ENGINEERING ANALYSIS OF A CHINESE-TYPE ANAEROBIC DIGESTER

by

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(ABSTRACT)

This study was undertaken to evaluate the performance of spherical Chinese digesters receiving dairy waste. Sixteen laboratory-scale (3L) reactors were operated in the mesophilic temperature range (35°C±2°C) and were subjected to hydraulic retention times (HRT) of 8, 10, 15, and 20 days and influent substrate concentrations (S_0) of 40.1, 57.8, 62.3, and 71.2 g BVS/L. Preliminary tracer experiments were performed to identify digester flow characteristics. A two-microbial culture mathematical model incorporating incomplete mixing and intermittent feeding was developed to predict effluent quality and gas production.

Stimulus-response data indicated that by positioning the outlet at the bottom of the digester, flow characteristics could be improved, leading to reductions in dead space and bypassing volumes by 47% and 91%, respectively. Digesters operated at HRT's of 10, 15, and 20 days performed normally. In these units, for a given S_0, as the HRT was increased the

volumetric methane production decreased while the unit methane production increased. The improvement in effluent quality was substantial when the HRT was increased from 8 to 10 days, and was modest when the HRT was increased beyond 10 days. The 8-day digesters were inhibited due to overloading. pH drops in these digesters were concurrent with alkalinity deficit. The optimum values for operational parameters were found to to be an HRT of 10 days, and a loading rate of 7.12 g BVS/L-d.

The two-culture mathematical model predicted gas yield and effluent concentration under retarded and normal digester operations. The three-step feed model best described digester activity following feed addition. The sensitivity analysis revealed that the digester model was decreasingly sensitive to the inhibition coefficient of methane-formers (KI2), the inhibition coefficient of acid-formers (KI1), the half-velocity concentrations (KS1, KS2), and the flow-parameters (A, B).

O Lord, how great are thy works!....

Ps. 92:5

The fear of the Lord is the begining of knowledge.....

Prov. 1:7

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dedicates this work to the memory of his late father,

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1.0 INTRODUCTION

The rising price of oil since 1973 has plunged oil importing countries into what is commonly termed the 'oil crisis', which is really a liquid fuels crisis. Petroleum is a finite resource and, even by the most optimistic standards, it will be exhausted early in the 21st century.

Among the various energy alternatives, biomass is perhaps the only energy source which is both available and affordable to the mass of the third world population. Biomass is a general term that refers to plant and animal material. Many conversion processes are available to release the energy stored in these materials. Anaerobic digestion, if harnessed efficiently, represents a valuable means of converting biomass to a more convenient and versatile fuel form - methane. Associated benefits of providing a nutrient-rich residue and pollution control also accrue.

1.1 SRI LANKA AND THE ENERGY CRISIS

Sri Lanka (formerly Ceylon) is a tropical island in the Indian Ocean situated south, and slightly east of southernmost India, and separated from that subcontinent by a narrow strip of shallow water. Sri Lanka has a total area

of 65,610 km^2 (25,332 $mile^2$) and is approximately the size of the state of West Virginia.

With a GNP per capita of $200, Sri Lanka ranks among the low-income group of countries. However, with respect to the physical quality of life index, Sri Lanka (with a value of 82) ranks between the upper-middle and high-income groups. In short, compared with its near neighbors, Sri Lanka enjoys a modestly high standard of living.

The Sri Lankan economy is based on agriculture, which employs nearly half of the labor force and accounts for one-fourth of the GNP. The main export crops - tea, rubber and coconut - are planted on about 40 percent of the total cultivated area, with paddy - the major food crop - occupying another 40 per cent. Minor crops include coffee, cashew nuts, citronella, cardamon, cinnamon, cloves, and tobacco.

1.1.1 THE SECOND ENERGY CRISIS

Total energy consumption of Sri Lanka in 1981 was 3.5 x 10^6 tons of oil equivalent (toe)[1] (Peramunetileke, 1983). As in most developing countries, non-commercial energy sources

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[1] 7 X 10^6 J
= 10.2 X 10^6 kcal
= 40.5 X 10^6 BTU

supply a significant portion of the energy needs. Approximately 60 percent of the total energy consumption is satisfied from fuel wood. The country's only other indigenous energy source is hydropower. Petroleum products are being imported to supply approximately 27% of the energy demand. Crude oil was the largest single item of import expenditure in 1981, accounting for nearly 25% of total import value (Quarterly Economic Review of Sri Lanka, 1981). Since 1974, Sri Lanka's trade balance has been chronically negative due to the increase in the cost of imported oil.

The problems associated with hydroelectricity, which supplies 13% of the energy requirement, can be presented by quoting from the Quarterly Economic Review of Sri Lanka (1984): "The most noteworthy feature of the energy situation in Sri Lanka during 1983 was that, owing to drought, hydroelectricity generation was severely curtailed, leading to an upsurge in imported heavy diesel for thermal electricity generation. Further, to balance supply and demand, power cuts were imposed in the latter part of the year throughout the island. To compensate for the additional costs incurred in increased thermal power production, electricity prices were revised upwards".

The vast majority of rural population in Sri Lanka, as well as a significant number of city dwellers, have traditionally

relied on biomass fuels to satisfy their energy needs. The most common fuels used are wood and crop residues. The predominant conversion method is direct burning. While these traditional methods have been used successfully for many years, their continuation may be in doubt due to population growth and associated pressure on the environment for provision of both food and fuel. In order to sustain current fuelwood use, widespread and rampant deforestation is being practiced leading to increased risk of flooding, erosion, siltation, and associated problems. The inadequacy of the present reforestation efforts to stem forest depletion has led to a severe shortage of wood. These problems, sometimes called the 'second energy crisis', are superimposed on those caused by the rising oil prices.

1.1.2 THE RURAL SETTING

The rural people of Sri Lanka are, in comparison to their urban counterparts, poor. Their main occupation is farming. Land holdings are small, averaging not more than 1.25 ha per family. Many farmers also raise a few cattle to supply their requirement of milk and fertilizer.

Although energy requirements in the rural areas are moderate in comparison to urban areas, rural families are often in the weakest position with regard to their capacity to absorb

energy price rises. Providing a sustainable and affordable energy source is an important component of rural development. Coupled with financial, technological, and other inputs, a relatively small increase in energy use can bring substantial improvements in agricultural productivity and can permit growth in rural industries and public services. Necessarily, any conversion technology implemented be simple, low cost and easily manageable. In addition, input to the system should be readily and locally available.

Anaerobic bioconversion of animal wastes is one process which meets these requirements. This process has many advantages, the more important ones being:

- Production of a clean form of energy (methane);
- Utilization of readily available feedstock;
- gas scrubbing usually not necessary;
- fertilizer value of feedstock essentially conserved;
- pollution control;
- pathogen and odor control;

- integrates well with farm operations.

1.1.3 BIOGAS TECHNOLOGY: PRESENT STATUS

The basic characteristics of rural digesters used in developing countries are their low capital and maintenance costs and low energy demand. These requirements are frequently achieved by constructing digesters with no provisions for either heating or mixing.

A survey of literature reveals that there are essentially two types of rural digesters commonly in use in the third world countries. The Indian-type digester is structurally more complex and therefore it requires higher capital cost than the Chinese digester. The latter has been in use for over 50 years. A recent study (Liljedahl et al., 1983) estimated that there were approximately 7,000,000 digesters in use in China. Basically, there are three types of Chinese digesters (Chen, 1982). These are the water pressure type, the floating cover type, and the membrane gas holder type. Of these, the water pressure type is by far the most popular. The wide acceptance of this design may be attributed to its ease of maintenance, and simple structure. In addition, the fixed dome achieves high gas pressures required to operate kitchen stoves.

The design most common in Sri Lanka is a modification of the Chinese water pressure type reactor. Being spherical in shape, it takes advantage of the soil pressure to counter balance its internal liquid pressure. Hence, it can be easily constructed with local material, requiring no additional reinforcement and associated cost. More importantly, like all other Chinese digesters, it is inherently buffered against fluctuating ambient temperatures. Chen (1982) reported that the temperature of the surrounding soil varies very slowly in response to more drastic changes of atmospheric air temperatures and the soil temperature was almost always in equilibrium with the digester temperature. It follows that the digester bacterial population is able to acclimatize to seasonal temperature changes. It is not surprising that these digesters are operated year round without heating.

A survey (Collins, 1984) conducted to determine the development of biogas technology and its role as a supplemental energy source for rural Sri Lanka indicated that anaerobic fermentation of animal waste is technically and economically feasible as an alternate energy source. The Chinese digester, because of its low initial and operating cost, and its simplicity, is particularly popular in Sri Lanka, in spite of a lack of concerted government support for construction and development.

In 1979 very few biogas digesters were in use (Collins, 1979) but by 1984 there were at least 800 units (Upawansa, 1984), indicating an increase of interest. According to Upawansa (1982), the cost of constructing a 6 cubic meter Chinese digester in Sri Lanka is in the range of Rs. 2800 to Rs. 3600 (U.S. $112 to U.S. $144) including the cost of pipeing, one stove, and one lamp. This is claimed to be the lowest among the developing nations (Upawansa, 1984). Upawansa (1984) states that small-scale Chinese biogas digesters can dramatically improve the lives of small landholders by stabilizing and increasing incomes, while improving health and sanitation in developing countries. Although these digesters have been reported to be stable, their operation is more of an art than science. Gas production from a typical unit ranges between 0.15 and 0.3 m^3/m^3- d. This compares with 0.93 - 3.76 m^3/m^3- d reported in other studies (Jeyanayagam and Collins, 1984; Gramms et al., 1971). Normally, performance is measured by production of some amount of gas, and if enough is produced to satisfy the owner's needs, performance is considered to be satisfactory.

In Sri Lanka, as in many other developing countries, while some rural famlies may afford installation of a digester, hundreds of others cannot afford such luxury. Hence, there exists an urgent need to design and operate the Chinese

digester to maximize gas production, thereby supplying the energy needs of more family units from fewer digesters.

1.2 SCOPE OF STUDY

It is clear that the potential for alternate energy sources in Sri Lanka is promising. If appropriate systems are developed, a shift in dependency from oil and fuel wood to renewable sources will follow. If anaerobic digestion is to play a major role in the rural community as a potential energy source, the following steps should be taken: (1) develop operational criteria for the digesters, and (2) educate the rural household to operate and to maintain a digester.

Inorder to accomplish the first step stated above, in this study, an engineering analysis of a Chinese digester, was conducted to evaluate its operating characteristics and performance. Specific objectives of this investigation were:

1. to establish digester flow characteristics and to determine structural changes necessary to improve these characteristics;

2. to observe digester response to changes in operational variables in the presence of intermittent (pulse) feeding and incomplete mixing;

3. to develop a kinetic model to predict gas production and effluent quality;

4. to define the operating regimen for maximum methane production and failure conditions;

5. to determine the effects of digester feeding more than once a day; and,

6. to recommend design modifications and operating methods likely to increase gas yields.

2.0 LITERATURE REVIEW

2.1 BIOCHEMISTRY AND MICROBIOLOGY OF METHANOGENESIS

The microbiological degradation of organic matter in an anaerobic environment is accomplished by microorganisms that are able to utilize molecules other than oxygen as hydrogen acceptors. The process is chemically complex involving numerous intermediate compounds and reactions. The ability of the organism to mediate any particular transformation or reaction depends on the availability of the enzyme specific to that reaction, and the ability of the substrate to pass through the cytoplasmic membrane of the cell.

In this section a discussion on the nature of the feedstock, the nutritional requirements of the organism involved, and the reactions of conversion of organic matter to gaseous end-products will be presented.

2.1.1 CONSTITUENTS OF DIGESTER FEEDSTOCK

Dairy cattle manure mainly includes cellulose and hemicellulose (Hills and Roberts, 1980). Other minor sources of carbohydrates are bacterial cells, gut secretion, and cells sloughed off intestinal walls. Undigested plant fibers

are always present in animal feces. These fibers consist of simple sugars linked together to form polysaccharides (Hobson et al., 1981). During hydrolysis, simple sugars are released and utilized by digester bacteria.

According to McInerney and Bryant (1981), Hobson et al. (1981), Downing and Kell (1980), Bryant (1979), and Toerein and Hatting (1969) degradation of protein proceeds via the extracellular hydrolysis, whereby peptides are formed. These are broken down into their component amino acids before being absorbed into the bacteria. Intracellular degradation follows resulting in the production of ammonia, carbon dioxide and volatile fatty acids. Non-protein nitrogen compounds like urea are rapidly degraded to ammonia, and are used by bacteria as an energy source. The source of lipids in animal waste is vegetable matter. However, the death of intestinal bacteria present in the feces may also contribute to the amount of lipids in the waste. Chynoweth and Mah (1971) reported that carbohydrate, protein and lipid reduction to fatty acids were 13%, 36% and 76% , respectively.

2.1.2 NUTRITIONAL REQUIREMENTS OF BACTERIA

In general, the nutritional requirements of microorganisms are reflected by their chemical composition. The composition

of bacteria is about 90% water. The dry weight is composed of nitrogen (10%), carbon (50%), hydrogen (10%), and oxygen (20%). In addition, inorganic matter in the form of metallic salts, various cell structures, and sulfur are also present.

Bryant (1974) stated that most rumen organisms have very simple nutritional requirements. Cell carbon is obtained from the substrate carbohydrate, amino acids, carbon dioxide, acetic acid or higher volatile fatty acids (Hobson et al. 1981). Ammonia or amino acids are the nitrogen sources for the bacteria (Hashimoto et al., 1980; Zeikus, 1977; Bryant et al., 1971). McInerney and Bryant (1981) included peptides, urea and nitrate as possible nitrogen sources. Sulfide or cysteine serve as sulfur sources for some bacteria. In addition, most strains need one or more B-vitamins for growth (Shuler, 1980).

Since carbon and nitrogen are the major elements required, the C/N ratio is a reflection of the nutritional value of the substrate. Work by various others (Sievers and Brune, 1978; De Renzo, 1977; Meynell, 1976; Sanders and Bloodgood, 1965; Kaplovsky, 1952; Kroeker et al., 1979) have resulted in recommendations of C/N ratios for successful digester operation. Specifically, for dairy manure, the optimum C/N ratio has been suggested as 25:1 (Hills, 1979).

2.1.3 THE TWO-STAGE SCHEME

Since the 1930's, methane fermentation was thought to involve only two major metabolic groups of bacteria. Price and Cheremisnoff (1981), Golueke (1977), and McCarty (1964a) found the two-stage process convenient to express the chemistry, microbiology and kinetics of anaerobic fermentation.

A simplified illustration of the two-stage scheme is presented in Figure 1. In the first stage, complex organics such as fats, proteins and carbohydrates are acted upon by a group of facultative anaerobic bacteria, and biologically converted to simpler products, namely organic acids. The bacteria responsible for this conversion are termed acid-forming or hydrolytic bacteria. The main functions of the hydrolytic bacteria are (a) to produce suitable enzymes to hydrolize the substrate extracellularly, and (b) to break down the hydrolysed substrate intracellularly to simpler compounds. Chemically this step is one of hydrolysis and fermentation, in which a small portion of energy is released for growth and a small portion of the organic waste is converted to cell mass.

The first stage merely converts organic matter to volatile fatty acids - a form suitable for the second stage of

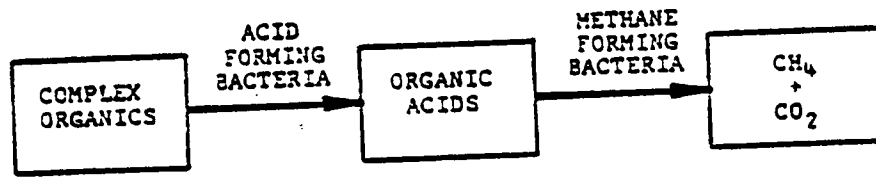


Figure 1. The Two-Stage Scheme

treatment. McCarty (1964a) listed as many as seven possible volatile acid intermediates. However, Toerien and Hatting (1969) and McCarty (1964a) have concluded that acetic and propionic acids are the most important intermediates in methanogenesis.

It is in the second stage of methane fermentation that true waste stabilization occurs. Organic acids are acted upon by a group of bacteria called methane-formers and converted to methane and carbon dioxide which are the most reduced and the most oxidized one carbon compounds.

The importance of methanogenic bacteria and acetate has been illustrated by McCarty (1964a). His scheme for the anaerobic fermentation process (Figure 2) indicates that methane-formers are responsible for most of the acetic acid formed, and this acid in turn amounts for nearly 72% of the gas produced. The percentages are based on chemical oxygen demand (COD) conversion. Mountfort and Asher (1978), Zeikus (1977), Smith and Mah (1966), and Jeris and McCarty (1962) have also stressed the importance of acetate in methane fermentation.

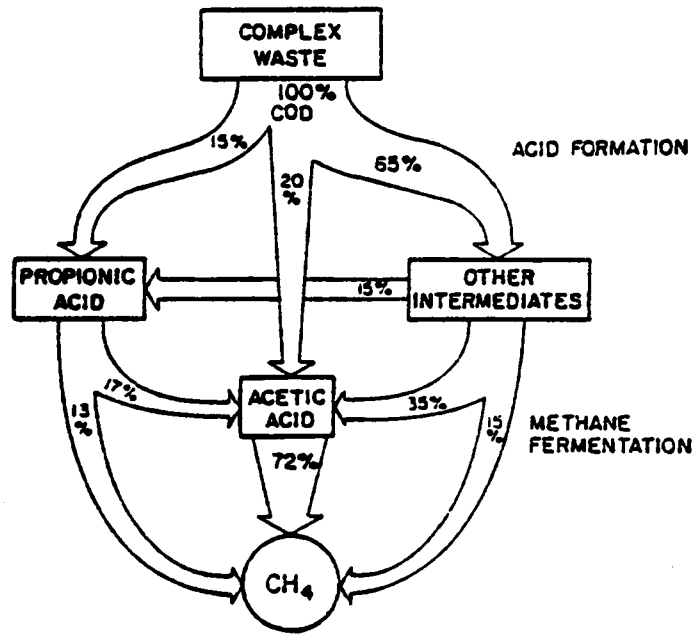


Figure 2. Pathways in Methane Fermentation (McCarty1964a)

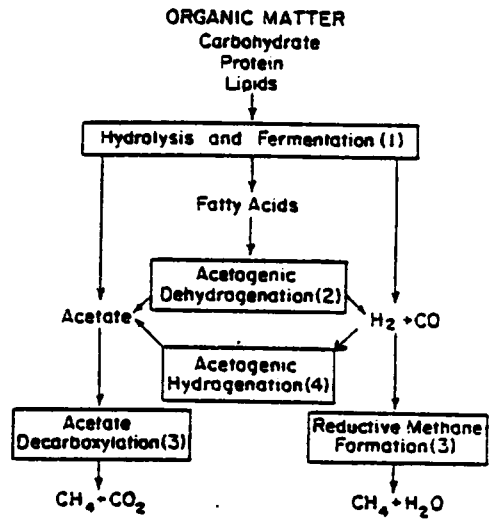


Figure 3. The Three-Stage Scheme (Bryant et al.1977)

2.1.4 THE THREE-STAGE SCHEME

Research by McInerney and Bryant (1981), and Bryant et al. (1977) indicated that a three-stage scheme for anaerobic fermentation (Figure 3) best fits the current information.

The first stage is the same as in the two-stage scheme, the end-products being fatty acids, alcohols, carbon dioxide, ammonia, and hydrogen. In the second stage, hydrogen-producing acetogenic bacteria convert these first stage products into hydrogen, carbon dioxide and acetic acid. Methanogenic bacteria, which form the third group, consist of two physiologically different organisms (McCarty, 1964a; Buswell and Mueller, 1952). One converts hydrogen to methane (hydrogen - utilizing methanogens), while the other forms methane by direct acetic acid cleavage (acetate - utilizing methanogens). The acetate-utilizing methanogens, although responsible for approximately 72% of the methane formed, are slow-growing (Hobson et al., 1974; McCarty, 1966) and often control the overall digester performance. The chemical representation of these two methane-forming mechanisms are:

$$CH_3COOH \rightarrow CH_4 + CO_2$$

$$CO_2 + 8H^+ + \rightarrow CH_4 + 2H_2O$$

Although three distinct stages of anaerobic fermentation have been identified, these actually proceed simultaneously. Further, the microorganisms responsible for the reactions have been observed to exhibit substrate preference (Russell and Baldwin, 1978). Hence, it is not surprising that more than one species of bacteria is necessary to complete a particular stage of the reaction.

2.1.5 REGULATORY ACTION OF HYDROGEN

The conversion of organic matter to methane is a closely coupled symbiotic relationship between the different groups of bacteria, with the dynamic balance between the production and utilization of the intermediate products (fatty acids, hydrogen) critical to the overall success of the fermentation process. Should this dynamic balance be disturbed, digester failure is imminent.

The significance of hydrogen in the digester environment has only recently been discovered (McInerney and Bryant, 1981; Hashimoto et al., 1980; Bryant, 1979; Zeikus, 1977). Propionic and butyric acids are the major end-products of the first stage and are substrate for the hydrogen-producing bacteria of the second stage:

$$CH_3CH_2COOH + 2\ H_2O \rightarrow CH_3COOH + CO_2 + 3\ H_2$$

$$\Delta G'_0 = +\ 76.1\ kcal/mol$$

$$CH_3CH_2CH_2COOH + 2\ H_2O \rightarrow 2CH_3COOH + 2H_2$$

$$\Delta G'_0 = +\ 48.1\ kcal/mol$$

The standard free energy change for these two reactions are positive at pH 7.0 and cannot proceed to the right as written. However, if the hydrogen is removed, thus maintaining a low hydrogen partial pressure, then the $\Delta G'_0$ values become progressively negative. In short, for the conversion of propionic and butyric acid to be thermodynamically favorable, low hydrogen concentrations must be maintained in the reactor. McCarty (1982) has determined that at hydrogen partial pressures of greater than 10^{-6} atmospheres, propionate conversion is hindered. This is confirmed by the investigations of Varel et al. (1977), McCarty et al. (1963), and Pholand and Bloodgood (1963).

McInnerny and Bryant (1981) and Bryant (1979) suggested that a phenomenon called 'interspecies hydrogen transfer' is responsible for maintaining low hydrogen concentrations in the reactor. Accordingly, the hydrogen-utilizing methane formers of the third group biologically remove hydrogen from the digester environment thereby maintaining an atmosphere suitable for propionic and butyric acid conversions. A

fourth group of microorganisms has also been recently implicated in the removal of H_2 leading to the formation of acetate (McInerney and Bryant, 1981). This close association between the hydrogen-producing and the hydrogen-utilizing bacteria is essential for proper digester performance. McCarty (1985) concluded that in almost all successful digesters a certain amount of attached growth is evidenced. The closeness of the organisms is believed to enhance hydrogen transfer.

2.2 SYSTEM BEHAVIOR

The anaerobic fermentation process involves a consortium of microorganisms, whose basic functions are to consume the substrate, and to propagate. But in so doing, they generate by-products of value to humans.

The efficiency of the biochemical reactions occurring during anaerobic digestion is greatly dependent upon the environment imposed on its biological population. Because of their size (microns in diameter), unicellular microorganisms have a large surface area-to-volume ratio and short path lengths for diffusion. On the one hand, this causes remarkably high metabolic rates in the microorganisms, while on the other hand, guarantees quick and significant changes to occur within the organism in response to changes in environmental

conditions (Edwards, 1970). Hence, a basic understanding of the microbe-environment interrelationship is of utmost importance for process prediction and control.

Temperature, pH, overloading, and the presence of toxic material may cause some of the physiological variables of the cell to increase, to decrease, to fluctuate, or to exhibit no apparent change. A retarded digester is the result of reduced microbial activity. Some of the symptoms of process inhibition are:

1. reduction in methane content and total volume of gas produced;

2. increase in volatile acid concentration;

3. depression of pH; and

4. increase in effluent substrate concentration.

2.2.1 TEMPERATURE EFFECTS

Anaerobic bacteria in general, and methane-formers in particular, are extremely sensitive to temperature fluctuations (Pohland and Bloodgood, 1963). For example, a spherical particle with a diameter of one micron will reach

a temperature near that of its environment within milliseconds, even if an unrealistically low thermal conductivity is assumed (Edwards, 1970).

In an early study, Fair and Moore (1934) concluded that there were four distinct temperature zones of microbial activity: thermophilic (above 42°C), intermediate (28°C - 42°C), temperate (10°C - 28°C), and cryophilic (below 10°C). In recent work, Downing and Kell (1980) suggested three temperature ranges: thermophilic (50°C - 60°C), mesophilic (25° - 38°C), and psychrophilic (5°C - 25°C). The mesophilic and thermophilic ranges are of interest in the treatment of agricultural, municipal and domestic wastes.

Temperature has a pronounced effect on waste stabilization. The investigations of De Renzo (1977), Pfeffer (1973), and Golueke (1958) indicated increased volatile solids destruction at higher temperatures. Using gas production data as a measure of the degree of substrate utilization, Pfeffer (1973) concluded that the first-order rate constant for substrate conversion varied directly with the temperature.

Pfeffer (1966) found that when the temperature was reduced from 35°C to 25°C over a 10-day period, the rate of gas production dropped. In another investigation, Pfeffer and

Liebman (1976) reported that the volatile solids destruction at 60°C and a 4-day solids retention time (SRT) was greater than at 40°C and a 30-day SRT. The influence of temperature on the period of digestion is illustrated in Figure 4

Cooney and Wise (1975) compared mesophilic and thermophilic digestion of domestic solid waste, and concluded that the gas produced was greater for the thermophilic range. Similar results were presented by Malina (1962). The dependence of gas production on temperature of the fermentation process is illustrated in Figure 5 (Pfeffer and Liebman, 1976). The optimum mesophilic and thermophilic temperatures are 40°C and 60°C, respectively (Price and Cheremisnoff 1981).

Garber (1977) stated that thermophilic anaerobic fermentation results in lower numbers of potentially pathogenic bacteria in the treated effluent. The stability of the anaerobic process is closely related to temperature fluctuations. A study conducted by McCarty and McKinney (1961) revealed an increase in the inhibitory effect of ammonia-nitrogen at increased temperatures. This is probably due to an increase in the ionization rate leading to a higher fraction of inhibitory free ammonia. Fisher and Greene (1945) found that over a short period of time a temperature fluctuation of 3°C can affect the digester performance significantly.

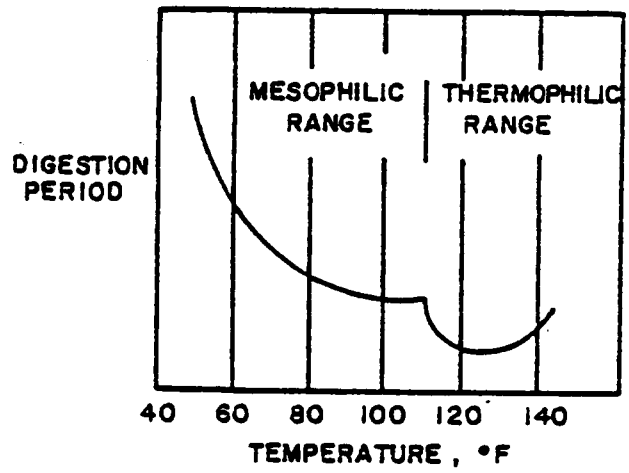


Figure 4. The Influence of Temperature on the: Period of Digestion (McCarty 1964b)

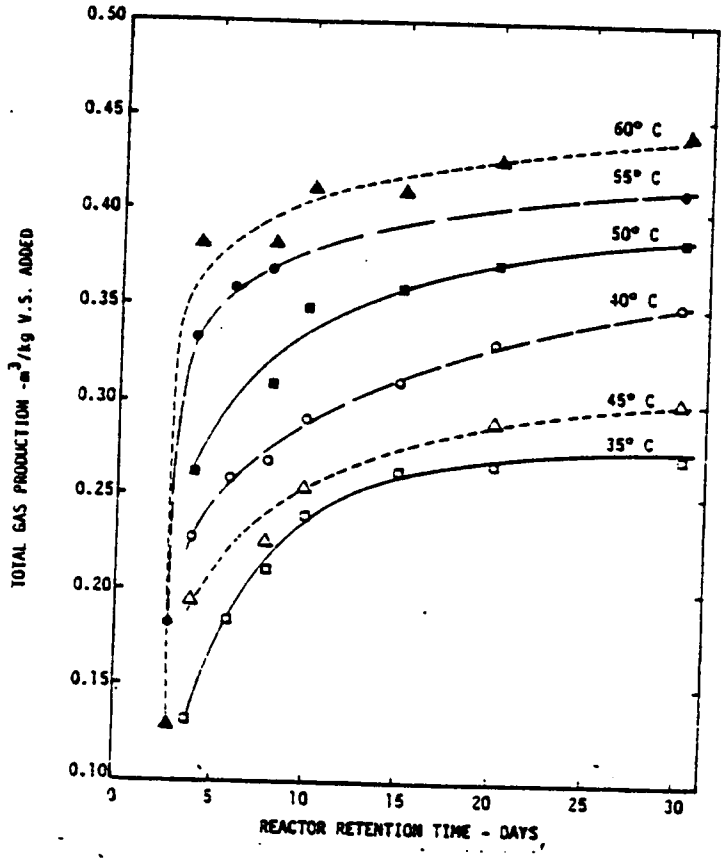


Figure 5. The Influence of Temperature on: Gas Production (Pfeffer et al. 1976)

Although it is important to keep the temperature relatively constant in order to maintain digester performance at its maximum, pilot-scale studies have indicated that even large temperature fluctuations did not cause permanent damage to the bacterial population (Stafford et al., 1980; Capri and Marais, 1975). Field digesters with large working volumes and high SRT values tend to be more tolerant of temperature fluctuations than small well-mixed laboratory digesters. Golueke (1958) stated that unstable conditions due to abrupt temperature changes result only if the microbial population in the digester is not well established.

Shifting from one temperature range to another should be performed cautiously. Different sets of bacteria predominate at these two ranges, and the transition should be gradual to avoid digester failure. The importance of choosing and maintaining optimum temperature need not be overemphasized.

The effects of temperature changes on the digestion process, although important, were not considered in the present investigation reported herein. All laboratory digesters were maintained at 35°C ± 2°C.

2.2.2 PH AND ALKALINITY

The heterogeneous bacterial population in an anaerobic digester comprises a wide variety of bacterial species. Each species has an optimum pH range in which its growth is best and where its metabolic processes function at optimum levels. The optimum pH range is the integral result of the contributions by the different reactions taking place. McCarty (1964b) reported that methane production proceeds quite well as long as pH is maintained between 6.2 and 7.6, with an optimum range between 6.6 and 7.2. At pH values below 6.2, volatile acid toxicity is acute (Hashimoto et al., 1980), while at pH levels greater than 7.6 the production of free ammonia at high organic loading rates causes inhibition (Jewell et al., 1976).

According to Stanier et al. (1964), the internal pH of the all living cells is approximately 7.0. Membranes of the living cells are only slightly permeable to hydrogen and hydroxyl ions (Stanier et al., 1964). Hence, most bacteria are not directly affected by the external concentrations of these ions. However, they are quite sensitive to un-ionized ions, the magnitude of which is pH-dependent. For example, weak acids are poorly dissociated at low pH values, and in their undissociated forms they easily migrate into the cells and thus change the internal pH. Strong acids, on the other

hand, are highly dissociated and therefore have a much less drastic effect. Weak bases and acids are thus toxic at high and low pH values, respectively, but are relatively harmless at neutral pH values (Stanier et al., 1964).

The alkalinity of an anaerobic digester is a measure of its buffering capacity, and is defined as the amount of strong acid or base required to change the pH by one unit (Buller, 1964). Buffers are, therefore, substances in solution that offer resistance to changes in pH as acids or bases are added to or formed within the solution. Buffer solutions usually contain a mixture of weak acids and their salts, or weak bases and their salts.

The microbially mediated reaction within the anaerobic ecosystem may be chemically represented as follows:

<u>ACID FERMENTATION (Oxidation)</u>

$$4C_3H_7O_2NS + 8H_2O \rightarrow$$

$$4CH_3COOH + 4CO_2 + 4NH_3 + 4H_2S + 8H^+ + 8e^-$$

<u>METHANE FERMENTATION (Reduction)</u>

$$8H^+ + 8e^- + 3CH_3COOH + CO_2 \rightarrow 4CH_4 + 3CO_2 + 2H_2O$$

ANAEROBIC FERMENTATION (Oxidation and Reduction)

$$4C_3H_7O_2NS + 6H_2O \rightarrow$$

$$4CH_4 + 6CO_2 + 4NH_3 + CH_3COOH + 4H_2S$$

With the exception of methane, the products of the above equation dissociate as weak acids or bases and form their own buffer systems in aqueous solution. Table 1 on page 32 lists the major acid-base systems encountered within the anaerobic ecosystem (Pholand and Engstrom, 1964; Albertson, 1961; Banta and Pomeroy, 1934). From the titration curves for these acids and bases, it could be infered that their buffer capacities are greatest at or close to pH values equal to their pKa values (Pohland, 1968). Since the sulfide concentration in dairy wastes is generally low, the pH in these digesters can be assumed to be controlled by the bicarbonate, the ammonia, and the VFA buffer systems.

Table 1. Major Buffer Systems in Anaerobic Ecosystem

ACID-BASE SYSTEM	pK_a
H_2CO_3 - HCO_3^-	6.4
NH_4^+ - NH_3	9.3
H_2S - S^-	6.9
Volatile Acids	4.8

Figure 6 depicts the domain of influence of the common buffers found in anaerobic digesters. The broken line represents the sum of all buffers at any given pH. Clearly, the VFA and the ammonia buffer systems exert their influence at pH values less than 6.0 and greater than 7.6, respectively, while in the pH range of normal digestion (6.2-7.6), the bicarbonate buffer system is dominant. The volatile acids and ammonia are completely ionized near neutral pH values and are ineffective as buffers. However, they act as a strong acid and a strong base, respectively, and interact with the bicarbonate system to establish the pH (Capri and Marais, 1975; Halderson et al., 1973).

The relationship between pH and carbonic acid is illustrated by the following equilibrium equation:

$$[H^+]\ [HCO^-] = K\ [H_2CO_3]$$

where,

$[H^+]$ = Hydrogen ion concentration, mol/L

$[HCO^-]$ = Bicarbonate ion concentration, mol/L

$[H_2CO_3]$ = Carbonic acid concentration, mol/L

K = First ionization constant for carbonic acid.

Based on this equation, McCarty (1964b) fixed the limits of anaerobic treatment (Figure 7).

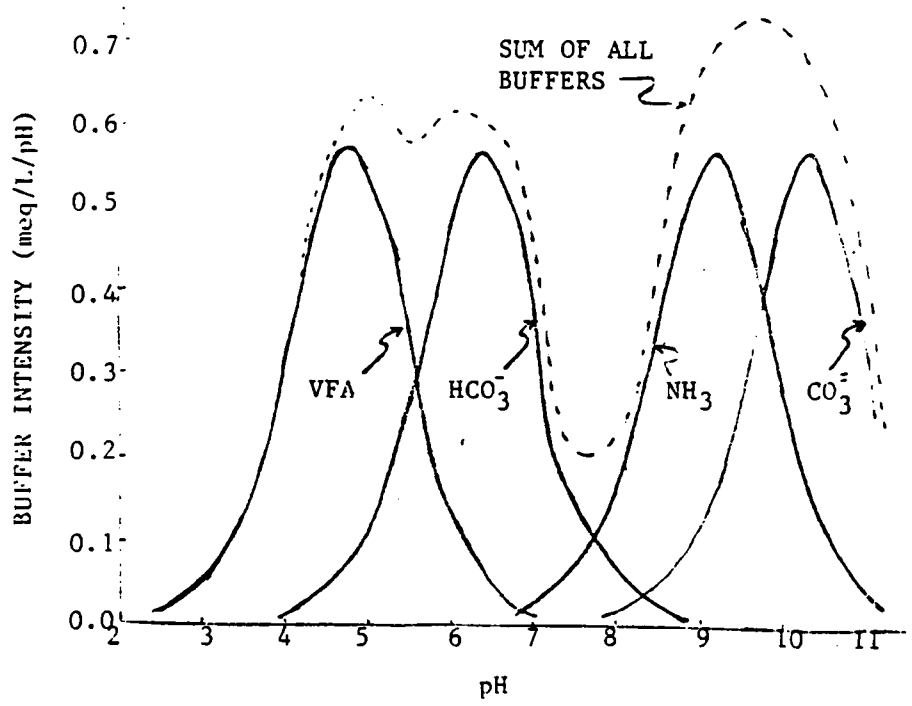


Figure 6. Buffer systems in Digesters (Georgacakis et al.,1984)

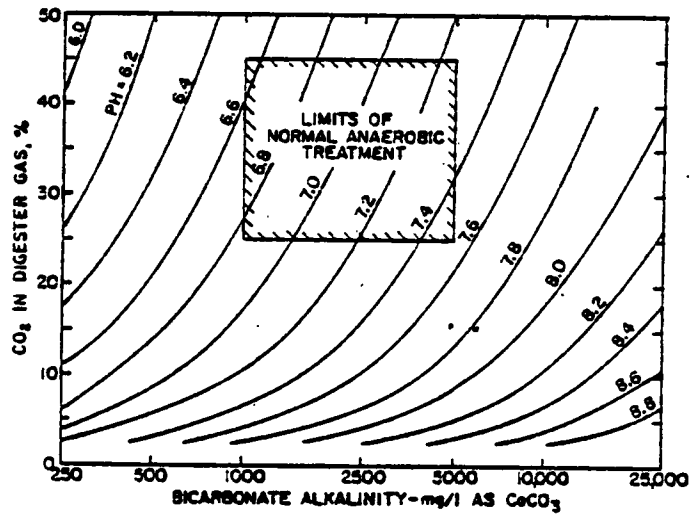


Figure 7 Limits of Anaerobic Treatment (McCarty 1964b)

The combined effect of all three buffers in a failing digester can be illustrated by Figure 8. Curves A, B and C describe the stability of the digester at three different points in time. Initially, the digester is stable with a low VFA concentration (IA) and a high bicarbonate buffer intensity (IIA). The pH of this system is very stable and is located at (1). As VFA increases, a corresponding decrease in the bicarbonate buffer will result due to the destruction of the alkalinity buffer. If this trend continues (curve C), a point will be reached where the bicarbonate alkalinity is essentially zero (II C). This represents complete failure of the digester with the pH shifting to position (3), between the VFA and ammonia buffer capacity peaks. It should be noted that at any point in time, electroneutrality must be satisfied. That is, the sum of the negative charges must equal the sum of the positive charges. Correcting a retarded digester involves overcoming the appropriate buffer system by altering the concentration of acids or bases by (1) internal generation, (2) removal from the system biochemically or hydraulically, or (3) external addition.

Georgackis et al. (1982) proposed that the C/N ratio is a good indicator of the bicarbonate - ammonia balance. Their study with swine manure digestion revealed that C/N ratios less than 10/1 exhibit ammonia inhibition, while ratios

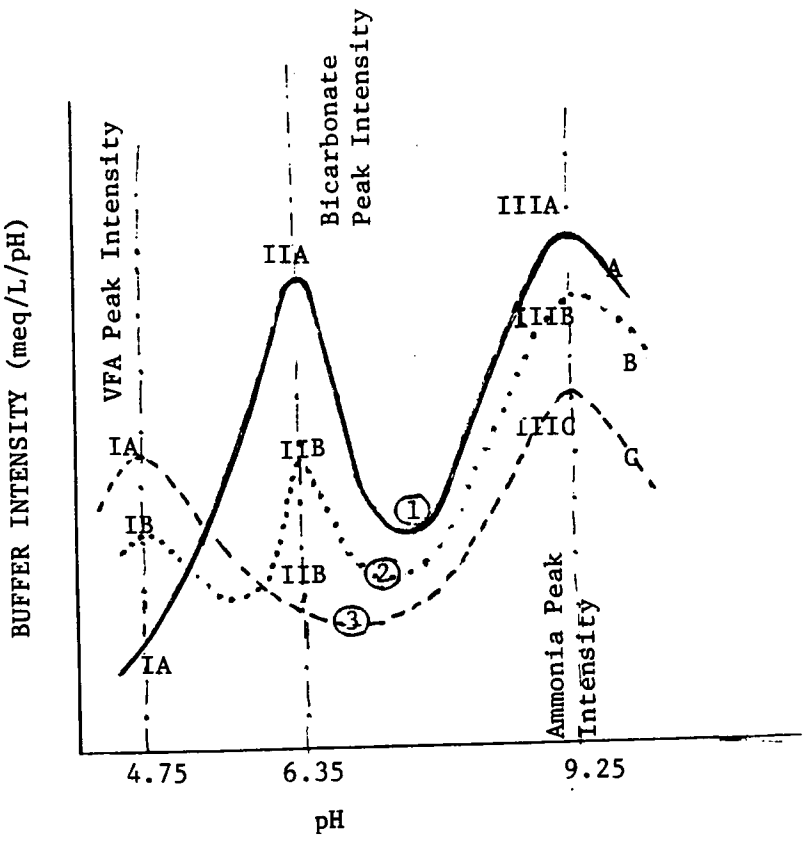


Figure 8. Buffer Intensity in Digesters (Georgacakis et al.,1984)

exceeding 17/1 would lead to failure due to low bicarbonate alkalinity. In summary, where anaerobic digesters receive wastes low in nitrogen (dairy waste), bicarbonate alkalinity is the chief source of stability control. The presence of ammonia will significantly enrich the bicarbonate alkalinity and, hence, the buffering capacity (Sievers and Brune, 1978). Swine and poultry manure possess an increased buffer stability due to naturally high levels of ammonia. However, the tendency for free ammonia inhibition in these digesters should be considered.

Determination of total alkalinity involves titrating to a pH end-point of 4.5. At near-neutral pH range, the total alkalinity of the digester contents is equal to the bicarbonate alkalinity. When volatile acids are present, they are neutralized by bicarbonate alkalinity resulting in the formation of acid salts. Under these conditions, when total alkalinity measurements are made, acid salts are also included. Hence, bicarbonate alkalinity can be approximated by the expression proposed by Pohland and Bloodgood (1963):

$$BA = TA - 0.833\ TVA \qquad (1)$$

where

BA = Bicarbonate alkalinity, mg/L as $CaCO_3$

TA = Total alkalinity, mg/L as $CACO_3$

TVA = Total VFA concentration, mg/L as acetic acid.

The term 0.833 TVA represents the amount of alkalinity required to neutralize the volatile acid. McCarty (1964a) included 0.85 to account for the fact that only 85 percent of the volatile acid alkalinity (acid salt) is measured during determination of total alkalinity. Hence, the modified form of equation (1) is:

$$BA = TA - (0.71)TVA \qquad (2)$$

A knowledge of the bicarbonate alkalinity reveals how much buffering capacity remains in the system. Adequate amounts are required to withstand fluctuations in the volatile acids concentration. The ratio of the volatile acids concentration (as mg/L acetic acid) to the bicarbonate alkalinity (as mg/L $CaCO_3$) is often used for characterizing anaerobic digesters (Gaudy and Lim, 1980). A ratio of 0.4 or less is indicative of sufficient buffering capacity. If the ratio is above 0.8, the system is likely to experience a severe drop in pH for small changes in volatile acids.

2.2.3 DIGESTER OVERLOADING

Digester overloading is frequently the result of careless operation and may be caused by increased flow rate (hydraulic overloading) or increased substrate concentration (organic overloading).

Hydraulic (quantitative) overloading results when residence times shorter than that required for a net production of bacteria is adopted. This leads to bacterial washout. Based on full-scale digester studies, ten days have been recommended as minimum solids retention time (SRT) for anaerobic digestion (McCarty, 1964b; Sawyer and Roy, 1955). Since average residence time is equal to the reactor working volume (V) divided by the average flow rate (Q) increasing the hydraulic flow rate or reducing the reactor volume would decrease the retention time. In digesters with incomplete mixing, dead zones may develop leading to decreased active volume and, hence, reduced retention times.

Organic (qualitative) overloading occurs when the influent stream contains organic matter in excess of the amount that could be utilized by the bacterial population. Almost always this type of overloading is associated with the differential response of the acid-formers and the methane-formers. When influent concentration is abruptly increased, the biodegradable organics are quickly converted to volatile acid by the acid-formers. However, methane-formers, being slow growing, cannot adjust to increased concentration of volatile acids. Consequently, fatty acid accumulation results leading to pH decrease and subsequent inhibition of the microbial population. Organic overloading may occur during digester start-up and when infrequent or pulse feeding is practiced.

2.2.4 RESIDENCE TIME DISTRIBUTION

The residence time of the digester contents is an important parameter. It is closely related to the selection and washout of the microbial population (Jenkins and Garrison, 1968; Adams and Pearson, 1965; Downing and Wheatland, 1962) and therefore dictates the fate of the process. Retention time, detention time, and holding time are synonymous terms for residence time and will be used interchangeably in this report.

According to Himmelblau and Bischoff (1968): "residence time of a fluid element is the time that elapses from the moment the element enters the vessel to the time it leaves it. The age of a fluid element at a given instant of time is the time that elapses between the element's entrance into the vessel and the given instant, and is, of course, less than or equal to the residence time." The concept of residence time can be extended to the solid and liquid components and are termed solids retention time (SRT) and hydraulic retention time (HRT), respectively. In a continuous flow completely mixed anaerobic unit, the hydraulic retention time and the solids retention time are equal. In the absence of adequate mixing, the SRT may differ from HRT.

All other environmental factors remaining constant, breakdown of the biodegradable fraction of waste is directly proportional to the residence time. Hence, in an anaerobic digester, the extent of treatment, and associated production of methane, are both directly affected by the detention time. Anaerobic digesters are usually designed to operate at a particular detention time. If V is the reactor volume and Q the influent flow rate, then the design retention time (θ) is given by V/Q. However, nonideal flow schemes may result in stagnancy and bypassing. In bypassing, some elements of fluid slip or pass through the vessel considerably faster than others, thereby escaping microbial degradation and contributing little to gas production. On the other hand, presence of stagnant regions cut down the effective or useful volume of the reactor, and possibly lead to unstable digester performance. An experiment can be performed with a tracer, such that, at an instant of time, all fluid elements entering the digester are marked. In a daily-fed anaerobic digester, this can be easily accomplished by adding a known concentration of a tracer to the influent. The digester flow pattern could then be determined by monitoring the tracer concentration in the effluent.

Two types of abstract or ideal flow schemes are commonly cited as limiting cases; these are plug flow and perfectly-mixed flow (Levenspiel, 1972; Himmelblau and

Bischoff, 1968; Aris, 1965; Kramers and Westerterp, 1963). Plug-flow occurs when the fluid velocity is uniform over the entire cross section of the reactor. Each element of fluid that enters the vessel and marches through in "single-file" without intermingling with other elements that enter earlier or later. At the other end of the spectrum, perfect mixing assumes that digester contents are completely homogeneous down to a molecular scale. It follows implicitly that the feed, on entering the digester, is immediately dispersed. Between these two extremes lie a variety of flow patterns found in practice.

In order to understand and predict digester behaviour, we need to know the length of time each molecule stays in the digester, or more precisely, the distribution of residence time in the flowing fluid. Elements of a fluid can take different routes as the fluid passes through a digester and may require different lengths of time to proceed from the inlet to the outlet. The effluent leaving the digester is, therefore, composed of elements that have remained in the digester for different detention times. If it is a plug flow digester, no tracer will appear until a time equal to the mean holding or residence time of the vessel has elapsed, at which point all the tracer will leave. On the other hand, if it is a perfectly mixed reactor, the tracer will be uniformly and instantaneously distributed upon entry. Hence, the

concentration of the tracer in the effluent will be high and equal to the tracer concentration within the reactor at time zero. It is then "washed out" of the vessel by the incoming nontracer fluid. Many vessels demonstrate intermediate behaviour.

2.2.5 INHIBITION AND TOXICITY

Inhibition has been defined as a rate reduction, while toxicity is the cessation of fermentation (Kugelman and Chin, 1971). McCarty (1964c) observed that 'toxic' and 'inhibitory' are relative terms and are strongly dependent on the concentration of the substance in question. At very low concentrations, the substance stimulates activity. As the concentration increases, the rate of biological activity decreases until inhibition begins. A further increase in the concentration brings about complete cessation of the process. The concentrations at which stimulation, inhibition and cessation occur, varies with the toxin. However, it should be recognized that microorganisms have a certain ability to adapt to inhibitory concentrations of some substances. According to Kugelman and Chin (1971), in waste the toxic substances build up slowly, hence acclamation is possible. The findings of McCarty and McKinney (1961) supported this concept.

The mechanism of inhibition is well presented by Webb (1963). Figure 9 is a simplified illustration of several potential sites at which an inhibitor may act. In short, substrate, or nutrients enter the cell and are utilized for cellular growth, for the synthesis of intermediates, and for the generation of energy which is used for accomplishing other metabolic functions (A, B & C) and in steps (1) and (2). According to Edwards (1970) the inhibitor can act outside the cell by blocking food supply at (1) or inside the cell at any of the five points, namely (2), (3), A, B & C. In almost all of these cases, the basic causes for inhibition are (1) change in chemical species of substrate or nutrient, (2) disruption of normal transport mechanisms into and through the cell, and (3) change in the activity of the enzyme or enzyme system.

Heavy metals, VFA, and ammonia are the common inhibitors of anaerobic fermentation and will be discussed in the following sections.

2.2.5.1 HEAVY METALS

Early studies of Hotchkiss (1923) established the stimulating and toxic effects of heavy metals. Kugelman and McCarty (1965) suggest that each cation may be responsible for enzyme activation in an organism. Eventually, when all the enzymes

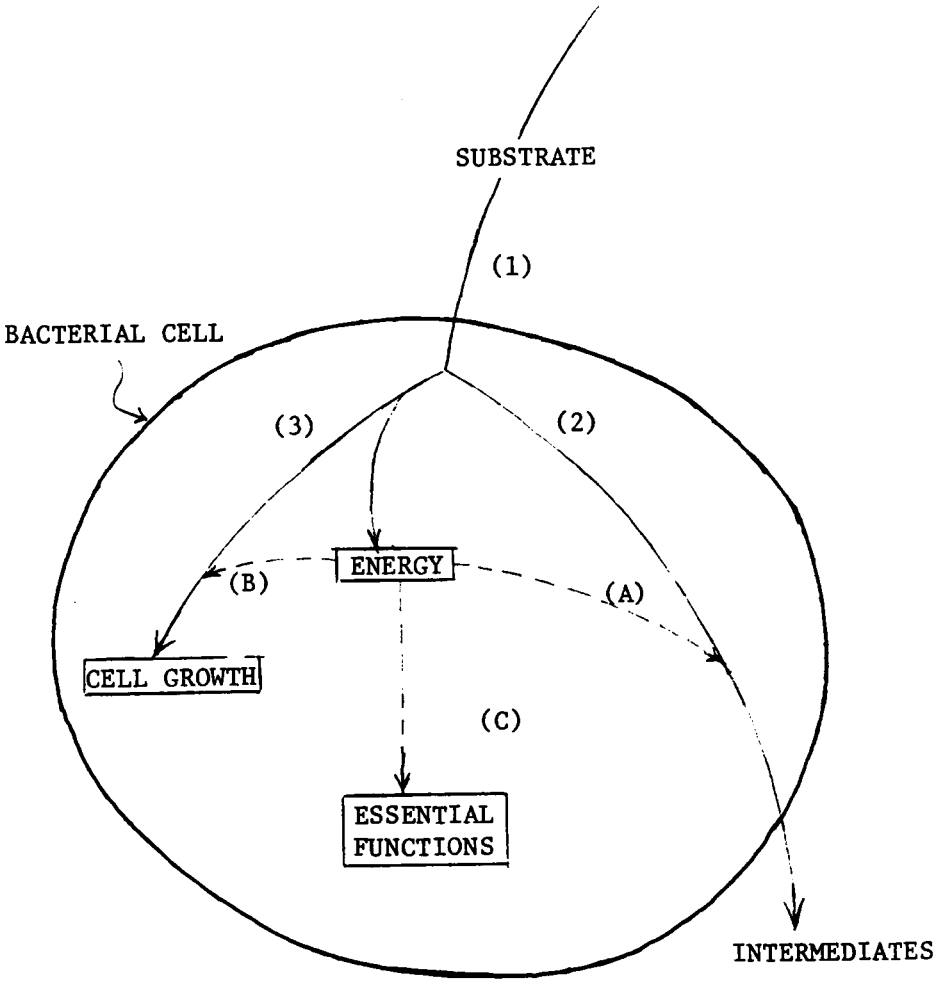


Figure 9. Possible Inhibition Sites (Edwards 1970)

are activated, any further increase in the cation concentration will only harm the enzyme. At this point the cation becomes toxic. McCarty and McKinney (1961) concluded that, on a weight basis, the monovalent cations were more toxic than the divalent cations. The effect of heavy metals like cadmium, chromium, nickel, zinc, copper and lead on anaerobic fermentation have been reported by Hayes and Theis (1978), Matsumoto (1978), Mosey (1976), and Kugelman and Chin (1971).

Control of heavy metals is by a complex-type reaction, which involves the precipitation of their sulfides. In swine waste digesters, copper was not found to be a problem as it was almost entirely removed as copper sulfide (Hobson et al., 1981). It has been reported that the amount of copper present in a swine waste anaerobic digester operated at an SRT of 10 days, and loaded at rate of 10% solids, would be about 85mg/L. This amount can be totally precipitated by the sulfides in the digester (Hobson and Shaw, 1976).

Heavy metal toxicity of dairy waste anaerobic digesters has not been reported. This may be attributed to the insignificant amounts of metal present in typical raw manure from dairy farms.

2.2.5.2 VOLATILE FATTY ACIDS

The effect of volatile acids produced during decomposition of complex organics is to reduce the pH. However, under balanced conditions, methane fermentation results in the destruction of volatile acids and reformation of bicarbonate buffer. Under unbalanced conditions, the acid formers outpace the methane formers, and volatile acid build-up occurs (McCarty 1964a).

Hobson and Shaw (1976), Bryant et al. (1971), Kugelman and Chin (1971), and McCarty and McKinney (1961) have reported that acetic and butyric acids are comparatively non-toxic to anaerobic digestion. On the other hand, propionic acid is inhibitory. The investigations of Hobson and Shaw (1976), Cooney and Ackerman (1975), Kugelman and Chin (1971), and Andrews (1969) further established the inhibitory nature of propionic acid.

Early studies resulted in more than one school of thought regarding the actual effect of high volatile acid concentration on the digestion process. Cassel and Sawyer (1959), and Kaplovsky (1952) believed that high acid concentration is the result of low activity of methane producing bacteria. They surmised that volatile acids are toxic to these organisms only in an indirect manner through

the reduction of pH, a condition which can be relieved by the addition of buffering material. Mudler et al. (1959), Andrews (1969), and Shulze and Raju (1958), on the other hand, concluded that it is the concentration of volatile acids rather than pH that directly inhibits methane formers. The toxic condition in this case can be relieved by reducing the organic load, or by dilution.

The most widely accepted explanation of VFA inhibition at the present time is the one postulated by Andrews (1969) who observed that the inhibitory effect of volatile acids at high concentration is due to the un-ionized portion of the acid (UVA). Kroeker et al. (1979) reported a trend towards digester failure as the UVA concentration increases above 10 mg/L. Any change in pH due to the change in volatile acid concentration is accompanied by changes in the concentration of ionized and un-ionized forms of the acids as illustrated by the following equation:

$$CH_3COOH \rightarrow CH_3COO^- + H^+$$

As pH decreases, the equilibrium shifts to the left and the un-ionized volatile acid (UVA) concentration increases. The cell membrane is much more permeable to the un-ionized molecule, hence this form is more inhibitory.

2.2.5.3 AMMONIA

Ammonia, although a necessary nitrogen source for bacteria and for enhancing digester stability, can be toxic when present in excess. Kroeker et al. (1979), Stevens and Shulte (1979), Sievers and Brune (1978), Converse et al. (1977), and Lapp et al. (1975) have all concluded that ammonia inhibition is a significant problem in the fermentation of ammonia-rich wastes such as those of swine and poultry.

As in the case of volatile acids, pH (H^+ concentration) has an effect on the equilibrium equation for ammonia.

$$NH^+_4 \rightarrow NH_3 + H^+$$

When the hydrogen ion concentration is sufficiently high (pH of 7.2 or lower), the equilibrium is shifted to the left, so that inhibition is related to the ammonium ion concentration. At higher pH levels, the equilibrium shifts to the right, resulting in free ammonia inhibition. Ammonia gas (free ammonia) is considered more toxic than ammonium ion (Kroeker et al., 1979; McCarty, 1964c).

McCarty (1964c) states that ammonia-nitrogen concentration between 1500 and 3000 mg/L is inhibitory at pH levels above 7.4, whereas, ammonia-nitrogen concentrations in excess of

3000 mg/L are supposed to be toxic at all pH values. These threshold levels were confirmed by Hobson and Shaw (1976). On the other hand, many investigators reported satisfactory anaerobic digestion at ammonia-nitrogen concentrations far beyond 1500 mg/L, even in the pH range 7.5 - 8.0. Melbinger and Donnellon (1971) observed this phenomenon in the digestion of concentrated sewage sludge, while Fisher et al. (1979), Kroeker et al. (1979), Converse et al. (1977), Van velsen (1977), Hobson and Shaw (1976), Lapp et al. (1975), Gramms et al. (1971), and Hart (1963) used animal wastes for their investigations. Lapp et al. (1975), and Melbinger and Donnellon (1971) attributed successful digestion at high ammonia-nitrogen concentration to acclimation.

2.3 THE CONTINUOUS CULTURE THEORY

All continuous flow systems consist essentially of a vessel (reactor) through which a steady flow of fluid is maintained. The design of the reactor and the flow rate dictate the length of time each molecule of the fluid spends within the vessel. By definition, a constant working volume is maintained in continuous-flow systems.

The advantages of continuous culture techniques are that precise manipulation and maintenance of the physical and chemical environment are possible and the microorganisms can

be held at steady-state and at constant physiological conditions for long periods. Thus, the investigator can control the environment at will to observe behavior of the system and to increase gas production.

Herbert (1960) presented a comprehensive classification of continuous culture systems employed in the production of yeast, ethanol, acetic acid, antibiotics, and vitamins. The discussion presented herein is limited to the continuously stirred tank reactor (CSTR) and its application in biological waste treatment.

The CSTR has been mathematically treated by Herbert (1960), Novick and Sziland (1950). The analysis of any continuous culture system must take into account (i) the flow characteristics, (ii) the kinetics of microbial growth, and (iii) a mass balance of the cells and substrates involved. The basic assumption of a completely stirred tank reactor (CSTR) is that each drop of incoming medium is mixed instantaneously and completely. This ensures uniform distribution of all reactants. If Q is the flow rate through the digester and V the reactor volume, then the inflowing substrate concentration is immediately diluted by a factor Q/V as it enters the reaction vessel. This ratio is called the dilution rate or flow rate per unit volume, and is designated by the symbol D. Thus, D is the reciprocal

of the mean hydraulic retention time for the reactor. Some of the other assumptions for a CSTR are:

1. pure culture,

2. growth controlled by a single substrate,

3. the Monod expression for bacterial growth adequately explains bacterial growth,

4. constant dilution rate,

5. decay rate is insignificant,

6. growth at exponential phase,

7. constant dilution rate,

8. decay rate is insignificant, and

9. growth at exponential phase.

2.3.1 MATERIAL BALANCES

In order to understand a biological system for waste treatment, it is necessary to know the exact changes

occurring in the composition and concentration of materials in a reactor, and the rate of such changes. Changes may be due to reaction between materials, biological activity, decay with time and mass transport. Significant information may be gathered by applying the law of conservation of mass to the various materials flowing through the reactor. A generalized material balance would include increase due to inflow, decrease due to outflow, and change in concentration due to reaction. Hence,

INPUT - OUTPUT ± REACTION = ACCUMULATION

If steady-state conditions are assumed to prevail, the accumulation term will be zero. The reaction occuring in the system may contribute (cell growth) or utilize (substrate consumption) material. Accordingly, the reaction term will be either positive or negative.

Figure 10 is a schematic representation of a completely-mixed anaerobic digester system without recycling. The dashed line represents the system boundary which is required to identify the flow into and out of the system. A constant flow rate (Q) through the system supplies the reactor with fixed substrate and cell concentrations of S_0 and X_0. As a consequence of complete mixing, the concentrations of substrate (S) and biomass (X) in the reactor and in the

effluent are the same. Since the rate of effluent removal (Q) equals influent flow rate, the volume (V) of culture remains constant.

The organism mass balance provides equations that show how the growth model is related to operational and control parameters in describing performance of the bioreactor. Figure 11 illustrates the fate of biomass (organism) in the reactor and aids in understanding the mathematical expression of biomass mass balance:

$$V(dX/dt) = QX_0 - QX + r_1V$$

$$(dX/dt) = D(X_0 - X) + r_1 \qquad (3)$$

where,

dX/dt = Mass rate of change in organism, mg/L.d

Q = Flow rate, L/d

X_0 = Influent organism concentration, mg/L

X = Effluent organism concentration, mg/L

r_1 = Growth rate, mg/L.d

V = Reactor volume, L

θ = Retention time, day

= V/Q

D = Dilution rate, 1/day

= $1/\theta$

= Q/V

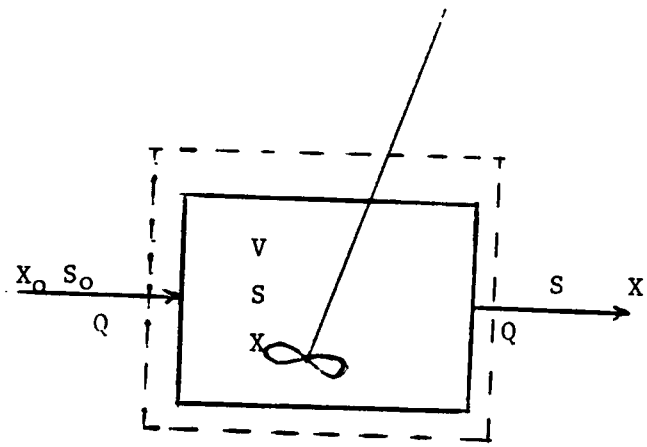


Figure 10. Well-mixed Reactor Without Cell Recycle

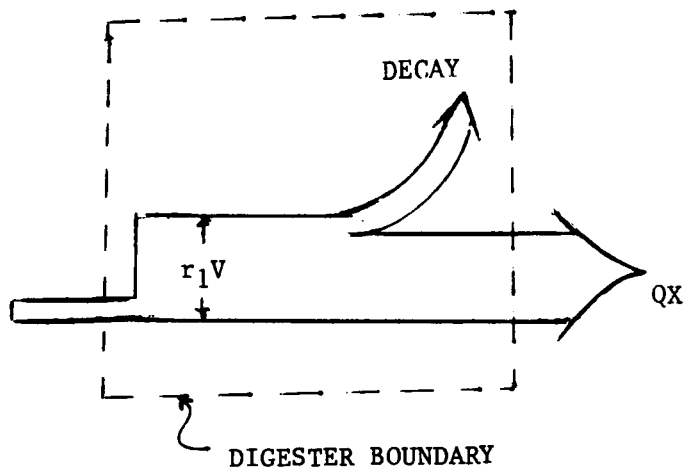


Figure 11. Fate of Biomass in an Anaerobic Reactor.

At steady-state, since there is no accumulation, $dX/dt = 0$. The term r_1 represents the change in organism concentration with time. The aim of continuously-fed digestion is to sustain the exponential growth phase which is characterized by "minimal and constant generation time, maximal and constant specific growth rate, maximum rate of substrate conversion, and achievement of steady-state" (Benefield and Randall, 1980). In the exponential phase, the rate of increase of cells (r_1) is proportional to the concentration of cells (X) in the reactor. Hence,

$$r_1 = \mu X$$

Where,

μ = Specific growth rate, d^{-1}

X = Concentration of microorganism, mg/L

Assuming that the concentration of the organism in the influent is negligible ($X_0=0$), equation (3) could be written as:

$$(dX/dt) = (\mu - D)X \qquad (4)$$

Equation (4) describes behavior of the system. At low flow rates, since $\mu > D$, dX/dt is positive and the biomass concentration (X) will increase, while if $D > \mu$ (that is, high flow rates), dX/dt is negative and X will decrease,

eventually becoming zero. Thus, the culture will be 'washed out' of the reactor. When $\mu=D$, $dX/dt=0$ and X does not change with time. This represents steady-state conditions.

Since μ is a function of substrate concentration (Monod, 1949), a substrate mass balance is needed in order to determine values of μ and D at which steady-state occurs. The fate of substrate in the digester (Figure 12) can be presented as follows:

$$V(dS/dt) = QS_0 - QS - r_2V \qquad (5)$$

where,

dS/dt = Rate of change of substrate, mg/L.d

S_0 = Influent substrate concentration, mg/L

S = Effluent substrate concentration, mg/L

r_2 = Rate of substrate utilization, mg/L.d

In equation (5), the term dS/dt represents rate of accumulation and is zero at steady-state. The rate of substrate utilized (r_2) by the bacterial population is given by:

$$r_2 = \mu X/Y$$

where, Y is the microorganism yield coefficient (g cells/g substrate). Thus, equation (5) becomes:

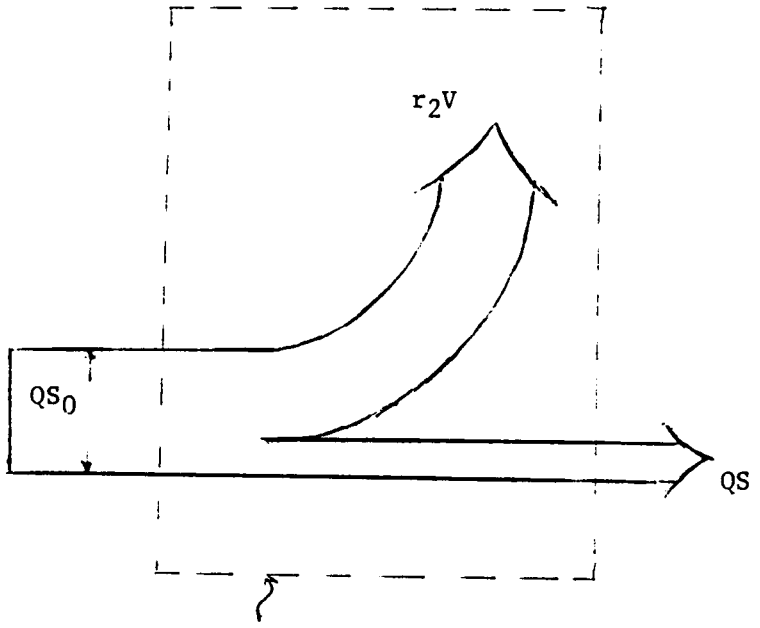


Figure 12. Fate of Substrate in an Anaerobic Reactor.

$$(dS/dt) = D(S_0 - S) - \mu X/Y \qquad (6)$$

As defined previously, μ is the growth rate per unit of biomass and is a function of the microbial environment, particularly the supply of essential growth nutrients. Many growth models have been formulated relating μ to substrate utilization (Contois, 1959; Moser, 1958; and Monod, 1949).

The most popular model, by far, used in the field of wastewater treatment, is the one proposed by Monod (1949). Monod observed that the specific growth rate of microorganisms responds directly to changes in the concentration of a growth-limiting nutrient when all other factors necessary for growth are supplied (Figure 13). The mathematical expression that resulted (equation 7) is similar to the one used by Michaelis-Menten in describing enzyme-substrate interactions.

$$\mu = \mu' \, S/(Ks + S) \qquad (7)$$

where,

μ = Specific growth rate, d^{-1}

μ' = Maximum specific growth rate, 1/d

S = Limiting substrate concentration, mg/L

Ks = Saturation (half velocity) constant, mg/L

The term Ks is the substrate concentration at $\mu = \mu'/2$. It is a constant that controls the shape of the growth curve as it approaches the maximum value. Low Ks values give a very sharply breaking curve while high values give a slowly breaking curve (Figure 13). In the past, Ks has been used to indicate the affinity of the organism for the substrate (Jacob and Monod,1961) and for the comparison of the growth supporting capacities of substrates (Christensen and Palmer, 1967; Monod, 1949).

The Monod model is an empirical expression that describes specific growth rate as a continuous function of substrate concentration. Although initially developed for pure cultures, it has been shown to satisfactorily fit data from heterogeneous cultures as well (Morris et al., 1977; Woods and O'Callaghan, 1974; Ghosh, 1969; Kornegay and Andrews, 1968; Adams and Pearson, 1965).

Replacing μ in equations (4) and (6) with the Monod expression (equation 5), we have:

$$(dX/dt) = [\mu'SX/(Ks+S)] - DX \qquad (8)$$

$$(dS/dt) = D(S_0-S) - (\mu'SX)/[Y(Ks+S)] \qquad (9)$$

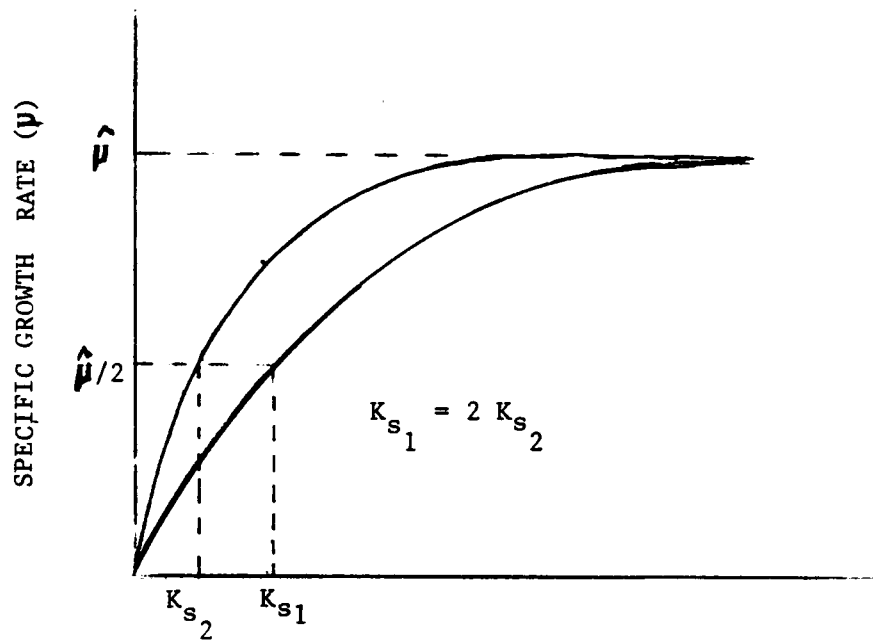


Figure 13. Microbial Growth Curve (Monod, 1949).

It can be shown that, starting from any initial substrate and biomass concentration, the system ultimately reaches steady-state. Initially, biomass concentration in the reactor (X) is small, and S is nearly equal to S_0. Since X is small, the specific growth rate (μ) is large and greater than the dilution rate (D). With time X increases and S decreases due to microbial action. Since, μ is a function of S (Monod, 1949), it will also decrease. This trend will continue, until eventually μ and D are equal. At this point the combined rates of substrate consumption and loss offset the rate of substrate addition and the system shows no further tendency to change. Steady-state is then said to prevail. It should be pointed out that fluctuations from steady-state values do occur. However, in most cases these deviations are small and they set up opposing reactions which will restore the status quo. Failure occurs when the deviations are so large that the system cannot self-adjust.

Mathematically, steady-state can be represented by setting $dX/dt = 0$, and $dS/dt = 0$. In other words, values of X and S must be determined which make the right-hand sides of equations (8) and (9) simultaneously zero. There are two possible solutions:

$$X = 0$$

$$S = S_0$$

and,

$$X = Y[S_0 - \{Ks / (\mu'\theta - 1)\}] \qquad (10)$$

$$S = Ks./ (\mu'\theta - 1) \qquad (11)$$

Since the first set of values corresponds to washout of all microorganisms, the second is the only desired steady-state conditions for X and S.

Petrie (1978) made a mathematical analysis of the steady-state operating point of the digester defined by equations (10) and (11). For the operating condition to be physically realizable, all parameters must be positive. Hence, from equations (10) and (11) we have $S_0 > Ks/(\mu'\theta - 1)$ to make X positive, and $\mu'\theta > 1$ to make S positive. Since $\theta = V/Q$, we have:

$$S_0 > QKs/(\mu'V - Q) \qquad (12)$$

Rearranging this inequality we get:

$$Q < \mu'VS_0/(Ks+S_0) \qquad (13)$$

The study presented herein is based on assumptions that the reactor volume (V), the kinetic parameters μ' and Ks, and the yield coefficient(Y) are fixed. Only Q and S_0 have been considered as process variables which may alter or be

altered. The expressions (12) and (13) specify an upper limit for the flow rate (Q) and a lower limit for S_0 to make the operating point physically meaningful. If Q exceeds this limit, washout occurs, while if S_0 drops below the defined lower limit, a healthy microbial population cannot be sustained.

Rearranging equation (11), an expression for solids retention time can be obtained:

$$\theta = (Ks + S)/\mu' S \qquad (14)$$

The economics of the system is greatly influenced by the minimum solids retention time (θm) that could be achieved for a particular influent substrate concentration (S_0). At θm the influent waste concentration (S_0) equals the effluent waste concentration (S). The minimum solids retention time can be determined from equation (14) by setting $S = S_0$ Hence we have,

$$\theta m = (Ks + S_0)/\mu' S_0 \qquad (15)$$

Finally, a discussion of the yield coefficient (Y) is in order. The utilization of substrate (carbon source) results in cellular growth (synthesis) of microorganisms. Gaudy and Gaudy (1980) state that the amount of biomass produced is

less than the amount of carbon source removed. The microorganism yield coefficient (Y) serves the purpose of establishing a relationship between the mass of cells formed (ΔX) and the mass of substrate consumed (ΔS). That is,

$$Y = \Delta X/\Delta S$$

Y is a function of the nature of the substrate, the microbial species present, and the environmental conditions available for growth. In this investigation, since these factors were kept reasonably under control, Y was assumed to be a constant. A review of anaerobic fermentation literature (Hill, 1982; Hill and Nordstedt, 1980; Hill and Barth, 1977; Andrews and Graef, 1971; Lawrence and McCarty, 1969; McCarty, 1966) suggests a working range for Y between 0.02 and 0.06 g organisms/g substrate. The value of Y for anaerobic digestion is very much less than that for aerobic treatment indicating that most of the organic matter degraded is converted to gaseous end products rather than to sludge (cells).

2.3.2 DEVIATIONS FROM CONTINUOUS CULTURE

The theoretical development of the continuous culture technique was based on certain implicit and explicit assumptions. While some of these are easily satisfied in

most experimental and field conditions, others do not hold in many cases.

In anaerobic digesters the complex nature of the substrate, the diverse microbial population, the presence of incomplete mixing, and intermittent feeding contribute to the diversion from the continuous culture theory.

Equation (9) predicts effluent substrate concentration at steady-state and is independent of the influent substrate concentration. The above concept holds for pure cultures but not for mixed cultures utilizing multiple component mixtures (Grau et al., 1975; Grady and Williams, 1975). Under these conditions, the substrate utilization model developed by Grau et al. (1975) adequately describes the effects of varying substrate concentration (Benefield and Randall, 1977). Thus, to maintain the same effluent quality for different influent substrate concentrations, the solid retention time must be varied.

It was assumed that the influent was free of microbial cells (that is, $X_0=0$). The rumen of cattle is in effect an anaerobic digester with a relatively short retention time. This ensures the presence of an active population of acid-formers and, possibly, a relatively small concentration of methane-formers in the influent.

The continuous culture theory assumes that the contents are well mixed on the micro and macro scales. In micromixing, individual molecules or reacting particles are free to mix with other molecules or reacting particles (Levenspiel, 1972). Therefore, mixing occurs at a molecular level and assures that all molecules are exposed to the same environment and possess equal chances of encountering molecules of other reactants. Macromixing, on the other hand, refers to bulk mass flow within the reactor. If micromixing is not achieved, a spatial distribution of reactant and product concentrations will be established. The absence of macromixing is evidenced by a residence time distribution which deviates from the ideal case (Danckwerts 1953). Farm anaerobic digesters are often undermixed at the micro and macro levels. Cholette and Cloutier (1959), and later Cholette et al. (1960), were the first to present mathematical models for incomplete mixing in continuous flow systems.

In developing microbial kinetics of suspended growth, it is assumed that the microbial cell is unattached and freely moving. In practice, this may not be realized in anaerobic systems. Cultures have been observed to exhibit oscillations of the total steady-state bacterial density. This behaviour has been attributed to wall-growth and mutual interactions (Casell and Sawyer, 1969; Bungay and Bungay, 1967). A

different type of attached growth was observed by McCarty (1985) where microorganism grew in clusters around substrate particles.

The continuous culture model is also subjected to the restriction of constant cell yield. Herbert (1958) presented an early paper on variable yield. Reduced yields have also been reported at low dilution rates (Gaudy and Gaudy, 1980) and may be attributed to the existence of maintenance energy requirements and/or endogenous respiration. Since cell yield depends on the species present as well as on the nature of the carbon source, one must expect a variation in the yield coefficient for a heterogeneous population (Ramanathan and Gaudy, 1972). Sherrard and Schroeder (1973) defined an observed yield coefficient obtained by subtracting the microbial maintenance requirement from the theoretical yield. The observed cell yield is not a true biological constant, but is a characteristic of the biomass and dilution rate.

3.0 MODELING ANAEROBIC DIGESTION

3.1 INTRODUCTION

"A model is simply a symbolic form in which physical and chemical principles are expressed. It may be an equation that is derived by consideration of the pertinent scientific principles, operated on by logic, and modified by experimental judgement" (Snyder and Stall, 1965).

In anaerobic digestion, the primary purpose of a mathematical model is to predict digester performance under varying operational conditions. The first step in developing a predictive model is to mathematically define the various interactions involved. Such an approach would eventually yield a set of non-linear, non-homogeneous, simultaneous, ordinary differential equations relating digester performance to several key parameters. The model so developed would make it possible to learn more about the conversion process without actually using the physical system or its prototype.

3.2 ANAEROBIC DIGESTION MODELS: A BRIEF OVERVIEW

Modeling a complex biological system requires an understanding of the behavior of the microorganisms and of the mathematical equations that describe them. Unfortunately in anaerobic systems the exact physiological nature of the organisms is not well defined. The task is further complicated by the fact that a consortium of microorganisms are involved. Hence, it is not surprising to find models of varying complexity in the literature. Many of them are tailor-made to describe a particular type of digester and are not universally applicable without adjustments.

Mathematical models for anaerobic treatment of animal waste may be classified according to the kinetic expression used to describe cell growth. The model of Hill and Barth (1979) incorporated the modified Monod kinetics of Andrews and Graef (1971) to account for inhibition. Morris et al. (1977) and Grady et al. (1972) used a first order growth model. The original Monod expression was adopted by Morris et al. (1977) in describing dairy waste digester performance. The Chen-Hashimoto model was based on Contois enzyme kinetics and possessed the ability to predict changes in effluent quality associated with variation in influent concentration (Chen and Hashimoto, 1979).

Steady-state models (Chen and Hashimoto, 1979; Morris et al., 1977) although easier to manipulate, are not applicable to transient behavior. Dynamic models, on the other hand, have the ability to describe process performance during start-up and under transient conditions resulting from overloading. The practical importance of dynamic models is realized when one considers that a failing digester is certainly not at steady-state. Andrews (1969) was a forerunner in applying dynamic modeling to anaerobic digestion. His model incorporated the effect of un-ionized volatile acids through a growth model based on the function presented by Haldane (1930). The dynamic model developed by Andrews and Graef (1971) considered the bicarbonate system and its significance in pH control. This model was developed using municipal and industrial waste. Hill and Barth (1977) modified the Andrews-Graef model for animal waste digestion.

Most early models considered the anaerobic digestion as a one-culture process (Chen and Hashimoto, 1979; Morris et al., 1977; Andrews and Graef, 1971). The basic assumption was that methane formation is the rate-limiting step. Therefore, these models implied that the influent substrate is volatile acid and the microorganisms of interest are the acid-formers; factors affecting the conversion of complex raw material to acetic acid were not considered.

Hill and Barth (1977), and later Hill and Nordstedt (1980), developed modeling techniques for a two-culture bacterial population. In effect, this involved twice the number of equations to fully describe behavior of the system. For the first time, the relationship between acid-formers and methane-formers was mathematically described. Accordingly, the model possessed the ability to predict volatile acid accumulation - a common occurence in actual digesters.

Hill (1983a) proposed a simplified two-culture model for animal waste digestion. He successfully exhibited the versatility of this model by applying it to various waste types (Hill, 1983a; 1983b; 1983c; 1983d). Hill (1982) presented a comprehensive dynamic model involving four physiologically different bacterial populations. Of necessity this model is complex and has been validated quantitatively with field operating data.

In recent work, Hill (1985) further improved the predictability of his model by incorporating a variable death rate. He postulated that as volatile acids concentration increased, microbial population decreased. Death rate, therefore, was assumed to play a much more dynamic role in removal of the viable microbial mass.

3.3 MODEL DEVELOPMENT.

Animal waste is chemically complex. It is often thought of as a mixture of fats, oils, proteins, carbohydrates, and inorganic compounds. Depending on the type of waste, it also contains a significant amount of refractory organics.

The anaerobic microbial population is also complex. Although there are several groups of microorganisms involved in the conversion of animal wastes, the model developed in this section considers a two-culture microbial population. Accordingly, different growth-limiting substrates need to be identified. From the microbiology and biochemistry of the process the growth-limiting substrate for the acid-formers is assumed to be the biodegradable organics (measured as VS or COD), while that for the methane-formers is the volatile fatty acids. The assumptions made in developing an appropriate mathematical model are:

1. The reactor receives feed intermittently (pulse-fed).

2. Digester contents are mixed prior to effluent withdrawal.

3. The process is mediated by a two-culture microbial population.

4. The biodegradable component of the organic waste (biodegradable volatile solids, or BVS) is the growth-limiting substrate for the acid-formers, while volatile acid (VFA) is the growth-limiting substrate for methane-formers.

5. Inhibition of both microbial populations is caused by un-ionized VFA.

6. Absence of inhibition due to free ammonia and other toxic materials.

The biodegradability (B_0) of the waste is the fraction of the raw waste that can be converted to soluble organics - a form that is directly consumed by the acid-formers. For stoichiometric purposes, glucose is assumed to be the soluble organic. In effect, B_0 reduces the raw waste to a compound that act as substrate for the acid-formers. If the total influent volatile solids concentration (St) is known, the influent BVS (S_0) may be computed as follows:

$$S_0 = B_0 \, St$$

B_0 is waste specific and may be established by using batch digestion data (Hashimoto, 1982).

Biodegradation of glucose by acid-formers yields short chain fatty acids which serve as substrate for the acid-formers. Although, many fatty acids may be formed during anaerobic digestion, formic, acetic, propionic and butyric have been most commonly reported (McCarty et al., 1963). Of these, acetic acid frequently is chosen as a representative of the total volatile acids of anaerobic fermentation. This assumption is justified for the following reasons: (1) acetic acid is the predominant volatile acid and is the precursor to nearly 72% of the methane formed (McCarty, 1964b), and (2) propionic and butyric acids, the next two most prevalent, have ionization characteristics very similar to acetic acid (Pholand and Engstrom, 1964; Jeris and McCarty, 1965).

Having defined the growth-limiting substrate for the different microbial cultures, the next logical step would be to develop mathematical expressions to represent the anaerobic process. The steps involved are:

1. Writing material balances for substrate and biomass.

2. Selecting kinetic relationships that relate bacterial growth to substrate utilization.

3. Combining material balances and growth kinetics to obtain a predictive model.

4. Modifying the basic model obtained in step 4 to account for incomplete mixing, and intermittent feeding.

Once the waste is reduced to the BVS and VFA components, the process may be modeled by writing mass balances and microbial growth equations as follows:

SUBSTRATE MASS BALANCES

$$dS/dt = (S_0-S)Q/V - \mu_1 X_1/Y_1 \qquad (16)$$

$$dVFA/dt = (VFA_0-VFA)Q/V + \mu_1 X_1(1-Y_1)/Y_1 - \mu_2 X_2/Y_2 \qquad (17)$$

Where,

S_0 = Influent BVS concentration, g/L

S = Effluent BVS concentration, g/L

VFA_0 = Influent VFA concentration, g/L

VFA = Effluent VFA concentration, g/L

θ = Detention time, d^{-1}

μ_1 = Specific growth of acid-formers, d^{-1}

μ_2 = Specific growth of methane-formers, d^{-1}

X_1 = Concentration of acid-formers, g/L

X_2 = Concentration of methane-formers, g/L

Y_1 = Yield coefficient of acid-formers, g/g

Y_2 = Yield coefficient of methane-formers, g/g

CELL MASS BALANCES

$$dx_1/dt = (X_{1_0} - X_1)Q/V + (\mu_1 - Kd_1)\, X_1 \quad (18)$$

$$dx_2/dt = (X_{2_0} - X_2)Q/V\ (\mu_2 - Kd_2)\, X_2 \quad (19)$$

Where,

X_{1_0} = Influent concentration of acid-formers, g/L

X_{2_0} = Influent concentration of methane-formers, g/L

Kd_1 = Specific death rate of acid-formers, (d^{-1})

Kd_2 = Specific death rate of methane-formers, (d^{-1})

Several growth models exist that establish a relationship between substrate utilization and organism growth. The one used in the study reported herein is analogous to an enzyme inhibition expression given by Dixon and Webb (1964):

$$\mu = \mu'/[1+(Ks/Sr) + (Si/Ki)] \quad (20)$$

where,

μ = Specific growth rate, d^{-1}

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

Ks = Half-velocity constant, g/L

Sr = Concentration of rate-limiting substrate, g/L

Si = Concentration of inhibitory substrate, g/L

Ki = Inhibition constant, g Si/L

All other terms are similar to the basic Monod model (equation 8). As stated before, the un-ionized component of the total volatile acids is the inhibitory (Si) and the growth limiting (Sr) substrate for methane-formers. At low concentrations, it is rate limiting, while at high concentrations it is inhibitory. For the acid-formers, the rate limiting substrate is the influent BVS, while the inhibitory substrate is the un-ionized volatile acids (UVA). Equation (6) can be rewritten for the acid-formers and the methane-formers as follows:

$$\mu_1 = \mu'/[1+(Ks_1/S) + (UVA/Ki_1)] \qquad (21)$$

$$\mu_2 = \mu'/[1+(Ks_2/UVA) + (UVA/Ki_2)] \qquad (22)$$

where,

μ_1 = Specific growth of acid-formers, d^{-1}

μ_2 = Specific growth of methane-formers, d^{-1}

The equilibrium between the ionized and un-ionized forms can be chemically represented by equation (23) which is the dissociation equilibrium for a weak acid:

$$UVA \rightarrow H^+ + VA^- \qquad (23)$$

$$[UVA] = [H^+]\,[VA^-]/Ka \qquad (24)$$

Where,

UVA = Un-ionized volatile acid concentration, g/L

H^+ = Hydrogen ion concentration, g/L

VA^- = Ionized volatile acid concentration, g/L

Ka = Ionization constant.

Clearly, the UVA concentration is strongly pH dependent. From equation (23), it is evident that as the pH of the system decreases (H^+ increases), the UVA concentration increases and becomes more inhibitory. Figure 14 is a graphical representation of Equation (22) and illustrates the effect of pH on microbial growth curves. It should be noted that the Monod growth expression (Equation 7) can not predict growth under varying pH conditions.

The low Ks value usually associated with methane-formers causes a sharp rise in the growth curve as it approaches the maximum specific growth rate (μ'). It is clear that the

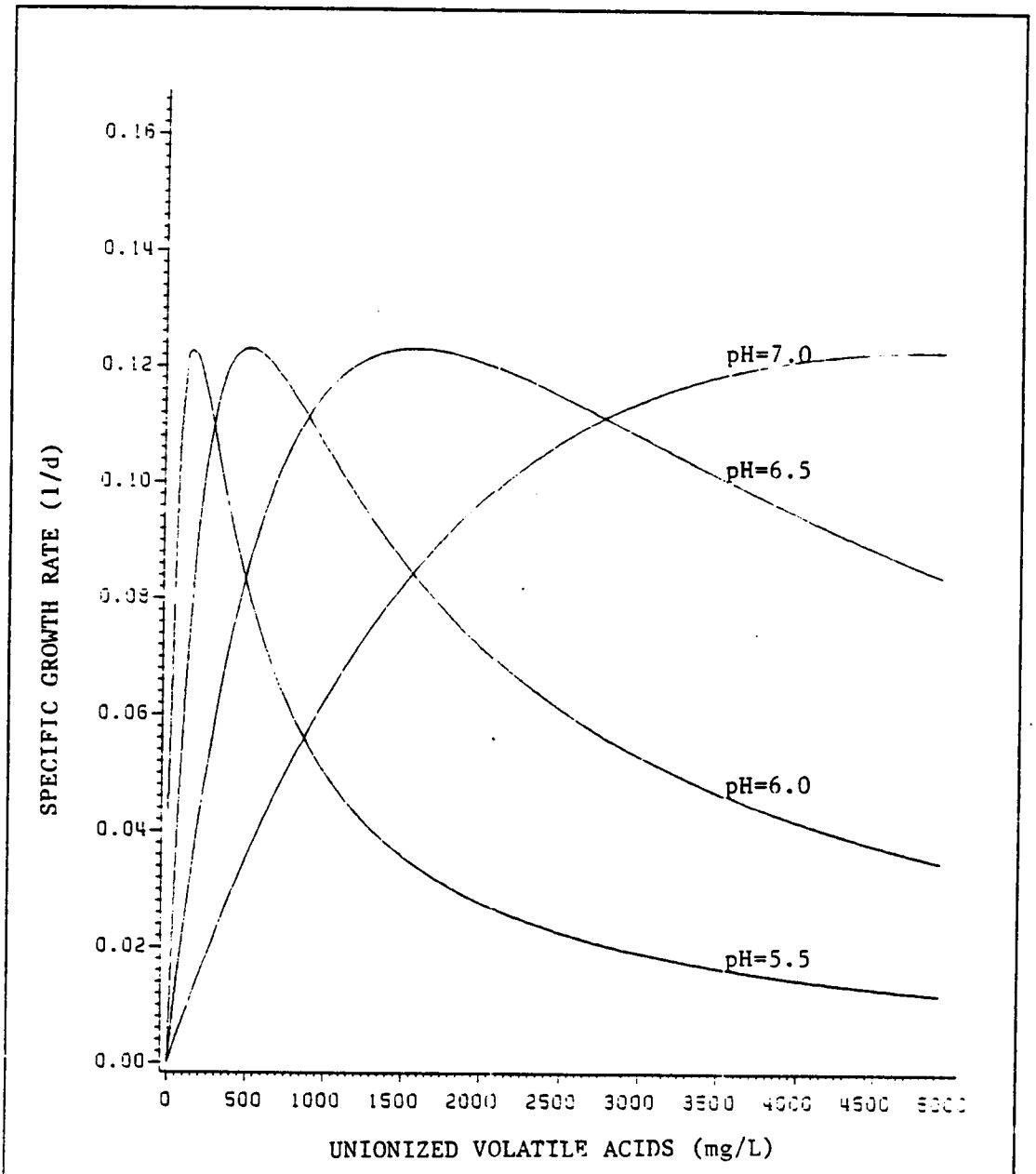


Figure 14. Effect of pH on Microbial Growth

specific growth rate (μ) is sensitive to small changes in the substrate concentration at very low values. On the other hand acid-formers, with a higher Ks value, approach μ' more slowly, and therefore is sensitive to changes in substrate concentration over a much broader range. In continuous cultures, organisms with higher Ks values tend to be more stable than those with lower Ks values.

A simplification can now be made. At any time the total volatile acid concentration (VFA) is the sum of the ionized and the un-ionized portions.

$$VFA = VA^- + UVA$$

With pH constrained between the limits 5.5 and 8, the predominant form of the volatile acids system is the ionized component, meaning that UVA is negligible. Therefore,

$$VFA \approx VA^-$$

Equation (24) can now be written as:

$$[UVA] = [H^+]\,[VFA]/Ka \qquad (25)$$

Equation (25) when combined with equations (21) and (22) will yield growth expressions that are sensitive to pH changes.

Lowering the pH results in progressively increased inhibition.

In order to determine the theoretical methane production, a conversion factor for the amount of methane produced from the conversion of a unit weight of biodegradable COD (or VS) destroyed is needed.

Assuming glucose as the soluble organic available to the acid-formers (Hill, 1982), its conversion to carbon dioxide and methane is given by:

$$C_6H_{12}O_6 \rightarrow 3\ CO_2 + 3\ CH_4$$

The oxygen demand of CH_4 is required to arrive at the COD of $C_6H_{12}O_6$. Hence

$$3\ CH_4 + 6\ O_2 \rightarrow 3\ CO_2 + 6\ H_6O$$

That is, the theoretical oxygen demand of glucose is 192/180 g, and 1 g of glucose yields 48/180 g of methane. Hence, the amount of methane produced per g of COD stabilized is:

$$g\ CH_4/g\ COD = 48 \div 180/192 \div 180. = 0.25$$

Finally, the methane productivity can be expressed in terms of the biodegradable COD (BCOD) by a simple conversion. Recall that the molecular weight of methane is 16 g/mol, and a mole of gas at Standard Temperature and Pressure occupies 22.4 L. Thus:

$$(0.25 \text{ X } 22.4)/16 = 0.35 \text{ L } CH_4/g \text{ COD}$$

Now, if the BCOD/BVS ratio of the waste is known, then theoretical gas production can be expressed in terms of BVS destroyed. In this study, the BCOD/BVS ratio was determined to be 1.46. Hence, the volume of gas that could be produced by the conversion of 1 g of volatile solids is (0.35 L/g biodegradable COD) (1.46g BCOD/g BVS) = 0.51 L CH_4/g BVS.

Hill (1982), working with a 3-step scheme involving five physiologically different microbial populations, arrived at a methane productivity of 0.55 L/g BVS destroyed. McCarty (1964e) has also demonstrated a direct correlation between volatile solids destruction and methane formation by specifying a value of 0.50 L/g biodegradable VS destroyed. Experimental data obtained for swine waste (Fisher et al., 1979) and dairy waste (Hills, 1980) suggest methane productivity values of 0.56 and 0.54 L /g VS respectively.

It is customary to report gas production as volumetric methane productivity (L/L-day) or as unit methane production. (L/g BVS added). Henceforth they will be referred to as VMP and UMP, respectively. Accordingly,

$$VMP = 0.5(S_0 - S)/\theta \qquad (26)$$

$$UMP = 0.5(S_0 - S)/S_0 \qquad (27)$$

Where,

VMP = Volumetric methane production, L/L-d

UMP = Unit methane production, L/g BVS destroyed

The process efficiency is generally measured by the degree of volatile matter reduction, and is generally expressed as a percent of influent substrate concentration. Thus,

$$E = [(S_0-S)/S_0] \ 100 \qquad (28)$$

$$Et = [(St_0-St)./St_0] \ 100 \qquad (29)$$

Where,

S_0 = Influent BVS concentration, g/L

S = Effluent BVS concentration, g/L

E = Biodegradable treatment efficiency, %

Et = Overall treatment efficiency, %

St_0 = Influent TVS concentration, g/L

St = Effluent TVS concentration, g/L

As indicated before, due to the presence of refractory material in most complex wastes, the biodegradable volatile solids (BVS) is often used for modeling purposes. However, from the point of view of effluent quality, the engineer is concerned not with the biodegradable component, but the total volatile solids.

Thus we have:

$$St = S + R\ St_0 \qquad (30)$$

where,

R = Refractory fraction.

Another useful parameter is the volumetric waste utilization rate (dF/dt) expressed as:

$$dF/dt = (S_0 - S)/\theta \qquad (31)$$

dF/dt can be used to arrive at the minimum retention time.

3.4 INCOMPLETE MIXING

Smooth operation of any biological system is possible only if constant environmental conditions are provided for the microbial population (Garrett and Sawyer, 1956). Aris (1965), Kramers and Westerterp (1963) and Levenspiel (1962) have documented the importance of mixing in rector design. Mixing serves several purposes:

1. to prevent short circuiting and dead volume,

2. to maintain a uniform temperature,

3. to disperse intermediates as they are formed,

4. to distribute substrate uniformly on entry,

5. to mix bacteria intimately with their substrate,

6. to prevent scum formation, and

7. to free trapped gases.

Continuously mixing field digesters demands large quantities of energy. In developing countries like Sri Lanka this additional power input is not justified. Hence, the digesters

in these countries tend to be undermixed. In an anaerobic digester, the elementary reacting particle for the substrate is the individual molecule, and for the microorganism is the individual cell. In reactors that are mixed only at the time of effluent withdrawal and feed addition, the elementary reacting particles are not freely dispersed at all times and are thus exposed to different environments. This would cause variations in the growth rate even within the same species. Further, since the volatile fatty acids will not be dispersed, localized regions of high volatile acid concentrations may occur leading to inhibition of microbial mass in these areas.

Feed addition and production of intermediates are the two major causes of varying digester environment. In batch processes, since feed is added only once, perfect mixing is easy to attained if agitation is maintained for a reasonably long period of time. In a continuous or intermittently fed system, on the other hand, a perfectly homogeneous mixture is difficult to achieve.

Cholette and Cloutier (1959) developed a flow model that appears to describe the flow pattern in an imperfectly mixed reactor. The model assumes that there is a perfectly mixed region, a dead space, and a bypass flow. Grieves et al. (1964) concluded that this method of volume apportionment

analysis of flow patterns is suitable for quantifying short circuiting and stagnancy (dead volume). Subsequent studies (Millbury et al., 1965; 1964) have supported this method of analysis.

The kinetic description of microbial growth and substrate utilization can be combined with the hydraulic model to elucidate the effect of short-circuiting and stagnant zones upon the anaerobic process. One of the effects of short circuiting and dead volume is to alter the theoretical dilution rate (D). By definition:

$$D = Q/V$$

In the present study, due to incomplete mixing, the actual dilution rate (D') differs from the the theoretical dilution rate. Thus,

$$D' = (B\ Q)/(A\ V) = (B/A)\ D \qquad (32)$$

where, A is the fraction of reactor volume that is completely mixed, and B is the component of the feed that enters the completely-mixed zone. Thus, the theoretical dilution rate is altered by a factor B/A. Obviously, if B>A, then D>D', and if B<A, then D <D'. Equations (32) can be incorporated into

the substrate and organism mass balances to yield the following four differential equations:

$$dS/dt = (S_0-S)D' - \mu_1 X_1/Y_1 \quad (33)$$

$$dVA/dt = (VA_0-VA)D' + \mu_1 X_1(1-Y_1)/Y_1) - \mu_2 X_2/Y_2 \quad (34)$$

$$dX_1/dt = (X_{10} - X_1)D' + (\mu_1 - Kd_1) X_1 \quad (35)$$

$$dX_2/dt = (X_{20} - X_2)D' (\mu_2 - Kd_2) X_2 \quad (36)$$

The presence of short circuiting also tends to decrease the effluent quality. The short circuited substrate will appear in the effluent and will increase the VS (or COD) concentration. If S and St are the reactor biodegradable and total substrate concentrations, respectively, then the actual effluent BVS concentration (Se) is:

$$Se = S + (1-R)(1-B) St_0 \quad (37)$$

where, R is the refractory fraction of the waste, and $(1-R)(1-B)St_0$ is the amount of biodegradable substrate short circuited. Likewise, the total effluent substrate concentration (Ste), which also includes the refractory fraction, is:

$$Ste = St + (1-B)\ St_0 \qquad (38)$$

It follows that the predicted values for gas production and performance efficiency will also be altered. In effect the above expressions are applied to a hypothetical region within the digester that is well-mixed. Hence, by definition, in this region SRT=HRT.

3.5 INTERMITTENT FEEDING

Digesters for animal wastes are often fed once daily. Pulse or intermittent feeding brings about a cyclic variation in the substrate concentration: high values immediately after feeding and low values prior to feeding. Hence, within a short time, the substrate concentration fluctuates from a maximum to a minimum. This fluctuation would be repeated every 24 hrs thus placing the biological population under tremendous physiological stress. Thus the achievement of steady-state conditions will be hindered leading to accumulation of volatile acids.

It has been observed that an abrupt increase in substrate concentration is accompanied by a similar increase in the substrate uptake rate with the the growth rate not being able

to switch to higher values (Van den Eynde et al., 1983). In a subsequent study, Van den Eynde et al. (1984) observed results that were not in accordance with the Monod concept of an immediate increase of the specific growth rate with higher concentration of substrate. The authors observed that initial substrate intake was too high. Consequently, excess substrate accumulated as reserves or was excreted as over-flow metabolites rather than producing growth. This finding has profound influence on the behavior of mixed cultures. Pulse feeding of anaerobic digesters results in the selection of species of acid-formers that can remove the initial substrate at a fast rate. The metabolites (VFA) that accumulate also need to be scavenged at a comparable rate. Since methane-formers are notoriously slow growing, their inability to keep pace with the acid-formers may lead to VFA accumulation and subsequent process inhibition. The Monod growth expression implies that, in response to changes in substrate concentration, the cell adjusts to a new growth rate instantaneously (Powell, 1967). However, cells growing at different rates have different composition, and it takes time to adjust the cell composition to that which is appropriate to the new growth rate. The Monod equation therefore applies strictly to steady-state conditions as it does not include a lag term normally associated with cells undergoing a transition in growth rate.

3.6 MODEL PARAMETERS

The digester model developed in this study contains four growth associated parameters that are considered constants for modeling purposes. This section describes the rationale behind assigning numerical values to these parameters.

Hashimoto et al. (1980), using extensive field data, have established a temperature dependent function for the maximum specific growth rate (μ'). This function, which is valid for a temperature range of 30°C to 60°C , is given as:

$$\mu' = 0.013\ T - 0.129$$

where, T is the temperature in degrees C. Using the above function, the maximum specific growth rate at 35°C is 0.326 d^{-1}. The same value was assumed for both cultures.

The half-velocity constant (Ks) is a measure of the sensitivity of the organism to changes in substrate concentration. It is therefore a function of the waste type and the microorganism involved. A range of values can be found in the literature. In the present study, half-velocity constants of 150 mg/L for the acid-formers and 25 mg/L for the methane-formers have been found to give results comparable to experimental values.

The inhibitor coefficient (Ki) defines the concentration of UVA beyond which inhibition is evidenced. The term UVA/Ki decreases μ by a factor related to the concentration of UVA. Obviously, Ki for methane-formers is lower than that for acid-formers because UVA is inhibitory to the former at lower concentrations. Ki values of 1000 mg UVA/l and 300 mg UVA/l were used in the study reported herein for the acid-formers and methane-formers, respectively. These values were recommended by Hill and Nordstedt (1980) and Hill and Barth (1977).

In the study reported herein, the microbial decay rate was assumed to be one-tenth the maximum specific rate and therefore is a constant at a given temperature (Hill, 1984; Hill and Nordstedt, 1980; Andrews and Pearson, 1975; Lawrence and McCarty, 1969). However it should be pointed out that a recent study (Hill, 1985), specifically designed to examine microbial death reported that the decay rate, like the growth rate, is a function of the organic acid concentration.

The yield coefficients used were derived from the stoichiometry of the process. Hill and Barth (1979) performed an elemental analysis of raw swine manure and determined its empirical chemical composition to be $C_6H_{13}NO_5$. They noted that dairy, beef and poultry wastes have similar carbon to hydrogen ratios. They also determined that raw

waste is converted to soluble organics (glucose; MW=180 g/mol) on a 1 to 1 weight and volume basis. Hence, we can chemically represent this initial extracellular enzymatic conversion as follows:

$$C_6H_{13}NO_5 + H_2O + H^+ \rightarrow C_6H_{12}O_6 + NH_4^+$$

The NH_4^+ generated in the above reaction is the source of nitrogen for the microbes (Hill, 1982). The conversion of glucose (soluble organic) to volatile acids may be described by the following reactions (Hill, 1982):

ACETOGENESIS

$$\text{Glucose} \rightarrow \text{Cells} + \text{acetate} + \text{propionate} + \text{butyrate} + CO_2$$

$$C_6H_{12}O_6 + 0.1115\ NH_4^+ + 1.05\ H^+ + 1.16\ e^- \rightarrow$$
$$0.1115\ C_5H_7NO_2 + 0.5\ CH_3CH_2COOH + 0.5\ CH_3CH_2CH_2COOH$$
$$+ 0.744\ CH_3COOH + 0.454\ CO_2 + 1.38\ H_2O \quad (39)$$

PROPIONATE HYDROGENESIS

Propionic acid → Cells + acetic acid + hydrogen + CO_2

$$CH_3CH_2COOH + 0.0458\ NH_4^+ + 0.0458\ e^- + 1.786\ H_2O \rightarrow 0.0458\ C_5H_7NO_2 + 0.924\ CH_3COOH + 2.87\ H_2 + 0.924\ CO_2 \qquad (40)$$

BUTYRATE HYDROGENESIS

Butyric acid → cells + acetic acid + H_2

$$CH_3CH_2CH_2COOH + 0.0545\ NH_4^+ + 1.84\ H_2O \rightarrow 0.0545\ C_5H_7NO_2 + 1.86\ CH_3COOH + 2.04\ H_2 \qquad (41)$$

From equation (39) we note that each molecule of glucose is converted to 0.1115 mols of cells and 0.5 mols each of propionate and butyrate. The conversion of 1 mol propionate and butyrate (equations 39 and 40) in turn produce 0.0458 mols and 0.0545 mols of cells, respectively. Hence, the total mol of cells formed as a result of the breakdown of 1 mol of glucose is, (0.1115 + 0.0458/0.5 + 0.0545/0.5) = 0.312 mols. Hence, the yield coefficient of acid-formers (Y_1) is:

Y_1=(0.312 mol X 113 g/mol)/(1 mol subs. X 180 g/mol)
= 0.196 g cells/g substrate

In order to compute the yield coefficient for methane formers (Y_2) it is assumed that the substrate is acetic acid (MW = 60 g/mol). Hence,

$$CH_3COOH + 0.0227\ NH_3 \rightarrow 0.0227\ C_5H_7NO_2 + 0.943\ CH_4 + 0.943\ CO_2 + 0.069\ H_2O$$

Since 1 mol of acetic acid converted results in the formation of 0.0227 mols of cells, the yield coefficient is 0.0227 mol cells/ mol substrate. That is:

Y_2=(0.0227 mol cell X 113 g/mol)/(1 mol subs. X 60 g/mol)

= 0.043 g org./g subs.

Most bacterial cells contain 50% carbon, 20% oxygen, 10-15% nitrogen, 8-10% hydrogen 1-3% phosphorus and 0.5-1.5% sulfur on dry weight basis (Gaudy and Gaudy, 1980). Although variations in their percentages occur in response to environmental conditions, a constant empirical expression is often assumed to simplify stoichiometric relationships. The most widely accepted formula is $C_5H_7NO_2$ with a molecular weight of 113 g/mol (Burkhead and McKinney, 1969; McCarty, 1966; Speece and McCarty, 1964). Table 2 summarizes the parameter values used in the present study.

Table 2. Parameter Values Used in Simulation

PARAMETER	VALUE
μ'	0.324 d^{-1}
Kd_1	0.0324 d^{-1}
Kd_2	0.0324 d^{-1}
Ks_1	0.15 g/L UVA
Ks_2	0.025 g/L UVA
Ki_1	1.0 g/L UVA
Ki_2	0.3 g/L UVA
Y_1	0.196 g/g
Y_2	0.043 g/g

4.0 EXPERIMENTAL PROCEDURE

In this section the materials and methods used in obtaining reactor performance data under controlled environmental conditions will be discussed. The study was conducted in several phases, most of which were concurrent.

4.1 DETERMINATION OF SUBSTRATE BIODEGRADABILITY

From the point of view of microbial degradation , the most important property of any waste is its assimilatory quality, or the availability of organic matter to the bacteria. Organic waste concentration is routinely expressed by three parameters: chemical oxygen demand (COD), biological oxygen demand (BOD), and volatile solids (VS) content, all of which have associated experimental errors. The COD technique requires sample dilution in order to stay within the range of operation. Thus strong wastes, such as dairy manure, must be diluted several times thereby increasing the magnitude of the error. Since determination of ultimate BOD is time consuming, it is approximated by the BOD value after 5 days (BOD_5). VS is generally measured by determining the loss of weight after ignition at 550°C. At this temperature, in addition to volatile organics, some inorganic material is

also lost. According to Lawrence and McCarty (1969), these losses would be insignificant at the relatively high solids concentration encountered with animal wastes.

Determination of COD and VS will permit the development of a COD/VS ratio for the dairy waste. A constant ratio over a period of time would indicate that both COD and VS are comparable parameters (Morris, 1977). However, since it is easier to determine, VS would be preferred.

Complex wastes, such as animal manure, contain a certain amount of volatile organic matter which is not biodegradable. Thus, the total volatile solids in digester influent consists of biodegradable and refractory portions. That is,

$$St_0 = S_0 + RVS$$

and,

$$R = RVS/St_0$$

where,

St_0 = total influent volatile solids (g/L);

S_0 = biodegradable volatile solids (g/L);

RVS = refractory volatile solids (g/L); and

R = refractory VS fraction.

Only S_0 serves as substrate for the acid-formers. Conceptually, as the solids retention time (SRT) approaches infinity, S_0 is completely removed. The VS remaining represents the refractory portion. In practice, biodegradability is the extent to which organic material is degraded under a given set of environmental conditions during a given time (Foree and McCarty, 1968). The biodegradable VS fraction varies with waste type and is affected by the species and age of animal, ration, manure age, and collection and storage methods.

In this investigation, batch digestion data was used to determine S_0 of dairy manure. A known concentration of substrate was digested in batch mode until a negligible amount of gas was produced. The VS remaining represents the RVS portion (Hashimoto, 1982).

4.2 BENCH-SCALE EXPERIMENTS

In order to evaluate the operating characteristics of the Chinese digester in the laboratory, scaled down replicas of the actual field digesters used in Sri Lanka (Figure 15) were constructed. Five litre boiling flasks were modified in the Virginia Tech Glass Instrument Laboratory (Chemistry Department) to structurally resemble the Chinese digester.

Initially, three laboratory digester designs were used, differing only in the position of the outlet as described below, and shown in Figure 16:

TYPE 1: Outlet placed at the 3L mark.

TYPE 2: Outlet placed at the 1.5L mark.

TYPE 3: Outlet placed at the bottom of the flask.

In all three types, the outlet orifice was completely submerged in the digester contents.

In a preliminary study, each of the three types of digesters was subjected to a tracer experiment. Based on the results, Type 3 digester was selected for the main investigation. The stimulus-response study and the basis of digester selection are described in sections 4.3 and 5.3, respectively.

Sixteen daily-fed digesters (Type 3) were involved in the main study designed to observe reactor performance under varying operational conditions. The digester units were distributed in two styrofoam boxes constructed for this purpose, and maintained in the mesophilic temperature range ($35^{\circ}C \pm 2^{\circ}C$). Glass jars (1L) within the boxes were filled with water and heated by 100 W aquarium heaters to maintain

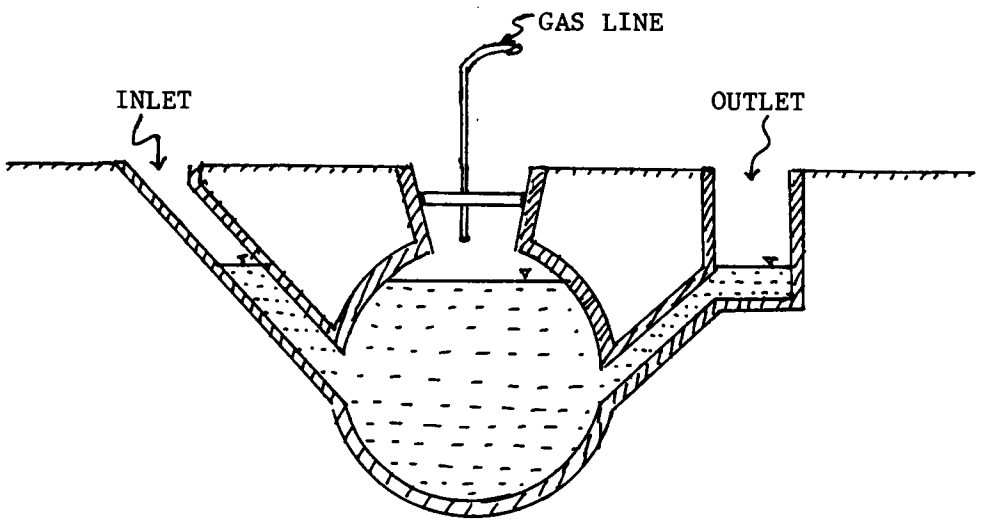


Figure 15. Large-scale Chinese Digester (Sri Lanka)

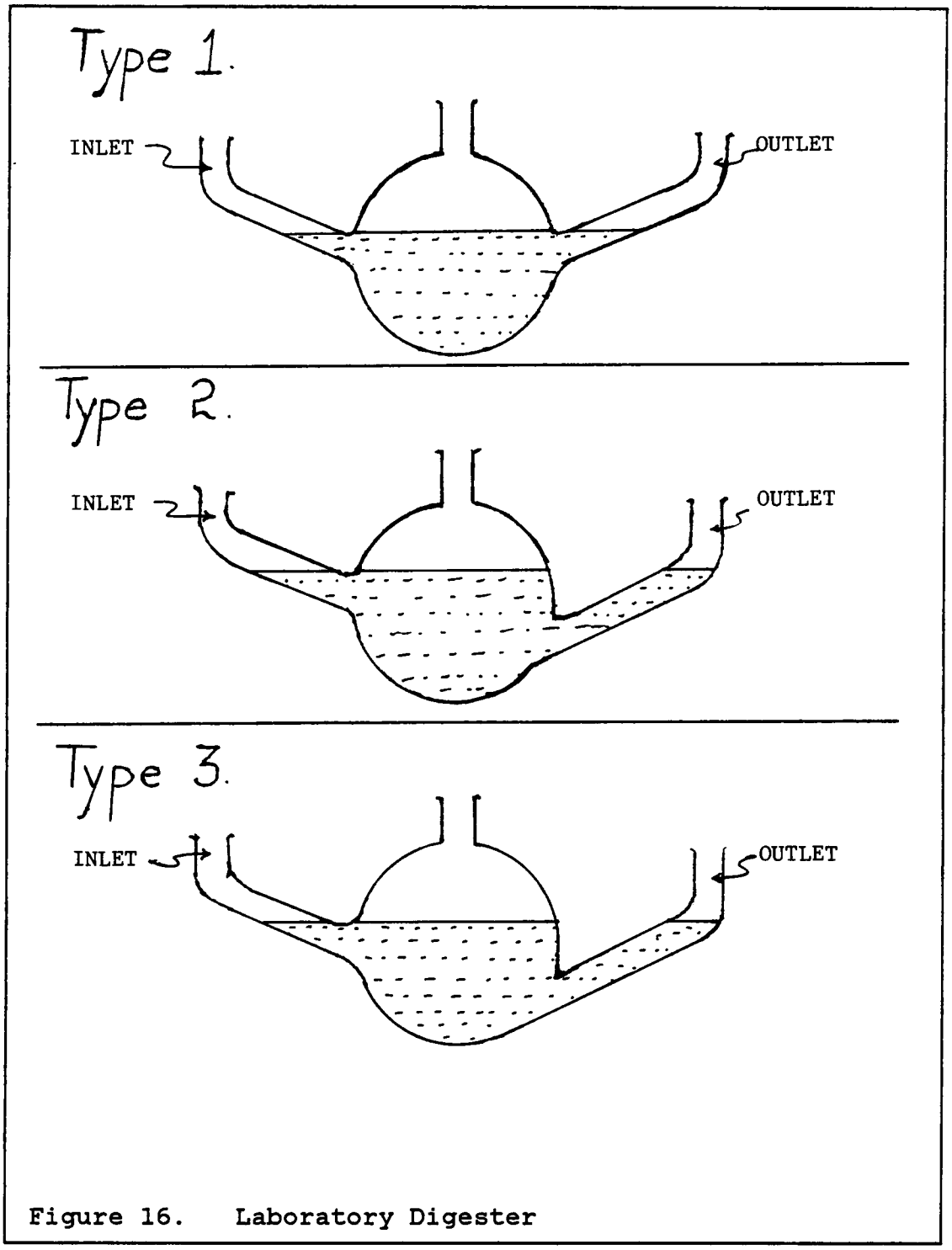


Figure 16. Laboratory Digester

box temperature. Dairy cattle manure from the Virginia Tech Dairy Center was used to prepare feedstock for the digesters.

4.2.1 DIGESTER SUBSTRATE

Dairy waste was used as substrate for the digesters. Manure was collected from concrete floors in enclosed barns at the Virginia Tech Dairy Cattle Center. Care was taken to collect only fresh manure, and to avoid inclusion of sand and other inert material. Glass jars (3.785 L) were used to transport manure to the laboratory where it was well mixed in a bucket, and five random samples where taken to determine total solids (TS), volatile solids (VS), nitrogen content (total and organic), and chemical oxygen demand (COD). The raw manure was subjected to a certain amount of 'cleaning' prior to analyses. Large particles of straw and seeds were removed to yield a relatively homogeneous waste. Previous experience (Jeyanayagam and Collins, 1984) indicated that presence of straw and seeds tends to interfere with the withdrawal of representative samples. The waste was stored in a freezer in glass jars until required for the digesters.

The laboratory digesters were fed once daily, similar to loading field units in Sri Lanka. Substrate for the digesters was prepared on a daily basis. Prior to preparation, the manure was thawed and diluted with tap water

to the desired influent TS concentration. Just before feeding, contents of each digester were mixed with a wooden ladle and a predetermined volume of effluent was withdrawn. This was followed by the addition of an equal volume of influent material.

In this investigation, the effect of sixteen different combinations of residence time and substrate concentration was observed. As illustrated in Table 3, each combination yielded a particular value of organic loading rate (LR) which was randomly assigned to a digester.

Table 3. Digester Loading Rates

FEED TS	RESIDENCE TIME (DAYS)			
(%)	8	10	15	20
6.9	5.01	4.01	2.67	2.00
10.0	7.23	5.78	3.86	2.89
10.7	7.78	6.23	4.15	3.12
12.2	8.90	7.12	4.75	3.56

Loading rates expressed in g BVS/L-day

Computations based on VS = 89% TS and BVS = 65% VS

Anaerobic sludge from a local municipal sewage treatment facility was used as inoculum. The digesters were filled with a 1:1 (by volume) mixture of inoculum and dairy waste. Quasi steady-state conditions were established after two to three retention cycles. Steady-state was assumed when evidence of constant gas yield and gas composition were observed.

4.2.2 MONITORING DIGESTER PERFORMANCE

Laboratory tests were conducted to develop response data for the parameters considered in this study. A summary of the sampling and analysis program is presented in Table 4. Determination of solids, pH, alkalinity, and chemical oxygen demand were performed according to Standard Methods (American Public Health Association, 1980).

Table 4. Sampling and Analysis Program

PARAMETER	RAW WASTE	INFLUENT	EFFLUENT		
	once	once	daily	biweekly	weekly
TS	X	X	X		
VS	X	X	X		
VFA		X	X		
COD		X	X		
PH			X	X	
ALKALINITY		X	X		
TKN		X			X
NH_4-N		X			X
GAS QUANTITY			X		
GAS QUALITY					X

4.2.2.1 SOLIDS

Total (TS) and volatile solids (VS) were determined for the raw waste, digester influent, and digester effluent samples. Five random samples of raw waste were placed in previously weighed crucibles and oven dried at 103°C for 24 hours to determine TS. Dried samples were then fired at 550° C in a muffle furnace for 5 hours to determine VS. A Mettler H 80 balance was used for weighing throughout this investigation.

4.2.2.2 PH AND ALKALINITY

A 20.0 mL sample of the daily effluent was used for the measurement of pH and alkalinity. The sample was constantly stirred with a magnetic stirrer and was titrated to pH 4.5 with 0.1N hydrochloric acid to determine digester alkalinity. The pH was measured using a Leeds and Northrup pH meter.

4.2.2.3 CHEMICAL OXYGEN DEMAND (COD)

A 10.0 mL representative sample of digester effluent was diluted to 1 L with distilled water. Precise 20.0 mL aliquots of diluted sample were placed in a 20/40 COD distillation flask. Then, 0.4 gm of mercuric sulfate, 10.0 mL of 0.25N potassium dichromate, and 30.0 mL of concentrated sulfuric acid containing silver sulfate catalyst were added.

Following 2.5 hours of refluxing, the sample was diluted to 150 mL. Titration with standard ferrous ammonium sulfate allowed for calculation of the sample COD.

4.2.2.4 VOLATILE FATTY ACIDS (VFA)

In order to determine the volatile acid concentration, 5.0 mL of effluent sample was pipetted into a culture tube containing 1.0 mL of 25% metaphosphoric acid and 5.0 mL of an internal standard (2.5 mL of 4-methyl valeric) in 1 L of distilled water, and then frozen. After thawing, samples were centrifuged for 20 minutes at 3000 rpm. Approximately 5.0 mL of sample was drawn into a 10 mL disposable syringe and forced through a membrane filter holder containing 2.0 micron metricel filter, and collected in a small culture tube. Exactly 2 mL of the sample was injected into a Perkin-Elmer 881 flame ionization gas chromatograph. The instrument parameters were: Nitrogen carrier gas at 40 mL/min., column at 120°C, injection port at 175°C, and detector at 210°C; 1.83 m X 3.175 mm glass column with 10% SP-1200/ 1% H_3PO_4 on 80/100 mesh chromasorb WAW.

Peaks were recorded using a Hewlett-Packard 3380 A integrator with a chart speed of 5 cm/min. Areas of peaks obtained from the integrator were compared with those of the standard solution to determine the volatile acid concentration.

4.2.2.5 DIGESTER GAS

Gas volume was measured by two different methods. The use of U-tube manometers facilitated gas measurement in a semi-continuous manner, while the use of Tedler gas sampling bags (Cole-Parmer) allowed accumulated daily gas volumes to be measured. An Orsat gas analyzer was used to determine gas composition assuming that the digester gas (biogas) was primarily a mixture of methane and carbon dioxide (Iannotti et al., 1985; Hashimoto, 1982; Gramms et al., 1971).

4.2.2.6 NITROGEN

Total nitrogen content of the manure was determined by placing 5 mL of sample in an 800 mL Kjeldahl digestion flask and diluting to 250 mL with distilled water. Ten mL of concentrated sulfuric acid, 6.7 g of potassium sulfate and 1.5 mL of mercuric sulfate were then added and the contents boiled until the solution became clear. Digestion was continued for another 30 minutes after which the flask was allowed to cool. The contents were then diluted with 200 mL of ammonia-free water, and 0.5 mL phenolphthalein indicator solution was added and mixed. Hydroxide thiosulfate reagent was carefully added so that it layered at the bottom. After mixing well, the flask was attached to the preheated distillation apparatus. Two-hundred mL of distillate were

collected in a boric acid trap and titrated with 0.1 N hydrocloric acid allowing for the calculation of total nitrogen.

4.3 STIMULUS-RESPONSE STUDY

Tracer studies allowed examination of flow characteristics of the reactors. Before explaining the experiments involved, it is necessary to discuss the digester hydraulic model and the associated mathematical expression for effluent tracer concentration.

First, let us consider a continuously stirred tank reactor (CSTR) subjected to a pulse input of a conservative (nonreactive) tracer. At time zero, the tracer is uniformly spread throughout the reactor at a concentration C_0. Influent flow to the reactor continues, but no more tracer is added. Thus, the tracer is slowly washed out of the system. A mass balance yields:

$$V\, dC_1/dt + Q\, C_1 = 0 \qquad (42)$$

where,

V = Reactor volume, L

C_1 = Reactor tracer concentration at time t, g/L

Q = Volumetric flow rate, L

Rearranging equation (42) and assuming the limits of integration to be from $C = C_0$ to $C = C_1$, and $t = 0$ to $t = t$, we have:

$$\int_{C_0}^{C_1} dC_1/C_1 = - \int (Q/V)\, dt$$

$$\ln (C_1/C_0) = - Qt/V \qquad (43)$$

Equation (43) is a theoretical expression of tracer concentration as a function of time for the CSTR.

In order to extend equation (43) to a poorly mix reactor, a digester flow model (Figure 17) was developed. Accordingly, only a fraction (A) of the digester volume (V) is completely mixed, leaving the complimentary fraction, 1-A as stagnant zone. Of the influent flow Q, a fraction B enters the completely mixed zone while the remaining (1-B), is short circuited.

Hence, equation (43) becomes:

$$C_1'/C_0 = \exp(-BQt/AV) \qquad (44)$$

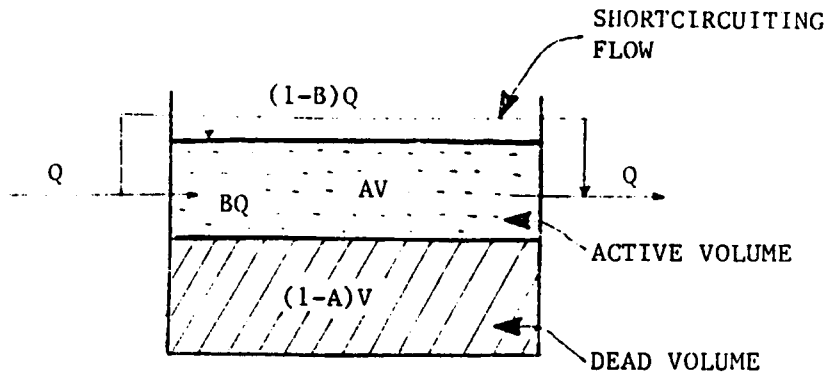


Figure 17. Digester Hydraulic Model

where, C_1' is the concentration of tracer in the completely-mixed zone (that is, volume AV) and will be diluted by the bypass flow. Hence, the effluent tracer concentration (C) is:

$$C = BQC_1'/(BQ+(1-B)Q)$$

That is,

$$C = B\,C_1' \qquad (44)$$

Combining equations (43) and (44), we have:

$$C/C_0 = B \exp(-BQt/AV)$$

Or,

$$\ln C/C_0 = \ln B - (B/A)(Qt/V) \qquad (45)$$

A semilog plot of equation (45) yields a straight line with a slope of -(B/A) and an intercept of ln B. This permits the quantification of the degree of mixing in terms of bypass flow and dead volume.

The choice of tracer for determining reactor flow characteristics is of fundamental importance. Bailey and Harkness (1978) outlined the criteria by which a tracer may be judged for its suitability. These are sensitivity of detection, safety, aesthetic characteristics, solubility,

adsorptive properties, cost, and stability. In this study, lithium chloride (LiCl) was used for the following reasons:

1. It is highly soluble (637 g/L at 20°C);

2. It does not decay;

3. It does not affect the anaerobic process;

4. It does not interfere with the determination of other parameters;

5. It is not present in dairy waste - does not need background correction;

6. Lithium concentrations down to 0.01 ppm can be detected with an atomic absorption unit;

7. Tests can be performed rapidly once equipment is calibrated;

8. Samples can be stored prior to analysis, and;

9. It is fairly inexpensive (approximate cost: $2.00 per lb.).

Digesters operated at retention times of 8, 10, 15, and 20 days were picked for the tracer study. Predetermined amounts of lithium chloride (LiCl) were mixed with the influent and fed to the digesters once at the beginning of the tracer experiments (pulse feeding). The effluent was monitored for lithium concentration on a continuous basis.

When lithium chloride is added to the digester, it ionizes. Some of the lithium will remain in the bulk solution while the rest will be adsorbed to the solids. Adsorption is a common phenomenon in solid-liquid systems and refers to the removal of solutes from solution by concentration at the surface of the solids. At any given time, the amount of solute remaining in the liquid will be in dynamic equilibrium with that adsorbed (Weber, 1972). The amount adsorbed appears to be influenced by agitation, adsorbent characteristics, solubility of adsorbate, pH, and temperature. Adsorption isotherms are helpful in describing distribution of solute between the liquid and solid phases. Three of the most common phases of mathematical relationships are the Langmuir, the Fruendlich, and the Brunaur-Emmett-Teller (BET) isotherms.

The data from this investigation was found to best fit the Fruendlich isotherm which is based on the assumption that the absorbent has a heterogeneous surface having different

affinities for the molecules of the absorbate. The equation developed is:

$$x/m = K\ C^{1}$$

where,

x = amount of solute adsorbed (mg),

m = weight of absorbent (mg),

C = concentration of solute remaining (mg/L),

K,n = constants.

Rearranging the above equation, we get:

$$\log(x/m) = \log K + (1/n) \log C$$

A plot of log(x/m) vs. log C will generate a straight line if the data follows Fruendlich theory. The values for K and n are obtained from the intercept and slope, respectively.

The experimental scheme adopted in developing the adsorption isotherm at 35°C is illustrated in Figure 18. Predetermined amounts of lithium chloride were added to sixteen effluent samples (50 mL) drawn from the sixteen digesters. A blank (filtered effluent) was also treated similarly. These samples were stored at constant temperature (35°C) for two

days to allow time for the adsorbed lithium to equilibrate with that in solution.

Each of the effluent samples was divided into two equal subsamples (25 mL). One portion was acid digested to extract the adsorbed lithium. The procedures given in Standard Methods (American Public Health Association, 1980) were followed. Accordingly, 5 mL of concentrated nitric acid was added to the sample and boiled for 25 minutes. This was followed by further addition of concentrated nitic acid and gentle refluxing (beaker covered with a watch glass) until digestion was complete as evidenced by a light-colored clear solution. The watch glass was then washed with water and contents of the beaker filtered. The filtrate was diluted to 100 mL and used to determine the total lithium in the sample. The undigested samples were first filtered and the filtrate analysed for dissolved lithium. The difference between this and the total lithium (as determined from the acid digested samples) was a measure of the adsorbed lithium.

A Perkin-Elmer Atomic Absorption unit was used in the programming mode for determination of lithium. The instrument was operated at a wavelength of 670.8 nm and a slit of 0.7 mm. An oxidizing (lean blue) air-acetylene flame was maintained and the lamp current was set at 15 mA. The atomic absorption unit was calibrated using standard

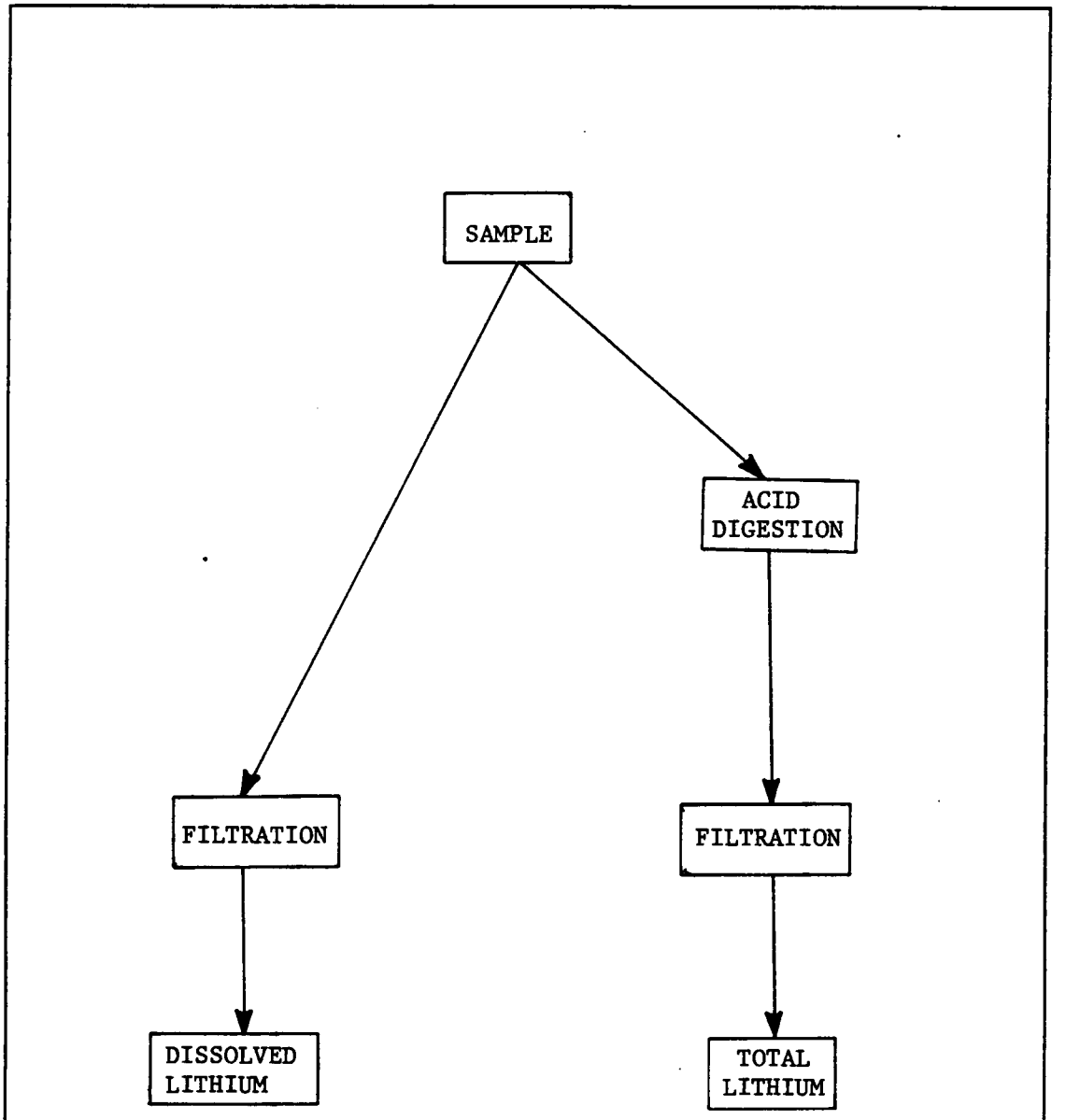


Figure 18. Determination of Lithium Distribution in Digesters

solutions containing 1.00, 5.00, and 10.00 mg/L lithium. Lithium carbonate was used in the preparation of these standards.

4.4 MODELING AND SIMULATION

The anaerobic digestion process was modeled as a two-culture microbial process. That is, raw waste was assumed to be converted to gaseous end-products by two physiologically different groups of microorganisms called acid-formers and methane-formers. The process was mathematically described by writing mass balances and growth expressions. In order to enhance accuracy of the model, effects of incomplete mixing and intermittent feeding were incorporated. A sensitivity analysis was performed to evaluate model response to variations in kinetic and digester flow parameters.

The flow chart used in simulating anaerobic digester performance is presented in Appendix B. The program was based on the nonhomogeneous differential equations (Equations 33 through 36) that predicted substrate utilization and organism growth. The solution algorithm was developed utilizing the Continuous Systems Modeling Program (IBM, 1972) and fortran library functions. In essence, the differential equations were solved using the fourth-order Runge-Kutta scheme with fixed integration interval. The output consisted

of organism and substrate concentrations as a function of time and was plotted with the SAS/GRAPH computer graphics system (SAS, 1985).

4.4.1 THE CONTINUOUS SYSTEM MODELING PROGRAM

The Continuous System Modeling Program (CSMP) is a problem-oriented program designed to facilitate the digital simulation of continuous processes. Perhaps one of the greatest assets of CSMP is the availability of 34 functional blocks (also called functions) plus means for the user to define functions specially suited to his particular simulation requirements. In addition, the flexibility of CSMP can be considerably extended to include the power of FORTRAN libraries and conditional logic and branching statements.

The program structure of CSMP is composed of three segments - INITIAL, DYNAMIC, and TERMINAL. Generally, data values and constants are defined in the INITIAL segment using PARAMETER statements. Also, calculations that are required to be performed only one time during simulation are placed in this segment. The statements that describe the dynamics of the system, or explicitly describe a set of differential equations, are placed in the DYNAMIC segment. In this segment, the program repeats the calculations as many times

as specified in the TIMER specification. The METHOD statement specifies the numerical integration method to be used. The TERMINAL segment usually contains the final computations and output control statements (PRINT, PRTPLT).

The CSMP functions used in this study include INTGRL, RAMP, IMPULS, and PULSE. A brief description of each of these functions follows.

The INTGRL statement represents the mathematical function of of integration and was written as:

```
Y = INTGRL(IC, X)
```

where,

```
IC = Y(0)
X  = dependent variable
```

The above expression states that the output Y is obtained by integrating X with respect to time, with the condition that Y at time zero is equal to IC. The mathematical representation is:

$$Y = \int X \, dt + IC$$

The RAMP function has a default slope of 1. This can be changed if required. It is also possible to combine several RAMP functions to generate other special signals. In this study, two RAMP statements were combined as follows:

```
Y1 = RAMP(0.0)
Y2 = -RAMP(3.0)
FEED = Y1 + Y2
```

The slope of Y1 was positive while that of Y2 was negative. In addition, the starting times of Y1 and Y2 were t=0 hrs. and t=3 hrs., respectively. A triangular signal (FEED) was generated by combining Y1 and Y2.

The IMPULS function was used to generated a train of signals every 24 hrs, starting at t=0 hrs. It was written as:

```
Y = S0 * IMPULS (0.0,24.0)
```

In effect, the IMPULS function produced a 'spike' input of magnitude S0 over a very short duration and therefore simulated once-a-day feed addition.

The PULSE function generated a step signal for a duration of 2 hours and was triggered when the value of TRIG was 1. It was defined as:

```
Y = SO * PULSE(2.0,TRIG)
```

Where, SO represented the magnitude of the step. The IMPULS statement was in turn used as a trigger function to assign a value of 1 to the variable TRIG every 24 hours starting at time=0 hrs. That is,

```
TRIG=IMPULS(48.0,24.0)
```

The PULSE statement in combination with the IMPULS function was used to define the three-step feed model.

5.0 RESULTS AND DISCUSSION

Results of this investigation will be discussed in four sections: (1) Dairy waste characteristics, (2) Digester flow patterns, (3) Digester performance, and (4) Simulation results.

Each of the sixteen digesters used in this study was subjected to a unique combination of hydraulic retention time (HRT) and influent BVS concentration. A numbering scheme, based on the operational variables involved, was developed to identify the digesters (Table 5). Each number consisted of two parts separated by a hyphen. The first part identified the HRT involved, while the numbers 1, 2, 3, and 4 were used in the second part to denote the influent BVS concentrations of 40.1, 57.8, 62.3, and 71.2 g/L, respectively. For example, the number 8-1 refers to the 8-day digester that was subjected to an influent BVS of 40.1 g/L.

Table 5. Indexing of Laboratory Digesters

DIGESTER	INFLUENT CONCENTRATION (g BVS/L)	HRT (day)	LOADING RATE (g/L-d)
8-1	40.1	8	5.01
8-2	57.8	8	7.23
8-3	62.3	8	7.78
8-4	71.2	8	8.90
10-1	40.1	10	4.01
10-2	57.8	10	5.78
10-3	62.3	10	6.23
10-4	71.2	10	7.12
15-1	40.1	15	2.67
15-2	57.8	15	3.86
15-3	62.3	15	4.15
15-4	71.2	15	4.75
20-1	40.1	20	2.00
20-2	57.8	20	2.89
20-3	62.3	20	3.12
20-4	71.2	20	3.56

5.1 MANURE CHARACTERISTICS

The raw manure was characterized by both basic and derived parameters. The basic properties were TS, VS, COD, pH and the nitrogen content (total and ammonia) and biodegradability. The derived parameters were the COD/VS and the NH_4-N/TKN ratios. A summary of the various parameter values is presented in Table 6.

Table 6. Raw Manure Characteristics #

PARAMETER	MEAN	STANDARD DEVIATION
TS (%)	17.1	1.18
TVS (% TS)	89.0	5.01
TCOD (1000 mg/L)	183.4	9.25
pH	7.1	0.30
Nitrogen (mg N/L)		
TKN	6515.3	1003.2
NH_4-N	1497.2	823.7
Biodegradable fraction*		
VS basis	0.65	
COD basis	0.69	
BCOD/BVS	1.44	
TCOD/TVS	1.32	
NH_4-N/TKN	0.23	

Sample size=24
* Based on batch digestion data

Although the manure used in this study exhibited variability, it was assumed that variation in parameter values was small. Accordingly, mean values were used throughout the entire experimental procedures.

The average TS content of the manure used in this study was higher than that cited in the ASAE data D384 (Agricultural Engineering Year Book, 1983). However, it agrees with that reported by Safely et al. (1984). It should be noted that the ASAE data is for fresh manure while that of Safely et al. (1984) is for scraped manure and therefore more closely relates to this investigation. The VS content was also higher than found in the literature (Agricultural Engineering Year Book, 1983; Safely et al., 1984; Taiganides, 1982). The 89.0 percent VS contained in the fresh manure is a reflection of the relatively high amount of organic solids present. It is this component that had to be stabilized during waste treatment.

The nitrogen levels determined compared well with those cited in the literature (Safely et al., 1984; Agricultural Engineering Year book, 1982). Organic nitrogen (org-N) was assumed to be the difference between the total Kjeldhal nitrogen (TKN) and ammonia nitrogen (NH_4-N). This can be attributed to the fact that collection was done during the cool morning hours, within a few hours of defecation.

Approximately 23% of the total nitrogen was present in the ammonium form.

The high COD values obtained were typical of livestock wastes. Specifically, the range reported here agreed with that of Taiganides (1982). The total COD : total VS ratio (TCOD : TVS) of 1.36 suggests that a substantial amount of COD existed as VS. Hence, the stabilization of TCOD was significantly affected by the TVS reduction.

The biodegradability of the waste was of fundamental importance as this defined the actual amount of waste that was readily available to organisms. This parameter was computed indirectly by first determining the refractory fraction (R) of the waste. Figure 19 illustrates the graphical determination of the refractory fraction both on the COD and VS basis. The results indicate that 65% of the TVS and 69% of the TCOD of the raw manure can be potentially degraded by the microbes and were termed the biodegradable VS (BVS) and the biodegradable COD (BCOD), respectively. These values were higher than encountered in the literature (Morris et al., 1977). This is to be expected as the manure was subjected to a certain amount of 'cleaning' aimed at removing straws, seeds, and trash.

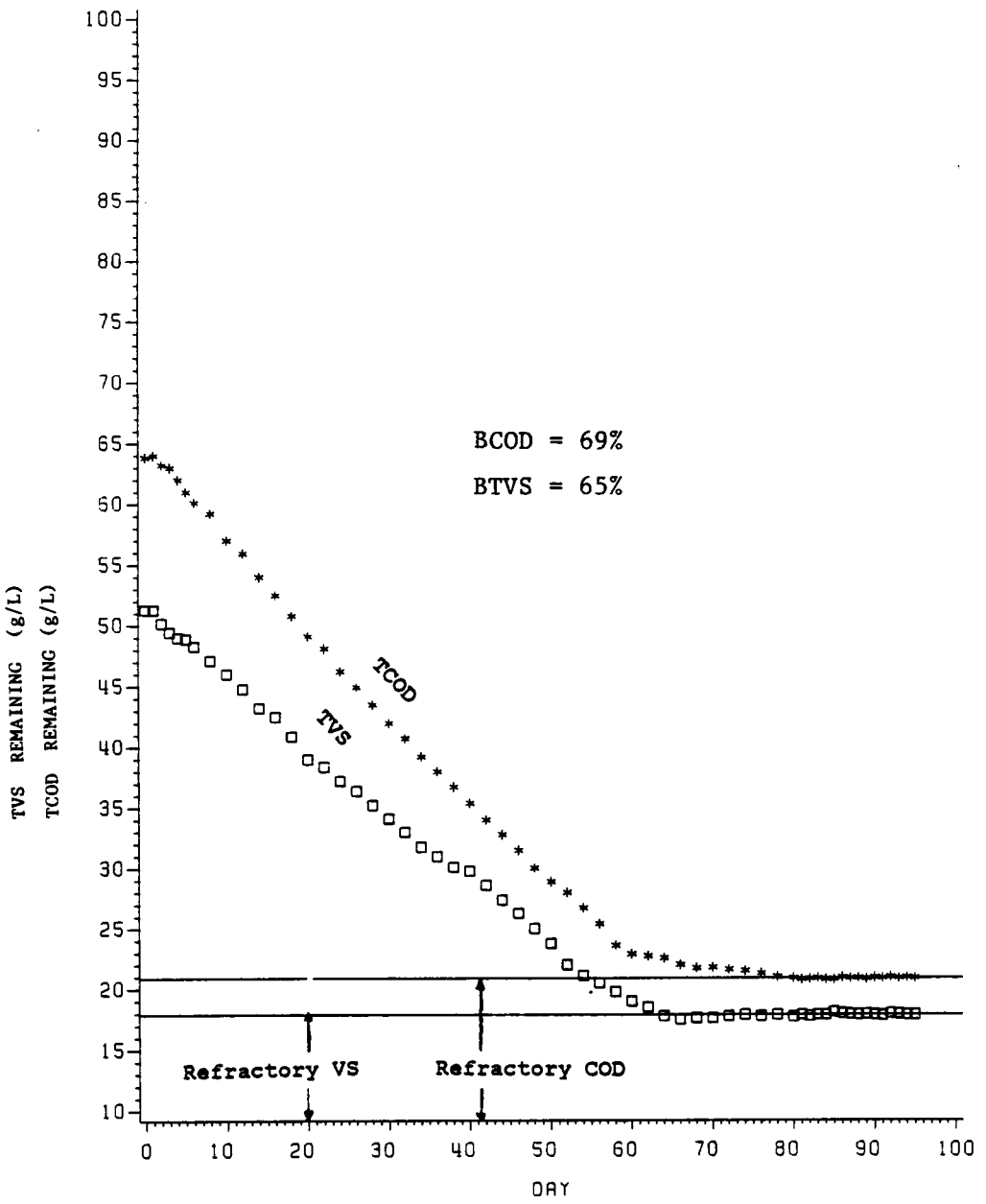


Figure 19. Determination of the Biodegradable Fraction.

5.2 THE COD-VS RELATIONSHIP

It was of practical value to determine the COD-VS relationship in this study. A constant ratio would indicate a direct relationship between COD and VS. Since VS is more easily determined, it could then be used as a digester performance indicator. Figure 20 establishes a linear relationship between TCOD and TVS for influent and effluent samples (r^2=0.96). The slope of the graph defines the TCOD/TVS ratio and was determined to be 1.36.

5.3 DIGESTER FLOW CHARACTERISTICS

The most important physical factor related to digester performance is its flow characteristics. Proper digester design and adequate mixing should combine to establish good flow patterns. In a properly mixed digester the hydraulic and solids retention times (HRT and SRT) are the same.

In the digesters used in this study, mixing was kept to a minimum, and it was hoped that the use of a chemical tracer would allow determination of the actual SRT values. An adsorption isotherm, necessary for this determination, was successfully developed by dosing effluent samples with predetermined quantities of lithium chloride (chemical tracer). Daily effluent samples were then analysed for

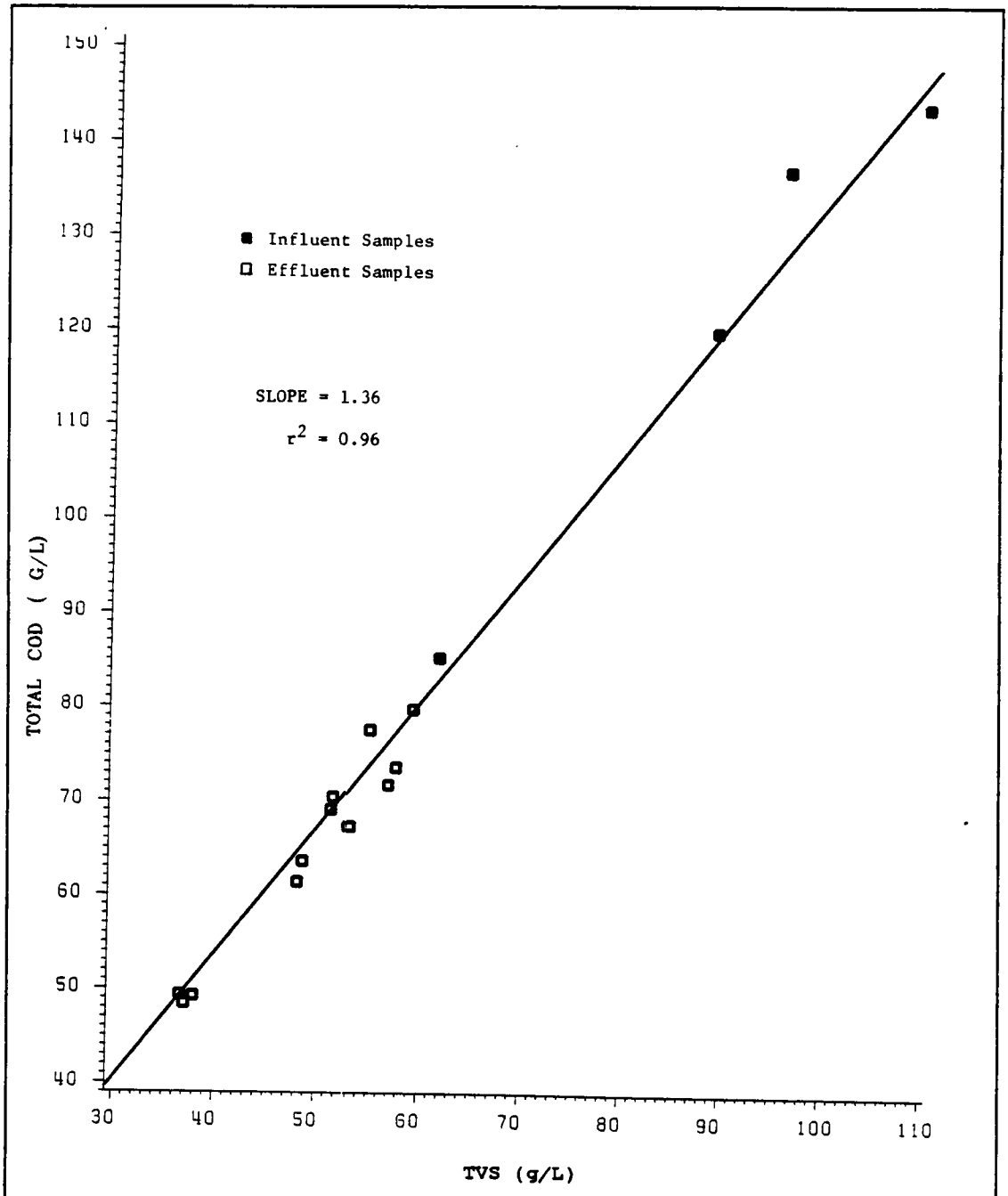


Figure 20. The COD-VS relationship

supernatent lithium concentrations. When these results were used in conjunction with the adsorption isotherm, contradictory information was obtained making it impossible to estimate SRT values. This was due to the poor adsorptive property of lithium. Hence, it can be stated that lithium chloride was not a suitable tracer for SRT determination. In view of this drawback, tracer analysis was used only to predict digester dead space and bypassing flow.

The total lithium concentration in the effluent was monitored and plotted as a function of time according to equation (45):

$$\ln C/C_0 = \ln B - (B/A)(Qt/V) \qquad (45)$$

The intercept and slope of a semilog plot of equation (45) yielded digester flow parameters A and B. Recall that in the hydraulic model, A was the fraction of the volume that was completely mixed, while B was the fraction of flow that entered the well-mixed region.

In this investigation, two sets of tracer studies were performed. The first (preliminary) tracer study involved Types 1, 2, and 3 digester units, and was used in selection of digester design for the main study. Four units of the selected digester type were subjected to a second tracer

experiment to determine the flow characteristics under different flow rates.

The first tracer study revealed that the Type 3 digester (Figure 16 on page 105), with the outlet originating from the bottom, possessed superior flow characteristics as defined by relatively higher values for parameters A and B (Table 7). The Type 1 digester, being a bench-scale model of the actual Chinese-type field digester presently in use in Sri Lanka, had its inlet and outlet placed radially opposite to each other, close to the liquid surface (3L mark). This design promoted short-circuiting and formation of a stagnant region as evidenced by extremely low values for A and B. In the Type 2 digester, the position of the outlet was altered by placing it at the 1.5L mark and the flow pattern was intermediate to that of Types 1 and 3.

Table 7. Flow Parameters of Type 1, 2, and 3 Digesters

DIGESTER	A	B
TYPE 1	0.27	0.33
TYPE 2	0.31	0.76
TYPE 3	0.61	0.94

A = Fraction of volume completely-mixed

B = Fraction of flow entering completely-mixed zone

Clearly, the position of the outlet relative to the inlet influenced the flow characteristics. Both Types 1 and 2 digesters exhibited significant amounts of bypassing flow and stagnant region. The Type 3 design, on the other hand, almost completely eliminated bypassing while reducing dead space considerably. Compared with the Type 1 digester, the improved design of the Type 3 digester resulted in a reduction of dead space and short circuiting volumes of 47% and 91%, respectively, and was selected as the digester design for the remainder of the investigation.

Results of the tracer study performed on the 8-day digesters are presented in Figure 21. The theoretical curve (equation 2) for the CSTR, where stagnancy and bypassing do not occur, is superimposed. The data for the 10-, 15-, and 20-day digesters (Appendix D) yielded similar curves. Table 8 lists the values for parameters A and B . Clearly, in all four digesters, greater than 90 % of the incoming flow entered the well-mixed (active) zone. It was also noted that as the flow rate increased (decrease in HRT), the dead volume, denoted by (1-A) V, decreased.

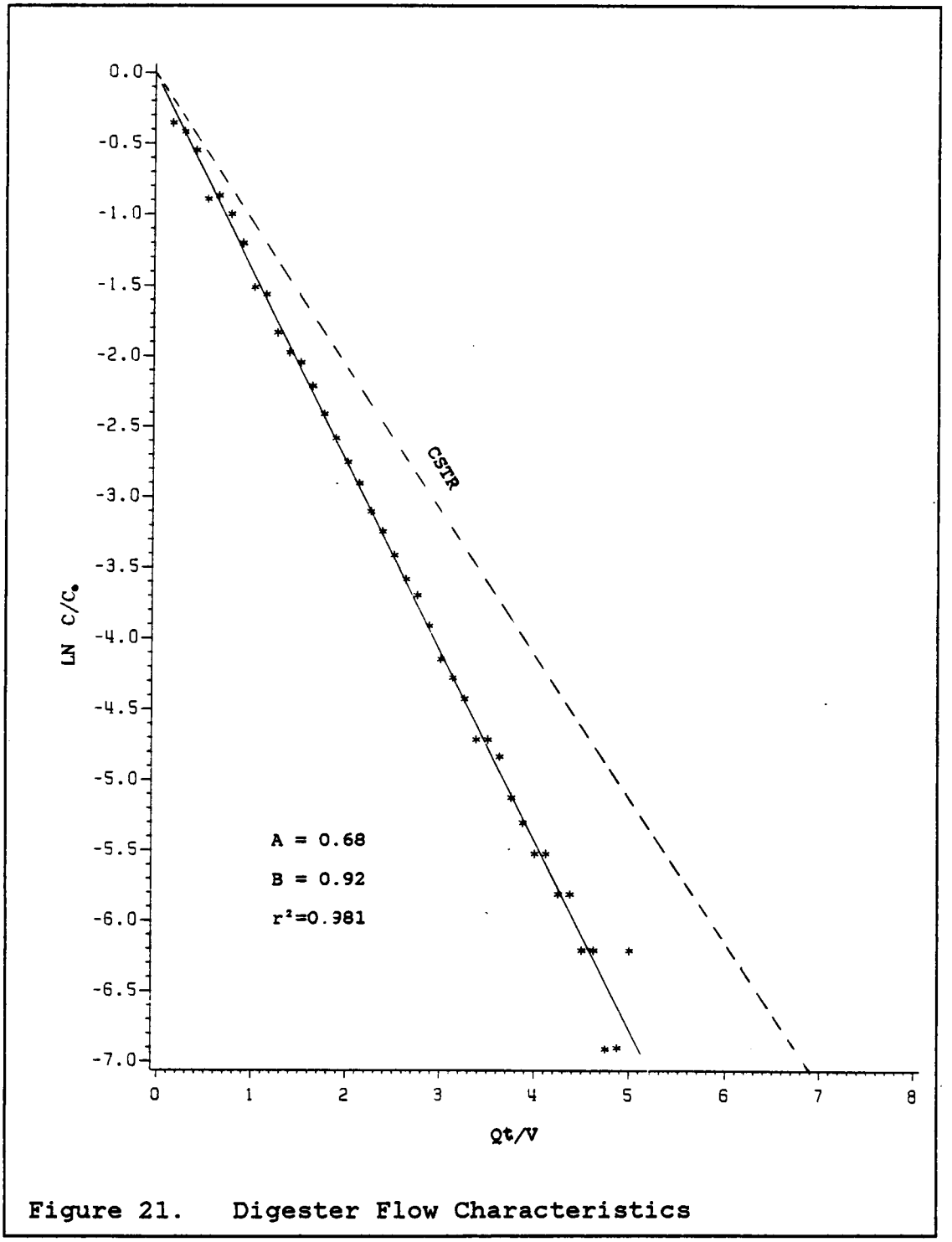


Figure 21. Digester Flow Characteristics

Table 8. Digester Flow Characteristics

HRT	D	A	B	A/B	HRT'	D'
8	0.125	0.68	0.92	0.73	5.91	0.169
10	0.100	0.64	0.92	0.69	6.96	0.140
15	0.067	0.60	0.93	0.64	9.68	0.100
20	0.050	0.56	0.92	0.60	12.35	0.080

D = Nominal dilution rate
D' = Actual dilution rate
HRT = Nominal HRT

HRT'= Actual HRT

As determined by the tracer study, the relative positions of the inlet and outlet hindered or promoted short circuiting. The digester design selected (Type 3) for this investigation effectively reduced bypassing as indicated by high values of A. The small fraction (1-B) that short circuited was entirely due to incomplete mixing. Likewise, since the digesters were spherical, the lack of complete mixing rather than digester geometry was the most likely reason for the occurrence of dead space in all digesters examined.

The effect of A and B was of importance for digester performance. Since (1-A) was the fraction of the influent that did not undergo treatment but passed directly to the outlet, the effect was an increase in the effluent substrate concentration. A low value of A indicated reduced active volume with an associated reduction of volumetric gas production.

More importantly, short circuiting and dead volume changed the dilution rate in the mixing zone. The theoretical dilution rate (D) was the inverse of HRT and is defined as

$$D = Q/V$$

Since only a fraction of Q and V were actually in the mixed region and were involved in the digestion process, the actual dilution rate (D') was:

$$D' = BQ/AV$$

$$D' = BD/A$$

Since in this study $B > A$, the effect was an increase in the dilution rate by a factor B/A. Under these conditions, a reactor which operates close to the washout dilution rate is in imminent danger of process failure if it is less then perfectly mixed. Cholette and Cloutier (1959) have shown that A and B proceed smoothly to unity as the degree of mixing is increased.

In this study nominal HRT values of 8, 10, 15, and 20 days were used to operate the digesters. However, due to incomplete mixing, the actual HRT's involved (HRT') were lower as given in Table 8. Also, since the tracer study was not successful in determining the SRT values, no distinction will be made between solids retention time (SRT) and hydraulic retention time (HRT). The tracer study established the fraction of the volume that was well-mixed. In this region, the HRT and the SRT are the same. It was assumed that dead volume does not take part in the biochemical reactions.

5.4 EXPERIMENTAL RESULTS

In this section, performance of the bench-scale digesters will be presented. Although data gathered from all digesters can be found in the Appendix D, discussion will be limited to selected units that represent typical digester performance observed in the laboratory. Of the sixteen digesters, the performances of four were retarded due to overloading. The behavior of normally operated digesters will be presented first followed by a discussion on the failed units.

As mentioned previously, digester performance was investigated by varying the loading rate. The loading rate of the digester was adjusted by changing the influent BVS concentration and the HRT (Figure 22). In a constant volume digester, HRT is varied by varying the flow rate (Q). In this study, sixteen loading rates were achieved by considering different combinations of HRT and influent BVS.

It should be stated that none of the sixteen digesters reached true steady-state conditions. Due to intermittent feeding and unique flow characteristics, the digesters exhibited quasi-steady state. For the sake of comparison, it is possible to define a 'steady-state' condition by sampling digesters at a common point in time (just prior to feeding in this study). If the relative changes in an

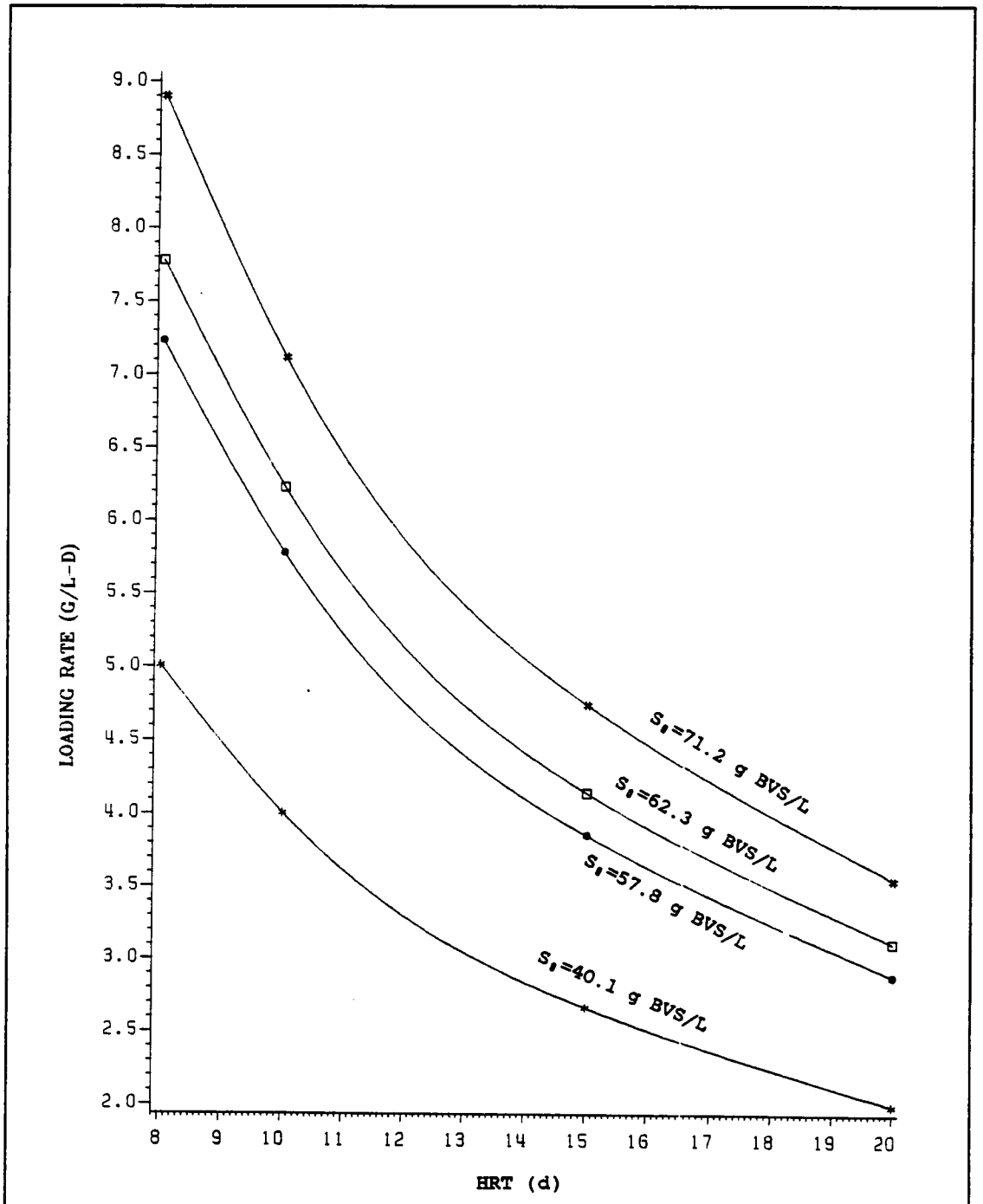


Figure 22. Variation of loading rate with S_0 and HRT.

indicator parameter are small, one could assume steady-state. In this investigation, gas production and effluent concentration data were used to determine 'steady-state' conditions. Between 2.5 to 3.0 retention cycles were required for the digesters to register 'steady-state' performance. Since these values were true only at a particular point in time, and were not representative values for an extended period, they have limited usefulness. For this reason, no statistical methods were used to compare mean values. A summary of the 'steady-state' results for the digesters is given in Table 9.

Table 9. Steady-State Digester Effluent Quality

DIGESTER	EFFLUENT QUALITY			
	Volatile Solids (g/L)		Chemical Oxygen Demand (g/L)	
	Biodegradable	Total	Biodegradable	Total
8-1*	29.34	50.93	55.75	82.23
8-2*	38.39	69.51	80.62	117.94
8-3*	42.14	75.69	92.72	135.41
8-4*	42.30	80.64	97.21	142.04
10-1	16.36	37.95	22.81	49.29
10-2	21.96	53.08	30.05	67.37
10-3	21.37	54.92	34.95	77.64
10-4	20.82	59.16	35.01	79.84
15-1	15.47	37.06	22.01	48.49
15-2	17.50	48.62	32.95	70.27
15-3	18.01	51.56	31.01	73.70
15-4	19.20	57.54	34.12	78.95
20-1	15.01	36.60	22.91	49.40
20-2	17.00	48.12	33.17	70.50
20-3	17.80	51.35	28.61	71.30
20-4	18.50	56.84	30.10	74.93

* Inhibited digesters

5.4.1 EFFLUENT QUALITY

The effluent quality presented in terms of TCOD (Figure 23) and TVS (Figure 24) exhibit the same trend. In general, there was a dramatic increase in the quality of the effluent with an increase in HRT from 8 days to 10 days. Very high effluent substrate concentrations at a short HRT of 8 days is due to digester inhibition. The graph also reveals that for HRT values longer than 10 days, there was no noticeable decrease in effluent quality, implying that the optimum HRT for efficient stabilization was 10 days. A relationship between influent and effluent substrate concentrations and HRT was also evident. For a given HRT, there was a general increase in the effluent concentration with an increase in the influent substrate concentration. This may be attributed to the fact that, due to short circuiting, a fraction of the influent substrate appeared in the effluent. Since this fraction was constant for a given flow rate, an increase in influent substrate concentration caused an increase in the concentration of bypassing material. The theory advanced by Daigger and Grady (1977) may also be important in anaerobic digestion where intermediates are formed. The authors explained that the total quantity of products of microbial metabolism is a function of the influent concentration. These products also showed up in the effluent and were measured as VS or COD.

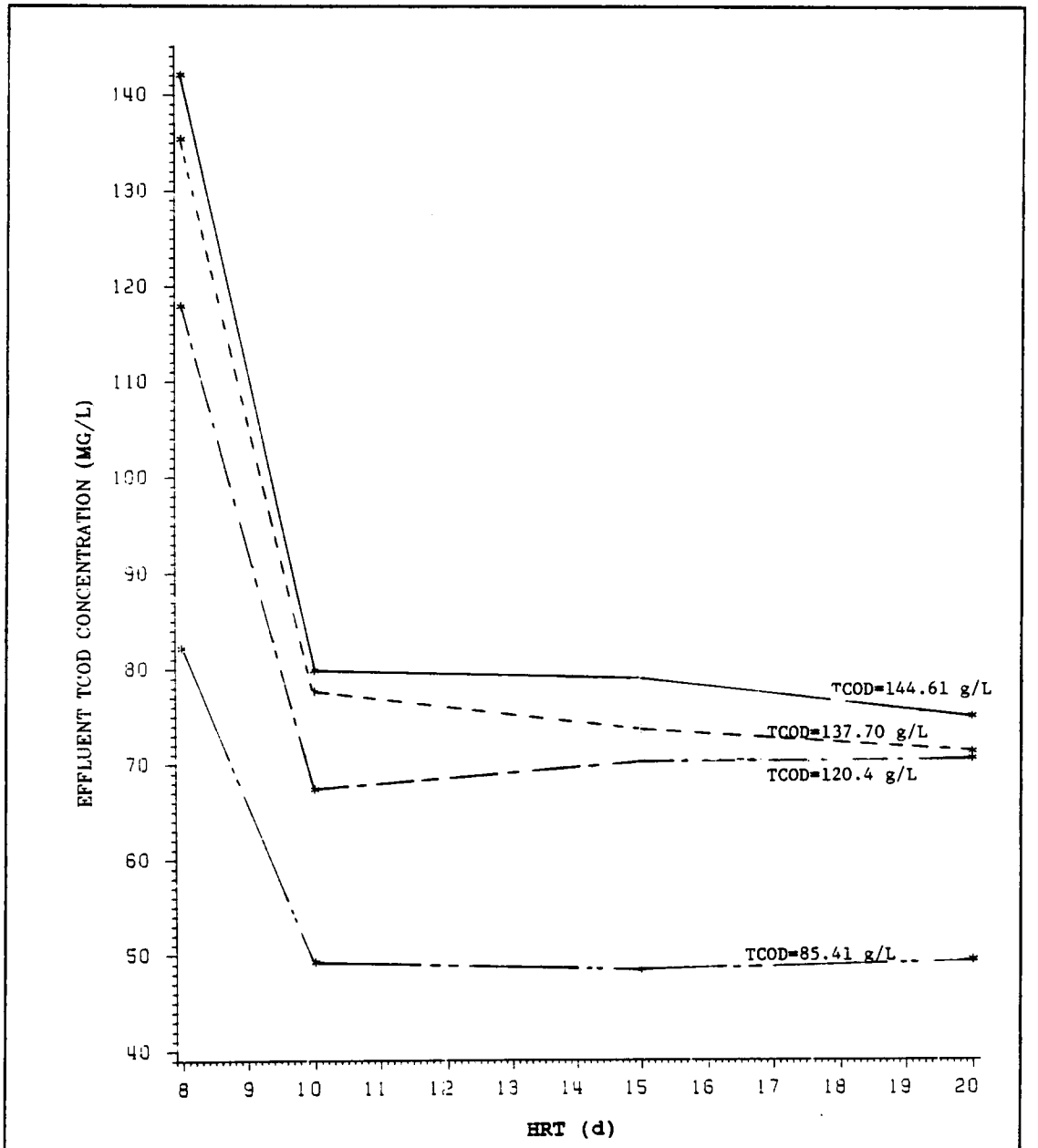


Figure 23. Steady State Effluent Quality (COD)

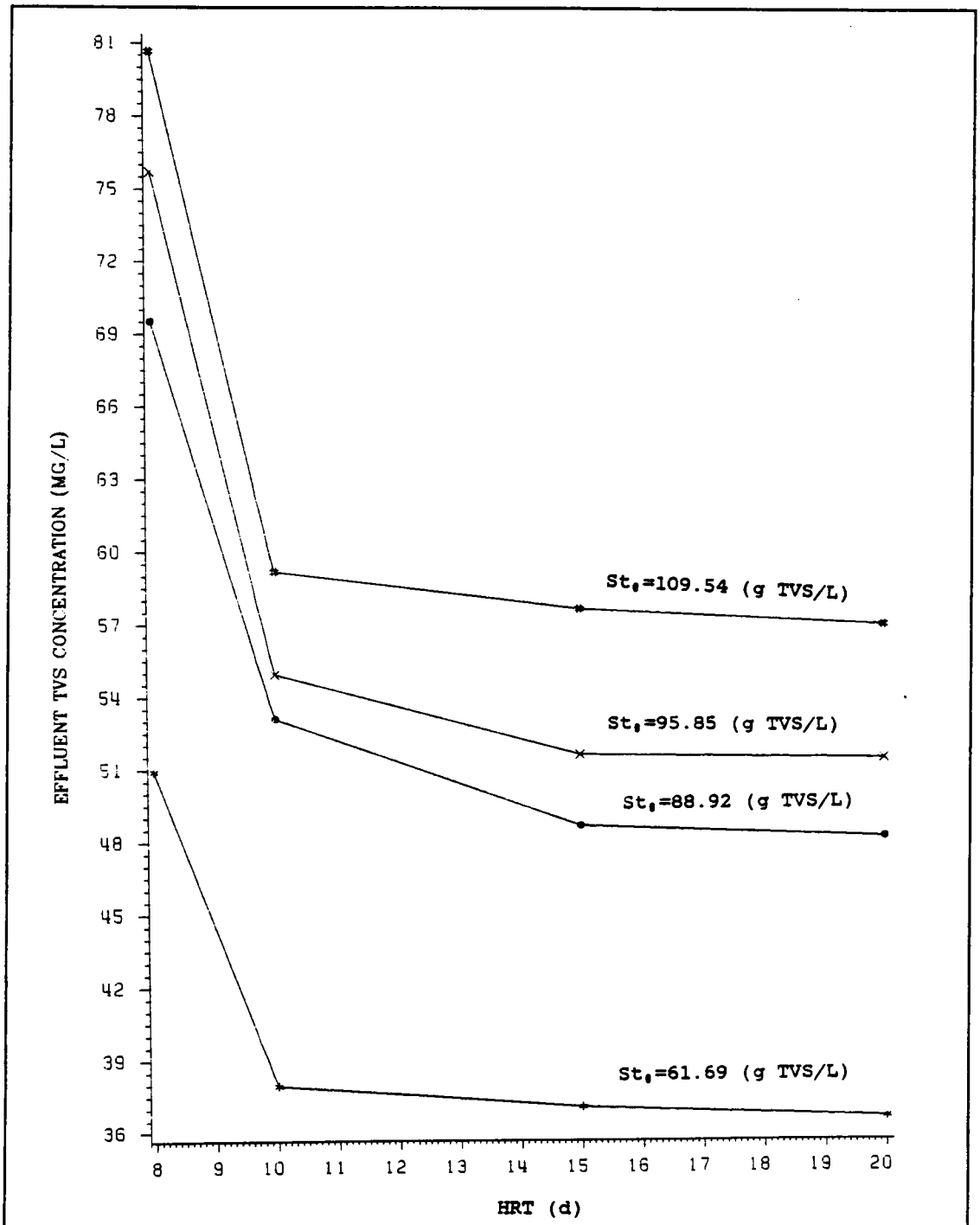


Figure 24. Steady State Effluent Quality (VS)

5.4.2 GAS PRODUCTION

Gas production data for each digester are summarized in Table 10. Data have been corrected to conditions of standard temperature and pressure. Both the quality (% methane) and quantity (L/L-day or L/g VS) were indicators of digester performance. A reduction in gas production and an associated increase in the carbon dioxide content were evidenced in the inhibited digesters. Reduced activity of the methanogenic bacteria was implicated.

Table 10. Digester Gas Production

DIGESTER	UMP*	VMP**	CH_4/CO_2
8-1	0.079	0.41	0.49
8-2	0.047	0.33	0.44
8-3	0.033	0.28	0.42
8-4	0.015	0.15	0.39
10-1	0.252	0.94	1.22
10-2	0.264	1.43	1.20
10-3	0.261	1.50	1.30
10-4	0.291	1.91	1.25
15-1	0.288	0.66	1.20
15-2	0.297	0.98	1.23
15-3	0.306	1.09	1.29
15-4	0.318	1.29	1.31
20-1	0.321	0.50	1.15
20-2	0.33	0.74	1.19
20-3	0.33	0.82	1.21
20-4	0.36	0.98	1.23

* L CH_4/g BVS

** L CH_4/L-d

The interrelationship between gas production (L/L-d) and the operational variables (S_0 and HRT) is illustrated by the three-dimensional plot presented in Figure 25. At all HRT values, with the exception of HRT=8 days, an increase in VMP with S_0 was witnessed. For the 8-day digesters, the VMP values were relatively low, with a dramatic drop as S_0 approached the maximum influent BVS concentration of 71.2 g/L (point A). Hence, it can be stated that the 8-day digesters were inhibited due to overloading. Within the scope of this investigation, it was not possible to identify whether the failure was due to hydraulic or organic overloading. However, some inference may be drawn by comparing loading rates of normally-operating and retarded digesters. Digester 8-1, with a loading rate of 5.01 g/L-d, was inhibited while digesters 10-1, 10-2, and 10-3, which were loaded at higher rates, exhibited high performance efficiencies (Figure 26). This indicates that digester 8-1 could not have failed due to organic loading. Now, from the tracer study, we know the actual HRT for the 8-day digesters was 5.91 days. That is, these digesters were, in effect, being operated well below the theoretical HRT of 8 days. It is possible that this could have caused cell washout. From these observations, it could be inferred that hydraulic overloading may have been the probable cause of failure in digester 8-1. Digesters 8-2, 8-3, and 8-4 were loaded at rates higher then any other

digester in the study. The failure of these digesters may have been due to hydraulic and/or organic overloading.

In the normally operating digesters, there was a trend towards increased VMP with increase in HRT (Figure 26). At constant influent VS concentrations, as the hydraulic retention time decreased, VMP increased until the system was loaded to its limit and VMP was maximized at a HRT of 10 days. Further decrease in the HRT resulted in a sharp decrease in VMP. From these results it could be stated that the optimal HRT is 10 days. At HRT values of less then 10 days, increased risk of inhibition may be encountered.

Methane production can also be expressed as L/g-BVS added, or called the unit methane production (UMP). Figure 27 illustrates the effect of HRT on UMP. At shorter values of HRT, there was an increase in the UMP indicating rapid conversion of biodegradable material. At longer HRT values, as most of the organics are stabilized, the curve levels out approaching the theoretical maximum methane yield per gram of BVS removed, and is assumed to be 0.5 L CH_4/g BVS. Hence, UMP can be used as an indicator of VS stabilization efficiency. The substantially lower gas yield at HRT = 8 days was due to digester retardation.

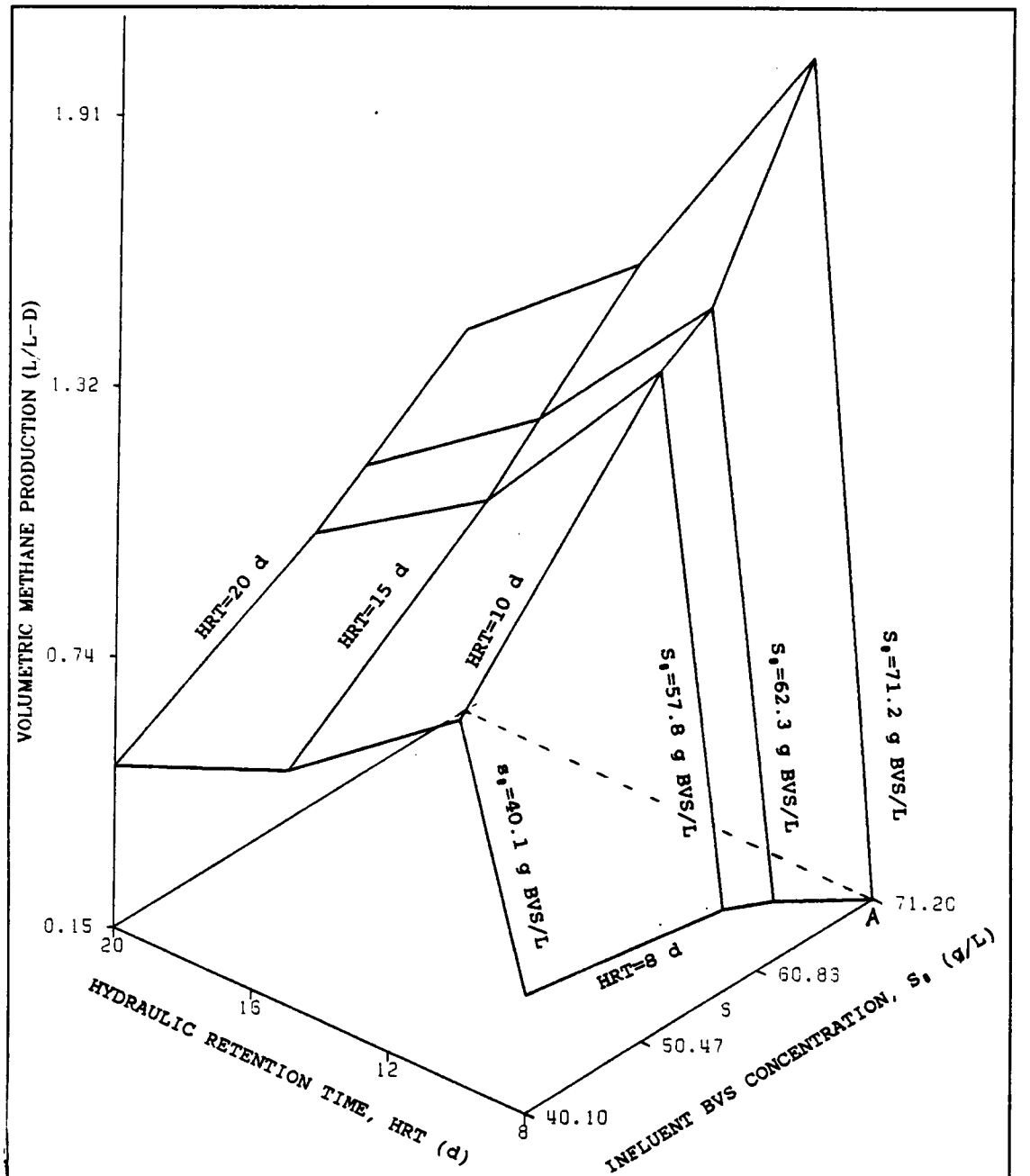


Figure 25. The Relationship Between VMP and Operational Variables

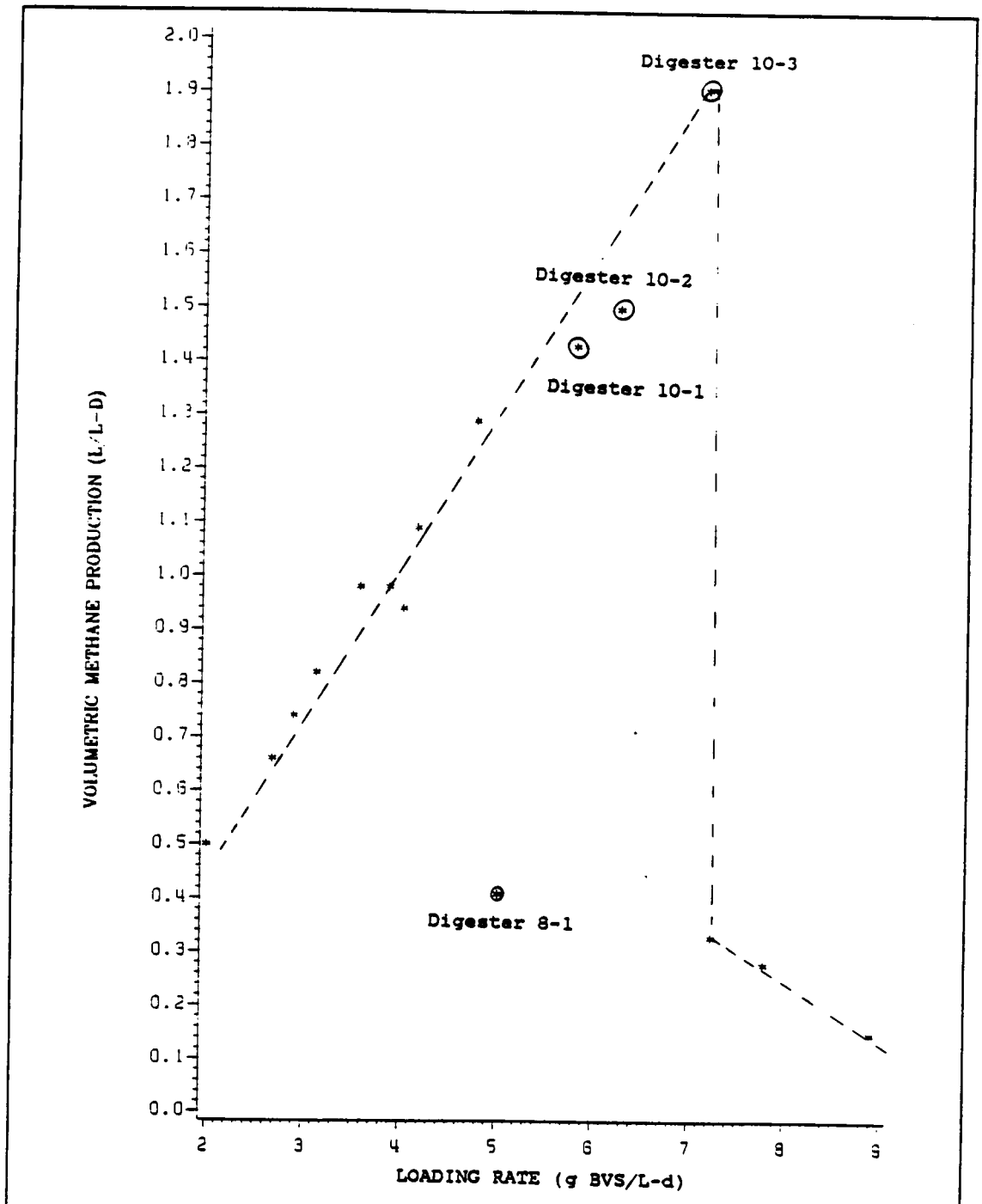


Figure 26 The Effect of Loading rate on VMP

The graph also reveals that the higher the influent BVS concentration (S_0), the greater was the UMP in the normally operated digesters. This pattern was reversed in the retarded units where lower gas production was associated with higher S_0 values.

The loading rate (LR) specifies the amount of substrate added to the digester per feeding and, therefore, has a direct bearing on the 'health' of the anaerobic process. The relationship between loading rate (LR) and influent BVS (S_0) is:

$$LR = S_0/\theta \qquad (46)$$

where θ is the solids retention time (HRT) in days. Clearly, LR can be varied by manipulating either S_0 or θ. If Q is the flow rate through the digester and V the digester volume, then $\theta = V/Q$. Since the volume of the digester was constant, θ was varied by altering the flow rate. S_0 was a direct function of the influent TVS. It is instructive to develop a relationship between digester gas yield and the operational parameters like HRT, influent VS, LR and θ. It is possible to generate families of curves of constant HRT and influent VS in a plot of gas yield (UMP) against loading rate (Figure 28). In this study, at constant influent VS concentration, the methane yield (L/g BVS) decreased when

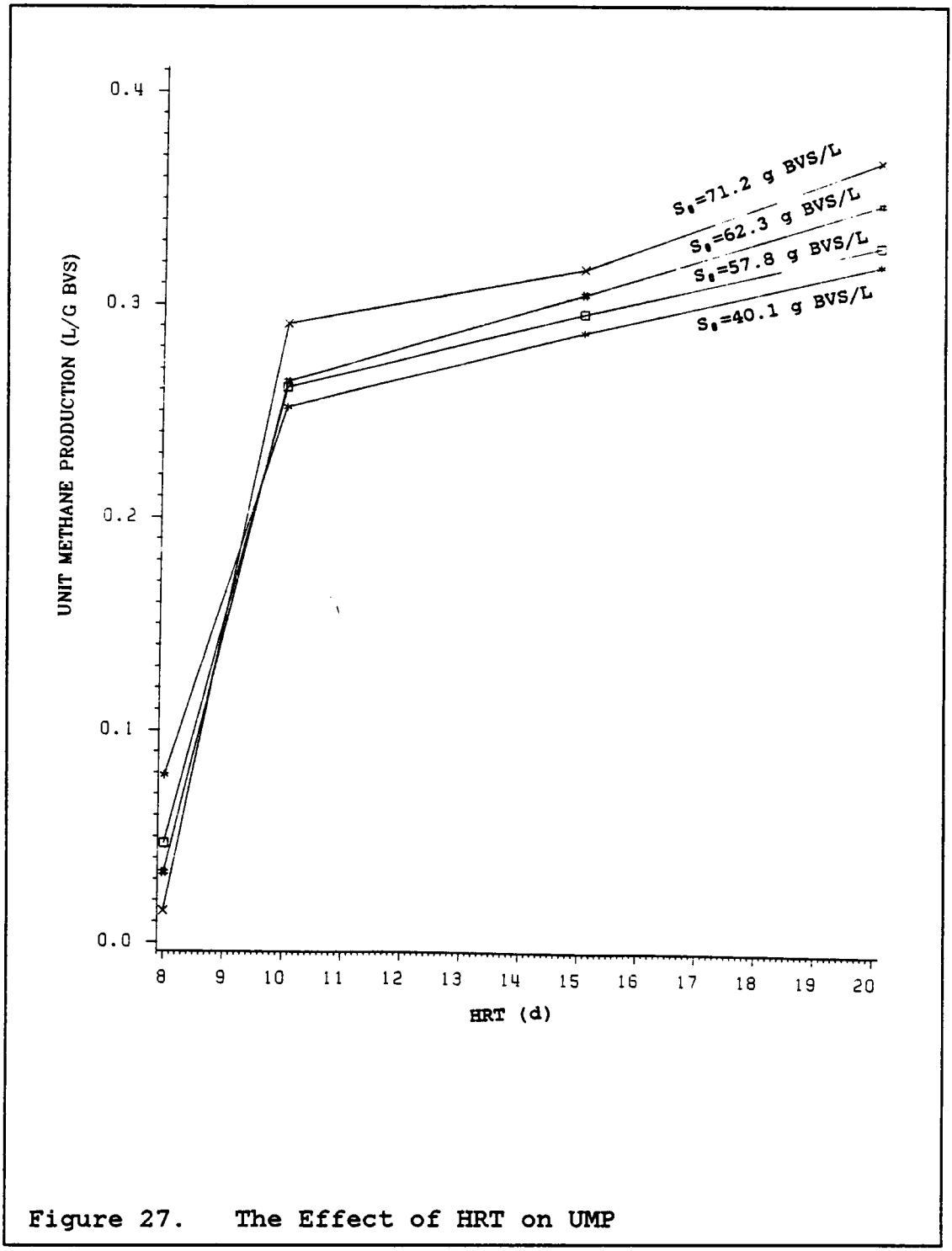


Figure 27. The Effect of HRT on UMP

loading rate was increased. This can be explained by the fact that at constant influent VS concentration (S_0), a decrease in HRT was the only way to increase the LR (equation 46). A decrease in HRT implies reduced exposure of substrate to the microorganisms and therefore reduced UMP. For a constant loading rate, higher influent VS concentration (S_0) resulted in higher methane yield. An increase in S_0 required a corresponding increase in θ for constant LR. Again, increased HRT led to greater volume of methane production per gram of BVS added.

The steady-state VMP values can be used to arrive at an optimum influent VS concentration. Chen and Hashimoto (1979) proposed a model based on Contois enzyme kinetics to describe steady-state volumetric methane production. The expression is:

$$VMP = [G_0 St_0/HRT]\ [1-(K/\theta\mu-1+K)] \qquad (47)$$

where,

VMP = Volumetric methane production, L/L-d

G_0 = Ultimate methane yield, L/g TVS

HRT = Hydraulic retention time, d

St_0 = Influent TVS concentration, g/L

μ = Maximum specific growth yield, d^{-1}

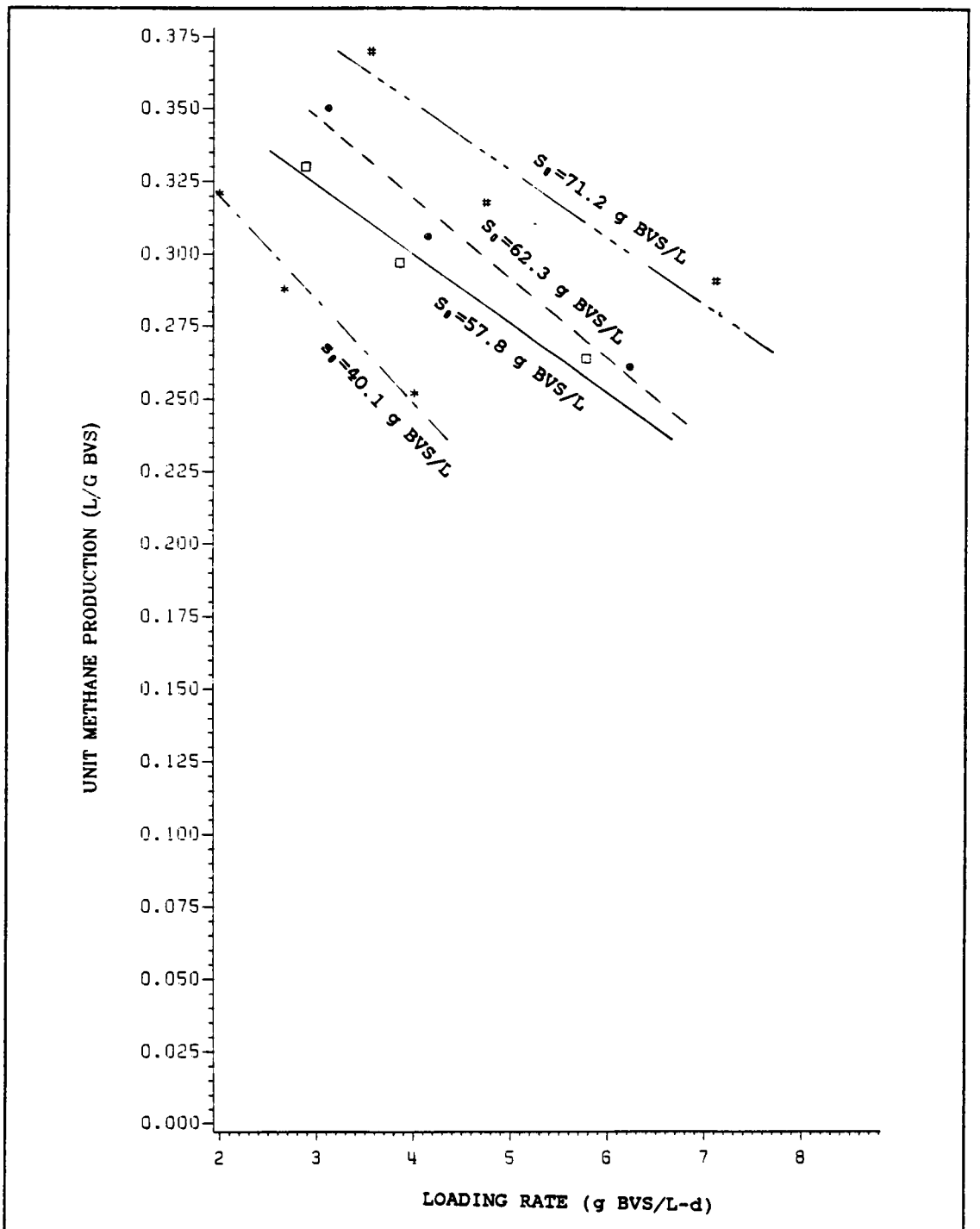


Figure 28. The Variation of UMP with Loading Rate

K = Kinetic parameter, dimensionless.

The ultimate methane yield (G_0) is the theoretical maximum amount of methane that can be produced from a given quantity of TVS. G_0 can be determined if the biodegradability of the manure and the methane yield from BVS are known. Hence, for the substrate used in this study:

$$G_0 = (0.65)\ (0.5)$$
$$= 0.33 \text{ L methane / g TVS}$$

Where,

0.65 = Biodegradability of the waste, g BVS/g TVS
0.5 = Methane yield, L/g BVS destroyed
BVS = Biodegradable VS
TVS = Total VS.

Expression (47) can be used to determine loading limits for anaerobic digestion of animal wastes. Rearranging equation (36) we get:

$$K=[(\theta\mu-1)G_0St_0/\theta\ VMP]-\theta\mu+1 \qquad (48)$$

It is evident that when G_0, St_0, and HRT are constant, VMP decreases as K increases. Thus, the increase in K is an

indication of some form of inhibition (Hill, 1983a; Hashimoto et al., 1980). The K value as expressed by equation (48) was used in conjunction with the observed and the simulated results of VMP (Figure 29) to establish maximum influent VS concentration. Clearly, K is relatively constant at low S_0 values, but began to increase at St_0 = 95.0 g TVS/L. This relationship seems logical since increasing S_0 amounts to overloading the reactor which leads to high concentrations of volatile fatty acids and reduced mass transfer of substrate and products.

Figure 30 shows the predicted K versus the experimental K for this study, and the line-of-perfect fit as determined by the computer. The data shows good fit (r^2=0.944) with a mean ratio of predicted K and experimental K of 1.09.

The reliability of experimental results was determined by comparing it to theoretical methane yields on the basis of BCOD and BVS removed. Table 11 presents the measured and predicted daily methane yields and their conversion efficiencies on COD and VS basis.

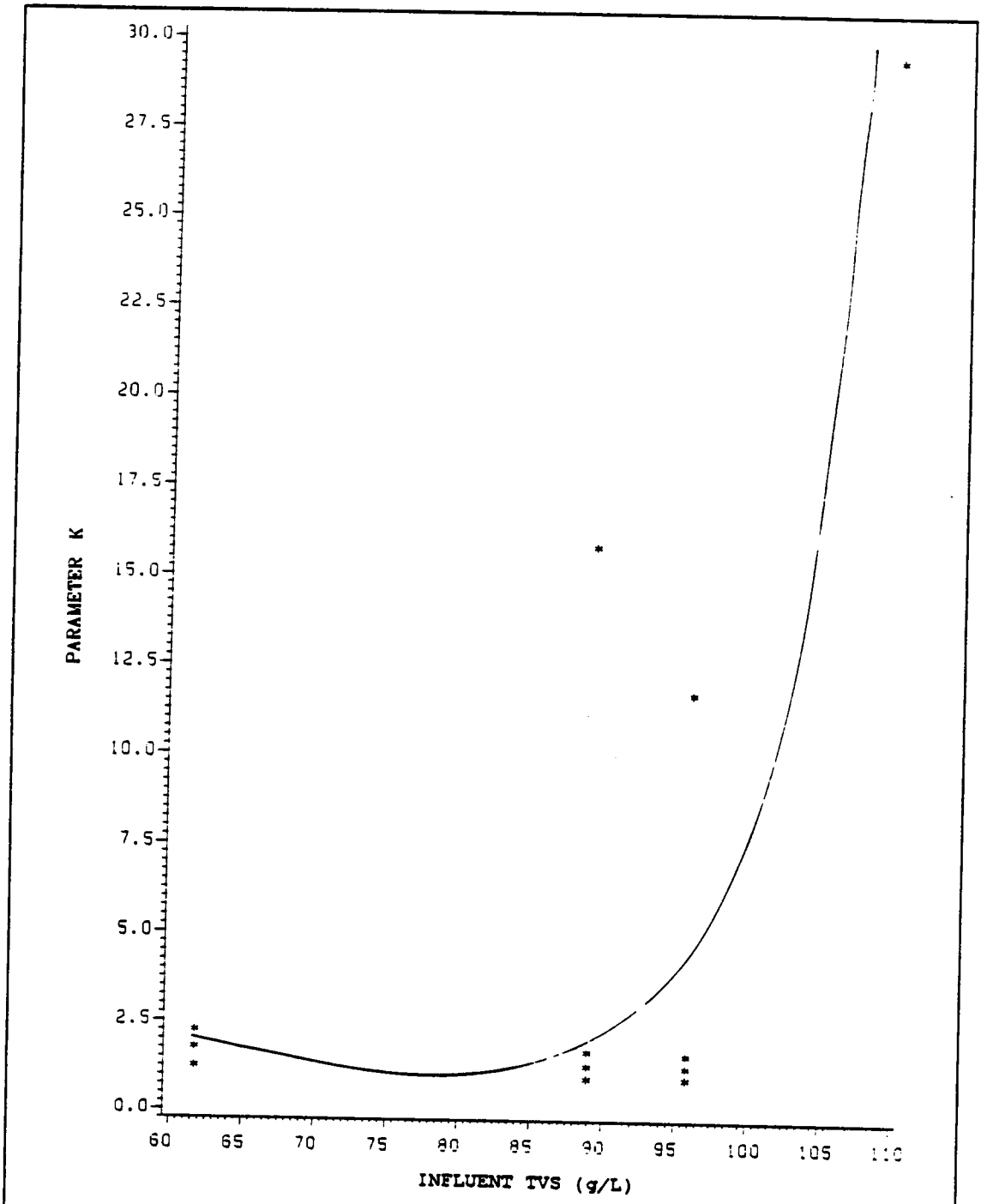


Figure 29 Variation of K with Influent Concentration

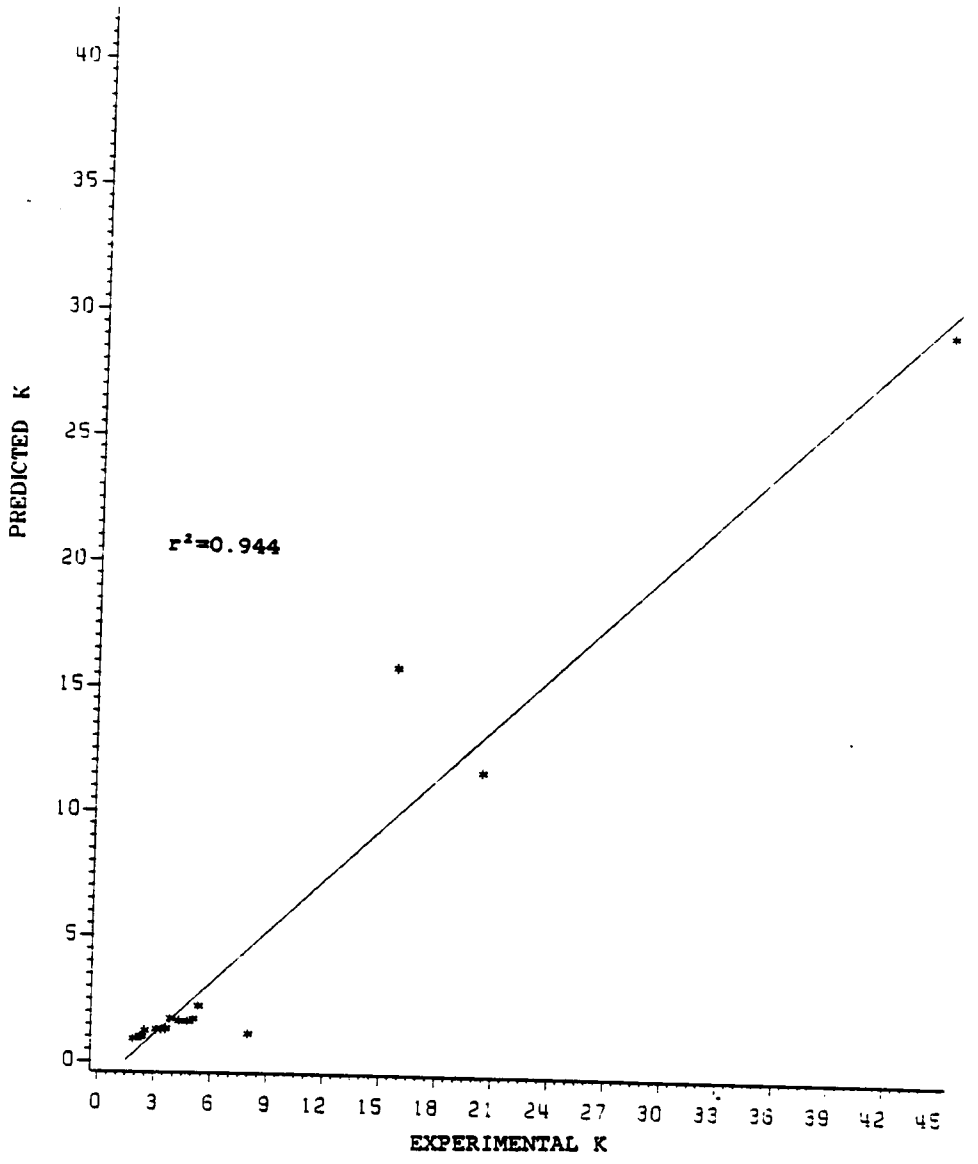


Figure 30 Predicted and Experimental Valus of K

Table 11. Measured and Predicted Methane Yields

DIGESTER	METHANE PRODUCTION (L)			MEASURED/PREDICTED (%)	
	Measured	Predicted			
		COD basis	VS basis	COD basis	VS basis
8-1	9.86	3.34	16.10	295.21	61.20
8-2	7.92	2.60	29.10	304.60	27.22
8-3	6.72	2.40	30.24	280.00	22.22
8-4	3.60	2.88	43.35	125.00	8.35
10-1	28.33	37.89	35.64	74.70	79.41
10-2	42.90	55.71	41.67	77.01	102.93
10-3	45.00	63.03	61.38	71.40	73.30
10-4	57.30	68.04	75.60	84.24	75.79
15-1	29.70	38.79	37.00	76.64	80.32
15-2	44.10	59.56	60.48	74.04	73.00
15-3	49.05	70.56	66.42	69.52	73.85
15-4	58.05	74.45	78.03	78.03	74.42
20-1	30.00	37.80	37.62	99.5	79.44
20-2	44.44	61.88	61.20	71.82	84.72
20-3	49.20	71.80	66.78	68.51	70.50
20-4	58.80	76.31	79.02	77.05	80.36

With the exception of the 8-day digesters, the experimental results were greater than 68% of the predicted results on COD and VS bases. The 20-day digesters in particular registered measured/predicted ratios close to 100. This suggests that at longer HRT, there was a reasonable degree of reliability associated with the experimental results. This could be explained by the fact that at HRT of 20-days, the amount of digester contents replaced was relatively small, being 1/20 of the volume. Hence, the digester environment was subjected to very little variation during pulse feeding. This may have contributed to more predictable digester performance. The unreasonably large values for the measured : predicted ratios in the retarded digesters (HRT=8 days) emphasized the inaccuracy associated with VS determinations in these units. This point will be discussed further in a following section.

The variability in conversion efficiencies may be attributed to (1) inaccurate measurement of gas production, VS and COD; (2) neglecting to correct for methane dissolved in the effluent; (3) neglecting to compensate for the fraction of organics synthesized into bacterial cells; (4) possible loss through gas leaks; and (5) the inability of the digester to reach true steady-state.

5.4.3 TREATMENT EFFICIENCY

Without doubt, the most practical measure of treatment efficiency is TVS or TCOD reduction. Table 12 lists these values for both total and biodegradable components in the digesters used in this study. The volumetric waste utilization rate (based on BVS) is also presented.

Table 12. Digester Treatment Efficiencies

DIGESTER	TREATMENT EFFICIENCY (%)				WASTE UTILIZATION RATE
	COD Basis		VS Basis		
	Biodegradable	Total	Biodegradable	Total	(g BVS/d)
8-1	5.40	3.70	26.83	21.12	1.34
8-2	2.98	2.10	33.58	21.81	2.43
8-3	2.40	1.70	32.36	21.00	2.52
8-4	2.57	1.80	40.60	26.40	8.30
10-1	61.3	42.30	59.20	38.50	2.37
10-2	63.80	44.00	62.01	38.55	3.58
10-3	63.20	43.60	65.78	42.70	4.09
10-4	64.90	44.84	70.80	46.05	5.04
15-1	62.60	41.09	61.40	40.03	1.64
15-2	68.30	47.10	69.70	45.30	2.69
15-3	70.70	48.80	71.12	46.20	2.95
15-4	71.00	49.02	73.03	47.55	3.47
20-1	61.12	42.20	62.62	40.70	1.25
20-2	70.00	48.90	70.60	45.84	2.04
20-3	72.00	49.70	71.43	46.44	2.25
20-4	72.80	50.20	74.00	48.10	2.64

All four 8-day digesters were inhibited. Accordingly, COD reductions in these digesters were extremely low. It was evident that low HRT's with high influent concentrations generate high loading rates that cannot be effectively handled by the methanogens. The treatment efficiency based on VS destruction gave misleading information in retarded digesters. Process inhibition was concurrent with volatile acid accumulation. These acids were lost during VS determination but were included in COD measurement. For this reason, VS reduction data overestimated treatment efficiency.

The biodegradable treatment efficiencies were low at shorter HRT values, but increased as HRT increased. The highest biodegradable VS reduction observed was 74.0% which occurred in the 20-day digester receiving influent substrate concentration of 71.2 g/L (that is, digester 20-4). It was also observed that the removal efficiency increased with S_0 for a constant HRT. As S_0 increases, a richer microbial population was developed which was capable of utilizing a greater quantity of organic matter, leading to improved treatment efficiency. It should be stated this trend will not continue unchecked and is limited by the organic loading rate at which inhibition occurs. Figure 31 depicts the removal efficiency as a function of HRT for both total and biodegradable VS. Although the maximum biodegradable treatment efficiency was 74%, the corresponding total VS

removal efficiency was only 31.4%. It should be noted that it is the latter that is of importance when evaluating treatment efficiencies.

5.4.4 VFA, PH AND ALKALINITY

The information gathered from retarded digesters is as important as that from normally operated units. In this section, laboratory data will be interpreted in order to establish loading rates beyond which inhibition is likely.

Volatile fatty acids (VFA) are microbial end-products of reactions mediated by the acid-forming bacteria and are substrates for the methane-formers. Hence, in a well-balanced reactor, uncontrolled variations of VFA do not occur because the microbial populations are in perfect harmony. Digester inhibition is usually a result of reduced activity of the methane-formers, and is accompanied by VFA accumulation. However, it should be kept in mind that a simple increase in the VFA concentration does not necessarily lead to process inhibition. It is the interaction between alkalinity and the VFA that is of interest.

Figure 32 is a simplified illustration of the chemical reactions associated with formation and destruction of alkalinity in an anaerobic environment. The digestion of

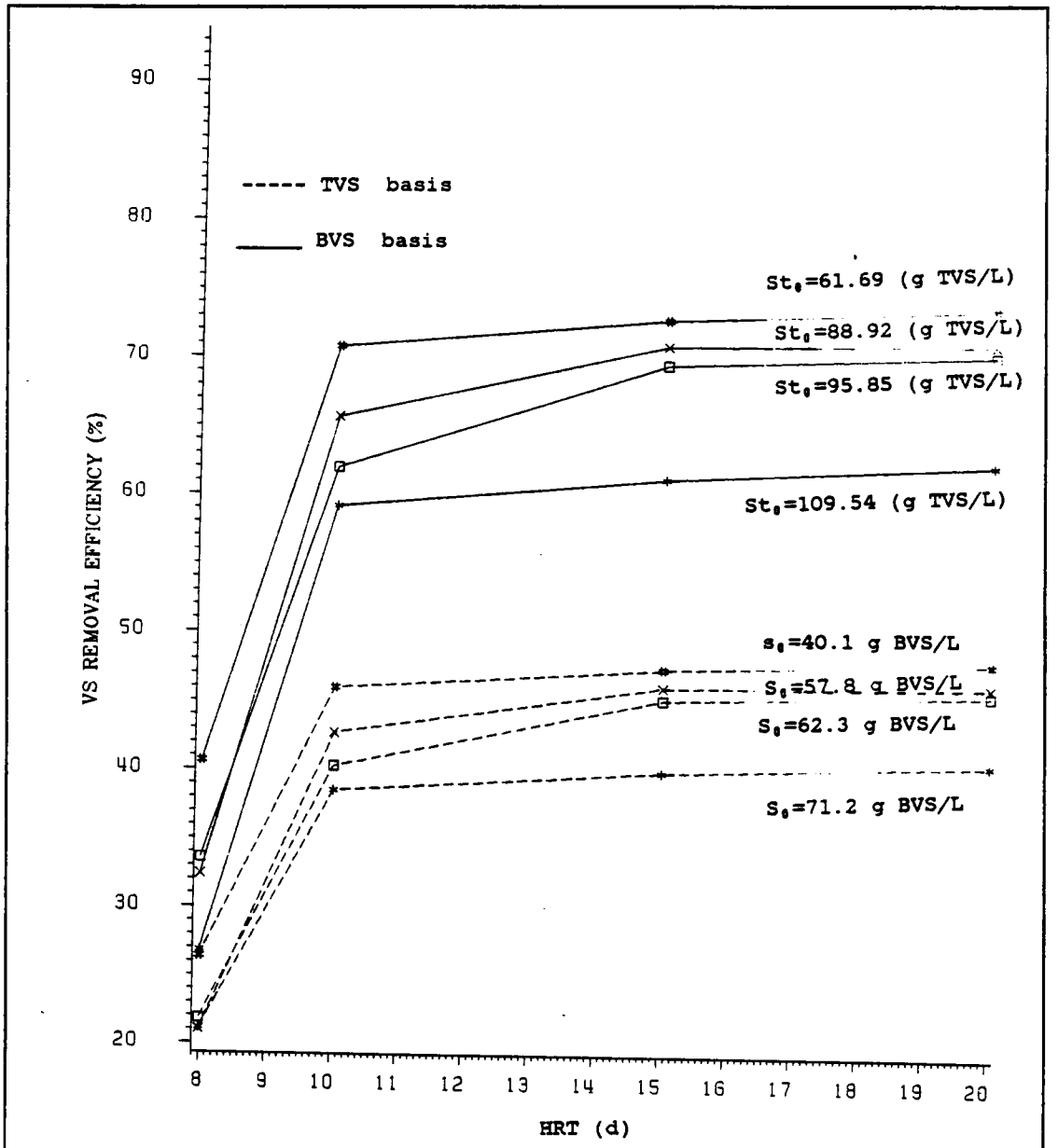


Figure 31. Removal Efficiency vs HRT

lipids, carbohydrates, and proteins releases organic fatty acids while ammonia is a by-product of protein degradation. The ammonia so formed combines with the bicarbonate from the carbon dioxide pool to form ammonia bicarbonate (NH_4HCO_3) and enhances the bicarbonate buffering capacity of the system (Georgacakis et al., 1982). Consequently, during the neutralization of volatile acids, bicarbonate alkalinity is destroyed and in its place an acid salt (ammonium acetate) is formed (Hindin and Dustan, 1960). Eventual biological degradation of the acid salt by methane-formers will again release alkalinity to the system, and the cycle may be repeated. Hence, in a continuously-fed digester, at steady-state, no net change in buffering capacity will result.

Under retarded conditions, volatile acid build-up occurs leading to the destruction of significant amounts of alkalinity and an associated reduction of the buffer capacity. Insufficient buffer will cause further increase in volatile acids. This cyclic effect subsequently leads to complete digester failure. It has been demonstrated that raising alkalinity in the digester tends to increase the operating level of the volatile acids over and above those values commonly considered maximum for the anaerobic fermentation process.

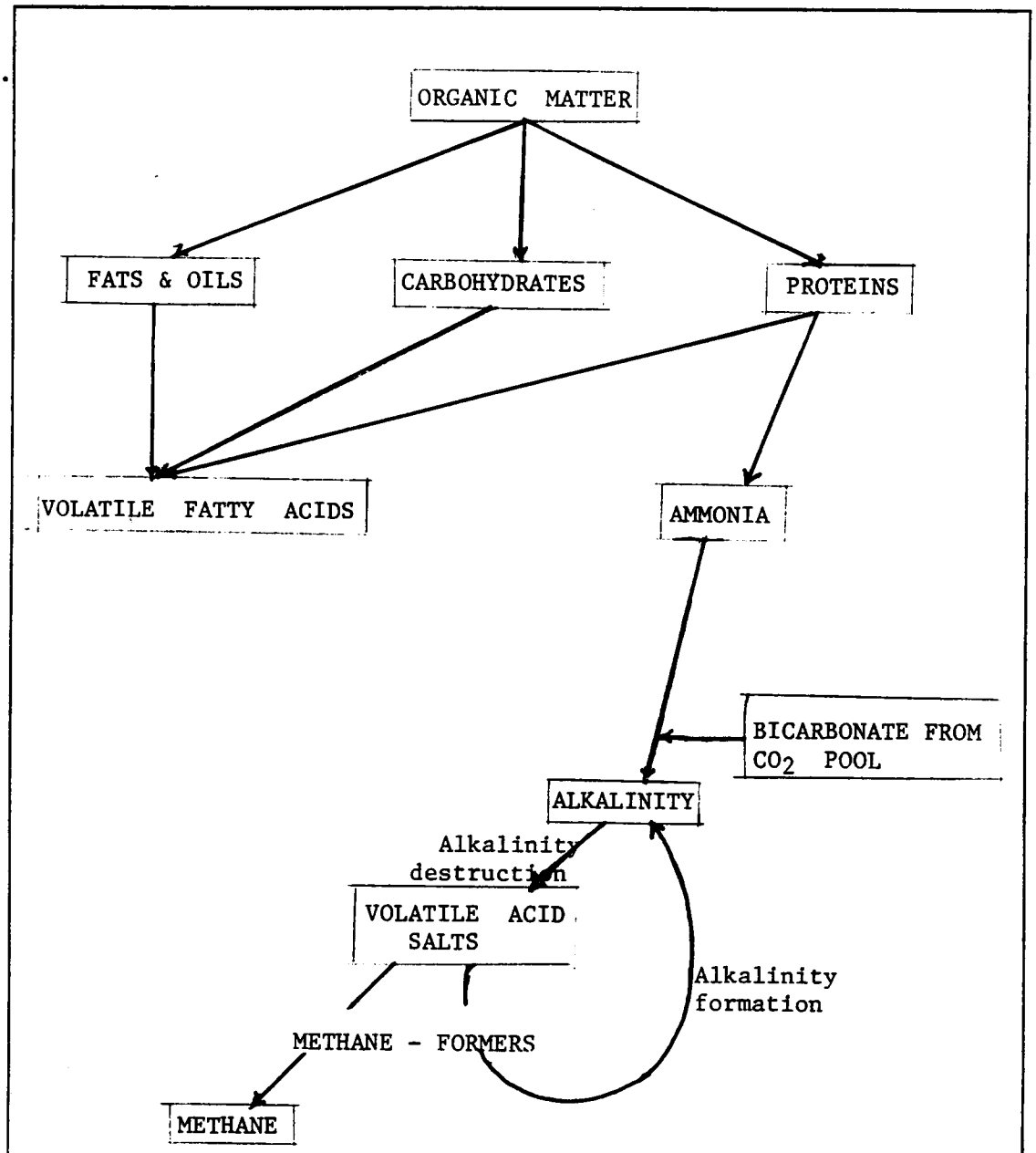


Figure 32. Alkalinity Formation and Destruction in Digesters

Alkalinity determination involves titrating with a strong acid to a pH of 4.3. At this pH all the bicarbonate alkalinity is assumed to be neutralized. However, if acid salts are present, they can, by consuming additional acid, overestimate the bicarbonate alkalinity. Hence, in order to arrive at the bicarbonate alkalinity, the value obtained by titration was adjusted by subtracting the apparent alkalinity contributed by the VFA. That is,

$$HCO_3 \text{ Alk.} = \text{Tot. Alk.} - 0.833 \text{ VFA} \qquad (49)$$

Where,

HCO_3 Alk = Bicarbonate alkalinity, mg/L $CaCo_3$

Tot. Alk. = Total alkalinity, mg/L $CaCo_3$

VFA = Volatile fatty acids, mg/L acetic

0.833 = Eq. Wt. of $CaCO_3$/Eq. Wt. of Acetic acid

Eq. Wt. = Equivalent Weight, mg/meq

The term 0.833 VFA represents the amount of alkalinity required to neutralize volatile fatty acids. If the VFA concentration is high, the bicarbonate alkalinity will be low because part of it will have combined with the VFA. If VFA is very high, then it may use up all the alkalinity that is available, and could lead to the presence of free volatile acids which cannot be further buffered. When this situation occurs, digester failure will follow. In other words, when

expression (49) becomes negative, digester buffer capacity has been surpassed. Any further increase in the VFA cannot be neutralized and will contribute to digester failure.

The calculated volatile acid-salts alkalinity (0.833 VFA), total alkalinity and pH in a normally operating digester (Digester 10-2) is presented in Figure 33. Data presented in the Appendix D can be used to generate similar curves for the digesters that were not retarded. An examination of the graph will indicate that a positive bicarbonate alkalinity was maintained at all times. Although in some of the digesters the variation of VFA was quite marked, it did not affect the pH, which remained within the normal working range of 6.5-7.5.

In the case of Digester 8-3, a different picture emerged. Due to inhibition, accumulation of VFA led to surpassing the neutralizing ability of the alkalinity (Figure 34). Coincident with this was a reduction in pH and increased inhibition of the digestion process, probably by the un-ionized form of VFA. Similar data (Appendix D) were obtained for the other retarded digesters.

Under normal operating conditions, the bicarbonate system is the major buffering system. Hence, the total alkalinity, which is determined by titrating with a strong acid to a pH

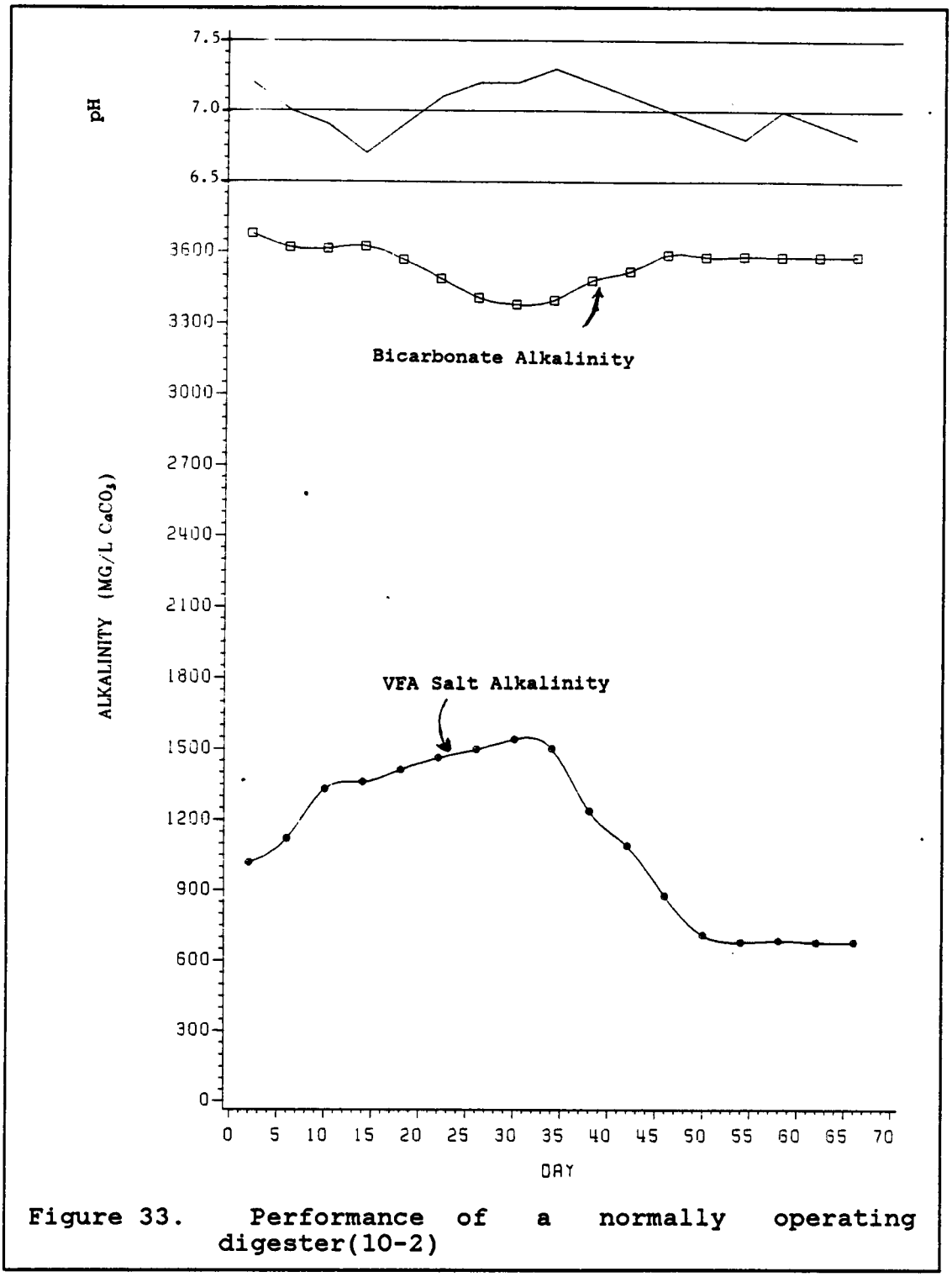


Figure 33. Performance of a normally operating digester(10-2)

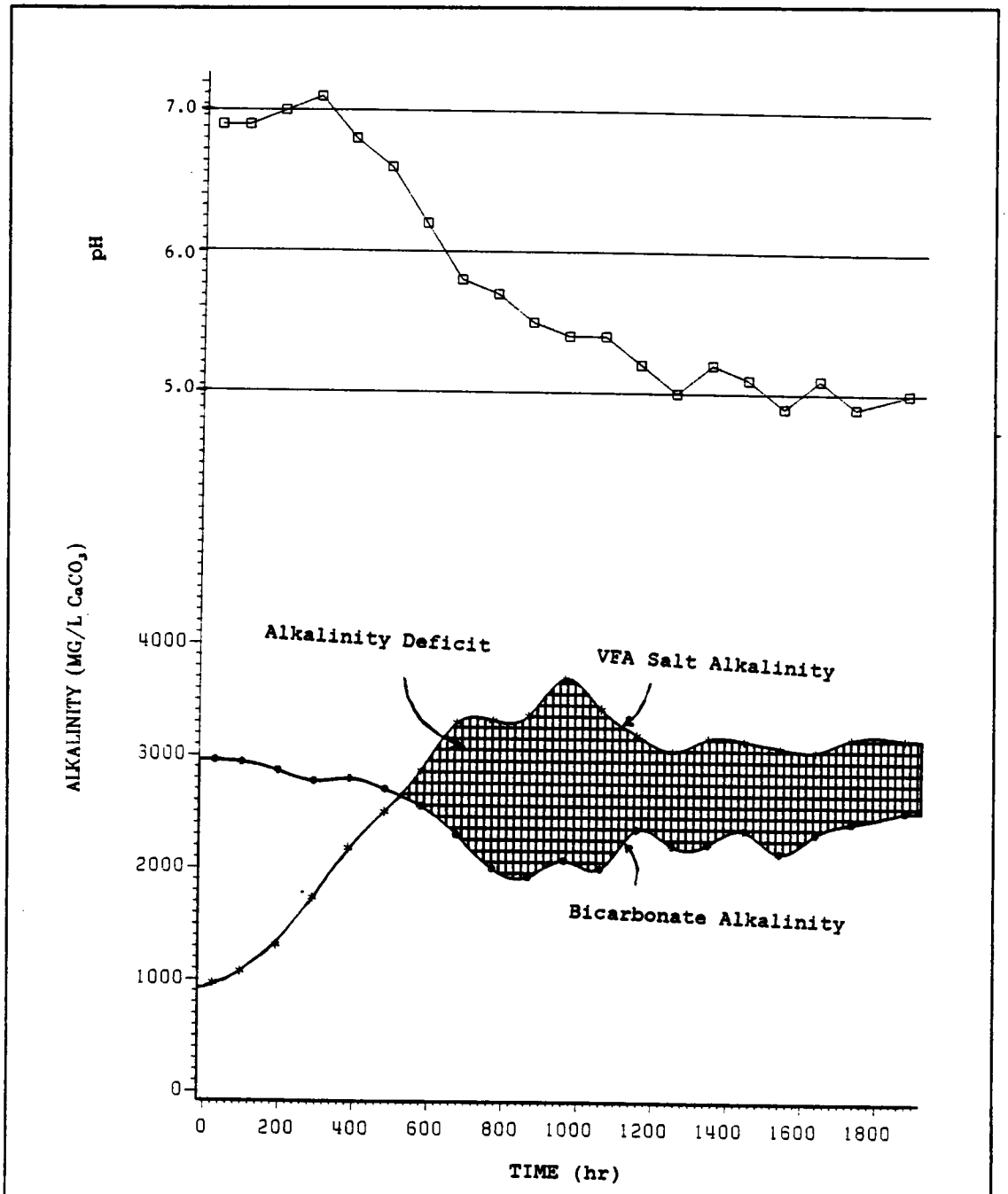
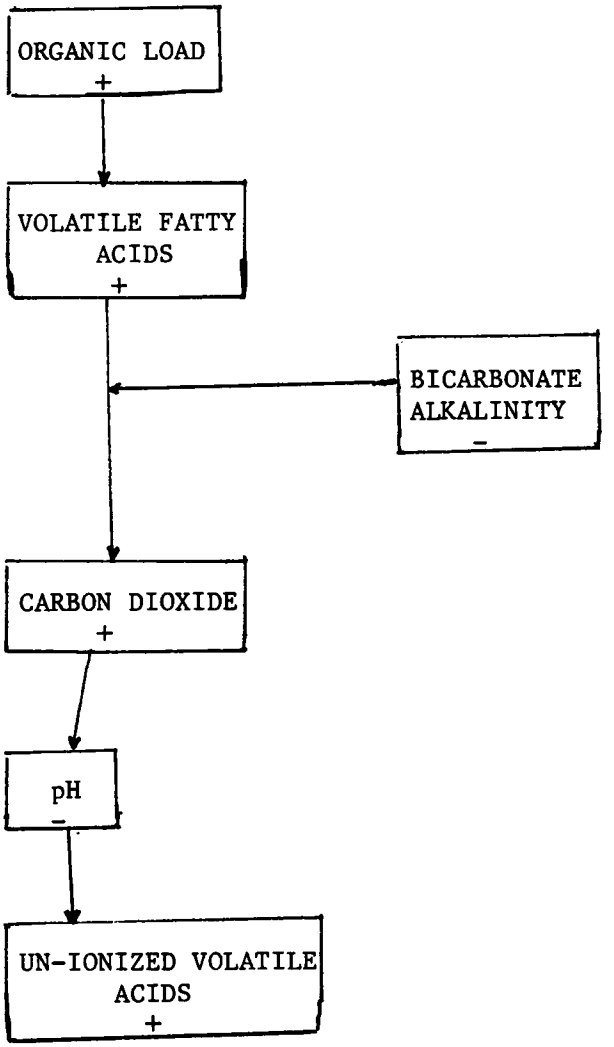


Figure 34. Performance of a retarded digester (8-3)

of 4.3, consists of the bicarbonate alkalinity only. However, in the presence of high concentrations of VFA, part of the alkalinity would have been destroyed leading to the formation of volatile acid salts.

The strong interactions among the different variables, and the effect on digester failure, is illustrated by Figure 35. In an overloaded digester, the formation of VFA by acid-formers is faster than its consumption by methane-formers. The VFAs that accumulate destroy alkalinity, forming acid salts and carbon dioxide. The increased carbon dioxide and decreased alkalinity will cause the pH to decrease. Low pH values and high VFA concentration result in high un-ionized volatile acid (UVA) levels which in turn cause inhibition of methane bacteria and an associated increase in VFA due to reduced consumption rates. This cycle is repeated until complete digester failure occurs.

The alkalinity of the system depends on the composition and concentration of the influent. High protein wastes typically have higher alkalinity because of the production of ammonia from proteins. High carbohydrate wastes typically have low alkalinity. Albertson (1961) has demonstrated that an increase in alkalinity tends to increase the operating level



+ Incraese
- Decrease

Figure 35. The Mechanism of Digester Failure

of the volatile acids over and above those values commonly considered maximum for the process.

Examination of the TVS data of the three stressed digesters (Table 13) indicates that VS removal is not an accurate performance parameter under retarded conditions. The substrate in these digesters, rather then being removed as a gaseous product, was converted to organic acids and was present in the effluent. Accordingly, effluent TCOD/TVS ratios of 1.6, 1.7, 1.8, and 1.8 were obtained. Clearly these were very much higher than the mean value of 1.36 established in this study. These high ratios are explained by observing that VFA are undetected in the VS determination method, while they are accounted for in the COD determination.

Table 13. TCOD/TVS Ratios for Experimental Digesters

DIGESTER	EFFLUENT TVS (g/L)	EFFLUENT TCOD (g/L)	TCOD/TVS
8-1*	50.93	82.23	1.6
8-2*	69.51	117.94	1.7
8-3*	75.69	135.41	1.8
8-4*	80.64	142.04	1.8
10-1	37.95	49.29	1.3
10-2	53.08	67.37	1.3
10-3	54.92	77.64	1.4
10-4	59.16	79.84	1.3
15-1	37.06	48.49	1.3
15-2	48.62	70.27	1.3
15-3	51.56	73.70	1.4
15-4	57.54	78.95	1.3
20-1	36.60	49.40	1.4
20-2	48.12	70.50	1.3
20-3	51.35	71.30	1.4
20-4	56.84	74.93	1.3

5.4.5 NITROGEN TRANSFORMATION

The fate of nitrogen in the digester is of special interest because of the fertilizer value associated with the digested sludge. Nitrogen can occur in different forms. In the anaerobic environment, the oxidized forms of nitrogen cannot exist. Hence, we are limited to organic nitrogen (org-N) and ammonia nitrogen (NH_4-N). It is customary to combine these two under total Kjeldhal nitrogen (TKN). That is,

$$TKN = (NH_4\text{-}N) + (Org\text{-}N)$$

Fresh manure contains substantial amounts of org-N. As noted earlier, manure used in this study had an average NH_4-N : TKN of 0.23. So, approximately 77% of the total nitrogen in the manure was in the organic form. Hashimoto (1983), Converse et al. (1977), and Gramms et al. (1971) reported similar results.

The 'steady-state' digester nitrogen concentrations are reported in Table 14. Mineralization of org-N in the anaerobic atmosphere was evidenced by the increase in NH_4-N : TKN values for all digesters that operated normally. On the other hand, in the three inhibited digesters, the NH_4-N levels were extremely low (6.04, 3.63 and 3.12 % of TKN).

This implies that the conversion of protenaceous material (a source of alkalinity) was inhibited.

The effect of an anaerobic environment is to promote the conversion of org-N to NH_4-N. Since the quantity of nitrogen lost in the gas phase as ammonia is less then 0.01% of TKN (Converse et al., 1981), close to 100% recovery of TKN is possible. A TKN mass balance would permit the determination of the percentage of the influent TKN that was recovered in the effluent. The values obtained ranged between 88.7% and 117.3%. Deviations from 100% recovery may be attributed to experimental error.

Table 14. Nitrogen Concentrations in the Digester

Digester	Influent TKN	Effluent TKN	Effluent NH_4-N	Effluent NH -N TKN	TKN Recovery (%)
8-1	1.71	1.61	119.80	7.44	94.2
8-2	2.48	2.10	126.85	6.04	84.7
8-3	2.67	2.71	98.35	3.63	101.5
8-4	3.05	2.90	90.15	3.12	95.1
10-1	1.71	1.85	638.25	34.5	108.2
10-2	2.48	2.91	1040.10	35.6	117.3
10-3	2.67	2.53	839.96	33.2	94.8
10-4	3.05	3.25	1039.94	32.1	106.6
15-1	1.71	1.82	684.18	37.8	105.9
15-2	2.48	2.20	803.00	36.5	88.7
15-3	2.67	2.57	866.11	33.7	96.3
15-4	3.05	2.95	1030.01	34.8	96.7
20-1	1.71	1.67	669.34	40.08	97.7
20-2	2.48	2.58	1020.13	39.5	104.0
20-3	2.67	2.60	990.60	38.1	97.4
20-4	3.05	3.30	1250.08	37.8	108.2

Based on these results, it can be stated that total nitrogen in the influent to an anaerobic digester was essentially conserved, and was available as a fertilizer nutrient. This finding supports those of earlier studies (Field et al., 1985; Field et al., 1984).

5.5 SIMULATION RESULTS

5.5.1 MODELING FEED ADDITION

In order to predict digester behavior as precisely as possible, it is necessary to simulate influent addition. In a continuously fed system, this is not a problem as S_0 is considered constant over the time scale of interest. Chinese digesters are conventionally fed once daily (pulse-fed). This type of feeding practice causes the digester variables to oscillate between two extremes corresponding to the condition immediately before and shortly after the loading period. Consequently, a variation in the digester environment is introduced requiring a lag period for microbial acclimation. This is even more critical in a system involving several physiologically different organisms where optimum performance will not be realized until the different microbial populations have adjusted. Growth expressions, however, predict an instantaneous utilization

of feed, and are inadequate to describe the actual growth response under these conditions.

In this study, feeding was first modeled as a pulse (that is, over a negligible period of time). Figure 36 illustrates the simulated gas yield as well as experimental results. In order to observe the changes due to pulse addition of feed, the digester contents were sampled at one-hour intervals for the first eight hours, and then four times over the remaining sixteen hours until the next feeding.

The poor fit between experimental and simulated results clearly indicates that, although substrate was supplied in the form of a pulse, the microbes did not utilize all at one time as predicted by the simulation. This indicates a need for describing microbial activity more precisely, which could be done in two ways: (1) directly modeling organism behavior by including a lag coefficient, or (2) modeling the feeding operation to fit the observed experimental results.

Obviously, the first method involves a thorough knowledge of microbiology and adequate data to correlate microbial behavior and substrate utilization. The second method is a black box approach. That is, it attempts to model microbial activity by observing gas production with no regard for the actual nature of the organisms involved. Considering the

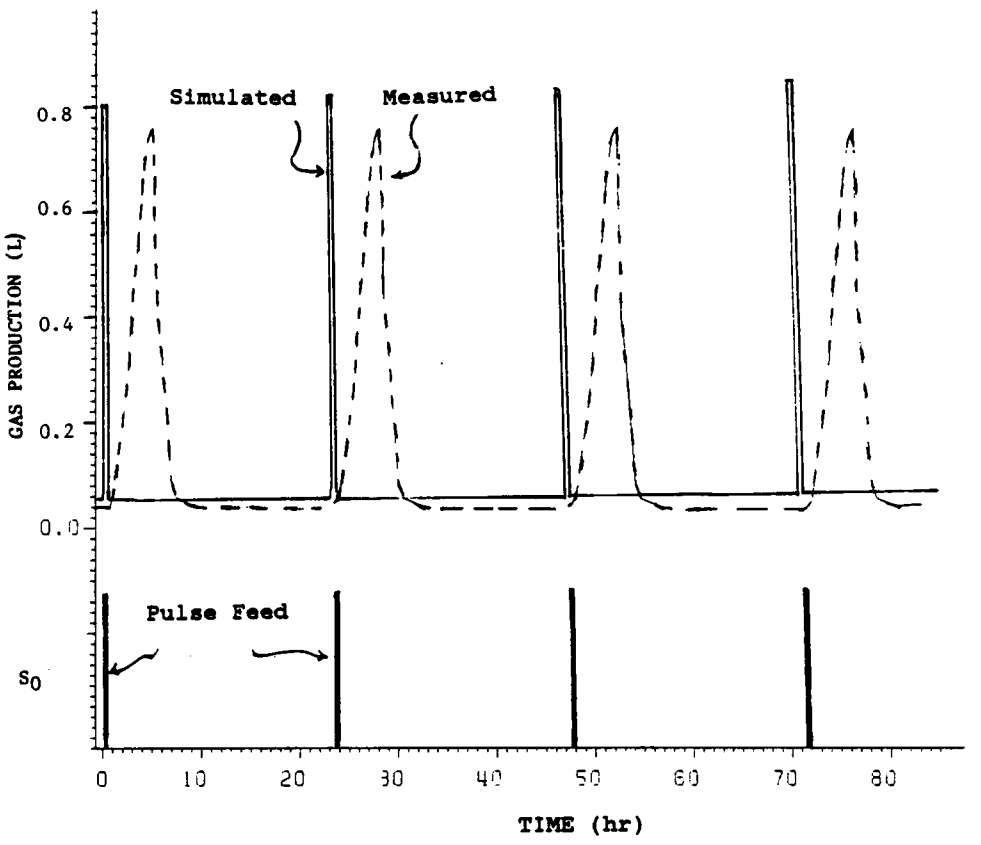


Figure 36. Cyclic Digester Behavior Following Feed Addition

complex interactions involved, this seems to be a reasonable approach.

The basic concept was to assign a time distribution to the feed. Experimental results (Figure 36) indicated that most of the substrate was utilized within approximately six hours after feed addition. Hence, feeding was modeled over a 6-hr period. The specific functions used to characterize the availability of feed were: the rectangular (Figure 37), the triangular (Figure 38), and the 3-step (Figure 39) functions. Comparing the predicted and measured methane production for each of these functions, it is apparent that the 3-step feed distribution best described the observed results.

According to Iannotti (1985), the actual response curve is skewed to the right due to slow initial substrate uptake. As the organisms acclimate, substrate utilization is increased, leading to a sharp increase in methane yield. Since the 3-step distribution approximated this type of behavior, it was adopted for this study.

5.5.2 SIMULATION OF NORMALLY OPERATED DIGESTERS

In this section simulation results of normally operated digesters will be presented and compared with experimental values. It is important to note that in simulation results

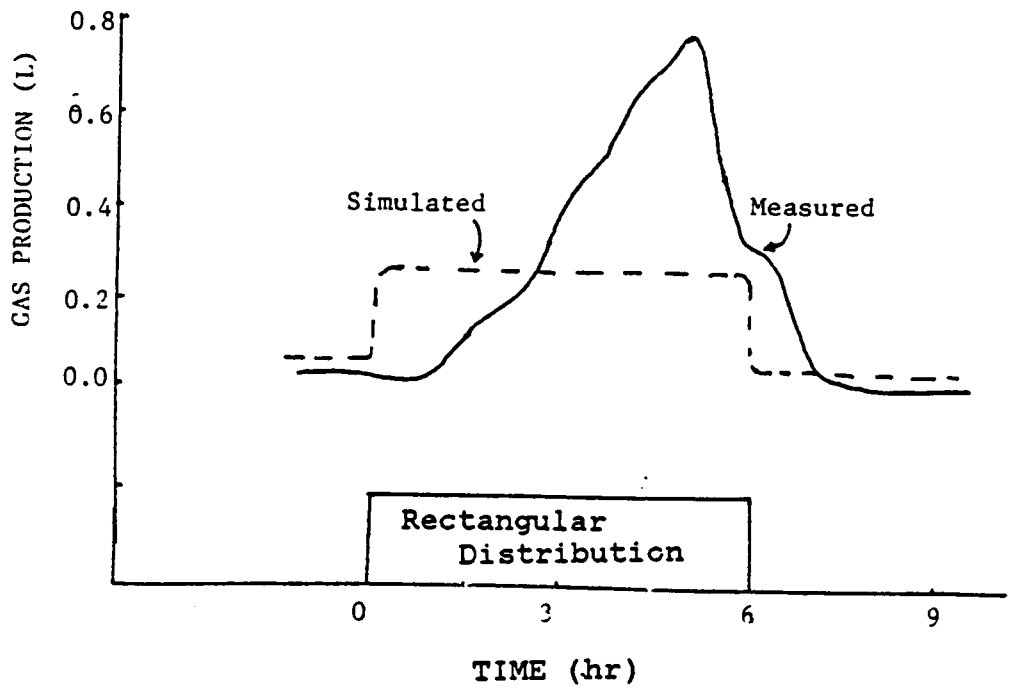


Figure 37. The Rectangular Feed Model

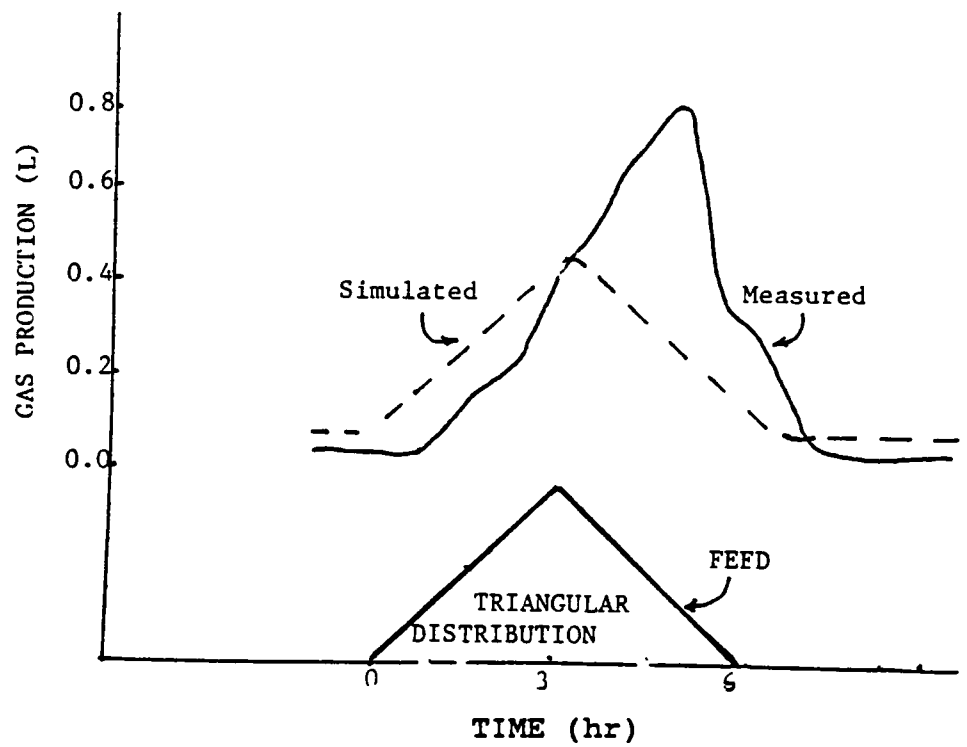


Figure 38. The Triangular Feed Model

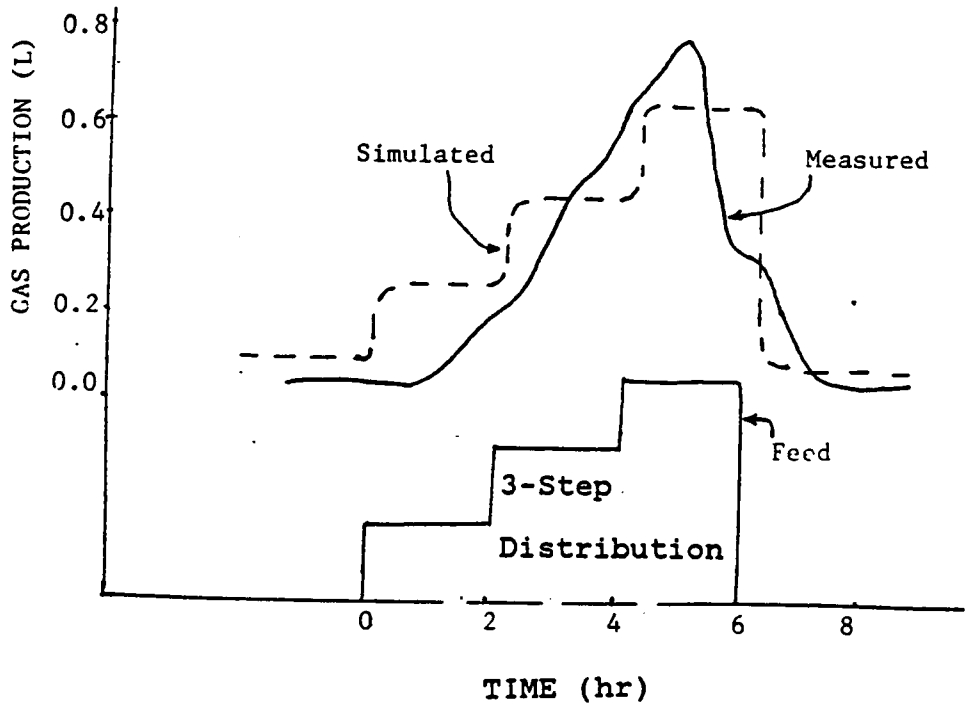


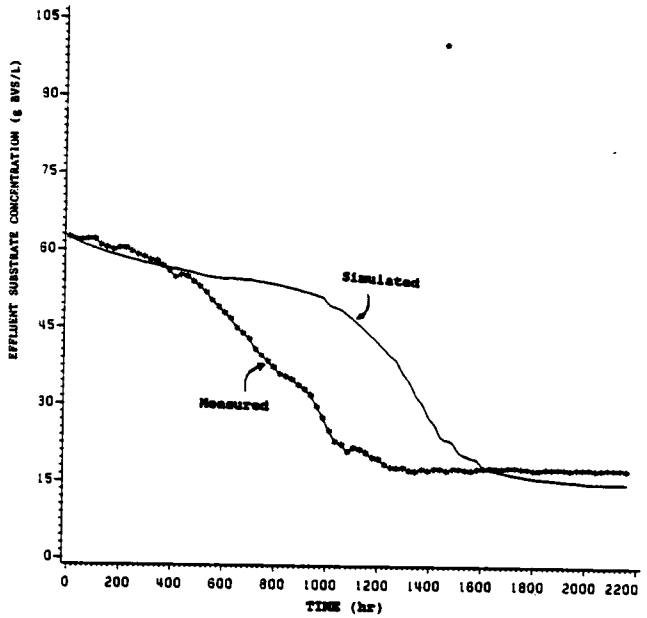
Figure 39. The Three-Step Feed Model

the absolute magnitude is not as informative as the shapes of the curves and their relation to observed trends.

Initial conditions are unimportant in these simulations because steady-state can be achieved regardless of initial conditions where enough operating time is given. Figure 40 presents experimental and simulated results of effluent VS concentration and volumetric methane production for a normally operating digester (Digester 10-4). In all cases, fairly good agreement between simulated and experimental results were observed. The simulated results consistently predicted lower S and higher VMP values than those observed in the laboratory. This can be attributed to: (1) error associated with assumed model parameter values, (2) not accounting for cellular growth, (3) the degree of mixing may be lower than that determined by tracer studies, and (4) the inability of the model to accurately simulate the effects of pulse feeding.

5.5.3 SIMULATION OF RETARDED DIGESTERS

As noted before, the results of dynamic simulation are most informative in inhibited digesters. Figure 41 depicts the response of effluent substrate concentration (COD) and volumetric methane production (VMP) as inhibition begins. Recall that inhibition refers to reduced activity of the



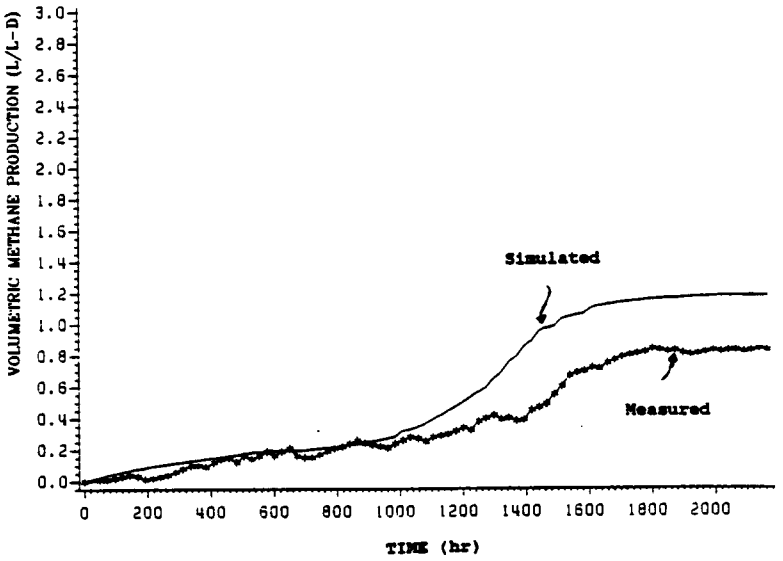


Figure 40. Steady State Simulation Results

methane-formers. As a consequence, COD reduction and associated methane production are hindered. The effluent COD and VMP are, therefore, good performance indicators.

The simulation results predicted failure in three of the four 8-day digesters. In the laboratory study, however, all four 8-day digesters failed. This inability to predict the performance of digester 8-1 need not be interpreted as model deficiency, but may be attributed to inability to determine the actual HRT accurately. In practice, the degree of mixing is a dynamic quantity and may vary from day to day, while continually changing digester flow pattern.

5.5.4 FREQUENCY OF FEEDING

Using computer simulations, the effect of increasing the frequency of feeding was investigated. The results are summarized in Figure 42 which shows the maximum and minimum values of methane production at 'steady-state.'

As the loadings per day is increased, a decrease in the difference between the maximum and minimum values of VMP is evident. For example, the deviation is 0.74 at ten loadings per day compared to 2.3 at a single daily loading. This is to be expected, since by increasing the number of feedings, the digester tends toward continuous feeding, hence a more

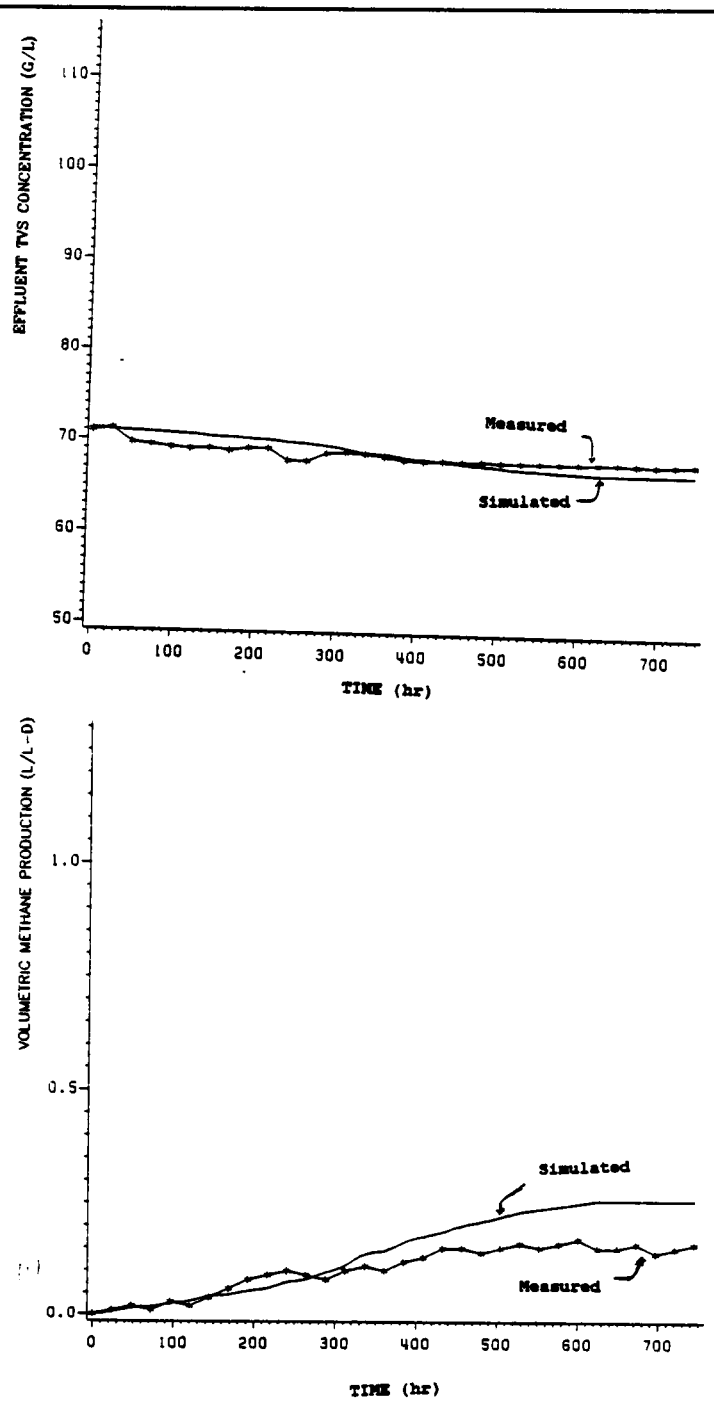


Figure 41. Behavior of an Inhibited Digester

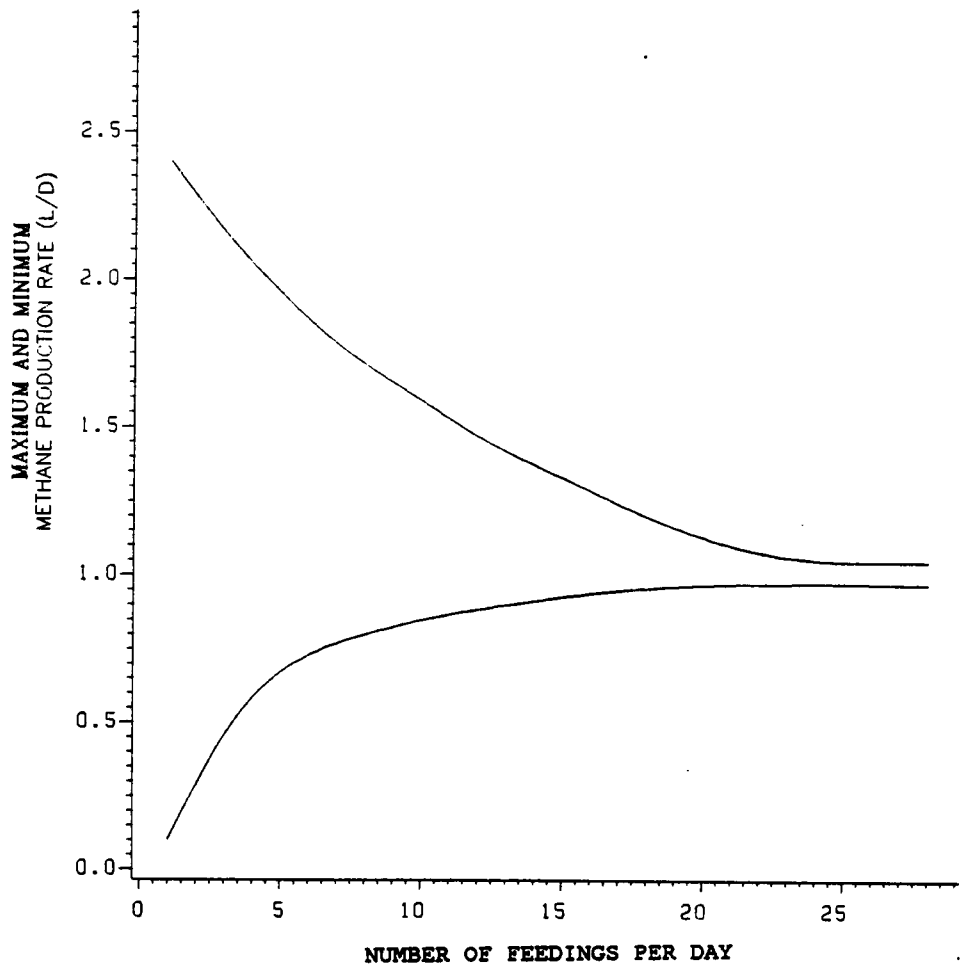


Figure 42 Effect of Feeding Frequency on Gas Production

balanced and predictable performance. Based on simulation results it could be stated that 20 feedings per day or more approximates continuous feeding.

Pulse feeding had profound influence on the dairy waste anaerobic digesters used in this study. A sudden increase in the influent concentration resulted in its degradation to VFA. Since dairy waste is relatively low in nitrogen as compared with chicken and swine manure, it lacks the necessary buffer to resist a drop in pH. One method of increasing the stability of intermittently fed digesters is to increase the frequency of feeding.

5.5.5 SELECTION OF SRT

Since the model used in this investigation considers a hypothetical well-mixed region (as defined by the tracer study), it was assumed that within this region SRT = HRT. Simulation results may be used to select design SRT values. In the following section, a discussion on this aspect will be presented.

There are two HRT values that are of importance in designing anaerobic systems. These are: the minimum SRT value at which process failure will occur (θ_m), and the SRT value at which the maximum volumetric waste utilization rate is achieved

(θu). By definition, process failure is evidenced when S = S_0. A system operating close to this point will be at its peak waste stabilization efficiency. Recall that the volumetric waste utilization (dF/dt) is given by equation (17) and refers to the amount of influent substrate converted on a daily basis. Thus,

$$dF/dt = (S_0 - S)/SRT$$

The simulated curves of dF/dt and effluent concentration (S) for S_0 = 72.1 g BVS/L are presented in Figure 43. Clearly, θm < θu. Similar curves may be generated for other values of S_0 as well. Anaerobic reactors designed to operate at θm may fail if a slight perturbation in digester environment is encountered. On the other hand, some margin of safety would be inherently provided by operating the system at SRT values close to the the maximum waste utilization rate (θu). In conclusion, θu is a better design parameter than θm.

5.5.6 SENSITIVITY ANALYSIS

A sensitivity analysis of the model was performed to evaluate the effects of kinetic and flow prameters on digester performance. The variables examined were KS1, KS2, KI1, KI2, A, and B. The variations in output and input values were compared as proportional differences from a datum. The value

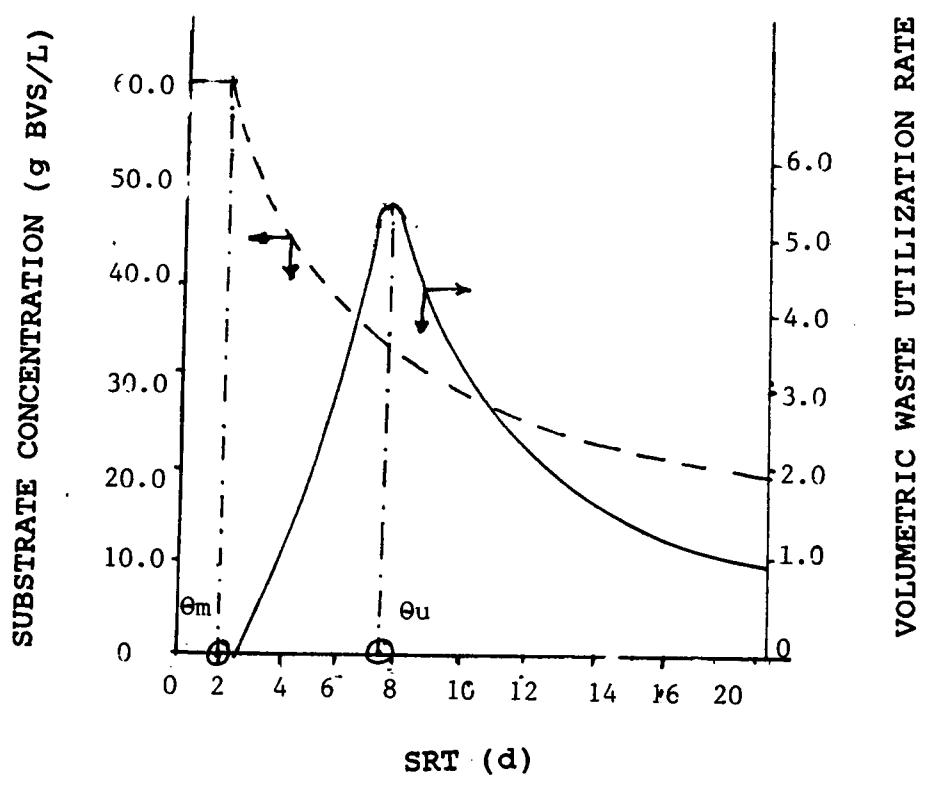


Figure 43 Determination of Design SRT Value

used in the main simulation model was the datum for each controlling parameter.

The parameters were varied within limits cited in the literature (Hill and Barth, 1979; Chen and Hashimoto, 1979; Andrews, 1969; Andrews and Graef, 1971; Hill and Nordstedt, 1980) and the corresponding change in the output (volumetric gas production) was used as a measure of the model's sensitivity to each of the input parameters. The sensitivity ratio (Stafford et al., 1980) used in this investigation is defined as:

$$S = Po/Pi$$

where, Po is the proportional difference in output from the baseline situation, and Pi is the proportional difference in controlling input from the baseline condition. The above expression can be written as:

$$S = [(Gi-Gb)/Gb] \; / \; [(Ii-Ib)/Ib]$$

where,

Gi = gas yield due to change in input, L/L-d

Gb = gas yield at baseline condition, L/L-d

Ii = input extreme

Ib = input at baseline condition

Table 15 shows the baseline values, control limits, gas yields, and sensitivity ratios for the different parameters. The inhibition coefficient of the methane-formers (KI2) is, by far, the most important variable followed by the inhibition coefficient of the acid-formers (KI1). The half-velocity constant of the methane-formers (KS2) and the fraction of the digester contents that is well-mixed (A) exert mild influence on model output.

In summary, sensitivity analysis was helpful in identifying parameters which had the greatest net effect on process modeling. Based on simulation results, the kinetic and flow parameters can be arranged in the order of importance as follows:

KI2 > KI1 > A > KS2 > KS1 > B

Table 15. Results of Sensitivity Analysis

PARAMETER	BASELINE VALUE	CONTROL LIMITS		BASELINE GAS YIELD	NET GAS YIELD*		SENSITIVITY RATIO	
		UPPER	LOWER		UPPER	LOWER	UPPER	LOWER
KS1	0.15	0.2	0.1	0.94	0.97	0.93	0.13	0.03
KS2	0.025	0.03	0.02	0.94	0.98	0.90	0.21	0.19
KI1	1.0	1.5	0.5	0.94	0.64	1.57	0.68	1.26
KI2	0.3	0.35	0.25	0.94	0.41	1.65	3.38	4.53
A	0.64	0.75	0.50	0.94	0.99	0.86	0.31	0.39
B	0.92	0.95	0.80	0.94	0.94	0.93	0	0.08

*Net change in gas yield due to change in control parameter value

KS1, KS2, KI1, and KI2 expressed in g/L
Gas yield in L/L-d

6.0 SUMMARY AND CONCLUSIONS

This investigation was initiated to study the behavior of a spherical Chinese biogas digester commonly found in Sri Lanka. The specific objectives were:

1. to determine operational and structural changes necessary to improve flow characteristics of the Chinese digester;

2. to observe digester response to operational variables;

3. to develop a mathematical model that can predict gas production and effluent quality in the presence of intermittent (pulse) feeding and incomplete mixing;

4. to define an operating regimen for maximum methane production and failure conditions;

5. to determine the effects of feeding more than once a day; and,

6. to recommend design modifications and operating methods likely to increase gas yields.

The conclusions presented in this section are valid for the reactors used in this investigation. Restating the experimental conditions: the laboratory - scale digesters (3L) were maintained in the mesophilic temperature range (35°C±2°C) and were subjected to four hydraulic retention times of 8, 10, 15 and 20 days. The influent BVS concentrations investigated were 40.1, 57.8, 62.3 and 71.2 g/L. Within the limits of the investigation, the conclusions are:

1. The bench-scale replicas of the field digesters exhibited significant amounts of stagnant volume and short circuited flow. By placing the outlet at the bottom of the digester (Type 3), dead space and bypassing volumes were reduced by 47% and 91%, respectively.

2. Digester stability and effluent quality are affected by incomplete mixing.

3. Pulse feeding causes digester parameters to exhibit cyclic behavior. As a consequence, true steady-state conditions are never attained. Increasing the frequency of feeding contributes to consistent digester performance. Simulation results indicate that 20 feedings per day or more approximates continuous feeding.

4. The response of the digester to pulse feeding is best described by assigning a three-step time-distributed model to the feeding process.

5. Based on the experimental results, the operating regime for optimum digester performance is:

   - Hydraulic retention time = 10 days
   - Influent total VS = 95.0 g/L
   - Loading rate = 7.12 g BVS/L-d

6. One method of improving the quality of the feedstock is to subject the raw manure to initial 'cleaning'. This operation demands minimum extra labor while decreasing the refractory fraction.

7. The value of the raw manure as a nitrogen fertilizer is essentially conserved. The percentage of influent TKN recovered in the effluent ranged between 88.7% and 117.3%.

8. The TVS can be used to define effluent quality in normally operating digesters. In retarded digesters, it is not as informative as the TCOD values.

9. pH is affected by volatile fatty acid concentration only when an alkalinity deficit exists.

10. The lithium chloride tracer method is an economical process for the determination of overall digester flow characteristics. It is not an accurate method for estimating solid retention times.

11. The two-culture dynamic model incorporating inhibition, incomplete mixing and pulse feeding successfully predicted effluent quality and gas yield under retarded and normal operating conditions.

12. The model was found to be most sensitive to variations of the inhibition coefficient of methane-formers followed by the variations of the inhibition coefficient of acid-formers. Digester flow parameters and half-velocity constants exerted a mild influence on the predictive ability of the model.

7.0 RECOMMENDATIONS

The results of this investigation are only a starting point. Their applicability to large-scale digesters will be limited by scale-up problems. A pilot scale study should be initiated to substantiate the findings reported herein. The recommendations suggested in this chapter are based on laboratory results and field observation and are aimed at enhancing the production potential of the Chinese digester:

1. The quality of the feedstock can be enhanced by removing leaves, straw, and other large objects.

2. A regular feeding pattern should be maintained. Dividing the daily feed into as many portions as practically feasible and loading the reactor at regular intervals is encouraged.

3. The recommended maximum feed concentration is approximately 10 g VS/L-d. Under certain circumstances it is possible to exceed this loading rate, but this should be done cautiously as inhibition may result.

4. If the digester is retarded, feeding should be terminated until recovery begins. Alternatively, the digester may

be 'flushed' with extremely diluted influent over a period of time.

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APPENDICES

APPENDIX A

Gas Volume Correction

Gas volume data corrected to Standard Temperature and Pressure (STP) using the following formula:

$$Vc = Vm\ (P-Pw)/(T+273)\ (Tstd/Pstd)$$

where,

Vc = Dry gas volume corrected to STP, L

Vm = Measured gas volume, L

P = Barometric pressure, 596 mm Hg

Pw = Water vapor pressure at T°C, 42.18 mm Hg

T = Digestion temperature, 35°C

Tstd = Standard temperature, 273 °K

Pstd = Standard pressure, 760 mm Hg

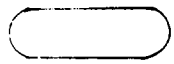
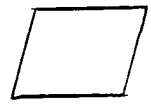
Blacksburg elevation assumed to be 2000 feet.

Values for P, Pw, Tstd, and Pstd were obtained from: Handbook of Tables for Applied Engineering Science, 2nd. Edition, 1980. CRC Press Inc. Boca Raton, Florida.

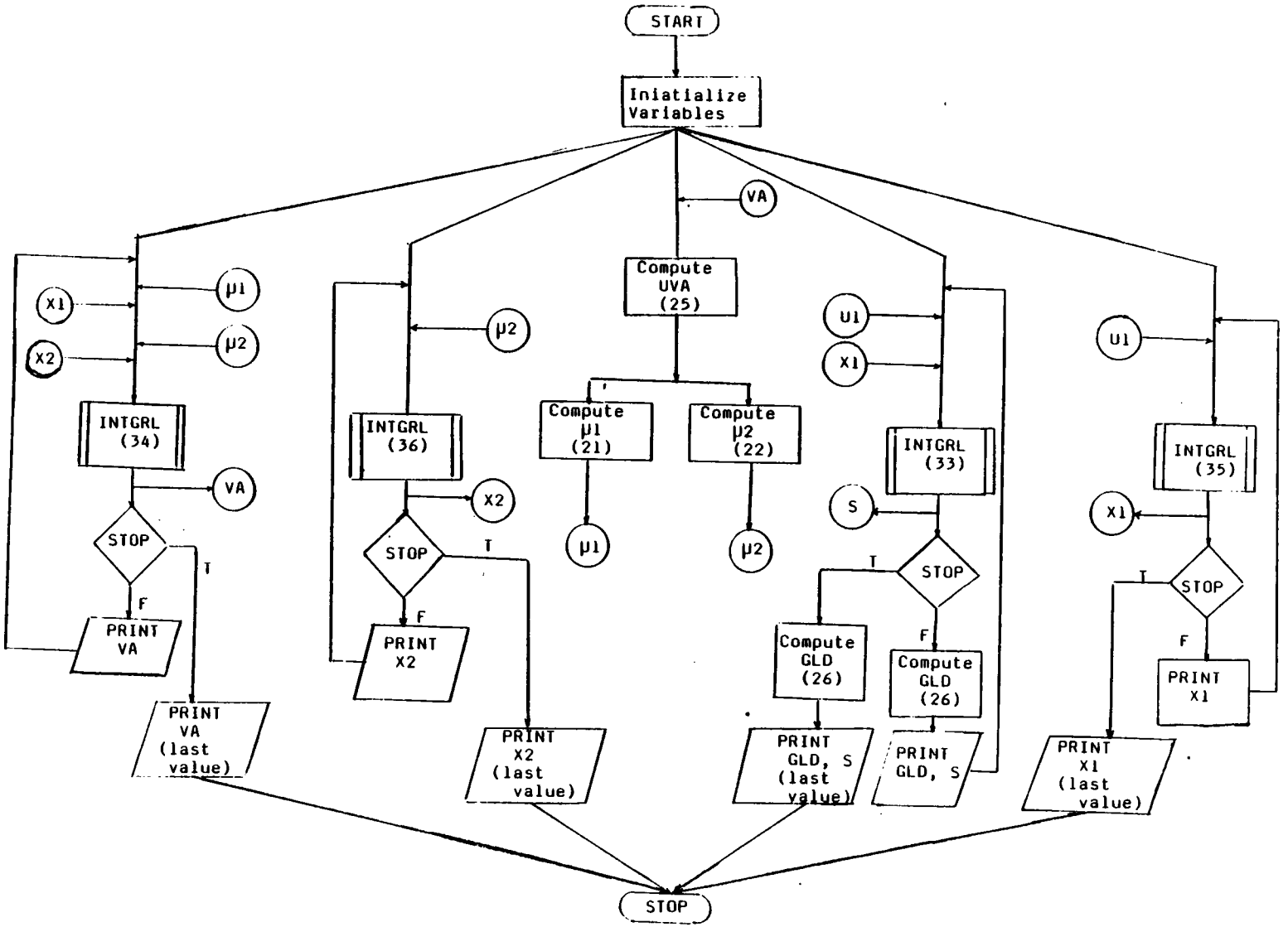
APPENDIX B. Flow Chart

(Definition of symbols and terms)

TERM	DEFINITION
UVA	Unionized volatile acids, mg/L
S	Substrate concentration, mg/L
GLD	Volumetric methane production, L/L-d
VA	Volatile fatty acids concentration, mg/L
X1	Concentration of acid-formers, mg/L
X2	Concentration of methane-formers, mg/L
μ1	Growth rate of acid-formers, d
μ2	Growth rate of methane-formers, d

SYMBOL	DEFINITION
	Terminal operation (START, STOP)
	Input - output (READ, PRINT)
	Compute, assign
	CSMP function (integration)
	Decision
	Onpage connector

- Numbers in parentheses refer to equations discussed in Chapter 3.
- Flowchart symbols taken from:
  Moore, J.B.1975. WATFIV: Fortran Programming with the WATFIV Compiler. Reston Publishing Company, INC., Reston, Virginia


START
Iniatialize Variables
VA
Compute UVA (25)
μ1
μ2
X1
X2
INTGRL (34)
VA
STOP
T
F
PRINT VA
PRINT VA (last value)
INTGRL (36)
X2
STOP
T
F
PRINT X2
PRINT X2 (last value)
Compute μ1 (21)
Compute μ2 (22)
μ1
μ2
U1
X1
INTGRL (33)
S
T
STOP
F
Compute GLD (26)
Compute GLD (26)
PRINT GLD, S (last value)
PRINT GLD, S
U1
INTGRL (35)
X1
T
STOP
F
PRINT X1
PRINT X1 (last value)
STOP

APPENDIX C. Program Listing

```
**********************************************************
* DIGESTER MODEL DEVELOPED TO PREDICT
* GAS PRODUCTION AND EFFLUENT QUALITY.
*
* THE MODEL ACCOUNTS FOR INCOMPLETE
* MIXING AND INTERMITTENT FEEDING.
**********************************************************
*
DEFINITION OF TERMS:

V  = VOLUME OF REACTOR CONTENTS
RT = HYDRAULIC RETENTION TIME
SF = INFLUENT SUBSTRATE CONCENTRATION
S  = REACTOR BVS CONCENTRATION
SE = EFFLUENT BVS CONCENTRATION
VA = VOLATILE FATTY ACID CONCENTRATION
UVA= UNIONIZED VOLATILE ACID CONCENTRATION
A  = FRACTION OF FEED ENTERING WELL-MIXED ZONE
B  = FRACTION OF DIGESTER VOLUME THAT IS WELL-MIXED
KA = IONIZATION CONSTATNT FOR ACETIC ACID
KD = SPECIFIC DEATH RATE
KI = INHIBITION COEFFICIENT
KS = HALF - VELOCITY CONSTANT
MUMAX = MAXIMUM SPECIFIC GROWTH RATE
MU = SPECIFIC GROWTH RATE
Y  = MICROBIAL YIELD COEFFICIENT
X  = CELL CONCENTRATION
HCONC = HYDROGEN - ION CONCENTRATION
VSD = VOLATILE SOLIDS DESTROYED
GLD = VOLUMETRIC GAS PRODUCTION
0  = DENOTES INITIAL CODITION
1  = DENOTES ACID - FORMERS
2  = DENOTES METHANE - FORMERS
*
*
**********************************************************
*  INPUT PARAMETERS RELATED TO
*  OPERATIONAL VARIABLES
**********************************************************
*
      PARAMETER RT=8.0, SF=40.1, VA0=0.645
      PARAMETER A=0.68, B=0.92
      PH=7.2
*
**********************************************************
*     KINETIC PARAMETERS
**********************************************************
*
      KA=31.6E-4
      KD1=0.1*MUMAX
      KD2=0.1*MUMAX
      KI1=1.0
      KI2=0.3
      KS1=0.15
      KS2=0.025
      MUMAX=0.324/24.0
      Y1=0.196
      Y2=0.06
*
**********************************************************
* INITIAL CONDITIONS
**********************************************************
*
      S0=SF
      S00=SF
      VA00=VA0
      X10=.1
      X20=.1
      X1=X10
      X2=X20
      PPH=-PH
      HCONC0=10.0**EXP(PPH)
      UVA0=HCONC0*VA0/KA
*
**********************************************************
* INITIAL COMPUTATIONS BASED
* ON OPERATIONAL VARIABLES
**********************************************************
*
      V=3.0
      HR=RT*24.0
      Q=V/HR
      THE=(B*Q)/(A*V)*DELT
      SY1=SF/12
      SY2=SF/6
      SY3=SF/3
*
*
DYNAMIC
*
**********************************************************
*  MICROBIAL GROWTH MODEL INCORPORATING
*  INHIBITION   EFFECTS OF UVA
**********************************************************
*
NOSORT
```

```
      IF(TIME.EQ.0.0)S=SF
      IF(TIME.EQ.0.0)UVA=UVA0
*
      MU1=MUMAX/(1.0+(KS1/S)+(UVA/KI1))
      MU2=MUMAX/(1.0+(KS2/VA)+(UVA/KI2))
SORT
*
************************************************************
* IMPULS FEED MODEL
************************************************************
*
NOSORT
      FEED=SF*IMPULS(24.0,24.0)
      SO=FEED
SORT
*
************************************************************
*  THREE - STEP FEED MODEL
************************************************************
*
NOSORT
     TRIG1=IMPULS(48.0,24.0)
     F1=SY1*PULSE(1.99,TRIG1)
     TRIG2=IMPULS(50.0,24.0)
     F2=SY2*PULSE(1.99,TRIG2)
     TRIG3=IMPULS(51.0,24.0)
     F3=SY3*PULSE(1.99,TRIG3)
     FEED=F1+F2+F3
     SO=FEED
SORT
*
************************************************************
*  RECTANGULAR FEED MODEL
************************************************************
*
NOSORT
       TRIG=IMPULS(48.0,24.0)
       FEED=(SF/6.0)*PULSE(6.0,TRIG)
       SO=FEED
SORT
*
************************************************************
* BVS AND VFA BALANCES
************************************************************
*
     DS=TERM1-TERM2
     TERM1=THE*(SO-S)
     TERM2=(MU1*X1/Y1)
     S=INTGRL(SOO,DS)
     DVA=THE*(VAO-VA)+(MU1*X1/Y1)*(1.0-Y1)-(MU2*X2/Y2)
     VA=INTGRL(VAOO,DVA)
*
************************************************************
* CELL BALANCES
************************************************************
*
      DX1=(MU1-KD1)*X1+THE*(X10-X1)
      X1=INTGRL(X10,DX1)
      DX2=(MU2-KD2)*X2+(X20-X2)*THE
      X2=INTGRL(X20,DX2)
*
************************************************************
* UVA DETERMINATION IS BASED ON THE CONCENTRATION OF VFA
* COMPUTED BY THE MODEL AND PH VALUE SPECIFIED.
************************************************************
*
     PPH=-PH
     HCONC=10.0*EXP(PPH)
     UVA=HCONC*VA/KA
*
************************************************************
* VS DESTRUCTION AND GAS PRODUCTION
************************************************************
*
      VSD=(SF-S)*100.0/SF
      GLD=0.5*(SF-S)/RT
       S=(1-B)SO+S
*
NOSORT
      CALL DEBUG(10,0.0)
SORT
*
METHOD RECT
PRINT S
TIMER FINTIM=2400.0,PRDEL=24.0,OUTDEL=24.0,DELT=0.1
END
STOP
ENDJOB
/*
//
```

ABBREVIATIONS

ALKAL = BICARBONATE ALKALINITY
VALK = VOLATILE FATTY ACID ALKALINITY

DAY 8-1	ALKAL. 8-1	VALK 8-4	ALKAL 8-4	VALK 8-1	PH 8-4	PH 8-4
1.0	2959.0	972.5	5268.0	1460.3	6.9	7.0
2.0	2958.0	999.5	5100.0	1501.0	6.9	6.9
4.0	2940.0	1080.0	4802.1	1921.0	6.8	6.7
6.0	2915.9	1160.58	4502.0	2231.9	6.9	6.6
8.0	2865.5	1310.62	4122.0	2501.3	7.1	6.5
10.0	2800.0	1588.77	3721.2	2900.6	7.0	6.3
12.0	2771.3	1731.52	3010.2	3001.0	7.2	6.3
14.0	2705.4	1901.5	2908.0	3111.0	7.1	6.1
16.0	2795.3	2178.30	2901.1	3191.2	6.9	5.9
18.0	2761.2	2310.20	2850.0	3232.0	6.8	5.8
20.0	2700.1	2502.41	2800.1	3290.0	6.8	5.7
22.0	2677.9	2677.52	2721.0	3331.0	6.6	5.7
24.0	2551.7	2871.31	2601.0	3432.0	6.4	5.6
26.0	2490.9	3063.72	2500.0	3531.0	6.2	5.5
28.0	2302.3	3298.31	2400.0	3600.0	6.1	5.4
30.0	2210.5	3481.60	2300.0	3541.0	5.8	5.4
32.0	2000.1	3323.52	2230.0	3503.0	5.6	5.3
34.0	1892.7	3259.55	2160.0	3481.0	5.7	5.3
36.0	1925.9	3367.12	2070.0	3500.0	5.6	5.2
38.0	2192.7	3459.52	1990.0	3631.0	5.5	5.3
40.0	2075.6	3699.13	2007.0	3581.0	5.6	5.4
42.0	1985.0	3502.3	2190.0	3630.0	5.4	5.2
44.0	2001.0	3425.1	2100.0	3701.0	5.5	5.1
46.0	2123.4	3310.02	2098.0	3701.0	5.4	4.9
48.0	2351.9	3200.30	2150.0	3801.2	5.3	5.0
50.0	2273.3	3151.52	2078.0	3798.0	5.2	4.9
52.0	2210.0	3053.5	2000.0	3921.0	5.1	4.8
54.0	2115.9	3167.12	1970.0	3811.0	5.0	4.7
56.0	2227.5	3171.56	1900.0	3703.0	5.1	4.8
58.0	2251.3	3268.33	1850.0	3803.1	5.2	4.9
60.0	2348.5	3149.15	1800.0	3723.3	5.1	5.0
62.0	2271.5	3113.28	1830.0	3898.2	5.1	5.1
64.0	2150.5	3090.32	1860.0	3711.2	5.0	4.9
66.0	2211.7	3005.3	1850.0	3831.2	4.9	4.9
68.0	2321.6	3061.2	1800.0	3703.2	5.2	5.0
70.0	2323.5	3169.1	1768.0	3708.3	5.1	4.9
72.0	2419.3	3172.6	1700.0	3817.5	4.9	4.8
74.0	2521.5	3175.1	1675.0	3790.2	4.9	4.7
78.0	2523.5	3167.9	1545.0	3699.8	5.2	4.8
80.0	2418.6	3169.0	1540.0	3700.0	5.0	4.8

DAY	ALK 8-2	VALK 8-2	PH 8-2	ALK 8-3	VALK 8-3	PH 8-3
1.0	4525.0	1017.1	7.2	4650.0	1200.3	7.1
2.0	4430.1	1140.0	7.2	4510.0	1356.1	7.0
4.0	4121.0	1483.1	7.1	4420.0	1600.7	6.9
6.0	3800.0	1811.8	7.0	4112.3	1921.8	6.7
8.0	3502.7	2131.2	7.1	3898.4	2321.1	6.6
10.0	3104.1	2301.7	7.0	3489.4	2781.7	6.5
12.0	2911.2	2601.2	6.9	3398.0	3371.5	6.7
14.0	2792.0	2721.7	6.7	3220.3	3521.6	6.4
16.0	2693.0	2951.0	6.5	3210.4	3875.7	6.1
18.0	2554.0	2721.0	6.3	3130.6	4023.5	5.9
20.0	2509.2	2822.1	6.1	3280.7	3983.5	5.8
22.0	2425.7	2732.2	5.9	3190.9	4225.0	5.7
24.0	2300.6	2823.1	5.7	3285.3	3917.5	5.5
26.0	2248.6	2800.2	5.5	3223.5	3675.0	5.3
28.0	2167.9	2821.0	5.3	3101.4	3975.0	5.1
30.0	2245.7	2721.0	5.0	3081.5	3990.9	5.2
32.0	2367.8	2834.2	5.1	3152.2	4075.5	5.3
34.0	2245.8	2802.0	5.2	3001.1	4321.7	5.1
36.0	2134.0	2723.2	5.2	2990.3	4427.8	5.0
38.0	2245.0	2801.2	5.1	2910.2	4621.9	4.9
40.0	2189.2	2902.3	4.8	2901.3	4731.8	4.8
42.0	2000.0	2913.4	4.8	3098.3	4700.0	5.1
44.0	2039.0	2986.8	4.9	2910.5	4621.2	5.2
46.0	1945.0	3002.2	4.8	2810.3	4631.7	5.3
48.0	2178.0	3021.0	4.9	2971.4	4781.7	5.4
50.0	2067.0	3050.2	5.0	2832.3	4832.2	5.3
52.0	2134.0	2909.2	5.1	2712.5	4723.2	5.2
54.0	2045.0	3021.0	5.3	2824.4	4831.5	5.0
56.0	1965.7	2911.6	5.4	2789.9	4531.5	4.9
58.0	1900.8	2902.3	5.3	2881.5	4785.6	5.0
60.0	1945.9	2821.5	5.1	2723.7	4634.6	4.9
62.0	2067.9	3034.8	5.2	2650.5	4431.1	5.1
64.0	2000.9	2811.2	5.2	2591.6	4600.0	5.2
66.0	1956.5	2922.1	5.1	2481.7	4599.9	5.0
68.0	2089.9	3002.2	4.9	2383.7	4222.2	4.9
70.0	1967.9	2902.0	5.0	2479.2	4335.0	4.9

ABBREVIATIONS:

ALKAL = BICARBONATE ALKALINITY
VALK = VOLATILE FATTY ACID ALKALINITY

DAY 10-1	ALKAL 10-1	VALK 10-3	ALKAL 10-3	VALK 10-1	PH 10-3	PH 10-3
1.0	2406.0	772.6	3751.0	1200.3	6.9	7.1
2.0	2400.0	783.1	3748.0	1187.2	7.0	7.0
4.0	2410.0	779.1	3765.0	1185.6	7.1	7.0
6.0	2395.0	780.1	3764.0	1201.9	7.0	7.0
8.0	2395.0	780.1	3766.0	1165.7	6.9	6.9
10.0	2401.0	778.77	3777.2	1171.6	6.8	7.0
12.0	2403.3	795.12	3787.7	1175.8	6.9	6.9
14.0	2410.5	798.15	3795.3	1181.9	7.2	6.9
16.0	2390.5	810.20	3781.4	1191.7	7.3	7.0
18.0	2370.5	825.10	3780.5	1195.8	7.4	6.9
20.0	2340.1	840.1	3781.1	1201.8	7.2	6.8
22.0	2305.1	853.12	3778.6	1225.9	7.3	7.0
24.0	2280.5	871.31	3778.7	1220.9	7.1	7.0
26.0	2265.1	1001.1	3769.7	1190.8	7.1	6.8
28.0	2250.7	1010.2	3777.2	1199.7	7.0	7.0
30.0	2245.1	980.60	3781.2	1210.7	7.0	6.8
32.0	2250.0	999.32	3774.6	1013.9	7.0	7.0
34.0	2260.7	1020.5	3779.6	1111.9	7.1	7.2
36.0	2265.9	1025.2	3765.2	1015.0	7.2	7.1
38.0	2280.7	1000.2	3670.2	999.70	7.2	7.1
40.0	2291.6	989.13	3600.3	981.00	7.2	7.1
42.0	2320.0	965.3	3681.2	879.8	7.2	7.0
44.0	2345.6	850.1	3701.2	857.20	7.3	7.0
46.0	2366.1	745.6	3721.9	899.90	7.2	7.0
48.0.	2379.9	730.30	3710.2	820.52	7.1	6.9
50.0	2385.3	621.52	3701.1	785.00	7.1	6.9
52.0	2401.0	698.5	3689.3	780.30	7.1	6.9
54.0	2405.9	694.12	3661.1	778.90	7.2	6.8
56.0	2435.1	590.56	3651.3	770.00	7.2	6.8
58.0	2451.5	574.8	3667.2	765.1	7.3	6.9
60.0	2449.1	573.15	3677.5	769.23	7.3	6.8
62.0	2453.5	575.28	3676.6	773.52	7.3	6.7
64.0	2452.5	576.32	3687.3	771.62	7.2	6.8
66.0	2448.7	574.3	3661.4	769.02	7.2	6.9
68.0	2450.6	575.9	3669.7	771.2	7.1	7.0
70.0	2449.5	574.1	3668.8	769.6	7.2	7.0

DAY 10-2	ALKAL. 10-2	VALK 10-4	ALKAL. 10-4	VALK 10-2	PH 10-4	PH 10-4
2.0	3678.0	1017.1	4003.0	1460.2	7.1	7.0
4.0	3599.1	1021.2	4002.0	1459.2	7.2	7.0
6.0	3621.1	1121.3	4001.3	1458.5	7.0	7.0
8.0	3653.4	1321.4	3998.4	1450.5	7.0	6.9
10.0	3615.2	1330.2	3965.2	1460.6	6.9	6.8
12.0	3635.3	1352.5	3942.7	1462.8	6.9	7.0
14.0	3625.4	1360.4	3881.3	1465.9	6.8	7.0
16.0	3600.3	1389.5	3779.4	1471.7	6.7	7.1
18.0	3570.1	1410.5	3707.4	1489.9	6.9	7.1
20.0	3540.5	1449.5	3649.1	1510.8	6.9	7.2
22.0	3490.4	1462.5	3600.0	1529.9	7.0	7.1
24.0	3450.5	1479.9	3541.7	1562.9	7.1	7.0
26.0	3410.5	1498.6	3501.7	1570.8	7.1	7.0
28.0	3390.4	1520.4	3484.2	1585.7	7.2	6.9
30.0	3381.4	1540.4	3460.2	1580.7	7.2	6.9
32.0	3385.6	1532.4	3570.6	1475.9	7.2	6.8
34.0	3401.2	1501.2	3535.6	1391.9	7.3	6.8
36.0	3440.4	1375.5	3551.2	1349.0	7.3	6.8
38.0	3481.6	1237.2	3557.2	1261.0	7.2	6.7
40.0	3521.5	1100.0	3571.3	1209.0	7.2	6.7
42.0	3521.2	1090.4	3601.2	1150.3	7.1	6.8
44.0	3570.4	881.1	3611.2	1043.0	7.1	6.9
46.0	3590.1	876.6	3621.9	931.90	7.0	6.9
48.0.	3587.9	725.30	3623.2	890.52	7.0	6.9
50.0	3580.3	710.52	3631.1	889.00	7.0	7.0
52.0	3576.0	700.5	3681.3	900.70	6.9	7.0
54.0	3581.9	681.12	3681.1	895.90	6.9	7.1
56.0	3584.1	685.56	3679.3	891.00	6.8	7.1
58.0	3579.5	687.8	3675.0	887.8	6.9	7.0
60.0	3576.1	682.15	3679.5	889.23	7.0	7.0
62.0	3579.5	681.28	3681.6	885.52	7.0	6.9
64.0	3582.5	682.32	3679.3	884.62	6.9	6.9
66.0	3581.7	681.3	3677.4	888.02	6.9	7.0
68.0	3579.6	684.9	3680.7	892.2	6.8	7.1
70.0	3577.5	681.1	3679.8	890.6	6.9	7.0

ABBREVIATIONS:

ALKAL = BICARBONATE ALKALINITY
VALK = VOLATILE FATTY ACID ALKALINITY

DAY	ALKAL 20-1	VALK 20-1	ALKAL 20-2	VALK 20-2	PH 20-1	PH 20-2
2.0	1001.0	772.63	1873.1	1017.5	7.1	6.8
4.0	1015.2	771.33	1870.1	1100.6	7.2	6.9
6.0	1721.8	1095.3	2971.8	1443.4	7.1	6.7
8.0	1006.0	780.3	1425.1	1231.6	7.0	6.9
10.0	995.83	783.23	1410.2	1345.6	7.1	6.9
12.0	990.23	779.23	1398.7	1571.8	6.9	6.8
14.0	992.33	801.24	1425.3	1563.9	6.8	7.0
16.0	989.33	802.34	1495.4	1498.7	6.9	6.9
18.0	987.34	821.34	1583.4	1453.9	7.0	7.0
20.0	975.35	801.37	1691.1	1401.8	7.1	7.1
22.0	980.33	811.55	1725.0	1397.9	7.0	7.0
24.0	977.63	880.86	1795.7	1321.9	7.2	6.9
26.0	975.85	851.66	1810.7	1301.8	7.1	6.8
28.0	970.54	878.94	1795.2	1278.7	7.3	6.9
30.0	969.54	890.77	1701.2	1228.7	7.1	6.9
32.0	965.46	921.32	1733.3	1208.2	7.2	7.0
34.0	966.72	935.82	1725.8	1197.9	7.1	7.1
36.0	965.64	953.75	1783.2	1198.0	7.2	7.2
38.0	969.76	965.82	1723.2	1100.0	7.3	7.2
40.0	980.85	978.40	1741.3	1098.0	7.1	7.1
42.0	979.72	983.74	1803.2	1097.9	7.2	7.0
44.0	975.84	970.80	1793.2	1191.0	7.1	6.9
46.0	972.41	983.72	1713.9	1124.0	7.2	7.0
48.0	970.69	995.80	1723.1	1125.2	7.1	6.9
50.0	970.88	999.98	1691.1	1111.0	7.2	7.0
52.0	968.70	998.78	1697.1	1102.0	7.1	7.1
54.0	966.73	1001.9	1683.1	1025.0	7.2	7.2
56.0	960.57	1010.6	1687.3	1000.7	7.1	7.1
58.0	960.45	1120.3	1701.0	998.96	7.0	7.0
60.0	958.51	1009.5	1700.5	995.63	7.0	7.1
62.0	955.45	1111.8	1725.6	996.92	6.9	7.2
64.0	954.85	1100.2	1728.3	1021.2	6.9	7.0
66.0	950.37	1121.9	1741.4	975.92	6.8	7.0
68.0	954.76	1121.3	1753.7	981.88	6.8	6.9
70.0	958.35	1010.2	2840.8	1289.9	6.9	6.9
72.0	951.3	1121.8	1731.5	996.5	6.9	6.8
74.0	921.4	1139.8	1743.9	997.8	7.0	6.8
76.0	895.6	1278.7	1721.5	1001.8	7.0	7.0
78.0	840.6	1100.7	1711.6	1121.8	7.1	7.0
80.0	885.6	1025.5	1723.5	1023.8	7.2	7.1
82.0	901.4	1195.5	1735.7	985.79	7.1	7.0
84.0	921.3	1078.7	1753.9	971.98	7.2	6.9
86.0	931.2	1091.5	1765.9	975.89	7.3	6.9
88.0	929.6	1086.9	1766.9	978.67	7.3	6.8
90.0	932.0	1085.7	1762.9	981.90	7.4	6.9

DAY 20-3	ALKAL 20-3	VALK 20-3	ALKAL 20-4	VALK 20-4	PH 20-3	PH 20-4
2.0	2002.0	1200.3	2437.1	1416.5	7.1	6.9
4.0	1985.2	1231.3	2430.1	1475.6	7.0	6.9
6.0	1920.9	1253.3	2440.8	1458.4	7.0	6.7
8.0	1810.1	1381.7	2429.1	1450.6	6.9	6.8
10.0	1767.9	1470.3	2395.2	1498.6	6.8	6.7
12.0	1732.3	1595.3	2366.7	1531.8	6.9	6.8
14.0	1685.3	1640.8	2284.3	1590.9	7.0	6.7
16.0	1671.3	1731.4	2200.4	1634.7	7.0	6.8
18.0	1690.4	1729.4	2160.4	1650.9	7.1	6.7
20.0	1695.0	1727.7	2120.1	1657.8	7.0	6.9
22.0	1721.3	1725.5	2100.0	1670.9	7.1	6.8
24.0	1743.3	1701.6	2110.7	1678.9	7.2	6.9
26.0	1765.5	1685.6	2085.7	1721.8	7.2	7.0
28.0	1781.4	1697.4	2117.2	1701.7	7.1	7.1
30.0	1799.9	1653.7	2129.2	1698.7	7.1	7.0
32.0	1823.6	1613.2	2078.3	1721.2	7.0	7.0
34.0	1810.2	1578.2	1923.8	1751.9	6.9	7.1
36.0	1805.4	1595.5	2178.2	1742.0	6.9	7.2
38.0	1835.6	1561.2	2191.2	1701.0	7.0	7.1
40.0	1841.5	1510.2	2203.3	1710.0	6.9	7.2
42.0	1821.2	1425.4	2310.2	1683.9	7.0	7.1
44.0	1802.4	1420.9	2121.2	1601.0	7.1	7.1
46.0	1821.1	1401.2	1999.9	1570.0	6.9	7.0
48.0	1836.9	1395.9	2010.1	1421.2	6.8	7.0
50.0	1830.2	1399.8	2113.1	1399.0	6.9	6.8
52.0	1827.0	1390.8	2005.1	1373.0	7.1	6.9
54.0	1810.3	1385.9	1981.1	1365.0	7.0	6.8
56.0	1827.7	1421.6	1985.3	1301.7	7.2	7.0
58.0	1801.5	1412.3	1978.0	1278.6	7.0	7.0
60.0	1791.1	1415.5	1995.5	1296.3	6.8	7.1
62.0	1798.5	1416.8	2001.6	1300.2	6.8	7.1
64.0	1803.5	1410.2	2110.3	1297.1	6.9	7.2
66.0	1821.7	1409.9	2100.4	1278.9	6.8	7.1
68.0	1853.6	1412.3	2021.7	1230.8	6.7	7.2
70.0	1831.5	1419.2	2083.8	1251.9	6.9	7.1

DAY	ALKAL 20-1	VALK 20-1	ALKAL 20-2	VALK 20-2	PH 20-1	PH 20-2
72.0	1813.0	1421.8	2131.5	1265.2	7.0	7.2
74.0	1795.9	1419.8	2033.9	1285.9	7.1	7.1
76.0	1775.9	1410.7	2124.5	1291.8	7.2	7.0
78.0	1783.9	1404.7	2194.6	1301.8	7.1	7.0
80.0	1823.6	1402.5	2178.5	1301.8	7.1	6.9
82.0	1845.1	1411.5	2100.7	1290.9	7.2	6.8
84.0	1849.8	1409.7	2156.9	1299.8	7.1	7.0
86.0	1821.9	1407.5	2164.9	1310.9	7.2	6.9
88.0	1837.8	1419.9	2150.9	1307.7	7.1	6.8
90.0	1841.6	1418.7	2170.9	1305.0	7.2	6.9

ABBREVIATIONS

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GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 8-1

HRS	S	SE	GLDE
.0	40.100	40.1	0.0
24.0000	39.273	40.2	0.0
48.0000	38.604	40.1	0.04
72.0000	38.030	39.9	0.03
96.0000	37.421	38.9	0.05
120.000	36.962	39.1	0.06
144.000	36.440	38.7	0.05
168.000	35.850	38.4	0.07
192.000	35.186	38.0	0.08
216.000	34.345	37.6	0.1
240.000	33.524	37.0	0.14
264.000	32.620	37.4	0.15
288.000	31.631	37.5	0.18
312.000	30.556	37.5	0.17
336.000	29.494	36.8	0.19
360.000	28.344	36.7	0.20
384.000	27.104	36.5	0.21
408.000	26.074	36.5	0.24
432.000	25.053	36.3	0.23
456.000	24.141	36.0	0.25
480.000	23.337	35.8	0.26
504.000	22.540	35.7	0.27
528.000	21.750	35.1	0.30
552.000	20.966	34.5	0.31
576.000	20.000	33.9	0.33
600.000	19.518	33.5	0.37
624.000	19.000	33.0	0.39
648.000	18.702	33.8	0.41
672.000	18.336	32.5	0.41
696.000	18.005	32.5	0.4
720.000	17.900	32.4	0.41
744.000	17.786	33.0	0.39
768.000	17.665	33.7	0.4
792.000	17.565	34.0	0.35
816.000	17.465	34.4	0.31
840.000	17.385	35.0	0.28
864.000	17.385	35.8	0.22
888.000	17.385	35.9	0.19
912.000	17.385	36.7	0.20
936.000	17.385	37.0	0.16
960.000	17.385	38.0	0.14
984.000	17.385	38.5	0.15

ABBREVIATIONS

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GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER B-2

HRS	S	SE	GLDE
.0	57.800	57.8	0.0
24.0000	57.180	57.9	0.0
48.0000	56.636	57.7	0.01
72.0000	56.148	57.8	0.01
96.0000	55.703	57.6	0.02
120.000	55.292	57.9	0.02
144.000	54.909	57.3	0.04
168.000	54.551	57.0	0.06
192.000	54.214	57.0	0.05
216.000	53.895	57.1	0.05
240.000	53.592	56.6	0.08
264.000	53.304	56.3	0.09
288.000	53.030	56.0	0.11
312.000	52.767	55.6	0.10
336.000	52.516	55.2	0.13
360.000	52.275	54.7	0.14
384.000	52.043	54.3	0.16
408.000	51.820	54.0	0.18
432.000	51.605	53.6	0.20
456.000	51.398	53.0	0.19
480.000	51.198	52.4	0.20
504.000	51.006	51.8	0.22
528.000	50.800	51.7	0.24
552.000	50.600	51.9	0.27
576.000	50.500	51.5	0.30
600.000	50.400	51.3	0.32
624.000	50.300	51.0	0.33
648.000	50.300	50.8	0.33
672.000	50.400	50.5	0.32
696.000	50.500	50.0	0.31
720.000	50.700	50.2	0.33
744.000	50.900	50.4	0.32
768.000	51.100	50.3	0.34
792.000	51.400	50.1	0.31
816.000	51.700	50.2	0.29
840.000	52.000	50.2	0.27
864.000	52.000	50.2	0.24
888.000	52.000	50.3	0.2
912.00	52.000	50.1	0.15
936.00	52.000	50.2	0.1
960.00	52.000	50.3	0.08
984.00	52.000	50.2	0.09

ABBREVIATIONS

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DIGESTER 8-3

HRS	S	SE	GLDE
.0	62.300	0.0	62.3
24.0000	61.944	0.01	62.5
48.0000	61.662	0.02	62.0
72.0000	61.439	0.02	62.0
96.0000	61.264	0.01	61.9
120.000	61.129	0.00	61.9
144.000	61.030	0.02	61.9
168.000	60.962	0.01	62.0
192.000	60.923	0.03	61.8
216.000	60.810	0.02	61.6
240.000	60.711	0.03	61.9
264.000	60.610	0.04	61.6
288.000	60.510	0.04	61.4
312.000	60.410	0.03	61.3
336.000	60.319	0.04	61.0
360.000	60.211	0.05	59.8
384.000	60.110	0.04	59.6
408.000	60.116	0.05	59.4
432.000	60.017	0.05	59.0
456.000	59.914	0.03	58.8
480.000	59.816	0.04	58.5
504.000	59.711	0.05	58.3
528.000	59.611	0.04	58.0
552.000	59.514	0.06	58.3
576.000	59.410	0.05	58.5
600.000	59.318	0.07	58.3
624.000	58.219	0.09	57.9
648.000	58.112	0.08	58.1
672.000	58.000	0.09	57.8
696.000	58.000	0.10	57.6
720.000	57.900	0.09	57.9
744.000	57.700	0.10	57.6
768.000	57.500	0.12	57.4
792.000	57.200	0.14	57.0
816.000	57.000	0.13	57.4
840.000	56.700	0.15	57.5
864.000	56.400	0.17	56.8
888.000	56.100	0.19	56.5
912.000	55.900	0.20	56.1
936.000	55.700	0.23	56.5
960.000	55.500	0.24	57.0
984.000	55.300	0.27	57.1
1008.00	55.100	0.25	56.7
1032.00	54.900	0.26	56.8
1056.00	54.800	0.27	56.6
1080.00	54.770	0.27	56.7
1104.00	54.770	0.29	56.8
1128.00	54.770	0.28	56.6
1152.00	54.770	0.29	56.7
1200.00	54.770	0.27	56.8
1224.00	54.770	0.28	56.7
1248.00	54.770	0.27	56.7

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DIGESTER 8-4

HRS	S	SE	GLDE
.0	71.200	71.20	0.0
24.0000	71.100	71.20	0.01
48.0000	70.953	69.70	0.02
72.0000	70.899	69.50	0.01
96.0000	70.784	69.30	0.03
120.000	70.688	69.10	0.02
144.000	70.505	69.20	0.04
168.000	70.451	69.00	0.06
192.000	70.325	69.30	0.08
216.000	70.224	69.30	0.09
240.000	70.008	68.00	0.10
264.000	69.894	68.00	0.09
288.000	69.661	68.90	0.08
312.000	69.399	69.00	0.10
336.000	69.005	68.90	0.11
360.000	68.880	68.60	0.10
384.000	68.583	68.30	0.12
408.000	68.383	68.21	0.13
432.000	68.209	68.30	0.15
456.000	67.992	68.20	0.15
480.000	67.840	68.25	0.14
504.000	67.683	68.21	0.15
528.000	67.500	68.20	0.16
552.000	67.400	68.21	0.15
576.000	67.300	68.21	0.16
600.000	67.200	68.21	0.17
624.000	67.100	68.30	0.15
648.000	67.100	68.25	0.15
672.000	67.100	68.21	0.16
696.000	67.100	68.19	0.14
720.000	67.100	68.20	0.15
744.000	67.100	68.30	0.16

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GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESER 10-1

HRS	S	SE	GLDE
.0	40.100	40.1	0.0
24.0000	39.272	39.1	0.01
48.0000	38.600	38.1	0.0
72.0000	38.023	37.6	0.02
96.0000	37.509	35.0	0.03
120.000	37.044	34.2	0.03
144.000	36.616	33.7	0.04
168.000	36.218	31.8	0.05
192.000	35.847	30.5	0.04
216.000	35.497	31.2	0.06
240.000	35.167	31.0	0.07
264.000	34.853	30.8	0.06
288.000	34.555	30.2	0.07
312.000	34.270	30.6	0.08
336.000	33.997	30.1	0.09
360.000	33.736	29.8	0.1
384.000	33.584	29.8	0.13
408.000	33.343	29.6	0.14
432.000	33.110	28.9	0.15
456.000	32.985	27.7	0.16
480.000	32.768	27.0	0.17
504.000	32.458	27.3	0.19
528.000	32.155	27.1	0.2
552.000	31.855	26.8	0.23
576.000	31.555	26.2	0.25
600.000	31.200	25.3	0.30
624.000	30.800	24.1	0.34
648.000	30.400	23.0	0.37
672.000	30.000	21.9	0.4
696.000	29.600	20.8	0.46
720.000	29.400	19.7	0.5
744.000	29.000	19.0	0.58
768.000	28.500	18.2	0.6
792.000	28.009	17.7	0.68
816.000	27.400	17.0	0.7
840.000	26.800	16.6	0.73
864.000	26.200	16.1	0.8
888.000	25.500	16.4	0.82
912.000	24.800	16.5	0.83
936.000	24.100	16.4	0.84
960.000	23.300	16.3	0.88
984.000	22.500	16.4	0.92
1008.00	21.800	16.5	0.94
1032.00	21.200	16.4	0.93
1056.00	20.600	16.3	0.95
1080.00	20.000	16.4	0.94
1104.00	19.500	16.5	0.93
1128.00	19.000	16.4	0 94
1152.00	18.500	16.3	0.95
1176.00	18.006	16.4	0.95
1200.00	17.500	16.4	0.94
1224.00	17.000	16.5	0.95
1248.00	16.500	16.3	0.94
1272.00	16.004	16.4	0.93
1296.00	15.500	16.3	0.94
1320.00	15.100	16.4	0.95
1344.00	14.800	16.3	0.94
1368.00	14.567	16.2	0.93
1392.00	14.567	16.3	0.95
1416.00	14.567	16.4	0.94
1440.00	14.567	16.4	0.95
1464.00	14.567	16.3	0.96
1488.00	14.567	16.4	0.95
1512.00	14.567	16.4	0.94
1536.00	14.567	16.4	0.95
1560.00	14.567	16.3	0.94
1584.00	14.567	16.4	0.95

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DIGESTER 10-2

HRS	S	SE	GLDE
.0	57.8	57.8	0.00
24.0000	56.5	56.0	0.03
48.0000	55.2	56.2	0.02
72.0000	54.0	55.3	0.01
96.0000	52.9	54.0	0.03
120.000	51.8	53.2	0.04
144.000	50.7	52.8	0.05
168.000	49.7	51.0	0.06
192.000	48.7	49.2	0.08
216.000	47.7	48.0	0.15
240.000	46.8	47.3	0.17
264.000	45.9	46.6	0.15
288.000	45.0	45.9	0.16
312.000	44.1	45.0	0.18
336.000	43.2	40.0	0.19
360.000	42.4	35.7	0.2
384.000	41.6	32.9	0.26
408.000	40.7	28.6	0.24
432.000	39.9	26.8	0.26
456.000	39.2	26.0	0.23
480.000	38.4	25.7	0.28
504.000	37.6	24.9	0.29
528.000	36.9	24.0	0.3
552.000	36.2	23.5	0.39
576.000	35.5	23.1	0.47
600.000	34.8	22.8	0.55
624.000	34.1	21.9	0.9
648.000	33.4	22.1	1.2
672.000	32.7	21.7	1.3
696.000	32.1	21.8	1.2
720.000	31.4	21.8	1.5
744.000	30.8	21.9	1.6
768.000	30.2	21.8	1.6
792.000	29.6	21.7	1.4
816.000	28.9	21.8	1.3
840.000	28.4	21.9	1.0
864.000	27.8	22.1	1.6
888.000	27.2	21.5	1.5
912.000	26.6	21.4	1.5
936.000	26.1	21.6	1.8
960.000	25.5	21.7	1.9
984.000	25.0	22.0	1.4
1008.00	24.4	21.9	1.1
1032.00	23.9	21.8	1.2
1056.00	23.4	21.7	1.3
1080.00	22.9	22.0	1.4
1104.00	22.4	22.1	1.5
1128.00	22.0	22.3	1.6
1152.00	21.6	22.1	1.4
1176.00	21.3	21.9	1.5
1200.00	20.9	22.0	1.6
1224.00	20.5	21.8	1.5
1248.00	20.2	21.6	1.4
1272.00	20.0	21.8	1.4
1296.00	19.8	21.9	1.5
1320.00	19.6	22.0	1.6
1344.00	19.4	21.9	1.7
1368.00	19.2	21.9	1.6
1392.00	18.9	21.8	1.5
1416.00	18.8	21.7	1.4
1440.00	18.7	21.6	1.8
1464.00	18.6	21.8	1.7
1488.00	18.5	21.9	1.6
1512.00	18.5	21.8	1.8
1536.00	18.4	21.7	1.6
1560.00	18.4	21.8	1.5
1584.00	18.4	21.9	1.4
1608.00	18.3	21.7	1.4
1632.00	18.3	22.0	1.4
1656.00	18.3	21.9	1.5

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 10-3

HRS	S	SE	GLDE
.0	62.300	62.3	0.00
24.0000	61.717	59.7	0.03
48.0000	61.198	59.0	0.04
72.0000	60.726	58.0	0.03
96.0000	60.293	57.1	0.03
120.000	59.889	56.0	0.05
144.000	59.511	54.9	0.09
168.000	59.156	53.0	0.13
192.000	58.819	52.0	0.16
216.000	58.499	51.4	0.19
240.000	58.194	49.0	0.23
264.000	57.903	47.5	0.27
288.000	57.623	44.0	0.25
312.000	57.355	43.8	0.27
336.000	57.098	42.5	0.26
360.000	56.849	40.0	0.30
384.000	56.610	38.0	0.32
408.000	56.379	35.7	0.33
432.000	56.155	33.8	0.4
456.000	55.939	30.1	0.42
480.000	55.629	28.7	0.43
504.000	55.326	28.0	0.44
528.000	55.029	27.0	0.45
552.000	54.838	25.1	0.5
576.000	54.752	23.6	0.53
600.000	54.601	23.0	0.56
624.000	54.500	22.7	0.6
648.000	54.300	22.0	0.65
672.000	54.100	21.8	0.7
696.000	54.000	21.0	0.78
720.000	53.800	21.0	0.9
744.000	53.500	21.6	0.85
768.000	53.200	21.4	0.95
792.000	52.900	21.5	1.10
816.000	52.500	21.4	1.0
840.000	52.100	21.3	1.3
864.000	51.600	21.3	1.3
888.000	51.000	21.0	1.5
912.000	50.400	19.7	1.6
936.000	49.700	21.2	1.4
960.000	49.000	19.8	1.3
984.000	48.200	20.0	1.5
1008.00	47.500	21.2	1.4
1032.00	45.700	21.3	1.6
1056.00	43.800	21.4	1.5
1080.00	41.800	21.4	1.4
1104.00	39.800	21.5	1.3
1128.00	37.100	21.4	1.4
1152.00	35.300	21.4	1.5
1176.00	33.700	21.5	1.6
1200.00	32.300	21.5	1.7
1224.00	31.100	21.6	1.6
1248.00	30.100	21.6	1.5
1272.00	29.000	21.7	1.4
1296.00	28.000	21.5	1.3
1320.00	27.000	21.4	1.2
1344.00	26.000	21.3	1.1
1368.00	25.000	21.1	1.3
1392.00	24.000	21.0	1.4
1416.00	23.000	21.2	1.5
1440.00	22.000	21.4	1.4
1464.00	21.000	21.5	1.6
1488.00	21.800	21.4	1.6
1512.00	21.500	21.3	1.7
1536.00	21.300	21.2	1.6
1560.00	20.000	21.1	1.5
1584.00	19.900	21.2	1.4
1608.00	19.700	20.9	1.5
1632.00	19.700	21.3	1.5
1656.00	19.700	21.1	1.4
1680.00	19.700	20.0	1.5
1704.00	19.700	19.9	1.4
1728.00	19.700	21.2	1.3
1752.00	19.700	21.3	1.4

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 15-1

HRS	S	SE	GLDE
.0	40.100	39.8	0.01
24.0000	39.272	39.7	0.02
48.0000	38.600	39.0	0.0
72.0000	38.023	39.4	0.03
96.0000	37.509	39.1	0.02
120.000	37.044	38.5	0.03
144.000	36.616	38.0	0.04
168.000	36.218	37.8	0.04
192.000	35.847	37.5	0.05
216.000	35.497	37.0	0.05
240.000	35.167	36.1	0.07
264.000	34.853	35.0	0.09
288.000	34.555	34.2	0.1
312.000	34.270	33.6	0.14
336.000	33.997	33.0	0.16
360.000	33.736	32.5	0.17
384.000	33.584	32.0	0.15
408.000	33.343	31.5	0.17
432.000	33.110	31.1	0.19
456.000	32.985	30.8	0.2
480.000	32.768	30.2	0.24
504.000	32.458	29.7	0.21
528.000	32.155	29.0	0.20
552.000	31.859	28.0	0.25
576.000	31.568	27.3	0.28
600.000	31.283	26.5	0.30
624.000	30.803	25.0	0.32
648.000	30.429	24.6	0.35
672.000	30.060	23.8	0.36
696.000	29.595	22.9	0.37
720.000	29.005	21.9	0.42
744.000	28.500	21.0	0.41
768.000	28.007	20.8	0.45
792.000	26.479	19.7	0.46
816.000	25.935	19.0	0.49
840.000	24.500	18.7	0.50
864.000	23.958	18.2	0.54
888.000	23.324	17.8	0.53
912.000	22.794	17.4	0.57
936.000	22.167	17.5	0.58
960.000	21.442	17.3	0.62
984.000	20.81	17.5	0.65
1008.00	20.103	17.4	0.63
1032.00	19.187	17.3	0.66
1056.00	18.274	17.5	0.68
1080.00	17.404	17.4	0.65
1104.00	16.696	17.3	0.64
1128.00	15.950	17.4	0.65
1152.00	15.207	17.5	0.65
1176.00	14.546	17.6	0.67
1200.00	14.007	17.5	0.68
1224.00	13.751	17.4	0.67
1248.00	13.556	17.5	0.65
1272.00	13.464	17.6	0.66
1296.00	13.302	17.7	0.65
1320.00	13.290	17.6	0.65
1344.00	13.110	17.5	0.66
1368.00	13.013	17.4	0.67
1392.00	13.013	17.5	0.65
1416.00	13.013	17.6	0.64
1440.00	13.013	17.6	0.66
1464.00	13.013	17.5	0.64
1488.00	13.013	17.6	0.65
1512.00	13.013	17.4	0.64
1536.00	13.013	17.5	0.65
1560.00	13.013	17.6	0.66
1584.00	13.013	17.5	0.65

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 15-2

HRS	S	SE	GLDE
.0	57.8	57.9	0.0
24.0000	56.5	56.8	0.0
48.0000	55.2	56.7	0.01
72.0000	54.0	56.8	0.01
96.0000	52.9	56.0	0.02
120.000	51.8	55.1	0.02
144.000	50.7	55.3	0.03
168.000	49.7	54.7	0.04
192.000	48.7	54.3	0.04
216.000	47.7	53.0	0.05
240.000	46.8	52.1	0.08
264.000	45.9	51.5	0.07
288.000	45.0	50.0	0.1
312.000	44.1	49.5	0.09
336.000	43.2	48.7	0.08
360.000	42.4	48.0	0.1
384.000	41.6	47.0	0.1
408.000	40.7	45.7	0.08
432.000	39.9	44.0	0.09
456.000	39.2	43.8	0.1
480.000	38.4	42.4	0.09
504.000	37.6	41.0	0.08
528.000	36.9	39.0	0.1
552.000	36.2	37.8	0.15
576.000	35.5	35.8	0.2
600.000	34.8	34.1	0.19
624.000	34.1	32.0	0.25
648.000	33.4	30.1	0.24
672.000	32.7	27.4	0.3
696.000	32.1	23.2	0.38
720.000	31.4	20.1	0.4
744.000	30.8	18.0	0.42
768.000	30.2	17.1	0.49
792.000	29.6	16.0	0.57
816.000	28.9	16.8	0.65
840.000	28.4	15.9	0.61
864.000	27.8	16.0	0.63
888.000	27.2	15.9	0.69
912.000	26.6	16.1	0.73
936.000	26.1	16.8	0.79
960.000	25.5	17.1	0.81
984.000	25.0	17.6	0.85
1008.00	24.4	17.2	0.87
1032.00	23.9	17.1	0.90
1056.00	23.4	17.4	0.90
1080.00	22.9	17.6	0.89
1104.00	22.4	17.5	0.91
1128.00	21.9	17.4	0.97
1152.00	21.3	17.5	0.98
1176.00	20.9	17.6	0.99
1200.00	20.6	17.5	0.97
1224.00	20.3	17.6	0.97
1248.00	20.1	17.6	0.96
1272.00	19.9	17.5	0.95
1296.00	19.7	17.3	0.96
1320.00	19.5	17.2	0.96
1344.00	19.3	17.3	0.95
1368.00	19.1	17.4	0.96
1392.00	18.9	17.5	0.97
1416.00	18.5	17.6	0.98
1440.00	18.0	17.5	0.98
1464.00	17.5	17.4	0.97
1488.00	17.0	17.5	0.98
1512.00	16.5	17.5	0.98
1536.00	16.1	17.4	0.99
1560.00	15.7	17.5	1.0
1584.00	15.5	17.6	0.99
1608.00	15.5	17.5	0.98
1632.00	15.5	17.4	0.99
1656.00	15.5	17.5	1.0
1680.00	15.5	17.5	0.99

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 15-3

HRS	S	SE	GLDE
.0	62.300	62.4	0.0
24.0000	61.717	62.0	0.01
48.0000	61.198	61.5	0.02
72.0000	60.726	61.2	0.01
96.0000	60.293	61.3	0.02
120.000	59.889	61.1	0.02
144.000	59.511	50.7	0.04
168.000	59.156	50.3	0.05
192.000	58.819	50.1	0.06
216.000	58.499	49.5	0.07
240.000	58.194	49.0	0.09
264.000	57.903	48.4	0.1
288.000	57.623	47.9	0.2
312.000	57.355	46.5	0.28
336.000	57.098	45.0	0.3
360.000	56.849	43.1	0.36
384.000	56.610	41.0	0.31
408.000	56.379	39.2	0.4
432.000	56.155	37.0	0.48
456.000	55.939	35.0	0.50
480.000	55.629	32.8	0.60
504.000	55.326	29.5	0.69
528.000	55.000	28.3	0.70
552.000	54.800	28.1	0.73
576.000	54.600	27.0	0.78
600.000	54.400	26.5	0.82
624.000	54.100	26.0	0.84
648.000	53.000	25.4	0.86
672.000	53.800	24.0	0.9
696.000	53.600	23.0	0.94
720.000	53.300	22.1	0.91
744.000	53.000	21.0	0.95
768.000	52.600	20.6	0.97
792.000	52.200	20.0	0.99
816.000	51.700	19.6	1.19
840.000	51.100	19.0	1.09
864.000	51.400	18.3	1.1
888.000	50.500	17.9	1.08
912.000	49.500	17.8	1.10
936.000	48.400	18.0	1.08
960.000	47.200	18.2	1.08
984.000	46.000	18.2	1.09
1008.00	45.700	18.3	1.1
1032.00	43.300	18.3	1.08
1056.00	41.900	18.2	1.07
1080.00	40.500	18.1	1.06
1104.00	38.900	18.3	1.08
1128.00	37.200	18.2	1.08
1152.00	35.400	18.2	1.1
1176.00	33.500	18.1	1.1
1200.00	31.500	18.1	1.09
1224.00	29.400	18.0	1.1
1248.00	27.300	18.1	1.09
1272.00	25.300	18.0	1.09
1296.00	23.500	17.9	1.09
1320.00	21.800	17.9	1.09
1344.00	20.300	18.0	1.1
1368.00	19.000	18.1	1.09
1392.00	18.000	18.2	1.09
1416.00	17.300	18.1	1.1
1440.00	16.800	18.2	1.1
1464.00	16.400	18.1	1.09
1488.00	16.400	18.2	1.09
1512.00	16.400	18.1	1.1
1536.00	16.400	18.2	1.09
1560.00	16.400	18.0	1.09
1584.00	16.400	17.9	1.1
1608.00	16.400	17.8	1.0
1632.00	16.400	17.9	1.09
1656.00	16.400	18.0	1.10
1680.00	16.400	18.2	1.10
1704.00	16.400	18.3	1.09
1728.00	16.400	18.2	1.0
1752.00	16.500	18.3	1.0
1776.00	16.400	18.3	1.09
1800.0	16.400	18.2	1.1
1824.0	16.400	18.2	1.1

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 15-4

HRS	S	SE	GLDE
24.0000	70.680	69.0	0.01
48.0000	70.208	69.1	0.00
72.0000	69.773	69.9	0.01
96.0000	69.368	68.4	0.02
120.000	68.989	68.2	0.02
144.000	68.600	67.5	0.03
168.000	68.300	67.0	0.02
192.000	67.800	66.2	0.03
216.000	67.400	65.6	0.02
240.000	66.900	65.0	0.02
264.000	66.400	64.3	0.05
288.000	65.000	63.8	0.10
312.000	64.500	63.0	0.09
336.000	64.000	62.0	0.1
360.000	63.400	60.5	0.14
384.000	62.800	59.0	0.14
408.000	62.300	59.4	0.13
432.000	61.700	58.0	0.15
456.000	61.000	56.7	0.16
480.000	60.200	55.0	0.17
504.000	59.400	54.0	0.19
528.000	58.500	52.6	0.21
552.000	57.500	51.0	0.23
576.000	56.500	48.0	0.28
600.000	55.400	45.0	0.30
624.000	54.200	44.9	0.32
648.000	53.100	40.5	0.35
672.000	52.000	35.8	0.38
696.000	51.900	31.0	0.40
720.000	50.800	29.5	0.38
744.000	49.700	28.6	0.41
768.000	48.700	26.8	0.45
792.000	47.700	24.5	0.48
816.000	46.600	23.7	0.5
840.000	45.600	21.0	0.52
864.000	44.600	23.5	0.6
888.000	43.600	23.0	0.68
912.000	42.600	22.0	0.7
936.000	41.600	21.0	0.73
960.000	40.600	20.5	0.8
984.000	39.600	19.9	0.83
1008.00	38.600	19.7	0.86
1032.00	37.600	19.5	0.85
1056.00	36.600	19.3	0.88
1080.00	35.600	19.1	0.92
1104.00	34.600	19.2	1.0
1128.00	33.600	19.0	1.0
1152.00	32.700	19.1	1.2
1176.00	31.800	19.0	1.0
1200.00	31.000	18.9	1.3
1224.00	30.300	18.9	1.29
1248.00	29.600	19.0	1.28
1272.00	29.000	19.1	1.25
1296.00	28.600	19.1	1.28
1320.00	28.200	19.0	1.29
1344.00	27.800	19.1	1.27
1368.00	27.400	18.9	1.29
1392.00	27.000	18.9	1.31
1416.00	26.600	19.0	1.33
1440.00	26.200	19.1	1.31
1464.00	25.800	18.9	1.32
1488.00	25.400	18.8	1.34
1512.00	25.000	18.9	1.32
1536.00	24.600	19.0	1.31
1560.00	24.200	19.1	1.34
1584.00	23.800	19.1	1.32
1608.00	23.300	19.0	1.31
1632.00	22.800	18.9	1.31
1656.00	22.200	18.9	1.32
1680.00	21.700	19.1	1.34
1704.00	21.400	19.0	1.35
1728.00	21.100	19.1	1.34
1752.00	19.900	19.0	1.35
1776.00	19.700	19.0	1.33
1800.00	19.500	18.9	1.32
1824.00	19.300	19.0	1.31
1848.00	19.100	19.1	1.32

1872.00	18.900	19.1	1.33
1896.00	18.700	19.0	1.33
1920.00	18.600	19.0	1.33
1944.00	18.600	18.9	1.31
1968.00	18.600	19.0	1.30

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 20-1

HRS	S	SE	GLDE
.0	40.100	40.1	0.0
24.0000	39.272	40.2	0.01
48.0000	38.600	40.0	0.01
72.0000	38.023	39.5	0.0
96.0000	37.509	39.0	0.02
120.000	37.044	38.1	0.01
144.000	36.616	38.0	0.02
168.000	36.218	37.8	0.03
192.000	35.847	37.0	0.03
216.000	35.497	36.5	0.05
240.000	35.167	35.8	0.05
264.000	34.853	35.0	0.06
288.000	34.555	34.2	0.08
312.000	34.270	33.6	0.09
336.000	33.997	33.6	0.10
360.000	33.736	33.0	0.09
384.000	33.584	32.0	0.08
408.000	33.343	31.4	0.12
432.000	33.110	30.1	0.11
456.000	32.985	29.3	0.13
480.000	32.768	29.5	0.14
504.000	32.458	29.3	0.16
528.000	32.155	29.0	0.17
552.000	31.859	28.3	0.18
576.000	31.568	28.0	0.17
600.000	31.283	27.5	0.16
624.000	30.803	26.0	0.18
648.000	30.429	25.5	0.19
672.000	30.060	25.0	0.20
696.000	29.595	24.5	0.19
720.000	29.005	24.1	0.22
744.000	28.579	23.2	0.25
768.000	28.007	23.2	0.26
792.000	26.479	23.4	0.28
816.000	25.935	23.0	0.27
840.000	24.595	22.0	0.26
864.000	23.958	21.0	0.28
888.000	23.324	20.4	0.29
912.000	22.794	20.2	0.30
936.000	22.167	19.5	0.29
960.000	21.442	19.1	0.31
984.000	20.810	19.0	0.33
1008.00	20.103	18.5	0.40
1032.00	19.187	18.3	0.46
1056.00	18.274	18.1	0.48
1080.00	17.304	17.8	0.47
1104.00	16.496	17.5	0.46
1128.00	15.650	17.4	0.47
1152.00	14.807	17.0	0.48
1176.00	14.206	16.8	0.47
1200.00	13.707	16.2	0.49
1224.00	13.151	15.5	0.50
1248.00	12.706	15.8	0.52
1272.00	12.404	15.4	0.51
1296.00	12.112	14.8	0.50
1320.00	12.110	14.9	0.49
1344.00	12.110	14.7	0.50
1368.00	12.110	14.9	0.51
1392.00	12.110	15.0	0.50
1416.00	12.110	15.1	0.49
1440.00	12.110	15.0	0.50
1464.00	12.110	14.9	0.51
1488.00	12.110	15.0	0.49

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 20-2

HRS	S	SE	GLDE
.0	57.8	57.5	0.0
24.0000	56.5	57.9	0.0
48.0000	55.2	57.0	0.03
72.0000	54.0	57.4	0.01
96.0000	52.9	57.3	0.02
120.000	51.8	57.1	0.03
144.000	50.7	57.0	0.02
168.000	49.7	56.3	0.01
192.000	48.7	55.7	0.03
216.000	47.7	55.8	0.02
240.000	46.8	55.0	0.03
264.000	45.9	54.5	0.04
288.000	45.0	54.0	0.05
312.000	44.1	53.7	0.07
336.000	43.2	53.4	0.05
360.000	42.4	53.5	0.10
384.000	41.6	53.0	0.15
408.000	40.8	52.0	0.20
432.000	40.0	51.9	0.22
456.000	39.2	49.8	0.19
480.000	38.4	49.0	0.28
504.000	37.6	47.9	0.32
528.000	36.8	46.8	0.39
552.000	36.0	45.7	0.42
576.000	35.2	44.8	0.47
600.000	34.4	43.6	0.54
624.000	33.8	42.0	0.59
648.000	33.2	41.0	0.65
672.000	32.6	40.5	0.72
696.000	32.0	39.3	0.58
720.000	31.4	38.0	0.55
744.000	30.8	37.0	0.57
768.000	30.2	35.8	0.59
792.000	29.6	34.0	0.61
816.000	28.9	33.8	0.60
840.000	28.4	32.7	0.62
864.000	27.8	32.9	0.59
888.000	27.2	32.7	0.63
912.000	26.6	31.0	0.64
936.000	26.1	30.8	0.65
960.000	25.5	29.4	0.67
984.000	25.0	28.6	0.64
1008.00	24.4	27.0	0.63
1032.00	23.9	25.8	0.64
1056.00	23.4	23.0	0.65
1080.00	22.9	22.6	0.66
1104.00	22.4	21.0	0.67
1128.00	21.9	20.5	0.69
1152.00	21.3	19.6	0.67
1176.00	20.9	18.8	0.64
1200.00	20.3	18.10	0.65
1224.00	19.9	17.9	0.66
1248.00	19.4	17.1	0.66
1272.00	18.9	17.0	0.67
1296.00	18.5	16.8	0.68
1320.00	18.1	16.5	0.69
1344.00	17.6	16.8	0.69
1368.00	17.3	17.3	0.71
1392.00	17.0	17.2	0.70
1416.00	16.8	17.3	0.69
1440.00	16.6	17.1	0.74
1464.00	16.4	17.0	0.74
1488.00	16.2	17.2	0.75
1512.00	16.0	17.0	0.73
1536.00	15.8	16.9	0.74
1560.00	15.6	17.1	0.76
1584.00	15.4	17.0	0.75
1608.00	15.2	17.1	0.74
1632.00	14.0	17.0	0.73
1656.00	14.9	17.3	0.74
1680.00	14.8	17.2	0.75
1704.00	14.7	17.1	0.76
1728.00	14.6	16.8	0.75
1752.00	14.6	16.9	0.74
1776.00	14.6	16.8	0.75
1800.00	14.6	17.0	0.76
1824.00	14.6	16.9	0.77

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 20-3

HRS	S	SE	GLDE
.0	62.3	62.5	0.0
48.0000	61.198	62.0	0.01
72.0000	60.726	62.2	0.01
96.0000	60.293	62.1	0.02
120.000	59.889	60.9	0.03
144.000	59.511	60.5	0.04
168.000	59.156	60.1	0.03
192.000	58.819	60.5	0.01
216.000	58.499	60.4	0.02
240.000	58.194	59.7	0.03
264.000	57.903	59.1	0.04
288.000	57.623	58.7	0.06
312.000	57.355	58.1	0.08
336.000	57.098	57.9	0.10
360.000	56.849	57.0	0.10
384.000	56.610	56.1	0.09
408.000	56.379	54.8	0.12
432.000	56.155	55.3	0.14
456.000	55.939	55.0	0.15
480.000	55.629	54.0	0.12
504.000	55.326	53.1	0.16
528.000	55.029	51.9	0.14
552.000	54.838	50.3	0.16
576.000	54.752	49.1	0.19
600.000	54.601	47.9	0.16
624.000	54.696	46.8	0.19
648.000	54.525	45.0	0.21
672.000	54.458	44.0	0.16
696.000	54.396	42.9	0.15
720.000	54.138	40.8	0.15
744.000	53.984	39.7	0.17
768.000	53.734	38.6	0.19
792.000	53.587	37.4	0.21
816.000	53.344	36.0	0.22
840.000	53.005	35.5	0.24
864.000	52.769	35.0	0.26
888.000	52.436	33.9	0.24
912.000	52.106	33.1	0.23
936.000	51.779	31.9	0.22
960.000	51.354	29.8	0.21
984.000	50.933	27.7	0.24
1008.00	49.515	25.1	0.26
1032.00	49.098	23.0	0.28
1056.00	48.485	22.4	0.27
1080.00	47.574	21.0	0.25
1104.00	46.565	21.9	0.28
1128.00	45.459	21.5	0.29
1152.00	44.355	20.8	0.30
1176.00	43.252	19.90	0.32
1200.00	42.003	19.7	0.34
1224.00	40.800	18.6	0.32
1248.00	39.600	18.0	0.38
1272.00	38.400	17.9	0.4
1296.00	36.100	18.1	0.42
1320.00	34.500	17.4	0.39
1344.00	32.000	17.3	0.4
1368.00	30.500	17.8	0.38
1392.00	28.000	17.4	0.39
1416.00	26.500	17.9	0.45
1440.00	24.000	17.8	0.47
1464.00	23.400	17.4	0.49
1488.00	22.800	17.9	0.55
1512.00	21.000	17.8	0.60
1536.00	20.400	17.6	0.67
1560.00	19.900	17.5	0.69
1584.00	19.500	17.9	0.70
1608.00	18.100	17.9	0.72
1632.00	17.700	18.10	0.71
1656.00	17.400	18.0	0.75
1680.00	17.100	17.9	0.77
1704.00	16.800	18.2	0.79
1728.00	16.600	18.1	0.8
1752.00	16.400	17.9	0.81
1776.00	16.200	17.8	0.82
1800.00	16.000	17.6	0.84
1824.00	15.900	17.7	0.83
1848.00	15.800	17.9	0.82

1872.00	15.700	17.8	0.83
1896.00	15.600	17.9	0.81
1920.00	15.500	17.8	0.80
1944.00	15.400	17.7	0.81
1968.00	15.300	17.9	0.82
1992.00	15.201	17.8	0.83
2016.00	15.101	17.9	0.82
2040.00	15.102	17.7	0.83
2064.00	15.102	17.8	0.83
2088.00	15.102	17.9	0.82
2112.00	15.102	17.8	0.83
2136.00	15.102	17.9	0.84
2160.00	15.102	17.7	0.83

ABBREVIATIONS

HRS = TIME IN HOURS
S = SIMULATED EFFLUENT CONCENTRATION
SE = MEASURED EFFLUENT CONCENTRATION
GLDE = MEASURED VOLUMETRIC GAS PRODUCTION

DIGESTER 20-4

HRS	S	SE	GLDE
24.0000	70.680	0.01	71.2
48.0000	70.208	0.01	70.6
72.0000	69.773	0.02	71.3
96.0000	69.368	0.05	70.2
120.000	68.989	0.04	69.5
144.000	68.631	0.04	69.0
168.000	68.292	0.04	70.01
192.000	67.870	0.05	69.90
216.000	67.463	0.05	67.54
240.000	66.970	0.06	65.00
264.000	66.488	0.05	63.6
288.000	65.008	0.06	60.80
312.000	64.558	0.07	57.00
336.000	64.007	0.08	55.67
360.000	63.466	0.1	53.89
384.000	62.832	0.11	51.47
408.000	62.306	0.12	49.78
432.000	61.787	0.11	47.00
456.000	61.005	0.12	45.35
480.000	60.200	0.14	43.06
504.000	59.400	0.15	42.25
528.000	58.500	0.18	40.86
552.000	57.500	0.19	39.85
576.000	56.500	0.20	35.78
600.000	55.400	0.22	36.89
624.000	54.200	0.24	34.67
648.000	53.005	0.25	32.39
672.000	51.800	0.26	30.66
696.000	50.600	0.28	31.25
720.000	49.400	0.30	29.36
744.000	48.200	0.32	27.64
768.000	47.000	0.38	25.81
792.000	45.800	0.39	23.59
816.000	44.600	0.38	22.89
840.000	43.400	0.40	20.86
864.000	42.200	0.38	21.89
888.000	41.009	0.40	21.06
912.000	39.800	0.45	20.89
936.000	39.600	0.5	20.00
960.000	39.400	0.55	19.67
984.000	38.200	0.57	19.00
1008.00	37.001	0.55	18.57
1032.00	35.800	0.60	18.10
1056.00	35.600	0.66	17.90
1080.00	34.400	0.72	18.1
1104.00	33.200	0.76	18.3
1128.00	32.000	0.80	18.24
1152.00	30.800	0.83	18.79
1176.00	29.600	0.86	18.5
1200.00	28.400	0.89	18.9
1224.00	28.100	0.92	18.7
1248.00	26.800	0.96	18.1
1272.00	25.500	0.95	18.8
1296.00	24.200	0.94	18.9
1320.00	23.000	0.95	18.8
1344.00	21.800	0.96	18.2
1368.00	20.700	0.96	18.5
1392.00	19.700	0.97	18.2
1416.00	18.900	0.97	18.1
1440.00	18.200	0.98	18.2
1464.00	17.700	0.97	18.5
1488.00	17.300	0.96	18.5
1512.00	17.300	0.97	18.1
1536.00	17.300	0.98	18.9
1560.00	17.300	0.97	18.1
1584.00	17.300	0.98	18.8
1608.00	17.300	0.96	18.1
1632.00	17.300	0.97	18.5
1656.00	17.300	0.95	18.7
1680.00	17.300	0.95	18.2
1704.00	17.300	0.96	18.5
1728.00	17.300	0.96	18.1
1752.00	17.300	0.97	18.5
1776.00	17.300	0.98	18.3
1608.00	17.300	0.99	18.2
1632.00	17.300	0.98	18.6
1656.00	17.300	0.97	18.3

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STIMULUS-RESPONSE DATA
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8-D DIGESTER

QT/V	LN C/C
0.125	-0.356
0.250	-0.416
0.375	-0.545
0.5	-0.892
0.62	-0.867
0.75	-0.994
0.875	-1.20
1.00	-1.51
1.125	-1.56
1.25	-1.83
1.375	-1.97
1.5	-2.04
1.625	-2.21
1.75	-2.41
1.875	-2.58
2.0	-2.75
2.125	-2.90
2.25	-3.10
2.375	-3.24
2.5	-3.41
2.625	-3.58
2.75	-3.69
2.875	-3.91
3.0	-4.14
3.125	-4.27
3.25	-4.42
3.375	-4.71
3.5	-4.71
3.625	-4.83
3.75	-5.12
3.875	-5.30
4.0	-5.52
4.12	-5.52
4.25	-5.81
4.375	-5.81
4.5	-6.21
4.625	-6.21
4.75	-6.91
4.875	-6.90
5.0	-6.21

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STIMULUS-RESPONSE DATA
****

10-D DIGESTER

QT/V	LN C/C
0.2	-0.446
0.4	-0.509
0.6	-1.171
0.8	-1.044
1.0	-1.605
1.1	-1.726
1.2	-1.625
1.3	-1.814
1.4	-2.189
1.5	-2.410
1.6	-2.350
1.7	-2.460
1.8	-2.660
1.9	-2.880
2.0	-2.880
2.1	-2.960
2.2	-3.320
2.3	-3.510
2.4	-3.770
2.5	-3.730
2.6	-4.020
2.7	-4.070
2.9	-4.510
3.1	-4.510
3.3	-4.830
3.5	-5.520
3.7	-5.520
3.9	-5.810
4.1	-6.210
4.3	-6.210

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STIMULUS-RESPONSE DATA
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15-D DIGESTER

QT/V	LN C/C
0.2	-0.478
0.4	-0.611
0.6	-0.798
0.8	-1.255
1.0	-1.427
1.2	-1.609
1.4	-2.120
1.5	-2.397
1.6	-2.489
1.8	-3.016
2.0	-3.170
2.2	-3.650
2.4	-3.817
2.6	-4.335
2.8	-4.509
3.2	-4.828
3.4	-5.116
3.6	-5.522
3.8	-5.809
4.0	-6.215

****
STIMULUS-RESPONSE DATA
****

20-D DIGESTER

QT/V	LN C/C
0.1	-0.3132
0.2	-0.465
0.3	-0.511
0.4	-0.656
0.5	-1.041
0.6	-0.919
0.7	-1.047
0.8	-1.339
0.9	-1.427
1.0	-1.755
1.2	-1.820
1.3	-2.040
1.4	-2.408
1.6	-2.513
1.7	-2.781
1.8	-3.058
1.9	-3.194
2.0	-3.352
2.1	-3.381
2.2	-3.611
2.3	-3.689
2.4	-4.017
2.5	-4.075
2.6	-4.343
2.7	-4.269
2.8	-4.510
2.9	-4.711
3.0	-4.962
3.2	-5.116
3.4	-5.809
3.6	-5.809
3.7	-6.215
3.9	-6.215

****
FRUENDLICH ADSORPTION
ISOTHERM DATA
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LOG X/M	LOG C
0.7724	-1.3010
0.4807	-1.3468
0.4094	-1.4202
0.3030	-1.5768
0.0414	-1.6021
-0.0079	-1.6778
-0.2218	-1.6990
-0.3969	-1.8539
-0.5229	-1.9208
-0.7011	-1.9586
-0.8041	-2.0969
-1.1024	-2.2218
-1.3979	-2.3010
-1.6021	-2.3979
-1.7212	-2.5229
-1.8239	-2.5229

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