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Civil and Sanitary
Ph.D. degree in Engineering

John A. Eastman
Major professor

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BIOGAS MANAGEMENT BY CONTROLLED FEEDING AND HEATING OF A DAIRY MANURE DIGESTER

By

Sarawoot Chayovan

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
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ABSTRACT

BIOGAS MANAGEMENT BY CONTROLLED FEEDING AND HEATING OF A DAIRY MANURE DIGESTER

By

Sarawoot Chayovan

Gas production dynamics were investigated using laboratory scale digesters fed daily with dairy manure and operated both at constant temperature and with imposed temperature fluctuations of ± 3.3°C about a mean of 35.8°C. Understanding digester dynamics would allow managing gas production to coincide more closely with its utilization, thereby reducing storage requirements. At constant temperature, a 14-liter control digester with a detention time of 19 days, fed with manure diluted to 25% and blended, behaved similarly to two 3-liter digesters fed whole manure at a detention time of 15 days. A second 14-liter digester fed with the diluted manure was operated with three phase relations between the 24 hour temperature cycle and the pulse feeding time. The higher the temperature at the time of feeding, the higher the peak gas production, up to 1.8 times the control. Gradually increasing the temperature after feeding results in sustained high gas production until the most rapidly degradable material is consumed. In all cases digester operation was stable as indicated by pH, alkalinity and total daily gas production. A mathematical model based on three substrate fractions having each first order kinetics and the Arrhenius temperature relationship successfully predicted gas production dynamics as long as hydrolysis remained the rate limiting step and the volatile acid pool did not change rapidly. For whole manure digested at 36.4°C,

the influent contained 19% fast fraction ($K = 1.15\ d^{-1}$), 35% moderate fraction ($K = 0.34\ d^{-1}$), and 46% slow fraction ($K = 0.0085\ d^{-1}$). For diluted and blended manure digested at 35.8°C, the influent contained 35% fast fraction ($K = 2.19\ d^{-1}$), 25% moderate fraction ($K = 0.17\ d^{-1}$), and 41% slow fraction ($K = 0.0075\ d^{-1}$). The temperature coefficient was found to be 1.25 corresponding to an Arrhenius activation energy of 42.5 kcal/deg Kelvin. Results show that gas storage can be reduced as much as 52% using managed heating and feeding for a situation in which gas is productively utilized for only eight hours of the day.

DEDICATED

TO MY PARENTS

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I. INTRODUCTION

This investigation provides an understanding of the fluctuations in rate of gas production as a result of imposing daily pulse feeding and temperature fluctuations on a digester fed with dairy manure. With this information, digester feeding and heating programs can be developed to more closely co-ordinate biogas production with its subsequent utilization, resulting in reduciton of gas storage without wasting gas, thereby improving the economics of the process.

In an ideal situation, all digester conditions such as temperature and feeding remain constant, resulting in constant methane generation rates. Also the uses of this methane would ideally remain constant throughout the day and week. Unfortunately, normal farm practices make such constant biogas usage impractical. Thus, in most cases, a high degree of gas utilization can only be obtained if large gas storage is provided or the production of methane and its utilization coincide. Because of high cost, storage for more than a fraction of one day's average gas production may not be economically justifiable. Gas storage of one day represents approximately one-third to one-half of the system cost for a 100-cow dairy (Heisler, 1981). For larger systems, the gas storage can represent an even greater fraction of the cost.

In order to reduce gas storage requirements it may be desirable to control the rate of gas production by scheduling feeding and heating cycles such that a maximum rate of methane is produced during hours when energy demand on the farm is high. Part of the methane produced (up to 40% in Michigan winters) must be used to maintain the digester operating

temperature and heating the influent manure. Depending on the detention time and amount of insulation, approximately 25 to 50 percent of the heat requirement is used to raise the incoming manure to the operating temperature. If this heating can be provided when the gas is not being heavily used for other productive purposes, reduction of gas storage needs would also result.

For such schemes to work, they must not jeopardize digester operation. Moreover, the effect of such temperature fluctuation and daily pulse feeding on the magnitude and timing of gas production must be known. The specific objectives are:

1. To determine the ability of digesters to acclimate to fluctuating temperatures without loss in total gas production;
2. To determine the amplitude and lag time of the 24-hour gas production cycle for a daily pulse feed digester;
3. To determine the amplitude and lag time of changes in the 24-hour gas production cycle caused by imposing temperature fluctuations on the daily pulse feeding; and
4. To develop a model from the experimental results such that some management strategies can be determined.

II. BIOCHEMICAL AND MICROBIOLOGICAL BACKGROUND

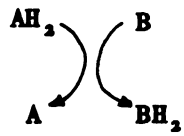
In this study, methane is produced through the anaerobic fermentation of dairy cattle manure. In order to understand the processes occuring in anaerobic digesters and evaluate the experimental results effectively, it is necessary to review some basic knowledge of Biochemistry and Microbiology involved in the anaerobic fermentation of dairy manure. The background material presented in this chapter covers A) microbial energetics, B) metabolic groups involved in anaerobic fermentation, C) properties of dairy cattle manure, and D) the anaerobic fermentation of dairy manure.

A. MICROBIAL ENERGETICS

The diversity of chemical activities found among the microbes is ascribed to the method the microbes have of obtaining energy to drive their metabolisms. In anaerobic fermentation, microbes obtain energy by the oxidation of organic material using electron acceptors other than molecular oxygen. The chemical energy released by the oxidation-reduction reaction is transferred through the electron transport system which is intimately linked with the interconversion of reducing equivalents and ATP. Some basic mechanisms of microbial energetics in anaerobic fermentation will be described in this section. For more detailed views of this subject, a number of text books such as Brock (1979), Gaudy and Guady (1980), Lynch and Poole (1979) should be consulted.

1. Oxidation-Reduction Reactions and Potentials

The breakdown of organic matter is generally oxidative and exergonic. In biological reactions, oxidation involves the removal of hydrogen or electrons, these being passed on to an acceptor, which is thereby reduced. In this way we can refer to the compound being oxidized as a hydrogen and/or electron donor, and the reaction sequence can be represented as:



where AH_2 and B are respectively the hydrogen donor and the hydrogen acceptor.

Such a representation stresses two important features of oxidation reduction (or redox) reactions. Each oxidation is accompanied by a reduction, and secondly, the two are coupled through the transfer of reducing equivelents in the form of hydrogen or electrons.

Each redox couple such as AH_2/A has a finite tendency to either donate its reducing equivalents and be oxidized ($AH_2 \rightarrow A$) or accept them and be reduced ($A \rightarrow AH_2$). When the two couples are combined in a complete redox reaction, the net flow of the reaction is determined by the relative tendency of each couple to donate or accept reducing equivalents. This tendency, or potential, can be measured and quantified by comparison with a standard redox couple. The standard redox couple is that present at the hydrogen electrode where hydrogen gas is in contact with hydrogen ions (protons) in solution in the presence of platinum as

a catalyst. The reaction is

$$H_2 = 2H^+ + 2e^-$$

and the tendency to donate reducing equivalents, in this case as electrons, is measured as the voltage or potential of the electrical current generated when the electrode is coupled in series with another redox couple electrode. At 25°C, 1 atmosphere of hydrogen and pH 7, the potential of the redox couple $H_2/2H^+$ is -420 mV. Table 2-1 presents the standard redox potentials (at pH 7.0) of a number of redox couples of interest in anaerobic sytems. A couple of lower redox potential will always donate reducing equivalents to a couple of higher potential. The couple CO_2/CH_4 has E_o' of -240 mV so that in combination with the redox couple $H_2/2H^+$ the complete redox reaction is given by:

$$4H_2 + CO_2 = CH_4 + 2H_2O$$

with the hydrogen donating electrons and being itself oxidized, while the carbon dioxide accepts the electrons and is therefore reduced. In anaerobic metabolism this CO_2 reduction reaction is mediated by methanogenic bacteria and is called methanogenesis.

TABLE 2-1. Standard Redox Potentials and Standard Free Energy Change of Some Redox Couples of Interest in Anaerobic Systems.

Redox Couple	E_o', mV	$\Delta G^{o\prime}$, Kcal/mol e^-
$2H^+/H_2$	-420	-9.7
$NADP^+/NADPH$	-324	-7.5
$NAD^+/NADH$	-320	-7.4
$ACETATE/CO_2$	-290	-6.7
CO_2/CH_4	-240	-5.5
$SO_4^=/H_2S$	-220	-5.1
NO/NO_2^-	-360	-8.3
NO_2^-/NO_3^-	-430	-9.9

2. Free Energy Change

During the oxidation of a substrate, reducing equivalents are transferred in the direction of increasing redox potential. This transfer is accompanied by the release of energy. The magnitude of standard free energy change is given by the relationship:

$$\Delta G^{\circ\prime} = -nF\Delta E_{\circ}^{\prime} \qquad (2\text{-}1)$$

where $\Delta G^{\circ\prime}$ is the standard free energy change, n is the number of electrons transferred, F is the Faraday constant ($96.649 KJV^{-1}\ mol^{-1}$) and $\Delta E_{\circ}^{\prime}$ is standard redox potential expressed in V. Standard free energy changes are provided in Table 2-1.

Free energy changes are useful for determining if reactions or combinations of reactions are thermodynamically possible. A chemical reaction can proceed only if the free energy change is negative or if it is coupled to another reaction such that the overall reaction has a negative free energy change. The existence of such a negative free energy change does not, however, in itself, mean that the reaction will occur since, in many cases there is an activation energy which must be overcome. One role of enzymes is to mediate a reaction by reducing the activation energy and providing favorable kinetics.

3. Adenosine Triphosphate (ATP)

As in all living organisms, energy transformation in anaerobes is mediated by the ATP system. Generally, the reactions of catabolic pathways are both oxidative and exergonic. The various specific dehydrogenases remove hydrogen from their substrates and donate them to one of a number of possible acceptors. Most often the acceptor is one

of the pyridine nucleotides, NAD^+ or $NADP^+$. The reduced forms of these primary hydrogen acceptors are the carriers by which reducing equivalents are transferred among the various metabolic reactions. NAD(P)H may be reoxidized by two general mechanisms. A coenzyme can donate its reducing equivalents to the reduction of organic substrates. Examples of this include fermentations and the biosynthetic sequences of anabolism. Alternatively, the reducing equivalents can be donated to the next carrier in the respiratory chain with consequent transduction of the redox energy into ATP. This redox energy is captured by the reaction of adenosine diphosphate (ADP) and inorganic phosphate (P_i) to form ATP. The energy conserved in the pyrophosphate bond is used for work when ATP is hydrolyzed either to ADP and P_i or to adenosine monophosphate (AMP) and pyrophosphate (PP_i).

B. METABOLIC GROUPS INVOLVED IN ANAEROBIC FERMENTATION

Effective bioconversion of organic matter to methane is a result of the combined and coordinated metabolic activity of a diverse, yet stable microbial population. This section describes the different metabolic groups and their syntrophic association in the anaerobic fermentation process. A general scheme of methanogenesis which incorporates present knowledge of the microbiology and biochemistry of anaerobic fermentation will be presented.

Until recently, methanogenesis was viewed as a two-stage process consisting of acid-formation and methane-formation (McCarty 1964, Kirsch and Sykes, 1971). In the first stage, the fermentative non-methanogenic bacteria, as a group, hydrolyze organic polymers and ferment the products to organic acids, alcohol, CO_2 and H_2, NH_3 and sulfide. In the

second stage, the end products of the metabolism of acid-forming bacteria in the first stage are converted to CH_4 and CO_2.

No methanogenic bacteria have been found, however, that utilize alcohols other than methanol or organic acids other than acetate and formate (Bryant et al., 1967, 1977). This finding indicates that the two-stage scheme is unsatisfactory. Bryant (1976) proposed a three-stage scheme by the addition of a new hypothetical group, the "H_2-producing acetogenic bacteria". This metabolic group degrades propionate and longer-chain fatty acids, alcohols and other organic acids with the production of acetate and H_2. The "S organism" from Methanobacillus omelianskii, for example, represents this group and is a part of a syntrophic association of two bacterial species. The "S organism" catabolizes ethanol to acetate and H_2. The formation of H_2 and acetate from ethanol is not energetically favorable unless H_2 is used by methanogenic bacteria to reduce CO_2 to CH_4. Therefore efficeint removal of H_2 by the methanogenic bacteria is essential for the non-methanogenic bacteria to catabolyze acids and alcohol for growth.

Figure 2-1 illustrates the relationship that exists between hydrogen partial pressure and free energy available to the hydrogen-producing and hydrogen-consuming groups. At standard conditions (25°C, pH 7 and all reactants and products at unit activity), ethanol, butyrate and propionate degradation are thermodynamically unfavorable (Bryant et al., 1967; McInerney et al., 1979; Boone and Bryant, 1980). In order for energy to be available to the organism oxidizing propionate to acetate and hydrogen, for example, the partial pressure of H_2 cannot exceed about 10^{-4} atmosphere (Thauer et al., 1977).

Zeikus (1980) and Wolfe (1979) added another metabolic group which

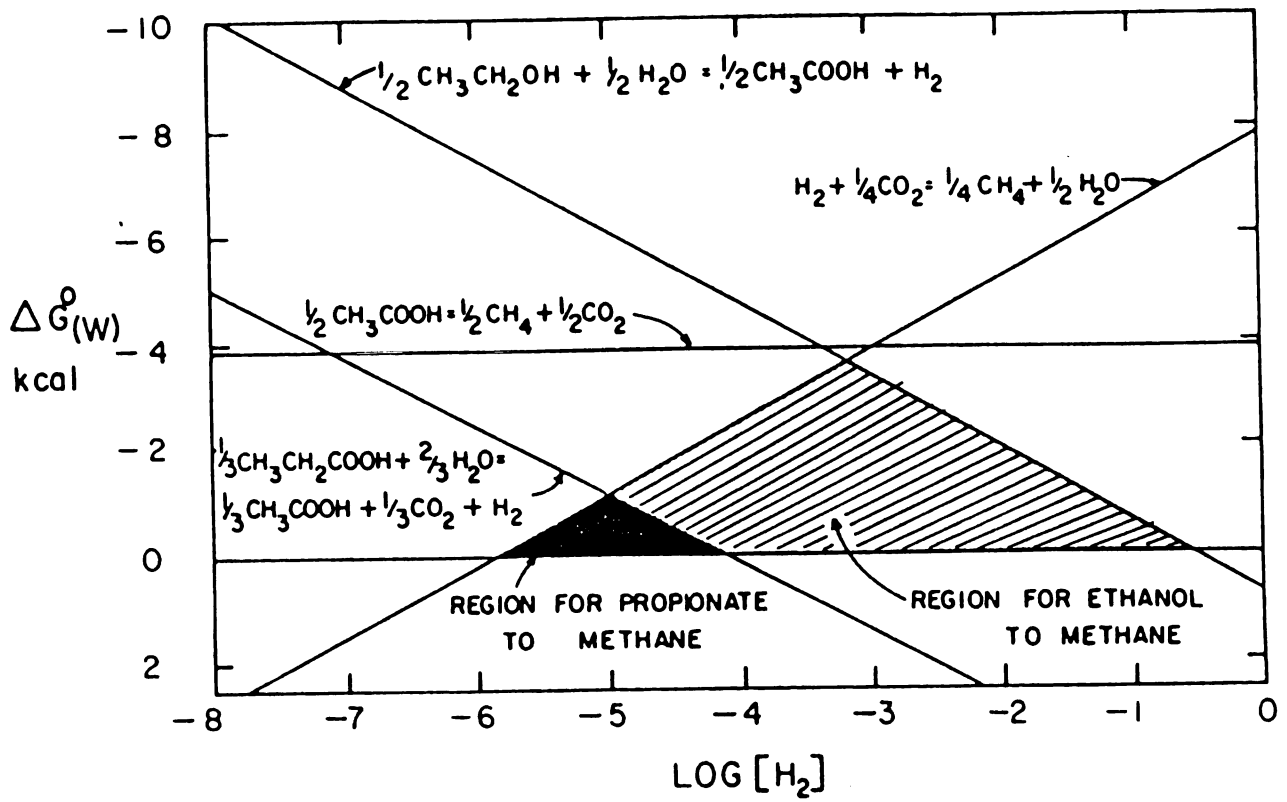


FIGURE 2-1. Effect of Hydrogen Partial Pressure on the Free Energy of Conversion of Ethanol, Propionate, Acetate and Hydrogen during Methane Fermentation. From McCarty (1981).

oxidizes H_2 anaerobically with the reduction of CO_2 to acetate, i.e. H_2-consuming acetogenic bacteria or homoacetogenic bacteria. The utilization of H_2 by this group, however, appears to be negligible compared with utilization by the methanogenic bacteria in the gastrointestinal enviroment (Prins and Lankhorst, 1977), therefore, its presence in the anaerobic digester may be insignificant.

The four metabolic groups described above can be incorporated into a three-stage scheme to describe the present knowledge of the microbiology and biochemistry of anaerobic digestion as shown in Figure 2-2.

C. DAIRY CATTLE MANURE

This section will be a review of the chemical nature of dairy cattle manure as a substrate for anaerobic fermentation. It will include the chemical composition followed by a discussion of biodegradability. Because of its complexity, dairy manure will be discussed in terms of the major classes of compounds present: proteins, carbohydrates, lipids and lignin. In addition, the characteristics of the non-biodegradable fraction as well as the methods used for its determination will be included.

1. Chemical Composition

The amount and composition of manure produced by dairy cattle varies from farm-to-farm and season-to-season, depending on the type of feed and bedding material used. Dairy cow manure contains about 12 to 18 percent total solids, about 80-90 percent of which are volatile solids including urea, fats, proteins, carbohydrates and lignin. A typical chemical composition of dairy cow manure (Hill, 1980) is shown in the first column of Table 2-2. In the second column, a typical composition

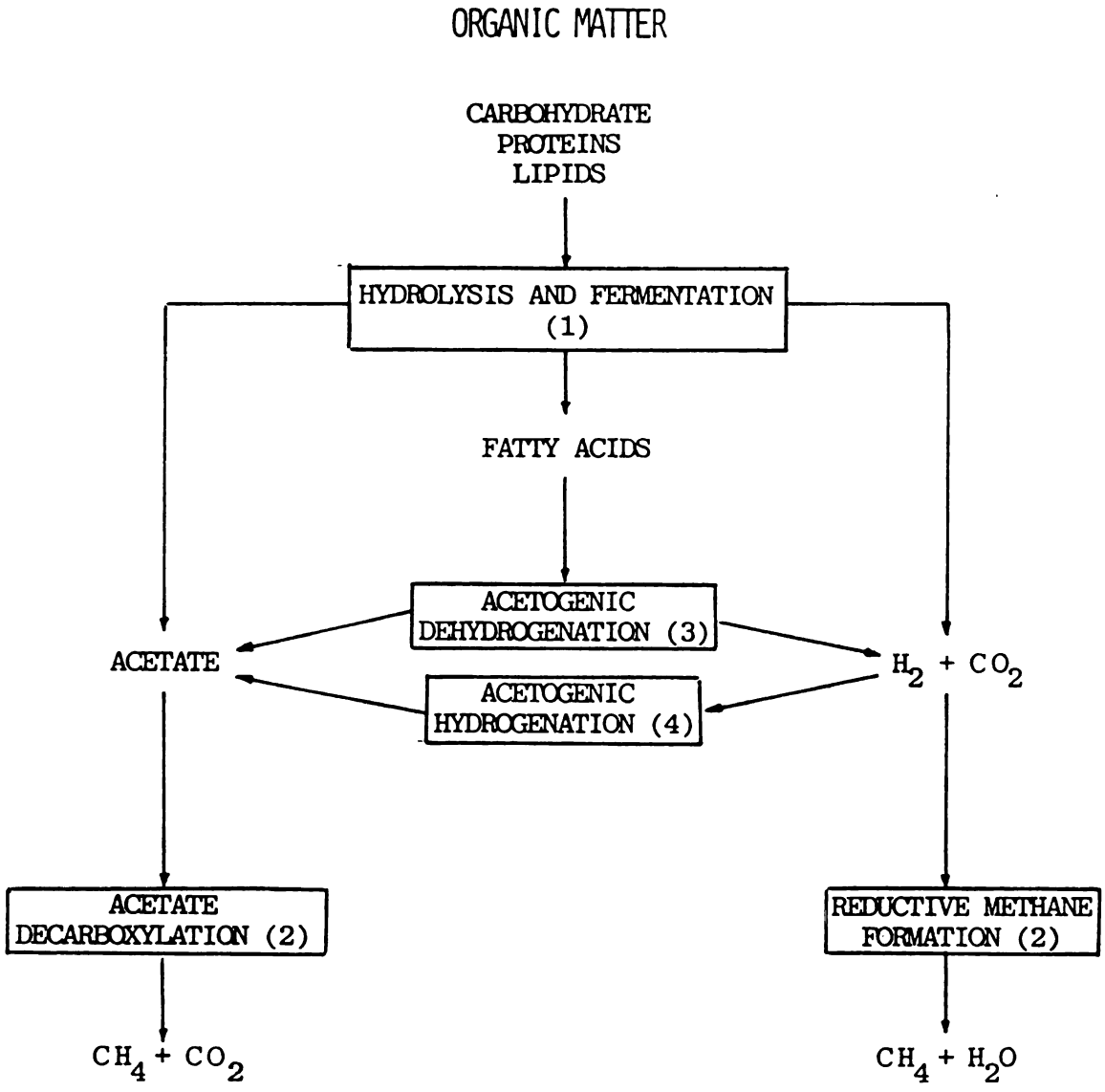


FIGURE 2-2. Summary of Three-Stage Scheme Consisting of Four Metabolic Groups.

TABLE 2-2. Comparison of Dairy Cow Manure and Domestic Primary Sludge.

Component	Dairy Cow Manure* % of VS	Domestic Primary Sludge+ % of VS
Carbohydrates	72	25
Cellulose	23	21
Hemicellulose	49	4
Lignin	16	9
Nitrogenous Materials	12	37
Lipid	-	29
Total	100	100

* adapted from Hill (1980)
+ adapted from Heukelekian and Balmat (1959)

of sewage sludge is presented for comparison. The dairy manure analyzed by Hill was scraped from the concrete floor of a dairy farm at the University of California, Davis. University of California, Davis. The manure was undiluted and contained relatively little urine. The animals were on a diet of approximately 80 percent cubed alfalfa, 15 percent rolled barley and 5 percent milo. The dairy manure contained 72 percent carbohydrates (cellulose and hemicellulose), 16 percent lignin, and 12 percent nitrogenous material. The lipid content was not measured probably because it is generally found in very small amounts in dairy manure.

Generally animals with a higher proportion of roughage feed produce manure containing a larger amount of lignin and other difficult to digest materials. The difference in diet also affects the amount of manure produced daily. For example, dairy cattle fed high roughage rations may excrete 32 to 45 kg of manure daily whereas a beef animal on a high grain diet may produce only 18 to 27 kg daily (Jewell et al., 1976).

Carbohydrates

Dairy cows are fed basically on plant materials. The plant leaves, stems and straw contain mainly starch, cellulose, hemicellulose, pectin and lignin. Starch is a polymer made up of glucose units joined by alpha 1,4 linkages and is often soluable in water. Cellulose, on the other hand, has beta 1,4-linked glucose units and is insoluble in water. While cellulose is the basic structural polysaccharide of plant cells, starch serves as the nutritional reservoir in plants. Some of the alpha 1,4-linked glucose chains are coiled or branched. These linkages tend to give starch granules a more open structure than that formed by the long, straight, beta-linked chains of cellulose molecules which can lie close together in fiber bundles. The open structure of starch is more easily dispersed in water than is the close-packed structure of the cellulose fiber and is more accessible to bacteria and their enzymes even when not completely dissolved.

Hemicellulose includes a variety of polysaccharides which are comprised largely of sugars other than glucose. Pentoses are abundant in hemi-cellulose. Hemicellulose generally has a lower molecular weight than cellulose. Pectins are polymers consisting primarily of the monosaccharide galacturonic acid. Hemicellulose and pectins are found in many plants, often in close association with cellulose molecules in plant fibers.

Lignin

Lignin, a very complex compound whose structure is still not fully determined, can not be degraded by anaerobic bacteria. Although celluloses are degradable they can be associated with lignin complexes which

are not anaerobically biodegraded. This is because the cellulytic enzymes can not penetrate the lignin matrix due to its steric hindrance effect (Van Velsen and Lettinga, 1980).

Because the microbial degradation of cellulose and hemicellulose is relatively slow, much remains undigested in the alimentary tract of the dairy cow. Starch and pectin in the feed, on the other hand are almost completely removed in the digestive tract and little reaches the dairy manure. All the lignin remains in the faeces. The lignin and ligno-cellulose complexes make up a non-biodegradable fraction of the digester feed.

Proteins

Most nitrogenous organic materials in nature are proteins. Other nitrogen-containing compounds include ammonia, urea, purine and pyrimidine. The nitrogenous compounds in dairy manure include proteins from feedstuffs which passed through the digestive tract, intestinal bacteria, gut secretions and sloughed-off intestinal cells in the faeces, and constituents of urine.

The amount and nature of nitrogenous constituents of the dairy manure can change as it is stored. So the composition of a slurry fed to an anerobic digester may not be the same as that of fresh excreta. In particular, bacterial action in collecting troughs and tanks may result in degradation of proteins to amino acids and then to ammonia. Urea is rapidly degraded to ammonia. Ammonia may then be lost by volatilization. The extent of such changes will depend on the time the manure is stored, but some changes can take place in a few hours, especially in warm weather.

Lipids

Fats (lipids) are digested by the animal but some will escape digestion to appear in the faeces. Besides residues from food lipids, faecal wastes will also contain the lipids of the intestinal bacteria, and these can amount to some five to ten percent of the bacterial weight. However, only small amounts of lipids are found in a typical dairy manure.

2. Substrate Biodegradability

In order to evaluate the efficiency of the conversion of organic matter to biogas, it is necessary to know the maximum fraction of organic matter (TVS) that is available for conversion to biogas, i.e. the biodegradability. Pfeffer and Quindry (1978), working with cattle waste under mesophilic conditions, estimated that the biodegradability of the manure ranged between 30% and 48% of the volatile solids added. Jewell et al. (1980) reported that 45% of the volatile solids in dairy cow manure were biodegradable and this fraction was not affected by fermentation temperature. In addition, a mixture of manure and straw bedding had a similar biodegradability.

Lignin has been regarded as the component which causes non-biodegradability. Not only is the lignin itself non-biodegradable but its presence within an organic complex also tends to shield the cellulose and other organic materials from enzymatic hydrolysis (Van Velson and Lettinga, 1980). The digestion study by Robbins et al. (1979) involving dairy manure plus chemically delignified wheat straw, indicated that approximately 44% of the degradable material was shielded by lignin. Several methods of pretreatment, such as thermal and/or chemi-

cal treatment by strong acid or base indicated a considerable improvement of subsequent digestion (Van Velsen and Lettinga, 1980). However, as yet it seems doubtful whether the costs of chemical additions and/or the extra energy input can be compensated by the increase in gas production.

The non-biodegradable or refractory fraction can be determined by a long term batch fermentation method used by Jewell et al. (1980). Samples are withdrawn at various intervals and analyzed for total volatile solids (TVS). The assumption is that as the solids retention time (SRT) approaches infinity, the biodegradable fraction of the manure will be destroyed, leaving only the refractory fraction. The ratio of sample TVS concentration (S_1) to the initial TVS concentration (S_0) is plotted against $1/S_0$(SRT) as shown in Figure 2-3. This will produce a linear relationship with the ordinate intercept being the refractory fraction.

The biodegradable fraction can also be determined by using data from continuous flow digesters operated at several hydraulic retention times. This method was developed by Chen and Hashimoto (1978) who proposed the following model.

$$B = B_0\left[1 - \frac{K}{\theta/\theta_m - 1 + K}\right] \qquad (2\text{-}2)$$

where B = liters of CH_4 at STP produced per gram COD added.

B_0 = liters of CH_4 at STP per gram COD produced at infinite retention time.

θ = hydraulic retention time

θ_m = the minimum or critical hydraulic retention time

K = a kinetic constant

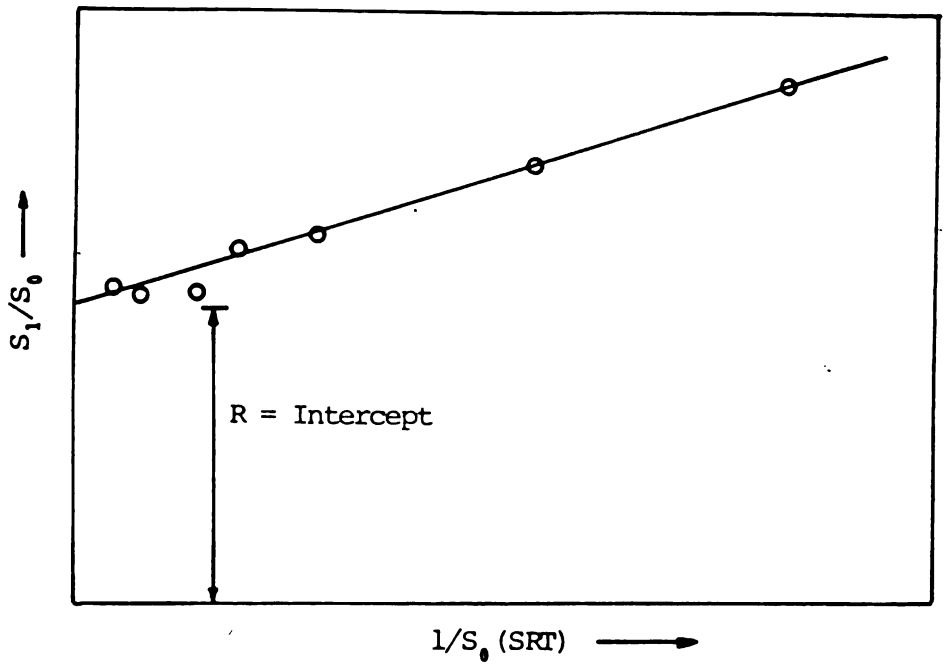


FIGURE 2-3. Graphical Determination of the Refractory Fraction by the Long Term Batch Fermentation Method. From Jewell (1980).

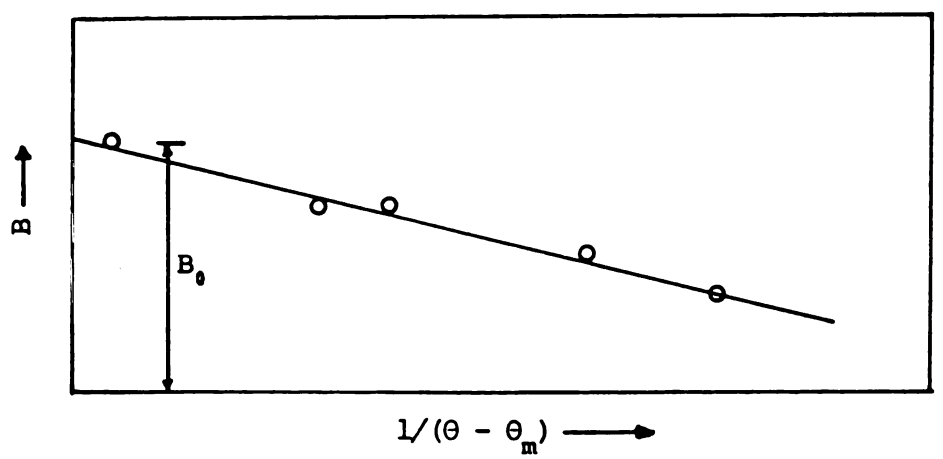


FIGURE 2-4. Graphical Determination of the Biodegradable Fraction from Continuous Feed Anaerobic Digestion. From Chen and Hashimoto (1978).

The plot of B vs $1/\theta$ should be a straight line with $B \rightarrow B_o$ as $\theta \rightarrow \infty$ (Figure 2-4). In this case, the weight equivalent of B_o divided by the total volatile solids of the influent (S_o) is the biodegradable fraction.

D. BIOCHEMISTRY OF DAIRY MANURE DECOMPOSITION

This section will review the biochemical background of the degradation of dairy cattle manure in an anaerobic digester. It will include the hydrolysis and fermentation of carbohydrates, followed by the hydrolysis and fermentation of proteins and lipids. Lastly, methane formation, the conclusion of the whole anaerobic digestion process, will be described. Most of the information presented in this section has been derived from reviews by Hungate (1975), Leng (1973), Latham (1979), Gaudy and Gaudy (1980) and Hobson et al. (1981) unless otherwise referenced.

1. The Hydrolysis and Fermentation of Carbohydrates

Most of the information on the biochemistry and enzymology concerning degradation of plant cells comes from the literature on rumen processes. The mechanisms and pathways of hydrolysis and fermentation of carbohydrates in anaerobic digesters are expected to be similar to those in the rumen.

Carbohydrate Hydrolysis

The carbohydrates in dairy manure are principally cellulose and hemicellulose derived from plant cell walls. These compounds are generally considered to be some of the most difficult polysaccharides for microorganisms to metabolize. The very high molecular weight, particu-

lar physical structure, and insolubility of these carbohydrates contribute to the difficulty of bacterial attack. Since the polysaccharides are too large to be taken into the bacterial cell, they must be degraded by extracellular enzymes. These may be released into the environment or may, in some cases, remain bound to the cell surface. In the latter case, the cell must make contact with the polysaccharide. Since many polysaccharides are insoluble, this is facilitated by growth of the microogrganism on the surface of polysacchraride materials such as on cellulose fibers. Becuse the hydrolysis of polysaccharides occurs extracellularly, the products of hydrolysis may be available to organisms other than the ones that produce the hydrolytic enzyme. Many different kinds of bacteria are present in, on and around plant fibers being degraded. These bacteria have been observed to be cooperative (Gaudy and Gaudy, 1980). Complete degradation of a heteropolysaccharide may require the action of more than one microorganism since a variety of enzymes may be required to break the different bonds and no one organism may be able to elaborate all of the enzymes needed.

Although the digester bacteria will consist of a mixture of different types, capable as a whole of degrading various forms of cellulose, the absolute rate at which the cellulose substrate is attacked still depends on its physical form. The resistance to attack is not only conferred by the orderly and close arrangement of the cellulose and hemicellulose molecular structures, but also by the prescence of substances inherently resistant to microbial enzymes such as waxes, lignin and even inorganic materials such as silica.

The major hydrolysis products of cellulose and hemicellulose are glucose, cellobiose and pentoses. Lack of accumulation of these soluble

carbohydrates in digesters is evidence that the rate of carbohydrate hydrolysis is slower than the fermentation of hydrolysis products (Eastman, 1977).

Carbohydrate Fermentation

As shown in Figure 2-5, soluble sugars released from the hydrolysis of cellulose, hemicellulose, starch, pectin and galactolipids are the major energy substrates for most of the rumen bacteria and they are fermented mainly to volatile fatty acids (VFA's), methane and CO_2.

The Embden-Meyerhof-Parnas (EMP) pathway is the major mode of hexose fermentatin in the rumen; aldolase, a characteristic enzyme of this pathway, is present in the majority of rumen bacteria. The major VFAs in the rumen are acetate, propionate and butyrate. Other VFAs, principally the branched VFAs, arise from amino acid catabolism. Acetate arises through the phosphoroclastic cleavage of pyruvate to acetyl phosphate and either formate or H_2 and CO_2. Formate is rapidly metabolized in the rumen to H_2 and CO_2. Extensive interconversion of acetate and butyrate occurs, with some butyrate arising as a result of organisms using acetate as an external electron acceptor. Propionate is formed by two routes, a major pathway involving formation of oxaloacetate and succinate and a minor pathway involving the formation of acrylate. Hydrogen, CO_2 and formate (indirectly through conversion to H_2) are substrates for methanogenesis.

Various electron-sink products derived from pyruvate are produced by the rumen bacteria in pure culture but do not normally accumulate in mixed cultures either in the rumen or in anaerobic digesters. These products include lactic and succinic acids, hydrogen and ethanol. In

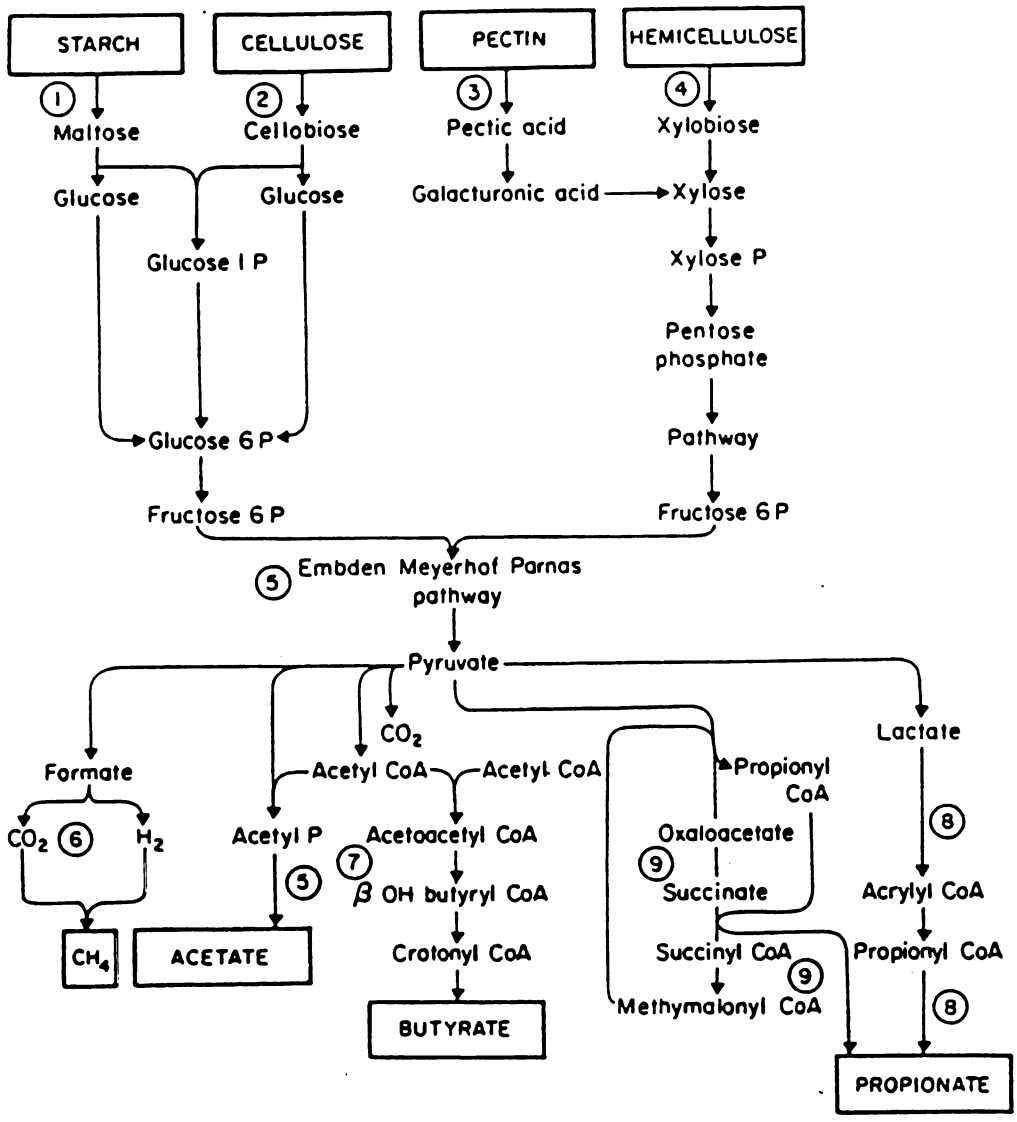


FIGURE 2-5. Pathways Involved in the Rumen Fermentation of the Major Insoluble Carbohydrates Present in Plants. From Latham (1979).

digesters, this phenomenon can be accounted for primarily by two mechanisms. Lactic and succinic acids are fermented by some bacteria to acetate and propionate. For instance $3x10^7$ bacteria fermenting lactic acid to acetic and propionic acid were found per ml of piggery-waste digester sludge (Hobson et al. 1974). Thus any lactic or succinic acid formed by fermentation of sugars would be immediately used up. Secondly the formation of lactic and succinic acids, ethanol, propionic and butyric acids will tend to be prevented by utilization of hydrogen by methanogenic bacteria (Wolin, 1974).

The primary breakdown of sugars in fermentations is to pyruvic acid, with liberation of hydrogen in the form of a hydrogen-carrier complex. This hydrogen can be released if the partial preserve is low enough or it could be used to reduce pyruvic acid to propionic acid. Pyruvic acid can also be reduced to ethanol by a different pathway:

$$CH_3COCOOH + 2H = CH_3CH_2OH + CO_2$$

or to lactic acid:

$$CH_3COCOOH + 2H = CH_3CHOHCOO^- + H^+$$

Pyruvic acid can also be converted to butyric acid (via acetic acid derivatives):

$$CH_3COCOOH = CH_3(CH_2)COOH + 2CO_2$$

or converted to succinic acid (via propionic acid):

$$CH_3COCOOH + CO_2 + 2(2H) = CH_2CH_2(COO)_2H_2 + H_2O$$

The production of acetic acid from pyruvic acid is:

$$CH_3COCOOH + H_2O = CH_3COOH + H_2 + CO_2$$

The hydrogen can then be used by the methanogenic bacteria to form methane and water:

$$4H_2 + CO_2 = CH_4 + 2H_2O$$

If the methanogenic bacteria are growing in the same culture with sugar-fermenting bacteria, the removal of hydrogen will induce the bacteria to form more hydrogen (Wolin, 1974). Thus instead of a mixture of acetic and propionic acids:

$$C_6H_{12}O_6 = CH_3COOH + CH_3CH_2COOH + CO_2 + H_2$$

acetic acid only would be produced:

$$C_6H_{12}O_6 + 2H_2O = 2CH_3COOH + 2CO_2 + 4H_2$$

The hydrogen formed in the initial split of glucose to pyruvic acid would be released as hydrogen gas and more hydrogen would be released in the formation of acetic acid. The H_2 would then be used to reduce CO_2 to form methane.

In a similar way the production of ethanol, lactic acid and the other reactions shown above, would be displaced in favor of acetic acid and hydrogen production.

The equations above show a strong tendency for glucose breakdown to result in production of acetic acid, hydrogen and carbon dioxide. Although in the mixed bacterial population of a digester, the fermentations would not be completely biased towards acetic acid and hydrogen,

experimental laboratory cultures with mixtures of methanogenic and acetogenic bacteria do show that this bias towards acetic acid production is strong in digesters (Iannott et al., 1973; Chung, 1972; Latham and Wolin, 1977).

2. Hydrolysis and Fermentation of Proteins

The anaerobic decomposition of proteins in nature and in anaerobic digesters is primarily the work of species of Clostridium which are active producers of proteolytic enzymes. Hydrolysis of proteins yields alpha-amino acids. The resulting amino acids can be fermented in two ways (Barker, 1961). Some, but not all, amino acids are fermented individually by pathways specific for each compound. The products of amino acid fermentation are generally ammonia, carbon dioxide, hydrogen, acetic acid, and butyric acid. Propionic and other low molecular weight acids and ethonal may also be formed depending on the amino acid fermented. Few of these pathways have been studied in detail (Barker, 1961; Gaudy and Gaudy 1980).

The second mechanism of amino acid degradation used by many species of Clostridium is the Stickland reaction. Pairs of amino acids are fermented with one being oxidized and the other reduced. This method of fermentation allows amino acids that can not be fermented individually to be used as an energy source (Barker, 1961). Table 2-3 presents a list of amino acids that are fermented by one or more species of Clostridium.

TABLE 2-3. Fermentation of Amino Acids by One or More Species of Clostridium.

Amino Acid	Fermented Singly	Stickland Reaction	
		Donor	Acceptor
Alanine	+	+	
Arginine	+		+
Aspartic Acid	+		+
Cysteine	+		+
Glutamic Acid	+		
Glycine			+
Histidine	+	+	
Hydroxyproline			+
Isoleucine		+	
Leucine	+	+	
Lysine	+		
Methionine	+		+
Phenylalanine	+	+	
Proline			+
Serine	+	+	
Threonine	+		
Tryptophan	+	+	+
Tyrosine	+	+	+
Valine		+	

Data from the chapter by Barker in Gunsalus and Stanier (1961), presented by Gaudy (1980).

3. Hydrolysis and Fermentation of Lipids

The primary products of lipid hydrolysis are long-chain fatty acids. The principal pathway for long-chain fatty acid degradation in anaerobic digestion has been demonstrated to be beta-oxidation (Jeris and McCarty, 1965). The long-chain fatty acids can be saturated or unsaturated. In the digester the unsaturated acids are hydrogenated by the bacteria to the saturated acids (Heukelekian and Mueller, 1958). The principal pathway for long-chain fatty acid degradation in anaerobic digestion has been demonstrated to be beta-oxidation (Jeris and McCarty, 1965). Beta oxidation is a pathway in which two carbon atoms at a time are split from the acid chain to form acetic acid and a shorter

long-chain acid. This is the repeated reaction :

$$CH_3\text{-}CH_2\ CH_2\text{-}CH_2\text{-}CH_2COOH + 2H_2O = CH_3\text{-}CH_2\ CH_2\text{-}COOH + CH_3COOH + 4H$$

This reaction results in the production of hydrogen. The reaction to the right is thermodynamically unfavorable unless hydrogen is removed to a low partial pressure by hydrogen-utilizing methanogens (McInerney et al., 1979).

Beta-oxidation of odd carbon fatty acids results in the production of one molecule of propionate from the last three carbons. Propionate is oxidized to acetate accompanied by the reduction of carbon dioxide to methane (Doelle, 1975).

4. Methane Formation

The main substrates for methanogenesis are acetic acid and hydrogen plus carbon dioxide. About 70 percent of the methane produced from sewage sludge came from the methyl group of acetate. Reduction of CO_2 by H_2 accounts for the rest of the methane production (Kugelman and McCarty, 1965; Smith and Mah, 1966). Methane production by decarboxylation of acetate is

$$CH_3COO^- + H_2O = CH_4 + HCO_3^-$$
$$\Delta G_0 = -6.74 \text{ KCal/mole}$$

and by CO_2 reduction:

$$CO_2(aq) + 4H_2 = CH_4 + H_2O$$
$$\Delta G_0 = -33.23 \text{ KCal/mole}$$

It should be noted that carbon dioxide reduction by hydrogen is thermodynamically very favorable. This explains why the hydrogen concentration in anaerobic digesters is extremely low. Well-balanced digesters have a partial pressure of hydrogen between 10^{-4} and 10^{-6} atm. (McCarty, 1981). On the other hand, the decarboxylation of acetate does not release much energy. Because of the limited energy generated from acetate catabolism, it is doubtful that active transport is involved in the passage of acetate into the cell. Thus, the slow growth rate of acetate utilizing methanogens may be limited by substrate uptake processes and require high external acetate concentrations to support significant growth on this substrate (Zeikus, 1980). Safford et al. (1980) demonstrated that methane production increased with incrasing acetate concentrations up to about 2000-3000 mg/1. At initial concentrations of 500, 1000, 2000 and 4000 mg/1 obtained by spike injection, the acetate removal rates were 69, 128, 143, and 40 mg/1/hr respectively. Laurence and McCarty (1969) also reported that acetate has no signifiant influence on its own removal rate at a concentration of 4000 mg/1. The effect of the concentrations of acetate and other VFAs will be reviewed in more detail when the effect of pulse feeding is discussed in the next chapter.

III. LITERATURE REVIEW ON PULSE FEEDING AND TEMPERATURE VARIATION EFFECTS

This chapter is divided into three sections. The first section reviews the effect of pulse feeding on biogas production. The second section reviews the effect of temperature variations. The last section discusses some potential instabilities which might occur due to a combination of pulse feeding and an imposed temperature variation.

A. EFFECT OF PULSE FEEDING

Only a few studies have been found which relate to pulse feeding. Jewell et al. (1980) fed dairy manure, at intervals of 1, 4, and 7 days to a digester. Data on gas production, percent methane and volatile acid concentration were collected on a daily basis. In each case, after acclimation, a stable pattern developed with some VA fluctuation (but no significant pH change) and high gas production during the first day, declining until the next feeding.

Mountfort and Asher (1978) demonstrated metabolic variations during the 24 hours following daily batch feeding of a laboratory digester with bovine waste. They found that the percentage of methane accounted for by acetate and CO_2 varied with time. During the first few hours after the digester was fed, up to 90 percent of the CH_4 produced came from acetate. This percentage declined to 70 percent at the end of the 24 hour feeding cycle. Reduction of CO_2 by H_2 accounted for the balance of CH_4 production. In addition, they found that after a two-hour lag following feeding, cumulative methane production increased linearly for 18 hours at which time the rate decreased slightly (Figure 3-1). Acetate

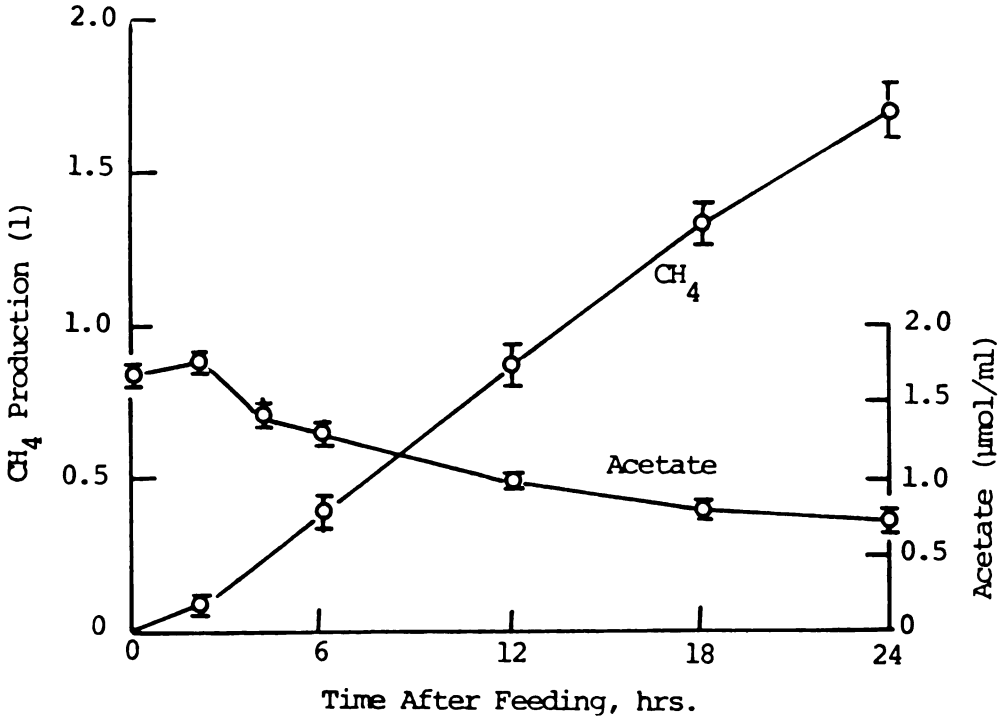


FIGURE 3-1. Methane Production and Pool Size of Acetate versus Time after Feeding Large Digester. From Mountford and Asher (1978).

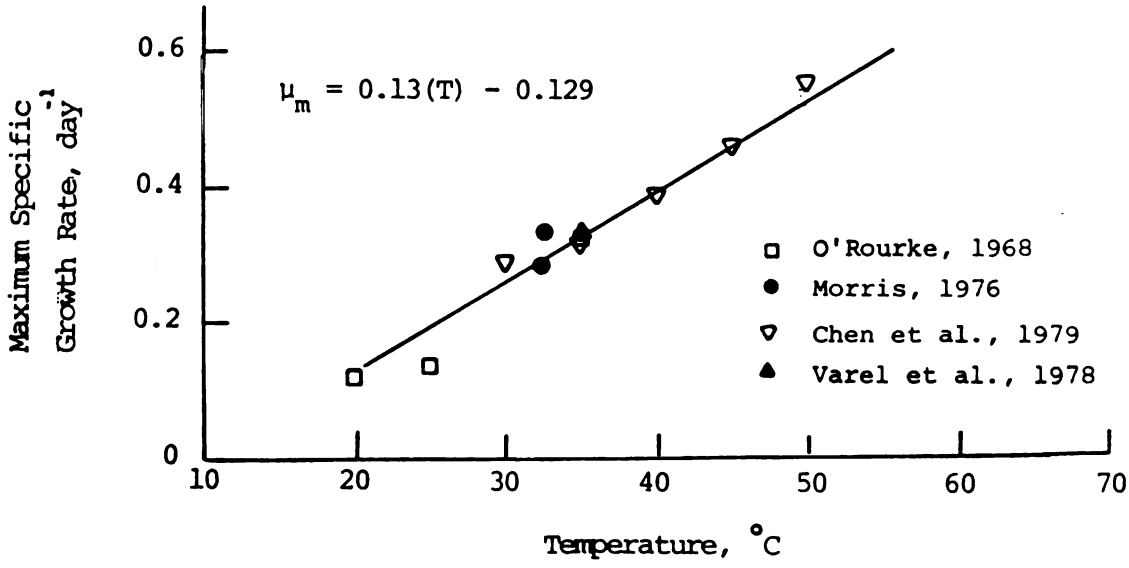


FIGURE 3-2. Effect of Temperature on μm. From Hashimoto et al. (1979).

levels increased from 1.68 to 1.75 μmol/ml between 0 to 2 hours after feeding and then gradually decreased to 0.75 μmol/ml at 24 hours.

Hawkes and Young (1980), working with poultry litter, presented data on changes in gas production rate over 24 hours following daily batch feeding. The data showed an approximate daily cycle of fluctuations in the rate of gas production. Because of starvation over the weekend and irregularity of stirring, steady state was not obtained.

B. EFFECT OF TEMPERATURE VARIATION

In most studies of the effect of temperature on anaerobic digestion, the temperature has been held constant at various levels. All studies agree that the rate of methane production from animal manure increases with increased temperature (Varel et al., 1980; Van Velsen, 1979; Jewell et al., 1980; Chen et al., 1980; O'Rourke, 1968). Hashimoto et al. (1979) reported that the maximum specific growth rate (μ_m) of fermentation increased linearly with increasing temperature. as shown in Figure 3-2.

A few studies have looked at short term temperature variations. Garber (1954) concluded that once established, a thermophillic sewage sludge digester resisted a temperature decrease of 9°F in 48 hours with no adverse effect. Speece and Kern (1970) imposed sharp temperature changes of 15°C and 25°C for durations of 15 minutes to two hours on digesters being fed acetate. They found that below 20°C, methane production nearly ceased but recovered immediately after the temperature was returned to normal. Because of the acetate feeding, however no conclusions can be reached concerning the balance between acid production and its removal. Van Velsen and Lettinga (1980), studying the influence

of temperature changes on the digestion of piggery manure containing 6 percent TS at 15 days HRT, demonstrated that when temperature changes between 20°C and 40°C were applied during five successive days, the digester was somewhat disturbed as indicated by a temporary increase in the VFA concentration. The digester, however, recovered completely within a 16 day period of normal constant temperature operation.

The literature reviewed above indicates that anaerobic digesters can tolerate some degree of temperature fluctuation. The temperature fluctuations imposed by Van Velsen and Lettinga (1980) are much more extreme than what one would expect in a managed farm scale digester. Using data provided by Jewell et al. (1980), the temperature of an insulated full scale digester might drop about 3.5°C in 24 hours during winter without feeding or 7°C with feeding cold manure. No previous work has been found which deals with small repeated temperature fluctuations of the magnitude investigated here.

C. PROCESS STABILITY

Increasing biogas utilization by imposing managed pulse feeding and managed temperature fluctuations requires some understanding of the nature of process instability and the biochemistry of fermentation of individual components in the substrate.

1. Process Instability

Process instability due to substrate overload or temperature shock is usually indicated by a rapid increase in the concentration of volatile fatty acids with a corresponding decrease in methane production. Varel et al. (1980) have shown that when a digester is stressed, propionate is the first component to increase. When further stressed,

acetate also increases. In severely stressed digesters butyrate, in particular, accumulates to high levels and, to a lesser degree, isobutyrate, isovalerate, and valerate. Kugelman and Chin (1971) reported that propionic acid was toxic to methanogenic bacteria at concentrations exceeding 4,000 mg/l. Stafford et al. (1980) suggested that under normal conditions, the propionic acid acted as a metabolic side shunt to allow acetic acid to be used for methane formation. Because of the slow growth of methanogens, the presence of propionate was more likely to slow the breakdown of complex polymers such as proteins, lipids and carbohydrates, but when it reached a high concentration, it probably began to exert inhibitory effects on methane fermentation itself.

The three environmental parameters of pH, alkalinity, and volatile acid concentration are all interrelated. Optimum methane production will result if the pH is between 6.6 and 7.6 (Kirsch and Sikes, 1971). Alkalinity in a digester provides the buffering capacity so that a small volatile acid accumulation will not allow the pH to drop substantially. If the alkalinity is insufficient, volatile acid accumulation may cause the pH to drop, indicating that the system is not in equilibrium and that methane forming bacteria in the system may be inhibited. Thus, if the volatile acid concentration continues to increase, the reactor will fail and gas production will cease.

2. Biochemistry

For stable operation of an anaerobic digester, acid formation and its removal must be balanced. Lipids undergo only minor hydrolysis in the acid phase, releasing constituent molecules such as glycerol and long chain fatty acids. The glycerol is fermented in the acid phase,

and long chain fatty acids are hydrogenated but not degraded further if methane production is inhibited (Heukelekian and Mueller, 1958; O'Rourke, 1968; Eastman, 1977). Although many proteins are rapidly hydrolyzed and fermented (Eastman and Ferguson, 1981), the resultant volatile acids are produced as their ammonium salts preventing a major pH drop. Because the hydrolysis of cellulose is slow, volatile acids from this source do not accumulate in large amounts. Thus, only readily degradable carbohydrates such as starch and soluble sugars are rapidly fermented in large quantities to free acids, posing a potential danger of digester upsets.

Because cellulose and hemicellulose are the major components in dairy manure, and readily degradable carbohydrates are relatively low, fermentation of manure has been shown to be quite stable with respect to pH. Jewell et al. (1980) reported that replacing up to one-fourth of the digester contents in one slug dose did not cause the pH to change by more than half a unit, and in all cases the pH stayed above 7.5.

IV. MATERIALS AND METHODS

In this chapter, the laboratory apparatus, experimental program, and analytical techniques are described.

A. DESCRIPTION OF THE APPARATUS

Two different completely mixed, manually fed, anaerobic digester systems were employed in this investigation. One system consisted of two 3-liter digesters placed in a constant temperature water bath. The digesters were designed to handle whole manure with a large tube for the feed and withdrawal port. This system was operated primarily to study the dynamic rate of gas production as a result of pulse feeding alone. The other system consisted of two 14-liter digesters. Each unit had a built-in cooling and heating system for temperature control. These digesters were used to investigate the combined effects of pulse feeding and cyclic temperature variation on the dynamic rate of gas production. The temperature control of one unit was modified to produce a daily temperature cycle which followed a ramp function. The other unit was operated at constant temperature serving as a control unit.

1. The 3-Liter Digester System

The system consisted of two identical anaerobic digesters shown schematically in Figure 4-1. Each digester consisted of a six inch diameter acrylic plastic cylinder having a liquid volume of 2.25 liters and a gas space of 0.75 liter. Complete mixing was accomplished mechanically with two flat paddles. The stirring shaft passed through an O-ring seal to prevent leakage of gas. The stirrers for both digesters

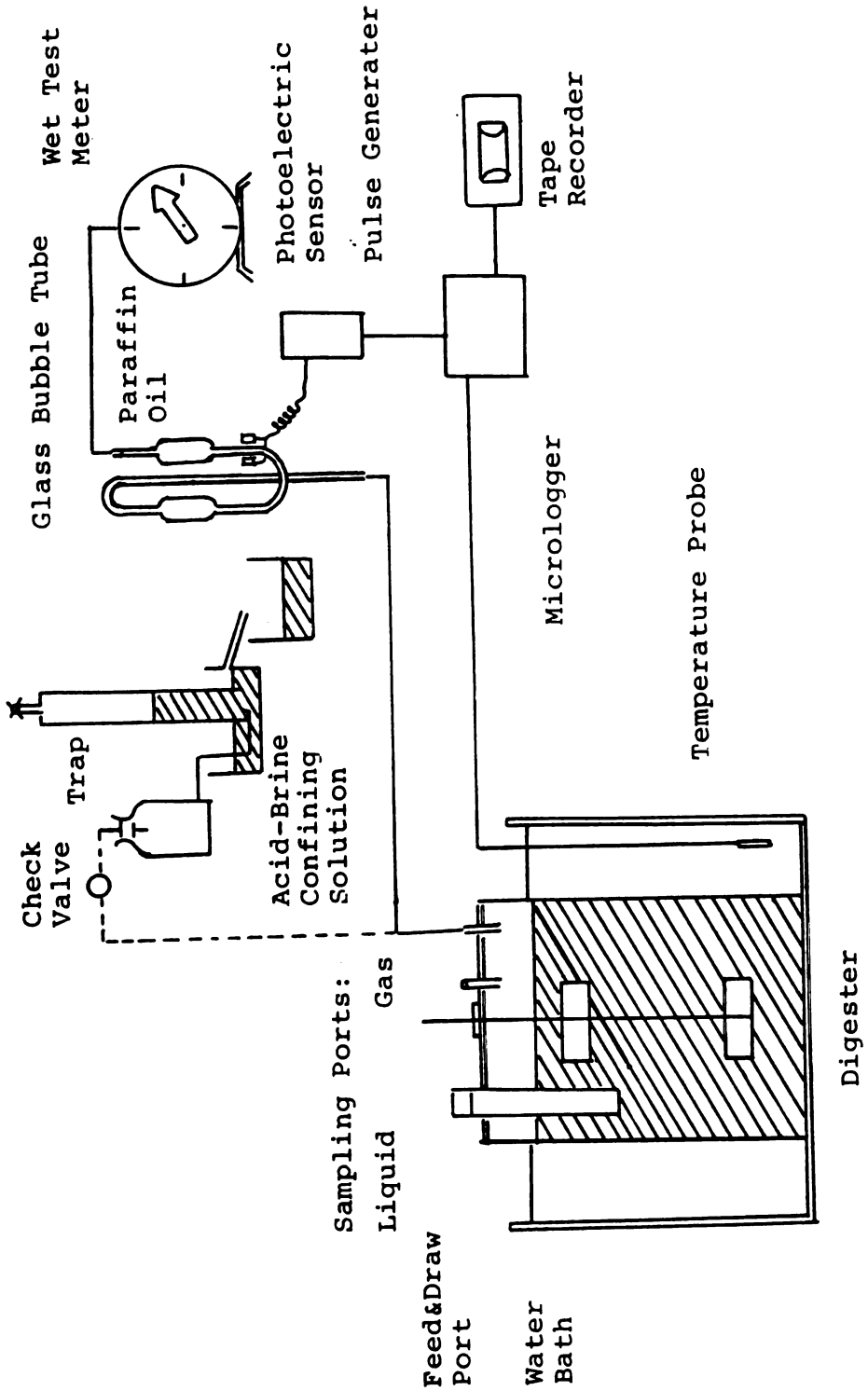


FIGURE 4-1. Schematic of a 3-Liter Digester System.

were driven with belts from a single variable speed motor (Model 565 with Model 903 controller, Bodine Electic Co., Chicago, Ill.)

Both digesters were contained in a circulating water bath for temperature control. The water depth in the bath was maintained at slightly above the liquid level in the digesters. The temperature of water in the bath was maintained at 36.40 ± 0.5°C.

Each digester was fed manually. A 1-1/8 inch diameter plastic tube projecting 2 inches below the liquid level was permanently inserted through the digeter lid. Through this a 30 c.c. syringe, with an enlarged opening , was inserted to withdraw a measured quantity of the digester contents. An identical amount of manure was then fed to reestablish the liquid level. When liquid samples were taken during the day, the amount withdrawn before feeding was reduced.

Gas samples were withdrawn directly from the digester head space by inserting a gas tight syringe through a serum stopper which capped a tube through the lid of the digester.

The Gas Measuring System

The gas measuring system consisted of bubble tubes, photoelectric sensors, pulse generator, a micrologger, a tape recorder and wet test meters.

A bubble tube was made of 7/8 in. I.D. glass tube, bent to form a U-shape with a radius of curvature of 1.5 inches. Paraffin oil was placed in the U-tube with a differential head of 1.5 to 2.0 inches. The dimensions of the U-tube were developed as a result of several trials to match the range of predicted gas production rates. Two 1-inch diameter bulbs were formed on either side of the U-tube so that bubbles could

rise and break in either leg depending on the direction of gas flow. The direction of gas flow may change temporarily during feeding or when samples are taken.

As the gas was produced the pressure in the digester head space increased, resulting in the lowering of the oil level on one leg of the U-tube. When the oil level reached the bottom of the U-tube, bubbles were released one by one. As each bubble rose it passed between a light emitting diode and a photocell connected to a pulse generator which sent a signal to a micrologger (Model CR21 Campbell Scientific Inc.). The micrologger was programmed to count pulses for every twenty minute interval. The data were stored in a buffer holding 30 to 48 data points. They were then transferred automatically to a cassette tape.

A wet test meter was connected to the outlet end of the bubble tube for calibration and determination of total daily gas production. During calibration the meter was read every hour. The readings were then correlated with the bubble count. Calibration curves were constructed and used to convert the bubble count into a gas production rate in ml/hr. The temperature of the water bath was also monitored continuously by the micrologger using a themister probe (Model 101, Campbell Scientific Co.).

Gas displacement of acid-brine solution was used as a backup system for gas measurement. When the backup was used, the pressure in the digester gas space was maintained at about 1.5 to 2 inches of water pressure above atmospheric. This was achieved by submerging the outlet of the gas line to the collection cylinder below the free surface of the acid brine solution.

2. The 14-Liter Digester System

The system consisted of two 14-liter anaerobic digesters (Bench Top Fermentor Model MF-102, New Brunswick Scientific Co., Inc.) shown schematically in Figure 4-2. Each digester jar was specially constructed to accommodate larger feed, sampling and overflow ports for handling the manure. The jar was made of 8 in. diameter PVC pipe and cap. A number 14 rubber stopper was inserted in the side wall. A 7/8 in. gravity overflow tube and a 3/4 in. feed and sampling tube were inserted through this stopper. The overflow tube was extended with flexible plastic tubing which was submerged 6 in. below the fluid level in a bottle to prevent gas escaping from the digester head space.

Temperature control was maintained using a water circulation system consisting of a pump, a cold water inlet line with an enlarged section for a water reservior and housing an inline immersion heater. A thermister controller connected to a solinoid valve on the cold water line and to the immersion heater controlled the temperature of water passing through a baffled heat exchanger in the digester jar (Figure 4-2).

The temperature controller of one digester was modified to produce a daily temperature cycle as a ramp function. The other digester was operated at constant temperature as a control unit. The gas measuring system was basically the same as described earlier for the 3-liter digesters.

B. EXPERIMENTAL PROCEDURES

This section describes the experimental procedures used for this study. The section will start with the collection, preparation and chemical characteristics of the substrate followed by details of the

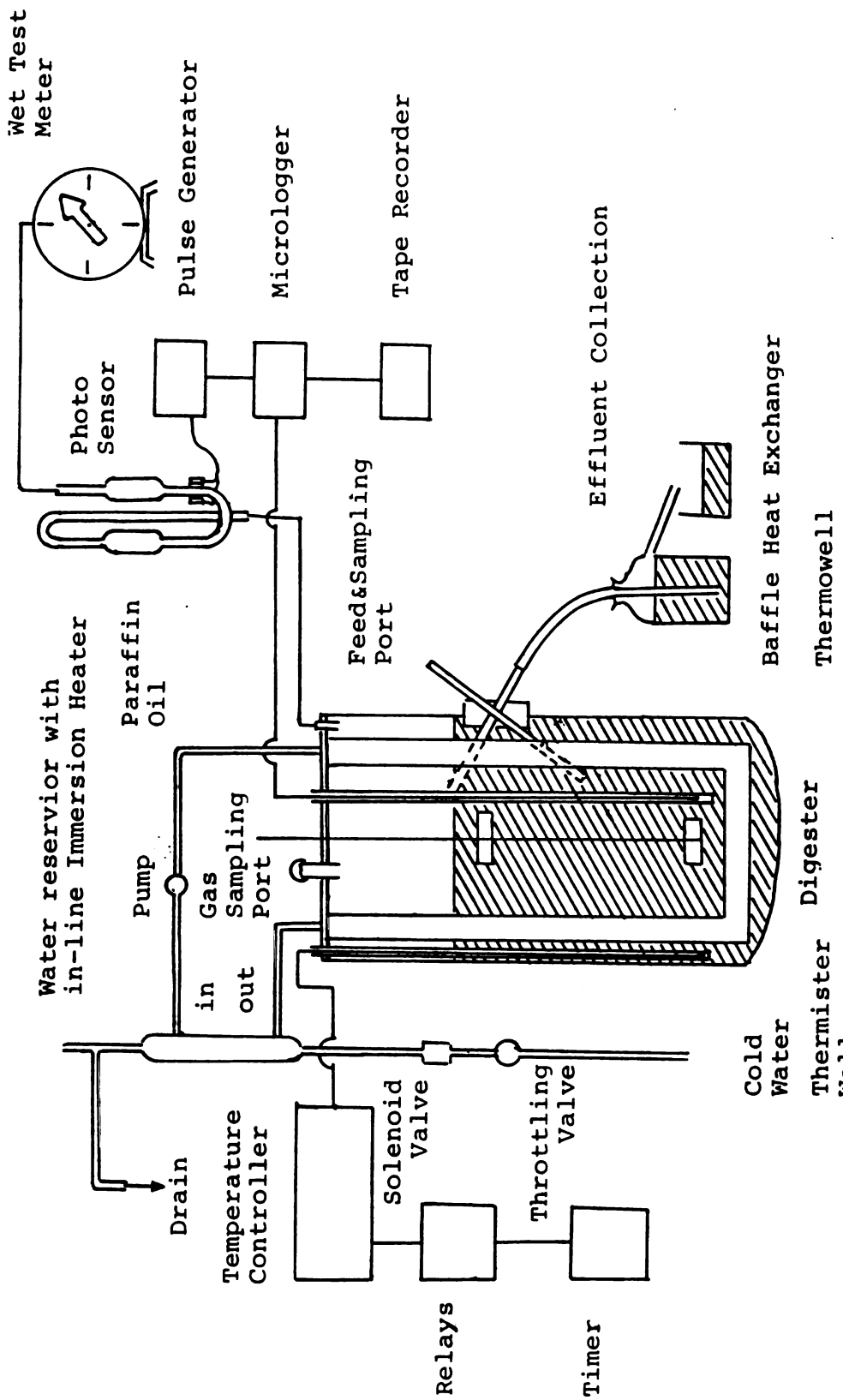


FIGURE 4-2. Schematic of a 14-Liter Digester System.

experimental program.

1. Substrate

The dairy manure used as the substrate was obtained from a dairy farm near Michigan State University. This farm, owned by Mr. Ben Arend, has about one hundred milking cows and was considered a typical Michigan dairy farm. The animals were on a diet of approximately 70 percent corn silage, 20 percent mixed grain (corn and soy bean 50:50) and 10 percent hay. Small amounts of vitamins, salts and trace minerals were added. No antibiotics were incorporated in the animal feed. Straw was used as bedding in the barn. The manure was scraped from the barn floor with a front end loader.

A one-inch mesh wire net was used to screen the manure to remove straw and other large particles that might have caused clogging problems in the laboratory digester operation. The screened manure was placed in one-quart plastic bags each containing about 400 ml. These bags were wrapped with rubber bands and stored in a freezer within twelve hours. When needed, the manure was removed from the freezer and thawed.

Throughout the investigation, no extra organic or inorganic nutrients were added to the digesters. Once established, the pH of all digesters remained constant within one half of a pH unit without any acid/base addition.

Substrate for the 3-Liter Digesters

Full strength manure was fed to the 3-liter digesters for four months. A single 15 gallon batch of manure was collected, dispensed into bags and stored in the freezer so that the influent would be constant over the entire period of this phase of experimentation. Each

day, one bag of frozen manure was thawed at room temperature for about 1 to 1.5 hour. An appropriate volume of thawed manure was then fed to each digester.

The chemical characteristics of the influent manure for the 3-liter digesters are shown in Table 4-1. The COD and volatile fatty acid samples were taken only during the stable period (after the digesters were operated for about two detention times). The samples for other parameters were taken over the whole period of operation. The total volatile solids were relatively constant over the entire period of this experiment with a standard deviation of 2.5 percent.

Substrate for the 14-Liter Digesters

Another single batch of 20 gallons dairy manure was collected and frozen for feeding to the 14-liter digesters. Prior to feeding, thawed manure was diluted to 25 percent by adding three volumes of tap water to one volume of whole manure. The mixture was blended in a one gallon high-speed blender (Waring) for one minute. An appropriate volume was then fed to each digester. The chemical characteristics of the influent for the 14-liter digesters are also listed in Table 4-1.

2. Experimental Program

The experimental program was designed primarily to evaluate the dynamic rate of gas production as a result of daily pulse feeding at a constant temperature alone and combined with an imposed temperature fluctuation. Two sets of different size, completely mixed, manually fed digesters as described in the last section were operated over a period of one year. Because of the pulse feeding, the substrate concentration in the digesters can never be constant so true steady state cannot be

TABLE 4-1. Chemical Characteristics of the Influent Manure.

Parameters	3-liter Digesters Ave.	Std. Dev.	N	14-liter digesters Ave.	Std. Dev.	N
pH	7.40	0.07	10	8.09	0.09	12
Total volatile solids, %	13.78	0.35	28	3.44	0.17	28
Chemical oxygen demand, mg/l	169,996	11,508	7	38,883	2,220	19
Total alkalinity, mg/l as $CaCO_3$	10,940	341	4	2,935	247	4
Bicarbonate alk., mg/l as $CaCO_3$	737	--	--	393	--	--
Volatile fatty acids, mg/l as COD:						
acetic acid	8,490	1,378	3	2,135	298	6
propionic acid	4,223	396	3	792	65	6
iso-butyric acid	173	81	3	130	184	6
butyric acid	3,287	206	3	407	117	6
iso-valeric acid	270	17	3	97	149	6
valeric acid	210	36	3	110	114	6
TOTAL	16,653	2,114	--	3,671	927	--

achieved. The measured daily gas production, however, was found to be relatively constant after an acclimation period of two or three detention times. From here on, this period of constant gas production will be referred to as a stable period. The demonstration of such a stable period for each experiment will be presented in the results. The experimental program is summarized in Table 4-2. It consists of two major groups of experiments, descriptions of which follow.

Experimental Group One was designed to evaluate the effect of daily pulse feeding alone. Two 3-liter daily-pulse-fed digesters were operated identically for duplication purposes. The digesters were fed with full strength manure at a constant temperature of 36.40 ± 0.5°C with a hydraulic retention time of 15 days. For the digester start up, active digester effluent from Baum's Dairy Farm (Springport, Michigan), was used for seeding. The effluent were collected in a five-gallon carboy and 2.5 liters was placed into each starting digester on the same day. Initially the digesters were fed 50 ml a day. This is gradually increased to the full amount of 150 ml a day.

The digesters were operated for about five detention times before an intensive program of data collection for the stable period started. Data collection included the continuous measurement of gas production rate, volatile fatty acid samples five times a day, gas composition analysis every two to four hours, and a daily sample of the effluent for determination of total volatile solids and chemical oxygen demand.

Experimental Group Two was conducted to study the combined effect of daily pulse feeding with an imposed temperature fluctuation. Two 14-liter daily-pulse-fed digesters were operated at a 19 day hydraulic retention time. Diluted dairy manure was used as the substrate. The

Table 4-2. Experimental Program.

Experimental Group	Operating Conditions
I	Daily pulse feeding at constant temperature Substrate: full strength dairy manure Hydraulic retention time: 15 days Operating temperature : 36.4 ± 0.5°C Digesters: two 3-liter digesters with 2.25-liters operating volume each, operated identically for duplication. Operation period: 4 months with daily feeding, 2 months without feeding
II	Daily pulse feeding with fluctuating temperature Substrate: diluted dairy manure, 1:3 ratio (manure to tap water by volume) Hydraulic retention time: 19 days Operating temperature: 35.8 ± 3.3°C, increased linearly for 12 hours, then decreased linearly for 12 hours Phase relation between feeding time and temperature cycle: A. feeding at the mid point of ascending temperature ramp B. feeding at the peak of the temperature cycle. C. Feeding at the bottom of temperature cycle. Digesters: two 14-liter digesters with 9.5-liter operating volume each, one operated as described above, another as a control digester operated at a constant temperature of 35.8 ± 0.5°C Operating period: 6 months for A, B and C above; 2 months extended from C without feeding.

seeding procedure was the same as that for Experimental Group One, except 9 liters of active effluent were blended before being placed into each starting digester. During the acclimation period, both digesters were operated identically at constant temperature. The digesters were considered to be stable after about three detention times. One digester was then imposed with a fluctuating temperature of ± 3.3°C about the mean of 35.8°C. The temperature increased linearly for twelve hours, then decreased linearly for twelve hours. The other digester was operated as a control unit with a constant temperature of 35.8 ± 0.2°C.

Using the first digester, three different phase relationships between the feeding time and the temperature cycle were studied and will be referred to as Experiments IIA, IIB and IIC from here on. For Experiment IIA, the digester was fed at the midpoint of the ascending temperature ramp. For Experiment IIB, feeding occured at the bottom, and for Experiment IIC the digester was fed at the peak of the temperature cycle. After each change to a new phase relationship, the digester was operated for about one more detention time before a stable period was assumed. The stability of the operation will be presented in the next chapter. The data and sample collection programs were the same as for Experimental Group I.

C. ANALYTICAL TECHNIQUES

The parameters of interest in this study include pH, alkalinity, total solids, total volatile solids, COD, individual volatile acids, gas composition and gas volume. The measurement procedures were based on Standard Methods, 14th Edition (1975) unless otherwise described here.

1. pH

Measurements of pH were made shortly after samples were withdrawn, using a pH meter (Corning, Model 12) with combination electrodes. The reference half-cell had Ag/AgCl internal elements with a ceramic junction. A commercial standard buffer solution with a pH of 7.00 at 25°C was used for calibrating the electrode and meter. Measurements were made to ± 0.05 pH unit.

2. Total Alkalinity

Total alkalinity was measured by titration to pH 4.5 using 0.02 N H_2SO_4. Results were reported in mg/l as $CaCO_3$. The total alkalinity in the digester is composed of bicarbonate alkalinity and fatty acid alkalinity. The bicarbonate alkalinity which is the measure of buffer capacity can be estimated using Equation 4-1.

$$BA = TA - (0.76 \times 0.833)(TFA) \qquad (4\text{-}1)$$

where BA = bicarbonate alkalinity, mg/l as $CaCO_3$

TA = total alkalinity, mg/l as $CaCO_3$

TFA = total fatty acid concentration, mg/l as acetic acid

The factor of 0.76 is the estimated fraction of unionized volatile fatty acids at pH 4.5, and 0.833 is the conversion factor of mg/l as acetic acid to mg/l as $CaCO_3$.

3. Total Solids

Total solids is a measure of all material (other than water) present in sludge, both in suspension and in solution. Prior to sampling, the evaporating dish was heated at 550°C for 20 minutes and weighed after complete cooling in the desiccator. A freshly drawn sam-

ple of 20 to 30 ml was poured into the dish and weighed rapidly. The sample was dried at 103°C overnight, cooled in a desiccator and weighed. The total solids data were expressed as percent by weight which can be calculated by Equation 4-2,

$$\% \text{ total solids} = \frac{(W_3 - W_1)(100)}{(W_2 - W_1)} \qquad (4\text{-}2)$$

where W_1 = weight of evaporating dish

W_2 = weight of wet sample and evaporating dish

W_3 = weight of dry solids and evaporating dish

4. Total Volatile Solids

The total volatile solids were measured from the dried solids of the above analysis by burning them completely in a muffle furnace at 550°C for 30 to 40 minutes depending on the size and concentration of the sample. The dishes were then air-cooled slightly and put in a desiccator for complete cooling before weighing. The percent total volatile solids can be determined by Equation 4-3,

$$\% \text{ total volatile solids} = \frac{(W_3 - W_4)(100)}{(W_2 - W_1)} \qquad (4\text{-}3)$$

where W_4 = weight of ash and evaporating dish

W_1, W_2 and W_3 are the same as in Equation 4-2.

5. Chemical Oxygen Demand (COD)

The chemical oxygen demand was determined by the dichromate reflux method. The procedure was based on Standard Methods, 14th Edition (1975). Freshly drawn samples were diluted between 1:400 and 1:800

depending on the estimated COD concentrations of the samples. A 20 ml aliquot of diluted sample was placed in a (COD) flask with 10 ml 0.25 N standard dichromate, 30 ml concentrated H_2SO_4 with Ag_2SO_4 and 0.4 g $HgSO_4$ and was refluxed for two hours. After diluting and cooling it was titrated with 0.25 N standard ferrous ammonium sulfate.

6. Individual Volatile Fatty Acid

The individual volatile fatty acids in the influent and effluent of the digesters were analyzed on a gas-chromatograph using a flame ioniza-iton detector. The volatile fatty acids analyzed include acetic, propionic, butyric, iso-butyric, valeric and iso-valeric acids.

A Varian 3700 gas chromatograph with a Varian CDS-111 data system and Model 9716 recorder were used in this analysis. A 6 ft 2.0 mm ID coiled glass column (Supelco Cat. No. 2-1721) packed with 10% SP-1200/1% H_3PO_4 on 80/100 mesh acid washed Chromosorb W (Supelco Cat.No. 1-1965, Supelco Inc., Bellefonte, PA) was connected to a flame ionization detector.

The gas chromatograph was operated isothermally at 115°C. The detector and injection port temperatures were 250°C and 160°C respectively. For acetate concentrations of about 150 mg/l as COD and lower, these operating conditions did not give a well-resolved acetate peak. After several trials, a column temperature of 90°C, with the detector at 150°C and the injection port at 190°C yielded a much better resolved acetate peak. Thus, this operating condition was used when acetate concentrations in the samples were 150 mg/l as COD or lower. Before use, the column was conditioned overnight at a temperature of about 50°C above the operating temperature with a nitrogen carrier gas flow rate of

30 ml/min. Hydrogen and air flow rates were adjusted to obtain a maximum sensitivity at 30 ml/min and 300 ml/min, respectively. The injeciton septum was replaced after 15-20 injections were made. The glass liner in the injection port was frequently checked for an excess accumulation of nonvolatile material which might cause a tailing peak or loss of sample. Whenever appropriate the glass liner was replaced with a clean one.

The data obtained were analyzed either automatically by the external standard method or manually calculated from a set of calibration curves. Parts of the data were verified by injecting the same samples into another gas chromatograph (Perkin-Elmer 900) located in the Soil-Science laboratory at Michigan State University. The results from both machines compared within ± 10 percent.

Fresh standards were prepared for each set of analyses from a stock mixture containing a known amount of each pure volatile fatty acid of interest. The standard solutions were prepared by diluting this stock solution to an appropriate volume. When data were analyzed using the external standard method, calibration samples were run for about every 3 or 4 samples analyzed. Three injections of one standard solution were normally made and the areas averaged. Results were reported in mg/l as COD. When the data were manually calculated, standard calibration curves were constructed for each set of samples. The standard calibration curves are shown in Figures 4-3 and 4-4. In all cases, the response of each component was linear over the entire concentration range of the standard solutions. For acetate at low concentrations tailing of the solvent peak caused a non-zero intercept in Figure 4-4 (dotted line) which does not affect the calculated concentrations. The

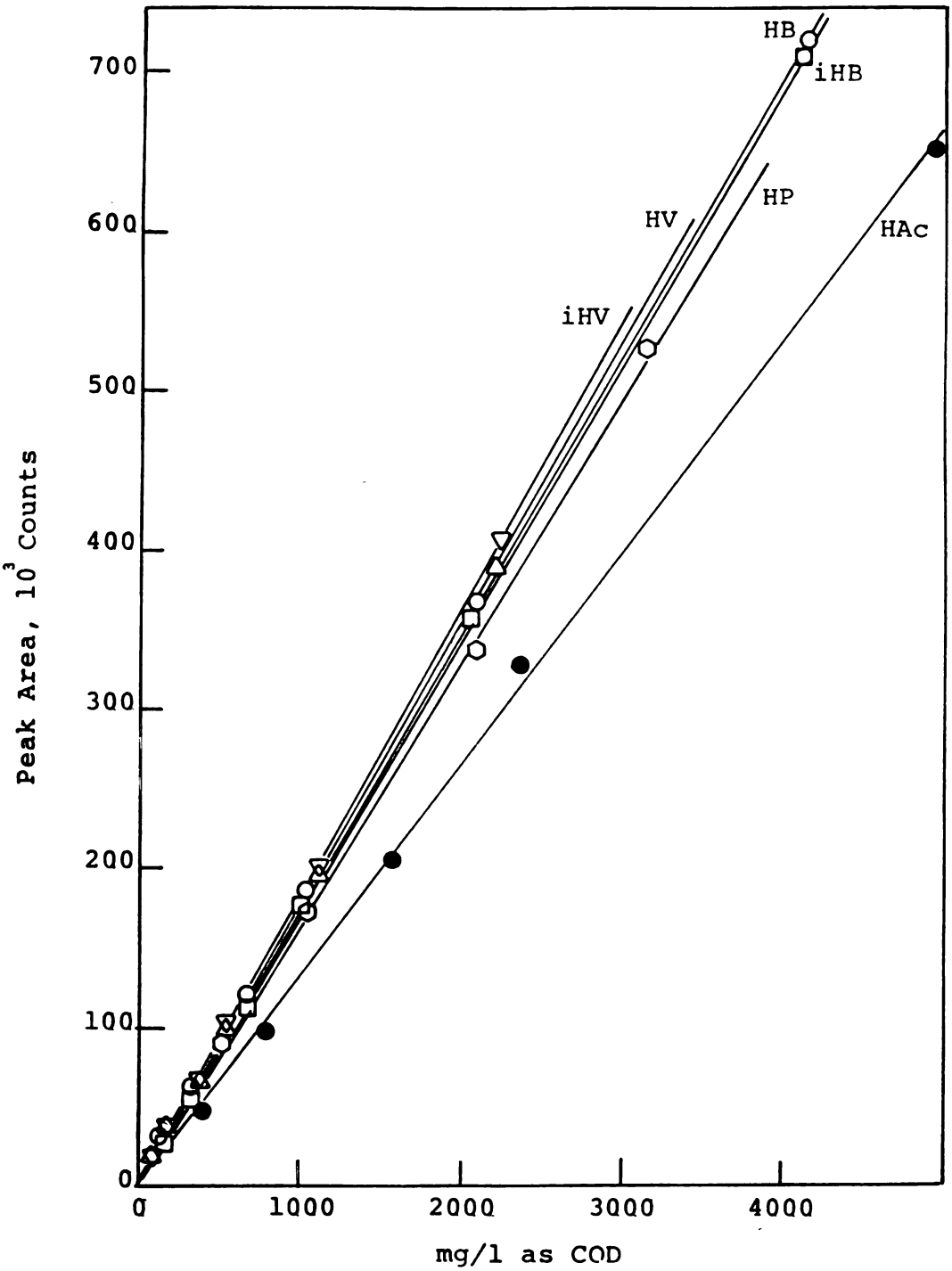


FIGURE 4-3. Volatile Fatty Acid Standard Curves for the Higher Concentration Range.

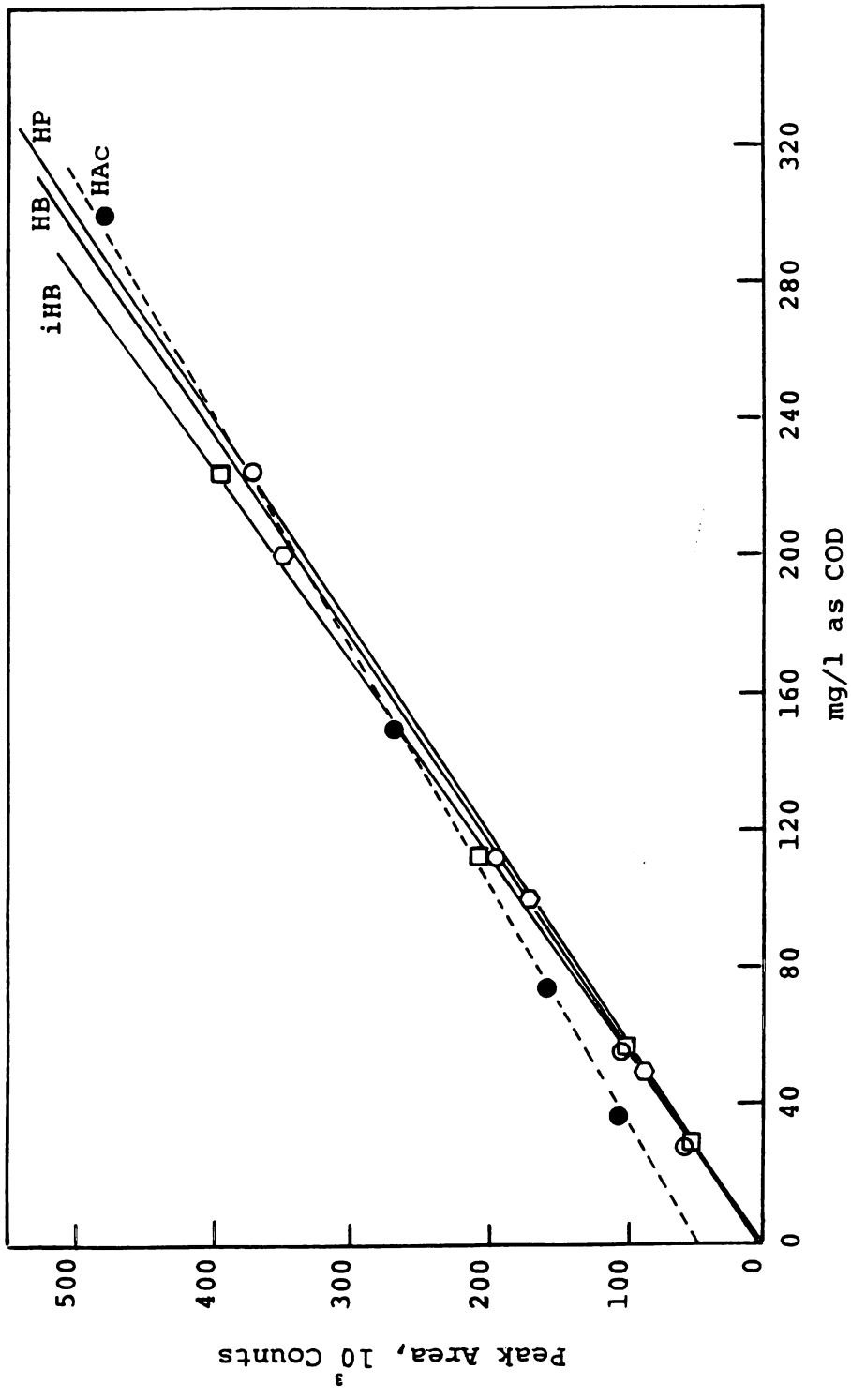


FIGURE 4-4. Volatile Fatty Acid Standard Curves for the Lower Concentration Range.

response of acetate in the lower range, however, remained linear with concentration.

Samples for volatile acid analysis were prepared by removal of suspended solids and acidification. A 20 ml sample was placed in a plastic centrifuge tube, capped and centrifuged for 10 min. at 14,400 rpm. The supernatant was filtered through a glass fiber filter followed by a 0.45 micrometer membrane filter (Millipore Type HA). The filtrate was acidified to a pH of 2 or below, capped and stored at 4°C. A one microliter sample was injected into the gas chromatograph using a 10 µl syringe (701N, Hamilton CO. Reno, Nev.). In most cases, peaks were well-resolved and baseline separation of all components was achieved.

7. Gas Composition

The gas composition was analyzed using the same gas chromatograph (Varian 3700) with a thermal conductivity detector. A 12 foot, 1/8 inch O.D. copper column was packed with 80/100 mesh Porapak Q (Water Associates, Inc., Milford, Mass.). The column was operated isothermally at 50°C with detector and injection temperatures of 150°C and 190°C respectively. Helium at a flow rate of 30 ml/min. was used as a carrier gas.

One milliliter samples were drawn from the digester head space with a one milliliter gas-tight syringe (1001N, Hamilton CO.) and injected immediately into the gas chromatograph. The major gases detected in the gas samples were nitrogen, methane, and carbon dioxide. The amount of nitrogen was small and primarily derived from the air that entered the digester during feeding. Therefore only methane and carbon dioxide were components of interest in the analysis. Standardization was accomplished by injecting various volumes of pure methane and carbon dioxide (Scotty II Mix 109 and Mix 105, Supelco Inc., Bellefonte, PA).

Figure 4-5 shows the peak area response to standard methane and carbon dioxide. The results of the analyses was normalized to include only methane and carbon dioxide and reported in percent by volume.

8. Bubble Tube Calibration

The bubble tubes, bubble counter and data acquisition device were described earlier. The calibration procedure will be detailed here.

After several trials of sizes and shapes, the bubble tubes were specially made to match the expected range of gas production rates. Paraffin oil (White Saybolt, Viscosity 125/135) was added into the tube and the amount of oil was adjusted so that the differential head was about 1-1/4 to 2-1/2 inches depending on the range of gas production rates to be measured. The higher the rate of gas production, the lower the differential head required to obtain a constant size and smooth rising of the bubbles. When the rate of gas production was relatively high, many bubbles tended to rise at one time (bursting). To prevent this, the differential head was readjusted for each set of experiments. A wet test meter (Precision Scientific Co., Chicago, IL) was connected to the outlet of the bubble tubes. During calibration, the wet test meter readings were made at 1/2 to 1 hour intervals over two or three days (feeding cycles). These readings were converted into rate of gas production in ml/hr and plotted against the corresponding bubble count data (Figure 4-6). showing a linear relationship over the entire range of interest. The correlation coefficients (R^2) of the linear regression analyses for all calibrations were 0.95 or higher. The bubble count data were then translated into gas production rates in ml/hr using these calibration curves.

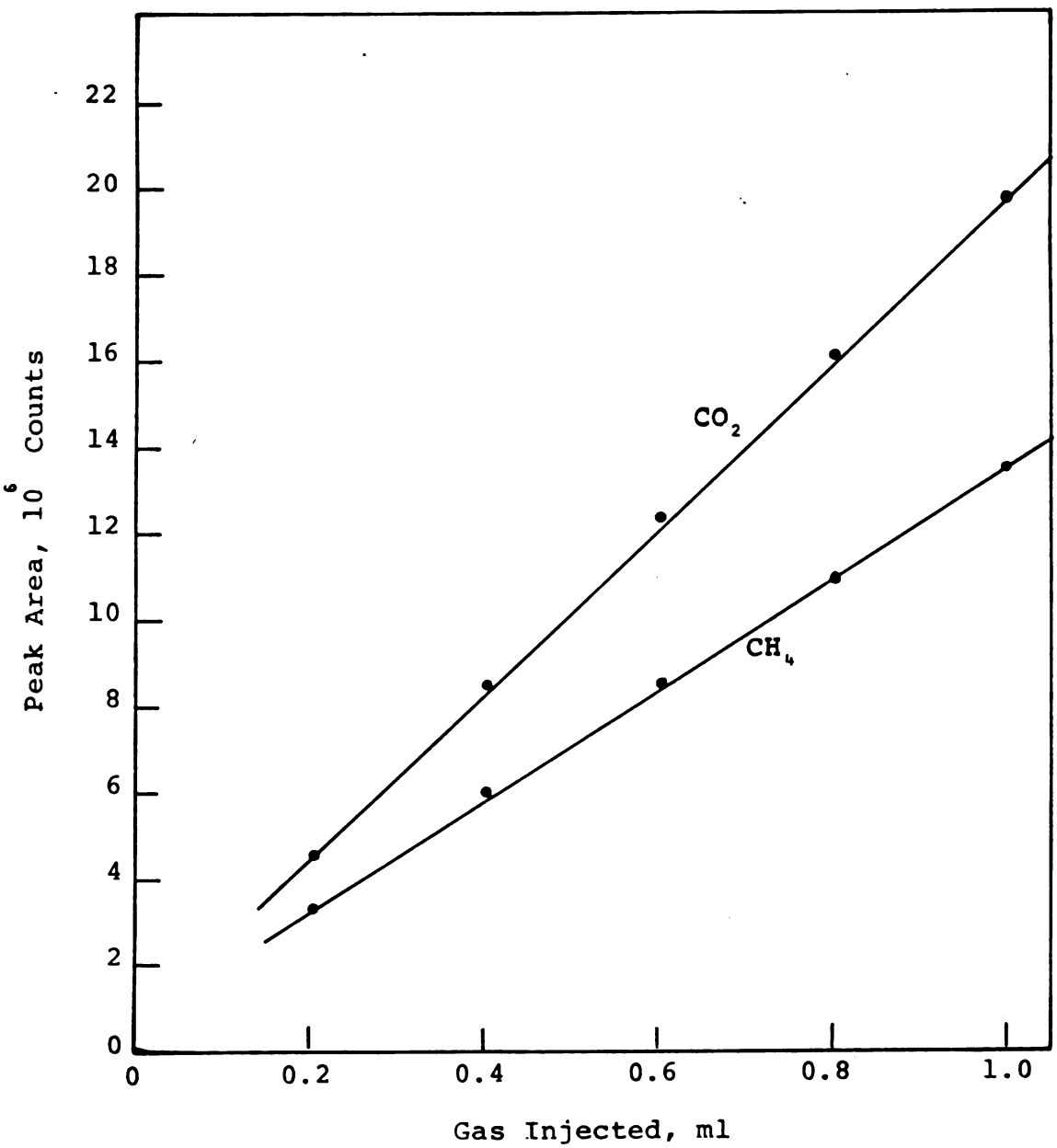


FIGURE 4-5. Calibration Curves for Methane and Carbon Dioxide.

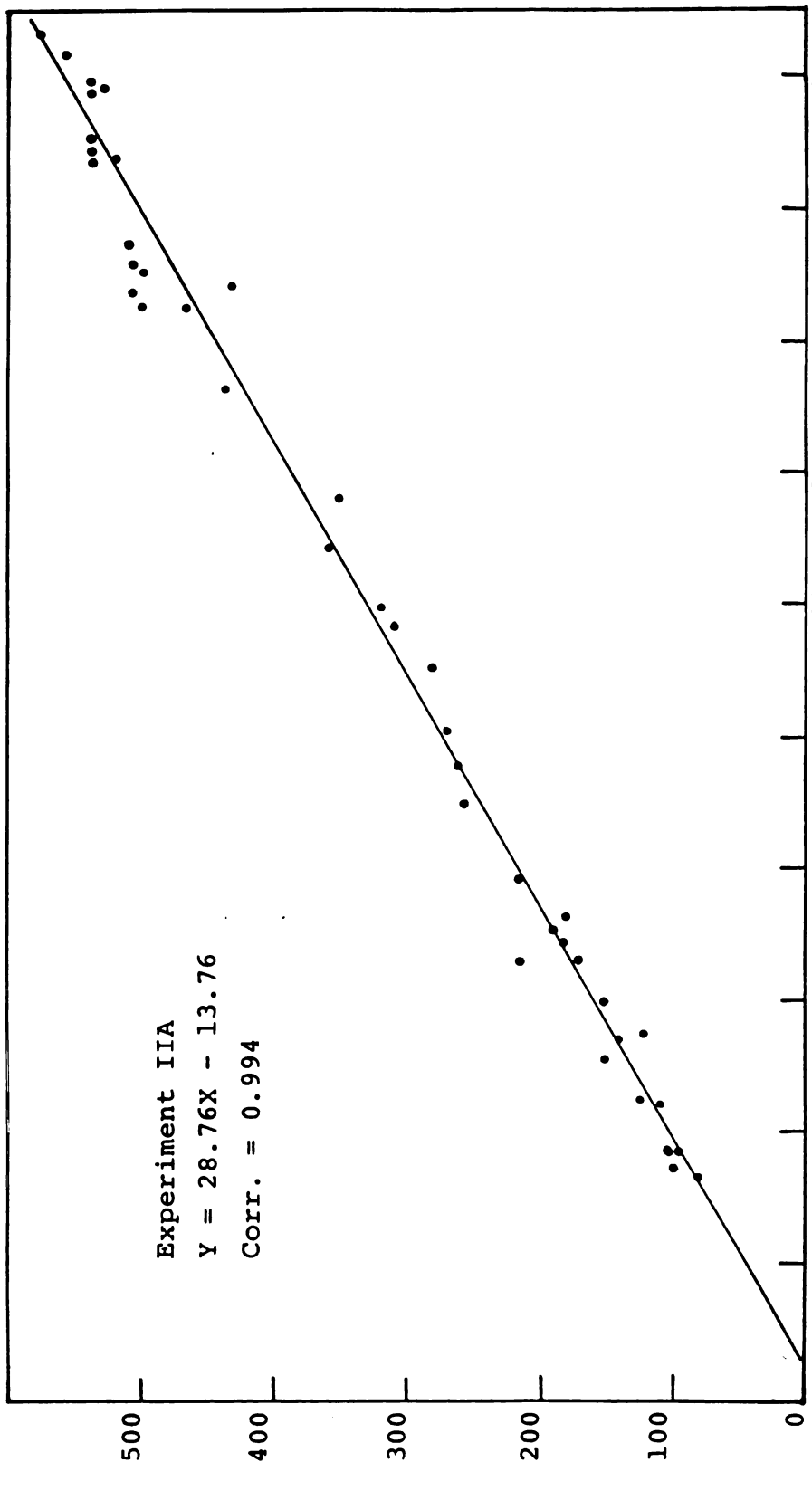


FIGURE 4-6. Example Bubble Tube Calibration Curve.

V. EXPERIMENTAL RESULTS

The experimental data presented in this chapter are divided into two sections in accordance with the two experimental groups: 1) 3-liter constant temperature, whole manure digesters; and 2) 14-liter , variable temperature, diluted manure digesters. A complete summary of the results, including statistical information, can be found in the Appendix. For a comparison of the experimental results with the chemical characteristics of the influent manure, see Table 4-1.

A. EXPERIMENTAL GROUP I

The results presented in this section were obtained from the two 3-liter, identically operated digesters fed with whole manure. The data collected during the stable period include the gas production dynamics, the overall extent of substrate degradation in terms of total volatile solids and chemical oxygen demand, and the individual volatile acids and gas composition at different times during the 24 hour feeding cycle. In addition, the data on daily gas production during the extended period of digester operation without feeding will be included.

1. Stable Period

As defined in the previous chapter, the stable period is considered to occur when the measured daily gas production is relatively constant for at least one detention time. The daily gas production for each digester measured using the wet test meter, is plotted in Figure 5-1. These data were recorded after the digesters had been operated for about four detention times. The mean daily gas production

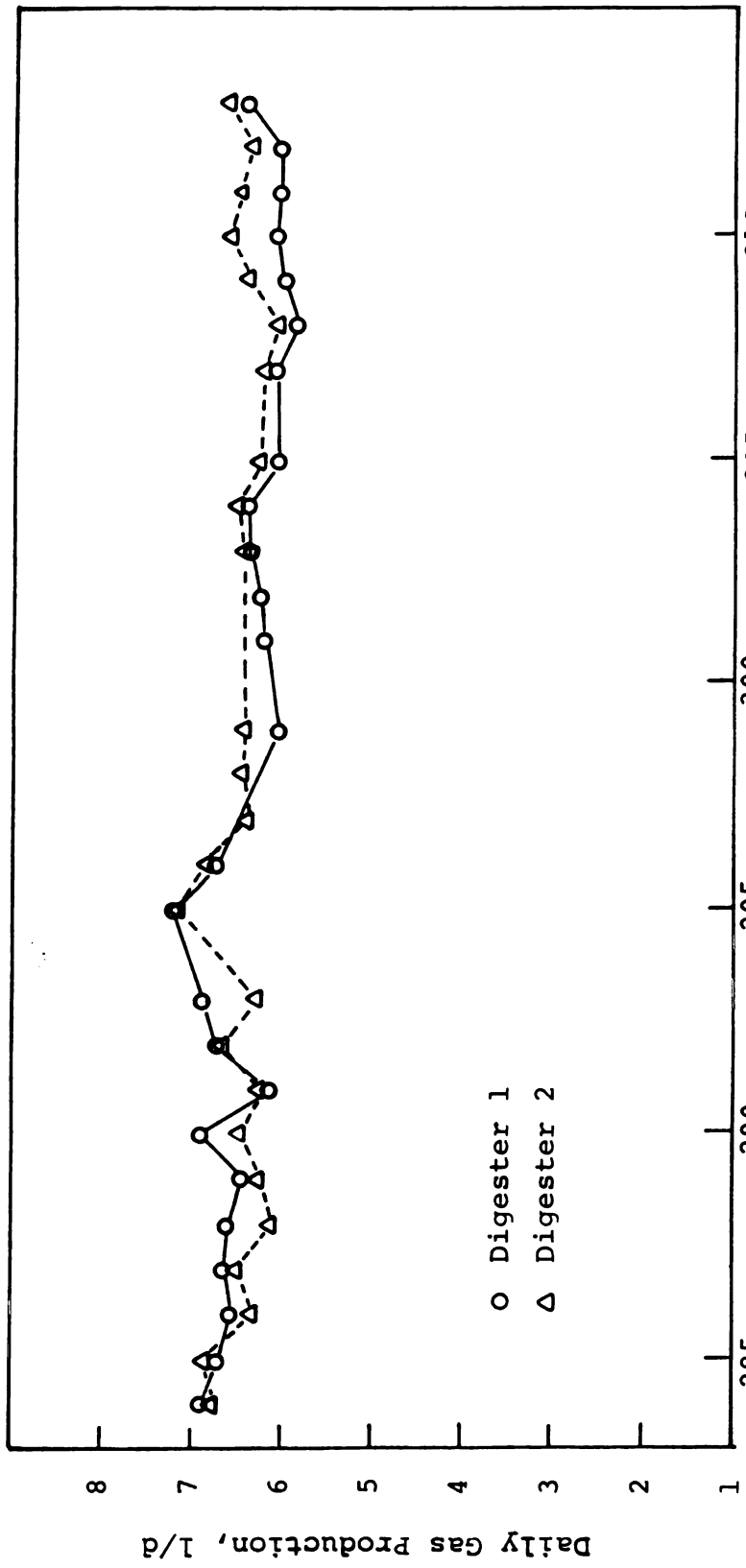


FIGURE 5-1. Daily Gas Production from Wet Test Meter Readings for Experiment I.

for the whole time period was 6.43 liters for Digester 1 and 6.48 liters for Digester 2 with standard deviations of 0.36 and 0.25 liter respectively. This variability was small and may have been caused, in part, by fluctuations in atmospheric pressure for which no correction was made. The variability was much less during the last 5 days when the continuous gas production data were taken. The mean daily gas production from wet test meter readings for this five day period was 6.14 liters for Digester 1 and 6.50 liters for Digester 2 with standard deviations of 0.16 and 0.12 liters respectively.

2. Gas Production Dynamics

Continuous readings of gas production were obtained using bubble counts during the last five days of the stable period (Julian days 309 to 314). The means of these data are plotted in Figure 5-2 along with the 99% confidence intervals. The gas production curves for both digesters followed the same pattern, rapidly increasing in the first two hours after feeding, peaking at about 2 to 4 hours, then gradually decreasing almost linearly to the end of the feeding cycle.

The mean daily gas production calculated from the bubble counts is 6.7 l/d for Digester 1 and 7.7 l/d for Digester 2, 11% and 18% higher than the wet test meter readings of the corresponding digesters. This discrepancy was significantly reduced for all later experiments as a result of a better adjustment of the oil level in the bubble tubes which led to a more consistent bubble size. Despite the difference in total daily gas production, the overall 24 hour patterns of gas production for Digesters 1 and 2 were almost identical.

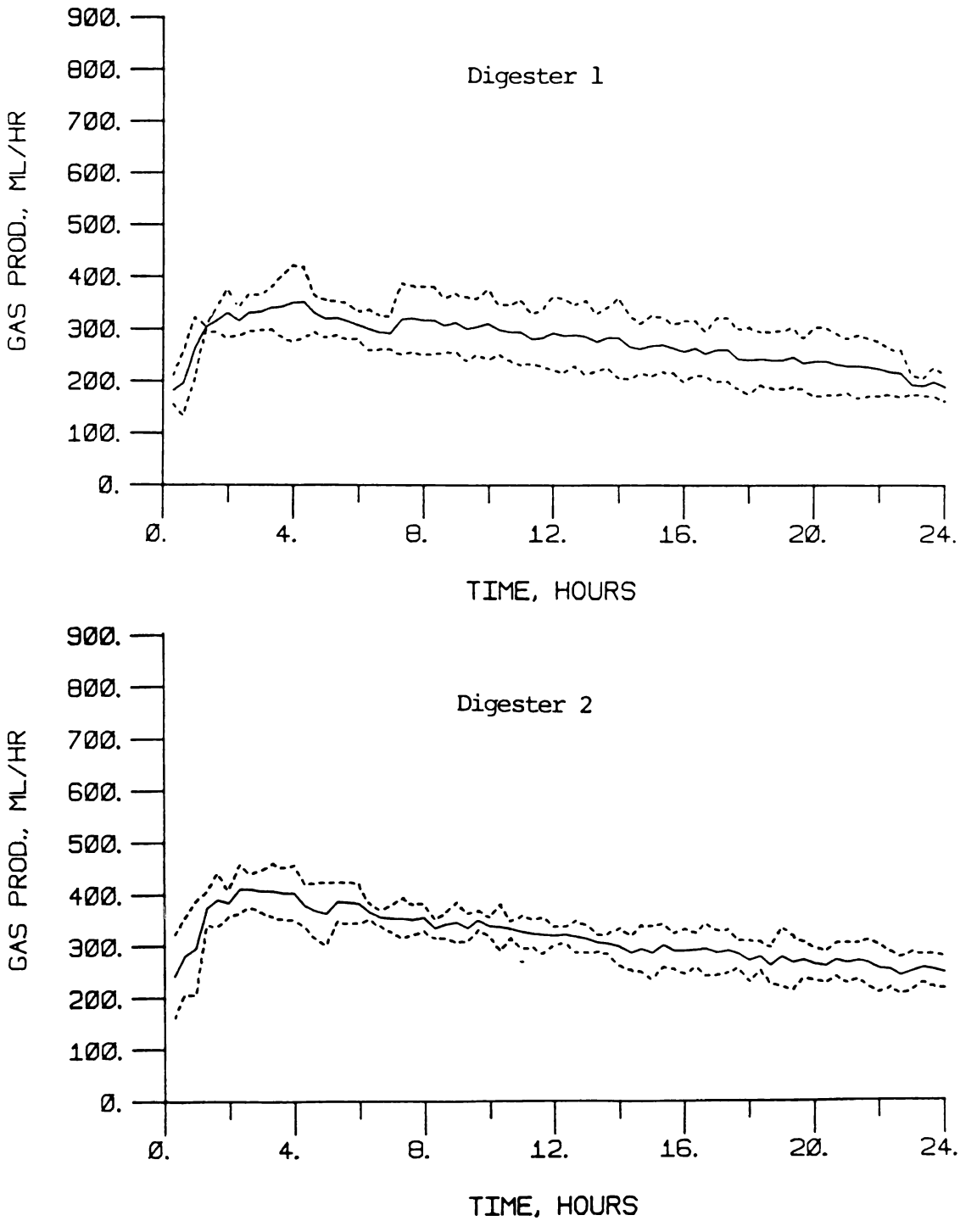


FIGURE 5-2. Mean Gas Production During the Stable Period of Experiment I. Dashed lines are the 99% confidence intervals on the mean (t test with n = 5).

TABLE 5-1. Substrate Degradation and COD Mass Balance for Experimental Group I.

Parameters	Influent	Effluent DIG 1	Effluent DIG 2
Total Volatile Solids, g/l			
Mean	137.8	88.9	88.0
S.D.	3.5	3.8	4.4
% Reduction	--	35.5	36.1
Total COD, g/l			
Mean	170.0	103.4	105.7
S.D.	11.5	10.4	9.3
% Reduction	--	39.2	37.8
COD/TVS	1.23	1.16	1.20
Gas Produciton, 1/d			
Mean	--	6.14	6.50
S.D.	--	0.16	0.12
Gas/COD*	--	0.97	1.06

* Gas/COD = ratio of gas measured by wet test meter to gas equivalent of COD reduction (0.382 liters of CH_4 at 25°C and 1 atm is equivalent to 1 gram COD assuming digester gas contains 60% CH_4).

3. Substrate Degradation and COD Mass Balance

Total volatile solids and total COD reduction were determined in order to evaluate the efficiency of the operating system. Because no oxidizing agent was added to the digesters, all the COD removed must be converted to methane or, in rare cases, hydrogen. Therefore the biogas equivalent of the measured COD reduction should balance the measured gas production. Table 5-1 summarizes the substrate degradation in terms of total volatile solids and COD.

The reductions of total volatile solids were 35.5 and 36.1 percent and the COD removals were 39.2 and 37.8 percent for Digester 1 and Digester 2 respectively. This suggested that the ratio of COD removal

to total volatile solids removal is approximately 1.08. A mass balance of the measured gas production and COD reduction was calculated using a conversion factor of 0.382 liters CH_4 at 25°C, 1 atm per gram COD, and assuming digester gas contains 60% CH_4.

Comparing the measured gas production with the gas equivalent of the measured COD reduction gives ratios of 0.97 and 1.06 for Digesters 1 and 2 respectively. Thus the discrepancy in the COD mass balance is less than 6 %.

4. Volatile Fatty Acids

The volatile fatty acid pool size is important in the study of anaerobic fermentation because it indicates how well the acid production balances with its removal. Acetic acid is a particularly important intermediate because it has been suggested as a rate limiting step for the soluble part of the substrate.

Samples for volatile acid analysis were taken at five times during the feeding cycle over two days during the stable period. The average values obtained in these analyses are plotted in Figure 5-3 for each digester. Because the concentrations of individual C_4 to C_6 acids were small, they are reported as a single group. The daily fluctuation of volatile acids in each digester over the 24 hour feeding cycle follows a similar pattern. After feeding, acetate increased about 4-5 fold due to the high level of acetate in the feed (filled circles) and remained relatively constant for about 4-5 hours, then slowly declined until the end of the feeding cycle. This follows the same pattern as the fluctuation in gas production rates. The high rate of gas production with a relatively constant volatile acid concentration during the several

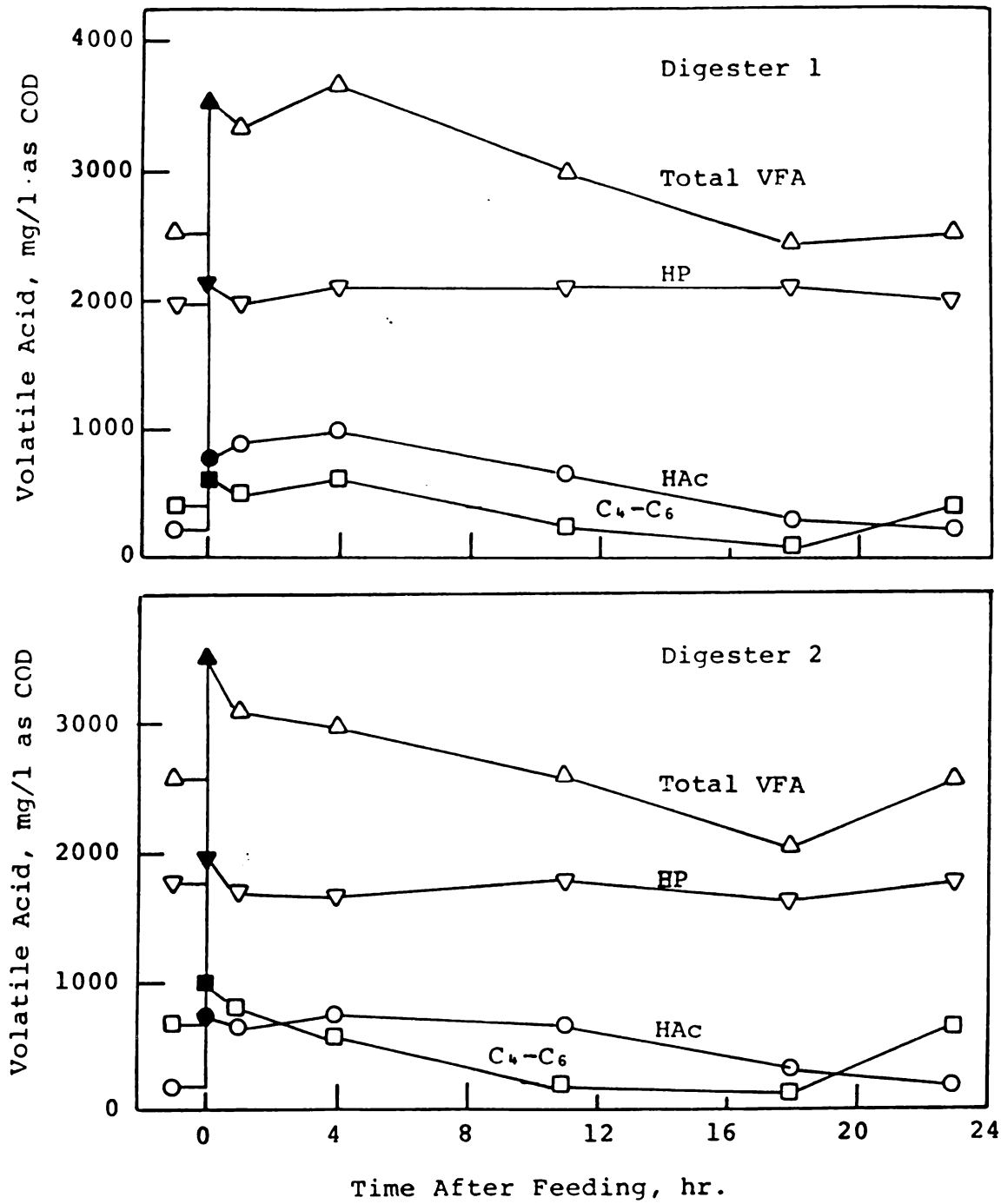


FIGURE 5-3. Individual Volatile Fatty Acid Concentrations During the Stable Period of Experiment I. Solid symbols represent calculated concentrations immediately following feeding.

hours after feeding suggests that some components other than volatile acids in the influent manure are rapidly degradable. The C_4 to C_6 volatile acids varied in about the same manner as acetate. The propionate concentrations in both digesters were very high and remained constant over the feeding cycle.

5. Gas Composition

Methane, carbon dioxide and nitrogen were the major components found in the digester gas. The nitrogen content was small, increasing sharply to about 3 to 5 percent following feeding, then decreasing to 1 to 2 percent a few hours later. This nitrogen seems to be derived from air which entered the digesters during the feeding process. Therefore, the gas composition results have been normalized to include only methane and carbon dioxide.

The methane content of the head space varied over the feeding cycle as shown in Figure 5-4. Both digesters showed a very similar variation of methane content. The methane percentage started declining following the feeding and reached a minimum of 58% after about 8 to 10 hours, then started rising till the end of the feeding cycle when the maximum was about 62%. The average methane content was 60%.

Because the gas sample taken from the head space is the mixture of newly produced gas and that remaining from earlier, the variation of methane content is also a function of the head space volume. For this experiment the head space volume is 0.75 liter which is about one fourth of the digester volume. In a typical farm digester, the head space proportion is normally higher. Thus a smaller variation of methane content can be expected.

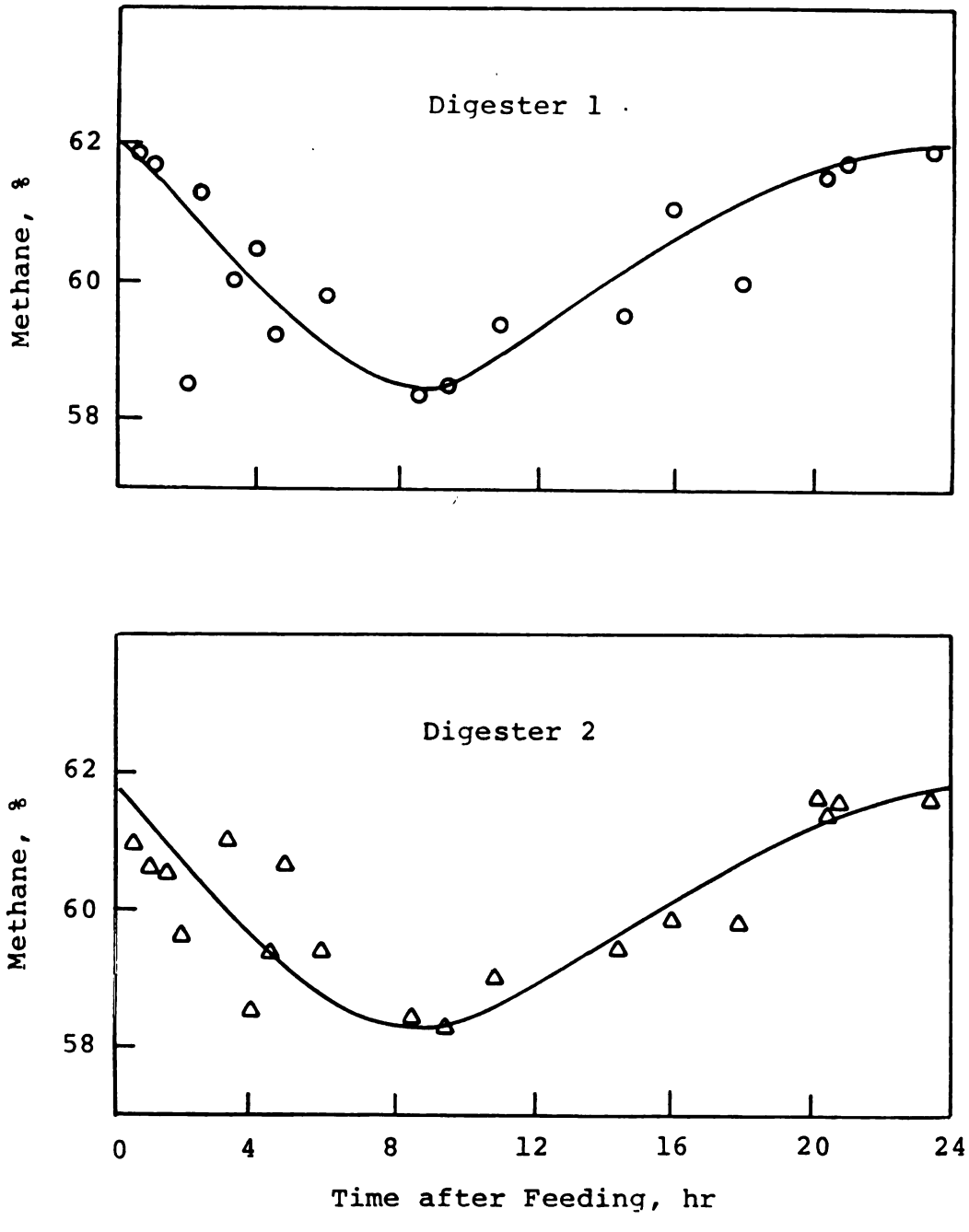


FIGURE 5-4. Methane Content in the Digester Head Space During the Stable Period of Experiment I.

6. pH and Total Alkalinity

Results for pH and alkalinity are plotted in Figure 5-5. The effluent samples for both parameters were withdrawn just before feeding. Several samples for pH measurement were also taken at different times during the feeding cycle but showed no variation. 30.p The pH over the entire experiment was almost constant at about 7.65 to 7.70 for both digesters. The pH of the effluent was slightly higher than for the influent manure which had pH 7.40. The alkalinity data were also constant with the effluent value about 50% higher than that of the influent manure. Since the volatile acid concentration of the influent manure was much higher than that of the effluent, the increase in alkalinity of the digesters was primarily due to an increase in bicarbonate alkalinity. The increase in pH is due both to the removal of volatile acids in the influent and to the hydrolysis and fermentations of proteins which release ammonia as shown by Jewell (1980) and Eastman and Ferguson (1981).

7. Gas Production during Extended Digester Operation Without Feeding

At the end of Experiment I, the operation of the two digesters were extended without feeding until the gas production stopped. The daily gas production values recorded from the wet test meters are shown in Figure 5-6. The rates of gas production for the two digesters recorded over 37 days were almost the same. Gas production dropped sharply after the first day without feeding and continued dropping moderately for 10 days before remaining relatively constant for another three weeks.

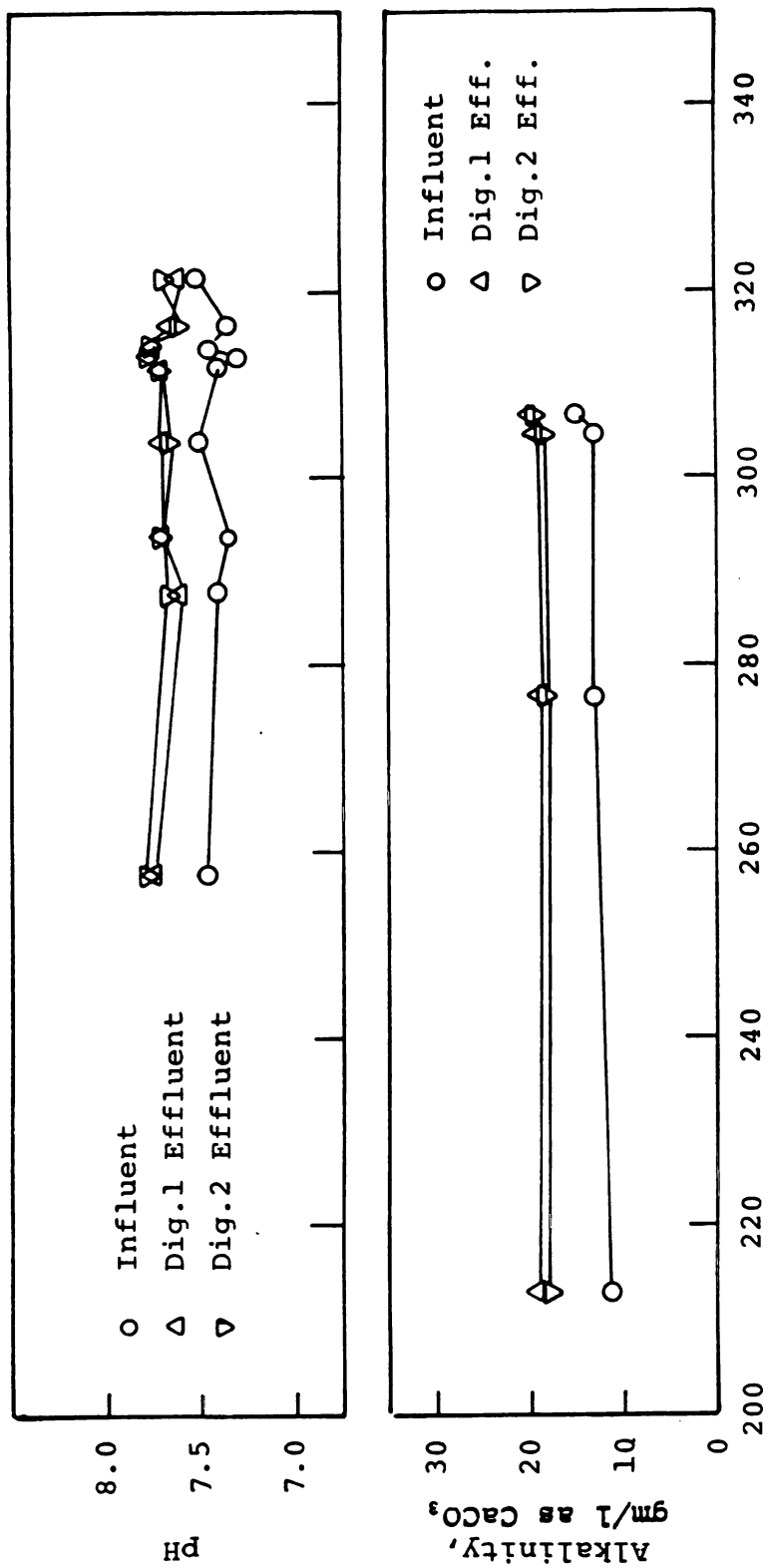


FIGURE 5-5. Total Alkalinity and pH Data for Experiment I.

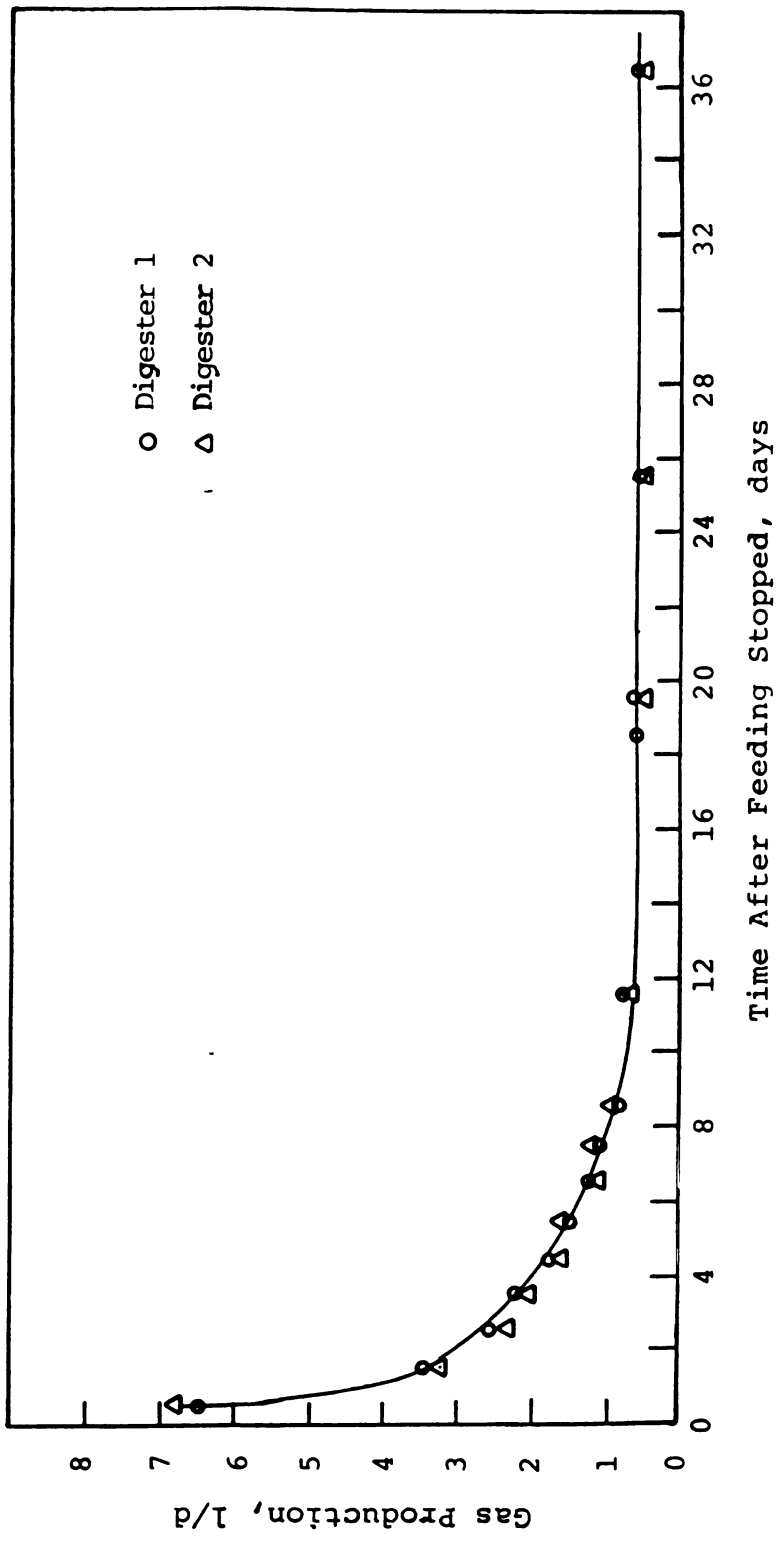


FIGURE 5-6. Gas Production During Extended Digester Operation without Feeding Following Experiment I.

B. EXPERIMENTAL GROUP II

The experimental data presented in this section describe the dynamics of gas production as a result of the combined effects of pulse feeding and temperature fluctuations. Other measured parameters include overall volatile solids and COD reduction, individual volatile acids and gas composition over the 24 hour feeding cycle. Also included are gas production data resulting from extended digester operation without feeding. These results were obtained from two 14-liter, daily pulse fed digesters. Three different phase relationships between the feeding and temperature cycles were investigated using one digester. The other was operated at a constant temperature as a control. For convenience the three phase relation experiments will be referred to as Experiments IIA, IIB and IIC in accordance with the phase relationships described in the previous chapter. The control unit will be referred to as Control.

1. Stabilization and Replication of the Two Digesters

Data collection began on Julian Day 85 after the full amount of influent manure had been fed for at least one detention time to each digester. This gave a detention time of 19 days. Time series of these data are shown in Figures 5-7 and 5-8. On Julian Day 111, the temperature of the control digester was increased from 35.4°C to 35.8°C to match the average temperature of the other digester. For several days after the increase of temperature, gas production increased by about ten percent, then dropped to about the same level as before. On several occasions, there were some problems with the temperature controller causing the temperature to remain at a high level (37 to 38°C) for some

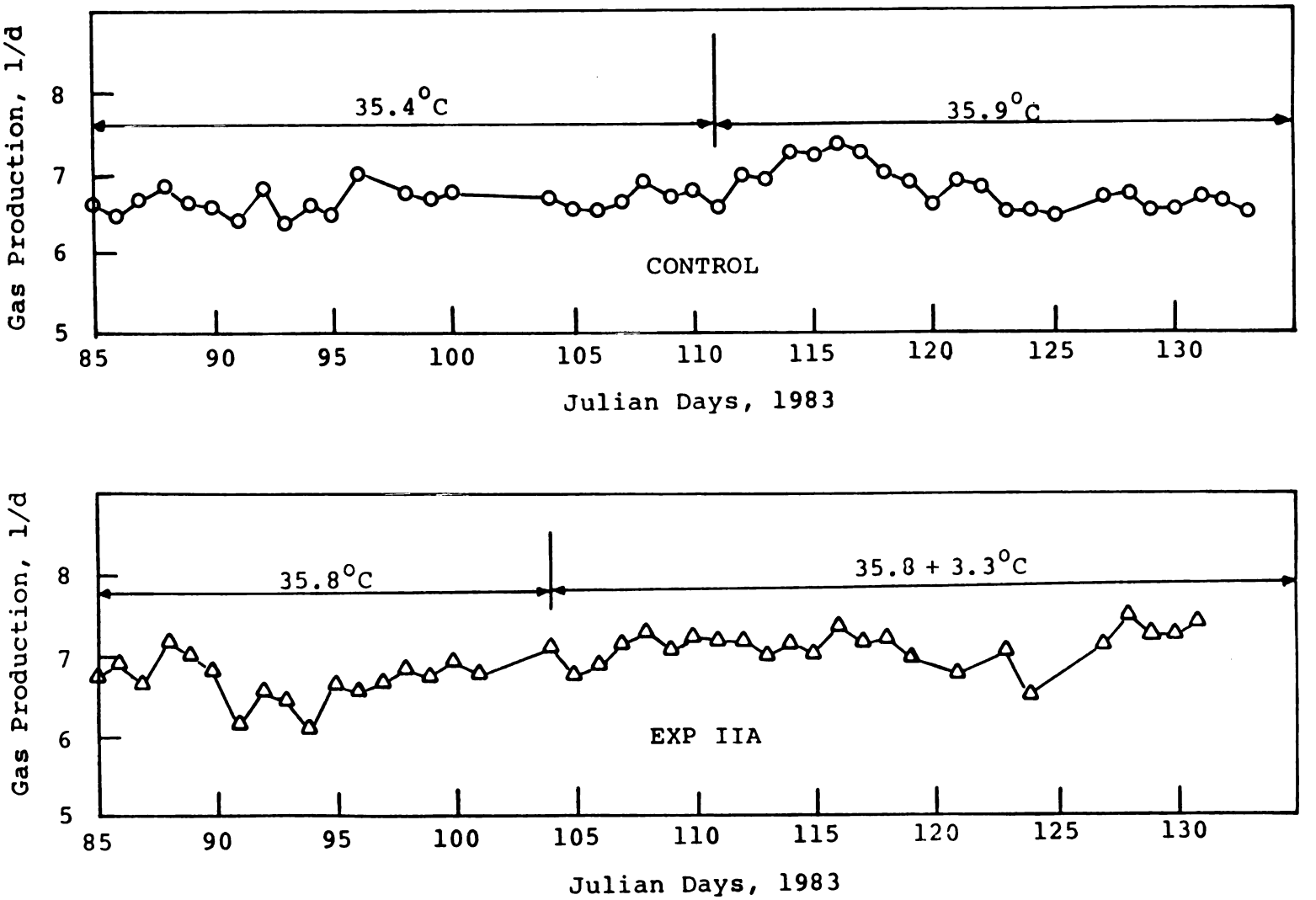


FIGURE 5-7. Daily Gas Production using the Wet Test Meter for Experiment IIA and the Control Digester.

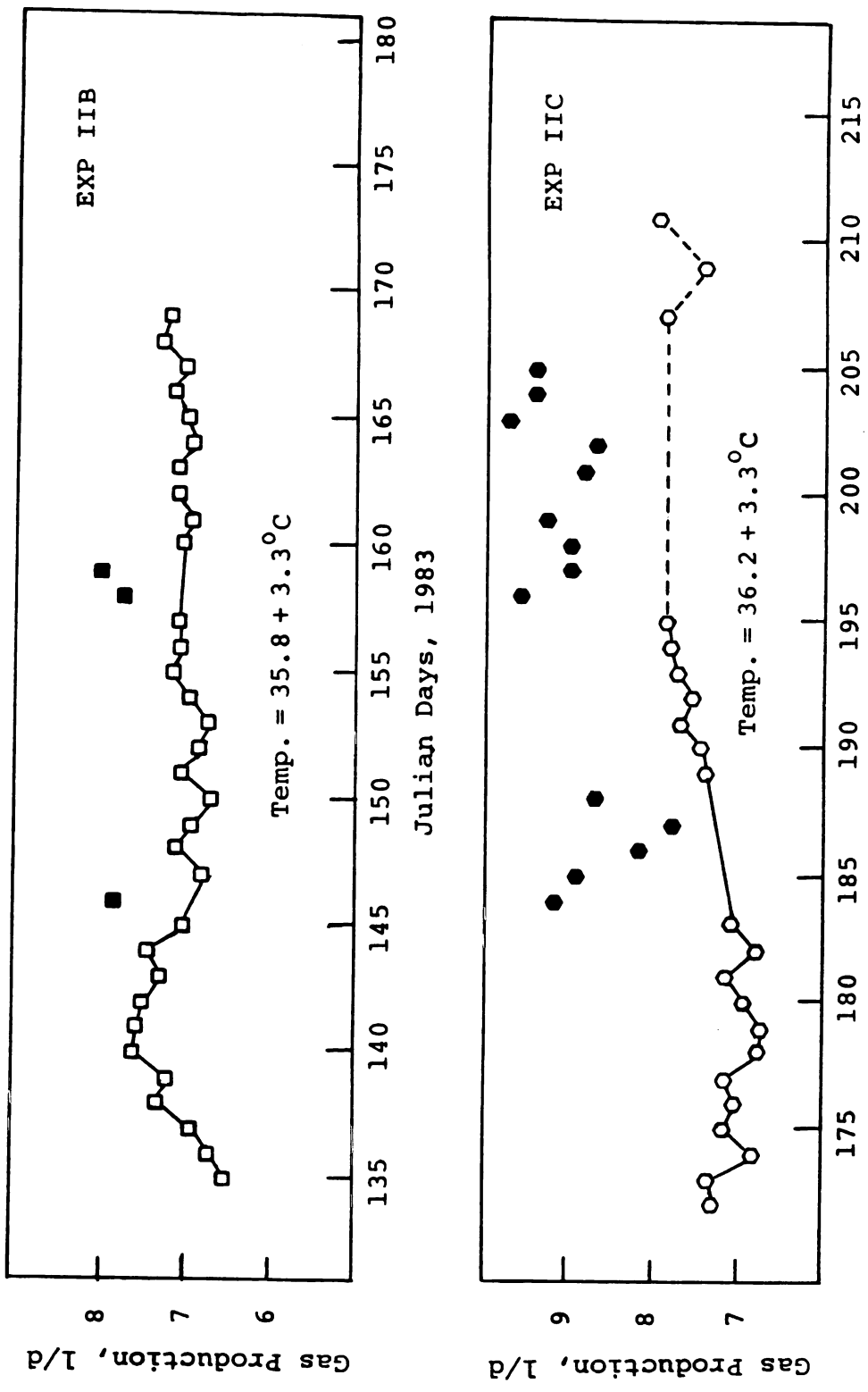


FIGURE 5-8. Daily Gas Production using the Wet Test Meter for Experiments IIB and IIC.

time before being noticed. This problem was worst at the end of Experiment IIC because the temperature was checked at the peak of its cycle which was, coincidently, the value at which the controller was locked. Data from this period have not been used in the following presentation.

In all cases, stable periods were assumed after digesters were fed with a constant amount of manure for at least two detention times (38 days). When the phase relationship was shifted the digester was operated for about one detention time before taking stable period data.

From Julian Day 86 to 103, both digesters were operated at constant temperature. The means and standard deviations of daily gas production for this period were 6.61 ± 0.17 l/d for the control digester, and 6.70 ± 0.28 l/d for the other digester. This indicates that a high degree of replication can be obtained for two digesters operated under the same conditions.

2. Gas Production Dynamics

Continuous measurement of gas production was obtained from bubble counts using the apparatus and procedure described in the previous chapter. When digesters reached the stable period for each experiment, the bubble tubes were calibrated and six days of data were obtained to determine the mean and standard deviation for each 20 minute period. The results are plotted in Figures 5-9 to 5-12 along with the corresponsing temperature cycle. Solid lines represent the mean values while the dashed lines represent the 99% confidence limits for the mean.

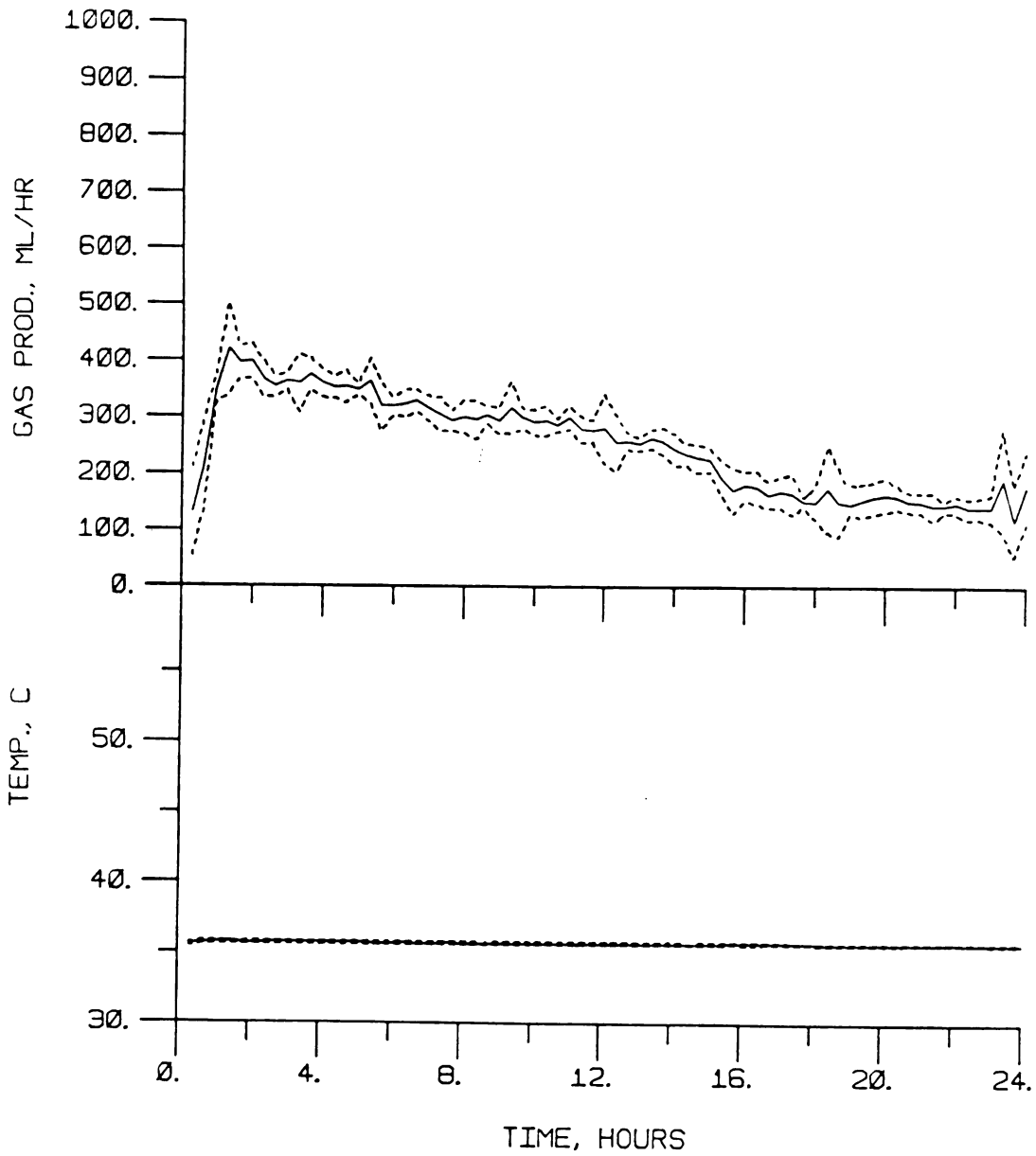


FIGURE 5-9. Mean Gas Production and Temperature During the Stable Period of Experiment II, Control. Dashed lines are the 99% confidence intervals on the mean (t test, n = 6).

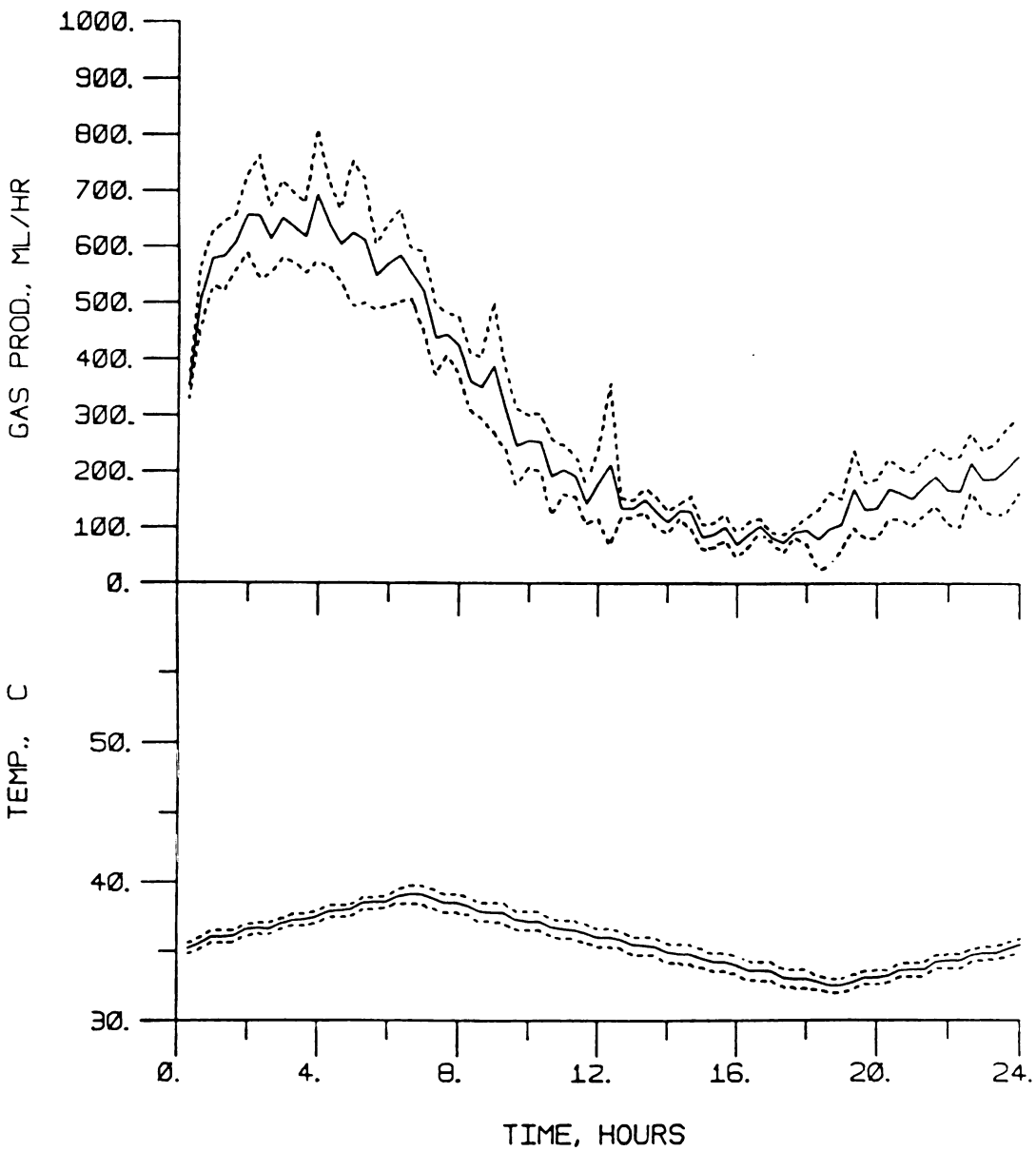


FIGURE 5-10. Mean Gas Production and Temperature During the Stable Period of Experiment IIA. Dashed lines are the 99% confidence intervals on the mean (t test, n = 6).

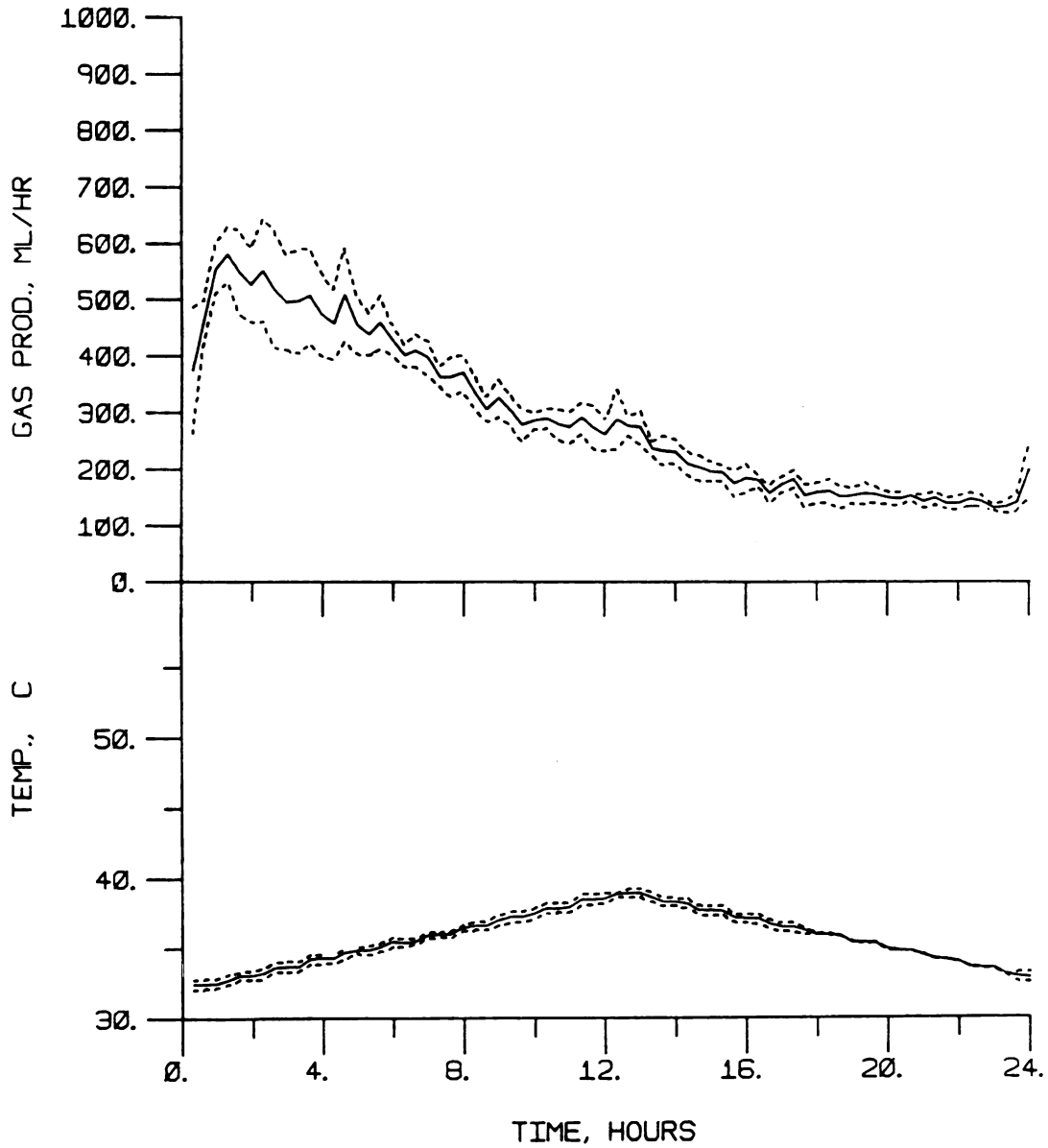


FIGURE 5-11. Mean Gas Production and Temperature During the Stable Period of Experiment IIB. Dashed lines are the 99% confidence intervals on the mean (t test, n = 6).

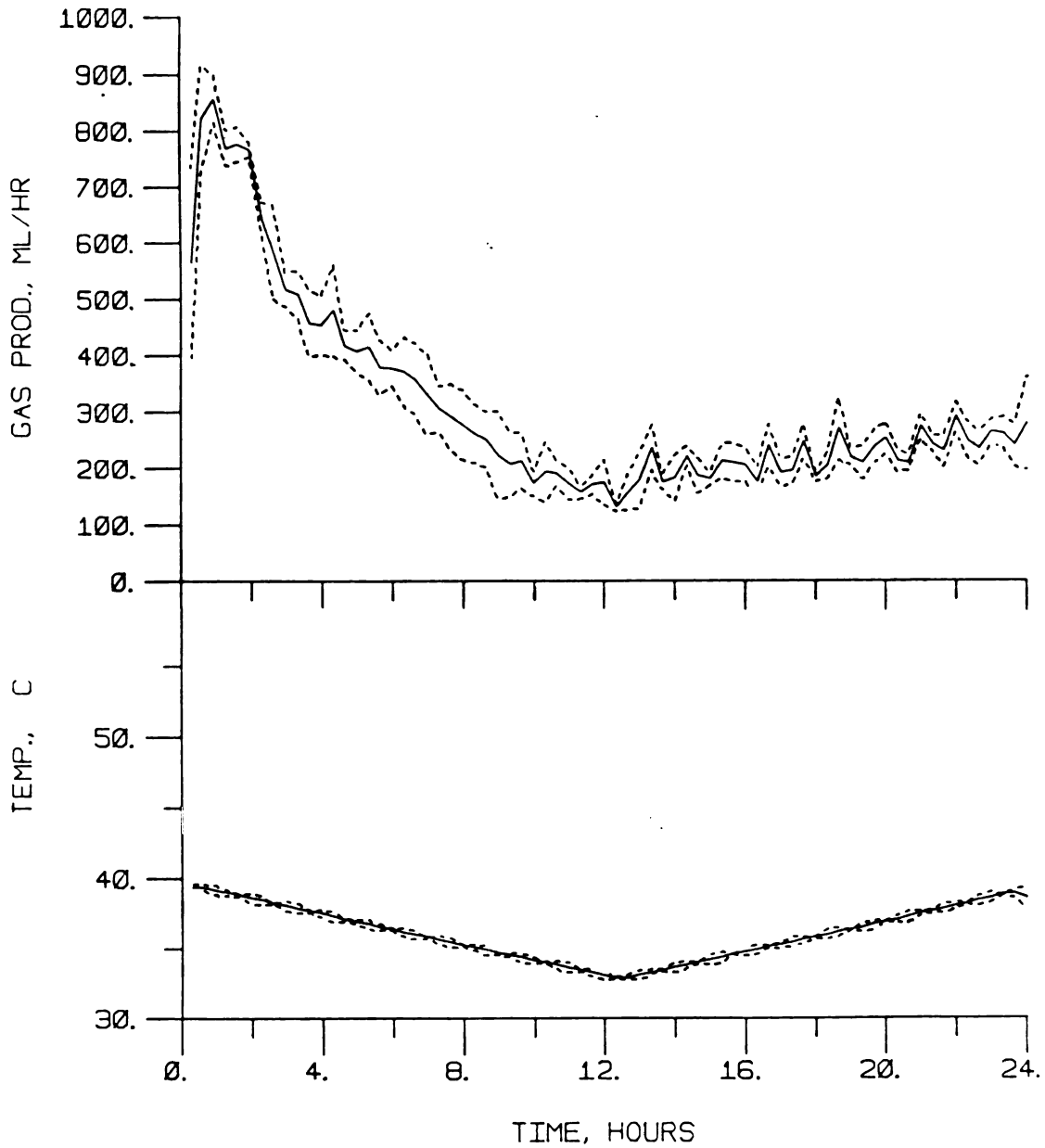


FIGURE 5-12. Mean Gas Production and Temperature During the Stable Period of Experiment IIC. Dashed lines are the 99% confidence intervals on the mean (t test, n = 6).

Control Digester

Within one and a half hours after feeding, the gas production rate increased from about 180 ml/hr to the peak of 420 ml/hr. The rate then decreased almost linearly to the end of the feeding cycle.

Experiment IIA

For this experiment, the influent manure was fed at the midpoint of the ascending temperature ramp. Two hours after feeding, the rate of gas production reached a peak of about 650 ml/hr then remained relatively constant for three hours. The rate started to decline shortly before the temperature reached its peak, suggesting that the readily degradable substrate was being depleted. The rate of gas production continued to decline until the minimum temperature was reached at which time gas production was only 85 ml/hr. As the temperature again increased, the gas production rate also increased in a parallel fashion.

Experiment IIB

For this experiment, the digester was fed when the temperature was at a minimum. The gas production reached a peak of 580 ml/hr about one and a half hours after feeding, then declined gradually to about 140 ml/hr at the end of the feeding cycle.

Experiment IIC

In Experiment IIC, the digester was fed when the temperature was at its maximum. The gas production rate reached a peak of 860 ml/hr about one hour after feeding. The gas production soon began to drop sharply until the minimum temperature was reached at which time the

rate was about 150 ml/hr. The rate then slowly increased with the increasing temperature.

3. Comparison of the Bubble Tube and Wet Test Meter Results

To check the accuracy of the bubble counting method of measuring gas, the total daily gas production computed from the bubble counts is plotted in Figure 5-13 together with the wet test meter results for the stable periods. The data from both methods are fairly close, except for the control unit where the wet test meter results were consistently higher than the bubble count values, indicating an error of about 9% in the calibration of the bubble tube for that digester.

4. Substrate Degradation and COD Mass Balance

The substrate degradation during the stable period in terms of total volatile solids and COD reduction is summarized in Table 5-2. The results show that the reduction of COD is about 4% greater than for volatile solids in all cases with the same pattern for both parameters among the four digesters. Particularly interesting is that the variable temperature digesters had consistently greater removal than the constant temperature control. The mean daily gas production data were included in the table to determine the mass balance for the system. The mass balance was done by comparing the measured gas production with the calculated gas equivalent of the COD reduction. The calculation was based on the assumption that the temperature of the gas was at 25°C and 1 atm. during measurement and that the digester gas contained 60% methane. These mass balance calculations show a maximum discrepancy of 15% which could be due to inaccuracies in COD measurement or assumed conversions.

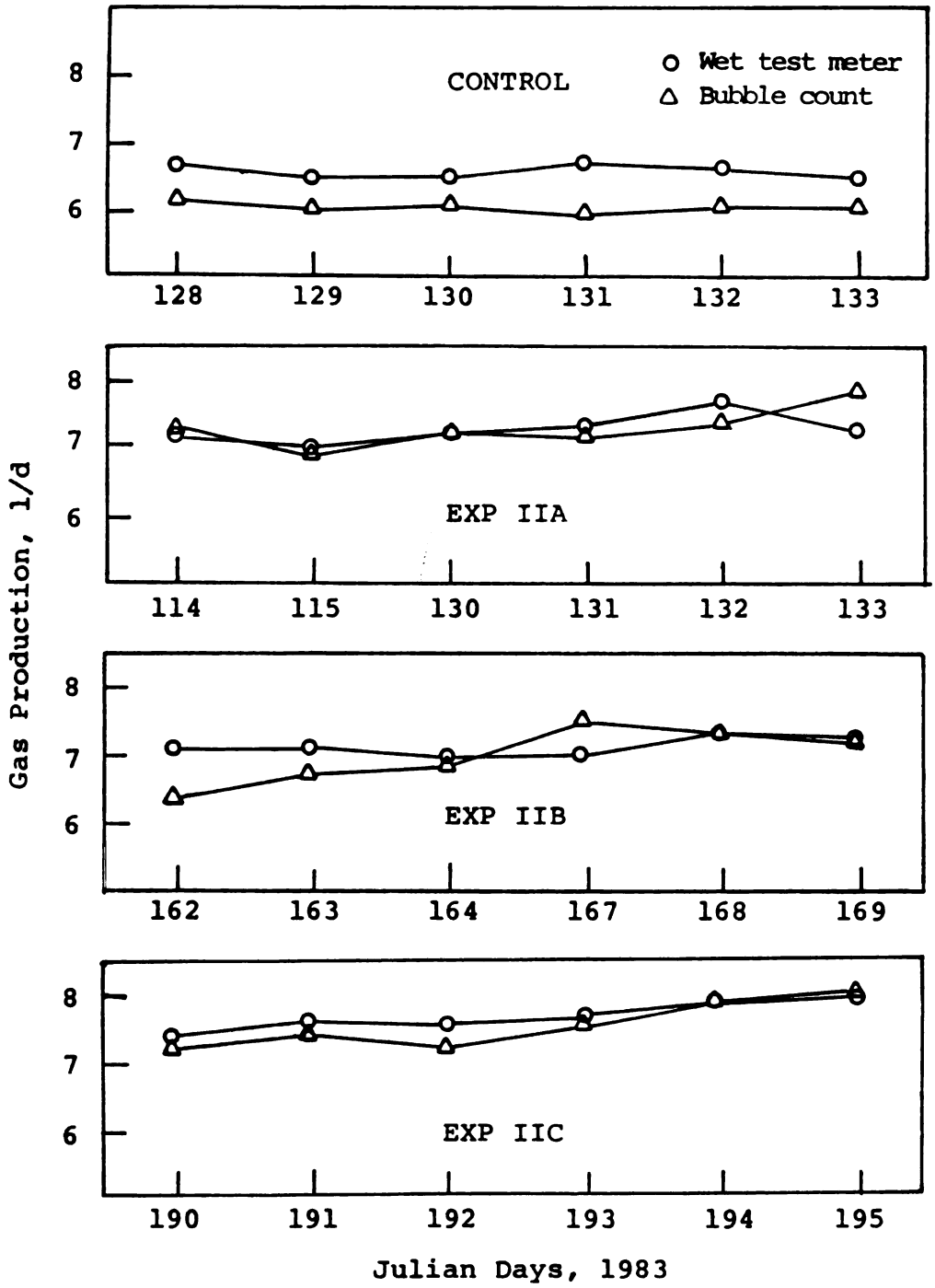


FIGURE 5-13. Comparison of Daily Gas Production During the Stable Period of Experiment II by Bubble Counts and by Wet Test Meter Readings.

TABLE 5-2. Substrate Degradation and COD Mass Balance for Experimental Group II.

Parameter	Inf. g/l	Effluent, g/l Control	Exp IIA	Exp IIB	Exp IIC
TVS, g/l					
Mean	34.4	19.9	16.7	17.7	17.0
S.D.	1.7	0.7	0.4	0.9	0.4
Removal, %		42.2	51.5	48.6	50.6
COD, g/l					
Mean	38.9	20.9	17.2	18.5	17.9
S.D.	2.2	1.8	1.3	1.4	2.2
Removal, %		46.2	55.7	52.5	53.9
COD/TVS	1.13	1.05	1.03	1.04	1.06
Gas Production, l/d					
Wet Test Meter	--	6.57	7.28	7.10	7.67
S.D.	--	0.11	0.25	0.13	0.16
Bubble Count	--	6.05	7.29	7.08	7.52
S.D.	--	0.08	0.33	0.41	0.35
Gas(wet test)/COD	--	1.15	1.06	1.09	1.15
Gas(bubble count)/COD	--	1.06	1.06	1.09	1.13

Gas/COD = ratio of the measured gas to the gas equivalent of COD reduction (0.382 liters of CH_4 at 25°C and 1 atm is equivalent to 1 gram COD assuming the digester gas contains 60% CH_4)

5. Volatile Fatty Acid Dynamics

Fluctuations in the concentration of volatile acids as the result of combined daily pulse feeding and temperature fluctuations are presented in Figures 5-14 to 5-17. In all digesters, acetic acid predominated followed by propionic acid. Butyric and iso-butyric acids had small but measurable concentrations and have been combined in the figures. Higher carbon volatile acids were barely detectable. In all cases the concentrations of volatile acids in the influent manure were higher than those in the digesters so that the volatile acid concentra-

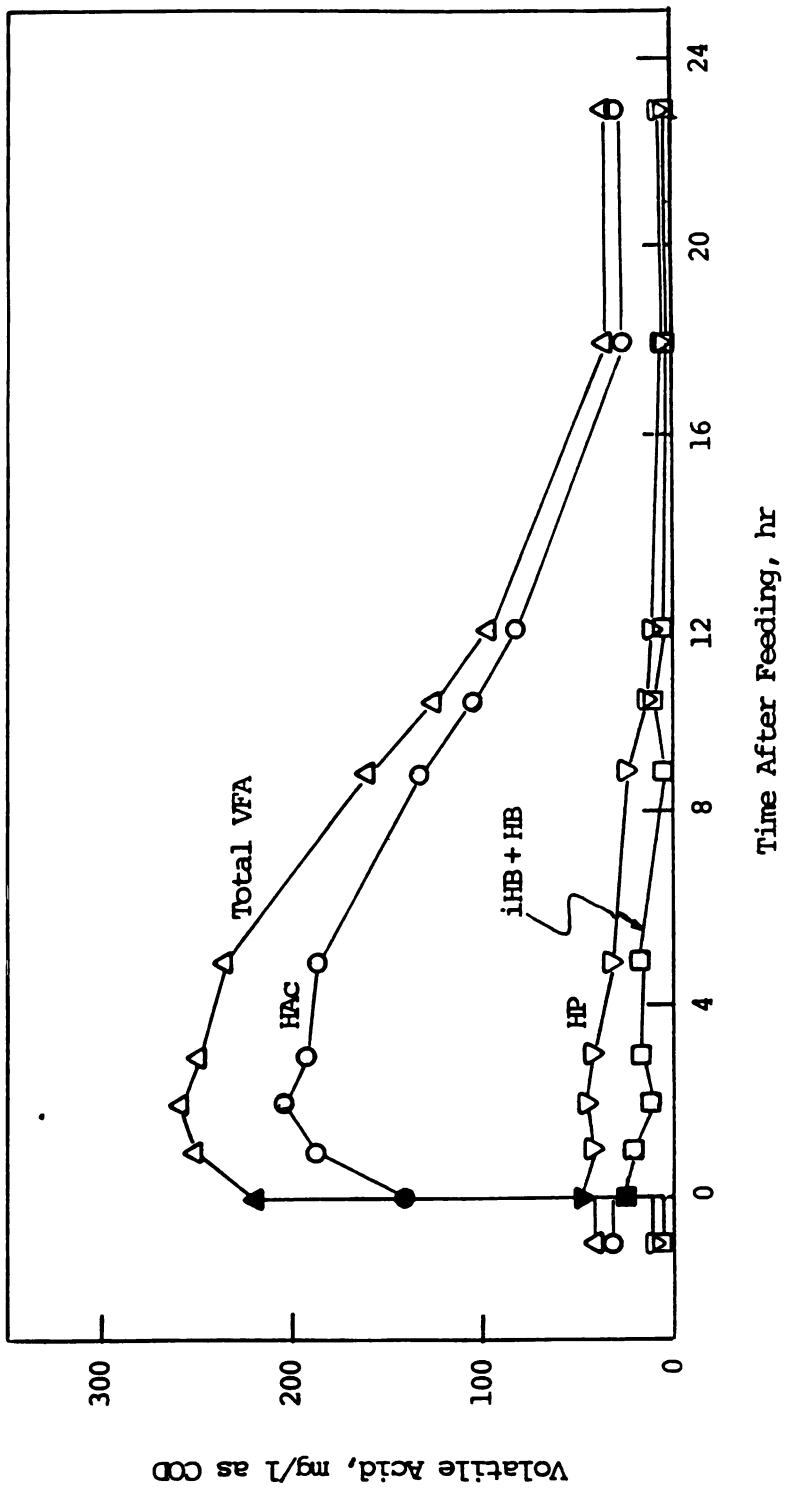


FIGURE 5-14. Individual Volatile Fatty Acid Concentrations During the Stable Period of Experiment II, Control. Solid symbols represent calculated concentratins immediatly following feeding.

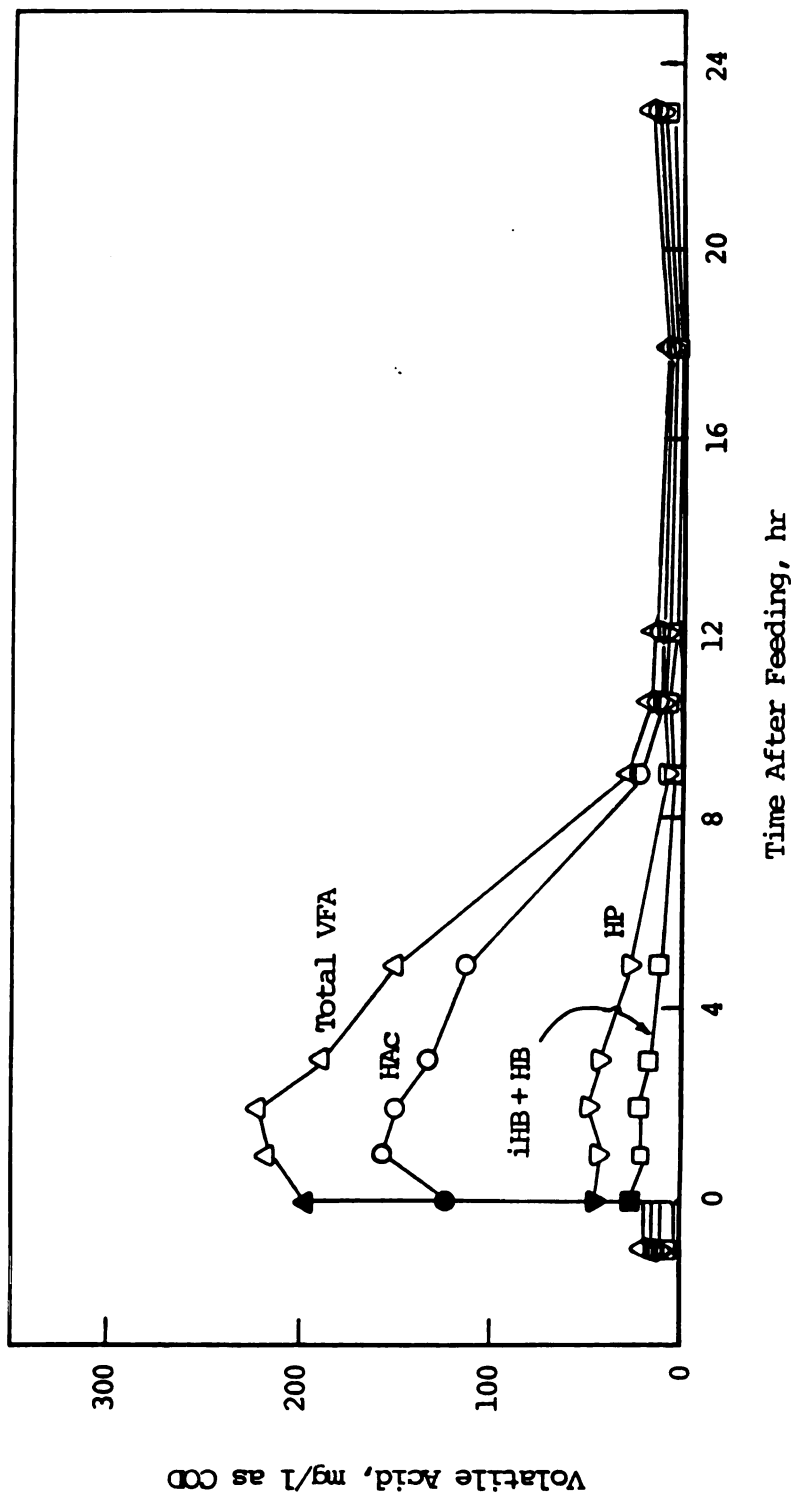


FIGURE 5-15. Individual Volatile Fatty Acid Concentrations During the Stable Period of Experiment IIA. Solid symbols represent calculated concentratins immediatly following feeding.

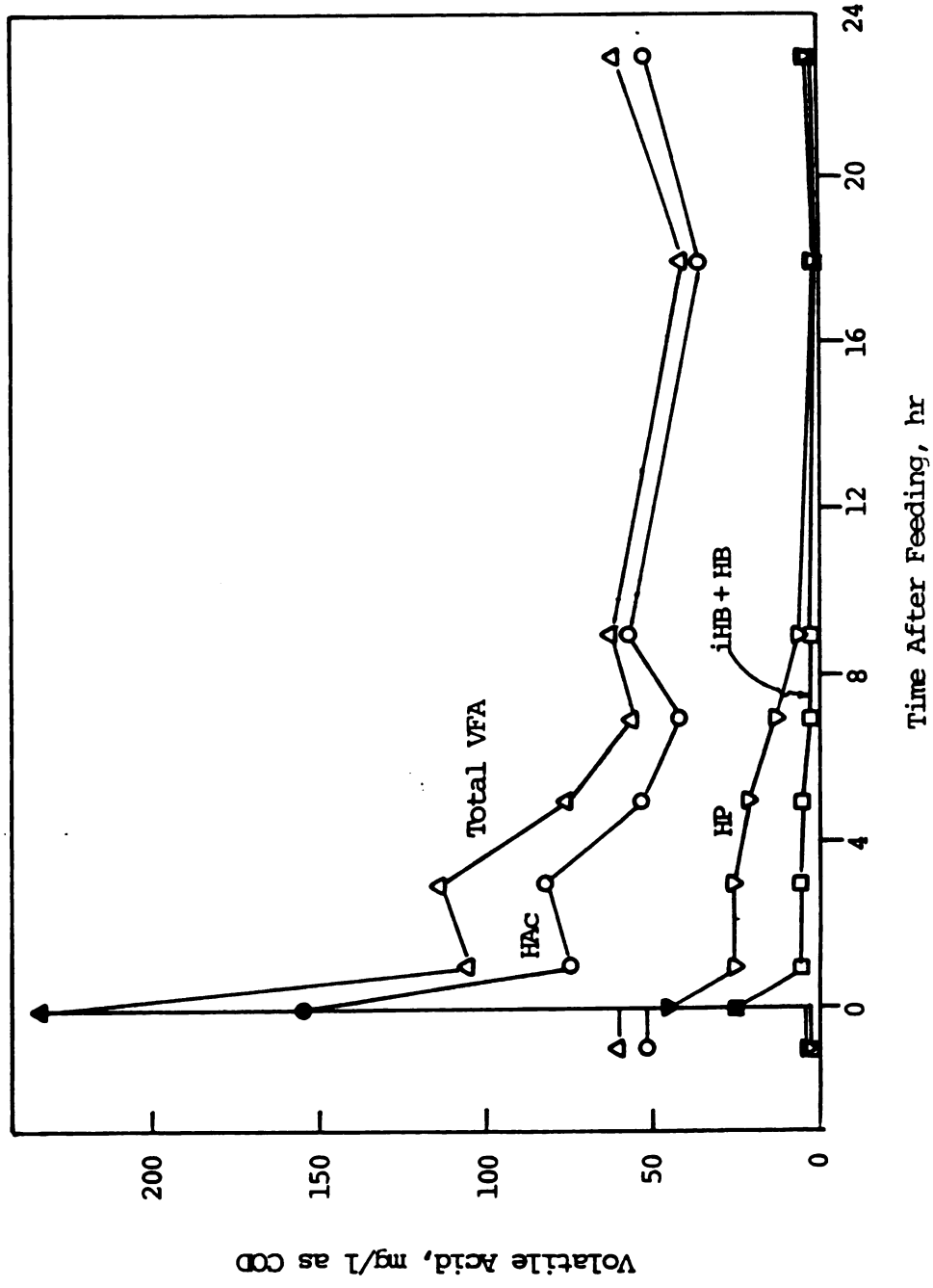


FIGURE 5-16. Individual Volatile Fatty Acid Concentrations During the Stable Period of Experiment IIB. Solid symbols represent calculated concentratins immediatly following feeding.

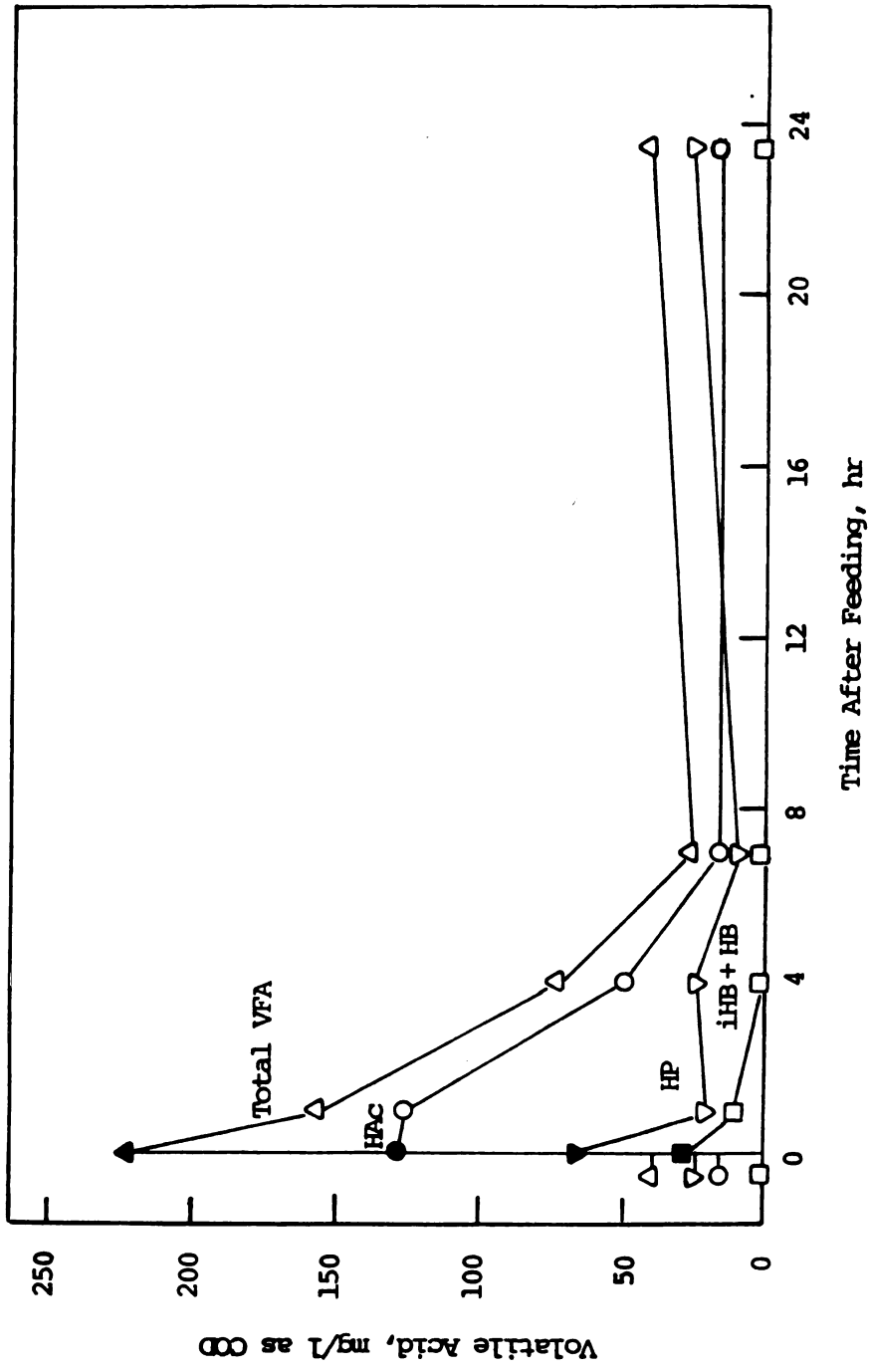


FIGURE 5-17. Individual Volatile Fatty Acid Concentrations During the Controller Malfunction where the Temperature Remained between 37 and 38°C. Solid symbols represent calculated concentrations immediately following feeding.

tion increased sharply as a result of feeding. In each figure, the filled symbols represent the concentrations of acids calculated from mixing the influent manure with the digester contents.

Control Unit

As a result of feeding, acetate increased in the control digester from 31 mg/l to 142 mg/l. Over the next two hours, acetate continued to increase, peaking at 203 mg/l, before declining steadily to the end of the day. After the initial increase due to feeding, propionate and butyrate declined slowly throughtout the day.

Experiment IIA

The pattern of volatile acids in Experiment IIA is very similar to that of the control unit, except that all the individual acids declined faster. At the end of twelve hours all acids were nearly depleted, totaling only 15 mg/l.

Experiment IIB

In Experiment IIB, all volatile acids dropped sharply in the first hour following feeding and all except acetic acid declined over the rest of the daily cycle. The acetic acid showed small increases at several times. Again, butyrate and iso-butyrate were at very low concentrations throughout. The overall level of total volatile acids was generally lower than in the control digester.

Experiment IIC

In Experiment IIC, all volatile acid samples were taken when the digester temperature stayed between 37°C and 38°C due to a faulty temperature controller which was not noticed until after the experiment

was terminated. Therefore, these data show the effect of operating at a constant temperature about 2 to 3 °C higher than normal rather than with a variable temperature. Under these conditions the volatile acid concentrations declined very rapidly in the 8 hours following feeding and remained at low levels for the rest of the cycle.

6. Gas Composition Dynamics

The gas composition data of Experiment II have been normalized to include only methane and carbon dioxide for the same reason described in Experiment I. Figure 5-18 shows the methane content of the digester gas for Control, Experiment IIA and Experiment IIB (Experiment IIC data are not presented due to the faulty temperature controller). The fluctuations of methane content for the three experiments are similar; all have a minimum methane content at about 7 to 8 hours after feeding. Exeriment IIA, however, has twice as much fluctuation as the Control and Experiment IIB. This is due to the fact that a larger amount of gas, 4.6 liters, was produced during the 8 hours after feeding for Experiment IIA than for the Control and Experiment IIB which produced 2.7 and 3.7 liters respectively.

7. pH and Total Alkalinity

Results for pH and alkalinity are plotted in Figure 5-19. The mean pH values for both digesters were almost equal at about 7.45 with a standard deviation of less than 0.1 unit throughout Experiment II. The mean pH of the influent manure was 8.1 with a standard deviation of 0.1. This influent pH was 0.7 unit higher than the influent manure of Experiment I due to stripping CO_2 during blending since the pH of the thawed manure measured before being diluted and blended was 7.4, about

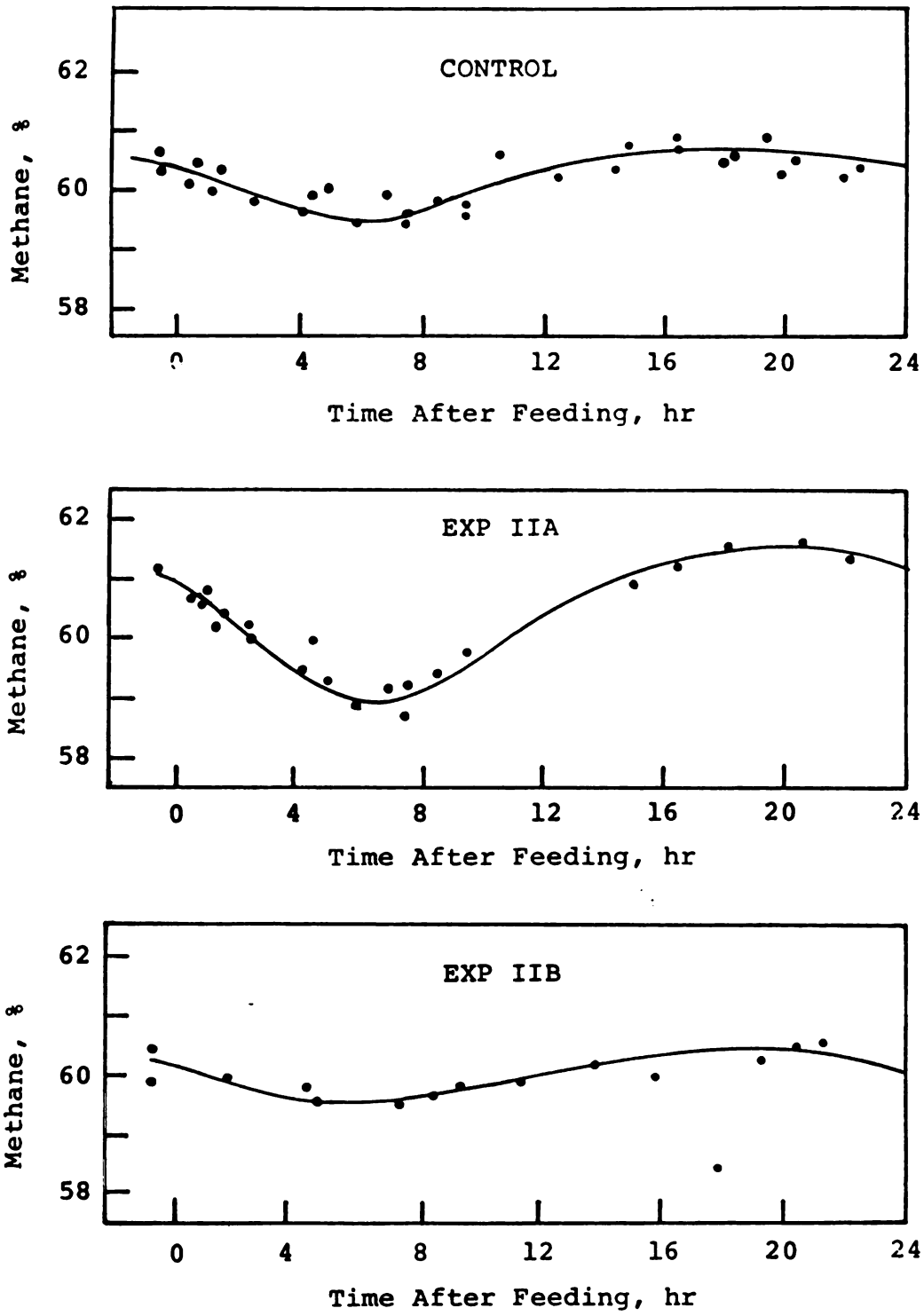


FIGURE 5-18. Methane Content in the Digester Head Space During the Stable Period for Experiment II.

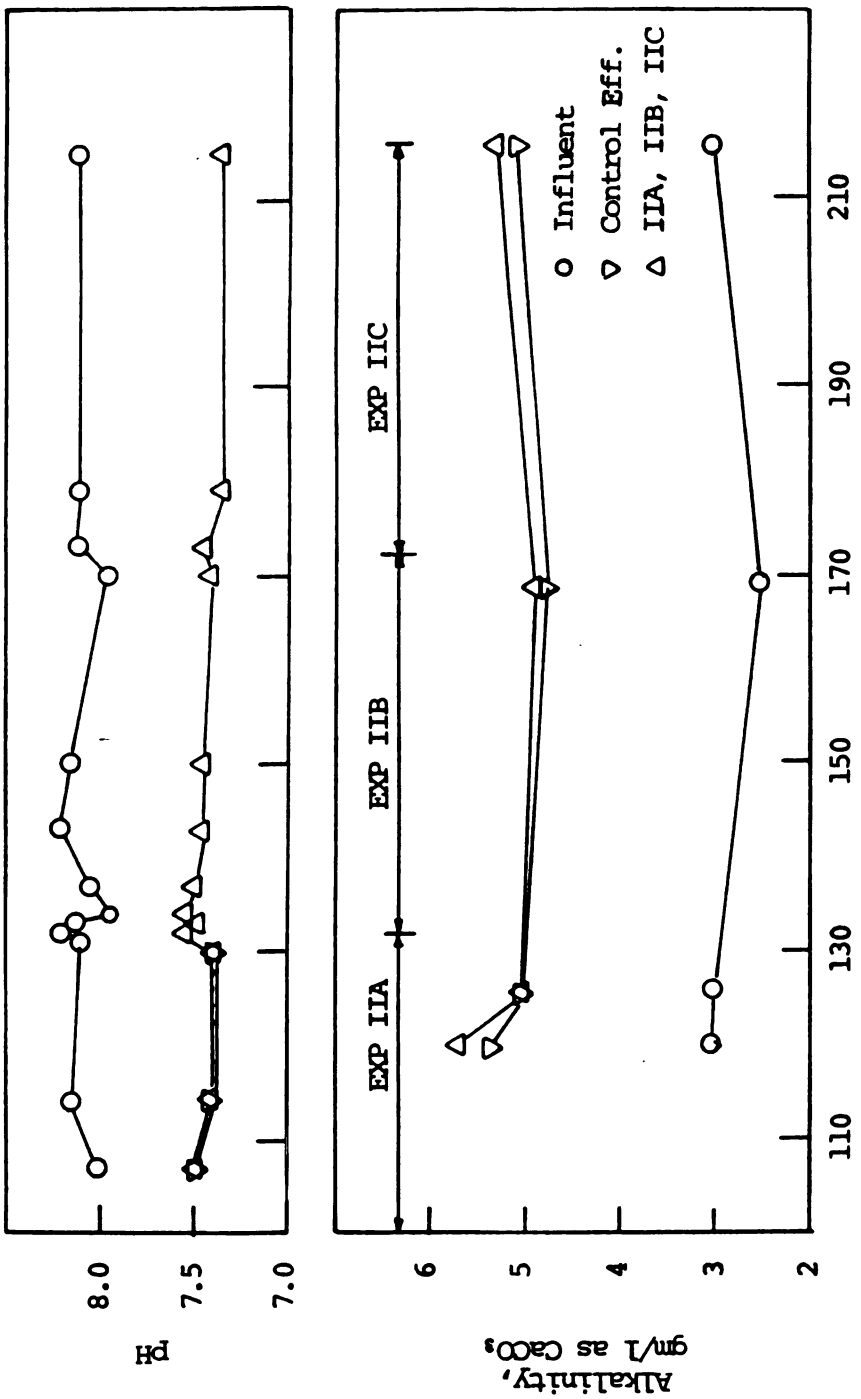


FIGURE 5-19. Total Alkalinity and pH for Experiment II.

the same as the influent manure of Experiment I.

Total average alkalinities of the effluents for both digesters were about 5,000 mg/1 as $CaCO_3$ compared with the influent of about 2,900 mg/1. The total alklinity of Experiment II was about one fourth that of Experiment I which is the dilution ratio for the influent manure.

8. Gas Production during Extended Digester Operation without Feeding

At the end of Experiment IIC, the operation of the digester was extended without feeding. The mixing conditions remained the same and the temperature controller was corrected to the proper Experiment IIC pattern. The data for daily gas production recorded from the wet test meter is shown in Figure 5-20. The pattern for the decline in rate of gas produciton is similar to that of Experiment I.

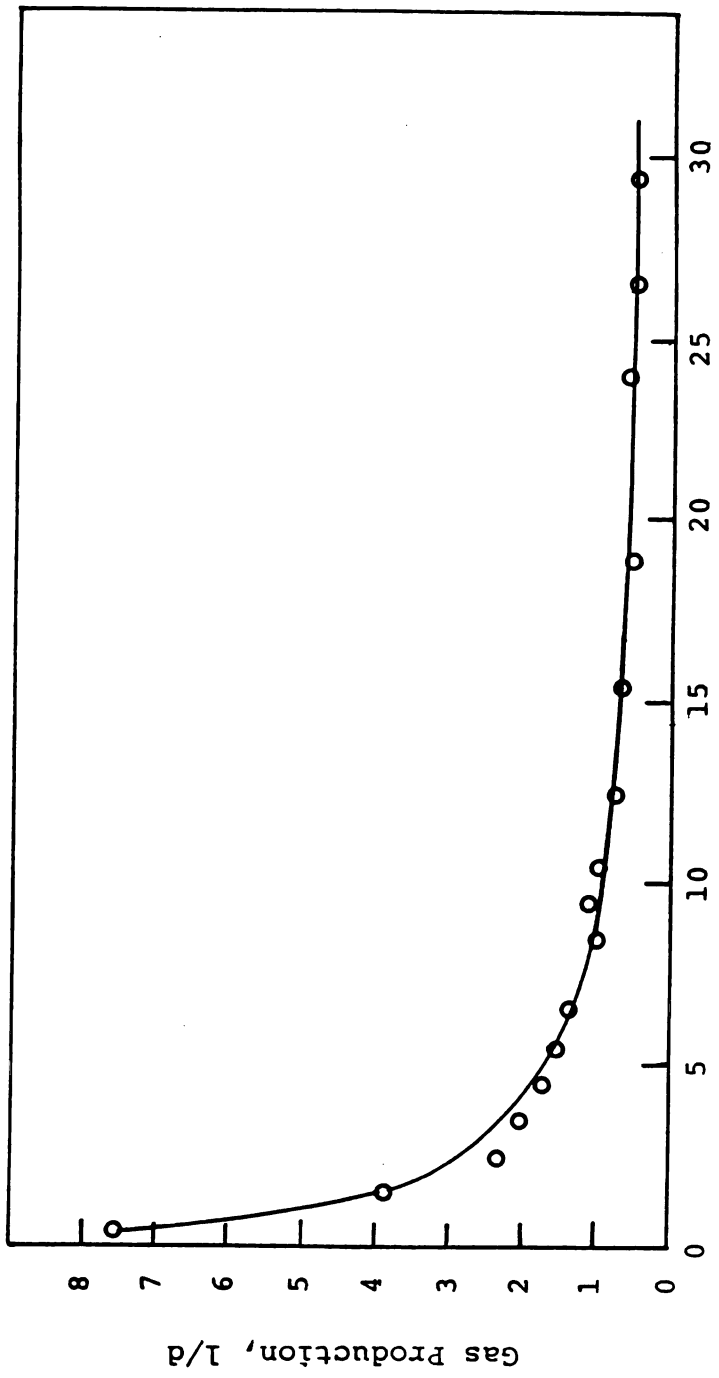


FIGURE 5-20. Gas Production During Extended Digester Operation without Feeding Following Experiment IIC.

VI. MATHEMATICAL MODEL OF GAS PRODUCTION DYNAMICS

The observed gas production dynamics have been presented in Chapters 5. In this chapter, a mathematical model is formulated to describe the effects of pulse feeding and temperature fluctuations on manure digestion. Values for the model parameters were obtained from the constant temperature experiments and the periods of extended operation without feeding. The theoretical results calculated from the mathematical model are graphically related to the experimental data from the other operating conditions.

A. MODEL DEVELOPMENT

For a homogeneous substrate, the rate of reaction depends on the composition of the substrate as well as the temperature and pressure of the system. The rate of reaction of component A may be written as:

$$R_A = f(\text{state of the system})$$
$$= f(\text{temperature, pressure, composition}) \qquad (6\text{-}1)$$

In the digesters being modeled in this investigation the pressure is held constant by the experimental conditions. Thus the reaction becomes:

$$R_A = f(\text{temperature, composition}) \qquad (6\text{-}2)$$

In this investigation we are concerned with the forms of this functional relationship. A general model with constant temperature will be developed first. The Arrhenius law will then be incorporated

into the model when temperature fluctutions are considered. One assumption for this model is that the digester is operated under stable conditions and an active bacterial culture exists.

1. Model for a Daily Pulse Feed Digester at Constant Temperature

Methane production is directly correlated with substrate reduction in terms of chemical oxygen demand (COD). Because the sulfate and nitrate content of the influent manure are insignificant, the only way COD reduction can occur is through the conversion of organic material to methane and carbon dioxide. The initial amount of substrate can therefore be measured in terms of its ultimate gas potential (G^o), the total amount of gas which could be produced from an infinite digestion period. In this model the ultimate gas potential represents the digester contents immediately after feeding rather than the amount of substrate in the feed.

Therefore, knowing the ultimate gas potential (G^o) immediately after feeding and the volume of gas produced, the remaining gas potential (G) in the digester can be calculated by:

$$G = G^o - \int^t R\, dt \qquad (6\text{-}3)$$

where G^o = ultimate gas potential in the digester, liters of gas at 1 atm and 25 °C;

G = gas potential in the digester at time t, liters of gas at 1 atm and 25°C; and

R = rate of gas production, 1/d of gas at 1 atm and 25°C.

Figures 6-1 and 6-2 show semi-log plots for the rate of gas production versus time for the experimental results obtained from extended operation, without feeding, of digsters from Experiment I and IIC respectively. Interestingly, both plots show three approximately linear relationships, suggesting that the substrate in each digester can be approximated by three components, each following first order kinetics as described in the following equation.

$$R_i = K_i G_i \tag{6-4}$$

where K_i = rate constant for component i, d^{-1};

R_i = rate of gas production for component i, 1/d of gas at 1 atm and 25°C; and

G_i = gas potential for component i, liters of gas at 1 atm and 25°C.

The three components can be combined in terms of both rate of gas production and remaining gas potential:

$$R_t = R_1 + R_2 + R_3 \tag{6-5}$$

$$G_t = G_1 + G_2 + G_3 \tag{6-6}$$

where R_1, R_2, R_3 are the rates of gas production from the slow, moderate and fast fractions respectively, 1/d ;

R_t is the total rate of gas produciton, 1/d;

G_1, G_2 and G_3 are the gas potentials of the three substrate fractions, liters; and

G_t is the total gas potential, liters.

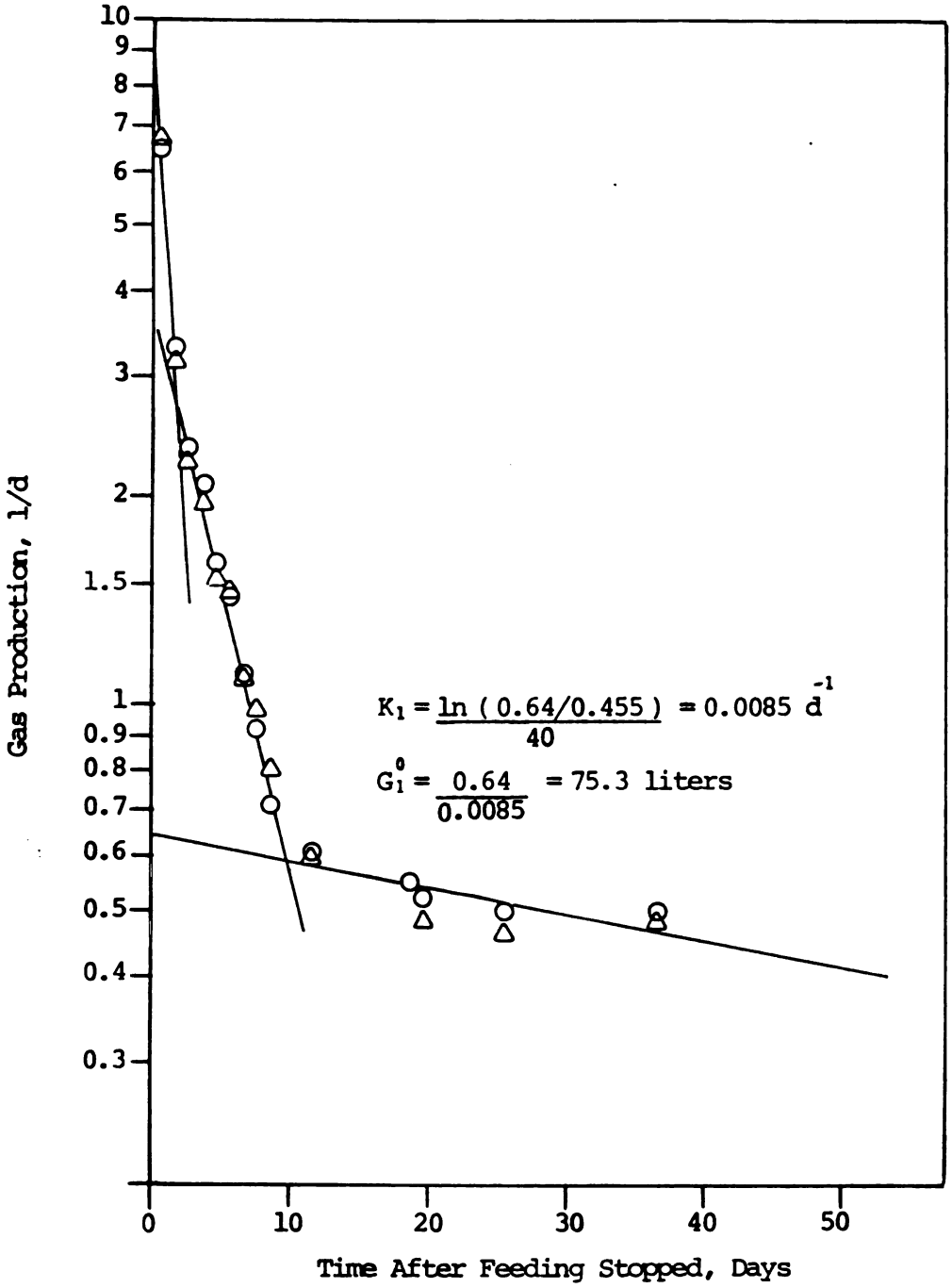


FIGURE 6-1. Graphical Estimation of the First Order Rate Constant and the Initial Gas Potential for the Slow Fraction for Experiment I.

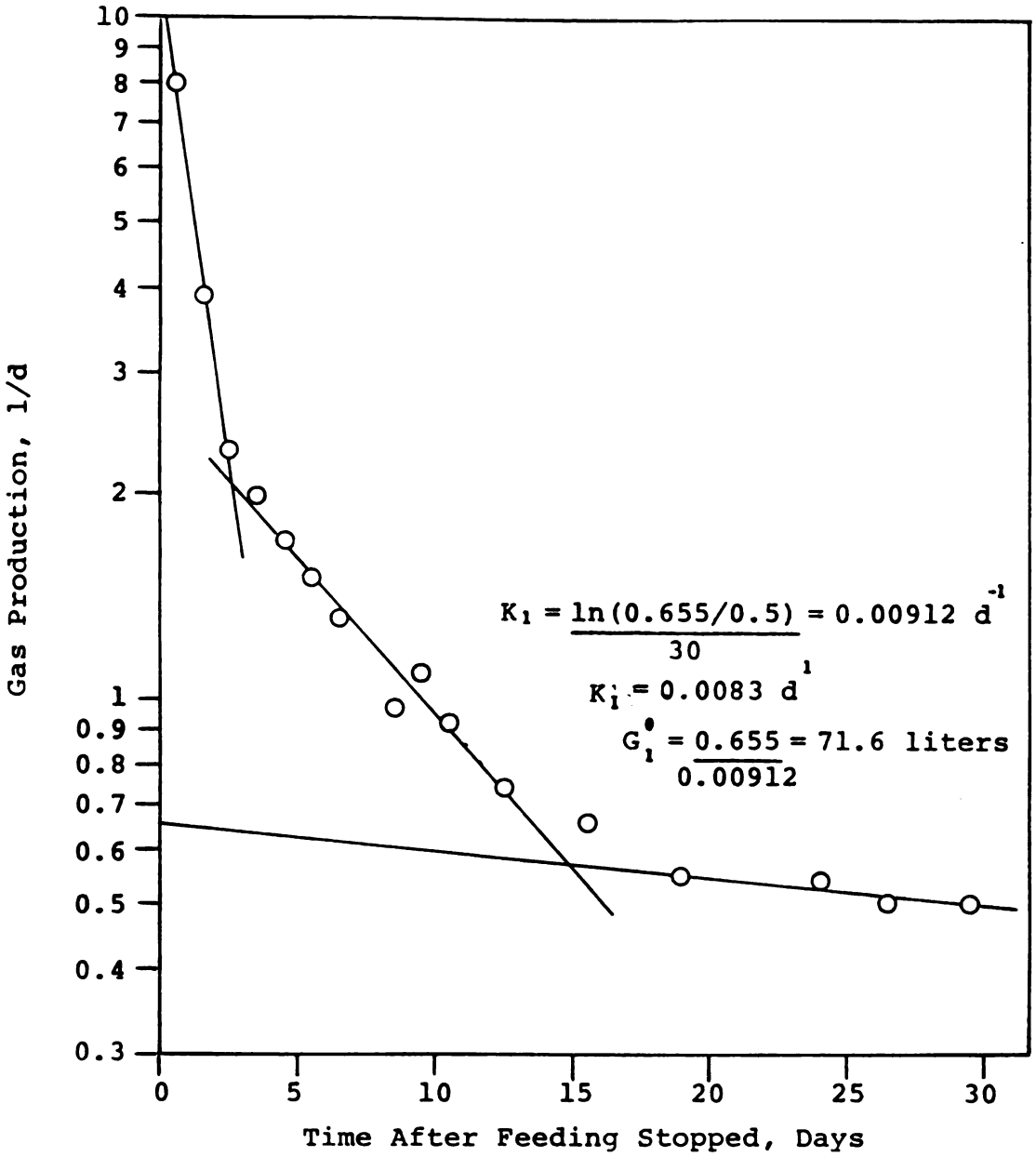


FIGURE 6-2. Graphical Estimation of the First Order Rate Constant and the Initial Gas Potential of the Slow Fraction for Experiment II.

*** K' = effective constant temperature rate constant that gives the same gas production as K gives with variable temperature (K'/K = 1.094).**

Substituting $R_i = - dG_i/dt$ into Equation 6-4 and integrating gives the following equation for a constant temperature digester.

$$G_i = G_i^\circ e^{-K_i t} \tag{6-7}$$

Combining Equations 6-4, 6-5 and 6-7 gives

$$R_t = K_1 G_1^\circ e^{-K_1 t} + K_2 G_2^\circ e^{-K_2 t} + K_3 G_3^\circ e^{-K_3 t} \tag{6-8}$$

For Experiment I, K_1 and G_1° were obtained from the lowest part of the curve in Figure 6-1 where $R_t = R_1$ since R_2 and R_3 are approximately zero due to substrate depletion. The slope is $-K_1$ and the intercept is $R_1^\circ = K_1 G_1^\circ$ from which G_1° can be determined.

The parameters, K_2 and G_2° were obtained by plotting $R_2 = R_t - R_1$ (Figure 6-3a) where $R_1 = K_1 G_1^\circ e^{-K_1 t}$. Then, the slope is $-K_2$ and the intercept is $K_2 G_2^\circ$. In a similar manner, K_3 and G_3° were obtained from Figure 6-3b by calculating $R_3 = R_t - R_1 - R_2$. The data and calculations involved are presented in Appendices C1 and C2. The results are summarized in Table 6-1.

Values for these kinetics parameters for Experiment II were similarly obtained from Figures 6-2 and 6-4. The data for the moderate and slow fractions came from the extended operation of Experiment IIC without feeding. The values for K_1 and K_2 obtained from Figures 6-2 and 6-4a were divided by a correction factor of 1.094 to account for the effect of the temperature cycle as described in Appendix D and then normalized to a reference temperature of 35.8°C. The data for the fast fraction came from the mean value of the stable period for the control digester. The data and calculations involved are presented in Appendices C3 and C4. The results are included in Table 6-1.

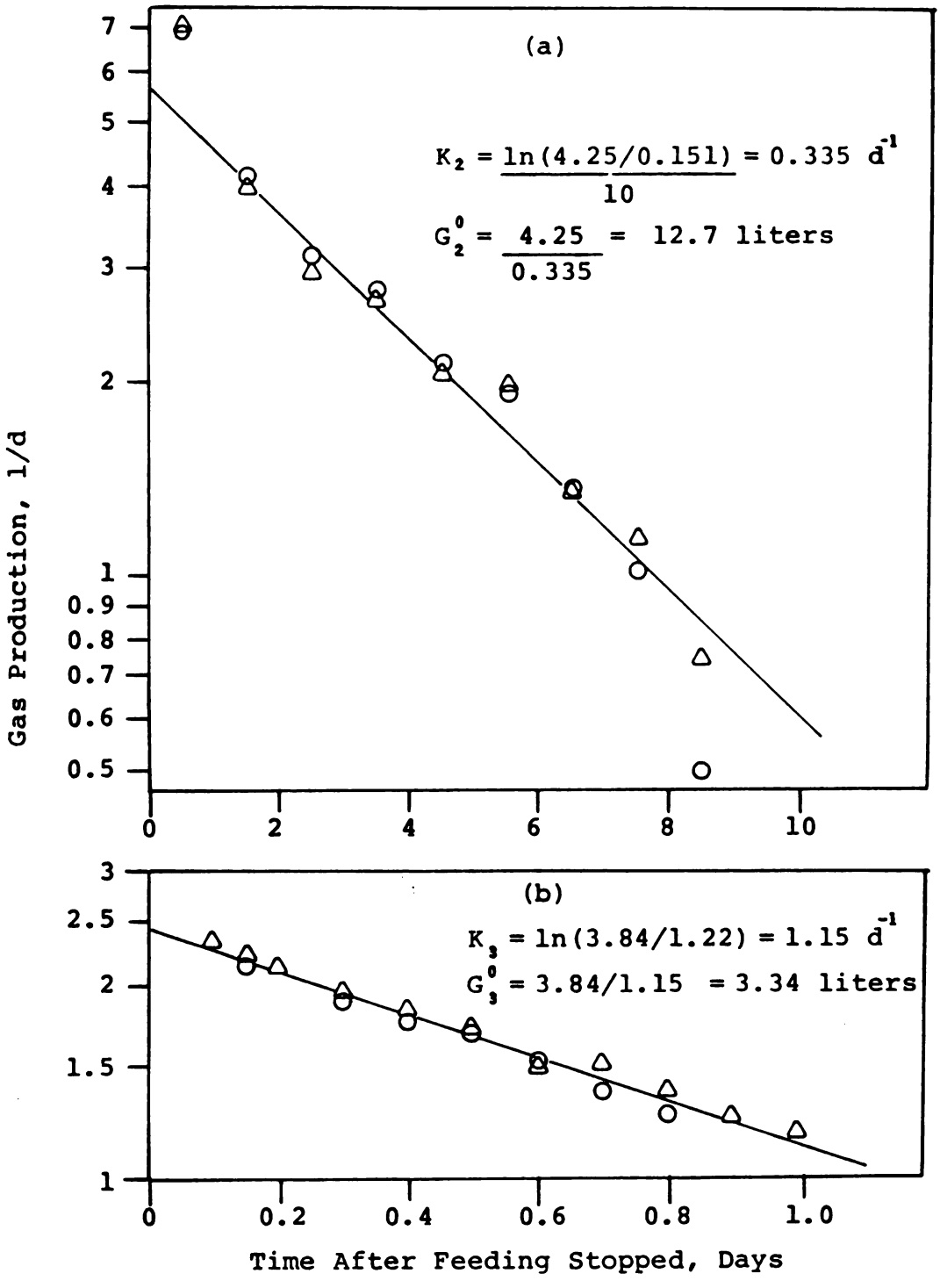


FIGURE 6-3. Graphical Estimation of the First Order Rate Constants and Intial Gas Potentials of (a) the Moderate and (b) the Fast Fractions for Experiment I.

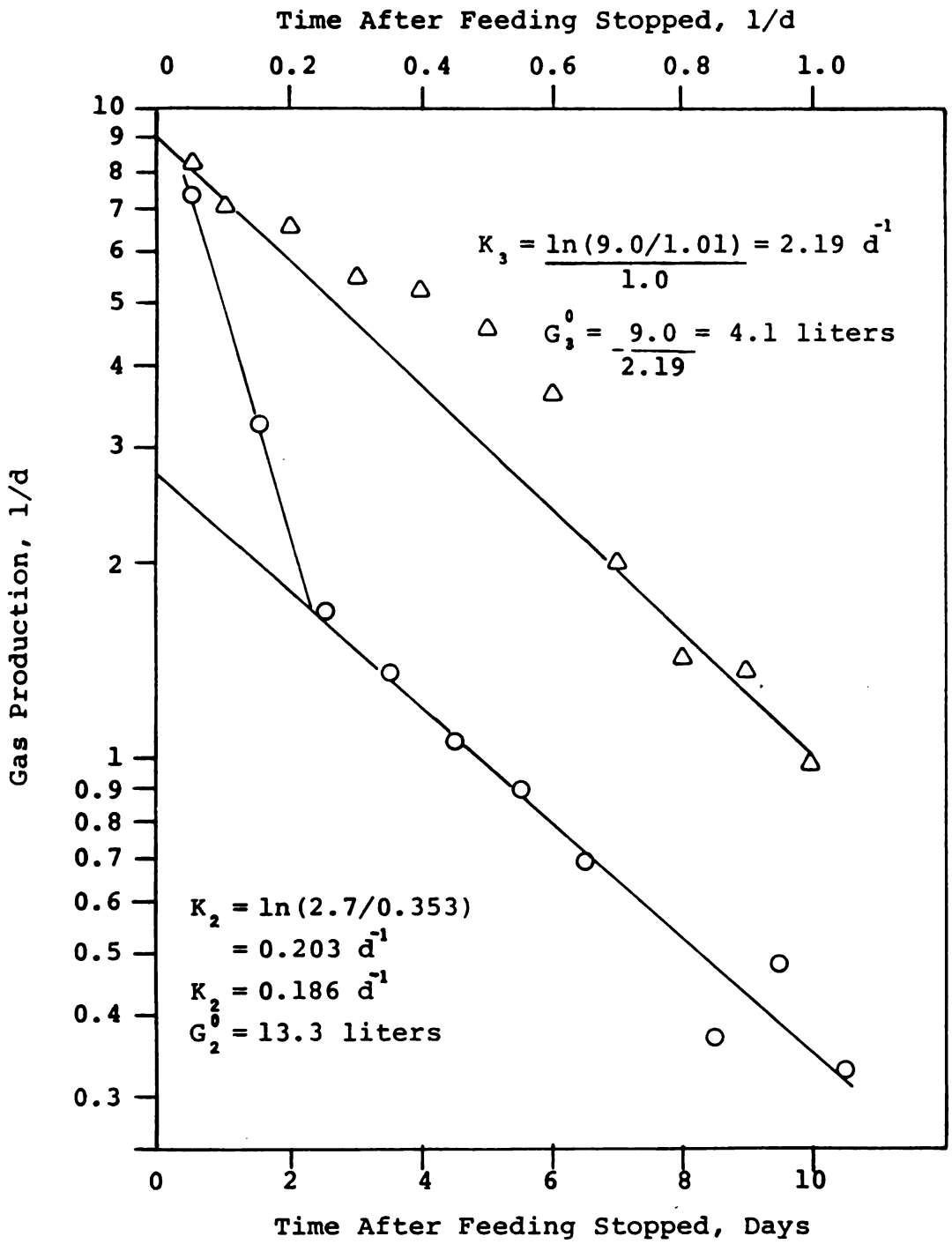


FIGURE 6-4. Graphical Estimation of the First Order Rate Constants and Initial was Potential of (a) the Moderate and (b) the Fast Fraction for Experiment II.

TABLE 6-1. Summary of Estimated Parameters for Mathematic Model (Normalized to wet test meter and constant temperature basis).

Parameters	Experiment I	Experiment II
T_r, °C	36.4	35.8
K_1, d^{-1}	0.0085	0.0075
K_2, d^{-1}	0.335	0.168
K_3, d^{-1}	1.15	2.19
G_1^o, liters	75.3	71.6
G_2^o, liters	12.7	13.3
G_3^o, liters	3.3	4.1
G_t^o, liters	91.3	89.0
$\theta_1 = \theta_2 = \theta_3$	1.25	1.25

To apply the model, R_t is plotted as a function of time using Equation 6-8. The model is compared with the experimental data in Figure 6-5 for Experiment I and Figure 6-6 for Experiment II Control. The solid lines represent the means of the observed data while the dashed lines represent the predicted gas production rates. The areas under the curves between each line represent the gas production accounted for by each fraction of the substrate.

2. <u>The Model with Temperature Variations</u>

Variations in reaction rate as a function of temperature can generally be represented by the Arrhenius equation:

$$K = A_o e^{E/RT} \qquad (6\text{-}9)$$

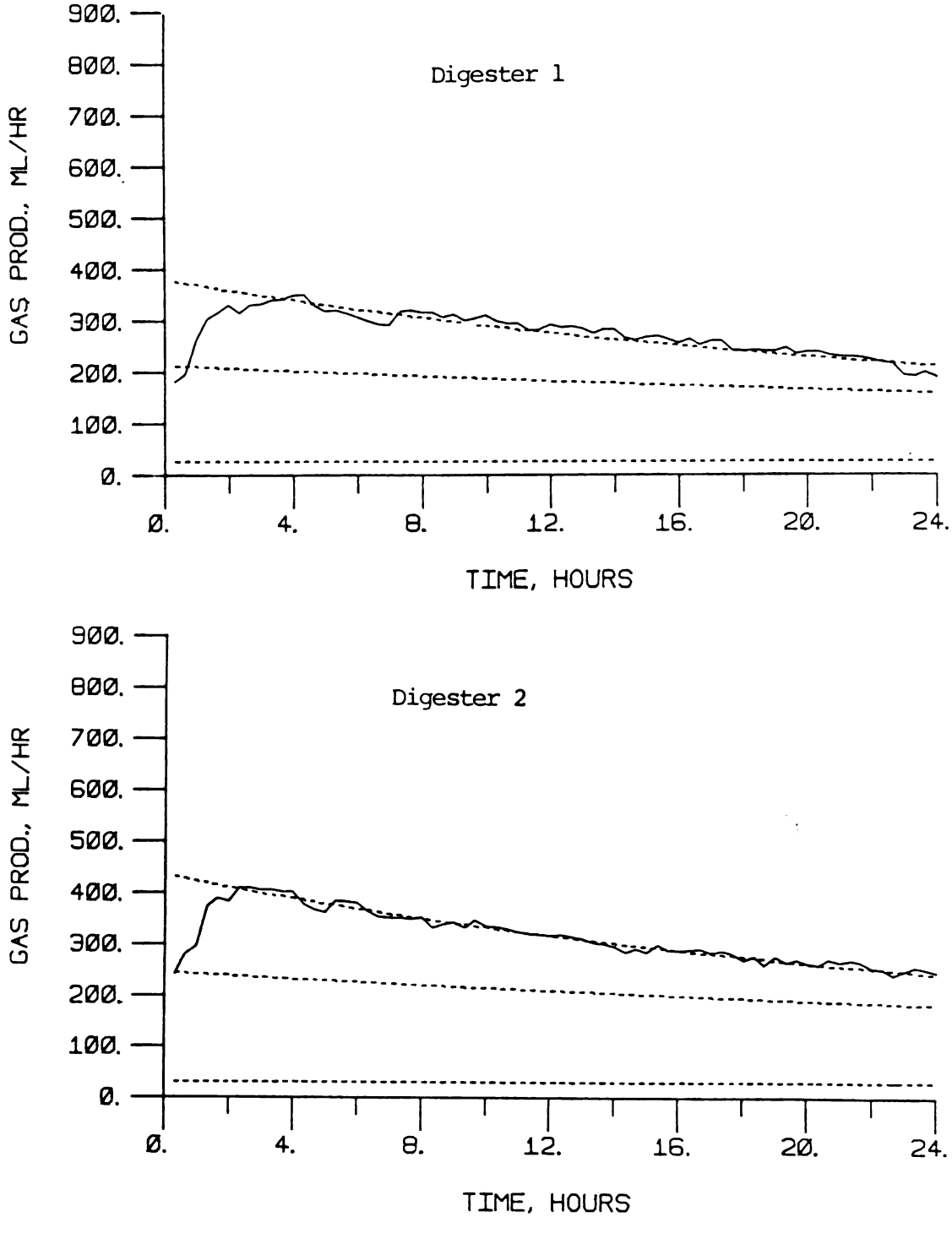


FIGURE 6-5. Comparison Between Model Results and Observed Data for Experiment I, (a) Digester 1 and (b) Digester 2.

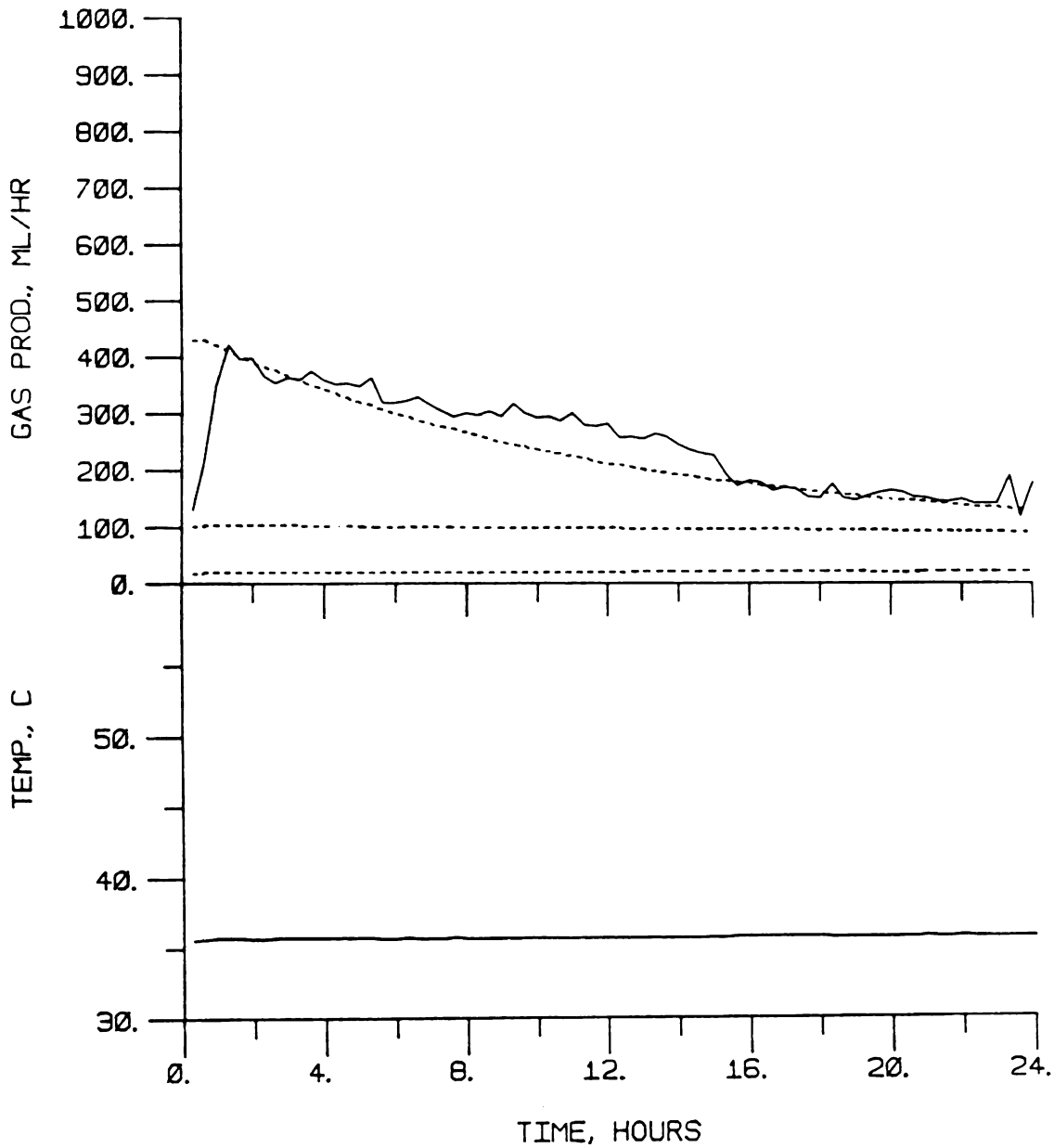


FIGURE 6-6. Comparison Between Model Results and Observed Data for Experiment II, Control.

or, in logarithmic form

$$\ln K = \ln A_e - E/RT \qquad (6\text{-}10)$$

where K = rate constant;

A_e = Arrhenius frequency factor;

E = Activation energy;

R = universal gas constant; and

T = the absolute temperature.

Strictly, the Arrhenius equation is applicable only to either a single stage reaction or to multistage raction in which the first step is rate determining (Weber, 1972).

The energy of activation, E, determines the fraction of the total number of molecules which are suffficiently activated at a given temperature to undergo reaction. The magnitude of E is therefore a direct determinant of the rate of a particular chemical reaction. The larger the value of E, the more the reaction is affeted by temperature.

When Equation 6-10 is evaluated against a reference temperature (T_r, K^r), the resulting expression is

$$\ln K/K^r = E(T-T_r)/RTT_r \qquad (6\text{-}11)$$

$$\text{or } K = K^r\theta^{T-T_r} \qquad (6\text{-}12)$$

Where θ is e^{E/RTT_r}. In Equation 6-12, T and T_r may be expressed as celsius temperature rather than absolute temperature because the difference is the same in each case.

Equation 6-4 now becomes:

$$R_i = K_i^r\ \theta^{T-T_r}\ G_i \qquad (6\text{-}13)$$

Where G_i must be evaluated by substituting Equation 6-13 into Equation 6-3. The result is

$$G_i = G_i^\circ - \int_\circ^t K_i^T \, \theta^{T-T_r} \, G_i \, dt \qquad (6\text{-}14)$$

in which T varies with time. For computational purposes this is written in finite difference form:

$$G_{i,t+\Delta t} = G_i^\circ - \sum_\circ^t K_i^T \, \theta^{T-T_r} \, G_{i,t} \, \Delta t \qquad (6\text{-}15)$$

The overall gas production rate is still given by Equation 6-5.

The model depends heavily on the value of the temperature coefficient, θ, which was estimated from the extended period following the last feeding of Experiment IIC with the same temperature cycle continued. For each day a value of θ was estimated from the ratio for the maximum to minimum gas production rates. These values were then averaged to give a mean θ of 1.25 with a standard deviation of 0.02 (n=7).

B. COMPARISON OF VARIABLE TEMPERATURE MODEL TO EXPERIMENTAL DATA

To compare the model results with the observed data the numerical integration procedure was incorporated into a FORTRAN program (Appendix C5) and executed on a DEC PDP-11/23 computer using a Δt of 5 minutes and the actual temperature data (Figures 5-10 to 5-12) observed for Experimental Group II. The results are shown in Figures 6-7 to 6-9 and discussed in the next chapter.

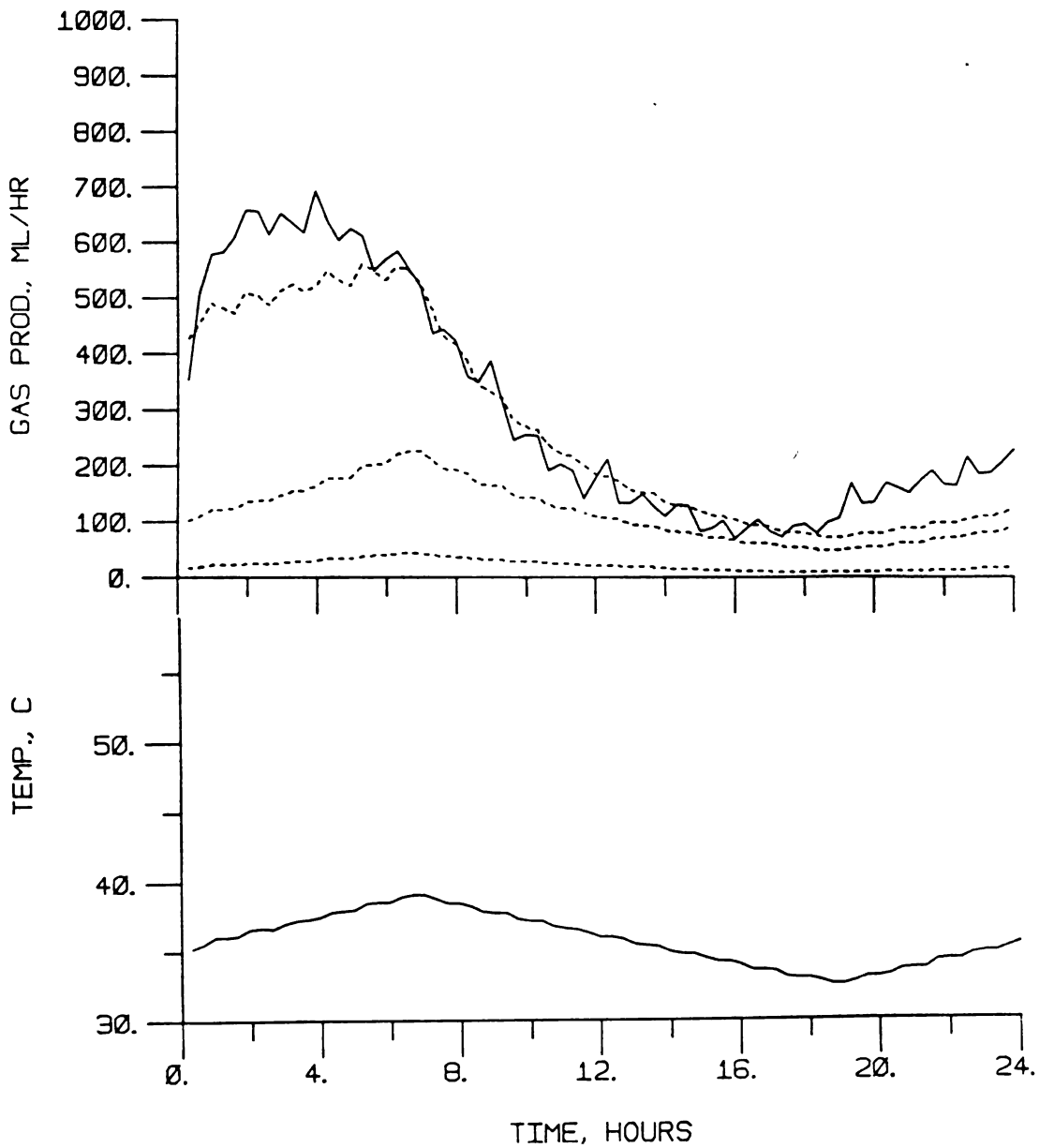


FIGURE 6-7. Comparison Between Model Results and Observed Data for Experiment IIA.

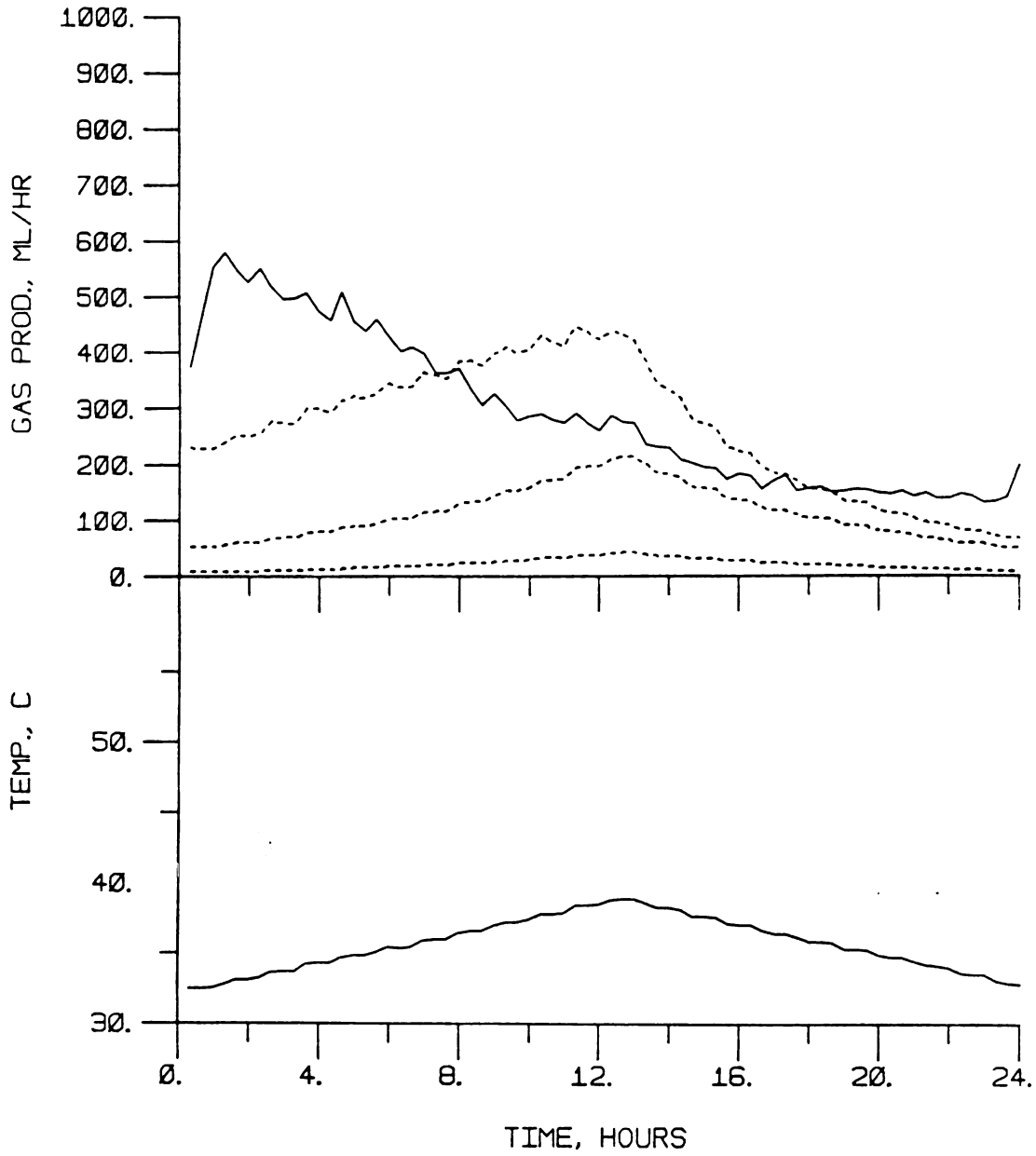


FIGURE 6-8. Comparison Between Model Results and Observed Data for Experiment IIB.

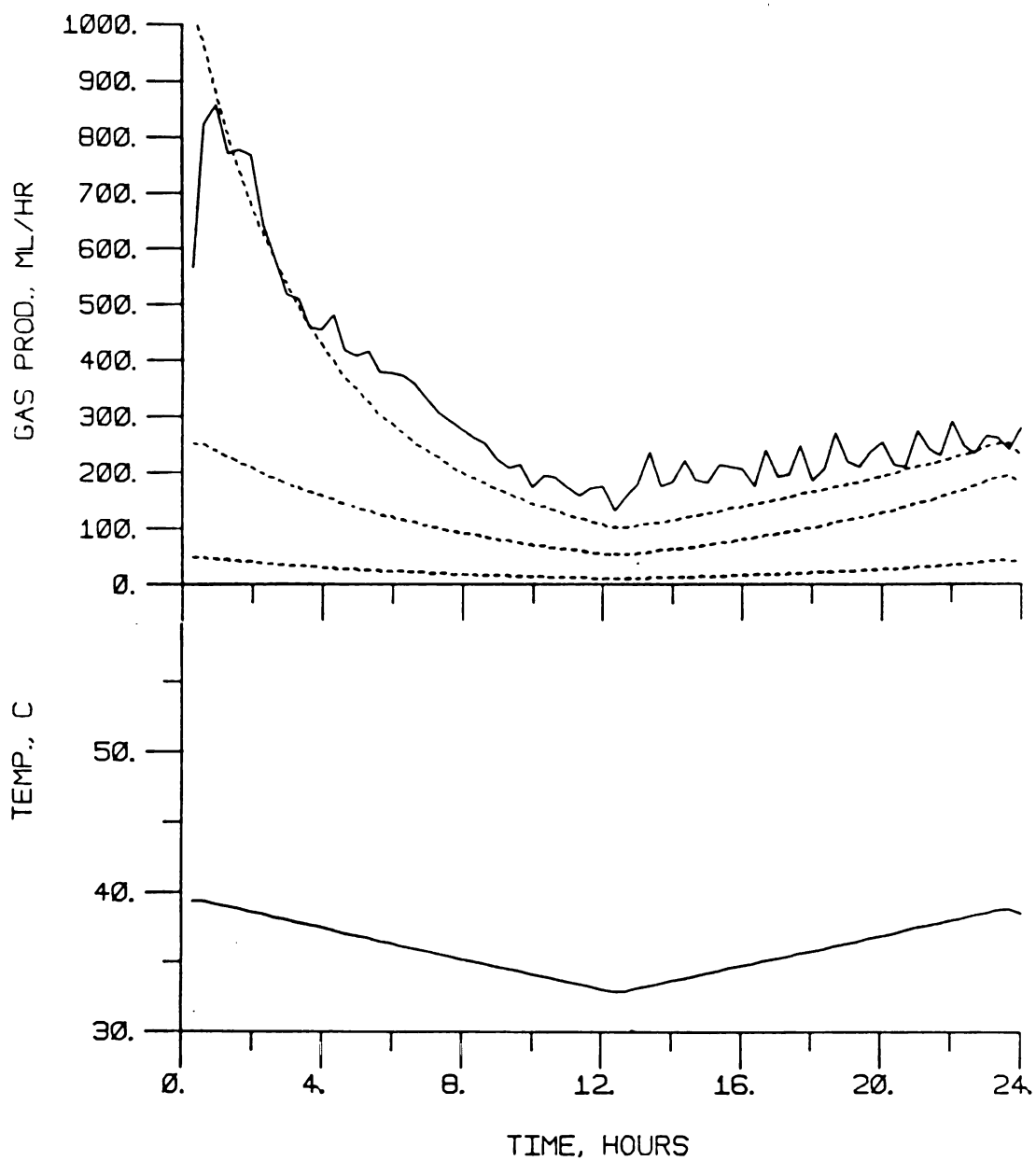


FIGURE 6-9. Comparison Between Model Results and Observed Data for Experiment IIC.

VII. DISCUSSION OF THE RESULTS

The discussion of the experimental results is organized around the following topics 1) evaluation of effects of the daily pulse feeding and temperature fluctuations on digester stability; 2) determination of the amplitude and timing of the 24 hour gas production cycle as a result of daily pulse feeding alone and combined with the temperature fluctuation cycle; 3) determination of the rate limiting step of the overall methane production process; and 4) comparison of total gas production between the constant and fluctuating temperature digesters.

A. DIGESTER STABILITY

Information obtained from this investigation indicates that a daily pulse feed digester, with or without small temperature fluctuations, can be operated with considerable stability. The stability can be evaluated by three different parameters: 1) constancy of daily gas production; 2) volatile acid pool size and its fluctuations; and 3) stability of pH and alkalinity.

1. Constancy of Daily Gas Production

For each of the experiments, the daily gas production, measured using the wet test meter, showed a high degree of constancy following the initial transition period during start up or following a phase shift. For Experiment I, using full strength manure at constant temperature, the data were recorded after the digesters had been operated for four, 15-day detention times. The 30 days of recorded data (Figure 5-1) show a standard deviation of less than 6 percent of the

mean for both digesters. The control digester for Experiment II (25% dilution, constant temperature) showed a standard deviation of only 2.6% of the mean over the 45-day period (Figure 5-7).

When temperature fluctuations were imposed during Experiments IIA, IIB and IIC, the digesters responded quickly with gas production (Figures 5-7 and 5-8) remaining generally stable except during periods when the temperature increased due to controller malfunction. At those times the gas production increased significantly but returned to normal when the temperature returned to the proper pattern. This indicates that there was no imbalance between the various groups of anaerobic bacteria.

2. Volatile Acids as an Indicator of Stability

For all experiments, the overall level of volatile acids was stable. The imposed temperature fluctuations did not cause any imbalance in the acid pool from day to day. In all cases, the volatile acid pool increased sharply following feeding due to high concentrations in the influent manure, then declined toward the end of the feeding cycle indicating that acid removal was faster than its formation.

In Experiment I, the concentration of total volatile acids in the influent was about 16,700 mg/l as COD. Following feeding, the total volatile acid pool was about 3,500 mg/l, declining to 2,600 mg/l at the end of the cycle (Figure 5-3). The data from both digesters during the two day sampling period were nearly identical, indicating the ability of the digester to remove the high concentrations of volatile acid in the influent manure without causing an imbalance.

The propionic acid in Experiment I, however, remained constant at

the relatively high levels of 2,000 and 1,700 mg/l as COD for Digesters 1 and 2 respectively. While the persistency of the propionic acid in Experiment I has not been explained, it was found for all the experiments conducted later with a 25% diluted influent manure and a 19-day detention time that propionic acid was nearly depleted at the end of the cycle. Therefore, it can be suggested that the propionic acid may be reduced by operating at a higher detention time and/or by diluting the influent manure. In spite of the high level of propionate in Experiment I, no sign of imbalance in volatile acids has been observed.

For Experiments IIA, IIB and IIC, where the digesters were imposed with temeprature variations, the results of the volatile acid pool fluctuations were much the same as for the control (constant temperature). In general, the overall levels for total acids were less than in the control digester. For all cases in Experiment II, the concentration of total volatile acids in the influent was about 3,700 mg/l as COD. Following feeding, the acid pool sizes were about 200 to 240 mg/l, declining to only 60 mg/l or lower depending on the experiment. These very low concentrations of total volatile acids at the end of the feeding cycle demonstrated that the overall daily acid removal was faster than its formation. In no case did volatile acid pools increase over the daily cycle.

3. Stability of pH and Alkalinity

In all digesters, the effluent pH and alkalinity remained constant over the entire experimental period. Furthermore the average effluent pH for Experiment I was within ± 0.3 pH unit of that for Experiment II. The total alkalinity in the effluent was approximately proportional to

the influent manure strength, having values of 18,000 mg/l as $CaCO_3$ for Experiment I and 5,000 mg/l for Experiment II. This high buffer capacity ensured that the pH did not change detectably during feeding.

4. Summary

The stability of the daily pulse feed digesters with or without temperature fluctuation has been discussed. The data for daily gas production, volatile acid pool, pH and alkalinity throughout this investigation demonstrated that the proposed operating conditions are perfectly feasible in terms of digester stability.

B. GAS PRODUCTION DYNAMICS

The experimental results showed that the rate of gas production varied greatly as a result of either daily pulse feeding or fluctuating temperature. In addition, the pattern of gas production can be controlled to a large extent by phase relationship between the feeding and temperature cycles. This section will first discuss the effects of daily pulse feeding and temperature variation separately. The combined effect will then be examined.

The influent manure contains a wide variety of substrates having different rates of degradation. As shown in the previous chapter, the manure used in this study can be approximately divided into three component groups on the basis of degradation rate. Data for these fractions, labeled slow, moderate and fast for covenience, are summarized in Table 7-1. The initial gas potential has been divided by the digester volume to normalize the data.

TABLE 7-1. Estimated Kinetic Parameters for the Three Substrate Fractions.

Parameter	Fast	Moderate	Slow
Experiment I			
Rate Constant (K) at 36.4°C, d^{-1}	1.15	0.335	0.0085
Initial Gas Potential (G^0), 1 gas/l digester	1.5	5.6	33.5
Experiment II			
Rate Constant (K) at 35.8°C, d^{-1}	2.19	0.168	0.0075
Initial Gas Potential (G^0), 1 gas/l digester	0.43	1.40	7.54

1. Daily Pulse Feeding Effect

In a constant temperature digester, the decline in gas production throughout the day due to pulse feeding results from the removal of substrate since the rate constants are not affected. Thus, most of the decline in gas production is caused by the removal of the fast fraction followed, to a lesser extent, by removal of the moderate fraction. The rate of degradation of the slow fraction is so low that gas production is unaffected by its removal within one day. These effects are clearly demonstated in Figures 6-5 in which the ordinate between each dotted line represents the rate of gas production for each fraction as calculated from the mathematical model.

The percentage of the total gas production contributed by each fraction at any time is determined by the product of the amount of that fraction present and the rate constant. The initial concentration of substrate at the beginning of the day is determined by the proportional

TABLE 7-2. Calculated Feed Concentrations of Substrate Fractions.

Removal	Detention Time (θ), d	Gas Potential, 1 gas/1 digester: Initial G° (t=0)	Effluent G (t=24hrs)	Feed Conc.*	%
Experiment I					
Fast Fraction	15	1.5	0.47	15.5	97
Moderate Fraction	15	5.6	4.0	28.3	86
Slow Fraction	15	33.5	33.2	37.3	11
Total	--	40.6	37.7	81.1	54
Experiment II					
Fast Fraction	19	0.43	0.05	7.3	99
Moderate Fraction	19	1.40	1.2	5.2	77
Slow Fraction	19	7.54	7.5	8.6	13
Total	--	9.37	8.75	21.1	59

* Feed Conc. = $\theta G^{\circ} - (\theta-1)G$

mixing of the feed manure with the digester contents. Thus a component which is rapidly degraded will have a low concentration in the reactor although its concentration in the feed may be high. This is illustrated in Table 7-2 in which the feed concentrations of each substrate fraction are calculated from the mass balance equation. The percentage removals of each fraction are also shown in the table.

A comparison of Experiment I with the Control of Experiment II shows significant differences in the fast and moderate fractions but not the slow fraction. In both experiments the slow fraction was largest; the difference in absolute magnitude is due to the four-to-one dilution of the feed manure in Experiment II. The fast fraction, however, was proportionally higher in Experiment II while the moderate

fraction was lower. It is suggested that these differences were caused by blending the manure when it was diluted so that particle size decreased and cell tissue was broken up. The increase in the rate constant for the fast material and decrease in the constant for the moderate material (Table 7-1) is also believed to be the result of blending the manure.

The effect of the changes caused by blending was to decrease the contribution of the moderate fraction and increase the contribution of the fast fraction to the overall gas production rate for Experiment II Control compared with Experiment I. Also, the higher rate constant of the fast fraction in Experiment II resulted in a more rapid decline in gas production during the daily cycle.

2. Temperature Variation Effect

Throughout the experimental program there were several indications that the rate of gas production responds rapidly to temperature changes. Whenever the temperature controller malfunctioned resulting in a sudden increase or decrease in temperature of a few degrees, the gas production rate also increased or decreased immediately and dramatically. When the temperature returned to normal, the gas production did also. Another piece of evidence showing the effect of temperature variation on gas production came at the end of Experiment IIC when the digester continued to operate with the same temperature fluctuation but without additional feeding. The gas production over the next 7 days closely matched the temperature cycle imposed on the digester. From this period of extended operation, the temperature coefficient (θ) was estimated as 1.25 corresponding to an Arrhenius activation energy of

42.5 kcal/degree Kelvin.

3. Combined Effect of Feeding and Temperature

As shown in Figures 5-10 to 5-12, imposing a temperature fluctuation of only ± 3.3 degrees celsius about the mean caused major changes in the magnitude and timing of the peak gas production resulting from daily pulse feeding. These changes can be largely explained by the mathematical model developed in Chapter 6. The discussion in this section will focus on each of the three phase relationships between the temperature cycle and the pulse feeding, discribing the resulting pattern of gas production in relationship to the model and explaining some of the descrepencies which remain. This information can then be used to develop strategies to provide better utilization of biogas by matching the gas production pattern to the energy needs of the farm.

Experiment IIA

In Experiment IIA (Figure 6-7), the calculated results from the model show that, following feeding, the rate of gas production continued to rise slightly for several hours until the temperature reached its peak. During this period, the increase in the overall rate is contributed largely by the moderate fraction (R_2), in spite of its lower rate constant. This is because the increase in rate due to rising temperature outweighs the effect of substrate removal which is relatively small with respect to its pool size. The rate of gas production contributed by the fast fraction (R_3) remained relatively constant during the period of increasing temperature since the increase in the constant was offset by depletion of substrate. When the temperature began to fall gas production from the fast fraction declined most rapidly fol-

lowed by the moderate and the slow fractions respectively. This can be explained similarly by the relative effects of the temperature and the change in individual substrate pool sizes.

The model results for this experiment match the experimental data fairly well, expecially in the important trends. Deviations from the experimental data occurred only in the first and last four hours when the model predictions were slightly low. In the last four hours the higher slope of the experimental data indicates a stronger temperature dependency than used in the model.

The gas production pattern of Experiment IIA demonstrates that it is possible to obtain high sustained gas produciton over an eight hour working day by heating the digester at a rate sufficient to balance the substrate removal effect. Allowing the digester to cool off for the remaining 16 hours would conserve energy during this time. Total gas storage requirements would be substantially reduced in this case.

Experiment IIC

The model results for Experiment IIC (Figure 6-9) match the experimental data very well. Following feeding, the gas production rate is maximum because both the temperature and the substrate concentrations are highest. The rate of gas production, however, stays at this peak for only a short time because both the temperature and the amount of the fast substrate fraction are decreasing simultaneously.

Although the gas production pattern during the first twelve hours is dominated by the decline of the fast fraction (R_3), the increase in gas production during the last twelve hours is due to the moderate fraction (R_2). The only significant deviation of the model predictions

from the experimental data occurred in the middle of the cycle when the predicted rate dropped too low. This observation and the lower slope for the experimental data during the period of increasing temperature indicate a slightly lower temperature dependency than used in the model, opposite to the observation from Experiment IIA.

The gas production pattern of Experiment IIC might be useful in cases when a large amount of gas is needed for a short period of time. In practice this pattern might be achieved by heating the feed material to a temperature higher than the digester prior to pulse feeding it. The digester could then be allowed to cool down gradually over the remainder of the cycle to keep gas production low when it isn't needed, reducing storage requirements.

Experiment IIB

In Experiment IIB the results predicted by the model do not fit the experimental data well as shown in Figure 6-8. As will be explained below, it is beleived that this is largely due to formulating the model entirely around the hydrolysis of particulates and ignoring the volatile acid pool.

The model predicts slowly increasing gas production caused by the moderate fraction (R_2) since the amount of the fast fraction is decreasing while the temperature is increasing as happened in Experiment IIA. The predicted gas production peaks at the same time as the temperature and then falls off rapidly as temperature decreases. The experimental results show a peak soon after feeding followed by decreasing gas production throughout the remaining period.

It is suggested that the discrepancy between the predicted and

observed results is due to changes in the acetic acid pool size which were not incorporated into the model. As shown in Figure 5-16, the acetic acid concentration was high immediately following feeding but decreased rapidly over the first few hours. The gas equivalent of the volatile acids removed in the first six hours is 1.07 liters which is close to the 1.25 liter discrepancy between the actual and predicted gas production during this time. Since the model includes the volatile acids in the fast fraction but does not include a separate degradation term, removal of these acids during the first 6 hours means they are not available for removal later. Thus, the actual gas production rate is lower than predicted by 0.94 liter during the middle eight hours.

The explanation of this phenomenon is based on the observations of Stafford et al. (1980) that methane production is appoximately proportional to acetic acid concentrations up to about 2,000 mg/l. Thus, the high acid concentration following feeding caused high methane production rates and hence high acetate removal rates. These high acetate removal rates could not be balanced by hydrolysis due to the low temperature. This effect was offset in Experiment IIA and IIC by the higher rate of hydrolysis at the higher initial temperatures and did not affect the results.

C. THE RATE LIMITING STEP

The experimental results obtained in this investigation combined with literature information indicate that hydrolysis of particulate substrates is the rate limiting step in the overall anaerobic digestion process. The principal evidence for this statement comes from the variation in volatile acid concentration over the feeding cycle (Figures

5-3 and 5-14 to 5-17). After an initial increase in acid concentration due to feeding, the volatile acid pools declined throughout the remainder of the day. Thus volatile acid removal by methane production was faster than volatile acid production by hydrolysis and fermentation.

The conclusion that hydrolysis of particulate substrate is the rate limiting step in manure digestion is supported by other investigations working with dairy manure (Jewell et al., 1980) and municipal sludge (Eastman and Ferguson, 1977). Furthermore, Eastman and Ferguson showed that fermentation of soluble hydolysis products was much faster than the hydrolysis process itself. This observation has also been assumed to hold in this investigation.

Although the basic pattern of volatile acid decline was true for all experiments, the rate and extent of the decline varied for each experiment. In general, both the rate and extent of volatile acid decline was faster in the variable temperature experiments than in the constant temperature experiments. In addition, the pattern of volatile acid decline, especially for acetic acid, roughly approximates the decline in gas production for each experiment.

The similarity in pattern between the acetic acid pool size and the gas production makes sense when the role of acetic acid is examined. When the acetic acid pool size is constant, the rate of methane production must equal, and be controlled by, the rate of hydrolysis and fermentation. Also Stafford et al. (1980) showed that, up to about 2,000 mg/l, the rate of methane production is approximately proportional to the acetic acid concentration. This indicates that the acetic acid pool size in balanced digestion may be largely controlled by the

rate at which acid COD, produced by hydrolysis is being converted to methane.

Knowledge of the rate limiting step provides improved understanding of digester kinetics. As long as hydrolysis of particulates remains the rate limiting step, the balance between acid formation and acid removal should not be damaged by pulse feeding or by temperature fluctuations. The balance can, however, be upset by pulse feeding of soluble substrates or particulates such as starch which have a very high rate of hydrolysis.

Furthermore, knowing that particulate hydrolysis is the rate limiting step results in considerable simplification in the formulation of the mathematical model because only the first step of the multistage reaction need be considered in most cases.

D. COMPARISON OF TOTAL GAS PRODUCTION BETWEEN THE CONSTANT AND FLUCTUATING TEMPERATURE DIGESTERS

Both the experimental and theoretical results in this study indicate that a fluctuating temperature digester produces more gas than a constant temperature digester operated at the same mean temperature.

The data for daily gas production for Experimental Group II are summarized in Table 7-3. The data measured by the wet test meter show that all the experiments imposed with temperature fluctuations have a higher total daily gas production than the constant temperature control unit by about 8 to 10 percent. For Experiment IIC, the increase in gas production was 17 percent, about half of which is estimated to be caused by the average temperature being 0.4°C higher than for the other units. This estimate assumes a temperature coefficient of 1.25.

TABLE 7-3. Evaluation of Gain in Total Gas Production Due to Temperature Fluctuations.

Parameter	Control	Exp IIA	Exp IIB	Exp IIC
Average Temperature, °C	35.80	35.82	35.77	36.20
TVS Removal, %	42.2	51.5	48.6	50.6
Increase Over Control, %		22	15	20
COD Removal, %	46.2	55.7	52.5	53.9
Increase Over Control, %		21	14	17
Daily Gas Production, l/d				
Wet Test Meter	6.57	7.28	7.10	7.67
Increase Over Control, %		11	8	17
Calculated (Model)	6.27	6.55	6.54	6.32
Increase Over Control, %		4	4	9

The increase in gas production rates are substantiated by the increase in substrate removal both in terms of volatile solids and COD (Table 7-3). In addition, the theoretical results calculated from the mathematical model developed in the previous chapter support the experimental observations in trend if not magnitude. These data suggest that the rate of degradation is non-linear with increasing temperature such that an increased removal at higher temperatures more than offsets decreased removal at lower temepratures resulting in a net gain of gas production for each temperature cycle as compared with the Control. The 9 percent increase calculated for Experiment IIC shows the effect of the higher average temperature as well as the temperature fluctuation in a manner paralleling the wet test meter results.

E. SUMMARY

This discussion can be summarized by relating the information presented above to the objectives stated in Chapter 1.

The first objective was to determine the ability of anaerobic digesters to acclimate to fluctuating temperature without loss in total gas production. Not only was it found that there was no loss in gas production when temperature fluctuations were imposed on the digestion of dairy cow manure, but gas production actually increased about 9%. This result was also predicted by the mathematical model although with a lesser increase.

The second and third objectives were to determine the amplitude and lag time of the 24-hour gas production cycle caused by daily pulse feeding alone and in combination with an imposed temperature fluctuation. This investigation has shown that the amplitude of the gas production cycle can be controlled to a large extent by the phase relationship between the pulse feeding and the temperature ramp. The higher the digester temperature at the time of feeding, the higher is the peak gas production and increasing the temperature after feeding can sustain high gas production until the most readily degradable material is consumed. The phase relationship did not, however, substantially change the timing of the initial large rise in gas production.

The fourth and final objective was to develop a model from the experimental results such that some management strategies can be determined. Such a model has been successfully developed based only on constant temperature experiments and on the periods of extended operation without feeding. The kinetic parameters obtained from these

periods of operation were used to predict the effects of imposed temperature fluctuations. The predicted results corresponded closely to the observed results in two cases. The discrepencies in the third case can be explained by the fact that volatile acid ultilization was not expressly incorporated into the model.

VIII. MANAGEMENT IMPLICATIONS

To minimize the gas storage requirement, feeding and heating of a digester must be scheduled such that the net gas produced during the high demand hours matches that demand. Consequently, a minimum fraction of the daily gas production remains to be stored. In this chapter, various management strategies for the reduction of gas storage will be discussed. Experimental data will be used to demonstrate how a gas storage requirement can be reduced compared to a conventional digester operated with uniform feeding at constant temperature.

To maintain digester temperature or impose a desired temperature fluctuation, energy is required for heating. Energy for heating may come from burning digester gas directly or from utilizing waste heat from productive processes such as electricity generation. In the former case, heating requirements are in competition with productive uses while in the latter case, heating coincides with productive uses. Furthermore, some portion of the heating requirements can be met by heating the influent separately to a temperature higher than that in the digester. The discussion in this chapter will be organized around these considerations.

A. HEATING COMPETITIVE WITH PRODUCTIVE GAS USE

Many productive uses of digester gas consume the gas without the generation of waste heat that can be diverted to digester heating. Examples include boiler operation, space heating and crop drying. In this case, gas storage requirements can be reduced by heating the digester during times when gas is not being productively utilized

and/or by increasing gas production at times when demand is highest.

To illustrate the potential for reduction in gas storage needs through digester management, a hypothetical situation will be examined. In this example, productive gas requirements are uniformly high for an eight hour working day and digester heating requires 25% of the daily gas production. For illustration purposes an idealized case will be considered in which 100% of the gas is used.

For a digester with uniform feeding and heating, the gas production would also be uniform as shown in Figure 8-1a. In this case the storage requirement would be 50% of the total daily gas production.

To illustrate the case of a managed digester, the pattern of Experiment IIA will be used to overlay the gas requirements as shown in Figure 8-1b. The sustained high gas production in this case requires increasing the temperature to offset the reduction of rapidly degradable substrate so the gas requirement for heating is not uniform but is twice as large for the twelve hours beginning at 1 AM dropping to zero at 1 PM. In addition, the pulse feed will be made one hour early, at 7 AM to allow time for gas production to rise by 8 AM. As shown by the area between the curves in Figure 8-1b, the gas storage requirement has been reduced to 24% of the total daily gas production. As an added benefit, the total gas production in this case can be expected to be 5 to 10 percent higher.

A similar analysis can be made for cases in which it is desired to have short periods of very high gas production. In these cases, the pattern of Experiment IIC would be appropriate. The digester should then be heated during the period when gas is not being productively used so that feeding would occur at, or shortly before, the point of

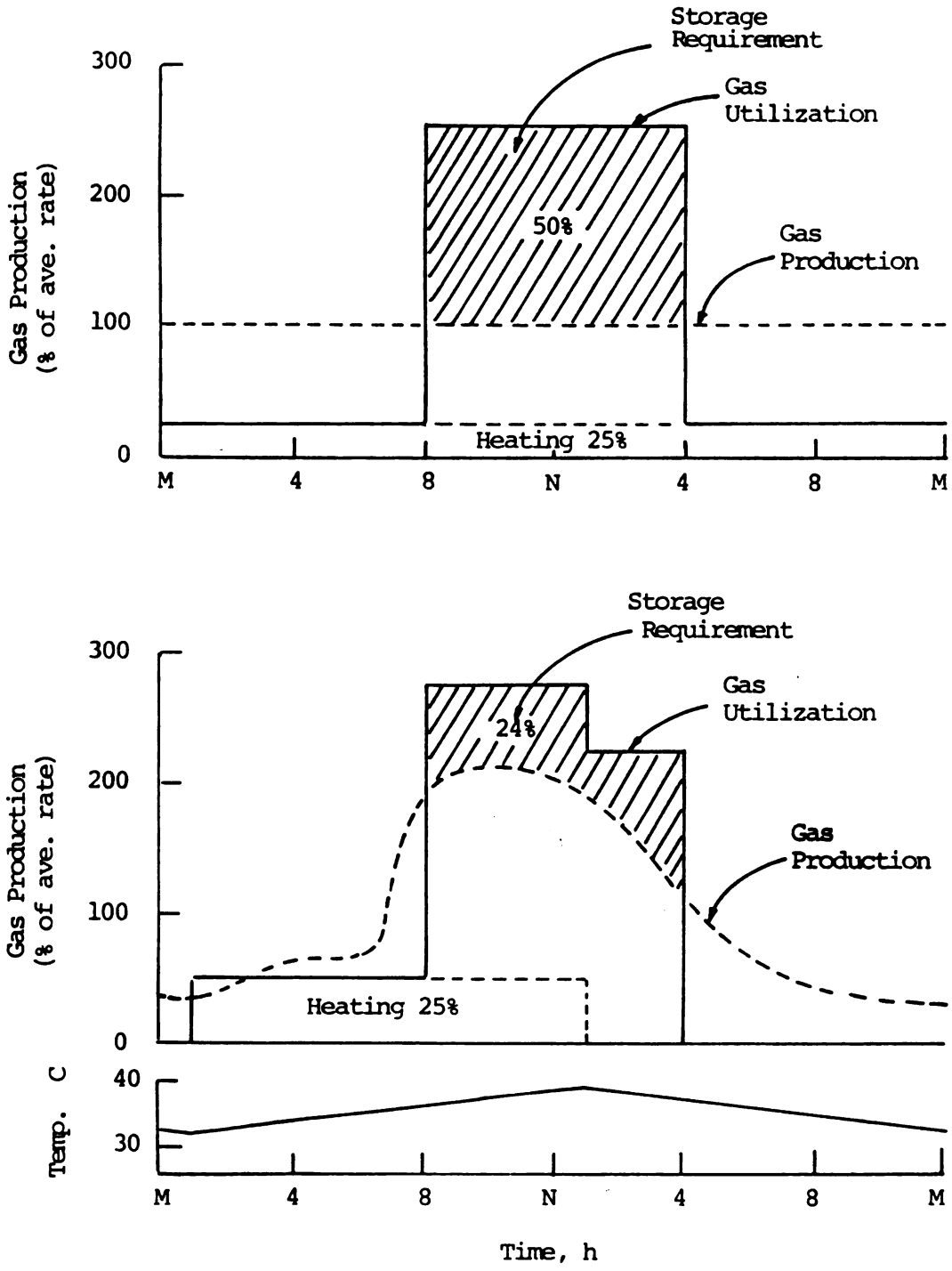


FIGURE 8-1. Gas Storage Requirements for (a) Digesters with Uniform Feeding and Heating, and (b) Managed Digesters Using Conditions of Experiment IIA.

maximum temperature. As an alternative, some of the heating could be accomplished by increasing the temperature of the influent material prior to adding it to the digester. This would keep gas production in the digester lower until it was needed.

B. HEATING COINCIDENT WITH PRODUCTIVE GAS USE

When digester gas is used to generate electricity only about 20 to 25 percent of the energy is actually converted to electricity. The remaining 75 to 80 percent is converted to heat, about 75% of which can be recovered for heating the digester and/or the influent material. This recovered heat is more than sufficient to maintain digester temperature. Because digester heating would occur at the same time as productive uses, the effect would be to sustain the gas production at relatively high levels as long as the rapidly degradable fraction had not been depleted.

On a dairy farm high electrical demand typically occurs twice a day during the milking operation. While it may not be possible to exactly match the gas production cycle to this demand, storage requirements would be reduced if the digester were fed twice a day approximately one hour before milking with the waste heat being used to sustain the gas production for several hours. By also heating the influent manure, the digester temperature could be increased sharply at the time of feeding to more closely coordinate gas production with utilization. The mathematical model, with some refinements, can be used to make more accurate predictions of gas production patterns for management strategies such as this which were not experimentally examined in this study.

IX. CONCLUSIONS

Based on the results of this study, the following conclusions can be made for dairy manure digesters operated with daily pulse feeding at constant temperature or with small temperature fluctuations.

1. Once established, a dairy manure digester can be operated in a stable manner in conjunction with pulse feeding and temperature fluctuations. Stable operation was achieved for all the conditions tested as indicated by low volatile acids, and constant pH (±0.05 units), alkalinity (±10%) and daily gas production (±6%).

2. Dairy manure contains a wide variety of substrates having different rates of degradation, some extremely rapid. The initial rise in gas production immediately following feeding is primarily due to substrates other than volatile acids since the acid pool did not decline to nearly the extent that gas production increased.

3. Hydrolysis of particulate substrates is the rate limiting step in the overall anaerobic digestion of dairy manure. Volatile acid pool size never increased and the literature indicates that hydrolysis products are fermented to acids as rapidly as they are produced.

4. The rate of gas production responds rapidly to temperature changes in either direction. This was true both for the gradual temperature changes intentionally imposed and for sudden temperature changes which occurred accidentally.

5. Within a daily cycle, the rate of gas production varies greatly as a result of pulse feeding and temperature fluctuations. The pattern of gas production can be controlled to a large extent by proper timing of the phase relationship between the feeding and temperature cycles. The constant temperature control digester showed a peak gas production 1.7 times the average occurring 1.5 hours after feeding. Feeding the digester at the peak of the temperature cycle caused a sharp peak 1.8 times as great as for the control but occurring at about the same time; gas production then decreased rapidly. Feeding the digester at the midpoint of the ascending temperature ramp caused a peak gas production about 1.4 times as great as the control; high gas production was maintained for 6 hours due to increasing temperature before falling rapidly with declining temperature.

6. A fluctuating temperature digester produces about 10% more total gas in 24 hours than a constant temperature digester operated at the same mean temperature. This reflects the non-linear nature of the Arrhenius temperature function. For moderately or slowly degradable substrates, increased removal rates at higher temperatures more than offset decreased removal rates at lower temperatures for a net gain in gas production. Degradation of rapidly degradable substrates is nearly complete in 24 hours in all cases so they do not contribute to the increased gas production due to fluctuating temperatures.

7. A mathematical model based on first order kinetics and the Arrhenius temperature relationship successfully predicted gas production dynamics as long as hydrolysis remained the rate limiting step and volatile acid pool size did not change rapidly. The data showed that the substrate could be approximated as three fractions based on the relative rates of degradation. For the whole manure digesters the size of these fractions in the influent as a percentage of the total gas potential and the first order rate constants at 36.4°C were:

   Fast Fraction: 19% with K = 1.15 d^{-1}

   Moderate Fraction: 35% with K = 0.335 d^{-1}

   Slow Fraction: 46% with K = 0.0085 d^{-1}

   For the blended and diluted manure these variables for the influent with the digester at 35.8°C were:

   Fast Fraction: 35% with K = 2.19 d^{-1}

   Moderate Fraction: 25% with K = 0.168 d^{-1}

   Slow Fraction: 41% with K = 0.0075 d^{-1}

   The temperature coefficient was estimated as 1.25 corresponding to an Arrhenius activation energy of 42.5 kcal/deg Kelvin.

8. The precision of the model for predicting the timing of gas production can be improved by directly incorporating changes in the volatile acid pool which can be significant for some phase relations between feeding and heating cycles.

9. Gas storage requirements can be substantially reduced by managing the feeding and temperature cycles. For a hypothetical situation in which gas is productively utilized eight hours a day, gas sto-

rage requirements can be reduced from 50% of daily gas production for a constant temperature, uniform feed digester to 24% by feeding at the midpoint of an ascending temperature ramp.

X. SUGGESTIONS FOR FUTURE WORK

Based on the results of this investigation, the following ideas are suggested for future research:

1. To verify that the results of the fluctuating temperature experiments are applicable to full strength manure, the conditions of Experiments IIA and IIC should be repeated with whole manure.

2. The combination of pulse feeding and temperature fluctuations may not result in stable operation with other types of substrate and the distribution of substrate fractions is likely to vary with type of substrate. Therefore, similar experiments should be conducted with a variety of waste materials.

3. The dynamics of volatile acid utilization need to be incorporated directly into the model. To do this, kinetic data for at least acetic acid must bbe obtained under similar operating conditions of pulse feeding and fluctuating temperature in a stable digester.

4. A theoretical study should be made with the mathematical model to determine the range of gas production patterns which would be predicted under various management strategies. Then does which would be most useful and those which would most severely test the model could be studied experimentally for further verification.

APPENDICES

APPENDIX A

TABLE A1. Area Counts for Volatile Fatty Acids Standard Solution (Data for Figure 4-3).

mg/l as COD	Area Counts 1	2	3	Average	Std. Dev.
Acetic Acid					
392.91	41,127	44,817	51,622	45,855	5,324
785.82	97,189	96,180	101,995	98,455	3,107
1571.64	197,132	217,029	202,007	205,389	10,371
2357.45	330,095	325,286	---	327,690	3,400
4714.90	649,235	653,615	---	651,425	3,097
9429.80	1,299,219	1,278,542	---	1,288,880	14,621
Propionic Acid					
527.14	89,521	93,774	90,606	91,300	2,210
1054.28	178,838	172,134	175,748	175,573	3,355
2108.56	334,581	324,080	349,493	336,051	12,770
3162.83	523,466	527,944	---	525,705	3,166
6325.67	1,043,196	1,040,493	---	1,041,844	1,911
12651.34	2,080,229	2,010,550	---	2,045,390	49,270
iso-Butyric Acid					
172.47	25,684	27,573	27,133	26,797	988
344.93	56,899	54,418	56,995	56,104	1,461
689.87	107,984	---	116,462	112,223	5,995
1034.80	175,860	177,527	---	176,694	1,179
2069.61	359,316	353,453	---	356,384	4,145
4139.22	727,149	696,297	---	711,723	21,816
Butyric Acid					
174.21	31,893	33,410	32,261	32,521	791
348.42	62,893	60,379	62,844	62,039	1,438
696.84	117,845	123,253	121,657	120,918	2,779
1045.25	184,531	185,930	---	185,230	989
2090.51	365,645	364,299	---	364,972	952
4181.01	731,939	708,388	---	720,164	16,653
iso-Valeric Acid					
94.05	17,842	18,216	16,750	17,603	762
188.10	34,156	33,288	33,554	33,666	445
376.20	64,448	69,895	67,767	67,370	2,745
564.30	101,290	101,829	---	101,560	381
1128.60	203,934	202,889	---	203,412	739
2257.21	407,712	400,414	---	404,063	5,160
Valeric Acid					
93.11	17,406	18,082	17,146	17,545	483
186.21	34,160	32,464	33,990	33,538	934
372.44	61,174	64,528	66,512	64,071	2,698
558.64	98,466	99,410	---	98,938	668
1117.29	196,532	195,756	---	196,144	549
2234.57	396,016	380,126	---	388,071	11,236

TABLE A2. Area Counts for Volatile Fatty Acids Standard Solution (Data for Figure 4-4).

mg/l as COD	Area Counts 1	2	3	Average	Std. Dev.
Acetic Acid					
37.72	115,124	92,311	104,618	104,018	11,418
75.45	266,264	149,491	166,268	160,641	9,656
150.90	278,060	267,539	259,972	268,524	9,084
301.80	463,633	481,052	484,642	476,442	11,237
Propionic Acid					
50.59	85,431	85,957	84,791	85,393	584
101.17	167,372	171,468	174,897	171,246	3,767
202.34	345,867	351,846	347,280	348,337	3,135
404.68	673,094	690,746	671,634	678,491	10,638
iso-Butyric Acid					
28.29	50,682	49,020	54,686	51,463	2,913
56.59	99,294	98,496	99,596	99,129	568
113.18	206,588	213,284	202,122	207,331	5,618
226.36	397,008	399,782	388,316	395,035	5,982
Butyric Acid					
28.29	62,964	51,458	51,568	55,330	6,611
56.59	101,600	97,686	102,036	100,441	2,396
113.18	191,304	195,470	194,788	193,854	2,235
226.36	371,728	380,276	362,886	371,630	8,695

APPENDIX B

TABLE B1. Daily Gas Production recorded from Wet Test Meter Readings, 1/d (Data for Figure 5-1).

J.D. 1982	Daily Gas Production, 1/d Digester 1	Digester 2
284	6.91	6.76
285	6.75	6.85
286	6.58	6.33
287	6.66	6.51
288	6.60	6.13
289	6.48	6.26
290	6.90	6.48
291	6.16	6.27
292	6.72	6.69
293	6.92	6.28
294	—	—
295	7.20	7.14
296	6.74	6.86
297	—	6.40
298	—	6.48
299	6.07	6.44
300	—	—
301	6.20	—
302	6.28	—
303	6.40	6.44
304	6.39	6.53
305	6.08	6.26
306	—	—
307	6.12	6.21
308	5.85	6.06
309	6.02	6.42
310	6.10	6.61
311	6.09	6.48
312	6.06	6.36
313	6.41	6.63
Mean	6.43	6.48
Std. Dev.	0.36	0.25
n	25	25

TABLE B2. Daily Gas Production Recorded by Wet Test Meters, l/d (Data for Figures 5-7 and 5-8).

CONTROL		EXP IIA		EXP IIB		EXP IIC	
JD	Gas Prod	JD	Gas Prod	JD	Gas Prod	JD	Gas Prod
85	6.59	85	6.71	134	--	170	--
86	6.45	86	6.92	135	6.52	171	--
87	6.63	87	6.66	136	6.72	172	7.32
88	6.82	88	7.19	137	6.91	173	7.35
89	6.62	89	7.03	138	7.31	174	6.82
90	6.55	90	6.83	139	7.19	175	7.16
91	6.37	91	6.18	140	7.60	176	7.04
92	6.78	92	6.59	141	7.54	177	7.16
93	6.32	93	6.47	142	7.48	178	6.76
94	6.57	94	6.10	143	7.28	179	6.70
95	6.45	95	6.67	144	7.43	180	6.90
96	6.97	96	6.55	145	7.02	181	7.12
97	--	97	6.68	146	7.86	182	6.77
98	6.70	98	6.84	147	6.81	183	7.07
99	6.63	99	6.74	148	7.12	184	9.15
100	6.73	100	6.92	149	6.94	185	8.93
101	--	101	6.78	150	6.70	186	8.16
104	6.67	104	7.09	151	7.05	187	7.76
105	6.52	105	6.78	152	6.83	188	8.68
106	6.49	106	6.88	153	6.74	189	7.39
107	6.61	107	7.16	154	6.97	190	7.43
108	6.84	108	7.29	155	7.15	191	7.68
109	6.65	109	7.05	156	7.07	192	7.54
110	6.74	110	7.22	157	7.10	193	7.72
111	6.53	111	7.18	158	7.76	194	7.81
112	6.94	112	7.16	159	8.04	195	7.85
113	6.88	113	7.00	160	7.05	196	9.57
114	7.22	114	7.14	161	6.96	197	8.96
115	7.19	115	7.00	162	7.09	198	8.96
116	7.32	116	7.34	163	7.08	199	9.25
117	7.20	117	7.16	164	6.92	200	9.90
118	6.94	118	7.20	165	7.00	201	8.83
119	6.83	119	6.94	166	7.14	202	8.70
120	6.57	120	7.38	167	7.02	203	9.70
121	6.88	121	6.73	168	7.30	204	9.42
122	6.78	122	7.49	169	7.20	205	9.42
123	6.48	123	7.02			206	--
124	6.50	124	6.48			207	7.86
125	6.42	125	7.56			208	8.72
126	--	126	7.81			209	7.42
127	6.67	127	7.08			210	8.96
128	6.70	128	7.45			211	7.93
129	6.47	129	7.22			212	5.35
130	6.50	130	7.77			213	8.64
131	6.68	131	7.34			214	8.31
132	6.61	132	7.73			215	8.31
133	6.46	133	--				

TABLE B3. Mean Gas Production Data for Experiment I.

Time, Hours	No. of Points	Gas Production, ml/hr DIGESTER 1 Mean	DIGESTER 1 Std.Dev	DIGESTER 2 Mean	DIGESTER 2 Std.Dev
0.33	4.	185.	21.	244.	58.
0.67	4.	199.	45.	283.	54.
1.00	4.	266.	43.	299.	67.
1.33	4.	305.	4.	378.	24.
1.67	4.	318.	16.	392.	37.
2.00	4.	333.	34.	386.	19.
2.33	4.	318.	20.	414.	33.
2.67	4.	333.	26.	413.	23.
3.00	4.	334.	25.	410.	30.
3.33	4.	342.	30.	411.	37.
3.67	4.	345.	43.	405.	36.
4.00	4.	352.	53.	406.	37.
4.33	4.	354.	49.	381.	30.
4.67	5.	332.	26.	372.	39.
5.00	5.	322.	26.	365.	44.
5.33	5.	323.	24.	388.	28.
5.67	5.	318.	25.	386.	30.
6.00	5.	310.	19.	384.	27.
6.33	5.	302.	29.	368.	10.
6.67	5.	296.	24.	357.	12.
7.00	5.	294.	23.	356.	20.
7.33	5.	322.	50.	356.	29.
7.67	5.	323.	46.	354.	21.
8.00	5.	319.	48.	358.	21.
8.33	5.	320.	47.	336.	13.
8.67	5.	310.	39.	343.	18.
9.00	5.	315.	41.	348.	28.
9.33	5.	304.	45.	337.	20.
9.67	5.	308.	39.	352.	14.
10.00	5.	314.	49.	340.	12.
10.33	5.	302.	35.	338.	33.
10.67	5.	297.	38.	334.	12.
11.00	5.	298.	47.	328.	23.
11.33	5.	285.	34.	325.	20.
11.67	5.	287.	39.	323.	26.
12.00	5.	296.	51.	321.	13.
12.33	5.	291.	51.	322.	11.
12.67	5.	291.	43.	320.	22.
13.00	5.	288.	51.	315.	19.
13.33	5.	278.	40.	307.	12.
13.67	5.	287.	42.	306.	15.
14.00	5.	287.	55.	300.	26.
14.33	5.	270.	45.	289.	24.
14.67	5.	266.	34.	297.	33.
15.00	5.	271.	42.	289.	37.
15.33	5.	273.	38.	303.	31.
15.67	5.	266.	34.	292.	26.
16.00	5.	260.	42.	291.	32.

TABLE B3 Cont.

Time, Hours	No. of Points	Gas Production, ml/hr DIGESTER 1 Mean	DIGESTER 1 Std.Dev	DIGESTER 2 Mean	DIGESTER 2 Std.Dev
16.33	5.	266.	38.	294.	24.
16.67	5.	257.	32.	296.	37.
17.00	5.	264.	44.	288.	31.
17.33	5.	263.	45.	291.	30.
17.67	5.	246.	42.	287.	20.
18.00	5.	244.	46.	272.	29.
18.33	5.	247.	37.	281.	21.
18.67	5.	245.	40.	263.	26.
19.00	5.	244.	40.	280.	42.
19.33	5.	249.	42.	270.	38.
19.67	5.	238.	36.	275.	25.
20.00	5.	242.	48.	267.	23.
20.33	5.	242.	48.	263.	21.
20.67	5.	237.	43.	275.	24.
21.00	5.	233.	38.	269.	28.
21.33	5.	232.	44.	274.	26.
21.67	5.	230.	40.	270.	33.
22.00	5.	227.	38.	257.	34.
22.33	5.	221.	31.	256.	25.
22.67	5.	219.	33.	245.	26.
23.00	5.	197.	13.	252.	27.
23.33	5.	193.	12.	259.	21.
23.67	5.	203.	21.	256.	24.
24.00	5.	192.	19.	251.	23.
	Daily Total =	6680.		Daily Total =	7672.

TABLE B4. Mean Gas Production Data for Experiment II, Control.

Time, Hours	No. of Points	Gas Prod, ml/hr Mean	Gas Prod, ml/hr Std.Dev	Temperature, °C Mean	Temperature, °C Std.Dev
0.33	6.	133.	57.	35.76	0.09
0.67	6.	215.	57.	35.80	0.06
1.00	6.	353.	18.	35.81	0.06
1.33	6.	423.	59.	35.81	0.07
1.67	6.	398.	21.	35.80	0.07
2.00	6.	400.	23.	35.81	0.08
2.33	6.	368.	23.	35.81	0.08
2.67	6.	356.	14.	35.81	0.08
3.00	6.	366.	11.	35.81	0.08
3.33	6.	362.	37.	35.81	0.08
3.67	6.	377.	20.	35.81	0.08
4.00	6.	362.	18.	35.81	0.07
4.33	6.	354.	13.	35.81	0.07
4.67	6.	356.	21.	35.81	0.07
5.00	6.	350.	7.	35.80	0.08
5.33	6.	366.	29.	35.80	0.08
5.67	6.	321.	31.	35.80	0.08
6.00	6.	321.	11.	35.80	0.08
6.33	6.	326.	17.	35.80	0.07
6.67	6.	332.	14.	35.80	0.07
7.00	6.	318.	17.	35.80	0.08
7.33	6.	307.	21.	35.80	0.08
7.67	6.	296.	13.	35.80	0.08
8.00	6.	302.	21.	35.79	0.08
8.33	6.	297.	25.	35.79	0.09
8.67	6.	307.	12.	35.79	0.08
9.00	6.	296.	16.	35.79	0.09
9.33	6.	320.	34.	35.79	0.09
9.67	6.	301.	14.	35.78	0.09
10.00	6.	293.	16.	35.78	0.08
10.33	6.	297.	20.	35.78	0.08
10.67	6.	289.	9.	35.79	0.08
11.00	6.	301.	15.	35.79	0.08
11.33	6.	281.	17.	35.78	0.08
11.67	6.	279.	13.	35.78	0.08
12.00	6.	283.	45.	35.78	0.08
12.33	6.	257.	36.	35.78	0.08
12.67	6.	260.	11.	35.78	0.07
13.00	6.	255.	9.	35.78	0.08
13.33	6.	265.	12.	35.78	0.08
13.67	6.	260.	17.	35.78	0.08
14.00	6.	245.	20.	35.78	0.08
14.33	6.	236.	14.	35.79	0.08
14.67	6.	231.	19.	35.79	0.08
15.00	6.	228.	15.	35.80	0.07
15.33	6.	195.	23.	35.81	0.06
15.67	6.	173.	29.	35.82	0.06
16.00	6.	182.	20.	35.83	0.07

TABLE B4 Cont.

Time, Hours	No. of Points	Gas Prod, ml/hr Mean	Std.Dev	Temperature, °C Mean	Std.Dev
16.33	6.	179.	21.	35.83	0.06
16.67	6.	166.	18.	35.82	0.06
17.00	6.	172.	21.	35.82	0.06
17.33	6.	168.	26.	35.81	0.05
17.67	6.	154.	5.	35.80	0.05
18.00	6.	152.	21.	35.80	0.05
18.33	6.	178.	57.	35.80	0.05
18.67	6.	153.	44.	35.80	0.06
19.00	6.	149.	12.	35.80	0.05
19.33	6.	155.	20.	35.79	0.05
19.67	6.	161.	21.	35.80	0.06
20.00	6.	166.	22.	35.80	0.06
20.33	6.	161.	15.	35.80	0.05
20.67	6.	154.	13.	35.80	0.04
21.00	6.	152.	13.	35.80	0.04
21.33	6.	146.	18.	35.80	0.04
21.67	6.	146.	8.	35.80	0.04
22.00	6.	149.	11.	35.80	0.03
22.33	5.	142.	14.	35.79	0.03
22.67	5.	143.	14.	35.79	0.04
23.00	5.	142.	16.	35.79	0.05
23.33	5.	191.	67.	35.79	0.06
23.67	6.	119.	44.	35.79	0.04
24.00	6.	178.	45.	35.80	0.03
	Daily Total =	6053.	Ave. Temp. =	35.80	

TABLE B5. Mean Gas Production Data for Experiment IIA.

Time, Hours	No. of Points	Gas Prod., ml/hr Mean	Std. Dev	Temperature, °C Mean	Std. Dev
0.33	6.	355.	18.	35.30	0.30
0.67	6.	510.	41.	35.65	0.31
1.00	6.	581.	35.	36.13	0.33
1.33	6.	586.	44.	36.18	0.33
1.67	6.	610.	37.	36.21	0.31
2.00	6.	660.	50.	36.68	0.31
2.33	6.	657.	80.	36.74	0.28
2.67	6.	615.	44.	36.72	0.30
3.00	6.	654.	51.	37.07	0.29
3.33	6.	636.	44.	37.32	0.31
3.67	6.	619.	46.	37.35	0.32
4.00	6.	697.	85.	37.56	0.30
4.33	6.	641.	56.	37.95	0.31
4.67	6.	605.	46.	37.97	0.31
5.00	6.	626.	95.	38.04	0.30
5.33	6.	614.	81.	38.52	0.31
5.67	6.	550.	42.	38.60	0.30
6.00	6.	571.	53.	38.62	0.30
6.33	6.	587.	60.	39.01	0.37
6.67	6.	555.	33.	39.12	0.46
7.00	6.	523.	52.	39.12	0.48
7.33	6.	438.	46.	38.83	0.50
7.67	6.	447.	28.	38.52	0.47
8.00	6.	428.	36.	38.50	0.47
8.33	6.	362.	37.	38.34	0.48
8.67	6.	353.	41.	37.92	0.48
9.00	6.	390.	84.	37.87	0.48
9.33	6.	313.	52.	37.83	0.49
9.67	6.	248.	49.	37.36	0.49
10.00	6.	257.	34.	37.26	0.48
10.33	6.	255.	38.	37.25	0.48
10.67	6.	193.	50.	36.88	0.50
11.00	6.	206.	33.	36.66	0.49
11.33	6.	195.	27.	36.64	0.49
11.67	6.	145.	26.	36.41	0.49
12.00	6.	180.	46.	36.07	0.48
12.33	6.	215.	104.	36.04	0.47
12.67	6.	137.	13.	35.93	0.47
13.00	6.	137.	12.	35.50	0.47
13.33	6.	152.	15.	35.44	0.47
13.67	6.	131.	20.	35.42	0.47
14.00	6.	112.	14.	34.99	0.48
14.33	6.	133.	10.	34.87	0.47
14.67	6.	130.	22.	34.85	0.48
15.00	6.	86.	16.	34.56	0.49
15.33	6.	90.	16.	34.29	0.47
15.67	6.	104.	17.	34.28	0.48
16.00	6.	71.	17.	34.09	0.48

TABLE B5 Cont.

Time, Hours	No. of Points	Gas Prod., ml/hr Mean	Std. Dev	Temperature, °C Mean	Std. Dev
16.33	6.	91.	16.	33.71	0.49
16.67	6.	106.	9.	33.67	0.47
17.00	6.	85.	7.	33.61	0.48
17.33	6.	74.	12.	33.18	0.49
17.67	6.	94.	6.	33.10	0.49
18.00	6.	98.	18.	33.09	0.49
18.33	6.	80.	39.	32.81	0.36
18.67	6.	100.	47.	32.63	0.36
19.00	6.	107.	33.	32.61	0.36
19.33	6.	171.	50.	32.88	0.34
19.67	6.	134.	35.	33.15	0.36
20.00	6.	136.	38.	33.17	0.36
20.33	6.	172.	40.	33.32	0.35
20.67	6.	164.	33.	33.71	0.36
21.00	6.	154.	35.	33.76	0.36
21.33	6.	177.	37.	33.80	0.35
21.67	6.	194.	38.	34.28	0.34
22.00	6.	169.	43.	34.35	0.36
22.33	6.	167.	46.	34.35	0.34
22.67	6.	220.	39.	34.75	0.34
23.00	6.	188.	39.	34.93	0.35
23.33	6.	190.	47.	34.93	0.36
23.67	6.	207.	55.	35.20	0.35
24.00	6.	232.	50.	35.51	0.36
	Daily Total = 7287.		Ave. Temp.= 35.82		

TABLE B6. Mean Gas Production Data for Experiment IIB.

Time, Hours	No. of Points	Gas Prod., ml/hr Mean	Std.Dev	Temerature, °C Mean	Std.Dev
0.33	5.	377.	81.	32.50	0.26
0.67	5.	463.	27.	32.55	0.26
1.00	5.	556.	31.	32.60	0.23
1.33	6.	583.	36.	32.87	0.24
1.67	6.	553.	54.	33.15	0.24
2.00	6.	528.	48.	33.17	0.25
2.33	6.	555.	67.	33.31	0.26
2.67	6.	521.	76.	33.72	0.27
3.00	6.	499.	62.	33.76	0.26
3.33	6.	500.	67.	33.79	0.24
3.67	6.	510.	62.	34.28	0.25
4.00	6.	476.	54.	34.36	0.24
4.33	6.	459.	45.	34.36	0.24
4.67	6.	512.	60.	34.74	0.27
5.00	6.	458.	38.	34.92	0.19
5.33	6.	441.	28.	34.95	0.23
5.67	6.	463.	35.	35.18	0.23
6.00	6.	431.	20.	35.50	0.24
6.33	6.	403.	15.	35.49	0.19
6.67	6.	411.	21.	35.57	0.16
7.00	6.	399.	21.	36.01	0.16
7.33	6.	366.	13.	36.05	0.15
7.67	6.	366.	25.	36.07	0.15
8.00	6.	374.	24.	36.56	0.18
8.33	6.	337.	21.	36.69	0.24
8.67	6.	308.	16.	36.70	0.24
9.00	6.	328.	24.	37.06	0.27
9.33	6.	306.	20.	37.32	0.27
9.67	6.	281.	22.	37.33	0.26
10.00	6.	289.	12.	37.52	0.27
10.33	6.	292.	12.	37.92	0.26
10.67	6.	283.	20.	37.95	0.27
11.00	6.	276.	21.	38.01	0.27
11.33	6.	294.	20.	38.52	0.28
11.67	6.	277.	28.	38.57	0.27
12.00	6.	263.	21.	38.58	0.28
12.33	6.	291.	39.	38.89	0.10
12.67	6.	279.	13.	39.00	0.23
13.00	6.	276.	22.	39.01	0.24
13.33	6.	238.	10.	38.72	0.25
13.67	6.	235.	19.	38.40	0.24
14.00	6.	233.	15.	38.37	0.24
14.33	6.	212.	16.	38.24	0.25
14.67	6.	205.	16.	37.79	0.24
15.00	6.	198.	13.	37.76	0.25
15.33	6.	196.	10.	37.73	0.25
15.67	6.	177.	17.	37.24	0.24
16.00	6.	187.	18.	37.14	0.24

TABLE B6 Cont.

Time, Hours	No. of Points	Gas Prod., ml/hr Mean	Std.Dev	Temerature, °C Mean	Std.Dev
16.33	6.	183.	7.	37.13	0.24
16.67	6.	159.	12.	36.75	0.23
17.00	6.	175.	10.	36.52	0.23
17.33	6.	185.	11.	36.51	0.22
17.67	6.	155.	15.	36.29	0.20
18.00	6.	162.	12.	36.02	0.02
18.33	6.	163.	16.	36.02	0.03
18.67	6.	153.	15.	35.93	0.02
19.00	6.	156.	10.	35.49	0.02
19.33	6.	159.	14.	35.43	0.03
19.67	6.	158.	10.	35.42	0.03
20.00	6.	152.	8.	34.97	0.02
20.33	6.	150.	8.	34.86	0.03
20.67	6.	155.	5.	34.85	0.02
21.00	6.	147.	9.	34.55	0.02
21.33	6.	152.	9.	34.28	0.02
21.67	6.	143.	7.	34.24	0.02
22.00	6.	143.	9.	34.07	0.00
22.33	6.	150.	9.	33.68	0.00
22.67	6.	147.	8.	33.65	0.02
23.00	6.	134.	4.	33.60	0.02
23.33	6.	136.	9.	33.12	0.05
23.67	6.	144.	11.	32.98	0.22
24.00	6.	201.	34.	32.96	0.24

Daily Total = 7075. Ave. Temp.= 35.77

TABLE B7. Mean Gas Production Data for Experiment IIC.

Time, Hours	No. of Points	Gas Prod, ml/hr Mean	Std.Dev	Temperature, °C Mean	Std.Dev
0.33	6.	568.	123.	39.26	0.07
0.67	6.	824.	69.	39.54	0.03
1.00	6.	860.	30.	39.57	0.02
1.33	6.	772.	23.	39.25	0.03
1.67	6.	779.	22.	38.97	0.04
2.00	6.	770.	10.	38.95	0.04
2.33	6.	645.	23.	38.80	0.03
2.67	6.	586.	62.	38.37	0.04
3.00	6.	519.	23.	38.34	0.04
3.33	6.	511.	32.	38.30	0.04
3.67	6.	460.	43.	37.80	0.04
4.00	6.	456.	38.	37.73	0.04
4.33	6.	482.	60.	37.72	0.03
4.67	6.	420.	19.	37.30	0.04
5.00	6.	410.	27.	37.11	0.03
5.33	6.	417.	43.	37.09	0.03
5.67	6.	381.	35.	36.84	0.03
6.00	6.	379.	23.	36.50	0.02
6.33	6.	373.	45.	36.47	0.03
6.67	6.	360.	45.	36.36	0.02
7.00	6.	332.	52.	35.93	0.02
7.33	6.	307.	30.	35.88	0.03
7.67	6.	294.	43.	35.86	0.02
8.00	6.	279.	45.	35.40	0.02
8.33	6.	264.	38.	35.29	0.00
8.67	6.	254.	36.	35.28	0.02
9.00	6.	225.	56.	34.95	0.04
9.33	6.	209.	42.	34.71	0.03
9.67	6.	216.	36.	34.68	0.03
10.00	6.	174.	16.	34.49	0.03
10.33	6.	196.	39.	34.12	0.02
10.67	6.	193.	16.	34.09	0.02
11.00	6.	176.	21.	34.03	0.02
11.33	6.	159.	8.	33.59	0.04
11.67	6.	173.	12.	33.51	0.04
12.00	6.	177.	30.	33.50	0.04
12.33	6.	132.	5.	33.08	0.06
12.67	6.	159.	22.	32.93	0.04
13.00	6.	180.	36.	32.92	0.04
13.33	6.	238.	30.	33.23	0.03
13.67	6.	178.	11.	33.49	0.04
14.00	6.	185.	30.	33.49	0.04
14.33	6.	224.	14.	33.66	0.03
14.67	6.	189.	22.	34.06	0.04
15.00	6.	183.	8.	34.07	0.04
15.33	6.	215.	22.	34.12	0.04
15.67	6.	212.	26.	34.62	0.04
16.00	6.	207.	22.	34.67	0.03

TABLE B7 Cont.

Time, Hours	No. of Points	Gas Prod, ml/hr Mean	Gas Prod, ml/hr Std.Dev	Temperature, °C Mean	Temperature, °C Std.Dev
16.33	6.	178.	18.	34.68	0.03
16.67	6.	242.	28.	35.12	0.05
17.00	6.	194.	18.	35.27	0.05
17.33	6.	199.	19.	35.27	0.05
17.67	6.	249.	22.	35.55	0.04
18.00	6.	187.	7.	35.85	0.03
18.33	6.	207.	18.	35.86	0.03
18.67	6.	273.	40.	35.99	0.03
19.00	6.	222.	11.	36.43	0.03
19.33	6.	212.	22.	36.45	0.03
19.67	6.	239.	22.	36.47	0.03
20.00	6.	256.	21.	36.95	0.02
20.33	6.	215.	15.	37.04	0.02
20.67	6.	212.	11.	37.05	0.02
21.00	6.	276.	16.	37.44	0.02
21.33	6.	245.	11.	37.67	0.02
21.67	6.	232.	21.	37.67	0.03
22.00	6.	294.	19.	37.90	0.03
22.33	6.	250.	24.	38.26	0.03
22.67	6.	238.	21.	38.28	0.04
23.00	6.	268.	16.	38.38	0.03
23.33	6.	264.	21.	38.88	0.02
23.67	6.	242.	28.	38.92	0.02
24.00	5.	280.	60.	38.93	0.03
Daily Total = 7523.		Ave. Temp. = 36.20			

TABLE B8. Total Volatile Solids During the Stable Period of Experiment I (in percent).

JD	Influent		Effluent	
	Sample 1	Sample 2	Digester 1	Digester 2
307	13.84	13.46	9.54	9.25
309	13.72	13.85	8.79	8.63
310	12.93	14.19	8.85	9.56
311	14.44	14.30	9.24	8.29
312	14.27	13.80	8.92	8.63
313	—	13.99	8.69	8.71
314	13.73	13.80	8.66	9.31
316	13.69	13.39	9.35	8.80
317	14.48	13.43	8.37	8.21
318	13.53	—	8.45	8.63
Mean	13.78		8.89	8.80
Std. Dev.	0.35		0.38	0.44
% TVS Reduction			35.5	36.1

TABLE B9. Total Volatile Solids Data During Stable Period of Experiment II (in percent).

JD 1983	Influent	Effluent			
		Control	Exp IIA	Exp IIB	Exp IIC
128	3.42	1.95	1.69	—	—
	3.38	1.93	1.72	—	—
130	3.70	2.02	1.70	—	—
	3.78	1.97	1.65	—	—
132	3.40	2.10	1.67	—	—
	3.66	2.04	1.63	—	—
134	3.49	2.03	1.69	—	—
	3.26	2.07	1.70	—	—
135	3.16	1.90	1.65	—	—
	3.13	1.88	1.60	—	—
164	3.50	—	—	1.75	—
	3.39	—	—	1.91	—
166	3.64	—	—	1.73	—
	3.46	—	—	1.69	—
167	3.57	—	—	1.76	—
	3.72	—	—	1.64	—
168	3.24	—	—	1.81	—
	3.21	—	—	1.89	—
191	3.49	—	—	—	1.66
	3.47	—	—	—	1.75
193	3.37	—	—	—	1.72
	3.53	—	—	—	1.68
211	3.60	—	—	—	—
	3.35	—	—	—	—
214	3.57	—	—	—	—
	3.32	—	—	—	—
216	3.24	—	—	—	—
	3.34	—	—	—	—
Mean	3.44	1.99	1.67	1.77	1.70
Std. Dev.	0.17	0.07	0.04	0.09	0.04

Note: For each sample, two replicates were analyzed.

TABLE B10. Total COD Data During Stable Period of Experiment I (in mg/l).

JD 1983	Influent Sample 1	Influent Sample 2	Effluent Digester 1	Effluent Digester 2
316	182,528	180,544	98,208	107,136
317	162,032	---	106,704	104,728
318	158,080	---	98,800	104,728
319	185,368	---	112,404	114,376
	---	---	116,348	114,376
320	169,936	162,032	88,130	88,999
Mean		169,996	103,432	105,724
Std. Dev.		11,508	10,401	9,310
% COD Reductions		---	39.16	37.81

TABLE B11. Total COD Data During the Stable Period of Experiment II (in mg/l).

JD 1983	Influent	Effluent Control	Exp IIA	Exp IIB	Exp IIC
128	38,801	21,164	17,637	—	
	40,917	—	19,400	—	
130	38,720	20,064	16,896	—	
	—	21,120	15,840	—	
131	—	22,880	17,600	—	
	—	24,640	15,840	—	
	—	19,972	—	—	
132	38,456	20,102	19,228	—	
	41,952	—	15,732	—	
134	37,393	19,131	16,522	—	
	—	19,131	17,392	—	
166	37,374	—	—	17,892	
	—	—	—	19,880	
167	35,712	—	—	17,856	
	—	—	—	21,030	
168	38,093	—	—	17,062	
	46,029	—	—	—	
	38,093	—	—	—	
169	39,680	—	—	17,856	
	37,299	—	—	17,856	
192	38,464	—	—	—	17,308
	—	—	—	—	16,155
194	38,417	—	—	—	21,073
	—	—	—	—	17,244
212	38,417	—	—	—	—
213	39,856	—	—	—	—
215	37,600	—	—	—	—
	37,600	—	—	—	—
Mean	38,883	20,192	17,209	18,490	17,945
Std. Dev.	2,220	1,819	1,323	1,413	2,151
% Red.	—	46.22	55.74	52.45	53.85

TABLE B12. Individual Volatile Fatty Acid Concentrations During the Stable Period for Digester 1, Experiment I, in mg/l as COD (Data for Figure 5-3).

Time	JD 1982	HAc	HP	iHB	HB	iHV	HV	HC	Total VFA
11 AM	323	182	1970	331	369	21	0	0	
	324	234	2182	85	0	108	6	0	
	325	194	1747	32	0	72	148	0	
	Ave.	203	1966	149	123	67	51	0	2559
1 PM	323	1150	2077	200	247	197	0	8	
	324	642	1833	62	140	109	20	6	
	Ave.	896	1955	131	194	153	10	7	3346
4 PM	323	1096	2220	326	319	222	47	0	
	324	850	1960	72	76	92	54	6	
	Ave.	973	2090	199	198	157	50	3	3670
11 PM	323	616	2108	109	0	192	0	32	
	324	669	2082	2	19	94	25	0	
	Ave.	642	2095	56	10	143	12	16	2974
6 AM	324	255	2093	93	0	43	0	1	
	325	327	2092	8	10	0	4	0	
	Ave.	291	2092	50	5	22	2	0	2462

TABLE B13. Individual Volatile Fatty Acid Concentrations During the Stable Period for Digester 2, Experiment I, in mg/l as COD (Data for Figure 5-3).

Time	JD 1984	HAc	HP	iHB	HB	iHV	HV	HC	Total VFA
11 AM	323	256	2223	339	0	57	0	0	
	324	104	1504	16	276	289	134	0	
	325	165	1507	621	235	0	14	12	
	Average	175	1745	325	170	115	49	4	2583
1 PM	323	525	1894	233	516	158	95	20	
	324	727	1490	203	216	67	40	37	
	Average	626	1692	218	366	112	68	28	3110
4 PM	323	645	1774	234	435	163	55	3	
	324	828	1550	47	74	111	0	0	
	Average	736	1662	140	254	137	28	2	2959
11 PM	323	733	1810	76	0	200	0	5	
	324	573	1703	0	19	48	17	0	
	Average	653	1756	38	10	124	8	2	2591
6 AM	324	280	1688	53	137	38	0	2	
	325	312	1514	0	8	0	6	0	
	Average	296	1601	26	72	19	3	1	2018

TABLE B14. Individual Volatile Fatty Acid Concentrations During the Stable Period of Experiment II Control, in mg/l as COD (Data for Figure 5-14).

Time		Individual VFA				Total
	JD	HAc	HP	iHB	HB	VFA
2:00 PM	129	50	3	0	0	57
	130	28	4	0	2	34
	131	32	5	0	8	45
	132	22	5	0	2	29
	133	25	6	0	4	35
	Average	31.4	4.6	0	4	40
4:00 PM	129	206	49	3	4	262
	131	186	44	4	20	254
	133	172	32	5	27	236
	Average	188	41.7	4	17	250.7
5:00 PM	130	203	44	5	6	258
6:00 PM	129	198	50	4	10	262
	131	184	32	2	18	236
	Average	191	41	3	14	249
8:00 PM	129	188	42	2	6	238
	130	186	36	1	1	224
	131	186	27	2	24	239
	133	185	24	2	29	240
	Average	186.2	32.2	1.75	15	235.2
12:00 PM	129	127	25	0	6	158
	130	138	21	0	0	159
	Average	132.5	23	0	3	158.5
1:30 PM	132	103	12	0	9	124
3:00 PM	132	80	12	0	4	96
9:00 AM	130	22	5	0	3	30
	131	31	7	0	0	38
	Average	26.5	6	0	1.5	34

TABLE B15. Individual Volatile Fatty Acid Concentrations During the Stable Period of Experiment IIA, in mg/l as COD (Data for Figure 5-15).

Time	JD	Individual VFA HAc	HP	iHB	HB	Total VFA
2:00 PM	129	10	4	0	0	14
	130	20	4	0	0	24
	131	0	3	0	5	8
	132	12	3	0	4	19
	133	8	4	0	2	14
	Average	10	3.6	0	2.2	15.8
4:00 PM	129	162	45	2	3	212
	131	151	42	3	20	216
	133	149	32	3	29	213
	Average	154	39.7	2.7	17.3	213.7
5:00 PM	130	148	46	2	18	214
6:00 PM	129	135	42	3	3	183
	131	131	35	2	22	190
	Average	133	38.5	2.5	12.5	186.5
8:00 PM	129	103	35	0	2	140
	130	117	32	1	5	155
	131	123	22	0	16	161
	133	104	16	0	22	142
	Average	111.8	26.2	0.2	11.2	149.5
12:00 PM	129	15	4	0	4	23
	130	23	4	0	3	30
	Average	19	4	0	3.5	26.5
1:30 AM	132	10	3	0	3	16
3:00 AM	132	10	3	0	2	16
9:00 AM	130	0	2	1	6	9
	131	0	4	0	0	4
	Average	0	3	0.5	3	6.5

TABLE B16. Individual Volatile Fatty Acid Concentrations During the Stable Period of Experiment IIB, in mg/l as COD (Data for Figure 5-16).

Time	JD	Individual VFA HAc	HP	iHB+HB	Total VFA
2:00 p.m.	165	54.0	3.0	4.0	61.0
	166	51.0	4.0	4.0	59.0
	Average	52.5	3.5	4.0	60.0
4:00 p.m.	165	75.0	24.0	7.0	106.0
	166	76.0	25.0	4.0	105.0
	Average	75.5	24.5	5.5	105.5
6:00 p.m.	165	89.0	25.0	6.0	120.0
	166	75.0	26.0	6.0	107.0
	Average	82.0	25.5	6.0	113.5
8:00 p.m.	165	54.0	21.0	4.0	79.0
	166	50.0	20.0	4.0	74.0
	Average	52.0	20.5	4.0	76.5
10:00 p.m.	165	44.0	12.0	3.0	59.0
	166	40.0	12.0	3.0	55.0
	Average	42.0	12.0	3.0	57.0
12:00 p.m.	165	55.0	3.0	4.0	62.0
	166	58.0	3.0	4.0	65.0
	Average	56.5	3.0	4.0	63.5
9:00 a.m.	165	34.0	0.0	3.0	40.0
	166	38.0	0.0	2.0	40.0
	Average	36.0	0.0	2.5	40.0

TABLE B17. Individual Volatile Fatty Acid Concentrations During the Stable Period of Experiment IIC, in mg/l as COD (Data for Figure 5-17).

Time	JD	Individual VFA HAc	HP	iHB+HB	Total VFA
2:30 p.m.	214	18.0	38.0	tr	56.0
	215	13.0	14.0	tr	27.0
	Average	15.5	26.0	tr	41.5
4:00 p.m.	214	115.0	13.0	8.0	136.0
	215	135.0	28.0	12.0	175.0
	Average	125.0	20.5	10.0	155.5
7:00 p.m.	215	41.0	25.0	tr	66.0
	216	56.0	21.0	tr	77.0
	Average	48.5	23.0	tr	71.5
10:00 p.m.	214	12.0	9.0	tr	21.0
	215	18.0	12.0	tr	30.0
	Average	15.0	10.5	tr	25.5

TABLE B18. Daily Gas Production for Extended Digester Operation without Feeding (wet test meter results, data for Figures 5-6 and 5-20).

Days	Exp I		Exp IIC
	Dig. 1	Dig. 2	
1	6.44	6.70	7.52
2	3.30	3.12	3.86
3	2.35	2.22	2.31
4	2.08	1.96	1.98
5	1.60	1.52	1.69
6	1.43	1.47	1.51
7	1.10	1.09	1.31
8	0.92	0.98	—
9	0.71	0.80	0.97
10	—	—	1.08
11	—	—	0.92
12	0.61	0.59	—
13	—	—	0.74
16	—	—	0.66
19	0.55	—	—
19.5	—	—	0.55
20	0.52	0.48	—
24.5	—	—	0.54
26	0.50	0.46	—
27	—	—	0.50
30	—	—	0.50
37	0.50	0.48	—

APPENDIX C

TABLE C1. Data for Estimation of Rate Constants and Initial Gas Potentials for the Slow and Moderate Fractions for Experiment I (wet test meter results, data for Figures 6-1 and 6-3a).

Time, Days	Overall Rate (R_t), 1/d		Calculated* R_1, 1/d	$R_2 = R_t - R_1$, 1/d	
	Dig. 1	Dig. 2		Dig. 1	Dig. 2
0	—	—	0.64	—	—
0.5	6.44	6.70	0.64	5.80	6.06
1.5	3.30	3.12	0.63	2.67	2.49
2.5	2.35	2.22	0.63	1.72	1.59
3.5	2.08	1.96	0.62	1.46	1.34
4.5	1.60	1.52	0.62	0.98	0.90
5.5	1.43	1.47	0.61	0.82	0.86
6.5	1.10	1.09	0.61	0.49	0.48
7.5	0.92	0.98	0.60	0.32	0.38
8.5	0.71	0.80	0.60	0.11	0.20
11.5	0.61	0.59	0.58	0.03	0.01
18.5	0.55	—	0.55	—	—
19.5	0.52	0.48	0.54	—	—
25.5	0.50	0.46	0.52	—	—
36.5	0.50	0.48	0.47	—	—
47.5	0.32	—	0.43	—	—

* Calculated $R_1 = K_1 G_1^\circ \exp(-K_1 t)$ where K_1 and G_1° are obtained from Figure 6-1.

TABLE C2. Data for Estimation of Rate Constants and Initial Gas Potentials for the Fast Fraction for Exp I (bubble count results normalized to wet test meter basis, data for Figure 6-2b).

Time, Days	Normalized R_t, 1/d		Calculated		$R_3 = R_t - R_1 - R_2$	
	Dig. 1	Dig. 2	R_1, 1/d	R_2, 1/d	Dig. 1	Dig. 2
0	4.39	5.73	0.64	4.25	—	—
0.1	7.39	8.34	0.64	4.11	—	3.59
1.15	7.79	8.03	0.64	4.05	3.10	3.34
0.2	7.06	7.73	0.64	3.93	—	3.11
0.3	7.06	7.22	0.64	3.85	2.57	2.73
0.4	6.66	6.85	0.64	3.72	2.30	3.49
0.5	6.42	6.49	0.64	3.60	2.18	2.25
0.6	5.96	5.90	0.64	3.48	1.84	1.78
0.7	5.60	5.86	0.64	3.37	1.60	1.86
0.8	5.29	5.49	0.64	3.25	1.40	1.60
0.9	4.92	5.19	0.64	3.15	—	1.41
1.0	4.04	4.96	0.63	3.04	0.36	1.28
1.5	3.30	3.12	0.63	2.57	0.09	—

Notes:

1. Normalized Rate = (Bubble count, 1/hr)x(24 hr/d)x(Factor)
   where Factor = wet test meter ave. rate/bubble count ave. rate
   = 6.14/6.68 for Dig. 1 and 6.50/7.67 for Dig. 2

2. Calculated $R_i = K_i G_i^\circ \exp(-K_i t)$ where K_i and G_i° are obtained from Figures 6-1 and 6-3.

TABLE C3. Data for Estimation of Rate Constants and Initial Gas Potentials for the Slow and Moderate Fractions for Exp II (fluctuating temperature results; Ave. Temp. = 36.25°C; wet test meter basis; data for Figures 6-2 and 6-4a).

Time, Days	Overall Rate (R_t), 1/d	Calculated* R_1, 1/d	$R_2 = R_t - R_1$, 1/d
0.5	7.96	0.65	7.31
1.5	3.87	0.64	3.23
2.5	2.31	0.64	1.67
3.5	1.98	0.63	1.35
4.5	1.69	0.63	1.06
5.5	1.51	0.62	0.89
6.5	1.31	0.62	0.69
8.5	0.97	0.60	0.37
9.5	1.08	0.60	0.48
10.5	0.92	0.59	0.33
12.5	0.74	0.58	0.16
15.5	0.66	0.57	0.09
19.0	0.55	--	--
24.0	0.54	--	--
26.5	0.50	--	--
29.5	0.50	--	--

* Calculated $R_1 = K_1 G_1^\circ \exp(K_1 t)$ where K_1 and G_1° are obtained from Figure 6-2.

TABLE C4. Data for Estimation of Rate Constants and Initial Gas Potentials for the Fast Fraction for Exp II (bubble count results from Control digester normalized to wet test meter basis; data for Figure 6-4b).

Time, Days	Normalized Rate R_t, 1/d	Calculated R_1, 1/d	R_2, 1/d	$R_3 = R_t - R_1 - R_2$
0	3.47	0.54	2.23	0.70
0.05	11.00	0.54	2.22	8.25
0.1	9.75	0.54	2.20	7.02
0.2	9.25	0.54	2.16	6.55
0.3	8.08	0.54	2.12	5.42
0.4	7.82	0.54	2.09	5.20
0.5	7.15	0.53	2.05	4.56
0.6	6.15	0.53	2.02	3.60
0.7	4.50	0.53	1.99	1.98
0.8	3.91	0.53	1.95	1.42
0.9	3.81	0.53	1.92	1.36
1.0	3.40	0.53	1.89	0.98

Notes:

1. Normalized Rate = (Bubble count, 1/hr)x(24 hr/d)x(Factor) where Factor = wet test meter ave. rate/bubble count ave. rate = 6.57/6.05

2. Calculated $R_i = K_i G_i^\circ \exp(K_i t)\theta^{(35.8-36.25)}$ where K_i and G_i° are obtained from Figures 6-2 and 6-4a; $\theta = 1.25$.

TABLE C5. Fortran Program for Comparison of Mathematical Model to Experimental Data.

```
      PROGRAM VARPLT
      REAL RP(72),TIME(72),T(72),GT(72)
      REAL K1,K2,K3
      K1=0.0165
      K2=0.236
      K3=2.88
      G1=47900.
      G2=11900.
      G3=2950.
      G1ZERO=47900.
      G2ZERO=11900.
      G3ZERO=2950.
      THETA1=1.2
      THETA2=1.2
      DELT=0.0034722
      TIME(1)=0.3333
      TYPE 5
5     FORMAT(' TYPE PLOT OUTPUT FILE NAME',/)
      CALL ASSIGN(2,'TT:',-1,'NEW')
      TYPE 6
6     FORMAT(' TYPE TEMP. FILENAME',/)
      CALL ASSIGN(1,'TT:',-1,'OLD')
      TYPE 7
7     FORMAT(' TYPE OUTPUT FILE NAME',/)
      CALL ASSIGN(3,'TT:',-1,'NEW')
      SUM=0.33333
      SUMA=0.0
      SUMB=0.0
      SUMC=0.0
      READ(1,102)
      DO 10 K=1,72
      READ(1,103)T(K)
10    CONTINUE
      READ(1,100)
      READ(1,103)TR
      TYPE *,'TR=',TR
      WRITE(3,104)THETA1,THETA2
      WRITE(3,105)K1,K2,K3
      WRITE(3,106)
      DO 500 J=1,72
      GT(J)=0.0
      DO 490 I=1,4
      SUMA=SUMA+(K2*G2*(THETA2**(T(J)-TR))*DELT)
      G2=G2ZERO-SUMA
      IF(G2.LE.0.0)TYPE *,'G2 IS LESS THEN ZERO'
      SUMB=SUMB+(K1*G1*(THETA1**(T(J)-TR))*DELT)
      G1=G1ZERO-SUMB
      IF(G1.LE.0.0)TYPE *,'G1 IS LESS THEN ZERO'
      SUMC=SUMC+(K3*G3*(THETA1**(T(J)-TR))*DELT)
      G3=G3ZERO-SUMC
```

```
      IF(G3.LE.0.0)TYPE *,'G3 IS LESS THEN ZERO'
480   CONTINUE
490   CONTINUE
      RP1=K1*G1*(THETA1**(T(J)-TR))
      RP2=K2*G2*(THETA2**(T(J)-TR))
      RP3=K3*G3*(THETA1**(T(J)-TR))
      RP(J)=(RP1+RP2+RP3)/24.
      GT(J)=G1+G2+G3
      WRITE(3,107)TIME(J),G1,G2,G3,GT(J),RP1,RP2,RP3,RP(J)
      SUM=SUM+0.3333
      TIME(J+1)=SUM
      WRITE(2,101)TIME(J),RP(J)
500   CONTINUE
101   FORMAT('RD',2G15.7)
102   FORMAT(/)
100   FORMAT('  ')
103   FORMAT(14X,F10.2)
104   FORMAT('THETA1=',F6.4,2X,'THETA2=',F6.4)
105   FORMAT('K1=',F7.5,2X,'K2=',F7.5,2X,'K3=',F7.5)
106   FORMAT(' TIME   G1      G2      G3     GTOT     RP1      RP2

     +RP3    RTOT')
107   FORMAT(F5.2,F8.0,F8.0,F8.0,F8.0,F8.0,F8.0,F8.0,F8.0)
      CALL CLOSE(1)
      CALL CLOSE(2)
      CALL CLOSE(3)
      STOP
      END
```

APPENDIX D

APPENDIX D

THEORETICAL GAIN IN GAS PRODUCTION

It was found in the analysis of the mathematical model that the higher gas production of the fluctuating temperature digester lies, in part, in the temperature dependence term based on the Arrhenius equation. The higher the activation energy or the temperature fluctuation, the higher the gas production will be compared with a digester at constant temperature. The demonstration of this relationship will be presented as follows.

Equation 6-11 from Chapter 6 can be rewritten as

$$K = K^r \exp[-E(T_r - T)/RT_r^2 \qquad (B-1)$$

where $T_r^2 \simeq TT_r$.

Let K' = effective constant temperature rate that gives the same gas production as K^r gives with variable temperature. Substitute Equation D-1 into Equation 6-4 and integrate with respect to time:

$$\int^t K^r G \exp[-E(T_r - T)/RT_r^2] \, dt = \int^t K'G \, dt \qquad (D-2)$$

When G remains relatively constant over a feeding cycle, G can be removed from Equation D-2 giving:

$$K^r \int^t \exp[-E(T_r - T)/RT_r^2] \, dt = K't \qquad (D-3)$$

Assume that the temperature fluctuation is a linear function of time as follows:

$$T = T_{max} - mt \tag{D-4}$$

where m = rate of temperature change, °C/day.

Substituting Equation D-4 into Equation D-3 and integrating with t = 0.5 day, half a cycle, gives:

$$K'/K^r = RT_r^2/E(T_{max}-T_{min})\left[\exp[-E(T_r-T_{max})/RT_r^2] - \exp[-E(T_r-T_{min})/RT_r^2]\right] \tag{D-5}$$

Equation D-5 gives the ratio of the gas production with a linearly fluctuating temperature to the gas production at constant temperature. Using the values of activation energy (E = 42.5 Kcal/degree Kelvin) and temperature range of 6.65°C (T_{max} = 39.57°C, T_{min} = 32.92°C) for the extended period of Experiment IIC, the calculated result is:

$$K'/K^r = 1.093 \tag{D-6}$$

Therefore, the estimated value of the gas production from the slow and moderate fractions in the fluctuating temperature digesters (EXP IIA, IIB, and IIC) are 9.3% higher than the gas production from these fractions in the control unit. However, since the fast fraction is almost completely degraded in 24 hours, gas production from this fraction is not much affected by temperature fluctuations. The estimation of gain in gas production for fluctuating temperature digesters compared to constant temperature digesters for various ranges of temperature fluctuation (ΔT) calculated by Equation D-6 are shown in Table D-1.

TABLE D1. Theoretical Gain in Gas Production Due to Fluctuating Temperature for a Slowly Degradable Substrate (percent increase over constant temperature).

E Kcal/°K	θ*	ΔT, °C 3.00	5.00	6.65	10.00
10	1.05	0.1	0.3	0.5	1.2
20	1.11	0.4	1.2	2.0	4.7
30	1.17	0.9	2.6	4.6	10.7
40	1.23	1.7	4.7	8.3	19.5
50	1.30	2.6	7.4	13.2	31.4
60	1.37	3.8	10.7	19.4	46.9
70	1.44	5.2	14.7	26.9	66.8
80	1.52	6.8	19.5	35.9	91.8

* $\theta = \exp(E/RT_r^2)$

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