A COMPREHENSIVE TREATABILITY STUDY ON ALCOHOL STILLAGE USING AEROBIC AND ANAEROBIC SUSPENDED GROWTH SYSTEMS

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LIST OF ABBREVIATIONS AND SYMBOLS

Alk	Alkalinity
BOD_5	Biochemical Oxygen Demand
CH_4	Methane
CH_0	Carbohydrate
CO_2	Carbondioxide
COD	Chemical Oxygen Demand
CST	Capillary Suction Time
EtoH	Ethanol
F	Flow Rate
F/M	Food over Microorganisms Ratio FS_i/XV
F_w	Waste Sludge Flow Rate
HRT	Hydraulic Retention Time, t = V/F
K	Lawrence and McCarty Maximum Substrate Utilization Rate
K_B	Substrate Loading at Which the Substrate Utilization is Half of Maximum Rate
K_e'	Eckenfelder's Second Order Substrate Removal Rate Constant
KS_1	Lawrence and McCarty's Saturation Constant
km	McKinney's Substrate Removal Rate
ki	Weston Inhibition Constant
k_d	Maintenance Energy or Decay Coefficient
MCRT	Mean Cell Residence Time
MGD	Million Gallons Per Day
mg/L	Milligrams Per Liter
MLSS	Mixed Liquor Suspended Solids

MLVSS	Mixed Liquor Volatile Suspended Solids
R_S	Weston Substrate Removal Rate
S_e	Effluent Substrate Concentration
S_i	Influent Substrate Concentration
SRT	Sludge Retention Time, Sludge Age, θ_c
SVI	Sludge Volume Index
TDS	Total Dissolved Solids
TKN	Total Kjeldal Nitrogen
TOC	Total Organic Carbon
TSS	Total Suspended Solids
U	Specific Substrate Utilization Rate
USDA	U.S. Department of Agriculture
VA	Volatile Acids
X	Biological Solids
X_e	Effluent Solids Concentration
X_o	Influent Solids Concentration
X_R	Underflow Solids Concentration
X_W	Pounds of Sludge Wasted
Y_t	True Cell Yield
ZSV	Zone Settling Velocity
α	Recycle Flow Ratio
θ_c	SRT
μ_n	Observed Growth Rate
μ_{max}	Maximum Growth Rate

CHAPTER I

INTRODUCTION

The oil importing nations face no greater challenge during the remaining one and a half decades of this century than finding viable alternative energy sources to replace petroleum to heat homes and offices, power factories, and maintain vital transportation systems.

While, on a percentage basis, the United States does not import as much oil as some other nations, it is still heavily dependent on imported oil for transportation. According to the final report (63) of the National Alcohol Fuels Commission, more than 50 percent of all petroleum consumed in this country is used in transportation. Four-fifths of that is in the form of gasoline for vehicles, primarily individual motor cars. The United States, because of its size, its pattern of industrial, commercial and residential development and its overall cultural habits is more dependent upon the automobile than almost any other nation. Although more fuel-efficient vehicles, conservation through decreased vehicular use, and increased public transportation availability will all help to reduce the consumption of gasoline, the country still faces another ten yars or longer in which to have available the quivalent of between 90 and 100 billion gallons of gasoline a year (14). The United States is now looking for alternatives to petroleum-based gasoline to fill that need, primarily through what are loosely defined as synthetic fuels from any material containing sugar, starch and/or cellulose.

One of the most attractive alternatives is alcohol fuel. From the perspective of the United States, alcohol fuels are almost "a perfect fuel". Domestic raw materials for producing alcohols are both vast, and, in some instances, renewable. Processes for conversion of starch and sugar to ethanol are in commercial operation as America's embryonic "gasohol" industry has made great strides.

The merits of gasohol over gasoline have been well demonstrated and documented. Pure alcohol is cleaner burning and more efficient than either gasoline or diesel fuel. Gasohol, a blend of 10% anhydrous fermentation ethanol and 90% unleaded gasoline is compatible to 100% premium unleaded gasoline.

It is not the intention of the author to advocate, by justifications, the use of alcohol fuel. However the point is that while increases in oil prices are impossible to predict accurately, fuel alcohol as a blending agent may be cost competitive within the 1900's, as many researchers forsee it.

Ethanol production requires considerable quantities of water with substantial amounts ending up in the thin stillage as a wastewater. And one of the serious problems ever associated with this fledgling industry is the production of the high temperature, high-strength and acidic wastewaters. The majority of the efforts to date have centered around fuel alcohol production with little importance to environmental concerns. Should the synthetic fuel option become a feasible addition to our nationi's energy alternatives, the environmental problems associated witht the wastewaters from alcohol production must be solved first.

Although a portion of these wastewaters can be recycled as one of the treatment alternatives, complete reuse is not practical due to the build up of salts and toxic by-products such as fusel-oil during the fermentation reactions. Present treatment practices typically consist of screening of grain solids and evaporation of the thin stillage. This is an energy intensive and cost expensive step.

The major objectives of the research reported here were (i) to characterize these high-strength wastewaters (ii) to develop biological treatment kinetics and performance evaluations with both aerobic and anaerobic suspended growth systems.

The wastewaters were collected from the Oklahoma State University Agricultural Engineer's 200,000 gallon per year fuel alcohol research facility and from the 3,000,000 gallon per year plant at Hydro, Oklahoma, for use in the above studies conducted for over three years. After gravity settling, the supernatant was pumped into bench-scale, complete mix, continuous flow aerobic and anaerobic activated sludge systems. These systems were carefully operated to control the growth rate or mean cell residence time (MCRT) and data were collected at steady state conditions.

These studies have determined the capability of biological treatment to handle this high strength wastewater. These studies have provided valuable information for treatability, performance evaluation, and development of biokinetic constants (which hitherto has never been documented) required for mathematically modeling the treatment process. This information provided the necessary data to develop preliminary concept designs of the aerobic and anaerobic activated sludge process along with the potentials for recycle and reuse options for fuel alcohol wastewaters.

CHAPTER II

LITERATURE REVIEW

2.1 Alcohol Manufacture

Alcohol fuels have recently attracted attention more as a petroleum extender and octane enhancer than as a replacement for petroleum. The Solar Energy Research Institute (SERI) has published a variety of books that cover the major factors involved in producing ethanol (EtOH). Facts about Ethanol (1) is an update of the 1979 SERI publication, Facts About Gasohol, and delineates ethanol issues in detail. Fuel from Farms (2) provides a comprehensive guide for farm-based ethanol production, describes fermentation procedures and offers worksheets and guidelines to help evaluate the farm-based production. Appendices provide feedstock data, equipment information, etc. Fermentation Guide for Common Grains (3) describes optimum procedures for manufacturing ethanol from corn, wheat, barley, or milo feed stocks. Fermentation Guide for Potatoes (4) outlines recommended procedures when using potatoes as the feedstock. Small-Scale Fuel Alcohol Production (5) which was later updated as "The Gasohol Hand Book" (6) by Daniel Hunt is a comprehensive volume covering all aspects of gasohol production. This information comprises technical, economical, environmental and utilization aspects. Another handout, Feed and Fuel from Ethanol Production (7) brought out in the same line discusses in 14 different articles the manufacture of fuel alcohol and the handling of wet distillers grains.

Ethanol Production and Utilization for Fuel (8), a report prepared by the Cooperative Extension Service, University of Nebraska, Lincoln, which has done a lot of spadework in gasohol, deals with the recent developments in the production processes and utilization of both ethanol and by-products.

Downs and Clary (9), (10), (11) who have been doing extensive research at Oklahoma State University have brought out a few reports which provide current, general information and data on the production and use of alcohol.

According to Tronnes (12), Keicker (Executive Director of the Minnesota Fuel Alcohol Association, who has vast experience with fuel alcohol vehicles) wants to show the farmers that alcohol produced on-farm is economical and to send a message to the American Vehicle manufactures to begin production of engines that can burn alcohol without any modification. A brief review of alcohol-combustion literature indicates that most of the commonly discussed options have been investigated in the past. In an article by Schrock (13), seven different engine fuel combinations were evaluated, with an emphasis on agricultural applications. Carburating ethanol into diesels, according to the author, appeared to be the most feasible near-term technology for using ethanol in diesel engines. Alcohol fuels (14) are efficient burning and environmentally benign and, because the production technologies are well understood, the pollution control technologies are known and the emissions and effluents are controllable. However, the other side of the coin is not quite encouraging. Jelinek (15) opined that no matter how high oil prices go, synfuels from new plants would never be economical. Goldemberg, (16) President of the Comphania

Energetica de Sao Paulo has a different outlook. According to him, "The ethanol program from sugarcane was a great success in Brazil. The production of ethanol has grown by a factor of ten in a matter of four years. The technology is now being exported to other countries," what many call, "the Brazilian Miracle." Observers according to Murphy, (17) now agree that Brazil will be close to its objective of producing 2.8 billion gallons of fuel ethanol by 1987 for an estimated 1.2 million vehicles running on ethanol or a 20 percent ethanol to petrol mix.

Over the past decades or so, the fermentation industry has been striding through phenomenal improvements owing to the interest in extraction of ethanol. Obviously several researchers have attempted to present innovative technologies to maximize EtOH production at minimal cost. Attempts have also been made to use cheaper and more readily available feedstocks for conversion into ethanol such as sweet potatoes, sugarcane, and cattails. Ladenburg (18) has investigated the industrial utilization of cattails in the production of ethanol. Included in this study was the natural and managed growth of cattail plants, the methods of harvesting, fermentation kinetics and overall economic evaluation.

A study was conducted at Texas A & M University, Texas, to evaluate the ethanol production characteristics of sweet potatoes. Egg (19) concluded that ethanol yields were as high as 137 liters per tonne of feedstock using procedures developed for grain. Major problems encountered were low ethanol concentrations in the beer and poor stillage dewatering properties.

The author is of the opinion that a comprehensive review of even the pertinent articles, as far as the manufacture is concerned, is beyond the scope of this research and hence restricts this review to only these selected references.

2.2 Reuse Options

Reuse, recycle and recovery can all be grouped under one domain, which precludes energy generation from these wastes. Eder (20) noted that evaporation and drying of distillery wash from grain distillation for use as feedstuffs were economically feasible provided that process energy can be achieved when the distillery and the evaporation plants are integrated with respect to heat economy. Riberio and Branco (21) investigated the use of stillage from fermentation ethanol production in Brazil and discussed how the proper selection of recovery processes can potentially bring additional revenue without compromising ethanol's competitiveness as a fuel.

Pollock (22) reviewed the processes for malting and brewing in terms of those major by-products which could be used to increase profits. Recycling for water savings (which, incidentally, is not accepted by many researchers because of the salts accumulation in the by-product), alcohol recovery from waste beer streams, drying organic solids for animal feed, liquefaction of carbon dioxide for carbonation, and recovery of heat were among the many processes discussed. Safely and Backus (23) concluded that a large portion of the protein in the spent stillage could be recovered using available separation equipment. Another article by Black, Waller, Steinmetz, and Ross (24) has attempted to give a detailed discussion on the nutritional requirements and economic value of fuel alcohol by-products. Their study indicated that ethanol by-products derived from corn were good sources of by-pass protein for ruminants. However their poor protein quality makes them less valuable for swine than for lactating dairy cows and rapidly growing feedlot beef cattle weighing less than 650 lbs.

Stock and Klopfenstein (25) supplement these points of view. But they add that when wet grains are produced during the summer months, the product, even if ensiled, may only last one week before mold growth occurs. Thus, preservation becomes another additional expenditure.

2.2.1 Characteristics of Stillage and Wastewater Management in the Fuel Alcohol Industry

The fuel alcohol industry can be classified as the advanced form of the fermentation industry. The basic sequential steps are almost the same. The wastewater characteristics are also similar but varying in their magnitude. Essentially all these wastewaters are high-temperature, high-strength and acidic in nature. Extensive research has been done throughout the world in this area. Most of these researchers agree that the fermentation industry wastewaters are very amenable to anaerobic treatment.

The EPA brought out a manual under the title "State of the Art: Wastewater Management in the Beverage Industry" (26). As stated, the general purpose of this paper was to investigate, through the literature, the water pollution impact caused by the wastes from the beverage industry and the methods available to combat the associated problems. The size of each industry was discussed along with production processes, wastewater sources and effluent characteristics. Wastewater management techniques were described in terms of in-plant recycling, by-product recovery and end-of-pipe treatment along with the economics of treatment.

Much of the experience on the treatment of spent molasses wastes by the anaerobic digestion process has been summarized in an early (1965)

review by Pettet, Tomlison and Hemens (27) and in a later review by Hiatt, Carr and Andrews (28). The latter are of the opinion that the reactors respond well to loading step changes of the order of 25-50 percent and return to normal operating conditions in about 10-15 days, only 70-80 percent of the waste COD is biodegradable, and the remainder would require an alternative form of treatment to anaerobic digestion. Polishing the anaerobic effluent by conventional aerobic activated sludge treatment appears to be a good option as seen by Bonkoski, Sointio and Gillespie (29). According to them, a major key to the process is the recycle of excess sludge from the aerobic stage to the anaerobic tank.

Sheehan and Greenfield (30) reviewed various disposal techniques either employed or investigated during the past 40 years in distillery industry. Methods used for product recovery, recycle, fertilizer applications, food supplements and single-cell protein (SCP) production were discussed separately from the various wastewater treatment alternatives (anaerobic digestion, anaerobic filters, activated sludge, and rotating biological contactors) that have been used by the industry.

In an investigation to develop useful by-products from molasses distillery wastes, Bhaskaran (31) reported another example of successful anaerobic digestion of molasses distillery wastes. Laboratory digesters were operated at detention periods of 9-20 days with loadings of 0.046 - 0.235 lb BOD/cuft/day. In all cases, greater than 90 percent reduction of BOD was reported. It is interesting to note that Bhaskaran considered recovery of fuel, Vitamin B_{12} and potasium salts from the waste to be economical. In a continuation of the work of Bhaskaran, further studies were performed by Radhakrishnan, De and Nath (32) on

molasses distillery wastes. These authors reported that higher loadings were possible if the waste was diluted. They attributed this effect to the lowering of the salt concentration in the reactors. Digestion was successfully carried out on a continuous basis with a detention period of 5 days, corresponding to a loading of 0.226 lb BOD/cuft/day. BOD removal was 89 percent.

Stander (33) reported on a full-scale anaerobic process treating wine distillery waste (spent wine) from a South African plant. This facility operated on an intermittent basis throughout the year. Stander reported periodic decline in anaerobic activity due primarily to three causes: (1) insufficient acclimatization of the original seed sludge; (2) decrease of the digester temperature to less than 20°C during the dormant period; and (3) process overloading due to hydraulic washout of actively digesting sludge. The digester was operated at loading as high as 2 lb volatile matter/cuft/day, with a detention period of 7.2 days. Removal of 97.6 percent COD based on an influent of 22.4 gm/L COD was achieved and gas yield was 14-15 volumes/volume of feed for normal operation at a temperature of 30°C. Operating pH was 7.6 for spent wine and 7.3 for spent wine stored in the holding lagoon. Stander reported that gas production declined and stopped within 2-4 hours after termination of feeding.

Jackson (34) presented a review of fermentation waste disposal in Great Britain in which he discussed various treatment methods including the anaerobic process. The author differentiated between industries by the final products as well as the raw materials utilized. In discussing waste treatment for molasses fermentation, he reported a successful pilot plant study in which 60 percent BOD removal was accomplished based

on a ten-day detention period. However Jackson felt that the method of choice for this waste would be spray combustion with recovery of heat of combustion and potasium carbonate, making the method economically self-supporting.

Dahab and Young (35) have attempted to simulate alcohol stillage in their lab to evaluate the treatability performance of an upflow anaerobic filter. Treatment efficiencies of around 90% were observed when operating at a COD loading rate of 2.0 $Kg/m^3/day$ (COD = 3,000 mg/L) (In a similar study, conducted in our laboratory with actual alcohol stillage, loading rate as high as 8.0 $Kg/m^3/day$ was observed by Stover, Gonzalez and Gomathinayagam (64) to give about 80% treatment efficiency using an upflow anaerobic filter). Dahab and Young have also given a good overview of alcohols, fatty acids and other fusel oil components in these wastewaters in order to relate with gas production.

Most of the research in anaerobic treatment has been, thus far, oriented towards type-design reactors, treatability studies and operational control with very little focus on process kinetics. However, for the last decade or two, researchers have attempted to define and explain the intrinsic principles of anaerobic fermentative pathways. In 1949, Monod described a kinetic equation which was simple and provided an accurate description of the growth of microbial cultures. Its widespread adoption virtually gave birth to the study of microbial growth kinetics. Subsequent works of Bauchop (36) in the same line, explain the mechanisms by which cells gain energy by converting ADP into ATP.

Despite the widespread use of anaerobic treatment, optimum process performance seldom is achieved because of the high degree of

empiricism. An approach to the meaningful evaluation of anaerobic treatment kinetics has been well documented by McCarty (37) (38) and his coworkers. Presently, there is a rather well-balanced effort in the areas of basic microbiology, bench and pilot plant studies to define the kinetics, and full-scale installation evaluations.

In an overview of scientific principles of "Anaerobic biotechnology" by Speece (39), he compared anaerobic and aerobic biotechnology per metric ton COD destroyed, with a specific reference to brewery wastes, as follows.

Power consumption during aerobic treatment was 1100 Kwh whereas anaerobic treatment consumed no electricity. Additionally, there was the benefit of methane generation at the rate of 1.1×10^7 Btu by the anaerobic system. Also, the net cell production during the aerobic treatment was 4 to 20 times greater (400-600 Kg) than that during the anerobic treatment (20-150 Kg).

A comprehensive review of distillery slops treatment has been made by De Renzo (40). He concludes that the incorporation of methane by-product recovery in a plant-scale installation can reduce unit treatment costs from 35% (in a 50,000 gpd facility with brewery wastes as a candidate) to 65% (in a 300,000 gpd facility), as compared with unit treatment costs for installations without recovery. It should be mentioned here that these figures obtained stoichiometrically are comparable to the actual figures seen in our laboratory.

There can be no two opinions that Europe can take credit for its innovative research in the area of brewery wastes treatment for over half a century. Various options including trickling filters, high-rate filters, Pasveer oxidation ditch have been attempted. The on-going

research at the University of Newcastle upon Tyne by Isaac and McFiggans (41) has demonstrated that distillery wastes are ideally treated by anaerobic methods. One of their interesting observations is that the application of a thermal shock, as in the "Bioenergy" process, would appear to be the most efficient method of encouraging satisfactory settling by inactivation of the bacteria, which in turn prevents gas production during the clarification stage (the major cause of poor settlement).

Sittig (42) has documented the adverse impact of brewery effluent on conventional effluent treatment systems. It caused a shift in the microbial biota which entailed a proliferation of slime bacteria. The profuse growth of this slime bacteria induced by brewery effluent caused operational upsets such as: bulking, clogging and general impairment of the operational efficiency in conventional sewage treatment systems. Carbohydrates, and particularly fermentable sugars in these wastes, intensely stimulated the growth of the disturbing slime bacteria.

Basu and Le Clerc (43) compared the anaerobic digestion of molasses distillery wastes at mesophilic ($35^{o}C$) and thermophilic ($55^{o}C$) temperatures. They concluded that, although thermophilic digestion gave slightly better results, mesophilic digestion was more of a practical proposition because of the costs of running a digester at $55^{o}C$.

Contact digesters were investigated by Roth and Lentz (44) as a method for treating rum stillage. Shock loadings as well as no loading for upto 30 days did not impair the digestions. In a similar study using sugar-beet waste as a candidate for digestion, Lettinga et al., (45) found that digesters were able to stand periods of shut-down of upto a year or more (useful in the treatment of seasonal wastes!) and

restart easily within one to three days. (These findings are in close accordance with the experience in our labs where the methanogens were totally deprived of feedstock well over eight days as part of a shock load study. The system recuperated in a matter of a few hours). Research in Austrailia by Barnes et al. (46) with a substrate formulated from molasses and yeast extract, endorses the above conclusions. They report that the analysis of the responses of the system to shock loads has indicated that the overall process response is similar to that observed for continuous loading.

Stafford, Hawkes and Horton (47), in an attempt to compare the relative treatment efficiencies for fermentation wastes by different alternatives, reported that anaerobic digestion produces the greatest removal (83%).

Chemical treatment gave hardly 10% BOD removal, electodialysis 28%, and activated sludge 30%. The performance of only a trickling filter was comparable (72%) to that of anaerobic digestion. They also observed a close relationship between laboratory, pilot, and full-scale operations, with particular reference to hydraulic retention time. Research by Loll (48) from West Germany agreed with the findings of these people and concluded that the half digestion period for brewery wastes is as low as two days, probably the lowest of all feedstock candidates for anaerobic digestion reported so far.

There are occasions where researchers have diametrically opposite conclusions too, for instance nutrient requirements in terms of C:N:P ratio. While Stafford, et al. (47) insisted on a C:N:P ratio of 30:1:1, Van den Berg and Lentz (49) reported for similar berwery wastes, a ratio of 300:5:1. Values obtained in our laboratory agreed with those of the

latter. This should be so because the cell yield is very low. But the same researchers (and almost every single researcher, without an exception) unequivocally reported about reasonably good sludge settleability. Bulking sludge was a rare phenomenon during our research on anaerobic treatment.

2.2.2 Energy Recovery

Of late, conversion of by-products to usable fuel has proven to be an environmentally effective action, favorable in the eyes of the public and a hedge against fuel price increases while remaining potentially profitable.

One of the companies on the island of Puerto Rico hardest hit by the energy and pollution control circumstances was Bacardi Corporation, distillers of Bacardi rum. One staff reporter (50) of Water/Engineering and Management reported that the company had found a way to substantially ease both these problems by using an innovative process based on anaerobic waste treatment technology. In another article, Szendrey, Schafer and Dorion (51) described the history behind this approach, current status and the future improvements envisaged. Apart from solving the energy and pollution crisis, a real bonus, already demonstrated during a scheduled distillery shut down was the ability of the process to go into an idle state and then be brought upto normal throughput rates easily and quickly.

In one more article (52) in the same line, another staff reporter (ASCE, Civil Eng.) concluded that when the total program would be in effect, the gas would replace nearly all the plant's fuel needs - equivalent to an annual estimated fuel savings of $1.5 million.

Willington and Marten (53) developed their article first by accounting the merits and the demerits of different options for handling stillage and finally concluded that selecting the most appropriate stillage management was a matter of trade-offs between energy, economic and environmental considerations. They were of the opinion that in the case of a molasses distillery, the potential fuel saving was significant if anaerobic treatment was an option.

According to Micheli (54), processes for the treatment of wastes of feedlot installations were of even greater interest, from the standpoint of recovery. In this case, in addition to energy recovery obtainable in the anaerobic digestion phase, it was possible to use the digested effluent, which contained substantial quantities of nitrogen and phospherous.

The concept of Integrated Utility Systems (IUS), similar to the ones documented here, was advocated by many researchers. Shah, Clark and Okos (55) suggested that on-site, renewable sources of energy could be integrated into the utility system and evaluated from an energy, economic, and management perspective.

Shaffer (56) supported the concept of IUS because the anaerobic digestion of food-processing wastes (including brewery wastes) offered the potential to achieve the objectives outlined in the Energy Security Act with respect to replacing imported nonrenewable energy resources with domestically produced, renewable energy. By utilizing a nonfossil fuel carbon source to produce energy, he added that the anaerobic digesters would not contribute to the increasing worldwide levels of carbon dioxide in the atmosphere, a phenomenon of great environmental concerns to scientists. He has evaluated a number of on-farm energy

production plants and concluded that at the current rates of crude and crude-product imports, 5.9 million barrels per day, on-farm energy production had the potential to off-set on a continuous basis, 7.2 percent of our petroleum imports. In addition, $9.08 billion in pollution control facilities could be offset.

The author has attempted to cull out certain articles, which are related to this research, but which could not be contained under a specific subtitle in the literature review. They are presented as follows. Mosey (57) has presented an article on "Anaerobic Biological Treatment of Food Industry Wastewaters" where he gave a vivid description of biochemical principles of methane fermentation. He mentioned that a conventional anaerobic digester treating a strong sugar or starch waste would remove about 75% of the COD at loading rates around 10 Kg/day/m^3, which is comparable to the performance of an upflow filter and occurs without production of surplus sludge.

In a continuous EtoH manufacturing plant, energy could be exchanged between cold streams and hot streams, but in a batch system, cooking, fermentation and distillation operations consumed predictable and unavoidable inputs of energy. Dunlap, Wang and Fischer (58) suggested to (i) use non-priority fuel (ii) use wet-spent-grains and (iii) to recycle spent liquor. Co-generation of methane from the stillage was one of the suggested alternatives.

According to a recent ENFOR (Energy from the Forest) study (59) anaerobic fermentation of wastes from two different kinds of pulp mill processes may produce enough biogas and realize enough cost savings to recover capital costs within four years. Not only can the process save the industry money, it reduces pollution as well.

While describing the performance of the ANAMET process treating sugar beet waste, Huss (60) (61) concluded that no nutrient addition was made inspite of a COD:N:P nutrient balance of 100:0.5:0.02.

Winter (62), of the Wall Street Journal reported that for many companies energy was the third largest business cost, after labor and raw materials, and it was rising more than twice as fast as the other two. He concluded that waste from breweries, food processing plants and other agricultural enterprises was being converted into alcohol, which could then be burned in boilers or in cars, trucks and tractors.

CHAPTER III

MATERIALS AND METHODS

The research work reported here was sponsored by the Oklahoma Water Research Center for a span of three years starting from July 1981.

The stillage or wastewaters used for the pretreatment and biological studies presented in this report were collected from the Oklahoma State University Agricultural Engineers' 200,000 gallon per year capacity fuel alcohol research facility and from the 3,000,000 gallon per year plant at Hydro, Oklahoma. These wastewaters were characterized and subjected to pretreatment investigations consisting of gravity settling with and without chemical conditioning agents to enhance flocculation and settling. Jar test studies were used to compare flocculating agents. The pretreated supernatant was then subjected to biological treatment studies in the aerobic and anaerobic activated sludge systems.

The temperature of the wastewaters that emanate out of the distillation columns were as high as $165^{o}(75^{o}C)$. The barrels in which the stillage was collected and stored were thoroughly cleaned and disinfected with chlorox prior to each collection. Originally the drums containing the wastes were stored in a walk-in-refrigerator, but later because of the non-availability of enough space, the wastes were then stored at the room temperature. The wastes were allowed to cool down to room temperture and the settled supernatant was fed into aerobic and anaerobic reactors.

3.1 Wastewater Characterization Studies

A series of jar test studies were performed in order to evaluate whether or not the addition of flocculating agents promote the thickening characteristics. Inorganic coalgulants like alum ($A\text{¢}_2(SO_4)_3 \cdot 18\ H_2O$), lime (Ash Grove Chemical Powder Co.) and ferric sulphate ($FeSO_4$) were first tried either singly or in combination. Later high molecular anionic and/or cationic polymers of the PERCOL products were used in different concentrations in the jar test studies again either singly or in combination, with or without adjusting the pH. One of the beakers was used as a control unit which received none of these flocculants/coagulants, but keeping all other conditions the same. In all jar test studies, the rapid mixing time was 30 seconds and the flocculation time monitored to 15 minutes. The contents were then allowed to settle for 30 minutes and the supernatant was syphoned, filtered and the filtrate analyzed for BOD, COD and TOC.

As a part of these characterization studies, a titration curve was plotted in order to determine the alkalinity to be added to the waste to run the reactors at about nutral pH. Because of the dissimilarities in the ionic characteritics between the corn stillage and the milo stillage, it was necessary to run the titration analyses on both the feedstocks.

The thin stillage was analyzed for the following in addition to the thickening characteristics mentioned above:

Total Solids, Total Dissolved Solids

Suspended Solids, Volatile Suspended Solids

Total COD, Soluble COD

Total BOD_5, Soluble BOD_5

Soluble TOC

Total P, Soluble P

Total TKN, Soluble TKN

Soluble NH_3-N

Total Protein, Soluble Protein

Total CHO, Soluble CHO

Soluble Glucose and pH

These characterization studies gave enough confidence to choose biological treatment as one of the best options. However everytime the waste was collected afresh, routine characteristic studies were performed.

The entire research work can be divided into five phases as follows:

1. Aerobic activated sludge treatment studies

2.1 Anaerobic activated sludge treatment studies

2.2 Anaerobic treatment followed by aerobic treatment

3. Anaerobic treatment - batch studies

4. Anaerobic treatment - gas studies

5. Anaerobic treatment - shock load studies.

Figure 1 is a profile of the time period for each phase of the operation. As is seen, more time was devoted to anaerobic studies because the waste was well amenable to anaerobic degradation.

3.2 Operation of the Bench Scale Units

3.2.1 Aerobic Activated Sludge Treatment

Bench scale, complete mix, continuous flow activated sludge systems similar to the one depicted in Figure 2 were used in these studies.

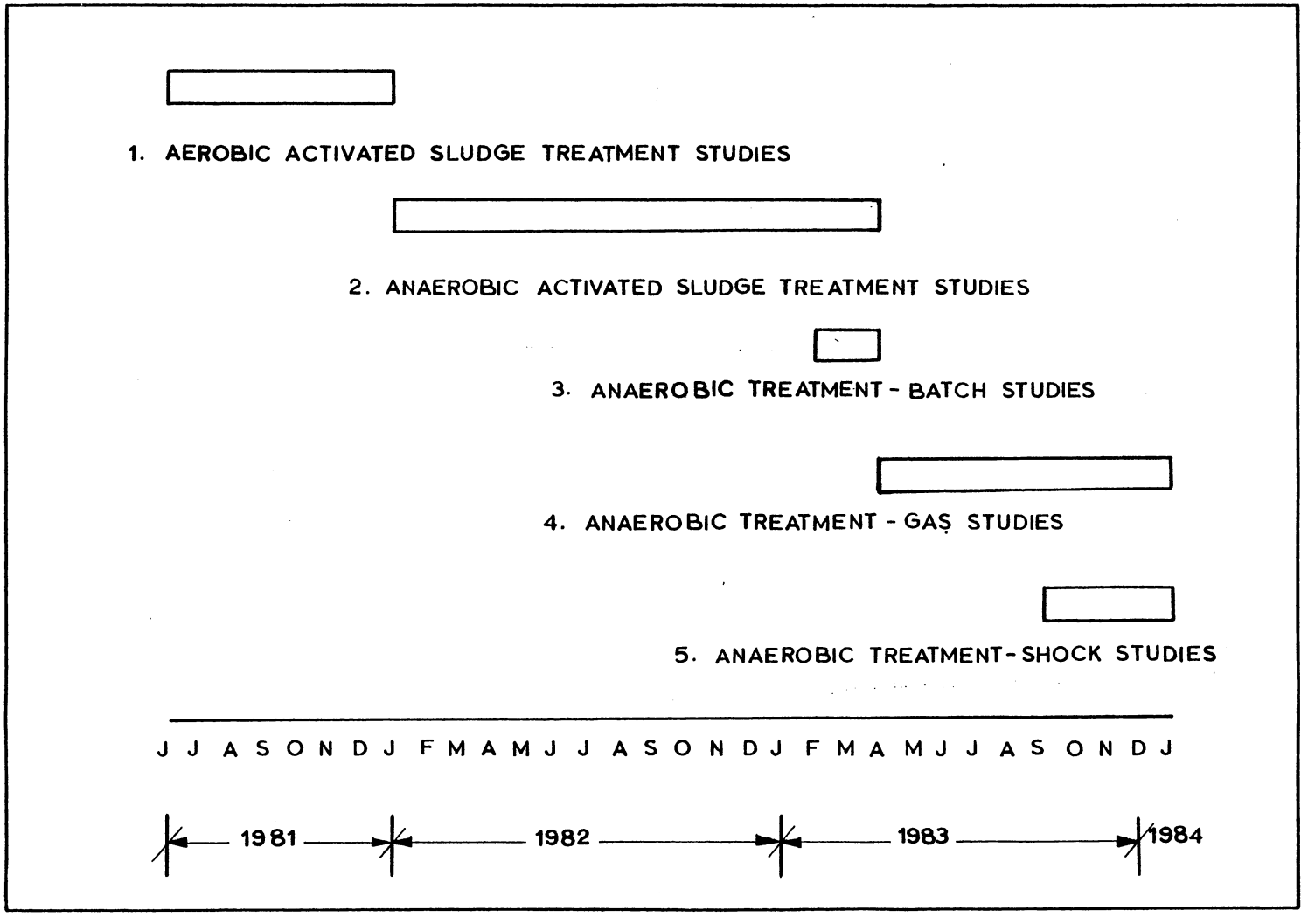


Figure 1. Schedule Depicting the Time Priod During Which Each Study was Performed.

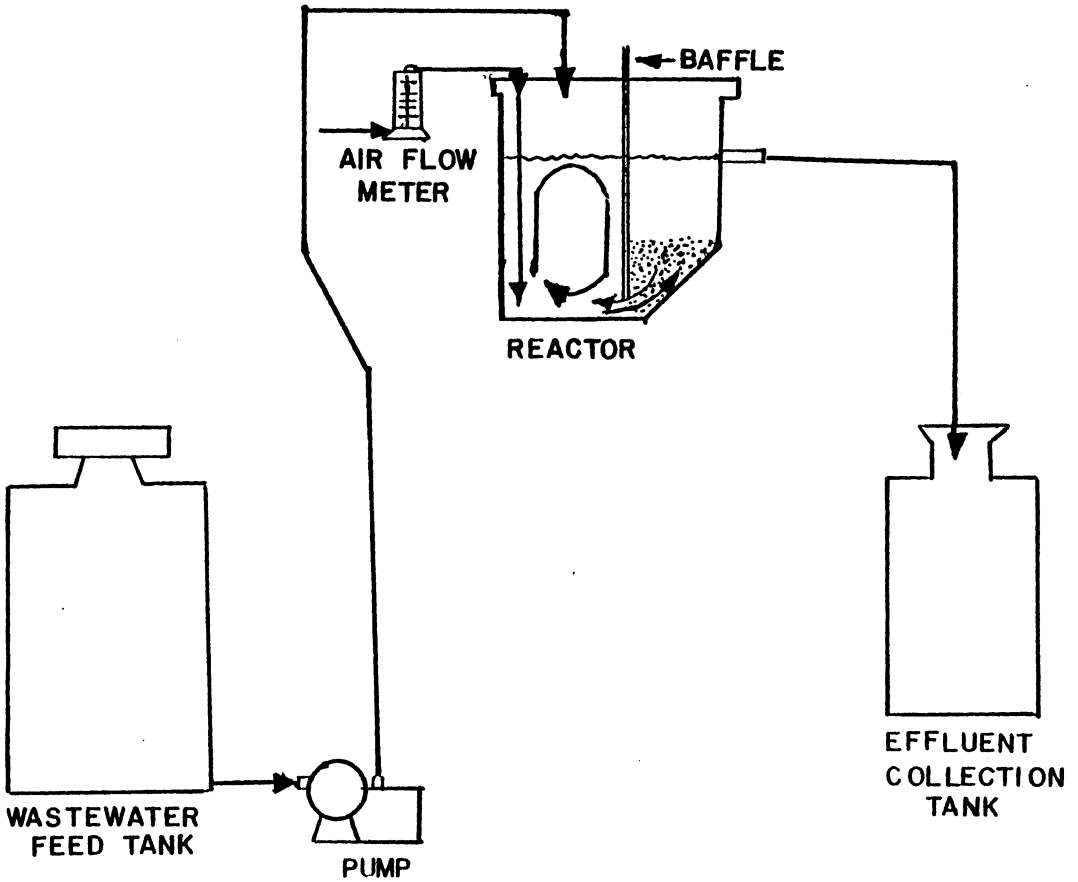


Figure 2. Schematic of Internal Recycle Reactors Employed for the Aerobic Activated Sludge Investigations.

These sytems were plexiglass internal recycle reactors with 7.2 liter aeration reactor volumes and 3.5 liter settling compartment volumes. The wastewaters were pumped from feed tanks to the aeration reactors, and the effluents flowed by gravity from the settling compartments to effluent collection tanks. The influent wastewater flow rates were regulated at 3.6 liters per day to provide hydraulic retention times of 48 hours. Compressed air passing through diffusers was used to supply oxygen to the microbial population as well as to mix the reactor contents. An adjustable plexiglass baffle was positioned so as to keep the clarifier sludge from compacting too tightly inside the baffle opening but, at the same time, to allow efficient sludge settling and recycling.

The reactors were initially filled with active microbial seed organisms obtained from Tulsa Wastewater treatment plant. The bench scale units were operated at a constant solids retentions time (SRT). Solids retention times of 20 days, 10 days, 6 days and 3 days were studied. Suspended solids analyses were performed on mixed liquor and effluent samples daily during steady-state conditions. Solids wastage, based upon that day's suspended solids analyses, was accomplished by removing the appropriate volume from the aeration basin. Influent flow rates were monitored at least once per day. Diffused air flow rates were adjusted to insure that the D.O. concentration in the reactor was not limiting (greater than 2 mg/L) and, at the same time, prevent the sludge from depositing on the reactor floor. After it was determined that the units were operating at steady-state conditions, the data used to determine the kinetic constants were collected.

3.2.2 Anaerobic Activated Sludge Treatment Units

The two bench scale plexiglass reactors used in the anaerobic studies were very much similar to the ones used in the aerobic studies. But they were completely sealed to avoid the entry of oxygen into and to facilitate the exit of the off-gas out of the reactor through a channelized tube as shown in Figure 3. One of the reactors was provided with a shaft and paddle system in order to mix the contents, whereas a magnetic bar was used in the other reactor for the same purpose. A thick mat of solids was observed in the latter inspite of this mixing. Hence another magnetic stirrer was set up on one side of the reactor at such a liquid level so as to break the scum mat. However, care was taken to avoid any latent oxygenation due to this mixing. A tee was used at the outlet. One arm of this tee was submerged by an inch into the clarifier as seen in the figure. The flow rate was controlled to 1.44 ℓ/day (1 ml/min) to give a hydraulic retnetion time of 5 days. Initially half the reactor was filled with active methanogenic bacteria brought from Stillwater wastewater treatment plant anaerobic digester in a well closed container. The rest of the reactor was filled with aerobic activated sludge already acclimated to 30 days SRT. Since no good COD reduction was observed for over a month, the unit was again fully reseeded with active anaerobic biomass. Oxygen, if any present, was expelled by purging with nitrogen gas. Careful control over all parameters, especially with reference to volatile acids and alkalinity, resulted in a good COD reduction within 10 days in both the reactors.

The continuous systems were operated to control the growth rate or sludge retention time (SRT) by wasting sludge on a daily basis. During

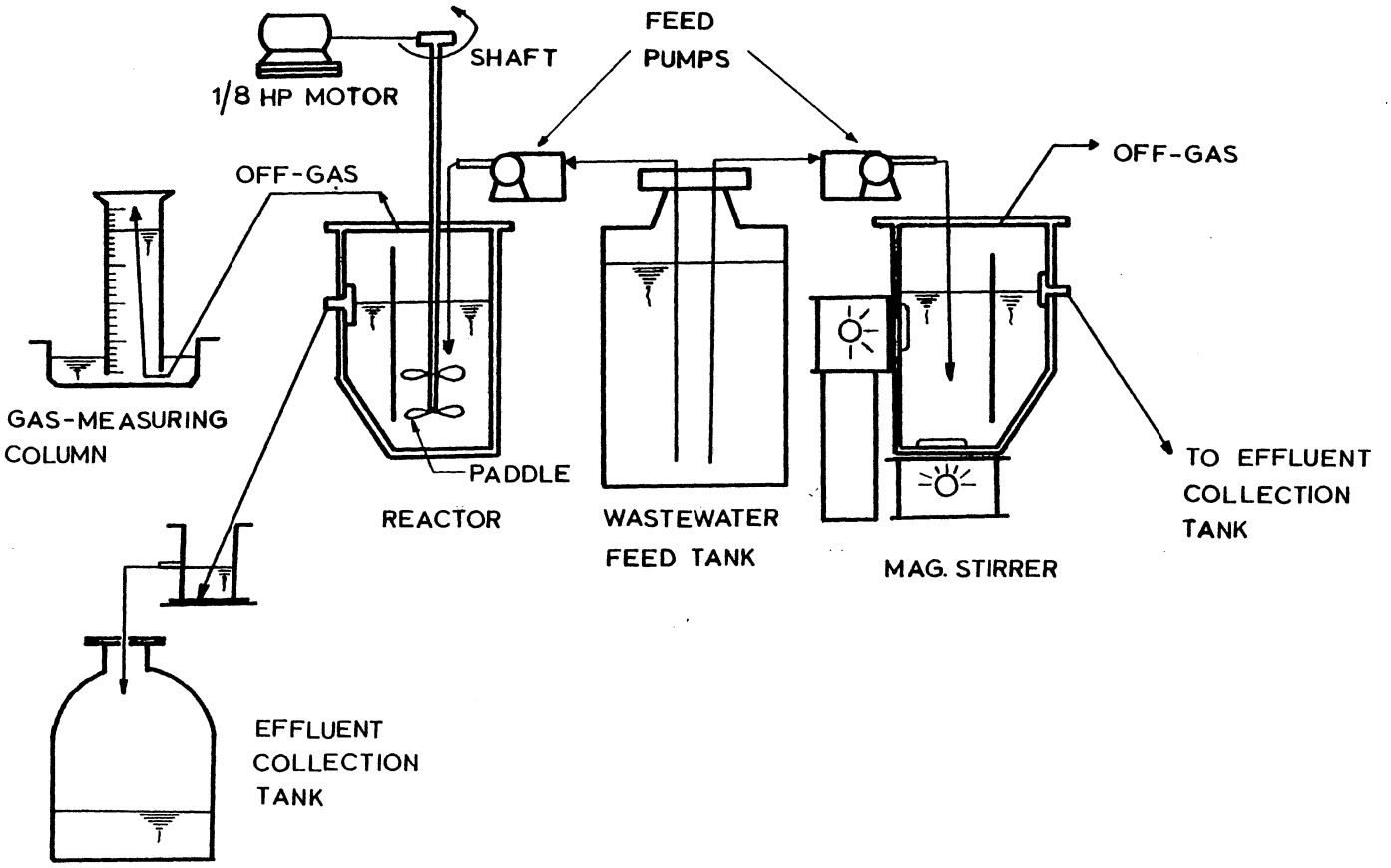


Figure 3. Schematic of the Complete Mix Anaerobic Systems

the treatability studies, the hydraulic retention time, the hydraulic flow rate and the sludge retention times were maintained constant. The influent wastewaters and the effluents of the biological systems were monitored with respect to BOD_5, COD and TOC. System operating characteristics were also monitored with respect to pH, effluent suspended solids, sludge settling and dewatering characteristics. The wastewater and mixed liquour pH was controlled by adding alkalinity in the form of sodium hydroxide. In order to keep the volatile acids accumulation under control, continuous monitoring on the volatile acids to alkalinity ratio was necessary. Especially, whenever there was a change-over in the feed concentration or in the SRTs, monitoring the pH for almost every three hours was necessary. The protein and carbohydrate contents of the biological sludges and stillage solids were also monitored for determination of reuse potential.

Most part of the substrate, during anaerobic degradation, is released as gas. Naturally, even a very small variation in any one of the system parameters such as influent substrate concentration, pH, temperature or microbial population will influence the production of gas to a measurable degree. Thus monitoring the gas production is the key in the successful operation of any anaerobic system. This could be accomplished by a perfect sealing of the reactor and stream-lining the gas to a common vent and then let it go through a gas measuring column. Such a "perfect sealing" was not possible during the operation of these reactors. So, the treatability performance was gauged more by substrate reduction than by gas production. Nevertheless, it was possible to redress this problem during the fourth phase of studies.

All the systems except the 30-day SRT systems were operated at around one-third of the full strength stillage substrate concentrations. The 2-day and 4-day SRT systems were operated as once - through systems, while all other systems were operated as sludge recycle systems. The treatment performance of these systems were greater than anticipated, and hence the organic loading rates were stepped up to two times and later to three times. The two 30-day SRT systems were operated at two-thirds of full strength and full strength substrate concentrations. Care was exercised to control the reactor pH around 7.0 and a temperature range of about 33°C to 37°C to provide a conducive environment for the methanogens.

Time and again researchers have attempted to polish the anaerobic effluent. With this in mind, an aerobic continuous flow activated sludge sytem was operated on the treated effluent from the 20 day SRT anaerobic system. This aerobic reactor consisted of a 3.0 liter aeration basin and 1.5 liter settling compartment. This system was also operated by controlling the SRT and monitoring the system performance in terms of BOD_5, COD and TOC. However the treatment performance of the anaerobic systems were so high that there was not enough carbon source available in the anaerobic effluent for being subsequently utilized for synthesis by aerobic microbes. Hence the aerobic system was only operated for a short time period.

3.2.3 Anaerobic Treatment - Batch Studies

Waste sludge from the anaerobic system was used periodically in batch anaerobic activated sludge studies in order to evaluate batch removal kinetics compared to continuous system kinetics. During this

study, the anaerobic microorganisms were allowed to go on a 'fast' for 24 hrs., prior to the start of each loading condition. Thus the residual COD in the settled supernatant was mostly due to the nonbiodegradable fraction. The reactor used for this study was a completely closed 1,000 ml flask with two outlets at the top, one for sampling and one for off-gas and one inlet for the entry of methane gas to counterbalance for the lost gas during sampling. Methane gas, from another continuous flow reactor, was provided for this purpose. The reaction time was extended as far as 48 hrs. even though most of the reactions were complete within 24 hrs. Temperature was controlled to be around 35°C to 39°C and the pH range was 6.9-7.3. Three sets of observations with reference to F/M ratio were made. During the initial period of observations, when the reaction was faster, samples were collected at shorter intervals. Gas production was measured at regular intervals.

3.2.4 Anaerobic Treatment - Gas Studies

The importance of gas measurement in an anaerobic system was emphasized earlier because gas production is by far the best diagnostic tool to evaluate the performance of any anaerobic reactor. Therefore another reactor was fabricated to be perfectly leak-proof. The mixing tank volume was 7.5 liter whereas the settling tank volume was 3.5 liter.

This system was operated at a constant SRT=30 day but at three different organic loading rates. The flow rate was maintained at 2.88 L/day which gave a hydraulic retention time of 2·6 days. The COD concentration was initially in the nieghborhood of 10,000 mg/L, then increased to two third full strength and finally to full strength.

Apart from monitoring all other parameters, gas production was monitored by using a graduated column. The volume of the water displaced in this column was considered to be equivalent to the gas produced in the reactor over a period of time measured as mℓ/hr and then expressed as cft/day. During every single loading rate study, the carbon dioxide content of the gas was also measured periodically as described in the hand-book "Operation of Wastewater Treatment Plants" (66).

3.2.5 Anaerobic Treatment - Shock Load Studies

Environmental shocks and microbial adjustments are nothing uncommon to wastewater treatment plants. During such shocks, the treatment plants in general and the consortium of microorganisms in particular either 'cope up' after a period of adjustment or simply 'give up'. The last phase of this project was to subject the above reactor to such changes which ranged from mild to severe. These shocks included step-up or step-down in infuent concentrations, variations in flow rates, reduction in the ratio of nutritional requirements, variations in the pH and finally depriving the microorganisms off feed completely over a week.

It was possible to collect very valuable information during this phase of study as for as feed shut-down load studies are concerned. Substrate removal performance and gas production were all monitored during these studies.

3.3 Analytical Techniques

Table I is a summary of the analytical techniques utilized in these investigations.

TABLE I

ANALYTICAL TECHNIQUES EMPLOYED IN
THESE INVESTIGATIONS

Analysis	Technique	Source
Suspended Solids	Samples were filtered through a dried, preweighed glass fiber filter (Reeve Angel 934-AH) and dried in a 103°C oven.	
Volatile Suspended Solids	Following suspended solids analyses, the filters were combusted to 550°C for twenty minutes then reweighed.	
pH	Orion Research Model 91-05 pH meter combination pH	
Dissolved Oxygen Concentration and Uptake	Orion Research Model 98-08-00 Probe; reduction of oxygen concentration monitored with time.	
TOC	Beckman Model 915 TOC Analyzer; Sample response compared to standard solution response curve.	
COD	Hach Chemical Company	Hach Chemical Co. Manual (69)
BOD	Standard Methods Technique with modified seed correction; Orion Research D.O. probe utilized.	Standard Methods for the Examination of Water & Wastewater, 14th Ed., (65)
TKN	Hach Chemical Company	Hach Chemical Co. Manual (69)

TABLE I (Continued)

Analysis	Technique	Source
Carbohydrate	Anthrone test - the intensity of color complex formed by furfural derivatives with the organic developer (Anthrone) measured as a function of concentration of carbohydrate	M-2 Manual (67)
Protein	1. Folin-Ciocalteu Test - The color development of protein with Folin-Ciocalteu reagent measured as a function of concentration of protein	M-2 Manual (67)
	2. Biuret Test - the peptide bonds in the protein molecule form a color with the biuret reagent	M-2 Manual (67)
	3. Coomassie dye binding technique - Colormetric	Biorad Biochemical Co. (68)
glucose	Glucostatic Reagent used, Enzymatic, colorimetric glucose analyses were performed and compared to standard solutions	Worthington Biochemical Corporation
Total P & Soluble P Soluble NH_3 - N Volatile Acids	Hach Chemical Company	Hach Chemical Co. Manual (69)
Carbohydrate and Protein content in sludges	Thickened sludge acid hydrolyzed, autoclaved and then analyzed for CHO and Protein after adjusting the pH to neutral	Performed in accordance with the techniques employed in our lab.
Alkalinity	Standard Methods Technique	Standard Methods for the Examination of Water & Wastewater, 14th Ed., (65)

TABLE I (Continued)

Analysis	Technique	Source
CO_2, CH_4	CO_2 content of the off-gas from the anaerobic reactor allowed to dissolve in the KOH saturated solution - the difference in level meaured as a percentage of CO_2 - Rest of the gas assumed as CH_4	operation of Wastewater Treatment Plants - Vol. II (66)
sludge settleability	Thickened sludge sample (5 ml) was placed in a capillary suction time apparatus. The time taken for the filtrate to traverse the gauged field measured as a function of settleability	

Mention should be made, at this juncture, of the COD recipe adopted in our lab. The acid reagent used in the COD analyses was only one half of the normality as against the 18N suggested in the Standard Methods. While this should not be purported to be an error, the author admits of the inadequacy of the COD analysis. A detailed discussion with reference to the discrepancy experienced in our lab in terms of the COD analyses and the corresponding gas production is given in Chapter IV.

Activated sludge mixed liquor and effluent suspended solids concentrations were monitored daily for both aerobic and anaerobic systems. Volatile suspended solids of the mixed liquor were monitored in order that the ratio of VSS to MLSS could be determined. While the temperature for the aerobic system was around 25 $\pm$ 2^{o}C, the same was monitored to be around 35 $\pm$ 2^{o}C in the anaerobic reactor. The alkalinity in the feed was adjusted to run the aerobic reactor around a pH of 7 $\pm$ 0.5 and extreme care was exercised to keep the pH close to neutral for the anaerobic reactor. The DO of the mixed liquor in the aerobic system was monitored to be around 2 mg/L.

Once these biological units attained steady-state conditions, as determined from consistent effluent conditions and MCRT, influent and effluent samples were regularly analyzed for BOD, COD and TOC. Only soluble (passing through Reeve Angel 934 - AH filters) influent and effluent BOD, COD and TOC were considered for modeling purposes.

Periodically mixed liquor was pulled out of the reactor and the settleability test was run using a 1,000 ml graduate cylinder. In the anaerobic system, when such a test was run, the sludge raised to the top portion due to the entrapped gas between the solids. However this buoyancy was reduced by mixing the sludge in an open container and

degasifying. After the settling test was over, the thickened sludge was analyzed for carybohydrate and protein in order to determine their fraction in the biological solids and also to assess the reuse potential. The procedures explained in the M-2 Manual (67) were followed for the carbohydrate analysis whereas the Biorad Coomassie dye binding techniques (68) were followed for the protein analysis. Similar analyses were also done on effluents on a regular basis.

3.4 Substrate Removal Kinetics-Principles

The data from the activated sludge systems were analyzed to provide performance information and the biokinetic constants required for design by the various activated sludge design models available.

The aim of these design models is to provide more accurate predictive equations which are in keeping with the underlying metabolic and biological principles governing the purification process. These models were developed by writing material balances describing the mass rate of change in substrate and in biomass. Substrate utilization and biomass increase are the two major concerns in the functional design of the biological reactor. Mathematical descriptioin of these two functions, especially substrate utilization rate or $(ds/dt)_g$, is where the various models differ. The biokinetic constants required for use in each of the following design models were determined: (70), (71), (72), (73).

The material balance may be conducted around the bioreactor, as in Gaudy's model and Weston's model, or around the entire process including the bioreactor and mixed liquor separator or final clarifier as shown in Figure 4. When the material balance for substrate is written around the entire process: (72)(73).

change of mass in reactor	=	mass entering reactor	-	mass leaving reactor in effluent	-	mass consumed biologically

$$\left(\frac{ds}{dt}\right)_R V = FS_i - FS_e - \left(\frac{ds}{dt}\right)_g V \quad (1)$$

For steady state conditions $\left(\frac{ds}{dt}\right)_R = 0$, and $\left(\frac{ds}{dt}\right)_g V = FS_i - FS_e$ (2)

Substitution of the appropriate substrate utilization rate term into the material balance equation and solving for the reactor volume, V, provides the required aeration tank volume by the desired design method. The required biokinetic constants or coefficients are determined by graphical analysis of the data developed from the treatability study. Use of these constants or coefficients in Equation 2 allows determination of V, as follows:

MASS BALANCE AROUND ENTIRE SYSTEM

Eckenfelder

First Order $$V = \frac{F(S_i - S_e)}{K_e S_e X} \quad (3)$$

Second Order $$V = \frac{FS_i(S_i - S_e)}{K_e' S_e X} \quad (4)$$

McKinney $$V = \frac{F(S_i - S_e)}{K_m S_e} \quad (5)$$

Weston $$V = \frac{F(S_i - S_e)}{R_s S_e \left(\frac{X}{S_i}\right)^{K_i}} \quad (6)$$

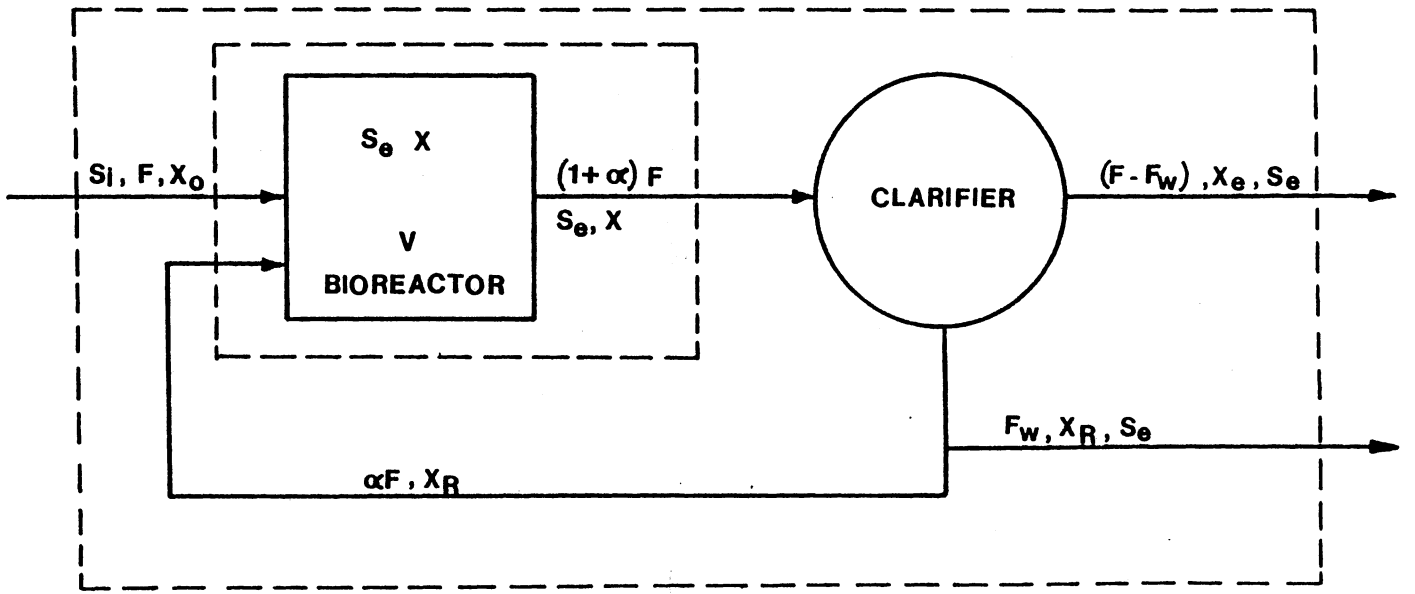


Figure 4. Flow Diagram, Activated Sludge Process Showing Notation and Mass Balance Envelopes.

Lawrence and McCarty

$$V = \frac{\theta_c Y_t F(S_i - S_e)}{(1 + K_d\theta_c) X} \quad (7)$$

Kincannon and Stover

$$V = \frac{FS_i/X}{\frac{U_{max} S_i}{S_i - S_e} - K_B} \quad (8)$$

MASS BALANCE AROUND BIOREACTOR

Gaudy

$$V = \frac{Y_t F[S_i - (1 + \alpha)S_e] + \alpha X_R F}{K_d X} - \frac{(1 + \alpha)F}{K_d} \quad (9)$$

Weston

$$V = \frac{F[S_i - (1 + \alpha)S_e]}{S_e R_s \left(\frac{X}{S_i/(1 + \alpha)}\right)^{K_i}} \quad (10)$$

Kincannon and Stover

$$V = \frac{FS_i/X}{\frac{U_{max} S_i}{S_i - (1 + \alpha)S_e} - K_B} \quad (11)$$

where:

- θ_c - sludge retention time or sludge age
- X_R - recycle solids concentration
- α - recycle ratio
- F - flow rate
- S_e - effluent substrate concentration
- S_i - influent substrate concentration
- X - biological solids concentration
- V - reactor volume

K - Lawrence and McCarty's maximum substrate utilization rate

K_B - substrate loading at which the rate of substrate utilization is one-half the maximum rate.

K_e - Eckenfelder's first order substrate removal rate constant

K_e' - Eckenfelder's second order substrate removal rate constant

K_i - Weston's inhibition descriptive constant

K_m - McKinney's substrate removal rate

K_s - saturation constant

R_s - Weston's substrate utilization rate constant

U_{max} - Kincannon and Stover's maximum substrate utilization rate

Y_t - true cell yield

μ_{max} - maximum growth rate

3.4.1 Variability Analysis of Substrate Removal Kinetics

The normal approach for analyzing and presenting biological system data to obtain the biokinetic constants or coefficients is to plot average values at each growth rate or sluge retention time. This appraoch masks the actual scatter of the data and provides an average value or 50 percent probable value to be used in design (74). This inherent biological system response variability shows up as variability in the biological kinetic analyses in all the design models except the Kincannon and Stover Model (72)(74). When using the other design models

to achieve specific effluent discharge criteria, the variability observed in the biokinetic coefficients must be considered.

During the design of activated sludge systems, to achieve scpecific effluent discharge criteria, it is very important to determine the variability expected and distinguish between the biokinetic constants and the variable biokinetic coefficients. Use of the 50 percent biokinetic coefficients will provide a system capable of achieving the specified effluent quality only 50 percent of the time. The allowed statistical variability of the effluent discharge criteria must be evaluated to determine the appropriate biokinetic coefficients to be used for design.

CHAPTER IV

RESULTS AND DISCUSSIONS

Every problem in environmental engineering must be approached initially in a manner that will define the problem. Once the problem has been defined quantitatively, the engineer is usually in a position to design facilities that will provide a satisfactory solution. One of the primary objectives of this research was to characterize the stillage in order to assess the pollution potential of the waste. Therefore, the major part of the initial phase of this research was oriented towards frequent sampling and running the pertinent analyses. In an attempt to get a typical 'fingerprint' of the stillage, samples were collected from an actual plant at Hydro, Oklahoma, about 100 miles from Stillwater, Oklahoma, and also from the Oklahoma State University Agricultural Engineers 200,000 gallon per year capacity fuel alcohol research facility.

4.1 Pretreatment - Jar Test Studies

A series of jar test studies were performed initially in order to evaluate the addition of flocculting agents to enhance the thickening characteristics of the wastewater. Inorganic coagulants like alum ($A\ell_2(SO_4)_3 \cdot 18H_2O$), lime (Ash Grove Chemical Powder Company) and ferric sulfate ($FeSO_4$) were first tried either singly or in combination and in different dosages. In all these jar test studies, the rapid mixing time was 30 seconds and the flocculation time monitored to 15 minutes. The

contents were then allowed to settle for 30 minutes. The control jar with the waste received no coagulant.

Later, high molecular anionic an/or cationic polymers (a product of Betz Company) of the PERCOL products were tried in different concentrations in these jar test studies again either singly or in combinations, with or without adjusting the pH.

Some of the observations of these jar test studies are summariezd as follows:

1. There was always a clear line of demarcation between the solids in the waste and the supernatant, both during and after settling. This line of separation was very descernible after a period of long settling. The settleability could be compared to that of a well settling typical activated sludge.
2. The settling characteristics improved considerably with the addition of PERCOL 726 anionic polymer. At a concentration of 20 mg/L of PERCOL 726 (0.5%) high strength anionic polymer, the floc size was very high as observed even during rapid mixing. The results obtained from the visual observations, in as much as settling is concerned, are presented in Table II.

   A simple technique to express the settleability has been used as follows. The volume of the waste sample used was 500 ml throughout this jar test study. After a period of 30 min. settling, if the separation line is seen at 400 ml, then the settling is

$$20\% \triangleq \left(\frac{500 - 400}{500}\right) \times 100\%$$

TABLE II

RESULTS OF THE JAR TEST STUDIES AND THICKENING CHARACTERISTICS OF STILLAGE

Coagulant	Dosage mg/L	Settling Character %	Remarks	Polymer	Dosage mg/L	Settling Character %	Remarks
	200	20	pH adjusted	PERCOL 726	5	60	Floc Size
Lime	300	30		0.5% High	10	60	increased
	600	20	to neutral	Anionic	15	60	as dosage
Control	-	20		Polymer	20	80	increased
					25	60	
				Control	-	20	
Lime +	100+100	20		PERCOL 757	5	20	even at 3,000
Alum	100+200	40	ph adjusted	High	10	20	mg/L no
	150+150	30		Cationic	20	20	difference
	300+300	20	to neutral	Polymer	50	20	observed.
Control	-	20			500	20	
				Control	-	20	
	100	20		Lime +	400+500	50	
Ferric	200	20	ph adjusted	PERCOL 726	400+1000	50	
sulfate	500	20		High Anionic	400+2000	60	-
Control	-	20	to netural	Polymer 0.05%	200+2000	50	
				Control	-	25	

TABLE II (Continued)

Coagulant	Dosage mg/L	Settling Character%	Remarks
Lime +	50+50+50	20	ph adjusted
alum +	100+200+50	30	
Ferric	0+300+50	25	to neutral
Sulfate	300+0+100	25	
Control	-	25	

(a) Using Coagulants

Polymer	Dosage mg/L	Settling Character %	Remarks
Lime +	400+200+1000	25	
$FeSO_4$ +	400+400+400	50	-
PERCOL 726	400+200+2000	50	
CONTROL	-	25	

(b) Using Organic Polymers

3. As seen from Table II, there was no difference in the settling characteristics between whether ferric sulfate was added or not; but it improved with the addition of lime (highest at 300 mg/L). The combination of lime and alum gave the best results at a dosage of 100 mg/L and 200 mg/L respectively.
4. Just like addition of ferric sulfate had little impact on the flocculation/sedimentation characteristics of the waste, so was the addition of PERCOL 757 high strength cationic polymer even at concentrations as high as 3,000 mg/L.
5. The combination of lime + PERCOL 726 anionic polymer also gave compatible results. Sixty percent settling was obtained at a concentration of 400 mg/L and 2000 mg/L of lime and PERCOL 726 respectively.
6. Invariably in all cases, when the concentration of the coagulant/polymer was the highest, the floc formation was also the highest. However, after certain time, the settled sludge raised to the top.
7. In one situation, the contents were allowed to settle for 24 hrs., after the addition of PERCOL 726 anionic polymer. When the control jar and the other jars which received the polymer were compared, all of them exhibited the same consolidation.
8. Addition of polymer/coagulent imparted little impact in the dewatering characteristics of the waste as observed by the CST analyses. For a sample whose thickened solids concentration was 22,400 mg/L the capillary suction time varied between 16 to 24 sec., indicating very good dewatering characteristics. This

range includes those samples which received PERCOL 726 high strength anionic polymer also.

9. It is obvious from Table II that the addition of PERCOL 726 high strength anionic polymer exhibited the best thickening characteristics for the waste.

4.2 Stillage Characterization

A summary of the stillage composition and concentration of these components are presented in Table III. While it has to be admitted that this is only a partial list of the components of the waste, this information was more than sufficient to perform the treatability studies. Therefore, as stated previously, the sampling effort was limited to arriving at a tyical finger print of the organic content of the stillage. The analyses on TKN, NH_3N, protein and phrosphate were run to estimate if any external nutrient needed to be added to the feedstock to meet the C:N:P ratio of 100:5:1.

The concentration in terms of COD, BOD and TOC best illustrate the magntiude of the pollutional potential of the stillage if it were to be discharged with little or no treatment. Milo feedstock exhibited a higher COD value than that of corn. It was also observed that about 30 to 40% of the SS in the milo reported here were due to the husks of milo. During the period of treatability studies using milo, care was taken to screen and skim these husks. The settled supernatant of milo exhibited a higher turbidity than that of corn.

As is seen from Table III, the waste was acidic. The milo waste was more acidic than the corn waste. The alkalinity demand in terms of $CaCO_3$ was much higher for milo waste than for corn waste. In Fig. 5,

TABLE III

RAW WASTEWATER (THIN STILLAGE) CHARACATERISTICS

Parameter*	Corn Feedstock		Milo Feedstock	
	Mean	Standard Deviation	Mean	Standard Deviation
TS	32,200	9,300	42,800	2,150
TDS	18,600	7,100	20,400	6,800
SS	11,800	3,700	22,500	5,100
VSS	11,300	3,500	19,500	2,600
Total COD	64,500	12,600	75,700	12,100
Soluble COD	30,800	6,200	40,700	9,100
Total BOD_5	26,900	800	34,900	2,000
Soluble BOD_5	19,000	2,100	21,700	1,360
Soluble TOC	9,850	2,200	14,900	2,600
Total P	1,170	100	1,280	100
Soluble P	1,065	75	1,075	150
Total TKN	755	115	--	--
Soluble TKN	480	95	--	--
Soluble NH_3-N	130	60	--	--
Total Protein	4,590	650	--	--
Soluble Protein	2,230	780	--	--
Total Carbohydrate	8,250	750	--	--
Soluble Carbohydrate	2,250	550	--	--
Soluble Glucose	< 750	--	--	--
pH (range)	3.3-4.0	--	2.5-4.0	--

* All units in mg/l except pH.

the titration curves for different feedstocks are plotted. For running the aerobic biological reactos, for example, a feed pH range of 7 to 9 had to be maintained. Sodium hydroxide was used for raising the pH. The alkanity demand to keep up to this pH was in the range of 1300 mg/l to 1650 mg/L for corn waste, whereas for milo waste, the range varied from 3950 mg/L to 4500 mg/L as $CaCO_3$.

In addition to these parameters analyzed, certain other characteristics, unique to this waste, need mention. There was absolutely no decay when the waste was preserved in the refrigerator. But when the waste was stored at room temperature, within a day or two, a thick mat of scum developed on the top layer. After a storing period of roughly five days, the waste did exhibit a pungent, rancid-butter smell.

Also, sometime in the middle of September 1982, the cooker in the Oklahoma State University Agricultural Engineers' alcohol plant broke down. Subsequent to the repair, it was observed by the alcohol plant personnel that the efficiency of the plant in ethanol extraction had also dropped. This drop in the efficiency of the alcohol plant had an impact on the stillage also. Before the break-down, the waste was mostly stable as far as the BOD and COD were concerned even after a storage for over a month. However after the repair, the waste started deteriorating in its organic strength at a faster rate. The possible reasons for this could be explained as follows.

Before the breakdown of the cooker, most of the ethanol was extracted from the fermented mash. As a result, the COD of the waste was mostly contributed by the organic matter in the stillage. The typical soluble COD values of the waste was around 30,000 $\pm$ 2,000 mg/L (for the corn feedstock) and was not fluctuating during this period

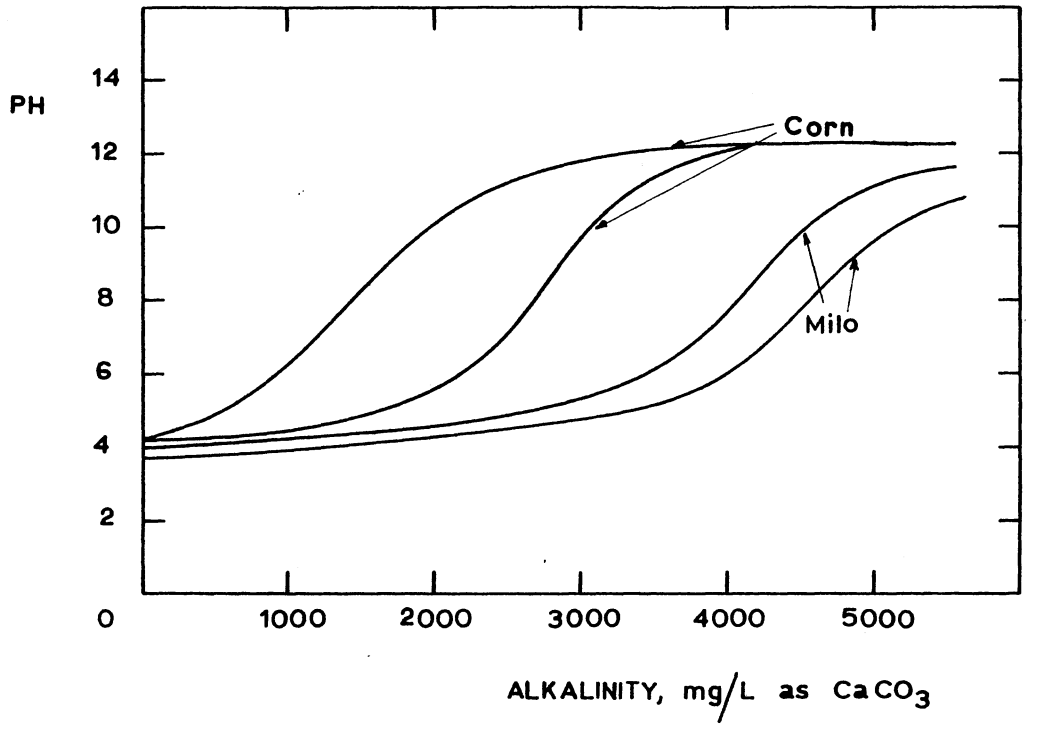


Figure 5. Typical Titration Curves for the Thin Stillage

irrespective of whether it was immediately after collection or during storing.

However, after the breakdown, a portion of the ethanol bled out along with the stillage which boosted the soluble COD values of the wastes, collected immediately after distillation, to as high as 36,000 mg/L. This value decreased slowly and somtimes reached a value as low as 18,000 mg/L. Such a reduction in the COD might be attributed to the fact that the unextracted ethanol, dissolved in the stillage, was evaporating slowly during the period of storage. A second reasoning that could explain this redution might be that the waste was being metabolized by some extraneous eucaryotic micro-organisms such as fungi. A better resolution of the concentration of ethanol in the fresh waste as well as the stored waste, preferably by using a GC and some microbial analyses on the formation of the scum mat on the top layer of the waste, might possibly explain these discrepancies in the COD vaues in a better manner.

4.3 Aerobic Activated Sudge Treatment Studies

4.3.1 Treatability Performance and Developing Bio-Kinetic Constants

As already outlined, the primary purpose of these biological investigations was to develop information and data that could be used to predict the treatability of this industrial wastewater.

From the pretreatment studies it was observed that it was possible to accomplish a good thickening of the stillage by using PERCOL 726 high strength anionic polymer. It was also observed that there was not a considerable variation in the capillary suction time irrespective of

whether the waste was subjected to pretreatment or not. Hence for the subsequent biological treatability studies, the gravity settled supernatant was used. The supernatant was diluted approximately 2:1 with tap water to provide the influent feed to be activated sludge systems.

The average influent and effluent charcteristics in terms of BOD_5, COD and TOC during this study are presented in Table IV. In Table V, the average continuous flow aerobic system operating characteristics are presented. As observed in Table IV, the treatment efficiency in terms of these parameters was very high throughout the entire period of study, always greater than 95%. The treatability data was analyzed to develop the average or 50 percent biokinetic constants or coefficients required for the design models of Eckenfelder, McKinney, Weston, Lawrence and McCarty, Gaudy, and Kincannon and Stover. All these constants or coefficients, as many of them should be called, are determined by graphical analysis. The results of these graphical analysis in terms of BOD_5 are shown in Figures 6-13. All the data is presented by the dots to show the actual scatter of the data observed during this study, and the average at each operating condition is presented by X's. The line represents the line of best fit for determination of the average or 50 percent biokinetic constants, as described by Stover, et al. (74). This type of scatter is typical in biological treatability due to the inherent variability of heterogeneous biological populations and is normally masked by just plotting the average values. There are procedures to handle this variability in determining the various probable values of the various biokinetic constants or coefficients, which are presented in the following part of this discussion.

TABLE IV

SUMMARY OF ACTIVATED SLUDGE TREATMENT PERFORMANCE

	SRT	Soluble BOD_5			Soluble COD			Soluble TOC		
F/M	(days)	Infl. (mg/l)	Eff. (mg/l)	Removal (%)	Infl. (mg/l)	Eff. (mg/l)	Removal (%)	Infl. (mg/l)	Eff. (mg/l)	Removal (%)
0.74	3	5300	290	94.5	9100	420	95.4	3090	100	96.8
0.45	6	5220	90	98.3	9100	200	97.8	3100	80	97.4
0.31	10	5315	70	98.7	10600	230	97.8	3570	90	97.5
0.24	20	5340	65	98.8	11100	180	98.4	3680	90	97.6

TABLE V

AVERAGE CONTINUOUS FLOW AEROBIC SYSTEM
OPERATING CHARACTERISTICS

	Influent		Effluent			
SRT (Days)	Flow (L/day)	Total BOD (mg/L)	SS* (mg/L)	VSS (mg/L)	Total BOD (mg/L)**	HRT (Hrs)
3	3.6	6,770	87	78	300	48
6	3.6	6,770	66	59	89	48
10	3.6	6,990	158	135	139	48
20	3.6	6,990	253	210	110	48

	Mixed Liquor*		Waste Activated Sludge**				
SRT days	MLSS (mg/L)	MLVSS (mg/L)	VS mg/L	ZSV (ft/hr)	CST (sec)	Protein (%)	CHO (%)
3	3,630	3,265	5,640	0.25	58.0	24	50
6	6,670	5,940	7,900	1.35	10.0	24	35
10	10,115	8,900	13,870	0.20	16.0	17	25
20	12,875	11,330	15,950	0.20	16.0	15	24
				Thin Stillage		21	50

* Mean values based upon 10, 9 15 and 12 sets of readings respectively.

** Mean values based upon 3 sets of readings.

ZSV - Zone settling velocity
CST - Capillary suction time
CHO - Carbohydrate

In Figure 6, the net specific growth rate (μ_n) is plotted as a function of the specific subtrate utilization rate (U) for determination of the true cell yield (Y_t) and the endogeneous decay or maintenance energy coefficient (K_d), as used in all the kinetic design models. The Y_t of 0.53 is the slope of the line, and K_d of 0.06 is the Y-axis intercept.

In Figure 7, U is plotted as a function of the effluent substrate concentration (S_e) for determination of Eckenfelder's first order substrate removal rate constant. The K_e of 0.004 is the slope of the solid line. In Figure 8, $S_i \cdot U$ is plotted as a funtion of S_e for determination of Eckenfelder's modified model (second order) subtrate removal rate constant. The K_e' of 20.7 is the slope of the solid line. The plot of U versus S_e actually yields a hyperbolic type plot with a maximum U value which indicates monomolecular kinetics. However, at the conditions activated sludge systems are normally operated only the lower portion of the curve is developed, and this part of the curve can be successively described by either monomolecular kinetics or first order kinetics. This aspect is shown in Figures 7 and 8 where the dashed line represents a break in the plots after Eckenfelder. The three average points on the solid line were used to calculate K_e and K_e', since the fourth operating condition definitely represented a point on the curve. An average line could have been drawn through the four data points to yield lower K_e and K_e' values of 0.0034 and 18, respectively; however it must be emphasized that the point on the dashed line is beyond the normal operating condition of most activated sludge plants.

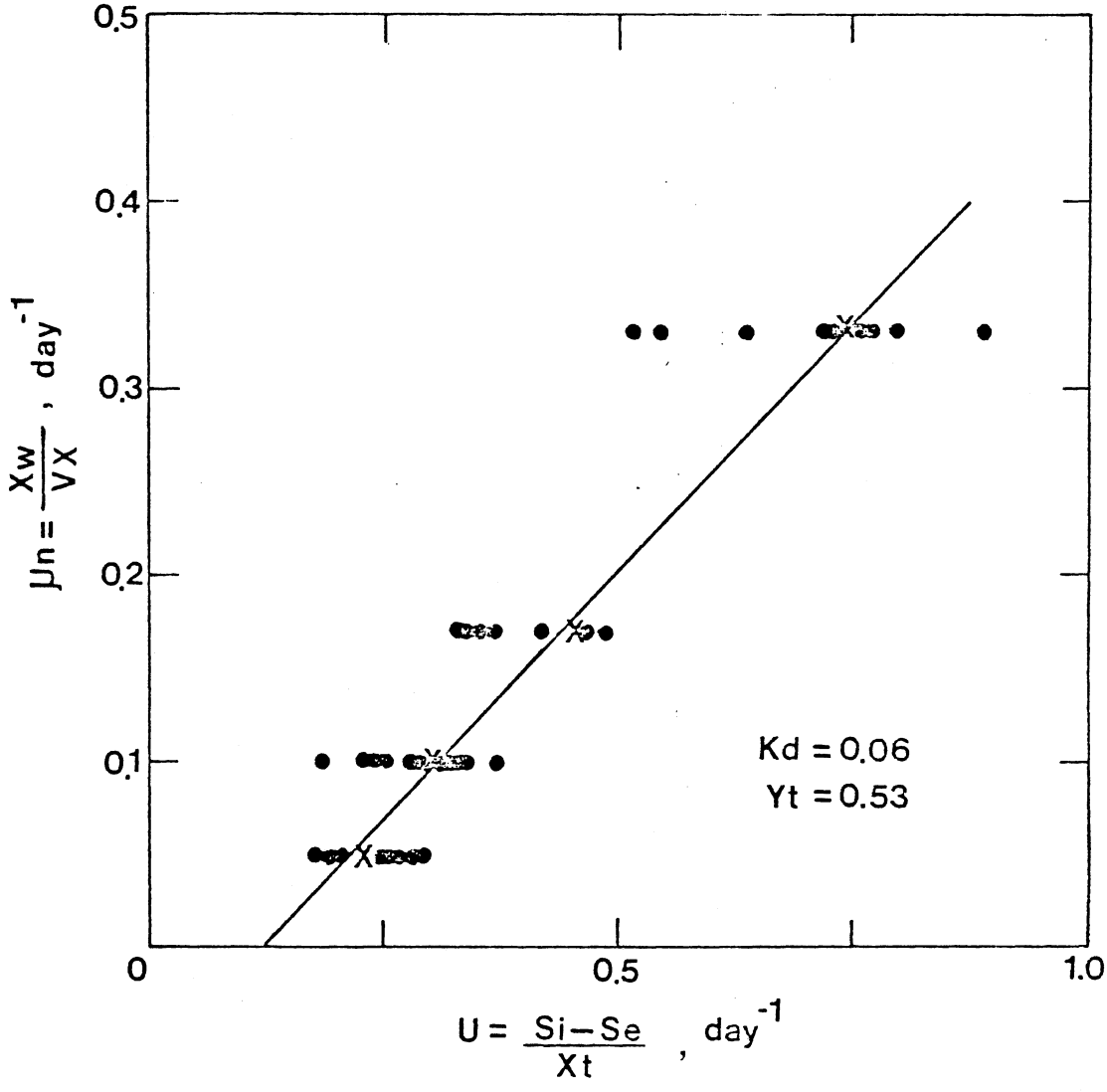


Figure 6. Graphical Determination of Y_t and K_d (BOD_5) for all Design Models.

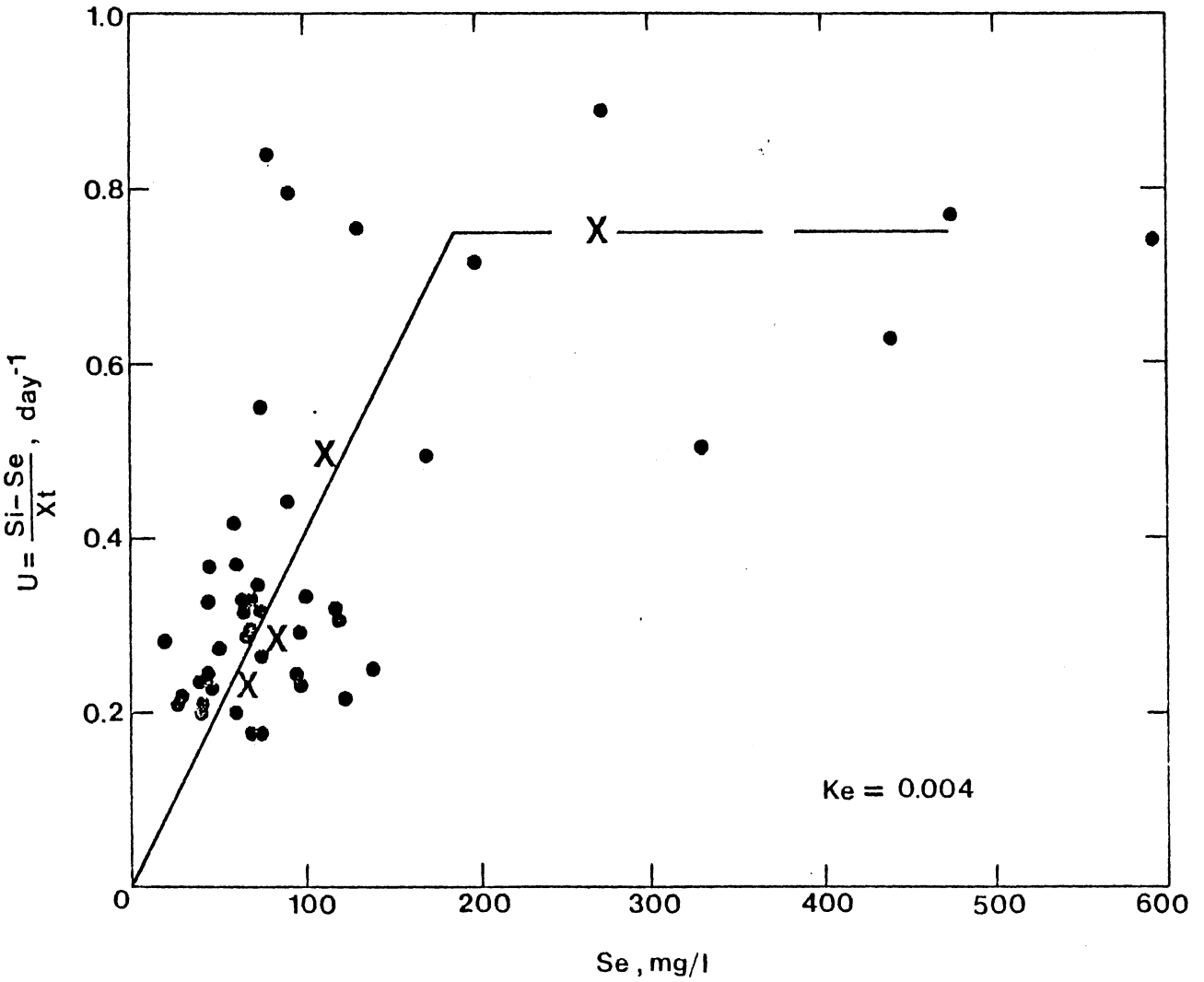


Figure 7. Graphical Determination of $K_e(BOD_5)$ for Eckenfelder's First Order Design Model.

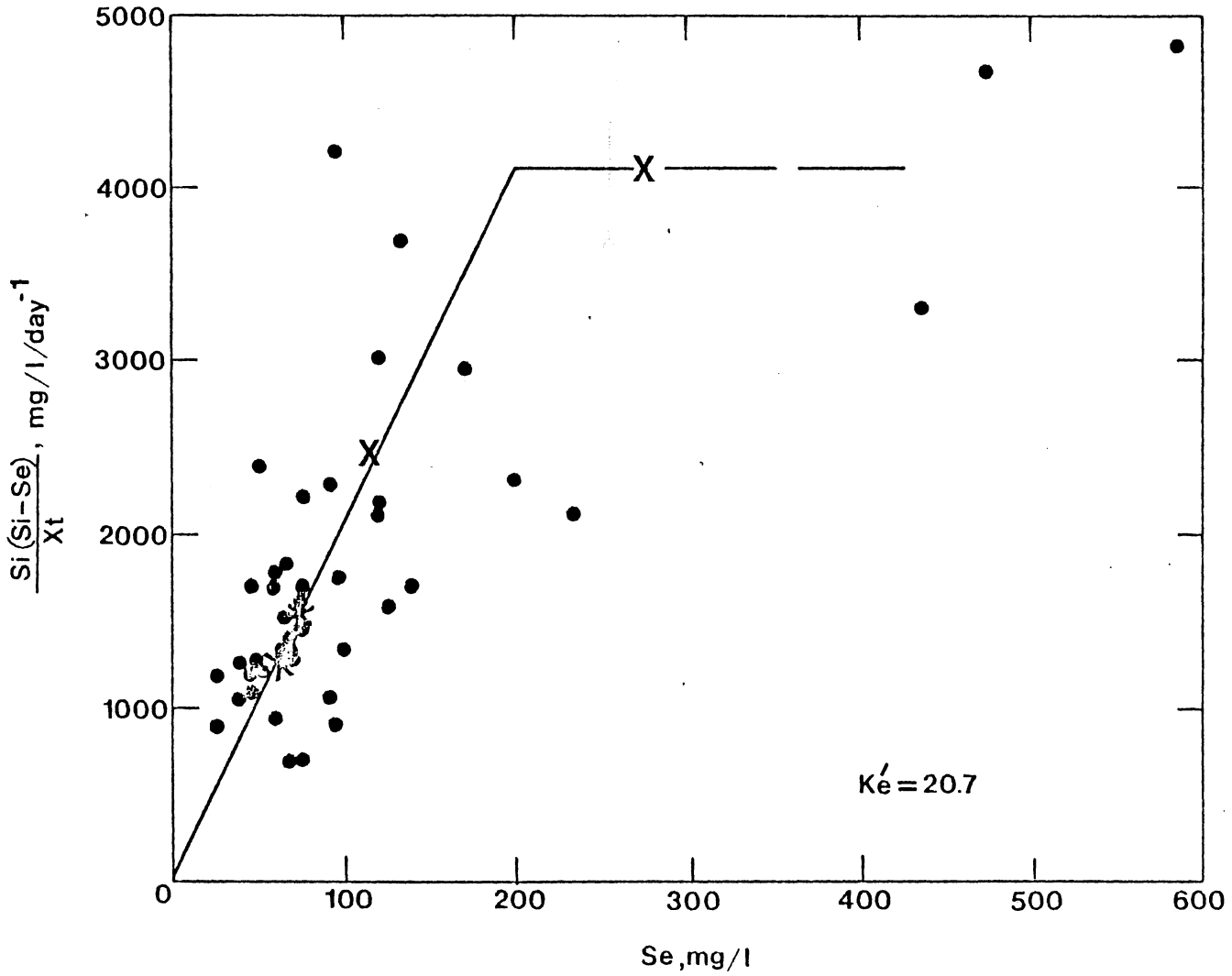


Figure 8. Graphical Determination of K_e' (BOD_5) for Eckenfelder's Modified Design Model.

In Figure 9, McKinney's substrate removal rate, K_m, is plotted as a function of the biological solids, X. As previously indicated by the substrate utilization rate terms of Eckenfelder and McKinney, $K_m = K_eX$ and the slope of the line is equal to the K_eX of 0.0042X. This K_e of 0.0042 compares well with the $K_e = 0.004$ of Figure 7. In Figure 9, the log of Weston's substrate reaction rate coefficient, r, is plotted as a function of the log of the BOD_5 to biological solids loading ratio, S_i/X, for determination of Weston's substrate utilization rate constant, R_s, and the inhibition descriptive constant, K_i. The R_s of 21.0 is the intercept at $S_i/X = 1.0$, and the K_i of 1.0 is the negative slope of the line. It is interesting to note that Weston's substrate reaction rate coefficient, $r = S_i - S_e/S_e \cdot t$ is the same as McKinney's substrate removal rate, $K_m = S_i - S_e/S_e \cdot t$ and that Weston's substrate utilization rate constant, $R_s = 21.0$, is the same as Eckenfelder's modified second order substrate removal rate constant, $K_e' = 20.7$ (73).

In Figure 11, the reciprocal of the specific growth rate, , is plotted as a function of the reciprocal of S_e for determination of the maximum specific growth rate, μ_{max}, and the saturation constant, K_s, as used in the Gaudy design model. The Y-axis intercept is the reciprocal of $\mu_{max} = 1.0$, and the slope is equal to K_s/μ_{max} with $K_s = 360$ mg/l. In Figure 12, the reciprocal of U is plotted as a function of the reciprocal of S_e for determination of the maximum U, K, and the saturation constant, K_s, as used in the Lawrence and McCarty design model. The Y-axis intercept is the reciprocal of K = 2.0, and the slope is equal to K_s/K with $K_s = 360$ mg/l. As previously indicated by the substrate utilization rate terms of Gaudy and Lawrence and McCarty, the relationship of $\mu_{max} = K \cdot Y_t$ can also be used to determine K. The

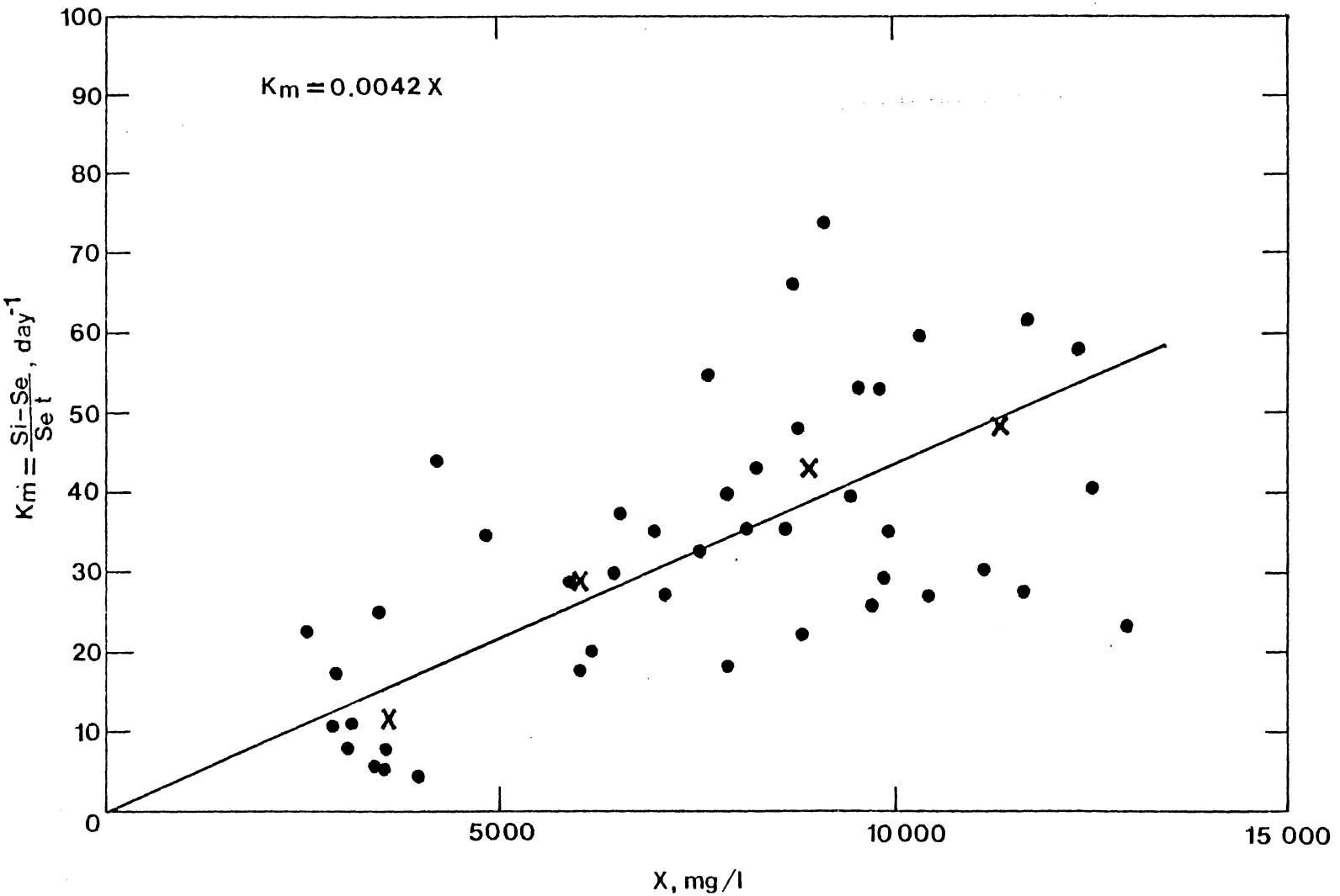


Figure 9. Graphical Determination of $K_m(BOD_5)$ for McKinney Design Model.

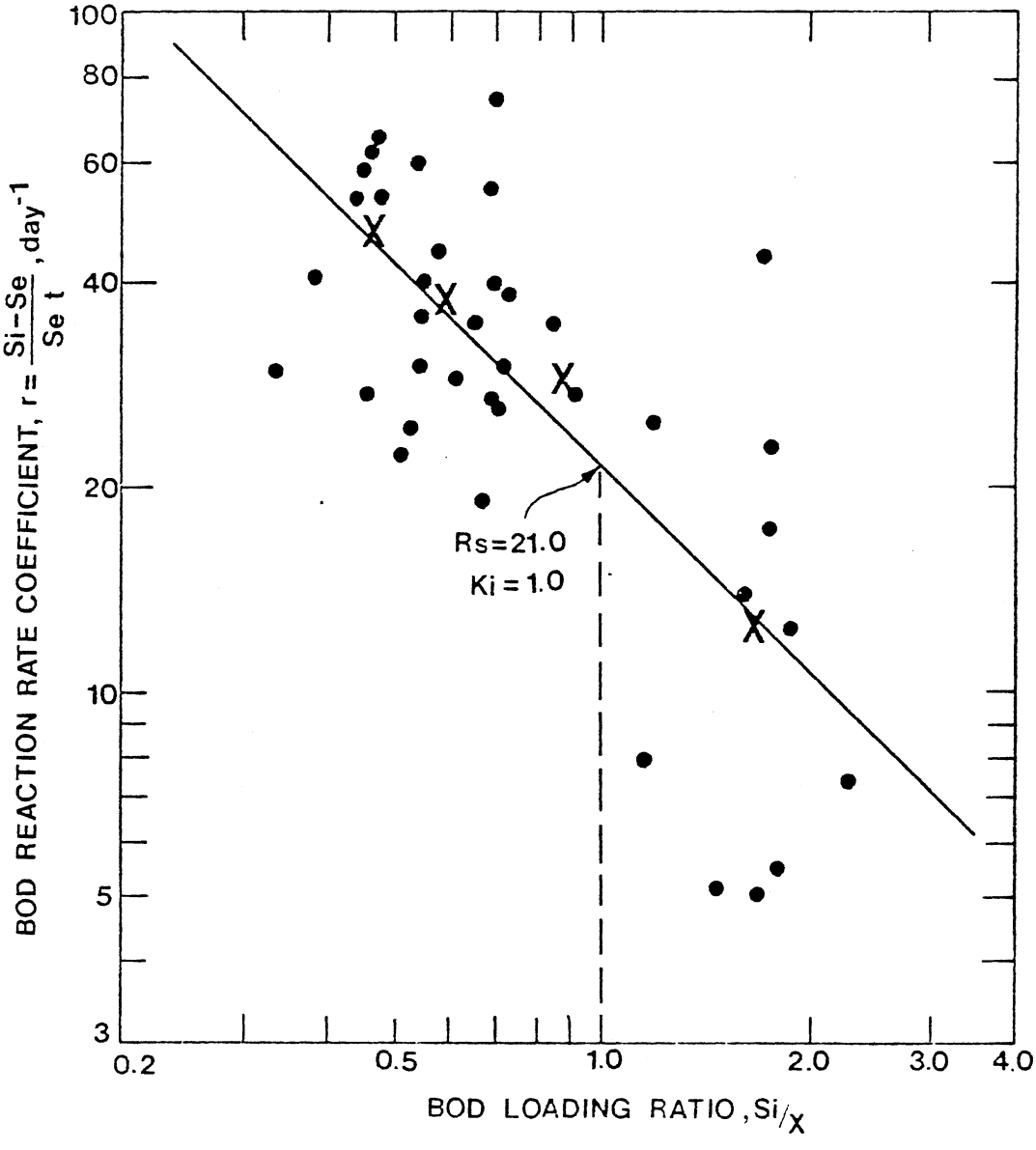


Figure 10. Graphical Determination of R_s (BOD_5) and K_i for Weston's Design Model.

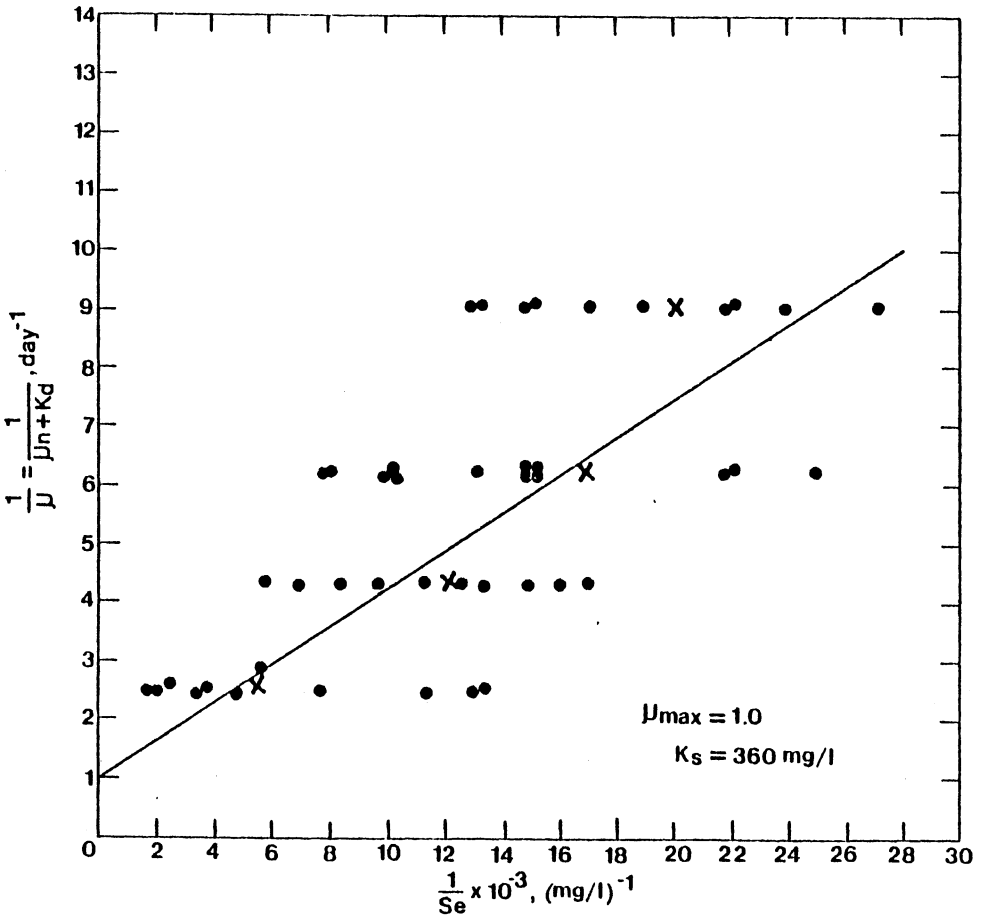


Figure 11. Graphical Determination of μ_{max} and K_s (BOD_5) for Gaudy Design Model.

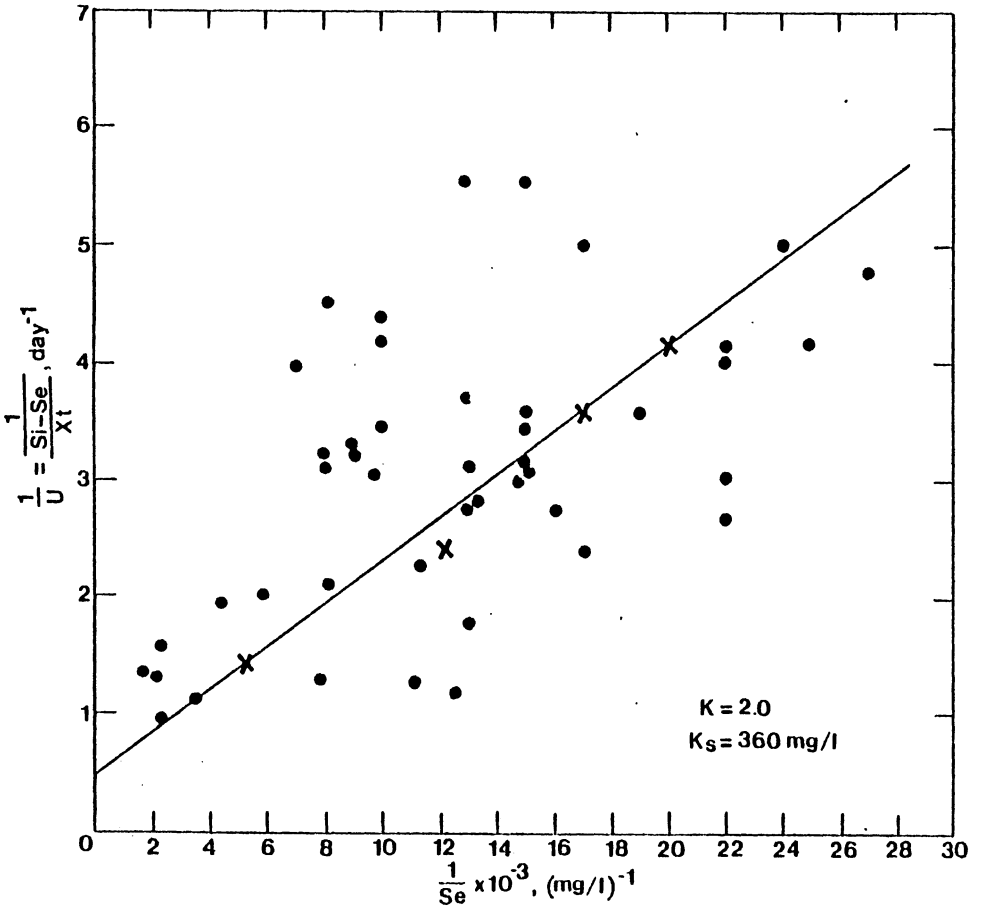


Figure 12. Graphical Determination of K and K_S (BOD_5) for Lawrence and McCarty Deign Model.

graphical determination of these constants from Figures 6, 11 and 12 agree with the kinetic assumptions; K_s = 360 mg/l in both Figures 11 and 12, Y_t = 0.53, μ_{max} = 1.0, and K = 2.0.

In Figure 13, the reciprocal of U is plotted as a function of the reciprocal of the specific loading rate, F/M, for determination of the maximum substrate utilization rate, U_{max}, and the substrate loading at which U is one-half of U_{max}, K_B, after Kincannon and Stover. The Y-axis intercept is the reciprocal of U_{max} = 16.7, and the slope is equal to K_B/U_{max} with K_B = 16.7. One advantage of this design method is the reduction in scatter of the data for determination of the biokinetic constants U_{max} and K_B. An excellent fit of the data can be observed in Figure 13 with the high correlation coefficient of 0.999. The elimination of the scatter by this design method is due to the fact that the substrate utlization rate terms in all the design models are expressed on a substrate mass basis, and the substrate utilization rate is actually a function of the mass loading rate. The Kincannon and Stover design model is the only model that expresses substrate utilization as a function of mass loading; all the other design models express substrate utilization as a function of concentration loading. These studies have shown that these wastewaters are highly biodegradable and can be successfully treated to high levels by the aerobic activated sludge process.

As stated in the beginning of this discussion, during the treatability studies the hydraulic retention time (t), the flow rate (F), and the sludge retention time (θ_c) were kept constant. The parameters that varied were effluent substrate concentration (S_e) and the mixed liquor volatile suspended solids concentration (X). The

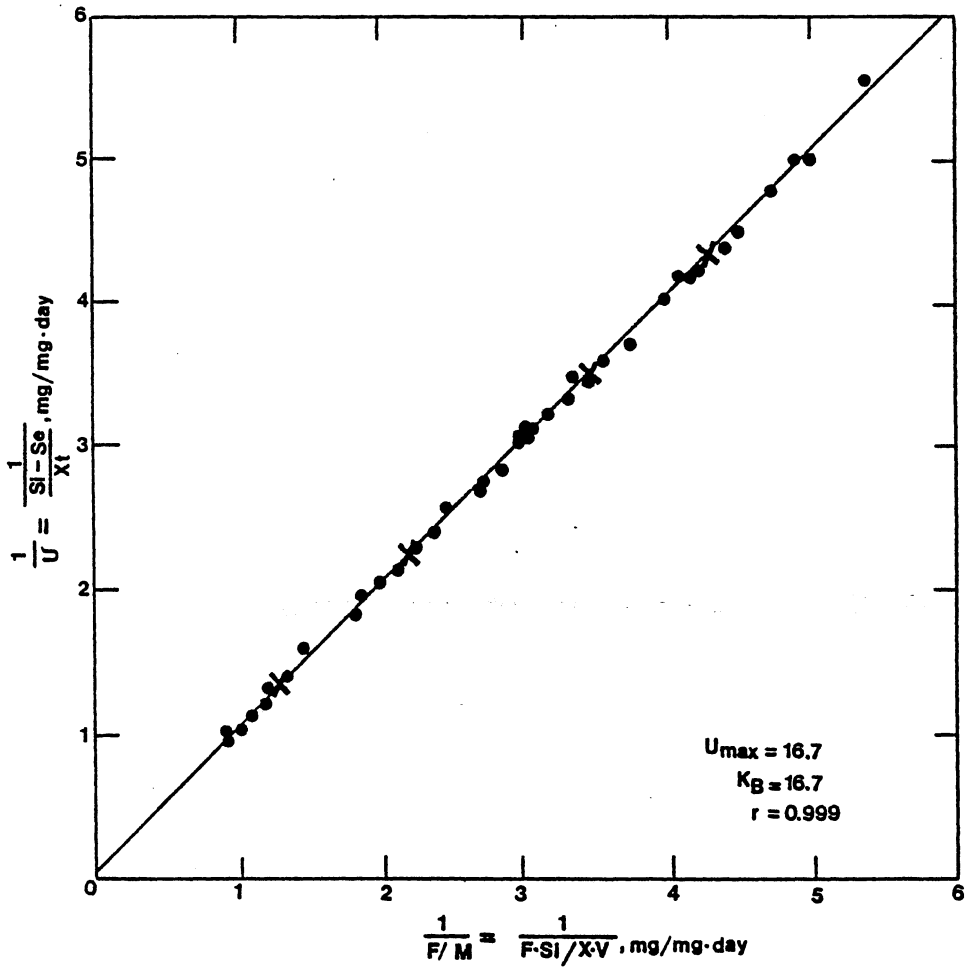


Figure 13. Graphical Determination of U_{max} and K_B (BOD_5) for Kincannon and Stover Design Model

influent BOD_5 concentration (S_i) also varied, even though attempts were made to keep it constant. Probability plots of these parameters can be developed over the data collection period to evaluate the variability observed for these parameters. Probability plots of the substrate utilization descriptor terms required for each design model, $U = \frac{(S_i - S_e)}{Xt}$, $S_i \cdot U$, $r = K_m = \frac{(S_i - S_e)}{S_e\ t}$ and S_i/X, can also be developed for use in evaluation of the variability in the biokinetic coefficients. Probability plots for these parameters required for variability analysis with each of the design models are shown in Figures 14-19 for the alcohol production wastewaters investigated during these studies. The separate lines on each figure represent the four different operating conditions or sludge retention times investigated.

In Figure 20 the net specific growth rate (μ_n) is plotted as a function of the specific subtrate utilization rate for determination of the true cell yield (Y_t) and the endogeneous decay coefficient (K_d), as used in all the kinetic design models. Y_t is the slope of the line and K_d is the Y-axis intercept. Since μ_n was kept constant, the variability in U was determined from Figure 14 to develop the probability lines of Figure 20. The average values of U are represented by the X's and fall approximately on the 50 percent line. Thus, by this approach Y_t and K_d can be determined for any probability level desired, for example at the 5, 25, 50, 75 and 95 percent probability levels. The desired probability value of U can be selected from Figure 14 for the different μ_n's or θ_c's investigated and plotted on Figure 20 against the respective μ_n or θ_c to yield the specified probability level of Y_t and K_d. An interesting aspect of Figure 20 is the variability of Y_t due to

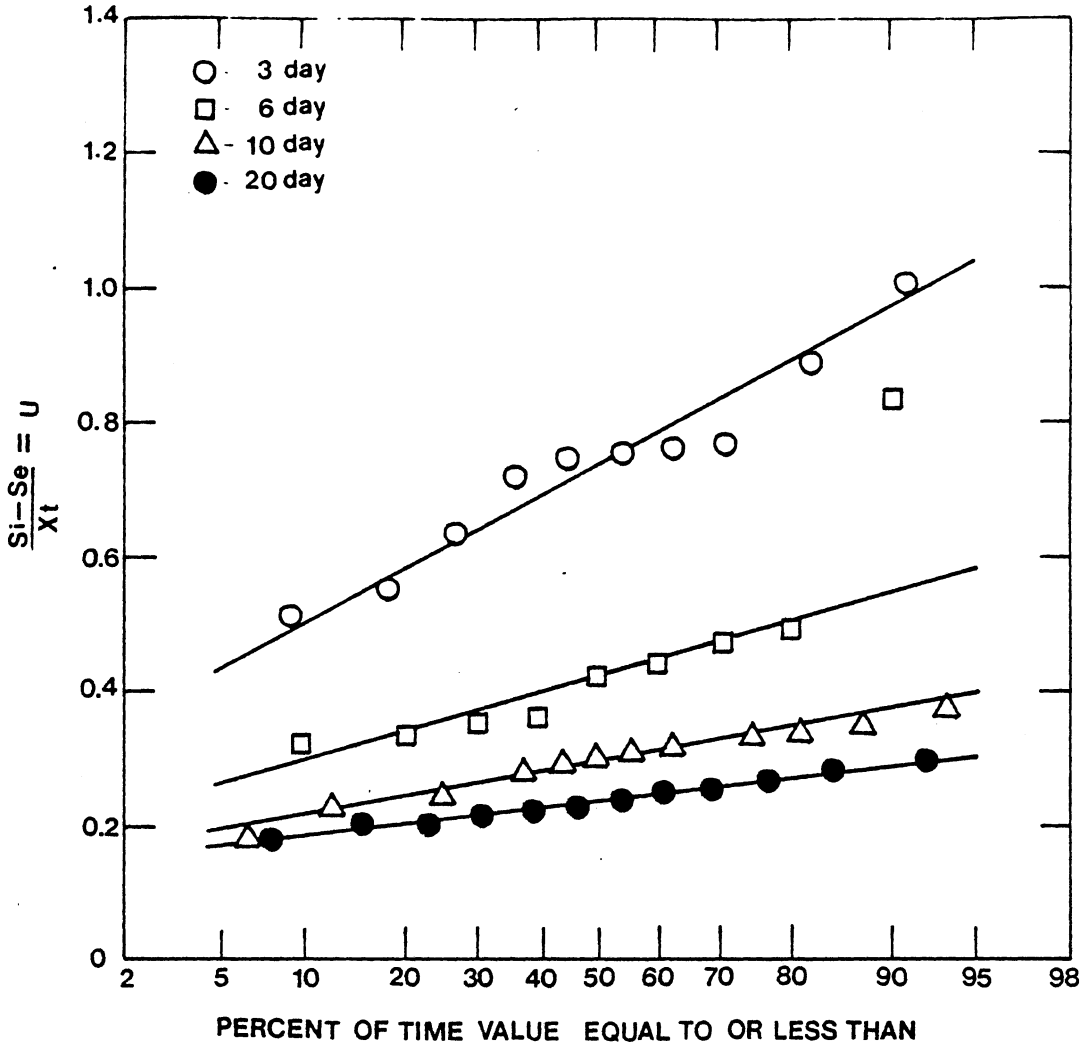


Figure 14. Frequency Analysis of U (BOD_5).

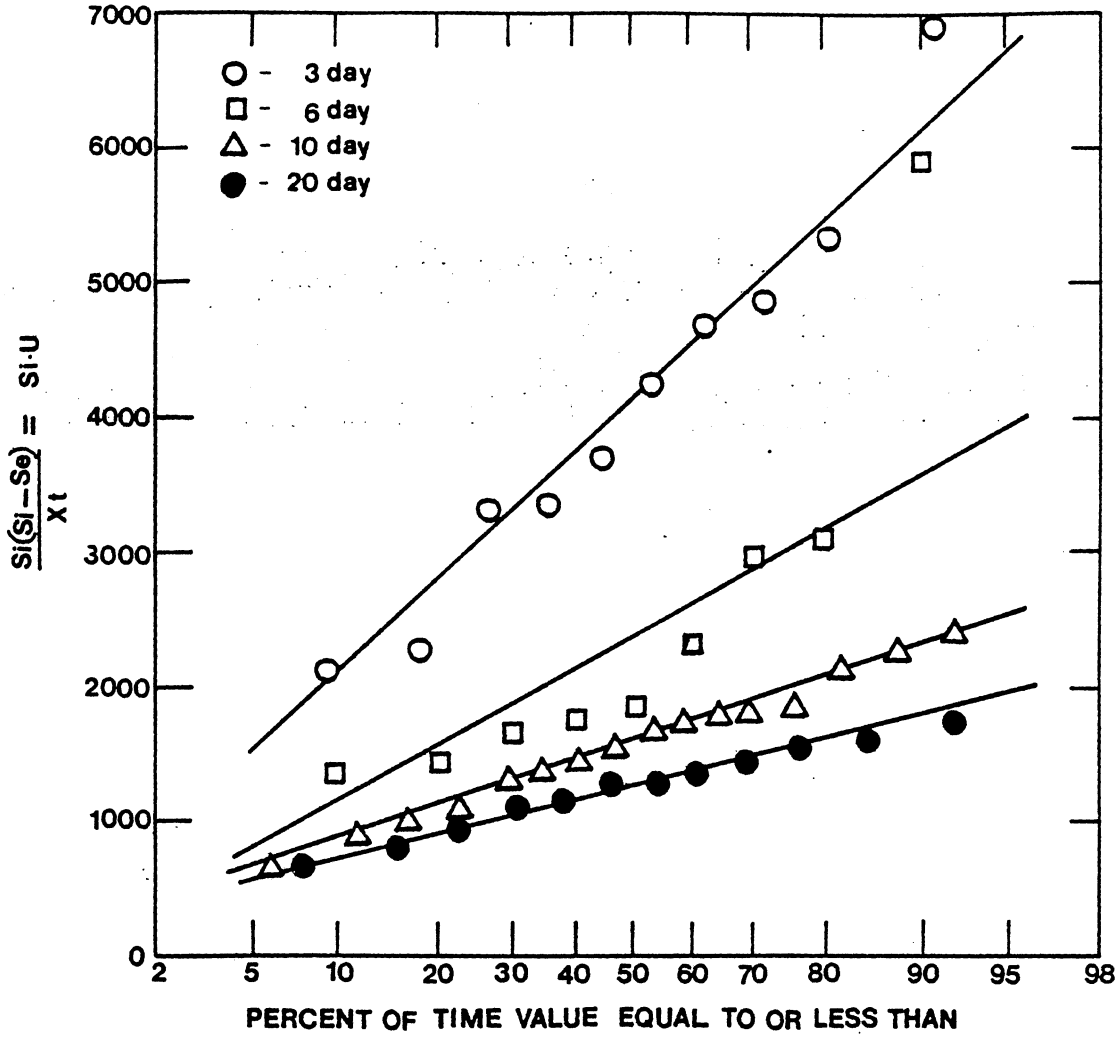


Figure 15. Frequency Analysis of Si · U (BOD_5)

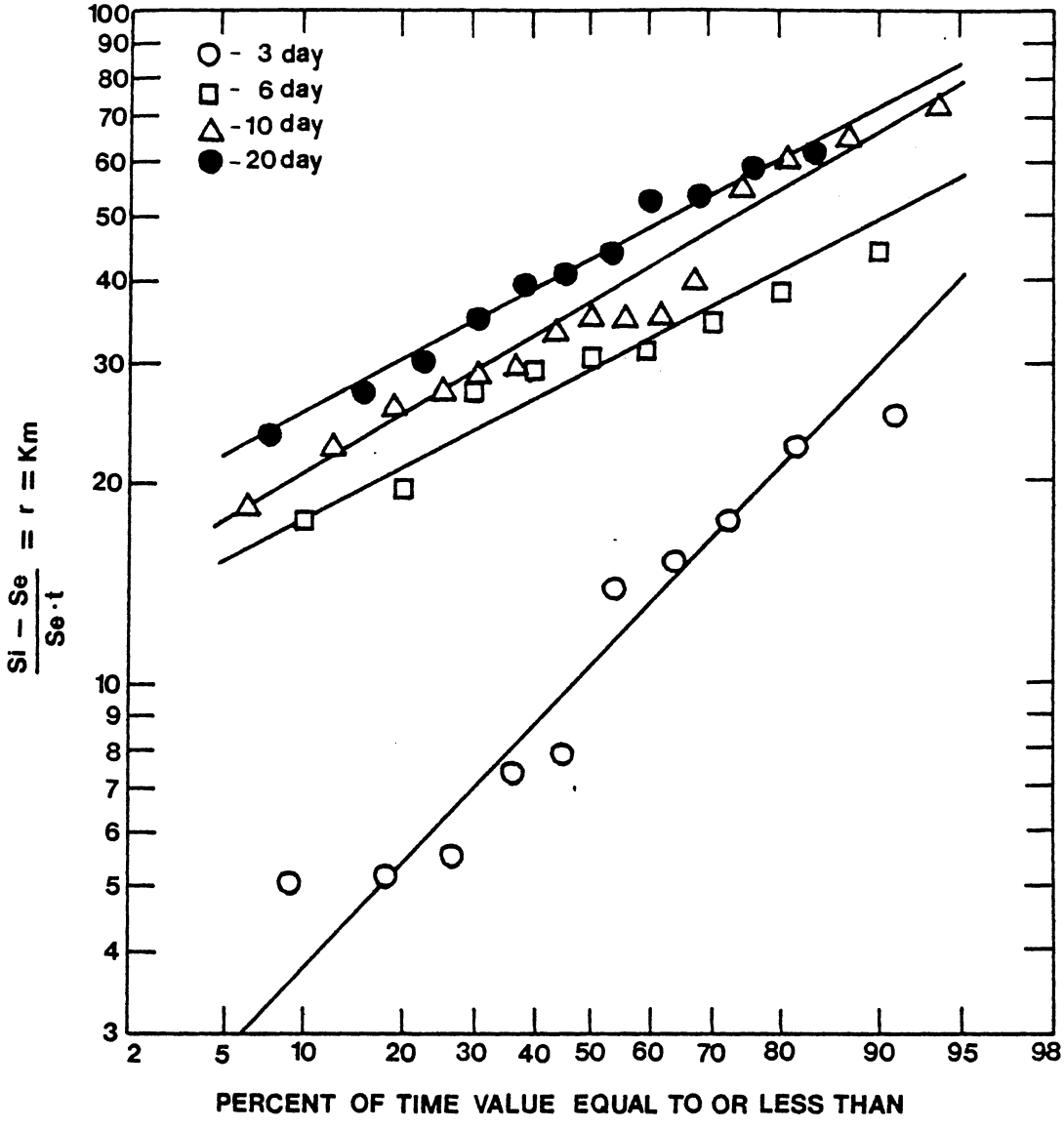


Figure 16. Frequency Analysis of r and K_m (BOD_5)

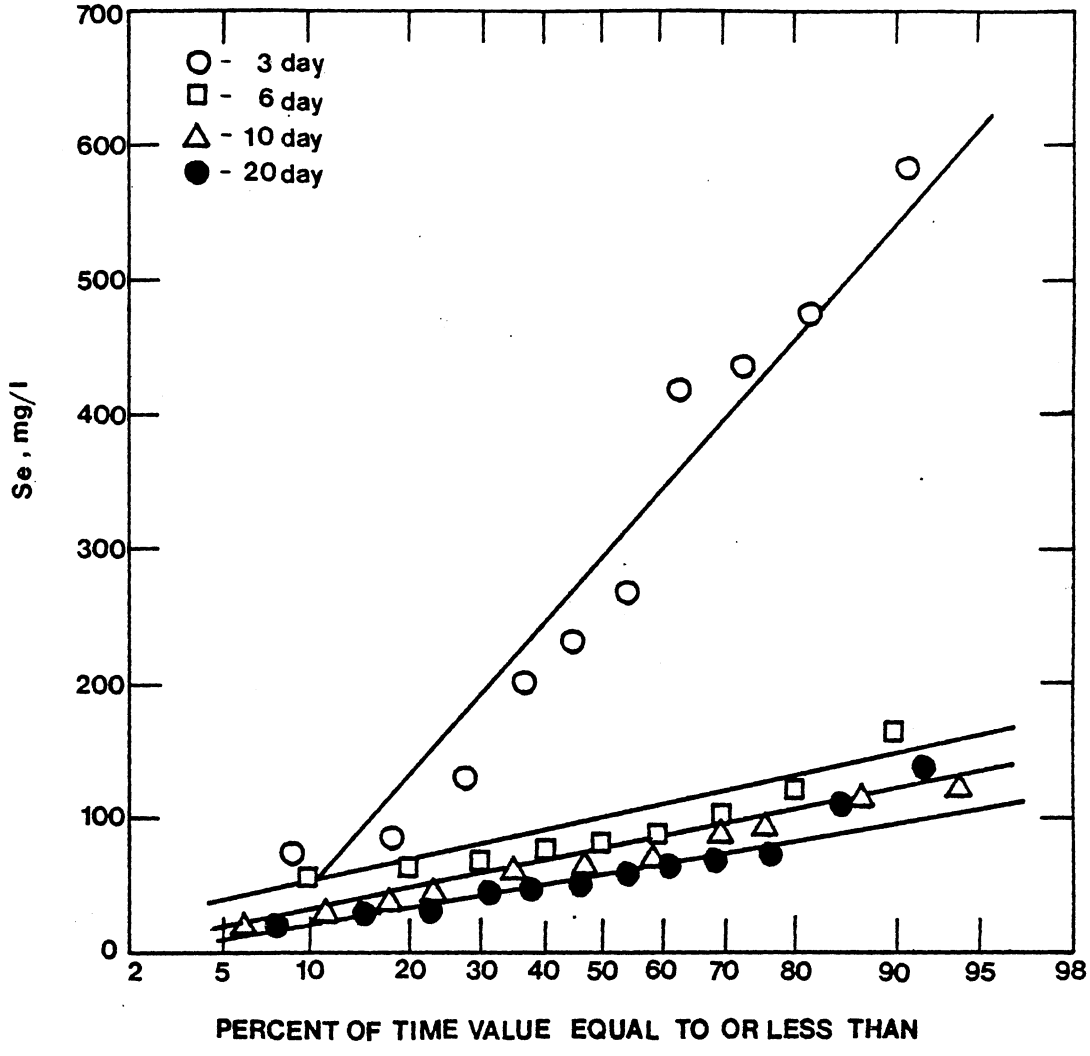


Figure 17. Frequency Analysis of S_e (BOD_5).

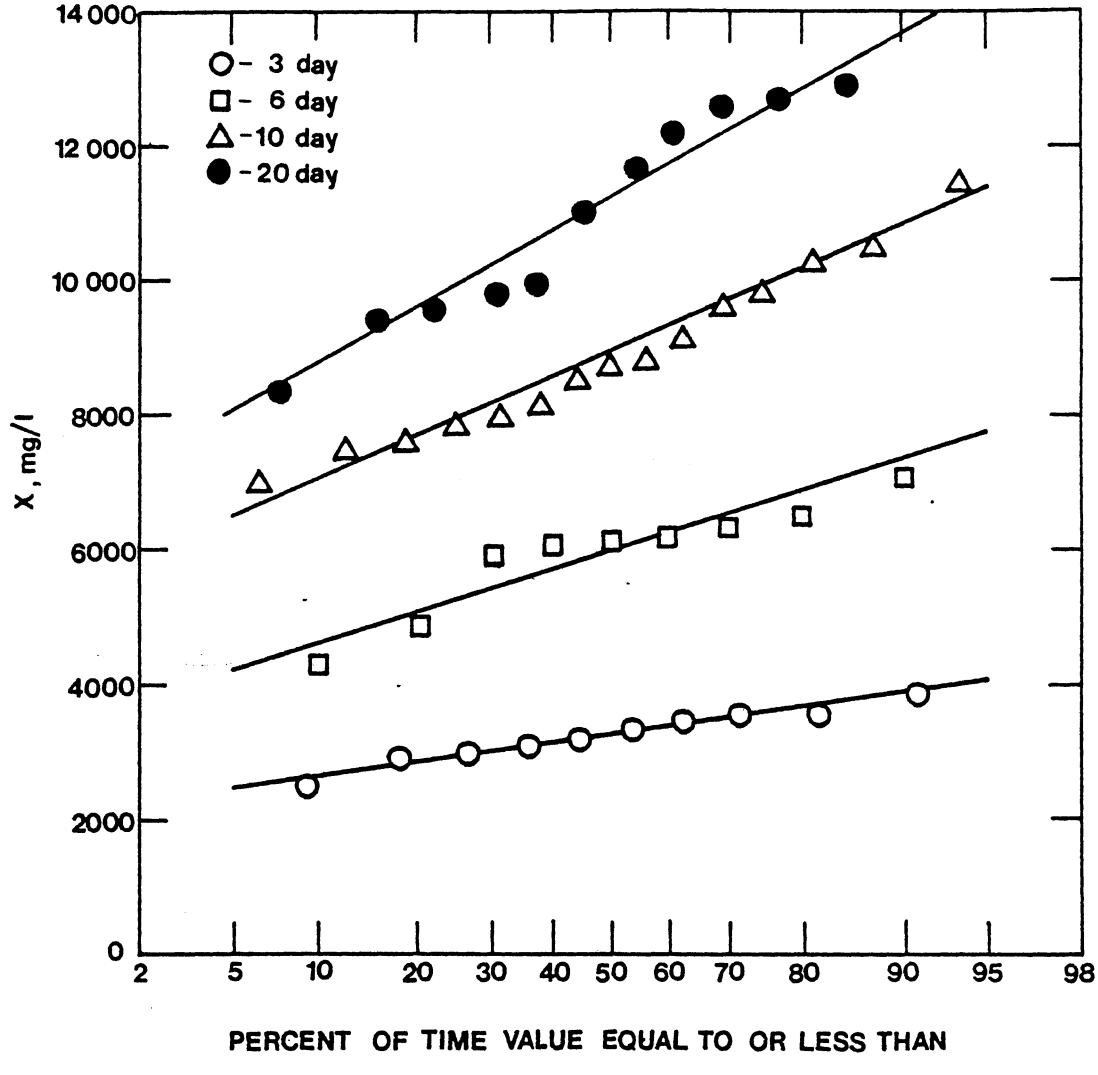


Figure 18. Frequency Analysis of X.

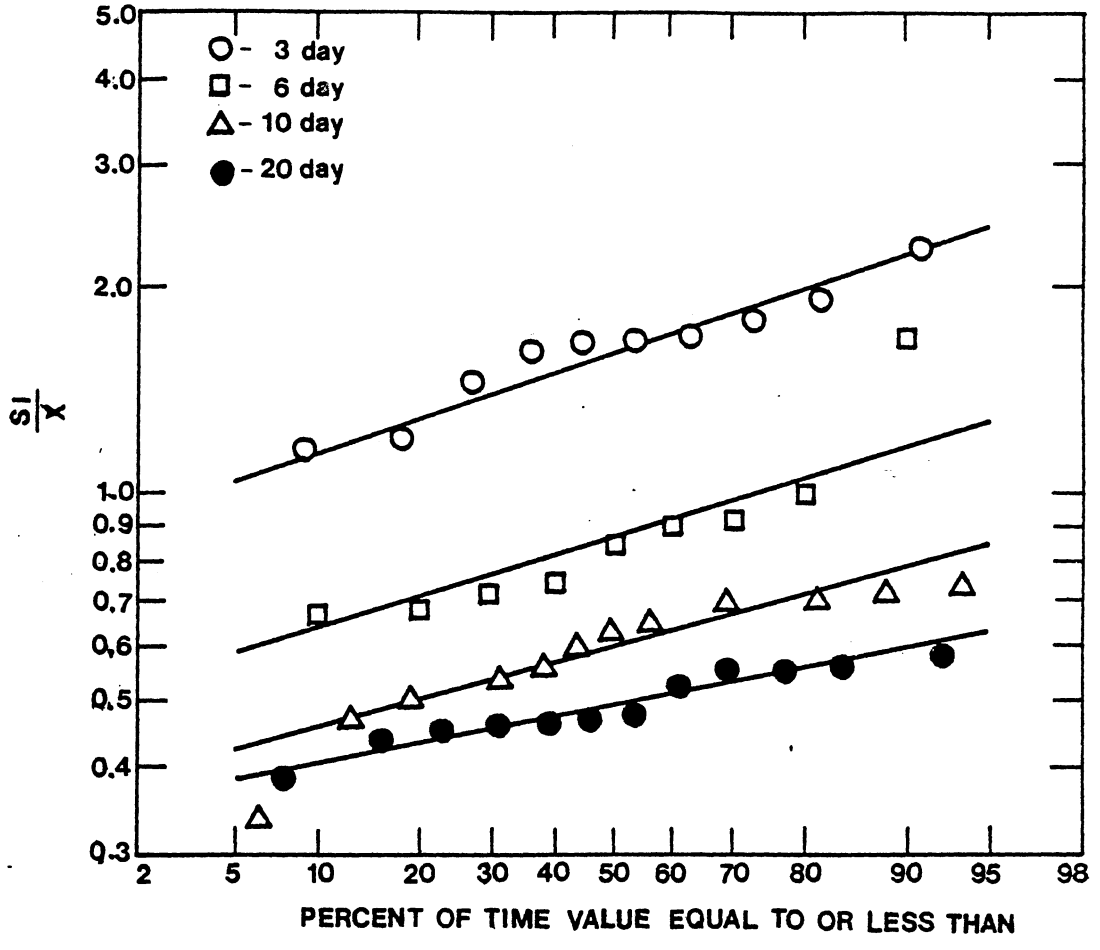


Figure 19. Frequency Analysis of S_i/X (BOD_5).

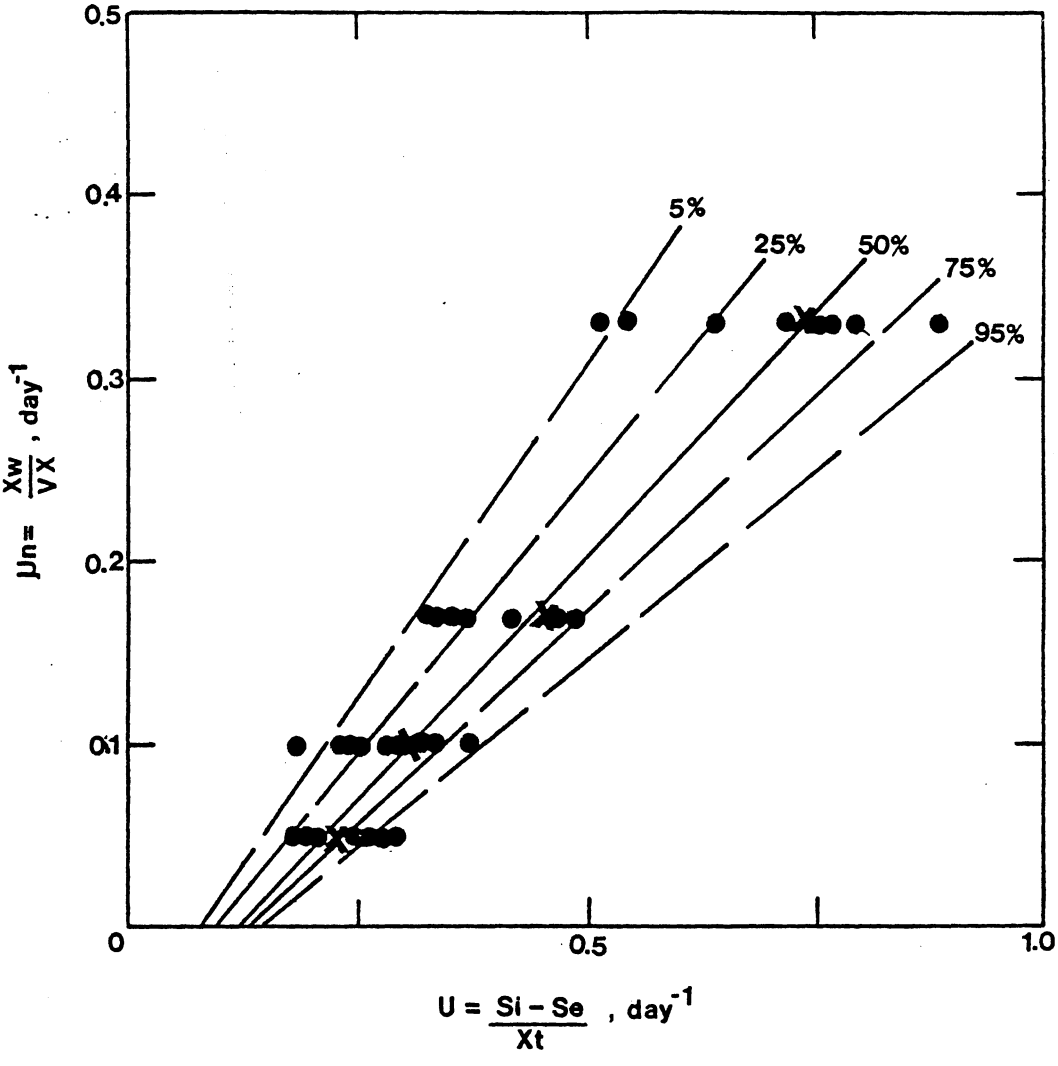


Figure 20. Graphical Determination of Y_t and K_d (BOD_5) for all Design Models.

the biological population dynamics throughout the study period, while all the lines converge to the same Y-axis intercept indicating that K_d remains constant. This is due to the fact that as μ_n increases or θ_c decreases the specific substrate utilization rate becomes more variable. As the μ_n is decreased the system becomes more stable with less variability in U. This observation points out that K_d can be treated as a true biokinetic constant, but Y_t varies with the population dynamics and should really be treated as a biokinetic coefficient rather than a biokinetic constant.

In Figure 21, U is plotted as a function of S_e for determination of Eckenfelder's constant, K_e, which is the slope of the line. As previously noted both U and S_e vary at the same μ_n or θ_c, and the lines in Figure 21 require variability analysis of both parameters from the probably plots of Figures 14 and 17. The Eckenfelder modified constant, K_e' can be determined by multiplying K_e by S_i or by plotting $S_i \cdot U$ versus S_e and determining the slope. The probability plots of Figures 15 and 17 could then be used to determine the desired probability levels of K_e' as shown in Figure 22. Due to this variability in both U and S_e, both K_e and K_e' vary and should really be treated as biokinetic coefficients rather than biokinetic constants.

In Figure 23, $K_m = \frac{(S_i - S_e)}{S_e\ t}$ is plotted as a function of X for determination of McKinney's constant, K_m, which is equal to the slope of the line multiplied by X. As previously indicated by the substrate utilization rate terms of Eckenfelder and McKinney, $K_m = K_e \cdot X$. Both K_m and X vary at the same μ_n or θ_c and the lines in Figure 23 require variability analysis of both these parameters from the probability plots of Figures 16 and 18. Due to the variability in both K_m and X,

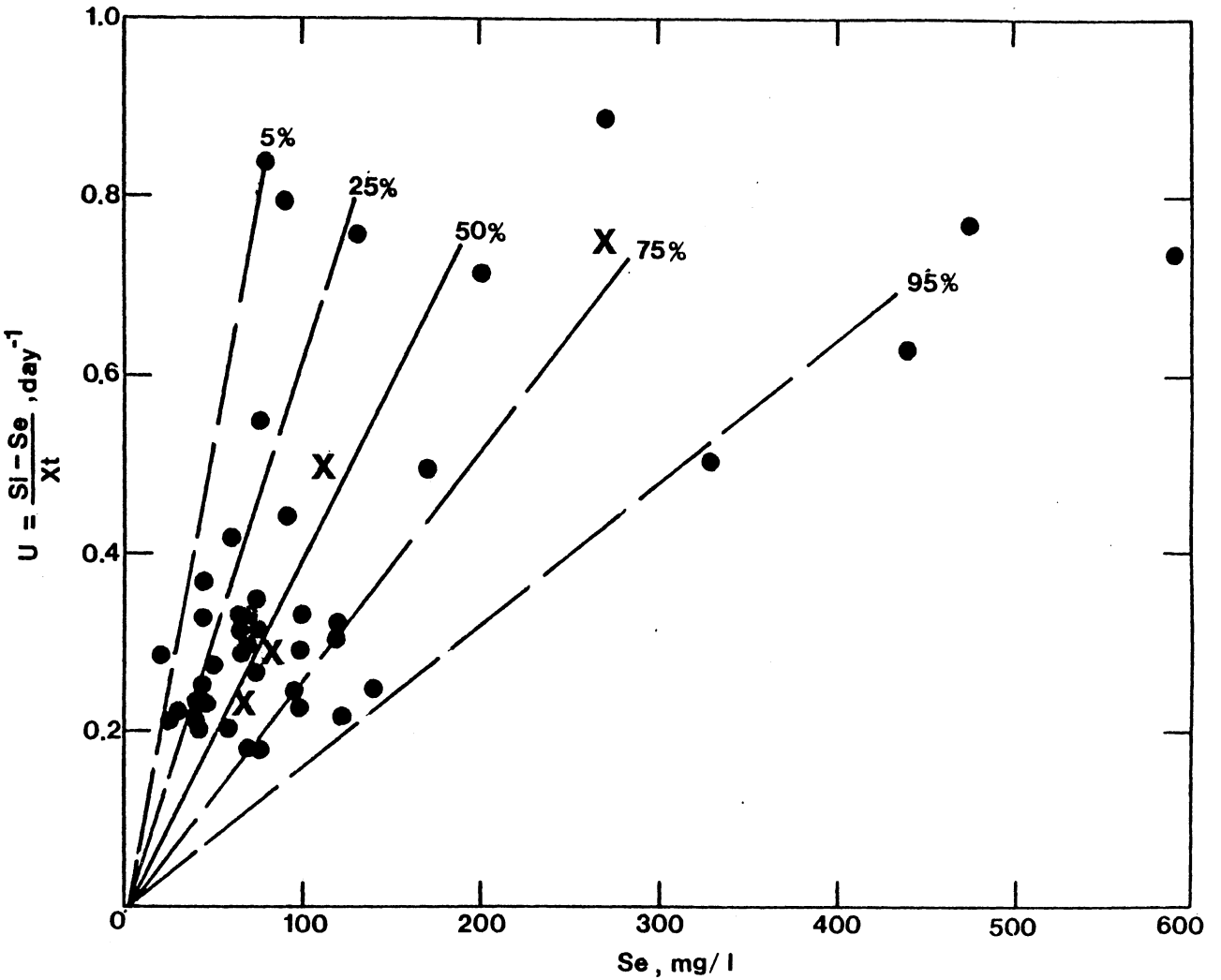


Figure 21. Graphical Determination of K_e (BOD_5) for Eckenfelder's First Order Design Model.

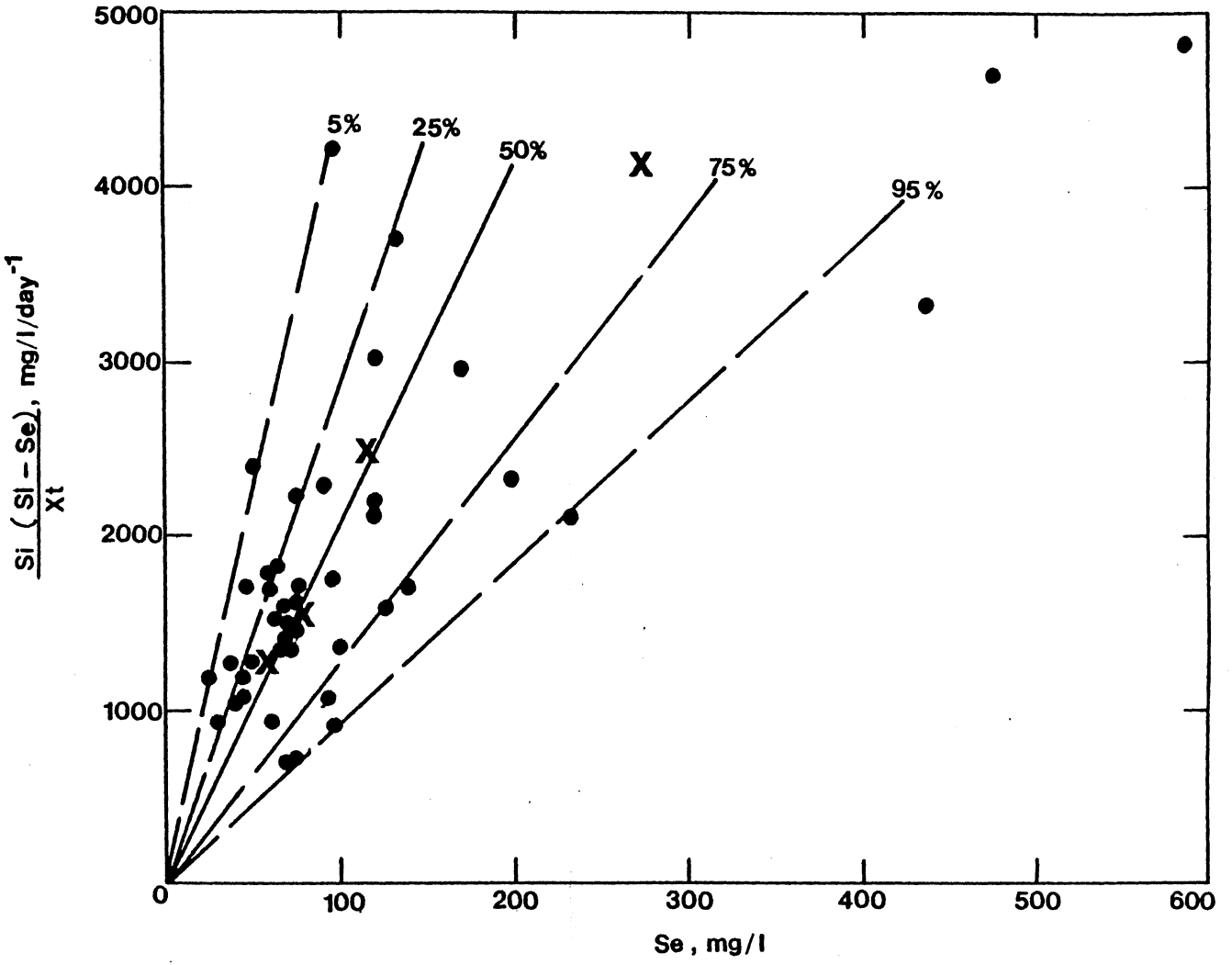


Figure 22. Graphical Determination of K_e' (BOD_5) for Eckenfelder's Modified Design Model .

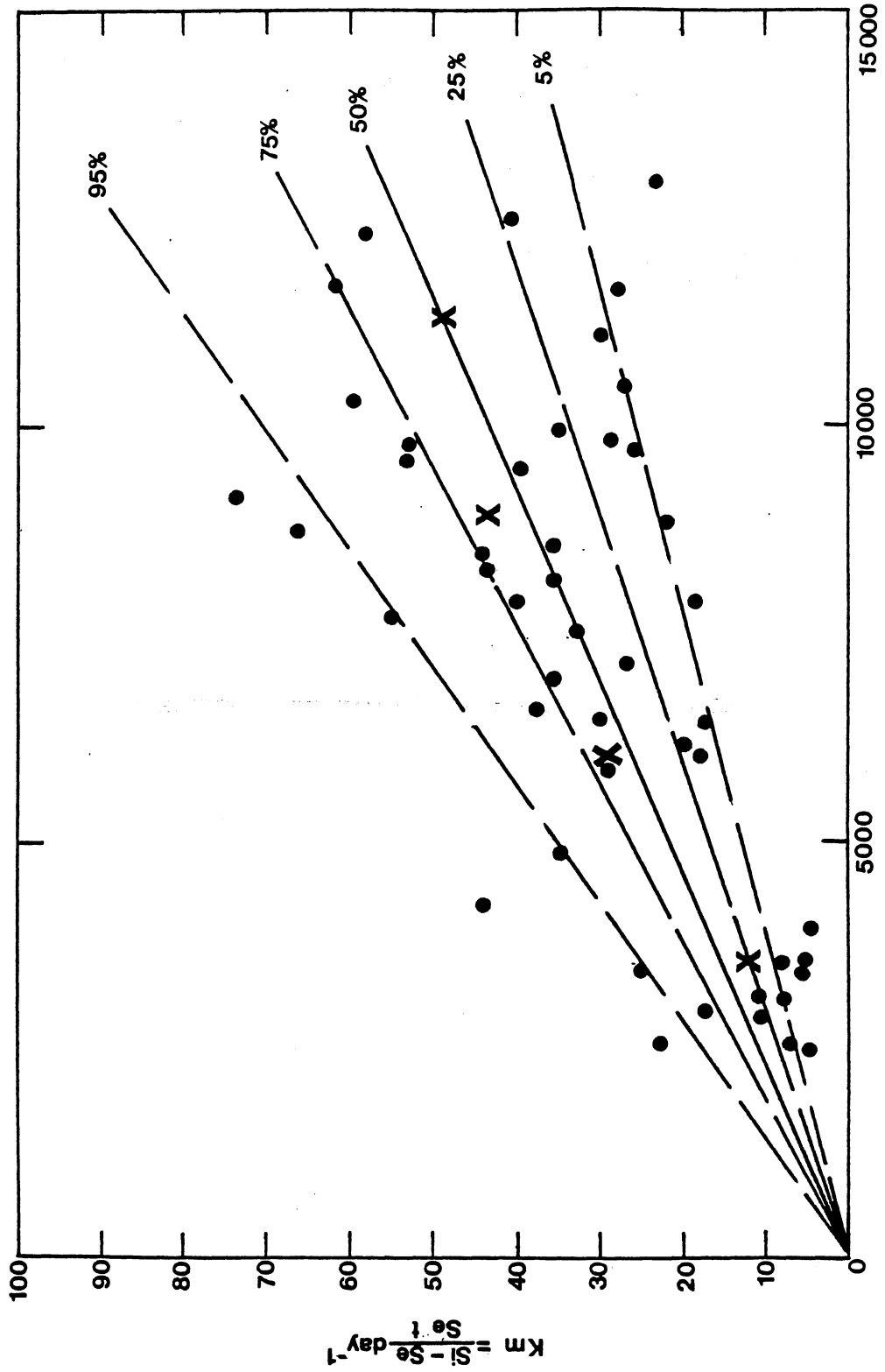


Figure 23. Graphical Determination of K_m (BOD_5) for McKinney Design Model.

$K_m = K_e \cdot X$ should really be treated as a biokinetic coefficient rather than a biokinetic constant.

In Figure 24 the log of Weston's substrate reaction coefficient, r, is plotted as a function of the log of the BOD_5 to biological solids loading ratio, S_i/X, for determination of Weston's substrate utilization rate constant, R_s, and the inhibition descriptive constant, $K_i \cdot R_s$ is the intercept at $S_i/X = 1.0$, and K_i is the negative slope of the line. Both r and S_i/X vary at the same μ_n or θ_c and the lines in Figure 24 require variability analysis of these parameters from the probability plots of Figures 16 and 19. Due to the variability in r and S_i/X, R_s should be treated as a biokinetic coefficient, and K_i should also be treated as a biokinetic coefficient since it is dependent on inhibition or toxicity to biological activity.

In Figure 25 the reciprocal of the specific growth rate (μ) is plotted against the reciprocal of the effluent substrate concentration (S_e) for determination of the maximum specific growth rate (μ_{max}) and the saturation constant (K_s) as used in the Gaudy design model. The Y-axis intercept is the reciprocal of μ_{max} and the slope is equal to K_s/μ_{max}. Since μ_n was controlled to be constant and K_d was found to be a true biokinetic constant μ ($\mu = \mu_n + K_d$) is constant and the variability observed in Figure 25 is due to the variability in the effluent subtrate concentration.

The S_e probability level desired is determined from Figure 17 for the appropriate specific growth rates and plotted on Figure 25 to determine the desired probability levels of μ_{max} and K_s. As observed in Figure 14 for U, the variability in S_e decreases as μ decreases due to the increased stability of the system at lower growth rates. Thus, the

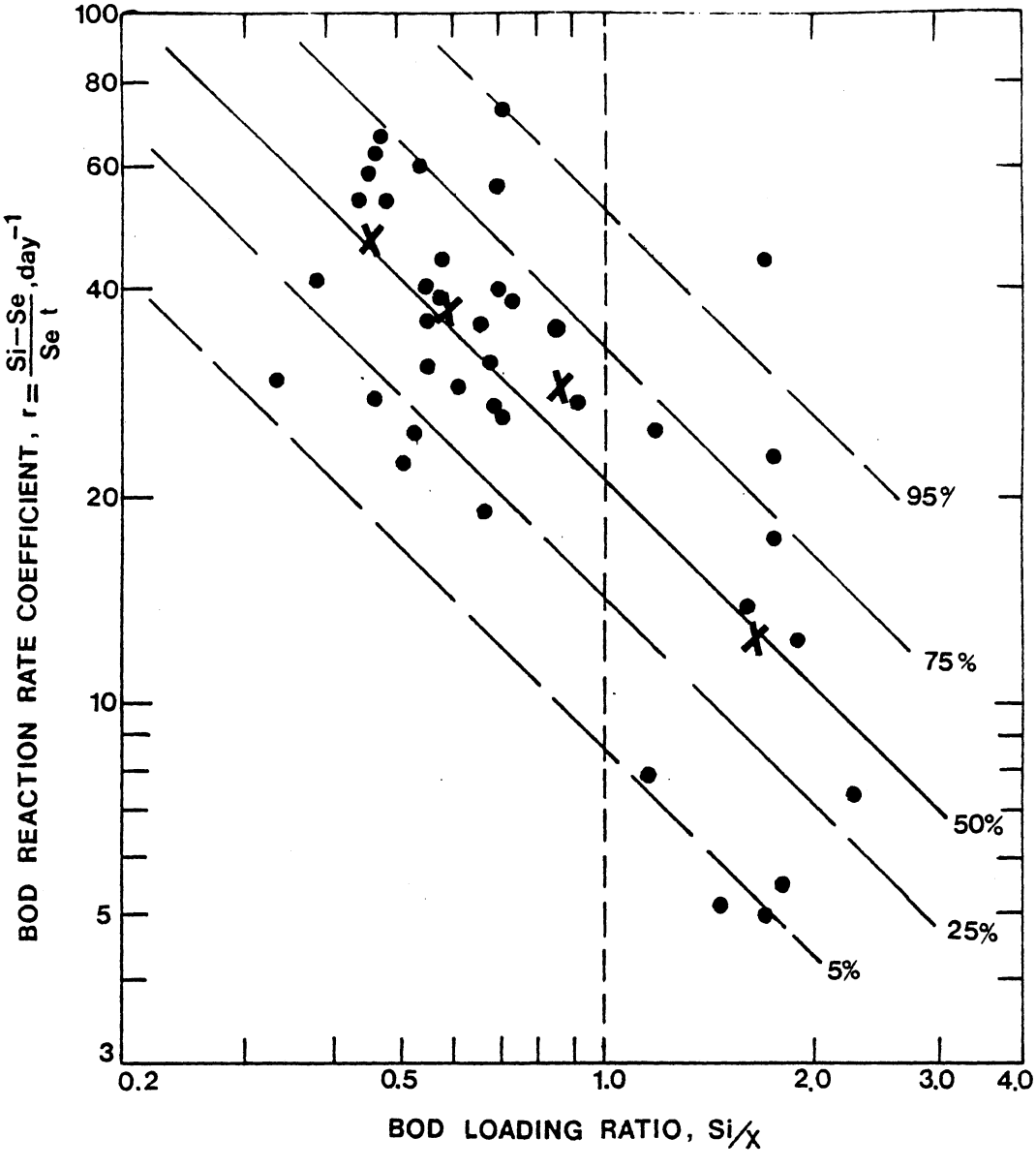


Figure 24. Graphical Determination of R_s (BOD_5) and K_i for Weston's Design Model.

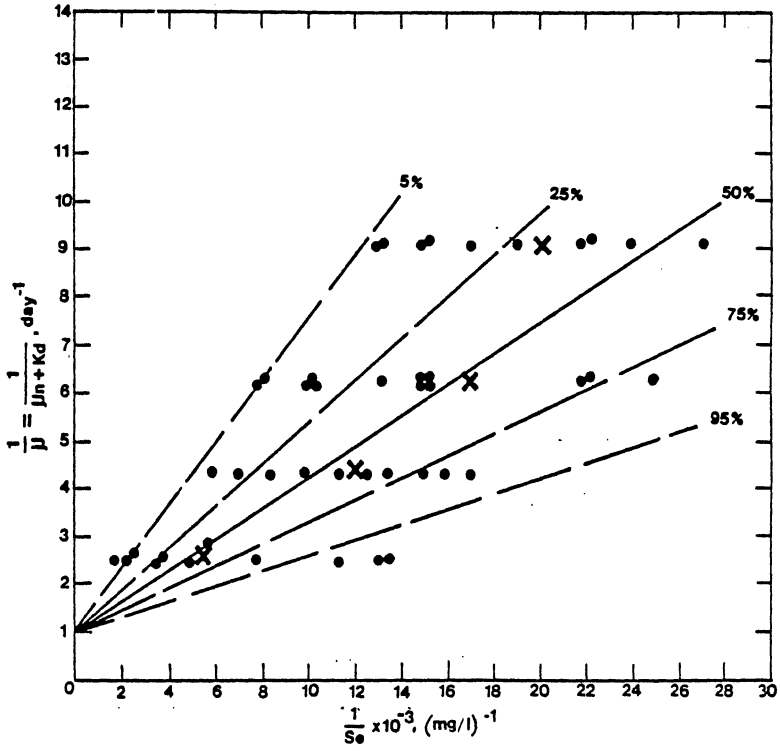


Figure 25. Graphical Determination of μ_{max} and K_s (BOD_5) for Gaudy Design Model.

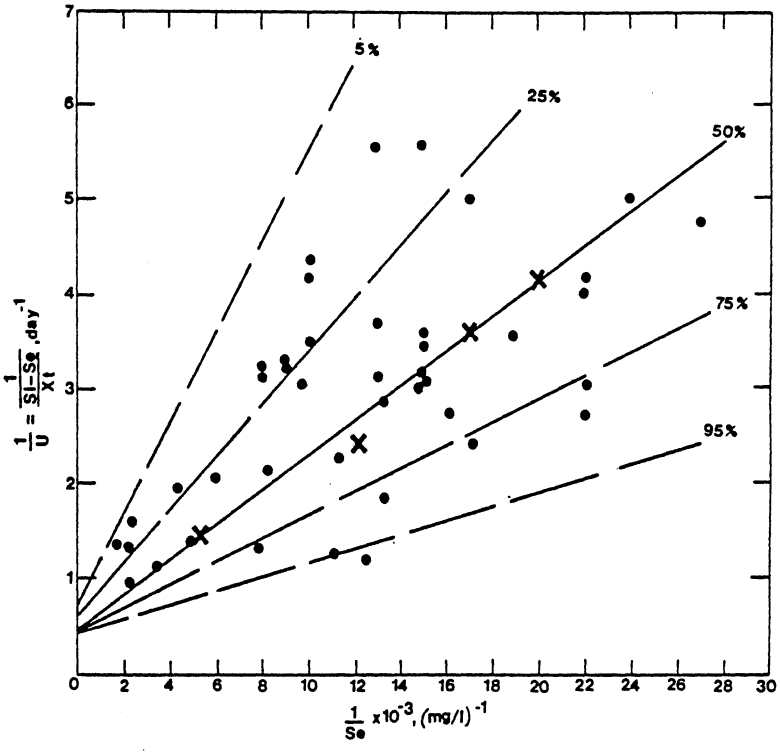


Figure 26. Graphical Determination of K and K_s (BOD_5) for Lawrence and MCarty Design Model.

different probability lines of all converge to the same intercept indicating that μ_{max} can realistically be treated as a true biokinetic constant, while K_s varies with the population dynamics and should really be treated as a biokinetic coefficient rather than a biokinetic constant.

The maximum specific subtrate utilization rate (K), as used in the Lawrence and McCarty design model, can be calculated from the relationship of $\mu_{max} = K \cdot Y_t$ or by making a plot of the reciprocal of the specific substrate utilization rate (U) versus the reciprocal of S_e. In this plot the reciprocal of the Y-axis intercept is equal to K and the slope is equal to K_s/K. A plot of this type is shown for the alcohol wastewater in Figure 26. As pointed out earlier, both U and S_e vary at the same μ_n or θ_c. Therefore, the probability lines in Figure 26 require variability analysis of both parameters from the probability plots of Figures 14 and 17.

Since the variability in both U and S_e decreases with decreasing growth rates, the different probability lines all converge toward the same intercept or the same K value. However, since $\mu_{max} = K \cdot Y_t$ and Y_t varies as shown in Figure 9, μ_{max} and K cannot both be constants. If $_{max}$ is treated as a constant in Figure 14 and Y_t varies as shown in Figure 9, K must vary as shown in Figure 26. If K were treated as a constant and Y_t varied, then $_{max}$ would vary and the one intercept in Figure 25 would look like the intercepts in Figure 26. Therefore, based on this kinetic analysis as shown in Figure 26, both K and K_s vary with shifts in the population dynamics and should really be treated as biokinetic coefficients rather than biokinetic constants.

During this kinetic analysis of the biological treatability of fuel alcohol production wastewater the observations were made that U_{max}, K_B, K_d, and μ_{max} could be treated as true biokinetic constants, while K_e, K_e', K_m, R_s, K_i, K, and K_s should all be treated as variable biokinetic coefficients expressing substrate utilization characteristics. The biological solids yield in terms of substrate removed, Y_t, should also be treated as a variable biokinetic coefficient. In Table VI the biokinetic constants are summarized along with the 5, 25, 50, and 75, and 95 percent probability values of the biokientic coefficients for the alcohol wastewater.

The recycle and reuse potential of both the stillage solids and the waste activated sludge (WAS) are presented in Table V. The protein and carbohydrate content of both stillage and WAS were essentially the same, indicating the mechanism of conversion of the soluble organics in this high strength wastewater to biological solids for use as cattle feed to be an important asset of biological treatment. The protein content observed in both the stillage solids and the WAS was lower than expected when compared to values previously reported in the literature. Possible explanations for this involve the efficiency of the starch preparation process and the capability of the biological solids to convert the high strength carbohydrate wastewater into cellular protein. If the starch was not broken down effectively to glucose and maltose, which are used by the yeasts, the excess carbohydrate would increase the carbohydrate percentage and decrease the protein percentage of the stillage. High strength carbohydrate wastewater, especially under nitrogen limiting conditions, has been shown to increase the carbohydrate content and decrease the protein content of the biological solids produced during activated sludge treatment (75).

TABLE VI

SUMMARY OF BIOKINETIC CONSTANTS AND COEFFICIENTS

Biokinetic Constant or Coefficient	Percent Probability				
	5	15	50	75	95
Y_t	0.74	0.63	0.53	0.48	0.41
K_d	0.06	0.06	0.06	0.06	0.06
K_e	0.0107	0.0060	0.0040	0.0026	0.0016
K_e'	48.0	30.0	20.7	13.0	9.0
K_m	0.0070X	0.0052X	0.0042X	0.0034X	0.0026X
R_s	8.7	14.0	21.0	32.5	51.0
K_i	1.0	1.0	1.0	1.0	1.0
μ_{max}	1.0	1.0	1.0	1.0	1.0
K	1.4	1.6	2.0	2.1	2.4
K_s	650	440	360	240	165
U_{max}	16.7	16.7	16.7	16.7	16.7
K_B	16.7	16.7	16.7	16.7	16.7

Waste sludge dewatering screening studies were also conducted by the Capillary Sution Time (CST) test procedure. The average test results of the CST screening are presented in Table V. These tests were conducted without conditioning agents and represent the relative dewatering characteristics of the waste sludge. The non-conditioned CST's of the sludges at the 6, 10, and 20 day sludge age operating conditions indicate a relatively easy to dewater sludge.

4.3.2 Start-Up and Operational Problems

Initially, the two reactors wre started at SRTS of 20 days and 10 days. Operating at such high SRTS and MLSS level is quite common with such high-strength organic wastes, because higher SRTS provide a lower loading of F/M ratio which would allow the system to withstand shock loads. Secondly, the amount of sludge to be wasted to the digester would be minimal.

To start with, the COD of the influent was only 1,000 mg/L and slowly stepped up to the neighborhood of 10,000 mg/L. But when the concentration was inceased more than 10,000 mg/L, operational problems were encountered. The effluent was turbid; the system started foaming; the DO uptake rate diminished. As it was surmised that because of the physcial limitations of the bench scale reactors such problems occured, it was decided to contain the COD concentration at about 10,000 mg/L.

Nutrients were added initially according to the BOD:N:P = 100:5:1 ratio that has been used to provide adquate nutrients for biological teatment. But as the SRTS were decreased to six days and three days, the systems started exhibiting similar problems addressed earlier. This should be so because at low SRTS, the growth rate of the cells is high,

and hence a high demand for nutrients. However, the BOD:N:P ratio was still maintained at the same level, which started deteriorating the performance of the systems. During such nutrient-deficient conditions in the reactors, bacterial cell replication was retarded and the bacteria capable of producing extracellular polysaccharide began producing profuse amounts of polysaccharide slime. This agreed very much with the finidngs of Stover (75), Wu (76) and Sittig et. al., (42). The formation of non-capsular inducible enzymes of bacteria required adequate nitrogen source and an acclimation period. Therefore BOD:N:P ratio was stepped up to approximately 100:10:2 and eventually, after a lag period of 15 days, the systems started operating normal.

Another problem observed during this study was raising sludge, which is normally common with extended aeration systems. The 20 day SRT reactor exhibited such problems. After the system began nitrifying the ammonia nitrogen, there were periods of time when the nitrogen addition was too high and the nitrate-nitrogen was denitrified under anaerobic conditions in the clarifier and floated sludge to the surface. This sludge floating to the surface caused increase in the effluent suspended solids, as observed in Table V. However, as observed in Table IV, the effluent soluble COD, BOD and TOC were all as low as usual even during the periods of increased effluent suspended solids.

During the entire period of aerobic studies, the feed pH had to be raised to the range of 9.0 to 10.0 whether the candidate was corn or milo. This would be equal to an addition of $CaCO_3$ alkalinity of 3000 mg/L and 4000 mg/L respectively. The observations with anaerobic reactors were totally different, which would be discussed later.

4.4 Anaerobic Suspended Growth Studies

Increasingly stringent environmental regulations coupled with rapidly rising energy costs make anaerobic treatment the most preferred process for the treatment of the high strength wastewaters produced by an alcohol plant. Anaerobic treatment of ethanol production wastewaters has proved to be by far the best treatment alternative. The foremost basic reasons are:

The high dissolved BOD (about 20,000 mg/L) of stillage, which exceeds economically attainable rates of O_2 transfer generally precludes aerobic treatment; no energy intensive mixing required.

The anaerobic fermentation process is characterized by low biomass yields, the intramolecular breakdown of complex organic compounds and the production of methane gas, a supplementary fuel.

The dewatering characteristics of the anaerobic sludge are much better than aerobic sludge and a lesser mass of waste solids is produced per unit volume of wastewater treated in the anaerobic process than in the aerobic treatment.

4.4.1 Anaerobic Suspended Growth System Performance

The operating characteristics of the continuous flow anaerobic system studies are presented in Table VII. In this table the influent feed, treated effluent, mixed liquor, waste sludge, and gas purity in terms of percent carbon dioxide are presented. All the systems except the 30 day SRT systems were operated at around one-third of the full strength stillage substrate concentrations. The 2-day and 4-day SRT

TABLE VII

AVERAGE CONTINUOUS FLOW ANAEROBIC SYSTEM
OPERATING CHARACTERISTICS

Mixed Liquor

SRT (days)	HRT (days)	MLSS mg/L	MLVSS mg/L	pH	Temp. °C	Protein %	Carbohydrate %
2	2	675	600	5.8-6.6	33-34	-	-
4	4	650	590	6.7-7.0	33-36	9.0	20.0
6	5.3	730	600	6.6-7.0	32-33	7.0	19.0
10	5.3	1670	1360	6.9-7.5	33-34	12.0	22.0
20	5.3	2300	1920	7.0-7.3	30-33	6.5	11.5
30(a)	5.0	8790	5785	7.2-7.6	34-36	9.0	9.4
30(b)	5.0	11740	8564	7.2-7.5	35-38	9.2	11.8

Influent (Feed)

SRT (days)	Flow (L/day)	SS mg/L	VSS Mg/L	$CaCO_3$ Alk. added (mg/L)	pH
2	5.60	100-200	100-200	3000	10-12
4	2.88	75-150	75-150	3000	10-12
6	1.44	100-200	100-200	3000	9-12
10	1.44	150-200	150-200	1500-2500	8-10
20	1.44	150-200	150-200	750-1500	7-8
30(a)	1.44	200-250	200-250	300	5-6
30(b)	1.44	300-400	300-400	200	3-5

TABLE VII (Continued)

Waste Sludge

SRT (days)	SS (mg/L)	VSS (mg/L)	SVI	ZSV (ft/hr)	CST (sec)	Gas % CO_2
2	-	-	-	-	-	-
4	-	-	-	-	-	5.0
6	3230	2730	370	4.1	19.5	10.0
10	6130	4600	67	4.5	9.0	15.1
20	18920	14640	25	0.7	9.0	19.1
30(a)	23650	17060	16	2.5	18.0	20.0
30(b)	30360	21870	17	0.3	16.5	23.5

Effluent

SRT (days)	SS (mg/L)	VSS (mg/L)	$CaCO_3$ Alk (mg/L)	Vol Acid (mg/L)	Soluble Protein (mg/L)	Soluble Carbohydrate (mg/L)
2	675	600	3500	1000	80	600
4	650	590	4400	2500	-	-
6	340	250	3220	0	165	825
10	320	240	3560	0	55	220
20	240	170	4800	0	76	40
30(a)	470	370	4950	0	71	100
30(b)	350	230	4880	0	85	108

SVI - Sludge Volume Index

ZSV - Zone Settling Velocity

CST - Capillary Suction Time

systems were operated as once-through systems, while all other systems were operated as sludge recycle systems. The treatment performance of these systems was much greater than expected, and therefore the higher strength wastewater studies were conducted. The two 30-day SRT systems were operated at two-thirds of full strength and full strength substrate concentrations.

All systems were operated to control the mixed liquor pH around 7.0 and the temperature at around 33°C to 36°C. Both pH and temperature control were easier to maintain as the SRT and the strength of the wastewater were increased. As noted in Table VII under the influent feed characteristics, the C_aCO_3 alkalinity addition requirements and pH control requirements decreased significantly with increasing SRT and wastewater strength. At the 30-day SRT and full strength wastewater feed of pH 3.0 to 5.0, the mixed liquor pH was very readily maintained at pH 7.2 to 7.5 with an average of only 200 mg/L C_aCO_3 alkalinity added.

The waste sludge settling, thickening, and dewatering characteristics were excellent throughout the entire study period that these systems were operated. The mixed liquor solids were very readily settled and thickened with concentrations of 2.0 to 3.0 percent very readily obtainable. These systems were operated for one year without any problems of sludge bulking or thickening as often occurs in aerobic activated sludge systems operating with high strength carbohydrate wastewater of this type. There were minor problems of floating sludge in the clarifiers due to gas production as observed in the high total effluent suspended solids concentrations of around 300 to 500 mg/L. The portion of the effluent suspended solids due to gas flotation were

readily settled in the effluent and were measured to account for about 20 to 40 percent of the total effluent suspended solids.

The protein and carbohydrate content of both the mixed liquor and effluent increased with decreasing SRT. As would be expected, both the protein and carbohydrate fraction of the biological solids increased as the growth rate inceased. The increase in protein and carbohydrate in the effluent corresponded with increases in BOD_5, COD and TOC. There was no volatile acid accumulation in any system until the SRT was decreased below 6 days. Both the gas production rate and the carbon dioxide fraction in the gas increased as the SRT increased.

The average F/M ratio in terms of MLVSS, influent substrate concentration, effluent substrate concentration, and treatment efficiency at each SRT are summarized in Table VIII. As observed in Table VIII 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 prcent were easily obtainable even with the full strength stillage at the SRT of 30 days. Greater than 97 percent BOD_5 removal was achieved at the F/M ($sBOD_5$/VSS) ratio of 0.85. Below the limiting SRT of 4.0-days, the volatile acids accumulated and the treatment efficiency dropped off dramatically. At the SRT of 2.0-days, the treatment efficiency was negligible with removal efficiencies around 10.0 percent.

4.4.2 Kinetic Analysis of Substrate Removal

In Figure 27 the net specific growth rate or net specific sludge production (μ_n) is plotted as a function of the specific substrate utilization rate in terms of BOD_5, COD, TOC for the continuous anaerobic

TABLE VIII

SUMMARY OF CONTINUOUS ANAEROBIC SYSTEM TREATMENT PERFORMANCE

SRT (days)	F/M	Influent (mg/L)	Effuent (mg/L)	Removal %
		SOLUBLE BOD_5		
2	2.44	3045	2840	6.7
4	1.50	2315	650	71.9
6	1.70	5400	1520	71.8
10	0.85	6120	180	97.1
20	0.52	5250	53	99.0
30(a)	0.32	9200	152	98.3
30(b)	0.37	16000	133	99.2
		Soluble COD		
2	5.21	6500	5900	9.2
4	2.25	5200	1200	76.9
6	2.82	8960	2470	72.4
10	1.29	9300	850	90.9
20	1.20	12250	460	96.2
30(a)	0.58	16790	1190	92.9
30(b)	0.67	28620	560	98.0
		Soluble TOC		
2	1.96	2450	2130	13.1
4	0.88	2070	835	59.6
6	0.83	2650	1290	51.3
10	0.51	3650	630	82.7
20	0.38	3820	320	91.6
30(a)	0.27	7800	230	97.1
30(b)	0.29	12280	430	96.5

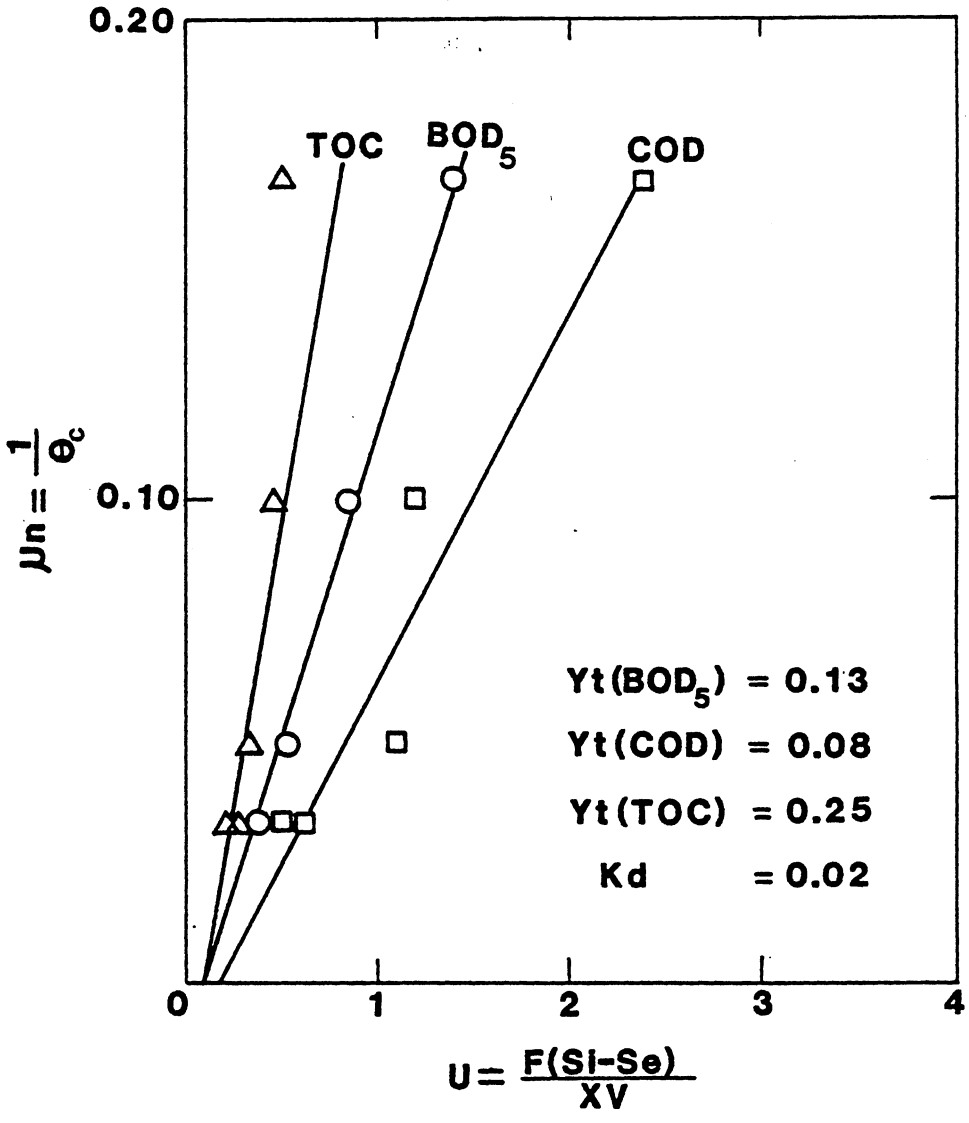


Figure 27. Graphical Determination of Yt and Kd in Terms of BOD_5, COD and TOC.

systems. This kinetic plot allows determination of the true cell yield (Y_t) and the endogenous decay coefficient (K_d) that are required for determination of the net sludge production. Y_t is the slope of the line, and K_d is the Y-axis intercept. The data points plotted in Figure 27 are the average of each SRT down to and including the 6-day SRT data. The data developed at SRT's below 6.0-days was not used due to volatile acid accumulations and lack of adequate growth of the methane forming bacteria. The true cell yields in terms of BOD_5, COD, and TOC were found to be 0.13, 0.08, and 0.25, respectively. The endogenous decay coefficient was found to be essentially independent of the specific subtrate parameter evaluated, with K_d = 0.02.

Since the methane forming bacteria became limiting at 4.0-day SRT's and less, the data developed at the 6.0-day SRT and greater were used for analysis of substrate removal kinetics. In Figures 28, 29, and 30, the specific substrate utilization rate is plotted as a function of the food-to-microorganism ratio in terms of BOD_5, COD, and TOC, respectively. These figures demonstrate the substrate removal characteristics as a function of the mass substrate loadings to the anaerobic systems following monomolecular kinetics. In Figures 31, 32, and 33, the reciprocal of U is plotted as a function of the reciprocal of F/M in terms of BOD_5, COD, and TOC, respectively, for determination of the maximum substrate utilization rate, U_{max}, and the subtrate loading at which U is one-half of U_{max}, K_B, after the Kincannon and Stover design model. Excellent correlation coefficients were observed in all three plots.

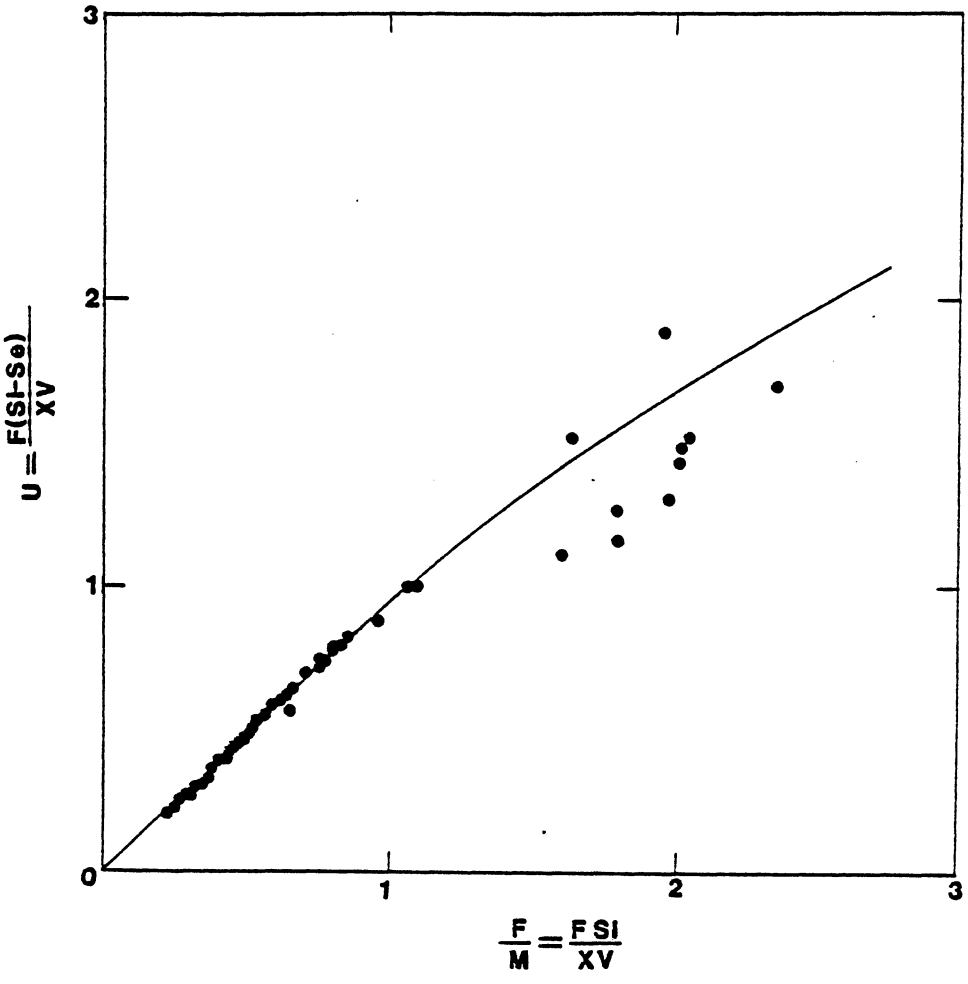


Figure 28. Substrate Utilization as a Function of Mass Substrate Loading in Terms of BOD_5.

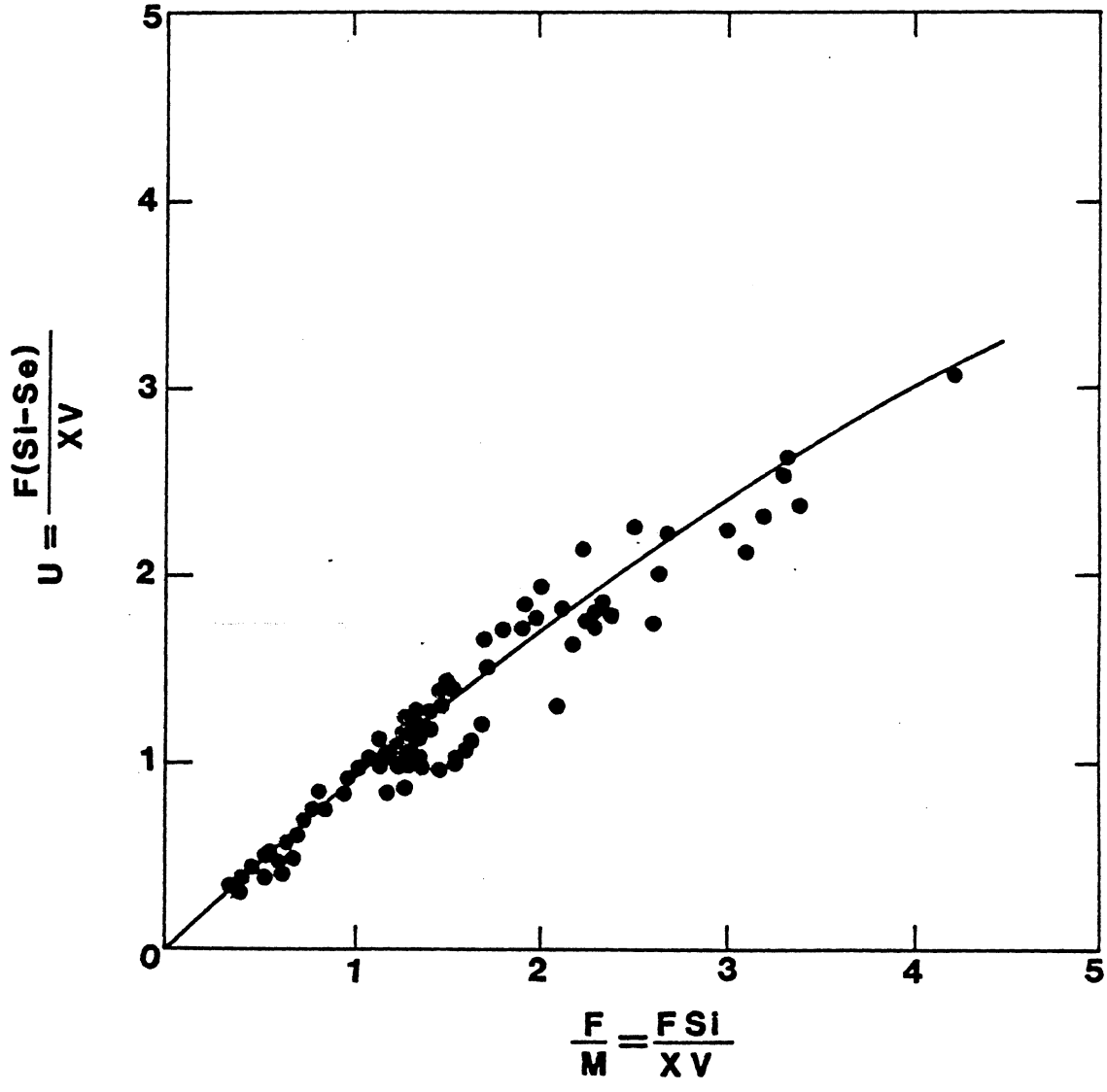


Figure 29. Substrate Utilization as a Function of Mass Substrate Loading in Terms of COD.

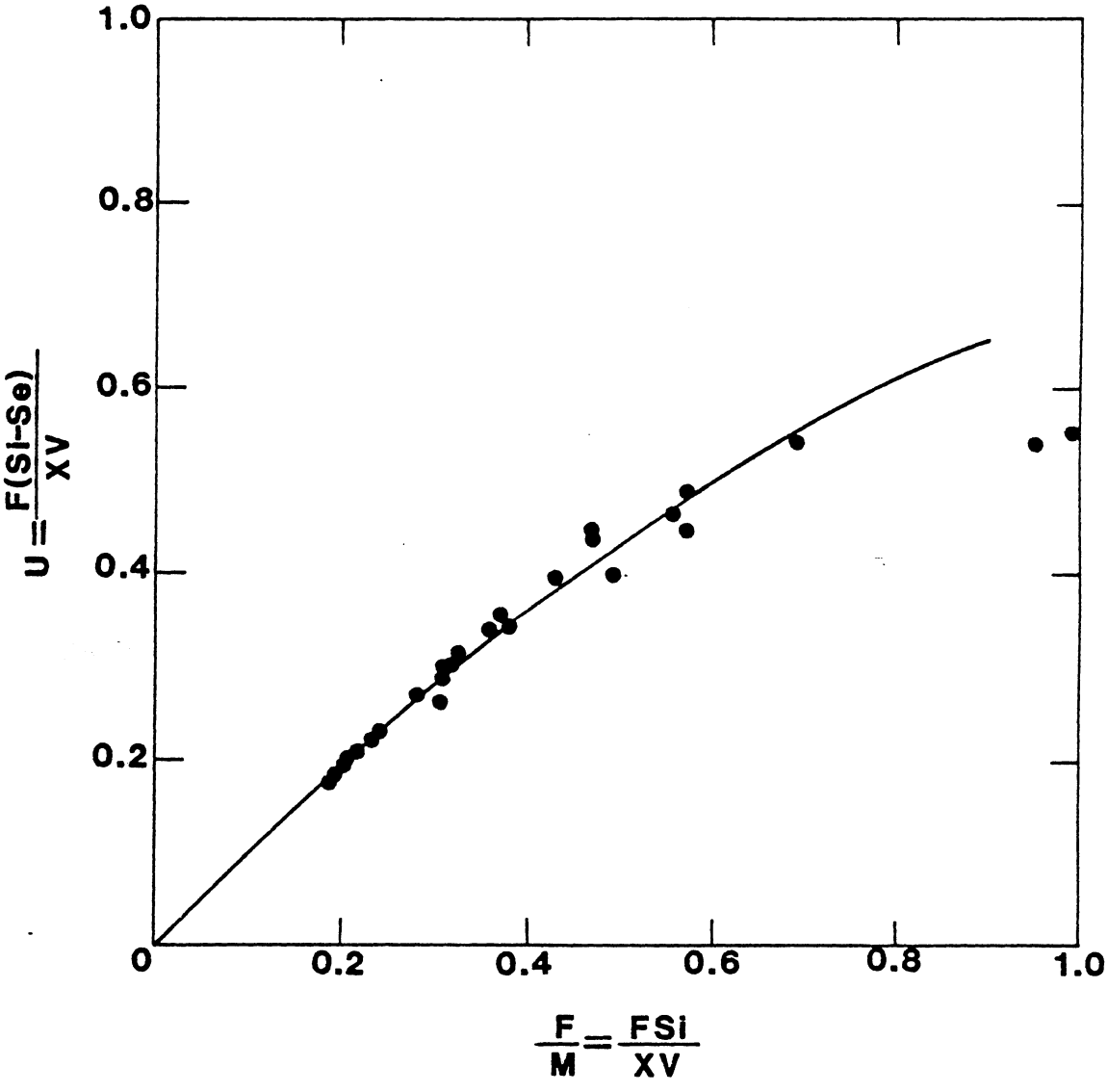


Figure 30. Substrate Utilization as a Function of Mass Substrate Loading in Terms of TOC.

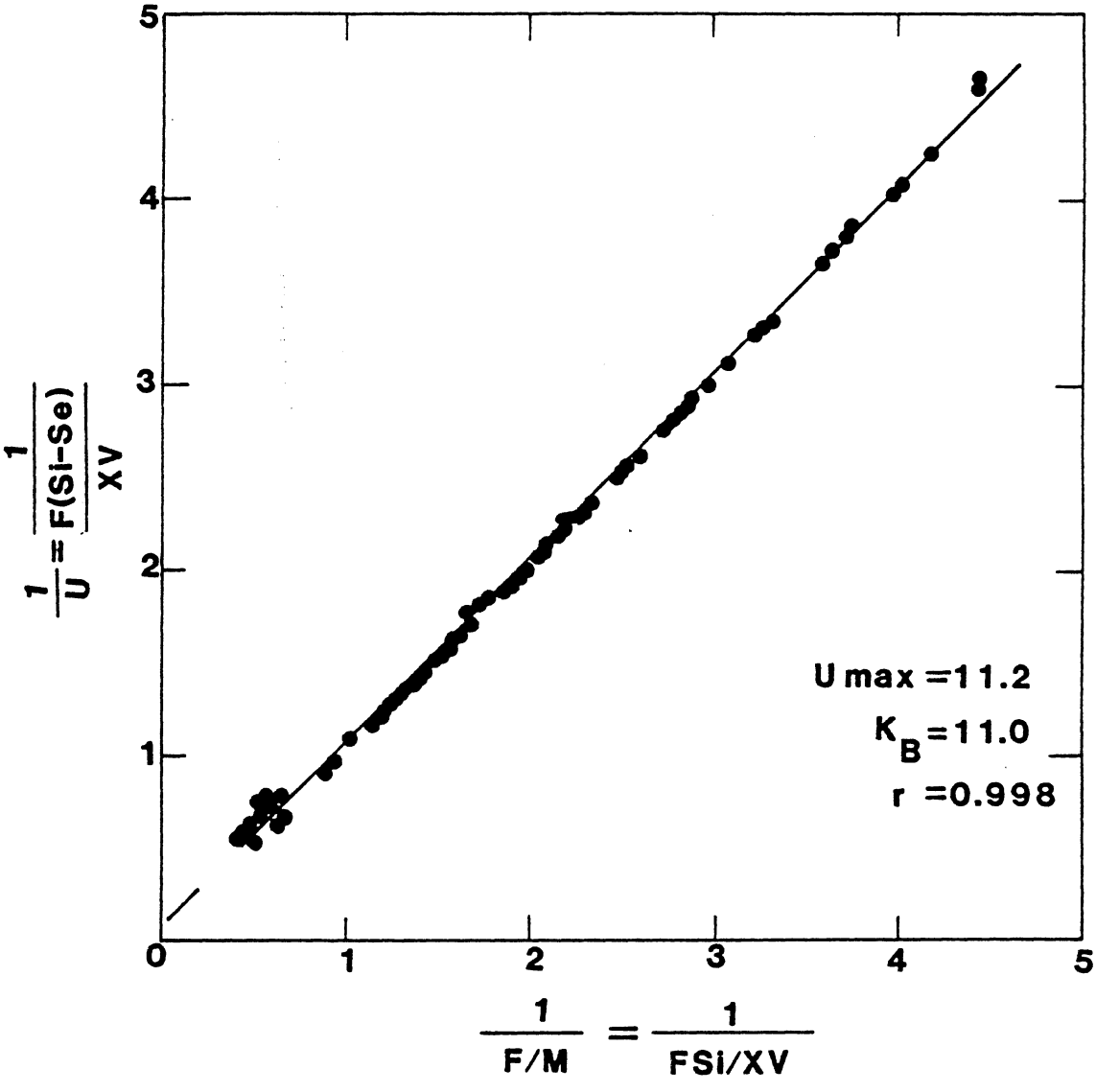


Figure 31. Graphical Determination of U_{max} and K_B in Terms of BOD_5.

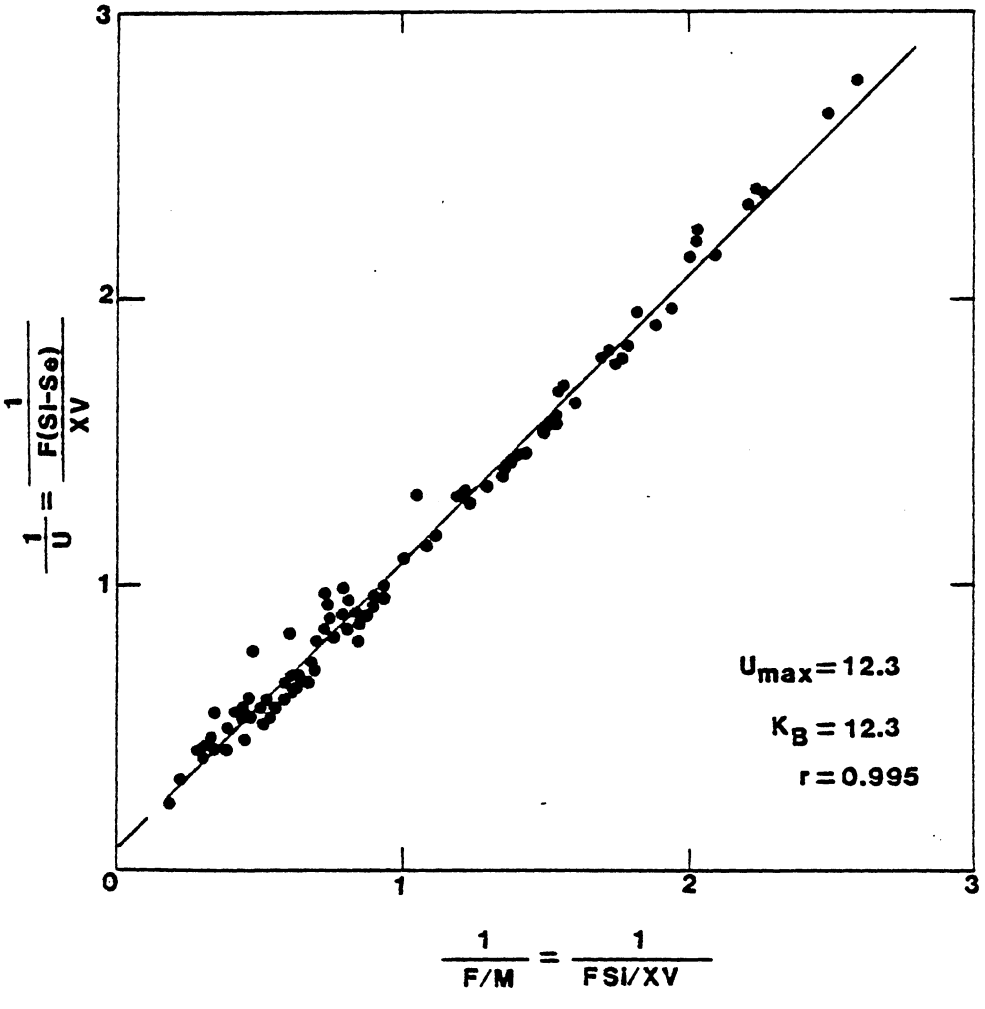


Figure 32. Graphical Determination of U_{max} and K_B in Terms of COD.

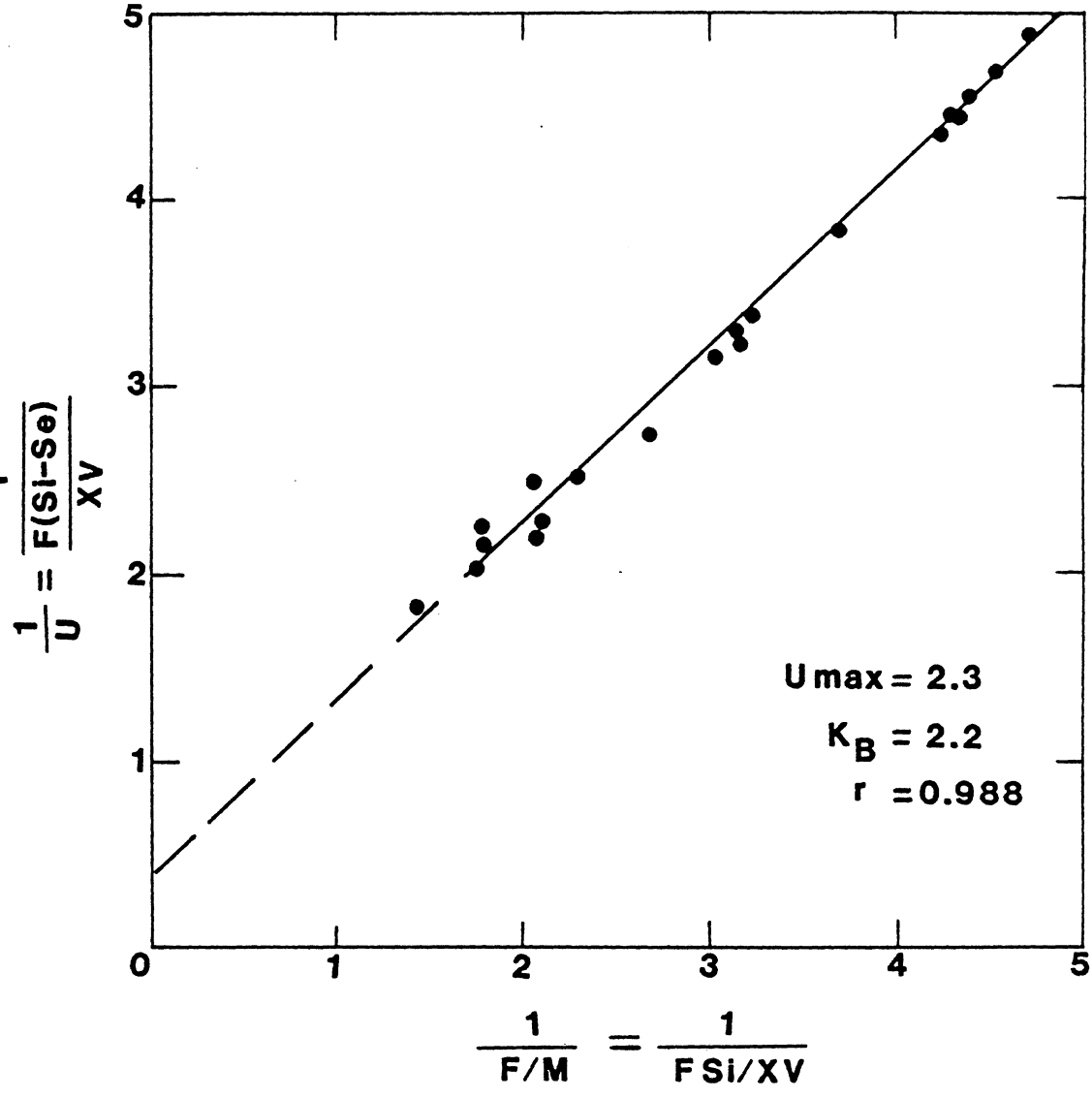


Figure 33. Graphical Determination of U_{max} and K_B in Terms of TOC.

4.5 Aerobic Polishing System Following Anaerobic System

As described earlier, in an attempt to polish the anaerobic effluent, an aerobic continuous flow activated sludge system was operated (SRT = 10 days) using the 20 day SRT anaerobic effluent. When the collection of data for this aerobic system was started in August, 1982, the anaerobic system was under acclimation. The BOD and COD of the effluent from the anaerobic system was around 500 mg/L and 1150 mg/L respectively. However by the middle of September, 1982, the anaerobic system performance was so high that not enough carbon source bled out in the anaerobic effluent for further cell metabolism in the aerobic reactor. As a result of this, the aerobic polishing reactor was operated for less than a month and a half.

In Figure 34, the chronological performance of the aerobic polishing step is presented. To start with, the F/M_{BOD_5} was about 0.1. But as the influent substrate reduced considerably, the F/M_{BOD_5} reached 0.01 during the above time period. It might be hard to accomplish a BOD/COD removal greater than 90% because a major fraction of the substrate that was bleeding out of the anaerobic system was composed of non-biodegradable organic matter. In other words, the percentage of ΔCOD available for cell synthesis in the aerobic step was very low. Similar was the experience of Huss (60), (61) using the Anamet Process. Huss could not get more than 74% BOD_5 reduction during the aerobic step. However, as it was experienced in our lab, Huss was able to get an overall BOD_5 reduction of greater than 95%.

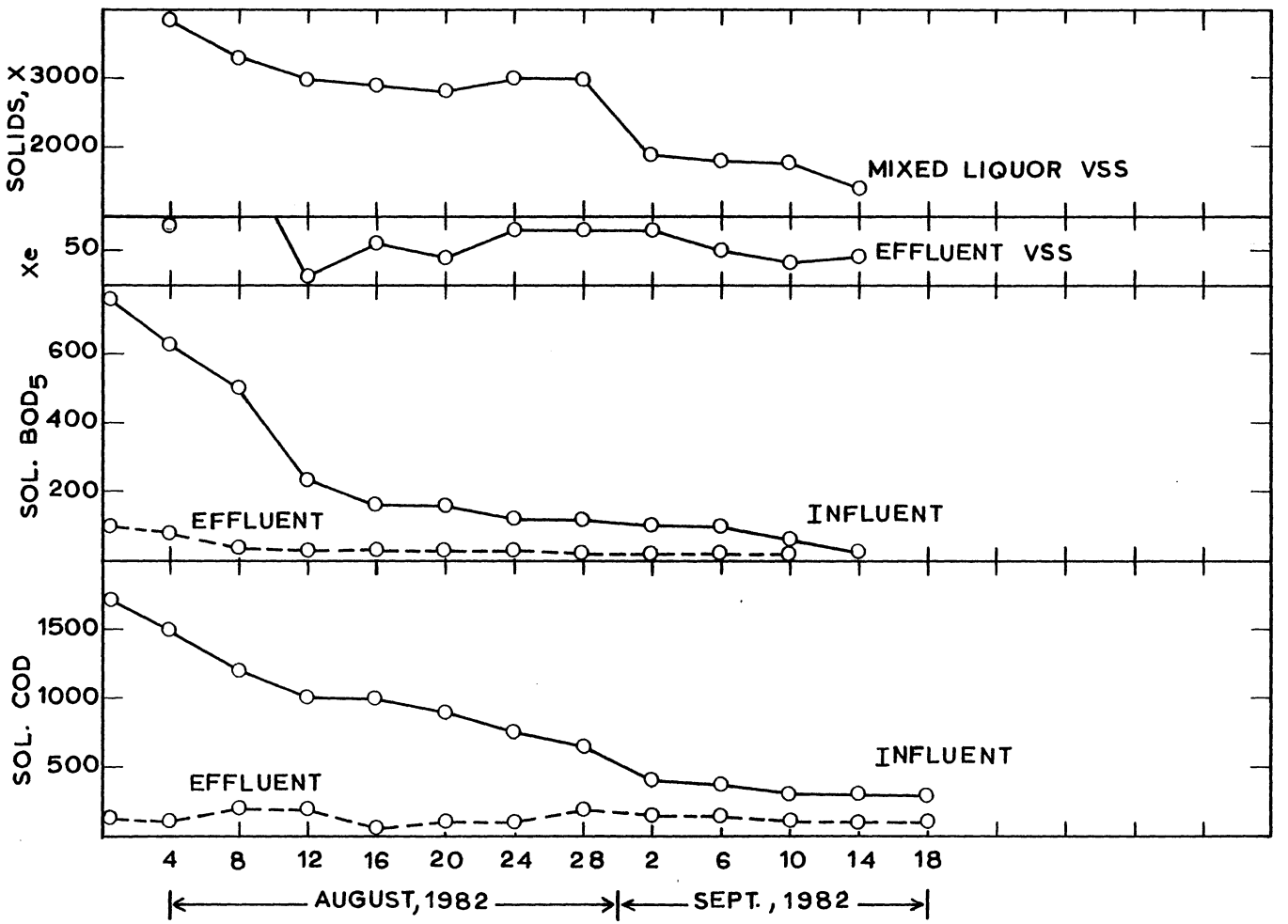


Figure 34. Chronological Performance of the Aerobic Polishing System

4.6 Anaerobic Treatment - Batch Studies

Fitting batch study kinetics into continuous system kinetics and evaluating the effects have been documented in literature to some extent as far as aerobic activated sludge systems are concerned. With a similar approach in mind, waste sludge from anaerobic system was periodically used in an anaerobic batch-fed activated sludge reactor. Four sets of experiments were run at about F/M ratios of 0.1, 0.25, 0.3 and 0.5 with respect to BOD_5.

The results of three of these experiments are summarized in Table IX. Runs number one and three are also summarized in Figures 35 and 36 for the low and high loaded systems, respectively. In the low loaded systems, volatile acids did not accumulate; however volatile acids did accumulate in the high loaded systems and appeared to inhibit the reaction kinetics. The apparent impact of volatile acid accumulation on reaction kinetics in the batch systems prevented fair comparisons with the continuous systems where volatile acids did not accumulate at the same F/M ratios. Thus the reaction kinetics of the batch and continuous systems appear different due to volatile acid accumulations in the batch systems above a certain F/M ratio. When the F/M ratio in the batch systems was maintained low enough to minimize volatile acid accumulation, the substrate removal kinetics approach the substrate removal kinetics in the continuous systems. These studies indicate that extreme caution should be exercised in designing batch anaerobic treatment experiments to develop data to use for designing continuous flow systems.

Another valuable piece of information obtained during and due to this batch study was with respect to the COD analysis on the alcohol

TABLE IX

TEST CONDITIONS AND RESULTS FROM BATCH STUDIES

Run No.	MLSS mg/L	S_i mg/L	S_e mg/L	% Removal	$\frac{F}{M}$	Gas Production			
						Vol. mL	% CO_2	CH_4 ft^3/lb	CH_4 Btu/lb
					COD				
1	2910	1780	900	49	0.61	420	10.5	6.78	6780
2	2550	1500	900	40	0.59	720	14.0	16.37	16370
3	2310	2340	1500	36	1.01	1675	22.0	24.62	24620
					BOD_5				
1	2910	450	100	78	0.15	420	10.5	17.05	17050
2	2550	920	600	35	0.36	720	14.0	30.44	30440
3	2310	1210	1100	-	0.52	1675	22.0	-	-

Test Conditions:

Reactor Vol. = 1,000 mL; Reaction time = 24 hrs; Temperature = 37-40°C; pH = 6.9-7.3

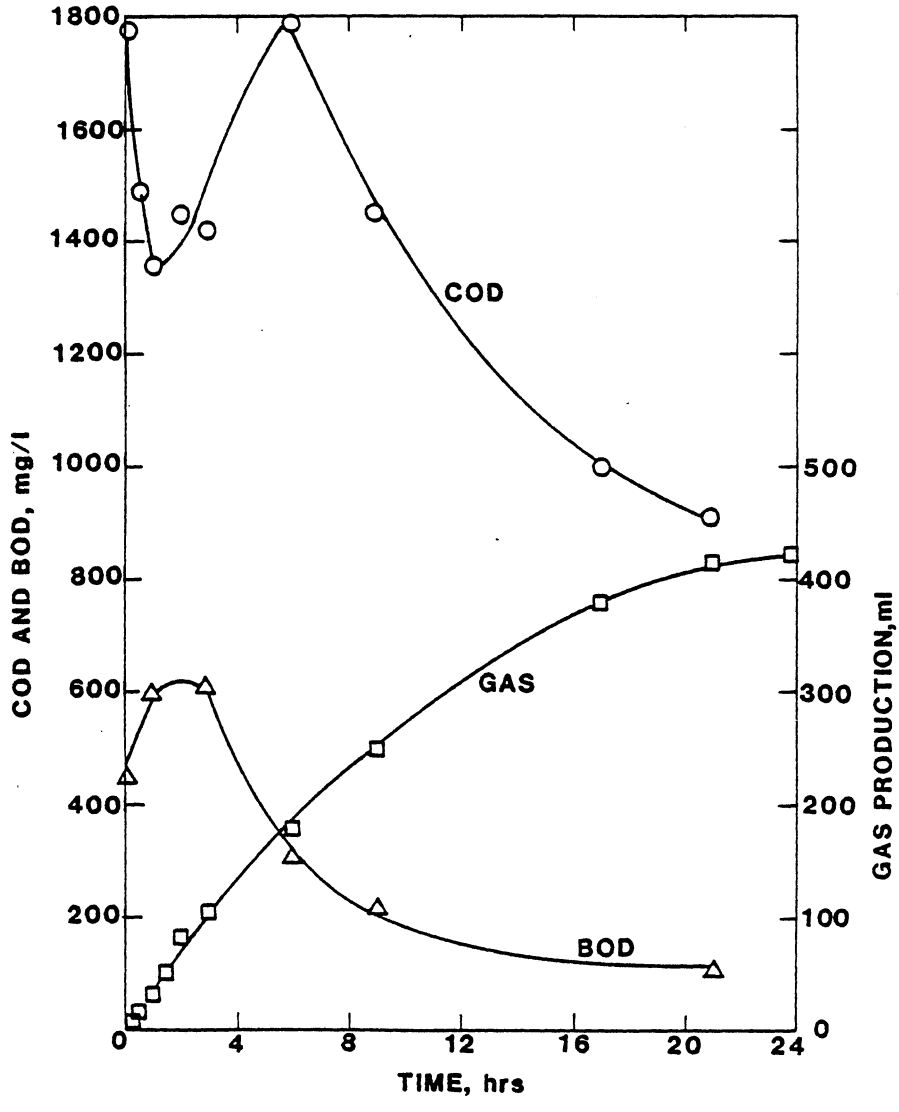


Figure 35. Batch Anaerobic System Removal Characteristics at Low F/M Ratio ≃ 0.1 (BOD).

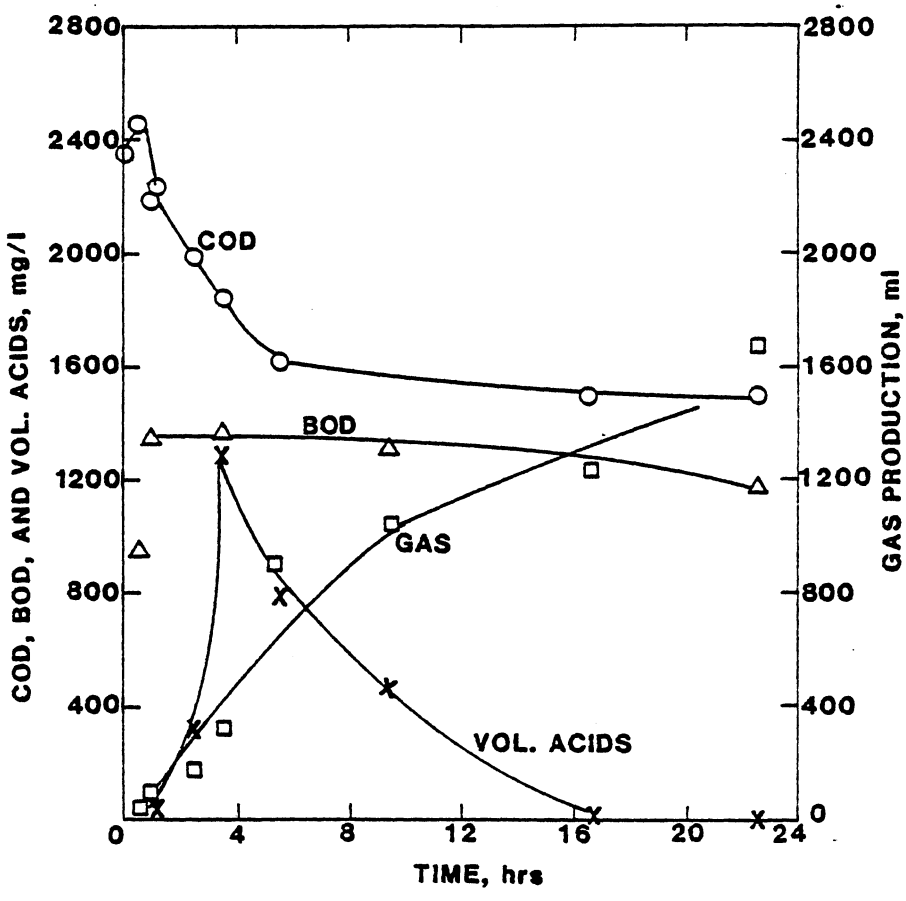


Figure 36. Batch Anaerobic System Removal Characteristics at High F/M Rate ≃ 0.5 (BOD).

waste and the corresponding gas production. It was mentioned in Chapter III that the Hach COD analysis method was inadequate in that it failed to resolve certain components of the alcohol waste, such as some long chain fatty acids and certain nucleic acids. As a result of this, the measured COD of the waste was less than what it actually was. The observations with regard to the COD concentration and all other relevant parameters for the batch fed anaerobic reactor for an $F/M_{BOD_5} = 0.25$ are presented in Figure 37. A close look at the COD values, from the start to about 6 hours, will reveal the following. As soon as the substrate was put in, the COD was 1500 mg/L. This substrate was being first acted upon by acidogens followed by acetogens. During this stage, the complex organic matter (that could not be perfectly resolved by COD analysis) was broken down into simpler forms. Due to this, the VFA concentration increased dramatically. It should have been possible for the COD analysis to resolve such simpler organic acids (as acetic acid) and hence the escalation in the COD concentration to 2000 mg/L. This logic was well supported when considering the gas production in terms of the COD destroyed. While writing a mass balance for COD and the corresponding gas produced, about 50% higher gas production was observed compared to the expected stoichiometric values.

Once these organic acids became available to the methanogens as substrates, the COD started dropping down. However it should be emphasized here that the whole process of anaerobic metabolism could go in the forward direction only if a consortium of multitudes of microorganisms performed the symbiotic and syntrophic (nutrient exchange), reactions without any interruptions. If this were so, the organic acids formed by the acid former should have been simultaneously

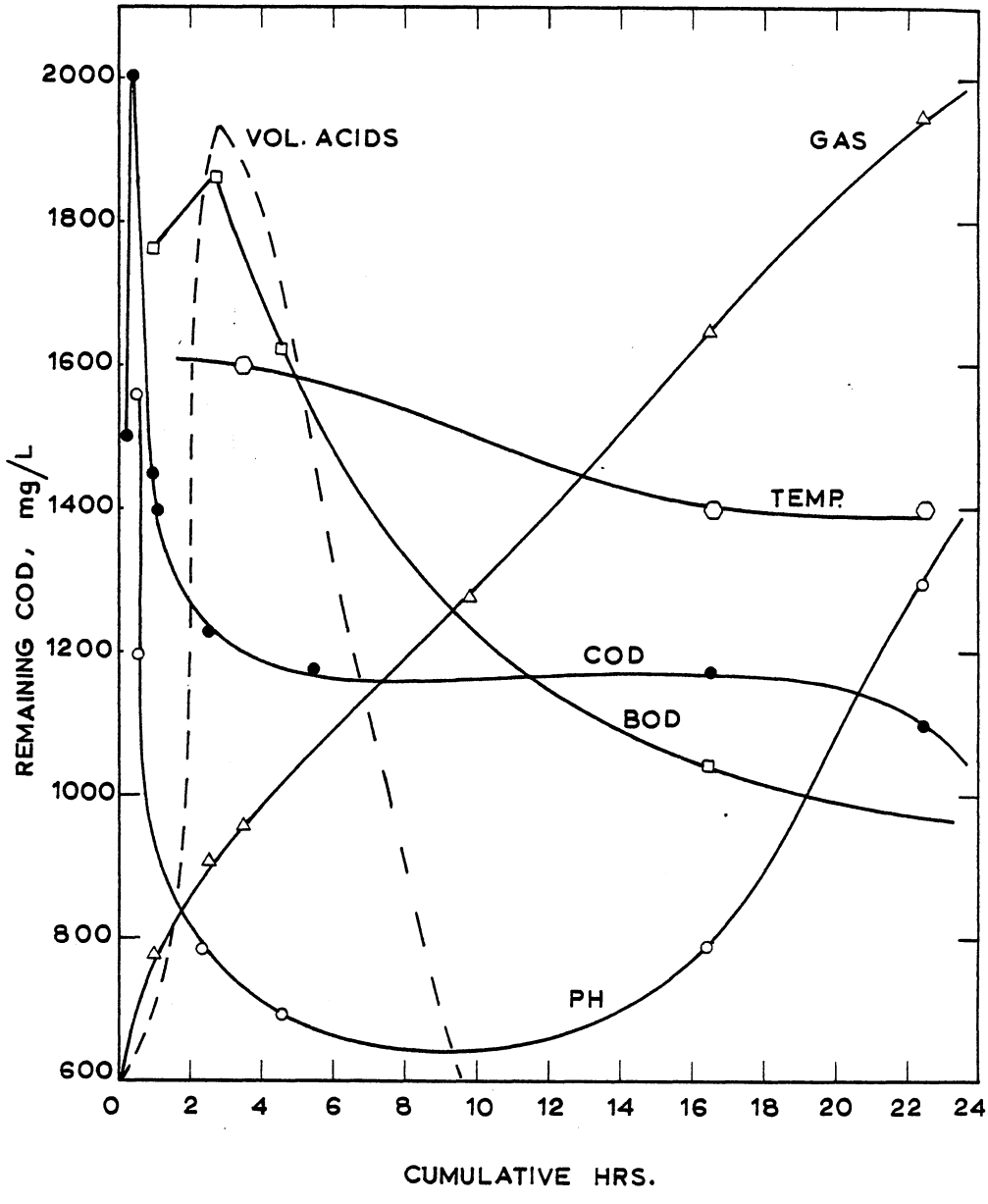


Figure 37. Batch Anaerobic System Removal Characteristics at F/M Ratio ≃ 0.25 (BOD_5).

utilized by methanogens. It could, therefore be concluded that what was measured as the highest COD could still be less than the actual COD.

Similar argument will hold good for the escalation of BOD also. In all the batch runs, there was a significant increase in the BOD within about 4 hrs since the start of the batch study.

In a BOD bottle when carbohydrate is available, it becomes the preferential substrate for the microorganisms as compared to other substrates such as protein and lipid. During the start of the batch study, the unbroken complex organic matter of the stillage was sampled out for BOD analysis. Similarly samples were also collected every half an hour for the same analysis. What should have happened, as explained for the COD analysis, that within this approximately 4 hrs. time, all of the complex and particulate organic matter should have been converted into simpler forms. In other words, it was not possible for the heterogeneous inocculum of cells in the BOD bottle to attack and cleave certain high molecular substrates such as protein or lipids. But, because the nonmethanogenic bacteria in the batch-fed reactor broke down these complex organic matter by their extracellular enzymatic activities, it paved way for the inocculum of cells in the BOD bottle to exhibit a better affinity for such simpler substrates as VFA's and other amino acids. It should be added here that lysine, an amino acid, one of the major constituents of the thin stillage, should have dissolved in the liquid medium which again should be one of the reasons for the boost up in the BOD values.

Incidentally, mention should be made at this juncture that when long term BOD was run on a continuous flow, complete-mix anaerobic

reactor effluent, it was found that the protein concentration of the effluent was approximately equal to the ultimate BOD.

Such an escalation in BOD could partly be attributed to the process of sequential removal of substrate: lysine serving as the substrate at the extinct of other major carbon sources. A pause or plateau in BOD exertion (O_2 uptake) was clearly discernible, and probably the diphasic oxygen uptake corresponded to the sequential utilization of carbohydrates followed by amino acids and peptides of protein.

In a time-bound research of this type, it was not possible to go beyond such suppositions and surmises. However, one definite conclusion that could be drawn from this phase of the research was that in the BOD analysis, a better resolution could possibly be accomplished for the same complex organic matter, if it were broken down by some means into simpler forms before running BOD analysis. Besides, the values should be better expressed in terms of total BOD instead of soluble BOD as done here. Such an approach would help to resolve the discrepancy encountered in the gas production too.

What the author wants to emphasize here, based upon the experience with this waste, is that the COD analysis does not measure all the organic content of the waste. Incidentally, it was observed that there was a near perfect mass balance between the TOC of the waste and the gas produced. However it will be appropriate to quantify these parameters in order to perfectly relate them. Hence this discussion will be further continued at that point where the gas studies are being discussed.

4.7 Anaerobic Treatment - Gas Studies

4.7.1 Treatment Performance

There is no single indicator which will reliably signal an imbalance between the two major populations of microbes in an anaerobic reactor. Consequently a number of indicators (such as concentration of volatile acids, bicarbonate alkalinity, pH, and rate of methane production) must be considered simultaneously. However, it is well accepted that the rate of methane production is a direct measure of the metabolic activity of the methanogenic bacteria and as such has a greater potential as a diagnostic tool of the anaerobic reactor performance than its counterparts. So, this phase of the research was oriented towards evaluating the gas production rate as a function of substrate utilization rate which in turn depended upon the substrate loading rate.

As discussed in Chapter III, this system was operated at a constant SRT = 30 day but at three different organic loading rates. The summary of the system performance in terms of BOD_5 and COD is presented in Table X. The gas production rate corresponding to each organic loading rate is also reported.

As seen from this table, very high treatment efficiency was achieved. Most biodegradable organic matter was stabilized. As a result of this, the effluent BOD was only 35 mg/L, even at the highest organic loading rate, giving an efficiency of greater than 99%. Comparing this SRT condition with that in Table VIII (30, a), one could see the similarities in the system performance. The former unit was run at 5 days HRT whereas the later was run at a HRT of 2.6 days. However

TABLE X

ANAEROBIC TREATMENT SYSTEM PERFORMANCE
IN TERMS OF BOD (COD)

(SRT = 30 Days)

Loading Rate F/M	Influent mg/L	Effluent mg/L	% Removal	MLVSS mg/L	Methane percent	Methane Production Ft^3/lb BOD (COD)
0.22	2,300	15	99.3	3,380	78	21.1
(0.50)	(5,125)	(380)	(92.6)			(9.9)
0.23	4,100	28	99.3	5,380	71	20.7
(0.56)	10,100	380	96.2			8.8
0.31	8,880	35	99.6	8,500	70	15.7
(0.55)	(16,000)	(425)	(97.3)			(8.5)

both systems gave compatible results establishing once again the fact that it was not the HRT but the SRT (F/M, in other words) which should govern the design. Also, it was interesting to observe that the influent BOD/COD ratio was 0.55 whereas this ratio was about 0.1 for the effluent during both sets of observations. These findings suggested that the secondary effluent from an anaerobic treatment needed no polishing steps so that the effluent stream could be put into a municipal sewer only to dilute municpal waste. The lowest BOD/COD ratio that could be obtained in the effluent using the aerobic activated sludge treatment was 0.30 (the highest BOD/COD = 0.70) indicating a higher substrate bleeding than by anaerobic treatment. The figures given here for aerobic treatment were when the loading was less than half of that for the anaerobic reactor, which readily explains one of the reasons for preference for anaerobic treatment for such high strength wastes.

4.7.2 Gas Production

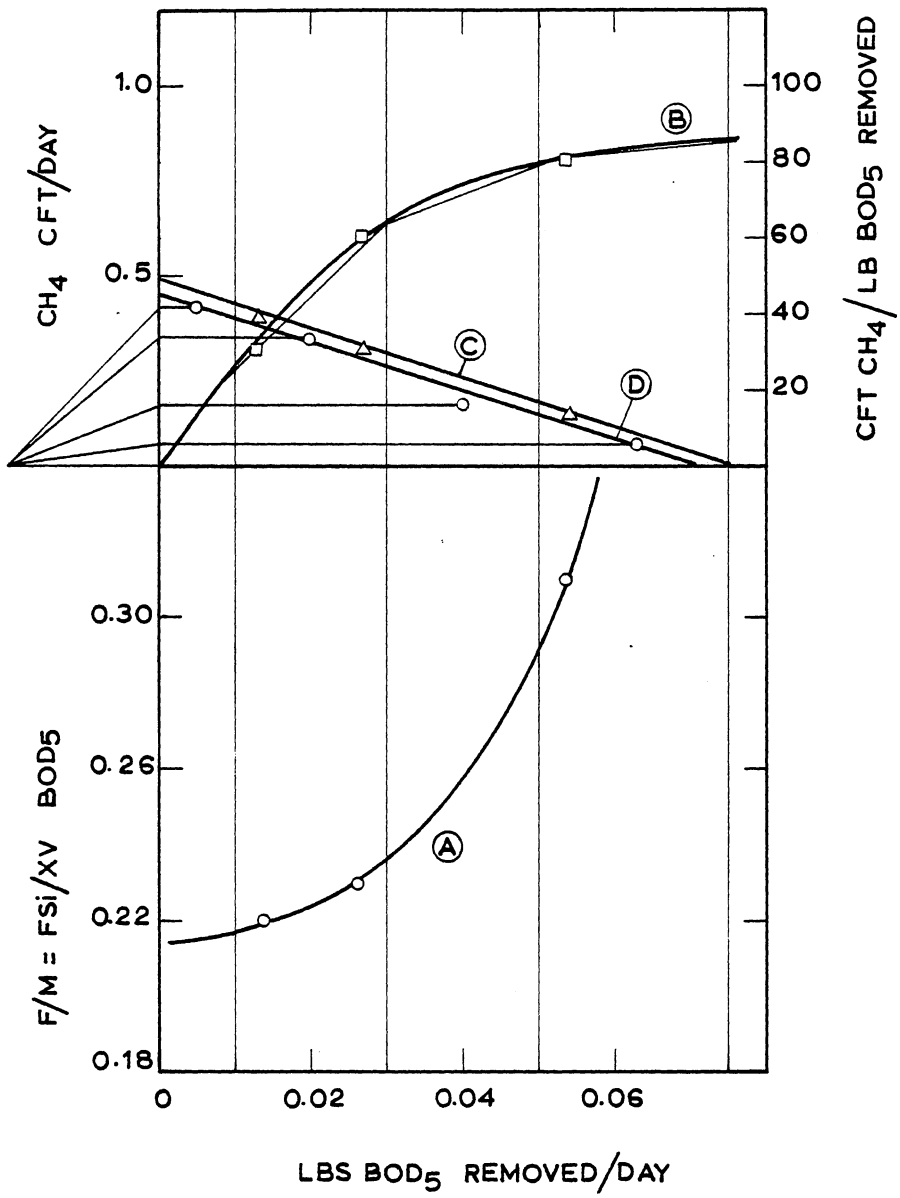
As it was mentioned elsewhere earlier, most of the stills do not extract all the ethanol from the fermented mash. In addition, a variety of other residual alcohol, fusel oils, long chain fatty acids and nucleic acids are reported to be present in the stillage in measurable concentrations, (35), (53). But, as stated in the Standard Methods (65), the COD analysis failed to measure such straight-chain aliphatic compounds and certain aromatic hydrocarbons. This inadequacy of COD analysis was reflected in the gas production rate which was higher than what was expected in our laboratory. Theoretically one pound of oxygen, equivalent to one pound of COD, is required to burn 0.25 lb methane as

seen in equation (13).

$$CH_4(0.25\ lb) + 2O_2(1b) = CO_2 + 2H_2O \qquad (12)$$

Volumetrically, 0.25 lb of CH_4 occupies 5.6 Cuft. But Dahab and Young (35) estimated this value of specific methane gas production rate for similar wastes at 6.3 Cuft CH_4/lb COD destroyed. However, as seen in Table X, an average methane production rate of 9.0 Ft^3/lb COD was observed in our lab for similar loading conditions. Such an escalated gas production (10 Ft^3/lb COD) was observed with the fixed-film system also (64) during a parallel research in this lab. Mention should be made at this point that the wastewater used by Dahab and Young was only a simulated, synthetic waste which did not duplicate the waste one hundred percent. The point is that the accuracy of assessing the rate of methane production depends very much upon a perfect resolution of the composition of the waste.

One can write a perfect mass balance only if the organic carbon contents of the waste is determined and if the gas production rates were to be related. The organic carbon determination lacks the many variables which plaque the BOD and COD analyses, resulting in more reliable and reproducible data. Such inadequacies and discrepancies which are inherrent in BOD/COD analysis can be minimized to a great extent if the mass balance were based upon TOC analysis, because at temperatures greater than 950°C, all the atoms of organic carbon molecules are oxidized to CO_2. Alternatively the waste can be acid hydroyzed first and cooked under more stringent oxidation conditions for COD analysis.



Ⓐ F/M VS LBS BOD_5 REMOV./DAY

Ⓑ PRIMITIVE CURVE

Ⓒ ACTUAL CH_4 PRODUCTION

Ⓓ DERIVATIVE CURVE OF B

Figure 38. Graphical Differentiation to Estimate Gas Production Rate.

When writing a substrate mass balance on the basis of TOC, it was seen that the observed rate of gas production was slightly less than the stoichiometric value. This should be true because a minimal portion of the carbon was utilized in the synthesis, respiration and replication of cells. It was seen that for every one pound of TOC destroyed, 31.0 Cft of gas (21.8 Cft CH_4) was generated.

Also, Dahab and Young reported that the percentage of methane in the gas was always in the range of 72-87 with CO_2 making up the remaining major component. As seen in Table X , the methane content was always greater than 70% even at high organic loading rates.

Speece (39) and McCarty (37) reported that at higher organic loading rates, it should be expected that the percentage of methane would go down than at lower organic loading rate because a higher percentage of substrate would be spent in the synthesis of cells than for being released as gas in order to keep the system in equilibrium. As observed from Table X, the results obtained with regard to methane percentage confirmed those conclusions.

Figure 38 is a graphical approach to estimate the cubic feet of methane produced per pound of BOD removed. Curve A of Figure 38 represents the pounds BOD removed/day as a function of the mass substrate loading. The methane produced as a function of the pounds of BOD removed is shown in curve B. It is graphically possible to differentiate the curve B, and D is the first derivative curve of B. Curve D will, therefore, represent the cubic feet of methane produced per pound of BOD removed. The line C represents the actual cubic feet of methane produced per pound of BOD removed. The Y axis on the right hand side represents the scale for the derivative curve. For any known

value of F/M and the corresponding pounds BOD removed/day, it becomes possible by using the derivative curve D, to estimate the cubic feet of methane produced per pound of BOD removed. These values are slightly lower than those of the actual values (represented by curve C) because the primitive curve (represented by curve B) is a line passing through the average values.

4.8 Anaerobic Treatment - Shock Studies

4.8.1 Organic and Hydraulic Shock Loading

After the anaerobic substrate removal kinetics were developed, one of the reactors, the 30 day SRT system was subjected to organic and hydraulic shock loads. This system was originally fed at a rate of 1 ml/min. During the period of shock load, the flow rate was doubled to 2 ml/min., but maintaining the feed concentration about the same and all other parameters constant.

During this period, the influent COD concentration varied between 5410 mg/L and 7170 mg/L.

Figure 39 is a graphical profile explaining the effects of doubling the flow rate. 0, on the X-axis is the day when the shock was initiated which was continued for 5 days. The numerals with the negative sign indicate the days prior to shock. Samples were collected 12 hours after shock and every 24 hours after shock.

As seen from the graph, when the flow rate was doubled, there was a spontaneous increase in all the system parameters, except for the pH. The alkalinity in the feed, necessary to neutralize the volatile acids accumulation, was not adjusted inadvertently when the flow rate was first doubled. As a result of this, the reactor pH plunged down to 6.5

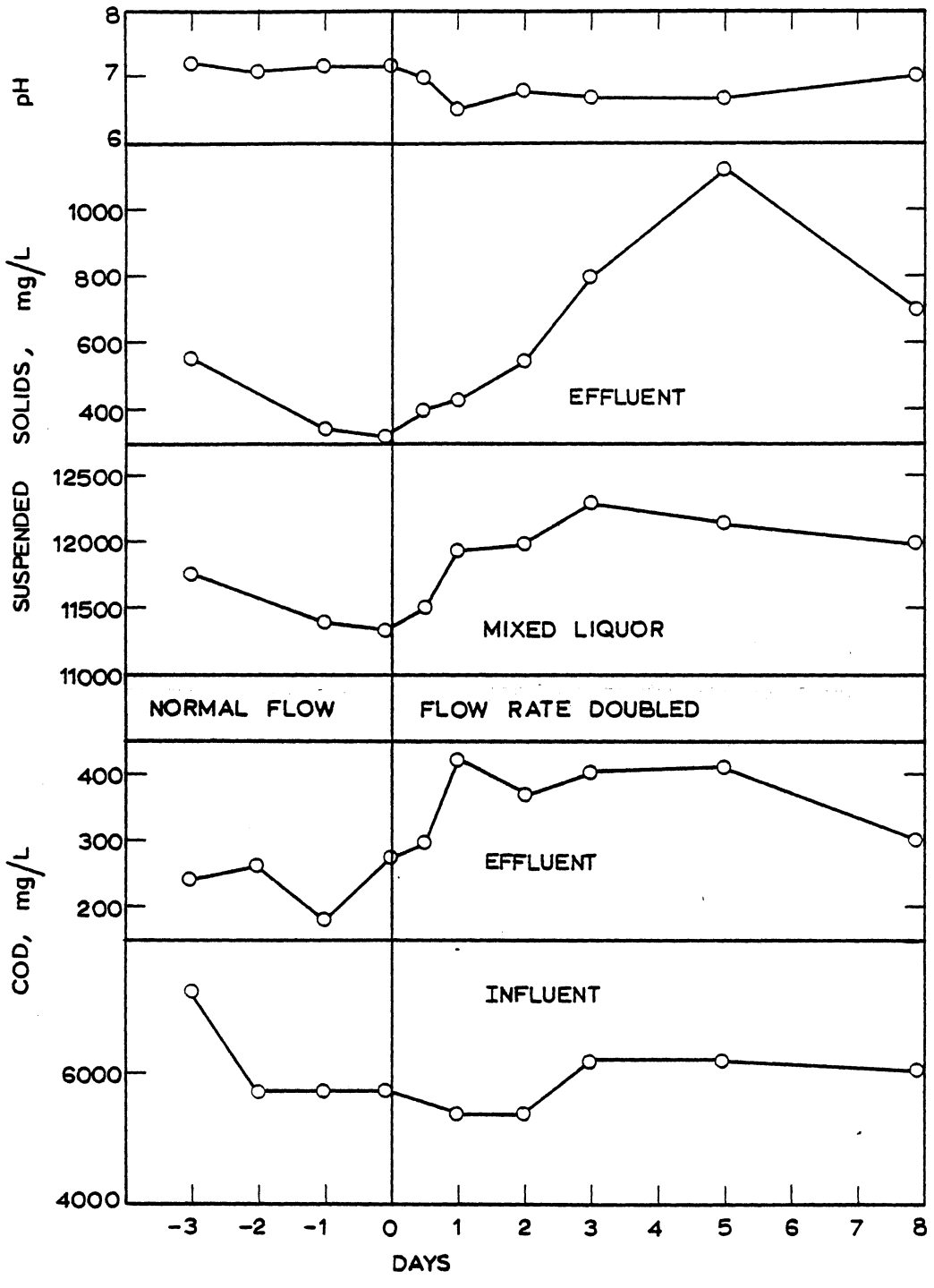


Figure 39. Effects of Organic (and Hydraulic) Shock Load.

from 7.2 due to the volatile acids accumulation. But, when the feed alkalinity was suitably increased, the reactor pH adjusted back to 6.8. Had the reactor pH gone below 6.5, the system might have reached failure conditions.

This is one of the periods of observation when the measurement of gas was not possible. On the day, when the shock was initiated, the effluent suspended solids was only 350 mg/L. But on the fourth day, the effluent suspended solids increased to 800 mg/L which then shot up to 1125 mg/L on the fifth day. Since the flow rate was doubled, the gas production rate also should have approximately doubled. But because of the physical limitations of the reactor, which could not handle such an increased gas production, the gas pushed some solids along with the effluent and hence the effluent suspended solids increased three fold. The effluent suspended solids reported here were obtained by completely mixing the effluent. However, it was interesting to observe that the effluent suspended solids run on the settled supernatant during this shock study was about the same as before shock.

The effluent COD, which was 275 mg/L on the day of shock, increased to 420 mg/L on the first day and stayed in that range until the fifth day when the shock load was stopped. The effluent COD then leveled off to the original range from the eighth while using a pilot scale anaerobic fluidized bed reactor in that they went to the extent of shocking the system to total failure.

Thus, it was possible to observe from this study that the anaerobic system was capable of withstanding such temporary organic and hydraulic shocks, provided enough care was taken to monitor the system.

In a similar attempt, when the flow rate was tripeled, almost similar changes were observed. But, because volatile acids built up to 2850 mg/L within 36 hours, and the pH plunged down to 6.3 (inspite of adding alkalinity), the shock was terminated.

4.8.2 Nutrient Shock Loading

Bauchop et al., (36) have suggested that the C:N:P ratio should be maintained at 100:5:1 irrespective of whether the treatment system was either aerobic or anaerobic. But, it was seen from the previous observations in this lab and from the literature (40), (41), (60), (61) that the cell yield in an anerobic system was about 1/5 to 1/10 of the aerobic system. On this basis, the TKN present in the waste should be sufficient to meet the N requirements of the reactor. Hence, during this phase of the study, no external source of nitrogen or phosphorus was added to the feed in order to study the effects of nutrient shock on an anaerobic system. Again, during this period of study, gas measurement was not possible.

One of the reactors, which was run at 10-day SRT, was used for this purpose. On July 22, 1984, this reactor received feed (whose COD was in the neighborhood of 5,000 mg/L) without the addition of any external nutrient. This shock was continued for about 24 days. Before shock, ammonium chloride salts and phosphoric acid were added as nutrients.

Figure 40 represents the chronological performance of the anerobic reactor, 8 days before and 24 days after shock. 0, on the X-axis, represents the zero day when the reactor was first nutrient shocked. Like in the previous case, numerals with negative sign indicate the days before shock.

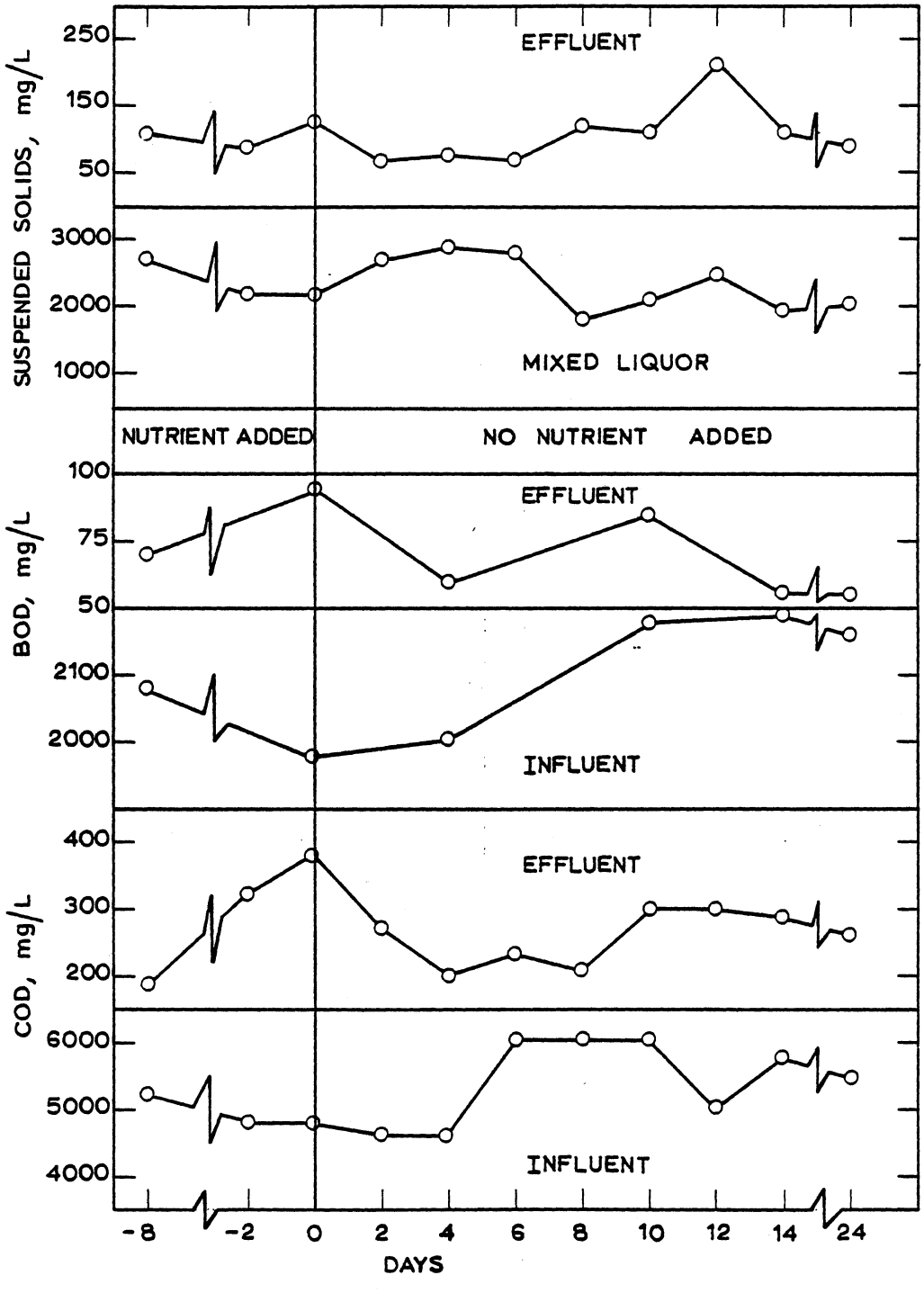


Figure 40. Effects of Nutrient Shock Load

It is obvious from the graph that depriving external nutrients had very little impact on all system parameters even for such a prolonged period of about 24 days. The performance of the system, before, during and after shock, was consistent in a definite range. Subsequent to such observations, the nutrient shock was terminated.

On further reference to literature, Grady and Lim (78) have documented that the nitrogen requirements for an anaerobic system, in mg N per mg COD removed, could be estimated from the equation NR = 0.105 Y_o, where Y_o is the observed yield. Based upon the already obtained kinetic values of $Y_{t(COD)}$ = 0.08 and Kd = 0.02 (Figure 27), one could calculate the value of Y_o as 0.1 for a system whose SRT = 10 days. Based upon this Y_o = 0.1, the nitrogen requirement in mg N would be 1.05 for every 100 mg COD removed. Therefore, for a waste whose COD was about 10,000 mg/L, the nitrogen requirement would be only 105 mg/L. However, the soluble TKN content that was present in the waste was adequate (120 mg/L) for a COD of 10,000 mg/L. Thus, it was possible to operate the system at a comparatively low SRT (10 days) without impairing the system performance even though no external nutrient was added.

This was yet another valuable piece of information obtained from the nutrient shock study. A large amount of chemicals, which would otherwise be added as nutrients, could be saved.

In a similar on-going research in this lab but using a fixed-film system, it was observed that the system performance has never deteriorated even though the addition of external nutrient was terminated for over two months.

4.8.3 pH Shock Loading

Actually, pH shock loading was not done during any specific period of time because of the fear that the unit would be stressed to failure. Once the anaerobic system fails, it takes anywhere between two to six months to recuperate the system. However, every now and then, during the entire period of this research, certain quantifiable results were obtained in terms of pH shocks. They are summarized as follows:

1. From the stand point of the pH, best operating conditions, during this study, were in the pH range of 6.8 to 7.2 which have been time and again supported by most researchers dealing with anaerobic studies. In this range, the VA/Alkalinity ratio was less than 0.1.

2. However, it was possible to stretch the above pH range to 6.5 and 7.5 respectively and still get compatible system performance. When the pH was about 6.4, the VA/Alkalinity ratio was around 0.5 indicating (a) the volatile acids accumulation and (b) that the system was heading to failure.

3. Below a pH of 6.5, volatile acids built up so much that 'sour' conditions developed, indicating chemical imbalance in the buffering system, and possible eventual failure. At this threshold level of total failure, about all that could be done was to reduce the organic loading rate to help prevent total failure. Such was the experience whenever there was either a switch over to a lower SRT or a sudden and persistent increased organic loading. No matter what the cause of the treatment imbalance, however, control of the pH to neutrality was essential for successful recovery.

Similarly in one situation, when the pH was greater than 7.8, the alkalinity was around 6500 mg/L and the alkalinity itself appeared to be toxic to the methanogens and the system failed.

4.8.4 Shock Load Due to Feed Shut-Down

Whenever, there are clean-up operations, over-hauling of the plant or mechanical break-down of components, production of ethanol has to be temporarily ceased. So, no waste is generated. Therefore the wastewater treatment unit receives no feed. The last phase of this research was to study the effects of plant shut-down on an anaerobic treatment plant, specifically with reference to gas production.

To start with, feed to the reactor was terminated for 24 hours. The gas production rate diminished considerably. There was no impact either on effluent substrate or on MLSS. Terminating the feed was, then, extended for another 24 hours. Gas production ceased almost completely. When addition of feed was restarted, gas production picked-up at the same rate it ceased.

Having gained this confidence, an attempt was made to terminate the feed for one week at a stretch and study the effects. Figure 41 is a graphical representation of the effects of feed-shut down for a week on the performance of the anaerobic system.

0, on the x-axis represents the day when the feed was stopped. Numerals with negative sign indicate the days before shock. After 7 days, addition of feed was restarted. Y axes represent analyses indicated.

As seen from the graph, the gas production rate which was in the range of 1300 to 1400 ml/hr plunged down to 25 ml/hr within 24 hours and

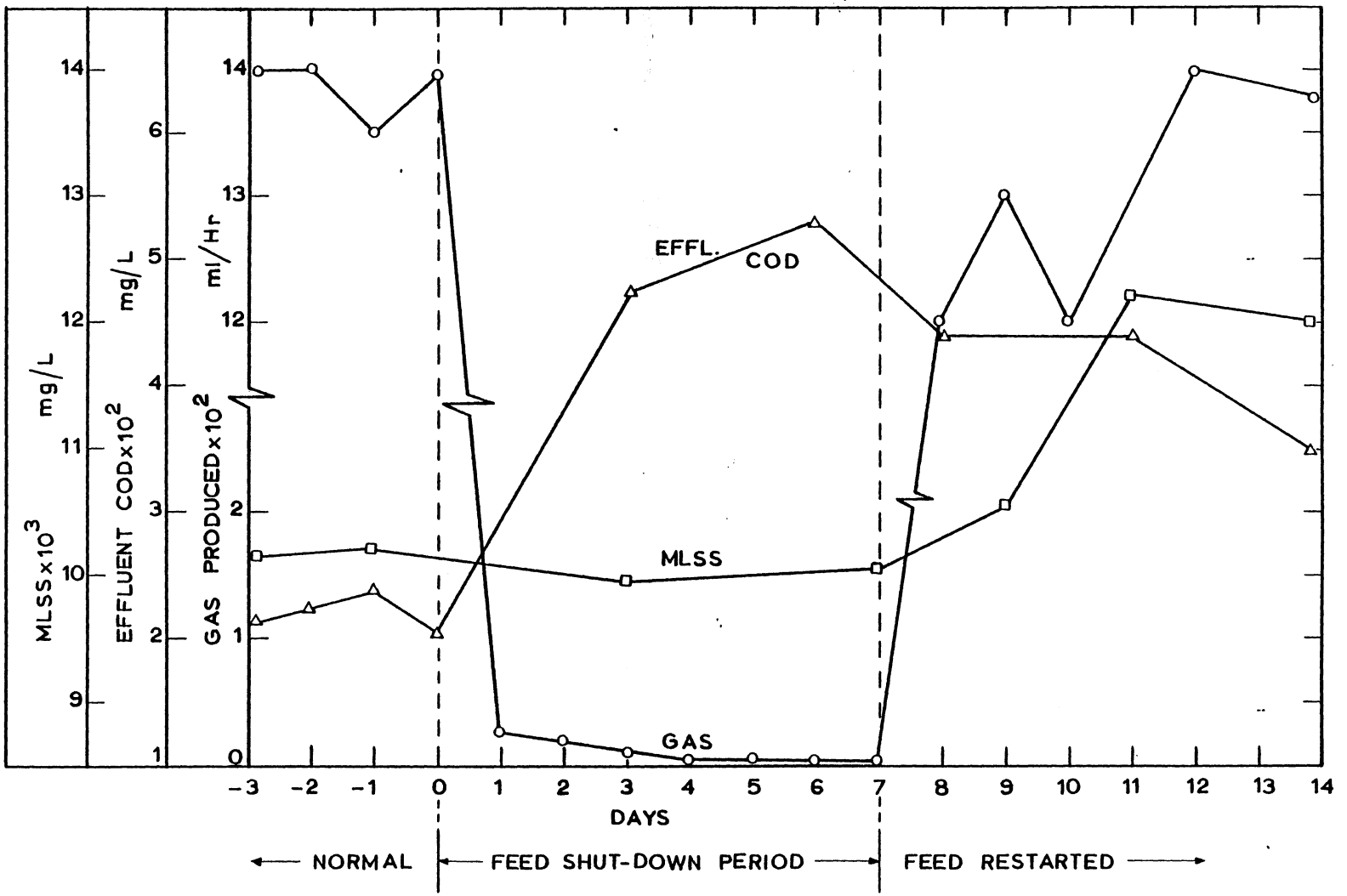


Figure 41. Effects of Feed-Shut-Down

touched the lowest value of 10 ml/hr on the 5th day, and continued at that rate until the 7th day when the feed was restarted. There was a spontaneous increase in the gas production rate which jumped back to 1200 ml/hr within 24 hrs. and reached the original range with 48 hrs. This established that the gas production rate was primarily a function of organic loading. Secondly, the system did not suffer any serious set-back due to the cessation of feed for a week. Szendrey et al., (51) have documented that there was a typical case of an anaerobic plant (treating food processing wastes) shut-down for over 150 days in a row, restored within 2 days when addition of substrate was restarted. The only requirement was to provide a conducive atmosphere to methanogens.

There was no significant change in th MLSS concentration during shock. However, the solids concentration in the reactor increased from 10,000 mg/L to 12,200 mg/L within 4 days of restart even though sludge wastage was maintained as before shock and levelled off only after 20 days.

The effluent COD, which was about 200 mg/L before shock, increased approximately three-fold during shock. Shah et al., (55) who experienced such an escalation in the effluent substrate during the feed shut down period with a fixed-film system, could find no possible explanation for this. However, it appeared that in the absence of the food, there might have been a chance for lysing of some cells during shock which effected an increase in the effluent COD values.

It is of prime importance that due to this phase of the research it was possible to conclude that feed-shut down had little impact on the performance of an anaerobic system. It might be even prudent to stop

mixing the solids in the reactor during this period in order to save some energy.

The fact that the methanogenic bacteria, responsible for the production of methane, could go under such 'hybernation' when their exogenous substrate was deprived could possibly be explained as follows.

First, it should be emphasized that the mechanism of methane formation from volatile acids is not fully understood and could well involve a mutualistic interaction between hydrogen-producing and hydrogen-utilizing bacteria. Thus the key for the production of methane is the intermediate, hydrogen. When CO_2 is used as the electron (hydrogen) acceptor methane is formed. Nevertheless, on certain occasions, molecular hydrogen gets released due to variations on partial pressure.

In a good operating anaerobic reactor hydrogen is continuously removed by the methanogenic culture to keep the partial pressure at low level. This reaction will not go in the forward direction unless the methanogenic bacteria continuously remove the molecular hydrogen produced by the nonmethanogens. Hydrogen accumulation inhibits the matabolic activities of the non-methanogenic bacteria if the methanogens fail to remove the molecular hydrogen. This we label and account for acid accumulation.

Now let us approach the above phenomenon of 'hybernation' with some suppositions.

If no hydrogen is formed, during the first stage, which is also sometimes possible, the nonmethanogenic phase results in insignificant reductions in COD because all electrons released in the oxidation of organic compounds are passed on to organic acceptors which remain in the

medium. Consequently the energy level of the entire system is lowered only by losses due microbial inefficiency. Contrarily when hydrogen is formed, however, it represents a gaseous product which escapes from the medium thereby causing a reduction in the energy content, and thus the COD, of the liquid.

If the hydrogen producing bacteria are not active and hence if they are not producing hydrogen, they must use organic compounds as acceptors for the electrons removed during biological oxidation. This results in the products such as butanol, ethanol, lactic acid and succinic acid; in addition to a smaller fraction of acetic acid. Thus, when organisms with very little active hydrogenase systems (which are only a subset of the acid-producing group) are present, the production of reduced end products is maximized and the production of acetate is minimized. These organic end products become available to methanogens as substrate.

This is probably what has been happening in the feed-deprived reactor.

However, before drawing the following conclusions, certain points need mention.

There was not any phenomenal decrease in the microbial population during the cessation of feed. Probably eight days are too short a period to positively conclude that there was cell lysing. The very fact, that there was spontaneous gas production as soon as the exogenous substrate was supplied, only confirm that these anaerobic microorganisms have been under a state of 'hybernation' and not undergoing bacterial decay. However, there would have been cell decay, had this period of depriving been extended for a prolonged time.

So, during the above hybernation period the hydrogen producing bacteria have been dormant. This immediately explains why the volatile acids concentration did not depelete as indicated by volatile acids analysis.

Now the question may be asked where do these volatile acids come from to be used as substrate.

It has been documented (78) that lipid degradation is incomplete in an anerobic reactor even when the MCRT is sufficiently long to prevent washout of methanogenic population. Hence it can be concluded that enough lipid, which the thin stillage has, was available as substrate.

Additionally, most of the effluent substrate was primarily composed of protein. This was seen when long term BOD was run on the continuous flow, complete-mix anaerobic reactor effluent. The protein concentration of the effluent was found to be approximately equal to the ultimate BOD.

Thus, during the period when the external substrate was deprived, the unused protein and lipid substituted for carbon source.

To quote from McKinney, "Anaerobic digestion is the uncharted wilderness in sanitary engineering". It is apparent that much work remains to be done before unfolding the mystery behind the dynamics of anaerobic metabolism is fully understood.

The phenomenon explained above is yet another mystery, for which some clues have become available due to this phase of the research.

CHAPTER V

SUMMARY AND CONCLUSIONS

The high-strength wastewaters (stillage) from fuel alcohol production facilities (both pilot scale and full-scale) were periodically collected and characterized. They were also subjected to different suspended growth biological treatment investigations primarily in (a) define the biokinetic constants necessary to size full-scale treatment plants (b) evaluate the feasibility of direct discharge, reuse and recycle options.

The following is the list of conclusions drawn from this research effort.

5.1 Stillage Characterization

1. Alcohol production wastewaters are high-strength, acidic and high-temperature.

2. The pretreatment investigations consisted of gravity settling with and without chemical conditioning agents to enhance flocculation and settling. Addition of PERCOL 726 (a product of Betz Co.,) high strength anionic polymer exhibited the best thickening characteristics for the waste.

3. There was not a considerable variation in the capillary suction time irrespective of whether the waste was subjected to pretreatment or not. Simple settling was more than sufficient to separate majority of the solids from the soluble.

4. For most of the time, it was observed that the TOC:BOD:COD ratio of the thin stillage was around 1:2:3 which was comparable to the values reported by researchers for similar wastes.

5. During storage, the unextracted ethanol dissolved in the stillage, evaporated slowly and thus reduced the COD/BOD concentration of the waste to about half of the original strength over a storage period of about 20 days.

5.2 Aerobic Suspended Growth Studies

1. These studies have shown that alcohol production wastewaters are highly biodegradable and can be treated to high levels of aerobic activated sludge process.

2. The data collected during the studies were analyzed to define the biokinetic constants required for design by the various activated sludge design models. All the design models could be used with a high degree of confidence. However, the Kincannon and Stover design model, that expressed substrate utilization as a function of mass loading, was capable of eliminating the scatter in the determination of biokinetic constants.

3. The waste activated sludge contained protein and carbohydrate contents similar to the spent yeast cells and thus should be a valuable by-product of wastewater treatment for use with the grain solids as cattle feed.

4. At low SRT (= 3 days) there was a profuse growth of slimy bacteria. Adequate nitrogen source and a relatively longer acclination period was required to overcome this.

5.3 Anaerobic Suspended Growth Studies

1. Fuel alcohol wastewaters were successfully treated to very high levels ($>$ 98%) by anaerobic suspended growth system. Such treatment performances were possible even at an organic loading rate three times higher than that of aerobic system.

2. The anaerobic systems were operated at several different hydraulic flow rates and different influent substrate concentrations to verify that the anaerobic reaction kinetics were indeed a function of the mass substrate loading rate. The substrate utilization rate was dependent on the F/M ratio as described by the Kincannon and Stover design model for activated sludge systems. The kinetic constants of U_{max} and K_B were determined with the very high correlation coefficients of 0.99.

3. The true cell yield of 0.13 in terms of BOD_5 was 4.0 times lower than that from aerobic systems (Y_t = 0.53) treating fuel alcohol wastewaters. (A summary comparing the various system parameters of aerobic and anaerobic systems is presented in Table XI).

4. Not only was substrate removal found to be a function of the mass substrate loading rate, but both the gas production rate and methane content of the gas were observed to be dependent on the applied substrate loading rate or the F/M ratio or SRT operating condition of the system. The carbon dioxide fraction of the gas increased as the F/M ratio decreased.

5. As far as the by-product recovery is concerned, the protein and carbohydrate content of the anaerobic biological sludge would make it suitable for use as cattle feed when dried and mixed with the stillage solids. By-product recovery in the form of the methane gas produced

during anaerobic treatment could be used as an energy source within the alcohol plant.

6. Extreme caution should be exercised while incorporating anaerobic batch treatment kinetics into those of continuous systems because the reaction kinetics of the batch systems appear different from the continuous system kinetics due to the build up of volatile acids above a certain F/M ratio.

7. The short-term aerobic activated sludge studies polishing the anerobic effluents showed that an additional 90 percent removal was possible. At the low loading condition aerobic system effluent BOD_5's of around 10.0 mg/L were obtained.

8. The regular COD analysis did not resolve all the organic carbon in the thin stillage. As a result of this, the methane production rate was higher by about 50 percent than the expected stoichiometric values. These high production rates were also due to the fact that the rates were reported in terms of soluble BOD and COD removed instead of total BOD and COD. An organic carbon (TOC) balance was conducted around the reactors, and the TOC balance confirmed the gas production rates to be correct.

5.4 Anaerobic Treatment Shock Studies

1. One of the reactors, which was subjected to temporary two-fold hydraulic (and therefore two-fold organic) shock loads, was capable of withstanding such shocks. But care was taken to monitor the volatile acids build up and the drop in pH. However when the flow rate (and therefore the organic loading rate) was tripled, within about 36 hours the system was heading towards failure and hence the shock was terminated.

2. From the standpoint of nutrient shock, depriving external nutrients had very little impact on the performance of the anaerobic system even for a prolonged period of 24 days. This was because there were enough nutrients in the waste itself to suffice the very low cell yield during the anaerobic metabolism.

3. No specific pH shock loading was done. From the informations available during the entire period of research, it was possible to conclude that best pH operating condition was between 6.8 and 7.2. Below a pH of 6.5, due to volatile acids accumulation (2850 mg/L), the VA/ALK ratio increased to greater than 0.5 indicating that the system headed to failure. At this threshold level of total failure, about all that could be done was (i) to reduce the organic loading rate (ii) not to waste the sludge (and thus increase the SRT). However, a similar attempt, to neutralize the pH, when the pH was getting greater than 7.8, proved futile.

4. The anaerobic system suffered no serious set-back in its performance due to the cessation of feed for a week, except in the gas production. The gas production rate plunged down to almost zero within 24 hours since the feed was terminated. There was a spontaneous increase in the gas production rate as soon as the feed was restored. This established that the gas production was primarily a function of organic loading.

5.5 Comparison of Aerobic vs Anaerobic System Performance

From Table XI, which summarizes and compares the system performance of aerobic reactor against the anaerobic reactor, it is apparent that the anaerobic treatment would definitely be a prudent option for a candidate of this type.

TABLE XI

COMPARISON OF AEROBIC AND ANAEROBIC REACTORS
SYSTEM PERFORMANCE

MCRT = 20 days			
COMPONENT	PARAMETER	AEROBIC SYSTEM	ANAEROBIC SYSTEM
FEED	BOD_5 MG/L	5,340	5,250
	pH	8 to 9	7
	Alk. added as $CaCO_3$ mg/L	3,000 to 4,000	750 - 1500
REACTOR	HRT days	2	5
	pH	~ Neutral	~ Neutral
	MLSS mg/L	12,900	2,300
	MLVSS mg/L	11,300	1,900
	Yt BOD_5	0.53	0.13
	Kd day^{-1}	0.06	0.02
	F/M	0.24	0.52
EFFLUENT	BOD_5 mg/L	65	53
	SS mg/L	250	240
	VSS mg/L	210	170
	% Removal	98.8	99
Gain or Loss		Needs 0.3 lb O_2/lb BOD removed	Generates ~ 15 Cft CH_4/lb BOD removed

5.6 Suggestions for Future Work

1. Studying the effects of influent solids (which are otherwise separated and sold as cattle feed) upon gas production as well as on substrate removal could be very valuable, if the integrated-utility-system (IUS) is one option.

2. A modified and improved COD analysis may be required to write a perfect mass balance for wastes such as the ones studied; acid hydrolyzing the waste and breaking down the complex organic matter before the COD analysis might possible be one approach. Similarly more TKN analyses, both on influent and effluent, need to be done to exactly quantify the nitrogen requirements during anaerobic metabolism.

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