SYNTHETIC FUEL (ALCOHOL PRODUCTION) WASTEWATER TREATMENT: SUSPENDED GROWTH ANAEROBIC STUDIES

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SUMMARY

Anaerobic suspended growth activated sludge treatability studies were conducted on fuel alcohol wastewater to develop performance information and the data necessary for evaluation of reaction kinetics. The kinetics of substrate removal were shown to be a function of the mass substrate loading. 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. The fuel alcohol wastewaters are highly biodegradable and can be successfully treated to high levels by anaerobic suspended growth systems.

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. The protein and carbohydrate content of the anaerobic biological sludge makes 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. The quality of the methane gas was determined to be a fuction of the F/M ratio or SRT operating condition of the system.

STATEMENT OF PROBLEM

Both government and the private sector have generally agreed that alcohol fuels can play a part in the national fuel policy. During the last few years, several alcohol production facilities ranging in size from 200,000 to 3,000,000 gallons per year have been developed in Oklahoma and adjoining states. There are problems in all of these facilities in handling and treatment of the wastes associated with the alcohol production process. Fuel alcohol technology is new and still in the developing stages. Thus, the majority of the efforts to date have centered around fuel alcohol production instead of environmental concerns. The environmental problems associated with the wastewaters from alcohol production must be solved for this synthetic fuel option to become a feasible addition to our nation's energy alternatives.

The high strength wastewaters produced during fuel alcohol production at the Oklahoma State University fuel alcohol research facility and the full-scale facility at Hydro, Oklahoma, have been subjected to characterization studies, pretreatment studies, and biological treatment studies by the activated sludge process. These wastewaters have been investigated with respect to treatment, recycle, and reuse options. These biological studies have consisted of aerobic activated sludge studies. 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 required for mathematically modeling the treatment process. This information provided the necessary data to develop preliminary concept designs of the activated sludge process for fuel alcohol wastewater treatment.

These research efforts have centered on only one treatment alternative, the aerobic activated sludge process. Other treatment alternatives must be investigated to provide the information required to determine the most feasible and economical alternative for fuel alcohol wastewater treatment. Aerobic treatment is possible, but may be expensive due to the high oxygen requirements and energy consumption. An alternative to aerobic treatment that has been investigated is anaerobic treatment. Anaerobic treatment of high strength wastewaters often offers advantages over aerobic treatment processes due to reduced operating costs and energy consumption. The process, on a large enough scale, can even be a significant source of energy. The methane gas produced could be used as a source of energy in the alcohol plant; for example, methane gas could be used for grain drying, cooking, and temperature control.

The purpose of the research reported here was to continue the wastewater treatment studies of fuel alcohol wastewater, including anaerobic treatment studies. The raw stillage or wastewaters were treated in anaerobic, bench-scale, continuous flow, activated sludge studies to determine the treatability, performance evaluation, and biokinetic constants for anaerobic treatment. Now the advantages and disadvantages of both aerobic and anaerobic treatment can be compared to determine the most feasible and economical alternative for biological treatment of fuel alcohol wastewater.

MATERIALS AND METHODS

Typical thin stillage or wastewater characteristics, as presentd in Table 1, were collected from the Oklahoma State University Agricultural Engineer's 200,000 gallon per year capacity fuel alcohol research facility and from the 3,000,000 gallon per year plant at Hydro, Oklahoma for use in the anaerobic activated sludge studies. These wastewaters were subjected to pretreatment by gravity settling, and the supernatant was then used in the biological treatment studies.

Bench-scale, complete mix, continuous flow anaerobic activated sludge systems were used in these studies to evaluate the anaerobic treatability of the fuel alcohol wastewaters. These systems were plexiglass with 7.2 liter mix tank reactor volumes and 3.5 liter settling compartment volumes. The wastewaters were pumped from feed tanks to the mix tank reactors, and the treated effluent flowed by gravity from the settling compartments to effluent collection tanks. The influent wastewater flow rates were regulated and carefully controlled to provide the desired hydraulic retention times.

An aerobic continuous flow activated sludge system was operated on the treated effluent from the 20-day SRT anaerobic system. This system consisted of 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. The purpose of this aerobic system was for polishing of the anaerobic system effluent. However, the treatment performance of the anaerobic systems were much higher than anticipated, and the aerobic system was only operated for a short time period.

Table 1. Raw Wastewater (Thin Stillage) Characteristics

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	--	3.5-4.0	--

*All units in mg/L except pH.

Waste sludge from the continuous flow anaerobic reactors were removed periodically for batch studies to evaluate batch treatment kinetics. The waste sludge was mixed for 12 hours for stabilization and then fed raw wastewater at different food-to-microorganism (F/M) ratios. The performance of these systems was monitored with time.

The continuous systems were operated to control the growth rate or sludge retention time (SRT) by wasting sludge on a daily basis. During the treatability studies, the hydraulic retention time, the hydraulic flow rate, and the sludge retention times were maintained constant. The data from these systems were analyzed to provide performance information and biokinetic constants required for design by the Kincannon and Stover design model.

The wastewaters and effluents of the biological systems were monitored with respect to BOD_5, COD and TOC according to the procedures in Standard Methods. System operating characteristics were also monitored with respect to pH, effluent suspended solids, sludge settling and dewatering characteristics. The wastewater and mixed liquor pH was controlled by adding alkalinity in the form of sodium hydroxide. The treated effluent alkalinity and volatile acid contents were continuously monitored. The protein and carbohydrate contents of the biological sludges and stillage solids were also monitored for determination of reuse potential.

The Kincannon and Stover activated sludge design model was employed for evaluation of the anaerobic system data because it is the only model that expresses substrate utlization as a function of mass substrate loading. A such, it is the only design model that eliminated scatter in the determination of biokinetic constants. Therefore, the Kincannon and Stover model provides a more conservative design based on consistent achievement of the effluent criteria when maintaining the specific loading rate of F/M ratio at the design value.

The design equation, derived for direct solution of the reactor tank volume, was developed by writing a material balance around the system describing the mass rate of change in substrate. Mathematical description of the substrate utilization rate or $(dS/dt)_g$ in the Kincannon and Stover model is based on monomolecular kinetics with $(dS/dt)_g$ expressed as a function of the mass loading rate or F/M ratio as follows:

$$\left(\frac{dS}{dt}\right)_g = \frac{U_{max} \; X \; \frac{FS_i}{XV}}{K_B + \frac{FS_i}{XV}} \qquad (1)$$

where:

F - flow rate

S_i - influent substrate concentration

X - mixed liquor solids concentration

V - reactor volume

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

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

Substitution of this substrate utilization rate term into the substrate material balance around the reactor or around the entire system and solving for the reactor volume, V, provides the required reactor tank volume by this design method as follows:

Mass Balance Around Entire System

$$V = \frac{FS_i/X}{\frac{U_{max}S_i}{S_i - S_e} - K_B} \quad (2)$$

Mass Balance Around Reactor

$$V = \frac{FS_i/X}{\frac{U_{max}S_i}{S_i - (1 + \alpha)S_e} - K_B} \quad (3)$$

where:

α = recycle ratio

The required biokinetic constants, U_{max} and K_B, are determined by graphical analysis of the data developed from the treatability study. When the reciprocal of $U = F(S_i - S_e)/XV$ is plotted as a function of the reciprocal of $F/M = FS_i/XV$, the y-axis intercept is the reciprocal of U_{max} and the slope is equal to K_B/U_{max}.

TEST RESULTS

The operating characteristics of the continuous flow anaerobic system studies are presented in Table 2. 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 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

Table 2. Average Continuous Flow Anaerobic System Opeating 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	C_aCO_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

(continued

Table 2. (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

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 to 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 2 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, the protein and carbohydrate fraction of the biological solids both increased as the growth rate increased. 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 3. As observed in Table 3, the treatment efficiency in terms of BOD_5, COD and TOC removals was very high when the SRT was maintained at 10 days or greater. Removal efficiencies of 98 to 99 percent were easily obtainable even with the full strength stillage at the SRT of 30 days. Greater than 97 percent $sBOD_5$ removal was achieved at the F/M ($sBOD_5$/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.

In Figure I 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, and TOC for the continuous anaerobic 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 I 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, repectively. The

Table 3. Summary of Continuous Anaerobic System Treatment Performance

SRT (days)	F/M	Influent (mg/L)	Effluent (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

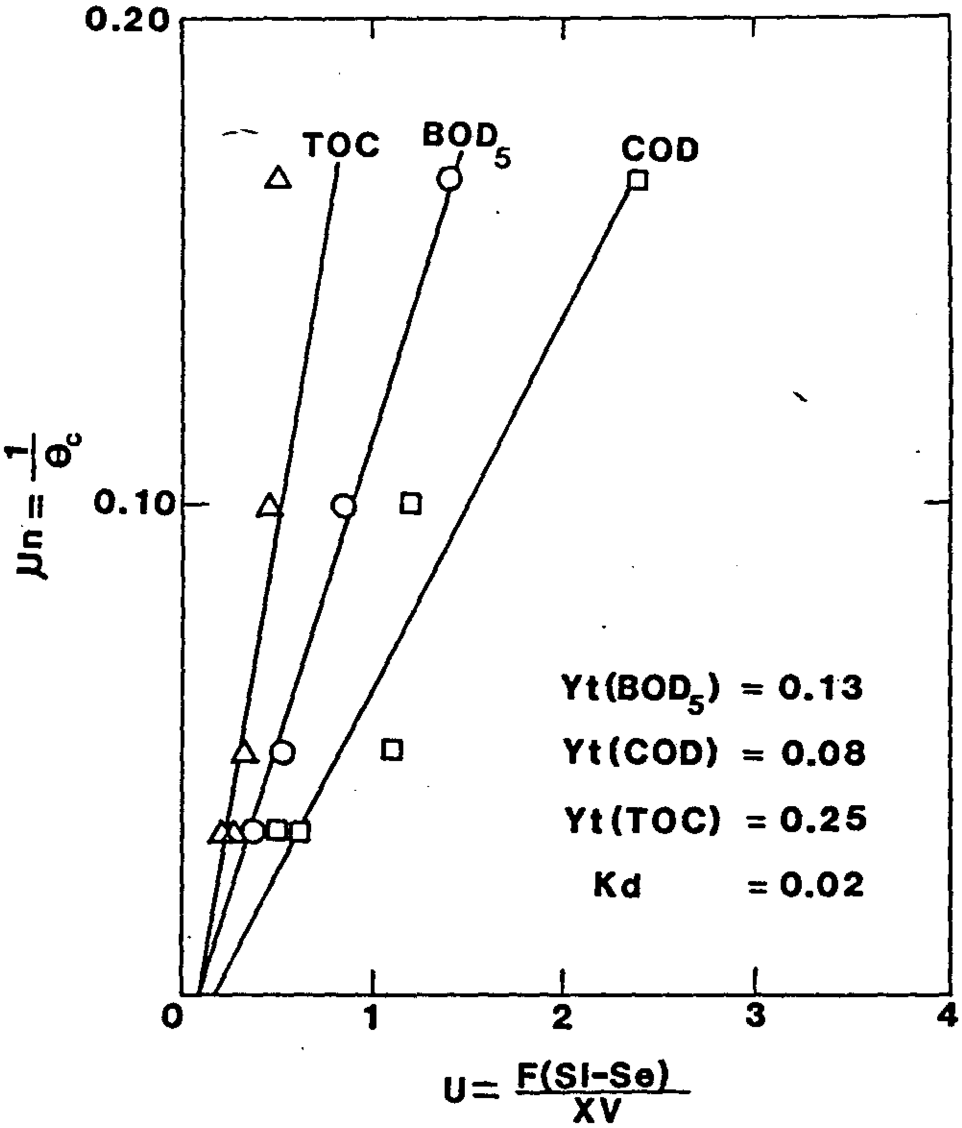

Figure 1. Graphical determination of Yt and Kd in terms of BOD_5, COD, and TOC.

endogenous decay coefficient was found to be essentially independent of the specific substrate 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 2, 3, and 4, 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. In Figures 5, 6, and 7, 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 substrate 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.

The results of the short-term aerobic activated sludge studies treating the effluent from the anaerobic systems are summarized in Table 4. Depending on the organic loadings and operating conditions of these systems, as high as 90 percent additional removal of the anaerobic system effluent BOD_5's were achieved. At the low loading condition aerobic system effluent BOD_5's of around 10.0 mg/L were obtained.

Waste sludge from the anaerobic systems was used periodically in batch anaerobic activated sludge studies to evaluate batch removal kinetics compared to continuous system kinetics. The results of three of these experiments are summarized in Table 5. Runs number one and three are also summarized in Figures 8 and 9 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

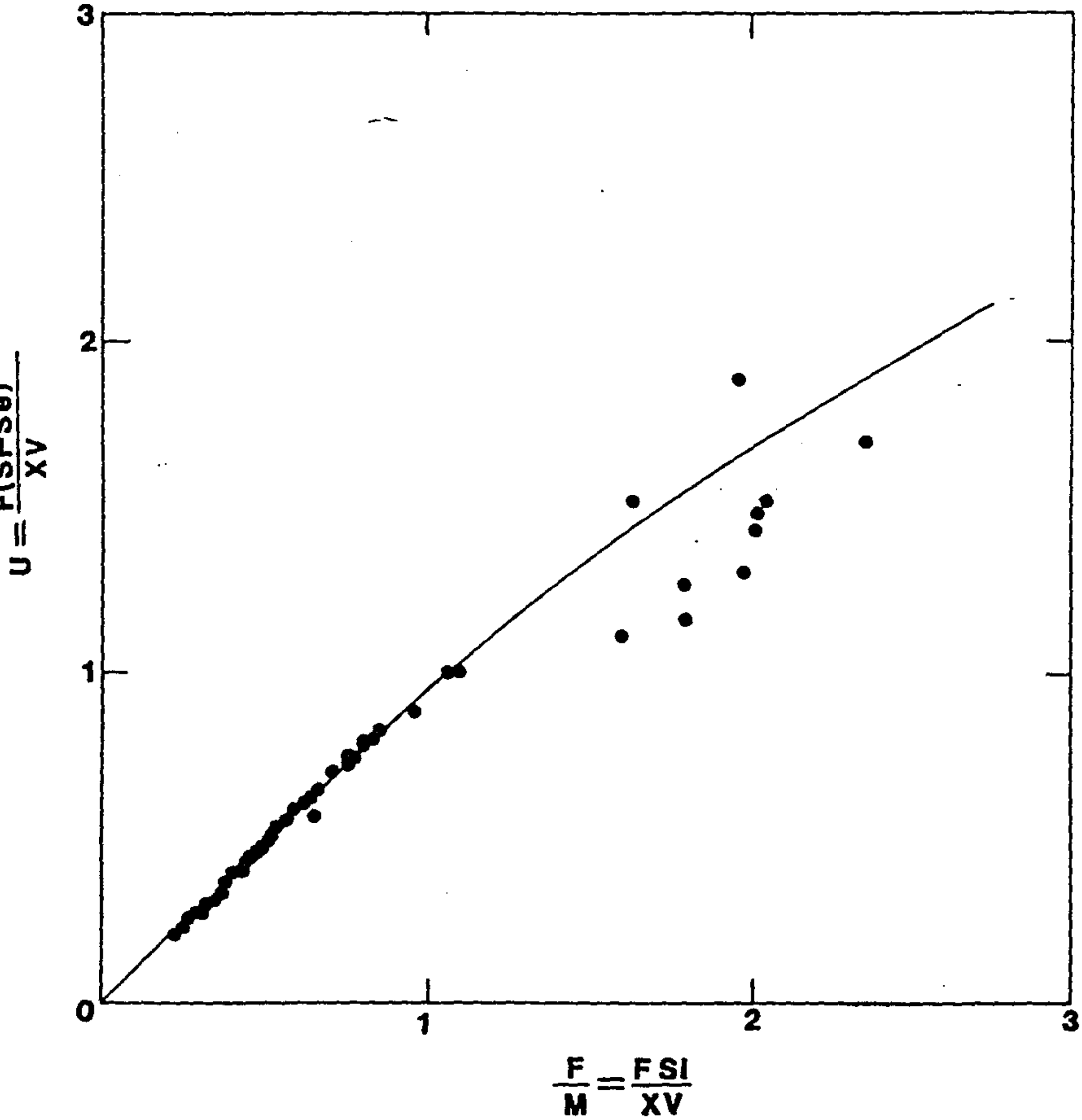

Figure 2. Substrate utilization as a function of mass substrate loading in terms of BOD_5.

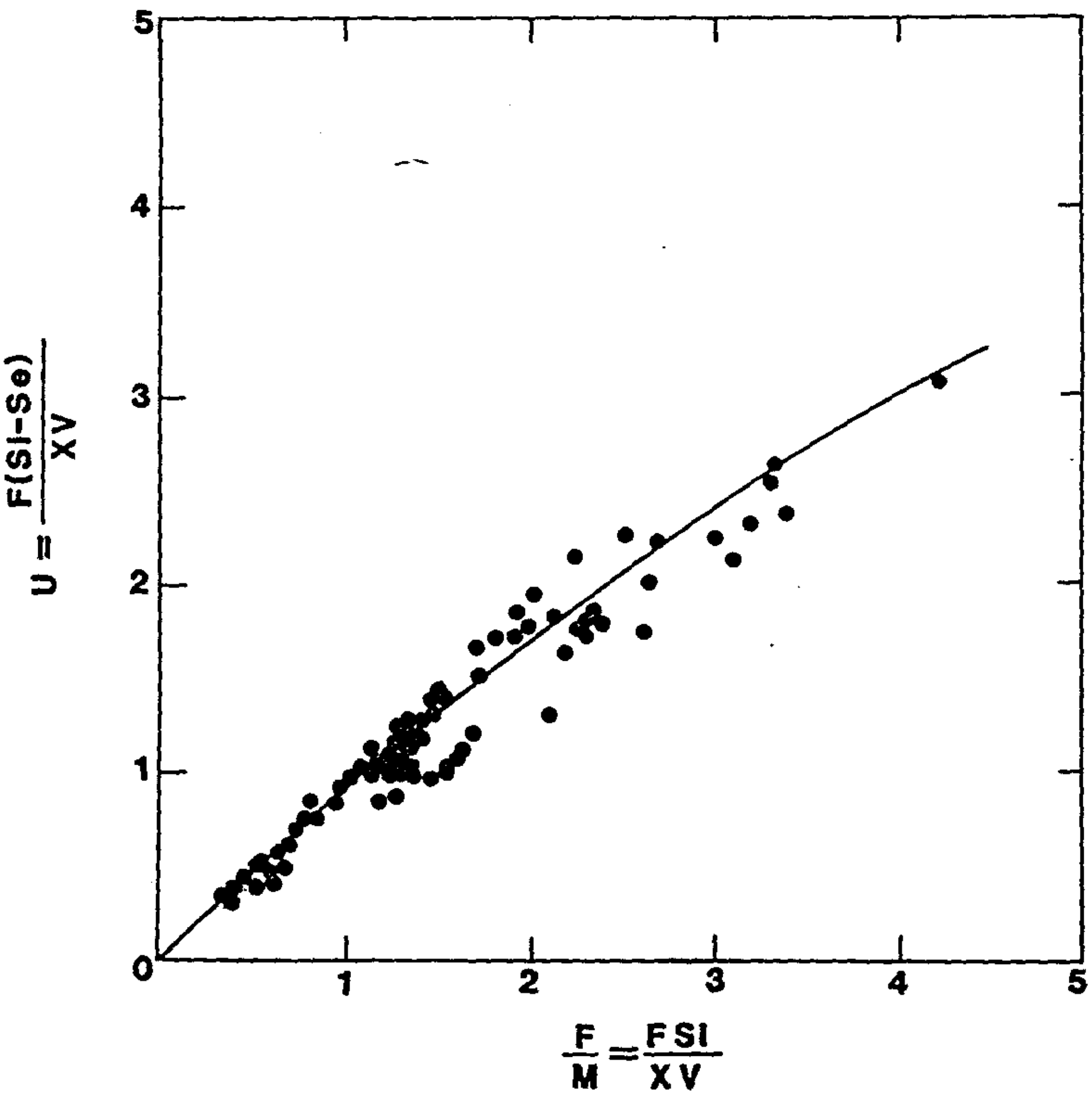

Figure 3. Substrate utilization as a function of mass substrate loading in terms of COD.

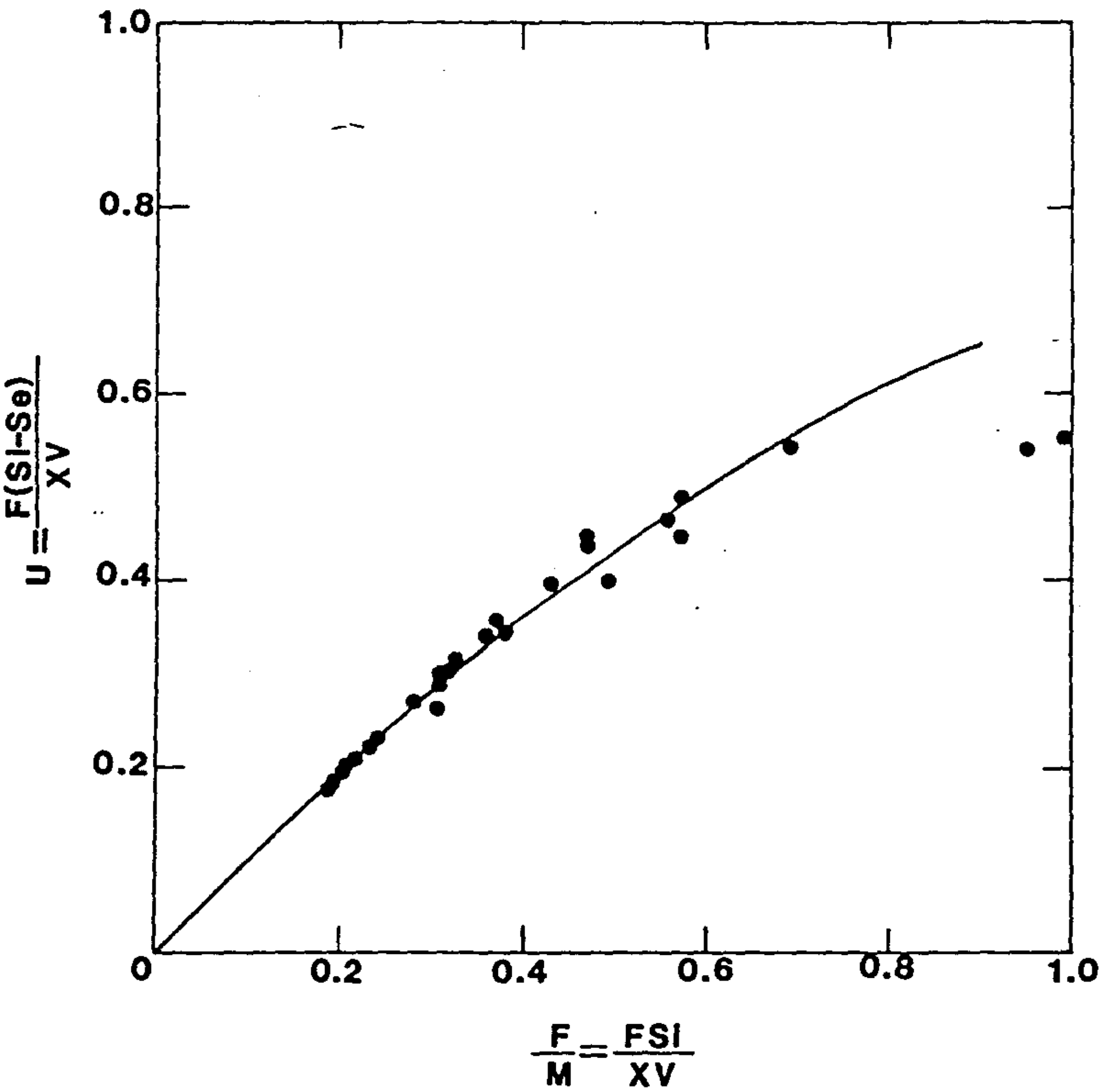

Figure 4. Substrate utilization as a function of mass substrate loading in terms of TOC.

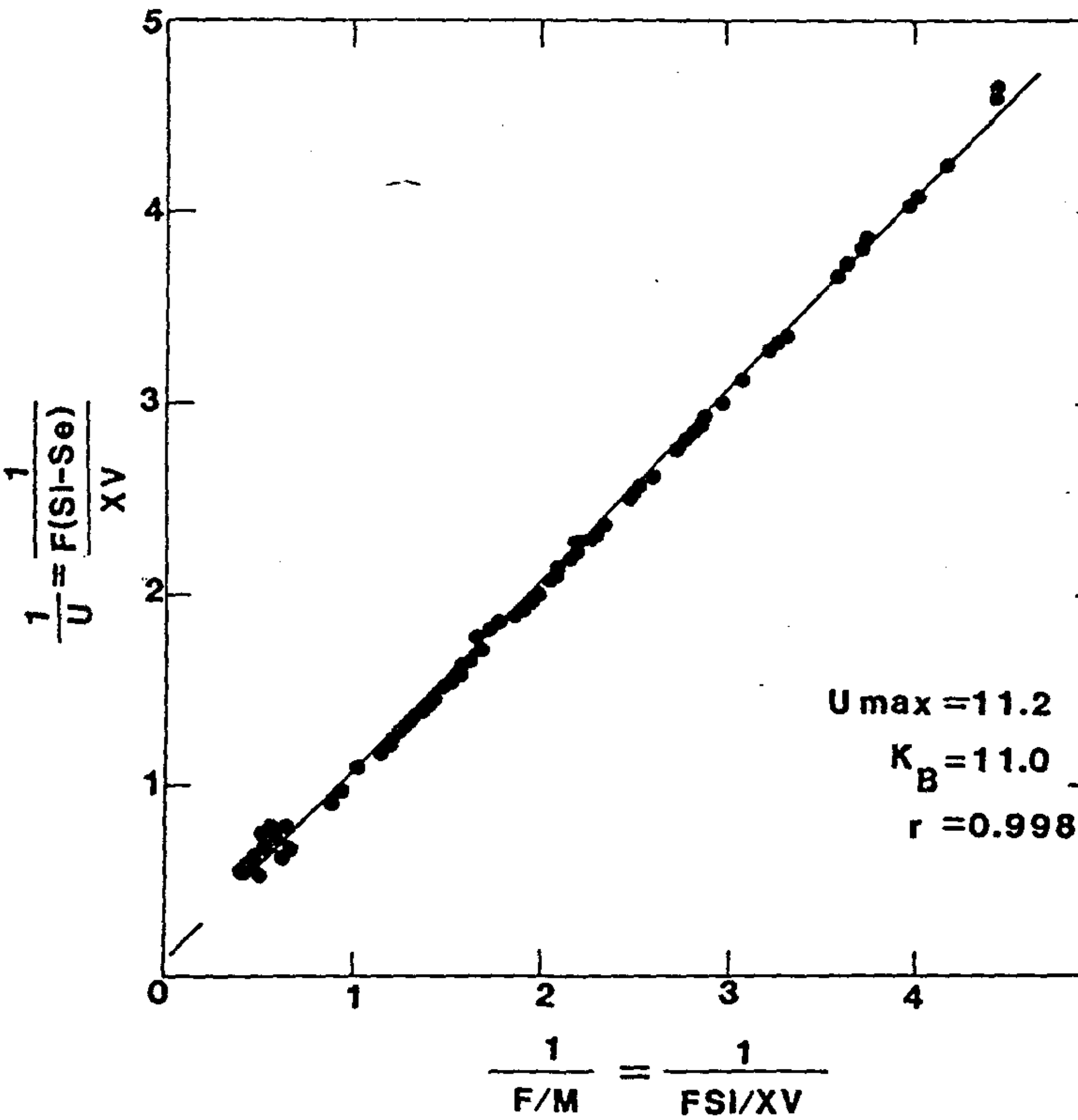

Figure 5. Graphical determination of U_{max} and K_B in terms of BOD_5.

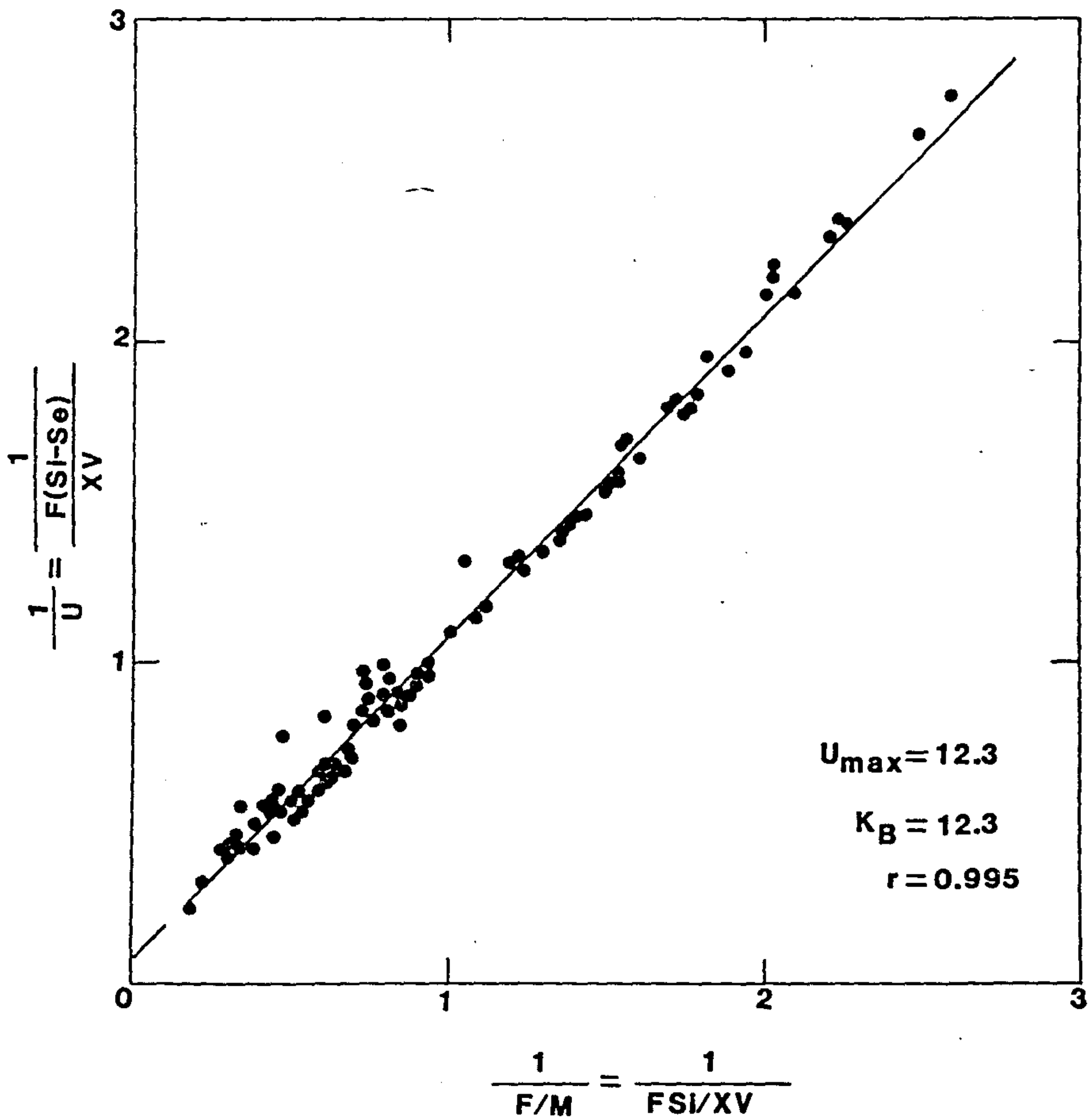

Figure 6. Graphical determination of U_{max} and K_B in terms of COD.

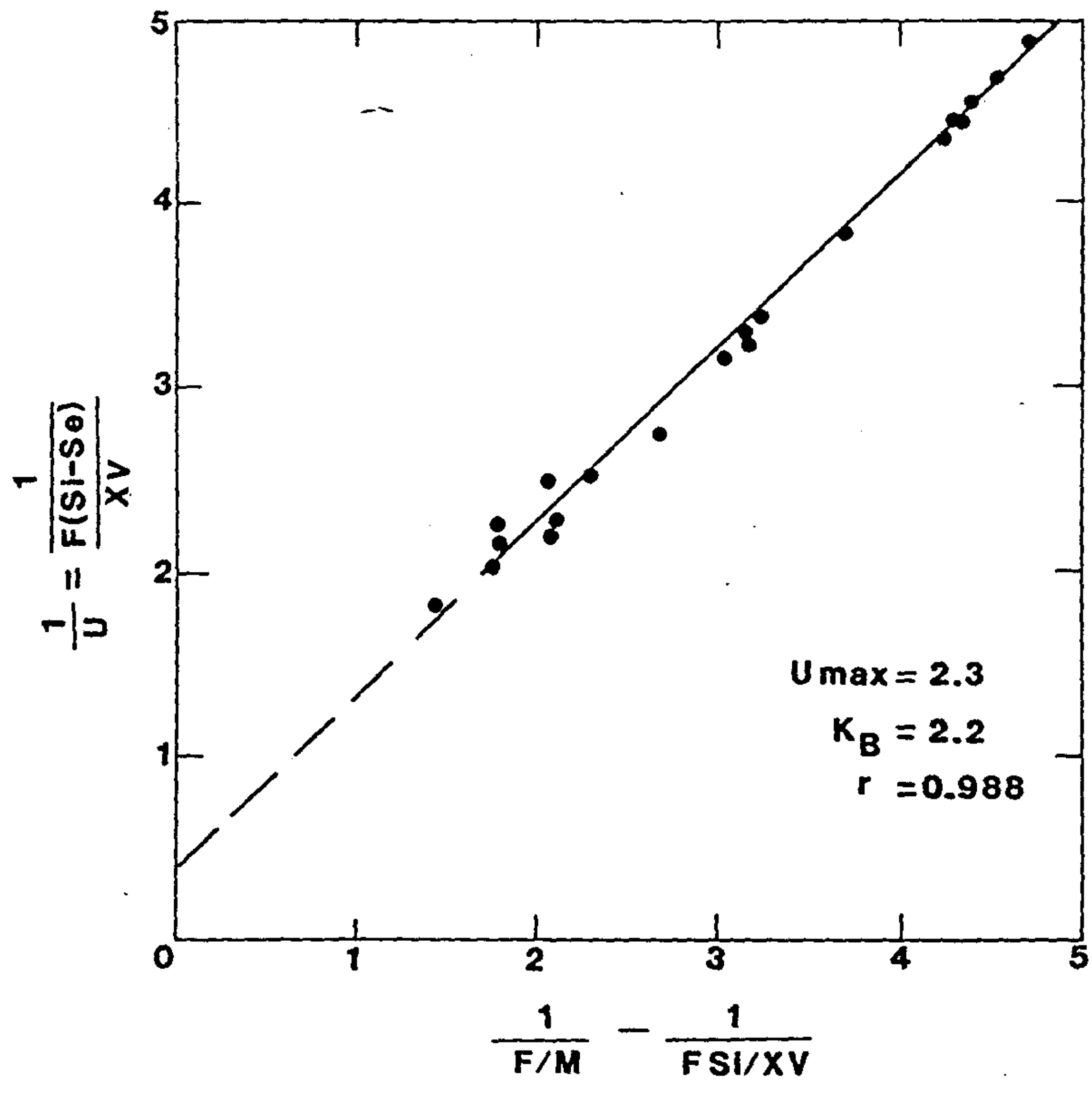

Figure 7. Graphical determination of U_{max} and K_B in terms of TOC.

Table 4. Performance Summary of Aerobic Systems Following Anaerobic Systems

F/M	MLVSS (mg/L)	Influent (mg/L)	Effluent (mg/L)	Removal %
		Soluble BOD_5		
0.03	1800	100	10	90.0
0.10	3500	700	80	88.6
		Soluble COD		
0.11	1800	400	120	70.0
0.15	3500	1100	180	83.6

Table 5. 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 hours

Temp. = 37-40°C

pH = 6.9-7.3

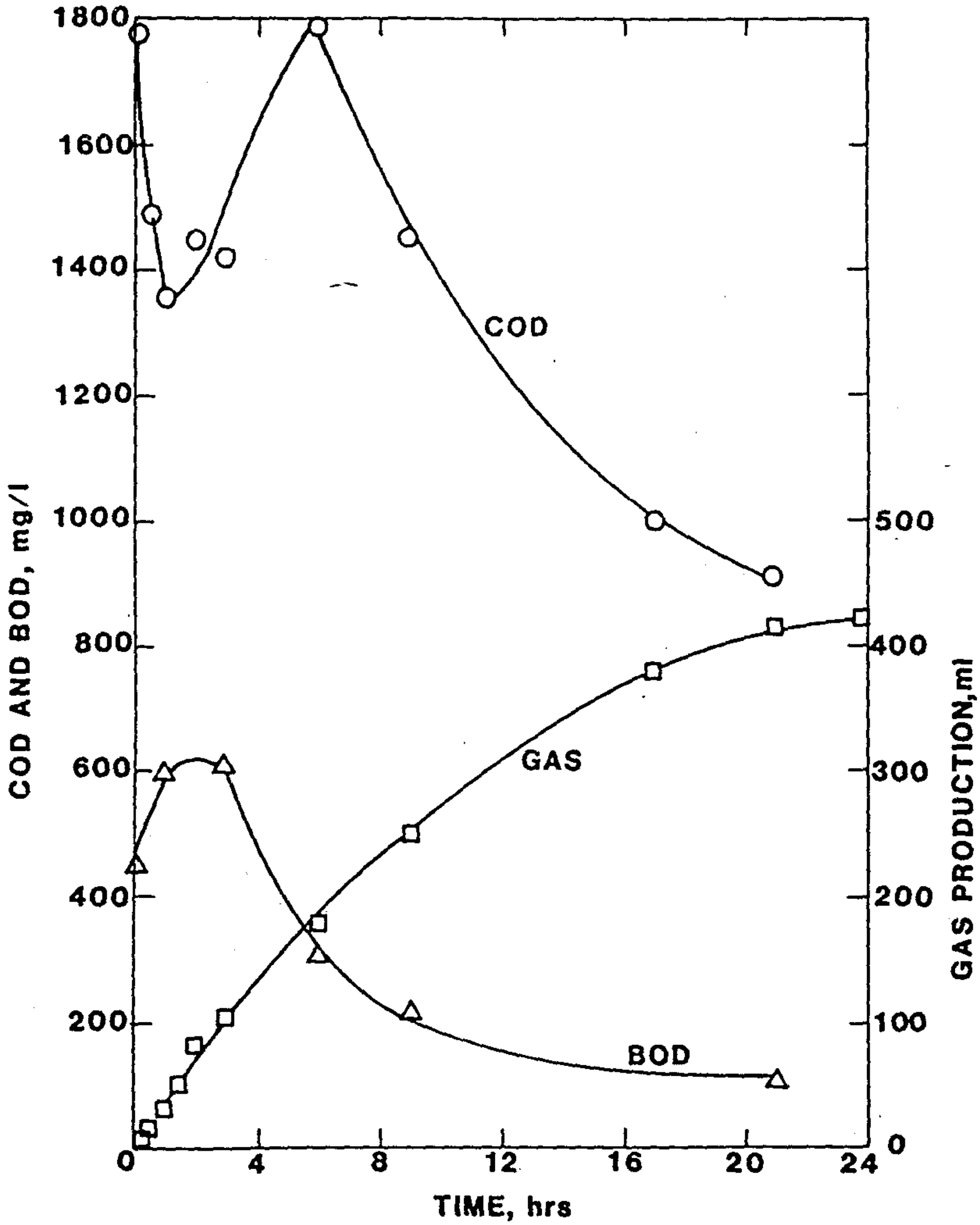

Figure 8. Batch anaerobic system removal characteristics at low F/M ratio.

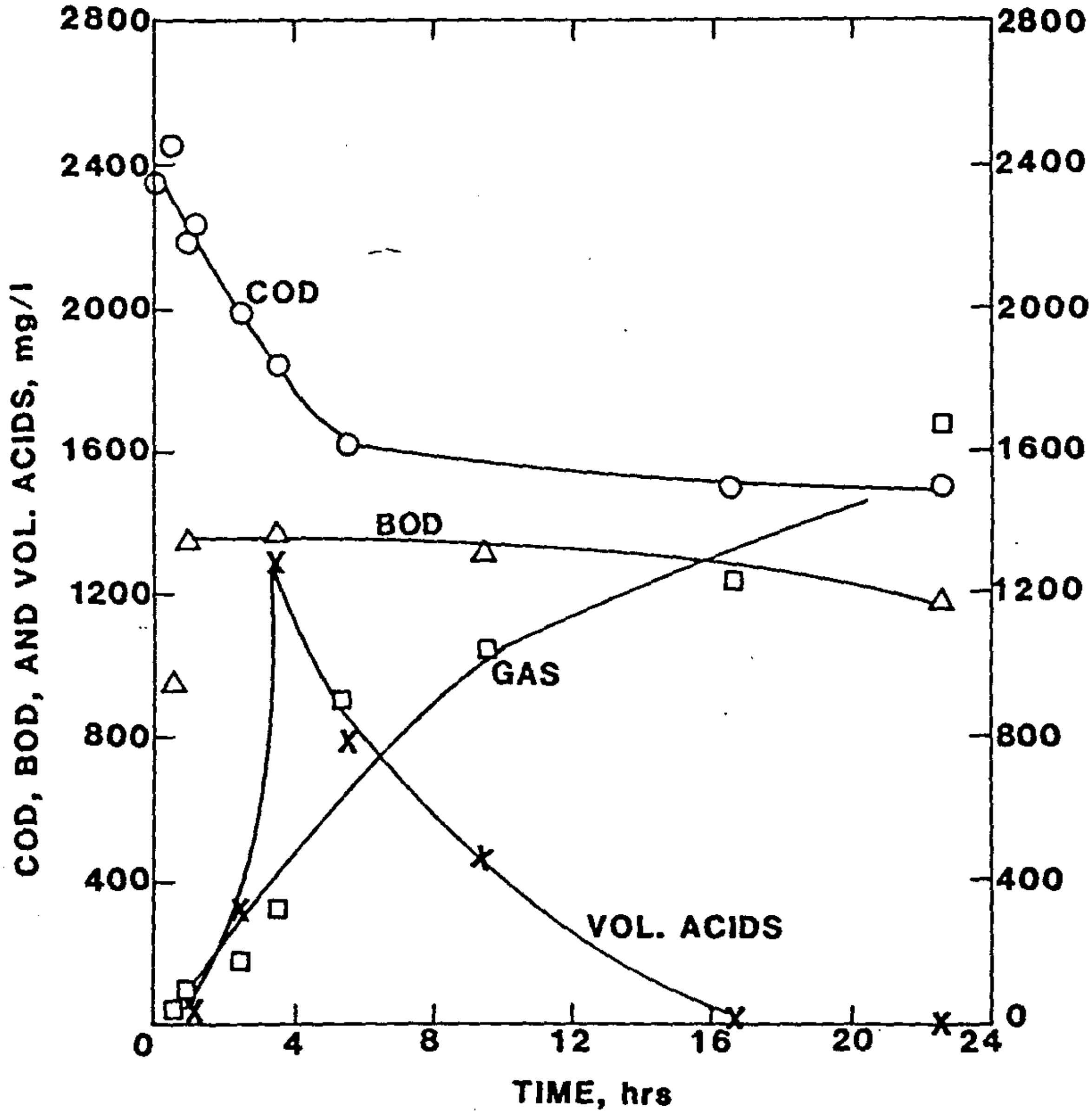

Figure 9. Batch anaerobic system removal characteristics at high F/M ratio.

MEETINGS ATTENDED, PRESENTATIONS AND PUBLICATIONS

Four technical papers have been presented at national meetings during the conduct of this project, as follows:

1. Stover, E. L. and Gomathinayagam, G., "Activated Sludge Treatability of Fuel Alcohol Production Wastewaters," presented at the 1982 Summer National American Institute of Chemical Engineers Meeting, Cleveland, Ohio (August 1982).
2. Stover, E. L. and Gomathinayagam, G., "Biological Treatment of Synthetic Fuel (Alcohol Production) Wastewater," presented at the 55th Annual Water Pollution Control Federation Conference, St. Louis, Missouri (October 1982).
3. Stover, E. L. and Gomathinayagam, G., "Biological Treatment Kinetics of Alcohol Production Wastewaters," presented at the 1982 Winter Meeting of the American Society of Agricultural Engineers, Chicago, Illinois (December 1982).
4. Stover, E. L., Gomathinayagam, Gl, and Gonzalez, R., "Anaerobic Treatment of Fuel Alcohol Wastewater by Suspended Growth Activated Sludge," presented at the 38th Annual Purdue Industrial Waste Conference, West Lafayette, Indiana (May 10-12, 1983).