KINETIC STUDIES AND PERFORMANCE EVALUATION OF AN ANAEROBIC FIXED-FILM REACTOR TREATING FUEL ALCOHOL WASTEWATER

By

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Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
December, 1987

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ACKNOWLEDGMENTS

I would like to sincerely thank Dr. Enos L. Stover for his guidance, encouragement, and friendship during my staying at OSU. His help has been really appreciated.

I would also like to thank Dr. John Veenstra and Dr. Gary Foutch for serving as committee members and for their valuable suggestions. Special thanks to Dr. Bobby Clary for serving as committee member and for his unconditional help providing the wastewater, as needed, throughout the course of this investigation

A very special thanks to my family for their support and encouragement, with special acknowledgment to my lovely wife Ana for her love, help, and sacrifice during the completion of my degree. I would like to dedicate this work to my daughters Fátima and Diana who always are my source of motivation.

Thanks to all my fellow graduate students, in particular Gomathinayagam Ganapathi, John Burton Barber Jr., Mohamed Abdulhafid, José A. González, and M. Karunanidhi, for their help and assistant when needed.

I also wish to thank Victor Wu and John Witt for their friendship and unconditional help in typing and editing this thesis.

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CHAPTER I

INTRODUCTION

The anaerobic treatment process has been important in organic stabilization since earlier times, but it is only in recent years that anaerobic microorganisms have been studied in sufficient detail to understand their role in the stabilization of organic wastes. With this better understanding, the anaerobic process has been successfully applied to the treatment of high-strength wastewaters. One of these applications is the anaerobic treatment of thin stillage generated during the production of ethanol.

Fermentation of ethanol from agricultural feed stocks such as corn and milo has been demostrated to be a promising energy alternative and a potential new agricultural industry. Gasohol, a blend of 10% anhydrous ethanol and 90% unleaded gasoline, has been shown to be compatible with 100% unleaded gasoline and has received widespread public acceptance. However, two very serious problems of the gasohol industry center around the energy consumption requirements to produce alcohol and the production of high temperature, high-strength, acidic wastewaters. The use of the anaerobic process for the treatment of alcohol wastewaters seems to be the right choice, since methane gas is generated as a by-product and could be used as an energy

source in the alcohol plant; for example, for grain drying, cooking, and temperature control, saving from 50% to 75% of the total energy requirements (1).

The anaerobic degradation of organic matter to methane involves a complex interaction of three major groups of interdependent bacteria and is performed in at least four important steps. The first step is the hydrolysis of complex long chain organics such as polysaccharides, proteins, and fats into their respective monomers. The hydrolytic reactions are catalyzed by enzymes released into the medium by the bacteria. The smaller molecules resulting from hydrolysis are used as carbon and energy sources by bacteria that carry out fermentations. The end products of those fermentations are primarily short-chain volatile fatty acids (such as acetic, propionic, butyric, valeric, and caproic), alcohols and other soluble organics. Their production or second step of the anaerobic metabolism is referred to as acidogenesis performed by the acidogens or acid-producing bacteria. The third step is carried out by a subgroup of the acidogenic bacteria, the acetogens, which oxidize volatile acids longer than acetic, as well as reduced organic compounds released by other bacteria, to acetic acid, carbon dioxide and hydrogen. The fourth and final step is the methanogenesis or methane formation by the methanogens. Methane is produced from acetic acid or from carbon dioxide and hydrogen, although small amounts can be produced from methanol and formic acid (2).

Two different types of anaerobic treatment systems, suspended-growth and fixed-film, have been investigated by the Environmental Engineering group at OSU (3,4), as part of an extensive fuel alcohol wastewater treatability study. Other treatment systems included activated sludge, rotating biological contactor (RBC), and aerated submerged biological filter (ASBF). The wastewater was collected from the OSU Agricultural Engineering fuel alcohol production research facility.

The objective of this research project was to focus on using a continuous upflow, fixed-film, anaerobic reactor in the treatment of fuel alcohol wastewater. A bench-scale reactor was operated for over two years and valuable information was obtained on kinetics, treatability, performance evaluation, and shock load conditions. The reactor was operated at several different substrate loading conditions to collect the appropriate data for definition of the biokinetic constants needed for reliable design and operation of an anaerobic fixed-film treatment system. The substrate removal kinetics, total gas production kinetics, and methane production kinetics were developed in terms of soluble BOD_5, COD, and TOC. Shock load studies were also performed to determine their impact on effluent quality, gas production, and reactor performance. The shock load studies included organic shock loads, temperature shocks, and shut-down periods. Substrate removal, total gas production, and

methane production kinetics were determined at low temperature (25 °C) for comparison purposes.

CHAPTER II

LITERATURE REVIEW

A. Energy from Biomass

Biomass is any material directly or indirectly derived from plant life and renewable in time periods of less than about 100 years. More conventional energy resources such as petroleum, coal, tar sands bitumen, etc., are also derived from plant life, but are not considered renewable. The energy in biomass is the chemical energy associated with the carbon and hydrogen atoms contained in oxidizable organic molecules (5). Processes for conversion of biomass to methane may be classified into two categories: thermal and biological. Thermal processes are limited to feeds with low water content, since the cost for heating and evaporation of the water is very high. Biological gasification, commonly known as anaerobic digestion, is a lower temperature process which is economic at different scales (6). The product gas is primarily methane and carbon dioxide. One study estimated that in the United States, the energy produced from biomass sources by the year 2010 will be less than 10% of the total energy consumed (7). On the other hand, the results of another study showed that the biomass contribution could be as much as 19% by the year 2000 (8).

Typical biomass resources are energy crops, farm and agricultural wastes, municipal waste, and animal waste. The energy crops include three major feedstocks: sugar, starch, and cellulose. Grain or starch crops include corn, wheat, rice, barley, and other cereals. The seed of these plants are typified by their high starch content that can be hydrolyzed to fermentable sugars for ethanol production. The sugar crops, including sugar cane, beet, and sweet sorghum, are preferable to the starch crops to the extent that sucrose is more readily hydrolyzed to fermentable sugars. Grasses, legumes, and short rotation trees are lignocellulosic crops which are less suitable for fermentation to ethanol. Also the crop residues or material left after harvesting are lignocellulosic material that as in the case of grasses are more suited to gasification or direct combustion as an energy source. Breaking of the lignin bonds of the cellulose makes difficult its conversion to ethanol. Processes for conversion of cellulosic biomass to ethanol are, however, being investigated and may prove viable.

In the United States grain crops are the most common feedstock for ethanol production (9). In the middle and late 1970's and early 1980's there was an enormous national interest in alcohol fuels, both as a partial solution to the energy shortage and as a potential new agricultural industry (10). Through 1980 ethanol was primarily used as a gasoline extender. In 1982 several oil companies started

incorporating ethanol into unleaded gasoline in amounts to 10% as a fuel additive, converting standard low-octane lead-free gasoline into a premium-grade fuel. In 1981 the production of ethanol for automotive applications was 100 million gallons (11) and in Oklahoma it was 10 million gallons (12). In 1978 it was implemented in Brazil the National Alcohol Program with the main objective of using alcohol as a fuel for brazilian cars to reduce oil imports. Today 1.2 million cars are supplied with hydrated alcohol as fuel (13). In Brazil the main feedstock for alcohol production is sugar cane.

Most economical analysis assume that a bushel of corn (and most other cereals) is converted to 2.5 gallons of alcohol (9). Egg (14) concluded from a study at Texas A & M University on ethanol production from sweet potatoes that ethanol yield was 137 liters per ton of feed stock, with the major problems being low ethanol concentrations in the beer and poor stillage dewatering properties. The production of ethanol from grains leaves behind a protein-rich stillage. This stillage combined with straw becomes an excellent nutritive source of animal feed (15). The solids can be separated from the water to reduce the volume and increase storage life. The liquid or thin stillage from the screen separation of the solids still contains a significant portion of dissolved proteins and carbohydrates. The concentration of the solids from the thin stillage is not simple and techniques such as evaporation are expensive.

Soil irrigation is an alternative for thin stillage disposal, but care must be taken to assure the soil acidity is not adversely affected since thin stillage is acidic. Another disposal alternative for the thin stillage is anaerobic digestion to produce methane. This alternative looks more viable since the methane produced can be used as an energy source at the alcohol production plant.

B. Treatment of Fuel Alcohol Stillage by Anaerobic Digestion

Different reactor configurations have been investigated in the anaerobic treatment of thin stillage generated during fuel alcohol production. Ward and Murphy (16) used conventional CSTR (Completely Stirred Tank Reactor) type reactor at long hydraulic retention time. The methane gas yield was 6.5 SCF per pound of solid per bushel of corn fermented. Similar results were obtained from milo substrate.

Takamura (17) evaluated the performance characteristics of the CSTR and the packed bed reactors. He fed centrifuged thin stillage as a substrate and observed better performance in terms of removal efficiency and stability in the packed bed reactor at loadings below 5 lbs COD/day/1000 sq. ft. (3.2 Kg COD/day/cu. m.) and hydraulic retention time of 15 days. The CSTR was capable of handling higher loads, at longer hydraulic retention time (20 days). The methane yield

was approximately the same in both cases, 0.45 cu. m. CH_4 per Kg of COD removed (7.2 cu. ft. CH_4/lb COD removed).

Dutt (18) expanded Takamura's work and his results demonstrated higher loadings in the packed bed reactor. Conventional and modified CSTR reactors performance, in single and two-stage configurations, also demonstrated unstability at the higher loadings. The organic concentration and total suspended solids content of the substrate applied to the packed bed reactor in Dutt's study averaged 44400 mg/L total COD and approximately 2% weight total suspended solids. The optimum loading observed, 7.4 Kg COD/day/cu. m. (11 lbs COD/day/1000 sq. ft.), was achieved at a hydraulic retention time of 6 days. At this loading condition the COD removal was 65%, the methane content in the gas was 63%, and the methane yield was 0.37 cu. m./Kg COD removed (5.9 cu. ft. CH_4/lb COD removed). Carbonate additions to the reactor were needed to raise the alkalinity and maintain the pH levels at higher loadings and shorter retention times. Calcium carbonate additions of up to 400 mg/L at 6 days retention time were needed.

Dahad and Young (19) studied the performance of a packed bed reactor treating thin stillage at low organic loadings, 2.0 Kg COD/day/cu. m. (3.0 lbs COD/day/1000 sq. ft.). At this loading condition, COD removal efficiency as high as 89% was obtained with methane yield of 0.375 cu. m. CH_4/Kg COD removed (6.0 cu. ft./lb COD removed). The system responded predictably when the loading rate was doubled.

Lanting and Gross (20) conducted a pilot-scale treatability study on ethanol stillage using an UASB (Upflow Anaerobic Sludge Blanket). At organic loading rate as high as 9.3 Kg COD/day/cu. m. (14 lbs COD/day/1000 sq. ft.) and hydraulic retention time of 10 hours, the system performed satisfactorily with COD removal of 76%, and was able to handle sudden fluctuations in the wastewater concentration with an average of 3400 mg/L. The methane yield was slightly lower compared to the results previously presented, 0.33 cu. m. CH_4/Kg COD removed (5.3 cu. ft. CH_4/lb COD removed). Addition of nitrogen and phosphorus, as nutrients, was found to be necessary and addition of caustic was also necessary to control the pH levels.

Stover et al. (3, 21,) conducted extensive bench-scale treatability studies on fuel alcohol thin stillage using both anaerobic suspended-growth and anaerobic fixed-film reactors. The suspended-growth activated sludge reactor was operated at different organic loading rates in order to develop the substrate removal kinetic constants. These kinetic constants were shown to be a function of the mass substrate loading rates (expressed as food to microorganism ratios, F/M). The system was operated to control the mixed liquor pH around 7.0 and the temperature around 33 ^{o}C to 36 ^{o}C. The alkalinity addition requirements and pH control requirements decreased significantly with increasing sludge retention time (SRT) and wastewater strength. The waste

sludge settling, thickening, and dewatering characteristics were excellent throughout the entire study period.

The average F/M ratios in terms of mixed liquor volatile suspended solids (MLVSS) and influent and effluent substrate concentrations (BOD_5, COD, and TOC) ranged from 0.37 to 2.44 in terms of BOD_5 (0.67 to 5.21 in terms of COD and 0.29 to 1.96 in terms of TOC). The treatment efficiency in terms of BOD_5, COD, and TOC removals was very high when the SRT was maintained at 10 days or greater. Removal efficiencies of 98 to 99 percent were easily obtainable even with the full strength stillage at the SRT of 30 days. Greater than 97 percent $sBOD_5$ removal was achieved at the F/M ratio of 0.85. Below the limiting SRT of 4.0 days, the volatile fatty acids accumulated and the treatment efficiency dropped off dramatically. At the SRT of 2.0 days, the treatment efficiency was negligible with removal efficiencies of around 10 percent. The true cell yields in terms of BOD_5, COD, and TOC were found to be 0.13, 0.08, and 0.25. The endogenous decay coefficient K_d was found to be essentially independent of the specific substrate parameter evaluated with a value of 0.02.

Waste sludge from the anaerobic system was used periodically in batch anaerobic activated sludge studies to evaluate batch removal kinetics compared to continuous system kinetics. The apparent impact of volatile fatty acids accumulation on reaction kinetics in the batch system prevented fair comparison with the continuous system where

volatile fatty acids did not accumulate at the same F/M ratios. When the F/M ratio in the batch system was maintained low enough to minimize volatile fatty acids accumulation, the substrate removal kinetics approached the substrate removal kinetics in the continuous system.

Stover et al. (22) presented a direct comparison of the F/M ratio in a suspended-growth system to the equivalent applied substrate loading rate in a fixed-film system. The mass substrate loading rate in suspended-growth systems is expressed as the food-to-microorganism ratio, while in fixed-film systems the mass substrate loading rate is expressed as the total applied loading rate in pounds of substrate applied per day per 1000 sq. ft. of media surface area. In the suspended-growth systems the mass of microorganisms is measured in pounds, while in the fixed-film systems the mass of microorganisms is expressed in terms of media surface area in 1000 sq. ft. available for attached growth. A graphical method for comparing the substrate removal and gas production in terms of F/M ratio and substrate loading (FSi/A) was developed, such that a direct comparison of F/M to FSi/A was made.

González (23) investigated the effects of high influent solids concentration upon the gas production in the treatment of fuel alcohol thin stillage using an anaerobic suspended-growth reactor, as part of the treatability studies conducted at OSU. Volatile suspended solids concentration of around 2400 mg/L added to the reactor

resulted in gas production increase. When the solids concentration was increased to around 3900 mg/L, its impact on the system could not be determined due to mechanical problems which caused the sludge retention time to decrease from 29 days to 14 days due to the loss of solids through the effluent line. At this condition the removal efficiency in terms of BOD_5 and COD decreased to 90% and the gas production dropped from 27 L/d to 18 L/d.

C. Anaerobic Treatment Process

For aerobic processes the cost of aeration increases with increased organic matter concentration, and above 5-10 Kg COD/cu. m. the system becomes oxygen transfer limited (24), and results in increasing hydraulic retention time to ensure sufficient oxygen supply. For such wastes, anaerobic treatment has been economical attractive.

C.1. Biochemistry

The biochemistry of anaerobic processes is much more complicated than that of aerobic processes, due to the many pathways available for an anaerobic community. The pathways and microorganisms responsible for the reactions are not known in detail, but during the last 15 years a broad outline of the processes has been described by a number of investigators (25, 26, 27, 28, 29).

A short review of the biochemistry of anaerobic process is presented in this section. The reactions start with the

complex organic substrates which must be metabolized to simple soluble organic compounds before being converted to energy for cell synthesis. In order for the bacteria to metabolize these complex organics, they must first be hydrolized to small molecules. The three major groups of complex organics are carbohydrates, proteins, and fats. Carbohydrates and proteins are hydrolyzed to simple sugars and amino acids, respectively, which can easily move across the cell wall into the bacteria. The fats are hydrolyzed to glycerol and long chain fatty acids. Glycerol can pass across the cell wall, but the fatty acids are too large to pass. They dissolve into lipids located on the bacteria cell surfaces and are pulled into the cell while being metabolized by beta oxidation. Hydrolysis is normally the first step in the chain of reactions to occur in an anaerobic reactor. Hydrolysis of complex organics occurs on the bacteria surface when the bacteria comes into direct contact with the organic solids. The bacteria surface is actually a series of hydrolytic enzymes held together with a lipo-polysaccharide framework. The enzyme reactions add water to the molecules in contact with the enzymes. The end products glucose, amino acids, and glycerol are soluble in water and diffuse through the cell wall. The fatty acids which can not diffuse across the bacteria cell wall dissolve in the lipids on the cell surface and move into the cell. Once they reach the interior of the cell wall the metabolic reactions begin with the terminal methyl group being

oxidized to a carboxyl group and then tie up with a CoA enzyme. Beta oxidation occurs with hydrogen being removed from the fatty acids and water added to the double bond that resulted. Hydrogen is removed from the hydroxy acid to yield a beta keto acid which is split by another CoA enzyme. The acetyl-CoA moves on to other reactive sites while the fatty acid, now two carbons shorter, undergoes further beta oxidation as it is literally pulled into the lipids on the bacteria surface. If the fatty acids contain an even number of carbon atoms, the ultimate breakdown is to acetyl-CoA. If the fatty acids contain an odd number of carbon atoms, the breakdown products will be acetyl-CoA and formyl-CoA. Simple organics diffuse through the bacteria cell wall and undergo metabolism. Glucose and fructose are broken down to short chain volatile acids while amino acids are hydrolyzed to form hydroxy acids. The hydroxy acids undergo beta oxidation to form acetyl-CoA and possibly, formyl-CoA. The end products also include reduced organics such as aldehydes, ketones, and alcohols. Part of the organics are reduced to methane and part are oxidized to carbon dioxide. The balance between carbon, hydrogen, and oxygen determine the ultimate end products. The methane bacteria use the hydrogen from the beta oxidation reactions to reduce the carbon dioxide in solution within the cell to form methane. The acetyl-CoA formed from metabolism of many of the organics can be split to yield methane and carbon dioxide.

In this reaction the CoA enzyme is regenerated to react with more substrate (30).

C.2. Microbiology

Early anaerobic microbial studies were done with mixed cultures rather than with pure cultures. The microorganisms were identified by size and shape. It appeared that bacteria were the primary anaerobic microorganisms with a few protozoa as secondary microorganisms. It was found that some of the anaerobic bacteria were not strict anaerobes, but were facultative. It was noted that some bacteria used special electron acceptors such as sulfates and carbon dioxide. These anaerobic bacteria produced various reduced compounds including hydrogen sulfide, and methane was an end product of carbon dioxide reduction. The facultative bacteria can metabolize either aerobically or anaerobically. The most common group of facultative bacteria are the Pseudomonas . Alcaligenes, Flavobacterium, Achromobacter and the various enteric bacteria are common facultative bacteria that have been identified in wastewater treatment systems (30). The obligate anaerobic bacteria are strict anaerobes sensitive to oxygen. Clostridium is the major group of strict anaerobes and they produce spores in order to survive in aerobic conditions. The sulfate reducing bacteria are also strict anaerobes that belong to Desulfovibrio. These bacteria are able to metabolize a large number of organic compounds while reducing sulfates to various intermediates,

including free sulphur and hydrogen sulfide. The methane bacteria are strict anaerobes that require a strongly reduced environment for metabolism. They are grouped primarily by shape, Methanobacterium (rods), Methanosarcina (curved), and Methanococcus (spheres). Four new genera have been added: Methanobrevibacter, Methanomicrobium, Methanogenium, and Methanospirillum (31). Only a few of the methane bacteria have been isolated in pure culture. Although bacteria are the primary microorganisms in anaerobic systems, protozoa have been noted in some systems. The protozoa appear when the organic load and the microbiological activity are quite high. Initially, the anaerobic protozoa are flagellated protozoa, Mastigophera, while a few free swimming ciliated protozoa, Ciliata, have appeared.

C.3. Rate-Limiting Step in Anaerobic Digestion

The rate limiting step in anaerobic digestion depends on the loading rate, the characteristics of the organic components being treated, and the predominant bacterial population (32). In anaerobic digestion of municipal wastewater and refuse sludges, hydrolysis is rate-limiting due to the slow degradation of the lipids fraction (33). In simple organics such as compounds found in petrochemical wastewaters, little or no hydrolysis is required. These organic acids, alcohols, aldehydes, ketones, etc., must be

converted to acetate, hydrogen, and carbon dioxide, and this step may be rate-limiting. Acetate conversion to methane may also be rate-limiting due to several reasons. One of these reasons may be a decrease in temperature which would reduce the rate of acetate conversion to methane due to the strong dependence of methanogenesis on temperature (34). Another reason which may cause acetate conversion to methane to become rate-limiting may be the absence of required nutrients, particularly lack of iron.

Conversion of acids to methane can be rate-limiting in the digestion of sewage sludge and purified cellulose, while the rate-limiting step in straw digestion is the degradation of the cellulosic substrate. Robbins et al. (35) tested the influence of lignin on cellulose degradation and methane production. They found that the delignified straw was almost entirely digestible whereas untreated straw was only about 32% degradable. Healy and Young (36) established that a number of compounds which make up the lignin polymer could be degradable to methane and carbon dioxide by adding domestic sludge digester bacteria.

Barber (37) studied the rate-limitation in the treatment of piggery waste using fixed-film reactors. He concluded that hydrolysis was the rate-limiting step up to an organic loading rate of 17 Kg COD/day/cu. m. (25 lbs COD/day/1000 sq. ft.). At a load of approximately 10 Kg COD/day/cu. m. (15 lbs COD/day/1000 sq. ft.) the rate of acetogenesis started decreasing while the rate of

methanogenesis did not, so acetogenesis becomes rate-limiting before methanogenesis. Also during this study, mathematical expressions were developed to describe the metabolic processes (hydrolysis, acidogenesis, acetogenesis, and methanogenesis).

CHAPTER III

MATERIALS AND METHODS

A. Experimental Approach

A.1. High Temperature Biokinetic Constants

In order to obtain the kinetics information on substrate removal, total gas production, and methane production at high temperature, a bench-scale, fixed-film, continuous upflow anaerobic reactor was operated at ten different organic loading conditions keeping the temperature at 36 $\pm$ 2 ^{o}C. At each condition, data was collected every other day for a period of two to three weeks. For every change in loading condition, a minimum period of one to two weeks was allowed to stabilize the system at that new condition. During these organic loading transition periods, the effluent volatile fatty acids (VFA), alkalinity, and pH were routinely monitored. When the VFA appeared to be stable and the ratio VFA to alkalinity was kept at less than 0.5, the system was considered to be operating at steady state. After steady state condition was reached, data collection started. The data collected included the following:

Influent

Flow rate, pH, alkalinity, suspended solids, volatile

suspended solids, soluble and total BOD_5, soluble and total COD, and soluble and total TOC.

Reactor Liquor

Volume wasted, pH, temperature, suspended solids, volatile fatty acids, and alkalinity.

Effluent

PH, temperature, alkalinity, volatile fatty acids, suspended solids, volatile suspended solids, soluble and total BOD_5, soluble and total COD, and soluble and total TOC.

Gas

Total gas production and carbon dioxide analysis.

Most of the organic loading conditions were established by keeping constant the influent flow rate and changing its strength. When the influent strength was kept constant and the flow rate was changed the same results were obtained. This confirm one more time that the performance and efficiency of fixed-film systems do not depend only upon the substrate concentration or hydraulic flow rate but, rather, upon total organic (substrate) loading as previously presented (38). In order to achieve the high organic loadings both flow rate and substrate concentration were changed.

A.2. Low Temperature Biokinetic Constants

To obtain the biokinetic constants at low temperature,

the same approach as for high temperature kinetics was followed. During this low temperature study, the temperature of the reactor was kept at 25 ± 2 °C while the system was operated at three different organic loading conditions.

A.3. Shock Load Studies

The capabilities of a fixed-film anaerobic reactor to handle shock loads relative to changes in flow rate, organic loading rate, temperature, and shut-down or no feeding periods were investigated. The impacts of changing organic loading rate were studied by doubling the influent flow rate for a period of 24 hours, at the same BOD_5 and COD concentrations. Throughout this experimental test period the reactor temperature was maintained at 36 ± 2 °C.

For a period of four days the temperature of the reactor was kept at 26 ± 2 °C to see the impacts of dropping the temperature 10 ± 2 °C. This low temperature test period started four days after the organic shock loading, once the system was at steady state condition.

Immediately after the low temperature test, the feed to the reactor was stopped for a period of 16 days keeping the temperature at 26 ± 2 °C to see the combined effects of low temperature and non-feeding. During days 15 and 16 of the shut-down period, the reactor temperature was increased back up to 36 ± 2 °C. The reactor was fed for a period of 7 days prior to being shut-down again for 11 days keeping the

temperature at 36 $\pm$ 2 ^{o}C. The temperature of the reactor was changed by changing the room temperature.

In order to define the impacts of these shock load conditions, data was collected prior to each shock load to have a reference or background. Also, data was collected during and after each shock load condition.

B. Wastewater Characterization

The wastewater or thin stillage used during this study was collected from the Oklahoma State University Agricultural Engineering 200,000 gallon per year capacity fuel alcohol research facility. This wastewater had been previously subjected to characterization and pretreatment investigations during previous studies at OSU (39) and the results of the wastewater characterization are presented in Table I. The wastewater was collected during batch operations of the research facility with a frequency of approximately one month. The temperature of the wastewater coming out of the distillation column was approximately 75 ^{o}C. The wastewater was allowed to cool down to room temperature and settle, before the supernatant was fed to the bench-scale reactor used for the studies. The waste was collected in 15 gallon stainless steel drums and stored at room temperature. Every new batch of wastewater was characterized immediately after collection, in terms of total and soluble BOD_5 and COD, suspended solids, and volatile suspended solids. The pH and strength of the

TABLE I

RAW WASTEWATER (THIN STILLAGE) CHARACTERISTICS*

Parameter**	Corn Feedstock		Milo Feedstock	
	Mean	Standard Deviation	Mean	Standard Deviation
TS	32200	9300	42800	2150
TDS	18600	7100	20400	6800
SS	11800	3700	22500	5100
VSS	11300	3500	19500	2600
Total COD	64500	12600	75700	12100
Soluble COD	30800	6200	40700	9100
Total BOD_5	26900	800	34900	2000
Soluble BOD_5	19000	2100	21700	1360
Soluble TOC	9850	2200	14900	2600
Total P	1170	100	1280	100
Soluble P	1065	75	1075	150
Total TKN	755	115	-	-
Soluble TKN	480	95	-	-
Soluble NH_3-N	130	60	-	-
Total Protein	4590	650	-	-
Soluble Protein	2230	780	-	-
Total Carbohydrate	8250	750	-	-
Soluble Carbohydrate	2250	550	-	-
Soluble Glucose	<750	-	-	-
pH (range)	3.3-4.0	-	3.5-4.0	-

* Taken from Reference (39)
** All units in mg/L except pH

wastewater decreased as it became older. This change could have been due to some biological activity still going on from the previous production processes causing its degradation.

C. Bench-Scale Unit

A bench-scale, fixed-film, continuous up-flow anaerobic reactor similar to the one shown in Figure 1 was used in this study. The reactor was fabricated of plexiglass with a total empty bed reactor volume of 0.5 cu. ft. (14.2 liters). The support media used was plastic media with a specific surface area of 42 sq. ft./cu. ft. and it was contained in 0.4 cu. ft. of the total reactor volume to yield a total surface area of 16.8 sq. ft. The influent wastewater was pumped into the bottom of the reactor and distributed by a distribution plate. The wastewater flowed up through the reactor bed and out the side of the reactor. A small amount of head space or freeboard (0.1 cu. ft., 2.8 liters) was provided at the top of the reactor. Also, a sample port was provided at the bottom of the reactor in order to monitor the reactor liquor at the bottom. To prevent solids accumulation at the bottom of the reactor, a constant volume of liquor, 200 mL, was arbitrary wasted on a daily basis.

The reactor was initially seeded with anaerobic bacteria brought from the Stillwater municipal treatment plant anaerobic digester. For a period of approximately one month, small amounts of acclimated seed (approximately 400

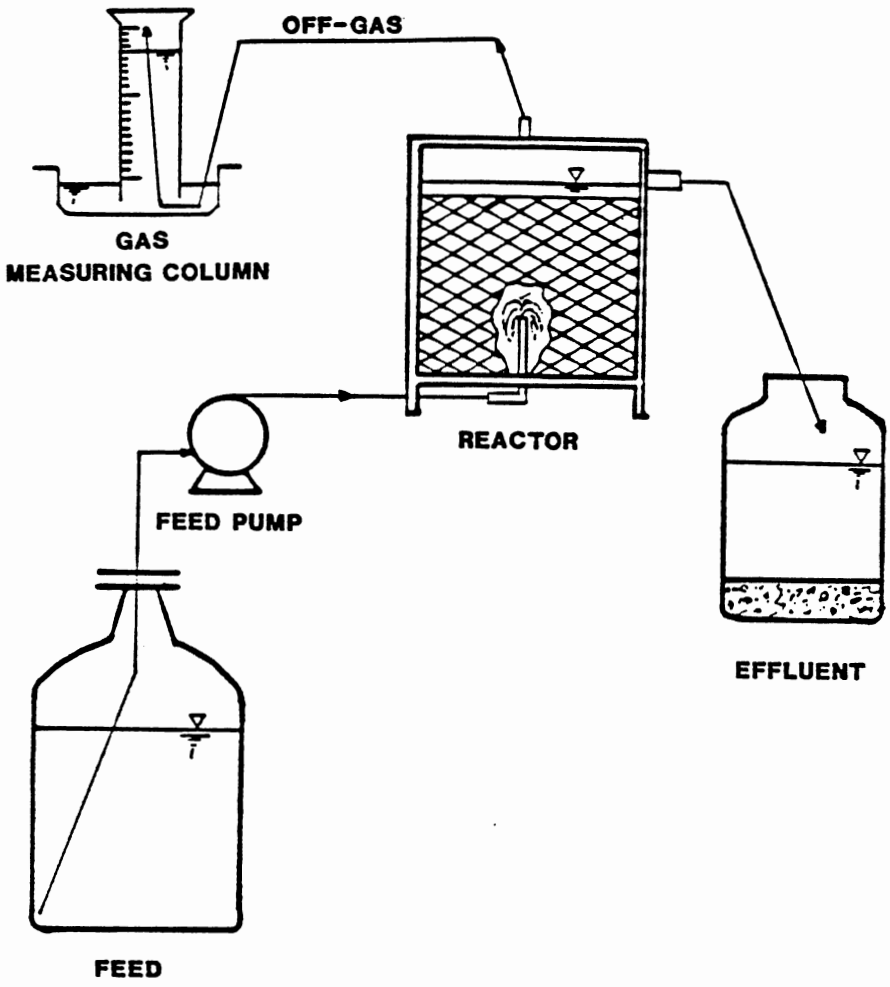

Figure 1. Schematic of the Bench-Scale Fixed-Film Anaerobic Reactor

mL), from another bench-scale, suspended growth anaerobic reactor, were added to the system on a daily basis until considerable attached growth was observed on the packing media and acclamation was obtained. The reactor was initially fed with diluted wastewater with a BOD_5 of 300 mg/L and the strength of the waste was slowly increased over a period of two months until the first organic loading condition for data collection was reached, BOD_5 of 2,000 mg/L.

The wastewater was pumped into the reactor at rates from 2.0 mL/min (2.88 L/day) to 11.6 mL/min (16.66 L/day) yielding hydraulic retention times from 4.0 to 0.7 days. The pH of the wastewater was adjusted with sodium hydroxide on a daily basis in order to keep the reactor liquor pH at around 7. This adjustment of the feed pH was only necessary when the system was operated at low organic loadings, while at high organic loadings the buffering capacity of the system appeared to increase not requiring any feed pH adjustments. Ammonium chloride and phosphoric acid were added to each feed in order to insure the presence of nutrients and keep the BOD_5:N:P ratio at 100:5:1.

The temperature of the reactor was kept at 36 $\pm$ 2 ^{o}C by controlling the room temperature.

D. Gas Production Measurement

Gas production is one of the best diagnostic tools

to evaluate the performance of any anaerobic reactor. The gas produced by the reactor was measured using water displacement from a graduate glass cylinder, as shown in Figure 1. The glass cylinder was filled with water several times a day in order to get an average of the daily gas production expressed in liters per day and corrected to standard temperature and pressure. The quality of the gas was determined on a weekly basis by measuring the carbon dioxide content of the gas.

E. Analytical Procedures

E.1. Biochemical Oxygen Demand, BOD_5

The BOD_5 of the samples was determined following the procedure outlined in Standard Methods for the Examination of Water and Wastewater (40). Since the alcohol wastewater was a very complex waste, seeding with acclimated micro-organisms was required and a seed correction factor was applied. An Orion Research Oxygen Electrode, Model 97-08-00, was used to measure the dissolved oxygen.

E.2. Chemical Oxygen Demand, COD

The COD tests were conducted following a modified procedure of the Hach Chemical Company COD test procedure explained in the Procedures Manual (41). This modified COD test procedure was inadequate in that it failed to measure certain components of the alcohol wastewater. The acid reagent used in this modified procedure was only one half of

the normality suggested in the Standard Methods (40). As a result of this, the measured COD of the wastewater was less than what it actually was.

The inaccuracy of this COD test procedure was observed toward the end of the study by additional testing at more stringent oxidation conditions. It was found that the COD values obtained using this modified COD test procedure were 1.4 times lower than the COD values obtained using the COD test procedure outlined in the Standard Methods (40). The COD values reported in Chapter IV were not corrected to the actual numbers. The use of these values yields conservative kinetics and explains the discrepancy between the stoichiometric and actual methane production rates.

E.3. Total Organic Carbon, TOC

The TOC of the samples was determined by using a Beckman Model 915, TOC analyzer and comparing the sample response curve to standard solutions response curves.

E.4. Suspended Solids, SS and Volatile Suspended Solids, VSS

Suspended solids were determined by filtering the sample through a preweighed glass microfibre filter (Whatman 934-AH, 4.25 cm dia.), drying in an oven at 103 ^{o}C $\pm$ 2 ^{o}C for at least one hour, and reweighing. Following suspended solids determination, the filter was combusted in a muffle

furnace at 550 °C ± 50 °C for twenty minutes and then reweighed.

E.5. pH

The pH determinations were made by using an Orion Research Model 601A/Digital Ionalyzer pH meter with an Orion combination pH 91-05 electrode.

E.6. Volatile Fatty Acids, VFA and Alkalinity

The volatile fatty acids were determined by the procedure developed by Dilallo and Albertson (42). In this method 50 mL of sample is titrated to pH 4 with the appropriate sulfuric acid strength, the volume of acid used is recorded to determine alkalinity, and then the titration is continued to pH 3.5 to 3.3. The sample is boiled for 3 minutes to remove dissolved carbon dioxide, then cooled to original temperature and back titrated from pH 4 to pH 7 with the appropriate sodium hydroxide strength. For the calculation of the volatile acids alkalinity (as $CaCO_3$), the following equation is used:

Volatile Acid Alkalinity = mL NaOH x Normality NaOH x 1,000

To convert from volatile acids alkalinity to volatile acids as acetic acid, a conversion factor should be used:
for volatile acids alkalinity (VAA) higher than 180 mg/L,

Volatile Acids (as acetic acid) = VAA x 1.5

For volatile acids alkalinity lower than 180 mg/L,

Volatile Acids (as acetic acid) = VAA x 1.0

The alkalinity can be obtained using the following formula:

Alkalinity (as $CaCO_3$) = mL H_2SO_4 x Normality H_2SO_4 x 1,000

E.7. Gas Analysis

Methane and carbon dioxide are the two major components of the off-gas from an anaerobic reactor. The methane content was measured indirectly by measuring the carbon dioxide content and assuming 2% of other gases, H_2S and H_2 (43).

% Methane = 100 - % CO_2 - 2

The carbon dioxide content of the off-gas was measured as described in the handbook "Operation of Wastewater Treatment Plants" (43). In this method, the carbon dioxide is absorbed into a potassium hydroxide solution and by difference in volumes the percent of carbon dioxide in the off-gas is determined.

CHAPTER IV

RESULTS AND DISCUSSION

A. Performance Evaluation

The bench-scale, fixed-film, anaerobic reactor was operated for a period of approximately two years in order to obtain the information needed to evaluate its performance treating fuel alcohol wastewater (thin stillage) and develop the biological kinetic constants.

Table II presents the average influent wastewater feed characteristics to the reactor at different organic loading conditions. The values presented in Table II are the average of data collected over a period of a minimum of two to three weeks at each condition. After making changes to a new condition, the system was allowed to reach steady state before collecting data. The period of acclimation ranged from one to two weeks.

Table III presents the average treated effluent characteristics and Table IV presents the analysis of the data in terms of substrate removal and gas production. The values from Tables III and IV are also the average of data collected over a period of two to three weeks at each condition.

An important observation made during the studies was

TABLE II

INFLUENT FEED CHARACTERISTICS

Loading Condition	Si* BOD$_5$ (mg/L)	Si* COD (mg/L)	Si* TOC (mg/L)	Flow (L/d)	pH	Alkalinity (mg/L as $CaCO_3$)	SS (mg/L)	VSS (mg/L)
1	1777	2512	763	2.88	6.6-8.5	2580	443	359
2	3968	5696	2858	2.81	6.0-6.5	2400	702	582
3	7485	10102	3088	2.87	5.2-5.9	3222	1250	1058
4	12167	18445	5917	3.22	5.1-5.6	2763	1409	1100
5	6450	8300	-	6.28	5.0-6.8	3900	563	554
6	15499	23911	-	4.45	5.1-6.3	3206	1352	887
7	6797	9851	-	9.30	5.2-7.3	-	576	491
8	12742	21429	-	11.54	5.1-7.4	4480	440	354
9	12233	16022	-	16.66	5.9-9.0	4311	456	321
10	15259	21362	-	14.40	-	-	-	-

*Si = Soluble BOD$_5$, COD, and TOC

TABLE III

EFFLUENT CHARACTERISTICS

Loading Condition	Se* BOD5 (mg/L)	Se* COD (mg/L)	Se* TOC (mg/L)	Temp. (°C)	pH	Alkalinity (mg/L as $CaCO_3$)	VFA (mg/l as Ac.Acid)	VFA / ALK	SS** (mg/L)	VSS** (mg/L)
1	34	131	80	32-34	7.0-8.1	1059	0(E)	0	156	117
2	57	215	179	30-32	7.8-7.9	1500	0(E)	0	234	159
3	140	271	183	31-35	7.8-8.0	1020	0(E)	0	318	207
4	390	756	479	31-36	7.1-7.7	1700	0(E)	0	804	550
5	515	742	-	35-37	6.5-7.1	1085	190(E)	0.17	542	400
6	2495	3159	-	36-39	5.6-7.7	2291	2405(E)	1.05	787	509
7	1024	1484	-	32-37	6.5-7.2	1854	605(E)	0.34	385	341
8	2974	3800	-	34-36	7.0-7.7	5050	3000(E) 300(B)	0.59 0.06	289	224
9	5493	5927	-	32-36	6.0-7.6	4036	3846(E) 598(B)	0.95 0.15	598	408
10	10955	14242	-	-	-	3100	3200(E) 2400(B)	1.03 0.77	-	-

*Se = Soluble BOD_5, COD, and TOC
** Clarifier Supernatant Solids
(E) = Effluent Sample
(B) = Sample from the Bottom of the Reactor

TABLE IV

SUBSTRATE REMOVAL AND GAS PRODUCTION

Loading Condition	Loading Rate* (lb/d/1000 sq. ft.)			Removal Rate* (lb/d/1000 sq. ft.)			Percent Removal			Actual Gas**			cu.ft.CH_4/lb Removed		
	BOD_5	COD	TOC	BOD_5	COD	TOC	BOD_5	COD	TOC	Production	$\%CO_2$	$\%CH_4$	BOD_5	COD	TOC
1	0.68	0.95	0.29	0.66	0.90	0.26	98	95	88	5.70	21	77	14.74	11.40	36.47
2	1.46	2.10	1.06	1.44	2.02	0.99	98	96	93	10.33	23	75	11.22	8.09	15.43
3	2.83	4.01	1.14	2.78	3.90	1.06	98	98	93	21.04	29	70	11.19	8.36	28.29
4	5.14	7.68	2.94	4.97	7.36	2.79	97	96	94	42.89	39	60	10.87	7.24	23.53
5	5.25	6.93	-	4.82	6.83	-	92	91	-	40.15	40	59	10.18	7.99	-
6	9.03	14.44	-	7.09	12.55	-	84	88	-	65.97	37	62	11.45	7.28	-
7	8.28	12.53	-	7.02	10.63	-	85	85	-	49.84	37	62	9.22	6.36	-
8	19.12	23.45	-	14.52	18.91	-	76	81	-	106.16	39	60	9.05	5.01	-
9	26.98	34.82	-	14.65	21.87	-	53	63	-	110.15	39	60	9.43	6.29	-
10	28.85	40.39	-	8.14	13.50	-	28	33	-	35.76	-	-	-	-	-

Soluble BOD_5, COD, and TOC

** Gas Volume Corrected to Standard Conditions (0 °C, 1 atm)
Gas Production in L/d

that the buffering capacity of the reactor appeared to increased with increasing organic loading rate. At low loading conditions, the feed pH had to be adjusted on a daily basis in order to keep the reactor liquor pH at around 7. But, at loading rates higher than approximately 3.0 lbs BOD_5/d/1000 sq. ft., the feed pH was adjusted to approximately 5.5 only at the time of feed preparation, and the pH of the reactor liquor held at around 7, as can be observed from Tables II and V.

From Tables III and IV it can be seen that no volatile fatty acids were observed in the effluent until the fifth loading condition, 5.25 lbs BOD_5/d/1000 sq. ft.. As the BOD_5 loading rate was increased above 5.25 lbs/d/1000 sq. ft., the volatile fatty acids concentration at the top of the reactor (effluent) increased faster that at the bottom of the reactor. This was due to the high loading rates in these plug flow reactors. At the bottom of the reactor, the substrate loading was higher than the system's acid formers could effectively convert into volatile fatty acids and the methane formers could effectively convert the volatile fatty acids to methane. However, as the substrate load progressed up through the reactor, more volatile fatty acids were produced. The volatile fatty acids production rate was faster than the methane production rate, and thus the volatile fatty acids concentration increased in a cumulative manner as the substrate load progressed upwards. Finally, the methane formers activity was severely hindered or

TABLE V

REACTOR LIQUOR CHARACTERISTICS

Loading Condition	pH	Temp. (°C)	Wastage (L/d)	SS (mg/l)	Observed Yield*		
					BOD_5 (lb sludge	COD prod./lb	TOC removed)
1	6.7-6.8	38-39	0.17	183	0.090	0.098	0.22
2	6.9-7.0	35-39	0.21	109	0.060	0.043	0.25
3	6.9-7.1	38-43	0.18	244	0.043	0.032	0.11
4	6.8-7.3	37-41	0.20	897	0.068	0.045	0.15
5	6.9-7.1	37-39	0.20	306	0.091	0.072	-
6	6.7-7.4	35-40	0.20	1794	0.061	0.038	-
7	6.9-7.1	36-41	0.20	880	0.067	0.046	-
8	7.3-7.7	37-41	0.20	342	0.030	0.016	-
9	7.2-8.2	36-41	0.20	224	0.089	0.059	-
10	-	-	-	-	-	-	-

* Soluble BOD_5, COD, and TOC

inhibited by the high volatile fatty acids concentration, and as the substrate load increased, the volatile fatty acids in the bottom of the reactor approached the same concentration as in the effluent. At the highest loading rate of 28.85 lbs BOD_5/d/1000 sq. ft., the volatile fatty acids content at the bottom and the top of the reactor were 2,400 and 3,200 mg/L respectively. At this loading rate, the reactor was unstable and difficult to operate and the treatment efficiency deteriorated to around 30% BOD_5 and COD removals. Cohen (44) reported the predominance of propionic acid during unstable anaerobic digestion as a common occurrence, and he stated that propionic acid is a preferred electron sink product at low pH conditions, and once formed is relatively difficult to degrade. Also, propionic acid is not a known methanogenic substrate and must pass through acetogenesis before methane can be formed.

An important parameter in the operation of any anaerobic reactor is the volatile fatty acids to alkalinity ratio, VFA/ALK. This ratio is an indicator of the performance of the system and as long as its value is less than 0.5, the system should be able to accommodate moderate variations in the volatile fatty acids concentrations with little fluctuation in pH. A rise in the ratio above 0.5; however, is indicative of an imbalance within the system as well as a lack of reserve buffering capacity. If the ratio rises above 0.8 the system is likely to experience a severe drop in pH from even small changes in volatile fatty acids.

As can be observed from Table III, the VFA/ALK ratio was very low for the first eight loading conditions, except for the sixth condition, indicating good performance with organic removal rates higher than 80%. At the ninth and tenth conditions, the VFA/ALK ratios increased to 0.95 and 1.03, respectively, along with the poor performance and the low organic removal rates experienced by the system at these high organic loadings previously discussed.

As can be readily observed in Table IV, both treatment efficiency and methane production rate decreased as the total substrate loading rate was increased. The gas quality was around 77% methane at an applied BOD_5 loading rate less than 1.0 lbs/d/1000 sq. ft.. The percent methane decreased until a BOD_5 loading of around 5.0 lbs/d/1000 sq. ft. had been reached where it leveled out at 60% methane. The total methane production rate per pound of BOD_5, COD, or TOC removed also decreased with increased loading rates.

The fourth and fifth loading conditions were very similar, around 5.0 lbs BOD_5/d/1000 sq. ft. (7.0 lbs COD/d/1000 sq. ft.), as can be observed from Table IV. The fourth condition was set by feeding to the reactor an influent concentration of 12,167 mg/L BOD_5 (18,445 mg/L COD) at a flow rate of 3.2 L/d, while the fifth condition was set by feeding an influent with around one half the concentration, 6,450 mg/L BOD_5 (8,300 mg/L COD), and twice the flow rate, 6.4 L/d. The performance of the system as far as substrate removal, gas production, and gas quality was

very similar at both the fourth and fifth loading conditions. The same situation was observed at the sixth and seventh loading conditions where the organic loading rate was around 9.0 lbs BOD_5/d/1000 sq. ft. (14.0 lbs COD/d/1000 sq. ft.). The fifth and seventh conditions were run in an attempt to prove that in anaerobic systems, as well as, aerobic systems (previously done by others, Ref.38), the performance and efficiency of fixed-film systems depend on the total organic loading rather than on only the substrate concentration or only the hydraulic flow rate.

Table V presents the average characteristics of the reactor liquor monitored by taking samples from the bottom of the reactor through the sample port provided. A constant volume of 200 mL of liquor was intentionally wasted from the bottom of the reactor in order to avoid solids accumulation. The sludge production or cell yield was very low, ranging from 0.03 to 0.09 lbs solids/lb BOD_5 removed (0.016 to 0.098 lbs solids/lb COD removed), since the new cells produced and attached to the media were not considered, and the yield coefficients of anaerobic processes are generally small as compared to those of aerobic processes. This is a result of the low ATP-yield, for example, 4 mole ATP/mole glucose under anaerobic conditions versus 38 mole ATP/mole glucose under aerobic conditions (24).

B. Substrate Removal Kinetics

The mathematical description of substrate utilization

rate is the major consideration in modeling and predicting both substrate removal and treatment efficiency or effluent quality. Mathematical description of the substrate utilization rate, as developed by Kincannon and Stover (45), is based in monomolecular kinetics with substrate utilization expressed as a function of the mass substrate loading rate, as follows:

$$U = \frac{U_{max} \frac{FSi}{A}}{K_B + \frac{FSi}{A}} \qquad (1)$$

where,

F = flow rate, MGD

Si = influent substrate concentration, mg/L

A = surface area of a specific volume of media, 1000 sq. ft.

U_{max} = maximum specific substrate removal rate, lbs/d/1000 sq. ft.

K_B = proportionality constant, lbs/d/1000 sq. ft.

$\frac{FSi}{A}$ = applied substrate loading rate, lbs/d/1000 sq. ft.

U = specific substrate utilization rate, lbs/d/1000 sq. ft.

This expression for substrate utilization can then be

substituted into the mass balance equation for substrate into and out of a particular volume of media in the anaerobic fixed-film reactor, as follows:

Mass of substrate into the volume of media	=	Mass of substrate out of the volume of media	+	Mass of substrate consumed biologically
FSi	=	FSe	+	UA (2)

where

Se = effluent substrate concentration, mg/L

By making this substitution the following relationship is obtained:

$$FSi = FSe + \frac{U_{max} \frac{FSi}{A}}{K_B + \frac{FSi}{A}} A \qquad (3)$$

Equation 3 can then be solved for either the required media surface area to achieve a specific effluent quality, or it can be solved for the effluent substrate concentration achievable with a specific media surface area, as follow:

$$A = \frac{FSi}{\frac{U_{max}\, Si}{Si - Se} - K_B} \qquad (4)$$

$$Se = Si - \frac{U_{max}\ Si}{K_B + \frac{FSi}{A}} \qquad (5)$$

Equation 4 can be used for design of anaerobic fixed film systems, and equation 5 can be used for predicting the effluent quality of a particular system.

In order to use these expressions, the biological kinetic constants, U_{max} and K_B, must be determined experimentally. These constants can be easily determined by operating an anaerobic fixed-film reactor at different substrate loading rates and monitoring the associated substrate removal characteristics. Examples of the types of data collected are presented in Tables II, III, and IV for the pilot fixed-film upflow anaerobic reactor.

The substrate data summarized in Table IV is presented graphically in Figures 2, 3, and 4, where the specific substrate utilization rate is plotted as a function of the applied substrate loading rate in terms of soluble BOD_5, COD, and TOC, respectively. The X's represent the average operating data at each test condition, and the circles represent all the data points with a significant amount of overlap of data points. These figures demonstrate the substrate removal characteristics as a function of the mass substrate loading rates applied to the anaerobic reactor. The curves in Figures 2, 3, and 4 can be linearized by plotting the reciprocal of the substrate utilization rate as

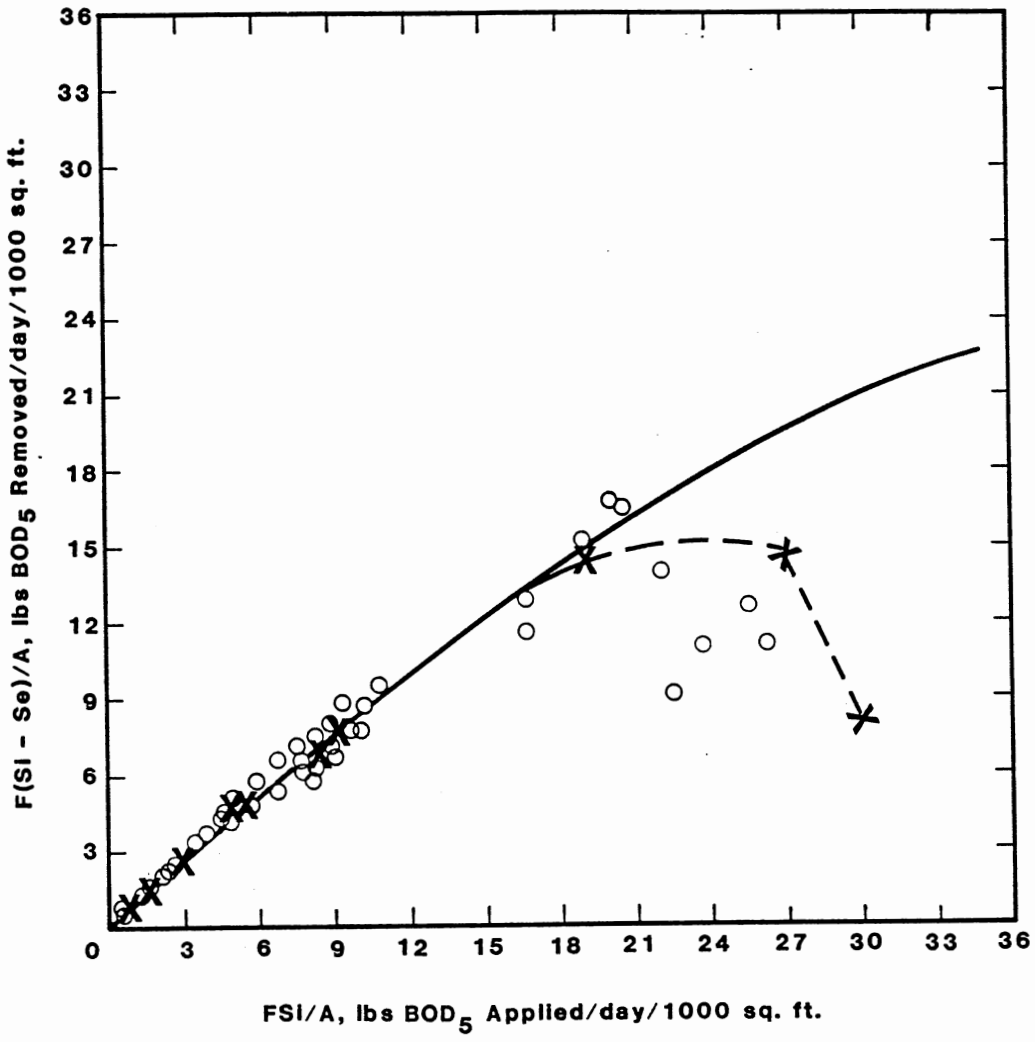

Figure 2. Substrate Utilization as a Function of Mass Substrate Loading in Terms of BOD_5

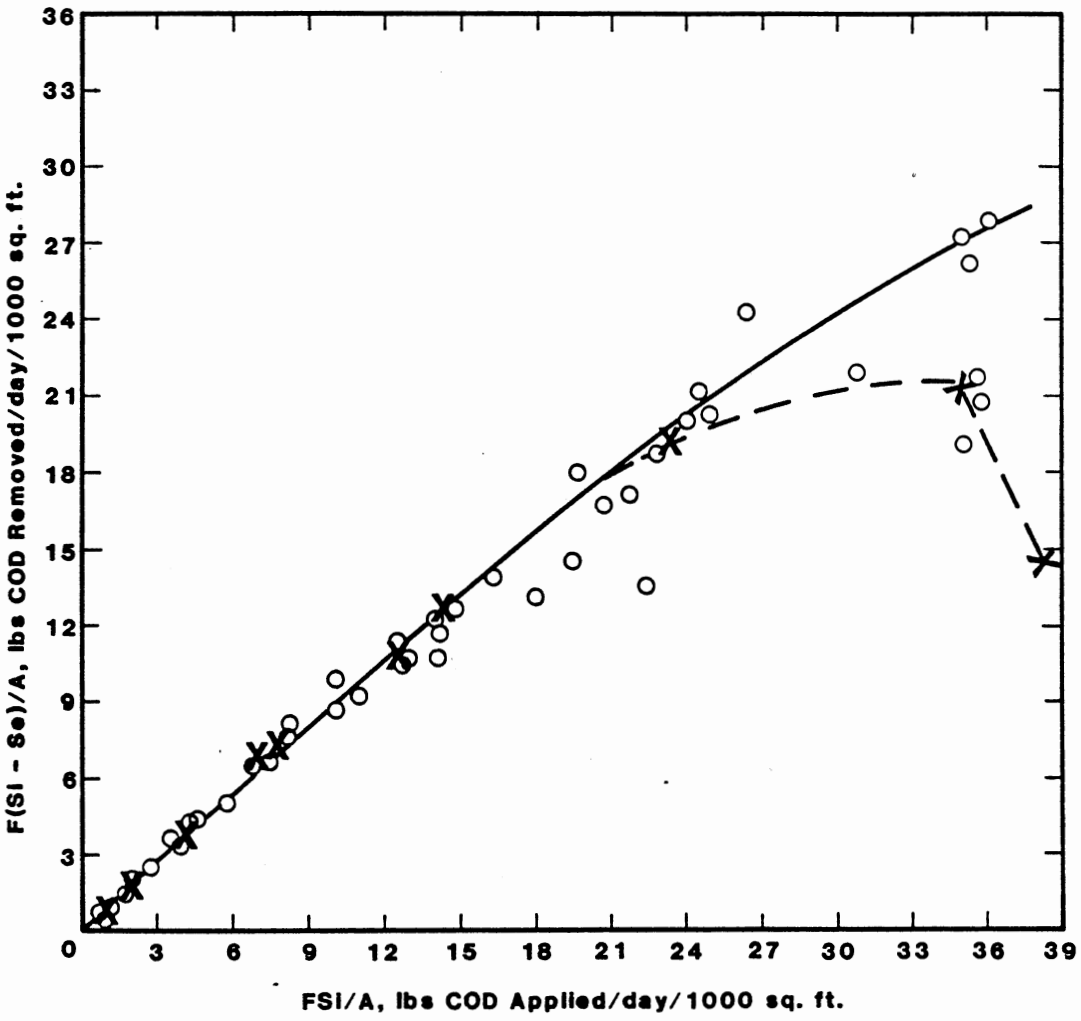

Figure 3. Substrate Utilization as a Function of Mass Substrate Loading in Terms of COD

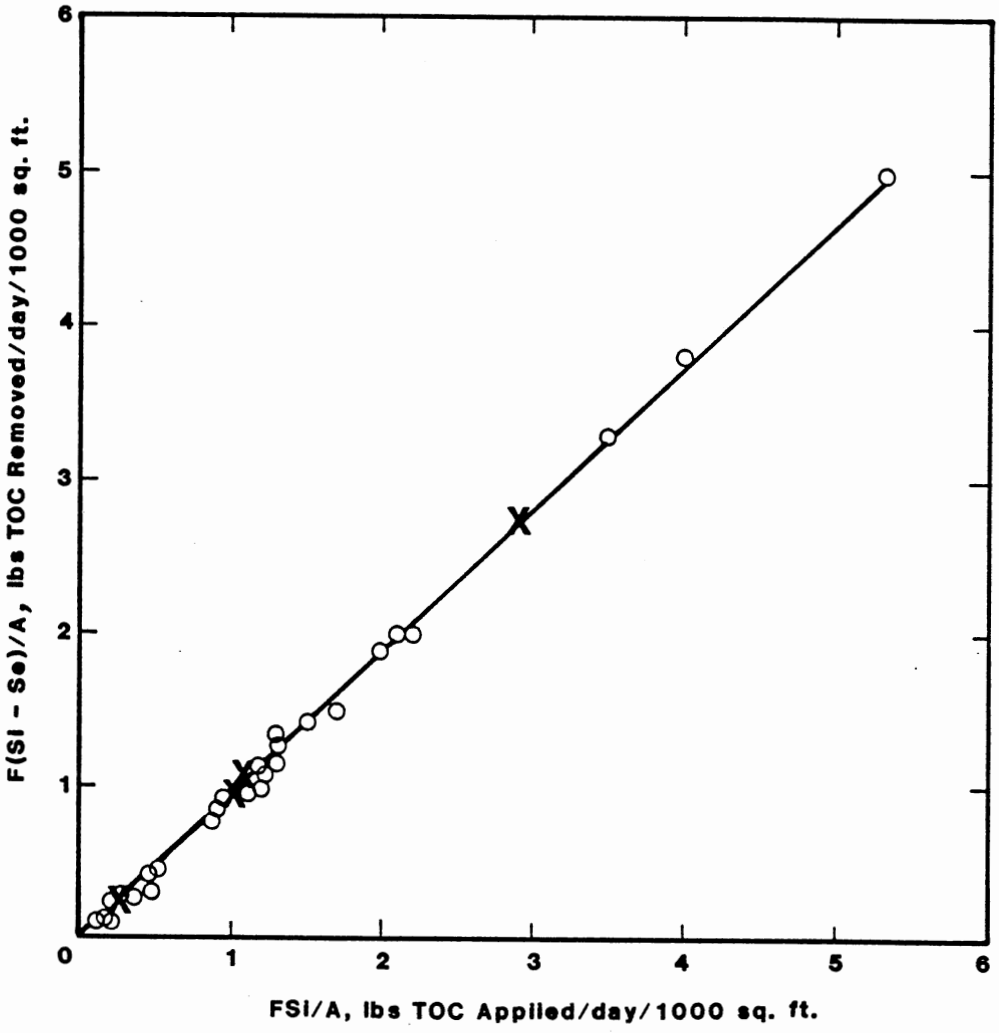

Figure 4. Substrate Utilization as a Function of Mass Substrate Loading in Terms of TOC

a function of the reciprocal of the applied substrate loading rate.

The associated reciprocal plots are shown in Figures 5, 6, and 7 for BOD_5, COD, and TOC, respectively. From these figures the biological kinetic constants, U_{max} and K_B, were determined from the Y-axis intercept and the slope of the line. U_{max} is the reciprocal of the Y-axis intercept, and K_B is the product of U_{max} and the slope of the line (K_B = slope * U_{max}). U_{max} and K_B in terms of soluble BOD_5 were 58.35 lbs/d/1000 sq. ft. and 58.08 lbs/d/1000 sq. ft., respectively. These kinetic constants in terms of soluble COD were much higher at 148.92 lbs/d/1000 sq. ft. and 142.55 lbs/d/1000 sq. ft., and in terms of soluble TOC they were lower, 27.74 lbs/d/1000 sq. ft. and 28.79 lbs/d/1000 sq. ft.. The correlation of all the data was excellent with correlation coefficients greater than 0.99. The lines in Figures 5, 6, and 7 were drawn using their respective equations, obtained using linear regression analysis. The results of these statistical analyses are presented in the Appendix.

The solid lines in Figures 2 and 3 were drawn using the kinetic constants determined in Figures 5 and 6 at loading rates below 27 (35) lbs BOD_5 (COD)/d/1000 sq. ft.. The calculated maximum substrate utilization rates were much higher than the actual observed rates due to limitations of the methane forming bacteria and increased volatile fatty acids accumulations at higher loading rates. The actual

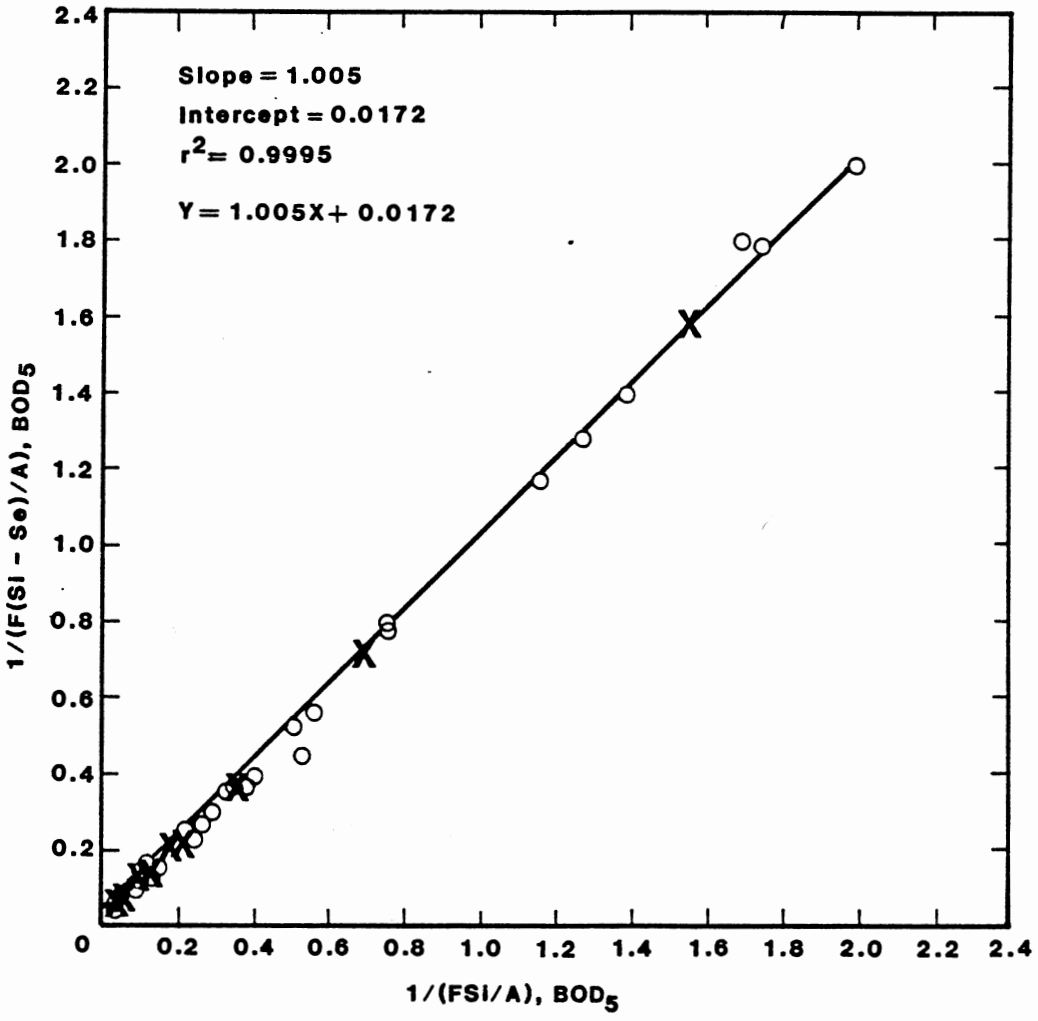

Figure 5. Graphical Determination of U_{max} and K_B in Terms of BOD_5

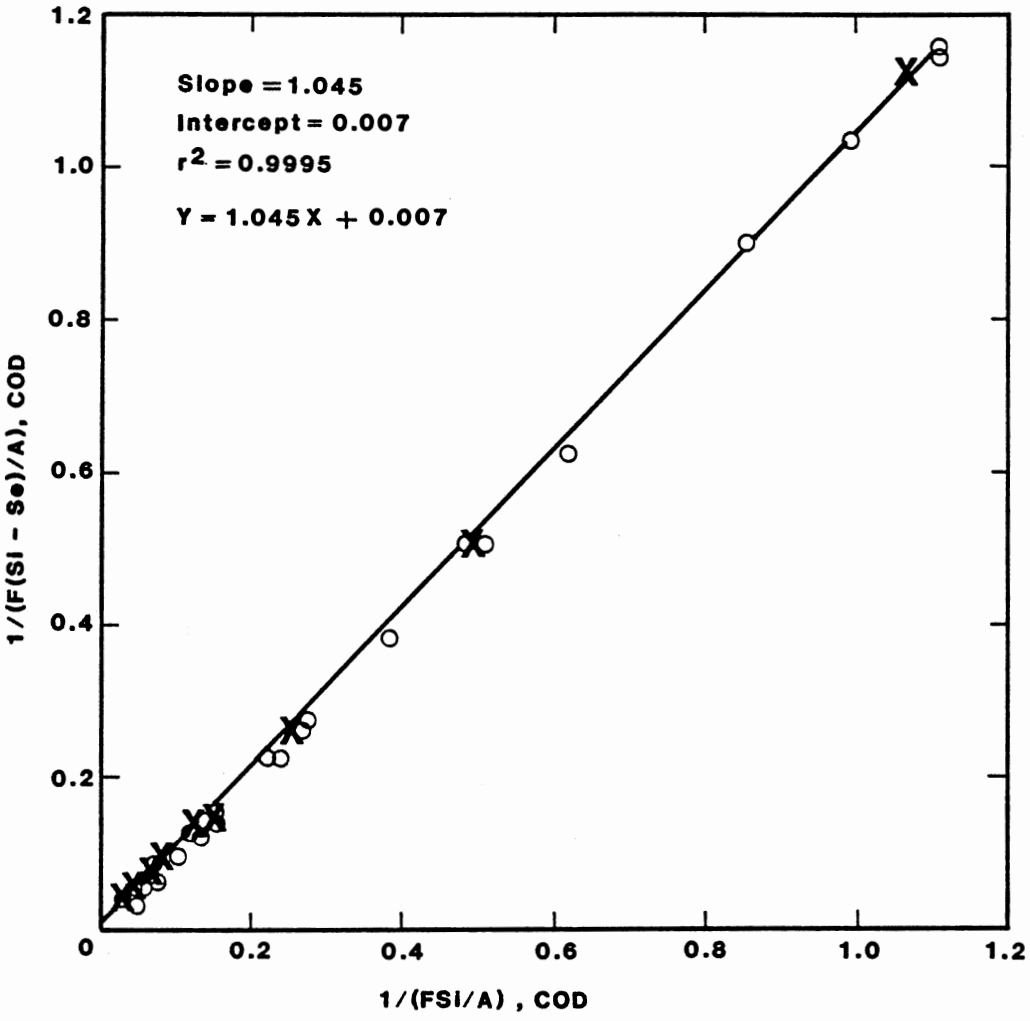

Figure 6. Graphical Determination of U_{max} and K_B in Terms of COD

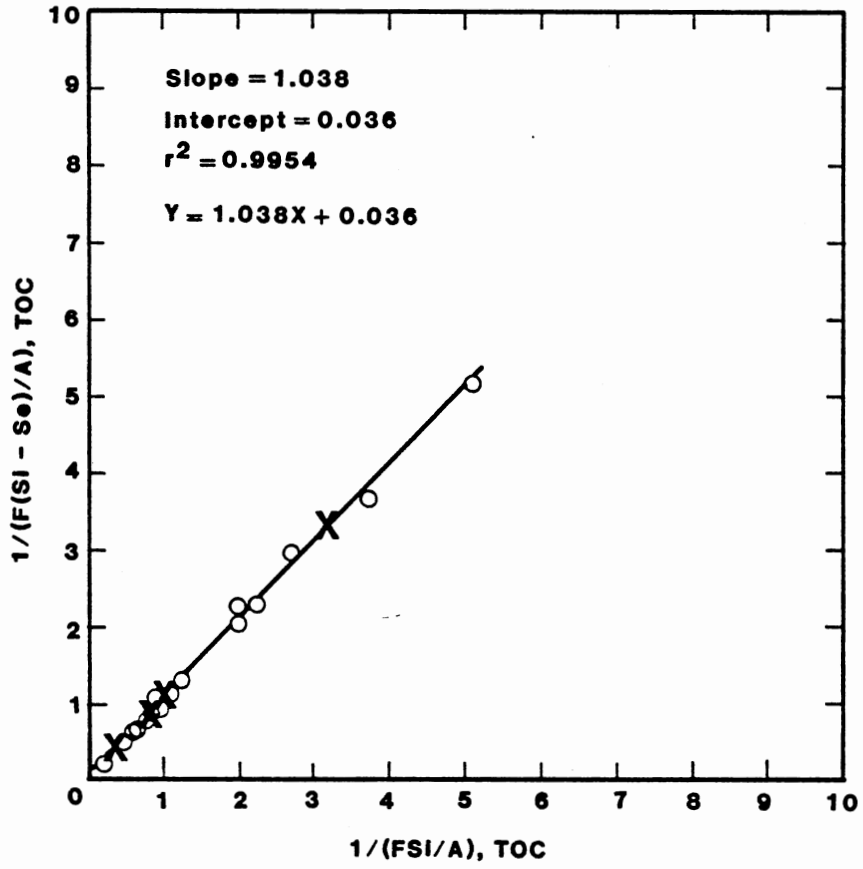

Figure 7. Graphical Determination of U_{max} and K_B in Terms of TOC

substrate utilization rates peaked out at around 15 (22) lbs BOD_5 (COD)/d/1000 sq. ft., as shown by the broken lines, compared to calculated values of 58.35 (148.92) lbs/d/1000 sq. ft.. At substrate loading rates greater than 27 (35) lbs BOD_5 (COD)/d/1000 sq. ft., the substrate utilization rate actually started decreasing due to volatile fatty acids build-up in the reactor and inhibition or retardation of the methane conversion reactions. The substrate loading rate of 28.85 (40.39) lbs BOD_5 (COD)/d/1000 sq. ft. was not included for the kinetics determination. It was shown in Figures 2 and 3 to indicate that at such a high loading condition the system almost completely fails.

Figure 4 shows the specific substrate utilization rate as a function of the applied substrate loading rate in terms of soluble TOC. This plot was developed based on only the first four loading conditions due to lost of TOC instrumentation capabilities during the rest of the study. For that reason, the impact of the high loadings on the system could not be seen in Figure 4 and the actual maximum substrate utilization rate was not determined to compare it to the calculated value obtained from Figure 7. The straight line in Figure 4 reflects the excellent performance of the system at low loading rates with very high removal efficiency.

Table VI presents a summary of the biological kinetic constants after the Stover and Kincannon mathematical description of the substrate utilization rate. These

TABLE VI

BIOLOGICAL KINETIC CONSTANTS FOR THE STOVER AND KINCANNON DESIGN MODEL

	U_{max} (lb/d/1000 sq.ft.)	K_B (lb/d/1000 sq.ft.)
BOD_5 KINETICS*	58.35	58.08
COD KINETICS*	148.92	142.55
TOC KINETICS*	27.74	28.79

* Kinetics in terms of soluble BOD_5, COD, and TOC

constants were determined in terms of soluble BOD_5, COD, and TOC for the treatment of fuel alcohol wastewater (thin stillage) using a fixed-film, upflow, anaerobic reactor.

C. Low Temperature Substrate Removal Kinetics

The bench-scale, fixed-film, anaerobic reactor was operated at 25 $\pm$ 2 °C for a period of approximately three months. During this period, the system was operated at three different organic loading conditions to determine the biological kinetic constants and compare them to the kinetic constants obtained at 36 $\pm$ 2 °C. The purpose of this study at low temperature was to determine the capabilities, removal efficiency, and gas production of a fixed-film anaerobic reactor when operated at low temperature, since the operation of an anaerobic system at lower temperature represents savings in energy consumption, reducing or eliminating the need for heating the reactor.

Tables VII and VIII present the influent and effluent characteristics, respectively, during the low temperature studies. Table IX presents the analysis of the data in terms of substrate removal and gas production and Table X presents the reactor liquor characteristics at the different loading conditions. The system was allowed to reach steady state condition after changing the loadings and before collecting any data.

TABLE VII

INFLUENT FEED CHARACTERISTICS FOR LOW TEMPERATURE STUDIES

Loading Condition	Si* BOD_5 (mg/L)	Si* COD (mg/L)	Flow (L/d)	pH	SS (mg/L)	VSS (mg/L)
1	367	564	7.18	7.1-8.7	35	32
2	841	1588	6.78	6.3-8.9	41	25
3	1501	2774	6.75	6.5-7.5	136	117

*Si = Soluble BOD_5 and COD

TABLE VIII

EFFLUENT CHARACTERISTICS FOR
LOW TEMPERATURE STUDIES

Loading Condition	Se* BOD_5 (mg/L)	Se* COD (mg/L)	pH	Temperature (°C)	Alkalinity (mg/L as $CaCO_3$)	VFA (mg/L as Ac.Acid)	VFA / ALK	SS** (mg/L)	VSS** (mg/L)
1	14	33	6.8-7.1	25	329	101	0.31	16	15
2	180	346	6.2-6.9	27	425	348	0.82	44	36
3	522	897	6.3-7.6	25	1420	903	0.64	120	90

*Se = Soluble BOD_5 and COD

** Clarifier Supernatant Solids

TABLE IX

SUBSTRATE REMOVAL AND GAS PRODUCTION
FOR LOW TEMPERATURE STUDIES

Loading Condition	Loading Rate* (lb/d/1000 sq.ft.)		Removal Rate* (lb/d/1000 sq.ft.)		Percent Removal		Actual Gas**			cu.ft.CH_4/lb Removed	
	BOD_5	COD	BOD_5	COD	BOD_5	COD	Production	$\%CO_2$	$\%CH_4$	BOD_5	COD
1	0.35	0.54	0.34	0.51	97	94	2.0	17	81	1.0	0.7
2	0.75	1.41	0.59	1.10	79	78	3.9	18	80	11.3	6.0
3	1.36	2.51	0.86	1.69	66	68	6.6	19	79	12.8	6.7

* Soluble BOD_5 and COD

** Gas Volume Corrected to Standard Conditions (0 °C, 1 atm)
Gas Production in L/d

TABLE X

REACTOR LIQUOR CHARACTERISTICS
FOR LOW TEMPERATURE STUDIES

Loading Condition	pH	Temperature (°C)	Wastage (L/d)	SS (mg/L)	Alkalinity (mg/L as $CaCO_3$)	VFA (mg/L as Ac.Acid)	VFA / ALK	Observed Yield* (lb sludge prod./lb removed) BOD$_5$	Observed Yield* (lb sludge prod./lb removed) COD
1	6.7-7.1	24	0.1	22	634	280	0.44	0.05	0.06
2	6.6-6.8	26	0.1	40	905	366	0.40	0.07	0.04
3	6.0-7.0	26	0.2	83	1875	474	0.25	0.12	0.03

* Soluble BOD_5 and COD

As can be observed from Tables VIII and X, volatile fatty acids were present in the effluent and in the reactor liquor at all the three organic loading conditions. By comparing to Table III it can be seen that no volatile fatty acids were present at such low organic loading (below 1.5 lbs BOD_5/day/1000 sq. ft.) when the system was operated at 36 $\pm$ 2 ^oC. Since not all the VFA produced were converted to methane, the gas production and the removal efficiency decreased as shown in Table IX compared to Table IV for low loading conditions (below 1.5 lbs BOD_5/day/1000 sq. ft.). Also, for these low loading conditions the gas quality was slightly different with lower percent CO_2 during the low temperature studies, since the solubility of the CO_2 increases with decreasing temperature.

From the previous comparison and from Tables IV and IX, it can be observed that for a decrease in temperature of approximately 10 ^oC, the BOD_5 and COD removals decreased approximately 18% at approximately 0.7 lbs BOD_5/day/1000 sq. ft. and approximately 30% at approximately 1.4 lbs BOD_5/day/1000 sq. ft.. The gas production decreased 32% at 0.7 lbs BOD_5/day/1000 sq. ft. and 36% at 1.4 lbs BOD_5/day/1000 sq. ft.. Another observation that can be made is that as the organic loading increased, the difference in BOD_5 and COD removals and in gas production, at the two temperatures, also increased. The summary of this comparison is presented in Table XI. Also, from Table IX it can be readily observed that the treatment efficiency and gas

TABLE XI

PERCENT REMOVAL AND GAS PRODUCTION COMPARISON
AT TWO DIFFERENT TEMPERATURES

36 °C				25 °C				Percent Decrease		
Loading Rate *	% Removal		Gas Production (L/d)	Loading Rate *	% Removal		Gas Production (L/d)	% Removal		Gas Production (L/d)
	BOD_5	COD			BOD_5	COD		BOD_5	COD	
0.68	98	95	5.70	**0.75**	79	78	3.90	19	17	32
1.46	98	96	10.33	**1.36**	66	68	6.60	33	29	36

* Loading Rate in lbs BOD_5/d/1000 sq. ft.

production decreased with increasing substrate loading rate which was previously observed from Table IV.

Changes in temperature cause changes in predominant population in an anaerobic system. There is some controversy as to whether there exists two temperature optima (mesophilic and thermophilic) for anaerobic digestion. Pfeffer (46) found 40 °C more favorable than 35 °C or 45 °C when the retention time was between 4 and 30 days. With the same retention times, he found a second optima at 60 °C even more favorable than 40 °C. The digesters performed more satisfactorily at 60 °C than either 55 °C or 65 °C. Buhr and Andrews (47) designed a dynamic process model to describe effects of temperature. This model predicts that the temperature which gives minimum volatile organic acids concentration increases with decreasing retention time so that at very low retention times (3.5 days) the optima temperature is high (around 50 °C). It also predicts greater maximum methanogenic rates at increasing temperature up to 60 °C. O'Rourke (33) studied the effects of temperature on anaerobic digestion of municipal raw sludge. He observed that the minimum SRT for lipids decomposition was about 4, 10, 12, and greater than 60 days, at temperatures of 35°, 25°, 20°, and 15 °C, respectively. Frequent changes in temperature should be avoided in an anaerobic system in order to keep the high efficiency and performance of the predominant group. It is more important to keep a constant temperature than to operate the system at the optima

temperature for each predominant group. Little is known about the performance of anaerobic systems at temperatures lower than 30 °C. However, it has been reported (34) that at temperatures between 15 °C and 25 °C the gas production decreased considerably and volatile fatty acids accumulation took place. This situation is due to the fact that the methanogenic bacteria are more sensitive to low temperatures than the acid forming bacteria. The response of methanogenic bacteria to temperature changes is immediate since these changes affect the rates of enzyme-catalized reactions.

Also, a significant difference was observed in the biological kinetic constants when the reactor was operated at 25 $\pm$ 2 °C. These kinetic constants were calculated based on soluble BOD_5 and COD after the Stover and Kincannon mathematical model. Figures 8 and 9 present the substrate utilization rate as a function of the mass substrate loading rate in terms of BOD_5 and COD, respectively. The X's represent the average operating data at each loading condition, and the circles represent all the data points with a significant amount of overlap of data points. As already discussed in a previous section, these figures demonstrate the substrate removal characteristics as a function of the mass substrate loading rates applied to the anaerobic reactor. The reciprocal plots for graphical determination of the biological kinetic constants are presented in Figures 10 and 11 in terms of soluble BOD_5 and COD, respectively. From Figure 10, U_{max} and K_B in terms of

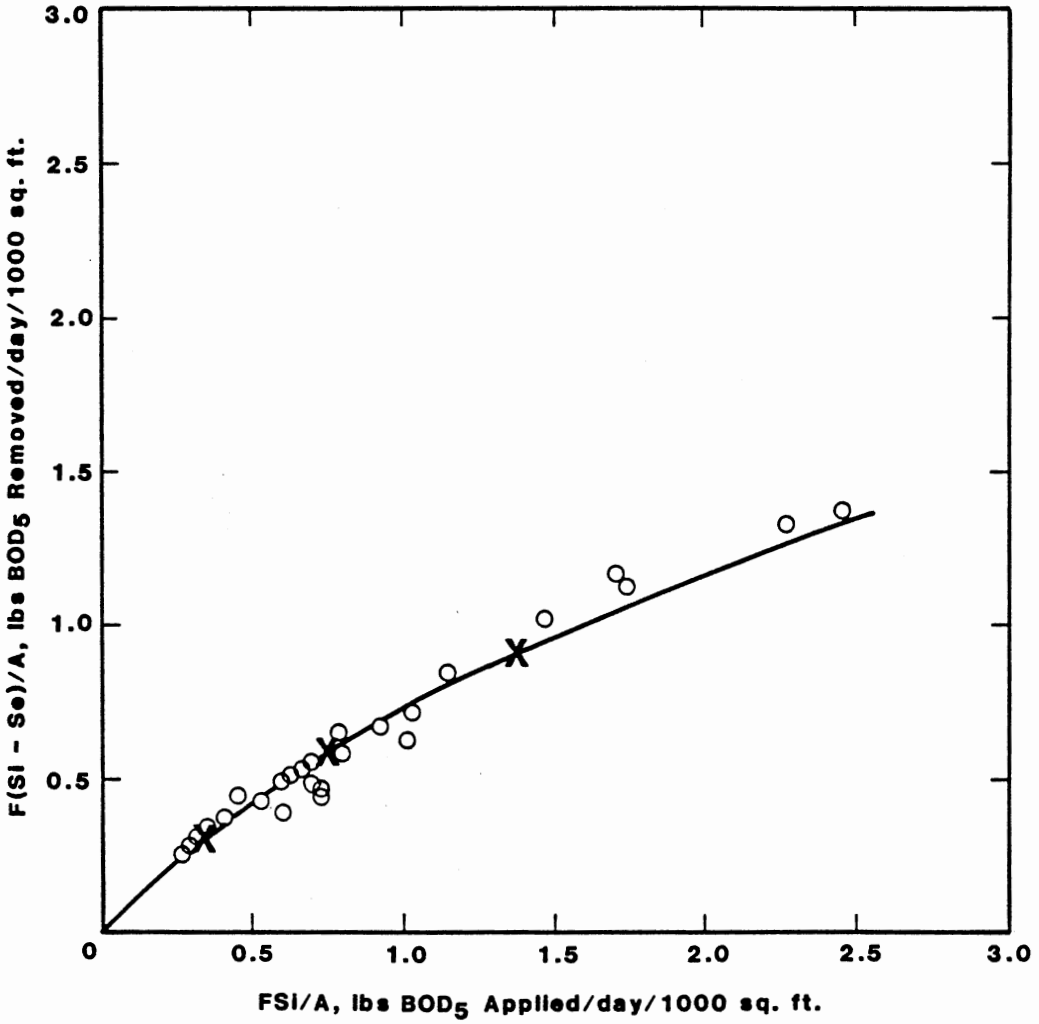

Figure 8. Substrate Utilization as a Function of Mass Substrate Loading in Terms of BOD_5 (Low Temperature)

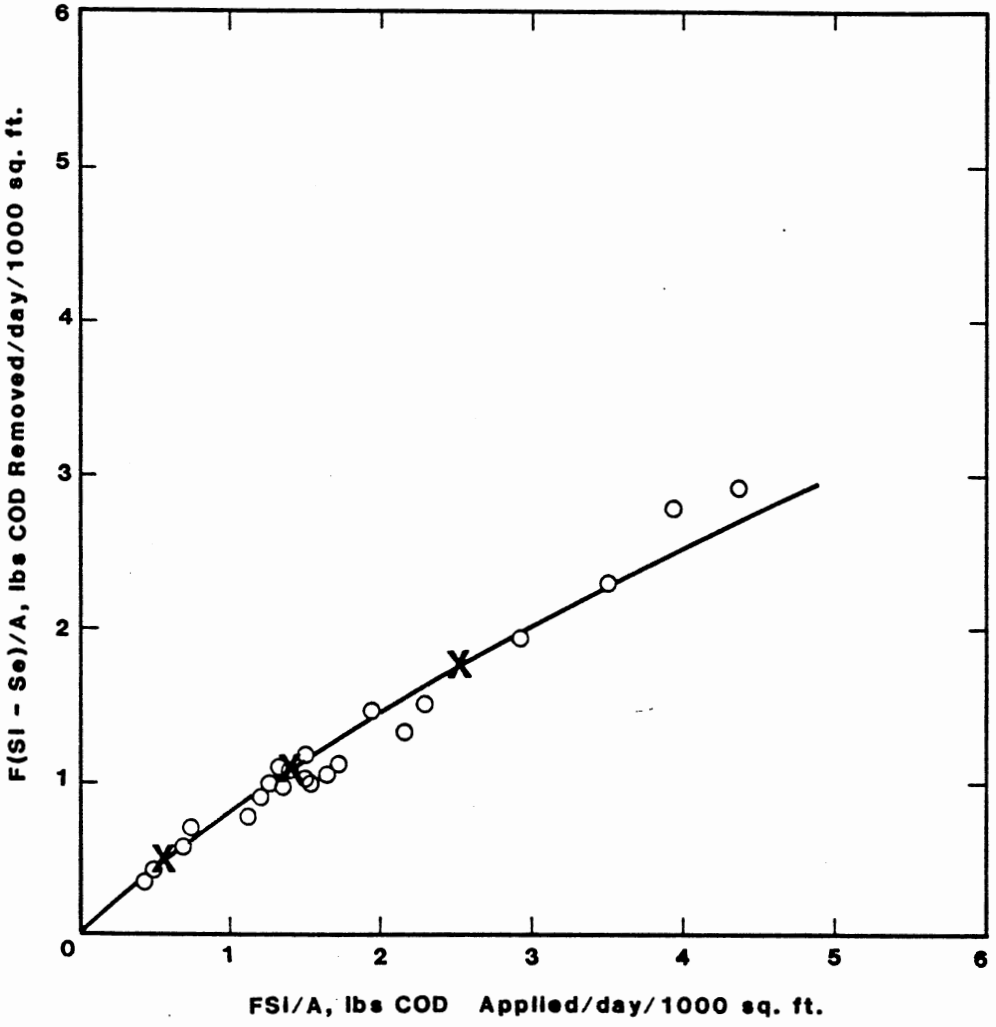

Figure 9. Substrate Utilization as a Function of Mass Substrate Loading in Terms of COD (Low Temperature)

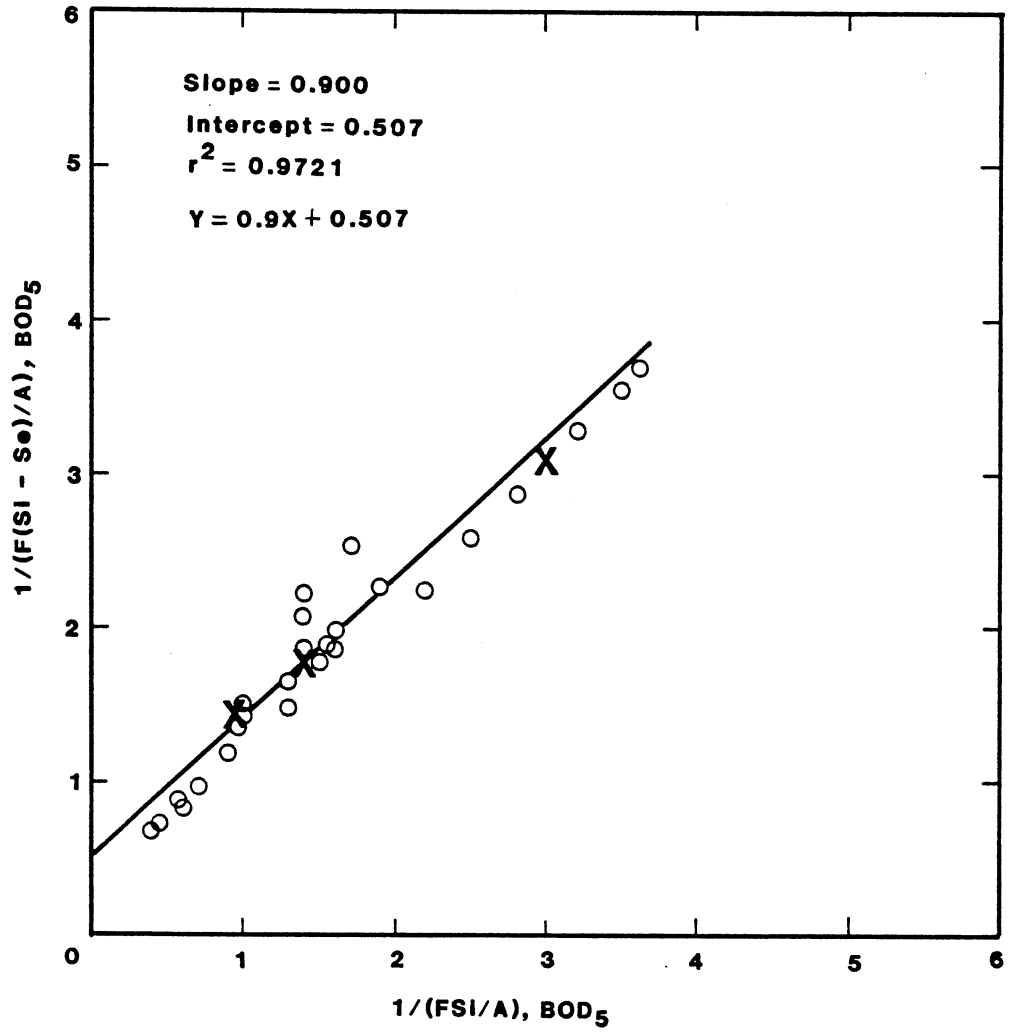

Figure 10. Graphical Determination of U_{max} and K_B in Terms of BOD_5 (Low Temperature)

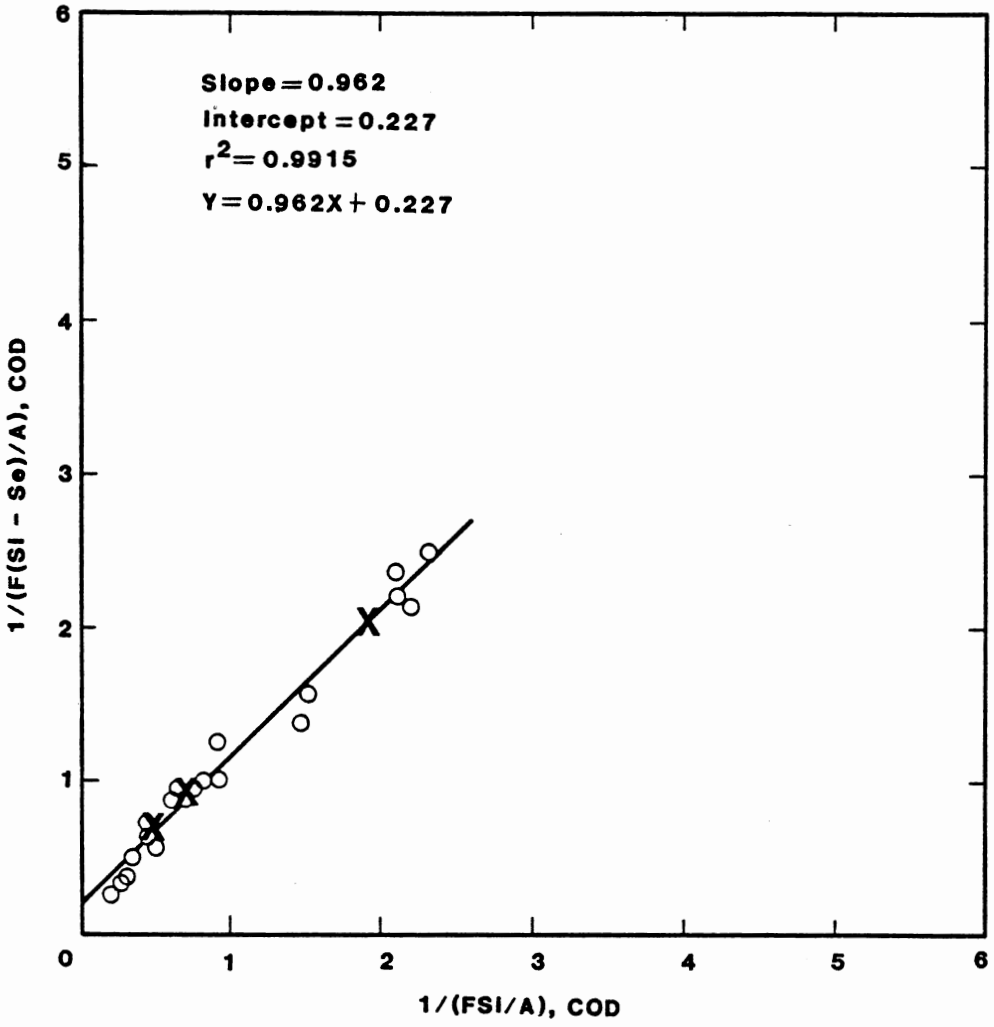

Figure 11. Graphical Determination of U_{max} and K_B in Terms of COD (Low Temperature)

soluble BOD_5 were 1.97 lbs/d/1000 sq. ft. and 1.78 lbs/d/1000 sq. ft., respectively, with a correlation coefficient of 0.9721. From Figure 11, U_{max} and K_B in terms of soluble COD were 4.41 lbs/d/1000 sq. ft. and 4.24 lbs/d/1000 sq. ft., respectively, with a correlation coefficient of 0.9915. The lines in Figures 10 and 11 were drawn using their respective equations obtained by linear regression analysis, and the results are shown in the Appendix. From Figures 8 and 9 and considering the trend of the lines, the calculated and the actual maximum substrate utilization rates appear to be close.

When comparing the biological kinetic constants at 25 $\pm$ 2 °C to the constants obtained at 36 $\pm$ 2 °C, shown in Table XII, the tremendous difference between them can be noticed. The reason for that difference is the very low performance of the methane forming bacteria at temperatures lower than 36 $\pm$ 2 °C. The acid forming bacteria are less sensitive to lower temperature, so when an anaerobic system is operated at those conditions, the acid formers keep producing intermediate volatile fatty acids at a higher rate than they can be consumed by the methanogens, causing an imbalance between the two major groups. If the organic loading to the system is increased, volatile fatty acids accumulation takes place causing the pH of the system to decrease to a point it becomes adverse to the methanogens and the system fails. For that reason, the fixed-film, upflow anaerobic reactor used in this study was not operated at high organic loadings at

TABLE XII

BIOLOGICAL KINETIC CONSTANTS AT TWO DIFFERENT TEMPERATURES (STOVER AND KINCANNON MODEL)

	36 °C		25 °C	
	U_{max} (lbs/day/1000 sq.ft.)	K_B	U_{max} (lbs/day/1000 sq.ft.)	K_B
BOD_5 KINETICS*	58.35	58.08	1.97	1.78
COD KINETICS*	148.92	142.55	4.41	4.24

* Kinetics in terms of soluble BOD_5 and COD

25 ± 2 °C. For the same reason, it is not recommended to operate a fixed-film anaerobic reactor at loadings higher than approximately 2.0 lbs BOD_5/day/1000 sq. ft. (4.4 lbs COD/day/1000 sq. ft.) if the temperature is kept at 25 ± 2 °C. Kennedy and van den Berg (48) evaluated the effects of temperature on the performance of anaerobic fixed-film reactors treating bean blanching wastes. They observed that in order to keep the COD removal rate constant at 88 ± 2%, it was necessary to decrease the COD loading rate by 37% when the reactor temperature was dropped from 35 °C to 25 °C. Speece and Kem (34) studied the effects of short-term temperature variations on methane production using bench-scale mesophilic (35 °C) digesters. The retention time was 20 days and the digesters were fed raw sludge once per day. Methane production was particularly sensitive to decreases in temperature and practically ceased when the temperature was dropped to 20 °C.

D. Gas Production Kinetics

The total gas production rate and gas composition are normally used to indicate the operational stability of anaerobic reactors. The rate of methane production is a direct measure of the metabolic activity of the methanogenic bacteria and as such has great potential as a diagnostic tool of anaerobic reactors performance. An imbalance between the two major populations (acidogens and methanogens) is likely to be manifested by a decrease in the production rate

of methane and an increase in the rate of carbon dioxide production. Therefore, a change in the composition is likely to show up before a change in the total production rate. The gas produced during anaerobic digestion consists of a mixture of methane and carbon dioxide with very small amounts of other gases, in particular, hydrogen sulfide and hydrogen (49).

The gas production characteristics of the fixed-film upflow anaerobic reactor summarized in Table IV are presented graphically in Figures 12 and 13 as a function of the applied BOD_5 and COD loadings, respectively. The methane content of the gas decreased and the carbon dioxide content increased as the applied loading was increased up to around 12 lbs BOD_5 (16.5 lbs COD)/day/1000 sq. ft. at which point the methane content leveled out at approximately 59% and the carbon dioxide leveled out at approximately 39%. Also, from Figures 12 and 13 it can be observed that the total gas production and methane production per pound of BOD_5 or COD removed decreased as the loading rates were increased over the entire range of loadings studied. The carbon dioxide per pound of BOD_5 or COD removed increased as the loading rates were increased up to approximately 12 lbs BOD_5 (15 lbs COD)/day/1000 sq. ft. and then appeared to start decreasing very slowly.

The gas production data presented in Figures 12 and 13 indicated that the total gas production and the total methane production were a function of the total applied

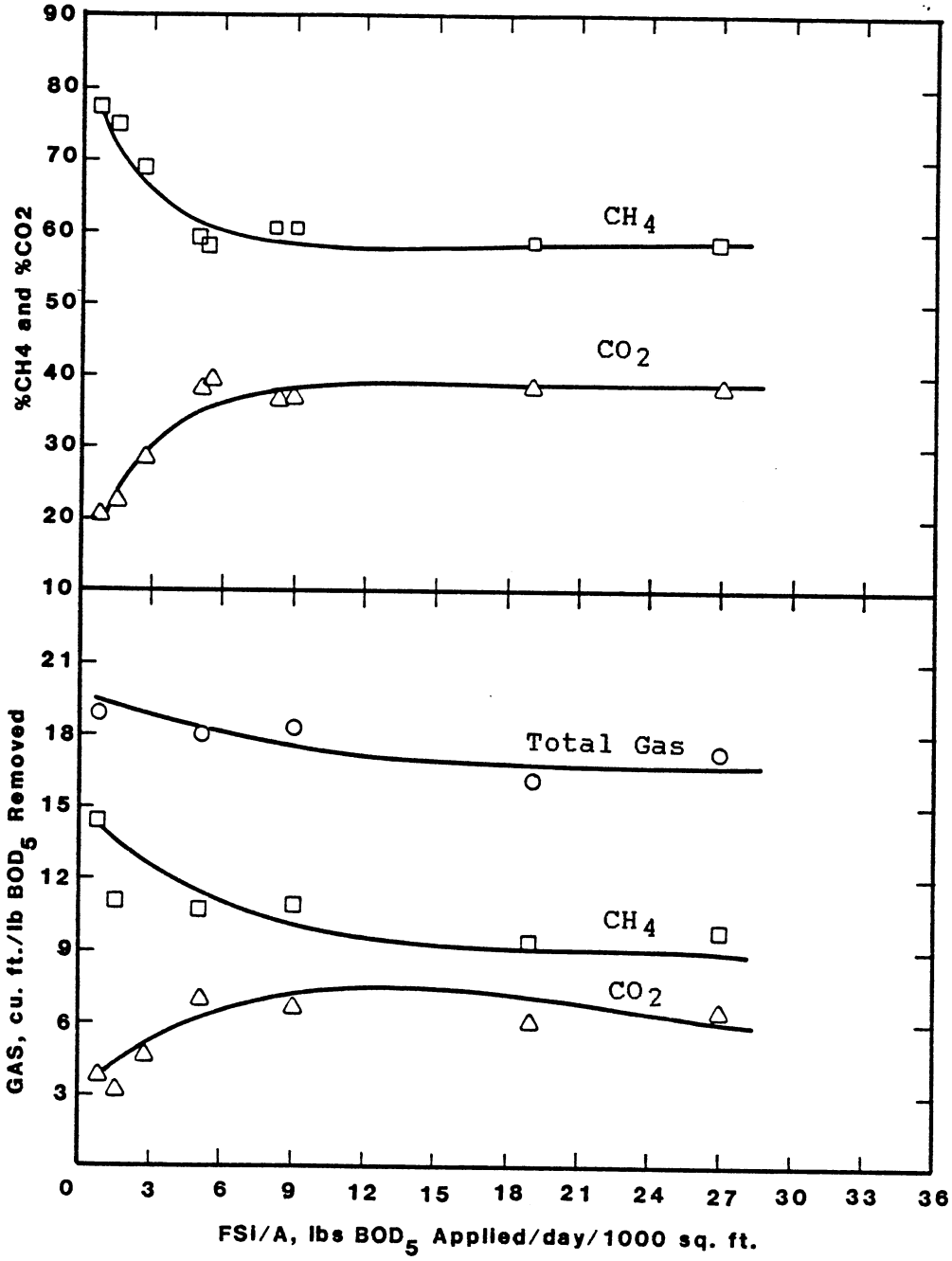

Figure 12. Gas Production Characteristics as a Function of Mass Substrate Loading in Terms of BOD_5

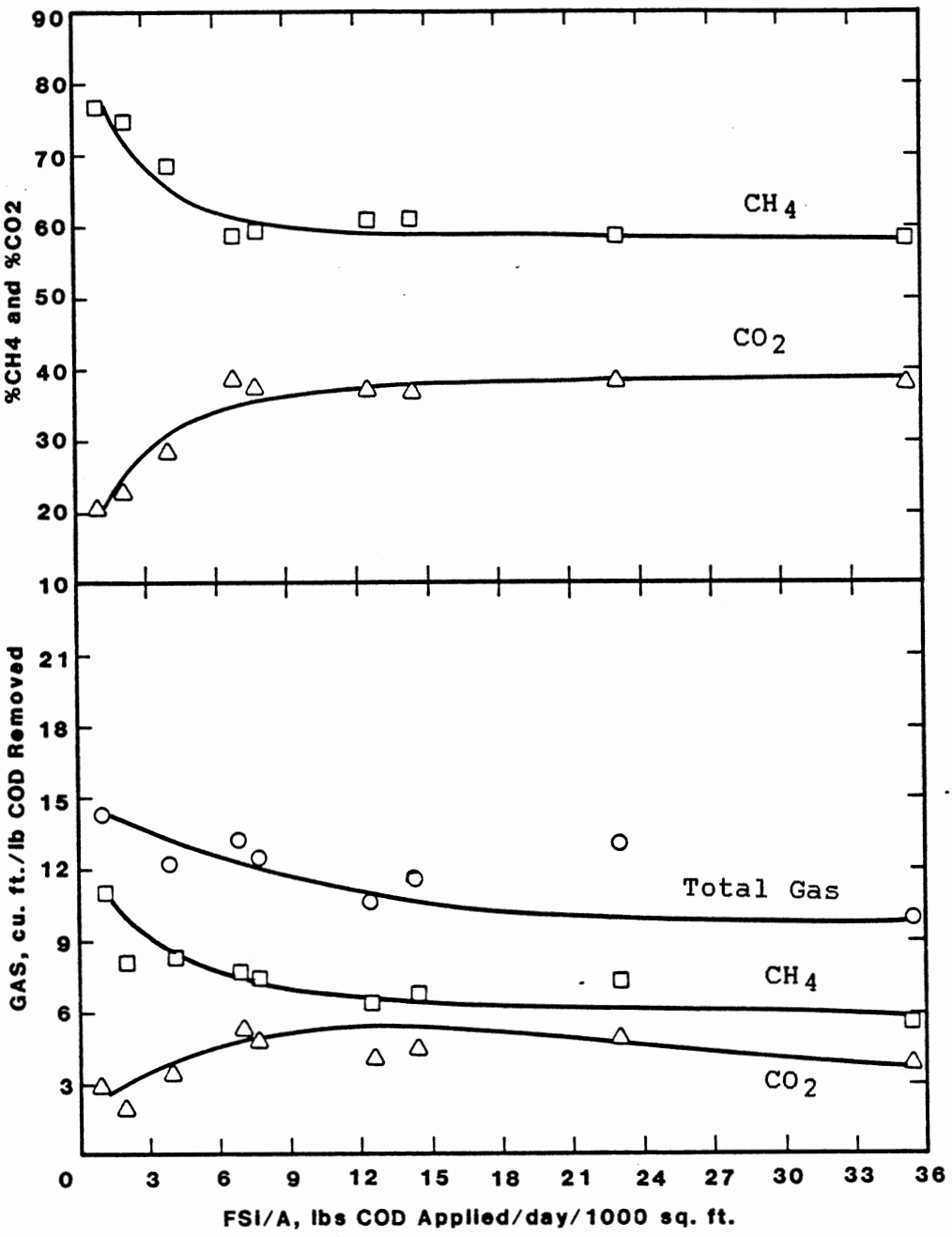

Figure 13. Gas Production Characteristics as a Function of Mass Substrate Loading in Terms of COD

substrate loading, and therefore, they should respond in a similar manner as the substrate utilization kinetics. In Figures 14 through 19 the total gas production and the methane production data were plotted as a function of the mass substrate loading (in terms of soluble BOD_5, COD, and TOC) in order to verify this assumption. As one might expect, the gas production kinetics were, in fact, a function of the applied substrate loading rates and could be described by monomolecular kinetics just like substrate utilization.

The reciprocal plots were also made to evaluate the possibility of determining biokinetic constants for use in prediction of gas quantity and quality. These plots are presented in Figures 20 through 25, and the biological kinetic constants were determined using the same method described in the determination of the substrate utilization kinetics. The total gas production and methane production biological kinetic constants, in terms of soluble BOD_5, COD, and TOC are presented in Table XIII.

The maximum total gas production rate, G_{max}, and the maximum methane production rate, M_{max}, were predictable. In fact, the maximum rates were found to be very close to each other irrespective of whether they were calculated in terms of BOD_5, COD, or TOC. The maximum specific total gas production rate, G_{max}, was found to be around 380 cu. ft./day/1000 sq. ft. while the maximum specific methane

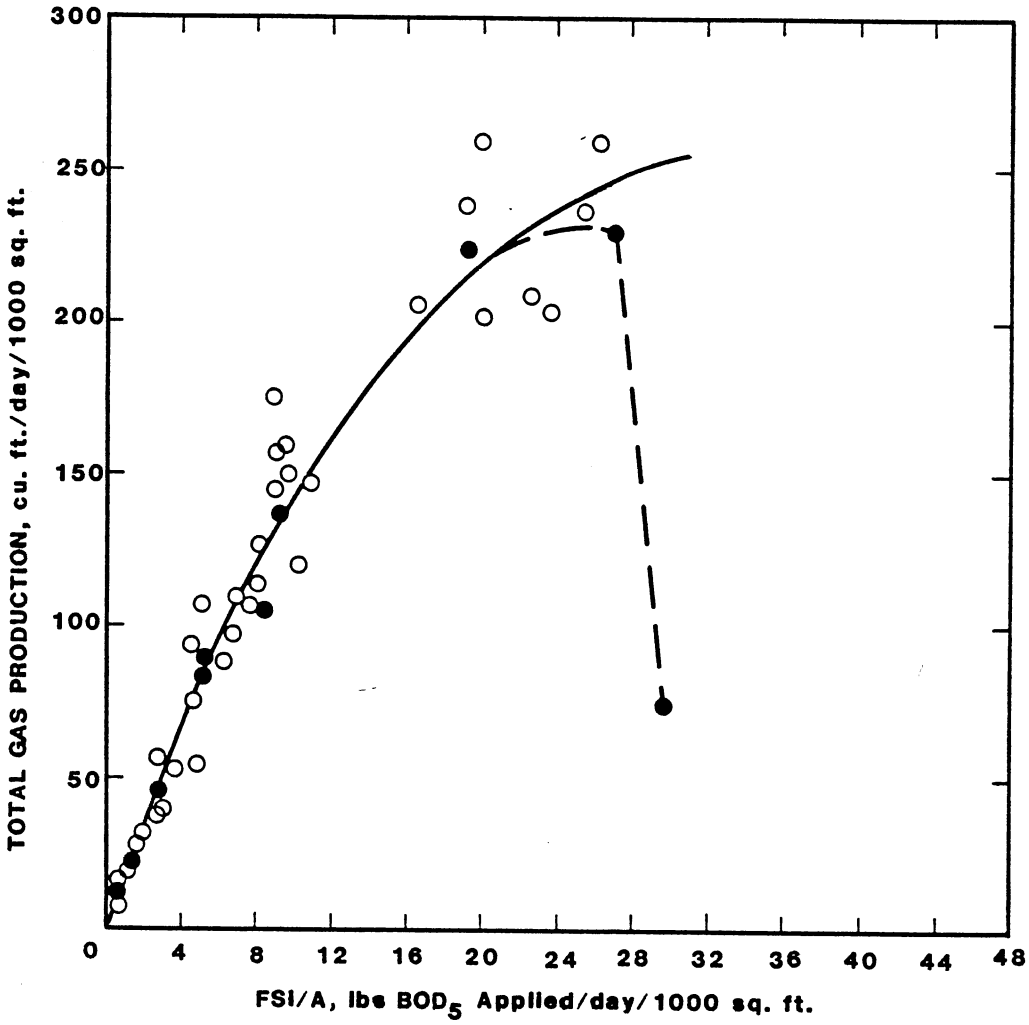

Figure 14. Total Gas Production as a Function of Mass Substrate Loading in Terms of BOD_5

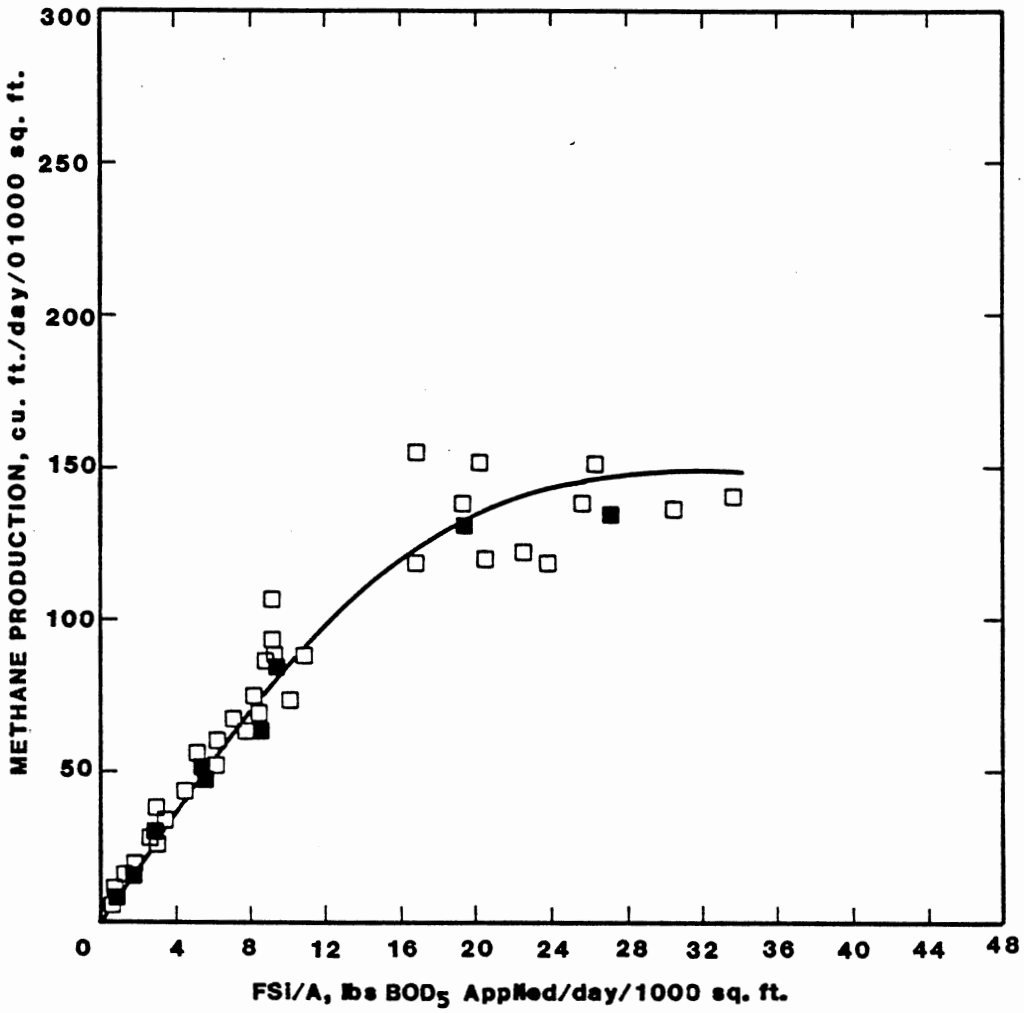

Figure 15. Methane Production as a Function of Mass Substrate Loading in Terms of BOD_5

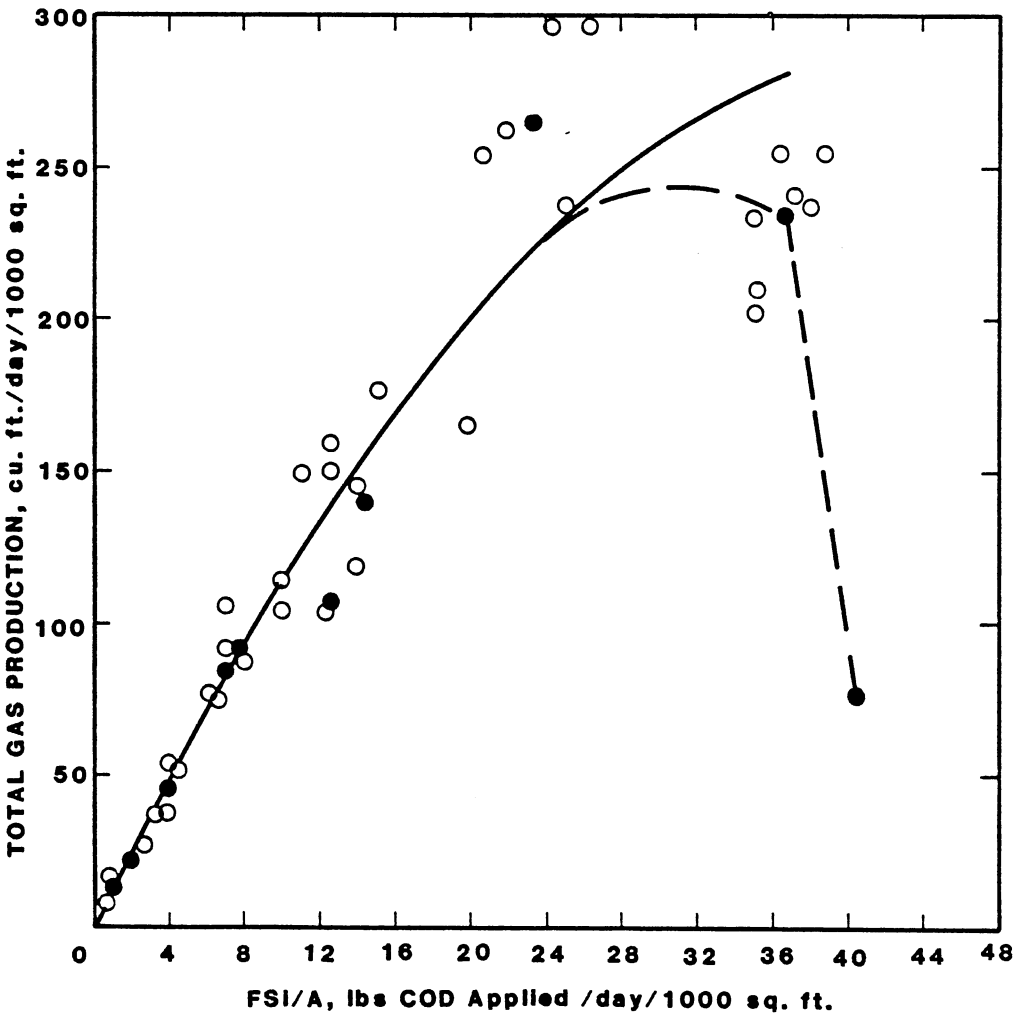

Figure 16. Total Gas Production as a Function of Mass Substrate Loading in Terms of COD

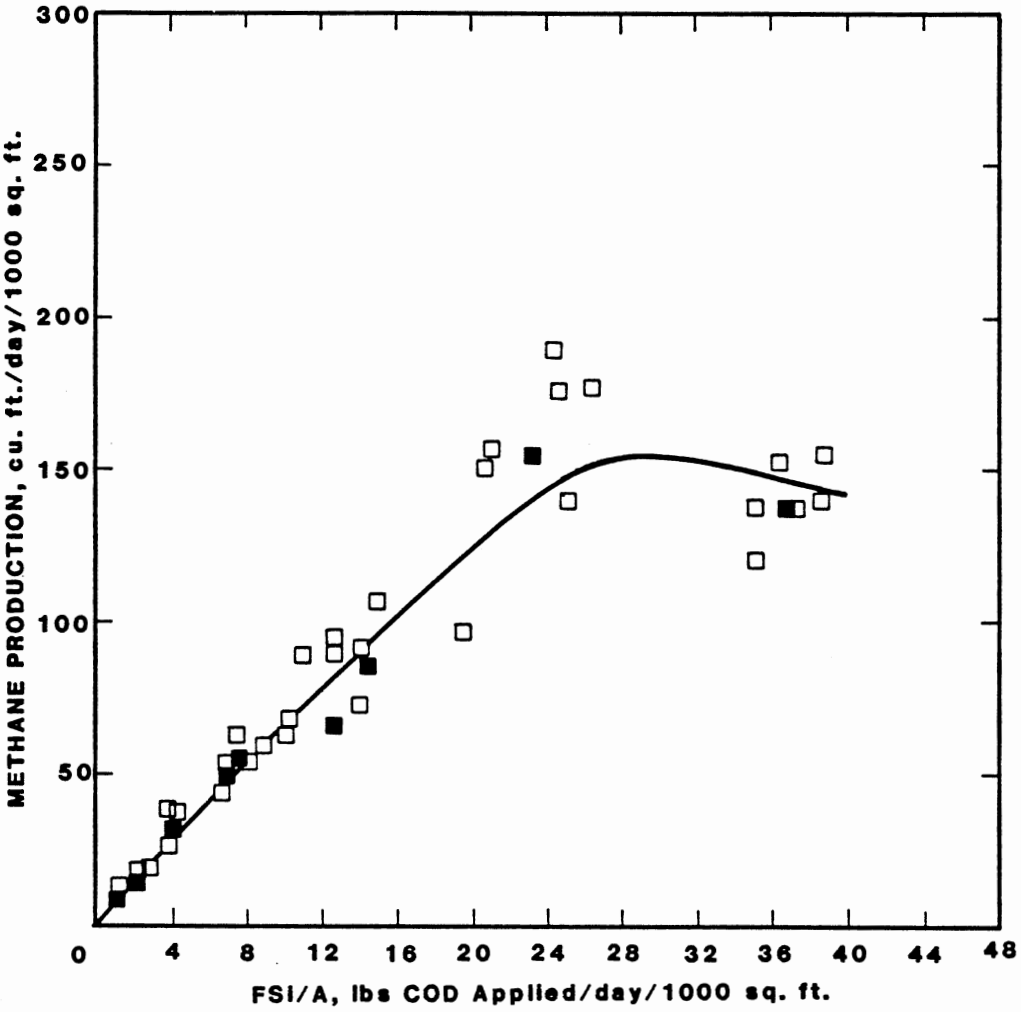

Figure 17. Methane Production as a Function of Mass Substrate Loading in Terms of COD

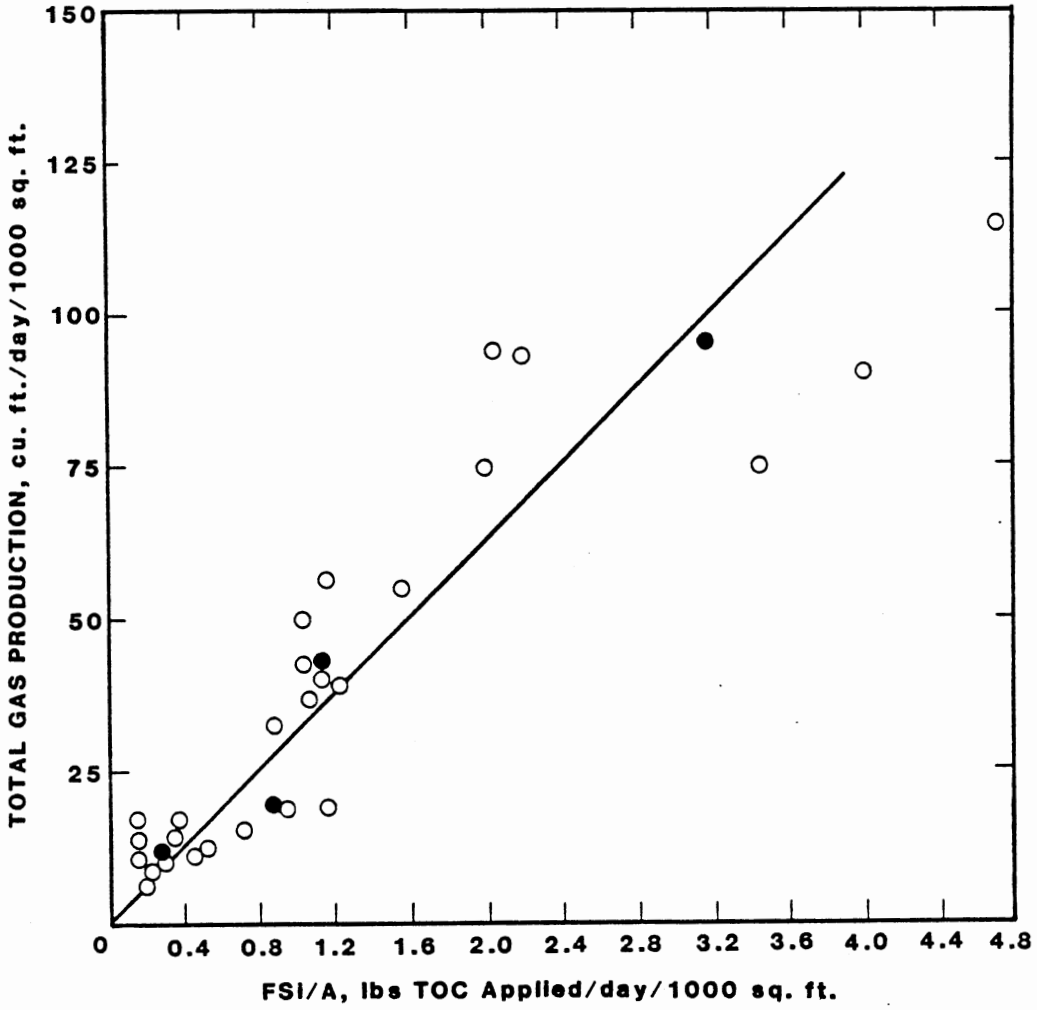

Figure 18. Total Gas Production as a Function of Mass Substrate Loading in Terms of TOC

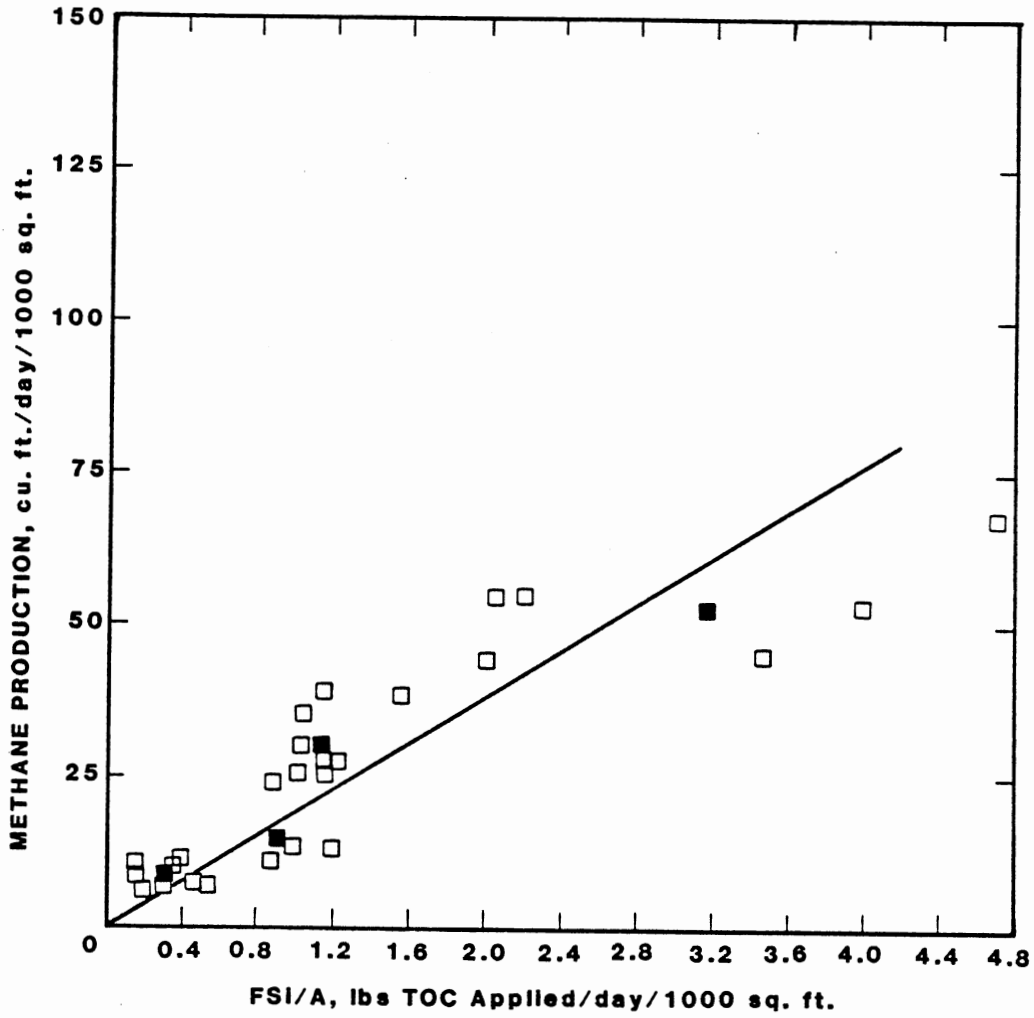

Figure 19. Methane Production as a Function of Mass Substrate Loading in Terms of TOC

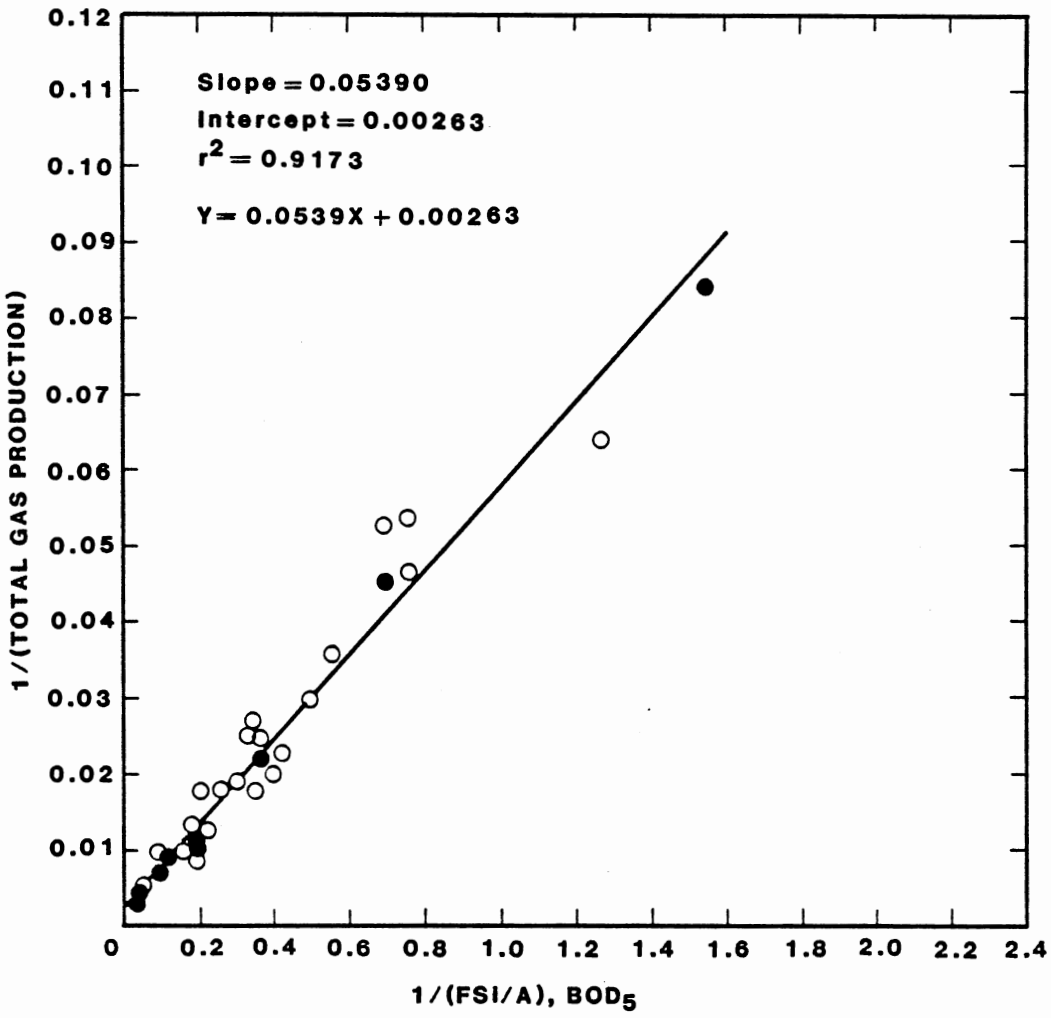

Figure 20. Graphical Determination of G_{max} and G_B in Terms of BOD_5

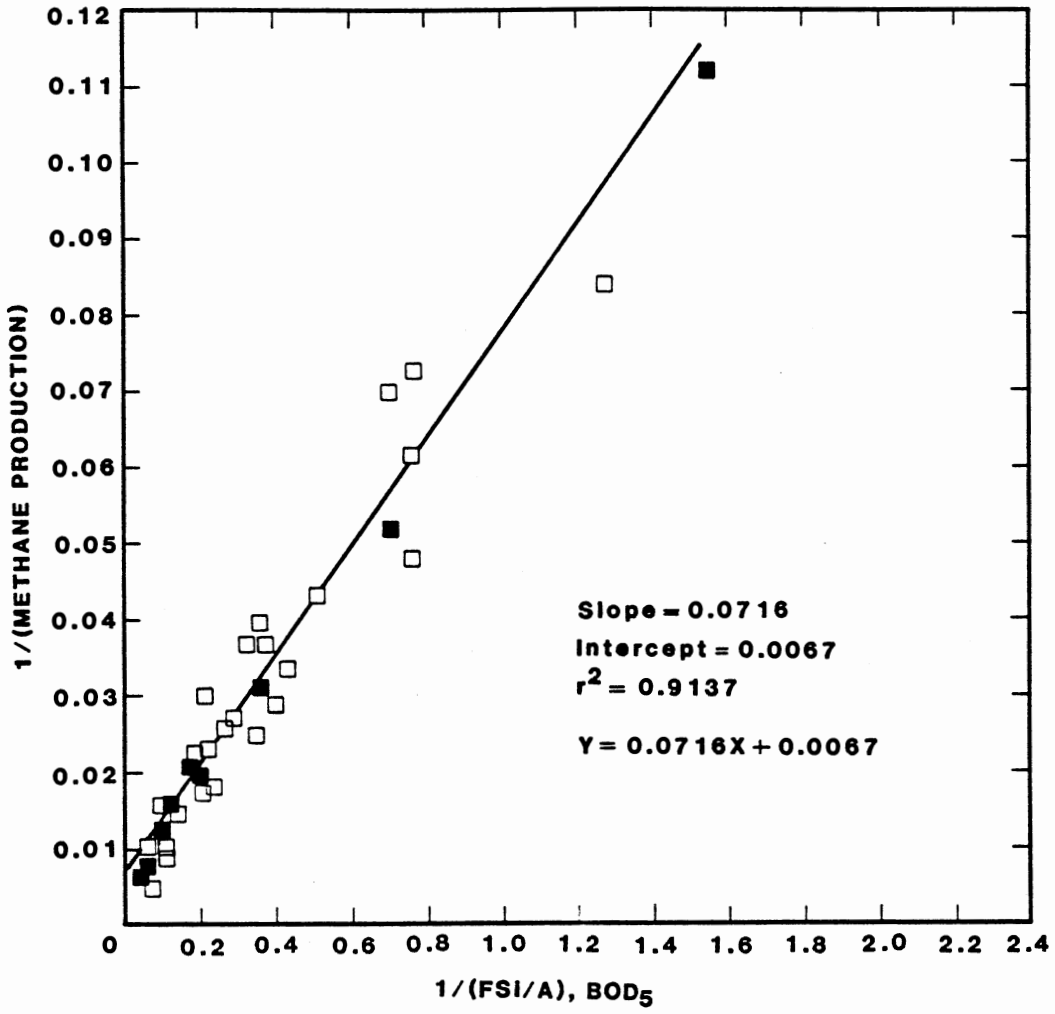

Figure 21. Graphical Determination of M_{max} and M_B in Terms of BOD_5

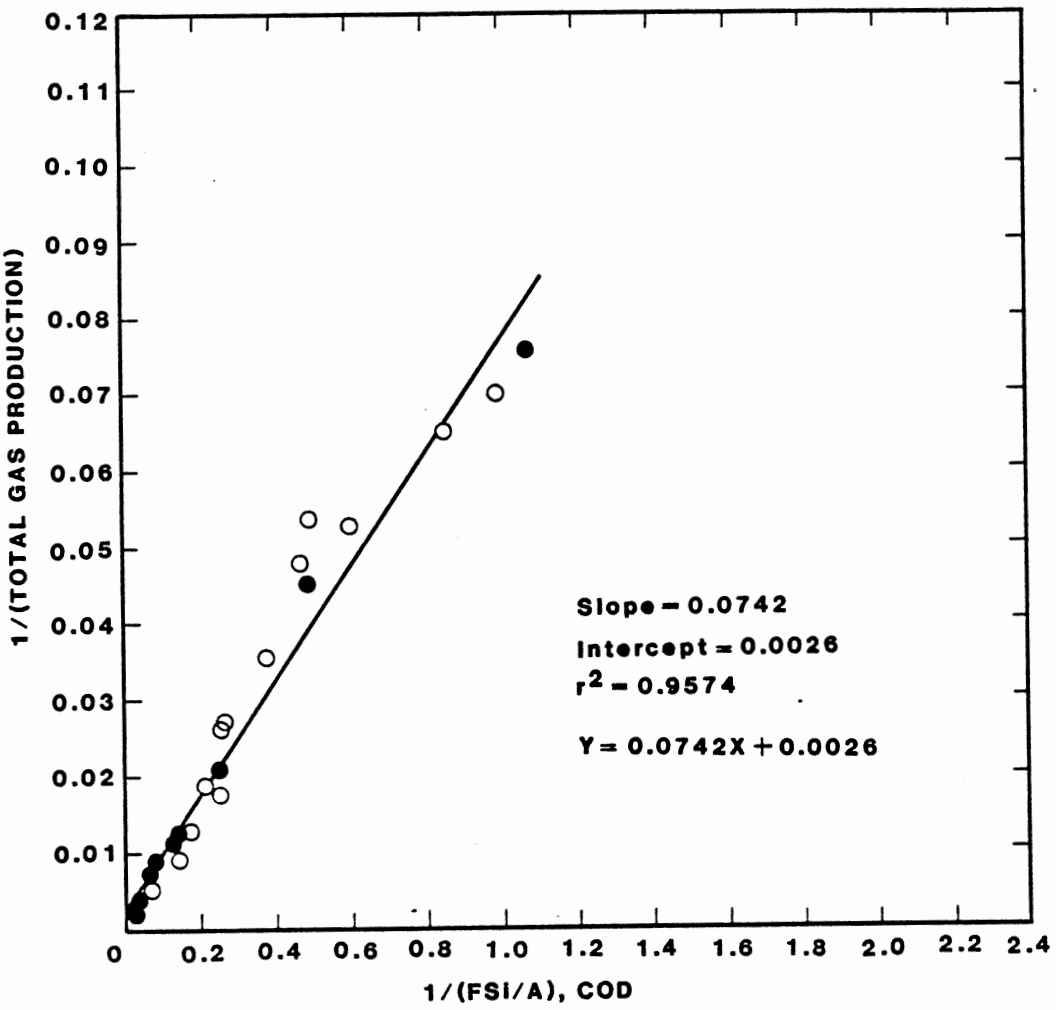

Figure 22. Graphical Determination of G_{max} and G_B in Terms of COD

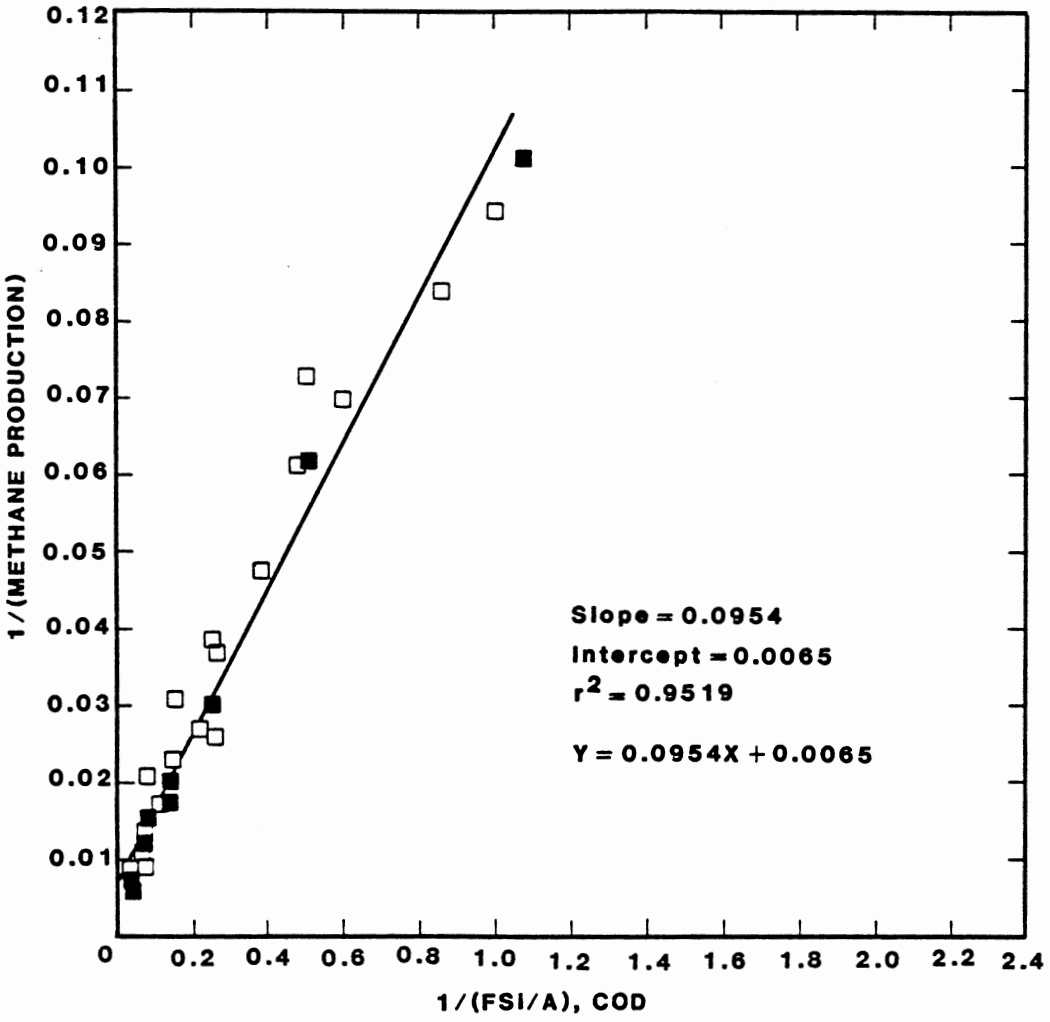

Figure 23. Graphical Determination of M_{max} and M_B in Terms of COD

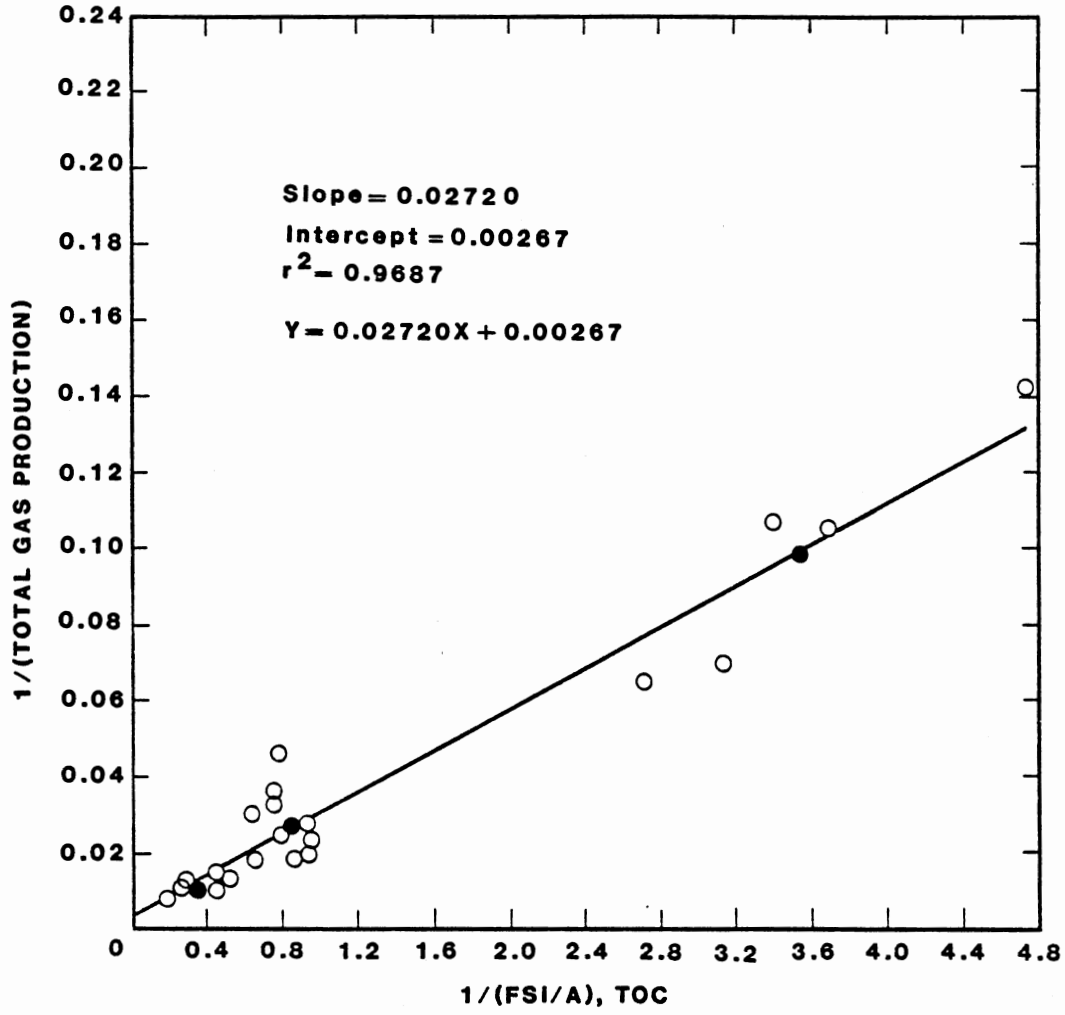

Figure 24. Graphical Determination of G_{max} and G_B in Terms of TOC

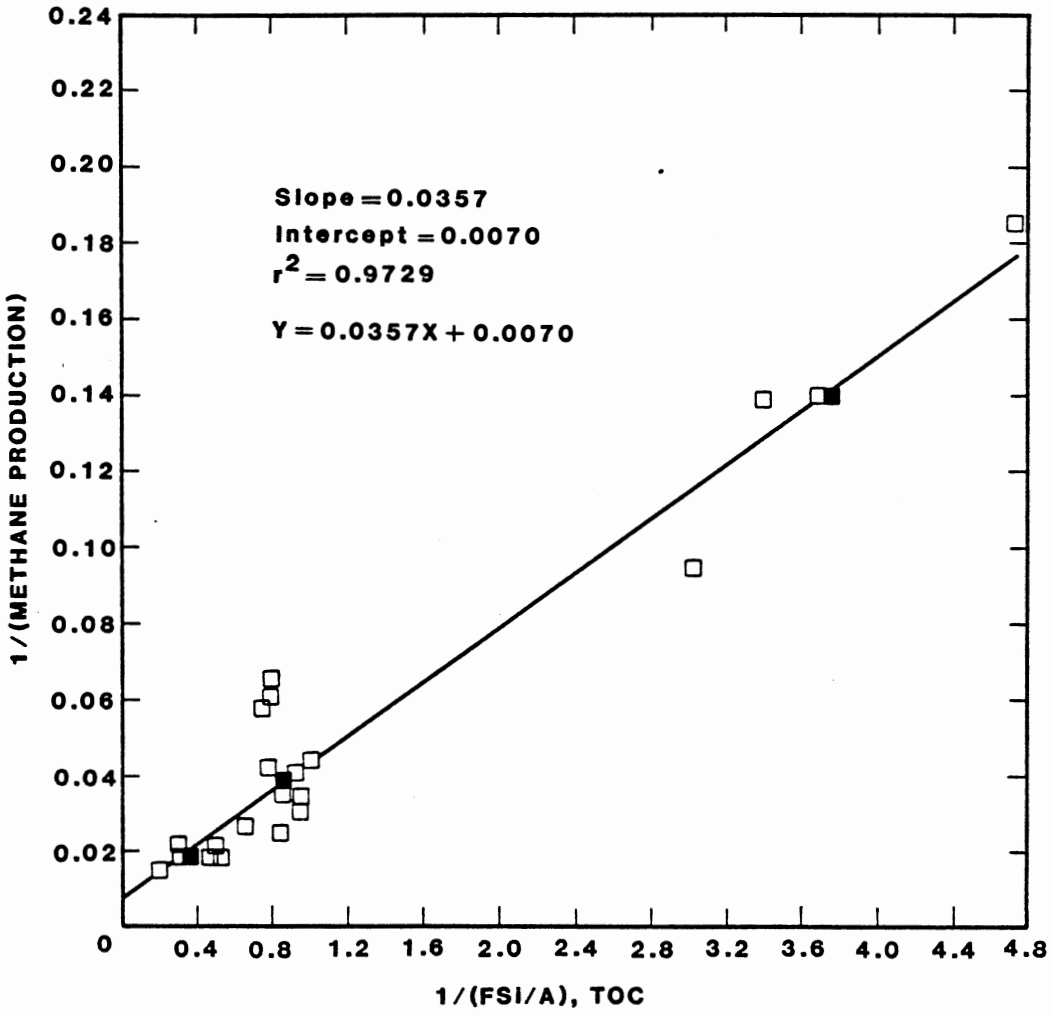

Figure 25. Graphical Determination of M_{max} and M_B in Terms of TOC

TABLE XIII

TOTAL GAS AND METHANE PRODUCTION
BIOLOGICAL KINETIC CONSTANTS

Constants	BOD_5* Kinetics	COD* Kinetics	TOC* Kinetics
G_{max} (cu.ft./d/1000 sq.ft.)	380.2	384.6	374.5
G_B (lbs/d/1000 sq.ft.)	20.5	28.5	10.2
M_{max} (cu.ft./d/1000 sq.ft.)	149.3	153.8	142.9
M_B (lbs/d/1000 sq.ft.)	10.7	14.7	5.1

* Kinetics in terms of soluble BOD_5, COD, and TOC

production rate, M_{max}, was around 150 cu. ft./day/1000 sq. ft..

Mathematical description of the total gas and methane production rates can therefore be modeled as the substrate loading rate by using monomolecular kinetics. Specific total gas production rate expressed as a function of the mass substrate loading rate follows:

$$G = \frac{G_{max} \frac{FSi}{A}}{G_B + \frac{FSi}{A}} \qquad (6)$$

where:

G = Specific total gas production rate, cu. ft./day/1000 sq. ft.

G_{max} = Maximum specific total gas production rate, cu. ft./day/1000 sq. ft.

G_B = Proportionality constant, lbs substrate/day/1000 sq. ft.

$\frac{FSi}{A}$ = Applied substrate loading rate, as previously described, lbs substrate/day/1000 sq. ft.

The specific methane production rate expressed as a function of the mass substrate loading rate follows:

$$M = \frac{M_{max} \frac{FSi}{A}}{M_B + \frac{FSi}{A}} \qquad (7)$$

where:

M = Specific methane production rate,
cu. ft./day/1000 sq. ft.

M_{max} = Maximum specific methane production rate,
cu. ft./day/1000 sq. ft.

M_B = Proportionality constant,
lbs substrate/day/1000 sq. ft.

Equations (6) and (7) can then be used to accurately predict the total gas production and methane production at any given substrate loading. These equations become an important tool in sizing the gas handling facility and predicting the amount of energy to be produced based on the methane production.

The solid lines in Figures 14 and 16 were drawn using the kinetic constants determined in Figures 20 and 22 at loading rates below 27 (35) lbs BOD_5 (COD)/day/1000 sq. ft.. The empty circles represent all the data points with a considerable amount of overlap and the filled circles represent the average operating data at each loading condition. The calculated maximum total gas production rate was higher than the actual observed rate due to the limitations of the bacteria at high loading rates, as

previously discussed in the substrate removal kinetics section. The actual total gas production rate peaked out at around 235 cu. ft./day/1000 sq. ft., as shown by the broken lines, compared to the calculated value of around 380. The total gas production rate suddenly decreased as the loading was increased to 28.85 (40.39) lbs BOD_5 (COD)/day/1000 sq. ft.. This last loading condition was not used for the kinetics determination, and it was shown in Figures 14 and 16 to indicate that at such a high loading condition the system almost completely fails.

The calculated and the actual maximum methane production rates were identical as shown by the solid lines in Figures 15 and 17. These lines peaked out at around 150 cu. ft./day/1000 sq. ft., which was the calculated value. The sudden decrease of methane production at loadings of 28.85 (40.39) lbs BOD_5 (COD)/day/1000 sq. ft. were not shown in these figures, since at that point the gas composition was not determined. In these figures, the empty squares represent all the data points with a considerable amount of overlap and the filled squares represent the average operating data at each loading condition. The actual maximum total gas production and maximum methane production rates in terms of TOC could not be compared to the calculated values, since only four TOC loading conditions were used in the calculations. However, the straight lines in Figures 18 and 19 indicate the high performance of the system at those low loading conditions. Again, the empty circles and squares

represent all the data points and the filled circles and squares represent the average operating data at each condition. The lines in Figures 20 through 25 were drawn using their respective equations obtained by linear regression analysis shown in the Appendix.

The actual methane production rates were higher than the expected stoichiometric values. There were two main possible reasons for this discrepancy, one of them was that the theoretical methane production rates were calculated based on soluble COD, since total COD was not consistently run on the influent and effluent. If total COD were used, the calculated theoretical methane production could be higher in proportion to the degree of substrate hydrolysis. In this particular case, the hydrolized fraction of the substrate was not determined. If the substrate were completely hydrolized, total COD should be used to calculate the theoretical methane production, considering that 0.35 L of methane are produced per 1 gr of COD removed, at STP (0 °C, 1 atm) (34). The other main reason was that the influent and effluent COD values were higher than those values reported by the modified Hach procedure employed during this study. The COD values were verified by additional testing of the raw wastewater under more stringent oxidation conditions toward the end of the study. By using corrected soluble COD's (corrected COD equal to 1.4 times the modified Hach procedure), the theoretical methane production rates were very close to the actual values. This means that the

remainder of the total COD may not have been hydrolized and the only reason for the difference between theoretical and actual methane production may have been the difference in COD's due to the analytical procedures.

E. Low Temperature Gas Production Kinetics

The total gas production and methane production characteristics during the low temperature studies are summarized in Table IX. It can be observed that as the substrate loading rate increased the percent BOD_5 and COD removals decreased, the percent methane decreased, and the percent carbon dioxide increased. The gas production data presented in Figures 26(a), 27(a), 28(a), and 29(a) indicate that the total gas production and the methane production are a function of the substrate loading rate, and the kinetics can be described by monomolecular kinetics, like substrate utilization and gas production at higher temperatures, discussed in previous sections. The graphical determination of the gas kinetics at low temperature are presented in Figures 26(b), 27(b), 28(b), and 29(b), and the kinetic values are summarized in Table XIV in terms of soluble BOD_5 and COD. In Figures 26 through 29, again, the empty circles and squares represent all the data points and the filled ones represent the average data at each loading condition.

The maximum total gas production rate, G_{max}, and the maximum methane production rate, M_{max}, were also found to be

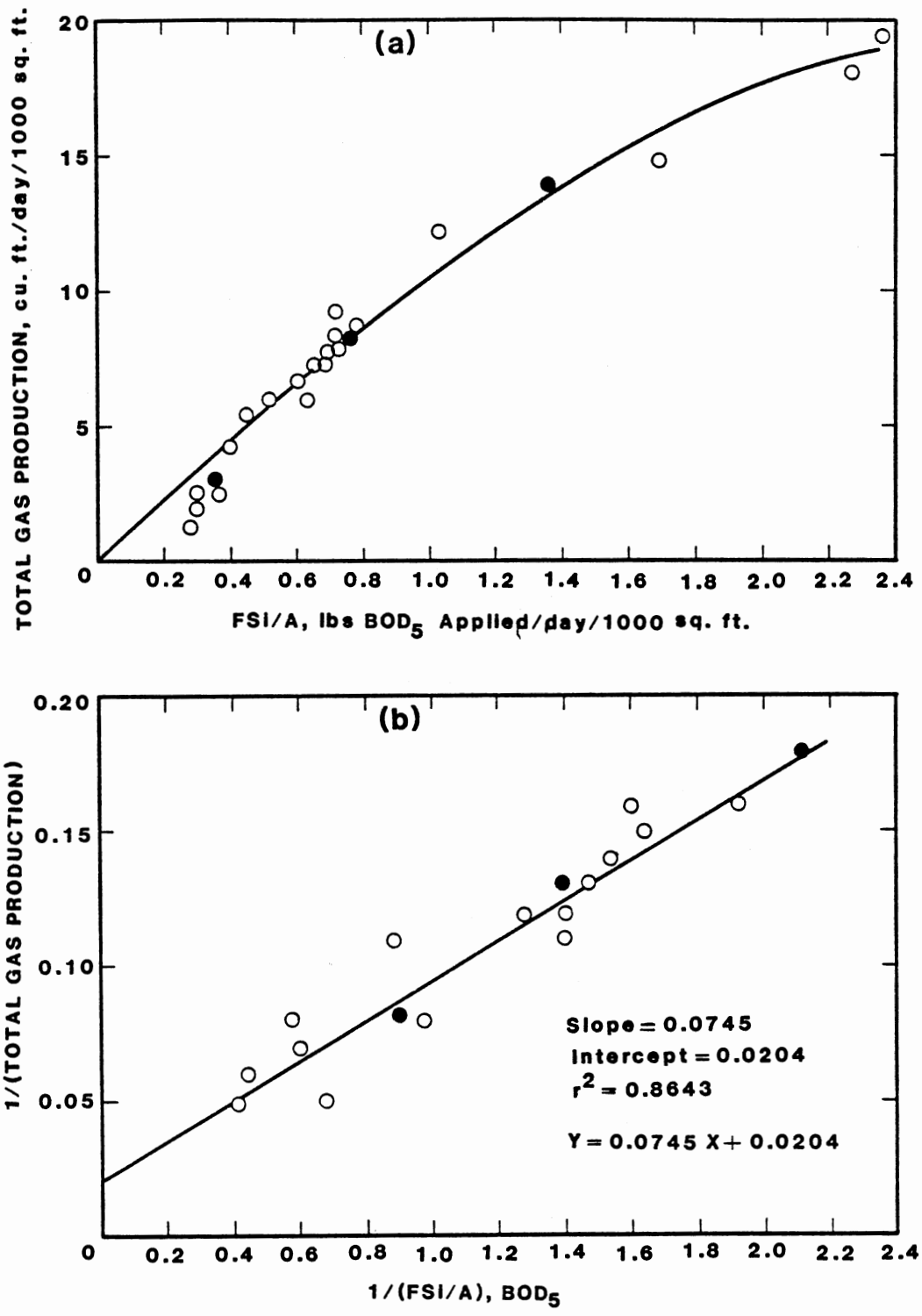

Figure 26. Total Gas Production Kinetics as a Function of BOD_5 Loading Rate (Low Temperature)

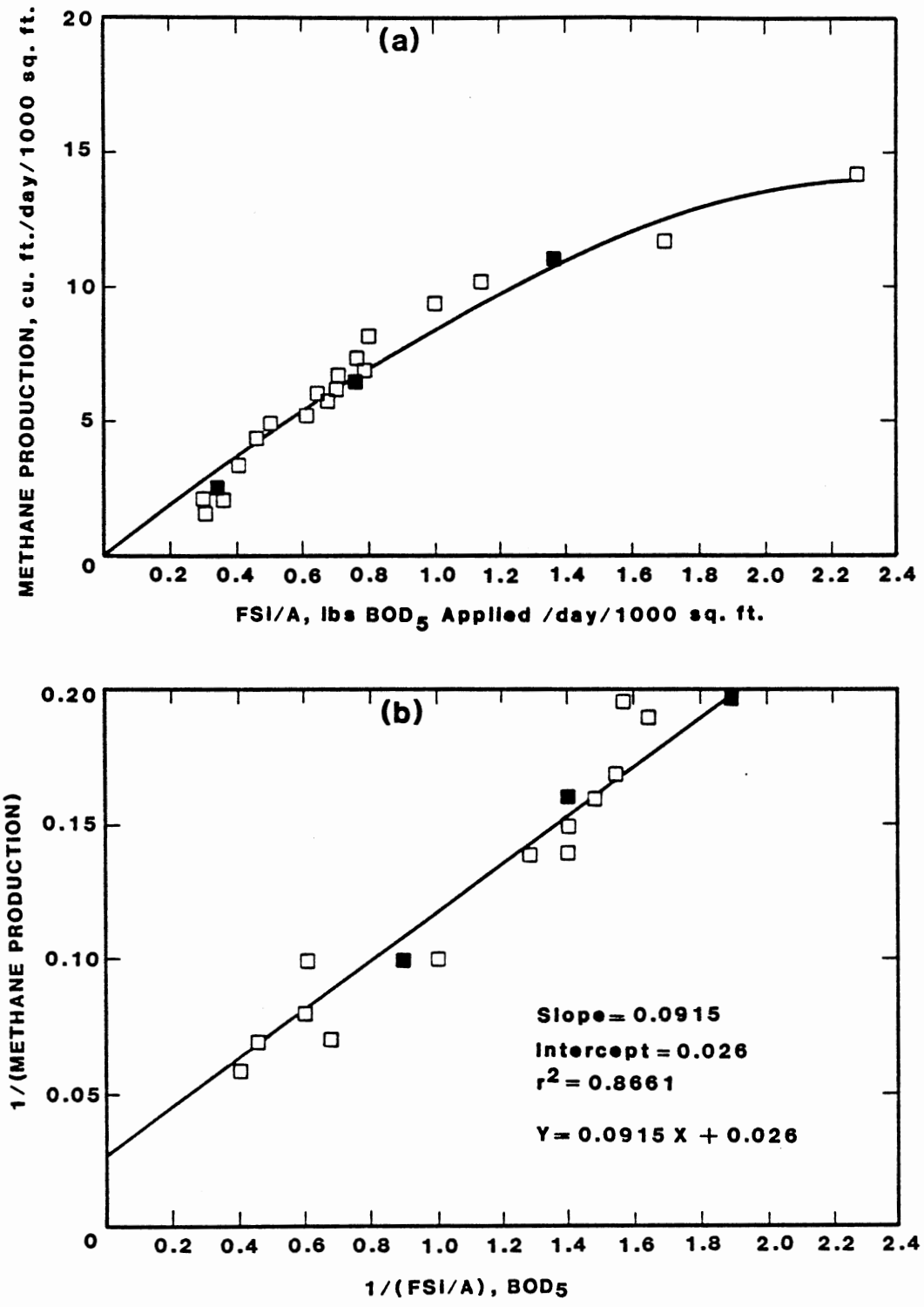

Figure 27. Methane Production Kinetics as a Function of BOD_5 Loading Rate (Low Temperature)

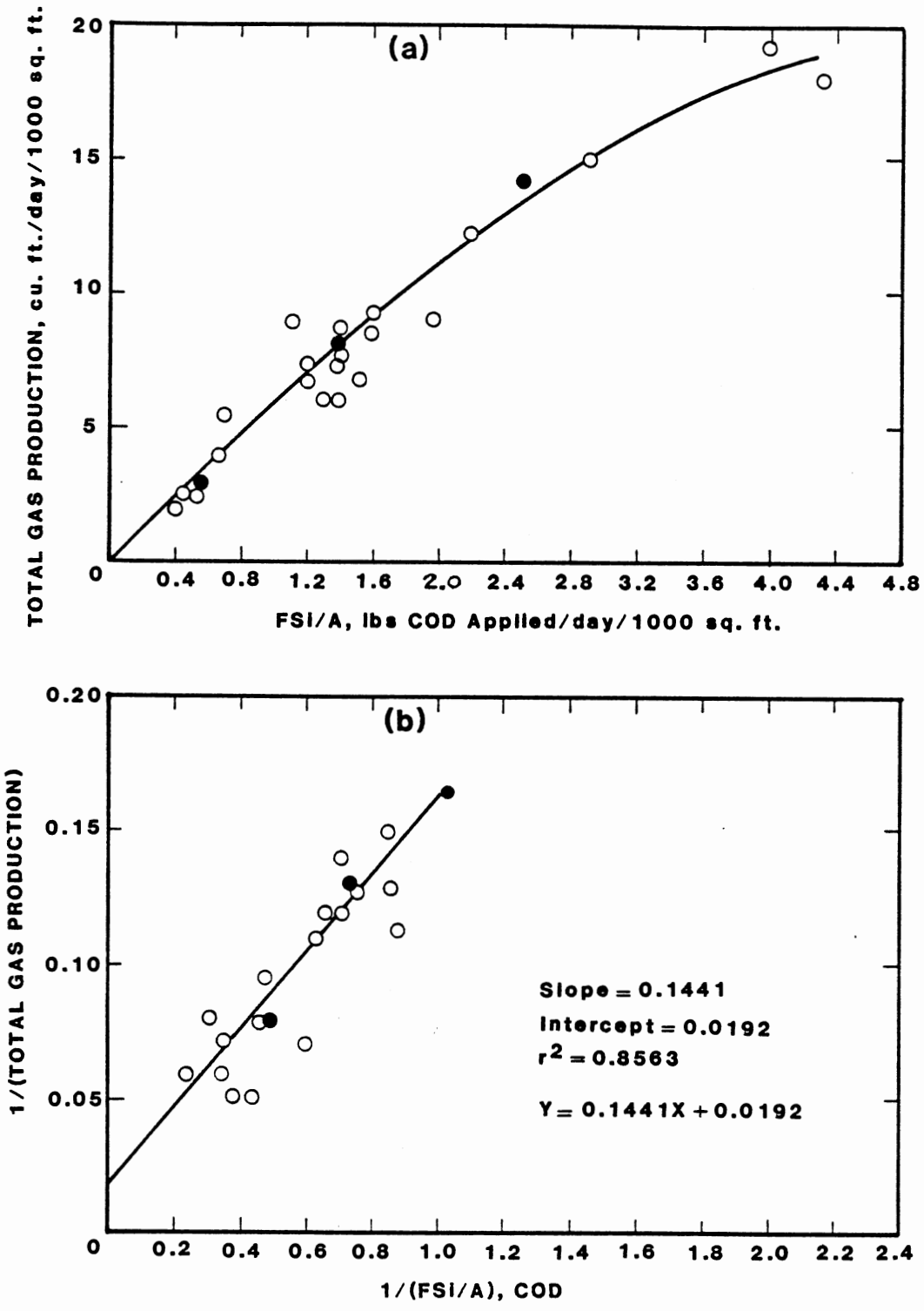

Figure 28. Total Gas Production Kinetics as a Function of COD Loading Rate (Low Temperature)

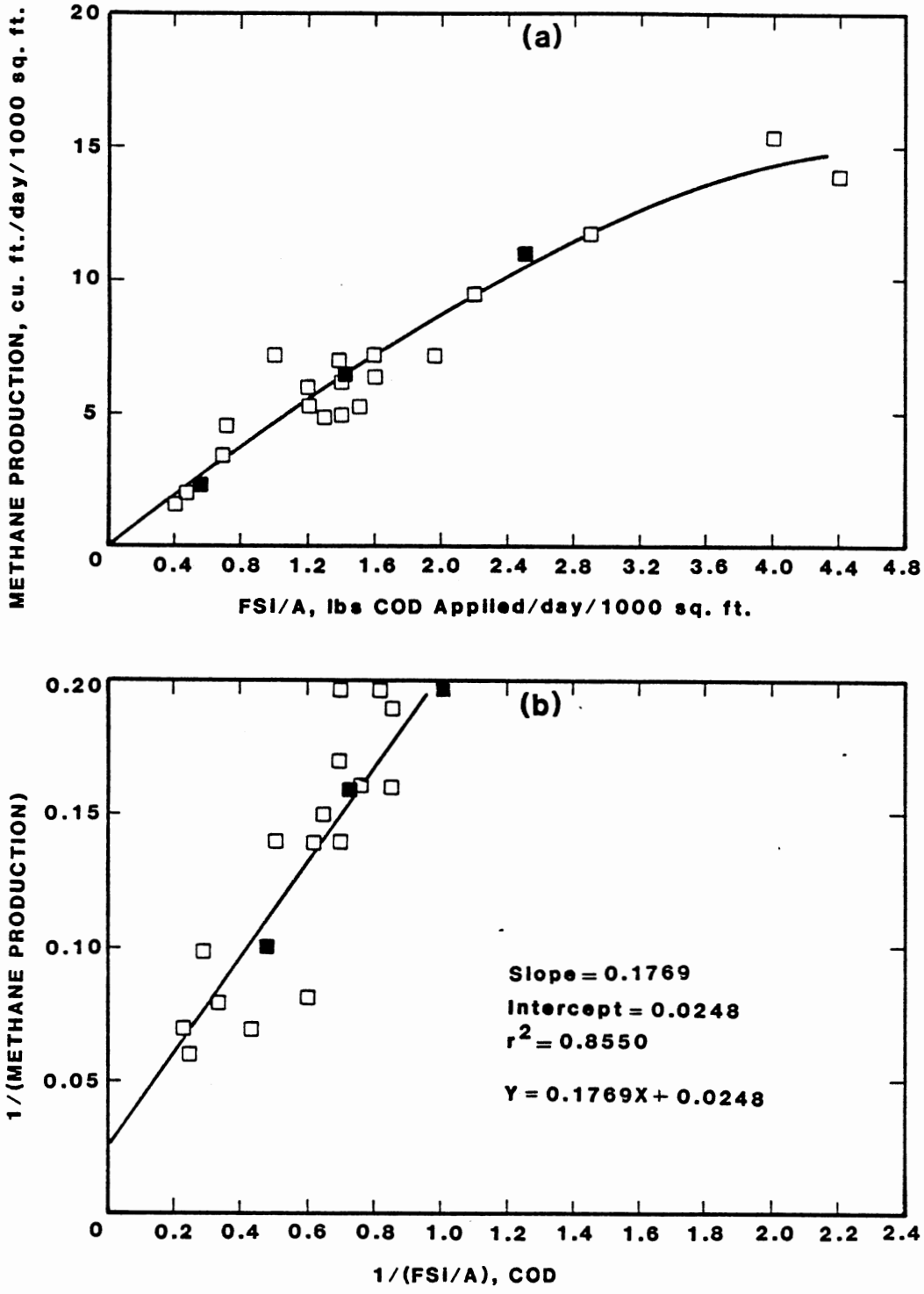

Figure 29. Methane Production Kinetics as a Function of COD Loading Rate (Low Temperature)

TABLE XIV

TOTAL GAS AND METHANE PRODUCTION KINETIC CONSTANTS (LOW TEMPERATURE)

Constants	BOD_5* Kinetics	COD* Kinetics
G_{max} (cu.ft./d/1000 sq.ft.)	49.0	52.1
G_B (lbs/d/1000 sq.ft.)	3.7	7.5
M_{max} (cu.ft./d/1000 sq.ft.)	38.5	40.3
M_B (lbs/d/1000 sq.ft.)	3.5	7.1

* Kinetics in terms of soluble BOD_5, and COD

very close to each other, irrespective of whether they were calculated in terms of BOD_5 or COD. G_{max} was found to be around 50 cu. ft./day/1000 sq. ft. and M_{max} was around 39 cu. ft./day/1000 sq. ft.. Again, equations (6) and (7) can be used to accurately predict the total gas and methane production rates for any given substrate loading condition, at 25 $\pm$ 2 ^{o}C. Also, during these low temperature studies, the actual methane production rates were higher than the stoichiometric values. The reason for this discrepancy has already been discussed in the previous section.

A comparison of the gas production kinetics in Tables XIII and XIV shows a tremendous difference between them. A similar difference was observed between the substrate removal kinetics at 25 $\pm$ 2 ^{o}C and 36 $\pm$ 2 ^{o}C. The reason for that difference, in both cases, was already discussed in previous sections.

F. Shock Load Studies

The key for maintaining process control and stable operations in biological treatment systems is to provide proper environmental conditions to the biomass or bacteria in the system. Changing environmental conditions, especially fluctuations in wastewater characteristics, tend to disrupt steady-state conditions, which the biological treatment facilities were designed to approach. The hydraulic flow rate and organic (BOD_5 or COD) loading rate, along with the variability in these parameters, are two of the most

critical parameters relative to maintaining stable operating conditions; of course, pH, temperature, nutrients, and lack of toxic or inhibitory substances are also critical to successful operations. Environmental changes tending to disrupt steady-state conditions (shock loads) which can not be, or have not been, smoothed by preventive engineering measures must be accommodated solely by successful biological response or by combined biological and operational remedial responses (55).

During production or manufacturing processes, wastewater discharge characteristics may vary significantly both in quantity and quality or temporarily ceased for clean-up operations, mechanical breakdown of equipment or overhauling of production facilities. Some facilities may have significant variations in wastewater discharges on a seasonal basis. There may also be significant periods of time where no wastewaters are generated. With these wastewater discharge characteristics in mind, the capabilities of anaerobic treatment systems to handle shock loads relative to changes in flow, organic loading rates, temperature, and shut-down or no feeding periods were investigated. The results from these experiments are discussed here to show the stability and response capabilities of these systems relative to substrate removal, effluent quality, gas production, and gas quality under changing conditions.

F.1. Organic and Hydraulic Shock Load

High loads of wastewater are generated when process tanks are emptied or cleaned, particularly from batch manufacturing. Any treatment system must be capable of meeting the average load and be able to accommodate shock loads with a minimum of effluent degradation.

During this particular shock load to the anaerobic fixed-film reactor, the organic loading rate was doubled by increasing the influent flow rate from 5.8 L/d to 11.9 L/d, maintaining the feed concentration constant at around 14,284 mg/L COD (11,050 mg/L BOD_5), for a period of 24 hours. Throughout this experimental test period the reactor temperature was maintained at 35 °C to 37 °C. The impacts on effluent quality and gas production of doubling the organic loading rate for 24 hours are summarized in Table XV and shown graphically in Figure 30. During the shock load period, the reactor was monitored by collecting samples every eight hours. The COD (BOD_5) loading rates were increased from around 11.0 (8.5) lbs/day/1000 sq. ft. to 22 (17) lbs/day/1000 sq. ft.. The average gas production increased from around 50 L/d to 86 L/d during the high loading period, then immediately dropped back to 43 L/d when the original loading rate was restored. Also, the gas quality slightly changed during this period, with a decrease in percent methane from 62 % to 59%, and then back to 62% after the shock load. The percent carbon dioxide increased from 36% to 39% and then back to 36%. The effluent COD,

TABLE XV

AVERAGE CONDITIONS BEFORE, DURING, AND AFTER SHOCK LOADING STUDY (ORGANIC LOADING RATE DOUBLED)

	Parameter	Conditions before the shock	Conditions during the shock	Conditions after the shock
Influent	Flow Rate L/d	5.8	11.9	5.8
	pH	7.3-7.5	7.4-7.9	7.3-7.4
	SS (VSS) mg/L	180 (140)	253 (174)	230 (162)
	COD (BOD_5) mg/L	14539 (11050)	14242 (11050)	14242 (11050)
	COD Load. (BOD_5 Load.) $lbs/d/1000ft^2$	11.0 (8.4)	22.2 (17.2)	10.8 (8.4)
Effluent	pH	7.4-7.6	6.9-7.5	7.4-7.6
	*VFA, mg/L as Acet.Ac.	1950 (480)	2625 (510)	1590 (465)
	*Alkalinity mg/L $CaCO_3$	2675 (3750)	2625 (3625)	2475 (3125)
	SS (VSS) mg/L	464 (393)	395 (306)	588 (380)
	COD (BOD_5) mg/L	3500 (2770)	4099 (3770)	2918 (2588)

TABLE XV (Continued)

	Parameter	Conditions before the shock	Conditions during the shock	Conditions after the shock
Efficiency	COD Removal	76	71	80
	(BOD_5 Remov.) %	(75)	(66)	(77)
Gas	**Production L/d	50	86	43
	Quality			
	% CH_4	62	59	62
	% CO_2	36	39	36

* Effluent (Bottom of the Reactor)
** Gas Volume Corrected to STP (0 °C, 1 atm)

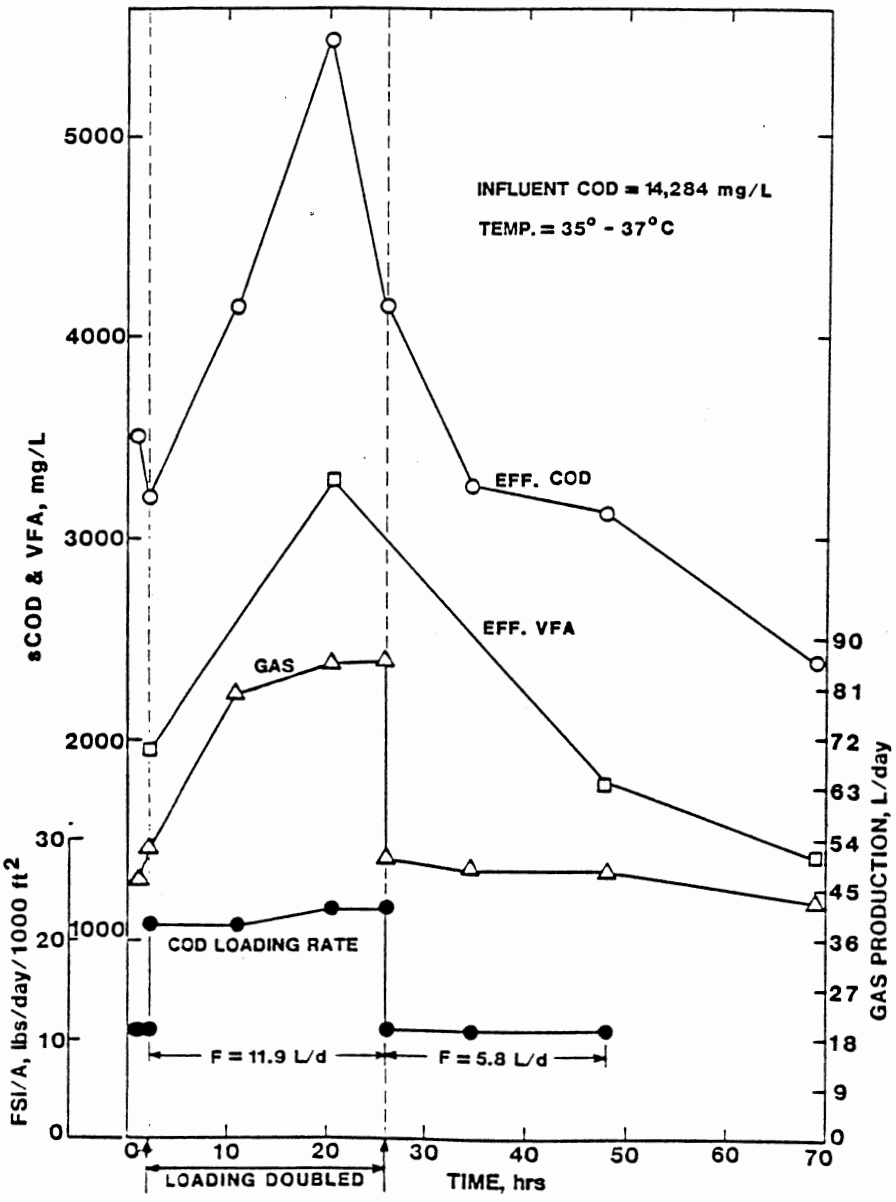

Figure 30. Organic Shock Load Results

BOD_5, and volatile fatty acids (VFA) all increased during the 24 hour shock load period reaching maximum values of 5,500 mg/L, 4,900 mg/L, and 3,300 mg/L as acetic acid, respectively, after 20 hours. They decreased back to around their original values within 24 hours after the loading rate was changed back to the original rate. The alkalinity in the effluent held constant at around 2,600 mg/L as $CaCO_3$. The treatment efficiency slightly dropped with decrease in COD (BOD_5) removals from 76% (75%) to 70% (66%) during the period of shock and immediately restored to 80% (77%) when the organic loading rate was taken back to the original rate.

Thus, it was possible to observe from this study, that the anaerobic fixed-film reactor was capable of withstanding temporary organic and hydraulic shocks with very little effluent substrate leakage and impact on gas production rates. Similar results were observed, at OSU when the organic loading to a suspended growth anaerobic reactor, fed with the same wastewater (thin stillage), was doubled by doubling the flow rate (39). Barnes et al., (50) had similar experiences when a pilot-scale fluidized bed anaerobic reactor was subjected to shock loads of high BOD_5 concentration, imposed over a period of one hour. The shock loads were twice the average daily loads.

F.2. Low Temperature Shock Study

The impacts of dropping the temperature 10 $\pm$ 2 ^{o}C (from

36 ± 2 °C to 26 ± 2 °C) in the fixed-film reactor are summarized in Table XVI and shown graphically in Figure 31. The reactor temperature was changed by changing the room temperature. The system was kept at 26 ± 2 °C for a period of four days. The COD (BOD_5) loading rate during this study period was around 13 (8) lbs/day/1000 sq. ft.. The effluent COD, BOD_5, and volatile fatty acids all increased during the low temperature period with maximum values of 6,500 mg/L, 5,500 mg/L, and 3,800 mg/L as acetic acid, respectively, after 160 hours. This poor performance of the system at lower temperature has been already discussed in a previous section. Once the temperature was increased back to 36 ± 2 °C, the effluent characteristics returned to similar values previous to the low temperature shock within one to two days. The average gas production dropped from 72 L/d to 32 L/d when the temperature was decreased, with a minimum value of 18 L/d, and increased back to 70 L/d when the temperature was increased back to 36 ± 2 °C. As expected, the COD (BOD_5) percent removals also decreased from 89% (91%) to 75% (72%), due to the gas production decrease and the increase in effluent COD, BOD_5, and VFA. The percent removals returned back to 87% (89%) as the temperature was increased to 36 ± 2 °C. As previously discussed, decrease in temperature during continuous feeding has significant negative impacts on both effluent quality and gas production.

Capri et al. (51) observed that when the temperature of a digester, normally operated at 35 °C, was reduced to 10 °C

TABLE XVI

AVERAGE CONDITIONS BEFORE, DURING, AND AFTER TEMPERATURE SHOCK STUDY

	Parameter	Conditions before the shock	Conditions during the shock	Conditions after the shock
Reactor	Temperature ^{o}C	35-37	24-28	35-40
Influent	pH	5.1-5.7	5.0-5.8	5.0-5.8
	SS (VSS) mg/L	425 (276)	456 (174)	440 (225)
	COD (BOD_5) mg/L	22154 (14450)	17950 (13450)	16320 (10000)
	COD Load. (BOD_5 Load.) lbs/d/1000ft^2	13.3 (8.6)	13.6 (10.2)	12.3 (6.8)
Effluent	pH	7.1-7.7	6.3-7.8	7.0-7.8
	*VFA, mg/L as Acet.Ac.	2100 (220)	3390 (360)	2430 (490)
	*Alkalinity mg/L $CaCO_3$	2691 (3030)	2775 (3125)	2700 (3250)
	SS (VSS) mg/L	795 (476)	344 (276)	324 (204)
	COD (BOD_5) mg/L	2423 (1313)	4462 (3823)	2084 (1130)

TABLE XVI (Continued)

	Parameter	Conditions before the shock	Conditions during the shock	Conditions after the shock
Efficiency	COD Removal (BOD_5 Remov.) %	89 (91)	75 (72)	87 (89)
Gas	**Production L/d	72	32	70

* Effluent (Bottom of the Reactor)
** Gas Volume Corrected to STP (0 °C, 1 atm)

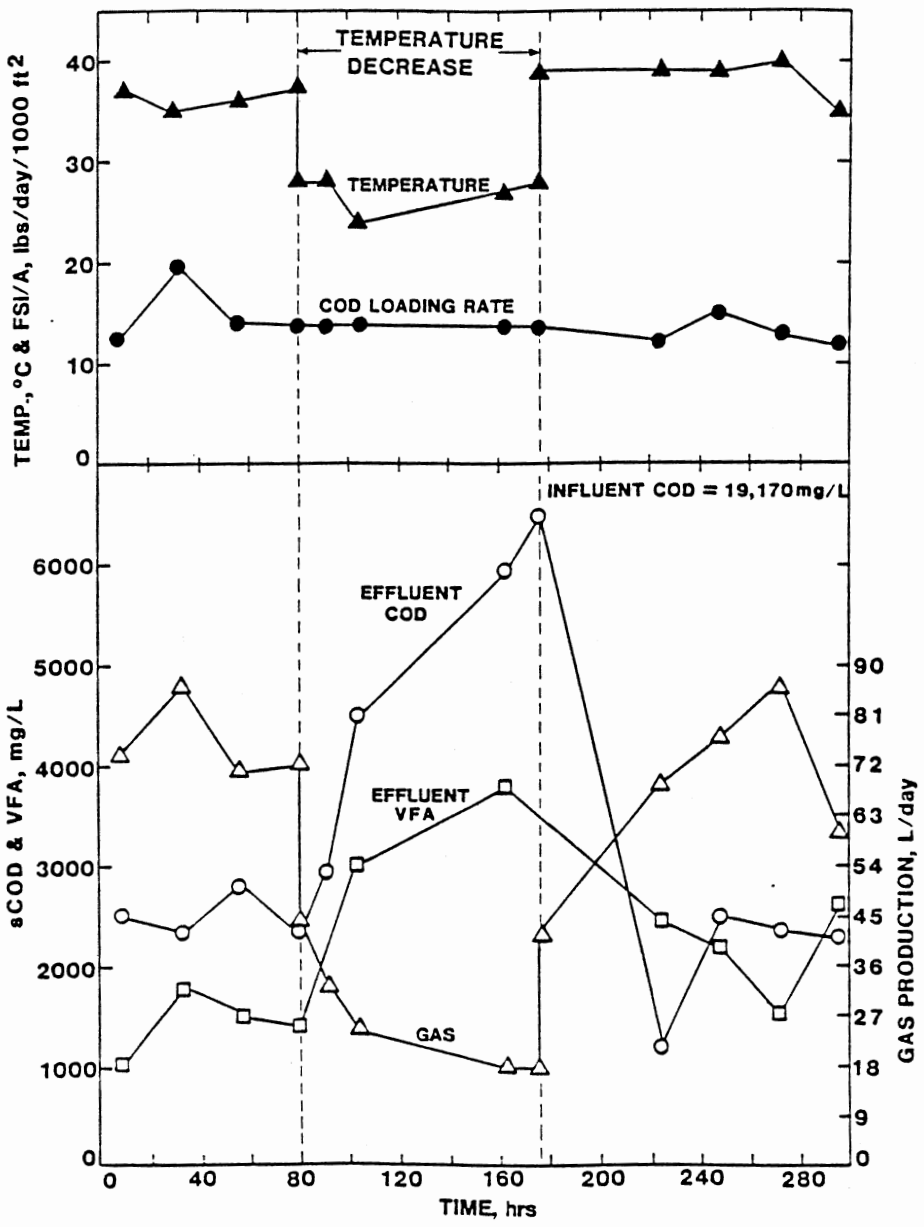

Figure 31. Temperature Shock Results

for 15 minutes and then raised again to 35 °C, the gas production decreased and resumed its former rate. He obtained similar results when the temperature was lowered to 10 °C for 2 hours although the gas production rate rose to its former level more slowly. Buhr and Andrews (47) model to describe effects of temperature, predicts that a sudden decrease in the temperature of a digester from 50 °C to 40 °C could cause digester failure within 2 to 3 days. Hickey (52) observed that an 11 degree drop from 35 °C to 24 °C resulted in only 10 percent reduction in COD removal rates over the entire loading range examined (15 to 37 Kg COD/day/m^3), during the treatment of cheese whey in an anaerobic fluidized bed system.

F.3. Feed Shut-Down Studies

Whenever there are cleanup operations, over-hauling of the plant or major mechanical break-downs, the production has to be temporarily ceased, so, no waste is generated and the anaerobic wastewater treatment system receives no feed. Because of these operational situations, the impacts of shut-down periods on the anaerobic reactor were investigated.

Figure 32 is a graphical profile showing the chronological impacts of feed shut-down over different time periods and different conditions on the performance of the pilot fixed-film reactor system. The COD (BOD_5) loading rate during this time period was around 5.0 (3.5) lbs/day/1000

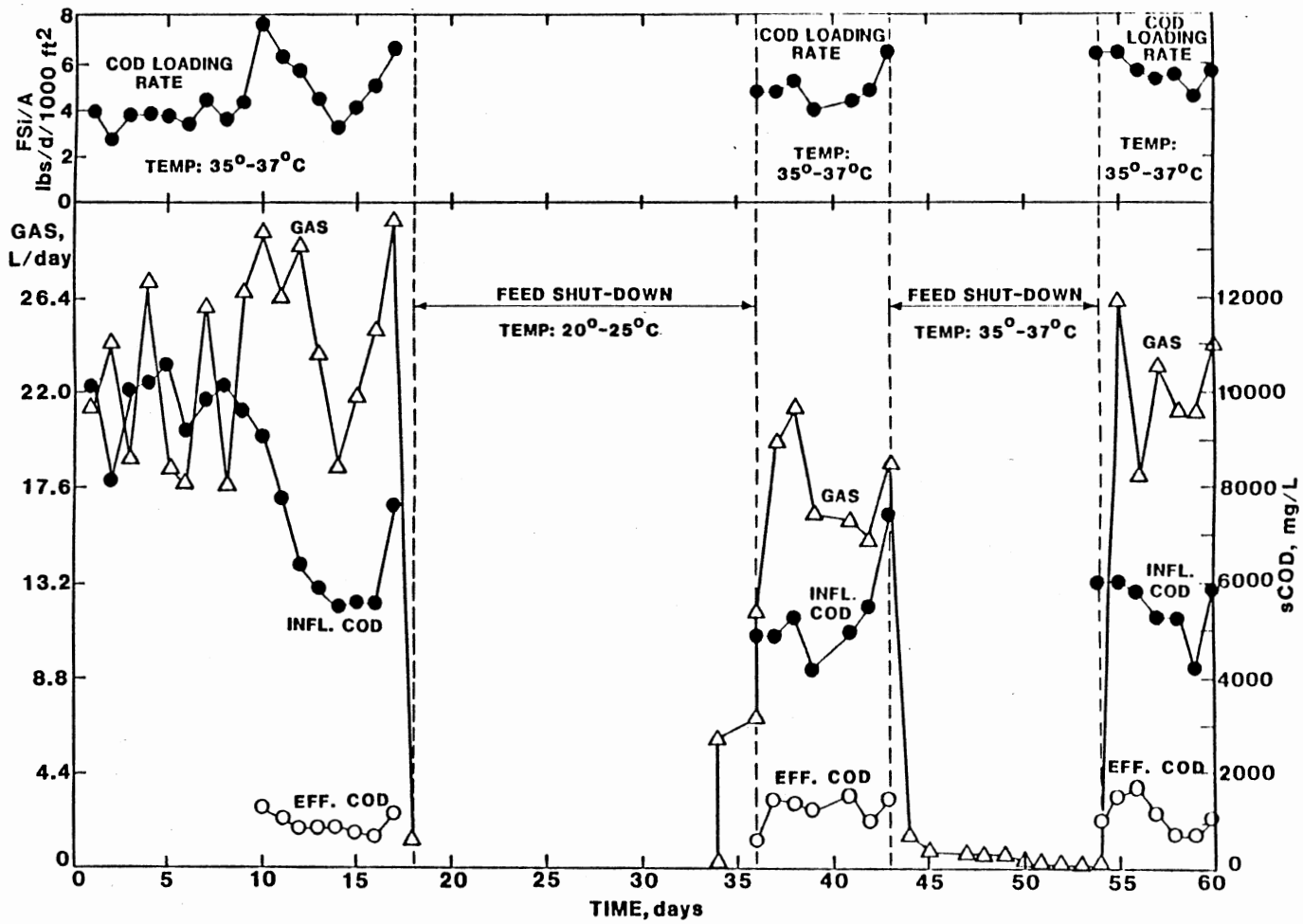

Figure 32. Effects of Shut-Down Periods

sq. ft.. The first non-feeding period was for 16 days with the reactor temperature dropped from 36 ± 2 °C to 20-25 °C. During days 15 and 16 of the shut-down period, the reactor temperature was increased back to 35 ± 2 °C with an immediate response in increased gas production prior to refeeding on day 16. The reactor was then restarted up (fed) for a 7-day period at 36 ± 2 °C prior to being shut-down again for 11 days at 36 ± 2 °C. The gas production dropped from around 20 to 25 L/d during the feeding periods to negligible amounts (between 0.34 and 1.82 L/d) during the non-feeding periods, while the concentrations of VFA in the reactor remained about the same, between 460 and 840 mg/L as acetic acid. The response capabilities of the reactor to non-feeding and start-up capabilities were similar irrespective of the reactor temperature during the dormant periods. This is an important consideration relative to shutting down an anaerobic system or placing it in a dormant state for long time periods without requirements for maintaining temperature control. Significant energy savings could be realized by not heating the reactor. Both the effluent quality and gas production capabilities of the system returned to around the initial values within 24 hours after the system was started up from both dormant periods. The test results during this series of testing are summarized in Table XVII.

The Bacardi Corporation anaerobic filter (53) treating distillery waste, has been shut-down for periods of three to

TABLE XVII

AVERAGE CONDITIONS DURING CONSECUTIVE FEED SHUT-DOWN (DORMANT PERIOD) STUDIES

	Parameter	Conditions before 1st dorm. per.	Conditions between dorm. per.	Conditions after 2nd dorm. per.
Influent	Flow Rate L/d	4.5	7.1	7.7
	pH	5.2-6.1	5.5-6.8	4.7-6.2
	SS (VSS) mg/L	146 (116)	146 (120)	133 (110)
	COD (BOD_5) mg/L	7774 (6028)	5390 (3830)	5427 (2864)
	COD Load. (BOD_5 Load.) lbs/d/1000ft^2	4.60 (3.19)	4.96 (3.65)	5.49 (4.32)
Effluent	pH	7.4-8.0	7.5-7.7	6.6-7.1
	*VFA, mg/L as Acet.Ac.	860 (690)	1079 (520)	978 (444)
	*Alkalinity mg/L $CaCO_3$	3400 (4350)	2670 (2778)	1180 (2490)
	SS (VSS) mg/L	135 (88)	190 (143)	147 (106)
	COD (BOD_5) mg/L	1127 (345)	1410 (205)	1155 (238)

TABLE XVII (Continued)

	Parameter	Conditions before 1st dorm. per.	Conditions between dorm. per.	Conditions after 2nd dorm. per.
Efficiency	COD Removal (BOD_5 Remov.) %	85 (94)	74 (95)	79 (92)
Gas	**Production L/d	23	18	22

* Effluent (Bottom of the Reactor)
** Gas Volume Corrected to STP (0 °C, 1 atm)

seven weeks without adverse effects on the system. The design feed rate was re-established within 24 hours after the distillery start-up. Szendrey et al. (54) documented a continuous shut-down period of over 150 days of an anaerobic plant treating food processing wastes. The system was restored within 2 days when the addition of substrate was restarted. A shut-down period of one week was performed on a suspended growth anaerobic reactor treating the same alcohol wastewater at OSU, without suffering any serious set-back (39).

Once the fuel alcohol wastewater treatability study at OSU was completed, the fixed-film anaerobic reactor was kept in a dormant stage, at room temperature, for approximately one year. After this dormant period, the reactor was fed with a different high strength wastewater (fish processing wastewater) and restored to normal operation within one week. The reactor was operated at 36 $\pm$ 2 ^{o}C treating fish processing wastewater for a period of 3 months. Since then, the reactor has been in a dormant stage, at room temperature, for over one year.

CHAPTER V

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

This research project was part of an extensive treatability study program performed on the wastewater generated at the Oklahoma State University Agricultural Engineering fuel alcohol production research facility. At this research facility ethanol was produced from grains such as corn, milo, and wheat, and the wastewater generated (thin stillage) was high-strength, acidic, and high-temperature.

The purpose of this research project was the kinetic analysis and performance evaluation of a continuous upflow, fixed-film, anaerobic reactor in the treatment of fuel alcohol wastewater. A bench-scale reactor was operated for a period of two years in order to develop the biological kinetic constants needed for reliable design and operation of a full-scale fixed-film anaerobic treatment system. The substrate removal kinetics, total gas production kinetics, and methane production kinetics were developed in terms of soluble BOD_5, COD, and TOC at 36 $\pm$ 2 ^{o}C, and in terms of soluble BOD_5 and COD at 25 $\pm$ 2 ^{o}C. Shock load studies including organic shock loads, low temperature shocks, and shut-down periods were also performed to determine their

impacts on effluent quality, gas production and reactor performance.

The following conclusions can be drawn from this study:

1. The fuel alcohol wastewaters are highly biodegradable and can be successfully treated to high levels by fixed-film anaerobic systems.

2. The substrate removal kinetics were found to be dependent and predictable as a function of the mass substrate loading rate applied. The substrate removal and treatment performance can be accurately predicted using the Stover and Kincannon mathematical design model. The application of this kinetic modeling approach was presented for design and optimization of the operation of full-scale anaerobic fixed-film treatment systems.

3. At substrate loading rates greater than 27 (35) lbs BOD_5(COD)/day/1000 sq.ft. the volatile fatty acid (VFA) concentrations increased to very high levels such that the methane conversion reactions were significantly reduced or inhibited.

4. The substrate removal kinetics developed at 25 $\pm$ 2 ^{o}C were considerably lower than the kinetics at 36 $\pm$ 2 ^{o}C due to the low rate of methane conversion at low temperatures.

5. The system was able to successfully treat the wastewater when operated at 25 $\pm$ 2 ^{o}C, for organic loading conditions lower than 2.0 (4.4) lbs BOD_5 (COD)/day/1000 sq. ft.

6. The total gas production kinetics and the methane production kinetics were a function of the applied substrate loading rates and could be described by monomolecular kinetics just like substrate utilization. Mathematical expressions to describe the total gas and methane productions were developed. These kinetic constants can be used for prediction of total gas and methane productions at any given organic loading conditions, as well as, for design of the gas handling facilities. Once the methane production is known, the amount of energy to be produced can also be predicted.

7. The maximum total gas production rate and the maximum methane production rate were predictable and were found to be identical irrespective of whether they were calculated in terms of soluble BOD_5, COD, or TOC.

8. The methane content of the gas decreased and the carbon dioxide content increased as the applied loadings were increased up to around 12 lbs BOD_5 (16.5 lbs COD)/day/1000 sq. ft. at which point the methane content leveled out at 59% and the carbon dioxide at 39%.

9. The total gas and methane production kinetics developed at 25 $\pm$ 2 ^{o}C were also considerably lower than the kinetics at 36 $\pm$ 2 ^{o}C. Also, the maximum rates (total gas and methane) were identical based on soluble BOD_5 and COD.

10. The organic loading rate to the system was doubled for a period of 24 hours without any serious adverse effects.

11. The low temperature shock load caused a decrease in gas production and an increase in effluent COD (BOD_5) and volatile fatty acids. Once the temperature was restored, the reactor performance went back to normal.

12. The reactor recuperated within 24 hours after being subjected to shut-down or dormant periods of up to two weeks.

13. Low temperatures during dormant periods of up to two weeks without feeding showed no negative impacts when continuous feeding was initiated.

14. The COD values reported in this study and obtained using a modified procedure of the Hach COD test procedure, were 1.4 times lower than the actual COD values, which were obtained using the procedure suggested in the Standard Methods (40). The substrate removal, total gas production, and methane production kinetic constants in terms of the soluble COD values reported in this study were 10% to 15% lower than the kinetic constants in terms of the actual COD values. This means that a design based on the lower kinetic constants would be a conservative design.

The concepts, methodology, and scientific approach used in this study are applicable to any anaerobic fixed-film reactor. The use of fixed-film anaerobic reactors offers advantages over other type of treatment systems. Some of these advantages are lower sludge production, able to handle high organic loading rates due to the high mass of microorganisms attached to the media, no need for mixing

which represents energy savings, methane production as a by-product, able to handle long shut-down periods.

It is recommended for further studies with fixed-film anaerobic systems the following:

1. Use an appropriate COD test procedure capable of accurately measuring the strength of the wastewater.

2. Use a wet test meter to measure the gas production rather than the water displacement method.

3. Analyze the off-gas by gas chromatography in order to accurately determine the gas composition.

4. Identify the volatile fatty acids in the influent and effluent in order to determine the rate-limiting step at different conditions.

5. Study the impacts of influent volatile suspended solids on the performance of the system, gas production, and gas quality.

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APPENDIX

LINEAR REGRESSION ANALYSIS
FIGURE 5

Predictor Variable (x): 1/(Loading Rate, BOD_5)
Number of Samples = 60
Mean = 0.337550
Median = 0.157000
Coefficient of Variance = 0.203285
Standard Deviation = 0.450871

Dependent Variable (y): 1/(Removal Rate, BOD_5)
Number of Samples = 60
Mean = 0.356883
Median = 0.174500
Coefficient of Variance = 0.205122
Standard Deviation = 0.452904

Regression Equation:
Y = 1.798862E-02 + 1.003984 * X

Significance of Slope :
T = 235.2901,
df = 58
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 2.007968)

Correlation Coefficient:
r^2 = 0.9995

Significance of Correlation:
The correlation coefficient is significantly different than 0

APPENDIX

LINEAR REGRESSION ANALYSIS
FIGURE 6

Predictor Variable (x): 1/(Loading Rate, COD)
Number of Samples = 55
Mean = 0.216236
Median = 0.090
Coefficient of Variance = 0.0921214
Standard Deviation = 0.303515

Dependent Variable (y): 1/(Removal Rate, COD)
Number of Samples = 55
Mean = 0.232909
Median = 0.102
Coefficient of Variance = 0.100638
Standard Deviation = 0.317235

Regression Equation:
Y = 7.014986E-03 + 1.044663 * X

Significance of Slope :
T = 226.5083
df = 53
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 2.089326)

Correlation Coefficient:
r^2 = 0.9995

Significance of Correlation:
The correlation coefficient is significantly different than 0

APPENDIX

LINEAR REGRESSION ANALYSIS
FIGURE 7

Predictor Variable (x): 1/(Loading Rate, TOC)
Number of Samples = 28
Mean = 1.208929
Median = 0.860
Coefficient of Variance = 1.195639
Standard Deviation = 1.093453

Dependent Variable (y): 1/(Removal Rate, TOC)
Number of Samples = 28
Mean = 1.290714
Median = 0.925
Coefficient of Variance = 1.299703
Standard Deviation = 1.140045

Regression Equation:
Y = 0.0360478 + 1.037833 * X

Significance of Slope :
T = 53.08742
df = 26
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 2.075666)

Correlation Coefficient:
r^2 = 0.9954

Significance of Correlation:
The correlation coefficient is significantly different than 0

APPENDIX

LINEAR REGRESSION ANALYSIS
FIGURE 10

Predictor Variable (x): 1/(Loading Rate, BOD_5)
Number of Samples = 26
Mean = 1.575769
Median = 1.400
Coefficient of Variance = 0.810713
Standard Deviation = 0.900396

Dependent Variable (y): 1/(Removal Rate, BOD_5)
Number of Samples = 26
Mean = 1.926154
Median = 1.905
Coefficient of Variance = 0.695688
Standard Deviation = 0.834079

Regression Equation:
Y = 0.5072368 + 0.9004601 * X

Significance of Slope :
T = 20.28569
df = 24
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 1.8009202)

Correlation Coefficient:
r^2 = 0.9721

Significance of Correlation:
The correlation coefficient is significantly different than 0

APPENDIX

LINEAR REGRESSION ANALYSIS
FIGURE 11

Predictor Variable (x): 1/(Loading Rate, COD)
Number of Samples = 26
Mean = 0.907308
Median = 0.705
Coefficient of Variance = 0.388941
Standard Deviation = 0.623651

Dependent Variable (y): 1/(Removal Rate, COD)
Number of Samples = 26
Mean = 1.100000
Median = 0.940
Coefficient of Variance = .366024
Standard Deviation = 0.604999

Regression Equation:
Y = 0.2273019 + 0.9618546 * X

Significance of Slope :
T = 37.35145
df = 24
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 1.9237092)

Correlation Coefficient:
r^2 = 0.9915

Significance of Correlation:
The correlation coefficient is significantly different than 0

APPENDIX

LINEAR REGRESSION ANALYSIS
FIGURE 20

Predictor Variable (x): 1/(Loading Rate, BOD_5)
Number of Samples = 59
Mean = 0.343051
Median = 0.1600
Coefficient of Variance = 0.205142
Standard Deviation = 0.452926

Dependent Variable (y): 1/(Total Gas)
Number of Samples = 59
Mean = 0.021814
Median = 0.0107
Coefficient of Variance = 0.000754
Standard Deviation = 0.027462

Regression Equation:
Y = 2.734394E-03 + 5.561615E-02 * X

Significance of Slope :
T = 17.39011
df = 57
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.1112323)

Correlation Coefficient:
r^2 = 0.9173

Significance of Correlation:
The correlation coefficient is significantly different than 0

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LINEAR REGRESSION ANALYSIS
FIGURE 21

Predictor Variable (x): 1/(Loading Rate, BOD_5)
Number of Samples = 59
Mean = 0.343051
Median = 0.1600
Coefficient of Variance = 0.205142
Standard Deviation = 0.452926

Dependent Variable (y): 1/(Methane)
Number of Samples = 59
Mean = 0.03127458
Median = 0.0181
Coefficient of Variance = 0.001260
Standard Deviation = 0.035492

Regression Equation:
Y = 6.712443E-03 + 7.159911E-02 * X

Significance of Slope :
T = 16.97438
df = 57
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.1431982)

Correlation Coefficient:
r^2 = 0.9137

Significance of Correlation:
The correlation coefficient is significantly different than 0

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LINEAR REGRESSION ANALYSIS
FIGURE 22

Predictor Variable (x): 1/(Loading Rate, COD)
Number of Samples = 52
Mean = 0.226956
Median = 0.1000
Coefficient of Variance = 0.095755
Standard Deviation = 0.309443

Dependent Variable (y): 1/(Total Gas)
Number of Samples = 52
Mean = 0.019465
Median = 0.0094
Coefficient of Variance = 0.000574
Standard Deviation = 0.023964

Regression Equation:
Y = 2.638097E-03 + 7.414347E-02 * X

Significance of Slope :
T = 23.44803
df = 50
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.1482869)

Correlation Coefficient:
r^2 = 0.9574

Significance of Correlation:
The correlation coefficient is significantly different than 0

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LINEAR REGRESSION ANALYSIS
FIGURE 23

Predictor Variable (x): 1/(Loading Rate, COD)
Number of Samples = 52
Mean = 0.226956
Median = 0.1000
Coefficient of Variance = 0.095755
Standard Deviation = 0.309443

Dependent Variable (y): 1/(Methane)
Number of Samples = 52
Mean = 0.028067
Median = 0.01575
Coefficient of Variance = 0.000963
Standard Deviation = 0.031036

Regression Equation:
Y = 6.400691E-03 + 9.546626E-02 * X

Significance of Slope :
T = 21.95499
df = 50
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.1909325)

Correlation Coefficient:
r^2 = 0.9519

Significance of Correlation:
The correlation coefficient is significantly different than 0

APPENDIX

LINEAR REGRESSION ANALYSIS
FIGURE 24

Predictor Variable (x): 1/(Loading Rate, TOC)
- Number of Samples = 24
- Mean = 1.416250
- Median = 0.8600
- Coefficient of Variance = 1.786564
- Standard Deviation = 1.336624

Dependent Variable (y): 1/(Total Gas)
- Number of Samples = 24
- Mean = 0.040908
- Median = 0.026255
- Coefficient of Variance = 0.001360
- Standard Deviation = 0.036880

Regression Equation:
- Y = 2.951463E-03 + 2.680097E-02 * X

Significance of Slope :
- T = 19.16967
- df = 22
- p = <10(-6)
- The slope of the line is significantly different than 0

Confidence Limits of Slope:
- (0, 0.0536019)

Correlation Coefficient:
- r^2 = 0.9687

Significance of Correlation:
- The correlation coefficient is significantly different than 0

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LINEAR REGRESSION ANALYSIS
FIGURE 25

Predictor Variable (x): 1/(Loading Rate, TOC)
Number of Samples = 23
Mean = 1.359565
Median = 0.8600
Coefficient of Variance = 1.787149
Standard Deviation = 1.336843

Dependent Variable (y): 1/(Methane)
Number of Samples = 23
Mean = 0.055491
Median = 0.0365
Coefficient of Variance = 0.002375
Standard Deviation = 0.048739

Regression Equation:
Y = 7.076362E-03 + 3.561061E-02 * X

Significance of Slope :
T = 20.87875
df = 21
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.0712212)

Correlation Coefficient:
r^2 = 0.9767

Significance of Correlation:
The correlation coefficient is significantly different than 0

APPENDIX

LINEAR REGRESSION ANALYSIS
FIGURE 26

Predictor Variable (x): 1/(Loading Rate, BOD_5)
Number of Samples = 21
Mean = 1.224762
Median = 1.280
Coefficient of Variance = 0.279456
Standard Deviation = 0.528636

Dependent Variable (y): 1/(Total Gas)
Number of Samples = 21
Mean = 0.111905
Median = 0.110
Coefficient of Variance = 0.002206
Standard Deviation = 0.046970

Regression Equation:
Y = 1.940636E-02 + 7.552358E-02 * X

Significance of Slope :
T = 7.033295
df = 19
p = 1.11054E-06
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.1510472)

Correlation Coefficient:
r^2 = 0.8500

Significance of Correlation:
The correlation coefficient is significantly different than 0

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LINEAR REGRESSION ANALYSIS
FIGURE 27

Predictor Variable (x): 1/(Loading Rate, BOD_5)
Number of Samples = 21
Mean = 1.224762
Median = 1.280
Coefficient of Variance = 0.279456
Standard Deviation = 0.528636

Dependent Variable (y): 1/(Methane)
Number of Samples = 21
Mean = 0.138571
Median = 0.140
Coefficient of Variance = 0.003333
Standard Deviation = 0.057731

Regression Equation:
Y = 2.445928E-02 + 9.317089E-02 * X

Significance of Slope :
T = 7.128875
df = 19
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.1863418)

Correlation Coefficient:
r^2 = 0.8532

Significance of Correlation:
The correlation coefficient is significantly different than 0

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LINEAR REGRESSION ANALYSIS
FIGURE 28

Predictor Variable (x): 1/(Loading Rate, COD)
Number of Samples = 21
Mean = 0.643333
Median = 0.66
Coefficient of Variance = 0.077873
Standard Deviation = 0.279058

Dependent Variable (y): 1/(Total Gas)
Number of Samples = 21
Mean = 0.111905
Median = 0.110
Coefficient of Variance = 0.002206
Standard Deviation = 0.046970

Regression Equation:
Y = 1.918555E-02 + 0.1441231 * X

Significance of Slope :
T = 7.22565
df = 19
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.2882462)

Correlation Coefficient:
r^2 = 0.8563

Significance of Correlation:
The correlation coefficient is significantly different than 0

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LINEAR REGRESSION ANALYSIS
FIGURE 29

Predictor Variable (x): 1/(Loading Rate, COD)
Number of Samples = 21
Mean = 0.643333
Median = 0.66
Coefficient of Variance = 0.077873
Standard Deviation = 0.279058

Dependent Variable (y): 1/(Methane)
Number of Samples = 21
Mean = 0.138571
Median = 0.14
Coefficient of Variance = 0.003333
Standard Deviation = 0.057731

Regression Equation:
Y = 2.477238E-02 + 0.1768897 * X

Significance of Slope :
T = 7.187384
df = 19
p = <10(-6)
The slope of the line is significantly different than 0

Confidence Limits of Slope:
(0, 0.3537794)

Correlation Coefficient:
r^2 = 0.8550

Significance of Correlation:
The correlation coefficient is significantly different than 0

VITA

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