# SYNTHETIC FUEL (ALCOHOL PRODUCTION) WASTEWATER TREATMENT:

# FIXED-FILM AND SUSPENDED GROWTH ANAEROBIC STUDIES

# E-032

by

# ENOS L. STOVER

# GANAPATHI GOMATHINAYAGAM

# REINALDO GONZALEZ

PROJECT COMPLETION REPORT WATER RESEARCH CENTER

PROJECT NO. 1-1-50660 (Y)

.

JULY 1984

# PROJECT COMPLETION REPORT

# SYNTHETIC FUEL (ALCOHOL PRODUCTION) WASTEWATER TREATMENT: FIXED-FILM AND SUSPENDED GROWTH ANAEROBIC STUDIES

#### SUMMARY

Anaerobic fixed-film and suspended growth treatability studies were conducted on alcohol wastewaters to develop performance information and the data necessary for evaluation of reaction kinetics. The kinetics of both substrate removal and gas production were found to be a function of mass loading. It was possible to establish that the substrate utilization rate in anaerobic systems was dependent on the F/M ratio as described by the Stover and Kincannon design model. Another important observation made during these studies was that both the gas production and gas quality were also found to be dependent on mass substrate loading. Additional observations using suspended growth systems, as a continuation of the previous years study confirmed these findings.

A mass balance was conducted around a one million gallon per year alcohol production plant, and it was estimated that using the methane gas, generated from an anaerobic treatment plant treating the thin stillage, could save 50% to 70% of the total energy requirements in fuel alcohol production.

#### 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 fullscale 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 and anaerobic 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 processes 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.

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 using anaerobic treatment systems. The raw stillage or wastewaters were treated in anaerobic, bench-scale, continuous flow completely mixed activated sludge and packed-bed reactors to determine the treatability, performance evaluation, and biokinetic constants for anerobic treatment. Now the advantages and disadvantages of both suspended growth and fixed-film aerobic and anaerobic treatment can be compared to determine the most feasible and economical alternative for biological treatment of fuel alcohol wastewater. The results of the anaerobic treatment studies are presented herein.

#### MATERIALS AND METHODS

Typical thin stillage or wastewater characteristics, as presented 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.

Parameter <sup>*</sup>	Corn Fee	dstock	Milo Feeds	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 <sub>5</sub>	26,900	800	34,900	2,000	
Soluble BOD <sub>5</sub>	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	<del>.</del> -		
Soluble TKN	480	95			
Soluble NH <sub>3</sub> -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		

Table 1. Raw Wastewater (Thin Stillage) Characteristics

\* All units in mg/l except pH.

.

#### Suspended Growth System

Bench scale, complete mix, continuous flow anaerobic activated sludge systems used in these studies were plexiglass reactors. The mixing compartment was 7.2 liters and the settling compartment was 3.5 liters in volume. The wastewaters were pumped from feed tanks to the reactors, and the treated effluent flowed by gravity from the settling compartment to effluent collection tanks. During the period of data collection, all system parameters, including the hydraulic retention time and the sludge retention time were maintained constant. 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. The successful operation of anaerobic treatment could be accomplished to a greater degree by a continuous watch on volatile acids and alkalinity. Hence, effluents were monitored for these in addition to the system operating characteristics such as pH, effluent suspended solids, sludge settling, and dewatering characteristics.

#### Fixed-Film System

The reactor was made out of plexiglass with a total empty bed reactor volume of 0.5 ft<sup>3</sup> (14.2 liters). The plastic media packing had a specific surface area of 42 ft<sup>2</sup>/ft<sup>3</sup> and was contained in 0.4 ft<sup>3</sup> of the total reactor volume yielding a total surface area of 16.8 ft<sup>2</sup>. The influent wastewater was pumped into the bottom of the reactor and distributed by a distribution plate. The wastewater flowed up through the reactor bed and out the side of the reactor. A small amount of headspace or freeboard (0.1 ft<sup>3</sup>, 2.8 liters) was provided at the top of the reactor. Both the hydraulic residence time and the total substrate loading were changed by varying both the hydraulic flow rate and substrate concentrations. Samples were collected both from the top of the reactor (or the effluent line) and from the bottom for comparison.

------

# SUBSTRATE REMOVAL KINETICS FOR SUSPENDED GROWTH SYSTEMS

When considering a reactor volume, a mass balance of substrate into and out of that reactor volume can be made as follows:

Mass of		Mass of		Mass of
substrate	-	substrate	+	substrate
into the	-	out of the	•	consumed
reactor		reactor		biologically

In the case of a suspended growth system, the reactor volume is expressed in million gallons with the resultant mass balance equation:

$$FS_{i} = FS_{e} + \left(\frac{dS}{dt}\right)_{G} V$$
 (A)

where

$$F = flow rate, MGD$$

$$S_{i} = influent substrate concentration, mg/l$$

$$S_{e} = effluent substrate concentration, mg/l$$

$$V = reactor volume in million gallons$$

$$\left(\frac{dS}{dt}\right)_{G} = specific substrate utilization rate, lb/lb·day$$

Mathematical description of this substrate utilization rate as a function of the substrate loading rate or food-to-microorganism ratio (F/M) based on monomolecular kinetics follows:

$$\left(\frac{dS}{dt}\right)_{G} = U = \frac{U_{max} \frac{FS_{i}}{XV}}{K_{B} + \frac{FS_{i}}{XV}}$$
(B)

where

FS<sub>i</sub> XV = F/M = food to microorganism ratio lb/lb·day U = specific substrate utilization rate, lb/lb·day U<sub>max</sub> = maximum specific substrate utilization rate, lb/lb·day K<sub>B</sub> = proportionality constant or substrate loading at which the rate of substrate utilization is one-half the maximum rate, lb/lb·day

Substitution of Equation (B) into Equation (A) and solving for the reactor volume, V, or the effluent quality,  $S_e$ , provides the design equation or the effluent quality predictive equation to be used for operations, respectively.

The operating characteristics and performance of the continuous flow anaerobic system studies are presented in Table 2. In this table, the loading rate (F/M), influent feed, and treated effluent, percentage of methane, and the system-performance are presented.

Table 2.	Anaerobic Treatment	System Perf	ormance
	In Terms of BOD	(COD).	

Suspended arowen systems					
Loading Rate F/M	Influent mg/l	Effluent mg/%	% Removal	Methane percent	Methane* Production Ft <sup>3</sup> /1b BOD (COD)
0.22	2,300	15	99.4	78	21.1
(0.50)	(5,125)	(380)	(92.6)*		(9.9)
0.23	4,100	28	99.3	71	20.7
(0.56)	(10,100)	(380)	(96.2)		(8.8)
0.31	8,800	35	99.6	70	15.7
(0.55)	(16,000)	(425)	(97.3)		(8.5)

Suspended Growth Systems

\*Based on soluble BOD (COD) removed.

### SUBSTRATE REMOVAL KINETICS FOR FIXED-FILM SYSTEMS

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

$$U = \left(\frac{dS}{dtA}\right)_{G} = \frac{U_{max} \frac{FS_{i}}{A}}{K_{B} + \frac{FS_{i}}{A}}$$
(C)

where

$$F = flow rate, million gallons per day (MGD)$$

$$S_{i} = influent substrate concentration, mg/l$$

$$A = surface area of a specific volume of media, 1000 ft^{2}$$

$$U_{max} = maximum specific substrate removal rate, 1bs/day/1000 ft^{2}$$

$$K_{B} = proportionality constant, 1bs/day/1000 ft^{2}$$

$$FS_{i} = applied substrate loading rate, 1bs substrate applied/day/1000 ft^{2}$$

$$U = \left(\frac{dS}{dtA}\right)_{G} = specific substrate utilization rate, 1bs substrate removed/day/1000 ft^{2}$$

This expression for substrate utilization can then be substituted into if the mass balance equation for substrate into and out of a particular volume of media in the anaerobic fixed-film reactor, as follows:

mass of substrate into the volume of media	=	mass of substrate out of the volume of media		+	mass of substrate consumed biologically	
FSi	2	FS <sub>e</sub>	+	$\left( \begin{array}{c} dS \\ \overline{dt} \end{array} \right)$	, A G	(D)

where

$$S_{a}$$
 = effluent substrate concentration, mg/L

By making this substitution the following relationship is obtained:

$$FS_{i} = FS_{e} + \frac{U_{max} \frac{FS_{i}}{A}}{\frac{K_{B} + \frac{FS_{i}}{A}}{A}} A$$
(E)

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

$$A = \frac{FS_{i}}{U_{max}S_{i}} - K_{B}$$
(F)

$$S_e = S_i - \frac{U_{max} S_i}{K_B + \frac{FS_i}{A}}$$
 (G)

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

In order to use these expressions, the biological kinetic constants,  $U_{max}$  and  $K_{B}$ , must be determined experimentally. These constants can be easily determined by operating an anaerobic fixed-film reactor at different substrate loading rates and monitoring the associated substrate removal characteristics.

The data in Tables 3, 4, and 5 was collected during treatability studies with high strength wastewaters generated during the production of fuel alcohol from grain by fermentation reactions. Table 3 presents the average influent wastewater feed characteristics to the reactor and Table 4 presents the average

S <sub>i</sub> * mg/l	F L/D	рН	Alk. mg/l as CaCO <sub>3</sub>	S.S. mg/l	۷.S.S. mg/l
1777 (2512)	2.88	6.6-8.5	2580	443	359
3968 (5696)	2.81	6.0-6.6	2400	702	582
7485 (10102)	2.87	5.2-5.9	3222	1250	1058
12167 (18445)	3.22	5.1-5.6	2763	1409	1100
6450 (8300)	6.28	5.0-6.8	3900	563	554
15499 (23911)	4.45	5.1-6.3	3206	1352	887
6797 (9851)	9.30	5.2-7.3	-:	576	491
12742 (21429)	11.54	5.1-7.4	4480	440	354
12233 (16022)	16.66	5.8-9.0	4311	456	321
15259 (21362)	14.40				

Table 3. Influent Feed Characteristics

\*S; = Soluble BOD(COD)

- - - - -

\_\_\_

- - -

. .

J.

Average values at each operating condition

÷,

Se <sup>*</sup> mg/L	рН	Temp. oC	Alk. mg/l as CaCO <sub>3</sub>	V.A. mg/l as CH <sub>3</sub> COOH	S.S.** mg/l	** V.S.S. mg/l
34 (131)	7.0-8.1	38-39	1059	0 (Eff)	156	117
57 (215)	7.8-7.9	35 <del>-</del> 39	1500	0 (Eff)	234	159
140 (271)	7.8-8.0	31-35	1020	0 (Eff)	318	207
390 (756)	7.1-7.7	31-36	1700	0 (Eff)	804	550
515 (742)	6.5-7.1	35-37	1085	190 (Eff)	542	400
2495 (3159)	5.6-7.7	36-39	2291	2405 (Eff)	787	509
1024 (1484)	6.5-7.2	32-37	1854 .	605 (Eff)	385	341
2974 (3800)	7.0-7.1	34-36	5050	3000(Eff) (300)(Bot	) 289 )	224
5493 (5927)	6.0-7.6	32-36	4036	3846(Eff) (598)(Bot	) 598 )	408
10955 (14242)			3100	3200(Eff 2400(Bot)	)	

Table 4. Effluent Characteristics

\*Soluble (BOD(COD) \*\* Clarifier Solids

\$F

Average values at each operating condition

(Eff) - Effluent Sample

(Bot) - Sample from bottom of reactor

Loading	Removal	%	Ga	s		
Rate Ibs/day/ 1000 ft <sup>2</sup>	Rate lbs/day/ l000 ft <sup>2</sup>	Removal	Production L/D	<sup>%C0</sup> 2	% CH	ft <sup>3</sup> CH <sub>4</sub> 1b removed
0.68 (0.95)	0.66 (0.90)	98 (95)	6.50	21	77	16.80 (13.0)
1.46 (2.10)	1.44 (2.02)	98 (96)	11.73	23	75	12.79 (9.22)
2.83 (4.01)	2.78 (3.90)	98 (98)	24.16	29	70	12.92 (9.59)
5.14 (7.68)	4.97 (7.36)	97 (96)	49.02	39	60	12.98 (8.69)
5.25 (6.93)	4.82 (6.83)	92 (91)	45.74	40	59	11.59 (9.10)
9.03 (14.44)	7.09 (12.55)	84 (88)	75.03	37	62	13.05 (8.30)
8.28 (12.53)	7.02 (10.63)	85 (85)	56.87	37	62	10.52 (7.26)
19.12 (23.45)	14.52 (18.91)	76 (81)	121.33	39	60	10.34 (5.73)
26.98 (34.82)	14.65 (21.87)	53 (63)	125.68	39	60	10.75 (7.18)
28.85 (40.39)	8.14 (13.5)	28 (33)	40.8			

54 -

Table 5. Substrate Removal and Gas Production

\*Soluble BOD(COD)

Average Values at each operating condition

treated effluent characteristics. This data was collected over a one and onehalf year time period. The system was stabilized at each operating condition prior to the data collection summarized in the tables.

The empty bed hydraulic residence time varied from less than one to around four days. Table 5 presents the analysis of this data in terms of substrate removal and gas production. As can be readily observed in Table 5, both the treatment efficiency and methane production rate decreased as the total substrate loading was increased. The gas guality was around 77 percent methane at an applied BOD loading rate less than 1.0 lb/day/1000 ft<sup>2</sup>. The percent methane decreased until a BOD loading of around 5.0 lbs/day/1000 ft<sup>2</sup> had been reached where it leveled out at 60 percent methane. The total methane production rate per pound of BOD or COD removed also decreased with increased substrate loading rates. The sludge production or cell yield averaged around 0.10 (0.07) pounds of sludge produced per pound of BOD (COD) removed. No volatile acids were observed in the effluent until substrate loadings greater than 5.0 lbs BOD/day/1000 ft<sup>2</sup> were applied to the reactor. As the BOD loading rate was increased above 5.0 lbs/day/ 1000 ft<sup>2</sup>, the volatile acid concentration at the top of the reactor (effluent) increased faster than at the bottom of the reactor. At the highest loading rate of 28.85 (40.39) lbs BOD (COD)/day/1000 ft<sup>2</sup>, the volatile acid content at the bottom and top of the reactor was 2400 and 3200 mg/L, respectively. At this highest loading rate, the reactor was very unstable and difficult to operate. The BOD and COD removals averaged around 30 percent. \*

The substrate data summarized in Table 5 is presented graphically in Figures 1 and 2, where the specific substrate utilization rate is plotted as a function of the applied substrate loading rate in terms of BOD and COD, respectively. The X's represent the average operating data at each test condition, and the circles represent all the data points with a significant amount of overlap of



FIGURE 1. SUBSTRATE UTILIZATION AS A FUNCTION OF MASS SUBSTRATE LOADING IN TERMS OF BOD5.



FIGURE 2. SUBSTRATE UTILIZATION AS A FUNCTION OF MASS SUBSTRATE LOADING IN TERMS OF COD.

data points. These figures demonstrate the substrate removal characteristics as a function of the mass substrate loading rates to the anaerobic reactor. The curves in Figures 1 and 2 can be linearized by plotting the reciprocal of the substrate utilization rate as a function of the reciprocal of the applied substrate loading rate.

The associated reciprocal plots are shown in Figures 3 and 4 for BOD and COD, respectively. From these figures the biological kinetic constants,  $U_{max}$  and  $K_{B}$ , can be determined from the Y-axis intercept and the slope of the line,  $U_{max}$  and  $K_{B}$  in terms of BOD were 58.08, respectively, while these kinetic constants in terms of COD were much higher at 148.92 and 142.55. The correlation of all the data was excellent with correlation coefficients greater than 0.999.

The solid lines in Figures 1 and 2 were drawn using the kinetic constants determined in Figures 3 and 4 at loading rates below 27 (35) lbs BOD (COD)day/ 1000 ft<sup>2</sup>. The calculated maximum substrate utilization rates were much higher than the actual observed rates due to limitations of the methane forming bacteria and increased volatile acid accumulations at higher loading rates. The actual substrate utilization rates peaked out at around 15 (22) lbs BOD (COD)/ day/1000 ft<sup>2</sup> compared to calculated values of 58.35 (148.92). At substrate loading rates greater than 27 (35) lbs BOD (COD/day/1000 ft<sup>2</sup>, the substrate utilization rate actually started decreasing due to volatile acid build-up in the reactor and inhibition or retardation of the methane conversion reactions.

56

#### GAS PRODUCTION KINETICS FOR FIXED-FILM SYSTEMS

Gas production characteristics of the anaerobic reactor data summarized in Table 5 are presented graphically in Figures 5 and 6 as a function of the applied BOD and COD loadings, respectively. The methane content of the gas



FIGURE 3. GRAPHICAL DETERMINATION OF Umax AND  $K_B$  in terms of  $\text{BOD}_{\frac{1}{2}}$  .



÷

\_\_\_\_





FIGURE 5. GAS PRODUCTION CHARACTERISTICS AS A FUNCTION OF MASS SUBSTRATE LOADING IN TERMS OF  $BOD_5$ .



FIGURE 6. GAS PRODUCTION CHARACTERISTICS AS A FUNCTION OF MASS SUBSTRATE LOADING IN TERMS OF COD.

decreased and the carbon dioxide content increased as the applied loadings were increased up to around 9 to 10 lbs/day/1000 ft<sup>2</sup>, at which point the methane content leveled out at 60 percent and the carbon dioxide leveled out at around 39 percent. At loading rates greater than 9 to 10 lbs B0D/day/ 1000 ft<sup>2</sup>, the volatile acid concentration in the effluent had increased significantly with concentrations greater than 1000 mg/ $\ell$ . The total gas production and methane production per pound of B0D or C0D removed decreased as the loading rates were increased over the entire range of loadings studied. The carbon dioxide per pound of B0D or C0D removed increased as the loading rates were increased up to around 9 to 10 lbs/day/1000 ft<sup>2</sup> and then appeared to start decreasing very slowly.

The gas production data presented in Figures 5 and 6 indicated that the total gas production and total methane production were a function of the total applied substrate loading, and therefore, they should respond in a similar manner as the substrate utilization kinetics. In Figures 7 and 8 gas production data was plotted as a function of the mass substrate loadings in order to evaluate the possibility of determining biokinetic constants for use in prediction of gas quantity and quality, as shown in these same figures. As one might expect, the gas production kinetics were, in fact, a function of the applied substrate loading rates and could be described by monomolecular kinetics just like substrate utilization. The gas production kinetics are summarized in Table 6.

The maximum total gas production rate and the methane production rate were predictable. In fact, the maximum rates were found to be identical irrespective of whether they were calculated in terms of BOD or COD. The specific total gas and methane production rates were found to be around 450 and 194 ft<sup>3</sup>day/1000 ft<sup>2</sup>, respectively.



FIGURE 7. TOTAL GAS AND METHANE PRODUCTION KINETICS AS A FUNCTION OF BOD LOADING RATE.



FIGURE 8. TOTAL GAS AND METHANE PRODUCTION KINETICS AS A FUNCTION OF COD LOADING RATE.

Kinetic Constants	BOD <sup>*</sup> Kinetics	COD <sup>*</sup> Kinetics
Maximum Gas Production Rate (ft <sup>3</sup> /day/1000 ft <sup>2</sup> )	446.3	451.3
Proportionality Constant (lbs/day/1000 ft <sup>2</sup> )	21.0	30.7
Correlation Coefficient	0.994	0.995
Maximum Methane Production Rate (ft3/day/1000 ft <sup>2</sup> )	193.9	194.8
Proportionality Constant (lbs/day/1000 ft <sup>2</sup> )	11.5	16.6
Correlation Coefficient	0.993	0.994

Table 6. Gas (Methane) Production Kinetic Constants

Kinetics in terms of soluble BOD and COD removal.

The observed gas production rates were higher than the expected stoichiometric values. These high production rates were due to the fact that the rates were reported in terms of soluble BOD and COD removed instead of total BOD and COD. This wastewater was also a highly complex wastewater containing long chain fatty acids, nucleic acids such as pyridine, and other compounds not readily amenable to the COD test.

Additional testing of the raw wastewater under more stringent oxidation iv conditions toward the end of the study indicated that the COD was actually higher than that reported by the Hach test procedure employed during these studies. Based on these observations, an organic carbon (TOC) balance was conducted around the reactors, and the TOC balance confirmed the gas production rates to be correct. Mathematical description of the gas (methane) production rates can therefore be modeled as the substrate loading rate changes by using monomolecular kinetics. Total specific gas production rate expressed as a function of the mass substrate loading rate follows:

$$G = \frac{G_{max} \frac{FS_i}{A}}{G_B + \frac{FS_i}{A}}$$
(H)

where

G = Specific gas production rate, ft<sup>3</sup>/day/1000 ft<sup>2</sup>  $G_{max} = Maximum specific gas production rate, ft<sup>3</sup>/day/1000 ft<sup>2</sup>$   $G_{B} = Proportionality constant, lbs substrate/day/1000 ft<sup>2</sup>$   $\frac{FS_{i}}{A} = Applied substrate loading rate, as previously described, lbs substrate/day/1000 ft<sup>2</sup>$ 

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

$$M = \frac{M_{max} \frac{FS_{i}}{A}}{M_{B} + \frac{FS_{i}}{A}}$$
(1)

where

 $M = \text{Specific methane production rate, ft}^3/\text{day}/1000 \text{ ft}^2$  $M_{\text{max}} = \text{Maximum specific methane production rate', ft}^3/\text{day}/1000 \text{ ft}^2$  $M_{\text{R}} = \text{Proportionality constant, lbs substrate/day}/1000 \text{ ft}^2$ 

#### DISCUSSION AND CONCLUSIONS

An extensive pilot program was conducted with the high strength wastewaters from fuel alcohol production processes to develop the biological treatment kinetics required for reliable design and operation of anaerobic fixed-film biological treatment systems. Stabilized operations were obtained at several different substrate loading conditions to collect the appropriate data for definition of the biokinetic constants. The kinetics of substrate removal, methane gas production, and gas quality were all found to be dependent and predictable as a function of the mass substrate application or loading rate. The kinetics were defined in terms of BOD and COD with greater than 99 percent removals reliably achievable. Gas production and quality were stable and reliable throughout the study period. Mathematical models were developed for accurate prediction of substrate removal, treatment performance, gas production, and gas methane content. The application of this kinetic modeling approach was presented, along with data analysis, for design and optimization of the operation of full-scale anaerobic fixed-film treatment systems.

The system was very stable when the mass substrate loadings were maintained below 27 (35) lbs BOD (COD)/day/1000 ft<sup>2</sup>. Above those loading rates the system was unstable with high volatile acid accumulation and pH control problems. At loading rates above 5 (7) lbs (BOD (COD) day/1000 ft<sup>2</sup> and below 27 (35) lbs BOD (COD)/day/1000 ft<sup>2</sup>, the volatile acid concentration increased faster in the reactor effluent than at the bottom of the reactor. This was due to the high loading rates in these plug flow reactors. At the bottom the substrate loading was higher than the system's acid formers could effectively convert into volatile acids and the methane formers could effectively convert the

volatile acids to methane. However, as the substrate load progressed up through the reactor, more volatile acids were produced. The volatile acid production rate was faster than the methane conversion rate, and thus the volatile acid concentration increased in a cumulative manner as the substrate load progressed upwards. Finally, the methane formers activity was severely hindered or inhibited by the high volatile acid concentrations, and as the substrate load increased, the volatile acids in the bottom of the reactor approached the same concentration as in the effluent. At this point the treatment efficiency of the system deteriorated to around 30 percent BOD and COD removal.

The research on anaerobic fixed-film systems for close to two years established the following potential advantages over the conventional contact process.

÷.

- even higher loading rates
- smaller tankage required
- larger inventory of immobilized biota
- more stable systems operations

#### MEETINGS ATTENDED, PRESENTATIONS AND PUBLICATIONS

Eight technical papers have been presented at national and state meetings during the conduct of this project as follows:

- Stover, E. L. and Gomathinayagam, G., "Activated Sludge Treatability of Fuel Alcohol Production Wastewaters." Presented at the Biological Treatment of Industrial Wastewaters Session of the 1982 Summer National AIChe Meeting, Cleveland, Ohio (August 29 - September 1, 1982).
- Stover, E. L., and Gomathinayagam, G., "Biological Treatment of Synthetic Fuel (Alcohol Production) Wastewater." Presented at the Water Pollution Control in Synfuels Production Session of the 55th Annual Water Pollution Control Federation Conference, St. Louis, Missouri (October 1982).
- Stover, E. L. and Gomathinayagam, G., "Biological Treatment Kinetics of Alcohol Production Wastewater." Presented.at the 1982 Winter Meeting American Society of Agricultural Engineers, Palmer House, Chicago, Illinois (December 14-17, 1982).
- 4. Stover, E. L., Gomathinayagam, G., 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).
- 5. Stover, E. L., Gomathinayagam, G, and Gonzalez, R., "Use of Methane Gas from Anaerobic Treatment of Stillage for Fuel Alcohol Production." Presented at the 39th Annual Purdue Industrial Waste Conference, West Lafayette, Indiana (May 8-10, 1984).

- 6. Stover, E. L., Gonzalez, R., and Gomathinayagam, G., "Anaerobic Fixed-Film Biological Treatment Kinetics of Fuel Alcohol Production Wastewaters." Presented at the Second International Conference on Fixed-Film Biological Processes, Arlington, Virginia (July 10-12, 1984).
- 7. "Anaerobic Treatment Kinetics of High Strength Industrial Wastewater -Comparison of Suspended Growth and Fixed-Film Reactors." Presented at the Industrial Waste Symposia, 57th Annual Water Pollution Control Federation Conference, New Orleans, Louisiana (October 1984).
- "Kinetic Analysis of Anaerobic Treatment of Alcohol Stillage Using Suspended-Growth and Fixed-Film Systems." Presented at the Seventh Annual Meeting of the Pollution Control Association of Oklahoma, Western Hills, Oklahoma (May 1984).

ie -