SYNTHETIC FUEL (ALCOHOL PRODUCTION) WASTEWATER TREATMENT

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by

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PROJECT COMPLETION REPORT

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INTRODUCTION

Interest has grown enormously in alcohol fuels, both as a partial solution to the energy shortage and as a potential new agricultural industry. In the last few years several grain-alcohol plants ranging in size from 200,000 to 3,000,000 gallons a year have been developed in Oklahoma and adjoining states. The production of fuel ethanol at commercial and smaller scales is still progressing rapidly. Due to the development of the gasohol market and to federal and state incentive programs, there now appears to be some profit potential for the commercial operator.

Ethanol plants can be divided into three broad types of operations. The first type produces anhydrous (pure, no water present) ethanol primarily for commercial blending of gasohol. These plants can normally produce more than 500,000 gallons of ethanol per year. The second type of ethanol plants produce relatively large volumes of 180 to 190 proof ethanol (proof = percent ethanol x 2). Ethanol from these plants can be blended with gasoline after upgrading to pure or anhydrous ethanol. The third type includes small on-farm units which can produce ethanol of 160 to 190 proof. Their production is generally less than 200,000 gallons of ethanol a year which is primarily suited for direct fuel use.

Recent advances in process technology, particularly in the areas of heat recovery, have made it possible to produce ethanol with at least a slightly positive energy balance. Properly designed plants should be able to produce anydrous ethanol with a process energy input of around 40,000 Btu per gallon of ethanol. An additional 30,000 to 40,000 Btu's per gallon are required to grow, harvest, and transport the grain feedstock, resulting in total production energy requirements of 70,000 to 80,000 Btu per gallon. The energy contained in a gallon of anhydrous ethanol is approximately 84,000 Btu. Thus the cost of alcohol production compared to the market value, and the energy output compared to the energy input, shows the present need for the most efficient possible design and operation of fuel alcohol plants.

The development of a successful fuel alcohol program requires the development of economical solutions to the following needs: (1) Need for the most efficient energy balance and yield in the starch-conversion process. (2) Development of scientific information to apply engineering principles to the fermentation processes for more efficient production. (3) Development of more efficient and economical uses of the by-products. (4) Development of capabilities for treating the wastewaters for reuse or discharge. There has been recent improvement in the energy balance in the area of heat recovery, but there is potential for more improvement especially in the area of direct recycle and reuse of by-products and wastewaters. Recycling and reusing waste by-products in the production process would maximize raw material usage, minimize overall energy requirements, and improve the overall materials balance to make the present slightly positive economic balance (when everything is working as designed) more positive and create a more economically favorable situation for the fuel alcohol industry.

The purpose of this research project was to characterize the high strength wastewaters from alcohol production facilities and evaluate the biological treatability of these wastewaters for discharge, reuse and recycle options. The biological treatment option investigated during these studies was the activated sludge process. This treatment process provides a treated effluent that can possibly be recycled back to the plant, used for irrigation purposes or discharged. Also, a waste biological sludge is produced that may be hydrolyzed and resused to provide growth nutrients or dried and used as cattle feed with the grain solids and spent yeast solids.

MATERIALS AND METHODS

The stillage or wastewaters used for the pretreatment and biological studies reported in this paper 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. 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 activated sludge systems.

Bench-scale, complete mix, continuous flow activated sludge systems were used in these studies to evaluate the biological treatability of the fuel alcohol wastewaters. These systems 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. The wastewaters and performance 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, dissolved oxygen, oxygen uptake rates, effluent solids, sludge settling characteristics and population dynamics by microscopic analysis. The protein and carbohydrate contents of the biological sludges and stillage solids were also monitored for determination of reuse potential.

The biological systems were operated to control the growth rate or sludge retention time by wasting sludge on a daily basis. During the treatability studies, the hydraulic retention time, the hydraulic flow rate, and the sludge retention time were maintained constant. The data from these 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 description 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: (1) (2) (3) (4)

Eckenfelder

First Order $$\left(\frac{ds}{dt}\right)_g = K_e X S_e$$

Second Order $$\left(\frac{ds}{dt}\right)_g = \frac{K_e' S_e X}{S_i}$$

McKinney $$\left(\frac{ds}{dt}\right)_g = K_m S_e$$

Weston $$\left(\frac{ds}{dt}\right)_g = R_s S_e \left(\frac{X}{S_i}\right)^{K_i}$$

Lawrence and McCarty $$\left(\frac{ds}{dt}\right)_g = \frac{K X S_e}{K_s + S_e}$$

Gaudy $$\left(\frac{ds}{dt}\right)_g = \frac{\mu_{max} X S_e}{Y_t(K_s + S_e)}$$

Kincannon and Stover $$\left(\frac{ds}{dt}\right)_g = \frac{U_{max} X \frac{FS_i}{XV}}{K_B + \frac{FS_i}{XV}}$$

where:

- 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

RESULTS AND DISCUSSION

A summary of the raw wastewater (thin stillage) characteristics from ethanol production from both corn and milo feedstocks at the Oklahoma State University fuel alcohol research facility is presented in Table 1. These results characterize the samples collected for pretreatment and activated

TABLE 1. RAW WASTEWATER (THIN STILLAGE) CHARACTERISTICS

Parameter*	Corn Feedstock Mean	Corn Feedstock Standard Deviation	Milo Feedstock Mean	Milo Feedstock 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.

sludge treatability studies. Successful pretreatment was accomplished by cooling and gravity settling for suspended solids removal.

The supernatant was then diluted approximately 2:1 with tap water to provide the influent feed to the activated sludge systems. The average influent and effluent characteristics in terms of BOD_5, COD and TOC during this study are presented in Table 2. As observed in Table 2, the treatment efficiency in terms of these parameters was very high throughout the entire study period. 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 presented in Table 3. Graphical determination of Y_t and K_d as used in all the design models is shown in Figure 1. Graphical determination of R_s and K_i as used in the Weston model and U_{max} and K_B as used in the Kincannon and Stover model are shown in Figures 2 and 3, respectively. The biokinetic constants or coefficients required by the remaining design models are determined by similar methods. (1) (2) (3) (4) (5)

These biological treatability studies have shown that these fuel alcohol production wastewaters are highly biodegradable and can be successfully treated to high levels by the activated sludge process. The biokinetic constants or coefficients can be used in the various design models to determine required aeration tank volumes to achieve a desired level of treatment. All the design models will provide similar answers, and they can all be used for design with a high degree of confidence.

TABLE 2. SUMMARY OF ACTIVATED SLUDGE TREATMENT PERFORMANCE

SRT	Soluble BOD_5			Soluble COD			Soluble TOC		
(days)	Infl. (mg/ℓ)	Eff. (mg/ℓ)	Eff. (%)	Infl. (mg/ℓ)	Eff. (mg/ℓ)	Eff. (%)	Infl. (mg/ℓ)	Eff. (mg/ℓ)	Eff. (%)
3	5300	290	94.5	9100	420	95.4	3090	100	96.8
6	5220	90	98.3	9100	200	97.8	3100	80	97.4
10	5315	70	98.7	10,600	230	97.8	3570	90	97.5
20	5340	65	98.8	11,100	180	98.4	3680	90	97.6

TABLE 3. BIOKINETIC CONSTANTS OR COEFFICIENTS

Model	Biokinetic Constant
Eckenfelder	
First Order	K_e = 0.004
Second Order	K_e' = 20.7
McKinney	K_m = 0.0042X
Weston	R_s = 21.0
	K_i = 1.0
Lawrence and McCarty	K = 2.0
	K_s = 360
Gaudy	μ_{max} = 1.0
	K_s = 360
Kincannon and Stover	U_{max} = 16.7
	K_B = 16.7
All Models	Y_t = 0.53
	K_d = 0.06
	a' = 0.30
	b' = 0.10

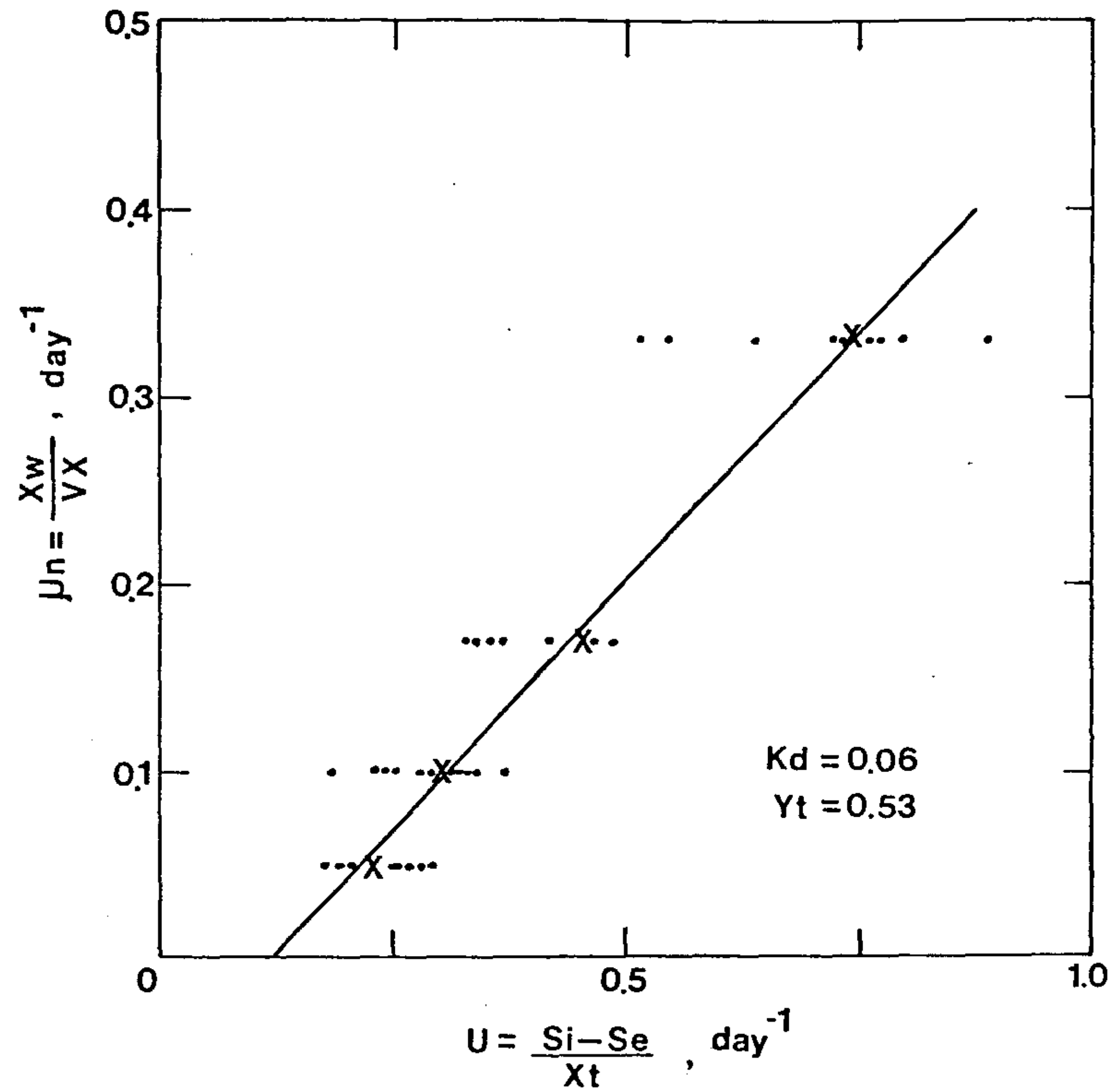

Figure 1. Graphical determination of Y_t and K_d (BOD_5) for all design models.

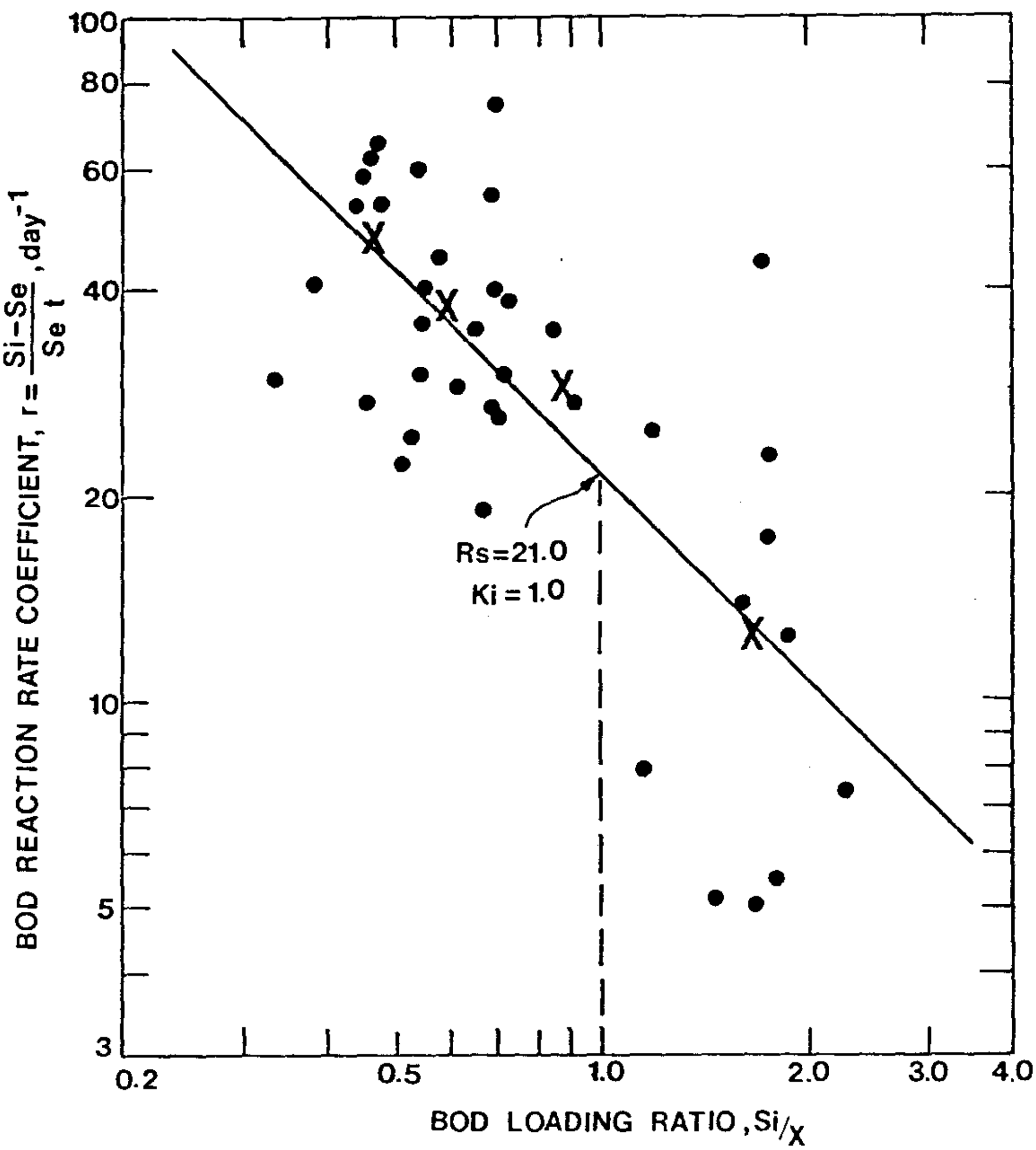

Figure 2. Graphical determination of $R_s(BOD_5)$ and K_i for Weston's design model.

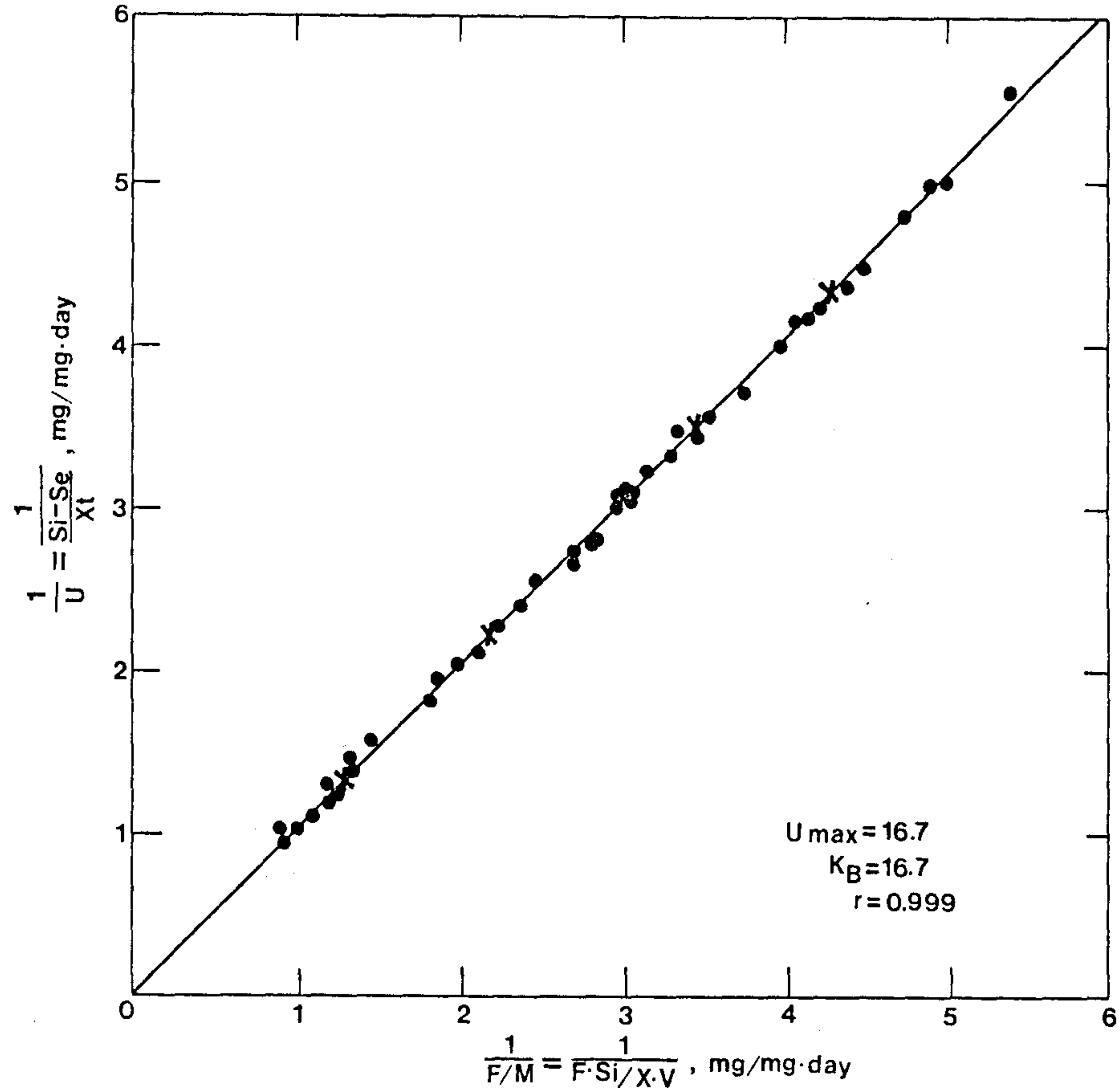

Figure 3. Graphical determination of U_{max} and K_B (BOD_5) for Kincannon and Stover design model.

Oxygen requirements were determined by conducting oxygen uptake analysis and determining the specific oxygen utilization rate at each operating condition. In Figure 4 the average specific oxygen utilization rate is plotted as a function of the average specific substrate utilization rate. The slope of this line represents the fraction of the substrate used for oxidation and the intercept represents the fraction per unit time of suspended or volatile suspended solids oxidized on an oxygen basis. These constants can be used to determine the oxygen requirements and size the aeration equipment for full scale activated sludge treatment.

The recycle and reuse potential of both the stillage solids and the waste activated sludge (WAS) are presented in Table 4. The protein and carbohydrate content of both stillage and WAS are 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 wastewater can now possibly be recycled or discharged, and the biological solids produced can be sold as a by-product along with the grain solids.

TABLE 4. PROTEIN AND CARBOHYDRATE CONTENT OF STILLAGE AND WASTE ACTIVATED SLUDGE (WAS)

	Percent* Protein	Percent* Carbohydrate
Thin Stillage	21	50
WAS		
SRT = 3	24	50
SRT = 6	24	35
SRT = 10	17	25
SRT = 20	15	24

*All analysis on a particulate or suspended solids basis.

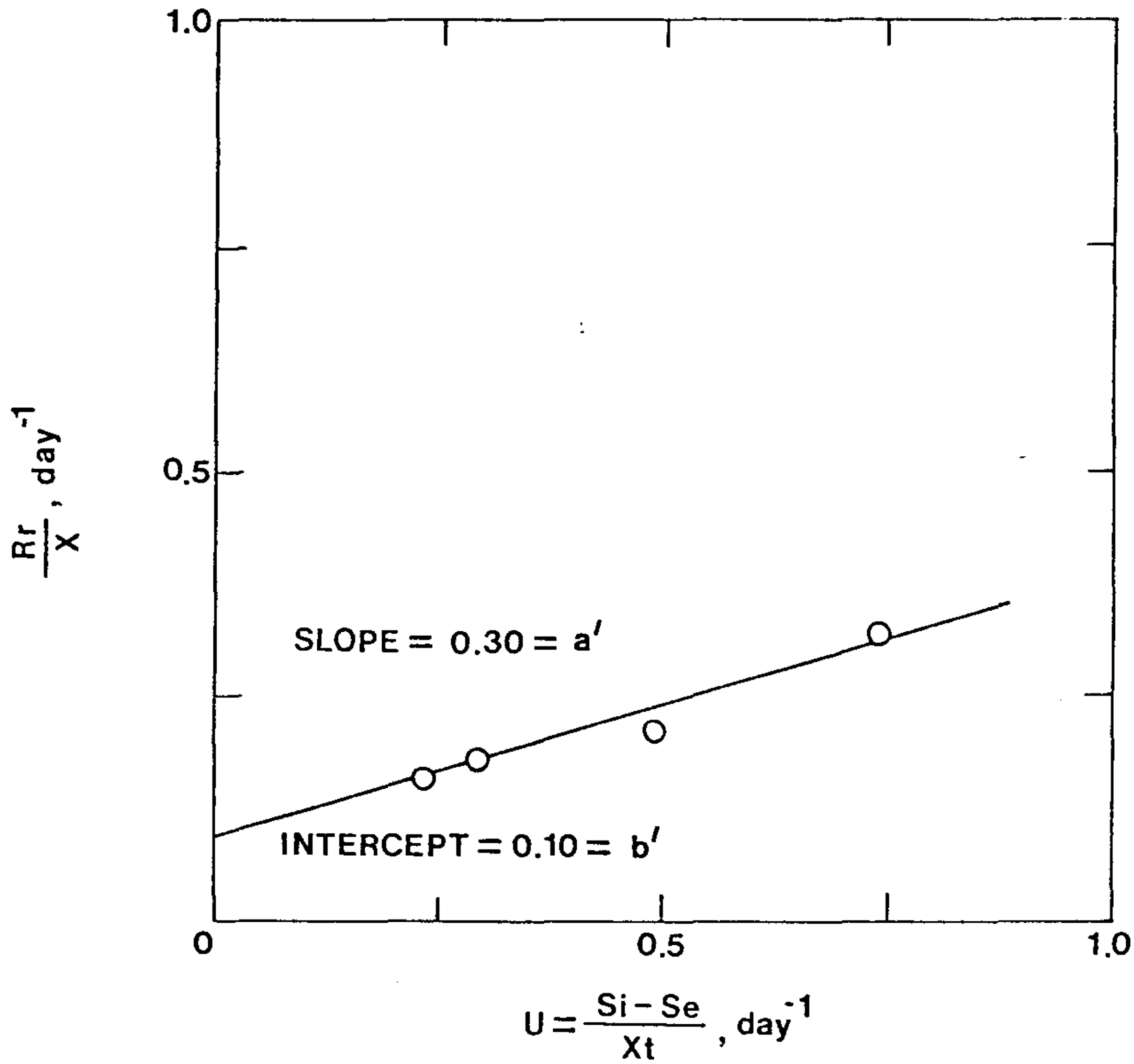

Figure 4. Oxygen requirements for activated sludge systems receiving fuel alcohol wastewaters.

SUMMARY AND CONCLUSIONS

The performance data and biokinetic constants show that the activated sludge process can be successfully used for treatment of the stillage or wastewaters from fuel alcohol plants for discharge or reuse. The waste activated sludge contains protein and carbohydrate contents similar to the spent yeast cells, and thus should be valuable as a by-product of wastewater treatment for use with the grain solids as cattle feed.

A biological treatment option to the activated sludge process that should be investigated is anaerobic treatment. Since this wastewater is a high strength wastewater, anaerobic treatment would offer certain advantages over aerobic treatment. Sludge production would be significantly less and possibly not as suitable for cattle feed; however, no oxygen would be required and methane gas would be produced. In large enough plants the methane gas produced could be used as an energy source within the alcohol plant. Anaerobic treatability studies need to be conducted.

This research work has resulted in the development of a research proposal entitled "Fuel-Alcohol Production Wastes--Treatment, Recycle, and Reuse Options" to Mitchell & Mitchell Economists, LTD. This research project was not funded. From this research work two technical papers have been accepted for presentation. The first paper is entitled "Activated Sludge Treatability of Fuel Alcohol Production Wastewaters" and will be presented at the 1982 Summer National American Institute of Chemical Engineers Meeting in Cleveland, Ohio in August 1982. A copy of this paper is attached. The second paper is entitled "Biological Treatment of Synthetic

Fuel (Alcohol Production) Wastewater" and will be presented at the 55th Annual Water Pollution Control Federation Conference in St. Louis, Missouri in October 1982.

LIST OF REFERENCES

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