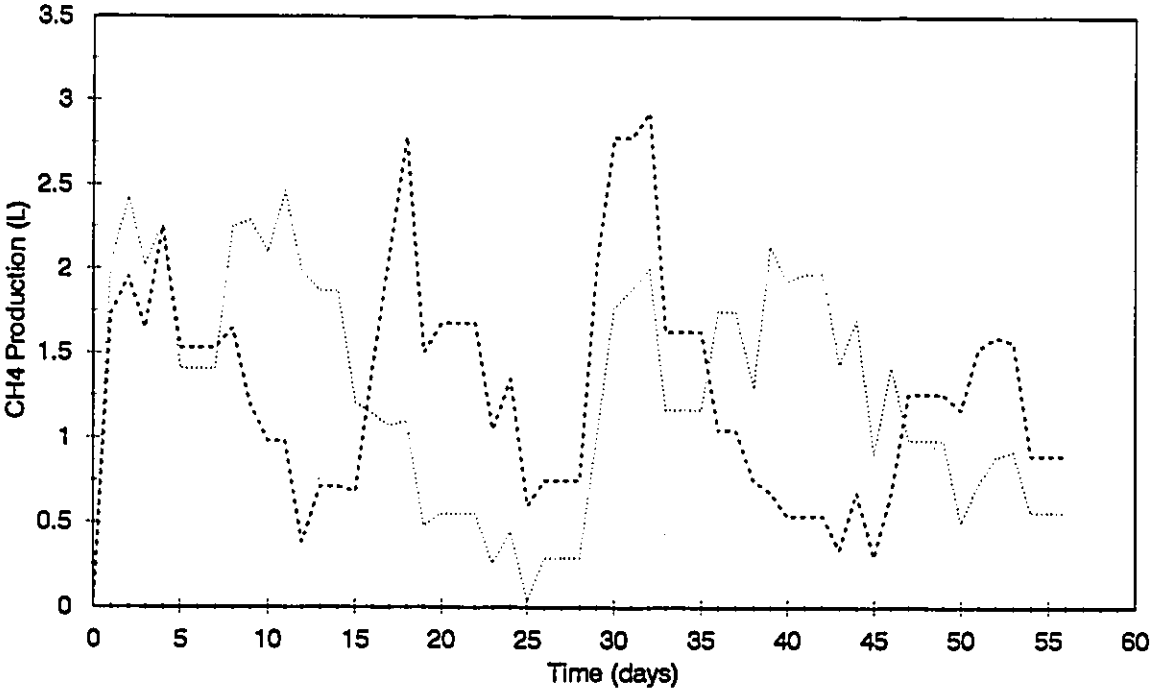


Fig. 4.23 Effect of cycle length on daily methane production. SBRs fed once a week, (test run 7), OLR = 1.63g COD/L-d, ------- SBRs 9-10, cycle length 14 days, ... SBRs 11-12, cycle length 28 days.

to process the swine manure slurry at a farm. Figure 4.24 shows the total daily methane production from two SBRs operated simultaneously at fill/react cycle lengths of 14 and 28 days. By comparing Figure 4.24 with Figure 4.23, it is obvious that a pair of SBRs provides a more uniform supply of methane than a single SBR. The daily variation in biogas production was due to the technique used to measure the biogas flow rate (wet cup gas meter). This device is affected by variations in barometric pressure. In practice on a farm, a gas pump will be used to supply the biogas to the burner. This gas handling system will not be affected by barometric pressure. As a result, the daily biogas production will be more uniform.

4.4.5 Effect of Sludge Acclimation

In the start-up run, SBRs were inoculated with fresh anaerobic sludge obtained from anaerobic digesters operated at 35°C and either fed with milk processing plant wastewater sludge (Agropur) or municipal sludge. The Agropur and municipal digesters were operated at sludge residence times of 26 and 2 weeks respectively. In this study no sludge had been wasted and the loss of VSS with the effluent was low. Therefore it was assumed that the sludge age in this study was the cumulative time since the sludge had been added to the SBRs and started to acclimatize to low temperature and swine manure

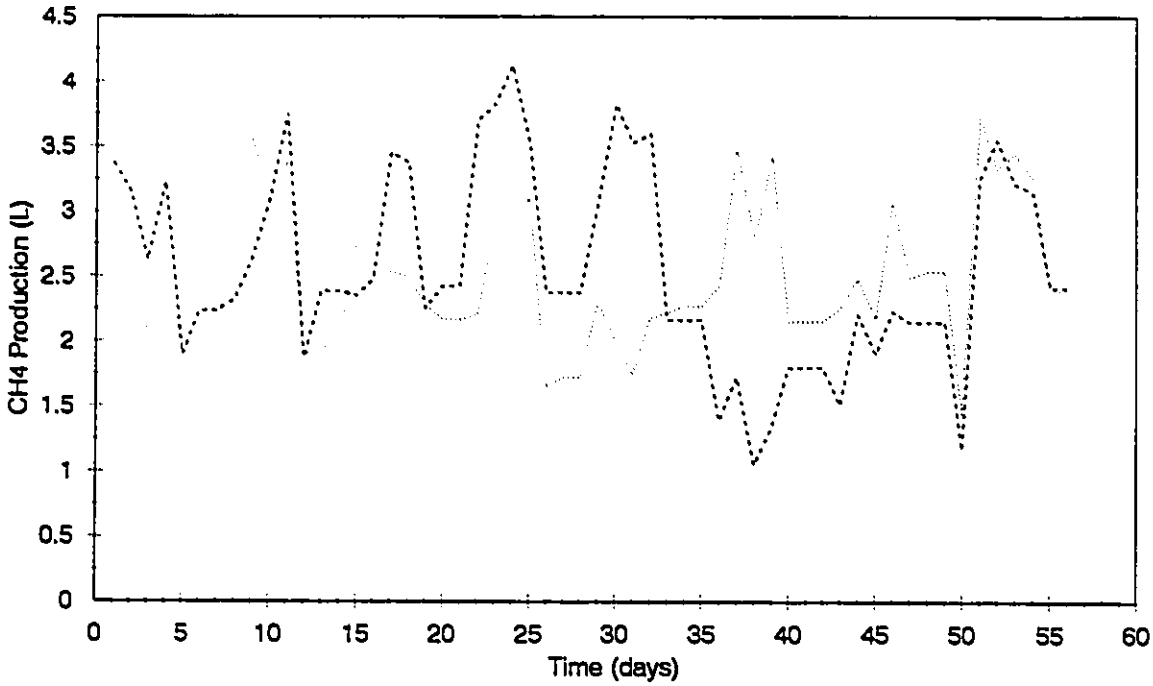


Fig. 4.24 Total methane production from two SBRs operated simultaneously, (test run 6).
OLR = 1.63g COD/L-d, ····· Cycle length 14 days, ····· Cycle length 28 days

slurry. Table 4.4 gives the estimated SBR's sludge ages at the beginning of each test run. The sludge age in this study largely exceeded the minimum and recommended design sludge age of 11 and 28 days respectively for anaerobic digesters operated at 18°C and fed with industrial wastes (McCarty, 1964).

Table 4.4 Sludge age at the beginning of each test run.

TEST RUN NO.	SBRs NUMBER	SLUDGE AGE AT THE START OF THE RUN (d) *
4	1-4	1
	5-8	1
5	1-4	1
	5-8	112
	9-12	112
6	1-4	97
	5-8	209
	9-12	209
7	9-12	306

* the sludge age in this study represent the cumulative time since the sludge started to acclimatize to low temperature and swine manure.

Figure 4.25 compares the SBRs response to sludge acclimation. Anaerobic sludge in digesters 7 and 8 in test run No. 4 was

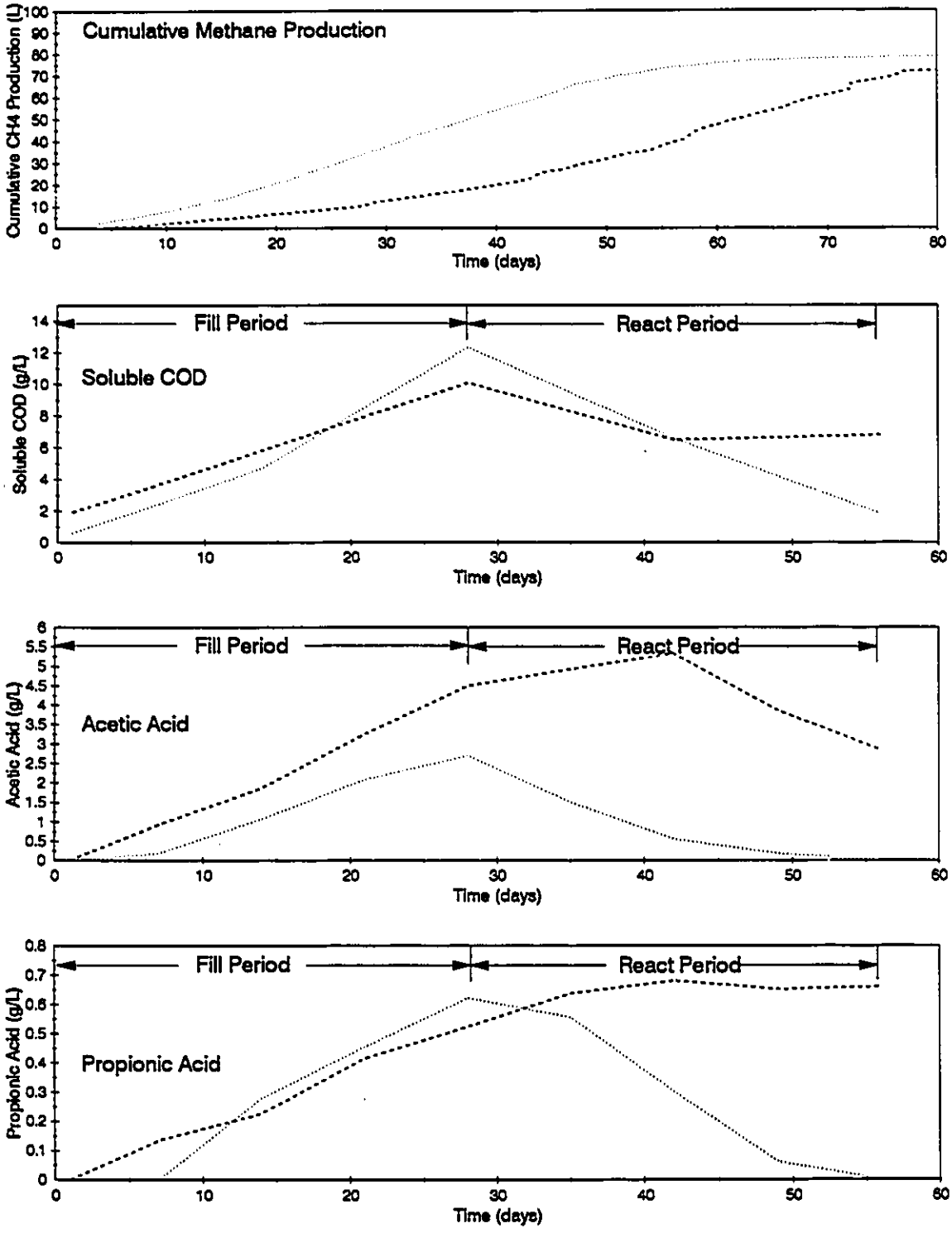


Fig. 4.25 Comparison of SBRs performance for different acclimatization times (no mixing).
------ Test run 4, SBRs 7 - 8, with a loading rate of 1.20g COD/L-d
..... Test run 5, SBRs 5 - 6, with a loading rate of 1.22g COD/L-d

exposed to swine manure slurry and low temperature for the first time. During this run there was a long lag phase in the biogas production during the feeding period. In test run No. 5 the same sludge already exposed to swine manure slurry and low temperature for a period of three months was fed about the same organic loading rate. The SBRs with an older sludge had: 1) a shorter lag phase and a substantially higher methane production rate; 2) substantially lower concentration of soluble COD, acetic and propionic acids at all times during the fill and react period; and 3) achieved complete removal of SCOD and VAs before the end of the react period. These experimental results indicate that sludge acclimation has a significant influence on the process response. The sludge acclimation that took place during the experiments could have involved shifts in microbial populations.

Figure 4.26 compares the cumulative methane production for each consecutive cycle during test run number six. These figures clearly indicate that the initial methane production rate and the total cumulative methane production for each cycle increased after each successive cycle and the lag phase at the beginning of the cycle decreased as the test progressed. The biogas production during cycle one is low because only a fraction of the soluble COD was converted to methane and carbon dioxide. The utilization of soluble COD increased after each successive cycle. This is clearly shown

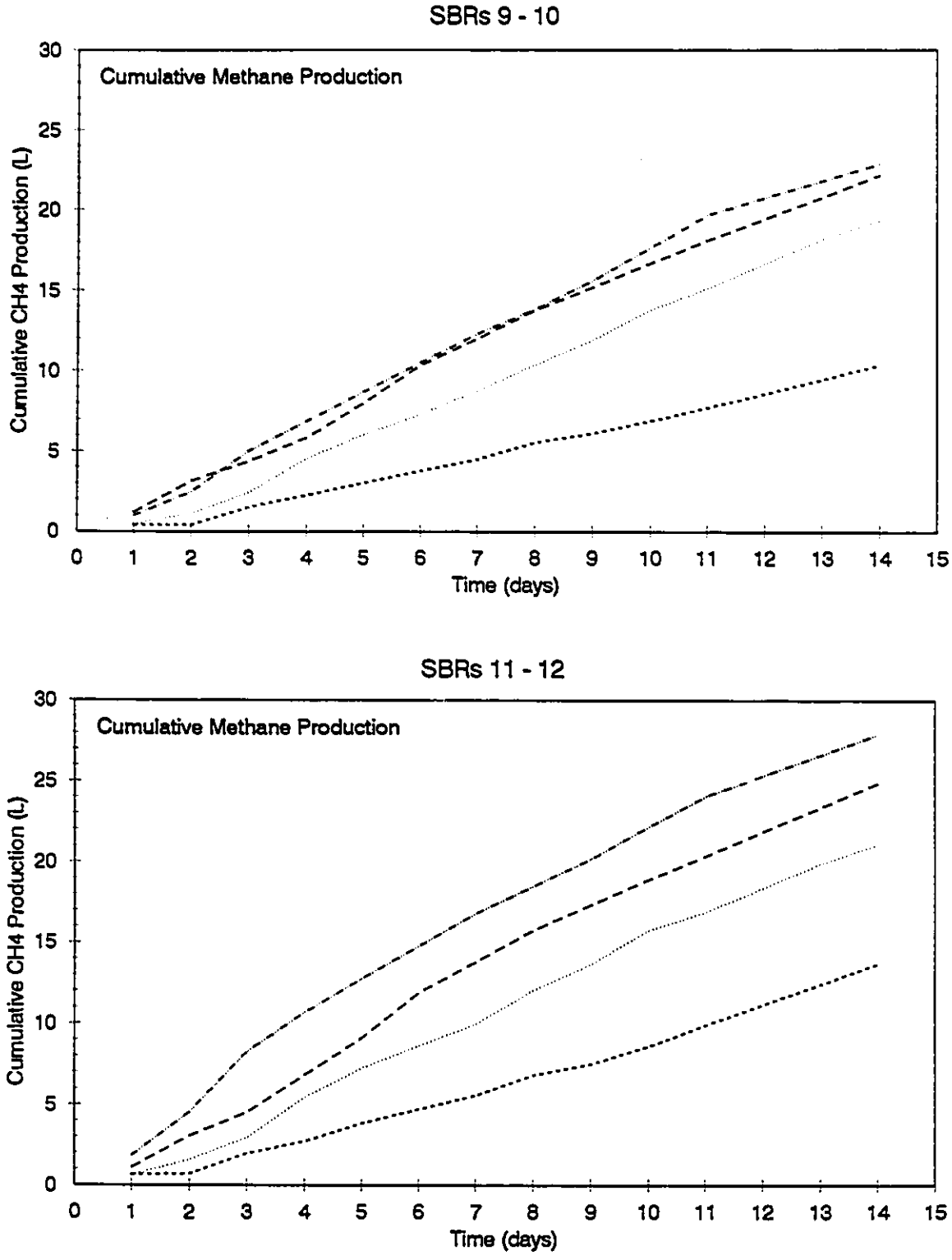


Fig. 4.26 Comparison of cumulative methane production for four successive cycles, (test run 6), SBRs 9 - 10 and 11 - 12. Each cycle lasted 14 days.
----- cycle 1, ... cycle 2, – – – cycle 3, —— cycle 4.

in Figures 4.20 and 4.21. These results clearly indicate that micro-organism acclimatization to low temperatures and swine manure slurry was taking place.

4.5 Methane Production

The biogas produced in test runs five, six and seven was of high quality with a methane concentration between 75 and 80% Table 4.5 gives the methane production as a function of unit mass of VS fed to the digester. The CH_4 production ranged from 0.48 to 0.66 L/g VS for most of the experimental run. Methane productions obtained in this study were substantially higher than methane production from swine manure obtained by digestion at 35°C in continuous flow digesters by Kroecker et al. (1979) who reported methane production of 0.45 L CH_4/g VS added for a loading rate of 2.5 kg VS/m^3-day, and by Hashimoto (1983) who reported 0.42 L CH_4/g VS added for a loading rate of 2.5 kg VS/m^3-day.

The higher methane production per gram of VS fed to the SBRs obtained in this study could be due to the lower organic loading rate and longer HRT. Another possible reason could be the lower operating temperature and the absence of mixing maintain a higher concentrations of hydrogen and carbon dioxide in the liquid phase. As a result more carbon dioxide can be converted to methane by the hydrogen utilizing methanogens. Also, with the continuous flow anaerobic

processes previously experimented, some CO_2, H_2 and CH_4 were lost with the digester effluents.

A high rate of methane production was not the main objective of this work but it is very useful to assess the system performance and stability. The steady production of methane per unit mass of VS fed indicates that anaerobic digestion of swine manure at 20°C in the laboratory-scale SBR digesters was a stable process.

4.6 Treatment Efficiency

Table 4.5 also gives the average level of removal of TCOD, SCOD and VS of two replicate tests for all runs. The total COD removal ranged from 27 to 82% and the VS removal ranged from 46 to 84%. Results for VS and total COD were highly variable due to sampling variation caused by rapid settling of heavy particulates. Some samples had less solids than others. This affected the VS and TCOD determination as well as the calculated methane production per gram of VS. The soluble COD test results were consistent. High SCOD removal was achieved during most of the experimental runs. Its removal ranged from 79% and 96% except in a few runs discussed below. Even during the start-up run the SCOD removal was high and ranged between

TABLE 4.5 Average methane production per unit of VS fed to the digesters and reduction in total COD, soluble COD and VS.

RUN NO.	DIGESTER NO.	LOADING RATE		FEEDING FREQUENCY	MIXING	FILL PERIOD	REACT PERIOD	NO. CYCLE	SLUDGE* TYPE	CH_4 PRODUCTION LCH4/g VS after 56 days	REMOVAL,%		
		g COD/ Feed	g COD/ L-d								TCOD	SCOD	VS
4	1-2	12.6	0.72	3	No	4	4	1	A	0.50	60.0	90.0	29.0
	3-4	12.6	0.72	3	No	4	4	1	B	0.66	70.0	96.0	74.0
	5-6	21.0	1.20	3	No	4	4	1	A	0.30	58.0	85.0	27.0
	7-8	21.0	1.20	3	No	4	4	1	B	0.52	73.0	91.0	56.0
5	1-2	14.25	0.81	3	No	4	4	1	B	0.66	54.0	90.0	46.0
	3-4	14.25	0.81	3	Yes	4	4	1	B	0.75	62.5	93.0	84.0
	5-6	21.40	1.22	3	No	4	4	1	B	0.62	41.0	88.0	64.0
	7-8	21.40	1.22	3	Yes	4	4	1	B	0.75	51.5	87.0	77.0
	9-10	28.50	1.63	3	No	4	4	1	B	0.61	50.1	86.0	68.0
	11-12	28.50	1.63	3	Yes	4	4	1	B	0.62	50.2	87.0	77.0
6	1-2	28.50	1.63	3	No	4	4	1	B	0.17	58.5	22.5	64.3
	3-4	85.50	1.63	1	No	4	4	1	B	0.12	69.9	21.6	73.1
	5-6	28.50	1.63	3	No	2	2	2	B	0.48	67.1	86.1	73.2
	7-8	85.50	1.63	1	No	2	2	2	B	0.53	73.9	85.1	73.6
	9-10	28.50	1.63	3	No	1	1	4	B	0.51	70.9	84.2	72.9
	11-12	85.50	1.63	1	No	1	1	4	B	0.60	82.9	84.8	68.3
7	9-10	66.00	1.26	1	No	1	1	1	B	0.69	78.3	86.8	77.9
	11-12	66.00	1.26	1	No	2	2	2	B	0.69	78.2	78.9	75.3

* Inoculum Type

A - Agropur Sludge
B - Combined Sludge (Agropur & Municipal)

85 to 96%. High SCOD removal occurred because of the low organic loading rate during the start-up run. Table 4.6 compares the SCOD removal in consecutive cycles. The soluble COD removal generally increased with each consecutive cycle. This also indicates that acclimatization of the anaerobic sludge at low temperatures was still taking place.

TABLE 4.6: Soluble COD removal in consecutive process cycles.

RUN NO.	SBRs NO.	SCOD REMOVAL			
		CYCLE 1	CYCLE 2	CYCLE 3	CYCLE 4
6	5-6	71.9	86.1	*	*
	7-8	81.8	85.1	*	*
	9-11	76.6	68	79.2	84.2
	11-12	72.7	67.5	81.9	84.8

* SBRs 5 to 8 had only two cycles over the 56 days of operation.

Table 4.7 gives the results of mass balances on TCOD carried out around some of the SBRs. This table shows that there was an imbalance between the sum of initial COD and fed COD and the sum of COD that accumulated and exited the SBRs. The percent imbalance ranged between 6.3 and 26.1%. This imbalance in COD was expected and it was likely due to the sampling difficulties and to a lesser extent to the experimental error with the analytical technique.

Reduction in swine manure slurry odours was one of the objectives of this study. The major volatile compounds that

Table 4.7 Mass Balance on COD Around SBRs

TEST No.	SBRs No. (g)	Initial COD (g)	Fed COD (g)	Biogas COD (g)	Effluent COD (g)	Sludge COD (g)	Percent* Imbalance
5, Cycle 1	7-8	477.7	250.0	254.0	36.5	374.8	8.6
5, Cycle 1	11-12	390.0	336.0	284.0	84.0	472.0	-16.1
6, Cycle 1	5-6	321.0	169.0	72.9	39.6	422.6	-9.0
6, Cycle 1	9-10	303.0	85.0	29.7	21.7	312.0	6.3
6, Cycle 2	9-10	279.0	84.8	55.4	19.5	368.7	-21.9
6, Cycle 2	11-12	299.0	84.8	60.3	21.3	402.0	-26.1

* % imbalance = $\frac{\text{((Initial COD + Fed COD) - (Biogas COD + Effluent COD + Sludge COD))}}{\text{(Initial COD + Fed COD)}}$

produce odours in animal manure slurries are volatile acids, amines, carbonyls, esters, hydrogen sulphide and ammonia. Laboratory staff observed that test runs that achieved complete removal of VAs and 70 to 96% of SCOD produced treated manure that was relatively odourless compared to raw manure. A large reduction in SCOD may result in complete utilization of amines, carbonyls and esters. The actual degree of reduction in odour intensity was not determined because the techniques recommended to measure odour intensity are complex, subjective, time consuming and could not feasibly be used within the time frame of this study. Quantification of odours will be addressed in future studies.

SBRs 1, 2, 3 and 4 in test run No. 6 had very low energy recovery and reduction in SCOD. These SBRs were started-up in test run 5 and their organic loading rate was doubled in test run 6. This large increase in organic loading rate might have caused their total failure.

The anaerobic sludge had excellent settling characteristics. In SBRs that were not mixed, a clear interface between the liquid and sludge bed zones started to occur near the end of the react period. At the end of the react period where the biogas production was very low the demarcation between the liquid and solids was even more evident. A thick layer of sludge was observable at the bottom of the digesters. In the

SBRs that were intermittently mixed there were no distinctive supernatant and sludge zones. For these SBRs, when mixing was stopped at the end of react period, it would take about 2 to 6 hours for a zone settling or liquid/solids interface to form and another 24 to 48 hrs for the sludge blanket to completely settle to the bottom of the SBR. Therefore the SBR provides excellent settling conditions to retain the slow growing microorganisms when the settling period is long enough.

4.7 Hydrogen gas concentration in SBR

Concentration of hydrogen was measured in both liquid and gas phases in digester 11 during test run 6, Cycle 3 and 4, and also in digester 10 during test run 7. Technical problems were experienced with the hydrogen measuring equipment (liquid and gas pumps as well as hydrogen cell) during test run 6. In test run 7, both hydrogen monitors were operated without any problems and complete sets of data for hydrogen concentrations in liquid and gas phases were obtained. Figure 4.27 illustrates the variation in dissolved and gaseous hydrogen concentrations over an operating cycle. SBR 10 was fed 66 g of COD (8.8 g COD/L) at the beginning of the cycle. Immediately after feeding, both concentration of dissolved and gaseous hydrogen increased rapidly until they reached maximum values and thereafter they started to decrease continuously. The dissolved hydrogen concentration reached a maximum after

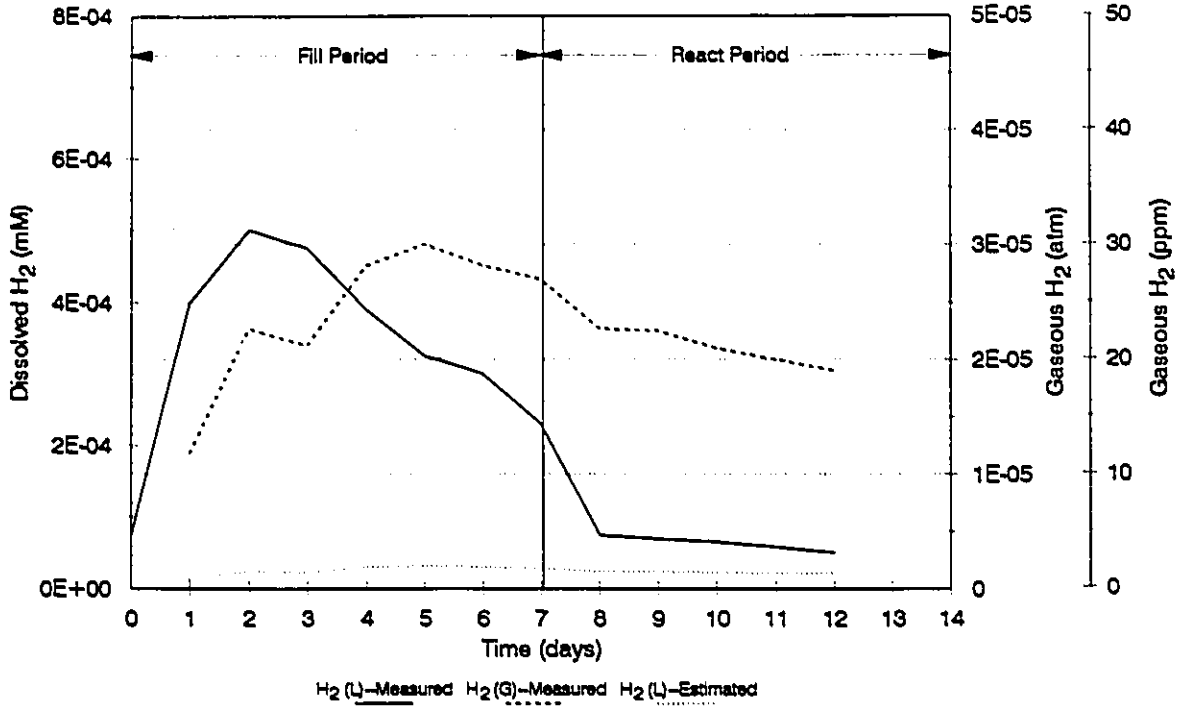


Fig. 4.27 Dissolved and gaseous hydrogen concentration in SBR 10, (test run 7). SBRs fed 66g. COD at the beginning of the cycle.

two days while the gaseous hydrogen concentration reached a maximum after five days. The rate of reduction in dissolved hydrogen concentration is substantially greater than the rate of reduction of hydrogen concentration in the gas phase.

Hydrogen concentration in the liquid phase depends mainly on biological activity and transfer rate, while the hydrogen concentration in gas phase depends on transfer rate as well as the rate of discharge of hydrogen with the biogas. Because there is a transfer limitation for the hydrogen gas at the gas and liquid interfaces, the hydrogen concentration reduction in the gas phase is mainly due to its rate of discharge with the biogas. The latter explained why at the end of the react period when the biogas production was low, the rate of reduction in hydrogen concentration in gas phase was also low. These results indicate that the responses or accumulation pattern of gaseous and dissolved hydrogen as a function of time are substantially different in a non-mixed SBR operated at 20°C.

Based on these results the hydrogen concentration in gas phase might not be an acceptable parameter to control or monitor the response of a non-mixed SBR. For a non-mixed system, the dissolved hydrogen concentration should be a more appropriate parameter to control and monitor the stability of an SBR. This is mainly because it indicates the actual concentration

of hydrogen to which the micro-organisms are actually exposed. Mosey (1983) and Rozzi et al. (1985) indicated that hydrogen gas concentration has a direct effect on the accumulation of individual VA in an anaerobic digester. They assumed that the hydrogen gas transfer rate between the liquid and gas phase was not limited. Based on this assumption, the partial pressure of hydrogen in gas phase and the Henry's constant for hydrogen were used to calculate the dissolved hydrogen concentration which is also shown in Figure 4.27 (indicated as estimated concentration). The estimated dissolved hydrogen concentration were 10 to 40 times lower than the actual concentrations. Pauss et al. (1990) obtained similar results and suggested that there is a hydrogen transfer limitation in anaerobic digesters.

Figure 4.28 shows the relative accumulation of dissolved hydrogen, acetic, propionic and butyric acids in the SBR over an operating cycle. The concentration of the individual VA increased rapidly just after feeding, acetic, butyric and propionic increased continuously for a period of two, four and one days respectively after feeding. Acetic and butyric acid concentrations started to decrease even when the dissolved hydrogen concentration was high. Acetic acid is decarboxylised to produce methane and carbon dioxide per Eq. (2.6); hydrogen gas is not involved. Therefore the increase in dissolved hydrogen was not expected to affect the

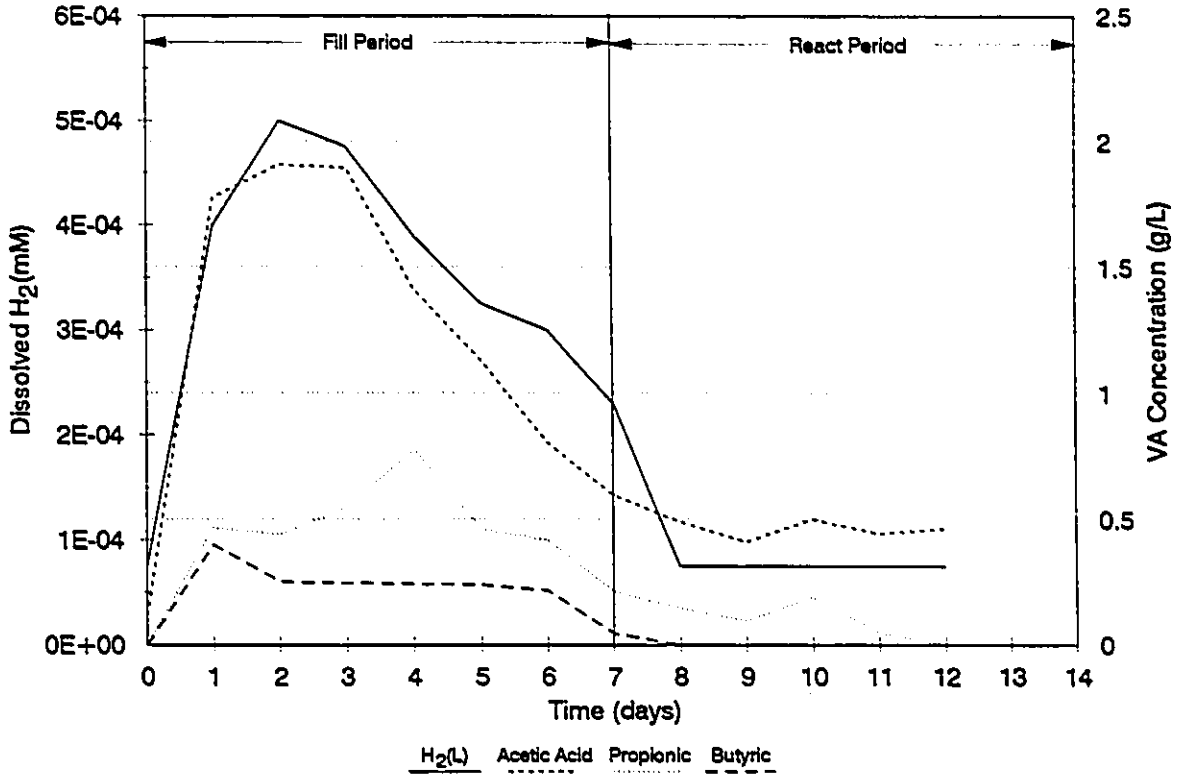


Fig. 4.28 Hydrogen and volatile acids accumulation in SBR 10, (test run 7). SBRs fed 66g. COD at the beginning of the cycle.

utilization rate of acetic acid. Propionic and butyric acids are converted to acetic acid and other intermediate products according to Egs. (2.4) and (2.5) respectively. Hydrogen gas is produced by both reactions. For these reactions to be thermodynamically feasible the dissolved concentration of hydrogen gas in the liquid phase must be very small. Harper and Pohland (1986) indicated than when the dissolved concentration of hydrogen exceeds 0.04 μM the utilization of propionic acid is not thermodynamically possible. Utilization of butyric acid will also cease when the hydrogen concentration exceeds 0.4 μM. These threshold values for hydrogen are functions of the environmental conditions in the anaerobic digester. The hydrogen gas threshold values were reevaluated for the environmental conditions of the SBR's used in this study. It was found that the utilization of propionic and butyric acids was not thermodynamically possible when the hydrogen gas concentration exceeded 0.1 and 1.0 μM respectively. Therefore the continuous utilization of butyric acid was expected in test 7. Figure 4.28 indicates that propionic acid was utilized by the acid formers even when it did not seem to be thermodynamically possible (when the dissolved hydrogen concentration exceeded 0.1 μM). This phenomenon was also observed by Pauss et al. (1989). They concluded that trophic microniche structures are present in digesters. This symbiotic association of microorganisms lowers the hydrogen gas concentration in the immediate

surroundings of the acid formers. As a result the transformation of propionic acid inside an acid forming bacteria becomes thermodynamically possible.

4.8 Mass transfer coefficient for H_2 gas

Experimental data in this study indicated that dissolved hydrogen and gaseous hydrogen are not in equilibrium. Therefore a mass transfer coefficient should be used to relate hydrogen gas concentration in liquid and gas phases.

The hydrogen mass transfer coefficient was determined by using the procedure described in section 2.4.1 and the experimental results obtained in this study. The mass transfer coefficient for H_2 in a non-mixed system was evaluated for each day of SBR operation. The experimental value of Kla_{H2} determined with Eq. (2.98) ranged between 0.18 to 0.70 d^{-1}.

4.9 Mass transfer coefficient for CO_2 Gas

The carbon dioxide mass transfer coefficient was determined by using the methodology discussed in section 2.4.2. The mass transfer coefficient for carbon dioxide in the non-mixed SBR was also estimated for each day of operation. It ranged between 0.25 and 0.50 d^{-1}. The mass transfer coefficient for CO_2 in this study for a non-mixed SBR operated at 20°C is very small when compared to literature values that range between 10 d^{-1} (Hill and Barth, 1977) and 100 d^{-1} (Andrews and Graef

1971). The low values for the hydrogen and carbon dioxide mass transfer coefficients could be due to the absence of mechanical mixing. The mass transfer coefficient for ammonia was not determined because of the lack of equipment. Based on the fact that the mass transfer coefficients for hydrogen and carbon dioxide in a non-mixed SBR were less than 1.0, it is probably reasonable to assume that the mass transfer coefficient for ammonia is also less than 1.0.

CHAPTER 5

ACCURACY OF MODELS

5.1 Simple Model Accuracy

This section examines the adequacy of the simple model in predicting the dynamic behaviour of the PAD of swine manure slurry in SBR. Experimental data from digesters 11 and 12 test run 5 (cycle length of 56 days) and digesters 5 and 6 test run 6 cycle 1 and 2 (cycle length of 28 days) were used to assess the accuracy of the simple model prediction. The operating conditions for these experimental runs are given in Table 3.1. The parameters used in this evaluation were VA, soluble chemical oxygen demand and methane flow rate.

The model biological kinetic constants obtained from the literature (Droste and Kennedy, 1988 and O'Rourke, 1968) are given in Table 5.1. These kinetic constants were used in the initial simulation run of Test 5, SBRs 11-12. They were adjusted after each simulation run to improve the model prediction. Table 5.2 gives the range of values considered in

the simulation runs for each kinetic constant. After each simulation run, the error of estimate (EE) and the percent error of estimate (PEE) were calculated to quantify the errors between predicted and measured values for soluble COD utilization, VA accumulation and methane production. The EE and PEE values were calculated according to Eqs (5.1) and (5.2). The biological kinetic constants were manipulated until minimum values were obtained for EE and PEE. The biological parameters that had the largest influence on the model prediction were the substrate utilization rates of the acid and methane formers.

$$EE = \sqrt{\frac{\Sigma(Calculated\ Value_i - Experimental\ Value_i)^2}{N}} \qquad (5.1)$$

$$PEE = \left(\frac{EE}{\frac{\Sigma(Experimental\ Value_i}{N}} \right) * 100 \qquad (5.2)$$

where:

EE = error of estimate

PEE = percent error of estimate

N = number of estimates

i = day number

Table 5.1. Initial Values of Biological Kinetic Constants Used in the Simple Model

	RANGE	
Constants	Acidogens	Methanogens
$Vmax_i$, mg/mg-d	0.4*	1.0*
Ks, mg/L	800*	200*
Y_i, mg/mg	0.12*	0.05*
k_{di}, d^{-1}	0.025*	0.025*
Kp, d^{-1}	0.05**	

* from Droste and Kennedy, (1988)

** from O'Rourke, (1968)

Table 5.2. Range of Values Considered for each Kinetic Constant.

	RANGE	
Constants	Acidogens	Methanogens
$Vmax_i$, mg/mg-d	0.1-0.80	0.1 - 1.4
Ks, mg/L	100-2500	500-3000
Y_i, mg/mg	0.05-0.25	0.01-0.20
k_{di}, d^{-1}	0.0005-0.04	0.0005-0.04
Kp, d^{-1}	0.01-0.08	

The yield factors for the acidogens and methanogens that provided the best fit were 0.1 and 0.05 mg/mg respectively. The other kinetic constants that provided the best fit are presented as part of Figures 5.1, 5.2 and 5.3. Some of these kinetic constants are different for each test run. Table 5.3 gives the lowest percent error of estimate (PEE) obtained for the kinetic constants that provided the best fit in each test run. The PEE values for VA, SCOD and Q_{CH4} are similar and within a reasonable range. These differences between measured and predicted parameters were expected. In this study it was not possible to determine the relative contributions to the errors between the measured and predicted values due to the simple model limitations, sludge acclimation or different operating conditions. Independent sets of experimental data would be required to clarify this.

Table 5.3. PEE for the Final Values of Kinetic Constant Used with the Simple Model

PEE			
Parameter	Test Run 5 Digesters 11-12	Test Run 6 Digester 5-6 Cycle 1	Test Run 6 Digester 5-6 Cycle 2
VA	37	20	23
SCOD	37	12	34
Q_{CH4}	27	30	28

Figures 5.1 to 5.3 compare the calculated and measured concentrations of VA, SCOD and Q_{CH4} as a function of time. These figures show that the simple model only predicted the general trend in methane production as well as VA and SCOD accumulations during the fill react periods.

5.2 Advanced Model Acceptability

The measured pH ranged from 7.4 to 7.8 during PAD of swine manure slurry in SBR. Clark and Speece (1971), indicated that there is no important pH effect on anaerobic process when the pH ranges between 6.0 to 8.0. The experimental results also indicated that: 1) there is in an important gas transfer limitation from the liquid to the gas phase for H_2 and CO_2; and 2) PAD in SBR was not affected by high concentrations of ammonia nitrogen and VAs. The experimental results in this study also strongly suggest the presence of both groups of acetoclastic methanogens. In some test runs the maximum concentration of acetic acid reached 6000 mg/L at the end of fill period and at the end of the treatment cycle the acetic acid concentration in some SBRs was less than 12 mg/L. Therefore assumptions 7, 11, 16, and 21 made in the development of the advanced model (Sec. 2.3.5.1) are validated by these experimental results.

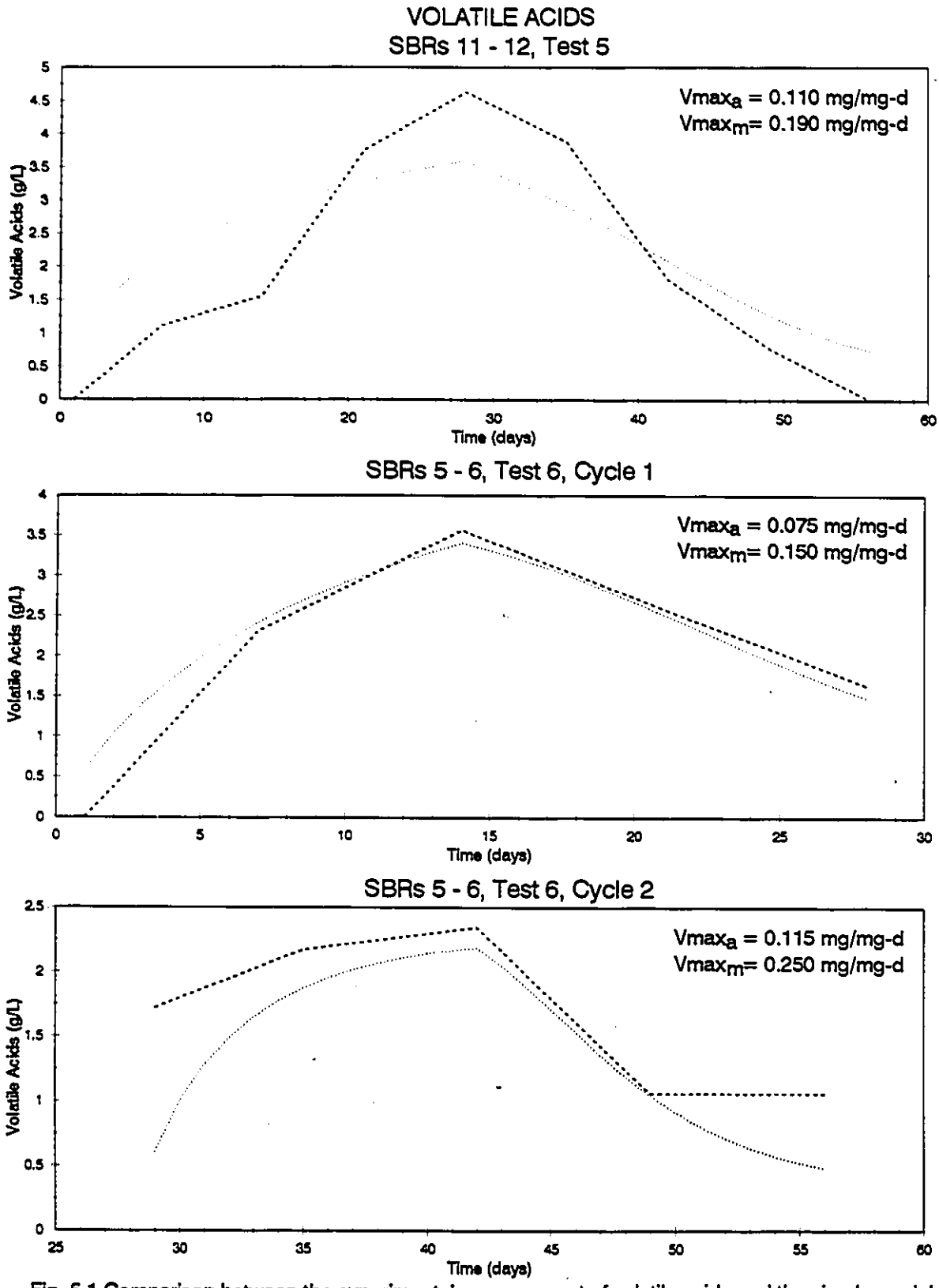


Fig. 5.1 Comparison between the experimental measurement of volatile acids and the simple model prediction, Ksa = 1500 mg/L, Ksm = 2500 mg/L, Kp = 0.04 d^{-1}, kdi = 0.001 d^{-1}, ------ Measured, ... Simple model prediction.

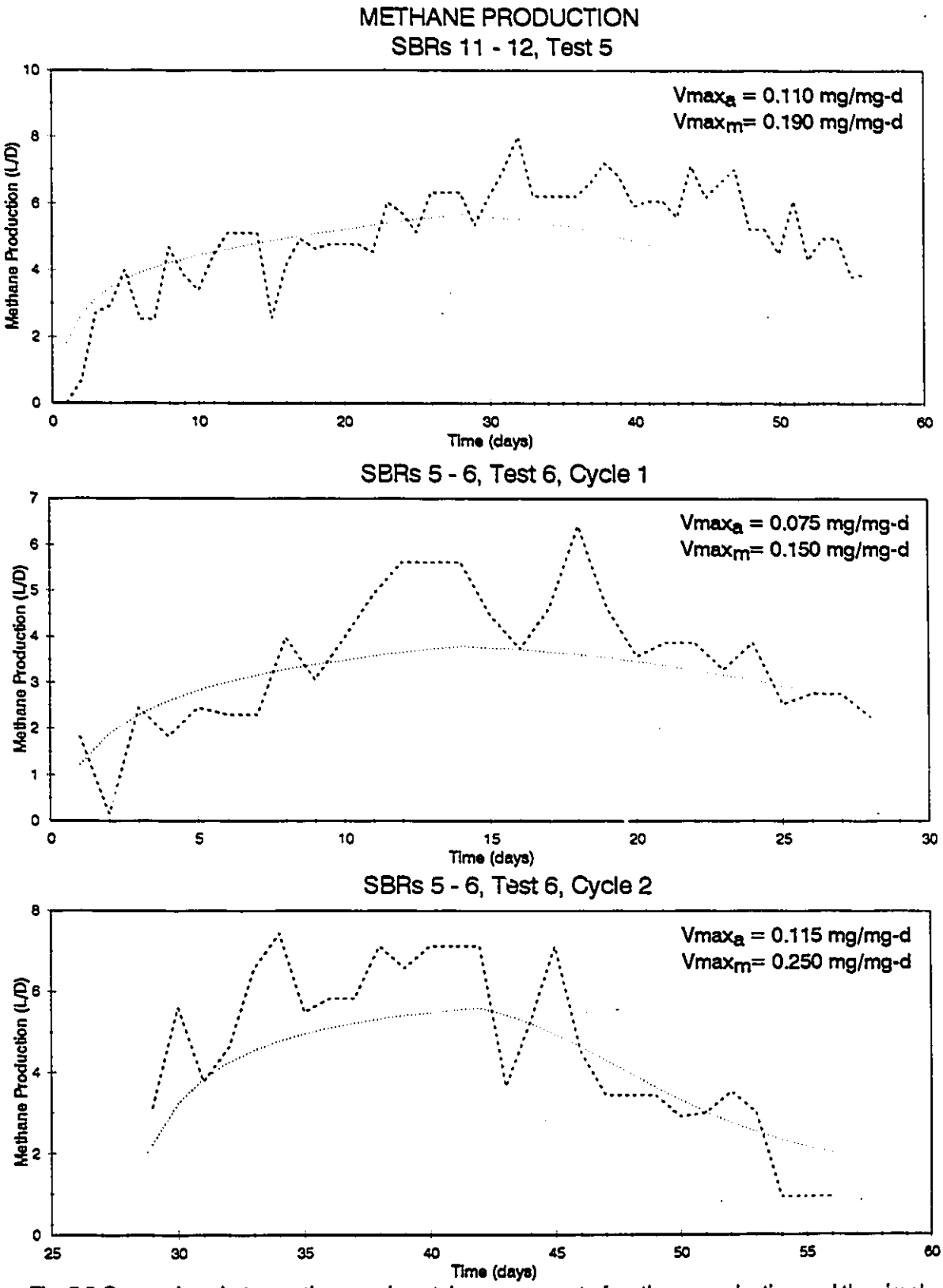


Fig. 5.2 Comparison between the experimental measurement of methane production and the simple model prediction, Ksa = 1500 mg/L, Ksm = 2500 mg/L, Kp = 0.04 d^{-1}, kdi = 0.001 d^{-1}, ------ Measured, ... Simple model prediction.

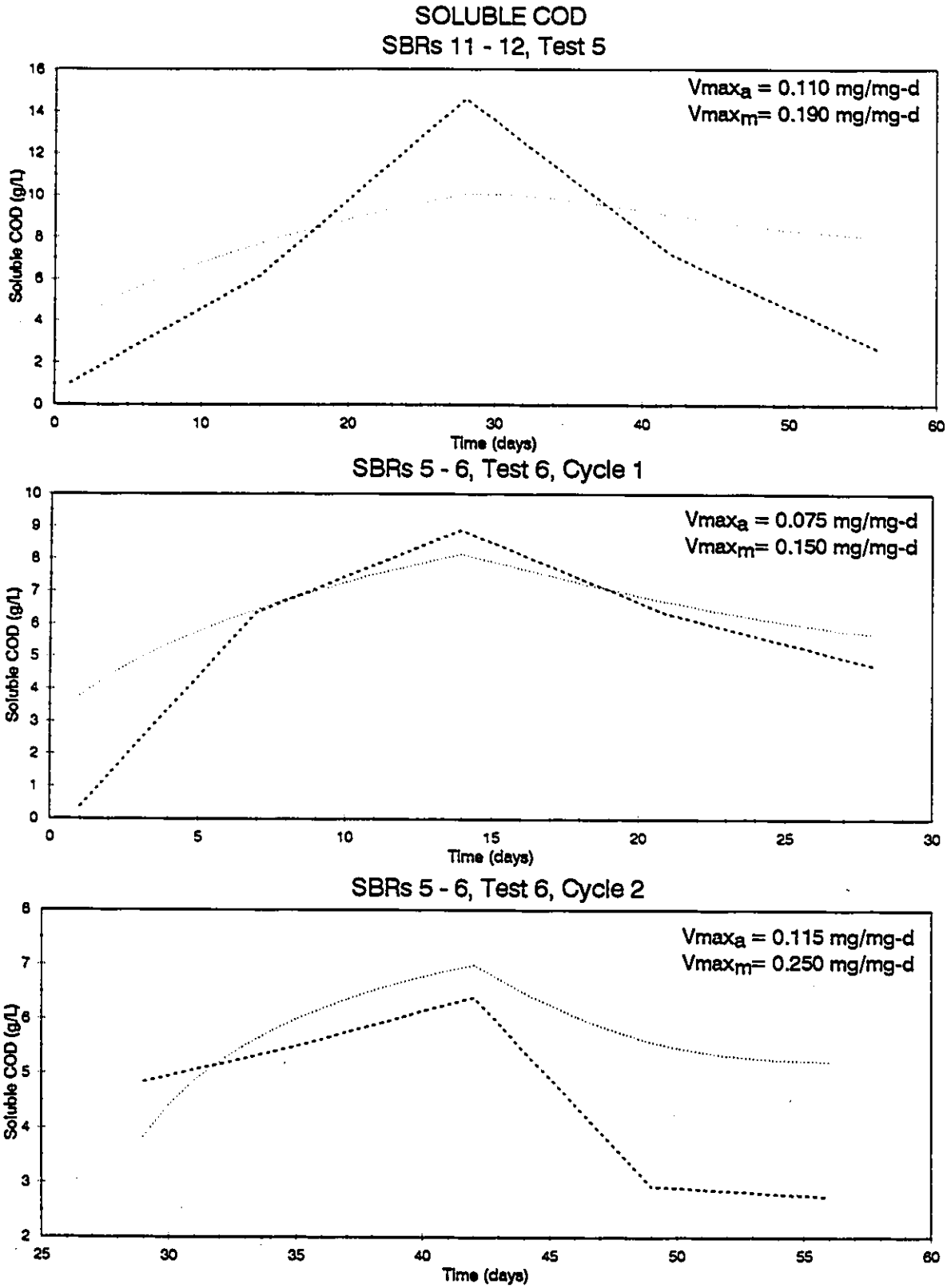


Fig. 5.3 Comparison between the experimental measurement of soluble COD and the simple model prediction, Ksa = 1500 mg/L, Ksm = 2500 mg/L, Kp = 0.04 d^{-1}, kdi = 0.001 d^{-1}, ····· Measured, ····· Simple model prediction.

The most important assumption (assumption 5) made in the development of the advanced model is based on Mosey's (1983) research work. This assumption assumed that P_{H2} is representative of the hydrogen gas concentration in the immediate surroundings of the bacteria. Therefore this assumption would be valid only if it meets the following conditions: 1) the accumulation pattern of hydrogen in the gas phase is identical to the accumulation pattern of the dissolved hydrogen; 2) the gaseous hydrogen diffuses both freely and rapidly into and out of the liquid phase; and 3) the partial pressure of hydrogen in gas phase is directly related to the dissolved concentration of hydrogen.

These conditions were not supported by the experimental results obtained in this study on PAD of swine manure slurry in non-mixed SBRs. Condition one was not met because the measured accumulation patterns of hydrogen gas in liquid and gas phase were totally different. Also conditions two and three were not met because the experimental results clearly indicate that there is a limitation in H_2 and CO_2 transfer from the liquid to the gaseous phase.

In order to model accurately PAD in SBR, it would be preferable that hydrogen regulation factors are based on the actual concentration (dissolved) of hydrogen in the immediate surroundings of the bacteria.

In this model as in Mosey's (1983) model, it is assumed that H_2 moves freely in and out of the cell and that the dissolved concentration of hydrogen in the cell is equal to the dissolved concentration of hydrogen in the surrounding media. Using an approach similar to Mosey's (1983) approach, the oxidation state of the NAD carrier molecule was related to the concentration of dissolved hydrogen in the liquid phase. This relationship is given in Eq. (5.3).

$$r = \frac{[NADH]}{[NAD^+]} = 1800\ [H_2] \qquad (5.3)$$

where:

r = ratio of reduced to oxidized carrier molecule

NADH = concentration of reduced carrier molecule

NAD^+ = concentration of oxidized carrier molecule

$[H_2]$ = dissolved hydrogen concentration, mM

Eq. (5.3) can now be substituted in Eqs. (2.15) to (2.19) to calculate the new hydrogen regulation factors for the individual VA production and utilization.

5.3 Advanced Model Kinetic Constants

The modified advanced model makes use of a large number of biological kinetic and physico-chemical constants. Most of these constants were obtained from the literature and some were determined experimentally.

5.3.1. Experimental Determination of VA Utilization Kinetics

Kinetic experiments were carried out in 3-litre batch reactors at a constant temperature of 20°C to determine the utilization rate of individual VAs. The concentration of VSS in the batch reactors was around 8000 mg/L. Acetic, propionic and butyric acids were fed to separate bottles to obtain initial concentrations of 2500, 2000 and 2000 mg/L respectively. Figures 5.4, 5.5, and 5.6 give the concentrations of the individual VAs as a function of time. The measured initial concentrations were slightly lower than expected. The measured concentrations were 2300, 1800 and 1750 mg/L for acetic, propionic and butyric acids respectively. The lower initial concentration as well as the rapid reduction in VAs at the beginning of the test should be due mainly to absorption phenomena. From the point where these VAs decreased steadily their removal was due to biological activity. It was assumed that the VAs utilization rate followed Monod kinetics.

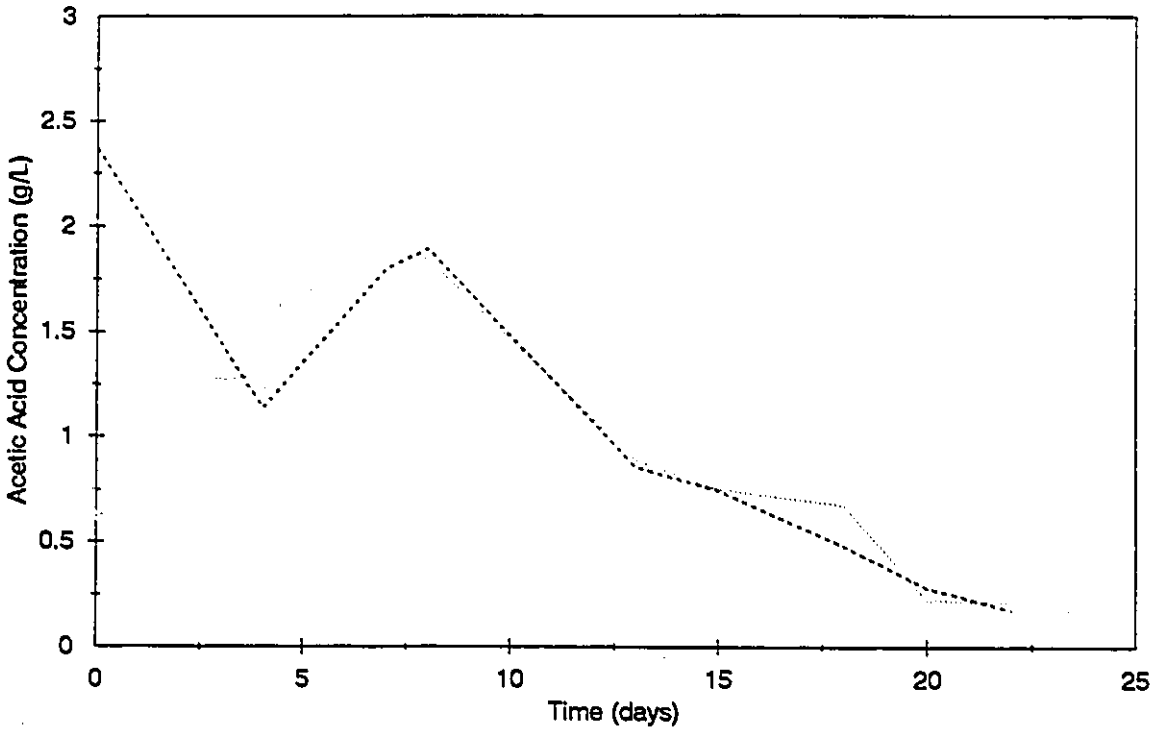


Fig. 5.4 Kinetic tests for acetic acid utilization rate. ------- test 1, ... test 2.

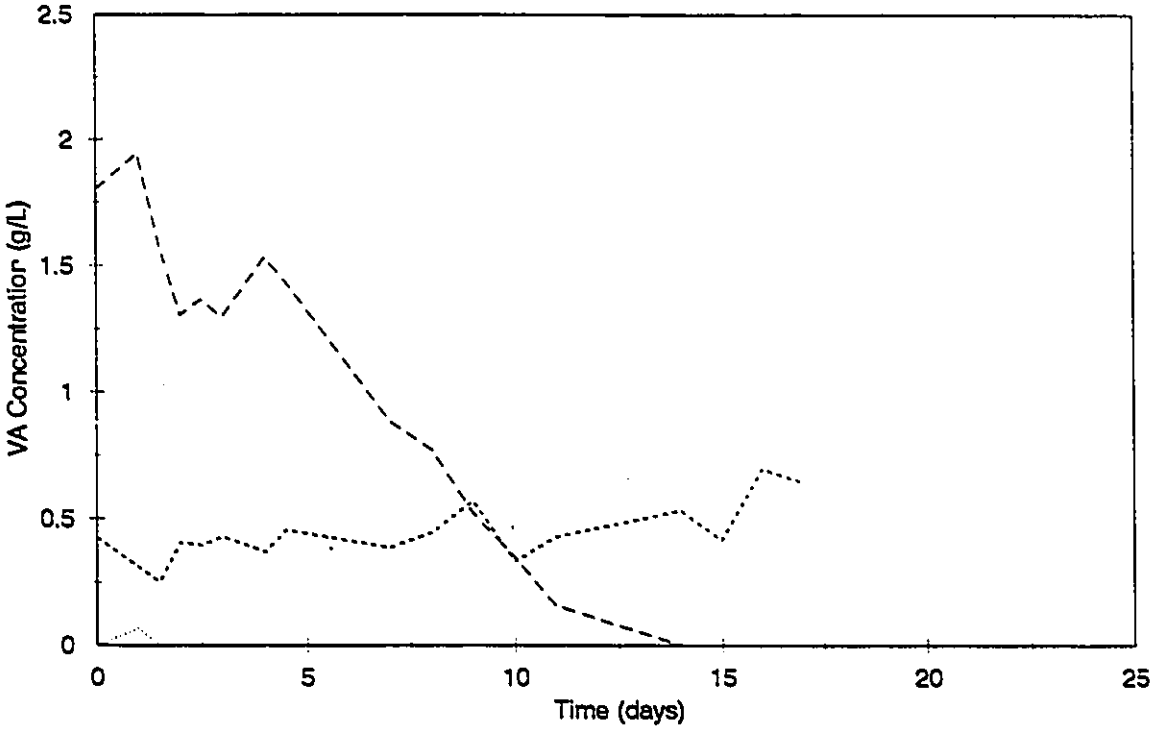


Fig. 5.5 Kinetic test for propionic acid utilization rate. (------- acetic, ... butyric, - - - - propionic).

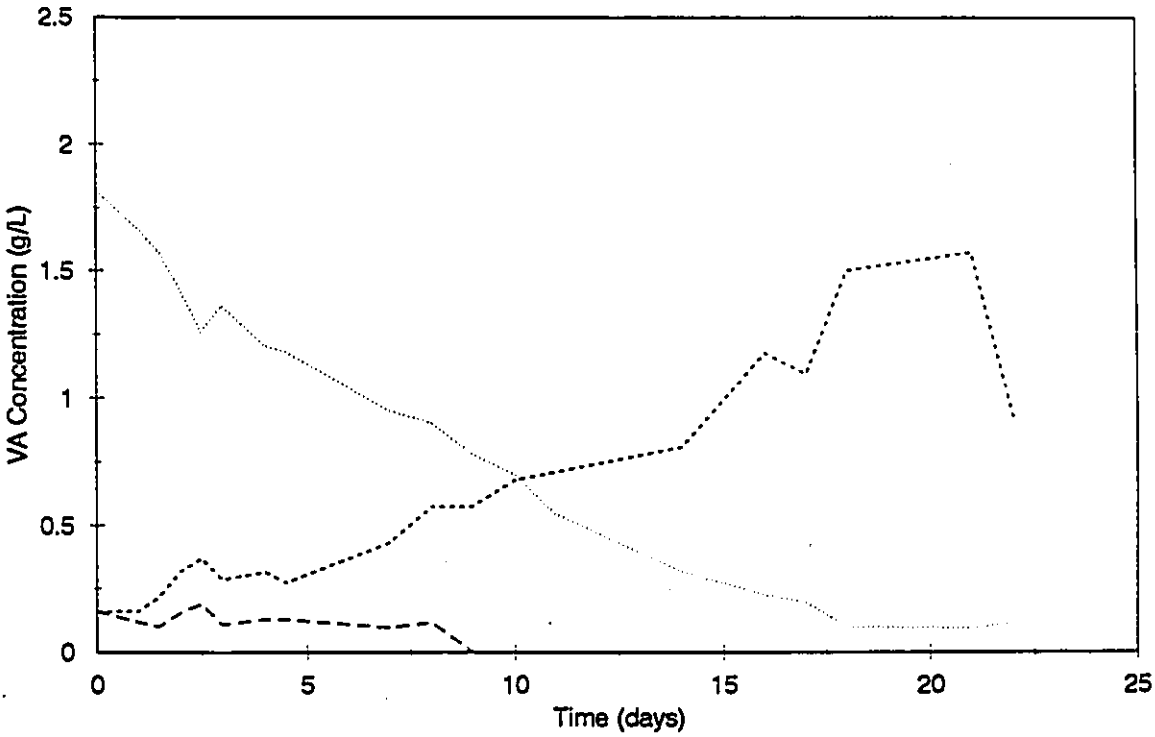


Fig. 5.6 Kinetic test for butyric acid utilization rate. (------- acetic, ... butyric, - - - - propionic).

$$\frac{dVA_i}{dt} = \frac{Vmax_i \, X_i \, VA_i}{K_{si} + VA_i} \qquad (5.4)$$

where:

$Vmax_i$ = maximum specific substrate utilization rate, mmol/mg-d

X_i = bacteria concentration, mg/L

VA_i = individual VA concentration, mM

K_{si} = saturation constant, mM

In order to determine the biological kinetic parameters $Vmax_i$ and K_{si} the exact concentration of the respective group of bacteria using the individual VA must be known. In this study the total and individual populations of bacteria were not known and could not be characterized accurately. Therefore the kinetic constants $Vmax_i$ and K_{si} could not be determined accurately.

Because the SBRs contained mixed cultures of bacteria as well as particulate organics a modified Monod kinetic expression was developed to determine the VAs utilization kinetics. This was made possible by defining a constant that combined the concentration of a group of bacteria with their corresponding maximum specific substrate utilization rate. The kinetics of VA utilization can now be determined by using the following expression.

$$\frac{dVA_i}{dt} = \frac{a_i S}{K_s + S} \qquad (5.5)$$

where:

$a_i = Vmax_i \; X_i$

The modified Monod expressions were rearranged and fitted to the experimental data.

$$\frac{dt}{dV_{A_i}} = \frac{K_S}{a_i}\frac{1}{S} + \frac{1}{a_i} \qquad (5.6)$$

The kinetic parameters for acetic, propionic and butyric acids were determined by a linear least-squares regression. They are listed in Table 5.4. As shown in that table the correlation coefficients for propionic and particularly butyric acids were rather low.

Table 5.4 Values of VA utilization kinetic constants.

Volatile Acids	Concentration range mM/L	a mM/d	K_s mM	Correlation Coefficient
Acetic	45.0 - 12.0 10.2 - 2.0	9.00 5.53	75.2 18.9	0.80 0.97
Propionic	28.0 - 4.0	3.48	7.9	0.76
Butyric	20.6 - 1.10	1.45	3.6	0.30

The substrate utilization rate constant 'a' is directly proportional to the population of microorganisms. This kinetic constant was adjusted to take into account the larger VSS concentration in the SBRs. The adjusted values are given in Table 5.5.

5.3.2 Kinetic Constants Obtained From the Literature

Other biological kinetic parameters and physico-chemical constants were required by the model. They were obtained from the literature, Gujer and Zehnder (1983), Merlini (1983) and Mosey (1983), Hill and Barth, (1977), and Perry and Chilton, (1973). These constants are listed in Tables 5.5 and 5.6.

5.4 Advanced Model Accuracy

As indicated earlier the startup run 4 was not considered in the simulation because of sludge acclimatization. Experimental runs 5 (SBRs 11-12), 6 (SBRs 5-6, cycle 1), 6 (SBRs 11-12, cycle 3) and 6 (SBRs 11-12, cycle 4) were simulated with the advanced model. Experimental run 5 was simulated to make comparisons with the simple model predictions and Test run 6 (SBRs 11-12, cycles 2 and 3) were selected because they were the only experimental runs where gaseous and dissolved hydrogen concentrations were measured. These runs were useful to validate the advanced model in predicting the accumulation of both gas and liquid phase hydrogen concentrations.

Table 5.5 Biological kinetic constants used in the initial simulation runs.

Parameter		Value
B_{inf}	0.75	*
K_d (d^{-1})	0.04	Gujer and Zehnder, 1983
Vo(l)	7.5	*
Vmaxc-Xc, (mM/d)	20.0	**
Ksc (mM)	12.0	**
YAc, (mg X/mmol of S to AC)	40.0	Mosey, 1983
YPr, (mg X/mmol of S to Pr)	20.0	Mosey, 1983
YBu, (mg X/mmol of S to Bu)	20.0	Mosey, 1983
Yc (mmol of X/mg S)	7.374×10^{-3}	***
Kda (d^{-1})	0.006	**
VmaxPr-XPr, (mM/d)	10.5	*
KsPr, (mM)	7.9	*
Ypp, (mg X/mmol of P_r to Ac)	10.0	Mosey, 1983
YP, (mmol Pr/mg X)	13.27×10^{-3}	***
KdPr, (d^{-1})	0.001	**
VmaxBu-XBu, (mM/d)	4.50	*
KsBu, (mM)	3.6	*
Ybb, (mg X /mmol of B_u to Ac)	20.0	Mosey, 1983
YB, (mmol Bu/mg X)	8.849×10^{-3}	***
KdBu, (d^{-1})	0.008	**
VmaxAc1-XAc1, (mM/d)	15.0	*
KsAc1, (mM)	18.9	*
Yaa1, (mg X/mmol of A_c to CH4)	2.5	Mosey, 1983
Ya1, (mmol Ac/mg X)	22.12×10^{-3}	***
Kdac1, (d^{-1})	0.008	**
VmaxAc2-XAC2 (mM/d)	25.0	*
KsAc2, (mM)	75.2	*
Yaa2, (mg X/mmol of A_c to CH4)	2.5	Mosey, 1983
Ya2, (mmol Ac/mg X)	22.12×10^{-3}	***
KdAc2, (d^{-1})	0.005	**
VmaxH2-XH2 (mM/d)	50.75	**
KsH2, (mM)	0.001	Costello et al. 1991
Yhh2, (mg X/mmol of H2 to CH4)	2.5	Mosey, 1983
Yh2, (mmol H2/mg X)	8.84×10^{-2}	***
KdH2, (d^{-1})	0.09	Costello et al. 1991
YprCO2, (mmol CO2/mg X_{pr})	4.42×10^{-3}	***
YBuCO2, (mmol CO2/mg X_{bu})	8.84×10^{-3}	***
YH2CO2, (mmol CO2/mg X_{ac})	4.42×10^{-3}	***

* constants determined experimentally in this study
** constants estimated from simple model simulation results and literatures
*** constants derived from stoichiometry of bacteria synthesis

Table 5.6 Physico-chemical constants used in the advanced model simulations.

Parameters	Value	Reference
Ka1	$10^{-6.33}$	Snoeyink and Jenkins, 1980
K_{a2}	$10^{-10.34}$	Snoeyink and Jenkins, 1980
K_{NH4}	$10^{-9.2}$	Hill and Barth, 1977
Ka_{Ac}	2×10^{-5}	Merlini, 1983
Ka_{Pr}	2×10^{-5}	Merlini, 1983
Ka_{Bu}	2×10^{-5}	Merlini, 1983
KH_{H2}, mM/atm-L	1.0729	Pauss et al. 1990
KH_{CO2}, mM/atm-L	34.35	Hill and Barth, 1977
KH_{NH3}, mM/atm-L	5.39	Hill and Barth, 1977
Kla_{H2}, (d^{-1})	0.50	*
KlaCO2, (d^{-1})	0.60	*
KlaNH3, (d^{-1})	0.10	**
Gas Standard Volume, 20°C, L	24.06	Perry and Chilton, 1973
Total Biogas Pressure, atm	1.0147	*

* value experimentally determined in this study.
** value estimated for the actual SBR's environmental conditions

The physico-chemical constants listed in Table 5.6 were used in all the simulation runs. The biological kinetic constants listed in Table 5.5 were only used as initial values for the first simulation run of SBRs 11-12 in Test 5. After each simulation run the EE and PEE were calculated to evaluate the error between the measured and predicted values for: 1) soluble carbohydrate utilization; 2) acetic, propionic and butyric acid accumulations, and dissolved hydrogen and gas

phase hydrogen accumulations; and 3) methane production. The specific substrate utilization rates were adjusted until minimum values were obtained for EE and PEE. The biological constants that provided the best-fit for SBRs 11-12, Test 5 were used in the initial simulation run for SBRs 5-6, Test 6. This approach was also used for subsequent tests.

The kinetic constants that gave the best fit were slightly different for each run investigated. The ranges observed for some biological parameters are given in Table 5.7. The biological kinetic constant that had the largest influence on the predictions of the advanced model was the maximum specific dissolved hydrogen utilization rate. A small variation in this kinetic constant had a major effect on the model predictions. Other parameters that had a significant effect on the advanced model predictions were, in order of importance, the specific utilization rates of carbohydrates, acetic, and propionic acids. Changes in the specific utilization rate of butyric acid did not have an important effect on the advanced model predictions. This is because the concentration of butyric acid was always small compared to the concentration of soluble COD, acetic and propionic acids.

TABLE 5.7 Range of Biological Constants that provided the best prediction.

Constants	SBRs 11-12 Test 5	SBRs 5-6 Test 6 Cycle 1	SBRs 11-12 Test 6 Cycle 3	SBRs 11-12 Test 6 Cycle 4
$Vmax_C \cdot X_c$, (mM/d)	10.0	13.0	13.0	15.0
K_{sC}, (mM)	9.4	9.4	9.4	9.4
$Vmax_{Pr} \cdot X_{Pr}$, (mM/d)	9.0	4.0	9.0	14.0
K_{sPr}, (mM)	9.0	9.0	9.0	9.0
$Vmax_{Bu} \cdot X_{Bu}$, (mM/d)	11.0	12.0	15.0	15.0
K_{sBu}, (mM)	4.0	4.0	4.0	4.0
$Vmax_{Ac1} \cdot X_{Ac1}$, (mM/d)	2.5	3.0	2.5	3.0
K_{sAc1}, (mM)	1.0	1.0	1.0	1.0
$Vmax_{Ac2} \cdot X_{Ac2}$, (mM/d)	6.0	8.0	12.0	14.0
K_{sAc2}, (mM)	20.0	20.0	20.0	20.0
$Vmax_{H2} \cdot X_{H2}$, (mM/d)	20.0	20.0	20.0	20.0
K_{sH2}, (mM)	0.0005	0.0005	0.0005	0.0005

Table 5.8 gives the percent error of estimates for the major variables measured and considered in the advanced model prediction. As shown in Table 5.8 the model prediction improved with sludge age. The PEE values for SCOD and VAs were large for Test run 5, SBRs 11-12 and test 6, SBRs 5-6. The model predictions were not very good for these tests because of the ongoing sludge acclimation and long feed and react periods. The PEE values were substantially lower for Test 6, Cycles 3 and 4. The better accuracy is likely due to the more stable bacterial sludge.

TABLE 5.8 Lowest Percent Error of Estimates Obtained During the Simulation.

Test No.	PEE			
	SCOD	Ac	Pr	QCH4
Test 5, Digester 11-12	60	48	33	29
Test 6, Digester 5-6 Cycle 1	80	37	30	33
Test 6, Digester 11-12 Cycle 3	21	29	7	23
Test 6, Digester 11-12 Cycle 4	26	18	17	27

The PEE obtained with the advanced model are very reasonable when considering that: 1) the advanced model is based on several assumptions; and 2) that most of the biological and physico-chemical constants required by the advanced model were not evaluated experimentally for the actual experimental conditions, they were instead obtained from the literature for digesters with a high level of mixing and different operating conditions.

Figures 5.7 to 5.13 compare the predicted and measured concentration of acetic, propionic and butyric acids, SCOD, dissolved and gas phase hydrogen as well as the production of methane.

Figures 5.7 to 5.10 show that the advanced model simulations were in good agreement with experimental results for Tests 6, Cycles 3 and 4. For these test run the model predicted well the trend in SCOD, acetic and propionic acids accumulation in the SBR.

Figure 5.11 compares the measured and predicted methane production. The large fluctuation in measured methane production was caused by changes in atmospheric pressure. The advanced model did predict reasonably the highly variable experimental methane production.

Figures 5.12 and 5.13 compare the measured and predicted dissolved and gas phase hydrogen concentrations respectively. The model predicted reasonably well the trend in accumulation of dissolved hydrogen. For the partial pressure of H_2 in the gas phase only the order of magnitude is predicted.

This advanced model represents an interesting tool to extend the knowledge of PAD in SBR, because it considers the interaction among the different microorganisms as well as the interaction between the biological, physico-chemical and gas phases.

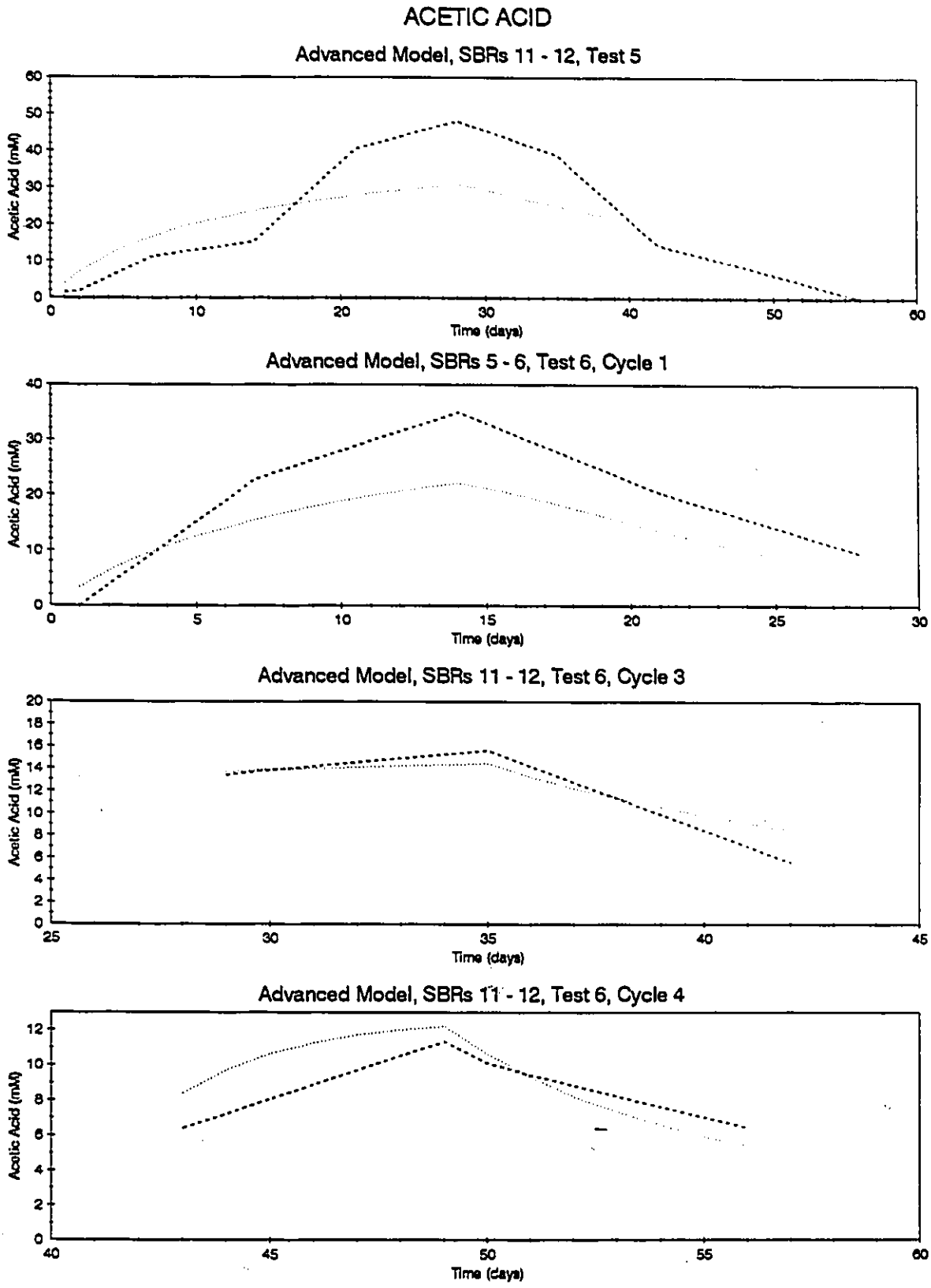


Fig. 5.7 Comparison between the measured and predicted acetic acid concentrations.
----- Measured, ... Advanced model prediction.

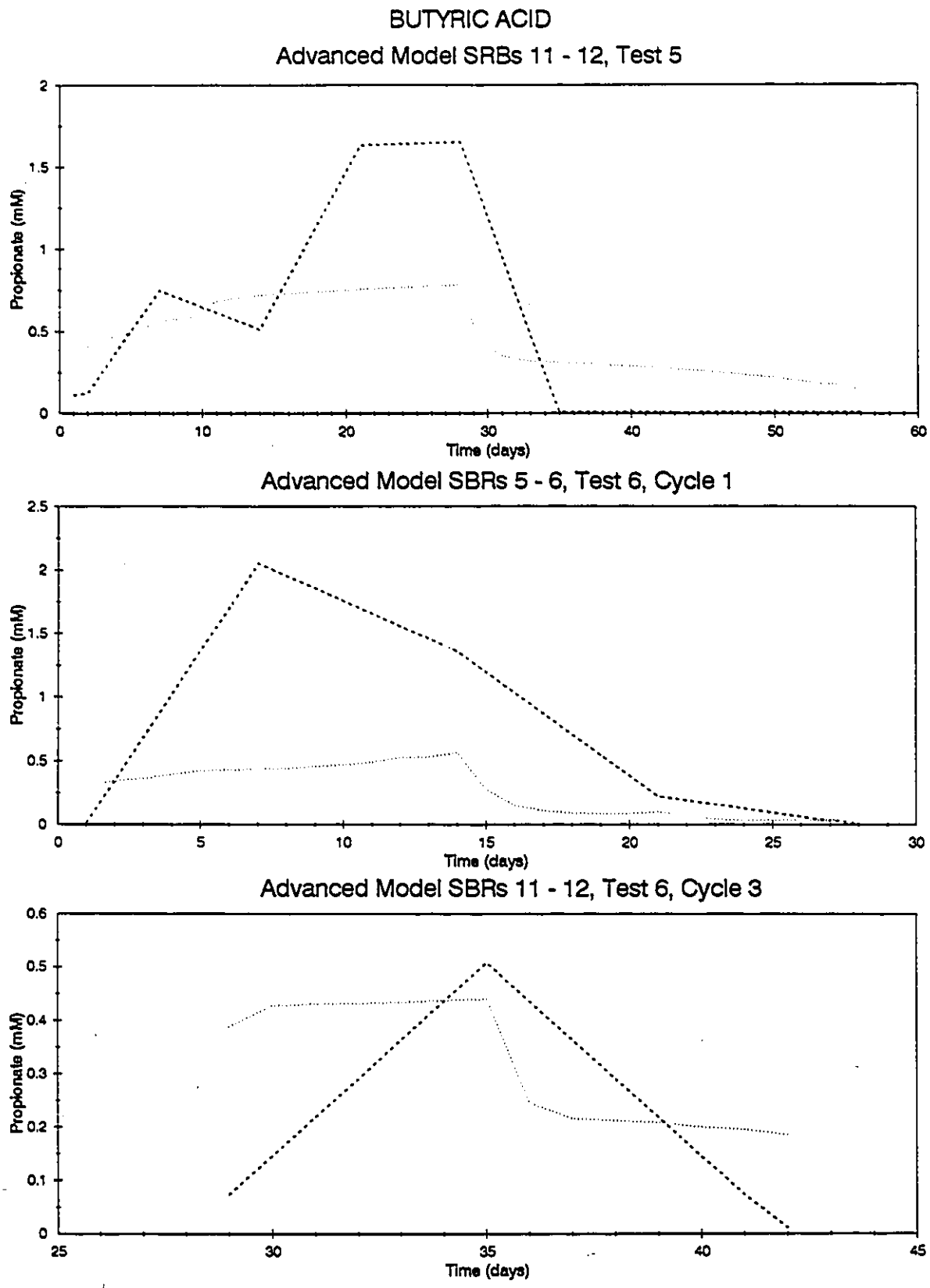


Fig. 5.8 Comparison between the measured and predicted butyric acid concentrations,
----- Measured, ... Advance model prediction.

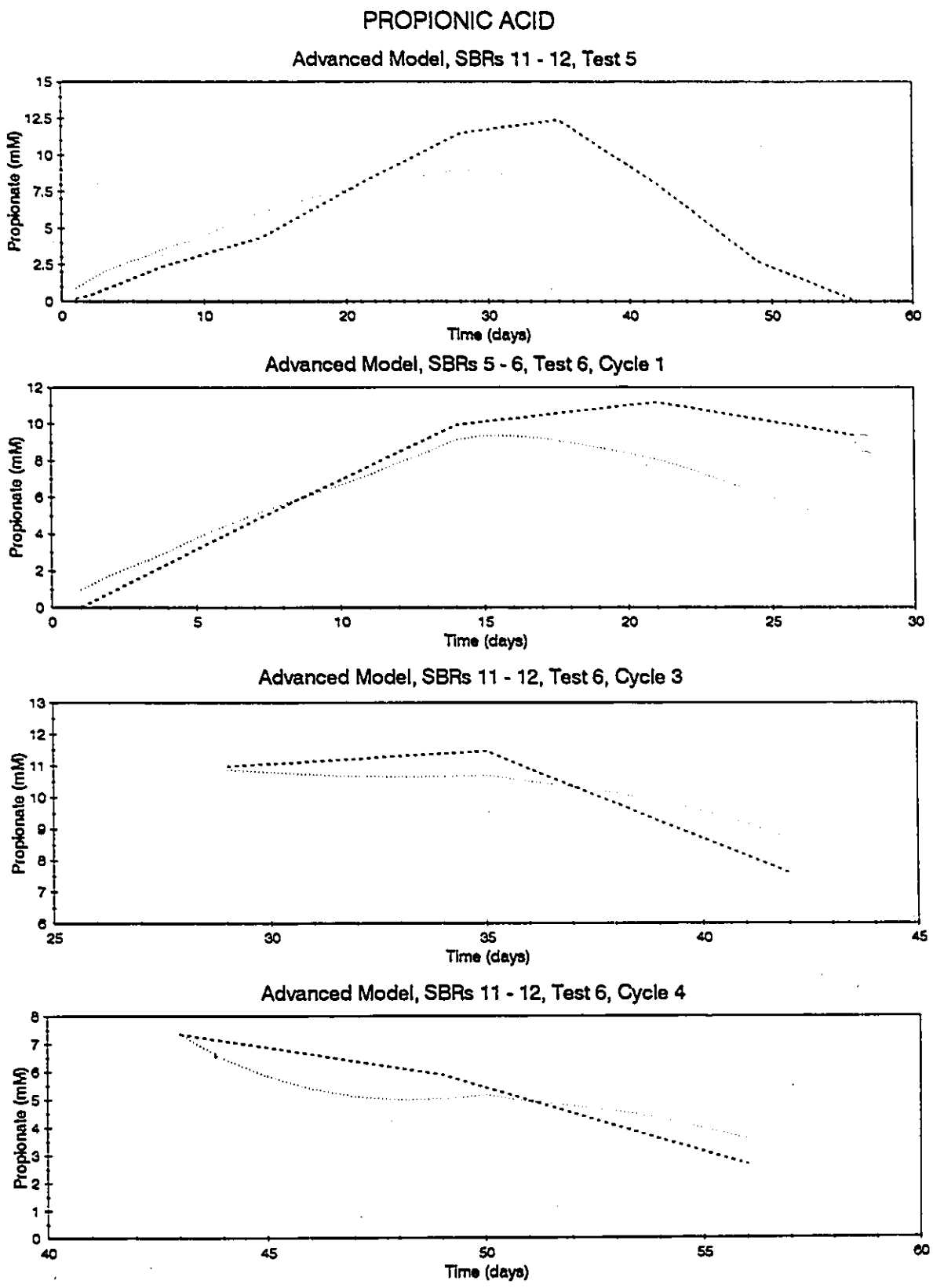


Fig. 5.9 Comparison between the measured and predicted propionic acid concentrations, ----- Measured, ... Advanced model prediction.

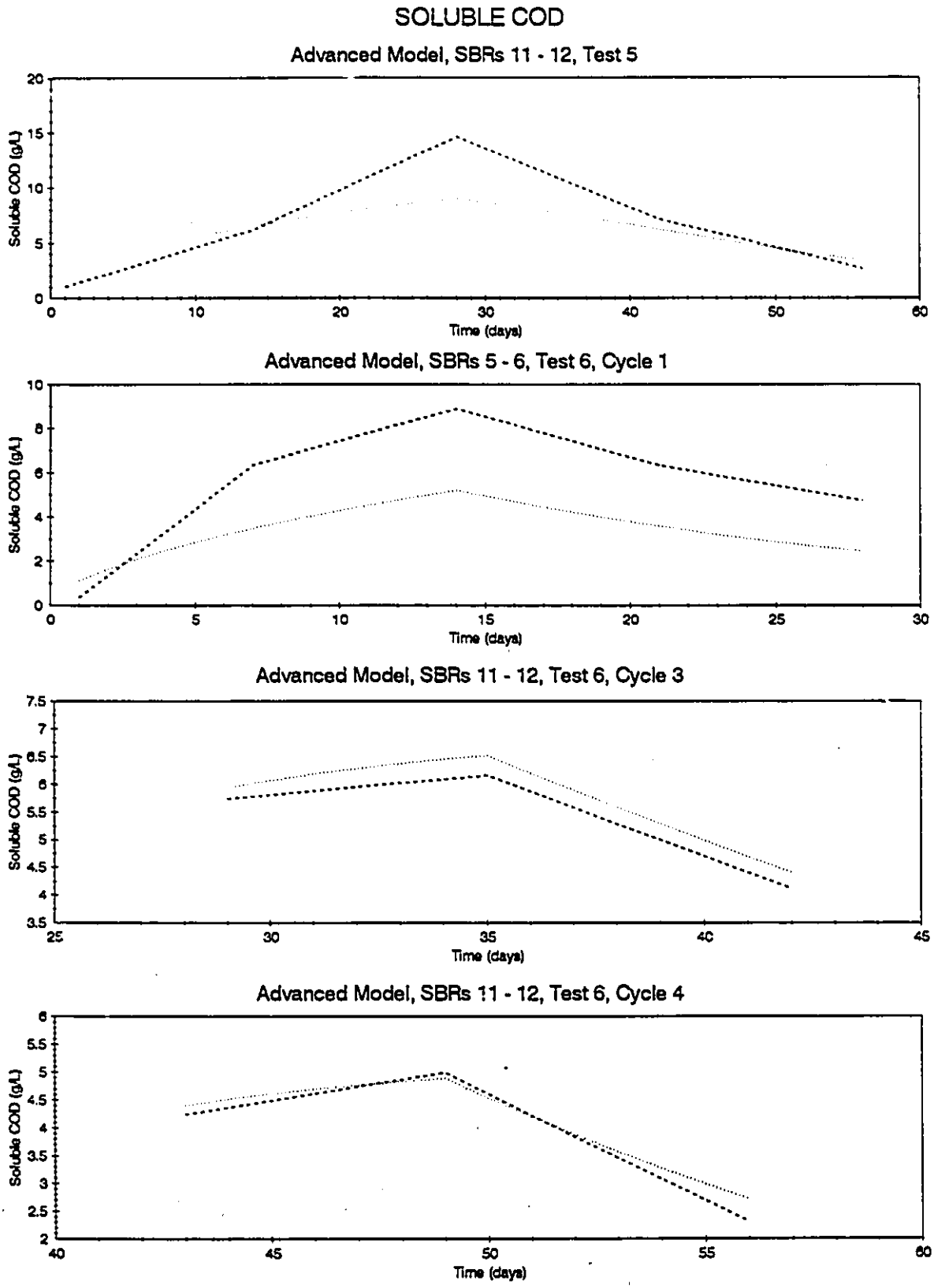


Fig 5.10 Comparison between the measured and predicted soluble COD concentrations,
----- Measured, ... Advanced model prediction.

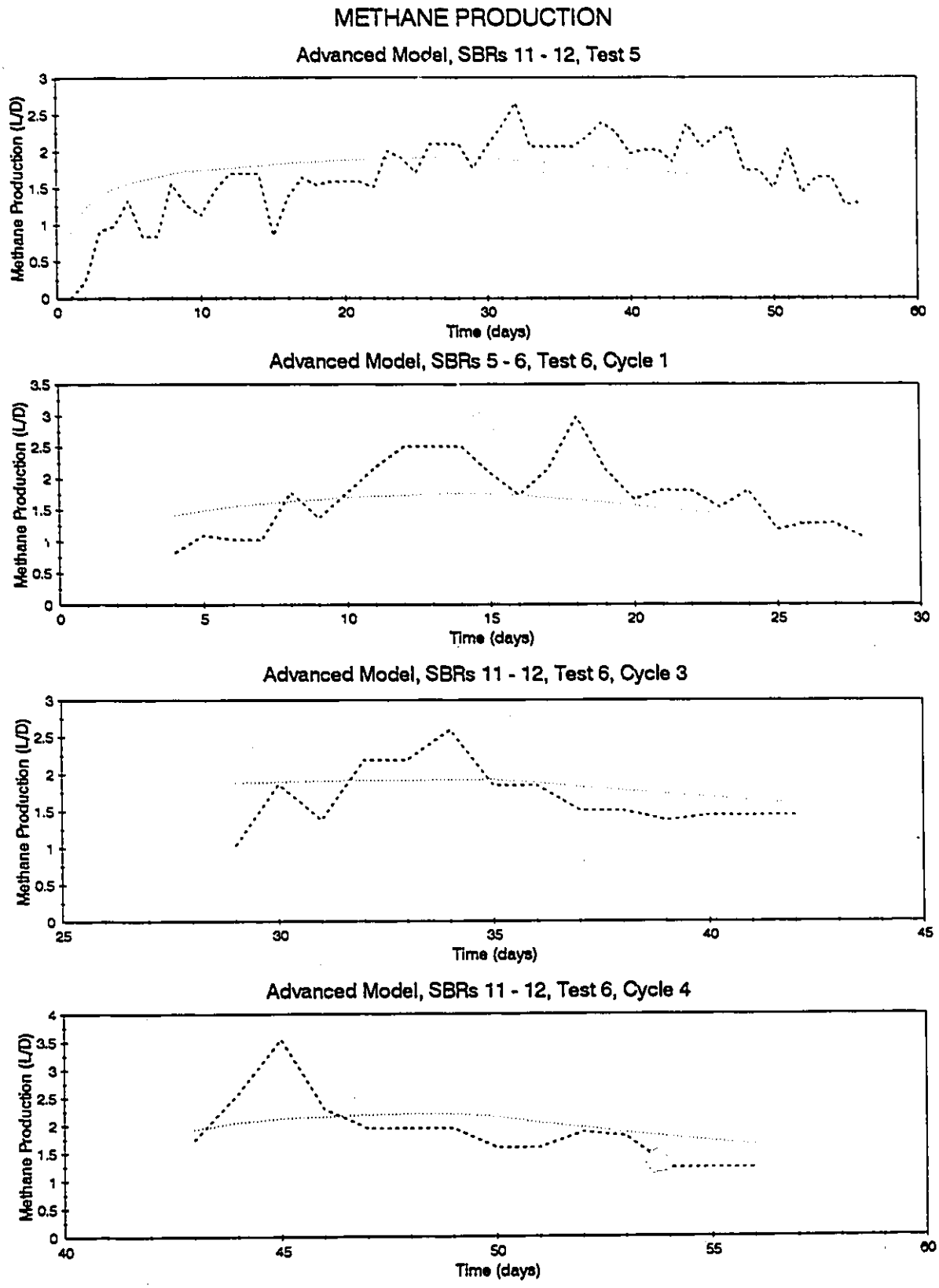


Fig. 5.11 Comparison between the measured and predicted methane production,
----- Measured, ... Advanced model prediction.

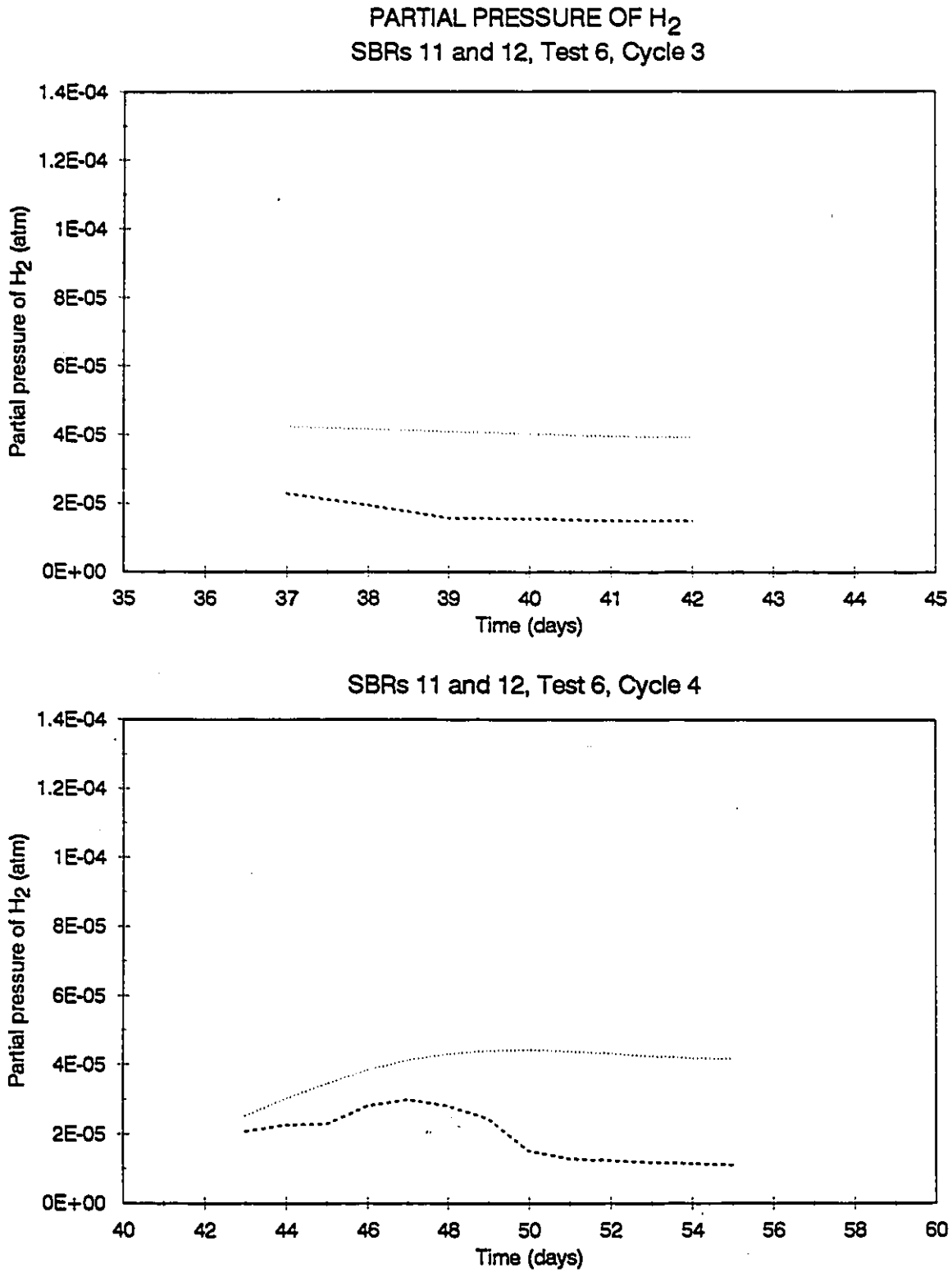


Fig 5.12 Comparison between the measured and predicted partial pressures of hydrogen,
----- Measured, ... Advanced model prediction

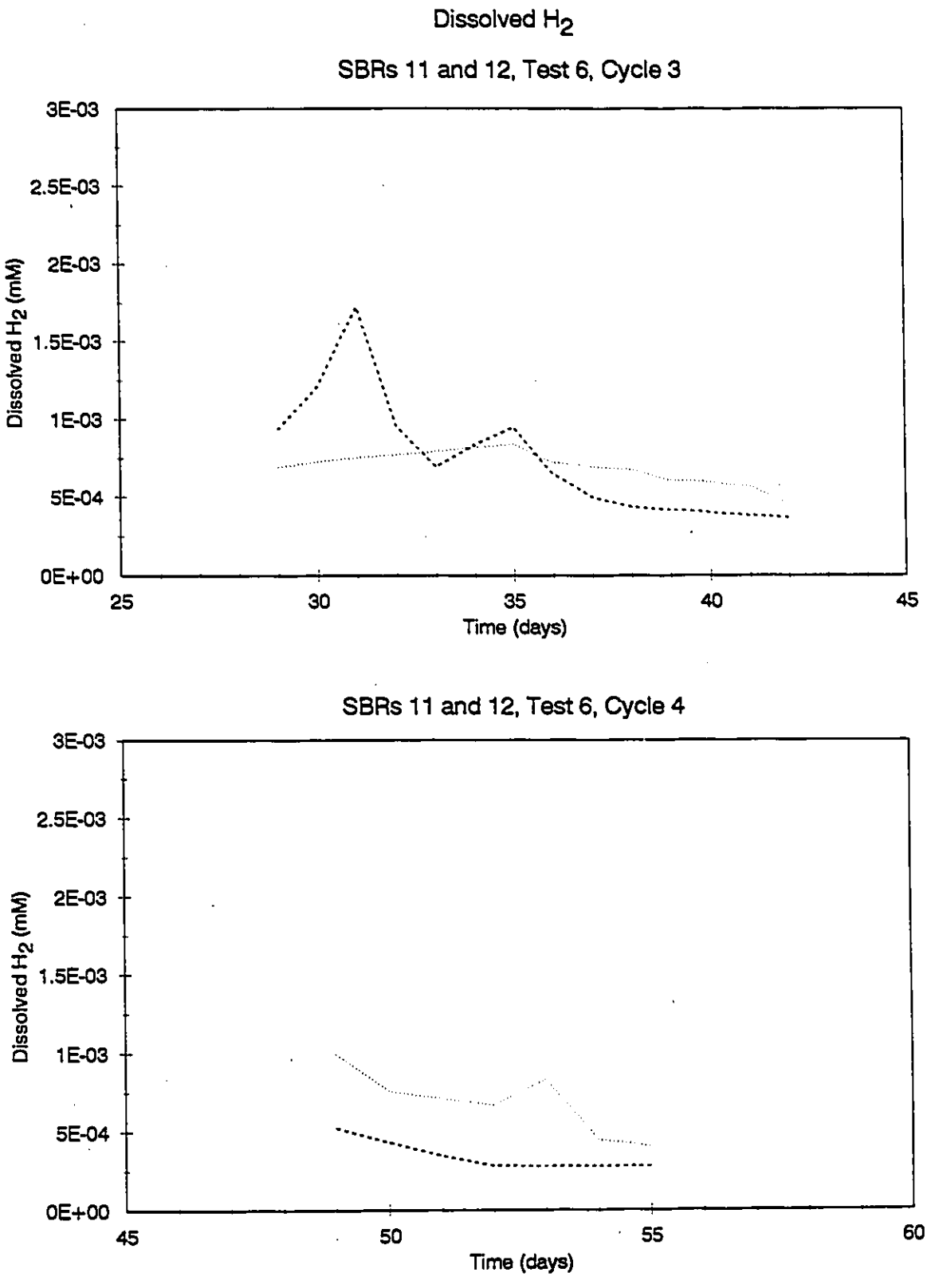


Fig. 5.13 Comparison between the measured and predicted dissolved concentration of hydrogen, ------- Measured, ... Advanced model prediction.

CHAPTER 6

CONCLUSION

Current animal manure management practices in several regions across Canada are detrimental to the environment and represent hazards to human and animal health. There are now more public and government pressures to encourage farmers to practice a more sustainable and environmentally sound agriculture. Therefore, there is an urgent need for a process that would eliminate odours, reduce pollution load and allow integration of animal manure into the overall production systems. Such a process will be of interest to the farm industry only if it has the following characteristics: 1) low cost; 2) stability; 3) simple and easy to operate; and 4) requires minimum labour skill.

The primary objective of this study was to evaluate the feasibility of PAD in SBR to treat swine manure slurry in order to reduce its pollution potential, recover energy and reduces odours. Experiments were carried out in 12 40-Litre SBRs operated under different conditions. These digesters have been in operation for over a year without showing any sign of failure or instability.

SBRs were started up without any problems. The experimental results for the startup run suggest that the organic loading rate should be reduced by 50% or the react period extended by about 20 days. Experimental results for the subsequent runs indicated that PAD of swine manure slurry at 20°C in intermittently fed SBR: 1) reduced the pollution potential of swine manure slurry by removing 85 to 95% of the soluble COD; 2) produced important quantity of biogas (0.48 to 0.66 L of CH_4 per gram of VS fed); and 3) was very successful to remove odours, the treated manure was almost odourless when compared to raw manure.

For all the experimental runs the PAD of swine manure slurry in SBR was found to be very stable. It was never affected by large concentrations of VAs and ammonia nitrogen even when their concentrations exceeded 6500 and 3500 mg/L respectively (previous systems would have failed under these conditions). Possible reasons for this very good stability are: 1) the SBRs provided quiescent settling conditions and were very efficient in retaining the slow growing bacteria in the system; 2) the high alkalinity in the SBRs (7000 to 14000 mg $CaCO_3$/L) allowed the pH to be maintained between 7.0 and 8.0 even when concentrations of VAs changed substantially; and 3) the long HRT and SRT provided in the system.

Other interesting findings were that PAD in SBR process does not require mixing. Because of this and that it operates at ambient temperature, this process might not require added energy and most of the energy produced should be available for utilization on the farm. The experimental results also indicated that this process can be intermittently fed only once a week without affecting the SBR stability and performance. This process will therefore minimize the interference with regular farm operations because it can be fed during regular manure removal from the barn and also the farmer will deal with the digester effluent only once a month or every two months. Based on this study, PAD in SBR represent a promising process to treat swine manure slurry on small and large farm operations.

The second objective of this study was to model PAD of swine manure slurry in SBR in order to extend knowledge of PAD in SBR and predict process performance.

Experimental results on dissolved and gas phase hydrogen concentrations indicated that: 1) the partial pressure of hydrogen in gas phase is not appropriate for evaluating the stability of a non-mixed SBR and 2) the hydrogen concentration in gas phase is not in equilibrium with the dissolved concentration. For these reasons recent advanced models of anaerobic digestion are not applicable to PAD of swine manure slurry in non-mixed SBRs.

Existing mathematical models of anaerobic digestion formed the basis for the two models used in this study. These two models were: 1) a simple model that considered only two populations of bacteria as well as particulates solubilization rate and 2) an advanced model that considered the interaction between the biological, liquid (physico-chemical) and gas phase. The new developments that have been incorporated in the advanced model were carefully made and were supported by experimental evidence. The advanced model assumed: 1) that six populations of bacteria are present in the SBR including two populations of acetoclastic bacteria; 2) that the hydrogen in gas phase is not in equilibrium with the dissolved hydrogen in the liquid phase and a mass transfer coefficient must be used to determine the hydrogen gas transfer rate; 3) that production of VA is regulated by the dissolved concentration of hydrogen in the liquid phase; and 4) that the process is not affected by large concentration of VA and ammonia nitrogen.

The simple model predicted reasonably well the trend in VA and SCOD accumulation as well as methane production. The advanced model which made use of a large number of kinetic constants also predicted reasonably well the methane production as well as the accumulation in acetic and propionic acids, dissolved

and gaseous hydrogen and SCOD. The advanced model represents an interesting tool to extend knowledge of PAD in SBR, because it considers the interaction among the different microorganisms and predicts the general trend in substrates utilization, accumulation of intermediate compounds and products formation.

CHAPTER 7

RECOMMENDATION FOR FUTURE RESEARCH

Future research should concentrate on biological, physical and chemical changes as well as odour reduction that occur in manure during PAD. These changes should also be evaluated with respect to process temperature, solids content, animal diet and presence of inhibitory elements such as antibiotics or food preservative. This information is necessary to evaluate precisely the feasibility of using PAD as a primary process to reduce manure odours and pollution potential, and increase the availability of manure nutrients.

In order to utilize the advanced model for evaluating control strategies, process stability and recommend design specifications for large scale PAD in SBR process, the following developments are also required:

1) modify the model to consider the metabolic pathway of fats and proteins;

2) extensive experimental investigation to determine the biological and physico-chemical kinetic constant by using bacterial sludge completely acclimatized to swine manure and low temperatures;

3) determine the relative concentrations of the different types of bacteria;

4) Verify if the model can predict eminence of process failure under operational conditions that caused SBRs failure;

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APPENDIX A

FORTRAN PROGRAM FOR THE SIMPLE MODEL

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      PROGRAM SBR
C     SBR-SIMPLE
C     DYNAMIC SIMULATION PROGRAM OF ASBR EXPERIMENTAL RUNS
C     INCLUDING EFFECTS OF FILL AND REACT PERIODS.
      CHARACTER*7 FNM,FNMO
      CHARACTER*9 CH2
      CHARACTER*11 CH3
      CHARACTER*14 CH26
      CHARACTER*16 CH27
      CHARACTER*18 CH6,CH7,CH11,CH24,DRIVE2
      CHARACTER*19 DRIVE
      CHARACTER*20 CH20, CH71,CH23,CH25
      CHARACTER*30 DFNM,DFNMO
      CHARACTER*42 CH9
      CHARACTER*22 CH10
      CHARACTER*24 CH61
      CHARACTER*48 CH91
      CHARACTER*22 CH101
      CHARACTER*26 CH22
      CHARACTER*28 CH1,CH5
      CHARACTER*29 CH51
      CHARACTER*44 CH8
      CHARACTER*43 CH4
      CHARACTER*47 CH12
      CHARACTER*48 CH13
      CHARACTER*51 CH41
      CHARACTER*54 CH81
      CHARACTER*79 CH32, CH33, CH42, CH43
      CHARACTER*80 CH28
      INTEGER RUNGE
      REAL*4 KP, Vo, KPI
      DIMENSION IDAY(100),Q(100),TCOD(100),SOLCOD(100),FC(100),
     1 QCH4(100),VAA(100),VAP(100),VAB(100),CH4P(100),QCH4o(100),
     2 VANCOD(100), X1L(100), X2L(100), S1(100),Y(6),F(6),
     3 S2(100), S6(100), TSS(100), ALK(100), VAAo(100), FTCOD(100),
     4 VAPo(100), VABo(100), P(100), Po(100), VAo(100), HRT(100),
     5 VS(100), V(100), VA(100), VSS(100), XLR(100), QCH4PP(100)
      DIMENSION TCODP(100), SOLCDP(100), QCH4P(100), XLP(100)
      COMMON RT3,RT4,RT5,RT6,RT7,RTH1,RTH2,RTH3,RTH4,RTH6,RTH7
      DATA TCOD/100*0./,SOLCOD/100*0./,QCH4o/100*0./
      DATA QCH4/100*0./,VA/100*0./,TSS/100*0./,VANCOD/100*0./
      DATA VAAo/100*0./,VAPo/100*0./,VABo/100*0./,Po/100*0./
      DATA P/100*0./,VS/100*0./,HRT/100*0./,V/100*0./,VAo/100*0./
      DATA Y1I/0./,B1I/0./,YASI/0./,VMAX1I/0./,HK1I/0./,QCH4PP/100*0./
     1 VMAX2/0./, HK2I/0./, Y2I/0./, B2I/0./, KP/0./, Vo/0./,
     2 FTCOD/100*0./
      DATA N1/0/,N2/0/,N3/0/,N4/0/,N5/0/,SMSLCD/0/, YAS/0./
     1 SMTCOD/0/,SMXF/0/,SMS2/0/,SMQCH4/0/,N12/0/,N22/0/,N32/0/,
     2 N42/0/,N52/0/,SMSLC2/0/,SMTCD2/0/,SMXF2/0/,SMS22/0/,SMQCH2/0/
      OPEN(11,FILE='LPT1')
      RT2 = 1./SQRT(2.)
      RT3 = 1. - RT2
```

```
      RT4 = 1. + RT2
      RT5 = 2.*RT3
      RT6 = 2.*RT4
      RT7 = RT2 - 0.5
      H = 0.10000000
      RTH1 = RT3*H
      RTH2 = RT2*H
      RTH3 = 0.5*H
      RTH4 = H/6.
      RTH6 = RT4*H
      RTH7 = RT7*H
C     ISVFL IS A FLAG TO SAVE CHANGES TO THE DEFAULT RATE CONSTANT FILE
      ISVFL = 0
C     NS IS NO. OF INCREMENT STEPS FOR 1ST VARIABLE
      NS = 0
C     NSS IS COUNTER CONTROL FOR NS
      NSS = -1
C     K2 IS A FLAG FOR SECOND VARIABLE INCREMENTING
      K2 = 0
C     NS2 IS NO. OF INCREMENT STEPS FOR SECOND VARIABLE
      NS2 = 0
C     NSS2 IS COUNTER CONTROL FOR NS2
      NSS2 = -1
      WRITE(*,1010)
1010  FORMAT('0',13X,' DYNAMIC SIMULATION FOR DSFF REACTORS',/,/, ' TH
     1 E STANDARD ERRORS OF ESTIMATE (SEE) WILL BE SHOWN ON THE SCREEN',
     2 /,/, 28X, ' PRINT OPTIONS')
      WRITE(*,1011)
1011  FORMAT('0',4X,'1. NO PRINTING',/,/, 5X, '2. PRINT STD. ESTIMATE
     1 OF ERROR',/,/, 5X, '3. PRINT SEE AND COMPARISON OF PREDICTED AND
     2 MEASURED EFF. SOLUBLE AND TOTAL       COD, VOL. ACIDS, METH.
PROD.,
     3 AND FILM VOLATILE SOLIDS.',/,/, 5X, '4. PRINT (3) + COMPLETE PRED
     4 ICTED DATA SUMMARY.',/,/)
      WRITE(*,'(A\)')'  Enter the line no. of your choice.  -->'
      READ(*,'(BN,I1)') IP
C     1 AND 2 REFER TO ACIDOGENS AND METHANOGENS RESPECTIVELY
C     VMAX- MAX SPEC. SUBSTRATE VEL.; HK- HALF VEL CONSTANT; Y- YIELD
C     FACTOR
C     YAS- ACID YIELD; B- DECAY RATE; ALL CONSTANTS EXCEPT Y ARE ON A
C     mg(COD)/L BASIS; Y IS mg VSS/mg COD
C     RATE CONSTANTS ARE ASSUMED TO BE THE SAME IN MIXED LIQ AND FILM
      CH1 = 'CURRENT RATE CONSTANT VALUES'
      CH2 = 'Acidogens'
      CH3 = 'Methanogens'
      CH4 = 'Max. specific substrate uptake rate (x/x/d)'
      CH5 = 'Half velocity constant (x/L)'
      CH6 = 'Yield factor (x/x)'
      CH7 = 'Decay rate (x/x/d)'
      CH8 = 'Yield of vol. acids from raw substrate (x/x)'
      CH9 = 'Max. Spec. Particulate Solub. Rate (x/x/d)'
      CH10 = 'SBR Initial Volume (L)'
```

```
      CH11 = 'x = mg    x = mMol'
C     OPEN FILE FOR DEFAULT RATE CONSTANTS
      OPEN(1,FILE='C:\FORTRAN\ANAEROB\DEFRAT1',STATUS='OLD')
      READ(1,1000)VMAX1,HK1,Y1,B1,VMAX2,HK2,Y2,B2,YAS,KP,Vo
1000  FORMAT(F8.5,F8.2,3F8.5,F8.2,3F8.5,F8.6,F8.2)
C     THE LETTER M SIGNIFIES CONSTANT ON A MOLAR BASIS
16    HKM1 = HK1/342./1.1228
      HKM2 = HK2/60./1.0667
      VMAXM1 = (VMAX1/1.1228/342.)*113.
      VMAXM2 = (VMAX2/1.0667/60.)*113.
      YM1 = (Y1/113.)*(1.1228)*342.
      YM2 = (Y2/113.)*(1.0667)*60.
      YASM = (YAS/1.0667/60.)*(342.)*1.1228
      WRITE(*,2000)CH1,CH2,CH11,CH4,VMAX1,VMAXM1,CH5,HK1,HKM1,CH6,Y1,
     1 YM1, CH7,B1,B1,CH8,YAS, YASM
2000  FORMAT('1',15X,A,/,23X,A,/,50X, A,/,' 1. ',A, 3X,F8.3,5X,
     1 F8.3,/,' 2. ',A, 18X,F8.1, 5X,F8.2,/,' 3. ',A,28X,F8.3,5X,
     2 F8.3,/,' 4. ',A, 28X, F9.5, 5X,F9.5,/,' 5. 'A, 2X,F8.3,5X,
     3 F8.3)
      WRITE(*,2001)CH3,CH11,CH4,VMAX2,VMAXM2,CH5,HK2,HKM2,CH6,Y2,YM2,
     1 CH7, B2, B2, CH9,KP, CH10,Vo
2001  FORMAT('0',22X, A,/,50X, A,/,' 6. ',A,3X,F5.3,4X,F8.3,
     1 /,' 7. ', A, 18X,F7.1,5X,F7.1,/,' 8. ',A, 28X,F8.3,5X,
     2 F8.3,/,' 9. ', A,28X, F9.5, 5X,F9.5,/,/,' 10. ', A,3X,
     3 F9.4,/,' 11. ',A, 17X, F8.3)
      CH12 = 'NOTE: Composition of m.o.s is C5H7NO2, M.W.-113'
      CH13 = 'YOU CAN ONLY CHANGE CONSTANTS ON A mg COD BASIS!'
      WRITE(*,2030)CH12,CH13
2030  FORMAT('0', 5X,A,/,5X,A)
      WRITE(*,'(A\)')' Do you wish to change a constant? (press Enter
     1 key for no; 1 for yes) -->'
      READ(*,'(BN,I1)') IANS1
      IF(IANS1.EQ.1)  GOTO 1
      GOTO 14
1     WRITE(*,'(A\)') ' Enter the line no. that you want to change.  -
     1 ->'
      READ(*,'(BN,I2)') IANS2
      ISVFL = 1
      GOTO(3,4,5,6,7,8,9,10,11,12,13)IANS2
3     WRITE(*,'(A\)')' Enter the new value for acidogens max. vel.  --
     1 >'
      READ(*,'(F10.5)') VMAX1
      GOTO 16
4     WRITE(*,'(A\)')' Enter the new value for acidogens half vel. con
     1 stant. - ->'
      READ(*,'(F10.5)') HK1
      GOTO 16
5     WRITE(*,'(A\)')' Enter the new value for acidogens yield factor.
     1 -->'
      READ(*,'(F10.5)') Y1
      GOTO 16
6     WRITE(*,'(A\)')' Enter the new value for acidogens decay rate.
```

```
     1 -->'
       READ(*,'(F10.5)') B1
       GOTO 16
7      WRITE(*,'(A\)')' Enter the new value for acetate yield from sucr
     1 ose.  -->'
       READ(*,'(F10.5)') YAS
       GOTO 16
8      WRITE(*,'(A\)')' Enter the new value for meth. max. vel.  -->'
       READ(*,'(F10.5)') VMAX2
       GOTO 16
9      WRITE(*,'(A\)')' Enter the new value for meth. half vel. constan
     1 t.  -->'
       READ(*,'(F10.5)') HK2
       GOTO 16
10     WRITE(*,'(A\)')' Enter the new value for meth. yield factor.  --
     1 >'
       READ(*,'(F10.5)') Y2
       GOTO 16
11     WRITE(*,'(A\)')' Enter the new value for meth. decay rate.  -->'
       READ(*,'(F10.5)') B2
       GOTO 16
12     WRITE(*,'(A\)')' Enter the new value for particulate solubiliza
     1 rate.  -->'
       READ(*,'(F10.5)') KP
       GOTO 16
13     WRITE(*,'(A\)')' Enter the new value for SBR initial volume.  -
     1 ->'
       READ(*,'(F7.4)') Vo
       GOTO 16
14     IF(ISVFL.EQ.0) GOTO 2
       WRITE(*,'(A\)')' Do you wish to make the change(s) permanent to
     1 data file?  (Enter 0 for no; 1 for yes)  -->'
       READ(*,'(BN,I1)') IANS3
       IF(IANS3.EQ.0) GOTO 2
       OPEN(2,FILE='C:\FORTRAN\ANAEROB\DEFRAT1',STATUS='NEW')
       WRITE(2,1000)VMAX1,HK1,Y1,B1,VMAX2,HK2,Y2,B2,YAS,KP,Vo
       CLOSE(2,STATUS='KEEP')
2      WRITE(*,'(A\)')' Do you wish to have one variable automatically
     1 incremented?  (Enter 0 for no; 1 for yes)  -->'
       READ(*,'(BN,I1)') IANS6
       IF(IANS6.EQ.0) GOTO 90
       WRITE(*,'(A\)') ' Enter the line no. that you want to increment.
     1 -->'
       READ(*,'(BN,I2)') IANS8
       IANS7 = IANS8
101    GOTO(103,104,105,106,107,108,109,110,111,112,113)IANS7
103    WRITE(*,'(A\)')' Enter the increment value for acidogens max. ve
     1 l.  -->'
       READ(*,'(F10.5)') VMAX1I
C      B ADDED TO VARIABLE REFERS TO ITS BEGINNING VALUE IN CASE IT'S
C      CHANGED DURING INCREMENTING
       VMAX1B = VMAX1
```

```
      GOTO 114
104   WRITE(*,'(A\)')' Enter the increment value for acidogens half ve
     1 l. constant. - ->'
      READ(*,'(F10.5)') HK1I
      HK1B = HK1
      GOTO 114
105   WRITE(*,'(A\)')' Enter the increment value for acidogens yield f
     1 actor.  -->'
      READ(*,'(F10.5)') Y1I
      Y1B = Y1
      GOTO 114
106   WRITE(*,'(A\)')' Enter the increment value for acidogens decay r
     1 ate.  -->'
      READ(*,'(F10.5)') B1I
      B1B = B1
      GOTO 114
107   WRITE(*,'(A\)')' Enter the increment value for acetate yield fro
     1 m sucrose.  -->'
      READ(*,'(F10.5)') YASI
      YASB = YAS
      GOTO 114
108   WRITE(*,'(A\)')' Enter the increment value for meth. max. vel.
     1 -->'
      READ(*,'(F10.5)') VMAX2I
      VMAX2B = VMAX2
      GOTO 114
109   WRITE(*,'(A\)')' Enter the increment value for meth. half vel. c
     1 onstant.  -->'
      READ(*,'(F10.5)') HK2I
      HK2B = HK2
      GOTO 114
110   WRITE(*,'(A\)')' Enter the increment value for meth. yield facto
     1 r.  -->'
      READ(*,'(F10.5)') Y2I
      Y2B = Y2
      GOTO 114
111   WRITE(*,'(A\)')' Enter the increment value for meth. decay rate.
     1 -->'
      READ(*,'(F10.5)') B2I
      B2B = B2
      GOTO 114
112   WRITE(*,'(A\)')' Enter the increment value for particulate solub
     1 ilization rate. -->'
      READ(*,'(F10.5)') KPI
      KPB = KP
      GOTO 114
113   WRITE(*,'(A\)')' Enter the increment value for SBR initial volu
     1 me -->'
      READ(*,'(F10.5)') VoI
      VoB = Vo
114   WRITE(*,'(A\)')' Enter the no. of increment steps (1-9).  -->'
      IF(K2.EQ.1) GOTO 116
```

```
      READ(*,'(BN,I1)') NS
      GOTO 117
116   READ(*,'(BN,I1)') NS2
      GOTO 90
117   WRITE(*,'(A\)')' Do you wish to have a second variable automatic
     1 ally incremented?  (Enter 0 for no; 1 for yes)  -->'
      READ(*,'(BN,I1)') IANS6
      IF(IANS6.EQ.0) GOTO 90
      K2 = 1
      WRITE(*,'(A\)') ' Enter the line no. that you want to increment.
     1 -->'
      READ(*,'(BN,I2)') IANS9
      IANS7 = IANS9
      GOTO 101
90    WRITE(*,'(A\)')' Enter the run no. (r4, r5, r6, r7, r8, r9) for
     1 evaluation  -->'
      READ(*,'(A6)')FNM
      WRITE(*,'(A\)')' enter the name of the output file-->'
      READ(*,'(A7)')FNMO
      DRIVE = 'C:\FORTRAN\ANAEROB\'
      DRIVE2 = 'C:\FORTRAN\OUTPUT\'
      WRITE(DFNM,'(A,A)') DRIVE, FNM
      OPEN(2,FILE=DFNM,STATUS='OLD')
      WRITE(DFNMO,'(A,A)') DRIVE2, FNMO
      OPEN(7,FILE=DFNMO,STATUS='OLD')
      READ(2,2039)FNM
      WRITE(7,2039)FNM
2039  FORMAT(A6)
C     ND IS THE NUMBER OF DAYS IN THE RUN
      READ(2,2040)ND
2040  FORMAT(I3)
C     MD IS THE FIRST RANGE OF NO. DAYS IN STD ERROR OF ESTIMATE
      READ(2,2041)MD
2041  FORMAT(I3)
      MD1=MD+1
      READ(2,2050)(IDAY(I), Q(I), FTCOD(I), FC(I), VAAo(I), VAPo(I),
     1 VABo(I), VAA(I), VAP(I), VAB(I), TCOD(I),SOLCOD(I),QCH4o(I),
     1 CH4P(I),VS(I), ALK(I), I=1,ND)
2050  FORMAT(I3,F8.5,10F9.2,F8.4,3F9.2)
C     WRITE(*,'(A\)')' ENTER OUTPUT FILE NAME-->'
C     READ(*,'(A12)')FILENAME
C     DRIVE = 'C:\FORTRAN\OUTPUT\'
C     WRITE(DFNM,'(A,A)') DRIVE, FILENAME
C     OPEN(UNIT = 10,FILE=DFNM,ACCESS='SEQUENTIAL',STATUS='NEW')
      DO 20 I=1,ND
      Po(I)=FTCOD(I)-FC(I)
      TSS(I) = (TCOD(I) - SOLCOD(I))/1.42
C     VOL. ACIDS ARE READ IN AS ACIDS AND MUST BE CONVERTED TO COD
      VAo(I) = (1.066*VAAo(I) + 1.512*VAPo(I) + 1.818*VABo(I))
      VA(I) = (1.066*VAA(I) + 1.512*VAP(I) + 1.818*VAB(I))
C     VANCOD IS SOLUBLE EFFLUENT COD DUE TO COMPONENTS OTHER THAN VOL
C     ACIDS
```

```
      VANCOD(I) = SOLCOD(I) - VA(I)
      IF (VANCOD(I) .LT. 0) VANCOD(I) = 0.1
C     QCH4 IS METHANE FLOWRATE/D, CH4P IS % CH4 WHICH MUST BE CONVERTED
C     QCH4O IS BIOGAS FLOWRATE/D
C     TO COD (2857 mg COD/L CH4)
      QCH4(I) = QCH4O(I)*CH4P(I)*2857./1000.
20    CONTINUE
C     COMPUTE SUMS OF PARAMETERS FOR LATER USE IN STD ERROR OF ESTIMATE
      DO 300 I=1,MD
      IF (SOLCOD(I).LT.0.01) GOTO 301
      N1 = N1 + 1
      SMSLCD = SMSLCD + SOLCOD(I)
301   IF (TCOD(I).LT.0.01) GOTO 302
      N2 = N2 + 1
      SMTCOD = SMTCOD + TCOD(I)
302   IF (VS(I).LT.0.01) GOTO 303
      N3 = N3 + 1
      SMXF = SMXF + VS(I)
303   IF (VA(I).LT.0.01) GOTO 304
      N4 = N4 + 1
      SMS2 = SMS2 + VA(I)
304   IF (QCH4(I).LT.0.01) GOTO 300
      N5 = N5 + 1
      SMQCH4 = SMQCH4 + QCH4(I)
300   CONTINUE
      DO 310 I=MD1,ND
      IF (SOLCOD(I).LT.0.01) GOTO 311
      N12 = N12 + 1
      SMSLC2 = SMSLC2 + SOLCOD(I)
311   IF (TCOD(I).LT.0.01) GOTO 312
      N22 = N22 + 1
      SMTCD2 = SMTCD2 + TCOD(I)
312   IF (VS(I).LT.0.01) GOTO 313
      N32 = N32 + 1
      SMXF2 = SMXF2 + VS(I)
313   IF (VA(I).LT.0.01) GOTO 314
      N42 = N42 + 1
      SMS22 = SMS22 + VA(I)
314   IF (QCH4(I).LT.0.01) GOTO 310
      N52 = N52 + 1
      SMQCH2 = SMQCH2 + QCH4(I)
310   CONTINUE
      N1T = N1 + N12
      N2T = N2 + N22
      N3T = N3 + N32
      N4T = N4 + N42
      N5T = N5 + N52
      VOL = 22.4
C     P1= Y(1), S1= Y(2), S2= Y(3), X1L= Y(4), X2L= Y(5), S6= Y(6)
140   Y(1) = 12000.0
      Y(2) = 1000.0
      Y(3) = 0.0
```

```
      Y(4) = 13500.0
      Y(5) = 6500.0
      Y(6) = 2000.0
C     X IS TIME, Y(I) ARE PASSED TO SUBROUTINE RUNGE
      X = 0.0
C     THE STOICHIMETRIC ACID YIELD, YAS, MUST BE ADJUSTED FOR M.O.
YIELD
C     TO OBTAIN THE TRUE ACID YIELD, YA
      YA = YAS - Y1*1.42
147   CONTINUE
      DO 30 J = 1,ND
C     SBR VOLUME AT TIME 0
      V(0) = Vo
C     SBR VOLUME AT TIME "t"
      V(J) = V(J-1) + Q(J)
      ICOUNT = 0
C     Hydraulic Residence Time at TIME t.
      IF (Q(J) .GT. 0.00) GOTO 19
      HRT(J) = 10.E+20
      GOTO 23
19    HRT(J) = V(J)/Q(J)
23    K = RUNGE(6,Y,F,X,H)
C     WHENEVER K = 1, COMPUTE DERIVATIVE VALUES
      IF (K.NE.1) GOTO 21
C     RG AND RD ARE MO GROWTH AND DECAY RATES
C     RS IS SUBSTRATE REMOVAL RATE
      DO 80 I = 1,6
      IF (Y(I).GT.0.0) GOTO 80
      Y(I) = 0.01
80    CONTINUE
      YX0 = Y(1)
      YX1 = Y(2)
      YX2 = Y(3)
      YX3 = Y(4)
      YX4 = Y(5)
      YX5 = Y(6)
      SPSUB1 = VMAX1*YX1/(HK1 + YX1)
      SPSUB2 = VMAX2*YX2/(HK2 + YX2)
      RS1L = SPSUB1*YX3
      RS2L = SPSUB2*YX4
      RD1L = B1*YX3
      RD2L = B2*YX4
C     F(1) IS THE RAW SUBSTRATE, S1, BALANCE
C     NOTE: IT IS ASSUMED THAT ALL DECAYED MO'S ARE CONVERTED INTO RAW
C     SUBSTRATE
C     F(1) IS THE PARTICULATE MASS BALANCE
      F(1) = ((Po(J)-YX0)/HRT(J)) - KP*YX0
C     F(2) IS THE BIODEGRADABLE SOLUBLE COD MASS BALANCE
      F(2) = ((FC(J) - VAo(J)) - YX1)/HRT(J) - RS1L +
     1 0.8*(RD1L + RD2L)*1.42 + 0.8*KP*YX0
C     F(3) IS THE VOLATILE ACIDS SUBSTRATE BALANCE
      F(3) = (VAo(J)-YX2)/HRT(J) - RS2L + YA*RS1L
```

```
C       F(4) IS THE LIQUID ACIDOGENS MASS BALANCE
        F(4) = -YX3/HRT(J) + Y1*RS1L - RD1L
C       F(5) IS THE LIQUID METHANOGENS MASS BALANCE
        F(5) = -YX4/HRT(J) + Y2*RS2L - RD2L
C       F(6) IS THE NON BIODEGRADABLE SOLUBLE COD MASS BALANCE
        F(6) = (4000-YX5)/HRT(J) + 0.2*(RD1L + RD2L)*1.42 + 0.2*KP*YX0
        GOTO 23
21      ICOUNT = ICOUNT + 1
        IF(ICOUNT.LE.9) GOTO 23
        DO 81 I = 1,6
        IF(Y(I).GT.0.0) GOTO 81
        Y(I) = 0.01
81      CONTINUE
        P(J) = Y(1)
        S1(J) = Y(2)
        S2(J) = Y(3)
        X1L(J) = Y(4)
        X2L(J) = Y(5)
        S6(J) = Y(6)
30      CONTINUE
        DO 35 I=1,ND
C       SOLUBLE COD IN SBR AT TIME t(I)
        SOLCDP(I) = S1(I) + S2(I) + S6(I)
C       TOTAL COD IN SBR AT TIME t(I)
        TCODP(I) = (X1L(I) + X2L(I))*1.42 + P(I)*1.5 + SOLCDP(I)
C       VOLATILE SUSPENDED SOLIDS IN SBR AT TIME t(I)
        VSS(I) = X2L(I) + X1L(I) + P(I)
C       MICRO-ORGANISMS RATIO IN SBR
        XLP(I) = X1L(I) + X2L(I)
        XLR(I) = X1L(I)/X2L(I)
C       QCH4P IS PREDICTED METHANE MASS FLOWRATE IN (g COD/DAY)
        QCH4PP(I) = V(I)*(1.- 1.42*Y2)*(VMAX2*S2(I)*X2L(I))/(HK2 + S2(I))
        QCH4P(I) = QCH4PP(I)/1000
35      CONTINUE
        SLCDSM = 0.
        TCODSM = 0.
        XFSM = 0.
        S2SM = 0.
        QCH4SM = 0.
C       COMPUTE STD ERROR OF ESTIMATE FOR MEASURED PARAMETERS, FIRST 20
C       DAYS.  ONLY DAYS ON WHICH MEASUREMENTS WERE MADE ARE CONSIDERED.
        DO 40 I=1,MD
        IF (SOLCOD(I).LT.0.01) GOTO 36
        SOLCDD = SOLCDP(I) - SOLCOD(I)
        SLCDSM = SLCDSM + SOLCDD**2
36      IF (TCOD(I).LT.0.01) GOTO 37
        TCODD = TCODP(I) - TCOD(I)
        TCODSM = TCODSM + TCODD**2
37      IF (VS(I).LT.0.01) GOTO 38
        XLD = VSS(I) - VS(I)
        XFSM = XFSM + XLD**2
38      IF (VA(I).LT.0.01) GOTO 39
```

```
      S2D = S2(I) - VA(I)
      S2SM = S2SM + S2D**2
39    IF (QCH4(I).LT.0.01) GOTO 40
      QCH4D = QCH4P(I) - QCH4(I)
      QCH4SM = QCH4SM + QCH4D**2
40    CONTINUE
      SESCD1 = SQRT(SLCDSM/N1)
      SETCD1 = SQRT(TCODSM/N2)
      SEEXF1 = SQRT(XFSM/N3)
      SEES21 = SQRT(S2SM/N4)
      SEQCH1 = SQRT(QCH4SM/N5)
      SLCDS2 = 0.
      TCODS2 = 0.
      XFSM2 = 0.
      S2SM2 = 0.
      QCH4S2 = 0.
C     COMPUTE STD ERROR OF ESTIMATE FROM DAY 21 ON
      DO 50 I=MD1,ND
      IF (SOLCOD(I).LT.0.01) GOTO 41
      SOLCDD = SOLCDP(I) - SOLCOD(I)
      SLCDS2 = SLCDS2 + SOLCDD**2
41    IF (TCOD(I).LT.0.01) GOTO 42
      TCODD = TCODP(I) - TCOD(I)
      TCODS2 = TCODS2 + TCODD**2
42    IF (VS(I).LT.0.01) GOTO 43
      XLD = VSS(I) - VS(I)
      XFSM2 = XFSM2 + XLD**2
43    IF (VA(I).LT.0.01) GOTO 44
      S2D = S2(I) - VA(I)
      S2SM2 = S2SM2 + S2D**2
44    IF (QCH4(I).LT.0.01) GOTO 50
      QCH4D = QCH4P(I) - QCH4(I)
      QCH4S2 = QCH4D**2 + QCH4S2
50    CONTINUE
      SESCD2 = SQRT(SLCDS2/N12)
      SETCD2 = SQRT(TCODS2/N22)
      SEEXF2 = SQRT(XFSM2/N32)
      SEES22 = SQRT(S2SM2/N42)
      SEQCH2 = SQRT(QCH4S2/N52)
      SESCOD = SQRT((SLCDSM + SLCDS2)/N1T)
      SETCOD = SQRT((TCODSM + TCODS2)/N2T)
      SEEXF = SQRT((XFSM + XFSM2)/N3T)
      SEES2 = SQRT((S2SM + S2SM2)/N4T)
      SEQCH4 = SQRT((QCH4SM + QCH4S2)/N5T)
      SMSLCT = SMSLCD + SMSLC2
      SMTCDT = SMTCOD + SMTCD2
      SMXFT = SMXF + SMXF2
      SMS2T = SMS2 + SMS22
      SMQCHT = SMQCH4 + SMQCH2
      SCOD1H = 100*N1*SESCD1/SMSLCD
      TCOD1H = 100*N2*SETCD1/SMTCOD
      XF1H = 100*N3*SEEXF1/SMXF
```

```
      S21H = 100*N4*SEES21/SMS2
      QCH41H = 100*N5*SEQCH1/SMQCH4
      SCOD2H = 100*N12*SESCD2/SMSLC2
      TCOD2H = 100*N22*SETCD2/SMTCD2
      XF2H = 100*N32*SEEXF2/SMXF2
      S22H = 100*N42*SEES22/SMS22
      QCH42H = 100*N52*SEQCH2/SMQCH2
      SCODH = 100*N1T*SESCOD/SMSLCT
      TCODH = 100*N2T*SETCOD/SMTCDT
      XFH = 100*N3T*SEEXF/SMXFT
      S2H = 100*N4T*SEES2/SMS2T
      QCH4H = 100*N5T*SEQCH4/SMQCHT
      IF(IP.LT.2) GOTO 70
      WRITE(11,2070)FNM,ND
2070  FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
      WRITE(7,2070)FNM,ND
      CH20 = 'RATE CONSTANT VALUES'
      CH41 = 'Max. spec. substrate uptake rate (mg COD/mg m.o./d)'
      CH51 = 'Half velocity constant (mg/L)'
      CH61 = 'Yield factor (mg/mg COD)'
      CH71 = 'Decay rate (mg/mg/d)'
      CH81 = 'Yield of vol. acids from raw substrate (mg COD/mg COD)'
      CH91 = 'Particulate solubilization rate (mg/mg/d)'
      CH101 = 'SBR initial volume (L)'
      WRITE(11,2060)CH20,CH2,CH3,CH41,VMAX1,VMAX2,CH51,HK1,HK2, CH61,
     1 Y1, Y2, CH71,B1,B2, CH81,YA,CH91,KP,CH101,Vo
2060  FORMAT('0',25X,A, /,/,56X,A, 3X,A,/,/,2X,A, 4X,F7.3,5X,F8.3,
     1 /,2X, A,25X, F6.1, 7X, F6.1,/,2X, A, 33X, F5.3,8X, F5.3,/,2X,
     2 A, 37X,F5.3, 8X, F5.3,/2X,A,3X, F8.3,/,2X,A, 15X,F8.4,
     3 /,2X, A,41X, F7.3,/,/)
      WRITE(7,2060)CH20,CH2,CH3,CH41,VMAX1,VMAX2,CH51,HK1,HK2, CH61,
     1 Y1, Y2, CH71,B1,B2, CH81,YA,CH91,KP,CH101,Vo
70    CH22 = 'STANDARD ERROR OF ESTIMATE'
      WRITE(*,2081)CH22
      IF(IP.LT.2) GOTO 71
      WRITE(11,2080)CH22
2081  FORMAT('1',25X,A)
      WRITE(7,2080)CH2
2080  FORMAT(23X,A)
71    CH23 = 'SOLUBLE EFFLUENT COD'
      CH24 = 'TOTAL EFFLUENT COD'
      CH25 = 'VOLATILE SOLIDS'
      CH26 = 'VOLATILE ACIDS'
      CH27 = 'METHANE FLOWRATE'
      CH28 = ' SEE(20D) TOT.(20D) NO.  % SEE(+20D) TOT.(+20D) NO.  % S
     1 EE(ALL) TOT.(ALL) NO.  %'
      WRITE(*,2091) CH23,CH28, SESCD1,SMSLCD,   N1, SCOD1H,
     1 SESCD2, SMSLC2,  N12, SCOD2H, SESCOD,SMSLCT,N1T,SCODH
      WRITE(*,2091) CH24,CH28, SETCD1,SMTCOD, N2, TCOD1H,
     1 SETCD2, SMTCD2,  N22, TCOD2H, SETCOD,SMTCDT,N2T,TCODH
      WRITE(*,2091) CH25,CH28, SEEXF1,SMXF, N3, XF1H,
     1 SEEXF2, SMXF2,  N32, XF2H,SEEXF,SMXFT,N3T,XFH
```

```
      WRITE(*,2091) CH26,CH28, SEES21,SMS2, N4, S21H,
     1 SEES22, SMS22,  N42, S22H,SEES2, SMS2T,N4T,S2H
      WRITE(*,2091) CH27,CH28, SEQCH1,SMQCH4, N5, QCH41H,
     1 SEQCH2, SMQCH2,  N52, QCH42H, SEQCH4,SMQCHT,N5T,QCH4H
      WRITE(*,2101)FNM,ND
2101  FORMAT(' ',5X,'RUN NO. = ',A, '; NO. OF DAYS = ',I3)
      IF(IP.LT.2) GOTO 99
2090  FORMAT(' ',1X,A,/,A,/,1X,E8.3,1X,E8.3,2X,I2,1X,F4.0,1X,E8.3,2X,
     1 E8.3, 2X, I2,1X,F4.0, 1X, E8.3, 1X, E8.3, 1X, I2, 1X, F4.0,/)
2091  FORMAT(' ',1X,A,/,A,/,1X,E8.3,1X,E8.3,2X,I2,1X,F4.0,1X,E8.3,2X,
     1 E8.3, 2X, I2,1X,F4.0, 1X, E8.3, 1X, E8.3, 1X, I2, 1X, F4.0)
      WRITE(11,2090) CH23,CH28, SESCD1,SMSLCD,   N1, SCOD1H,
     1 SESCD2, SMSLC2,  N12, SCOD2H, SESCOD,SMSLCT,N1T,SCODH
      WRITE(11,2090) CH24,CH28, SETCD1,SMTCOD, N2, TCOD1H,
     1 SETCD2, SMTCD2,  N22, TCOD2H, SETCOD,SMTCDT,N2T,TCODH
      WRITE(11,2090) CH25,CH28, SEEXF1,SMXF, N3, XF1H,
     1 SEEXF2, SMXF2,  N32, XF2H,SEEXF,SMXFT,N3T,XFH
      WRITE(11,2090) CH26,CH28, SEES21,SMS2, N4, S21H,
     1 SEES22, SMS22,  N42, S22H,SEES2, SMS2T,N4T,S2H
      WRITE(11,2090) CH27,CH28, SEQCH1,SMQCH4, N5, QCH41H,
     1 SEQCH2, SMQCH2,  N52, QCH42H, SEQCH4,SMQCHT,N5T,QCH4H
      WRITE(7,2090) CH23,CH28, SESCD1,SMSLCD,   N1, SCOD1H,
     1 SESCD2, SMSLC2,  N12, SCOD2H, SESCOD,SMSLCT,N1T,SCODH
      WRITE(7,2090) CH24,CH28, SETCD1,SMTCOD, N2, TCOD1H,
     1 SETCD2, SMTCD2,  N22, TCOD2H, SETCOD,SMTCDT,N2T,TCODH
      WRITE(7,2090) CH25,CH28, SEEXF1,SMXF, N3, XF1H,
     1 SEEXF2, SMXF2,  N32, XF2H,SEEXF,SMXFT,N3T,XFH
      WRITE(7,2090) CH26,CH28, SEES21,SMS2, N4, S21H,
     1 SEES22, SMS22,  N42, S22H,SEES2, SMS2T,N4T,S2H
      WRITE(7,2090) CH27,CH28, SEQCH1,SMQCH4, N5, QCH41H,
     1 SEQCH2, SMQCH2,  N52, QCH42H, SEQCH4,SMQCHT,N5T,QCH4H
      IF(IP.LT.3) GOTO 99
      WRITE(11,2100)FNM,ND
2100  FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
      CH32 = ' DAY   Q         SOLUBLE COD    VOL. ACIDS      TOT. EFF.
C
     1OD'
      CH33 = '                 MEAS   PRED    MEAS   PRED      MEAS
PRE
     1D'
      WRITE(7,2100)FNM,ND
      WRITE(11,2110)CH32,CH33
2110  FORMAT(1X,A,/,1X,A)
      WRITE(7,2110)CH32,CH33
      WRITE(11,2120)(IDAY(I),Q(I),SOLCOD(I),SOLCDP(I),VA(I), S2(I),
     1 TCOD(I), TCODP(I), I=1,ND)
2120  FORMAT(' ',1X,I3, 1X, F5.3, 3X, F7.0, 1X, F7.0, 3X, F5.0, 1X,
     1 F6.0, 4X, F6.0, 1X, F6.0,)
      WRITE(7,2120)(IDAY(I),Q(I),SOLCOD(I),SOLCDP(I),VA(I), S2(I),
     1 TCOD(I), TCODP(I), I=1,ND)
      WRITE(11,2121)FNM,ND
2121  FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
```

```
      CH32 = ' DAY    Q           VOL.SOLIDS              CH4 FLOW'
      CH33 = '                   MEAS     PRED          MEAS     PRED'
      WRITE(7,2121)FNM,ND
      WRITE(11,2122)CH32,CH33
2122  FORMAT(1X,A,/,1X,A)
      WRITE(7,2122)CH32,CH33
      WRITE(11,2123)(IDAY(I),Q(I),VS(I),VSS(I),QCH4(I),QCH4P(I),
I=1,ND)
2123  FORMAT(' ',1X,I3, 1X, F5.3, 7X, F6.0, 1X, F6.0, 7X, E8.3, 1X,
     1 E8.3)
      WRITE(7,2123)(IDAY(I),Q(I),VS(I),VSS(I),QCH4(I),QCH4P(I), I=1,ND)
      WRITE(11,2121)FNM,ND
      CH42 = ' DAY    Q                   VOLUME                  HRT'
      CH43 = '                             (L)                    (d)'
      WRITE(7,2121)FNM,ND
      CH42 = ' DAY    Q                   VOLUME                  HRT'
      CH43 = '                             (L)                    (d)'
      WRITE(11,2129)CH42,CH43
2129  FORMAT(1X,A,/,1X,A)
      WRITE(7,2129)CH42,CH43
      WRITE(11,2124)(IDAY(I),Q(I),V(I),HRT(I), I=1,ND)
2124  FORMAT(' ',1X,I3, 1X, F5.3, 11X, F9.3,11X, E10.3)
      WRITE(7,2124)(IDAY(I),Q(I),V(I),HRT(I), I=1,ND)
      IF(IP.LT.4) GOTO 99
      WRITE(11,2100)FNM,ND
      WRITE(7,2100)FNM,ND
      WRITE(11,2125)
2125  FORMAT(' ',/,/,1X,'  DAY  FEED     Po     S1     S2     X1L     X2L
     1 X1L/X2L         S6')
      WRITE(7,2125)
      WRITE(11,2130)(IDAY(I), FC(I), P(I), S1(I), S2(I), X1L(I),
     1 X2L(I),  XLR(I), S6(I), I=1,ND)
2130  FORMAT(3X, I3,1X, F6.0, 2X, F6.0,4F7.0,2X,F5.1,F7.0)
      WRITE(7,2130)(IDAY(I), FC(I), P(I), S1(I), S2(I), X1L(I),
     1 X2L(I),  XLR(I), S6(I), I=1,ND)
99    IF(K2.EQ.0) GOTO 161
      NSS2 = NSS2 + 1
      IF(NSS2.EQ.NS2) GOTO 161
      IANS7 = IANS9
      GOTO 162
161   NSS = NSS + 1
      IF(NSS.EQ.NS) GOTO 199
      NSS2 = 0
      IANS7 = IANS8
      GOTO(170,171,172,173,174,175,176,177,178,179,180)IANS9
170   VMAX1 = VMAX1B
      GOTO 162
171   HK1 = HK1B
      GOTO 162
172   Y1 = Y1B
      GOTO 162
173   B1 = B1B
```

```
      GOTO 162
174   YAS = YASB
      GOTO 162
175   VMAX2 = VMAX2B
      GOTO 162
176   HK2 = HK2B
      GOTO 162
177   Y2 = Y2B
      GOTO 162
178   B2 = B2B
      GOTO 162
179   KP = KPB
      GOTO 162
180   Vo = VoB
162   GOTO(123,124,125,126,127,128,129,130,131,132,133)IANS7
123   VMAX1 = VMAX1 + VMAX1I
      GOTO 288
124   HK1 = HK1 + HK1I
      GOTO 288
125   Y1 = Y1 + Y1I
      GOTO 288
126   B1 = B1 + B1I
      GOTO 288
127   YAS = YAS + YASI
      GOTO 288
128   VMAX2 = VMAX2 + VMAX2I
      GOTO 288
129   HK2 = HK2 + HK2I
      GOTO 288
130   Y2 = Y2 + Y2I
      GOTO 288
131   B2 = B2 + B2I
      GOTO 288
132   KP = KP + KPI
      GOTO 288
133   Vo = Vo + VoI
288   GOTO 140
      CLOSE(7,STATUS='KEEP')
199   END
      INTEGER FUNCTION RUNGE(N,Y,F,X,H)
      DIMENSION PHI(6),SAVEY(6),Y(N),F(N),QQ(6),QQ2(6)
      COMMON RT3,RT4,RT5,RT6,RT7,RTH1,RTH2,RTH3,RTH4,RTH6,RTH7
      DATA M/0/
      M = M + 1
      GOTO (1,2,3,4,5) M
1     RUNGE = 1
      RETURN
2     DO 22 J=1,N
      SAVEY(J) = Y(J)
      PHI(J) = F(J)
      QQ(J) = F(J)
22    Y(J) = SAVEY(J) + RTH3*F(J)
```

```
        X = X + 0.5*H
        RUNGE = 1
        RETURN
3       DO 33 J=1,N
        PHI(J) = PHI(J) + RT5*F(J)
        QQ2(J) = F(J)
33      Y(J) = SAVEY(J) + RTH7*QQ(J) + RTH1*F(J)
        RUNGE = 1
        RETURN
4       DO 44 J=1,N
        PHI(J) = PHI(J) + RT6*F(J)
44      Y(J) = SAVEY(J) - RTH2*QQ2(J) + RTH6*F(J)
        X = X + 0.5*H
        RUNGE = 1
        RETURN
5       DO 55 J=1,N
55      Y(J) = SAVEY(J) + (PHI(J) + F(J))*RTH4
        M = 0
        RUNGE = 0
        RETURN
        END
```

APPENDIX B

FORTRAN PROGRAM FOR THE ADVANCED MODEL

```
      PROGRAM BIOREACTOR
C     r = 1800 H2(aq)
C     RESULTS ARE PRINTED ON A HARD COPY
C     ----------------------------------
C     NOTE: THIS PROGRAM USE A NEW CONSTANT FOR THE MAXIMUM VELOCITY
C           OF SUBSTRATE UTILIZATION RATE.
C           Vmaxi(NEW) = Vmaxi*Xi
C            WHERE:  Vmaxi = max. specific substrate uptake rate.
C                 Xi = Concentration of m.o. in SBR.
C           Vmaxi.Xi is determined as a single constant from
C            the experimental data.
C     ADVANCED MODEL
C     DYNAMIC SIMULATION PROGRAM OF ASBR EXPERIMENTAL RUNS
C     INCLUDING EFFECTS OF FILL AND REACT PERIODS.
      CHARACTER*6 FNM
      CHARACTER*3 CH105,CH106,CH107
      CHARACTER*9 CH2
      CHARACTER*38 CH102
      CHARACTER*16 CH100
      CHARACTER*18 CH24
      CHARACTER*19 DRIVE,CH4
      CHARACTER*20 CH20,CH71,CH26
      CHARACTER*24 CH23
      CHARACTER*30 DFNM,CH3
      CHARACTER*40 CH104
      CHARACTER*22 CH103,CH25
      CHARACTER*46 CH11,CH10
      CHARACTER*51 CH62
      CHARACTER*49 CH63
      CHARACTER*44 CH64
      CHARACTER*48 CH61
      CHARACTER*52 CH452
      CHARACTER*52 CH453
      CHARACTER*52 CH454
      CHARACTER*52 CH455
      CHARACTER*52 CH456
      CHARACTER*29 CH552
      CHARACTER*29 CH553
      CHARACTER*29 CH554
      CHARACTER*29 CH555
      CHARACTER*29 CH556
      CHARACTER*50 CH41
      CHARACTER*48 CH652
      CHARACTER*48 CH662
      CHARACTER*44 CH663
      CHARACTER*44 CH664
      CHARACTER*44 CH665
      CHARACTER*44 CH666
      CHARACTER*48 CH653
```

```
      CHARACTER*48 CH654
      CHARACTER*48 CH655
      CHARACTER*48 CH656
      CHARACTER*20 CH722
      CHARACTER*20 CH723
      CHARACTER*20 CH724
      CHARACTER*20 CH725
      CHARACTER*20 CH726
      CHARACTER*39 CH91
      CHARACTER*23 CH101
      CHARACTER*26 CH22,CH5,CH7,CH27
      CHARACTER*28 CH1
      CHARACTER*29 CH51,CH6,CH9
      CHARACTER*45 CH8
      CHARACTER*52 CH81
      CHARACTER*79 CH32, CH33, CH42, CH43
      CHARACTER*80 CH28
      INTEGER RUNGE
      REAL*8 KP,NH4,NH3l,KlaCO2,KHCO2,KPi,KLah2,Ka1,KHNH3,Kaac,
     1 KaPr,KNH4,HKac1,Kabu,KlaNH3,NH3gt,NH4lt,KHH2,Ka2,NH4nc,
     2 Mch4,NH4onc,NH4o,NH4p
      DIMENSION IDAY(100),Q(100),TCOD(100),SCOD(100),
     1 QCH4P(100),QCH4o(100),pH(100),TCODo(100),SCODo(100),
     2 Y(21),F(21),pHo(100),Pbio(100),CBbio(100),Pobio(100),
     3 CBobio(100), ALK(100), ALKo(100), CNBo(100),
     4 HRT(100),H2l(100),QCH4(100),H2g(100),
     5 VS(100),PrP(100),AC(100),PR(100),BU(100),NH4(100),
     6 ACo(100),BUo(100),PRo(100),BuP(100),Ac_(100),
     7 Zo(100),CO3(100),Hp(100),HCO3_(100),Pr_(100),
     8 Vl(100),Vg(100),Mch4(100),Bu_(100),Z(100),H2gp(100),
     9 CO2o(100),CO2(100),HCO3o(100),HCO3(100),CO3o(100)
      DIMENSION AcP(100),CBbioP(100),Pbiot(100),VsP(100),
     1 CBbiot(100),CNBt(100),BUt(100),Prt(100),Act(100),Xct(100),
     2 Xprt(100),Xbut(100),Xac1t(100),Xac2t(100),Xh2t(100),
     3 Qch4t(100),Qgt(100),H2gt(100),H2lt(100),NH3gt(100),
     4 CO2lt(100),Zt(100),Ht(100),ACoo(100),BUoo(100),PRoo(100),
     5 ACnc(100),BUnc(100),PRnc(100),NH4nc(100),CO2gt(100),
     6 NH4lt(100),Tcarbo(100),Tcarbop(100),NH4onc(100),NH4o(100),
     7 CO2p(100),H2lp(100),NH4p(100),CO2gp(100),VAo(100),VA(100),
     8 VAp(100),SCODP(100),TCODP(100)
      COMMON RT3,RT4,RT5,RT6,RT7
      COMMON RTH1,RTH2,RTH3,RTH4,RTH6,RTH7
      DATA Pbiot/100*0./,CBbiot/100*0./
      DATA CNBt/100*0./
      DATA Prt/100*0./,Act/100*0./,Xct/100*0./,Xprt/100*0./
      DATA Xbut/100*0./,Xac1t/100*0./,Xac2t/100*0./,Xh2t/100*0./
      DATA Qch4t/100*0./,Qgt/100*0./,H2gt/100*0./,H2lt/100*0./
      DATA NH4lt/100*0./,CO2lt/100*0./,CO2gt/100*0./,Zt/100*0./
      DATA Ht/100*0./,ACoo/100*0./,BUoo/100*0./,PRoo/100*0./
```

```
      DATA ACnc/100*0./,BUnc/100*0./,PRnc/100*0./,NH4nc/100*0./
      DATA TCOD/100*0./,SCOD/100*0./,QCH4o/100*0./,CNBo/100*0./
      DATA QCH4P/100*0./,QCH4/100*0./,But/100*0./,Hp/100*0./
      DATA VS/100*0./,HRT/100*0./,ALK/100*0./,Q/100*0./
      DATA ACo/100*0./,BUo/100*0./,PRo/100*0./,VsP/100*0./
      DATA AC/100*0./,BU/100*0./,PR/100*0./,ALKo/100*0./
      DATA NH3l/0./,pH/100*0./,H2g/100*0./,H2gp/100*0./
      DATA pHo/100*0./,Pobio/100*0./,CBobio/100*0./,Pbio/100*0./
      DATA CBbio/100*0./,CtCO3o/0./,CtCO3/0./,VAo/100*0./
      DATA Eo/0./,E/0./,CO2o/100*0./,CO2/100*0./,CO2gp/100*0./
      DATA HCO3o/100*0./,HCO3/100*0./,CO3o/100*0./,CO3/100*0./
      DATA Vl/100*0./,Vg/100*0./,Zo/100*0./,Z/100*0./
      DATA NH4/100*0./,H2l/100*0./,Nh3gt/100*0./VA/100*0./
      DATA HCO3_/100*0./,Mch4/100*0./,Tcarbo/100*0./
      DATA CO2p/100*0./,H2lp/100*0./,NH4p/100*0./
      DATA VAp/100*0./,SCODp/100*0./,TCODp/100*0./
      DATA Tcarbop/100*0./,NH4onc/100*0./,NH4o/100*0./
      DATA VMAXac1/0./,VMAXac2/0./,TCODo/100*0./,SCODo/100*0./
      DATA RAC/0./,RPR/0./,RBU/0./,RPPR/0./,RBBU/0./,R/0./,YC/0./
      DATA SPSUBc/0./,SPSUBbu/0./,SPSUBpr/0./,HKc/0./,HKbu/0./
      DATA SPSUBac1/0./,SPSUBac2/0./,VMAXh2/0./,Biod/0./
      DATA HKpr/0./,VMAXc/0./,VMAXbu/0./,VMAXpr/0./,RSc/0./
      DATA RSbu/0./,RSpr/0./,YN/0./
      DATA Ybuco2/0./,Yprco2/0./,Yh2co2/0./
      DATA YAC/0./,YPR/0./,YBU/0./,Ybb/0./,Ypp/0./
      DATA Ya1/0./,Ya2/0./,YB/0./,YP/0./,Yh2/0./,Yhh2/0./
      DATA KP/0./,Vo/0./,PT/0./,R/0./
      DATA HKac2/0./,HKh2/0./,Vstp/0./,Bionh4/0./
      DATA Yaa1/0./,Yaa2/0./,Bc/0./,Vo/0./
      DATA VMAXbu/0./, Vo/0./,wo/0./,w1/0./,w2/0./
      DATA wo2/0./,w12/0./,w22/0./,Ac_/100*0./,Pr_/100*0./
      DATA Bu_/100*0./,BioCH4/0./,BioH2/0./
      DATA N1/0/,N2/0/,N3/0/,N4/0/,N5/0/,SMC/0./
      DATA SMAc/0./,SMPr/0./,SMBu/0./,SMQCH4/0./,N12/0/,N22/0/,N32/0/
      DATA N42/0/,N52/0/,SMC2/0./,SMAc2/0./,SMPr2/0./,SMBu2/0./
      DATA Bbu/0./,Bpr/0./,Bac1/0./,Bac2/0./,Bh2/0./
      DATA RSac1/0./,RSac2/0./,SMQCH2/0./,Pco2/0./
      DATA TrH2/0./,TrNH3/0./
      OPEN(11,FILE='LPT1')
      CALL RTTH
C     ISVFL IS A FLAG TO SAVE CHANGES TO THE DEFAULT RATE CONSTANT FILE
      ISVFL = 0
C     INTEGRATION STEP
      HH = 0.0002
C     NS IS NO. OF INCREMENT STEPS FOR 1ST VARIABLE
      NS = 0
C     NSS IS COUNTER CONTROL FOR NS
      NSS = -1
C     K2 IS A FLAG FOR SECOND VARIABLE INCREMENTING
```

```
      K2 = 0
C     NS2 IS NO. OF INCREMENT STEPS FOR SECOND VARIABLE
      NS2 = 0
C     NSS2 IS COUNTER CONTROL FOR NS2
      NSS2 = -1
      WRITE(*,1010)
1010  FORMAT('0',13X,' DYNAMIC SIMULATION FOR DSFF REACTORS',/,/, ' TH
     1E STANDARD ERRORS OF ESTIMATE (SEE) WILL BE SHOWN ON THE SCREEN',
     2/,/, 28X, ' PRINT OPTIONS')
      WRITE(*,1011)
1011  FORMAT('0',4X,'1. NO PRINTING',/,/, 5X, '2. PRINT STD. ESTIMATE
     1OF ERROR',/,/, 5X, '3. PRINT SEE AND COMPARISON OF PREDICTED AND
     2MEASURED EFF. SOLUBLE AND TOTAL       COD, VOL. ACIDS, METH. PROD.,
     3AND FIlM VOLATILE SOLIDS.',/,/, 5X, '4. PRINT (3) + COMPLETE PRED
     4ICTED DATA SUMMARY.',/,/)
      WRITE(*,'(A\)')'  Enter the line no. of your choice.  -->'
      READ(*,'(BN,I1)') IP
      CH1 = 'CURRENT RATE CONSTANT VALUES'
      CH2 = 'Acidogens'
      CH3 = 'Acetogens (Propionic)'
      CH4 = 'Acetogens (Butyric)'
      CH5 = 'Methanogens (methanothrix)'
      CH6 = 'Methanogens (methanosarcinas)'
      CH7 = 'Methanogens (H2 utilizers)'
      CH8 = 'Max. substrate uptake rate, Vmax.Xi (mM/d)'
      CH9 = 'Half velocity constant (mM/L)'
      CH10 = 'Microorganism yield (mg of X /mM of Substrate)'
      CH11 = 'Substrate use for the formation of X (mM/mg X)'
      CH100 = 'Decay rate (1/d)'
      CH104 = 'Max. Spec. Particulate Solub. Rate (1/d)'
      CH102 = 'Biodegradable Fraction of Particulates'
      CH103 = 'SBR Initial Volume (L)'
      CH105 = 'Yac'
      CH106 = 'Ypr'
      CH107 = 'Ybu'
C     OPEN FILE FOR DEFAULT RATE CONSTANTS
      OPEN(1,FILE='C:\FORTRAN\ANAEROB\DEFRAT11',STATUS='OLD')
      READ(1,1000)Biod,KP,Vo,VMAXco,HKc,YAC,YPR,YBU,Yc,Bc
1000  FORMAT(10F12.5)
      OPEN(1,FILE='C:\FORTRAN\ANAEROB\DEFRAT12',STATUS='OLD')
      READ(1,1001)VMAXpro,HKpr,Ypp,Yp,Bpr,VMAXbuo,HKbu,Ybb,Yb,Bbu
1001  FORMAT(10F12.5)
      OPEN(1,FILE='C:\FORTRAN\ANAEROB\DEFRAT13',STATUS='OLD')
      READ(1,1002)VMAXac1o,HKac1,Yaa1,Ya1,Bac1,VMAXac2o,HKac2,Yaa2,
     1Ya2,Bac2
1002  FORMAT(10F12.5)
      OPEN(1,FILE='C:\FORTRAN\ANAEROB\DEFRAT14',STATUS='OLD')
      READ(1,1003)VMAXh2o,HKh2,Yhh2,Yh2,Bh2
1003  FORMAT(5F12.5)
```

```
1600 WRITE(*,2000)CH1,CH2,CH8,VMAXco,CH9,HKc,CH10,CH105,YAC,
    1CH106,YPR,CH107,YBU,CH11,YC,CH100,Bc,CH104,KP,CH102,Biod
2000 FORMAT(1X,A,/,3X,A,/,5X,' 1. ',A,15X,F12.5,/,5X,' 2. ',
    1A,31X,F12.5,/,5X,' 3. ',A,5X,A,6X,F12.5,/,
    25X,' 4. ',51X,A,6X,F12.5,/,5X,' 5. ',51X,A,6X,F12.5,/,5X,' 6.
    3A,14X,F12.5,/,5X,' 7. ',A,44X,F12.5,/,5X,' 8. ',A,20X,F12.5,/,
    45X,' 9. ',A,22X,F12.5,)
     WRITE(*,'(A\)')' To continue? (press Enter key) -->'
     READ(*,'(BN,I1)') IANS1
     WRITE(*,2001)CH3,CH8,VMAXpro,CH9,HKpr,CH10,Ypp,
    1CH11,Yp,CH100,Bpr
2001 FORMAT(3X,A,/,/,5X,' 10. ',A,14X,F12.5,/,5X,' 11. ',
    1A,30X,F12.5,/,5X,' 12. ',A,13X,F12.5,/,
    25X,' 13. ',A,13X,F12.5,/,5X,' 14. ',A,43X,F12.5)
     WRITE(*,'(A\)')' To continue? (press Enter key) -->'
     READ(*,'(BN,I1)') IANS1
     WRITE(*,2002)CH4,CH8,VMAXbuo,CH9,HKbu,CH10,Ybb,
    1CH11,Yb,CH100,Bbu
2002 FORMAT(3X,A,/,/,5X,' 15. ',A,14X,F12.5,/,5X,' 16. ',
    1A,30X,F12.5,/,5X,' 17. ',A,13X,F12.5,/,
    25X,' 18. ',A,13X,F12.5,/,5X,' 19. ',A,43X,F12.5)
     WRITE(*,'(A\)')' To continue? (press Enter key) -->'
     READ(*,'(BN,I1)') IANS1
     WRITE(*,2003)CH5,CH8,VMAXac1o,CH9,HKac1,CH10,Yaa1,
    1CH11,Ya1,CH100,Bac1
2003 FORMAT(3X,A,/,/,5X,' 20. ',A,14X,F12.5,/,5X,' 21. ',
    1A,30X,F12.5,/,5X,' 22. ',A,13X,F12.5,/,
    25X,' 23. ',A,13X,F12.5,/,5X,' 24. ',A,43X,F12.5)
     WRITE(*,'(A\)')' To continue? (press Enter key) -->'
     READ(*,'(BN,I1)') IANS1
     WRITE(*,2004)CH6,CH8,VMAXac2o,CH9,HKac2,CH10,Yaa2,
     1CH11,Ya2,CH100,Bac2
2004 FORMAT(3X,A,/,/,5X,' 25. ',A,14X,F12.5,/,5X,' 26. ',
     1A,30X,F12.5,/,5X,' 27. ',A,13X,F12.5,/,
     25X,' 28. ',A,13X,F12.5,/,5X,' 29. ',A,43X,F12.5)
     WRITE(*,'(A\)')' To continue? (press Enter key) -->'
     READ(*,'(BN,I1)') IANS1
     WRITE(*,2005)CH7,CH8,VMAXh2o,CH9,HKh2,CH10,Yhh2,
     1CH11,Yh2,CH100,Bh2,CH103,Vo
2005 FORMAT(3X,A,/,/,5X,' 30. ',A,14X,F12.5,/,5X,' 31. ',
     1A,30X,F12.5,/,5X,' 32. ',A,13X,F12.5,/,
     25X,' 33. ',A,13X,F12.5,/,5X,' 34. ',A,43X,F12.5,
     3/,/,5X,' 35. 'A,37X,F12.5)
     WRITE(*,'(A\)')' To continue? (press Enter key) -->'
     READ(*,'(BN,I1)') IANS1
2030 FORMAT('0', 5X,A,/,5X,A)
     WRITE(*,'(A\)')' Do you wish to change a constant? (press Enter
    1key for no; 1 for yes) -->'
     READ(*,'(BN,I1)') IANS1
```

```
      IF(IANS1.EQ.1) GOTO 1009
      GOTO 1400
1009  WRITE(*,'(A\)') ' Enter the line no. that you want to change.  -
     1->'
      READ(*,'(BN,I2)') IANS2
      ISVFL = 1
      GOTO(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,
     123,24,25,26,27,28,29,30,31,32,33,34,35)IANS2
     1WRITE(*,'(A\)')' Enter the new value for acidogens max. vel.  --
     1>'
      READ(*,'(F10.5)') VMAXco
      GOTO 1600
2     WRITE(*,'(A\)')' Enter the new value for acidogens half vel. con
     1stant. - ->'
      READ(*,'(F10.5)') HKc
      GOTO 1600
3     WRITE(*,'(A\)')' Enter the new value for acidogens yield factor
     1(mg Xa/ mM carbohydrate to acetic acid)-->'
      READ(*,'(F10.5)') YAC
      GOTO 1600
4     WRITE(*,'(A\)')' Enter the new value for acidogens yield factor
     1(mg Xa/ mM carbohydrate to propionic acid)-->'
      READ(*,'(F10.5)') YPR
      GOTO 1600
5     WRITE(*,'(A\)')' Enter the new value for acidogens yield factor
     1(mg Xa/ mM carbohydrate to butyric acid)-->'
      READ(*,'(F10.5)') YBU
      GOTO 1600
6     WRITE(*,'(A\)')' Enter the new value for amount of carbohydrate
     1use in the formation of 1 gr of acid formers (mM/mg)-->'
      READ(*,'(F10.5)') YC
      GOTO 1600
7     WRITE(*,'(A\)')' Enter the new value for acidogens decay rate.
     1-->'
      READ(*,'(F10.5)') Bc
      GOTO 1600
8     WRITE(*,'(A\)')' Enter the new value for particulate
     1solubilization rate. -->'
      READ(*,'(F10.5)') KP
      GOTO 1600
9     WRITE(*,'(A\)')' Enter the new value for biodegradable
     1fraction of carbohydrates.  -->'
      READ(*,'(F10.5)') Biod
      GOTO 1600
10    WRITE(*,'(A\)')' Enter the new value for acetogens (propionic)
     1max. vel. -->'
      READ(*,'(F10.5)') VMAXpro
      GOTO 1600
11    WRITE(*,'(A\)')' Enter the new value for ace.(prop.) half vel.
```

```
     1constant. -->'
      READ(*,'(F10.5)') HKpr
      GOTO 1600
12    WRITE(*,'(A\)')' Enter the new value for ace.(prop.) yield
     1factor (mg Xpr/ mM propionic to acetic)-->'
      READ(*,'(F10.5)') Ypp
      GOTO 1600
13    WRITE(*,'(A\)')' Enter the new value for amount of propionic
     1acid used for synthesis of 1g of acetogenic X.    -->'
      READ(*,'(F10.5)') Yp
      GOTO 1600
14    WRITE(*,'(A\)')' Enter the new value for ace.(prop.) decay
     1rate.     -->'
      READ(*,'(F10.5)') Bpr
      GOTO 1600
15    WRITE(*,'(A\)')' Enter the new value for acetogens (butyric)
     1max. vel. -->'
      READ(*,'(F10.5)') VMAXbuo
      GOTO 1600
16    WRITE(*,'(A\)')' Enter the new value for ace.(buty.) half vel.
     1constant. -->'
      READ(*,'(F10.5)') HKbu
      GOTO 1600
17    WRITE(*,'(A\)')' Enter the new value for ace.(buty.) yield
     1factor (mg Xpr/ mM butyric to acetic)-->'
      READ(*,'(F10.5)') Ybb
      GOTO 1600
18    WRITE(*,'(A\)')' Enter the new value for amount of butyric
     1acid used for synthesis of 1g of acetogenic X.    -->'
      READ(*,'(F10.5)') Yb
      GOTO 1600
19    WRITE(*,'(A\)')' Enter the new value for ace.(buty.) decay
     1rate.     -->'
      READ(*,'(F10.5)') Bbu
      GOTO 1600
20    WRITE(*,'(A\)')' Enter the new value for acetoclastic
     1methanothrix max. vel. -->'
      READ(*,'(F10.5)') VMAXac1o
      GOTO 1600
21    WRITE(*,'(A\)')' Enter the new value for methanothrix half vel.
     1constant. -->'
      READ(*,'(F10.5)') HKac1
      GOTO 1600
22    WRITE(*,'(A\)')' Enter the new value for methanothrix yield
     1factor (mg Xpr/ mM acetic to CH4)-->'
      READ(*,'(F10.5)') Yaa1
      GOTO 1600
23    WRITE(*,'(A\)')' Enter the new value for amount of acetic
     1acid used for synthesis of 1g of methanothrix X.  -->'
```

```
      READ(*,'(F10.5)') Ya1
      GOTO 1600
24    WRITE(*,'(A\)')' Enter the new value for methanothrix decay
     1rate.      -->'
      READ(*,'(F10.5)') Bac1
      GOTO 1600
25    WRITE(*,'(A\)')' Enter the new value for acetoclastic
     1methanosarcinas max. vel. -->'
      READ(*,'(F10.5)') VMAXac2o
      GOTO 1600
26    WRITE(*,'(A\)')' Enter the new value for methanosarcinas half vel.
     1constant. -->'
      READ(*,'(F10.5)') HKac2
      GOTO 1600
27    WRITE(*,'(A\)')' Enter the new value for methanosarcinas yield
     1factor (mg Xpr/ mM acetic to CH4)-->'
      READ(*,'(F10.5)') Yaa2
      GOTO 1600
28    WRITE(*,'(A\)')' Enter the new value for amount of acetic
     1acid used for synthesis of 1g of methanosarcinas X.     -->'
      READ(*,'(F10.5)') Ya2
      GOTO 1600
29    WRITE(*,'(A\)')' Enter the new value for methanosarcinas decay
     1rate.      -->'
      READ(*,'(F10.5)') Bac2
      GOTO 1600
30    WRITE(*,'(A\)')' Enter the new value for H2 utilizer
     1methanogens max. vel. -->'
      READ(*,'(F10.5)') VMAXh2o
      GOTO 1600
31    WRITE(*,'(A\)')' Enter the new value for H2 red. methanogens
     1half vel. constant. -->'
      READ(*,'(F10.5)') HKh2
      GOTO 1600
32    WRITE(*,'(A\)')' Enter the new value for H2 red. yield
     1factor (mg Xpr/ mM H2 to CH4)-->'
      READ(*,'(F10.5)') Yhh2
      GOTO 1600
33    WRITE(*,'(A\)')' Enter the new value for amount of H2
     1acid used for synthesis of 1g of H2 red. X.  -->'
      READ(*,'(F10.5)') Yh2
      GOTO 1600
34    WRITE(*,'(A\)')' Enter the new value for H2 red. decay
     1rate.      -->'
      READ(*,'(F10.5)') Bh2
      GOTO 1600
35    WRITE(*,'(A\)')' Enter the new value for SBR initial volume.  -
     1->'
      READ(*,'(F7.4)') Vo
```

```
      GOTO 1600
1400  WRITE(*,'(A\)')' Do you wish to have one variable automatically
     1incremented?  (Enter 0 for no; 1 for yes)  -->'
      READ(*,'(BN,I1)') IANS6
      IF(IANS6.EQ.0) GOTO 90
      WRITE(*,'(A\)') ' Enter the line no. that you want to increment.
     1  -->'
      READ(*,'(BN,I2)') IANS8
      IANS7 = IANS8
1006  GOTO(101,102,103,104,105,106,107,108,109,110,111,112,113,
     1114,115,116,117,118,119,120,121,122,123,124,125,126,127,
     2128,129,130,131,132,133,134,135)IANS7
101   WRITE(*,'(A\)')' Enter the increment value for acidogens max. ve
     1l.  -->'
      READ(*,'(F10.5)') VMAXcI
C     B ADDED TO VARIABLE REFERS TO ITS BEGINNING VALUE IN CASE IT'S
C     CHANGED DURING INCREMENTING
      VMAXcB = VMAXco
      GOTO 1140
102   WRITE(*,'(A\)')' Enter the increment value for acidogens half ve
     1l. constant. - ->'
      READ(*,'(F10.5)') HKcI
      HKcB = HKc
      GOTO 1140
103   WRITE(*,'(A\)')' Enter the increment value for acidogens yield
     1factor YAC. -->'
      READ(*,'(F10.5)') YACI
      YACB = YAC
      GOTO 1140
104   WRITE(*,'(A\)')' Enter the increment value for acidogens yield f
     1actor YPR. -->'
      READ(*,'(F10.5)') YPRI
      YPRB = YPR
      GOTO 1140
105   WRITE(*,'(A\)')' Enter the increment value for acidogens yield f
     1actor YBU. -->'
      READ(*,'(F10.5)') YBUI
      YBUB = YBU
      GOTO 1140
106   WRITE(*,'(A\)')' Enter the increment value for YC
     1mM of Carbo./ mg Xc  -->'
      READ(*,'(F10.5)') YCI
      YCB = YC
      GOTO 1140
107   WRITE(*,'(A\)')' Enter the increment value for Bc, 1/d
     1.    -->'
      READ(*,'(F10.5)') BcI
      BcB = Bc
      GOTO 1140
```

```
108  WRITE(*,'(A\)')' Enter the increment value for KP, 1/d
    1-->'
     READ(*,'(F10.5)') KPI
     KPB = KP
     GOTO 1140
109  WRITE(*,'(A\)')' Enter the increment value for Biod
    1onstant.  -->'
     READ(*,'(F10.5)') BiodI
     BiodB = Biod
     GOTO 1140
110  WRITE(*,'(A\)')' Enter the increment value for acetogens max. ve
    11, VMAXpr. -->'
     READ(*,'(F10.5)') VMAXprI
     VMAXprB = VMAXpro
     GOTO 1140
111  WRITE(*,'(A\)')' Enter the increment value for acetogens half ve
    11. constant, HKpr. - ->'
     READ(*,'(F10.5)') HKprI
     HKprB = HKpr
     GOTO 1140
112  WRITE(*,'(A\)')' Enter the increment value for acetogen yield
    1factor Ypp. -->'
     READ(*,'(F10.5)') YppI
     YppB = Ypp
     GOTO 1140
113  WRITE(*,'(A\)')' Enter the increment value for Yp,
    1mM of pr/mg of Xpr. -->'
     READ(*,'(F10.5)') YPI
     YpB = Yp
     GOTO 1140
114  WRITE(*,'(A\)')' Enter the increment value for Bpr, 1/d
    1.    -->'
     READ(*,'(F10.5)') BprI
     BprB = Bpr
     GOTO 1140
115  WRITE(*,'(A\)')' Enter the increment value for acetogens max. ve
    11, VMAXbu. -->'
     READ(*,'(F10.5)') VMAXbuI
     VMAXbuB = VMAXbuo
     GOTO 1140
116  WRITE(*,'(A\)')' Enter the increment value for acetogen half ve
    11. constant, HKbu. - ->'
     READ(*,'(F10.5)') HKbuI
     HKbuB = HKbu
     GOTO 1140
117  WRITE(*,'(A\)')' Enter the increment value for acetogens yield
    1factor Ybb. -->'
     READ(*,'(F10.5)') YbbI
     YbbB = Ybb
```

```
      GOTO 1140
118   WRITE(*,'(A\)')' Enter the increment value for Yb,
     1mM of bu/mg of Xbu. -->'
      READ(*,'(F10.5)') YbI
      YbB = Yb
      GOTO 1140
119   WRITE(*,'(A\)')' Enter the increment value for Bbu, 1/d
     1.    -->'
      READ(*,'(F10.5)') BbuI
      BbuB = Bbu
      GOTO 1140
120   WRITE(*,'(A\)')' Enter the increment value for methanothrix
     1 max vel, VMAXac1. -->'
      READ(*,'(F10.5)') VMAXac1I
      VMAXac1B = VMAXac1o
      GOTO 1140
121   WRITE(*,'(A\)')' Enter the increment value for CH4-X half ve
     11. constant, HKac1. - ->'
      READ(*,'(F10.5)') HKac1I
      HKac1B = HKac1
      GOTO 1140
122   WRITE(*,'(A\)')' Enter the increment value for CH4-X yield
     1factor Yaa1 -->'
      READ(*,'(F10.5)') Yaa1I
      Yaa1B = Yaa1
      GOTO 1140
123   WRITE(*,'(A\)')' Enter the increment value for Ya1,
     1mM of ac/mg of Xac1. -->'
      READ(*,'(F10.5)') Ya1I
      Ya1B = Ya1
      GOTO 1140
124   WRITE(*,'(A\)')' Enter the increment value for Bac1, 1/d
     1.    -->'
      READ(*,'(F10.5)') Bac1I
      Bac1B = Bac1
      GOTO 1140
125   WRITE(*,'(A\)')' Enter the increment value for methanosarcina
     1s max vel, VMAXac2. -->'
      READ(*,'(F10.5)') VMAXac2I
      VMAXac2B = VMAXac2o
      GOTO 1140
126   WRITE(*,'(A\)')' Enter the increment value for CH4-nas half ve
     11. constant, HKac2. - ->'
      READ(*,'(F10.5)') HKac2I
      HKac2B = HKac2
      GOTO 1140
127   WRITE(*,'(A\)')' Enter the increment value for CH4-nas yield
     1factor Yaa2 -->'
      READ(*,'(F10.5)') Yaa2I
```

```
      Yaa2B = Yaa2
      GOTO 1140
128   WRITE(*,'(A\)')' Enter the increment value for Ya2,
     1mM of ac/mg of Xac2. -->'
      READ(*,'(F10.5)') Ya2I
      Ya2B = Ya2
      GOTO 1140
129   WRITE(*,'(A\)')' Enter the increment value for Bac2, 1/d
     1.    -->'
      READ(*,'(F10.5)') Bac2I
      Bac2B = Bac2
      GOTO 1140
130   WRITE(*,'(A\)')' Enter the increment value for H2 utilizer
     1s max vel, VMAXh2. -->'
      READ(*,'(F10.5)') VMAXh2I
      VMAXh2B = VMAXh2o
      GOTO 1140
131   WRITE(*,'(A\)')' Enter the increment value for H2 util. half v
     1el. constant, HKh2. - ->'
      READ(*,'(F10.5)') HKh2I
      HKh2B = HKh2
      GOTO 1140
132   WRITE(*,'(A\)')' Enter the increment value for H2 util. yield
     1factor Yhh2 -->'
      READ(*,'(F10.5)') Yhh2I
      Yhh2B = Yhh2
      GOTO 1140
133   WRITE(*,'(A\)')' Enter the increment value for Yh2,
     1mM of H2/mg of Xh2. -->'
      READ(*,'(F10.5)') Yh2I
      Yh2B = Yh2
      GOTO 1140
134   WRITE(*,'(A\)')' Enter the increment value for Bh2, 1/d
     1.    -->'
      READ(*,'(F10.5)') Bh2I
      Bh2B = Bh2
      GOTO 1140
135   WRITE(*,'(A\)')' Enter the increment value for SBR initial volu
     1me -->'
      READ(*,'(F10.5)') VoI
      VoB = Vo
1140  WRITE(*,'(A\)')' Enter the no. of increment steps (1-9).  -->'
      IF(K2.EQ.1) GOTO 1160
      READ(*,'(BN,I1)') NS
      GOTO 1170
1160  READ(*,'(BN,I1)') NS2
      GOTO 90
1170  WRITE(*,'(A\)')' Do you wish to have a second variable automatic
     1ally incremented?  (Enter 0 for no; 1 for yes)  -->'
```

```
      READ(*,'(BN,I1)') IANS6
      IF(IANS6.EQ.0) GOTO 90
      K2 = 1
      WRITE(*,'(A\)') ' Enter the line no. that you want to increment.
     1  -->'
      READ(*,'(BN,I2)') IANS9
      IANS7 = IANS9
      GOTO 1006
90    WRITE(*,'(A\)')' Enter the run no. (eq. TRxyz) for evaluation -->'
      READ(*,'(A6)')FNM
      DRIVE = 'C:\FORTRAN\ANAEROB\'
      WRITE(DFNM,'(A,A)') DRIVE, FNM
      OPEN(2,FILE=DFNM,STATUS='OLD')
      READ(2,2039)FNM
2039  FORMAT(A6)
C     ND IS THE NUMBER OF DAYS IN THE RUN
      READ(2,2040)ND
2040  FORMAT(I3)
C     MD IS THE FIRST RANGE OF NO. DAYS IN STD ERROR OF ESTIMATE
      READ(2,2041)MD
      MD1 = MD + 1
2041  FORMAT(I3)
      READ(2,2050)(IDAY(I), Q(I), TCODo(I), SCODo(I), ACoo(I),
     1BUoo(I), PRoo(I), TCOD(I), SCOD(I), ACnc(I), BUnc(I), PRnc(I),
     2VS(I), QCH4o(I), pHo(I), pH(I), ALKo(I), ALK(I), NH4onc(I),
     3NH4nc(I), H2l(I),H2g(I), I = 1,ND)
2050  FORMAT(I3,F8.5,11F9.2,3F8.4,4F9.2,F15.7,F15.10)
C     nc means that concentrations are in mg/l
      DO 2020 I=1,ND
C     1.066 mg COD/mg C6H12O6
C     180 mg C6H12O6 / mM of C6H12O6
C     TOTAL VA on a COD basis
      VAo(I) = 1.06*ACoo(I) + 1.51*PRoo(I) + 1.818*BUoo(I)
      VA(I) = 1.06*ACnc(I) + 1.51*PRnc(I) + 1.818*BUnc(I)
C     INFLUENT CONCENTRATION OF PARTICULATE CARBOHYDRATE IN mM/L.
C     Po(I) = ((TCODo(I) - SCODo(I))/1.066)/180
C     INFLUENT CONCENTRATION OF SOLUBLE CARBOHYDRATE IN mM/L.
C     CBo(I) = ((SCODo(I) - VAo(I))/1.066)/180
C     INFLUENT CONCENTRATION OF PARTICULATE CARBOHYDRATE IN mM/L.
      Pobio(I) = Biod*(((TCODo(I) - SCODo(I))/1.066)/180)
C     INFLUENT CONCENTRATION OF SOLUBLE CARBOHYDRATE IN mM/L.
C     CBobio(I) = CBo(I)
      CBobio(I) = Biod*(((SCODo(I) - VAo(I))/1.066)/180)
      IF (CBobio(I).gt.0.0) GOTO 766
      CBobio(I) = 0.01
C     NON-BIODEGRADABLE INFLUENT CONCENTRATION OF SOLUBLE ORGANICS IN
      1mM/L.
C     ASSUMED THAT NON-BIODEGRADABLE SOLUBLE ORGANIC IS MADE OF
      1CARBOHYDRATE.
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766   CNBo(I) = ((CBobio(I)))*(1 - Biod)
C     SBR CONCENTRATION OF PARTICULATE CARBOHYDRATE IN mM/L.
      Pbio(I) = (((TCOD(I) - SCOD(I))/1.066)/180)
C     SBR CONCENTRATION OF SOLUBLE CARBOHYDRATE IN mM/L.
      CBbio(I) = (((SCOD(I) - VA(I))/1.066)/180)
      IF (CBbio(I).gt.0.0) GOTO 765
      CBbio(I) = 0.01
C     TOTAL CH2O IN SBR
765   Tcarbo(I) = Pbio(I) + CBbio(I)
C     NON-BIODEGRADABLE SBR CONCENTRATION OF SOLUBLE CARBOHYDRATE IN mM/L.
C     CNB(I) = (CBbio(I))*(1 - Biod)
C     NOTE: CAN NOT USED THE ABOVE EXPRESSION BECAUSED 'Biod' IS
C     VARIABLE IN THE SBR, IT IS LARGE AT THE END OF FILL PERIOD
C     AND IT IS VERY SMALL AT THE END OF THE REACT PERIOD.
C     QCH4 IS BIOGAS FLOWRATE L/D, WHICH MUST BE CONVERTED
C     TO mMOLE of CH4 per day)
C     QH2O = 2% of QCH4
      QCH4(I) = 0.98*(QCH4o(I)/25.0)*1000
C     CONVERT CONCENTRATIONS FROM mg/l to mM/l
      ACo(I) = ACoo(I)/60.0
      BUo(I) = BUoo(I)/88.0
      PRo(I) = PRoo(I)/74.0
      AC(I) = ACnc(I)/60.0
      BU(I) = BUnc(I)/88.0
      PR(I) = PRnc(I)/74.0
      NH4o(I) = NH4onc(I)/18.0
      NH4(I) = NH4nc(I)/18.0
C     DISSOCIATION CONSTANT VALUES AT 20 oC
      Ka1 = (1.0/10.0**6.33)
      Ka2 = (1.0/10.0**10.34)
C     DETERMINATION OF CO2, HCO3, CO3 in INFLUENT from pH and Alkalinity.
C     Eo = H**2.0 + H*Ka1 + Ka1*Ka2
      Eo = (1/10**pHo(I))**2.0 + (1/10**pHo(I))*(Ka1) +
     1(Ka1)*(Ka2)
      wo = ((1/10**pHo(I))**2.0)/Eo
      w1 = (1/10**pHo(I))*(Ka1)/Eo
      w2= (Ka1)*(Ka2)/Eo
C     ALKALINITY IS EXPRESSED IN eq.
      CtCO3o = ((ALKo(I)/50000.0) + (1/10**pHo(I)) -
     1((1/10**14)/(1/10**pHo(I))))/(w1 + 2*w2)
C     CONCENTRATIONS IN mM/l
      CO2o(I) = wo*CtCO3o*1000.0
      HCO3o(I) = w1*CtCO3o*1000.0
      CO3o(I)  = w2*CtCO3o*1000.0
C     DETERMINATION OF CO2, HCO3, CO3 in SBR DIGESTER from pH and
      1Alkalinity.
C     E = [h]**2.0 + [H]*Ka1 + Ka1*Ka2
      E = (1/10**pH(I))**2.0 + (1/10**pH(I))*(Ka1) +
     1(Ka1)*(Ka2)
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      wo2 = ((1/10**pH(I))**2.0)/E
      w12 = (1/10**pH(I))*(Ka1)/E
      w22 = (Ka1)*(Ka2)/E
C     ALKALINITY IS EXPRESSED IN eq.
      CtCO3 = ((ALK(I)/50000.0) + (1/10**pH(I)) -
     1((1/10**14)/(1/10**pH(I))))/(w12 + 2*w22)
C     CONCENTRATIONS IN mM/l
      CO2(I) = wo2*CtCO3*1000.0
      HCO3(I) = w12*CtCO3*1000.0
      CO3(I)  = w22*CtCO3*1000.0
C     Zo = MEASURED (Cation - Anion) in Feed (Influent)
      Zo(I) = HCO3o(I) - NH4o(I) + ACo(I) + Pro(I) + BUo(I)
C     Z = MEASURED (Cation - Anion) in ASBR DIGESTER
      Z(I) = HCO3(I) - NH4(I) + AC(I) + Pr(I) + BU(I)
2020  CONTINUE
C     COMPUTE SUMS OF PARAMETERS FOR LATER USE IN STD ERROR OF ESTIMATE
      DO 300 I=1,MD
      IF (CBbio(I).LT.0.01) GOTO 301
      N1 = N1 + 1
      SMC = SMC + CBbio(I)
301   IF (Ac(I).LT.0.01) GOTO 302
      N2 = N2 + 1
      SMAc = SMAc + Ac(I)
302   IF (Pr(I).LT.0.01) GOTO 303
      N3 = N3 + 1
      SMPr = SMPr + Pr(I)
303   IF (Bu(I).LT.0.01) GOTO 304
      N4 = N4 + 1
      SMBu = SMBu + Bu(I)
304   IF (QCH4o(I).LT.0.01) GOTO 300
      N5 = N5 + 1
      SMQCH4 = SMQCH4 + QCH4o(I)
300   CONTINUE
      DO 310 I=MD1,ND
      IF (CBbio(I).LT.0.01) GOTO 311
      N12 = N12 + 1
      SMC2 = SMC2 + CBbio(I)
311   IF (Ac(I).LT.0.01) GOTO 312
      N22 = N22 + 1
      SMAc2 = SMAc2 + Ac(I)
312   IF (Pr(I).LT.0.01) GOTO 313
      N32 = N32 + 1
      SMPr2 = SMPr2 + Pr(I)
313   IF (Bu(I).LT.0.01) GOTO 314
      N42 = N42 + 1
      SMBu2 = SMBu2 + Bu(I)
314   IF (QCH4o(I).LT.0.01) GOTO 310
      N52 = N52 + 1
      SMQCH2 = SMQCH2 + QCH4o(I)
```

```
310   CONTINUE
      N1T = N1 + N12
      N2T = N2 + N22
      N3T = N3 + N32
      N4T = N4 + N42
      N5T = N5 + N52
C     Y(1) = Particulate in SBR,mM/l
C     Y(2) = Soluble C6H12O6 in SBR, mM/l
C     Y(3) = Non Biodegradable Organic in SBR, mM/l
C     Y(4) = Bu in SBR,mM/l
C     Y(5) = Pr in SBR,mM/l
C     Y(6) = Ac in SBR,mM/l
C     Y(7) = Xc,mg/l
C     Y(8) = Xpr,mg/l
C     Y(9) = Xbu,mg/l
C     Y(10) = Xac1,mg/l
C     Y(11) = Xac2,mg/l
C     Y(12) = Xh2,mg/l
C     Y(13) = Qch4,mM/d
C     Y(14) = Qbiogas,l/d
C     Y(15) = H2g,atm
C     Y(16) = H2l,mM/l
C     Y(17) = NH3g,atm
C     Y(18) = NH4l+,mM/l
C     Y(19) = CO2g,atm
C     Y(20) = Cation 'Z',mM/l
C     Y(21) = CO2l,mM/l
C     Hp(J) = H+,mM/l
C
C
140   Y(1) = 0.4*0.88*pbio(1)
      Y(2) = 0.8*CBbio(1)
      Y(3) = 0.2*CBbio(1)
      Y(4) = BU(1)
      Y(5) = PR(1)
      Y(6) = AC(1)
      Y(7) = 9028
      Y(8) = 281.0
      Y(9) = 366.0
      Y(10) = 490.0
      Y(11) = 820.0
      Y(12) = 1652.0
      Y(13) = 0.0
      Y(14) = 0.0
      Y(15) = 0.000040
      Y(16) = .0001
      Y(17) = 0.005
      Y(18) = NH4(1)
      Y(19) = 0.20
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      Y(20) = Z(1)
      Y(21) = CO2(1)
C     CONSTANT VALUES AT 20 oC
      KNH4 = 6.0 E-10
      Vstp = 24.45
      Klah2 = .50
      KHh2 = 1.0729
      Klanh3 = 0.10
      KHnh3 = 5.39
      Klaco2 = 0.9
      KHco2 = 34.35
      YN = 0.008
      Kaac = 2.0 E-5
      Kapr = 2.0 E-5
      Kabu = 2.0 E-5
      YbuCo2 = 8.84 E-3
      YprCo2 = 4.42 E-3
      Yh2Co2 = 44.24 E-3
      Hp(1) = 0.00000002
      HCO3_(1) = 185.0
      Pco2 = 0.20
C     X IS TIME, Y(I) ARE PASSED TO SUBROUTINE RUNGE
      X = 0.0
      DO 3000 J = 1,ND
C     SBR Volume at Time Zero.
      Vl(0) = Vo
C     SBR Biogas Volume = (Total SBR Volume - SBR Liquid Volume)
      Vg(0) = (37.0 - Vo)
C     Liquid Volume at time t.
      Vl(J) = Vl(J-1) + Q(J)
C     Gas Volume at time t.
      Vg(J) = Vg(J-1) - Q(J)
      ICOUNT = 0
C     Hydraulic Residence Time at TIME t.
      IF (Q(J) .GT. 0.00) GOTO 1900
      HRT(J) = 10.E+20
      GOTO 2300
1900  HRT(J) = Vl(J)/Q(J)
2300  K = RUNGE(21,Y,F,X,HH)
C     WHENEVER K = 1, COMPUTE DERIVATIVE VALUES
      IF (K.NE.1) GOTO 21000
C     RG AND RD ARE MO GROWTH AND DECAY RATES
C     RS IS SUBSTRATE REMOVAL RATE
      DO 80 I = 1,21
      IF (Y(I).GT.0.0) GOTO 80
      Y(I) = 0.000000001
80    CONTINUE
      YX1 = Y(1)
      YX2 = Y(2)
```

```
      YX3 = Y(3)
      YX4 = Y(4)
      YX5 = Y(5)
      YX6 = Y(6)
      YX7 = Y(7)
      YX8 = Y(8)
      YX9 = Y(9)
      YX10 = Y(10)
      YX11 = Y(11)
      YX12 = Y(12)
      YX13 = Y(13)
      YX14 = Y(14)
      YX15 = Y(15)
      YX16 = Y(16)
      YX17 = Y(17)
      YX18 = Y(18)
      YX19 = Y(19)
      YX20 = Y(20)
      YX21 = Y(21)
C     NOTE: Vmaxi.Xi decreased during the fill period becaused of dilution
C     UNREGULATED SOLUBLE CARBOHYDRATES UTILIZATION RATE BY ACID
C     FORMERS
      VMAXc = VMAXco*(Vl(0)/Vl(J))
      SPSUBc= VMAXc*YX2/(HKc + YX2)
      RSc = SPSUBc
C     UNREGULATED BUTYRIC ACID UTILIZATION RATE BY ACETOGENS
      VMAXbu = VMAXbuo*(Vl(0)/Vl(J))
      SPSUBbu = VMAXbu*YX4/(HKbu + YX4)
      RSbu= SPSUBbu
C     UNREGULATED PROPIONIC ACID UTILIZATION RATE BY ACETOGENS
      VMAXpr = VMAXpro*(Vl(0)/Vl(J))
      SPSUBpr = VMAXpr*YX5/(HKpr + YX5)
      RSpr= SPSUBpr
C     ACETIC ACID UTILIZATION RATE BY THE ACETOCLASTICS
C     1) METHANOTHRIX SPP
      VMAXac1 = VMAXac1o*(Vl(0)/Vl(J))
      SPSUBac1 = VMAXac1*YX6/(HKac1 + YX6)
      RSac1= SPSUBac1
C     2) METHANOSARCINAS
      VMAXac2 = VMAXac2o*(Vl(0)/Vl(J))
      SPSUBac2 = VMAXac2*YX6/(HKac2 + YX6)
      RSac2= SPSUBac2
C     HYDROGEN UTILIZATION RATE BY THE METHANOBACTERIUM BRYANTII
      VMAXh2 = VMAXh2o*(Vl(0)/Vl(J))
      SPSUBh2 = VMAXh2*YX16/(HKh2 + YX16)
      RSh2= SPSUBh2
      RDc = Bc*YX7
      RDbu = Bbu*YX9
      RDpr = Bpr*YX8
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      RDac1 = Bac1*YX10
      RDac2 = Bac2*YX11
      RDh2 = Bh2*YX12
C     RATIO OF OXIDISED TO REDUCED ELECTRON CARRIER MOLECULE
C     R = NAD+ / NADH
      R = 1800*YX16
C     Regulation by hydrogen: conversion of carbohydrates to acetic
      RAC = 1/((1 + R)**3)
C     Regulation by hydrogen: conversion of carbohydra. to propionic
      RPR = R/((1 + R)**2)
C     Regulation by hydrogen: conversion of carbohydrates to butyric
      RBU = R/((1+R)**3)
C     Regulation by hydrogen: conversion of propionic to acetic
      RPPR = 1/(1+R)
C     Regulation by hydrogen: conversion of butyric to acetic
      RBBU = 1/(1+R)
C     TOTAL GAS PRESSURE IN DIDESTER
C     PT = 1 ATM + FAC*(6 inches water)
      PT = 1.0147
C     F(1) IS THE PARTICULATE MASS BALANCE, M/l
      F(1) = ((Pobio(J)-YX1)/HRT(J)) - KP*YX1
C     F(2) IS THE SOLUBLE CARBOHYDRATES MASS BALANCE, M/l
      F(2) = (CBobio(J) - YX2)/HRT(J) - RSc*(RAC + RPR + RBU) +
     1KP*YX1 - YC*(YAC*(RAC*RSc) + YPR*(RPR*RSc) +YBU*(RBU*RSc)) +
     2.00737*(RDc + RDpr + RDbu + RDac1 + RDac2 + RDh2)
C     Where YC = Amount of Carbohydrates used in the formation of
C     one gramme of acid formers.
C     F(3) IS THE NON-BIODEGRADABLE SOLUBLE ORGANICS MASS BALANCE, M/l
      F(3) = (CNBo(J) - YX3)/HRT(J)
C     F(4) IS THE BUTYRIC ACID SUBSTRATE BALANCE
      F(4) = (BUo(J) - YX4)/HRT(J) + RBU*RSc - RSbu*RBBU -
     1YB*RSbu*Ybb
C     F(5) IS THE PROPIONIC ACID SUBSTRATE BALANCE
      F(5) = (PRo(J) - YX5)/HRT(J) + 2*RPR*RSc - RSpr*RPPR -
     1YP*RSpr*Ypp
C     F(6) IS THE ACETIC ACID SUBSTRATE BALANCE
      F(6) = (ACo(J) - YX6)/HRT(J) + 2*(RAC*RSc) + (RSpr*RPPR) +
     12*RSBU*RBBu - RSac1 - RSac2 - Ya1*RSac1*Yaa1 - Ya2*RSac2*Yaa2
C     F(7) IS THE LIQUID ACIDOGENS MASS BALANCE
      F(7) = - YX7/HRT(J) + YAC*(RAC*RSc) + YPR*(RPR*RSc) +
     1YBU*(RBU*RSc) - RDc
C     F(8) IS THE LIQUID ACETOGENIC (PROPIONIC) MASS BALANCE
      F(8) = - YX8/HRT(J) + Ypp*(RSpr*RPPR) - RDpr
C     F(9) IS THE LIQUID ACETOGENIC (BUTYRIC) MASS BALANCE
      F(9) = - YX9/HRT(J) + Ybb*(RSbu*RBBU) - RDbu
C     F(10) IS THE LIQUID ACETOCLASTIC(METHANOTHRIX) MASS BALANCE
      F(10) = - YX10/HRT(J) + Yaa1*(RSac1) - RDac1
C     F(11) IS THE LIQUID ACETOCLASTIC(METHANOSARCINAS) MASS BALANCE
      F(11) = - YX11/HRT(J) + Yaa2*(RSac2) - RDac2
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C     F(12) IS THE LIQUID H2 UTILIZING METHANOGENS MASS BALANCE
      F(12) = - YX12/HRT(J) + Yhh2*(RSh2) - RDh2
C     BIOLOGICAL PRODUCTION OF H2, mM/l-dt
      BioH2 = 4*RSc*RAC + 2*RSc*RBU - 2*RSc*RPR + 2*RSbu*RBBU +
     13*RSpr*RPPR - RSh2 - Yh2*Rsh2*Yhh2
C     BIOLOGICAL PRODUCTION OF NH4+, mM/l-dt
3114  BIOnh4 = - YN*(YAC*RSc*RAC + YPR*RSc*RPR +
     1YBU*RSc*RBU + Yaa1*RSac1 +Yaa2*RSac2+ Ybb*RSbu*RBBU +
     1Ypp*RSpr*RPPR + YHH2*RSh2) + YN*(RDc + RDac1 + RDac2 + RDpr +
     1RDbu + RDh2) + 0.105*Kp*YX1
C     BIOLOGICAL PRODUCTION OF CH4, mM/l-dt
      BioCH4 = RSac1 + RSac2 + 0.25*RSh2
      IF (BioCH4.GT.0.0) GOTO 3115
      BioCH4 = 0.0
C     BIOLOGICAL PRODUCTION OF CO2, mM/l-dt
3115  BIOco2 = 2*RSc*RAC + 2*RSc*RBU - Ybuco2*RSbu*Ybb -
     1Yprco2*RSpr*Ypp + RSac1 + RSac2 - 0.25*RSh2 + RSpr*RPPR -
     1Yh2co2*RSh2*Yhh2
C     H2 GAS TRANSFER, mM/l-d
      TrH2 = Klah2*((KHh2*YX15) - YX16)
C     AMONIA-NITROGEN IN LIQUID PHASE, mM/l
      NH3l = YX18*Knh4/HP(J)
C     NH3 GAS TRANSFER, mM/l-d
      TrNH3 = Klanh3*((KHnh3*YX17) - NH3l)
C     CO2 GAS TRANSFER, mM/l-d
      TrCO2 = Klaco2*((KHco2*YX19) - YX21)
C     METHANE PRODUCTION, mM/l-dt
      Mch4(J) = BioCH4
C     METHANE PRODUCTION, mM/dt
      F(13) = Vl(J)*Mch4(J) + 0.8*Q(J)
C     TOTAL BIOGAS FLOWRATE, mM/l-dt
C     TOTAL BIOGAS FLOWRATE Qm = Mch4 + frac*Mco2 + Mnh3 + Mh2o + Mh2
C     OR Qg = Mch4/(1 - (Pco2 + Ph2o + Pnh3 + Ph2)
C     Partial pressures of H2 and NH3 are neglectable.
C     Partial pressure of H2O is 0.02 at 20 oC
C     Qm = (Mch4/(0.98 - (Pco2))*Vl, mM/dt
      Qm = (Vl(J)*Mch4(J))/(0.98 - Pco2)
C     TOTAL BIOGAS FLOWRATE, l/d
      F(14) = ((Vstp/1000)*Qm)
C     HYDROGEN GAS MASS BALANCE(gas phase), dpH2/dt,(atm/d)
      F(15) = ((-PT*(Vl(J)/Vg(J))*TrH2) -
     1((YX15/Vg(J))*Qm))*(Vstp/1000.0)
C     HYDROGEN GAS MASS BALANCE(liquid phase), mM/l-dt
C     (dH2/dt)aq = (in - dilution) + (dH2/dt)bio. - (dH2/dt)transf.
      F(16) = -YX16/HRT(J) + BioH2 + TrH2
C     Amonia nitrogen mass balance(gas phase), dNH3/dt,(atm/d)
      F(17) = ((-PT*(Vl(J)/Vg(J))*TrNH3) -
     1((YX17/Vg(J))*Qm))*(Vstp/1000.0)
C     Amonium nitrogen mass balance(liquid phase)
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C     (dnh4/dt) = (NH4(J) - nh4) + (dnh4/dt)BIO - (dnh4/dt)Tr
      F(18) = (NH4o(J) - YX18)/HRT(J) + BIOnh4 + TrNH3
C     CARBON DIOXIDE GAS MASS BALANCE(gas phase), dCO2/dt,(atm/d)
      F(19) = ((-PT*(Vl(J)/Vg(J))*TrCO2) -
     1((YX19/Vg(J))*Qm))*(Vstp/1000.0)
C     CARBON DIOXIDE GAS MASS BALANCE(liquid phase)
C     (dco2/dt)aq = (in - dil.) + (dco2/dt)bio + (dco2/dt)c + (dco2/dt)tr
C     WHERE:
C     (dco2/dt)bio =Biological production rate of CO2, mM/l-d
C     (dco2/dt) =  Chemical production rate of CO2, mM/l-d
C     (dco2/dt)tr = Transfer rate of CO2 from gas to liquid phase, mM/l-d
C     CATIONS AND ANIONS MASS BALANCE
      F(20) = (Zo(J) - YX20)/HRT(J)
      CHEMco2 = (HCO3o(J) - HCO3_(J))/HRT(J) + F(4) + F(5) + F(6) -
     1F(20) - F(18)
      F(21) = (co2o(J) - YX21)/HRT(J) + BIOco2 + CHEMco2 + Trco2
C     BICARBONATE SYSTEM
      Ac_(J) = Kaac*YX6/(Hp(J) + Kaac)
      Pr_(J) = Kapr*YX5/(Hp(j) + Kapr)
      Bu_(J) = Kabu*YX4/(Hp(j) + Kabu)
C     Determination of bicarbonate concentration, mM/l
      HCO3_(J) = YX20 + YX18 - Ac_(J) - Pr_(J) - Bu_(J)
C     HCO3_ can not be negative, and if = 0.0 cannot determine the pH,
    1divid. by 0
      IF (HCO3_(J).GT.0.0) GOTO 3117
      HCO3_(J) = 1.0
C     Determination of Hydrogen ion concentration, mM/l
3117  Hp(J) = Ka1*YX21/HCO3_(J)
      GOTO 2300
21000ICOUNT = ICOUNT + 1
      IF(ICOUNT.LE.4999) GOTO 2300
      DO 81 I = 1,21
      IF(Y(I).GT.0.0) GOTO 81
      Y(I) = 0.000000001
81    CONTINUE
      Pbiot(J) = Y(1)
      CBbiot(J) = Y(2)
      CNBt(J) = Y(3)
      But(J) = Y(4)
      Prt(J) = Y(5)
      Act(J) = Y(6)
      Xct(j) = Y(7)
      Xprt(J) = Y(8)
      Xbut(J) = Y(9)
      Xac1t(J) = Y(10)
      Xac2t(J) = Y(11)
      Xh2t(J) = Y(12)
C     Methane flow rate M/d
      QCH4t(J) = 0.025*Y(13)
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      Qgt(J) = Y(14)
      H2gt(J) = Y(15)
      H2lt(J) = Y(16)
      Nh3gt(J) = Y(17)
      Nh4lt(j) = Y(18)
      CO2gt(j) = Y(19)
      Pco2 = CO2gt(J)
      Zt(J) = Y(20)
      Co2lt(J) = Y(21)
      Ht(J) = Hp(J)
C     VALUE OF Hp(J) for the next iteration
      Hp(J+1) = Hp(J)
C     TO determine the daily cumulative gas production Y(13)
C     and Y(14) become:
      Y(13) = 0.0
      Y(14) = 0.0
3000 CONTINUE
      DO 3500 I=1,ND
C     SOLUBLE CARBOHYDRATE IN SBR AT TIME t(I)
      CBbiop(I) = CBbiot(I)
C     TOTAL CH2O IN SBR AT TIME t(I), mM/l
      Tcarbop(I) = CBbiot(I) + Pbiot(I)
C     VOLATILE SUSPENDED SOLIDS IN SBR AT TIME t(I)
      AcP(I) = Act(I)
      PrP(I) = Prt(I)
      BuP(I) = But(I)
      QCH4p(I) = QCH4t(I)
C     VOLATILE SUSPENDED SOLIDS IN SBR AT TIME t(I)
C     Vss/Vs ratio = 0.88
      VsP(I) = (((Pbiot(I))*180) + Xct(I) +
     1Xprt(I) + Xbut(I) + Xac1t(I) + Xac2t(I) + Xh2t(I))/0.88
      NH4p(I) = NH4lt(I)
      CO2p(I) = CO2lt(I)
      CO2gp(I) = CO2gt(I)
      H2lp(I) = H2lt(I)
      H2gp(I) = H2gt(I)
      Hp(I) = -(ALOG10(Ht(I)))
C     VAp(I) = COD BASIS
      VAp(I) = 1.07*AcP(I)*60. + 1.51*PrP(I)*74. + 1.818*BuP(I)*88.
      SCODp(I) = (((CBbiot(I) + CNBt(i))*180*1.066)) + VAp(I)
      TCODp(I) = (((Pbiot(I))*180*1.066)) + SCODp(I) +
     1(Xct(I) + Xprt(I) + Xbut(I) + Xac1t(I) + Xac2t(I) +
     1Xh2t(I))*1.41
3500 CONTINUE
      CBbioM = 0.
      AcM = 0.
      PrM = 0.
      BuM = 0.
      QCH4SM = 0.
```

```
C     COMPUTE STD ERROR OF ESTIMATE FOR MEASURED PARAMETERS FOR FIRST 20
C     DAYS.  ONLY DAYS ON WHICH MEASUREMENTS WERE MADE ARE CONSIDERED.
      DO 40 I=1,MD
      IF (CBbio(I).LT.0.01) GOTO 36
      CBbioD = CBbioP(I) - CBbio(I)
      CBbioM = CBbioM + CBbioD**2
36    IF (Ac(I).LT.0.01) GOTO 37
      AcD = AcP(I) - Ac(I)
      AcM = AcM + AcD**2
37    IF (Pr(I).LT.0.01) GOTO 38
      PrD = PrP(I) - Pr(I)
      PrM = PrM + PrD**2
38    IF (Bu(I).LT.0.01) GOTO 39
      BuD = BuP(I) - Bu(I)
      BuM = BuM + BuD**2
39    IF (QCH4o(I).LT.0.01) GOTO 40
      QCH4D = QCH4P(I) - QCH4o(I)
      QCH4SM = QCH4SM + QCH4D**2
40    CONTINUE
      SECB1 = SQRT(CBbioM/N1)
      SEAc1 = SQRT(AcM/N2)
      SEPr1 = SQRT(PrM/N3)
      SEBu1 = SQRT(BuM/N4)
      SEQCH1 = SQRT(QCH4SM/N5)
      CBbioM2 = 0.
      AcM2 = 0.
      PrM2 = 0.
      BuM2 = 0.
      QCH4S2 = 0.
C     COMPUTE STD ERROR OF ESTIMATE FROM DAY 21 ON
      DO 50 I=MD1,ND
      IF (CBbio(I).LT.0.01) GOTO 41
      CBbioD = CBbioP(I) - CBbio(I)
      CBbioM2 = CBbioM2 + CBbioD**2
41    IF (Ac(I).LT.0.01) GOTO 42
      AcD = AcP(I) - Ac(I)
      AcM2 = AcM2 + AcD**2
42    IF (Pr(I).LT.0.01) GOTO 43
      PrD = PrP(I) - Pr(I)
      PrM2 = PrM2 + PrD**2
43    IF (Bu(I).LT.0.01) GOTO 44
      BuD = BuP(I) - Bu(I)
      BuM2 = BuM2 + BuD**2
44    IF (QCH4o(I).LT.0.01) GOTO 50
      QCH4D = QCH4P(I) - QCH4o(I)
      QCH4S2 = QCH4D**2 + QCH4S2
50    CONTINUE
      SECB2 = SQRT(CBbioM2/N12)
      SEAc2 = SQRT(AcM2/N22)
```

```
      SEPr2 = SQRT(PrM2/N32)
      SEBu2 = SQRT(BuM2/N42)
      SEQCH2 = SQRT(QCH4S2/N52)
      SESCB = SQRT((CBbioM + CBbioM2)/N1T)
      SESAc = SQRT((AcM + AcM2)/N2T)
      SESPr = SQRT((PrM + PrM2)/N3T)
      SESBu = SQRT((BuM + BuM2)/N4T)
      SEQCH4 = SQRT((QCH4SM + QCH4S2)/N5T)
      SMSCB = SMC + SMC2
      SMSAc = SMAc + SMAc2
      SMSPr = SMPr + SMPr2
      SMSBu = SMBu + SMBu2
      SMQCHT = SMQCH4 + SMQCH2
      TCB = 100*N1*SECB1/SMC
      TAc = 100*N2*SEAc1/SMAc
      TPr = 100*N3*SEPr1/SMPr
      TBu = 100*N4*SEBu1/SMBu
      QCH41H = 100*N5*SEQCH1/SMQCH4
      CB2H = 100*N12*SECB2/SMC2
      Ac2H = 100*N22*SEAc2/SMAc2
      Pr2H = 100*N32*SEPr2/SMPr2
      Bu2H = 100*N42*SEBu2/SMBu2
      QCH42H = 100*N52*SEQCH2/SMQCH2
      CBH = 100*N1T*SESCB/SMSCB
      AcH = 100*N2T*SESAc/SMSAc
      PrH = 100*N3T*SESPr/SMSPr
      BuH = 100*N4T*SESBu/SMSBu
      QCH4H = 100*N5T*SEQCH4/SMQCHT
      IF(IP.LT.2) GOTO 70
      WRITE(11,2070)FNM,ND
2070  FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
      CH20 = 'RATE CONSTANT VALUES'
      CH41 = 'Max. substrate uptake rate(mM CH2O/d)'
      CH51 = 'Half velocity constant (mM/L)'
      CH61 = 'Yield factor (mg Acidogens/mM Organic to Acetic)'
      CH62 = 'Yield factor (mg Acidogens/mM Organic to Propionic)'
      CH63 = 'Yield factor (mg Acidogens/mM Organic to Butyric)'
      CH64 = 'Organic use for formation of 1g of Acidogens'
      CH71 = 'Decay rate (1/d)'
      CH81 = 'Yield of vol. acids from raw substrate (mg COD/mg COD)'
      CH91 = 'Particulate solubilization rate (1/d)'
      CH101 = 'SBR initial volume (L)'
      WRITE(11,2060)CH20,CH2,CH41,VMAXco,CH51,HKc, CH61,
     1YAC, CH62,YPR, CH63,YBU, CH64,YC, CH71,Bc, CH91,KP, CH102,
     1Biod,CH101,Vo
2060  FORMAT('0',25X,A, /,2X,A,/,/,2X,A,8X,F12.5,/,2X, A,29X,
     1F12.5, /,2X, A, 10X, F12.5,/,2X,
     2A, 7X,F12.5,/2X,A,9X, F12.5,/,2X,A, 14X,F12.5,
     3/,2X, A,38X, F12.5,/,2X,A,19X,F12.5,/,2X,A,20X,F12.5,
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     4/,2X,A,35X,F12.5)
      CH452 = 'Max. substrate uptake rate,(mM Prop./d)'
      CH552 = 'Half velocity constant (mM/L)'
      CH652 = 'Yield factor (mg Acetogens/mM Propionic to Acetic)'
      CH662 = 'Propionate use for formation of 1g of Acetogens'
      CH722 = 'Decay rate (1/d)'
      WRITE(11,2061)CH3,CH452,VMAXpro,CH552,HKpr, CH652,
     1Ypp, CH662,Yp,CH722,Bpr
2061  FORMAT('0',/,/,2X,A,/,/,2X,A,6X, F12.5,
     1/,2X, A,29X, F12.5, /,2X, A, 10X, F12.5,/,2X,
     2A, 10X,F12.5,
     3/,2X, A,38X, F12.5)
      CH453 = 'Max. substrate uptake rate (mM Buty./d)'
      CH553 = 'Half velocity constant (mM/L)'
      CH653 = 'Yield factor (mg Acetogens/mM Butyric to Acetic)'
      CH663 = 'Butyrate use for formation of 1g of Acetogens'
      CH723 = 'Decay rate (1/d)'
      WRITE(11,2062)CH4,CH453,VMAXbuo,CH553,HKbu, CH653,
     1Ybb, CH663,Yb,CH723,Bbu
2062  FORMAT('0',/,/,2X,A,/,/,2X,A,6X, F12.5,
     1/,2X, A,29X, F12.5, /,2X, A, 10X, F12.5,/,2X,
     2A, 14X,F12.5,
     3/,2X, A,38X, F12.5)
      CH454 = 'Max. substrate uptake rate (mM Acetate/d)'
      CH554 = 'Half velocity constant (mM/L)'
      CH654 = 'Yield factor (mg Methanothrix/mM acetic to Methane)'
      CH664 = 'Acetate use for formation of 1g of Methanothrix'
      CH724 = 'Decay rate (1/d)'
      WRITE(11,2063)CH5,CH454,VMAXac1o,CH554,HKac1, CH654,
     1Yaa1, CH664,Ya1,CH724,Bac1
2063  FORMAT('0',/,/,2X,A,/,/,2X,A,6X, F12.5,
     1/,2X, A,29X, F12.5, /,2X, A, 10X, F12.5,/,2X,
     2A, 14X,F12.5,
     3/,2X, A,38X, F12.5)
      CH455 = 'Max. substrate uptake rate (mM Acetate/d)'
      CH555 = 'Half velocity constant (mM/L)'
      CH655 = 'Yield factor (mg Methanosarcinas/mM acetic to Methane)'
      CH665 = 'Acetate use for formation of 1g of Methanosarcinas'
      CH725 = 'Decay rate (1/d)'
      WRITE(11,2064)CH6,CH455,VMAXac2o,CH555,HKac2, CH655,
     1Yaa2, CH665,Ya2,CH725,Bac2
2064  FORMAT('0',/,/,2X,A,/,/,2X,A,6X, F12.5,
     1/,2X, A,29X, F12.5, /,2X, A, 10X, F12.5,/,2X,
     2A, 14X,F12.5,
     3/,2X, A,38X, F12.5)
      CH456 = 'Max. substrate uptake rate (mM Hydrogen/mg m.o./d)'
      CH556 = 'Half velocity constant (mM/L)'
      CH656 = 'Yield factor (mg H2 utilizer/mM CO2)'
      CH666 = 'Hydrogen use for formation of 1g of H2 utilizer'
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      CH726 = 'Decay rate (1/d)'
      WRITE(11,2065)CH7,CH456,VMAXh2o,CH556,HKh2, CH656,
     1Yhh2, CH666,Yh2,CH726,Bh2
2065  FORMAT('0',/,/,2X,A,/,/,2X,A,6X, F12.5,
     1/,2X, A,29X, F12.5, /,2X, A, 10X, F12.5,/,2X,
     2A, 14X,F12.5,
     3/,2X, A,38X, F12.5)
70    CH22 = 'STANDARD ERROR OF ESTIMATE'
      WRITE(*,2081)CH22
      IF(IP.LT.2) GOTO 71
      WRITE(11,2080)CH22
2081  FORMAT('1',25X,A)
2080  FORMAT(23X,A)
71    CH23 = 'SOLUBLE ASBR COD (mM/l)'
      CH24 = 'ACETIC ACID (mM/l)'
      CH25 = 'PROPIONIC ACID (mM/l)'
      CH26 = 'BUTYRIC ACID (mM/l)'
      CH27 = 'METHANE FLOWRATE (mM/day)'
      CH28 = ' SEE(20D) TOT.(20D) NO.  % SEE(+20D) TOT.(+20D) NO.  % S
     1EE(ALL) TOT.(ALL) NO.  %'
      WRITE(*,2091) CH23,CH28, SECB1,SMC,      N1, TCB,
     1SECB2, SMC2,   N12, CB2H, SESCB,SMSCB,N1T,CBH
      WRITE(*,2091) CH24,CH28, SEAc1,SMAc, N2, TAc,
     1SEAc2, SMAc2,  N22, Ac2H, SESAc,SMSAc,N2T,AcH
      WRITE(*,2091) CH25,CH28, SEPr1,SMPr, N3, TPr,
     1SEPr2, SMPr2,  N32, Pr2H,SESPr,SMSPr,N3T,PrH
      WRITE(*,2091) CH26,CH28, SEBu1,SMBu, N4, TBu,
     1SEBu2, SMBu2,  N42, Bu2H,SESBu, SMSBu,N4T,BuH
      WRITE(*,2091) CH27,CH28, SEQCH1,SMQCH4, N5, QCH41H,
     1SEQCH2, SMQCH2,     N52, QCH42H, SEQCH4,SMQCHT,N5T,QCH4H
      WRITE(*,2101)FNM,ND
2101  FORMAT(' ',5X,'RUN NO. = ',A, '; NO. OF DAYS = ',I3)
      IF(IP.LT.2) GOTO 99
2090  FORMAT(' ',1X,A,/,A,/,1X,E8.3,1X,E8.3,2X,I2,1X,F4.0,1X,E8.3,2X,
     1E8.3, 2X, I2,1X,F4.0, 1X, E8.3, 1X, E8.3, 1X, I2, 1X, F4.0,/)
2091  FORMAT(' ',1X,A,/,A,/,1X,E8.3,1X,E8.3,2X,I2,1X,F4.0,1X,E8.3,2X,
     1E8.3, 2X, I2,1X,F4.0, 1X, E8.3, 1X, E8.3, 1X, I2, 1X, F4.0)
      WRITE(11,2090) CH23,CH28, SECB1,SMC,     N1, TCB,
     1SECB2, SMC2,   N12, CB2H, SESCB,SMSCB,N1T,CBH
      WRITE(11,2090) CH24,CH28, SEAc1,SMAc, N2, TAc,
     1SEAc2, SMAc2,  N22, Ac2H, SESAc,SMSAC,N2T,AcH
      WRITE(11,2090) CH25,CH28, SEPr1,SMPr, N3, TPr,
     1SEPr2, SMPr2,  N32, Pr2H,SESPr,SMSPr,N3T,PrH
      WRITE(11,2090) CH26,CH28, SEBu1,SMBu, N4, TBu,
     1SEBu2, SMBu2,  N42, Bu2H,SESBu, SMSBu,N4T,BuH
      WRITE(11,2090) CH27,CH28, SEQCH1,SMQCH4, N5, QCH41H,
     1SEQCH2, SMQCH2,  N52, QCH42H, SEQCH4,SMQCHT,N5T,QCH4H
      IF(IP.LT.3) GOTO 99
      WRITE(11,2100)FNM,ND
```

```
2100 FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
     CH32 = ' DAY   Q          ACETATE      PROPIONATE        BUTYRATE'
     CH33 = '                 MEAS   PRED    MEAS   PRED     MEAS   PRE
    1D'
     WRITE(11,2110)CH32,CH33
2110 FORMAT(1X,A,/,1X,A)
     WRITE(11,2120)(IDAY(I),Q(I),Ac(I),AcP(I),Pr(I), PrP(I),
    1Bu(I), BuP(I), I=1,ND)
2120 FORMAT(' ',1X,I3, 1X, F5.3, 3X, F6.2, 1X, F6.2, 3X, F6.2, 1X,
    1F6.2, 4X, F6.3, 1X, F6.3)
     WRITE(11,2111)FNM,ND
2111 FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
     CH32 = ' DAY   Q       DISSOLVED H2     DISSOLVED CO2  AMONIA-NH4'
     CH33 = '               MEAS   PRED       MEAS   PRED   MEAS  PRED'
     WRITE(11,2112)CH32,CH33
2112 FORMAT(1X,A,/,1X,A)
     WRITE(11,2113)(IDAY(I),Q(I),H2l(I),H2lP(I),CO2(I),CO2p(I),
    1NH4(I), NH4P(I), I=1,ND)
2113 FORMAT(' ',1X,I3, 1X, F5.3, 1X, F10.8, 1X, F10.8, 1X, F5.1, 1X,
    1F5.1, 2X, F5.1, 1X, F5.1,)
     WRITE(11,2114)FNM,ND
2114 FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
     CH32 = ' DAY   Q     PARTIAL PRESSURE H2    HYDROGEN ION H+'
     CH33 = '               MEAS        PRED       MEAS      PRED'
     WRITE(11,2115)CH32,CH33
2115 FORMAT(1X,A,/,1X,A)
     WRITE(11,2116)(IDAY(I),Q(I),H2g(I),H2gp(I),pH(I),
    1HP(I), I=1,ND)
2116 FORMAT(' ',1X,I3,1X,F5.3,1X,F10.7,1X,F10.7,4X,F5.2,5X,
    1F5.2,)
     WRITE(11,2121)FNM,ND
2121 FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
     CH32 = ' DAY   Q          VOL.SOLIDS             CH4 FLOW'
     CH33 = '                 MEAS    PRED          MEAS     PRED'
     WRITE(11,2122)CH32,CH33
2122 FORMAT(1X,A,/,1X,A)
     WRITE(11,2123)(IDAY(I),Q(I),VS(I),VsP(I),(QCH4o(I)*.95),QCH4P(I),
    1I=1,ND)
2123 FORMAT(' ',1X,I3, 1X, F5.3, 7X, F6.0, 1X, F6.0, 6X, F10.3, 1X,
    1F10.3)
     WRITE(11,2121)FNM,ND
     CH42 = ' DAY   Q      TOTAL COD, mg/l    SOLUBLE COD, mg/l   '
     CH43 = '              MEAS       PRED    MEAS        PRED    '
     WRITE(11,2126)CH42,CH43
2126 FORMAT(1X,A,/,1X,A)
     WRITE(11,2124)(IDAY(I),Q(I),TCOD(I),TCODp(I),SCOD(I),
    1SCODp(I), I=1,ND)
2124 FORMAT(' ',1X,I3, 1X, F5.3, 1X, F7.1,4X, F7.1,2X, F7.1,4X,F7.1)
     WRITE(11,2121)FNM,ND
```

```
      CH42 = ' DAY    Q         HCO3, mM/l              pCO2     '
      CH43 = '                MEAS        PRED          PRED     '
      WRITE(11,2131)CH42,CH43
2131  FORMAT(1X,A,/,1X,A)
      WRITE(11,2134)(IDAY(I),Q(I),HCO3(I),HCO3_(I),CO2gp(I), I=1,ND)
2134  FORMAT(' ',1X,I3, 1X, F5.3, 1X, F7.2,4X, F7.2,7X, F7.2)
      IF(IP.LT.4) GOTO 99
      WRITE(11,2118)FNM,ND
2118  FORMAT('1',2X,'RUN NO. ',A,/,' NO. OF DAYS IN RUN = ',I3)
      WRITE(11,2125)
2125  FORMAT(' ',/,/,1X,'  DAY     Xc      Xac1      Xac2      Xpr
     1Xbu      XH2')
      WRITE(11,2130)(IDAY(I), XCt(I), Xac1t(I), Xac2t(I), Xprt(I),
     1Xbut(I), Xh2t(I), I=1,ND)
2130  FORMAT(3X, I3,4X,F6.0,2X,F6.0,4X,F6.0,4X,F6.0,3X,F6.0,3X,F6.0)
99    IF(K2.EQ.0) GOTO 1611
      NSS2 = NSS2 + 1
      IF(NSS2.EQ.NS2) GOTO 1611
      IANS7 = IANS9
      GOTO 162
1611  NSS = NSS + 1
      IF(NSS.EQ.NS) GOTO 199
      NSS2 = 0
      IANS7 = IANS8
      GOTO(170,171,172,173,174,175,176,177,178,179,180,181,182,
     1183,184,185,186,187,188,189,190,191,192,193,194,195,196,197,
     1198,201,202,203,204,205)IANS9
170   VMAXco = VMAXcB
      GOTO 162
171   HKc = HKcB
      GOTO 162
172   YAC = YACB
      GOTO 162
173   YPR = YPRB
      GOTO 162
174   YBU = YBUB
      GOTO 162
175   YC = YCB
      GOTO 162
176   BC = BCB
      GOTO 162
177   KP = KPB
      GOTO 162
178   Biod = BiodB
      GOTO 162
179   VMAXpro = VMAXprB
      GOTO 162
180   HKpr = HKprB
      GOTO 162
```

```
181  Ypp = YppB
     GOTO 162
182  Yp = YpB
     GOTO 162
183  Bpr = BprB
     GOTO 162
184  VMAXbuo = VMAXbuB
     GOTO 162
185  HKbu = HKbuB
     GOTO 162
186  Ybb = YbbB
     GOTO 162
187  Yb = YbB
     GOTO 162
188  Bbu = BbuB
     GOTO 162
189  VMAXac1o = VMAXac1B
     GOTO 162
190  HKac1 = HKac1B
     GOTO 162
191  Yaa1 = Yaa1B
     GOTO 162
192  Ya1 = Ya1B
     GOTO 162
193  Bac1 = Bac1B
     GOTO 162
194  VMAXac2o = VMAXac2B
     GOTO 162
195  HKac2 = HKac2B
     GOTO 162
196  Yaa2 = Yaa2B
     GOTO 162
197  Ya2 = Ya2B
     GOTO 162
198  Bac2 = Bac2B
     GOTO 162
200  VMAXh2o = VMAXh2B
     GOTO 162
201  HKh2 = HKh2B
     GOTO 162
202  Yhh2 = Yhh2B
     GOTO 162
203  Yh2 = Yh2B
     GOTO 162
204  Bh2 = Bh2B
     GOTO 162
205  Vo = VoB
     GOTO 162
162  GOTO(143,144,145,146,147,148,149,150,151,152,153,154,155,156,
```

```
    1157,158,159,160,161,1622,163,164,165,166,167,168,169,1701,1711,
    11721,1731,1741,1751,1761,1771)IANS7
143  VMAXco = VMAXco + VMAXcI
     GOTO 288
144  HKc = HKc + HKcI
     GOTO 288
145  YAC = YAC + YACI
     GOTO 288
146  YPR = YPR + YPRI
     GOTO 288
147  YBU = YBU + YBUI
     GOTO 288
148  YC = YC + YCI
     GOTO 288
149  Bc = Bc + BcI
     GOTO 288
150  KP = KP + KPI
     GOTO 288
151  Biod = Biod + BiodI
     GOTO 288
152  VMAXpro = VMAXpro + VMAXprI
     GOTO 288
153  HKpr = HKpr + HKprI
     GOTO 288
154  Ypp = Ypp + YppI
     GOTO 288
155  Yp = Yp + YpI
     GOTO 288
156  Bpr = Bpr + BprI
     GOTO 288
157  VMAXbuo = VMAXbuo + VMAXbuI
     GOTO 288
158  HKbu = HKbu + HKbuI
     GOTO 288
159  Ybb = Ybb + YbbI
     GOTO 288
160  Yb = Yb + YbI
     GOTO 288
161  Bbu = Bbu + BbuI
     GOTO 288
1622 VMAXac1o = VMAXac1o + VMAXac1I
     GOTO 288
163  HKac1 = HKac1 + HKac1I
     GOTO 288
164  Yaa1 = Yaa1 + Yaa1I
     GOTO 288
165  Ya1 = Ya1 + Ya1I
     GOTO 288
166  Bac1 = Bac1 + Bac1I
```

```
      GOTO 288
167   VMAXac2o = VMAXac2o + VMAXac2I
      GOTO 288
168   HKac2 = HKac2 + HKac2I
      GOTO 288
169   Yaa2 = Yaa2 + Yaa2I
      GOTO 288
1701  Ya2 = Ya2 + Ya2I
      GOTO 288
1711  Bac2 = Bac2 + Bac2I
      GOTO 288
1721  VMAXh2o = VMAXh2o + VMAXh2I
      GOTO 288
1731  HKh2 = HKh2 + HKh2I
      GOTO 288
1741  Yhh2 = Yhh2 + Yhh2I
      GOTO 288
1751  Yh2 = Yh2 + Yh2I
      GOTO 288
1761  Bh2 = Bh2 + Bh2I
      GOTO 288
1771  Vo = Vo + VoI
288   GOTO 140
199   END
      INTEGER FUNCTION RUNGE(N,Y,F,X,HH)
      DIMENSION PHI(21),SAVEY(21),Y(N),F(N),QQ(21),QQ2(21)
      COMMON RT3,RT4,RT5,RT6,RT7,RTH1,RTH2,RTH3,RTH4,RTH6,RTH7
      DATA M/0/
      M = M + 1
      GOTO (1,2,3,4,5) M
1     RUNGE = 1
      RETURN
2     DO 22 J=1,N
      SAVEY(J) = Y(J)
      PHI(J) = F(J)
      QQ(J) = F(J)
22    Y(J) = SAVEY(J) + RTH3*F(J)
      X = X + 0.5*HH
      RUNGE = 1
      RETURN
3     DO 33 J=1,N
      PHI(J) = PHI(J) + RT5*F(J)
      QQ2(J) = F(J)
33    Y(J) = SAVEY(J) + RTH7*QQ(J) + RTH1*F(J)
      RUNGE = 1
      RETURN
4     DO 44 J=1,N
      PHI(J) = PHI(J) + RT6*F(J)
44    Y(J) = SAVEY(J) - RTH2*QQ2(J) + RTH6*F(J)
```

```
      X = X + 0.5*HH
      RUNGE = 1
      RETURN
5     DO 55 J=1,N
55    Y(J) = SAVEY(J) + (PHI(J) + F(J))*RTH4
      M = 0
      RUNGE = 0
      RETURN
      END
      SUBROUTINE RTTH
      COMMON RT3,RT4,RT5,RT6,RT7,RTH1,RTH2,RTH3,RTH4,RTH6,RTH7
      DATA RT2/0./
      RT2 = 1./SQRT(2.)
      RT3 = 1. - RT2
      RT4 = 1. + RT2
      RT5 = 2.*RT3
      RT6 = 2.*RT4
      RT7 = RT2 - 0.5
      HH = 0.0002
      RTH1 = RT3*HH
      RTH2 = RT2*HH
      RTH3 = 0.5*HH
      RTH4 = HH/6.
      RTH6 = RT4*HH
      RTH7 = RT7*HH
      RETURN
      END
```

APPENDIX C

ICP TEST PARAMETERS AND SENSITIVITY

ICP PARAMETERS

The unit was an ARL 34000 which is a vacuum polychromator with 34 fixed channels.

RE power generator: Henry Radio Model 2500 PGC/27

Generator Conditions

Output frequency	27.12 MHz
Incident power	1200 w
Reflected power	0

Excitation Conditions

Observation height	15 mm
Coolant gas flow	12 l/min
Plasma gas flow	0.6 l/min
Carrier gas flow	1 l/min
Sample uptake rate	2.5 ml/min
Nebulizer	Meinhard concentric, Type C
Spray-chamber	ARL conical model

Analytical Conditions

Pre-integration time	30 s
Integration time	10 s
Number of integrations	3

Spectrometer

Grating	1080 lines/mm
Primary slit size	20 μ

Computer

Digital PDP 11/03
RX 02 floppy disc drives

TABLE A1. Wavelength and Sensitivity of the ICP

Element	Wavelength	Determination Limits (ppm in solution)	Detection Limits (ppm)
Al	308.2	0.820	0.0026
As	189.0	1.130	0.0226
Ba	493.4	0.010	0.0002
Ca	317.9	0.070	0.0014
Cd	226.5	0.160	0.0032
Co	228.6	0.170	0.0034
Cr	267.7	0.120	0.0024
Cu	324.8	0.115	0.0023
Fe	259.9	0.060	0.0012
K	766.4	2.500	0.0500
Mg	279.1	0.685	0.0137
Mn	257.6	0.030	0.0006
Mo	202.0	0.340	0.0068
Na	589.5	1.500	0.0300
Ni	231.6	0.685	0.0137
Pb	220.3	2.300	0.0460
Sb	217.6	1.885	0.0377
Se	196.0	2.115	0.0423
Si	251.6	0.415	0.0083
Sn	189.9	0.790	0.0158
V	292.4	0.080	0.0016
Zn	213.9	0.200	0.0040

APPENDIX D

EXPERIMENTAL RESULTS

TEST RUN NO. 4

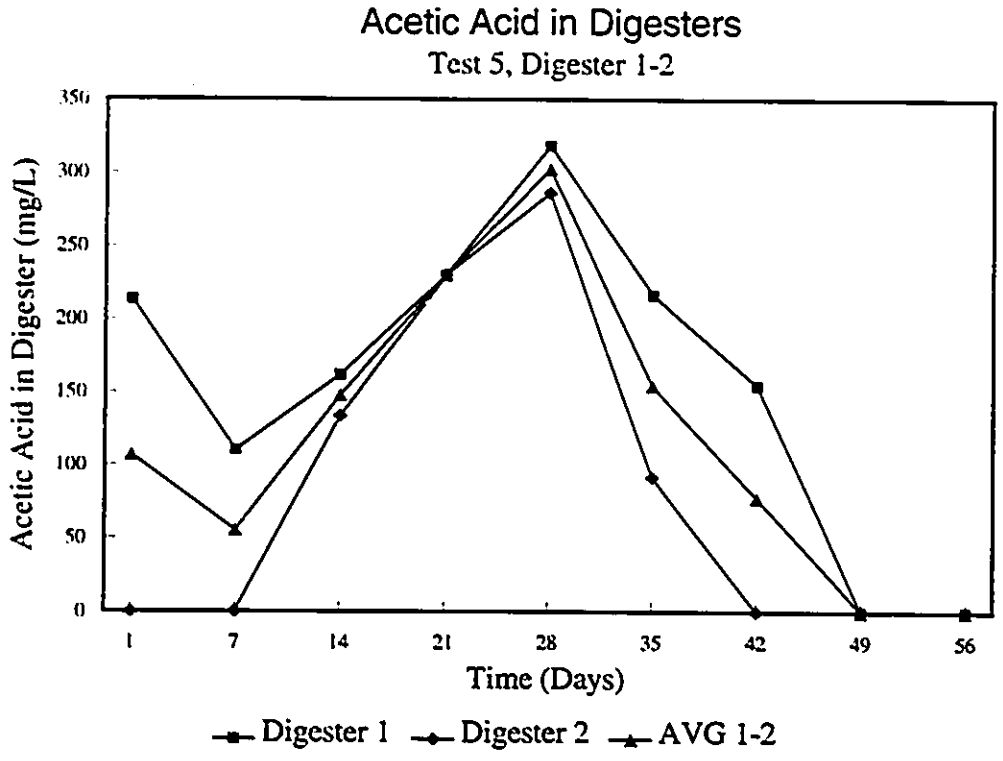
Test	Date		1	2	3	4	5	6	7	8
pH	14/6	1	7.64	7.62	7.56	7.58	7.61	7.56	7.60	7.51
	21/6	7	7.65	7.64	7.51	7.54	7.64	7.57	7.48	7.52
	28/6	14	7.58	7.53	7.46	7.44	7.48	7.45	7.40	7.40
	5/7	21	7.60	7.45	7.42	7.61	7.60	7.57	7.38	7.46
	12/7	28	7.63	7.50	7.58	7.38	7.65	7.49	7.36	7.55
	19/7	35	7.58	7.59	7.45	7.60	7.49	7.53	7.62	7.39
	26/7	42	7.85	7.73	7.60	7.81	7.69	7.74	7.82	7.49
	2/8	49	8.05	7.63	7.55	7.83	7.66	7.49	7.58	7.70
	9/8	56	7.74	7.70	7.78	7.68	7.67	7.68	7.72	7.78
	VA		14/6	1	93.5			89.0		
Acetic	21/6	7	1007.2	575.2	693.7	668.2	1229.7	986.6	890.1	958.3
Acid	28/6	14	1655.1	1831.3	1356.0	938.4	1834.3	1722.3	1789.9	1953.8
	5/7	21	3057.0	3141.9	2170.6	2058.6	3578.4	3766.0	3139.9	3353.0
	12/7	28	3772.8	3966.4	3209.0	3211.9	4713.4	4713.4	4520.5	4481.0
	19/7	35	3874.9	3967.6	3947.6	3644.4	4524.1	4679.1	4845.0	4999.5
	26/7	42	3144.4	3329.3	3367.0	3390.3	4273.1	4600.1	5130.7	5532.5
	2/8	49	2043.7	2270.8	2401.5	2296.2	3029.3	3389.0	3742.0	3986.6
	9/8	56	1374.4	1492.6	1450.3	1332.0	2290.5	2681.1	2833.3	2845.6
VA	14/6	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Propionic	21/6	7	131.9	51.5	115.3	105.4	206.9	185.7	128.9	140.3
Acid	28/6	14	284.5	298.0	143.0	117.4	246.6	307.2	211.1	239.9
	5/7	21	427.7	402.9	256.5	218.6	496.7	620.4	404.4	424.4
	12/7	28	616.5	542.8	313.3	333.6	622.7	664.7	525.7	519.4
	19/7	35	738.4	700.0	448.0	382.1	812.4	869.7	644.3	629.9
	26/7	42	787.8	674.2	340.8	335.5	881.6	940.0	699.5	661.3
	2/8	49	757.9	703.5	297.5	260.8	905.6	991.9	660.9	642.9
	9/8	56	784.7	710.4	267.7	212.9	952.8	1028.3	682.9	639.1
VA	14/6	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Butyric	21/6	7	134.0	0.0	109.5	139.6	245.6	214.7	91.3	147.9
Acid	28/6	14	215.2	219.0	120.1	123.8	77.4	156.2	84.1	139.5
	5/7	21	244.7	151.5	139.9	146.9	246.8	289.6	229.5	236.9
	12/7	28	285.4	218.1	199.8	188.8	137.6	178.3	182.7	188.2
	19/7	35	286.8	225.8	178.9	156.5	231.8	253.7	202.9	260.7
	26/7	42	254.0	88.4	58.7	58.5	99.8	118.0	98.7	91.8
	2/8	49	181.0	98.2	46.5	56.5	84.1	95.8	65.9	59.7
	9/8	56	213.1	91.3	64.2	40.8	71.2	71.9	0.0	57.0
CaCO3	14/6	1	16337	17670	14670	16670	15670	17337	16003	15336
(mg/l)	21/6	7	18670	19671	16003	13336	15670	14670	15003	15003
	28/6	14	17337	16670	15003	17670	17003	15003	14336	13336
	5/7	21	14836	19004	16503	13503	16003	14503	14336	13003
	12/7	28	18004	18670	16337	15003	19337	17170	16170	15336
	19/7	35	19004	17337	15503	14003	16003	18837	14336	15837
	26/7	42	19171	20717	15836	16003	16170	20337	15170	15837
	2/8	49	18837	15670	13169	12836	15170	15503	12836	12503
	9/8	56	17170	19337	13169	16003	15670	18670	18337	14503

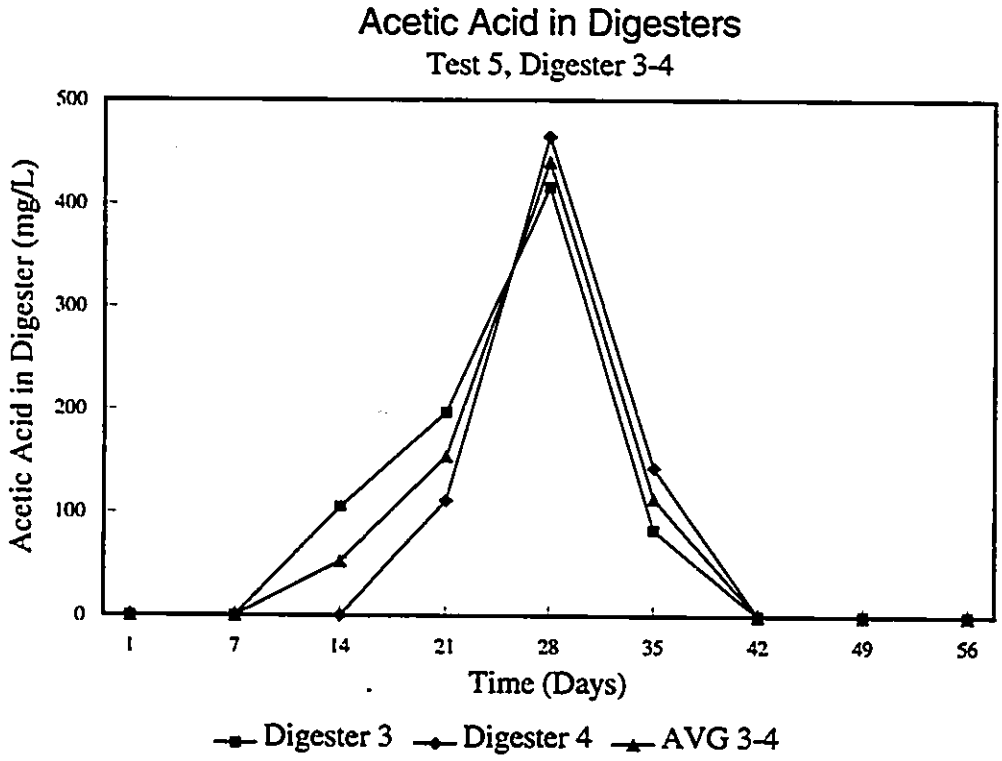
NH3-N	14/6	1	2322	2340	2110	2119	2339	2352	2089	2078
(mg/l)	21/6	7	2610	2571	2405	2413	2748	2784	2466	2459
	28/6	14	2927	2939	2548	2639	2964	3051	2683	2692
	5/7	21	3097	3033	2718	2725	3227	3298	2945	2995
	12/7	28	3244	3238	2916	2904	3389	3480	3139	3175
	19/7	35	3404	3382	3016	3070	3678	3668	3297	3297
	26/7	42	3280	3255	2936	2915	3491	3564	3237	3248
	2/8	49	3299	3270	2918	2913	3534	3590	3250	3289
	9/8	56	3210	3250	2957	2960	3545	3620	3291	3325
TCOD	14/6	1	42946	39277	60202	62053	69423	80647	34482	70643
(mg/l)	21/6	7	51662	52076	46710	43278	49758	48036	45336	46533
	28/6	14	54636	56758	40900	67226	57305	57135	39042	42555
	5/7	21	54504	60649	42724	47107	54555	59666	52691	50683
	12/7	28	54308	54034	49551	48499	59675	59937	49350	53421
	19/7	35	55633	51848	45852	52287	64707	58246	46565	44874
	26/7	42	50861	48987	44800	45109	53374	55449	46675	46857
	2/8	49	58328	55420	51761	51010	59083	62074	53962	54136
	9/8	56	54039	50225	45728	27684	56808	59120	48664	50019
TSCOD	14/6	1	0	1100	185	180	183	2033	3844	0
(mg/l)	21/6	7	2473.11	3151.11	1908.11	1948.44	2695.44	4339.67	5327.78	2142.44
	28/6	14	5358.41	5544.07	3918.41	4011.63	5626.63	7030.78	7058.85	4641.96
	5/7	21	8243.70	7957.04	5928.70	6074.81	8557.81	9721.89	8789.93	7141.48
	12/7	28	11129	10330	7939	8138	11489	12613	10521	9641
	19/7	35	6081	6538	4855	5073	7496	7167	6587	6020
	26/7	42	5874	5843	4771	4676	7114	7647	6411	6491
	2/8	49	7694	7529	6327	5976	9844	10917	9184	9457
	9/8	56	5456	5499	4301	7185	7843	9027	6665	6920
VS	14/6	1	39003	39564	34440	35667	39298	39435	32206	34214
(mg/l)	21/6	7	39046	39095	33985	34912	38338	38718	33649	32653
	28/6	14	38607	38237	33561	34344	40845	39582	33149	33582
	5/7	21	38466	39051	33425	33425	36997	36057	34862	33167
	12/7	28	38910	38964	33649	34476	37862	37931	33865	33112
	19/7	35	38516	39875	34277	34277	36996.5	36938	34314	30815
	26/7	42	37090	36843	32753	32753	36131	35945	31531	31531
	2/8	49	36801	36818	33178	32799	35930	35729	31906	31199
	9/8	56	36233	35969	31928	32228	35075	35669	31906	31199

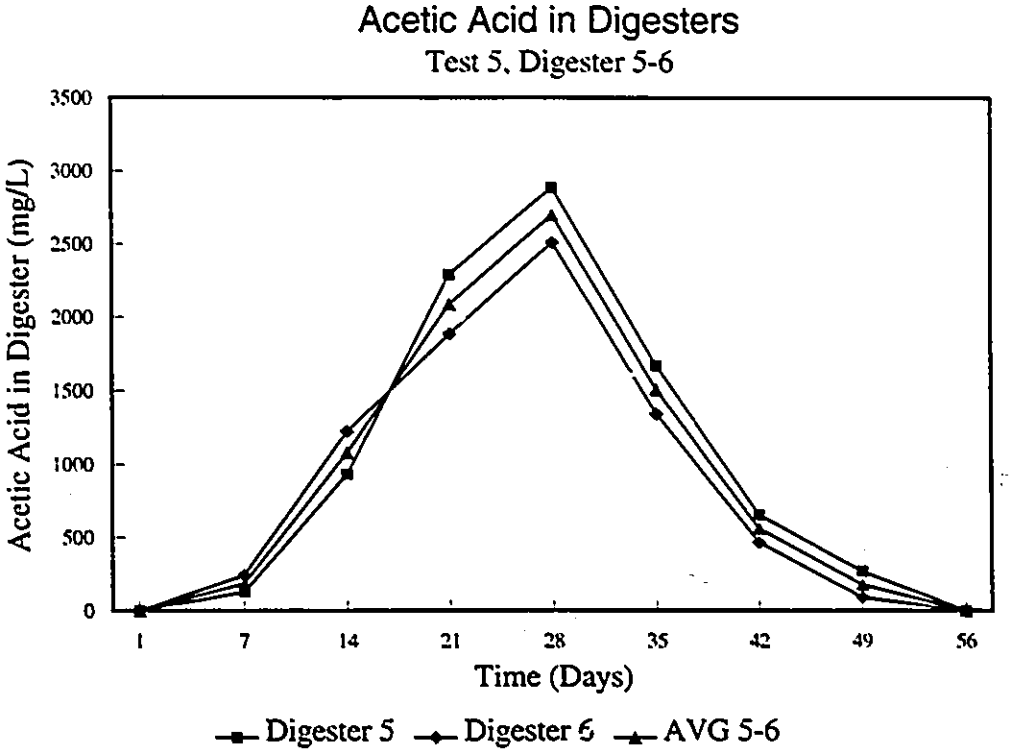
TEST RUN NO. 5

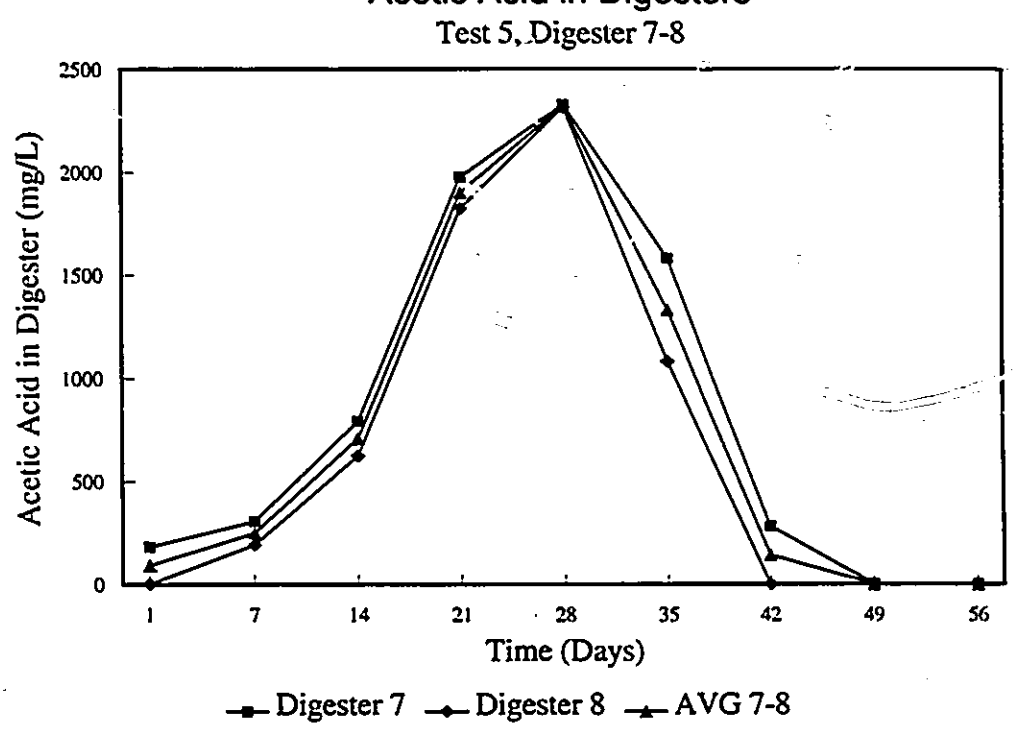
Test	Date	Day	1	2	3	4	5	6	7	8	9	10	11	12
pH	4/10/93	1	7.62	7.56	7.52	7.58	7.88	7.89	7.75	7.76	7.80	7.60	7.86	7.90
	12/10/93	7	7.59	7.57	7.59	7.58	7.57	7.53	7.49	7.46	7.49	7.38	7.50	7.48
	18/10/93	14	7.57	7.52	7.48	7.49	7.48	7.48	7.45	7.48	7.45	7.42	7.48	7.47
	25/10/93	21	7.68	7.68	7.63	7.54	7.60	7.69	7.58	7.59	7.55	7.52	7.59	7.49
	1/11/93	28	7.35	7.30	7.20	7.29	7.36	7.45	7.39	7.48	7.45	7.53	7.39	7.39
	8/11/93	35	7.14	7.28	7.13	7.16	7.33	7.33	7.34	7.34	7.38	7.38	7.34	7.32
	15/11/93	42	7.38	7.31	7.39	7.37	7.57	7.26	7.55	7.56	7.63	7.58	7.57	7.54
	22/11/93	49	7.18	7.34	7.26	7.29	7.48	7.47	7.48	7.50	7.53	7.56	7.54	7.55
	28/11/93	56	7.80	7.83	7.58	7.66	7.75	7.91	7.82	7.85	7.72	7.74	7.77	7.65
VFA	4/10/93	1	213.6	0.0	0.0	0.0	0.0	0.0	181.2	0.0	0.0	246.1	0.0	0.0
Acetic	12/10/93	7	110.2	0.0	0.0	0.0	128.1	241.4	307.5	193.1	320.6	407.6	786.1	568.1
Acid	18/10/93	14	162.0	133.6	105.1	0.0	931.2	1221.1	793.7	625.6	1208.5	1543.3	987.9	853.0
(mg/L)	25/10/93	21	230.2	230.2	197.2	111.5	2292.0	1883.1	1976.5	1822.8	2405.6	2268.3	2180.6	2671.1
	1/11/93	28	318.3	286.1	415.9	464.6	2886.9	2510.9	2325.9	2314.8	2763.7	2669.8	3004.8	2777.3
	8/11/93	35	216.5	91.4	82.9	143.1	1669.7	1338.4	1579.9	1082.7	3063.0	2095.5	2614.6	2053.2
	15/11/93	42	154.5	0.0	0.0	0.0	651.5	463.7	281.5	0.0	526.2	794.0	879.8	848.0
	22/11/93	49	0.0	0.0	0.0	0.0	267.4	88.7	0.0	0.0	418.8	400.8	460.6	441.3
	28/11/93	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
VFA	4/10/93	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Propionic	12/10/93	7	0.0	0.0	0.0	0.0	0.0	0.0	114.9	0.0	113.2	166.8	209.9	137.4
Acid	18/10/93	14	0.0	0.0	0.0	0.0	262.0	293.9	250.8	230.0	377.4	408.1	336.8	308.1
(mg/L)	25/10/93	21	0.0	0.0	0.0	0.0	448.5	458.8	428.2	310.5	662.8	694.9	592.9	602.1
	1/11/93	28	0.0	0.0	0.0	0.0	593.8	648.6	472.8	410.7	833.2	813.8	859.5	838.7
	8/11/93	35	88.6	0.0	0.0	0.0	522.0	586.3	348.4	176.3	1360.6	1001.1	1034.6	803.5
	15/11/93	42	0.0	0.0	0.0	0.0	305.6	295.3	0.0	0.0	635.8	968.5	651.3	533.9
	22/11/93	49	0.0	0.0	0.0	0.0	123.7	0.0	0.0	0.0	438.0	594.8	274.8	126.5
	28/11/93	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
VFA	4/10/93	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Butyric	12/10/93	7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	131.3	0.0
Acid	18/10/93	14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	125.7	90.1	0.0
(mg/L)	25/10/93	21	0.0	0.0	0.0	0.0	86.0	0.0	0.0	0.0	0.0	84.5	175.9	111.7
	1/11/93	28	0.0	0.0	90.5	0.0	107.6	83.0	0.0	92.6	100.4	105.5	147.7	143.6
	8/11/93	35	0.0	0.0	0.0	0.0	0.0	0.0	61.5	0.0	67.2	0.0	0.0	0.0
	15/11/93	42	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	22/11/93	49	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	28/11/93	56	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaCO3	4/10/93	1	5001	5334	4334	3667	6001	10002	9002	10002	7668	7335	7668	8668
(mg/L)	18/10/93	14	7668	7001	7001	6335	8002	11336	11336	10002	7668	8335	11336	9669
	1/11/93	28	9335	7335	6668	6335	7668	8668	9335	8668	8668	8002	9335	6335

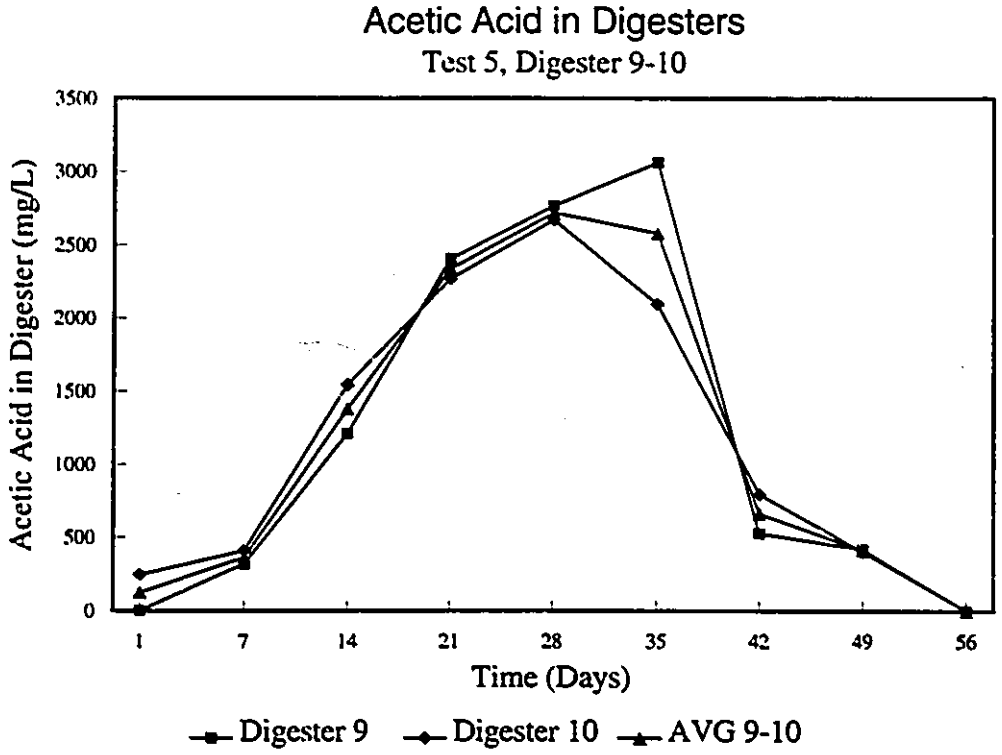
	15/11/93	42	10669	9002	7668	6668	9335	11002	10669	10669	11336	12669	10335	11669
	28/11/93	56	8335	7668	8335	7335	11002	9335	12336	11002	11336	11336	16337	17003
NH3-N	4/10/93	1	671	631	723	655	1190	1503	1507	1444	1251	1206	1453	1434
(mg/L)	18/10/93	14	1291	1309	1362	1301	2017	2110	2264	2109	2176	2280	2345	2392
	1/11/93	28	1990	1995	1767	1841	2798	2584	2900	2592	2781	3005	3092	2846
	15/11/93	42	2117	2172	2258	2165	2696	2841	3158	3031	2949	3159	3118	3200
	28/11/93	56	1874	1889	1898	1900	2575	2240	2919	2646	2794	2965	3192	3147
TCOD	4/10/93	1	15194	13688	15877	12102	36808	32607	32959	31153	30510	27020	30721	29487
(mg/L)	18/10/93	14	28831	11525	18909	22653	25577	28753	37473	34961	26964	28268	44184	41384
	1/11/93	28	56049	53663	59785	39187	36234	42670	60553	66803	39544	43160	54891	49107
	15/11/93	42	48796	43879	54607	51869	22015	31717	32666	55946	28214	27896	36818	33283
	28/11/93	56	45544	44903	76934	87521	19458	37331	34326	34109	23282	27000	41229	41204
SCOD	4/10/93	1	396	388	0	0	462	738	1385	1238	1093	828	1202	815
(mg/L)	18/10/93	14	41	166	172	402	4570	4894	4705	3341	6576	6202	6767	5600
	1/11/93	28	7292	7004	7307	6355	12462	12209	13384	11948	14029	14098	15236	13991
	15/11/93	42	4463	2925	4226	3675	7296	5810	5679	5071	4805	4957	6607	7748
	28/11/93	56	351	1037	1860	470	1996	1705	2222	1865	3435	4439	2896	2458
TS	4/10/93	1	56213	42342	60937	49504	31096	44731	42314	43909	35050	35414	42185	43157
(mg/L)	18/10/93	14	43204	45689	59222	43392	30572	40093	52738	52707	43258	32860	46996	49810
	1/11/93	28	44606	48749	58099	51031	41234	40146	56381	55677	36661	36313	53118	47133
	15/11/93	42	43249	49699	65932	52015	27739	38371	54761	64582	32324	35745	35955	42871
	28/11/93	56	42306	43032	51360	44132	27391	34467	48057	41830	31718	31548	54801	42899
VS	4/10/93	1	34209	18914	30634	26579	14935	19956	28702	19074	16385	16666	18432	18373
(mg/L)	18/10/93	14	24826	26020	31499	27000	15912	19173	22564	22751	21844	17479	25425	28632
	1/11/93	28	25102	26768	31074	27919	15000	20255	25505	25461	19817	19759	26345	23318
	15/11/93	42	24247	27114	32707	28343	14953	19014	24271	49574	17013	18738	18466	20790
	28/11/93	56	23710	23293	32707	28343	13936	16562	22148	18736	14978	16189	26304	20825
VSS	4/10/93	1	31909	9702	30045	21702	14164	19449	21163	18569	15982	15464	17677	17632
(mg/L)	18/10/93	14	24309	25306	30456	20826	14777	18113	21213	21444	16654	15532	11496	11501
	1/11/93	28	21206	22513	25013	22474	18549	16482	21230	21129	16556	15289	21410	17227
	15/11/93	42	20198	23225	26888	22754	11503	15681	20849	23671	12751	14578	14525	17306
	28/11/93	56	21973	22721	24768	19841	13009	15359	21633	21594	14431	15236	13944	21249
VSS/VS	4/10/93	1	0.93	0.51	0.98	0.82	0.95	0.97	0.74	0.97	0.98	0.93	0.96	0.96
	18/10/93	14	0.98	0.97	0.97	0.77	0.93	0.94	0.94	0.94	0.76	0.89	0.45	0.40
	1/11/93	28	0.84	0.84	0.80	0.80	1.24	0.81	0.83	0.83	0.84	0.77	0.81	0.74
	15/11/93	42	0.83	0.86	0.82	0.80	0.77	0.82	0.86	0.48	0.75	0.78	0.79	0.83
	28/11/93	56	0.93	0.98	0.76	0.70	0.93	0.93	0.98	1.15	0.96	0.94	0.53	1.02

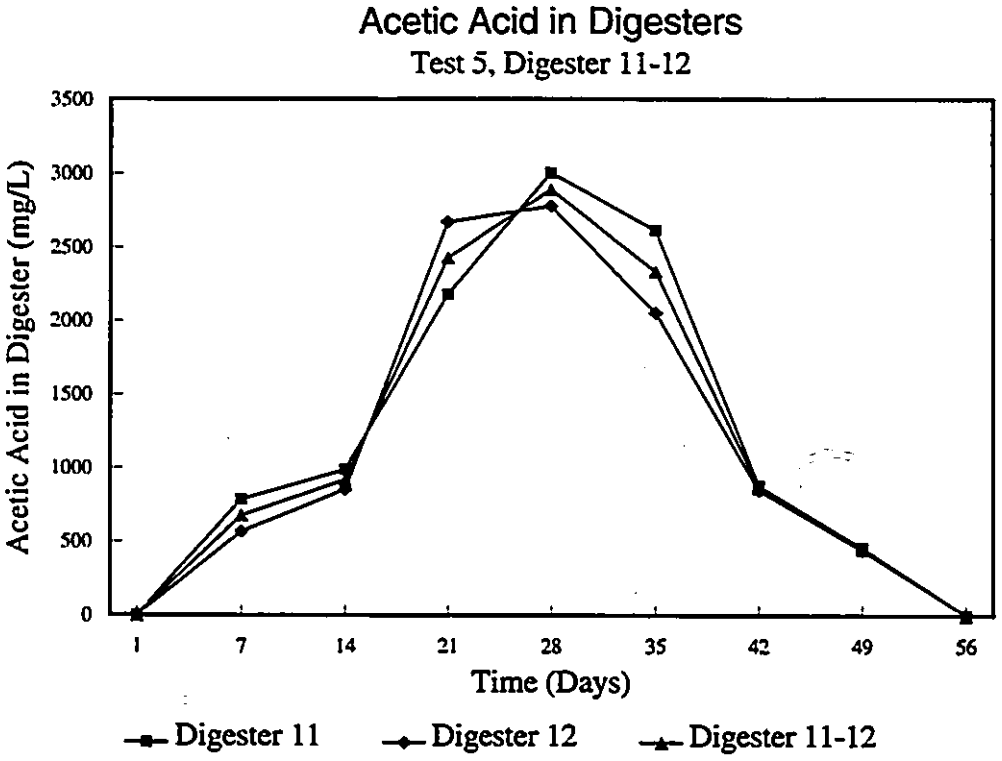

Acetic Acid in Digesters
Test 5, Digester 1-2
Acetic Acid in Digester (mg/L)
350
300
250
200
150
100
50
0
1
7
14
21
28
35
42
49
56
Time (Days)
Digester 1
Digester 2
AVG 1-2

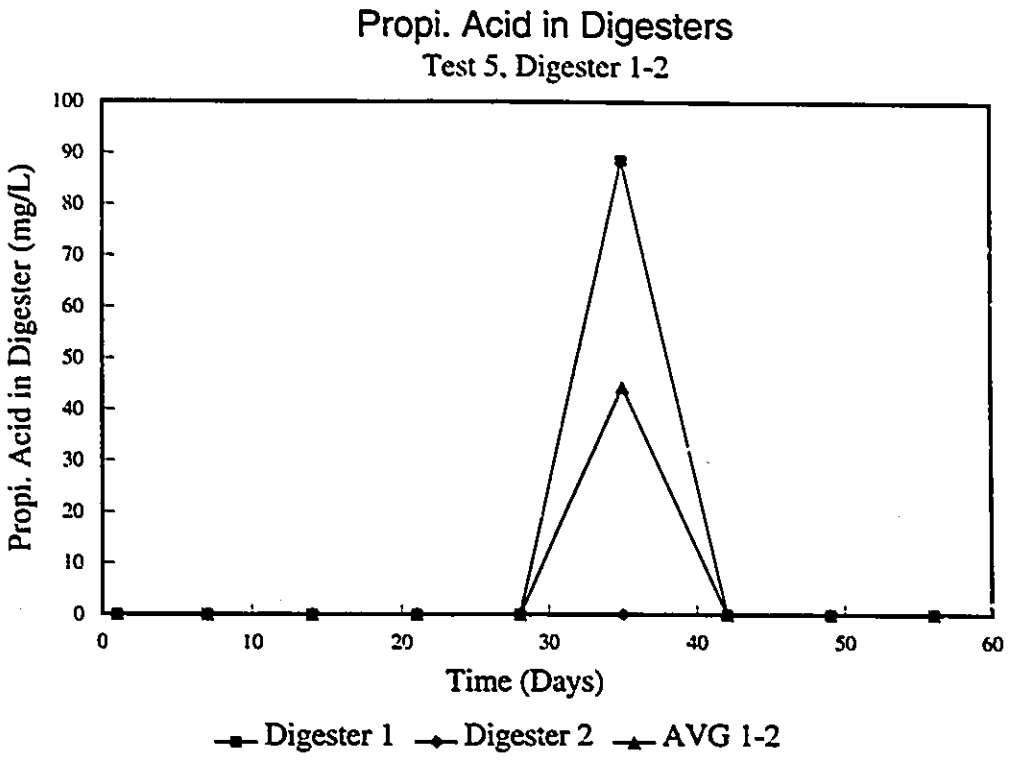

Acetic Acid in Digesters
Test 5, Digester 3-4
Acetic Acid in Digester (mg/L)
500
400
300
200
100
0
1
7
14
21
28
35
42
49
56
Time (Days)
Digester 3
Digester 4
AVG 3-4

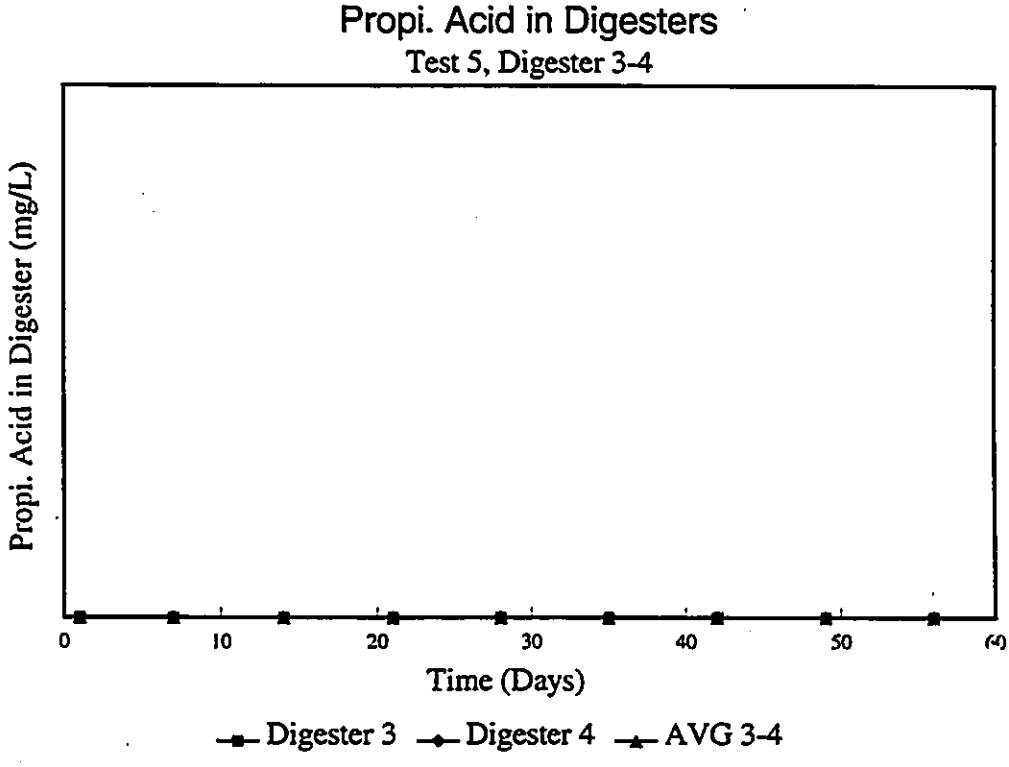

Acetic Acid in Digesters
Test 5, Digester 5-6
Acetic Acid in Digester (mg/L)
3500
3000
2500
2000
1500
1000
500
0
1
7
14
21
28
35
42
49
56
Time (Days)
Digester 5
Digester 6
AVG 5-6

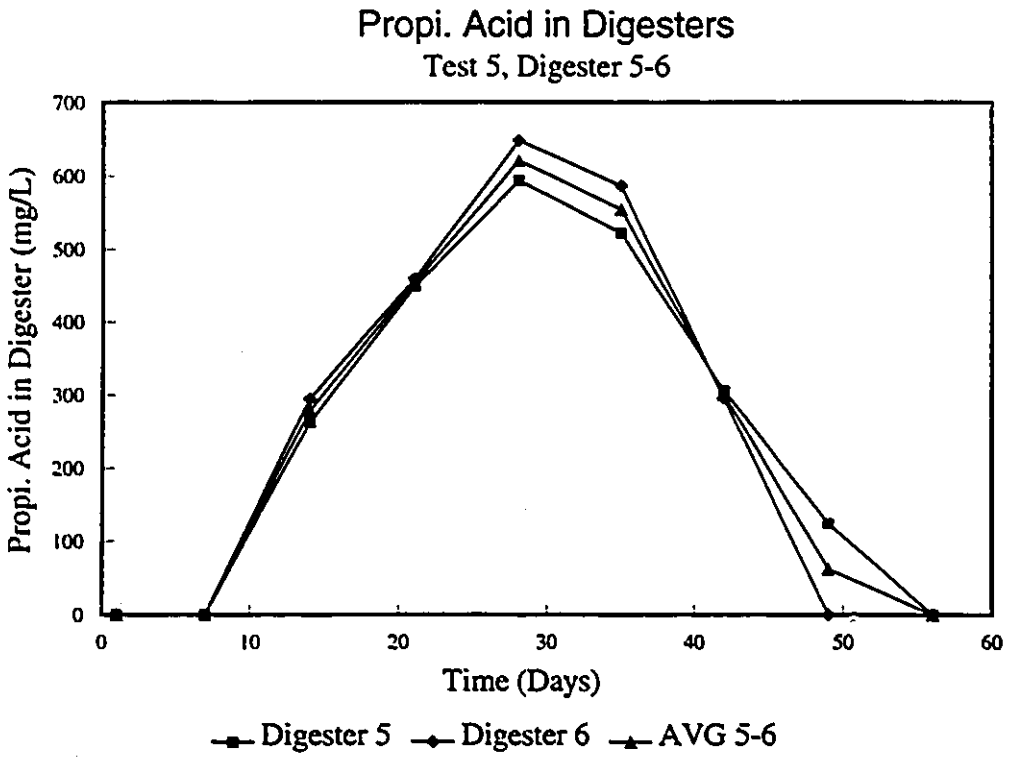

Acetic Acid in Digesters
Test 5, Digester 7-8
Acetic Acid in Digester (mg/L)
2500
2000
1500
1000
500
0
1
7
14
21
28
35
42
49
56
Time (Days)
Digester 7
Digester 8
AVG 7-8

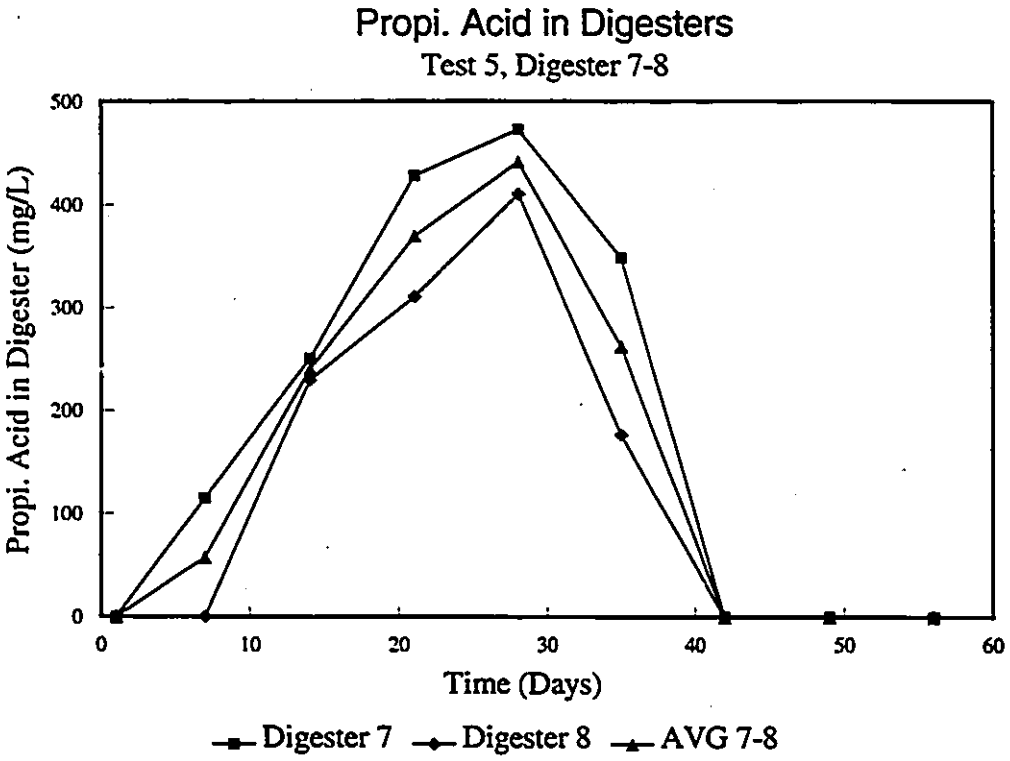

Acetic Acid in Digesters
Test 5, Digester 9-10
Acetic Acid in Digester (mg/L)
3500
3000
2500
2000
1500
1000
500
0
1
7
14
21
28
35
42
49
56
Time (Days)
Digester 9
Digester 10
AVG 9-10

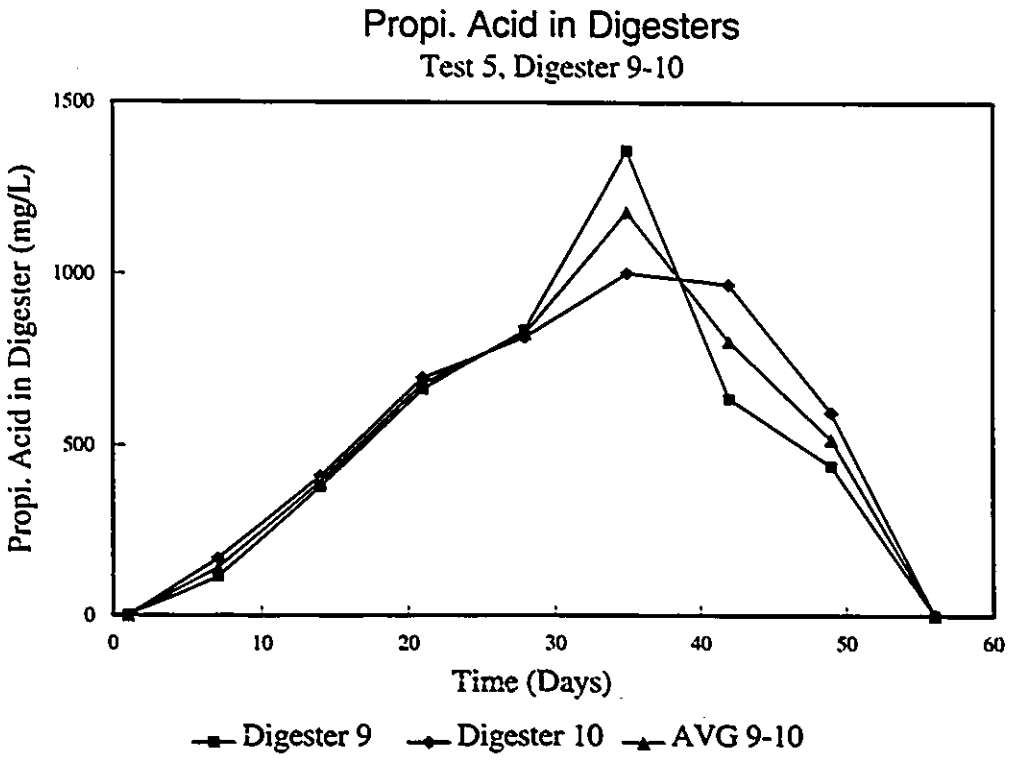

Acetic Acid in Digesters
Test 5, Digester 11-12
Acetic Acid in Digester (mg/L)
3500
3000
2500
2000
1500
1000
500
0
1
7
14
21
28
35
42
49
56
Time (Days)
Digester 11
Digester 12
Digester 11-12

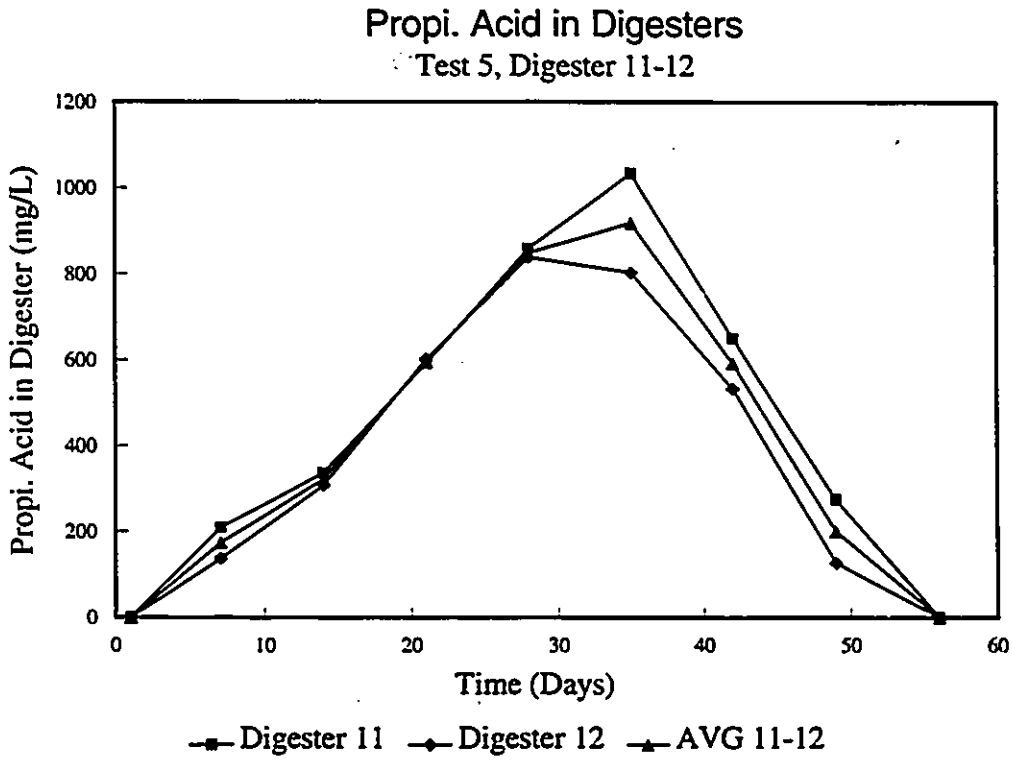

Propi. Acid in Digesters
Test 5, Digester 1-2
Propi. Acid in Digester (mg/L)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (Days)
Digester 1
Digester 2
AVG 1-2

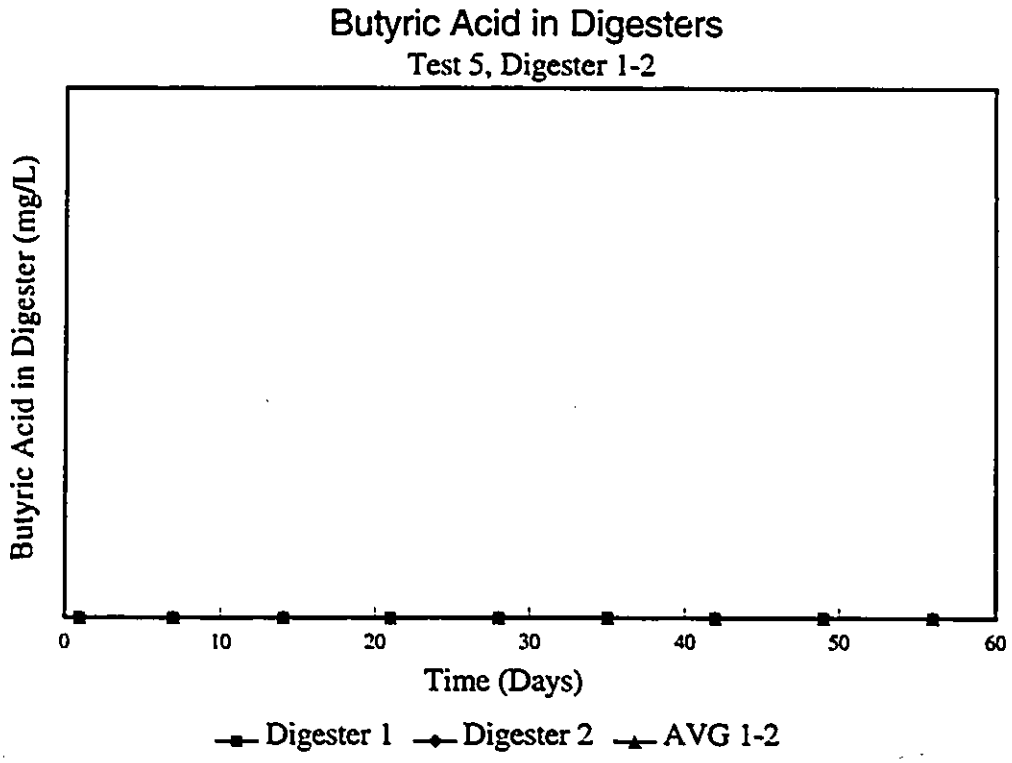

Propi. Acid in Digesters
Test 5, Digester 3-4
Propi. Acid in Digester (mg/L)
0
10
20
30
40
50
Time (Days)
Digester 3
Digester 4
AVG 3-4

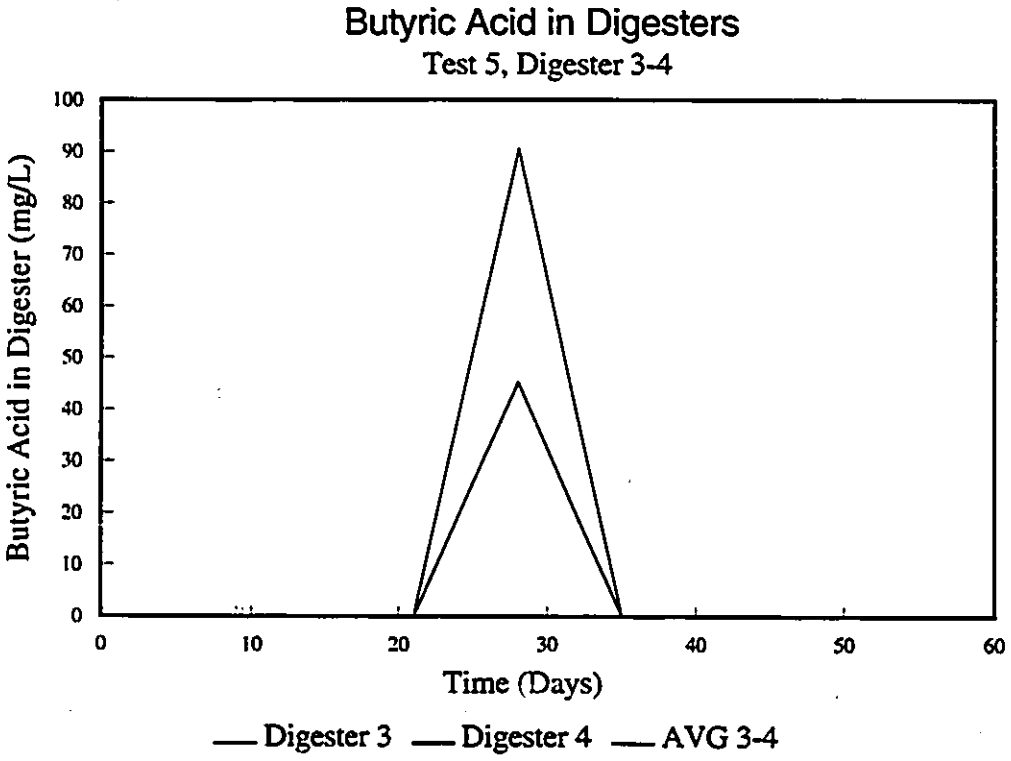

Propi. Acid in Digesters
Test 5, Digester 5-6
Propi. Acid in Digester (mg/L)
700
600
500
400
300
200
100
0
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6

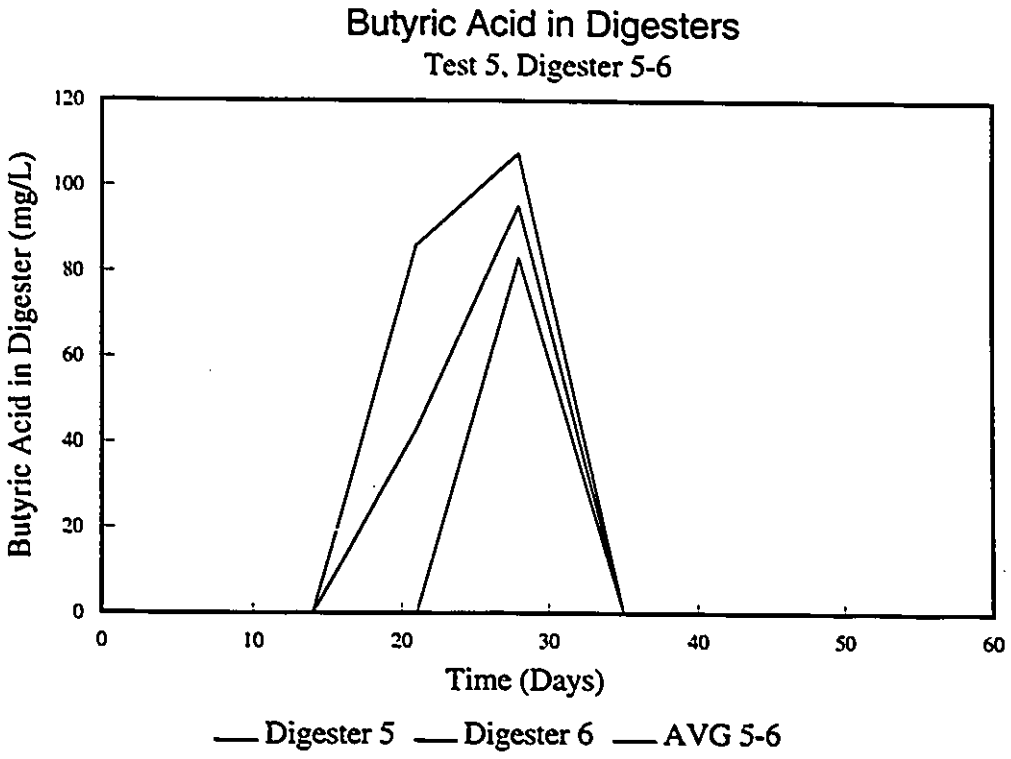

Propi. Acid in Digesters
Test 5, Digester 7-8
Propi. Acid in Digester (mg/L)
500
400
300
200
100
0
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8

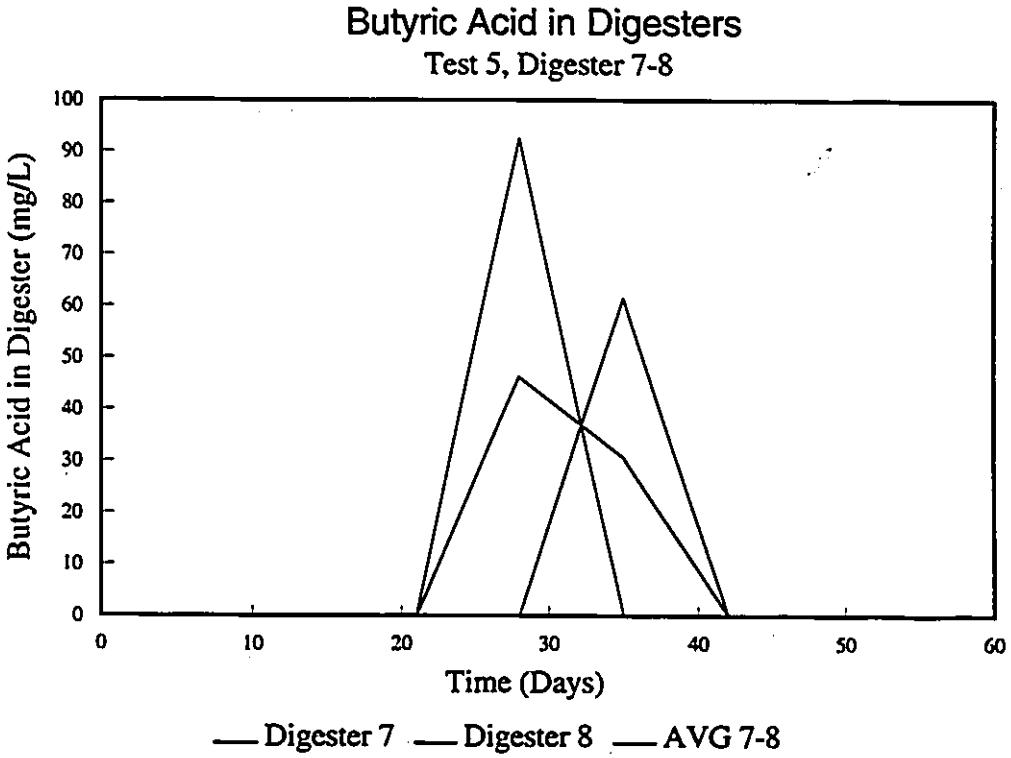

Propi. Acid in Digesters
Test 5, Digester 9-10
Propi. Acid in Digester (mg/L)
1500
1000
500
0
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

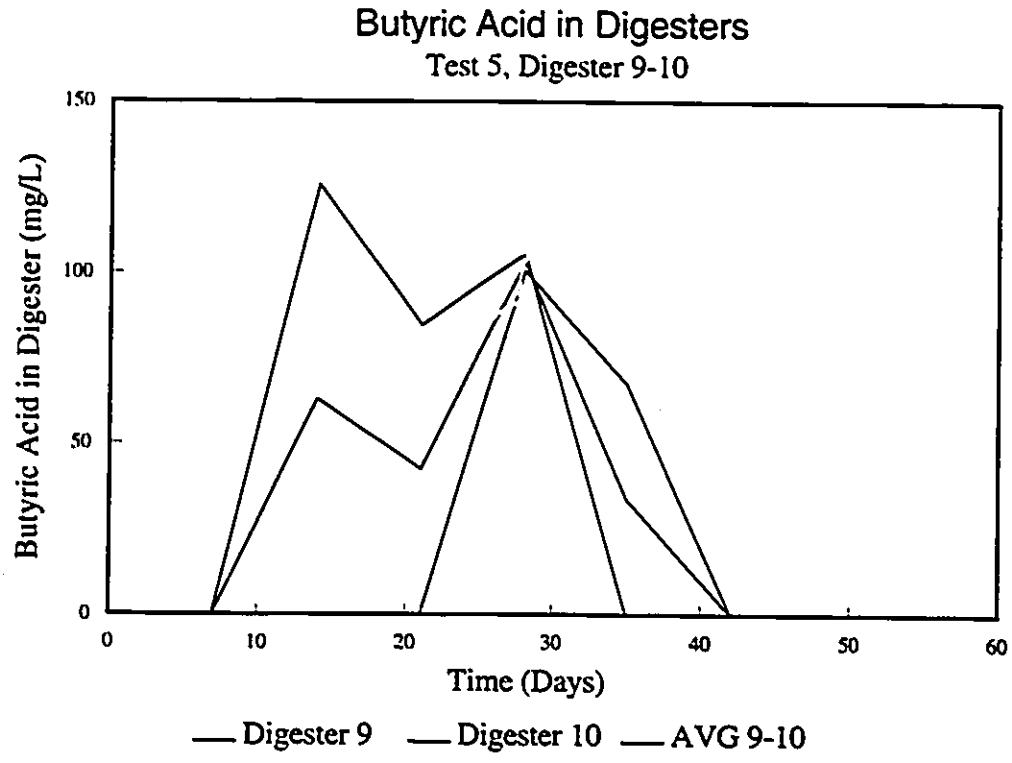

Propi. Acid in Digesters
Test 5, Digester 11-12
Propi. Acid in Digester (mg/L)
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

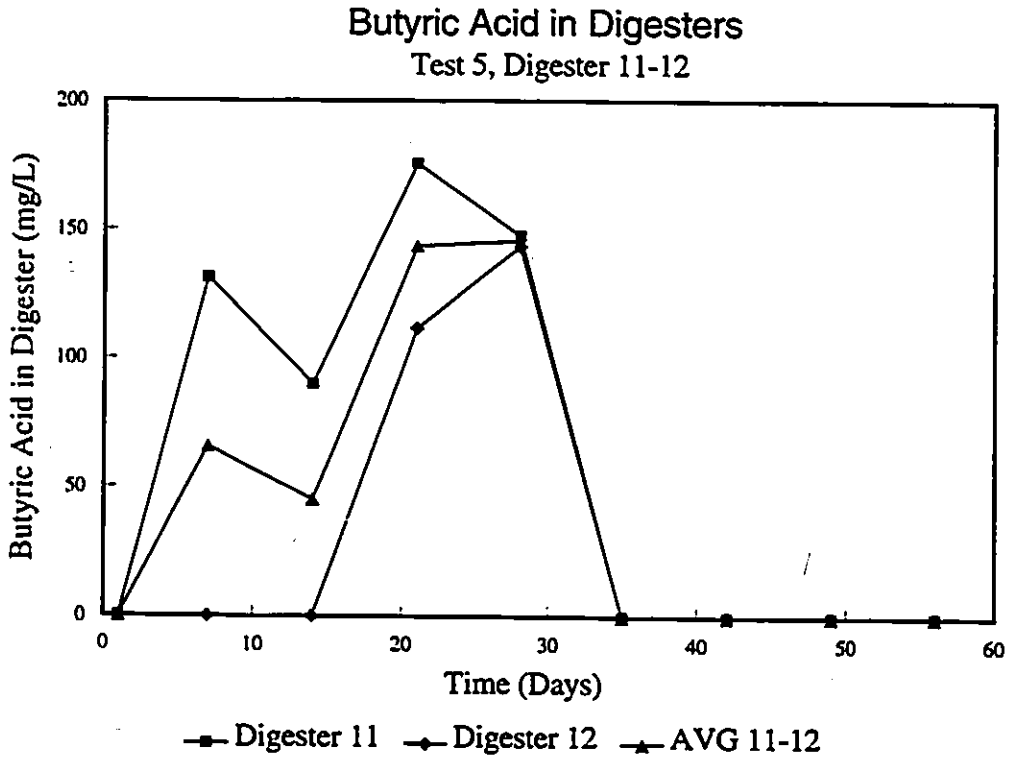

Butyric Acid in Digesters
Test 5, Digester 1-2
Butyric Acid in Digester (mg/L)
0
10
20
30
40
50
60
Time (Days)
Digester 1
Digester 2
AVG 1-2

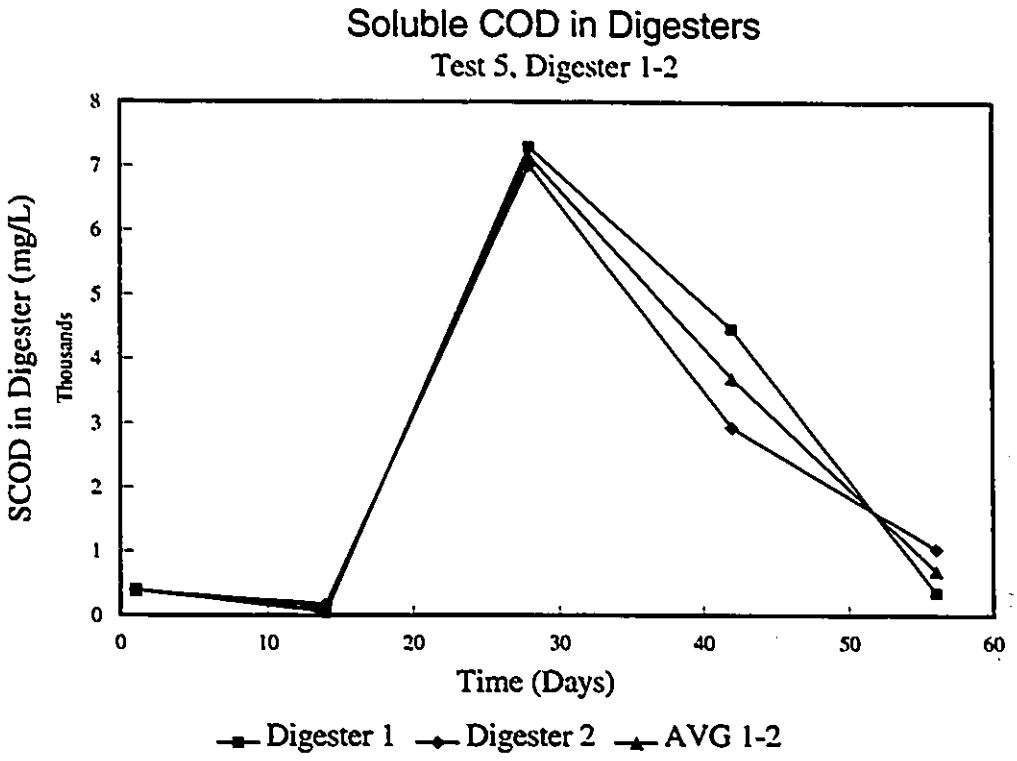

Butyric Acid in Digesters
Test 5, Digester 3-4
Butyric Acid in Digester (mg/L)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (Days)
Digester 3
Digester 4
AVG 3-4

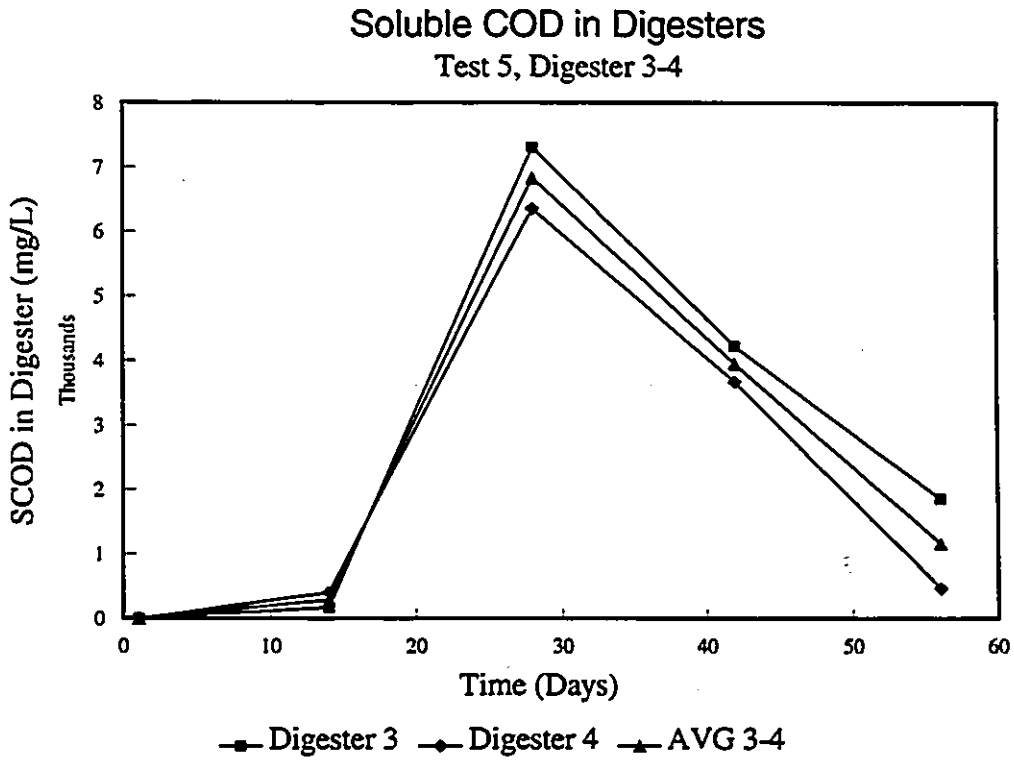

Butyric Acid in Digesters
Test 5, Digester 5-6
Butyric Acid in Digester (mg/L)
120
100
80
60
40
20
0
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6

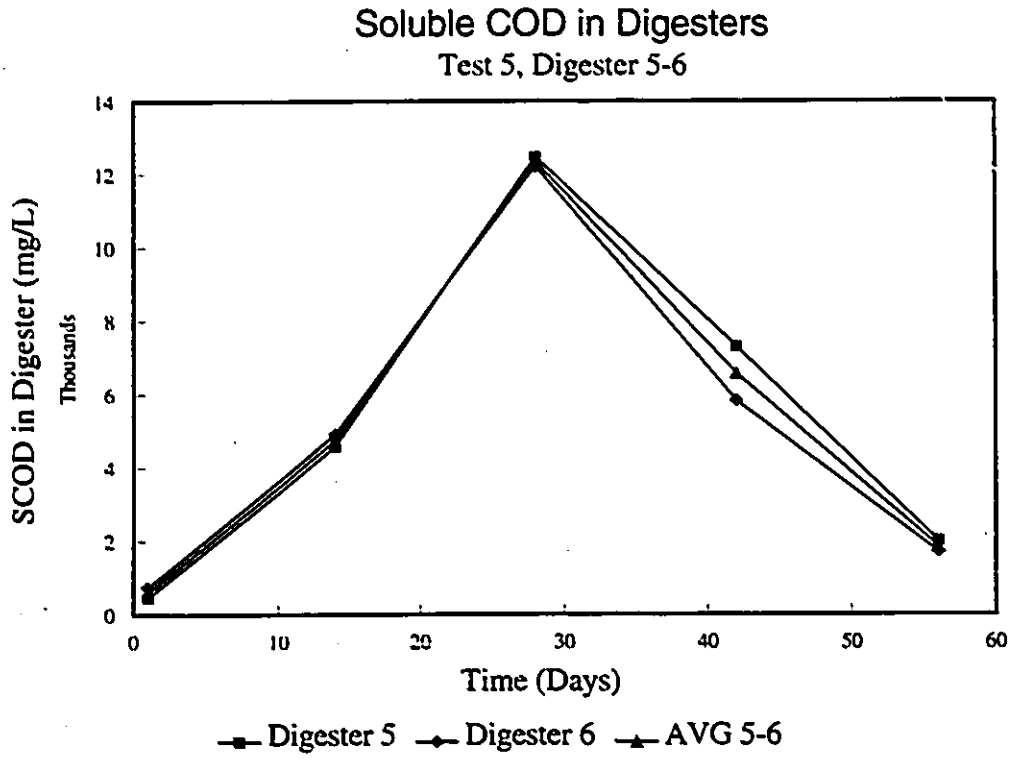

Butyric Acid in Digesters
Test 5, Digester 7-8
Butyric Acid in Digester (mg/L)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8

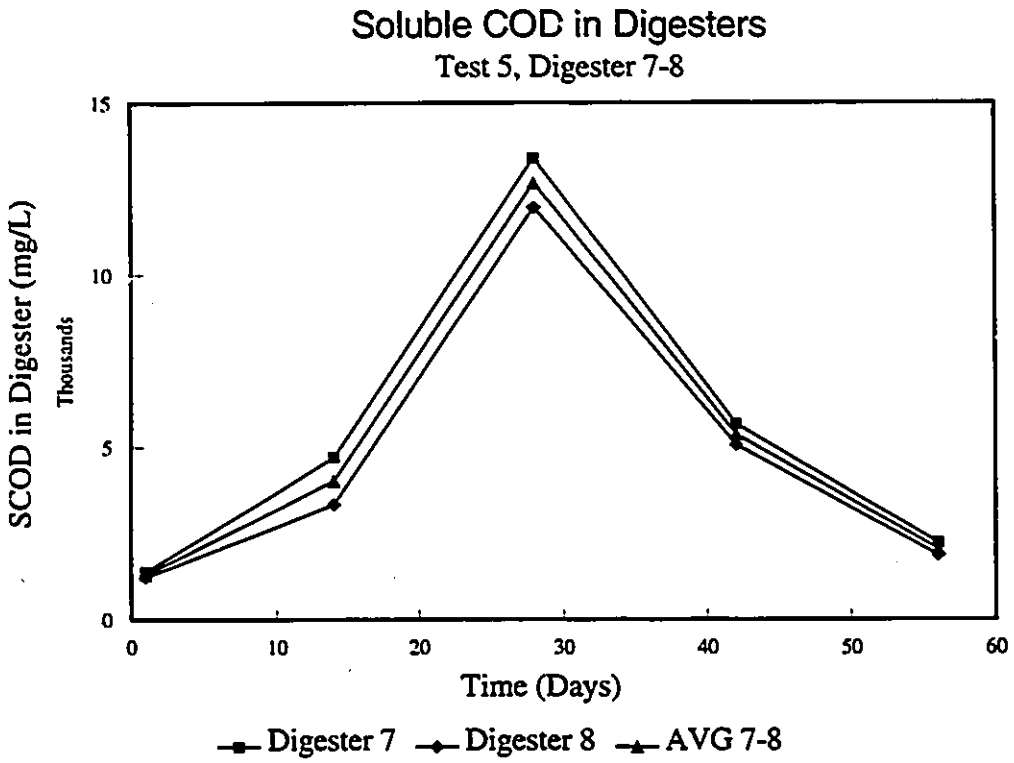

Butyric Acid in Digesters
Test 5, Digester 9-10
Butyric Acid in Digester (mg/L)
150
100
50
0
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

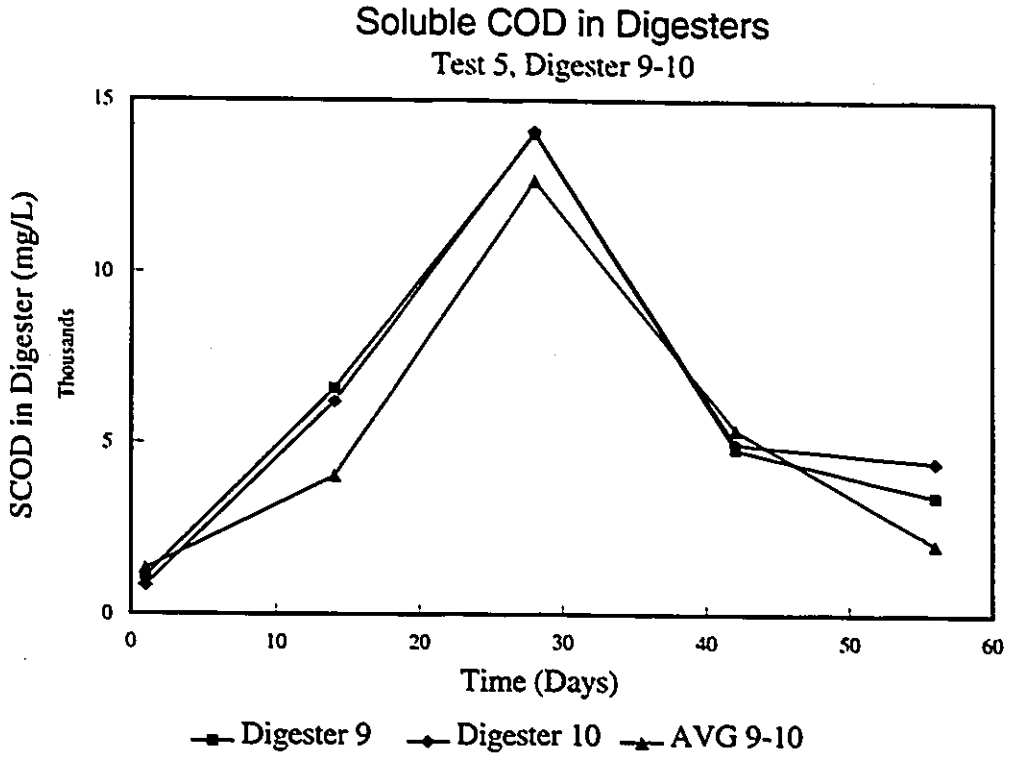

Butyric Acid in Digesters
Test 5, Digester 11-12
Butyric Acid in Digester (mg/L)
200
150
100
50
0
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

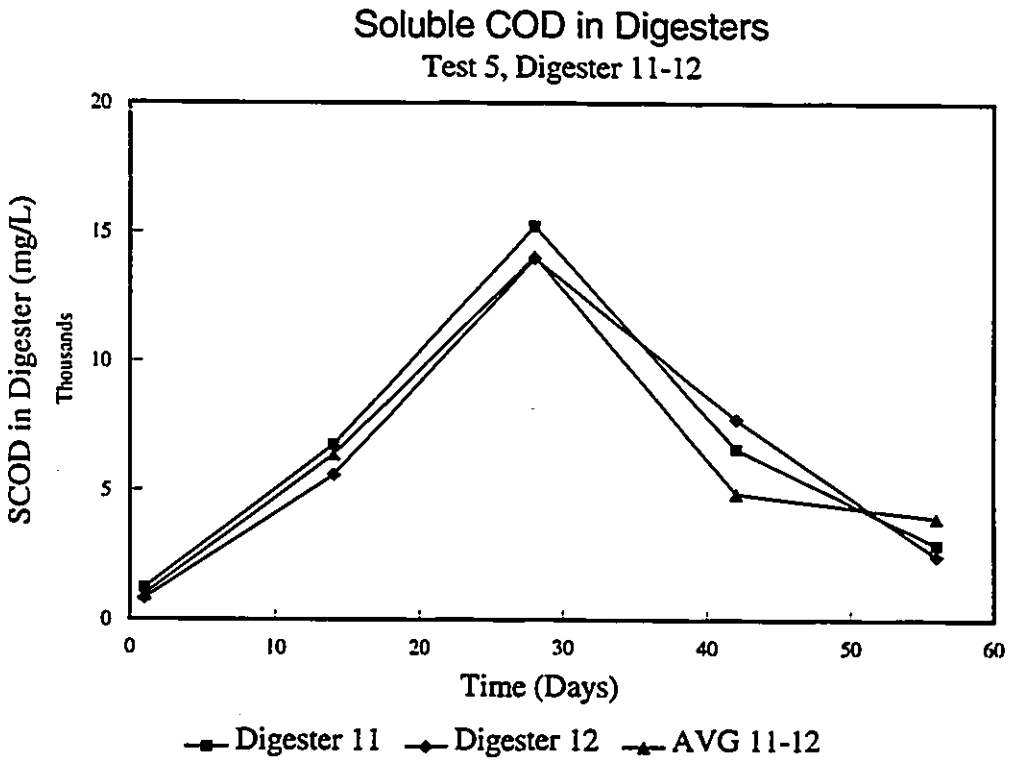

Soluble COD in Digesters
Test 5, Digester 1-2
SCOD in Digester (mg/L)
Thousands
0
1
2
3
4
5
6
7
8
0
10
20
30
40
50
60
Time (Days)
Digester 1
Digester 2
AVG 1-2

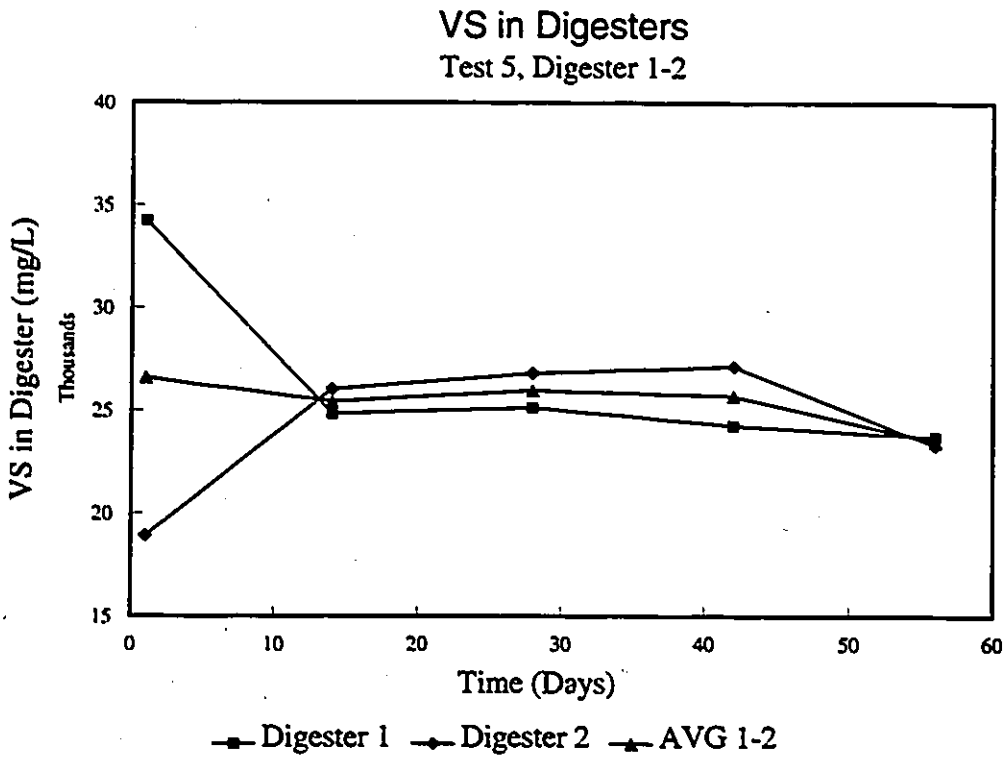

Soluble COD in Digesters
Test 5, Digester 3-4
SCOD in Digester (mg/L)
Thousands
0
1
2
3
4
5
6
7
8
0
10
20
30
40
50
60
Time (Days)
Digester 3
Digester 4
AVG 3-4

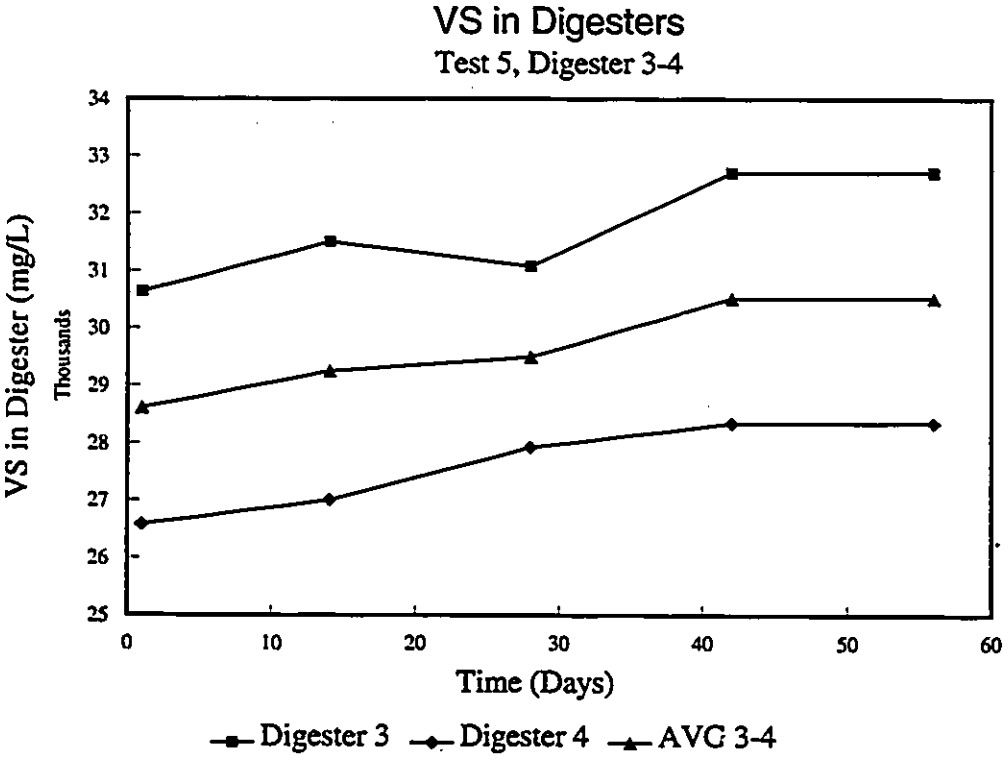

Soluble COD in Digesters
Test 5, Digester 5-6
SCOD in Digester (mg/L)
Thousands
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6

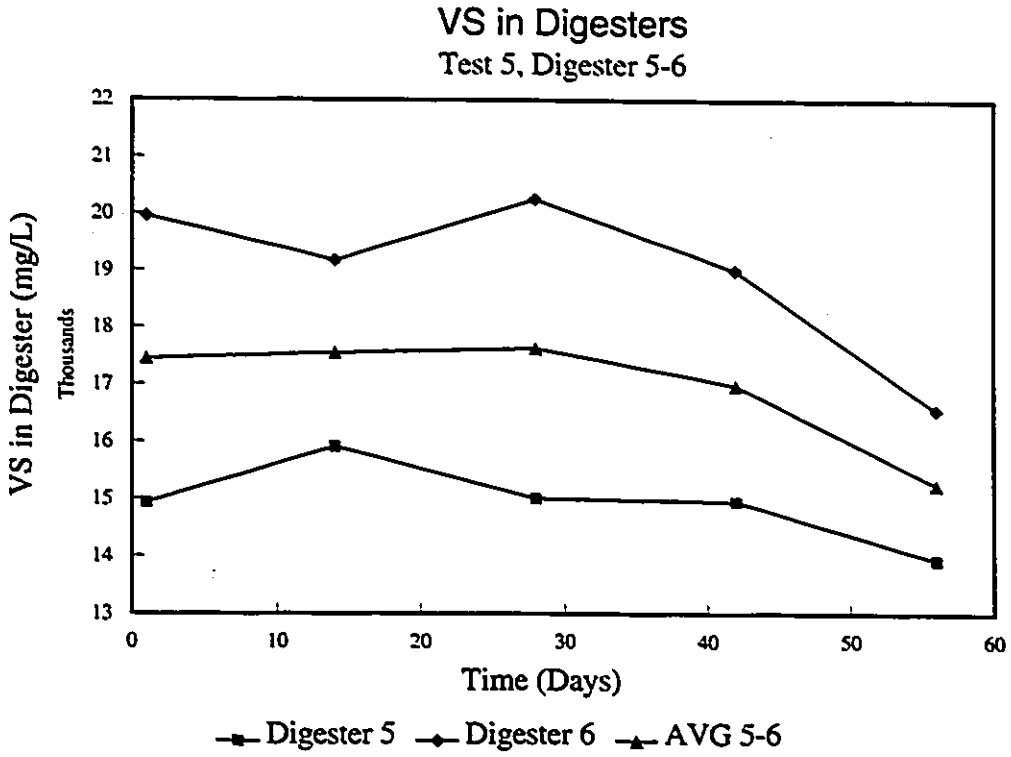

Soluble COD in Digesters
Test 5, Digester 7-8
SCOD in Digester (mg/L)
Thousands
15
10
5
0
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8

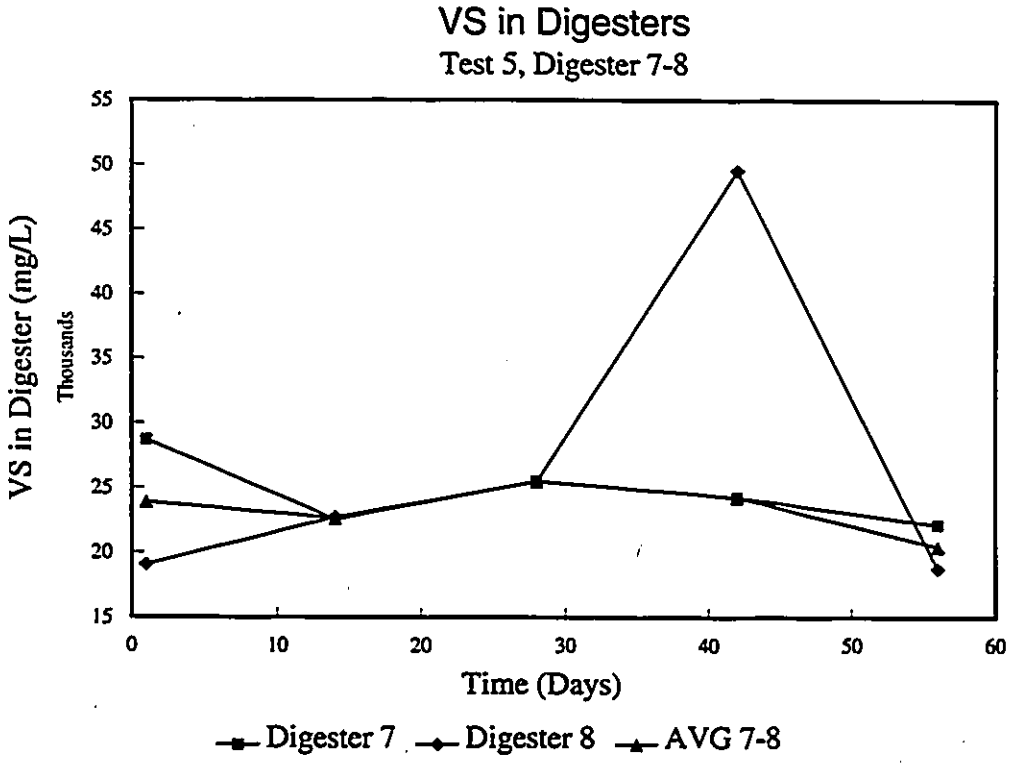

Soluble COD in Digesters
Test 5, Digester 9-10
SCOD in Digester (mg/L)
Thousands
15
10
5
0
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

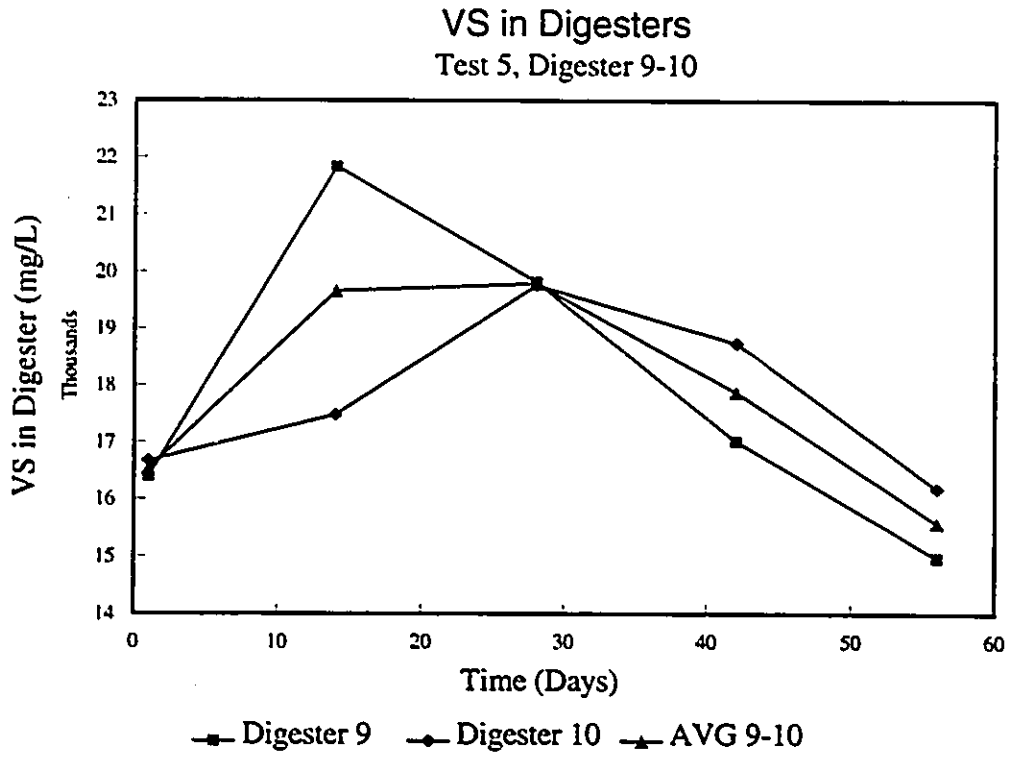

Soluble COD in Digesters
Test 5, Digester 11-12
SCOD in Digester (mg/L)
Thousands
20
15
10
5
0
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

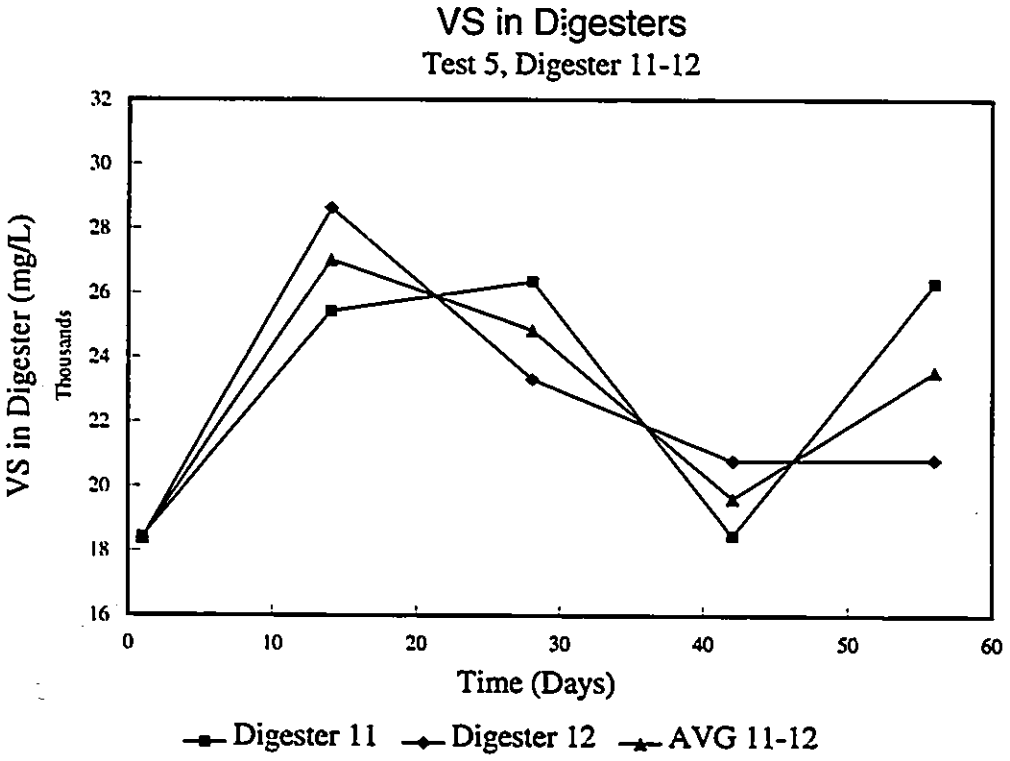

VS in Digesters
Test 5, Digester 1-2
VS in Digester (mg/L)
Thousands
40
35
30
25
20
15
0
10
20
30
40
50
60
Time (Days)
Digester 1
Digester 2
AVG 1-2

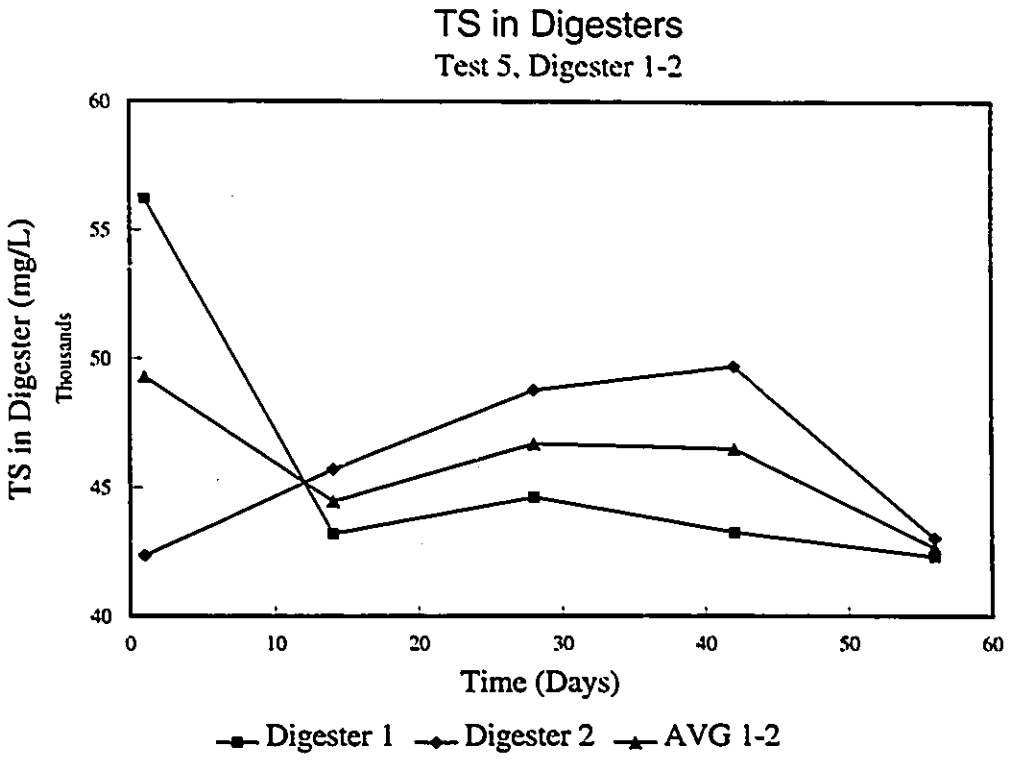

VS in Digesters
Test 5, Digester 3-4
VS in Digester (mg/L)
Thousands
34
33
32
31
30
29
28
27
26
25
0
10
20
30
40
50
60
Time (Days)
Digester 3
Digester 4
AVG 3-4

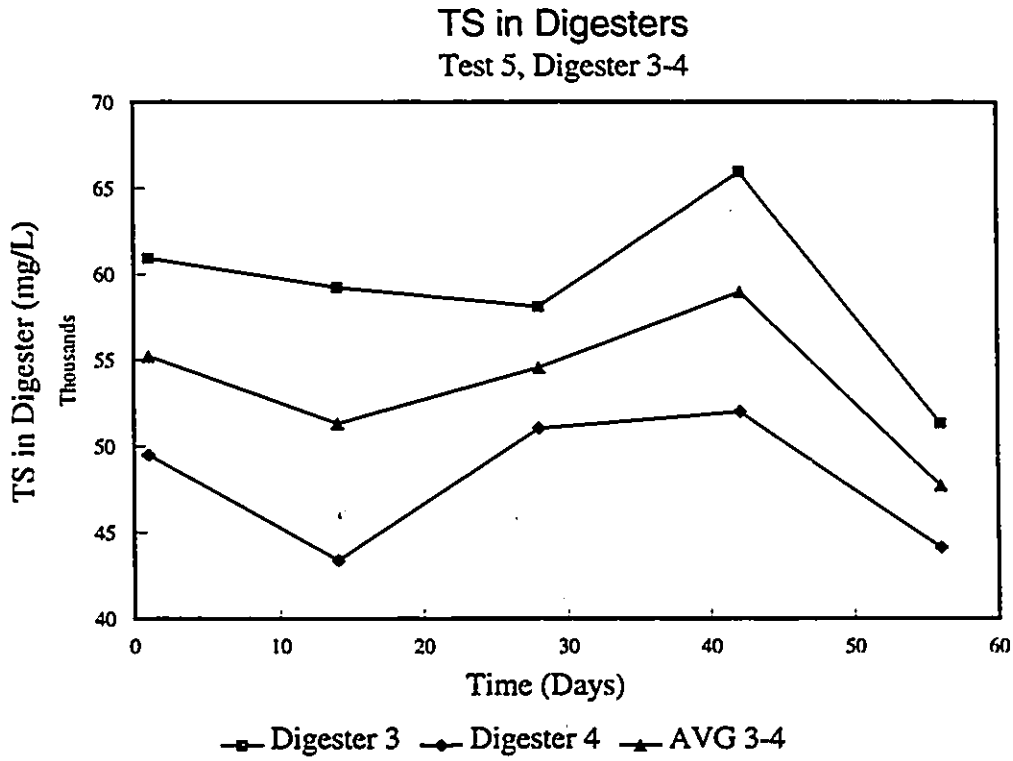

VS in Digesters
Test 5, Digester 5-6
VS in Digester (mg/L)
Thousands
22
21
20
19
18
17
16
15
14
13
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6

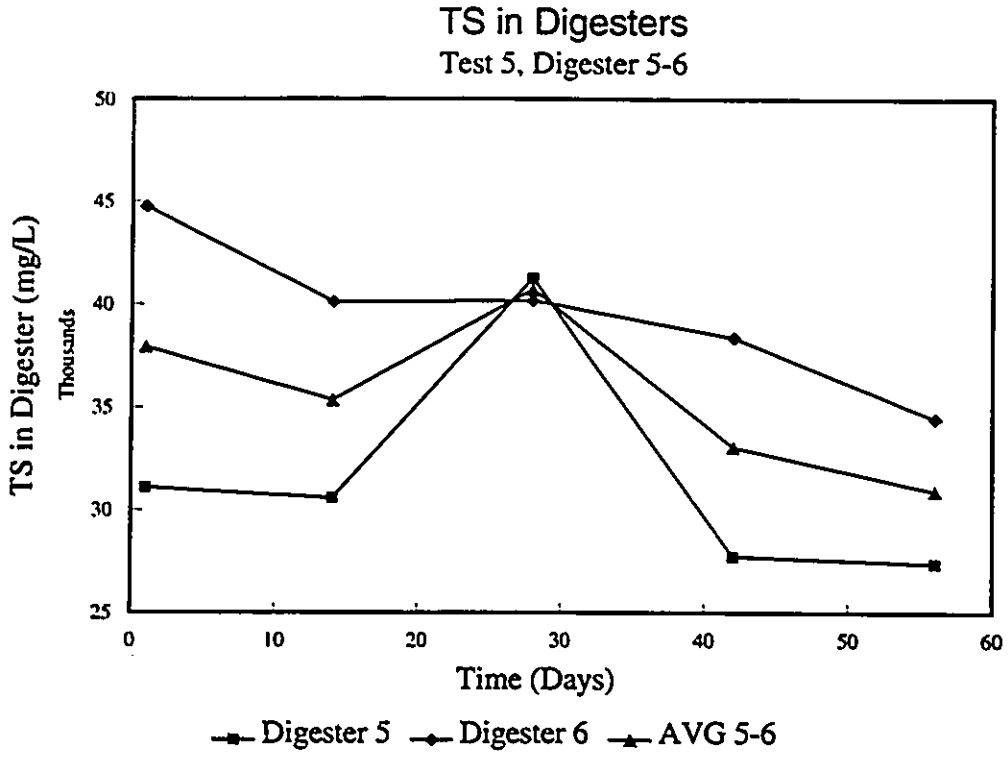

VS in Digesters
Test 5, Digester 7-8
VS in Digester (mg/L)
Thousands
55
50
45
40
35
30
25
20
15
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8

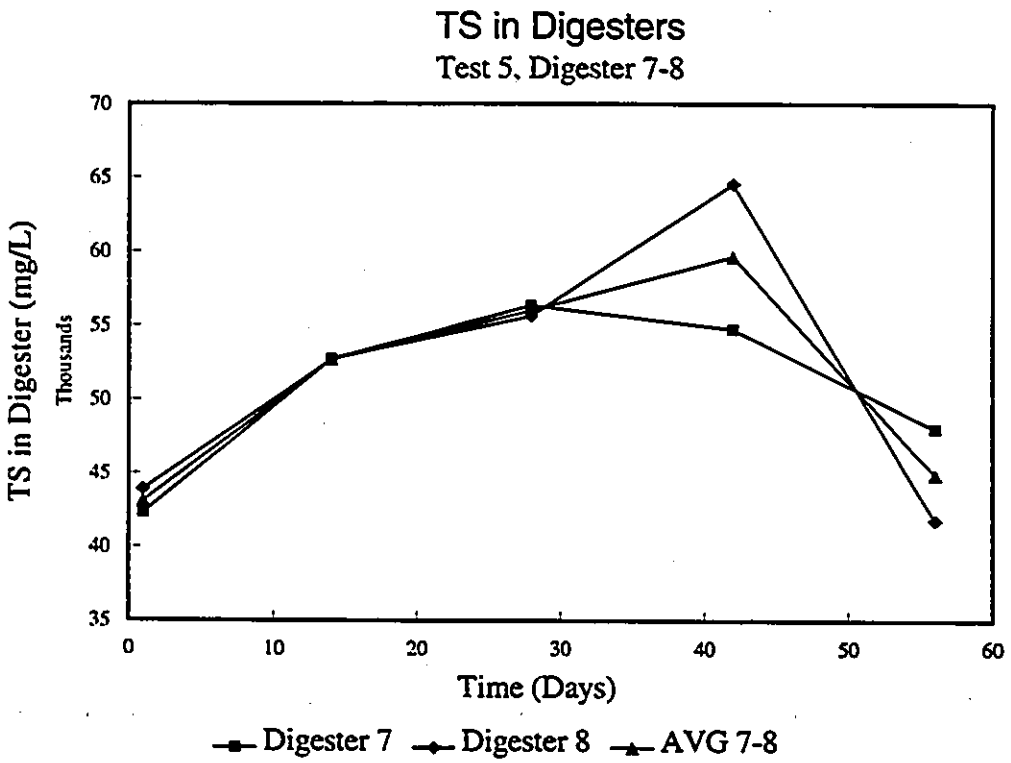

VS in Digesters
Test 5, Digester 9-10
VS in Digester (mg/L)
Thousands
23
22
21
20
19
18
17
16
15
14
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

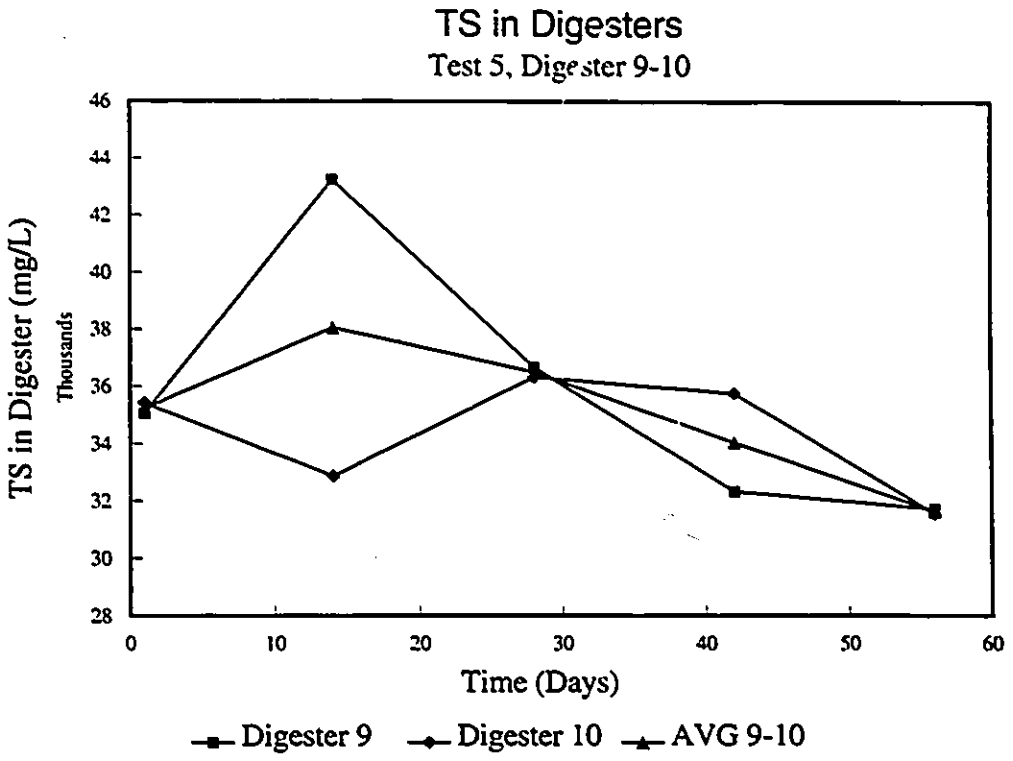

VS in Digesters
Test 5, Digester 11-12
VS in Digester (mg/L)
Thousands
32
30
28
26
24
22
20
18
16
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

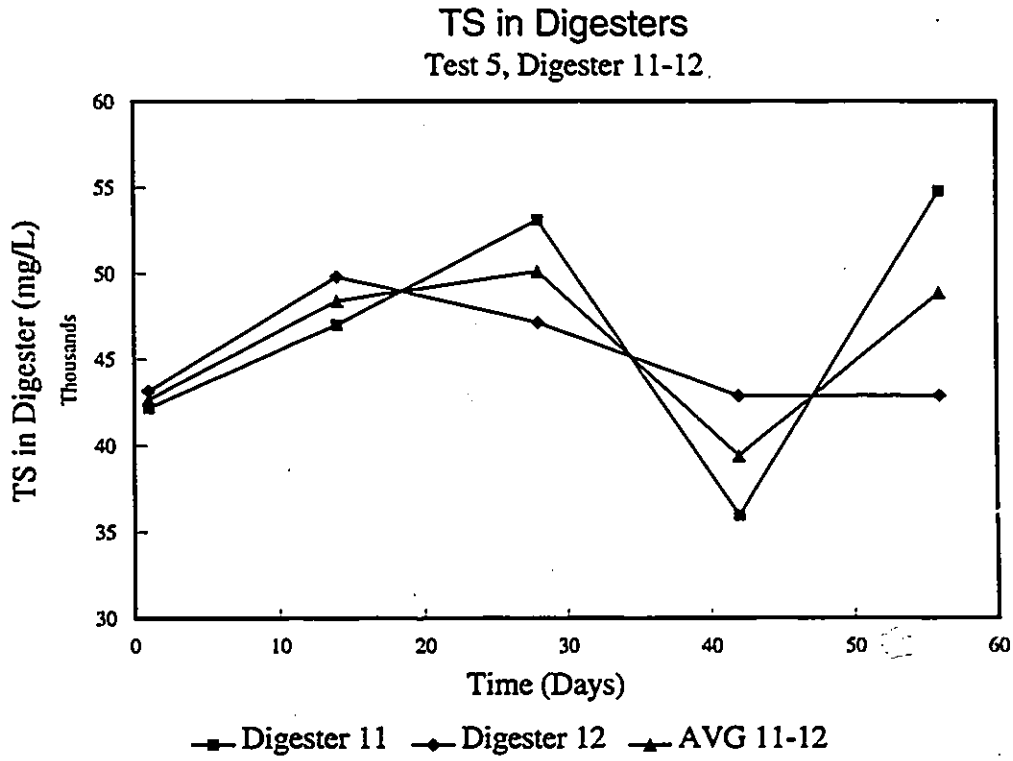

TS in Digesters
Test 5, Digester 1-2
TS in Digester (mg/L)
Thousands
60
55
50
45
40
0
10
20
30
40
50
60
Time (Days)
Digester 1
Digester 2
AVG 1-2


TS in Digesters
Test 5, Digester 3-4
TS in Digester (mg/L)
Thousands
70
65
60
55
50
45
40
0
10
20
30
40
50
60
Time (Days)
Digester 3
Digester 4
AVG 3-4


TS in Digesters
Test 5, Digester 5-6
TS in Digester (mg/L)
Thousands
50
45
40
35
30
25
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6


TS in Digesters
Test 5, Digester 7-8
TS in Digester (mg/L)
Thousands
70
65
60
55
50
45
40
35
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8

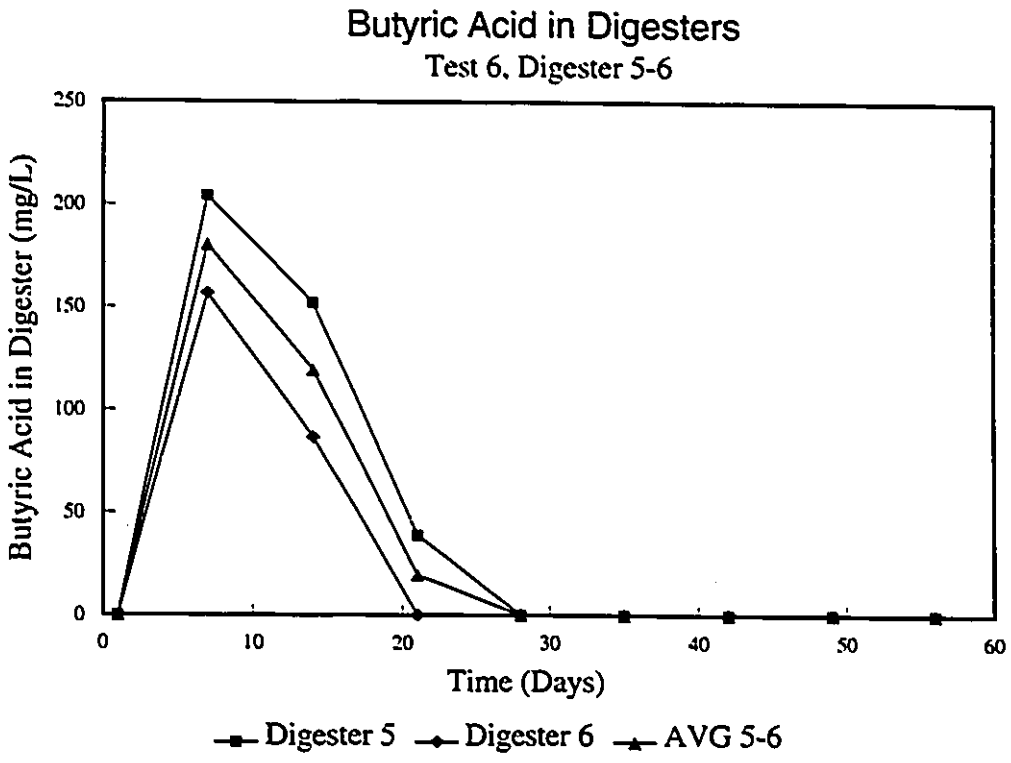

TS in Digesters
Test 5, Digester 9-10
TS in Digester (mg/L)
Thousands
46
44
42
40
38
36
34
32
30
28
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

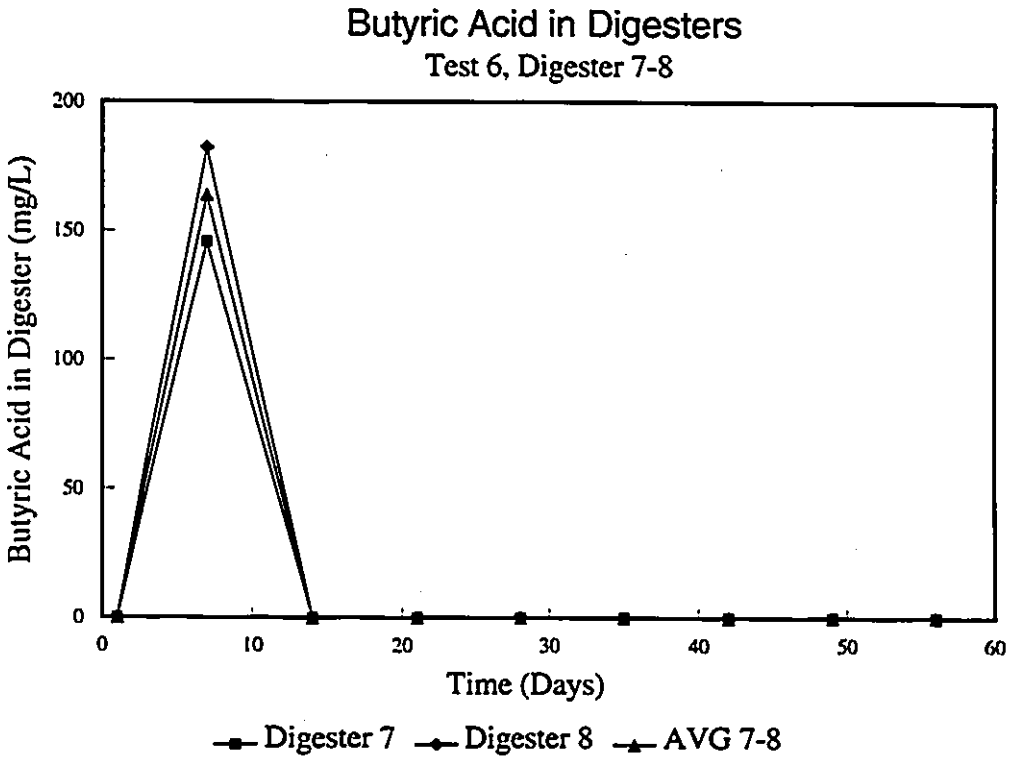

TS in Digesters
Test 5, Digester 11-12
TS in Digester (mg/L)
Thousands
60
55
50
45
40
35
30
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

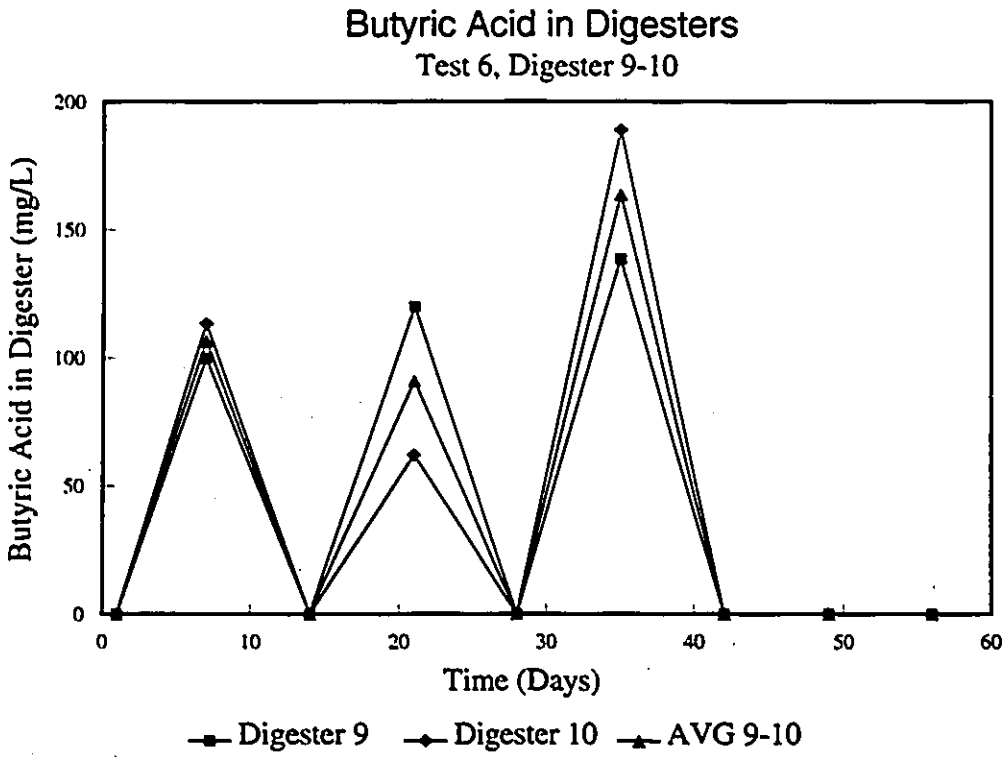
TEST RUN NO. 6

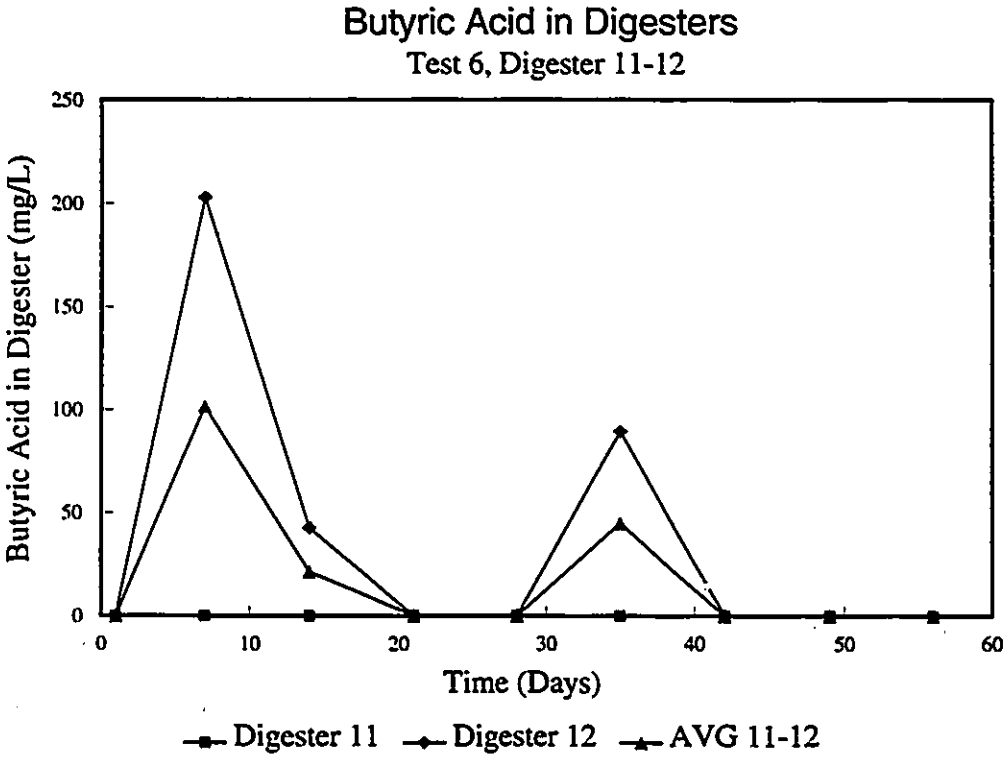
Test	Date	Day	1	2	3	4	5	6	7	8	9	10	11	12
pH	10/1/94	1	7.46	7.47	7.47	7.42	7.55	7.53	7.48	7.50	7.59	7.76	7.70	7.67
	17/1/94	7	7.64	7.57	7.47	7.44	7.50	7.53	7.57	7.68	7.58	7.59	7.65	7.56
	24/1/94	14	7.43	7.45	7.31	7.38	7.50	7.45	7.56	7.62	7.48	7.44	7.62	7.38
	31/1/94	21	7.40	7.34	7.22	7.24	7.58	7.59	7.59	7.63	7.54	7.48	7.62	7.45
	7/2/94	28	7.50	7.32	7.38	7.37	7.75	7.65	7.66	7.66	7.72	7.60	7.65	7.62
	14/2/94	35	7.32	7.29	7.22	7.21	7.62	7.59	7.66	7.73	7.59	7.59	7.56	7.65
	21/2/94	42	7.36	7.29	7.22	7.29	7.75	7.68	7.74	7.69	7.63	7.66	7.64	7.70
	28/2/94	49	7.33	7.26	7.16	7.20	7.75	7.73	7.71	7.74	7.72	7.70	7.68	7.77
	7/3/94	56	7.32	7.24	7.19	7.28	7.82	7.82	7.75	7.76	7.77	7.77	7.78	7.72
VFA	10/1/94	1	67.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acetic	17/1/94	7	1355.7	1369.6	1886.9	1494.9	1605.8	1123.4	1199.4	1140.7	1523.4	1746.9	1338.6	1280.1
Acid	24/1/94	14	2220.3	2710.8	3185.4	2862.7	2329.2	1867.1	1185.2	1820.5	1061.5	1108.9	744.3	1287.7
(mg/L)	31/1/94	21	3427.5	4051.0	4614.4	3866.2	1500.3	946.3	418.2	442.0	1643.9	2193.3	1408.6	1483.3
	7/2/94	28	4195.4	4206.0	5270.8	4864.8	659.7	465.1	245.3	508.6	918.7	1028.8	875.7	693.2
	14/2/94	35	4414.0	4551.1	5858.5	5437.8	1012.6	873.1	495.6	359.6	1059.2	1056.5	930.1	946.6
	21/2/94	42	5204.0	5915.9	6439.2	5955.1	1147.0	1001.2	298.8	265.4	457.9	543.1	350.8	319.2
	28/2/94	49	4598.7	5588.5	6186.5	6032.7	938.0	500.0	343.2	227.0	793.7	783.3	765.4	594.3
	7/3/94	56	4598.7	5588.5	6186.5	6032.7	938.0	500.0	343.2	227.0	793.7	783.3	765.4	594.3
VFA	10/1/94	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Propionic	17/1/94	7	63.6	0.0	0.0	61.4	371.8	327.4	354.8	395.0	397.3	395.0	342.4	401.1
Acid	24/1/94	14	126.7	114.4	139.4	218.7	739.3	729.2	644.1	646.8	506.1	369.4	414.4	559.3
(mg/L)	31/1/94	21	145.6	192.7	257.3	393.4	828.3	825.3	650.4	684.0	800.2	780.5	682.4	791.5
	7/2/94	28	254.1	323.9	440.7	503.2	673.5	707.2	398.1	457.7	844.1	776.0	719.2	894.6
	14/2/94	35	237.1	250.7	415.0	509.9	571.9	971.7	312.0	183.0	875.6	815.3	581.1	1114.3
	21/2/94	42	280.6	354.3	479.1	590.4	657.3	930.7	108.5	63.8	642.5	637.6	267.8	857.2
	28/2/94	49	278.0	364.8	448.4	549.1	128.8	260.7	0.0	0.0	375.6	385.0	254.9	616.6
	7/3/94	56	278.0	364.8	448.4	549.1	128.8	260.7	0.0	0.0	289.8	234.3	200.7	193.3
VFA	10/1/94	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Butyric	17/1/94	7	118.1	0.0	180.8	99.4	204.3	156.8	145.8	182.3	99.9	113.3	0.0	202.8
Acid	24/1/94	14	114.7	126.6	391.8	270.1	152.1	86.7	0.0	0.0	0.0	0.0	0.0	42.6
(mg/L)	31/1/94	21	191.6	224.3	515.5	474.9	38.8	0.0	0.0	0.0	119.9	61.8	0.0	0.0
	7/2/94	28	343.7	456.1	746.5	653.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	14/2/94	35	285.7	360.0	610.3	559.2	0.0	0.0	0.0	0.0	138.5	188.9	0.0	89.4
	21/2/94	42	324.4	401.6	541.9	448.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	28/2/94	49	236.2	317.7	410.7	367.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	7/3/94	56	236.2	317.7	410.7	367.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaCO3	10/1/94	1	6668	7668	6001	5334	5001	5668	6001	6001	6335	7335	9669	6668
(mg/L)	24/1/94	14	10669	11336	10669	8002	10669	12002	11336	11002	13003	9335	13003	12002
	7/2/94	28	12669	18004	11669	14670	12669	16003	12002	15670	13336	18004	16003	17337
	21/2/94	42	15670	9002	12002	12002	17670	15003	16670	16670	16670	16003	16337	16337
	7/3/94	56	13169	12336	16337	12002	13003	14003	15670	16003	17670	18004	10669	20004

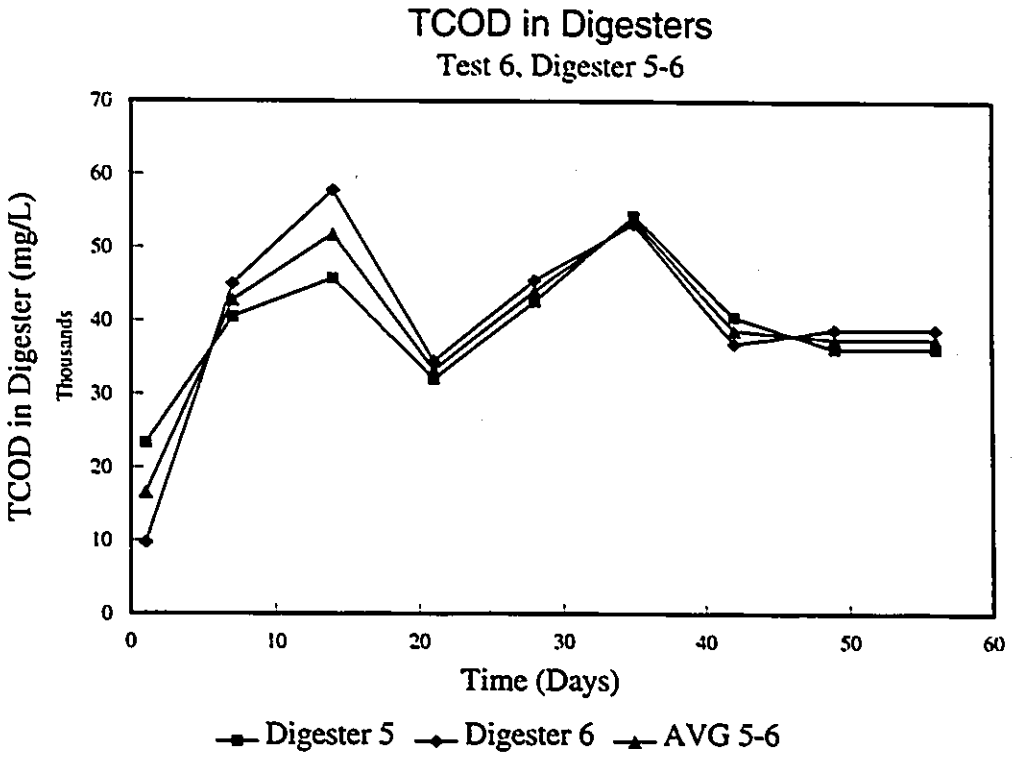
NH3-N	10/1/94	1	1484	1582	1394	1136	1130	1110	1137	1236	1367	1546	1711	1371
(mg/L)	24/1/94	14	2608	2657	2865	2632	2941	2463	2916	2917	2632	2322	2613	2686
	7/2/94	28	3346	3589	3684	3558	3073	2959	2979	2911	3153	2959	3312	3448
	21/2/94	42	2665	2682	2997	2668	2972	2978	3122	2838	2535	2218	2668	2635
	7/3/94	56	2665	2682	2997	2668	2972	2978	3122	2838	2535	2218	2668	2635
TCOD	10/1/94	1	55187	38037	25943	11047	23299	9724	15000	7384	12530	22848	24568	8514
(mg/L)	17/1/94	7	61493	53366	55251	34777	40588	45022	40129	44472	38731	42298	33337	41644
	24/1/94	14	55458	52182	47189	41936	45770	57827	48557	42102	37570	36808	35537	44204
	31/1/94	21	46504	46170	49719	40561	32023	34459	43792	32132	39550	38487	38900	52085
	7/2/94	28	51450	57465	69702	56965	42570	45459	38860	32388	39033	47233	36422	57787
	14/2/94	35	48312	48312	78006	56040	54312	53213	52934	54887	53583	48833	40535	54405
	21/2/94	42	49371	49371	51399	54010	40484	36853	35558	48006	43392	53691	35402	48257
	28/2/94	49	46206	54066	52667	55101	36189	38821	33537	38151	43507	42531	38417	53967
	7/3/94	56	62481	46134	62200	53619	36189	38821	33537	38151	47218	51043	18241	49111
SCOD	10/1/94	1	0	0	23	349	617	99	844	0	479	25	486	831
(mg/L)	17/1/94	7	5661	5504	6628	6170	6649	6014	6044	5819	5760	6063	5761	7119
	24/1/94	14	7402	8328	10221	9498	8767	9004	8870	7474	4750	4646	5385	6253
	31/1/94	21	10181	11040	12971	12575	6584	6055	5151	4499	8705	7432	6893	7967
	7/2/94	28	13133	14302	15088	14255	4730	4730	3684	3379	5246	5192	5752	5578
	14/2/94	35	14145	14720	16318	15407	5315	5676	3274	3661	6970	6247	5670	6651
	21/2/94	42	14632	14776	15886	15177	6081	6717	4851	4286	4818	4843	3201	5035
	28/2/94	49	13344	13660	15693	14644	2688	3183	2167	2876	5723	6154	4143	5829
	7/3/94	56	13532	14309	15365	15586	2375	3115	1821	2085	2731	2885	1502	3119
TS	10/1/94	1	42846	55576	47322	29054	23018	24398	23608	22184	25832	22384	35361	25530
(mg/L)	24/1/94	14	52525	52793	54414	38842	41500	50424	47695	41051	43663	35923	39783	41089
	7/2/94	28	47711	61675	64389	60367	48381	39585	43116	38304	42644	43293	47451	60690
	21/2/94	42	47077	45649	52485	45039	44934	50622	53130	50133	47681	51082	36149	56891
	7/3/94	56	62639	53952	86092	71157	16525	25828	39813	27904	74349	72656	27483	73112
VS	10/1/94	1	24572	29110	25549	16250	11759	12253	11606	11082	12901	11594	16967	12794
(mg/L)	24/1/94	14	29390	29037	29583	22465	21600	24885	22878	20231	21901	18490	19057	21698
	7/2/94	28	26787	33483	35380	34178	23454	19301	20507	18213	21253	21672	21627	28755
	21/2/94	42	26712	25486	29116	26231	21939	24167	24826	23499	23410	28826	17087	43075
	7/3/94	56	26712	25486	29116	26231	21939	24167	24826	23499	23410	28826	17087	43075
VSS	10/1/94	1	23818	28466	25516	16675	11326	11790	9662	10584	12480	10892	16193	12297
(mg/L)	24/1/94	14	27542	30958	27116	15713	19700	23256	20917	18281	20292	17135	17677	20065
	7/2/94	28	24899	30962	32492	32465	22676	25782	18186	16686	23511	16205	19864	25616
	21/2/94	42	24700	23207	26594	24008	25808	24861	19529	22299	25765	17282	18508	11897
	7/3/94	56	24700	23207	26594	24008	25808	24861	19529	22299	25765	17282	18508	11897
VSS/VS	10/1/94	1	0.97	0.98	1.00	1.03	0.96	0.96	0.83	0.96	0.97	0.94	0.95	0.96
	24/1/94	14	0.94	1.07	0.92	0.70	0.91	0.93	0.91	0.90	0.93	0.93	0.93	0.92
	7/2/94	28	0.93	0.92	0.92	0.95	0.97	1.34	0.89	0.92	1.11	0.75	0.92	0.89
	21/2/94	42	0.92	0.91	0.91	0.92	1.18	1.03	0.79	0.95	1.10	0.60	1.08	0.28
	7/3/94	56	0.92	0.91	0.91	0.92	1.18	1.03	0.79	0.95	1.10	0.60	1.08	0.28

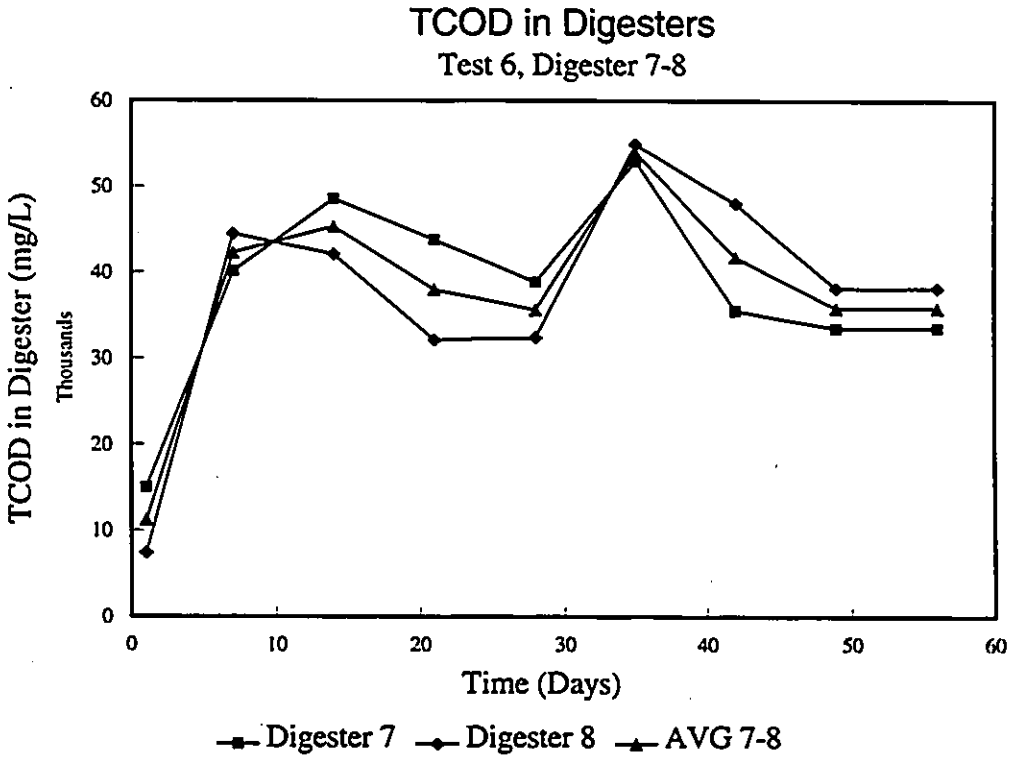

Butyric Acid in Digesters
Test 6, Digester 5-6
Butyric Acid in Digester (mg/L)
250
200
150
100
50
0
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6

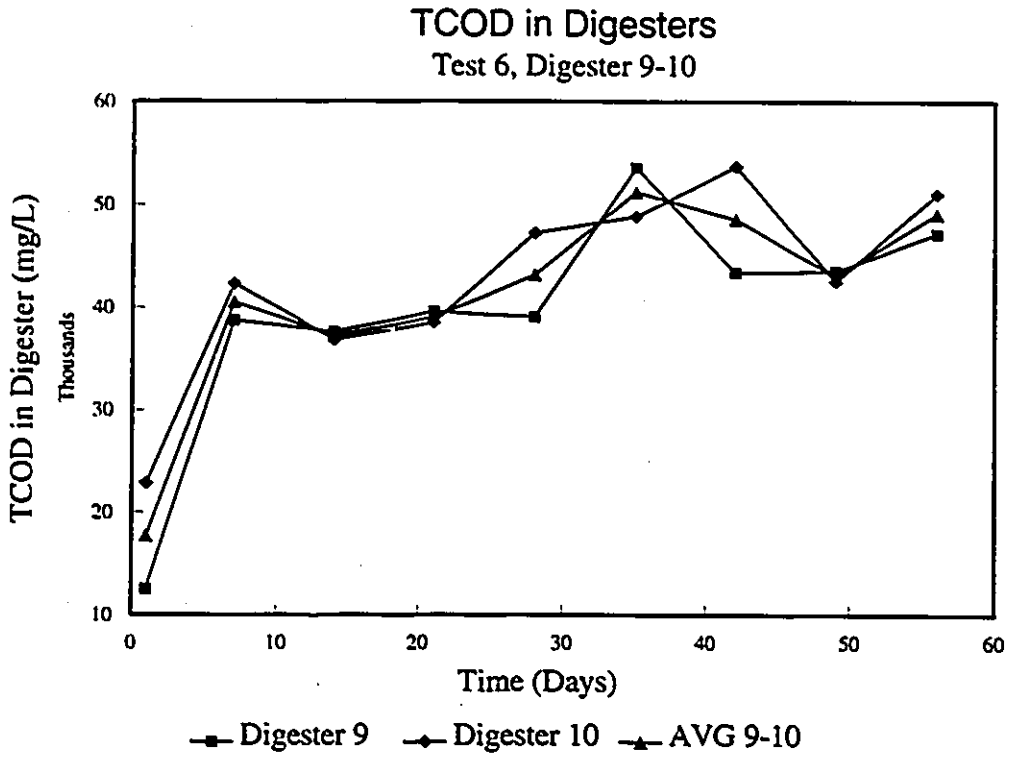

Butyric Acid in Digesters
Test 6, Digester 7-8
Butyric Acid in Digester (mg/L)
200
150
100
50
0
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8

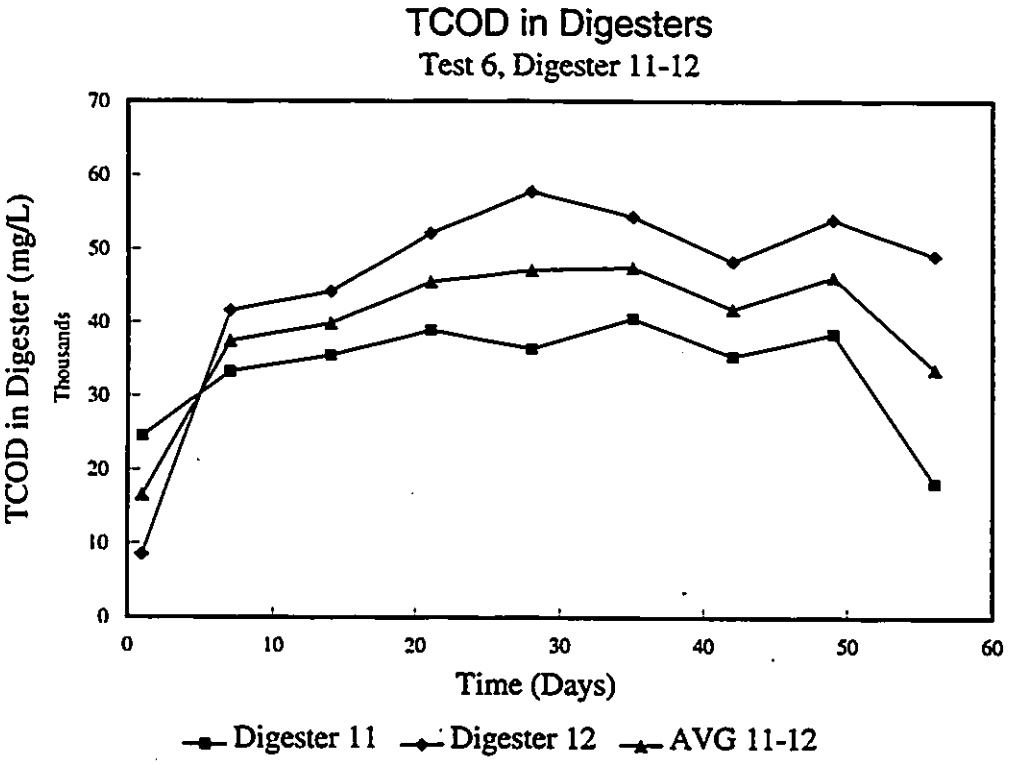

Butyric Acid in Digesters
Test 6, Digester 9-10
Butyric Acid in Digester (mg/L)
200
150
100
50
0
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

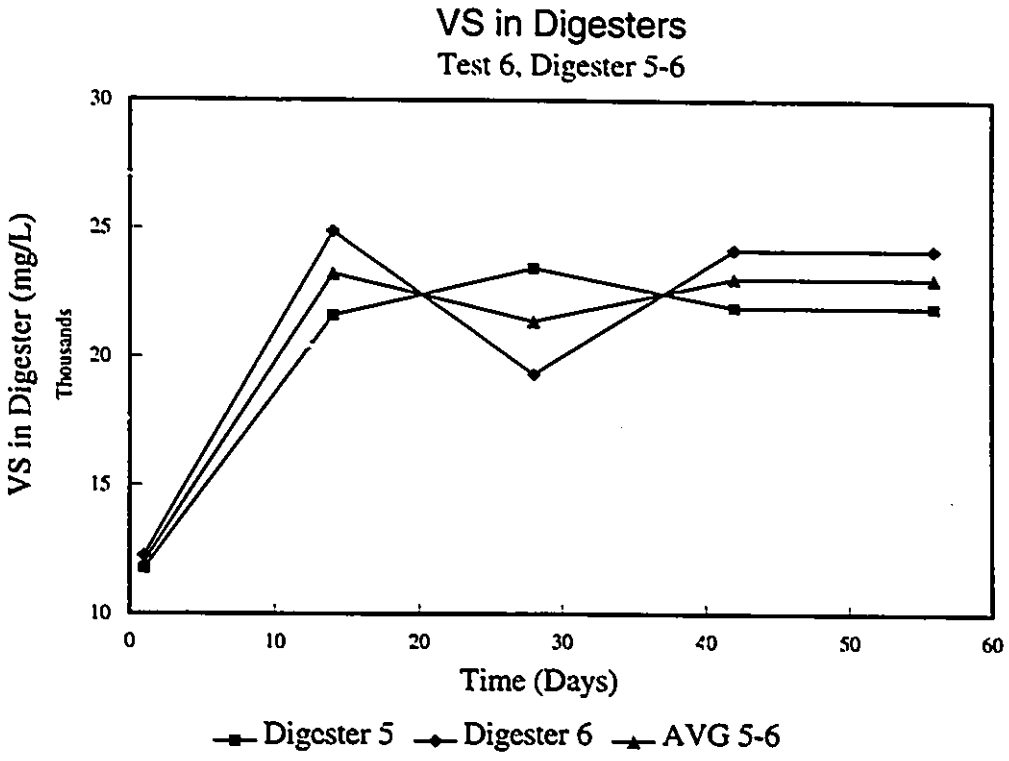

Butyric Acid in Digesters
Test 6, Digester 11-12
Butyric Acid in Digester (mg/L)
250
200
150
100
50
0
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

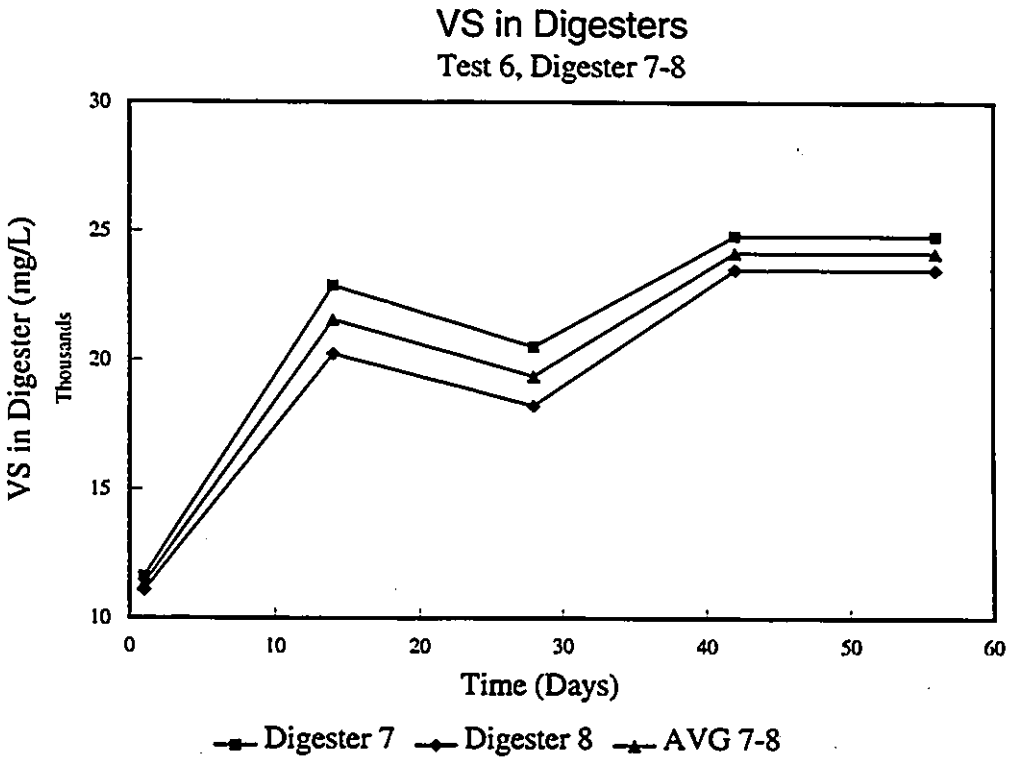

TCOD in Digesters
Test 6, Digester 5-6
TCOD in Digester (mg/L)
Thousands
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6

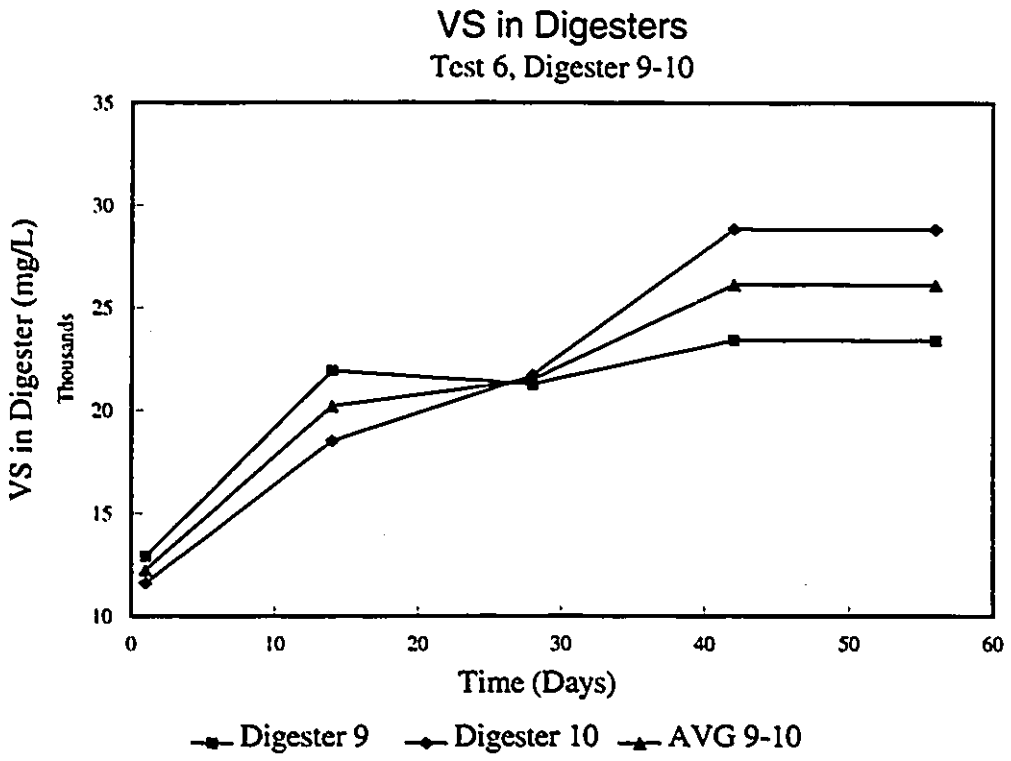

TCOD in Digesters
Test 6, Digester 7-8
TCOD in Digester (mg/L)
Thousands
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8

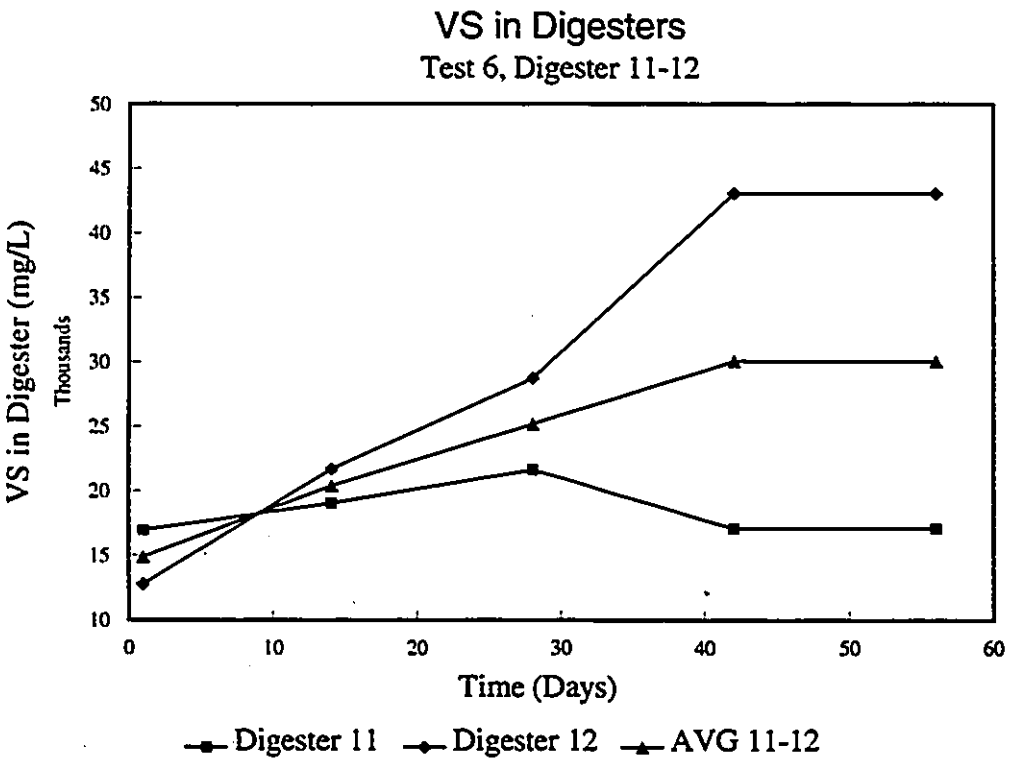

TCOD in Digesters
Test 6, Digester 9-10
TCOD in Digester (mg/L)
Thousands
60
50
40
30
20
10
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

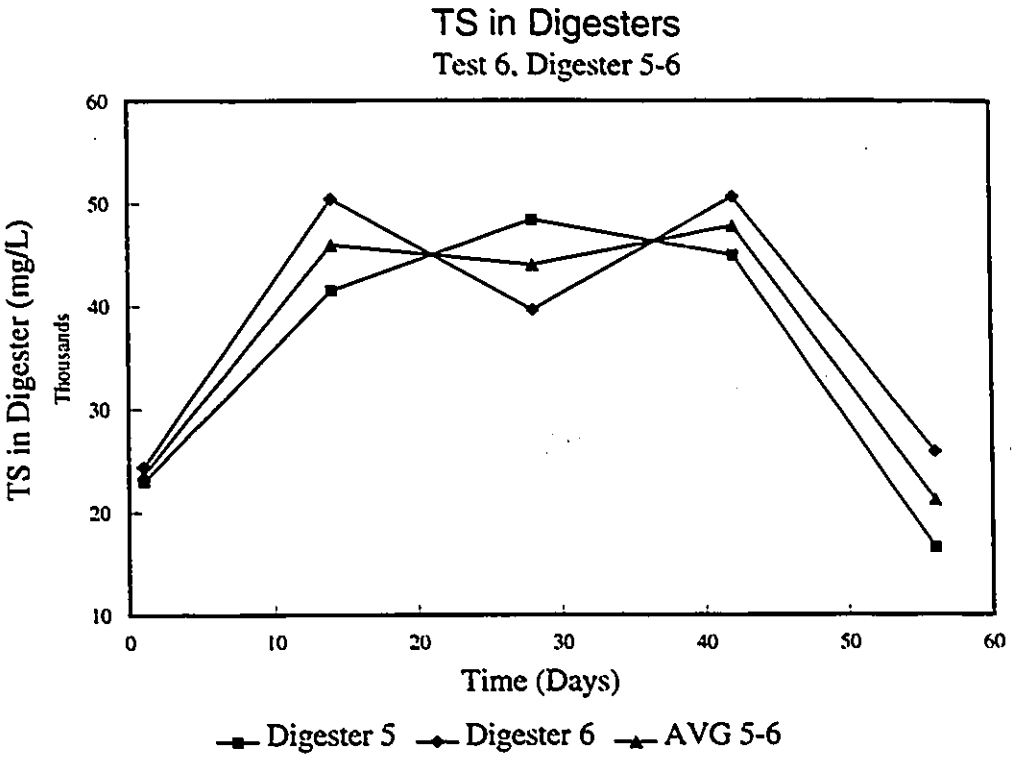

TCOD in Digesters
Test 6, Digester 11-12
TCOD in Digester (mg/L)
Thousands
70
60
50
40
30
20
10
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

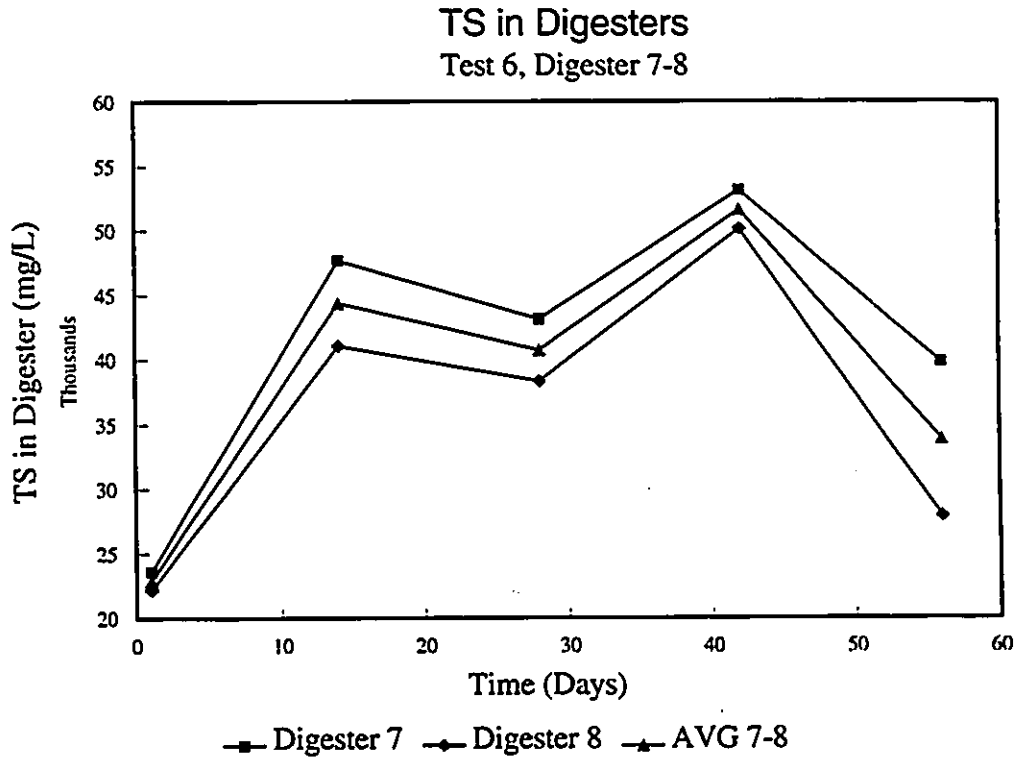

VS in Digesters
Test 6, Digester 5-6
VS in Digester (mg/L)
Thousands
30
25
20
15
10
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6

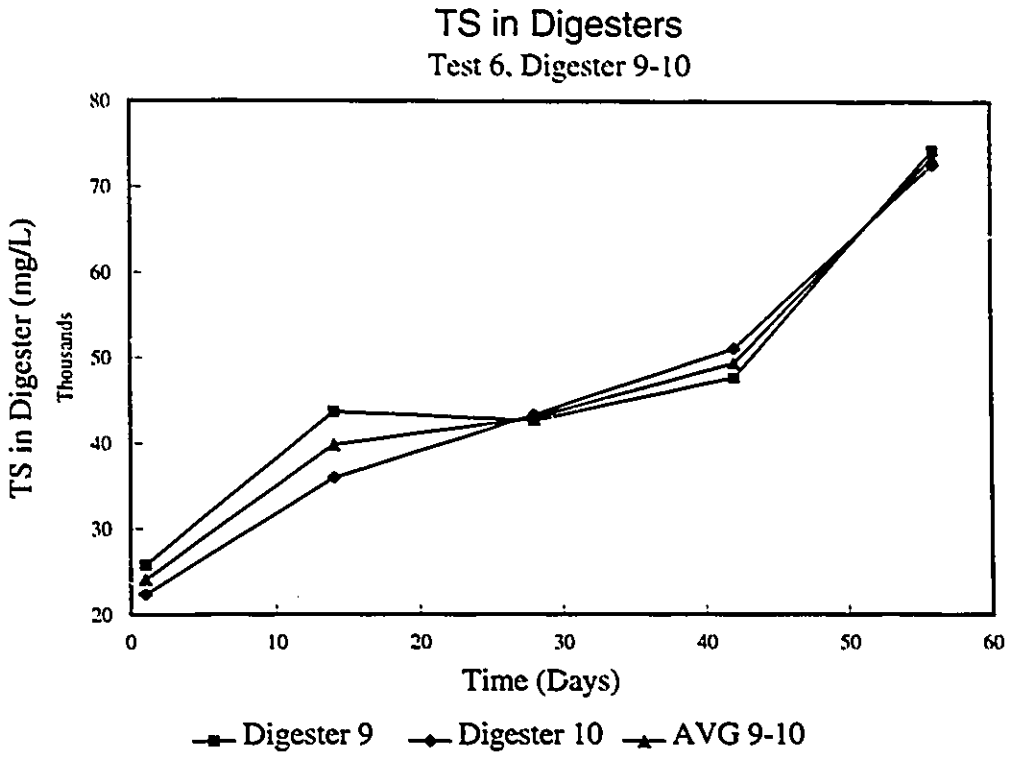

VS in Digesters
Test 6, Digester 7-8
VS in Digester (mg/L)
Thousands
30
25
20
15
10
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8

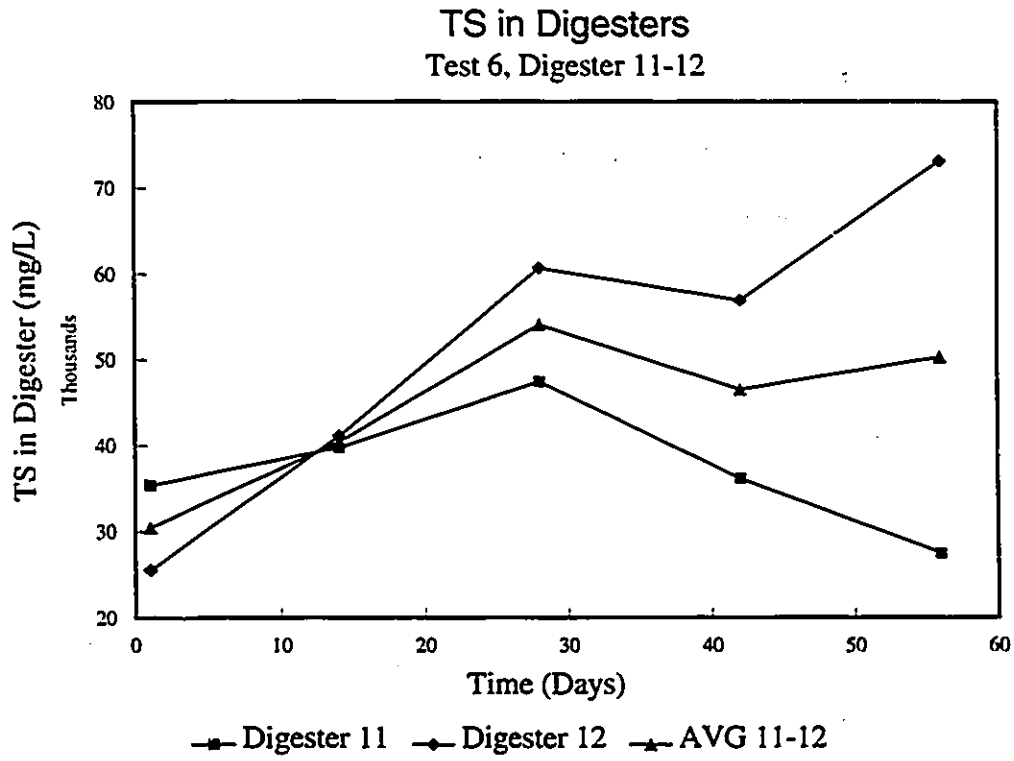

VS in Digesters
Test 6, Digester 9-10
VS in Digester (mg/L)
Thousands
35
30
25
20
15
10
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10


VS in Digesters
Test 6, Digester 11-12
VS in Digester (mg/L)
Thousands
50
45
40
35
30
25
20
15
10
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12


TS in Digesters
Test 6, Digester 5-6
TS in Digester (mg/L)
Thousands
60
50
40
30
20
10
0
10
20
30
40
50
60
Time (Days)
Digester 5
Digester 6
AVG 5-6


TS in Digesters
Test 6, Digester 7-8
TS in Digester (mg/L)
Thousands
60
55
50
45
40
35
30
25
20
0
10
20
30
40
50
60
Time (Days)
Digester 7
Digester 8
AVG 7-8


TS in Digesters
Test 6, Digester 9-10
TS in Digester (mg/L)
Thousands
80
70
60
50
40
30
20
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10


TS in Digesters
Test 6, Digester 11-12
TS in Digester (mg/L)
Thousands
80
70
60
50
40
30
20
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

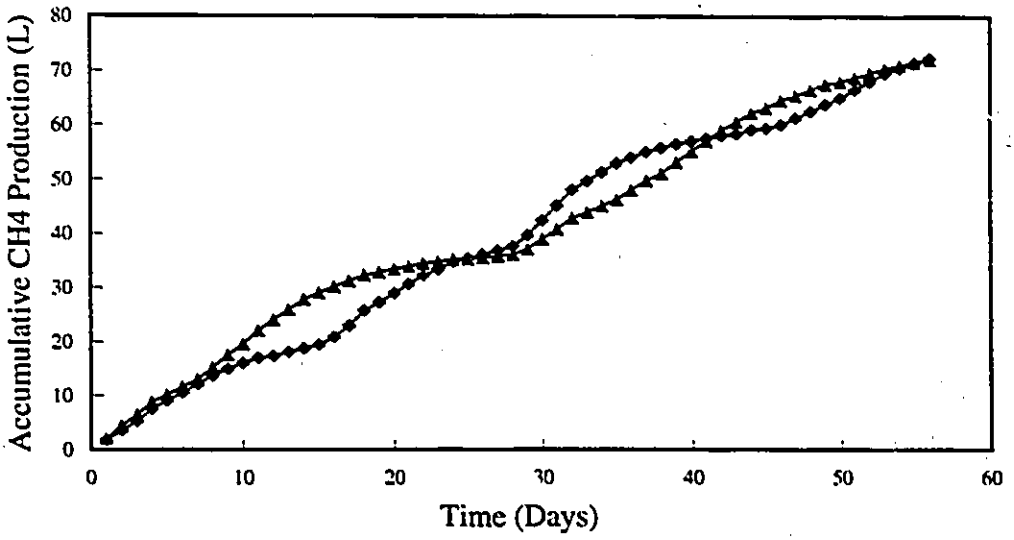
TEST RUN NO. 7

Test	Date	Day	9	10	11	12
pH	14/3/94	1	7.73	7.71	7.67	7.73
	21/3/94	7	7.70	7.68	7.62	7.78
	28/3/94	14	7.75	7.77	7.73	7.82
	4/4/94	21	7.70	7.70	7.66	7.79
	11/4/94	28	7.94	8.01	7.93	8.06
	25/4/94	42			8.04	8.04
	2/5/94	49	8.07	7.96	7.99	8.11
	9/5/94	56	8.16	8.05	8.11	8.17
VFA	14/3/94	1	140.0	115.3	119.2	96.4
Acetic	21/3/94	7	557.2	480.1	301.2	328.3
Acid	28/3/94	14	641.2	507.9	481.5	607.6
(mg/L)	4/4/94	21	329.9	361.6	285.6	220.5
	11/4/94	28	174.5	156.1	86.4	105.6
	25/4/94	42			551.5	1310.2
	2/5/94	49	512.5	1687.7	386.2	440.5
	9/5/94	56	170.2	245.4	167.4	228.0
VFA	14/3/94	1	0.0	0.0	0.0	0.0
Propionic	21/3/94	7	163.0	95.4	76.5	0.0
Acid	28/3/94	14	141.5	0.0	114.1	138.3
(mg/L)	4/4/94	21	75.9	0.0	0.0	0.0
	11/4/94	28	0.0	33.0	0.0	0.0
	25/4/94	42			108.5	324.6
	2/5/94	49	294.2	718.2	93.3	121.5
	9/5/94	56	63.1	139.1	34.6	28.1
VFA	14/3/94	1	0.0	0.0	0.0	0.0
Butyric	21/3/94	7	66.5	0.0	0.0	0.0
Acid	28/3/94	14	0.0	0.0	0.0	0.0
(mg/L)	4/4/94	21	0.0	0.0	0.0	0.0
	11/4/94	28	0.0	22.7	0.0	0.0
	25/4/94	42			19.1	87.9
	2/5/94	49	142.8	452.3	63.6	46.4
	9/5/94	56	63.0	49.5	0.0	0.0
CaCO3	14/3/94	1	16003.0	18670.0	11669.0	21671.0
(mg/L)	28/3/94	14	15670.0	12669.0	11336.0	12669.0
	11/4/94	28	17670.0	8168.0	8168.0	13169.0
	25/4/94	42			10335.0	12669.0
	9/5/94	56	23004.6	19837.3	14169.5	20837.5
NH3-N	14/3/94	1	3653.0	3625.0	2190.0	4341.0
(mg/L)	28/3/94	14	4087.0	3666.0	3068.0	4565.0
	11/4/94	28	20963.5	32834.8	31141.1	22298.9
	25/4/94	42			28883.0	21409.7
	9/5/94	56	19219.5	22693.9	28339.9	20438.6

TCOD	14/3/94	1	36447.0	34901.0	31991.0	42829.0
(mg/L)	21/3/94	7	36918.0	36905.0	36519.0	34984.0
	28/3/94	14	38582.0	42620.0	34268.0	43522.0
	4/4/94	21	39323.0	27247.0	27770.0	25828.0
	11/4/94	28		25401.9	14403.3	21125.7
	25/4/94	42			10412.5	12463.5
	2/5/94	49	51888.6	39022.3	19898.6	26756.1
	9/5/94	56	43118.5	42584.4	18798.6	27899.0
SCOD	14/3/94	1	2347.0	2397.0	2548.0	3668.0
(mg/L)	21/3/94	7	3665.0	3743.0	2118.0	3626.0
	28/3/94	14	2843.0	3345.0	2860.0	2963.0
	4/4/94	21	3828.0	2757.0	1925.0	4112.0
	11/4/94	28	4428.5	2743.5	3336.0	4441.6
	25/4/94	42			1665.3	3531.9
	2/5/94	49	4511.8		1867.0	3971.7
	9/5/94	56	3749.9	3102.5	2320.0	4233.2
VS	14/3/94	1	24748.0	23891.0	21689.0	28803.0
(mg/L)	28/3/94	14	23383.0	21947.0	18900.0	22095.0
	11/4/94	28	19728.4	9657.2	5369.9	9205.0
	25/4/94	42			10808.5	14050.8
	9/5/94	56	29342.7	27541.7	10461.4	15737.3

Effect of Cycle Length on Accumulative CH4 Production

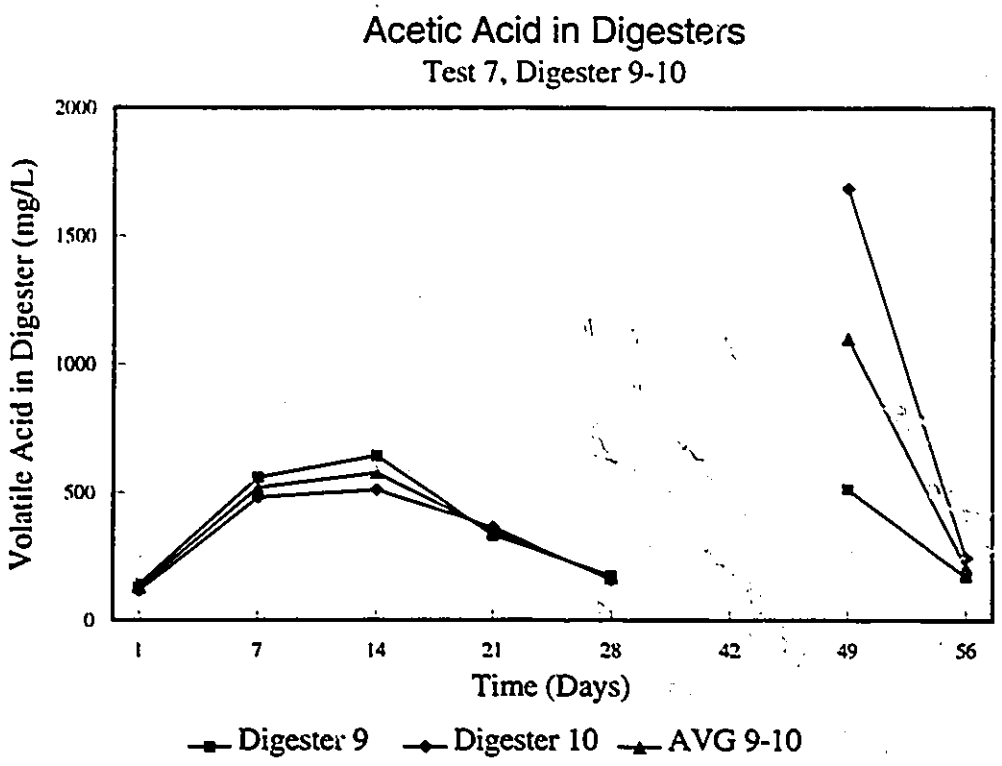
Test 7, Digester 9-10 & 11-12

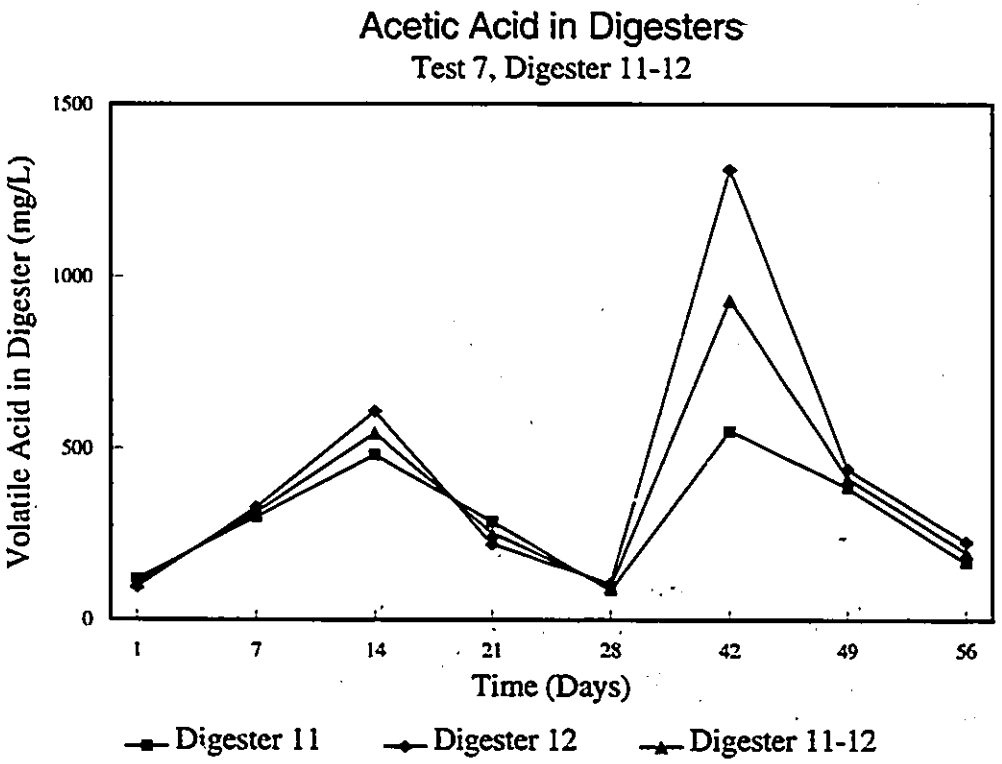


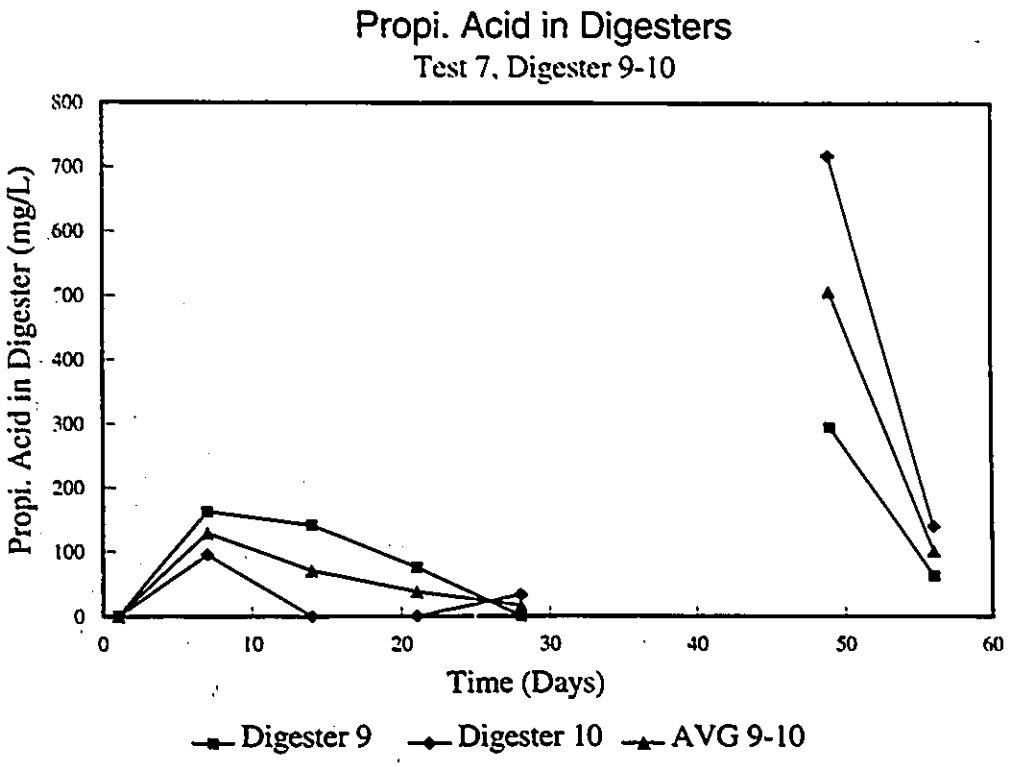
Digester 9-10, Cycle length was 14 days

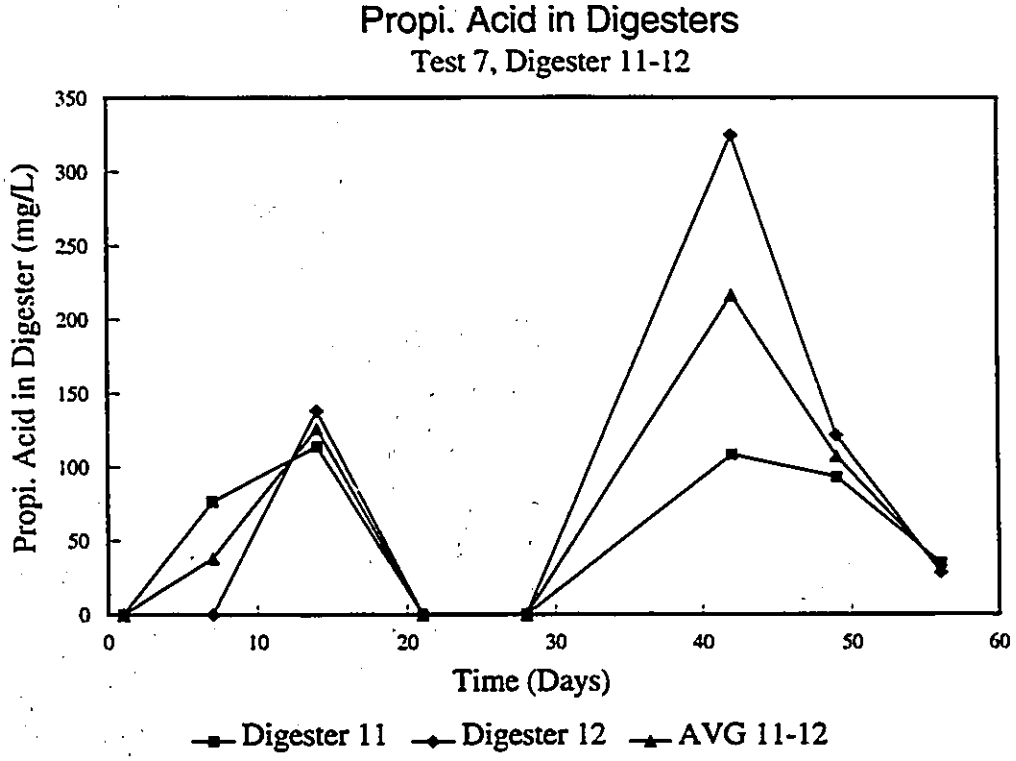
Digester 11-12, cycle length was 28 days

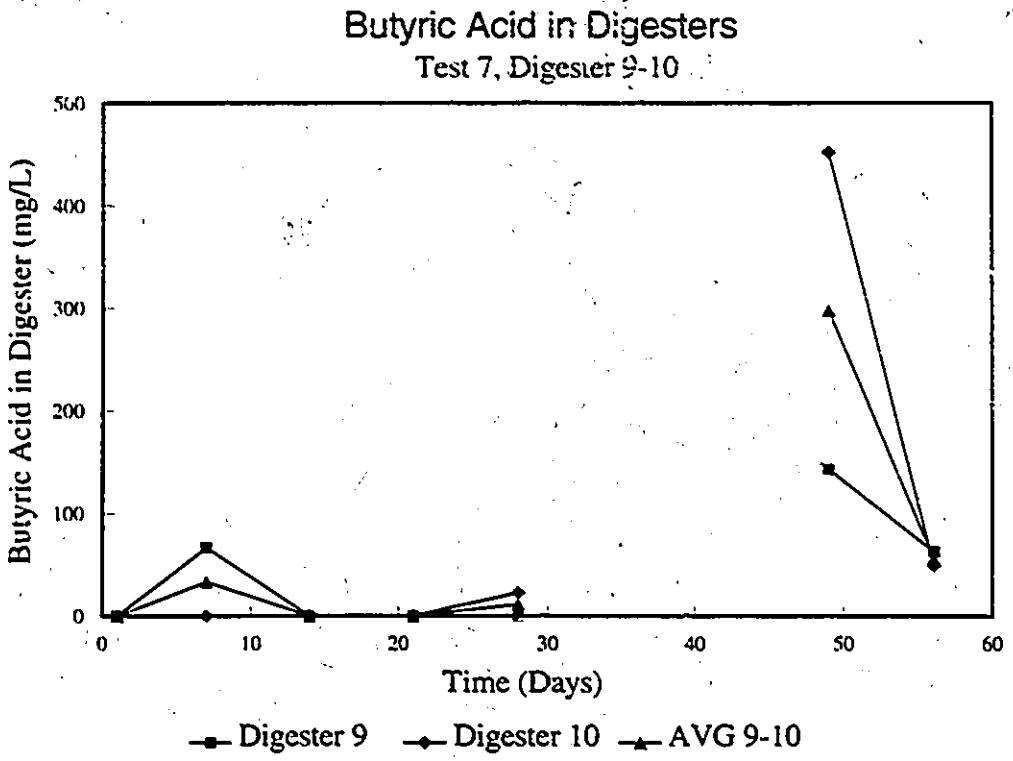
Feeding once a week and the loading rate was 1.26 g COD/L.D

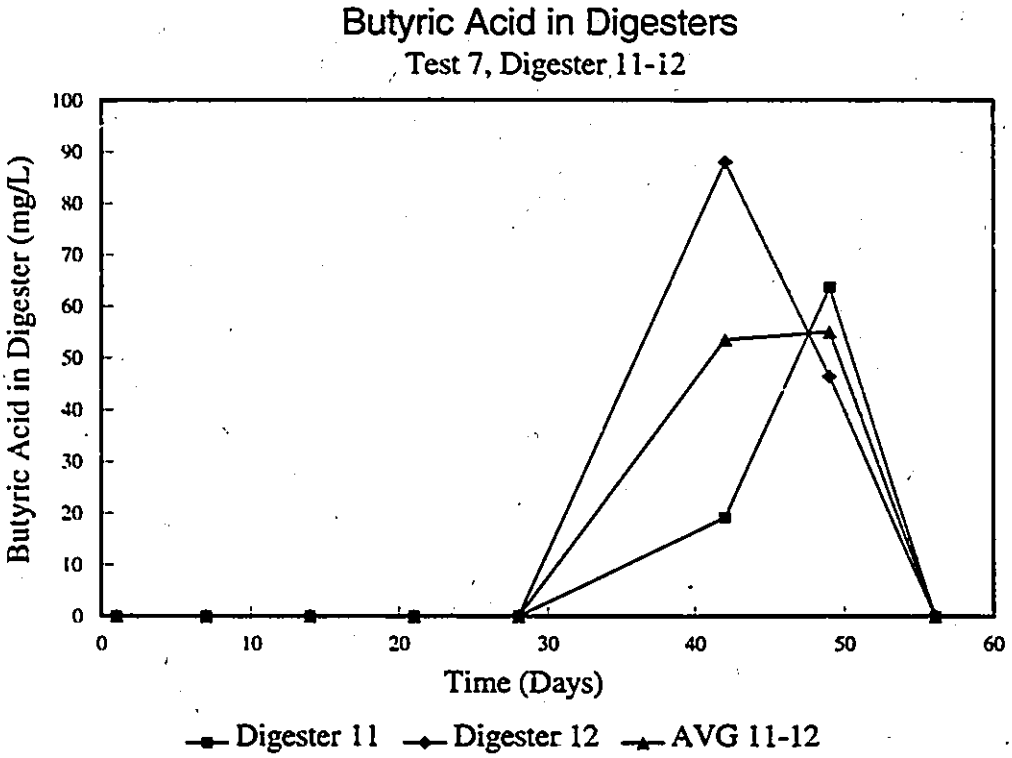

Acetic Acid in Digesters
Test 7, Digester 9-10
Volatile Acid in Digester (mg/L)
2000
1500
1000
500
0
1
7
14
21
28
42
49
56
Time (Days)
Digester 9
Digester 10
AVG 9-10

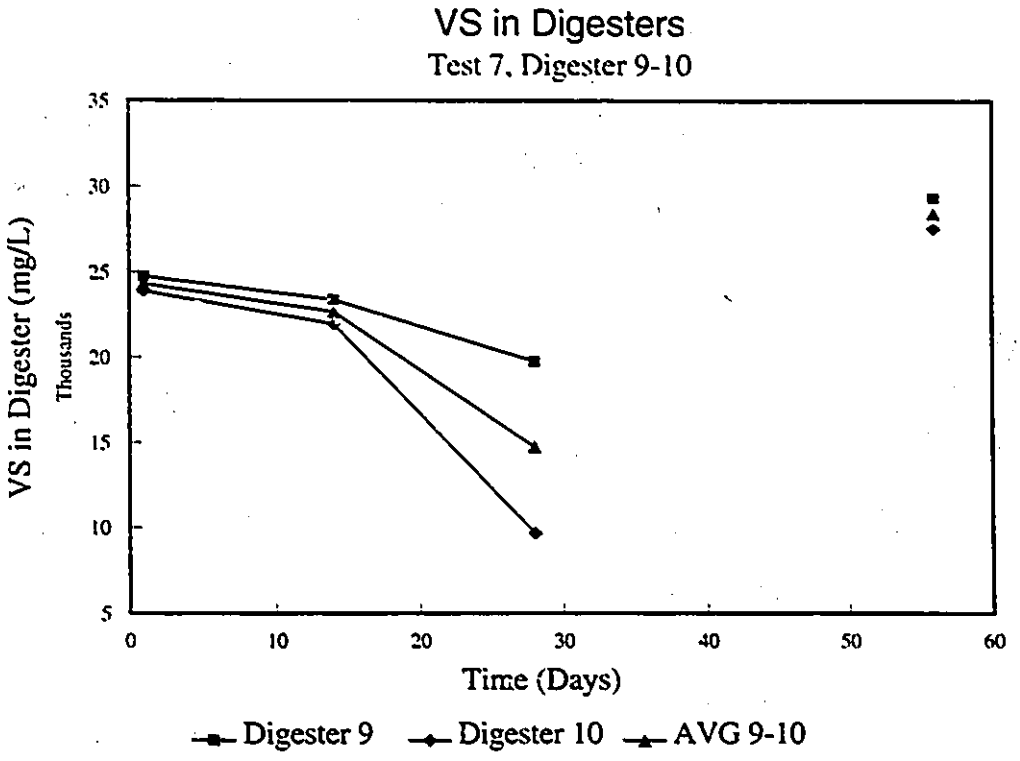

Acetic Acid in Digesters
Test 7, Digester 11-12
Volatile Acid in Digester (mg/L)
1500
1000
500
0
1
7
14
21
28
42
49
56
Time (Days)
Digester 11
Digester 12
Digester 11-12

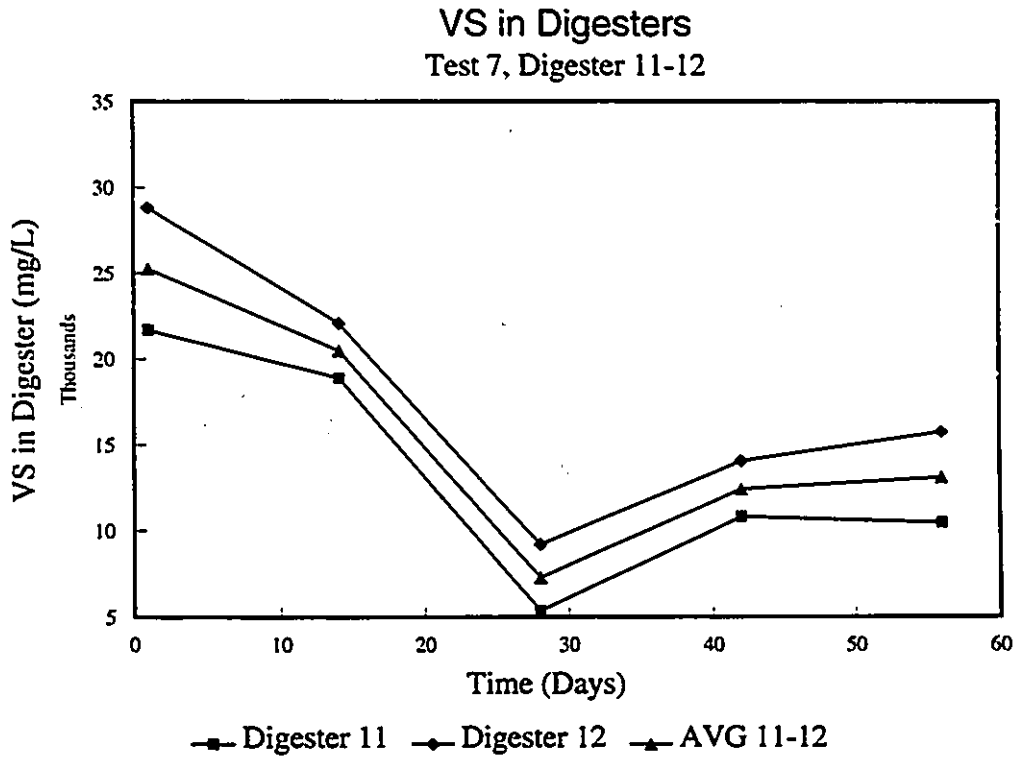

Propi. Acid in Digesters
Test 7, Digester 9-10
Propi. Acid in Digester (mg/L)
800
700
600
500
400
300
200
100
0
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

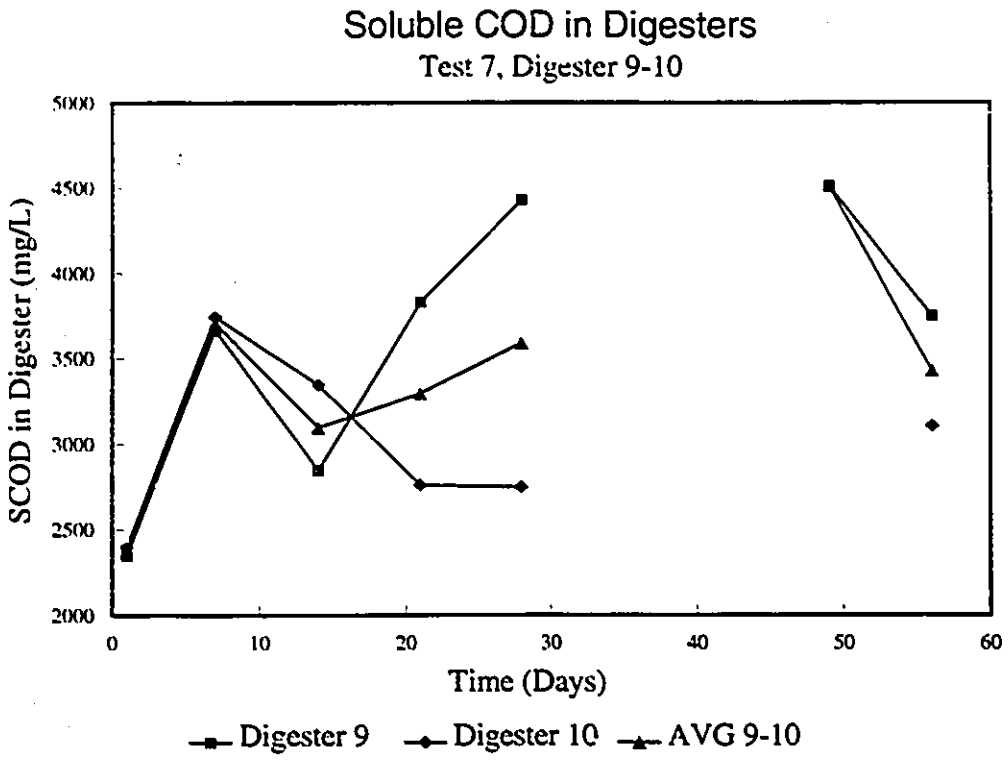

Propi. Acid in Digesters
Test 7, Digester 11-12
Propi. Acid in Digester (mg/L)
350
300
250
200
150
100
50
0
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

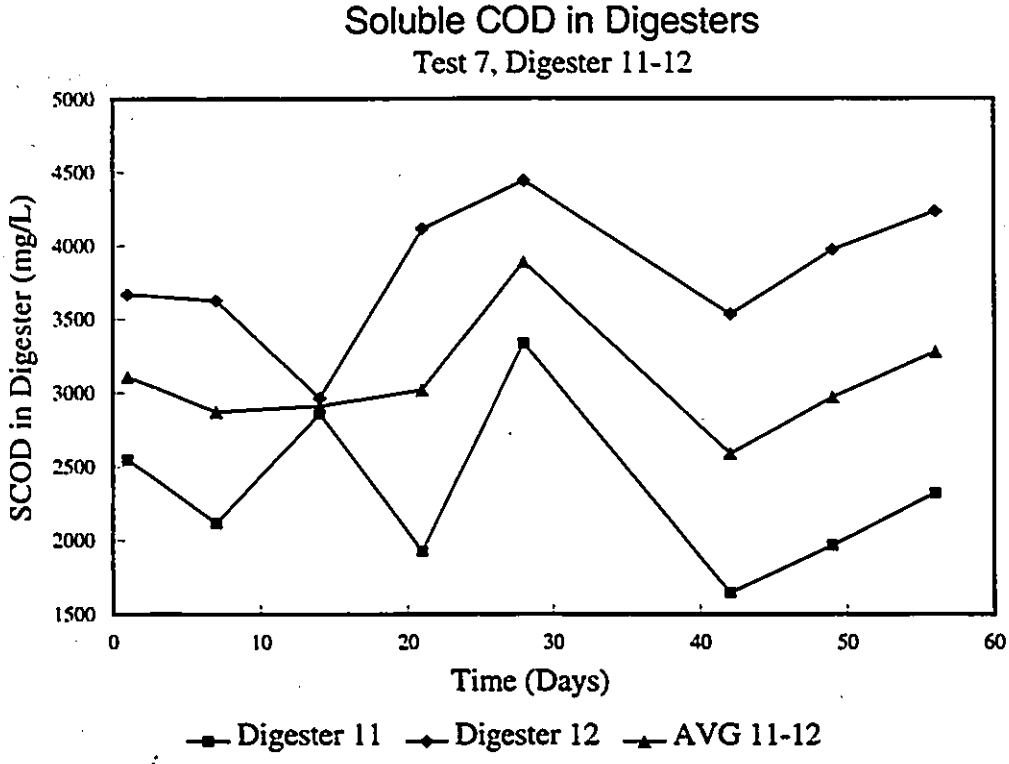

Butyric Acid in Digesters
Test 7, Digester 9-10
Butyric Acid in Digester (mg/L)
500
400
300
200
100
0
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10

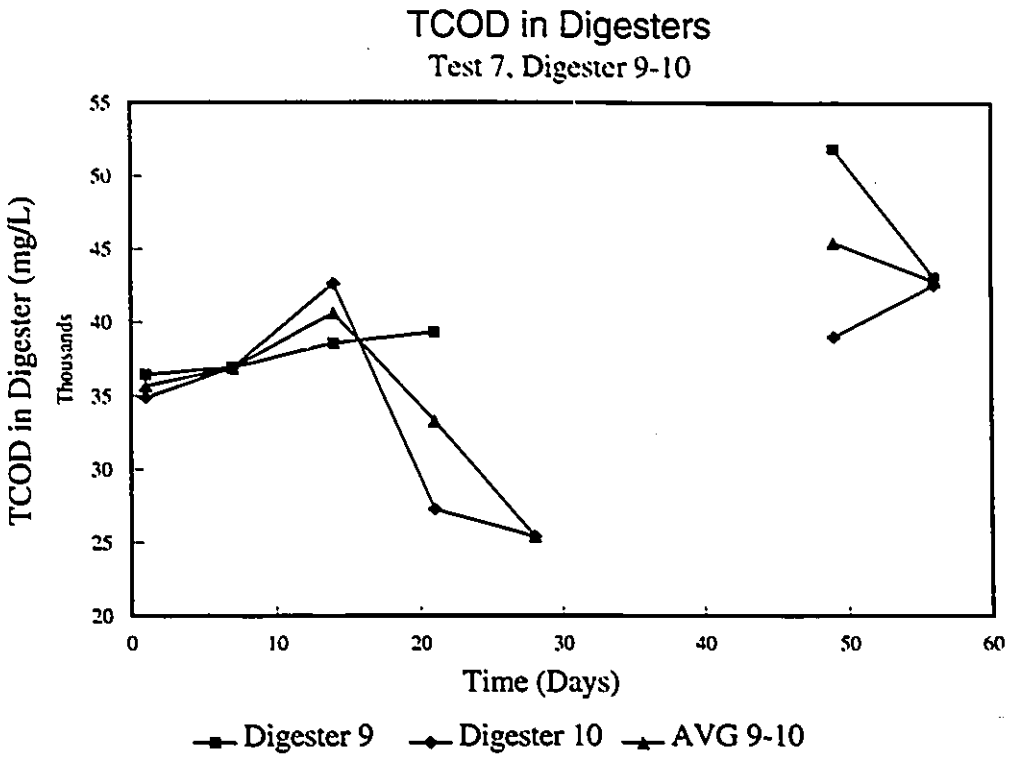

Butyric Acid in Digesters
Test 7, Digester 11-12
Butyric Acid in Digester (mg/L)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12

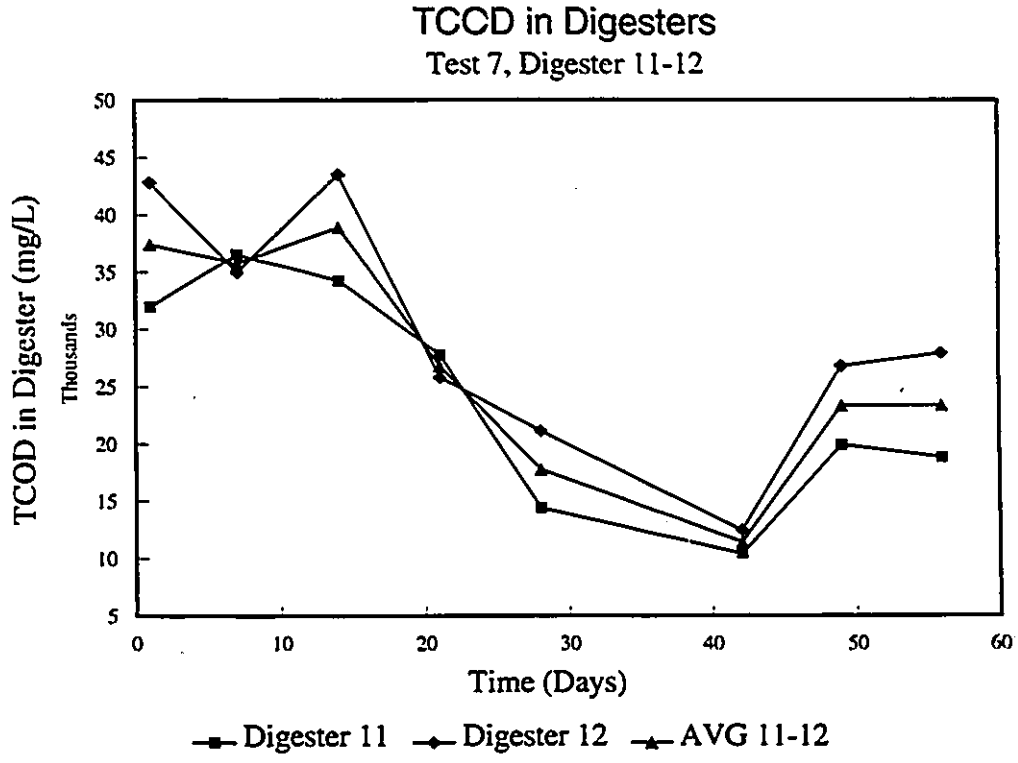

VS in Digesters
Test 7, Digester 9-10
VS in Digester (mg/L)
Thousands
35
30
25
20
15
10
5
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10


VS in Digesters
Test 7, Digester 11-12
VS in Digester (mg/L)
Thousands
35
30
25
20
15
10
5
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12


Soluble COD in Digesters
Test 7, Digester 9-10
SCOD in Digester (mg/L)
5000
4500
4000
3500
3000
2500
2000
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10


Soluble COD in Digesters
Test 7, Digester 11-12
SCOD in Digester (mg/L)
5000
4500
4000
3500
3000
2500
2000
1500
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12


TCOD in Digesters
Test 7, Digester 9-10
TCOD in Digester (mg/L)
Thousands
55
50
45
40
35
30
25
20
0
10
20
30
40
50
60
Time (Days)
Digester 9
Digester 10
AVG 9-10


TCCD in Digesters
Test 7, Digester 11-12
TCOD in Digester (mg/L)
Thousands
50
45
40
35
30
25
20
15
10
5
0
10
20
30
40
50
60
Time (Days)
Digester 11
Digester 12
AVG 11-12