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FUEL GAS PRODUCTION FROM ANIMAL AND AGRICULTURAL RESIDUES AND BIOMASS

Quarterly Coordination Meeting, March 15-16, 1979,
Tampa, Florida; Third Quarterly Progress Report

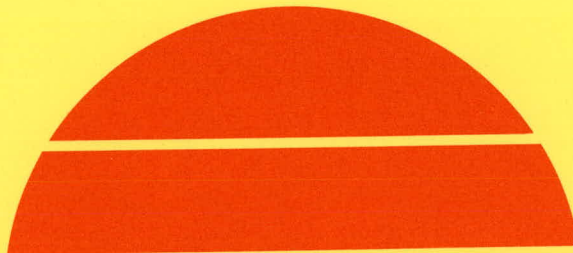
By
D. L. Wise
E. Ashare
R. L. Wentworth

MASTER

April 24, 1979
Date Published

Work Performed Under Contract No. ET-78-C-02-5099

Dynatech R/D Company
Cambridge, Massachusetts



U.S. Department of Energy



Solar Energy

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FUEL GAS PRODUCTION FROM ANIMAL AND
AGRICULTURAL RESIDUES AND BIOMASS

Quarterly Coordination Meeting

March 15-16, 1979

Tampa, Florida

Third Quarterly Progress Report

D.L. Wise
E. Ashare
R.L. Wentworth

Dynatech Project No. DOE-5
Dynatech Report No. 1883

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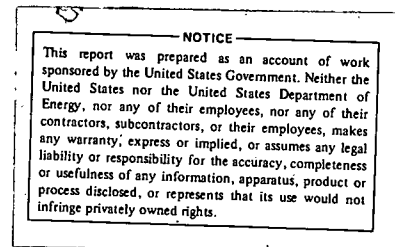
Prepared for:

United States Department of Energy
Fuels From Biomass Systems Branch

Under Contract No. ET-78-C-02-5099.A000

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"The contributors to this report have indicated that no patentable material has been presented in their summary reports."

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SUMMARY

The eleventh quarterly coordination meeting of the methane production group of the Fuels From Biomass Systems Branch, U.S. Department of Energy was held at Tampa, Florida, March 15-16, 1979. Progress reports were presented by the contractors and a site visit was made to Kaplan Industries, Bartow, Florida to see the Hamilton Standard demonstration facility for digestion of environmental feedlot residue to methane.

A meeting agenda, a list of attendees, and progress reports are presented.

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AGENDA

Coordination Meeting
ANAEROBIC DIGESTION TECHNOLOGY
March 15, 16, 1979
Host International Hotel
Tampa International Airport
P.O. Box 24107
Tampa, Florida 33622
(813) 879-5151

THURSDAY, March 15, 1979 - Citrus Room

2:00 - 2:05 pm	R.L. Wentworth	Introduction
2:05 - 2:45 pm	W.B. Coe	Status of the 25 TPD Experimental Facility
2:45 - 3:25 pm	E. Coppinger	Operation of an Anaerobic Digester at Monroe, WA
3:25 - 4:05 pm	E. Ashare	Digester Design Concepts
4:05 - 4:45 pm	Yud-Ren Chen	Digester Operation and Heat Transfer Studies at MARC
4:45 - 5:25 pm	J.L. Gaddy	Farm Energy and Chemicals from Biomass
7:00 pm	Dinner - Pasco Room Host International Hotel	

(cont.)

FRIDAY, March 16, 1979 - Citrus Room

8:20 - 9:00 am	W.J. Jewell	Anaerobic Fermentation of Agricultural Residues
9:00 - 9:40 am	P.L. McCarty	Thermochemical Treatment for Increasing Anaerobic Biodegradability
9:40 - 9:55 am	BREAK	
9:55 - 10:35 am	J.T. Pfeffer	University of Illinois Progress Report
10:35 - 11:15 am	R.E. Speece	Methane Fermentation Toxicity Recovery Characteristics
11:15 - 11:30 am	R.F. Ward	Closure
11:30 - 12:30 pm	Luncheon, Assorted Sandwich Buffet, Citrus Room	
1:00 - 2:00 pm	Travel: Host International, Tampa, to Kaplan Industries, Bartow	
2:00 - 4:00 pm	W.B. Coe/D.J. Lizdas/L.W. Umstadter Tour of the Facility at Kaplan Industries	
4:00 - 5:30 pm	Return to Tampa Airport	

LIST OF ATTENDEES

Coordination Meeting
Host International Hotel
Tampa International Airport
Tampa, Florida
(813) 879-5151
March 15, 16, 1979

Cornell Univeristy 202 Riley-Robb Hall Ithaca, NY 14853	William J. Jewell K. Fanfoni A.P. Leuschner R. Cummings	(607) 256-4533
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John H. Ryther

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PIPELINE FUEL GAS FROM AN
ENVIRONMENTAL FEEDLOT
CONTRACT NO. EG-77-C-01-4015
PROGRESS FROM DECEMBER 1, 1978 TO FEBRUARY 28, 1979
PREPARED FOR THE
QUARTERLY COORDINATION MEETING
MARCH 15-16, 1979

HAMILTON STANDARD

Windsor Locks, Connecticut 06096



1.0 PROGRAM OBJECTIVE

The objective of the program is to design, fabricate and operate an experimental anaerobic fermentation facility at an environmental cattle feedlot. The 25 ton per day (dry matter basis) facility will be utilized to identify the technical and economic feasibility of producing fuel gas and a cattle refeed product from the feedlot residues.

Design and constuction are complete. The operational evaluation beganon March 1, 1979.

2.0 PROGRESS DURING THE QUARTER

Dedication ceremonies were held on December 8 with approximately 300 people in attendance. Dr. Robert San Martin, Director of the Division of Distributed Solar Technology of DOE and U.S. Representative Andrew P. Ireland of Florida were among the speakers.

During December, all electrical wiring details were completed and the electrical system was 95% checked out. Mixer seals and stuffing boxes were installed. All liquid pumps were checked out. The mixer on tank No. 1 was checked out with a full tank of water.

During January, the construction trailer was moved to its new location and the electrical wiring, benches and test equipment were installed, completing the conversion into the on-site laboratory.

The system operational manual was completed and training of operational personnel continued. Work continued on the "as-built" system drawings.

During the first few days of January, portions of the cover of Tank No. 2 were damaged. The cause was the inadvertant isolation from the tank of the pressure relief/vacuum breaker valve by a maintenance valve, coupled with unusually low ambient temperatures that caused vacuum conditions in the tank. The tank cover was repaired, and the maintenance valve removed from the system. A backup pressure relief/vacuum breaker valve has been added to each tank, and a procedure has been developed to allow checking of the pressure relief/vacuum breakers without isolating them from the tank.

The remainder of January was spent completing final checkout of all electrical wiring, the system boiler, steam lines, and steam injectors. Checkout of the main steam injector indicated that the drive mctor was inoperative due to water penetration and corrosion. the motor was replaced under warranty and additional motor protection was implemented. The system was ready for startup at the end of January. (See Figure 1).

Startup was initiated on February 7 by filling tank No. 1 with 3000 pounds of sodium bicarbonate and water to the six foot level, raising the temperature to 55°C, and adding manure to the twelve foot level while maintaining the temperature. Problems were encountered with temperature control; temperature fluctuation were consistently beyond specification value. The problem was found to be a leaking thermal sensor for the steam regulator. Replacing the sensor decreased the fluctuations to a marginally acceptable value. A revised steam control was defined and placed on order.

Startup did not proceed as anticipated. (See Attachment 1). At the end of February, TVA had leveled off and there was no significant gas production. Causes for this behavior are under investigation.

3.0 ACTIVITIES DURING NEXT QUARTER

The investigation into the startup problem will continue; it is expected that design point operating conditions will be achieved during the next quarter.

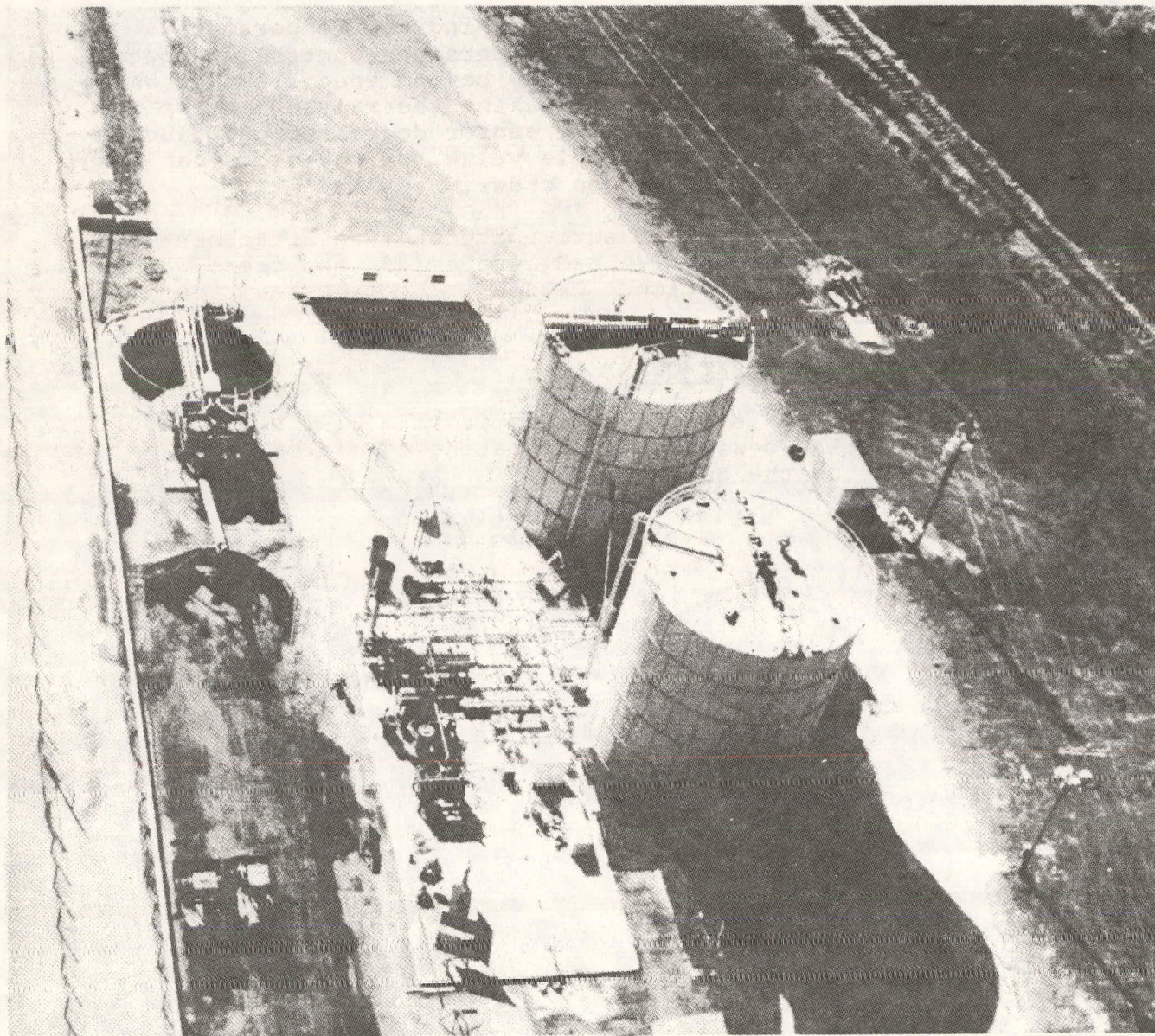


Figure 1
System Ready For Start Up

ATTACHMENT 1

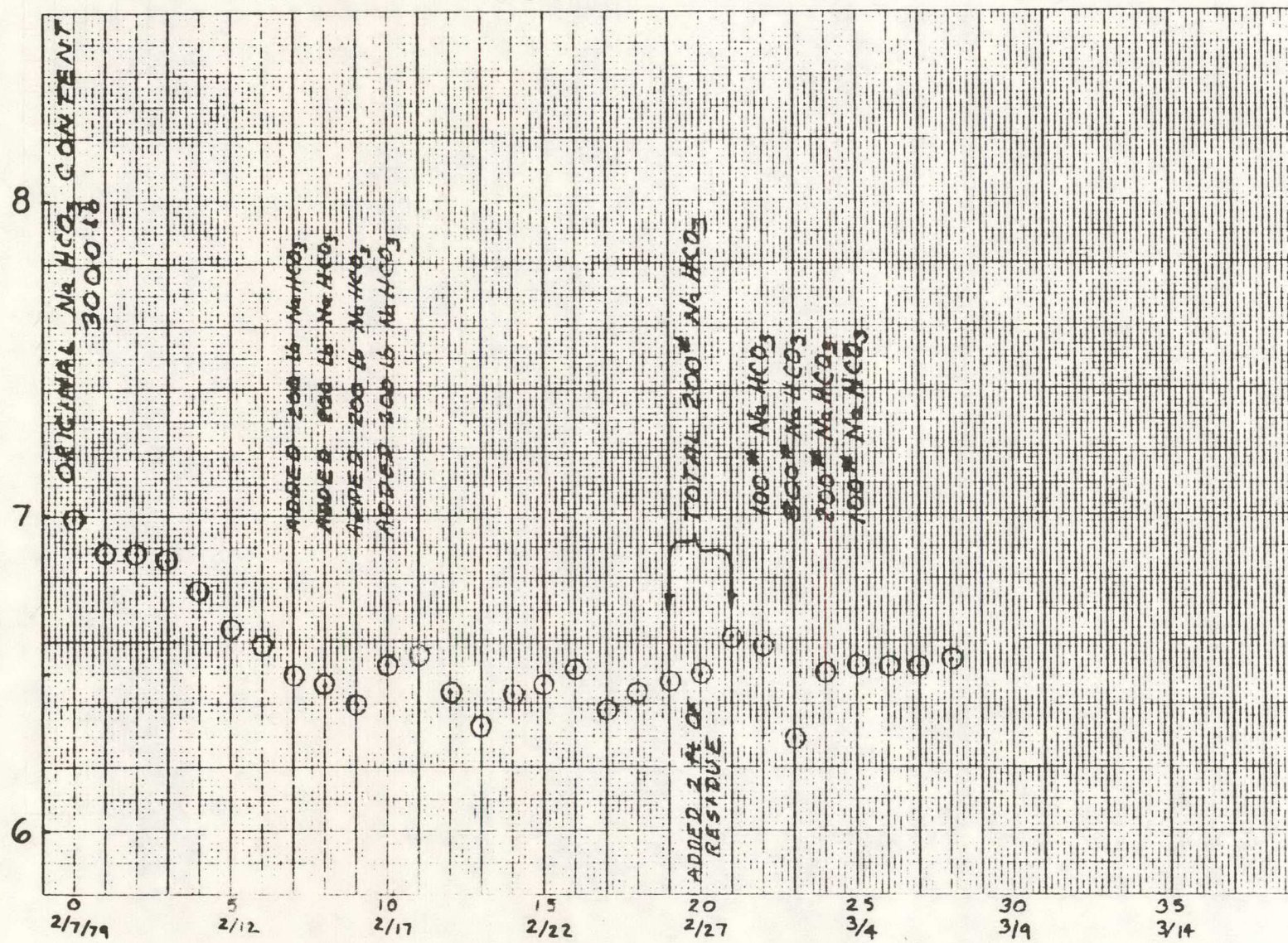
START UP DATA

DOE-K
FEBRUARY, 1979

HSD-K
MAY, 1975

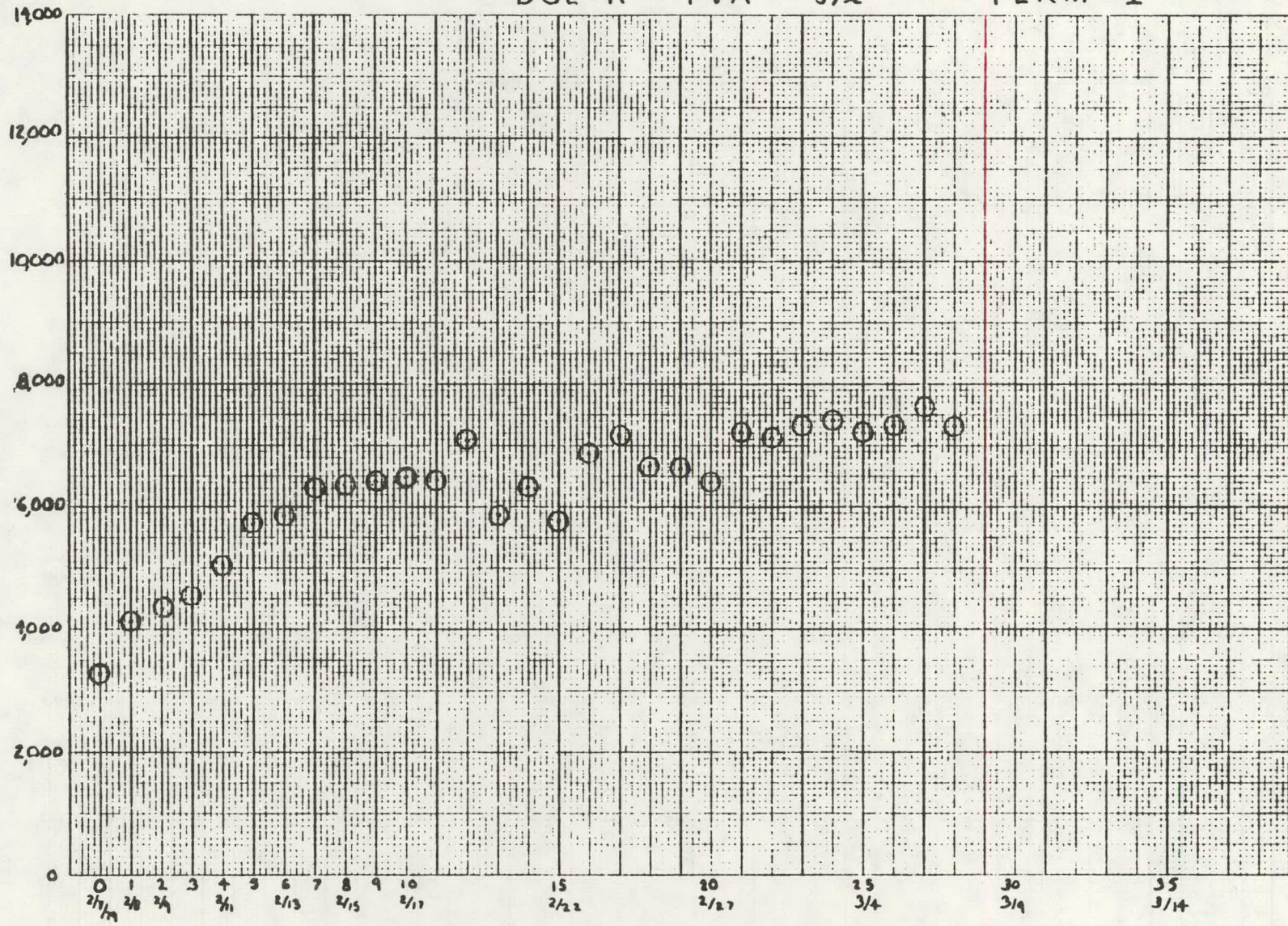
DOE-K pH

FERM 1



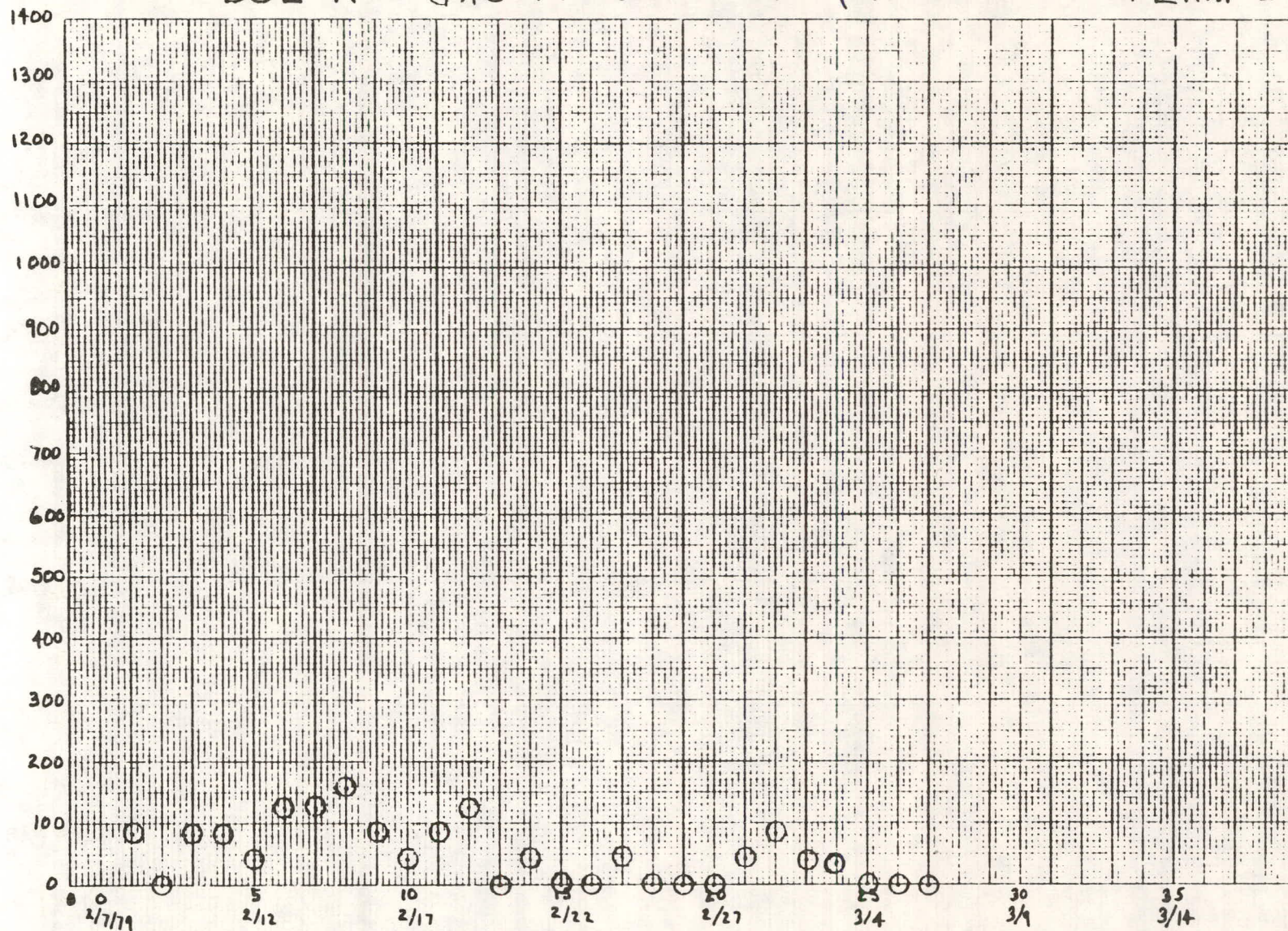
DOE-K TVA mg/l

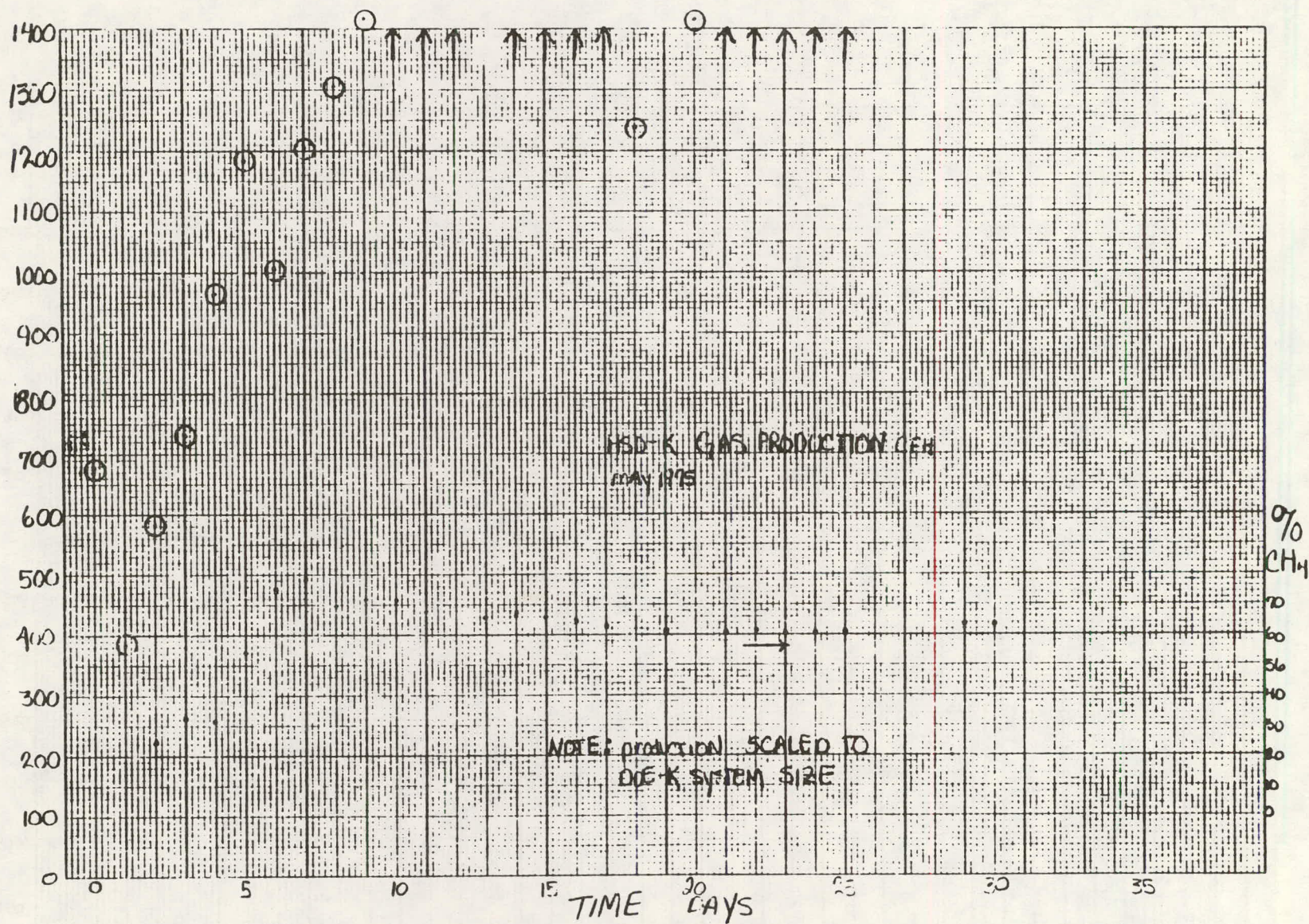
FERM 1

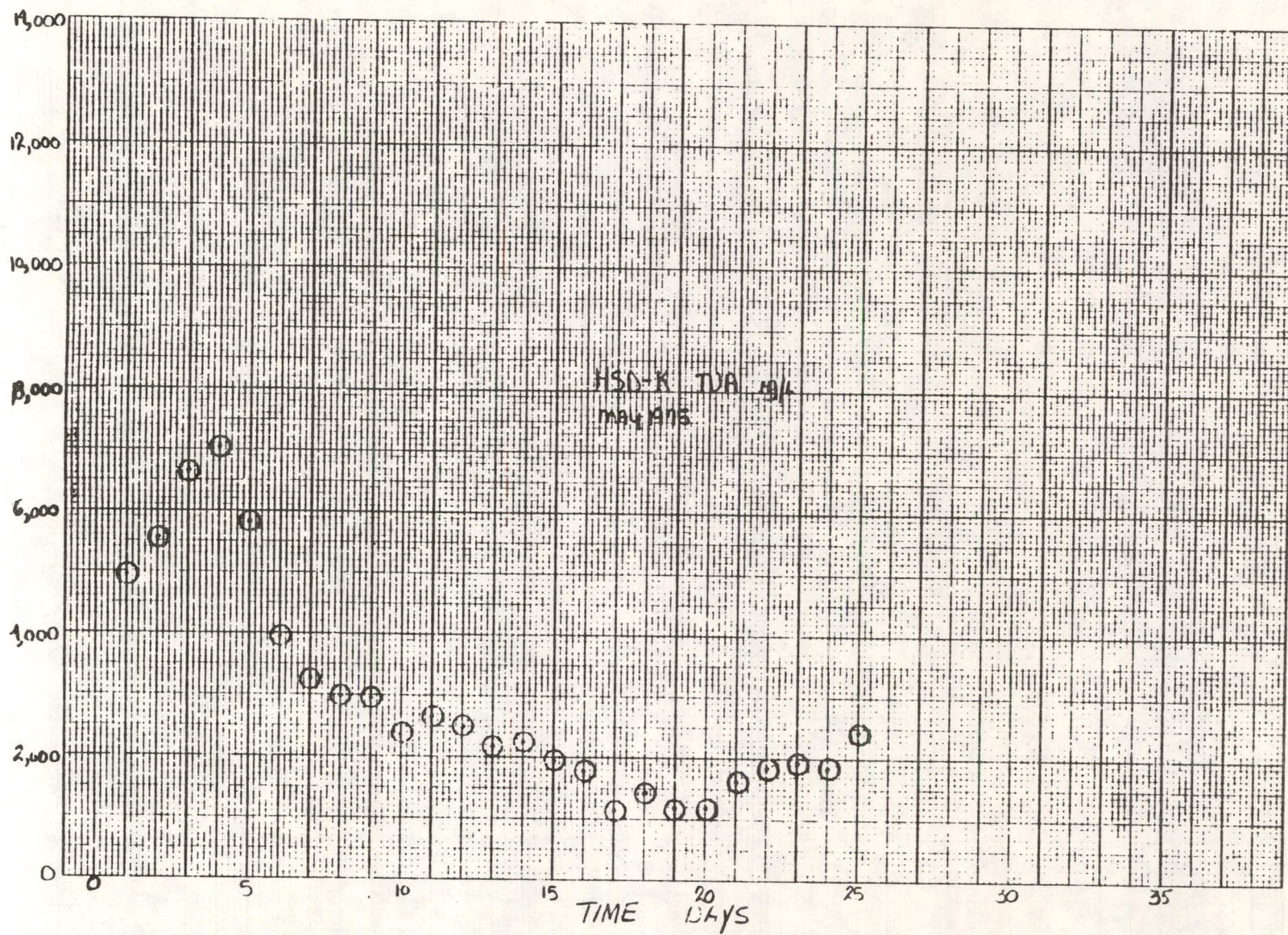


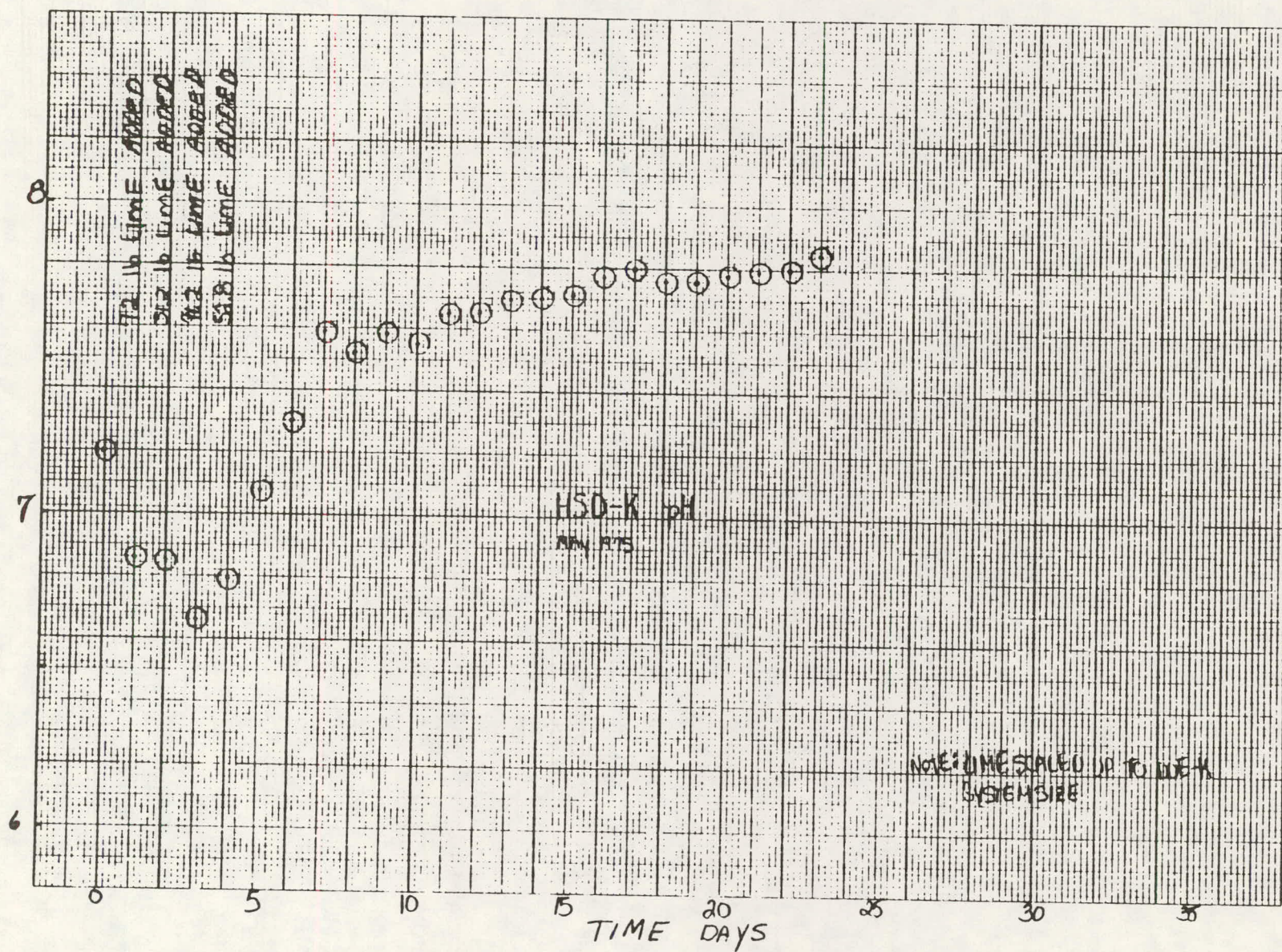
DOE-K GAS PRODUCTION (WET SCFH)

FERM 1









Operation of a 50,000 Gallon Anaerobic Digester
at the Monroe State Dairy Farm
near Monroe, Washington

Seventh Quarterly Technical Status Report
November 1, 1979 -- February 28, 1979
and
Milestone Plan and Management Report

This project is jointly sponsored by
The U.S. Department of Energy
Washington State Department of Ecology
Washington Department of Social and Health Services

9 March 1979

Ecotope Group
Seattle, WA 98112

Project manager: Elizabeth Coppinger
Project liaison: David Baylon
Principal Researchers: Jack Brautigam
Bruce Lampcov
David Smith

Prepared for:

The United States Department of Energy
under Contract #EG-77-C-06-1016

Digester Performance

The digester at Monroe has experienced a wide variety of loading rates during the past quarter. Loading was erratic in December due to scraping problems and averaged 3.74 Kg/m^3 reactor. Two weeks of below freezing weather at the beginning of January prevented any manure from being scraped due to severe freezing in the loafing shed. Gas production fell to less than 20 m^3 of biogas/day. Loading resumed on January 12 and gas production began to recover.

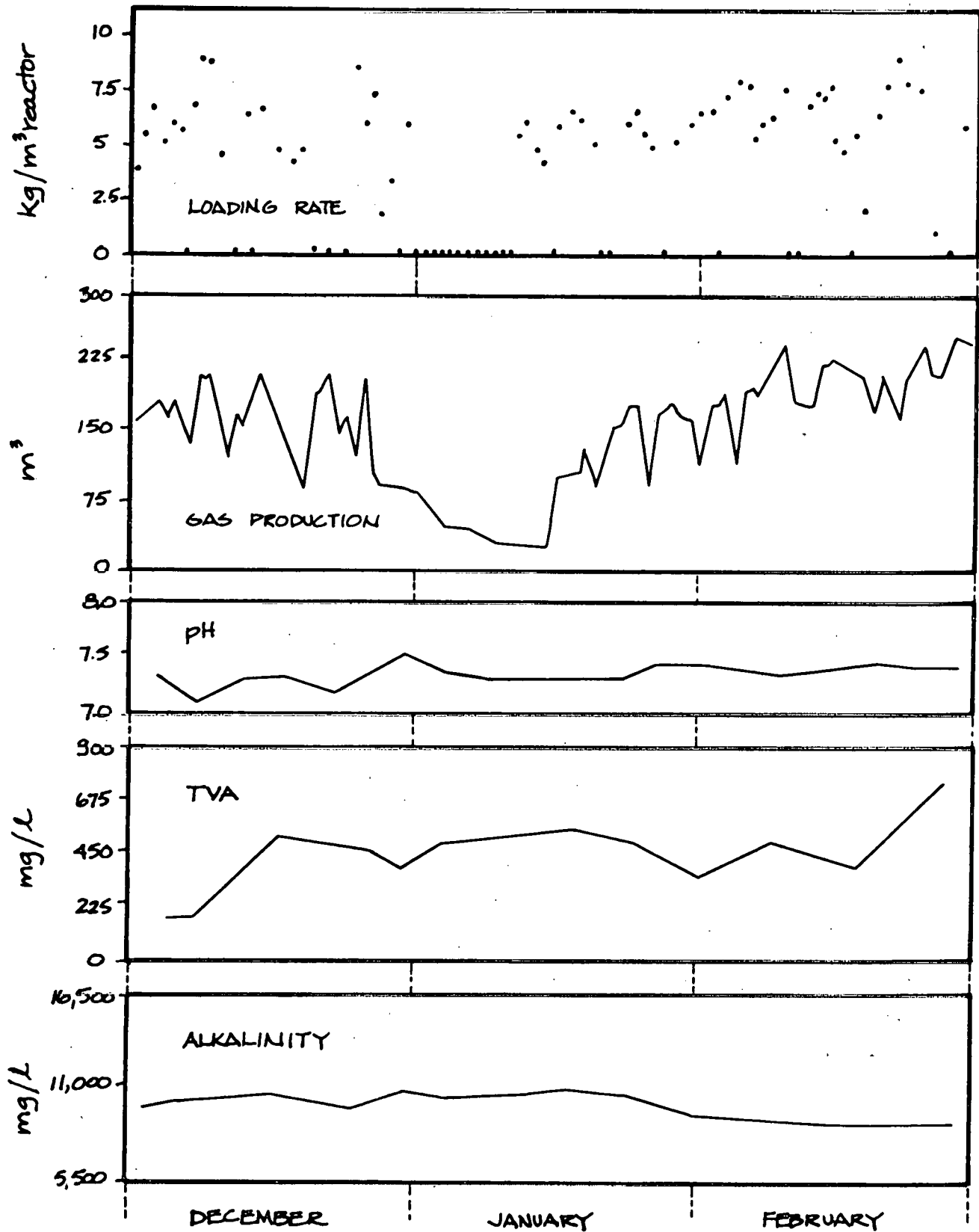
Manure from a calf pen is now scraped to the digester. This has brought the loading rate up to 5.27 Kg/m^3 reactor, and gas production is returning to the high rates of last June. This increased loading rate has resulted in a rise in TVA to 712 mg/l from 300 mg/l , and alkalinity has fallen to 9150 mg/l from its former level of $10,200 \text{ mg/l}$. These values are still well within a safe range and pH has remained stable.

The % reduction has risen to 30%. However, the gas produced per volatile solids destroyed has fallen from $.952$ to $.732 \text{ m}^3/\text{KgV.S.}$ As a result the gas produced per volatile solids added has remained at $.22 \text{ m}^3/\text{KgV.S.}$

Net Energy

The average ambient temperature for the quarter was 1°C , which is exceptionally cold for the Pacific Northwest. Consequently, 68% of the gas produced was used to heat the digester. This situation was aggravated by the two weeks of no loading in January. This was a reflection of the uncharacteristic nature of the weather. Manure was freezing on the concrete floor of the loafing shed since it is open and unheated. As a result of the period of no loading, gas consumption exceeded production for a period of one week. When loading was resumed the gas storage became essential for the first three days since the gas production was insufficient to meet the energy demands of influent heating.

MONROE DIGESTER PERFORMANCE DECEMBER 1 - FEBRUARY 28



MONROE DIGESTER PERFORMANCE

DECEMBER 1 - FEBRUARY 28

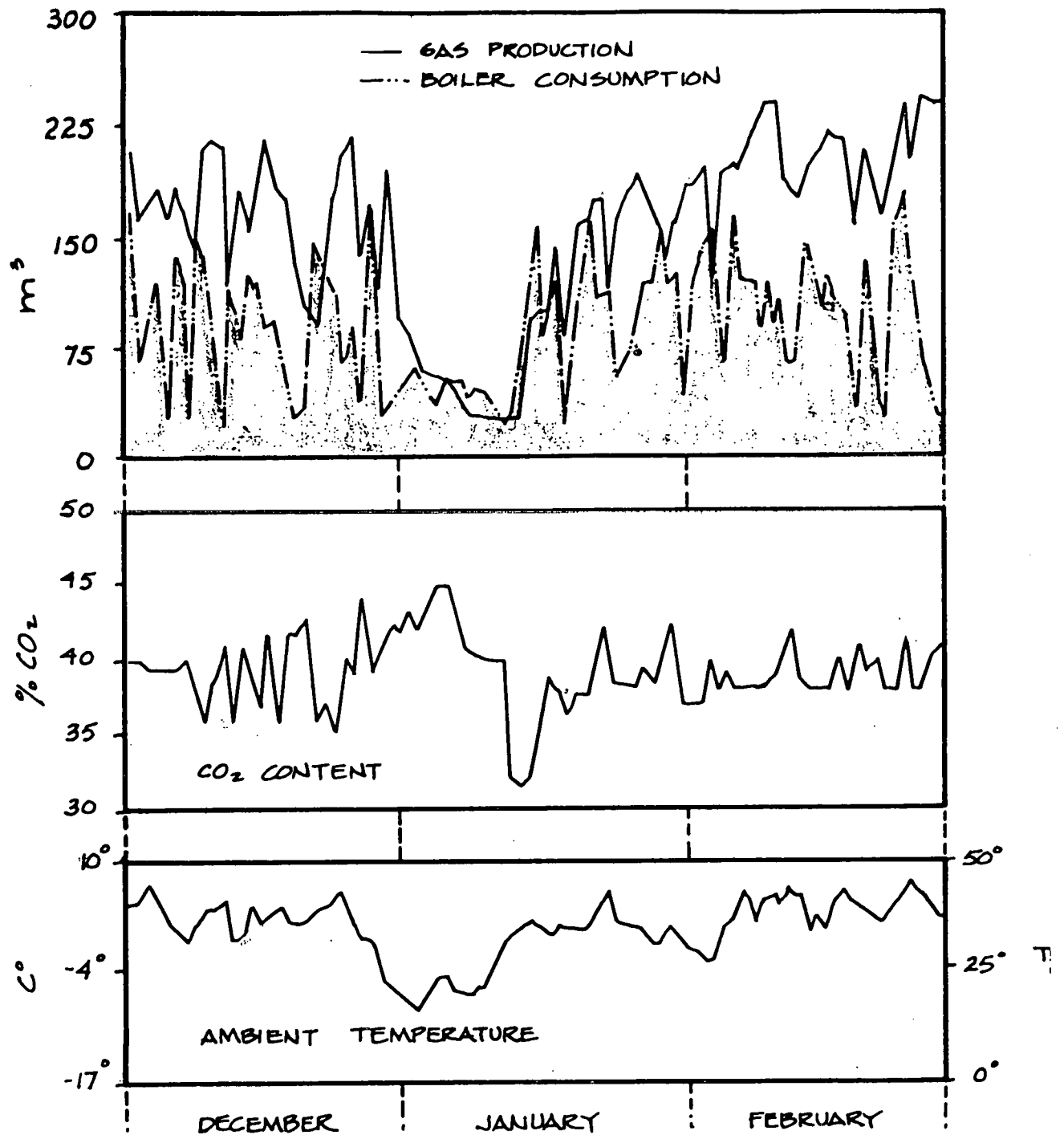


Table 1
Mass Balances

week starting	loading rate kg VS/m ³ -reactor	m ³ /kg VS added	m ³ /kg VS destroyed	%VS destroyed
11-17	5.03	.178	.492	36.1
12-4	5.44	.182	1.04	17.5
12-11	3.97	.247	.815	30.1
12-18	3.46	.250	.931	26.9
12-25	1.46	.486	.947	51.3
1-1	-	-	.763	33.0
1-8	2.44	.108	.220	33.0
1-15	3.81	.197	.821	24.0
1-22	3.76	.242	.950	25.4
1-29	5.41	.171	.604	28.3
2-5	4.55	.262	.766	34.2
2-12	5.71	.210	.673	31.2
2-19	6.73	.164	.519	31.6

Table 2
Energy Balance

week starting	energy production GJ	boiler consumption GJ	net production GJ	% energy for heating	average ambient temperature
11-27	24.7	16.1	8.6	65.3	1.7°C
12-4	27.8	16.9	10.9	60.8	2.4
12-18	24.7	15.1	9.6	61.1	3.6
12-25	19.3	10.8	8.6	55.7	-4.7
1-1	8.2	7.5	7.0	91	-5.6
1-8	7.9	10.1	-2.2	128	.5
1-15	22.2	6.8	5.3	76	1.8
1-22	25.7	17.2	8.5	67	.5
1-29	26.4	16.6	9.8	63	-1.5
2-5	33.8	16.7	17.1	49	4.5
2-12	33.7	17.7	16.0	52	3.5
2-19	31.0	18.2	12.7	59	4.2

System Improvements

Loading Pump. A Moyno pump (Model 2GOGSI 11 kW motor) has been received and installed to replace the inoperative Marlow diaphragm pump. The pump delivery was delayed for two weeks due to the closure of all country roads, which were not built to withstand freezing. After two weeks of severe weather the ground froze down to 18". Consequently, all trucks were banned from county roads, and we were unable to transport the pump to the site.

The pump is now plumbed in and we have begun using it for influent loading through the heat exchanger. The pump has been wired in with a high pressure cut-off switch that turns the pump off in case of a clog in the discharge line. We have also installed a 1"x2" mesh screen on the influent line to keep large particles out of the pump.

In its preliminary operation, the pump has performed well. In addition to easily loading through the heat exchanger, the pump can now load manure at whatever thickness it is received. This results in a tremendous savings in operator time. A flow switch to shut the pump off in the case of a clog in the suction line has not yet been installed. Therefore, the pump has not yet been operated through a full range of conditions.

Engine/Generator. The Waukesha engine and Kato electrical generator were restarted in February after a year of no use. The engine had been run for less than 200 hours and required a tune up, but no major work. The engine/generator ran at a conversion efficiency of only 7%. This is significantly lower than the 11% efficiency achieved last year. However, the electrical consumption is less than 10% of its value at this time last year.

We had hoped to be hooked up to the utility grid sometime in February. Despite assurance from the local utility that they were interested and willing to hook us to the grid, the inevitable delay encountered when working on such a new project has prevented that from happening. Although we fully expect to be able to hook up to the utility before the end of this project year, we feel

that we can no longer depend on the utility time estimate for when this will occur.

The engine/generator is now being wired to a load that can be varied from 1.5 kW to 40 kW. Heating elements are being used. The advantage of using a purely resistive load is that it will not introduce a situation where the voltage and current can get out of phase. We will now run the generator under a variety of load conditions and monitor the conversion efficiency and waste heat recovery.

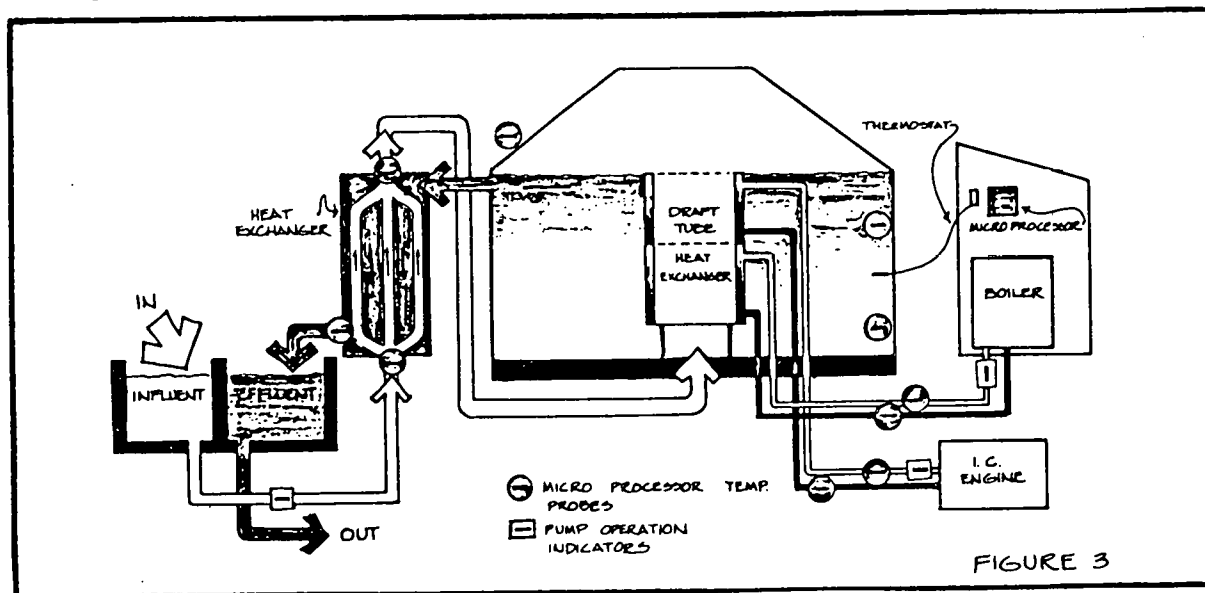
Temperature Control. The original temperature measuring and controlling devices for the digester tank were all of mechanical design with capillary tubes from the sensor to the switch. One probe was connected to a microswitch that controlled the digester temperature by turning the boiler water pump on and off. The other was connected to a meter calibrated in 2 °F increments. The sensors were mounted in two separate wells in the side of the digester.

The temperature control had a 2 °F bandwidth for turning the pump on and off. The gas consumption of the boiler was very erratic on a day-to-day basis, and the pump often stayed on for many hours longer than necessary. The reading of the temperature indicator also varied several degrees on sunny days.

From this information it was decided that a more sensitive and accurate temperature control would be needed to determine the characteristics of the temperature inside the tank. A simple portable temperature indicator was made using a battery powered Wheatstone bridge circuit with a 50 μ A meter to read 30 to 40 °C. The probe was mounted at the end of a pole that could be inserted into the digester through the sampling ports. The temperature was found to be within $\pm 1^\circ\text{C}$ at any location inside the digester after a day of not loading. During loading the temperature would drop a few degrees and slowly rise with some hotter and colder spots (about 1 °C) occasionally passing the probe. It was noticed that loading with or without the gas recirculation mixer set up entirely different temperature stratifications and in fact, by monitoring the temperature changes, the effectiveness of the digester mixing could be monitored.

A combination temperature control and measuring unit was designed and installed. (See Appendix #1) Its on/off bandwidth could be varied from .1 to 1.5 °C; it was set to .1 °C. This very noticeably stabilized the temperature of the digester and resulted in the ability to predict gas consumption on a daily basis, given the loading volume and temperature.

Microprocessor. A microprocessor has been installed to monitor the heat flows of the system. Temperature probes have been installed in ten sites (See figure 3)



The microprocessor samples and records the history of time and temperature on magnetic tape for detailed performance evaluation. Ten channels log temperatures taken by YSI "Thermilinear Thermistors" #44202 that have an accuracy and interchangeability of ± 0.15 °C and a linearity deviation of ± 0.065 °C. The overall accuracy of the system (from -5 °C to 50 °C) is ± 0.2 °C, and overall resolution is ± 0.1 °C. Three discrete channels are used to log pump operation. The 14th channel logs internal time.

The sampling rate is set on site. Each channel can also be disabled so that it is neither recorded or displayed.

A cyclic routine displays the last sample of each channel and current time in

minutes, hours, and days. This provides an immediate on-site readout to verify current operation.

An internal clock with a stability of $\pm 0.01\%$ provides timing for display and logging.

The sampled data is temporarily stored in an internal buffer that holds 95 samples. When full, the buffer is automatically transferred to magnetic tape using Kansas City Standard format.

An internal calibration subroutine provides a continuous sample of a selected channel for hook-up verification and calibration.

Powered from standard 115 volt, 50 to 60 hz, and operating over the temperature range of 0 °C to 70 °C, the unit will continue to operate in case of power failure for over 24 hours on common lead-acid automobile battery back-up power without any performance degradation.

The microprocessor will allow us to obtain more accurate information on the components of heat demand, the efficiency of the influent/effluent heat exchanger, the efficiency of heat delivery in the digester, the efficiency of the boiler, and the amount of heat delivered from the Waukesha engine. This information will allow us to better quantify the cost effectiveness of various actions to improve the system's energy.

Net Energy

The economic feasibility of anaerobic digestion for energy production on a farm is determined by the capital cost, operation and maintenance costs, and the net usable energy produced. In considering the design of a system the trade-off between these three factors must be considered. (See Appendix #2)

In our work in the last quarter we focused on the operation and maintenance of our plant. Small and intermediate scale systems cannot justify hiring a person to tend the plant. Therefore, minimizing the operator time involved is crucial for the feasibility of the system.

Our work this past quarter and for the rest of the project will focus on the net energy of the system. By quantifying the elements of the energy requirements of the system, design decisions can be made as to the cost effectiveness of any action that will improve the system's net energy. Likewise, the information will be useful in determining the overall economics of a system in a given climate.

The energy requirements of a system are electricity for mixing, pumping, gas handling, etc., and the heat needed to warm incoming manure and to replace the digester heat lost through the skin.

Equation [1]:

$$Q = (UA\Delta T) \cdot (t) + (C_p \omega \Delta T) - (q_r V_g)$$

where:

Q = heat required

UA = heat loss per degree hour

ΔT = temperature of the digester - temperature of the ambient

t = time in hours

C_p = specific heat of slurry

ω = weight of slurry

q_r = heat of reaction per volume of methane

V_g = volume of methane produced

Biogas can be burned to keep the digester up to temperature and the excess used for process heat. Electricity must then be supplied by an outside source. The other option is to burn the gas to produce electricity to run the plant and for other options-- and possibly to feed into the utility grid. In this case, waste heat can be used to heat the digester and for other farm operations requiring low grade heat.

Equation [2]:

$$NE_g = E_p - (Q/\eta_g) - (e/\eta_e)$$

where:

- NE_g = net energy of gas
- E_p = energy produced
- Q = heat required [1]
- η_g = efficiency of heat delivery
- e = electricity used
- η_e = efficiency of electrical conversion

Equation [3]:

$$NE_e = (E_p \cdot \eta_e) - (Q \cdot \eta_g) - e + w$$

where:

- NE_e = net energy of electricity
- w = energy of waste heat utilized

Electrical Consumption

Electrical consumption of a digestion system is a critical factor-- especially in areas of high electrical cost. In addition, a system that is a net gas producer could be a net energy loser when the conversion efficiency of the

central station power providing electrical energy is considered.

This was the case at the beginning of our project. (See Figure 4) Consequently, a strong emphasis was placed on decreasing the electrical consumption of the system. As a result of decreasing the amount of in-tank mixing and improving the influent mixing system, electrical consumption was reduced from an equivalent of 64,000 GJ in November 1977 to 2,000 GJ in January 1979. (An increase to 4,000 in February was a result of experimentation with the heat exchanger. See the heat exchanger section.) Another major result of this decrease has been the reduction of machine use, and thereby lesser maintenance costs.

Mixing and loading the influent now replaces mixing the digester contents as the major electrical use. Consequently, more work is being done to decrease both the electrical consumption and the operator time involved in this operation.

Heat Demand

Between 40-45% of the total gas production of our system goes back into keeping the digester up to temperature. The major components of the heat demand are replacing heat lost through the digester skin and heating the cold influent.

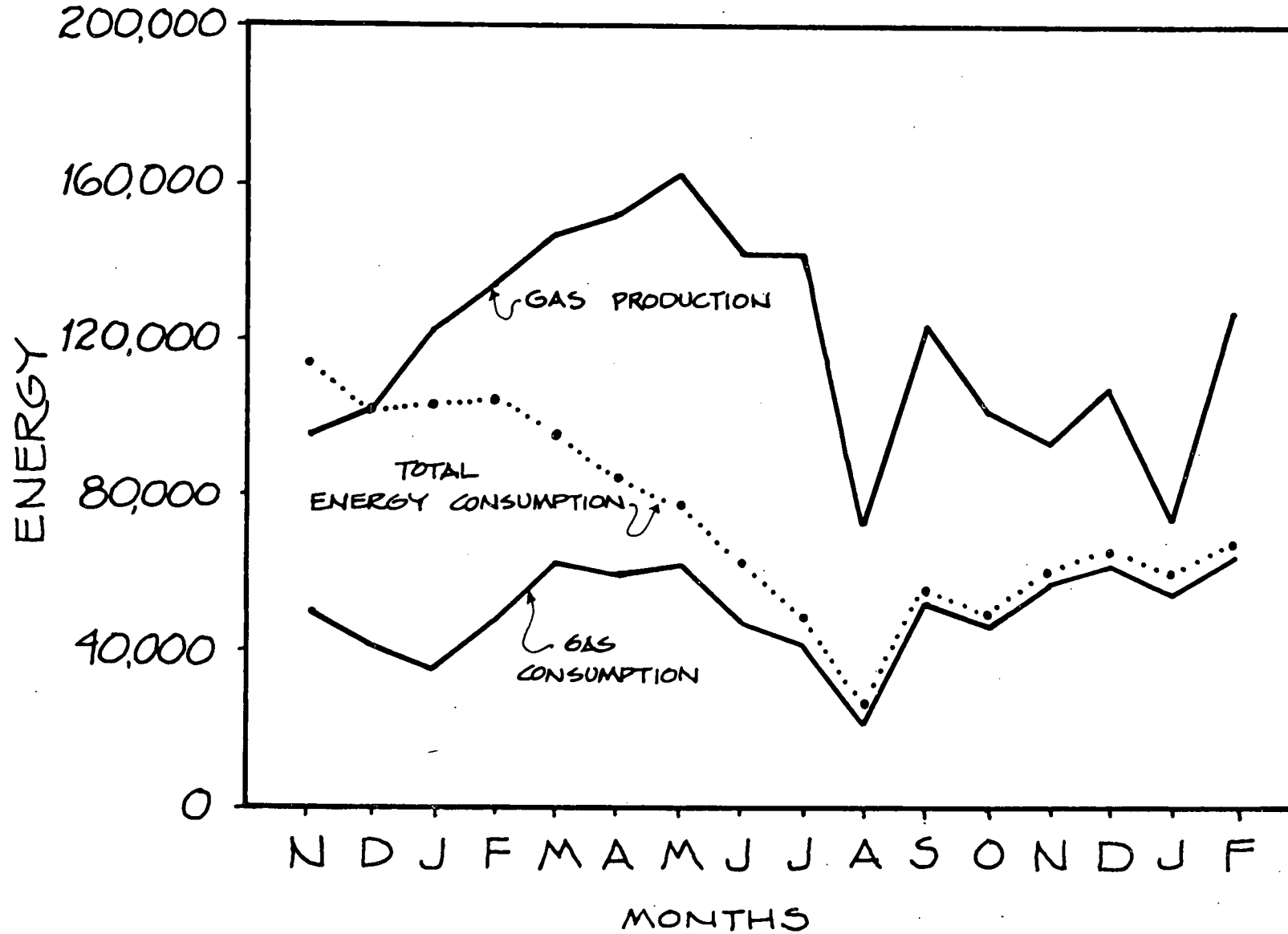
Skin Loss

Skin losses from our tank would be $613.3 \text{ GJ/hr-}^{\circ}\text{C-m}^2$ if the tank was uninsulated. Under those conditions the digester temperature could not be maintained even in the relatively mild Western Washington climate. Consequently, all exposed surfaces of the tank were insulated. 4" of Dow styrofoam SM_{tm} was installed on the exterior walls and 3" of polyurethane foam was sprayed on the inside of the roof. The calculated heat loss from the insulated tank is $299.7 \text{ kJ/hr-}^{\circ}\text{C}$. (See Appendix #3.)

NET ENERGY

FOR MONROE DIGESTER

GIGA JOULES



During a period of not loading at the beginning of January the thermostat was turned down and the temperature of the digester fell $.42\text{ }^{\circ}\text{C/day}$, which corresponded to a heat loss of $.293\text{ GJ/day}$. The predicted heat loss for the same condition is $.255\text{ GJ/day}$. The predicted heat of reaction for the gas produced is $.027\text{ GJ}$. Adjusting for this contribution gives a total heat loss of $.227\text{ GJ}$.

Because the tanks are insulated, skin loss accounts for only 20-25% of our heat demand. The question of how much insulation to install in a system is an economic one that is determined by average ambient temperature, local energy costs, and the diminished returns for each added amount of insulation.

Figure 5 depicts the interaction of these variables. The graph represents the economic trade-off between the value of energy saved by each additional increment of insulation (assuming a value of $\$3.32/\text{GJ}$), and the cost of adding that insulation. The two curves represent the energy savings realized at various R values for a climate having an average winter temperature of $4\text{ }^{\circ}\text{C}$, and an average winter temperature of $-7\text{ }^{\circ}\text{C}$. The straight line represents the annualized incremental cost of each inch of insulation.

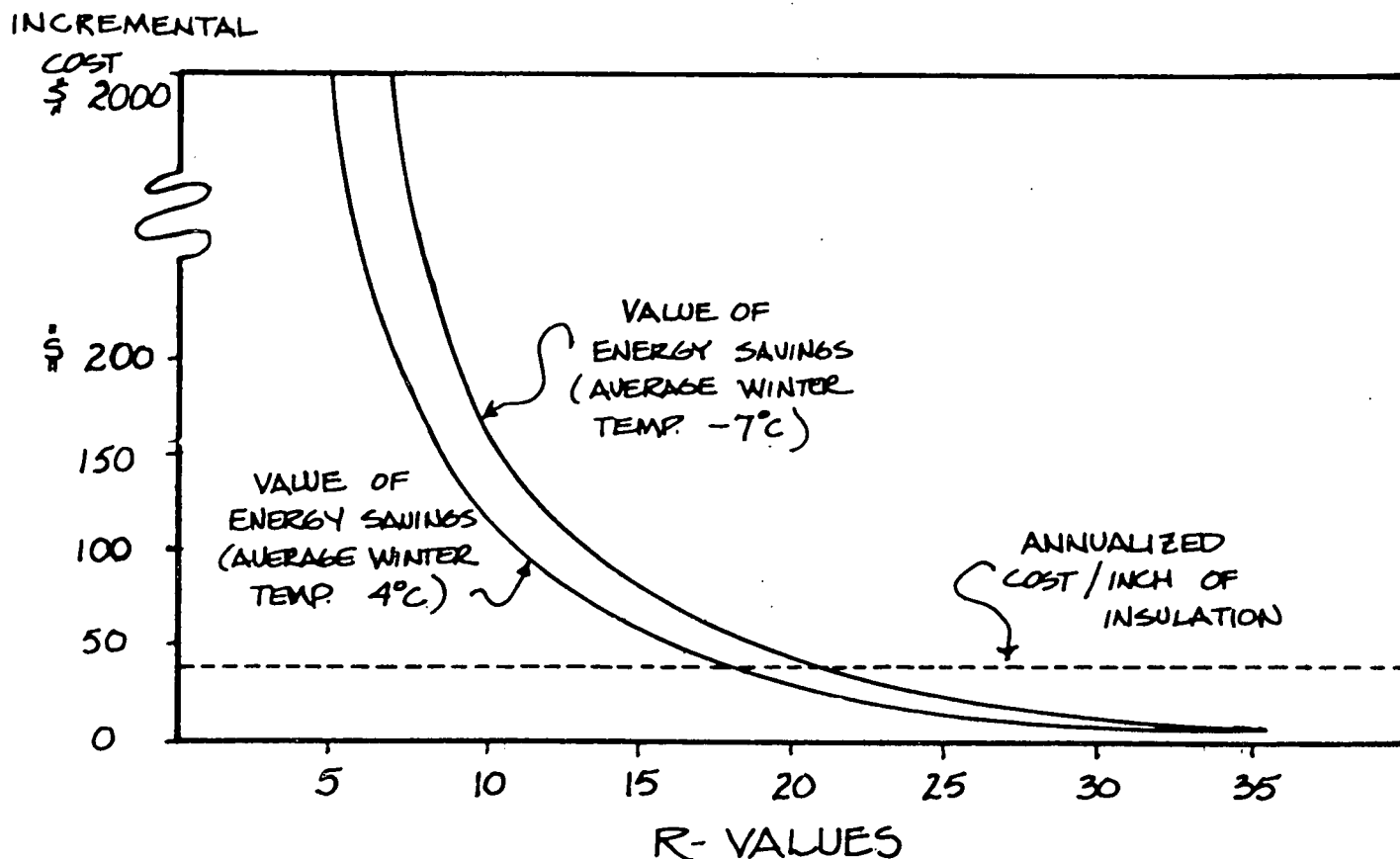


Figure 5

For a tank such as ours in this locality the breakdown point between incremental cost of insulation and increased energy savings is around $R = 18$. For the same tank in a colder climate (averaging a winter temperature of -7°C) with the same gas costs, the breakeven point would be $R = 22$.

Influent Heat Demand

With an insulated digester the heat required for warming incoming manure will account for 75-90% of the total system's heat demand. The two major means of decreasing this heat demand are reducing or eliminating the use of mixing water, and utilizing an influent/effluent heat exchanger.

Mixing Water

In addition to reducing the heat demand of the influent, eliminating mixing water also reduces the digester volume needed and cuts down on operating time. Both of these have a positive economic benefit. Our system was designed for loading at 4% T.S. Over the past year the % solids loaded has been raised 10% and now will be raised to 12-14%. By increasing the solids loaded from 4% to 12%, the influent heating demand is reduced by 2/3.

Figure 6 shows the relationship between the amount of energy needed for heating a given volume of manure at various dilutions.

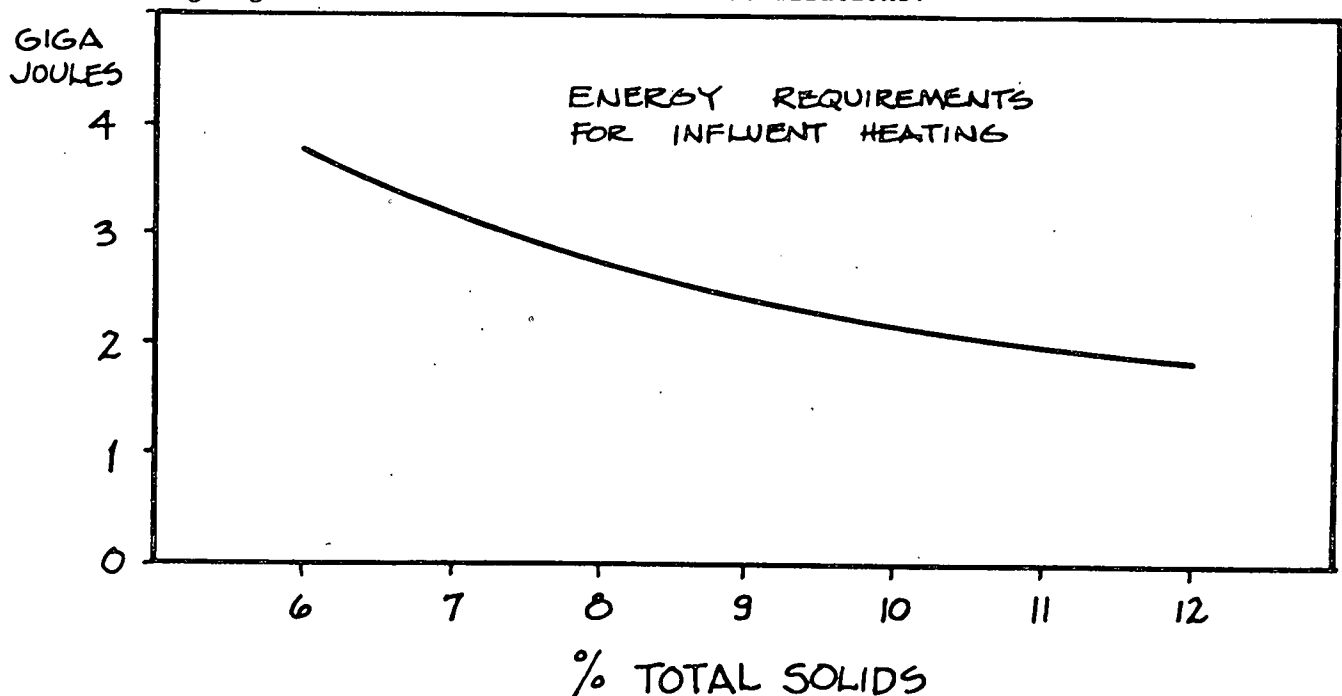


Figure 6

The benefit of dilution is that the slurry is more easily mixed and pumped. To save the maximum amount of energy little or no water should be added. The problem then becomes one of finding a pump that can mix and load the slurry. This problem is especially acute if bedding is used.

It is difficult to quantify the economic trade-offs in reducing the mixing water, since its impact will be specific to any application. The positive benefits are a smaller digester volume and less heating demand. Its costs are a pumping system that can handle a thick substrate.

Heat Exchanger

Trade-offs may exist between the option of loading a thick slurry and the use of an influent/effluent heat exchanger. Likewise the use of a heat exchanger may prevent the use of a totally gravity fed system and require the use of a pump. From a net energy standpoint the energy trade-off between a heat exchanger and the use of a transfer pump is very favorable, even taking into account the electrical conversion efficiency.

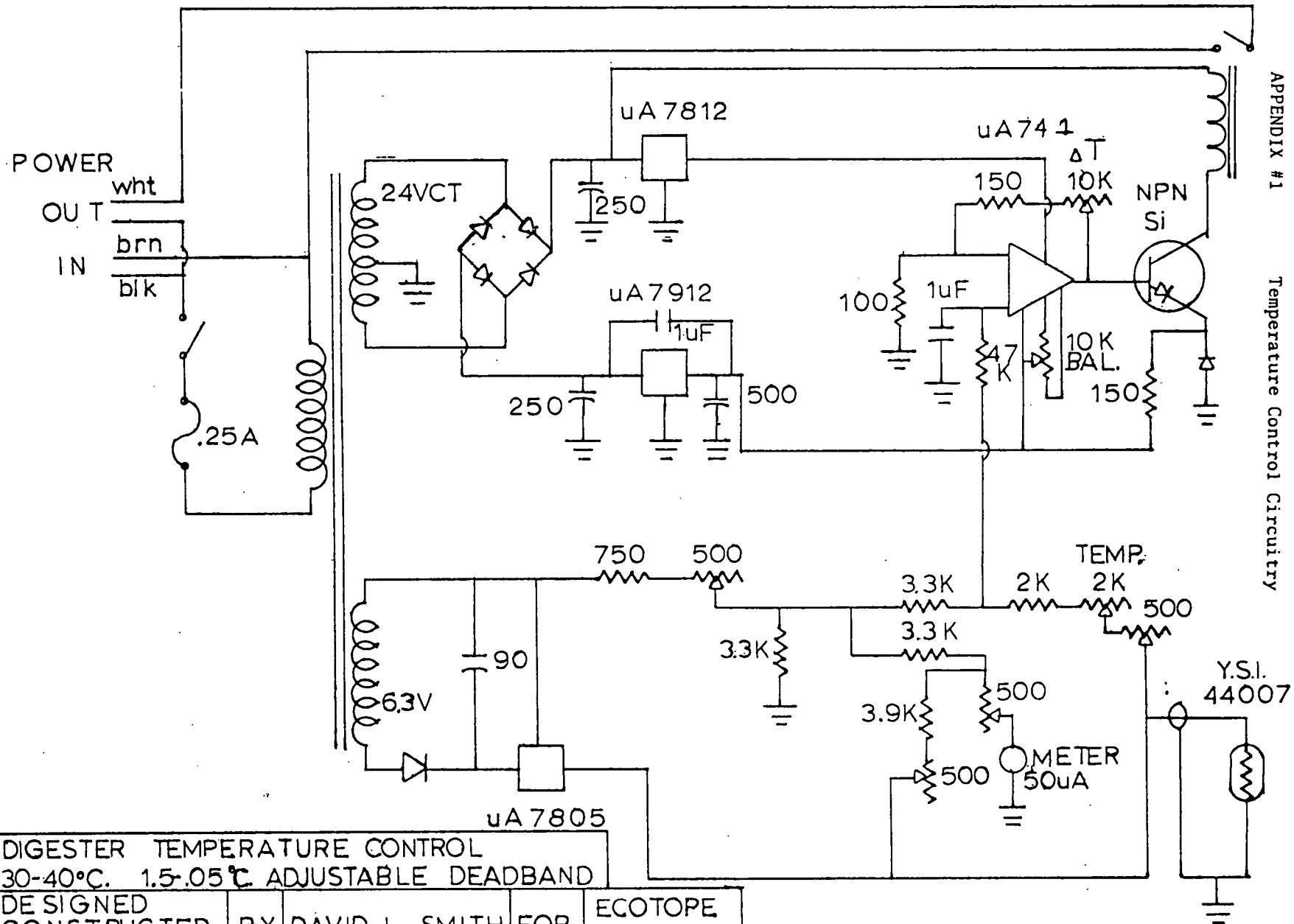
Another aspect of slurry-to-slurry heat exchange is the importance of agitation for efficient heat exchange. Preliminary data from the use of our tube-in-shell heat exchanger indicates severe channeling at low flow rates, which greatly reduces heat exchange and points to the need for agitation. Some work was done this quarter to investigate the use of the influent and effluent tanks as a heat exchanger. An efficiency of 33% over a 24-hour period was obtained through a 6" concrete wall; however, it required constant slurry agitation. The energy cost of this increased agitation greatly reduces the value of the heat recovered. If effective heat exchangers do require the use of pumps for transfer and agitation, the economic trade-off must be carefully examined.

The economics of that energy involve not only the cost of the electricity used, but also the capital operation and maintenance costs involved with the pump. Pumps have been our major maintenance expense. Machinery used

around manure is subject to extraordinary corrosion. For small and intermediate size operations the question of pump use can be critical.

Heat Delivery

Another area that significantly affects the gas consumption of a system is the efficiency of heat delivery. Preliminary measurements indicate that in our system the boiler transfers heat with only a 50-60% efficiency. When the digester was turned down during the freeze 25.7 m³/ day of gas was consumed just to keep the boiler up to temperature. This value represents over 10% of our daily gas consumption. This figure will probably be lower on days when the boiler is running, but it does indicate that significant improvements in net energy could be realized by improving the efficiency of heat delivery.



DIGESTER TEMPERATURE CONTROL
30-40°C. 1.5-.05°C ADJUSTABLE DEADBAND

DESIGNED	BY	DAVID L. SMITH	FOR	ECOTOPE GROUP
CONSTRUCTED		12-18-78		
DRAWN				

APPENDIX #2

Life Cycle Energy Analysis for HP-97 Desk Calculator

by David Baylon, Ecotope Group

Rate of Return/ Energy Cost of Production Program (Life Cycle)

This program computes the energy benefits from "on-site" energy production in two ways:

- 1) rate of return, that is, net benefit divided by invested capital and capital cost (interest)
- 2) energy cost (\$/MBTU or \$/kWh), that is, the cost of energy production divided by the total energy production

INPUT

Primary Storage Registers

E	capital cost
D	capital credits (direct tax credits, rebates, etc.)
C	interest rate (opportunity cost of capital)
B	inflation rate (+1)
A	fuel escalation rate (+1) of competitive energy
9	life of facility
8	annual energy cost of facility operation in \$
7	annual energy production (BTU, kWh, GJ)
6	current energy cost of competitive energy (\$/MBTU)

Secondary registers

0	labor cost of operation (annual)
1	maintenance cost of operation (annual)
2	tax bracket of owner of facility (for depreciation credit)
5	loan life

Economic Formulas and Assumptions

1. Capital Cost

$$CC = C - CR$$

(Clean Water Act)
Investment Credits
Renewable Energy Credits

$$AC = cc \left(\frac{i}{1 - (1+i)^{-N}} \right)$$

Total Capital Cost (present value)

$$TCC = AC \left(\frac{1 - (1+r)^{-N}}{\ln(1+r)} \right)$$

2. Depreciation (straight line)

$$DC = TR \cdot \frac{CC}{N} \cdot \left\{ \frac{1 - (1+r)^{-N}}{\ln(1+r)} \right\} = \text{Depreciation}$$

3. Operating Costs, Total O.C.

$$OC = (M + L)N$$

4. Total Energy Costs (present value) (Production or Consumption)

$$E = EV \cdot EP \cdot N$$

$$TE = E \left\{ \frac{\left(\frac{1+e}{1+r} \right)^N - 1}{\ln \left(\frac{1+e}{1+r} \right)} \right\} = EC$$

5. Rate of Return (present value)

$$(1+M) = \left(\frac{TE - OC - EC + DC}{TCC} \right)^{1/N}$$

6. Average Cost of Energy (present value)

$$CE = \frac{TCC + OC + EC - DC}{EP \cdot N}$$

7. Payback Period

$$K = \frac{\ln \left(\left(\frac{1}{E} \cdot EV \right) \cdot \left(\ln \frac{1+e}{1+r} \right) \cdot (TCC) + 1 \right)}{\ln \left(\frac{1+e}{1+r} \right)}$$

Where:

i = interest rate or opportunity cost on initial capital
r = inflation rate
e = fuel cost escalation
N = life of project
C = total construction cost
CR = federal credits (Clean Water Act, 1977) and tax credits (Renewable Tax Credits,
Investment Tax Credits)
CC = capital cost
AC = annual capital cost with interest
TCC = total capital cost over project life
DC = depreciation tax credit
TR = tax rate
M = maintenance
L = operator labor
OC = operating cost
E = annual energy cost (present)
TE = total energy value over project life
EC = total energy cost (plant operation)
R = rate of return
CE = value of energy produced
EP = total energy production (BTU, kWh, etc.)
EV = present energy cost/unit

40

001	*LEL1	21 01	044	÷	-24	087	F2S	16-51	129	ST+4	35-55 04	171	ST00	35 00
002	DSP2	-63 02	045	1/X	52	088	RCL9	36 09	130	ST-5	35-45 05	172	STX1	35-35 01
003	SFC	16-11	046	STX0	35-35 00	089	x	-35	131	RTN	24	173	RCLC	36 15
004	RCLC	36 15	047	R1	-31	090	ST+4	35-55 04	132	*LEBLA	21 11	174	RCLD	36 14
005	PRTX	-14	048	GSBD	23 14	091	ST-5	35-45 05	133	P2S	16-51	175	-	-45
006	RCLD	36 14	049	RCL0	36 00	092	RCL5	36 05	134	RCL1	36 01	176	STX1	35-35 01
007	PRTX	-14	050	x	-35	093	RCL0	36 00	135	PRTX	-14	177	RCLC	36 13
008	-	-45	051	ST+4	35-55 04	094	÷	-24	136	ST03	35 03	178	1	01
009	ST00	35 00	052	ST00	35 00	095	X#0?	16-45	137	F19	16 23 01	179	+	-55
010	RCL9	36 09	053	RCLA	36 11	096	0	00	138	RTN	24	180	P2S	16-51
011	PRTX	-14	054	PRTX	-14	097	RCL9	36 09	139	RCL0	36 00	181	RCL5	36 05
012	GSBD	23 14	055	RCLB	36 12	098	1/X	52	140	PRTX	-14	182	P2S	16-51
013	ST01	35 01	056	PRTX	-14	099	YX	31	141	RCL3	36 03	183	ST05	35 05
014	RCLC	36 15	057	÷	-24	100	1	01	142	+	-55	184	YX	31
015	x	-35	058	ST02	35 02	101	-	-45	143	ST03	35 03	185	1/X	52
016	RCL9	36 09	059	RCL9	36 09	102	DSP4	-63 04	144	SF0	16 21 00	186	CHS	-22
017	÷	-24	060	YX	31	103	SFC	16-11	145	RTN	24	187	1	01
018	P2S	16-51	061	1	01	104	PRTX	-14	146	*LEBLD	21 14	188	+	-55
019	RCL2	36 02	062	-	-45	105	SFC	16-11	147	RCLB	36 12	189	RCLC	36 13
020	PRTX	-14	063	RCL2	36 02	106	DSP3	-63 03	148	XZY	-41	190	÷	-24
021	x	-35	064	LN	32	107	RCL4	36 04	149	YX	31	191	1/X	52
022	P2S	16-51	065	÷	-24	108	RCL7	36 07	150	1/X	52	192	STX1	35-35 01
023	ST05	35 05	066	ST02	35 02	109	÷	-24	151	CHS	-22	193	RCLB	36 12
024	CHS	-22	067	RCL8	36 08	110	RCL9	36 09	152	1	01	194	RCL5	36 05
025	ST04	35 04	068	PRTX	-14	111	÷	-24	153	+	-55	195	YX	31
026	P2S	16-51	069	X#0?	16-42	112	PRTX	-14	154	RCLB	36 12	196	1/X	52
027	RCL5	36 05	070	GSBD	23 02	113	SFC	16-11	155	LN	32	197	CHS	-22
028	P2S	16-51	071	RCL7	36 07	114	CF1	16 22 01	156	÷	-24	198	1	01
029	PRTX	-14	072	PRTX	-14	115	F0?	16 23 00	157	RTN	24	199	+	-55
030	ENT1	-21	073	RCL6	36 06	116	RTN	24	158	R/S	51	200	RCLB	36 12
031	ENT1	-21	074	PRTX	-14	117	P2S	16-51	159	*LEBLE	21 15	201	LN	32
032	ENT1	-21	075	x	-35	118	RCL3	36 03	160	RCL6	36 06	202	÷	-24
033	RCLC	36 13	076	RCL2	36 02	119	P2S	16-51	161	RCL7	36 07	203	STX1	35-35 01
034	PRTX	-14	077	x	-35	120	RCL9	36 09	162	x	-35	204	1	01
035	1	01	078	ST+5	35-55 05	121	x	-35	163	RCL8	36 08	205	ST+1	35-55 01
036	+	-55	079	GSBD	23 12	122	ST-4	35-45 04	164	-	-45	206	RCL1	36 01
037	XZY	-41	080	RTN	24	123	ST+5	35-55 05	165	1/X	52	207	LN	32
038	YX	31	081	*LEBLB	21 12	124	GSBD	23 13	166	ST01	35 01	208	RCL0	36 00
039	1/X	52	082	CF0	16 22 00	125	RTN	24	167	RCLA	36 11	209	÷	-24
040	CHS	-22	083	SF1	16 21 01	126	*LEBL2	21 02	168	RCLB	36 12	210	SPC	16-11
041	1	01	084	*LEBLC	21 13	127	RCL2	36 02	169	÷	-24	211	PRTX	-14
042	+	-55	085	GSBA	23 11	128	x	-35	170	LN	32	212	RTN	24
043	RCLC	36 13	086	RCL5	36 03									

OPERATION: GSB 1

OUTPUT:

Capital cost	94200.00
Credit	3500.00
Life	25.00
Tax Rate	0.20
Life of loan	25.00
Interest rate	0.10
Fuel escalation rate	1.15
Inflation rate	1.07
Energy cost of operation	390.00
Energy production	2833.00
Energy cost/unit (present)	5.50
Maintenance costs	1500.00
Rate of return without labor costs	0.0740
Energy cost (life) without labor costs	2.317
Maintenance cost	1500.000
Labor cost	1750.000
Rate of return with labor costs	0.0710
Energy cost (life) with labor costs	2.935
Payback period (E)	0.247

APPENDIX #3

Heat Loss Through Skin

Areas

wall: 25' diameter 13.5 ft high = 1050 ft^2

roof: 25' diameter 13.3 ft rise = 520 ft^2

floor: 12" cement mortar floor (assume heat loss only around the perimeter)

perimeter: 78.5 ft

Insulation

wall: 4" Dow Styrofoam SM_{tm}, $R = 4.0/\text{in} = 16$

(expanded polystyrene extruded, cutcell surface, $1.8 \text{ lb}/\text{ft}^3$)

$$U = 1/16 = 0.063 \text{ BTU}/\text{hr}\cdot\text{ft}^2\cdot^{\circ}\text{F}$$

roof: 3" sprayed polyurethane foam (interior), $R = 6.25/\text{in} = 19$

(expanded polyurethane, $1.5 \text{ lb}/\text{ft}^3$)

$$U = 1/19 = 0.053 \text{ BTU}/\text{hr}\cdot\text{ft}^2\cdot^{\circ}\text{F}$$

floor: 12" cement mortar floor (assume loss only around the perimeter)

$$q = .8 \text{ BTU}/\text{hr}\cdot\text{ft}^2\cdot^{\circ}\text{F}$$

$$p = 78.5 \text{ ft}$$

$$\Delta T = 95 - T_A$$

Heat Loss

$$\begin{aligned} \text{wall: } q &= 0.63 \text{ BTU}/\text{hr} \cdot \text{ft}^2 \cdot ^{\circ}\text{F} \cdot 1050 \text{ ft}^2 \cdot 24 \text{ hours} \\ &= 1587.6 \text{ BTU}/^{\circ}\text{F} \cdot \Delta T_{\text{OF}} \end{aligned}$$

$$\begin{aligned}\text{roof: } q &= .053 \text{ BTU/hr} \cdot \text{ft}^2 \cdot ^\circ\text{F} \cdot 520 \text{ ft}^2 \cdot 24 \text{ hours} \\ &= 674.16 \text{ BTU} \cdot \Delta T_{\text{OF}}\end{aligned}$$

$$\begin{aligned}\text{floor: } q &= .81 \text{ BTU/hr} \cdot \text{ft}^2 \cdot ^\circ\text{F} \cdot 78.5 \text{ ft} \cdot 24 \text{ hours} \\ &= 1526.05 \text{ BTU/}^\circ\text{F} \cdot \Delta T\end{aligned}$$

Daily Heat Loss

$$\begin{aligned}& (1587.6 \text{ BTU/}^\circ\text{F} + 674.16 \text{ BTU/}^\circ\text{F} + 1526.04 \text{ BTU/}^\circ\text{F}) \cdot (T_D - T_A) \\ &= 3787.80 \text{ BTU/}^\circ\text{F} (T_D - T_A)\end{aligned}$$

Calculated Heat Loss and Actual Heat Loss January 9--11

Average temperature of the digester = 97.3°F

Average temperature of the ambient = 33.3°F

Temperature drop = $.75^\circ\text{F/day}$

Digester volume = 6250 ft^3

$\rho = 63.08 \text{ lb/ft}^3$

$C_p = .94 \text{ BTU/lb-}^\circ\text{F}$ (7% T.S.)

$$\begin{aligned}\text{Calculated Daily Heat Loss} &= .3787.80 \text{ BTU/}^\circ\text{F} (97.3^\circ - 33.3^\circ) \\ &= .242 \times 10^6 \text{ BTU}\end{aligned}$$

$$\begin{aligned}\text{Actual Daily Heat Loss} &= .94 \text{ BTU/lb-}^\circ\text{F} \cdot 63.08 \text{ lb/ft}^3 \cdot 6250 \text{ ft}^3 \cdot .75^\circ\text{F/day} \\ &= .278 \cdot 10^6 \text{ BTU/day}\end{aligned}$$

MILESTONE AND MANAGEMENT REPORT

Ecotope Group
Monroe State Honor Farm
Anaerobic Digestion Project

	Jl	Au	Sp	Oc	Nv	Dc	Ja	Fe	Mr	Ap	My	Je	Jl	Ag
SYSTEM IMPROVEMENTS														
1. Automate system														
2. Modify plumbing														
3. Continue mixing studies														
4. Decrease retention time														
5. Operate digester in thermophilic range														
6. Farm gas utilization														
7. Farm cadre training														

HEAT EXCHANGER OPERATION

1. Preliminary engineering analysis														
2. Order pump														
3. Pump delivery and installation														
4. Increase % solids loaded														
5. Evaluate heat exchanger operation														

INTERNAL COMBUSTION ENGINE EVALUATION

1. Contact local utility														
2. Install waste heat monitoring equipment														
3. Restart engine-generator														
4. Operate engine-generator														
5. Monitor waste heat utilization														
6. Hook up to utility grid														
7. Evaluate performance and efficiency of operation														

REPORTS

▲ ▲ ▲ ▲ ▲

ANALYSIS OF DIGESTER DESIGN CONCEPTS

Prepared by:

Edward Ashare and Elizabeth H. Wilson

ABSTRACT

Engineering economic analyses were performed on various digester design concepts to determine the relative performance for various biomass feedstocks. A comprehensive literature survey describing the state-of-the-art of the various digestion designs is included. The digester designs included in the analyses are CSTR, plug flow, batch, CSTR in series, multi-stage digestion and biomethanation. Other process options investigated included pretreatment processes such as shredding, degritting, and chemical pretreatment, and post-digestion processes, such as dewatering and gas purification. The biomass sources considered include feedlot manure, rice straw, and bagasse.

The results of the analysis indicate that the most economical (on a unit gas cost basis) digester design concept is the plug flow reactor. This conclusion results from this system providing a high gas production rate combined with a low capital "hole-in-the-ground" digester design concept. The costs determined in this analysis do not include any credits or penalties for feedstock or by-products, but present the costs only for conversion of biomass to methane. The batch land-fill type digester design was shown to have a unit gas cost comparable to that for a conventional stirred tank digester, with the potential of reducing the cost if a land-fill site were available for a lower cost per unit volume.

The use of chemical pretreatment resulted in a higher unit gas cost, primarily due to the cost of pretreatment chemical. A sensitivity analysis indicated that the use of chemical pretreatment could improve the economics provided a process could be developed which utilized either less pretreatment chemical or a less costly chemical.

The use of other process options resulted in higher unit gas costs. These options should only be used when necessary for proper process performance, or to result in production of a valuable by-product.

Figure 33

Unit Gas Cost for Digestion of Rice Straw

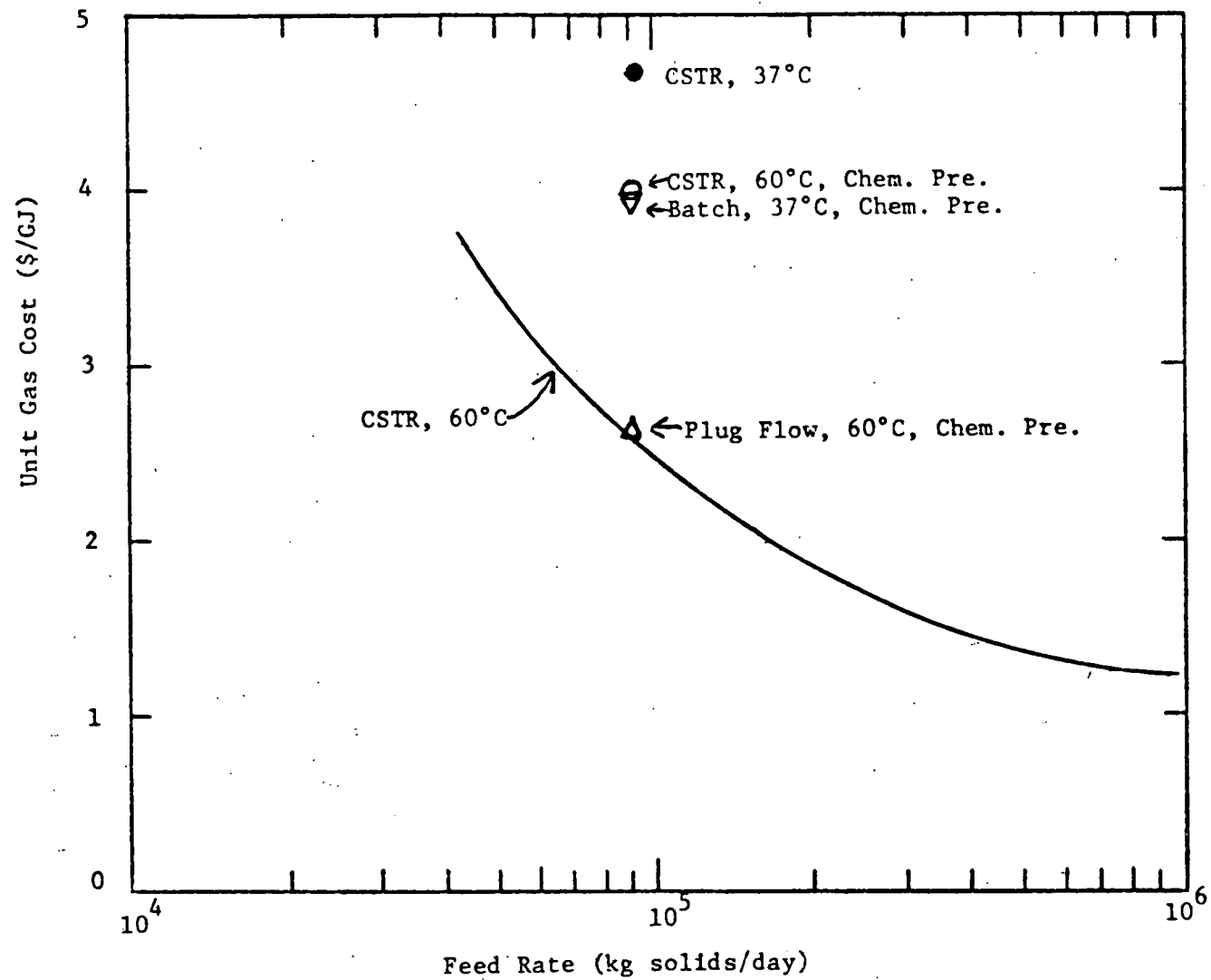


Figure 34

Unit Gas Cost for Digestion of Bagasse

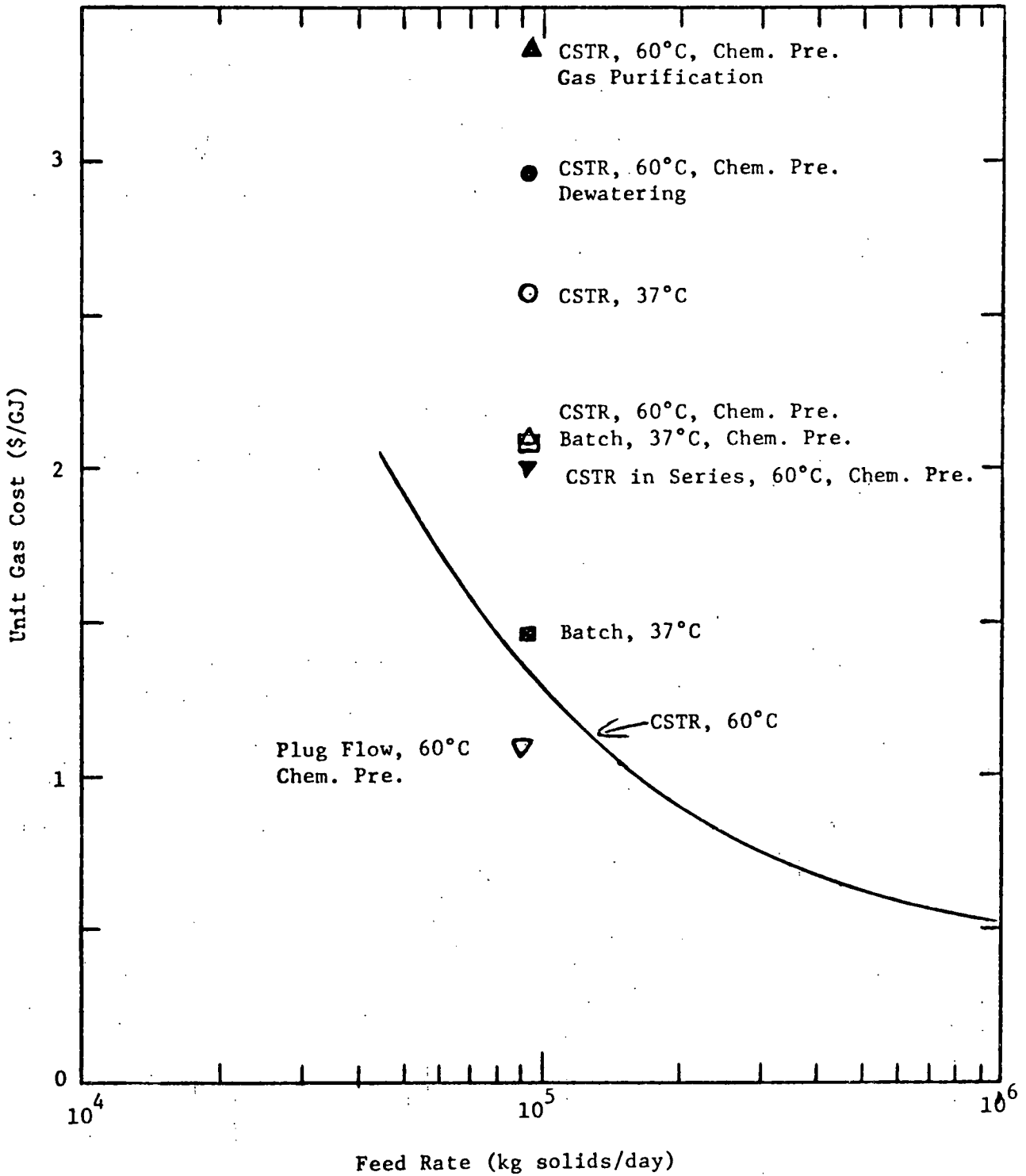
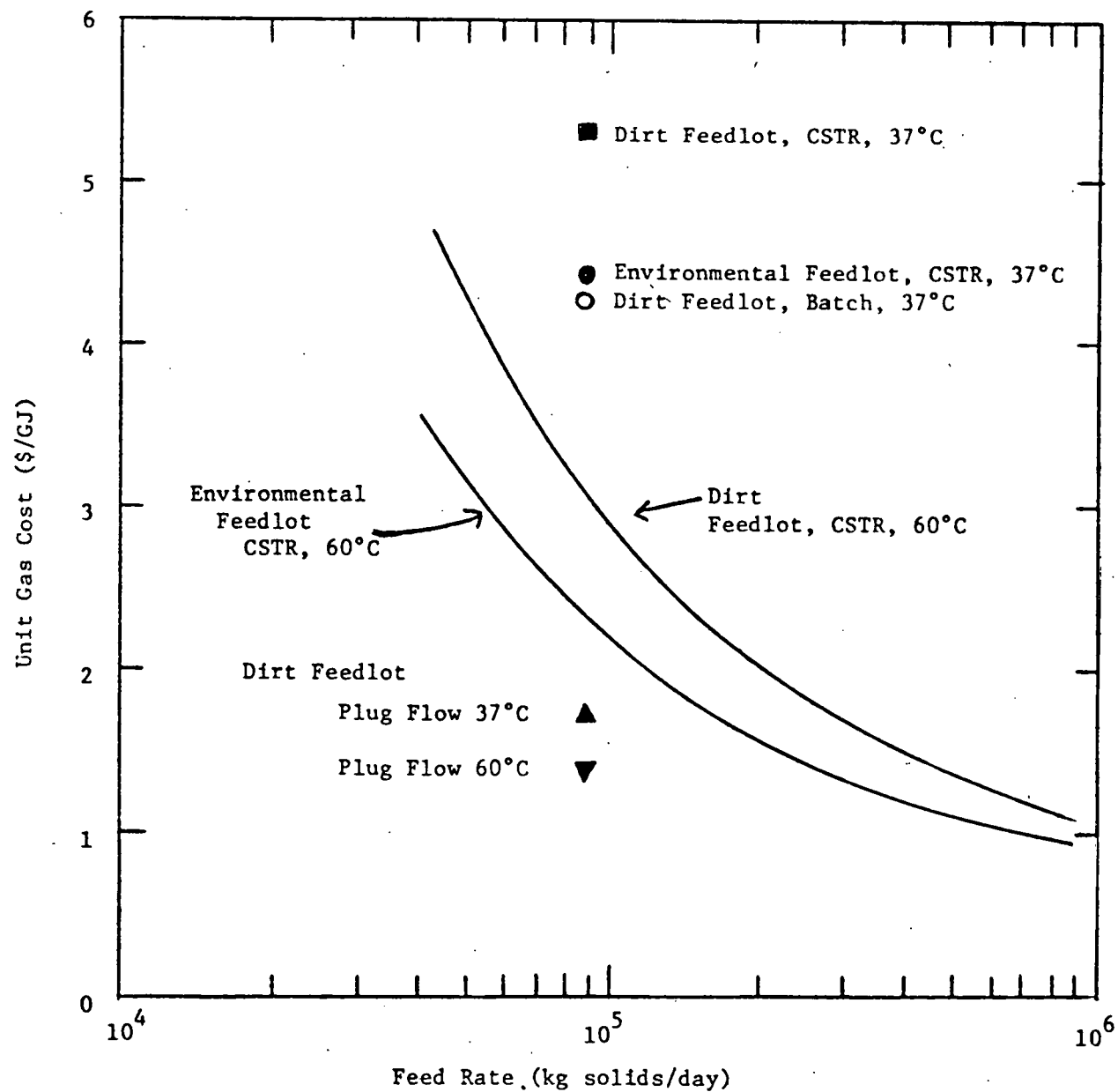


Figure 32

Unit Gas Cost for Digestion of Feedlot Manure



ANAEROBIC FERMENTATION OF LIVESTOCK AND CROP RESIDUES

QUARTERLY PROGRESS REPORT
DECEMBER, 1978 to FEBRUARY, 1979
TAMPA, FLORIDA

Y. R. CHEN
A. G. HASHIMOTO

ROMAN L. HRUSKA U.S. MEAT ANIMAL RESEARCH CENTER.
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CLAY CENTER, NEBRASKA 68933

PREPARED FOR

U.S. DEPARTMENT OF ENERGY
DIVISION OF SOLAR TECHNOLOGY
FUELS FROM BIOMASS SYSTEMS BRANCH
INTERAGENCY AGREEMENT EX-76-A-29-1058

INTRODUCTION

The overall objective of this project is to evaluate the technical and economic feasibility of the anaerobic fermentation process to recover methane and high protein biomass from beef cattle and crop residues. The specific objectives of interest to the Department of Energy are: a) to develop design criteria for optimum production of methane from anaerobic digestion of beef cattle and crop residue; and b) to determine the capital and operating costs, and energy, manpower and safety requirements for anaerobic fermentation systems associated with livestock operations. This report summarizes the operation of the pilot-scale fermentor and the results of the study of energy requirements and methane production cost for anaerobic fermentation systems during the reporting period.

PILOT-SCALE FERMENTOR

During this reporting period, we attempted to recycle the effluent centrate as make-up water for the influent feed. The purpose of this study was to determine whether increased methane production rates could be obtained by recycling the bacterial cells and nutrients in the centrate (e.g., volatile fatty acids, organic matter, etc.). This question intrigued us since the centrifuge only recovers about 20% of the protein (i.e., cells) and the centrate contains about 2000 mg/l total volatile acids, 8000 mg/l alkalinity and other nutrients. Also, recovering the effluent heat would produce a more favorable heat balance for the fermentation system.

Figures 1, 2, 3, and 4 show the pH and alkalinity, ammonia, TVA and volumetric gas production rate profiles during the reporting period. The centrate was recycled on day 750 at a seven-day retention time. The alkalinity, ammonia, and TVA all began to increase dramatically after day 750. The gas production increased up to day 754, then decreased on day 755 because it was not fed. On

day 759, the fermentor was not fed again because of excessive foaming. On day 760 and 761, the fermentor was fed at 12 days retention time, not fed on day 762, fed at 12 days retention time on days 763 to 765, and not fed on days 766 to 774. It is obvious from this study that recycling the centrate resulted in some form of toxicity to the system, and would not be a recommended practice for livestock residue fermentors.

During the rest of the reporting period, the fermentor has been operated to recover from the stress imposed by this study.

ENERGY REQUIREMENTS FOR ANAEROBIC FERMENTATION SYSTEMS

Pumping and mixing are integral operations in a completely mixed, continuous flow methane fermentation system. Realistic estimates of the pumping and mixing requirements are necessary in order to properly size the equipment, and to estimate the total energy requirement and utility costs of the system.

The rheological properties of the material being pumped and mixed have a direct influence on the power requirements. Livestock waste slurries generally display non-Newtonian, pseudoplastic behavior. The relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) was modeled by a power law formula:

$$\tau = K\dot{\gamma}^n \quad (1)$$

where: K and n are rheological consistency and behavior indices, respectively.

The rheological properties of the fermentor contents and the process slurry were obtained by a rotational viscometer. Figure 5 and 6 are two typical rheological property plots (τ vs. $\dot{\gamma}$) for fermentor contents and process slurry.

Pumping Power Requirements

The power requirement for pumping is equal to the total pressure loss multiplied by the flow rate.

The pressure drop is equal to:

$$\Delta P = f \frac{2L}{D} (\rho V^2) \quad (2)$$

where: f = friction coefficient, dimensionless

L = pipe length, m

D = pipe diameter, m

V = flow speed, m/sec, and

ρ = slurry density, Kg/m³.

The friction coefficient for flow in smooth pipes is given by (Chen and Hashimoto, 1976):

$$f = \begin{cases} 16/N_{Re}' & \text{for } N_{Re}' \leq 3100 \\ 0.0306 (N_{Re}')^{-0.18} & \text{for } N_{Re}' > 4300, \end{cases} \quad (3)$$

and N_{Re}' is the Generalized Reynolds number, which can be calculated by:

$$N_{Re}' = \frac{(\rho DV)}{K} \left(\frac{8V}{D} \right)^{(1-n)} \left[\frac{4n}{3n+1} \right]^n \quad (4)$$

In the laminar flow region ($N_{Re}' \leq 3100$), the friction coefficient is independent of pipe surface roughness. Therefore, Equation (3) for $N_{Re}' \leq 3100$ can also be used to calculate the friction coefficient for a rough pipe. There is no known report on the effect of surface roughness on pumping livestock waste slurries in turbulent flow region. We suggest that the f for rough pipe in the turbulent region be approximated by multiplying the f obtained from Equation (3) (for $N_{Re}' > 4300$) by the ratio of the f 's of the rough and smooth pipes from the Moody diagram for Newtonian liquids at the same Reynolds number.

There is little available information on calculating the frictional losses in flow through pipe fittings such as expansions, contractions, connectors, and elbows. Until more applicable data becomes available, the friction losses of slurries flowing through pipe fittings can be estimated by the method currently used for Newtonian liquids (i.e., using effective pipe lengths for various fittings).

Tables 1 and 2 list the designed pipe diameter, pumping rate, number of

pumps and the total influent and effluent volume to be pumped for different feedlot size. Five days retention was assumed. Power required per 100 m is listed in Tables 1 and 2. The pumping time per day was assumed to be 10 hours so that the same unit can be used for pumping both influent and effluent. The rheological consistency and behavior indices were taken to be $K = 4.0 \text{ dyne} \cdot \text{sec}^n / \text{cm}^2$ and $n = 0.6$ for the influent and $K = 3.0 \text{ dyne} \cdot \text{sec}^n / \text{cm}^2$ and $n = 0.5$ for the effluent. The pump efficiency was assumed to be 50%.

Table 1 shows that for the influent, the power requirement per 100 m is 0.987 Kw for a 1,000-head feedlot and 98.4 Kw for a 100,000-head feedlot. Power requirement increases directly with feedlot size for feedlots greater than 25,000 head.

The power per unit volume per 100 m of pipe varies from 22.6 w/m^3 to 40.5 w/m^3 . This number depends on the pipe size chosen.

Table 2 shows that power requirement is less for pumping effluent because of the lower total solids concentration (i.e., lower apparent viscosity). The power requirement per unit volume pumped varies from 11.75 w/m^3 to 20.5 w/m^3 .

Mixing Power Requirements

The power required to mix livestock waste slurries can be estimated from the plot of the Generalized Reynolds number with the power number. The Generalized Reynolds number for mixing is given by (Metzner and Otto, 1959):

$$N_{Re}' = \frac{\rho D^2 N (11N)^{1-n}}{K} \left[\frac{4n}{3n+1} \right]^n \quad (5)$$

where: N is the impeller rotational speed and D is the impeller diameter. The power number is calculated by:

$$N_p = \frac{P}{\rho D^5 N^3} \quad (6)$$

where: P is the power applied by the impeller on the slurry.

For an impeller to tank diameter ratio of 0.33, we found that, when propellers are used, the power curve of the slurries coincides with the power curve of Newtonian liquids; however, when turbines are used, the power curve deviates from the Newtonian power curve in the transition range (N_{Re}' between 10 to 1000) and coincides in the laminar range. For turbine, the power number for the slurries is about 25% higher than the power number for Newtonian liquids at the same Reynolds number in some transition range.

Figures 7 and 8 are plots of the mixing power number for Newtonian liquid and fresh cattle manure slurry for propeller to tank diameter ratios 0.33 and 0.2.

The marked effect of N_{Re}' on the power consumption is shown in Figure 9. The choice of N_{Re}' for mixing depends on the required degree of mixing. We found that N_{Re}' of 3,000 for turbine and 10,000 for propeller gave sufficient mixing.

Tables 3 and 4 give the required digester tanks and propellers for mixing fermentor contents and process slurry for beef feedlots ranging from 1,000 to 100,000-head. The maximum tank height was assumed to be 10 m. The propeller to the tank diameter ratio was assumed to be 0.2 with the maximum propeller diameter of 4 m. The propeller was assumed to be operated at $N_{Re}' = 10^4$ with $N_p = 0.45$ (Figure 8).

The mixing power per cubic meter of volume was found to decrease from 13.4 w/m³ for 1,000-head feedlots to 4.01 w/m³ for 25,000-head feedlots and is constant for feedlots greater than 25,000-head. For premixing the slurry, the power requirement decreases from 68.1 w/m³ for 1,000-head feedlots to about 6 w/m³ for 25,000-head feedlots and is constant for feedlots larger than 25,000-head.

Heating Requirements

The total heat required to maintain the fermentor at a desired temperature can be expressed as follows:

$$Q_T = Q_d + Q_w + Q_g + Q_i - Q_r \quad (7)$$

where: Q_T = total fermentor heat requirement, J/day,

Q_d = heat loss through fermentor walls, floor and top, J/day,

Q_w = heat loss through evaporation, J/day,

Q_g = heat loss through the gas leaving fermentor, J/day,

Q_i = heat required to raise the influent slurry to the desired fermentor temperature, J/day, and

Q_r = heat of reaction from the formation of methane fermentor, J/day.

The heat loss from the fermentor wall (Q_d) is the sum of the heat losses through the top, side walls, and bottom of the digester:

$$Q_d = (U_1A_1 + U_2A_2 + U_3A_3) (t - t_a) \quad (8)$$

where: $U_{1,2,3}$ = overall heat transfer coefficients of top, side walls, and bottom of the fermentor, J/d·m²·°C,

$A_{1,2,3}$ = surface areas of the top, side walls, and bottom of the fermentor, m²,

t = fermentor temperature, °C, and

t_a = ambient temperature, °C.

The heat loss due to evaporated water is the sum of the sensible heat loss of the stream and heat of evaporation of water:

$$Q_w = W_w [H_v + (C_p)_v (t - t_a)] \quad (9)$$

where: W_w is the mass flow rate of water vapor leaving the fermentor, H_v is the evaporation heat, J/kg, $(C_p)_v$ is the water vapor specific heat, J/kg °C.

At fermentor temperature 35°C, $H_v = 2.42$ MJ/kg and $(C_p)_v = 1.886$ KJ/kg °C.

The mass flow rate of water vapor in the biogas stream has been estimated by Ashare et al. (1977):

$$W_w = 0.804 (V \cdot \gamma_V) X_w / f(1 - X_w) \quad (10)$$

where: f is the volume fraction of CH_4 in the biogas, V is the fermentor working volume, m^3 , γ_V is volumetric CH_4 production per volume of fermentor per day, $\text{m}^3 \text{CH}_4/\text{m}^3/\text{d}$, and X_w is the mole fraction of water in the biogas stream:

$$X_w = 1.27 \times 10^6 \exp [-5520/(t + 273)] \quad (11)$$

where: t is the fermentor temperature, $^\circ\text{C}$.

The sensible heat loss with the dry biogas leaving the fermentor are the sum of the sensible heat in CH_4 and CO_2 . Following Ashare et al. (1977), the sensible heat loss with the dry biogas leaving fermentor is given by:

$$Q_g = \left[1676 + 1772 \frac{(1 - f)}{f} \right] (V \cdot \gamma_V) (t - t_a) \quad (12)$$

The heat of reaction is estimated to be 54.5 KJ per mole of methane produced, assuming the degraded waste is all cellulosic material (Ashare et al., 1977). The total heat produced in the fermentor is, therefore, given by:

$$Q_r = 2.43 \times 10^6 (V \cdot \gamma_V) \quad (13)$$

The heat required to raise the raw waste slurries to the fermentor operating temperature can be calculated by:

$$Q_i = W C_p (t - t_s) \quad (14)$$

where: t_s is the process slurry temperature, $^\circ\text{C}$, W is the total weight of slurry to be added to the fermentor per day, and C_p is the specific heat of the process slurry. The specific heat of the process slurry depends on its total solids concentration. The specific heat of beef cattle waste slurry was found to be:

$$C_p = 4.17 [1 - 0.00812 (TS)] \quad (15)$$

where: C_p is in J/g °C and TS is in %.

The amount of slurry to add to the fermentor depends on the operational hydraulic retention time (θ) and the slurry density (ρ), so:

$$Q_i = \frac{\rho V}{\theta} C_p (t - t_s) \quad (16)$$

Table 5 gives the total methane energy production and heat requirements for digesters operating at 55°C and five day retention time ($\gamma_V = 3.7$ L CH₄/L digester/d, Hashimoto et al., 1979) for different feedlot sizes.

The net heat energy requirements for 1,000-head feedlots are $Q_d = 0.46$ GJ/d, $Q_w + Q_g = 0.09$ GJ/d, $Q_i = 6.75$ GJ/d. The heat produced due to chemical reaction is 1.67 GJ/d. So the total heat energy requirement to maintain the digester at 55°C requires 7.42 GJ/d, assuming boiler efficiency to be 75%. This is about 29% of the total daily energy production of the system.

Calculations show that Q_d is 6% of Q_i for a 186 m³ digester and is about 2% of Q_i for a 18600 m³ digester. This implies that for a large fermentor, the insulation of the fermentor becomes less critical. It also shows that the heat energy generated in the fermentor due to chemical reaction (Q_r) is 24% of the heat energy required to heat the process slurry (Q_i). Table 5 also shows that Q_i is the major heat requirement for this system and indicates the necessity for recovering the effluent heat energy, which comprises the major heat energy loss of the system.

The net energy production, i.e., the amount of methane energy production minus heat energy requirement (assuming boiler efficiency of 75%) ranges from 18.3 GJ/d for a 1000-head feedlot to 1868 GJ/d for a 100,000-head feedlot.

Figure 10 is a plot of the net energy production per unit volume of the fermentor operating at different retention time for different feedlot size. Since the capital and operational cost of the system is generally directly

related to the fermentor volume, the net energy production per unit volume gives a good indication of the energy production per capital cost. Figure 10 shows that the net energy production per capital cost has an optimum value at 4.5 days retention time, which is longer than the retention time (3.5 day) where the maximum volumetric methane production rate ($\gamma_{V_{max}}$) occurs (Hashimoto et al., 1978).

Figure 10 also shows that the net energy production per unit volume increases with the amount of waste to be processed at the same retention time. In this case, the maximum net energy production per unit volume increases from 87.8 MJ/m³·d for a 100-head feedlot to 100 MJ/m³·d for a 100,000-head feedlot.

Figure 11 summarizes the daily pumping and mixing energy requirement as compared to the energy requirement for gas compression for different feedlot size. It was assumed that the mixer operates 24 hours a day and the power requirement for gas compression is 4.2 watts per cubic meter per day gas produced. Figure 11 shows that for large feedlots even with the mixer operating 24 hours a day, it comprises a small portion of the total electrical energy required.

ANNUAL AND METHANE PRODUCTION COSTS

In the following calculations, we will assume that no heat is recovered from the effluent heat, effective pumping length is 300 m, the fermentor mixer is operating for 24 hours a day, the electricity cost is 4¢/Kw hr and water cost is 11¢ per cubic meter. The influent total solids is 94 g/L and volatile solids is 80 g/L. The volumetric methane production is 3.7 L CH₄/L digester/d at 5 days retention time (Hashimoto et al., 1979).

Assuming the capital cost ranges from \$1130/m³ for digester volume of 186 m³ to \$320/m³ for digester volume of 18,600 m³. These capital costs are considered to be upper limits of the estimated installment costs of these systems. The

annual fixed cost is taken to be 21% of the capital cost.

Table 6 shows that the annual cost of this system ranges from \$83,000 for 1,000-head feedlots to \$1,739,000 for 100,000-head feedlots. The methane production cost decreases from \$12.58/GJ for 1,000-head feedlots down to \$2.57/GJ for 100,000-head feedlots.

If the capital cost is reduced by 60%, it will lower the methane production cost as shown in Table 7. The methane production cost decreases from \$8.57/GJ for 1,000-head feedlots to \$1.46/GJ for 100,000-head feedlots. Considering the current natural gas price of about \$2/GJ, the 25,000-head feedlot will produce methane at a competitive price.

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TABLE 1

POWER REQUIREMENT FOR PUMPING INFLUENT^{1/}
PER 100 m^{2/}

FEEDLOT SIZE (UNIT 1000 h)	1	2	5	10	25	50	100
VOLUME OF SLURRY TO BE PUMPED IN TEN HOUR PERIOD (m ³ /10 hr)	37.2	74.4	186	372	930	1860	3720
PIPE DIAMETER IN METER IN INCH	0.0508 2	0.0508 2	0.0762 3	0.0762 3	0.1016 4	0.1016 4	0.1016 4
FLOW RATE IN m ³ /sec IN GPM	0.00103 16.3	0.00207 32.7	0.00517 81.7	0.01033 163.2	0.02583 408	0.02583 408	0.02583 408
GENERALIZED REYNOLDS NUMBER	35.1	93.2	137.6	363	694	694	694
NUMBER OF PUMP UNIT	1	1	1	1	1	2	4
POWER IN Kw ^{3/}	0.987	3.02	4.19	12.68	24.6	49.2	98.4
POWER PER UNIT SLURRY VOLUME (w/m ³)	26.5	40.5	22.6	34.1	26.5	26.5	26.5

^{1/}Influent assumed to be 10% TS, $K = 4.0 \text{ dyne} \cdot \text{sec}^n / \text{cm}^2$, $n = 0.6$.

^{2/}Length includes the effective length due to suction, expansion, contraction of flow. Assume no elevation.

^{3/}Pump efficiency 50% assumed.

TABLE 2

POWER REQUIREMENT FOR PUMPING EFFLUENT^{1/}
PER 100 m^{2/}

FEEDLOT SIZE (UNIT 1000 h)	1	2	5	10	25	50	100
VOLUME OF MIXED LIQUOR TO BE PUMPED IN TEN HOUR PERIOD (m ³ /10 hr)	37.2	74.4	186	372	930	1860	3720
PIPE DIAMETER IN METER IN INCH	0.0508 2	0.0508 2	0.0762 3	0.0762 3	0.1016 4	0.1016 4	0.1016 4
FLOW RATE IN m ³ /sec IN GPM	0.00103 16.3	0.00207 32.7	0.00517 81.7	0.01033 163.2	0.02583 408	0.02583 408	0.02583 408
GENERALIZED REYNOLDS NUMBER	63.9	182.2	260.9	737	1419	1419	1419
NUMBER OF PUMP UNIT	1	1	1	1	1	2	4
POWER IN Kw ^{3/}	0.535	1.525	2.19	6.17	11.89	23.78	47.6
POWER PER UNIT MIXED LIQUOR VOLUME (w/m ³)	14.4	20.5	11.75	16.6	12.78	12.78	12.78

^{1/} Effluent 5% TS, $K = 3.3 \text{ dyne} \cdot \text{sec}^n / \text{cm}^2$, and $n = 0.5$ assumed.

^{2/} Includes effective length due to suction, expansion and contraction of flow and elbow. No elevation assumed.

^{3/} Pump efficiency 50% assumed.

TABLE 3

POWER REQUIREMENT FOR PROPELLER MIXING^{1/} OF FERMENTOR CONTENTS^{2/}

FEEDLOT SIZE (UNIT 1000 h)	1	2	5	10	25	50	100
VOLUME OF MIXED LIQUOR (m ³)	186	372	930	1860	4650	9300	18600
TANK DIAMETER (m)	6.2	7.8	10.9	15.4	24.3	24.3	24.3
TANK HEIGHT TO DIAMETER RATIO	1.0	1.0	0.92	0.65	0.41	0.41	0.41
TANK NUMBER	1	1	1	1	1	2	4
NUMBER OF DUEL PROPELLER	1	1	1	2	4	8	16
PROPELLER DIAMETER (m)	1.25	1.6	2.0	2.5	3.0	3.0	3.0
ROTATIONAL SPEED (RPM)	54.3	38.2	27.72	20.2	15.5	15.5	15.5
POWER PER DUEL PROPELLER ^{3/} (Kw)	2.49	2.97	3.49	4.09	4.66	4.66	4.66
POWER REQUIRED (Kw)	2.49	2.97	3.49	8.18	18.60	37.3	74.6
POWER PER UNIT VOLUME (w/m ³)	13.4	7.99	3.75	4.40	4.01	4.01	4.01

^{1/} $Re = 10^4$, $N_p = 0.45$, $D_I/D_T = 0.2$.^{2/} 5% TS, $K = 3.3 \text{ dyne} \cdot \text{sec}^n / \text{cm}^2$, $n = 0.6$ assumed.^{3/} Motor efficiency 75% assumed, factor for duel propeller 1.8 used.

TABLE 4 POWER REQUIREMENT FOR PROPELLER MIXING^{1/} OF PROCESS SLURRY^{2/}

FEEDLOT SIZE (UNIT 1000 h)	1	2	5	10	25	50	100
VOLUME OF PROCESS SLURRY (m ³)	37.2	74.4	186	372	930	1860	3720
TANK DIAMETER (m)	3.6	4.6	6.2	7.8	10.9	15.4	15.4
TANK HEIGHT TO DIAMETER RATIO	1	1	1	1	0.92	0.65	0.65
TANK NUMBER	1	1	1	1	1	1	2
NUMBER OF DUEL PROPELLER	1	1	1	1	1	2	4
PROPELLER DIAMETER (m)	0.73	0.91	1.25	1.6	2.0	2.5	2.5
ROTATIONAL SPEED (RPM)	133.6	97.3	61.8	43.5	31.6	23.0	23.0
POWER PER DUEL PROPELLER ^{3/} (Kw)	2.53	2.97	3.72	4.44	5.20	6.10	6.10
POWER REQUIRED (Kw)	2.53	2.97	3.72	4.44	5.21	12.20	24.40
POWER PER UNIT VOLUME (w/m ³)	68.1	39.9	20.0	11.93	5.60	6.56	6.56

^{1/} $N_{Re} = 10^4$, $N_p = 0.45$, $D_I/D_T = 0.2$.

^{2/}10% TS, $K = 4.0 \text{ dyne} \cdot \text{sec}^n / \text{cm}^2$, $n = 0.5$ assumed.

^{3/}Motor efficiency 75% assumed, factor for duel propeller 1.8 used.

TABLE 5 ENERGY PRODUCTION MINUS HEAT ENERGY REQUIRED FOR FERMENTOR OPERATING AT 55°C^{1/}

FEEDLOT SIZE (UNIT 1000 h)	1	2	5	10	25	50	100
VOLUME OF THE FERMENTOR (m ³)	186	372	930	1860	4650	4650	4650
NUMBER OF TANK	1	1	1	1	1	2	4
TANK DIAMETER (m)	6.2	7.8	10.9	15.4	24.3	24.3	24.3
TANK HEIGHT TO DIAMETER RATIO	1	1	0.92	0.65	0.41	0.41	0.41
METHANE ENERGY PRODUCTION (GJ/D)	25.75	51.5	128.8	257.5	643.8	1288	2575
DIGESTER SURFACE HEAT LOSS (GJ/D)	0.40	0.63	1.16	1.85	3.40	6.8	13.6
HEAT LOSS THROUGH GAS LINE (GJ/D)	0.09	0.18	0.43	0.90	2.26	4.52	9.04
HEAT GAIN DUE TO REACTION (GJ/D)	1.67	3.34	8.36	16.5	41.8	83.6	167.2
HEATING INFLUENT (GJ/D)	6.75	13.50	33.75	67.5	168.7	337.4	675
TOTAL HEAT REQUIRED (BOILER) ^{2/}	7.42	14.62	36.0	71.4	176.8	353.5	707
NET HEAT ENERGY AVAILABLE (GJ/D)	18.33	36.9	92.8	186.2	467	935	1868

^{1/} Influent: TS = 9.41%; VS = 80 g/L; % CH₄ = 50; process slurry temperature 10°C

Ambient temperature 10°C, U = 2.04 KJ/hr·m²·°C

γ_V = 3.7 L CH₄/L digester/d, θ = 5 days

^{2/} Boiler Efficiency = 75%

TABLE 6 ANNUAL COSTS AND METHANE PRODUCTION COST OF THERMOPHILIC ANAEROBIC FERMENTATION SYSTEMS FOR DIFFERENT FEEDLOT SIZE (HIGH CAPITAL COST ASSUMED)

FEEDLOT SIZE (UNIT 1000 h)	1	2	5	10	25	50	100
CAPITAL COST (\$1000 x)	210	334	617	982	1860	3340	5980
ANNUAL COST ^{1/}							
FIXED	44.1	70.1	129.6	206	392	702	1256
LABOR	33.9	41.3	53.8	65.6	85.3	104.1	127
MATERIALS AND UTILITIES ^{2/}	5.09	8.64	19.23	36.9	90.1	178.6	356
TOTAL ANNUAL COST ^{1/}	83.1	120.1	202.6	309	567	984	1739
METHANE PRODUCTION COST (\$/GJ)	12.58	9.04	6.06	4.60	3.37	2.92	2.57

^{1/}Costs are in \$1000/yr

^{2/}Electricity cost 4¢/Kw hr assumed
 Water cost 11¢/m³ of water assumed
 Pumping length 300 m assumed

TABLE 7 ANNUAL COSTS AND METHANE PRODUCTION COST OF THERMOPHILIC ANAEROBIC FERMENTATION SYSTEMS FOR DIFFERENT FEEDLOT SIZE (LOW CAPITAL COST ASSUMED)

FEEDLOT SIZE (UNIT 1000 h)	1	2	5	10	25	50	100
CAPITAL COST (\$1000 x)	84	134	247	393	747	1336	2392
ANNUAL COST ^{1/}							
FIXED	17.6	28.1	51.8	82.5	157	281	502
LABOR	33.9	41.3	53.8	65.6	85.3	104	127
MATERIALS AND UTILITIES ^{2/}	5.09	8.64	19.2	36.9	90.1	178.6	356
TOTAL ANNUAL COST ^{1/}	56.6	78.0	124.8	184.9	332	563	985
METHANE PRODUCTION COST (\$/GJ)	8.57	5.87	3.74	2.76	1.97	1.67	1.46

^{1/}Costs are in \$1000/yr

^{2/}Electricity cost 4¢/Kw hr assumed

Water cost 11¢/m³ of water assumed

Pumping length 300 m assumed

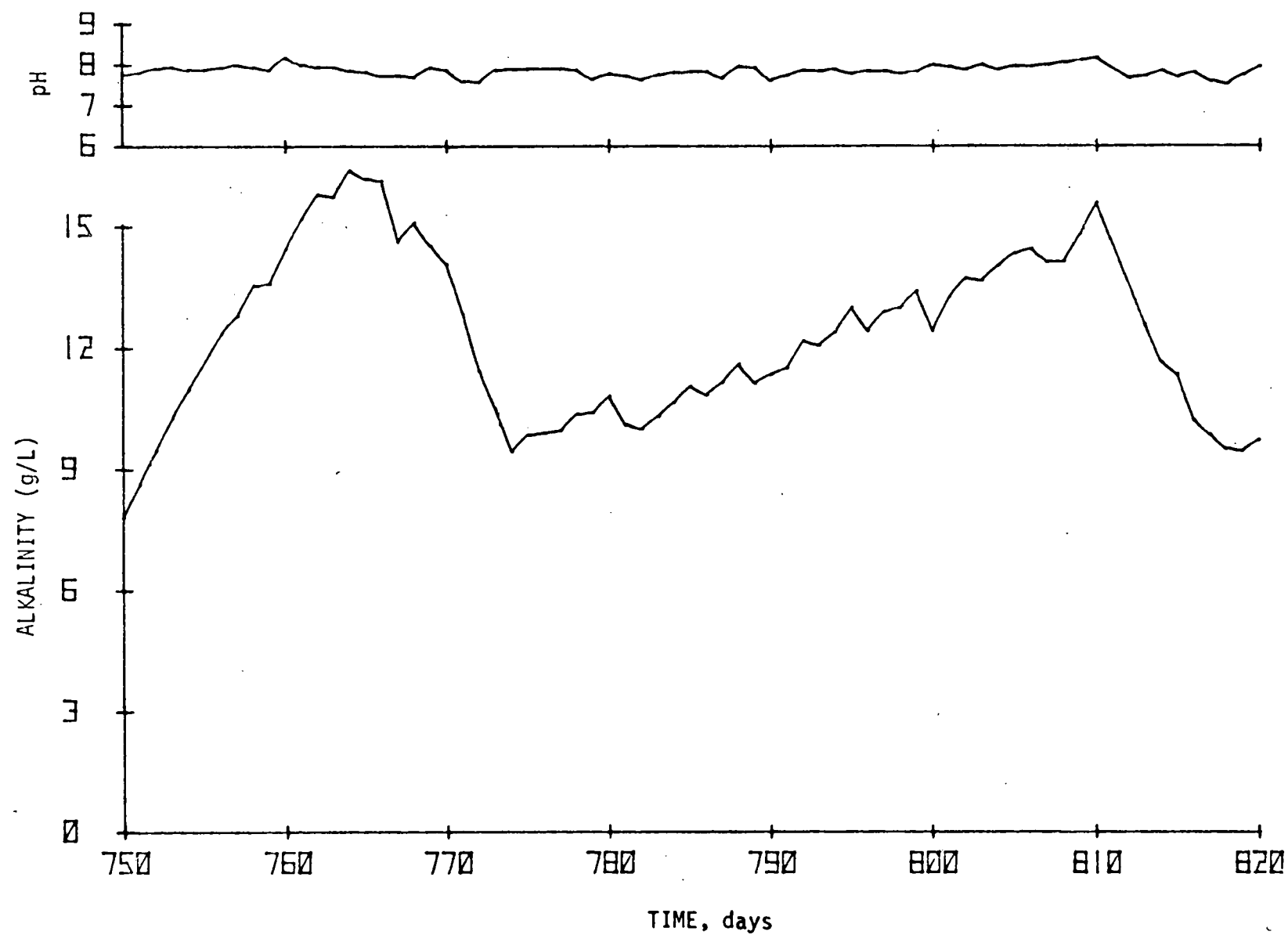


Figure 1. Effluent Alkalinity and pH Profiles

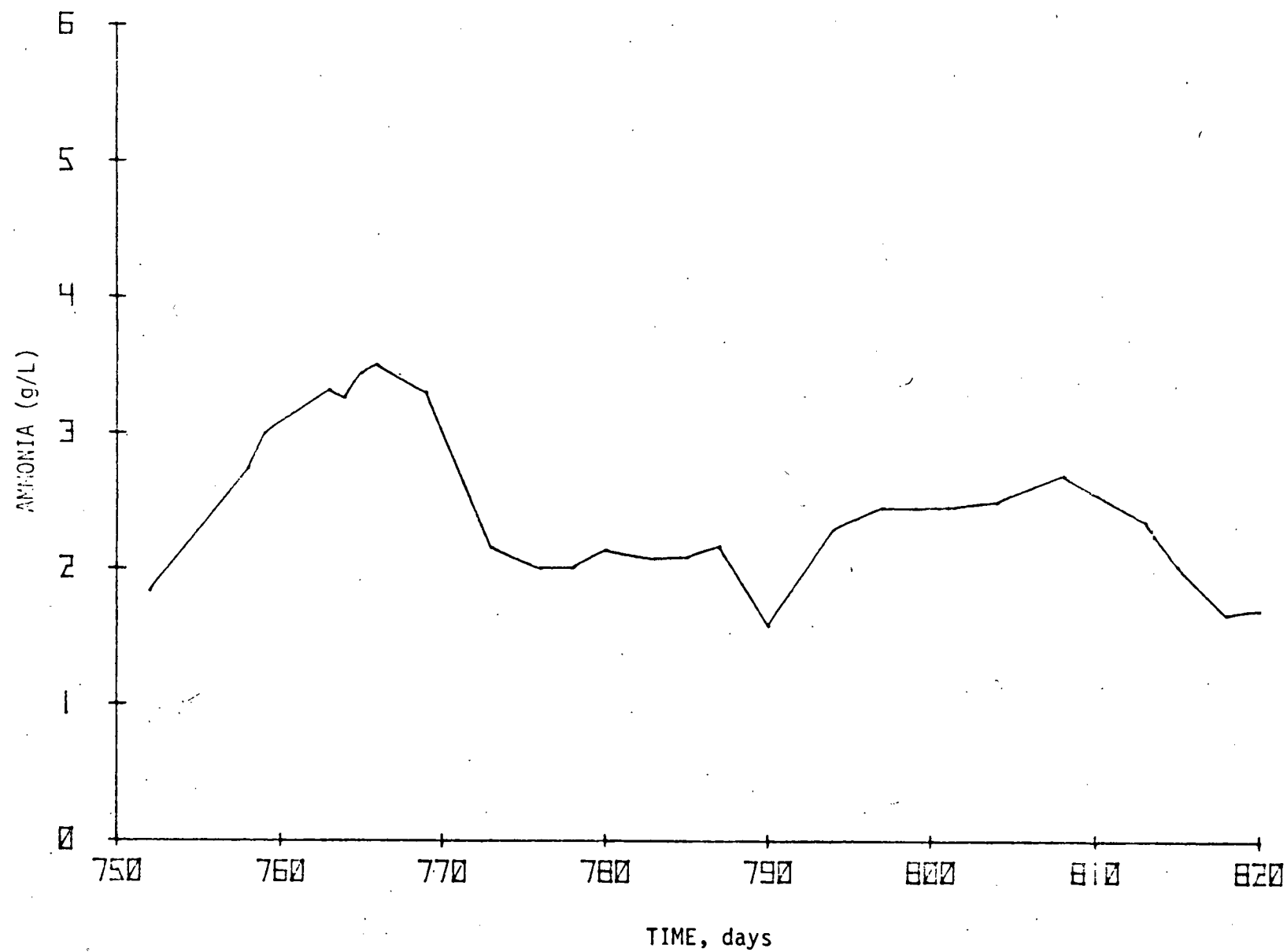


Figure 2. Effluent Ammonia Profile

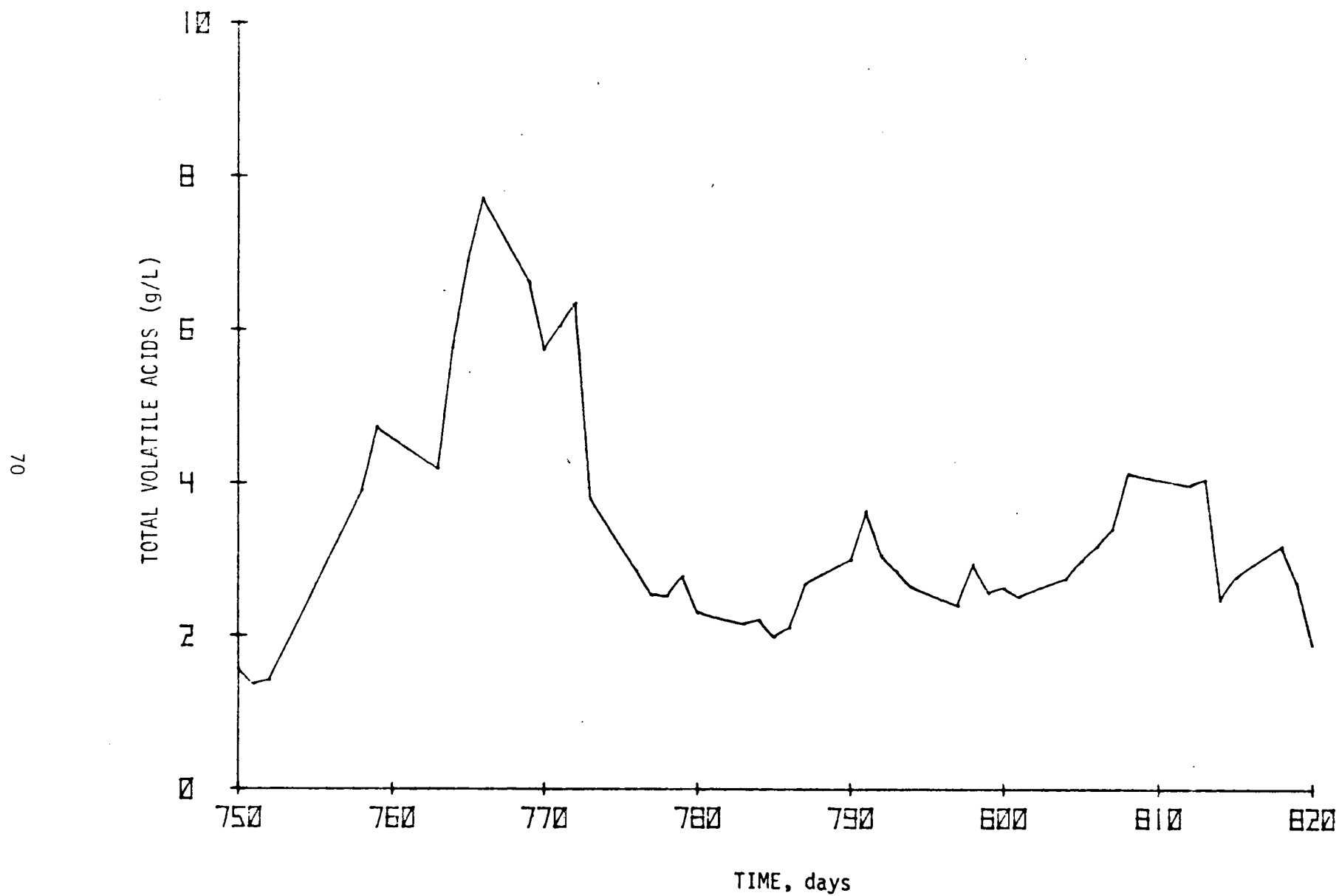


Figure 3. Effluent Total Volatile Acids Profile

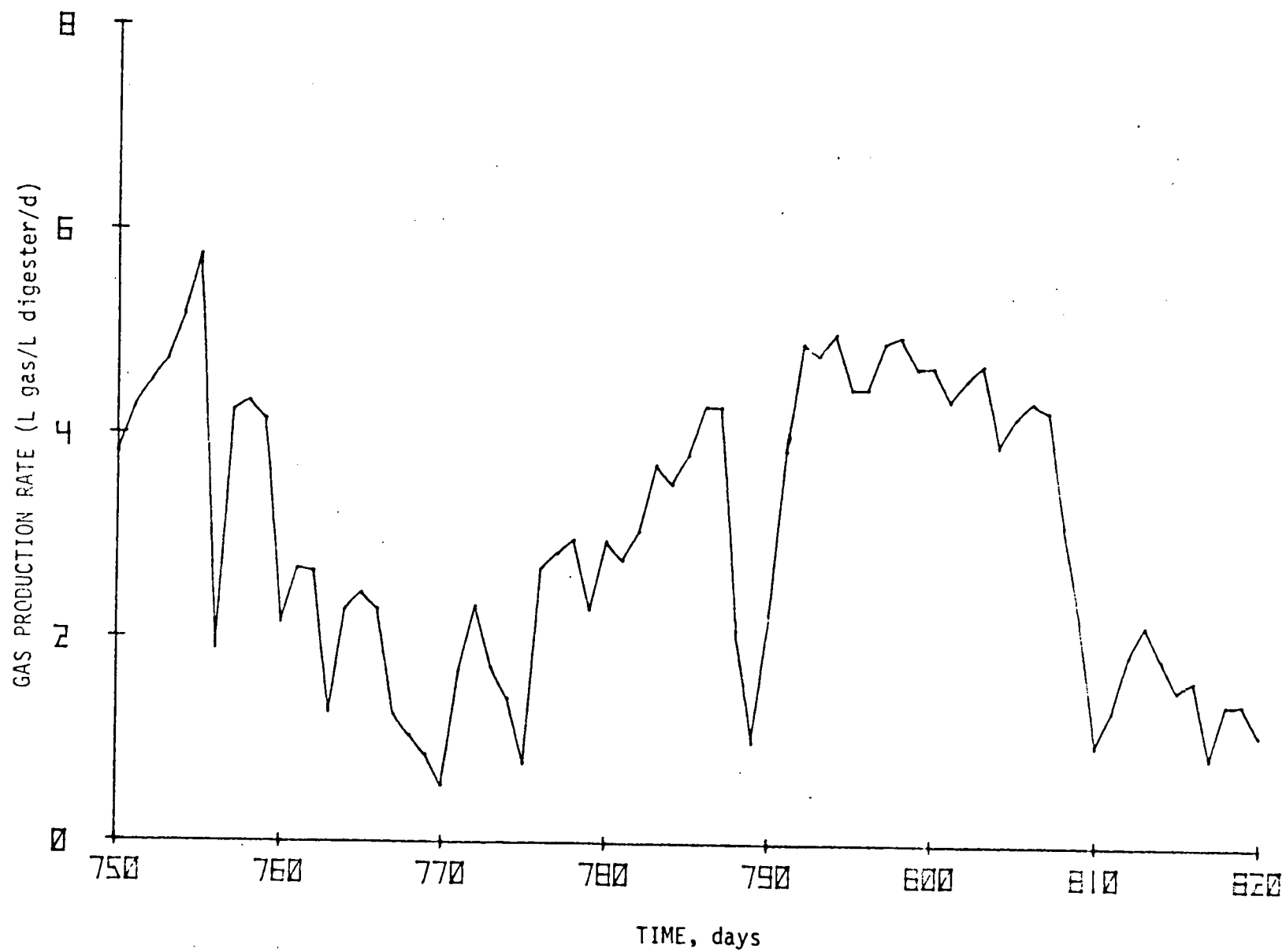


Figure 4. Volumetric Gas Production Rate Profile

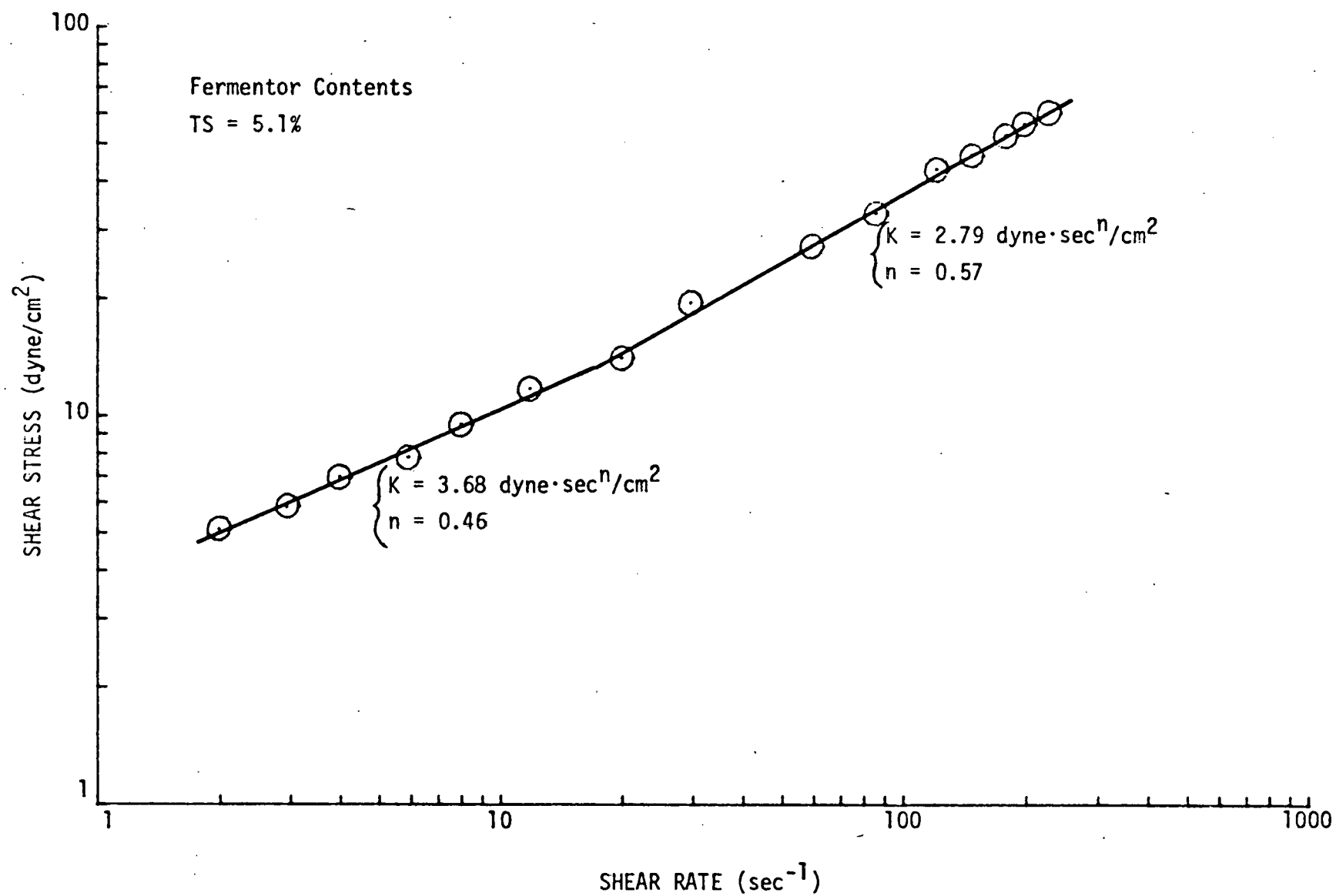


Figure 5. Rheological Properties of Fermentor Contents (TS = 5.1%)

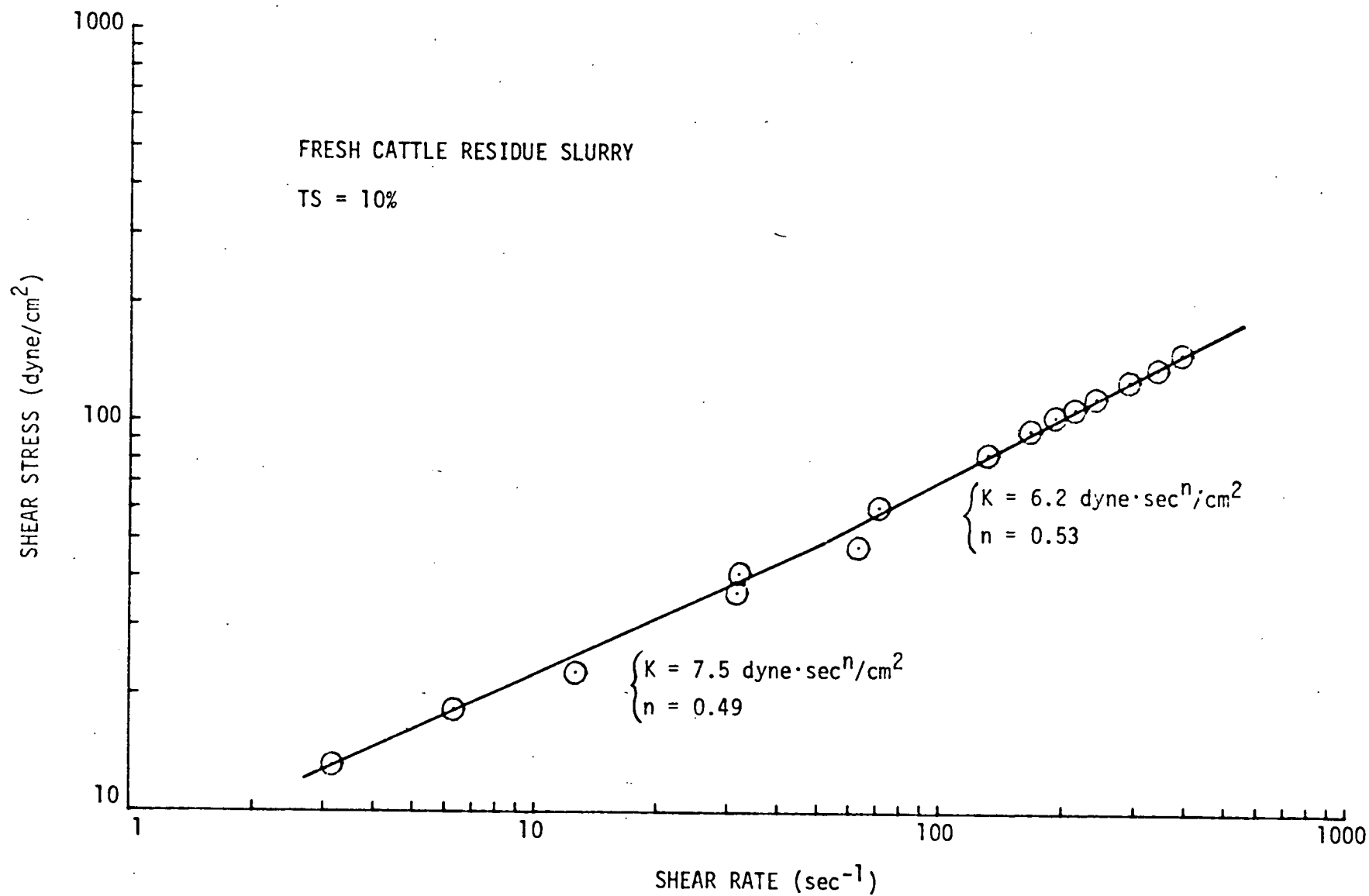


Figure 6. Rheological Properties of Fresh Cattle Residue Slurry (TS = 10%)

Propeller (Diameter 10.2 cm, 3 Blade Marine Type)
 Propeller to Tank Diameter Ratio = 0.33
 Tank 29.8 cm ID, Baffled

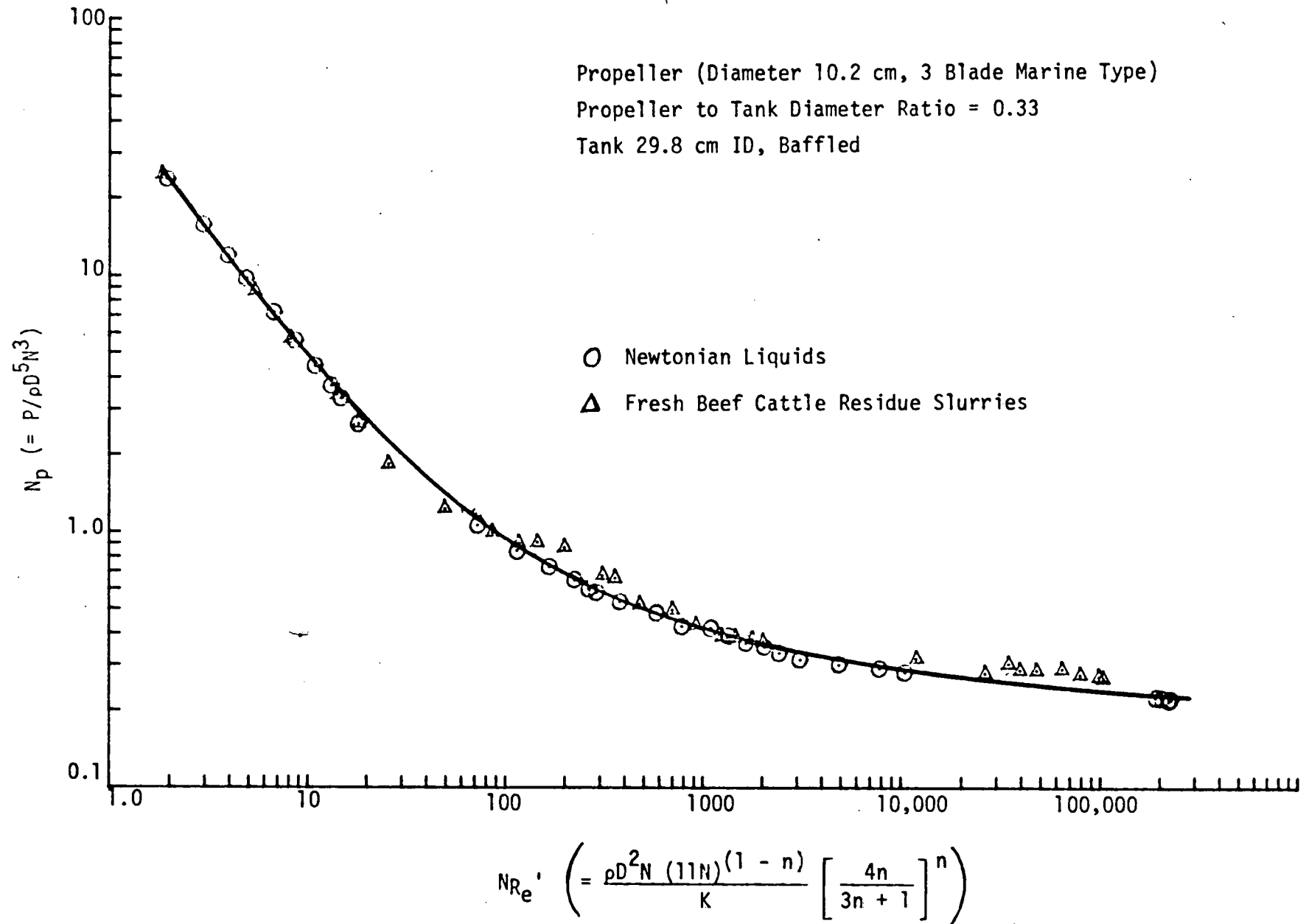


Figure 7. Propeller Power Number vs. Generalized Reynolds Number (Propeller to Tank Diameter Ratio = 0.33)

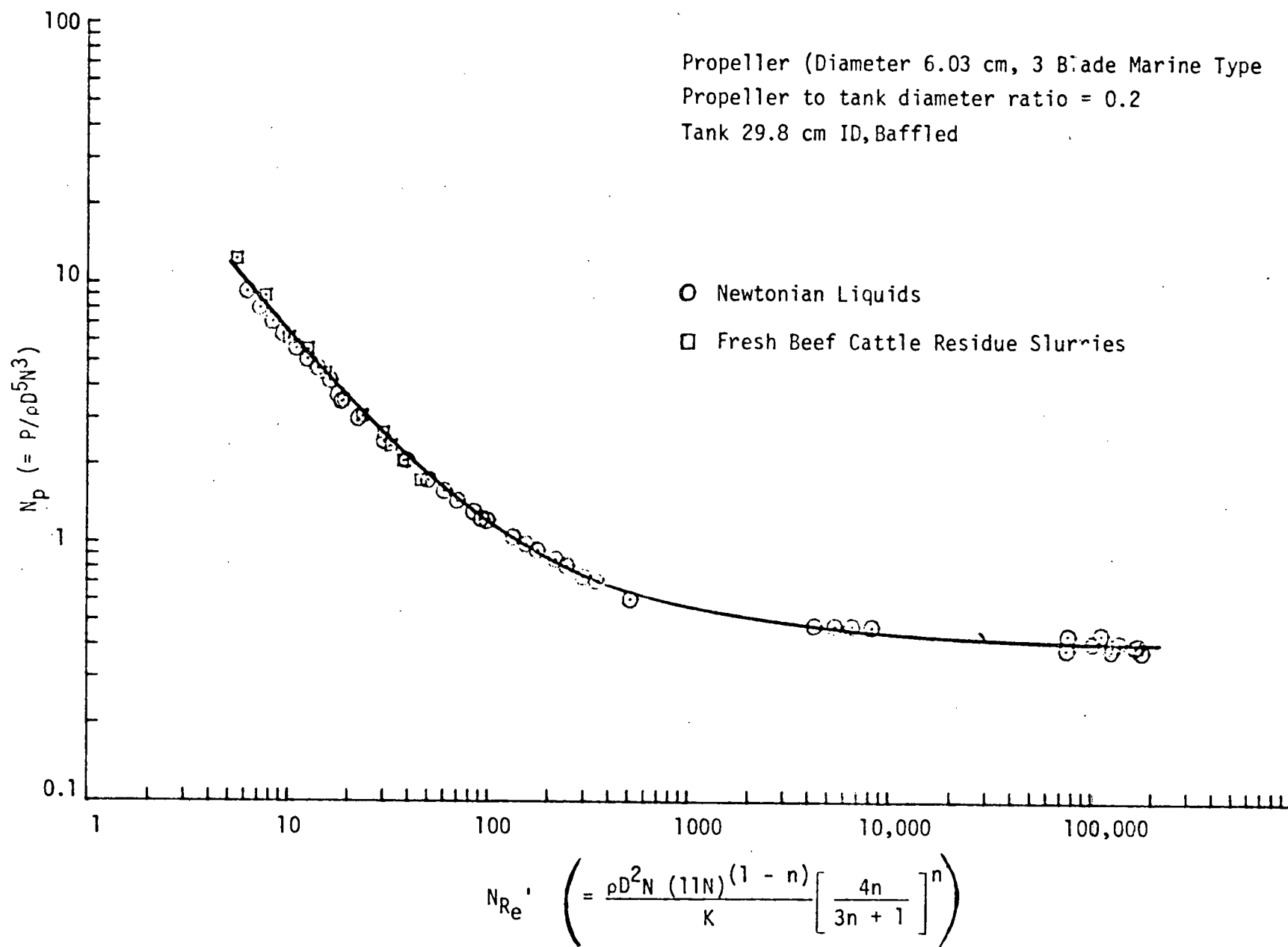


Figure 8. Propeller Power Number vs. Generalized Reynolds Number
 (Propeller to Tank Diameter Ratio = 0.2)

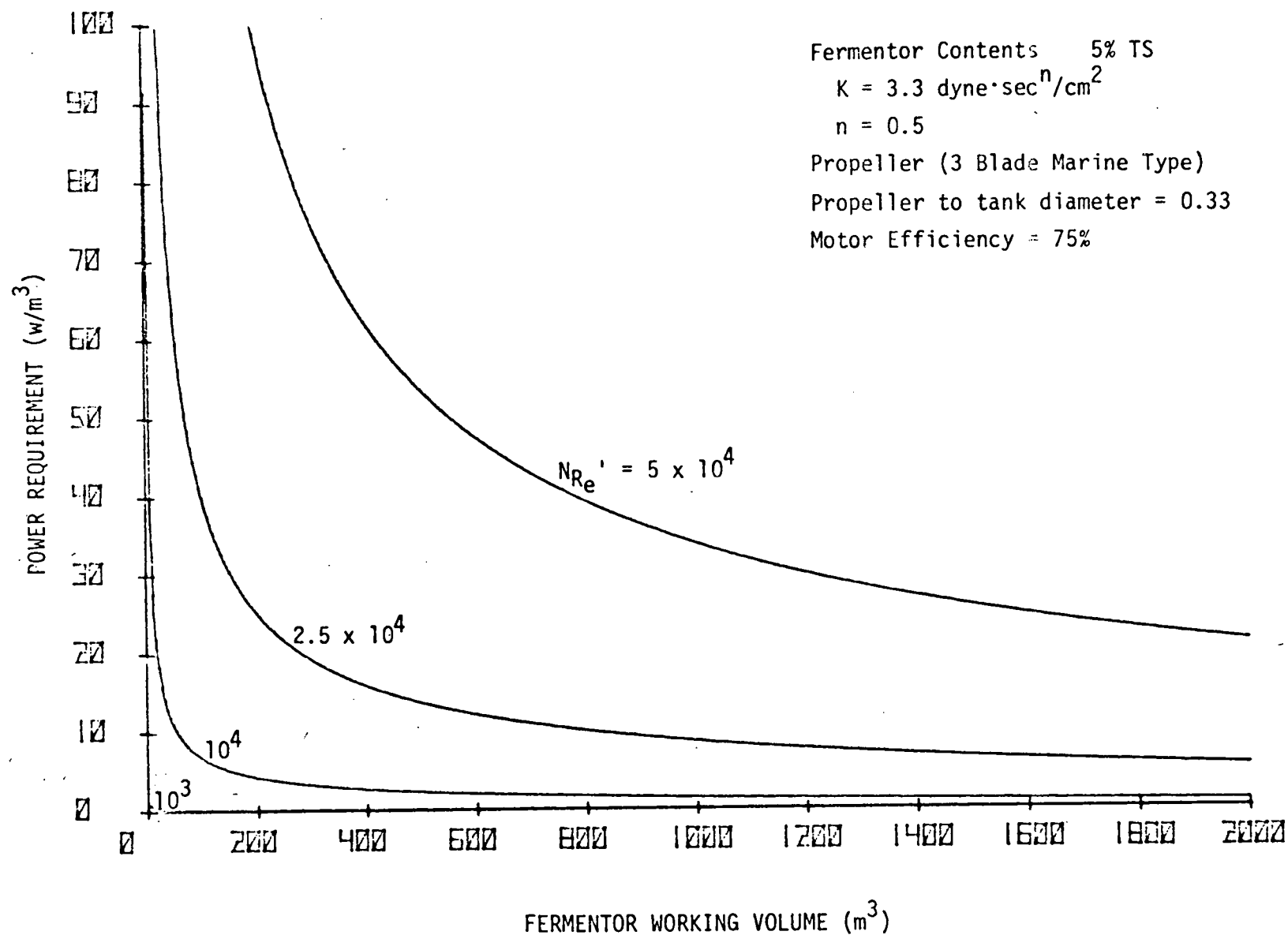


Figure 9. Power Requirements for Propeller Mixing at Different Generalized Reynolds Number

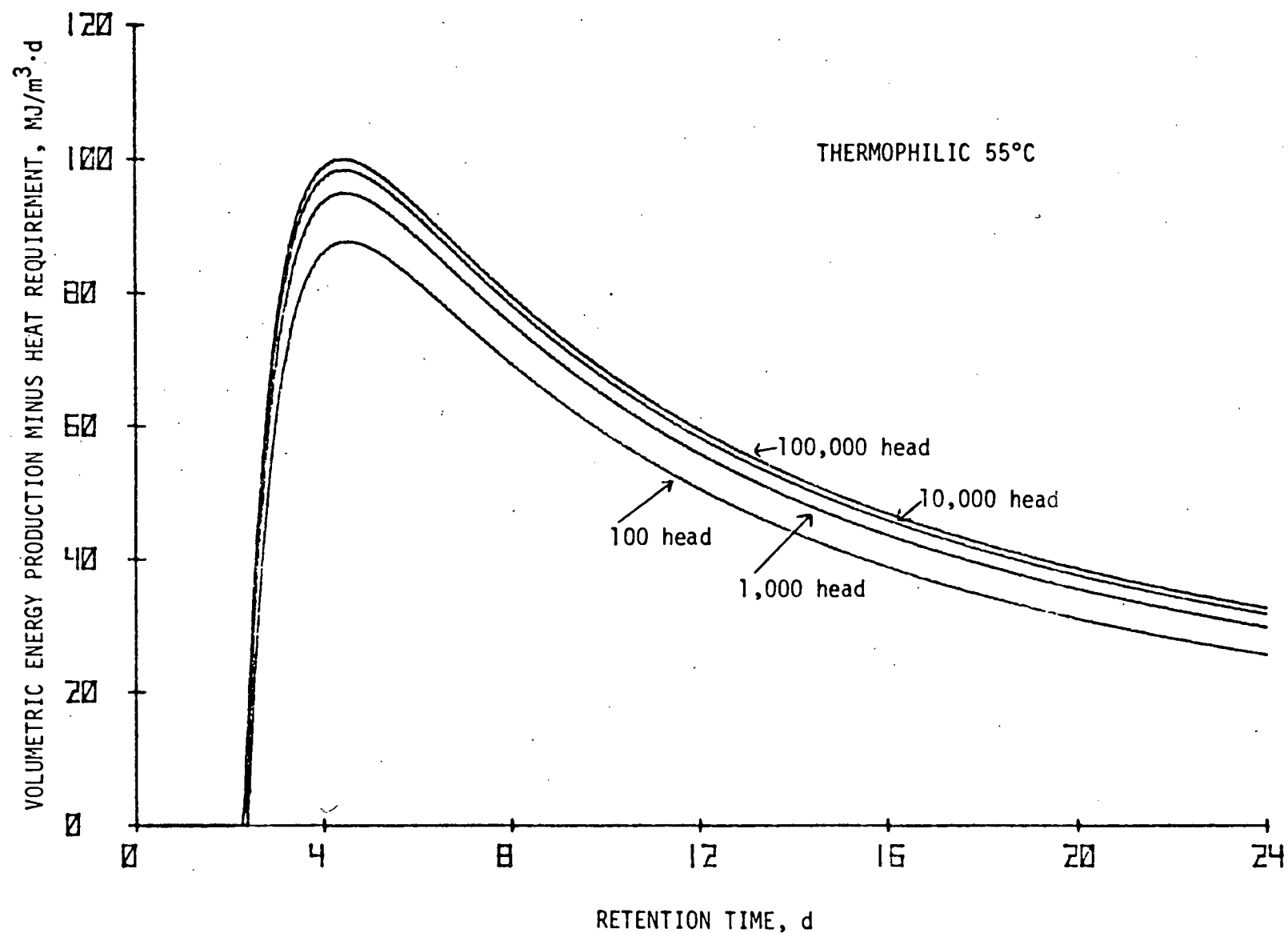


Figure 10. Net Thermal Energy Production vs. Retention Time for Thermophilic Anaerobic Fermentation Systems

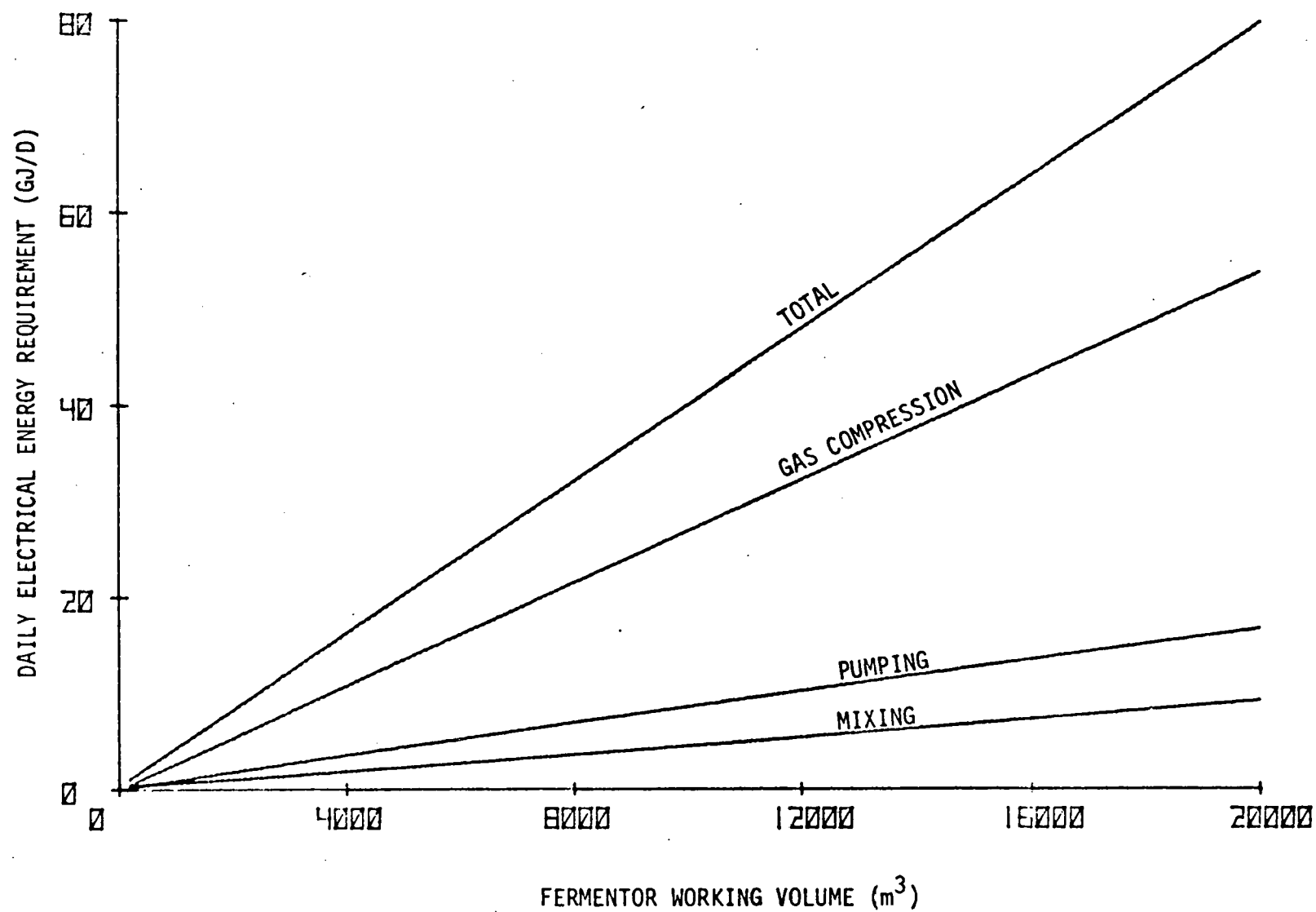


Figure 11. Daily Electrical Energy Requirements for Anaerobic Fermentation Systems

Summary of Proposed Research Entitled

ECONOMIC AND KINETIC STUDIES OF THE PRODUCTION
OF FARM ENERGY AND CHEMICALS BY FERMENTATION OF BIOMASS

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DOE-SERI Contract No. XJ-9-8020-1

Economic and Kinetic Studies of the Production of Farm Energy and Chemicals By Fermentation of Biomass

The proposed research contract, dated March 6, 1979 and to continue through March 6, 1980, is composed of two distinct parts. The first phase consists of testing a farm digester to produce the heat and electricity for a local farm. The second part of this research deals with the laboratory investigation of the production of chemicals and methane from the stages of anaerobic digestion. Each phase is described briefly in the following:

A. Feasibility of Producing Farm Energy from Biomass

A digester-system has been constructed on a 240 acre farm located in Drury, MO. This system is composed of four batch reactors, agitated mechanically. The reactors are housed in a building heated with exhaust heat from an electrical generator. Gas (50 percent CH_4 and CO_2) will be stored and used in the home and farm buildings for heat. A portion of the gas will be used to generate electricity for farm usage.

Preliminary economic projections indicate that heat can be supplied for \$3-4/ $\bar{\text{M}}$ BTU and electricity generated for \$.04 -.06/kwh. The general objective of this phase of the project is to evaluate the technical and economic feasibility of this system utilizing native grasses or other herbaceous feedstocks available on the farm. Briefly, the work to be accomplished includes:

- 1) Identify vegetation types or crops and management systems that are most appropriate for small-scale production of feedstock for anaerobic digestion systems. Emphasis shall be placed on high yield/low energy input cropping systems.
- 2) Operate an existing test anaerobic digestion facility on a cooperating farm, using native grasses as feedstock. Inoculum requirements shall be determined. Gas volumes and concentrations shall be monitored daily and samples analyzed. Initial operations shall be conducted on a 60-day batch-cycle. Seasonal variation, in operating efficiencies and conditions shall be monitored.

- 3) Evaluate the effluent from the reactors as a soil amendment.
- 4) Provide a preliminary economic evaluation of the experimental operation at the conclusion of the first year of research.

B. Production of Chemicals and Methane from The Stages of Anaerobic Digestion

Separation of the three stages of the anaerobic digestion process (hydrolysis, acidogenesis and methanogenesis) affords an opportunity to operate each stage at its optimal conditions of pH, temperature, nutrient and culture. Hydrolysis can be accomplished with mineral acids at faster rates and with better yields. Pure cultures may be more efficient in converting pentoses and hexoses to acids or methane. Intermediate chemicals products can be produced and may prove to be more valuable than methane.

The purpose of this phase of the study is to determine the feasibility of producing methane in three separate stages and to compare the economics of this mode of operation with a single mixed culture. The production of intermediate chemicals will also be evaluated. The specific objectives are:

- 1) Conduct hydrolysis of corn stover and/or grasses with a two stage sulfuric acid treatment to produce xylose and glucose.
- 2) Produce organic acids in both mixed culture and a pure culture of Propionibacterium from the xylose and glucose fraction from step 1).
- 3) Produce methane in mixed culture from the acids of step 2) and from the biomass fed to step 1).
- 4) Measure reaction kinetics, yields and conversions for each stage.
- 5) Provide a preliminary economic evaluation of the production of methane and chemicals by the above processes.

Project Status

Construction of the farm system is nearing completion. Agitators are being installed in the reactors and the reactors are expected to be charged and inoculated around mid-April. Installation of gas storage and generator will continue beyond the start-up date. Full operation is anticipated by July 1.

Biomass identification studies have begun and effluent evaluation will begin when reactor effluent is available.

Laboratory equipment for study of the stages of digestion is being assembled. This work will begin when students become available in early summer.

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ANAEROBIC FERMENTATION OF AGRICULTURAL RESIDUES-- POTENTIAL FOR IMPROVEMENT AND IMPLEMENTATION

Eleventh Quarter Progress Report for Period From
December 16, 1978 to March 15, 1979

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ANAEROBIC FERMENTATION OF AGRICULTURAL RESIDUES--
POTENTIAL FOR IMPROVEMENT AND IMPLEMENTATION

SUMMARY

The Cornell University project on production of methane from agricultural residues has as its main goal the development of a low-cost methane gas generation system for use on small agricultural operations. This progress report covers the activities included in the next-to-last quarter of this study.

Five different types of anaerobic fermentor reactor designs are presently being operated, with the majority of effort focussed on two full scale reactors (both about 35m³) designed to process the residues produced by 65-cow dairies. Three pilot units (5m³ volume) are being operated to determine the limits of operation variables--temperature, labor inputs, mixing, and bedding composition. Variables being evaluated with the pilot reactors include: temperature of operation (25°C and 35°C), straw and sawdust bedding addition, intermittent feeding (once per day to once per week), mixing (none to once per 4 days), and moisture content (90 percent to 60 percent moisture).

The low-cost full scale plug flow reactor has now been operated for nearly one year, including the winter with the lowest temperature (down to minus 25°C) for the longest period recorded for the northern New York area. Preliminary analysis of the data indicates more efficient solids conversion with the plug flow design (41 percent TVS destruction efficiency) than with the completely mixed full scale system (31.7 percent TVS destruction efficiency) when operating at a 30-day hydraulic retention time at 35°C.

Although analysis of the thermal data is incomplete, comprehensive heat loss studies were conducted during the cold period. The efficiency of the boiler-hot water heating system varied between 40 and 55 percent. The net energy production during the coldest conditions (worst case) was estimated to be 44 percent at a 15-day HRT at 35°C with the low-cost plug flow system.

Considerable operational problems with the full scale systems occurred during the coldest winter period; but these problems were not caused by the weather. Both units have been out of operation for several weeks but were back in full scale operation by mid-March.

Activities in the next quarter will conclude all pilot plant analysis and most of the full scale testing. It is anticipated that completion of testing the full scale units and preparation of the final reports will take place during the 13th quarter (summer 1979).

REPORT OUTLINE

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Anaerobic Fermentation of Agricultural Residues--
Potential for Improvement and Implementation

INTRODUCTION

The concern for U.S. energy supplies was heightened during the last three months because of the recent events in the Middle East. The abrupt cutoff of Iranian oil during this time of crisis served to underscore the serious negative implications of a continued, increasing dependence on this volatile part of the world for future oil supplies that are a key part of a thriving U.S. economy. There is an urgent need for accelerated programs of energy conservation and alternative energy development. As new sources of energy are sought, fuels from biomass should receive increased emphasis since the potential of generating a significant amount of clean, renewable fuel from photosynthetically fixed solar energy appears to be economically and technically feasible in many instances.

This is the eleventh quarter progress report describing the activities of an ongoing three-year research effort to facilitate the development of new and/or improved technology that will result in the widespread implementation of anaerobic fermentation as a source of renewable energy for small-scale agriculture. This report describes the progress of events in the last three months contributing to the continued demonstration of low-cost, simplified reactor concepts at the pilot and full scale levels in the conversion of dairy farm manure residues to methane.

The methane project is now obtaining data from simplified pilot and full-scale fermentors operated on dairy cow manure. The following reactor types have been constructed and operated:

1. Pilot scale randomly fed and mixed, three-cow residue handling capacity when operated at a 30-day HRT;
2. Pilot scale plug flow reactor, three-cow residue handling capacity when operated at a 30-day HRT;

3. Pilot scale semi-solid reactor operating with wheat straw and dairy manure.
4. Full-scale plug flow reactor, 65-cow residue handling capacity when operated at a 10-day HRT; and
5. Full-scale conventional completely mixed control, same residue handling capacity as the full-scale plug flow fermentor.

The overall progress attained with the main phases of the project is estimated to be about 2.5 to 3 months behind schedule, and 5 months behind the original proposed starting date of June 1, 1976. An accelerated experimental program planned for the next quarter should bring the tasks up to the time schedule as proposed, with only a few tasks remaining variables to be tested during the summer of 1979.

Activities for the eleventh quarter, extending from December 16, 1978, to March 15, 1979, have included the following:

1. Collection of steady state data from the full scale plug flow reactor and control unit operated at 30 days HRT, 35°C and 10-12% TS manure feed.
2. Replacement of the internal heat grid on the full scale plug flow reactor under adverse subzero weather conditions.
3. Replacement of the internal gas collection liner of the full scale conventional control reactor.
4. Initiation of the full scale plug flow reactor into the next scheduled condition of 15 days HRT, 35°C, 10-12% TS manure feed.
5. Continued experimentation with bedding addition to the dairy manure feedstock of the pilot scale plug flow fermentor. During this feeding mode steady state data was obtained at 15 days HRT and 35°C, and 30 days HRT and 25°C.
6. Collection of steady state data from the random mix reactor operated on manure and bedding (straw) at 35°C, 16 days HRT, fed and mixed every four days, 11-13% TS feed. Using the same feedstock, the reactor was then changed in its operation to 25°C, 28 days HRT, fed and mixed once per week.

7. Startup and operation of a semi-solid reactor operated with initial solids content of around 30%.
8. The initial planning of the content and format of the final report, including the preparation of a detailed, preliminary outline for this document.

OBJECTIVES

The general approach of this new phase of the project will be to define unique approaches to methane generation that will result in economical methane alternatives for small scale agriculture. Specific objectives of this study will be to:

1. Develop the basis for minimal acceptable cost and management required for small-scale fermentor development;
2. Demonstrate cost-effective designs and manageable technology for typical farming operations using the dairy as an example at the 65-head herd size (about 0.5 tons dry matter feed rate per day);
3. Define lower limits for major parameter specification for successful fermentor operation in terms of mixing, insulation, temperature, feed rate, and management requirements in a cold climate with full-size fermentors;
4. Review alternative construction materials useful for decreased capital cost of fermentor construction and operation; and
5. Develop a practical feasibility manual for small scale fermentor design, construction, and operations, using the study results.

PROJECT STATUS

Proposed Status

The work plan originally submitted with the proposal is presented in Figure 1. A bar chart schedule indicating the proposed and actual progress of certain project components is presented in Figure 2. Throughout the eleventh quarter, the pilot and full scale fermentors were to continue in their operation, progressing well into the final conditions for each reactor. The pilot scale random mix reactor (5.0 m^3) was to conclude its experimental testing with manure and bedding feed at low temperatures and cease in its operation. The pilot scale plug flow reactor (5.6 m^3) was to continue its operation on the manure and bedding feedstock. Also scheduled for the eleventh quarter was the continued operation of the full scale plug flow and conventional control reactor (34 m^3) on a manure and bedding feedstock at a lower temperature (25°C).

Present Status

Long-term operation of the full scale low-cost reactor has now been ongoing continuously for just less than a year. Successful operation of this design has provided a basis for suggesting that small scale methane generation may be technically and economically feasible, thus providing positive information on the main goal of this study.

The overall progress is presently about three months behind the proposed schedule. The operation of the pilot scale reactors has thus far adhered closely to the work plan. However, the full scale demonstration phase has had delays due to the adversity of severe winter weather during the initial construction (December 1977 - March 1978) and some reactor modifications that were made during the last quarter. The revised experimental plan was drafted to accelerate the testing program and to narrow the schedule gap, as shown in Figure 3. Progress

WORK PLAN

Eleventh Quarter Progress Report, March 15, 1979

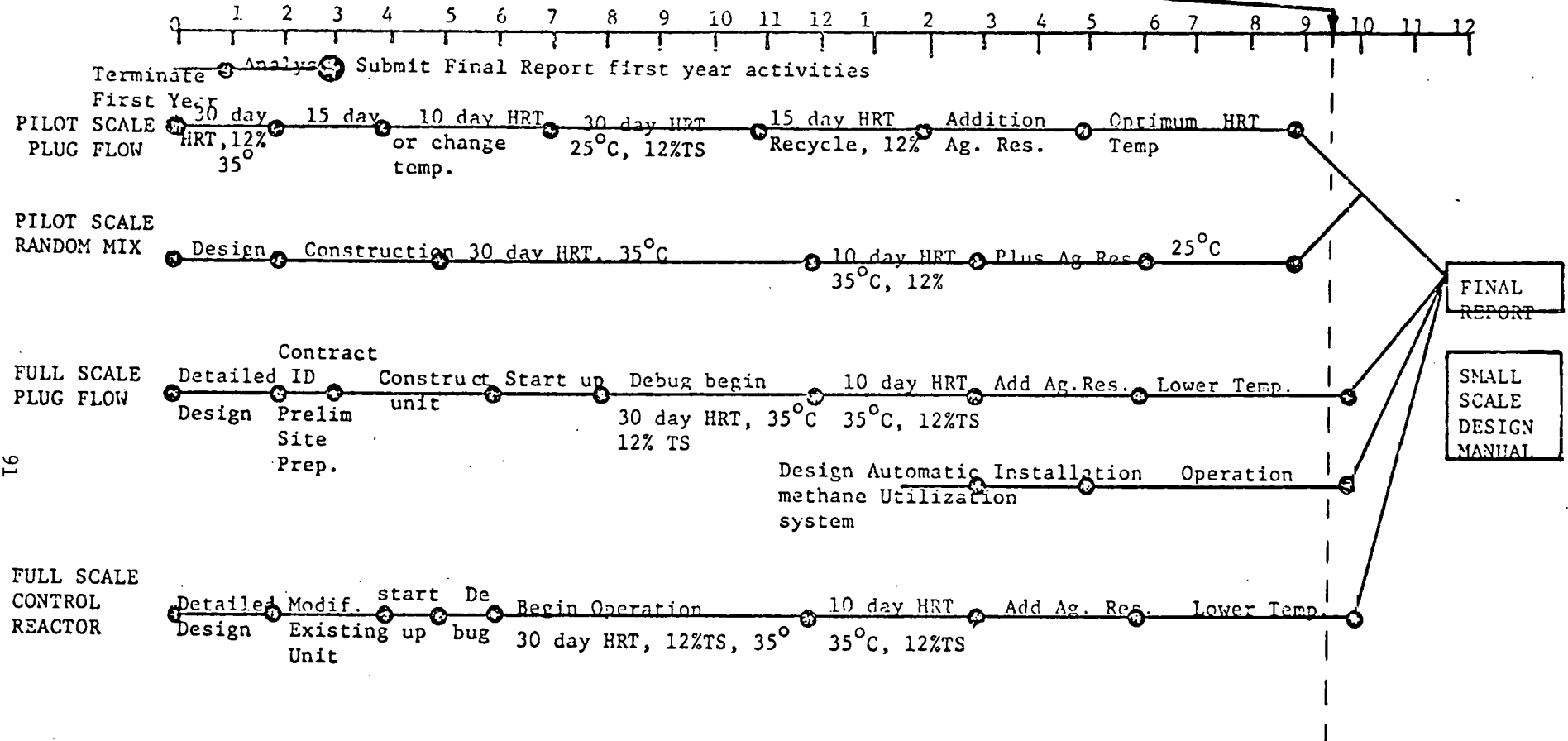


Figure 1. Detailed work plan for the development and demonstration of low cost fermentors.

FIGURE 2. CORNELL UNIVERSITY METHANE PROJECT WORK PLAN FOR 1977-1979.

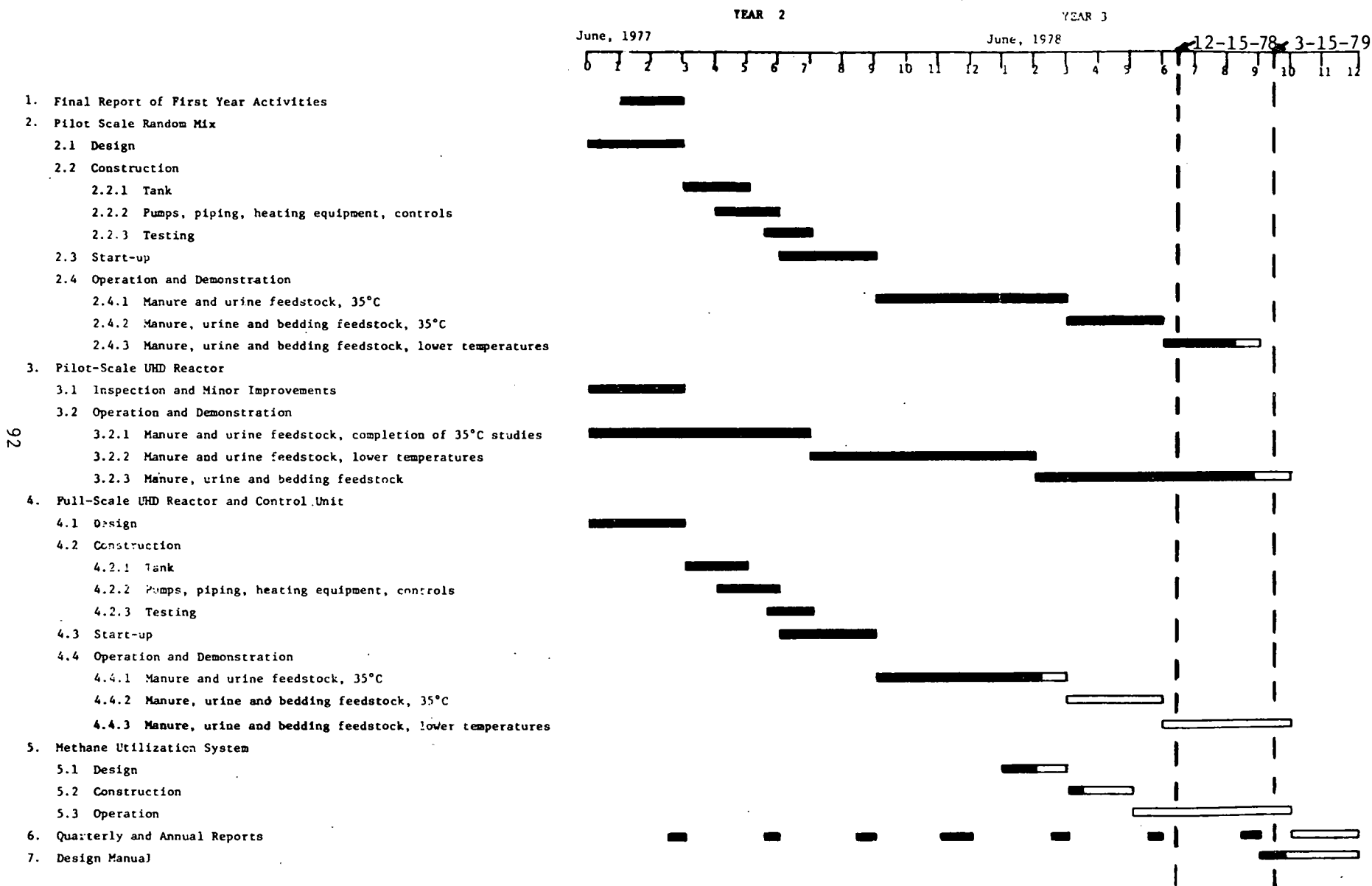
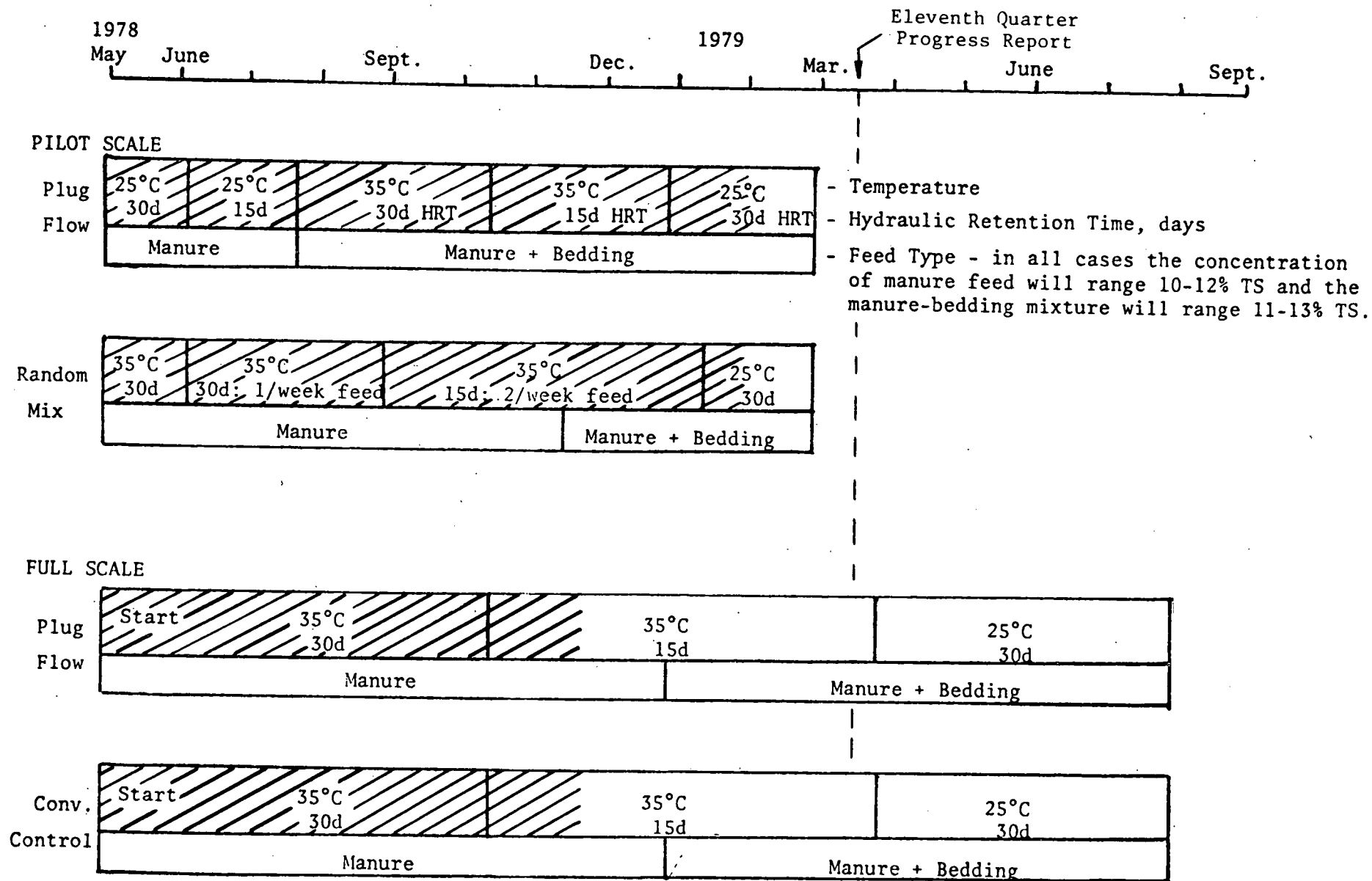


Figure 3. EXPERIMENTAL TESTING PROGRAM



in reference to the new schedule is indicated, showing a 2 1/2 month overall delay behind the accelerated work plan.

Progress review meetings were held with the methane project group on a weekly basis throughout the eleventh quarter for periodic progress review and discussion of various tasks and problems encountered during this demonstration period in the coldest season of the year. The notes and minutes from these sessions are available upon request from the investigators.

Pilot Scale Random Mix Reactor

During the latter weeks of the tenth quarter period, the PVC internal heat exchanger of the pilot scale random mix unit was replaced with a steel heat grid because of some previous mechanical problems described in the Tenth Quarter Progress Report (December 15, 1978). Following a repair period of 15 days, the random mix reactor was restarted by filling the system with 900 gallons of effluent from the pilot scale plug flow reactor and with 300 gallons of manure and straw mixture. Throughout most of the eleventh quarter the random mix unit was operated on a manure and straw feed mixture (11 to 13% TS), 16 days HRT, 35°C and fed once every four days. Straw was added to the influent manure on the basis of a bedding utilization rate of 0.93 Kg/cow/day (2.0 lbs/cow/day). At this operating mode the random mix reactor produced biogas at an average rate of about $2.0 \text{ m}^3/\text{m}^3 \text{ reactor/day}$ ($1.2 \text{ m}^3/\text{m}^3/\text{day CH}_4$) with a concomitant TVS destruction of 26.9 percent. A comparison of reactor performances at this condition and other previous operating modes is provided in Table 1. It is probably that the difference in TVS destruction efficiency between the two long HRT tests is more related to the biodegradable fraction change than a mixing effect.

During most of the experimental period when the random mix reactor was operated at 16 days HRT, 11-13% TS chopped straw and manure feed, and 35°C, the gas production and solids destruction performance was maintained at constant and uniform levels. Within twenty days of the end of the experimental run, however,

TABLE 1. PERFORMANCE DATA FOR THE RANDOM MIX REACTOR OPERATED AT 35°C

Operational and Performance Parameters	Operating Conditions			
	10-12% TS Manure 30 days HRT	10-12% TS Manure 28 days HRT	10-12% TS Manure 16 days HRT	11-13% TS Manure & Straw 16 days HRT
Feeding Frequency	once/day	once/7 days	once/4 days	once/4 days
Mixing Frequency	once/10 days	once/7 days	once/4 days	once/4 days
Days of Operation	104	90	52	70
Average Gas Production				
m^3/day	10.1	6.4	8.2	10.0
$\text{m}^3/\text{m}^3 \text{ reactor/day}$	2.0	1.3	1.6	2.0
Methane Production				
m^3/day	6.3	3.7	4.9	5.9
$\text{m}^3/\text{m}^3 \text{ reactor/day}$	1.3	0.74	0.98	1.2
Effluent pH	7.8	7.7	7.6	7.8
TVS Destruction, Percent	37.0	31.4	28.7	26.9

the reactor exhibited a significant decrease in gas production from an average value of about 10.0 m^3 per day to 5.2 m^3 per day. Other parameter measurements for pH, volatile acids and alkalinity did not suggest a distressed situation for the fermentation process during the low-performance period, thereby indicating that a variation in manure biodegradability may have caused the observed decrease in gas production. Throughout this bedding addition condition, no significant amount of solids accumulation was observed. This is an important observation in relation to minimum mixing needs for reactors using animal manures with straw and hay bedding.

Upon completion of the bedding addition study at 35°C , the random mix reactor operation was changed to a lower temperature, 25°C , using the same straw-manure feedstock. The reactor is presently operated at a 28-day HRT, 11-13% TS feed, feeding and mixing once per week. Gas production and trouble-free operation at this lower temperature is surprisingly good. The experimental progress for this unit is nearly on schedule.

Pilot Scale Plug Flow Fermentor

The pilot scale plug flow fermentor completed two experimental runs during the eleventh quarter while operating on feed mixtures of manure and bedding. After completing an experimental run at a feeding mode of 11-13% TS wood chips and manure influent, 30 days HRT, and 35°C , the same reactor conditions were repeated in the first portion of the eleventh quarter using chopped straw (cut into 2.5 cm lengths) for bedding addition at a blending rate of 0.68 Kg/cow/day (1.5 lbs/cow/day). Under this mode of operation a gas production rate of $4.67 \text{ m}^3/\text{day}$ ($0.84 \text{ m}^3/\text{m}^3 \text{ reactor/day}$) was observed with a total volatile solids destruction efficiency of 35.2 percent. In the course of the 35°C experiment, a fibrous float formed to a thickness of 0.15 m (6.0 inches) at the feed end of the plug flow unit, increasing through the reactor to a depth of 0.76 m (2.5 feet) at the effluent end. Solids measurements at various points in the reactor and a soluble tracer study indicated

that eventually only 60 percent of the total volume of the reactor was functional in fermentation. The data also suggested that the float formation rate reached steady state in that the depth of the float remained stable for several weeks. When solids ceased to accumulate in the float, steady state data was obtained from the pilot scale plug flow fermentor.

The next operating condition was established at a 15-day HRT, 35°C and 11-13% TS manure and chopped straw feed. Once again, at the shorter retention time the depth of the floating straw solids remained constant and, after a month of operation, steady state from this condition was also obtained according to schedule, thus concluding the bedding addition study at 35°C.

Steady state data from three experimental runs comprising the bedding addition study conducted at 35°C are presented for comparison purposes in Table 2. In general, the wood chip addition in the reactor seemed to produce more methane than the chopped straw addition experiments conducted under the same temperature and hydraulic retention time conditions. The nature of the bedding types used and the fact that the wood chips were added at a higher rate (1.36 Kg/cow/day or 3.0 lbs/cow/day) than those rates applied to the straw addition experiments (0.68 Kg/cow/day or 1.5 lbs/cow/day), thus resulting in a higher influent solids concentration for the wood chip experiments, were partially responsible for the difference. Float accumulations occurred with the straw addition experiments, resulting in only 60 to 70 percent of the fermentor volume being usable. Hence, the hydraulic retention time of the system was significantly less than 30 and 15 days, respectively. It is particularly interesting to note, however, that the highest methane gas production rates were observed with the straw-addition experiment employing a 15-day HRT to the pilot scale plug flow reactor while the system continued to maintain the same float solids depth throughout the testing period. At an estimated effective hydraulic retention time of 10-12 days, the pilot scale plug flow reactor gas production rate was an impressive $1.0 \text{ m}^3/\text{m}^3 \text{ reactor/day}$ in biogas produced.

TABLE 2. SUMMARY OF PERFORMANCE DATA FOR THE PILOT SCALE PLUG FLOW FERMENTOR OPERATED ON DAIRY MANURE AND BEDDING FEEDSTOCKS, 35°C, 11-13% TS FEED.

Performance Parameter	Operating Conditions		
	30 days HRT Wood Chips*	30 days HRT Chopped Straw**	15 days HRT Chopped Straw**
Days of Operation	44	89	32
Influent Solids g/l TS	123	119	118
Effluent Solids g/l TS	91.9	81.3	92.2
Solids Destruction			
TS %	25.5	31.5	21.7
TVS %	28.9	35.2	25.1
Effluent pH	7.5	7.5	7.8
Effluent Alkalinity g/l	16.8	13.6	19.6
Gas Production			
m ³ /day	5.50	4.67	5.85
m ³ /m ³ reactor/day	0.98	0.84	1.05
Methane Production			
m ³ /day	3.30	2.61	3.39
m ³ /m ³ reactor/day	0.59	0.47	0.61
m ³ CH ₄ /Kg VS _D	0.55	0.38	0.35
Gas Composition (Percent CH ₄)	60	56	58

*Data from the tenth quarter period.

**Data from the eleventh quarter period.

Following the collection of steady state data for the concluding bedding-addition experiment at 35°C, the plug flow reactor temperature was lowered to 25°C. Presently, the plug flow reactor is operating at a 30-day HRT, manure and straw feedstock (11-13% TS), 25°C. Testing for this unit is close to schedule. Preliminary gas production rates are only slightly less than comparable conditions at 35°C.

Full Scale Plug Flow Fermentor and Completely Mixed Control Unit

Early in the eleventh quarter, the full scale plug flow and conventional control fermentors reached steady state under operating conditions of 35°C, 30 days HRT, and 10-12% TS dairy manure feed. A summary of the entire body of steady state gas production and solids destruction data obtained from these units is presented in Table 3 as compared to performances observed from bench and pilot scale reactors. Final data comparisons in Table 3 indicate that the full scale plug flow and conventional control fermentors operated at gas production and solids destruction efficiencies comparable to those obtained with the smaller reactor prototypes operated at the bench and pilot scale level. Both full scale reactors produced biogas at rates of 1.26 and 1.13 m³/m³ reactor/day for the plug flow and conventional control systems, respectively. A detailed comparison of the steady state operation of the two full scale systems is given in Table 4.

The operation of the full scale plug flow and conventional control fermentors through Ithaca winter weather conditions has allowed a better understanding of the problems associated with conserving energy in these systems for temperature maintenance when operating in cold climates. The determination of the rate of heat lost from the low-cost full scale plug flow reactor is necessary to the calculation of the net energy production that can be derived from the system at various times of the year. The winter season becomes most crucial to the overall energy balance of anaerobic fermentation systems since low ambient air temperatures generally produce a greater demand on the farm for heating energy just when the

TABLE 3. COMPARISON OF RESULTS OBTAINED FROM VARYING SIZES OF REACTORS AT 35°C and 30-day HRT.

PLUG FLOW REACTOR DESIGN

Scale	Gas Production			Gas Comp. (% CH ₄)	% TVS Reduction	Reactor Volume (ft ³)
	vol/vol	l/gm VS _A	ft ³ /lb VS _A			
Bench ¹	0.91	0.357	5.7	56	49.1	0.1
Pilot	1.10	0.333	5.3	61	25.7	200
Full	1.26	0.364	5.8	57	40.6	1360

COMPLETELY MIXED REACTOR DESIGN

Scale	Gas Production			Gas Comp. (% CH ₄)	% TVS Reduction	Reactor Volume (ft ³)
	vol/vol	l/gm VS _A	ft ³ /lb VS _A			
Bench ²	0.92	0.246	4.0	64	32.0	0.1
Bench ³	0.81	0.350	5.6	63	36.0	0.5
Pilot	--	--	--	--	--	--
Full	1.13	0.310	5.0	58	31.7	1250

NOTES:

1. UHD Reactor Run at 8% TS
2. Control Reactor for Pilot Scale Plug Flow Run at 12% TS
3. Morris Data Run at 8% TS

TABLE 4. COMPARISON OF STEADY STATE OPERATION OF FULL SCALE DAIRY MANURE DIGESTION SYSTEM

	Completely Mixed Reactor	Plug Flow Reactor
Condition, HRT, days	28.5	28.1
Feed Rate, gal/day	328	363
Days of Operation	111	111
Days of Steady State	57	57
Total Solids, gm/l		
Influent	119.5	111.7
Effluent	87.4	72.2
Reduction	32.1	39.5
Reduction, %	26.9	35.4
Volatile Solids, gm/l		
Influent	103.6	96.9
Effluent	70.8	57.6
Reduction	32.8	39.3
Reduction, %	31.7	40.6
Biodegradable Volatile Solids		
Refractory Fraction	0.55	0.55
Refractory Solids, gm/l	57.0	53.3
Influent, gm/l	46.6	43.6
Effluent, gm/l	13.8	4.3
Reduction, gm/l	32.8	39.3
Reduction, %	70.4	90.1
Gas Production (all values at STP)		
ft ³ /day	1412	1717
% CH ₄	58	57
ft ³ CH ₄ /day	820	980
Gas Production Predicted From Measured Biodegradable Volatile Solids Destruction		
ft ³ CH ₄ /day	722	957
Energy Produced, Btu/day	7.86 x 10 ⁵	9.71 x 10 ⁵
Energy Required, Btu/day	4.96 x 10 ⁵	11.32 x 10 ⁵
Energy Used in System, % Total	63	117

digester itself requires more of its own biogas to maintain temperatures at 35°C. In order to determine the energy demand of the full scale reactors, conducted heat loss tests were initiated consisting of simply shutting down the boiler, ceasing wasting and feeding for a 48-hour period, and measuring the resultant decrease in temperature of the reactor contents. Three heat loss studies were performed on the full scale plug flow reactor, one test performed before the top flexible liner was insulated and two conducted after three inches of fiberglass insulation and a protective sheet of hypolon rubber was laid over the gas collection cover. Conducted heat loss testing was also conducted on the full scale conventional control fermentor.

The data from these heat loss studies, presented in Table 5, show the significant benefit to be realized in insulating the top gas collection liner of the reactor. This is most convincingly seen from the fact that the observed digester heat loss of 496,000 Btu/day at an ambient air temperature of 33.5°F was reduced to 359,000 Btu/day even though the average air temperature had dropped from 1°C to minus 18°C. Specifically, heat loss calculations predicted a decrease in heat loss from the digester gas cover of more than 82 percent leading to a dramatic reduction in the total conducted heat loss by about 58 percent in spite of colder ambient air temperatures. As seen in Table 5, the overall conducted heat loss was reduced by about 28 percent. There are two possible reasons for the differences in the predicted and actual energy savings realized. First, the effluent overflow zone of the reactor, insulated during the first heat loss test, was only partially insulated during the second heat-loss run; the heat loss value given for the effluent zone is an estimate and could range as high as 200,000 Btu for the second trial. Second, the insulation blanket for the flexible cover had been disturbed during a previous repair operation, thereby possibly reducing its total effectiveness to conserve heat.

The total energy input required relative to the energy produced each day was estimated at 63 percent for the first test and 44 percent for the second.

TABLE 5. HEAT BALANCE DATA OBTAINED FOR
THE PLUG FLOW FERMENTOR

Parameter	Plug Flow Reactor Heat Loss Tests	
	Uninsulated Liner	Insulated Liner
Digester Temperature, °F	95	95
Ambient Temperature, °F	33.5	0.6
48-Hour ΔT , Digester, °F	12	8.7
<u>Calculated Heat Losses, Btu/day</u>		
Heat Loss to Soil	29,600	36,700
Heat Loss to Air		
Cover	437,000	76,700
Moat	25,000	38,900
Baffle Zone	6,500	58,900
Total Conducted Heat Loss	498,000	211,000
<u>Observed Conducted Heat Loss, Btu/day</u>	496,000	359,001
Observed/Calculated Heat Loss	0.99	1.70
Hydraulic Retention Time, days	30	15
Energy to Heat Raw Feed, Btu/day	143,000	303,000
Total Energy Required (Observed), Btu/day	639,000	662,000
Biogas Energy Produced, Btu/day	971,000	1,500,000*
Ratio Btu Required/Btu Produced	0.66**	0.44**

* Anticipated energy production rate based on past observations of methane production rates from the pilot scale plug flow fermentor operated at 95°F, 15 days HRT and 10-12% is dairy manure feed.

** This ratio does not take into account the overall heat transfer efficiency of the boiler and digester heat exchanger.

The measured thermal loss characteristics are useful in examining the net energy production capability of the system under adverse conditions. A comparison of the low-cost plug flow system operational characteristics to those of a well insulated completely mixed system is given in Table 6. Note that the net energy production at a 15-day HRT when the air temperature averages less than minus 18°C is 44 percent of the total production. This value is based on actual increased thermal properties, but on gas production data extrapolated from pilot data. This data is illustrated in Figure 4.

Previous pilot plant operation at 25°C indicates that this may be an optimum temperature for units susceptible to large energy losses. The present operation of the two pilot units and the eventual operation of the full scale units at 25°C as the last test condition will confirm the advantages. A comparison of the impact of the operation of the plug flow unit at 35°C and 25°C is shown in Figure 5. Note the significant increase in net energy that appears to result when a lower temperature is chosen.

At certain times during the eleventh quarter, both full scale units were under repair, though for different reasons. About midway through the quarter, the PVC heat exchange grid inside the full scale plug flow unit experienced excessive leaking. It was then decided to remove the PVC grid and replace this heating system with black steel pipe, four inches in diameter. Personnel from a number of other research projects in the Department of Agricultural Engineering assisted Methane Project members in the repair of this system.

A major concern was that the subzero temperatures of -30°F to -10°F and wind conditions could make installation very difficult. Another concern was whether the flexible liner material could be handled without causing cracks and holes during the cold when removed from the top of the reactor and during replacement. After pumping the plug flow reactor empty, the research team removed the PVC gas collection system over a two-day period and then installed the steel pipe grid over a period of about a week. The cover was replaced and within 10 days of

TABLE 6. COMPARISON OF ENERGY GENERATION WITH THE TWO FULL SCALE SYSTEMS OPERATING UNDER COLD CONDITIONS

Parameter	Plug Flow Reactor			Completely Mixed Reactor		
	30 Day HRT	15 Day HRT*	15 Day. HRT*	30 Day HRT	15 Day HRT	15 Day HRT*
Ambient Air Temperature,(°C)	1	1	-18	1	1	-18
Heat Loss to Surroundings, (Btu/day)	496,000	111,000	170,000	78,250	78,250	123,900
Feed Temperature, (°F)	50	50	40	50	50	40
Heat Loss to Heat Feed, (Btu/day)	143,000	246,000	303,000	130,340	242,210	302,760
Total Heat Required,(Btu/day)	639,000	357,000	473,000	208,490	320,460	426,660
Total Heat Supplied,(Btu/day)	1,132,00	638,000	845,000	496,000	736,000*	1,015,860
Heating System Efficiency, (%)	56	56	56	42	42*	42
Total Biogas Produced,(ft ³)	1717	2500	2500	1412	2500*	2500
Total Energy Produced, (Btu/day)	971,000	1,500,00	1,500,000	786,000	1,500,000*	1,500,000
Energy Used, (Btu/day)	1,132,000	638,000	845,000	496,000	736,000*	1,015,860
Net Energy, (Btu/day)	0	862,000	655,000	290,000	764,000*	484,140
Energy Used, (% of Total)	117	43	56	63	49*	68
Net Energy, (% of Total)	0	57	44	37	51*	32

*Calculated values from measured thermal characteristics.

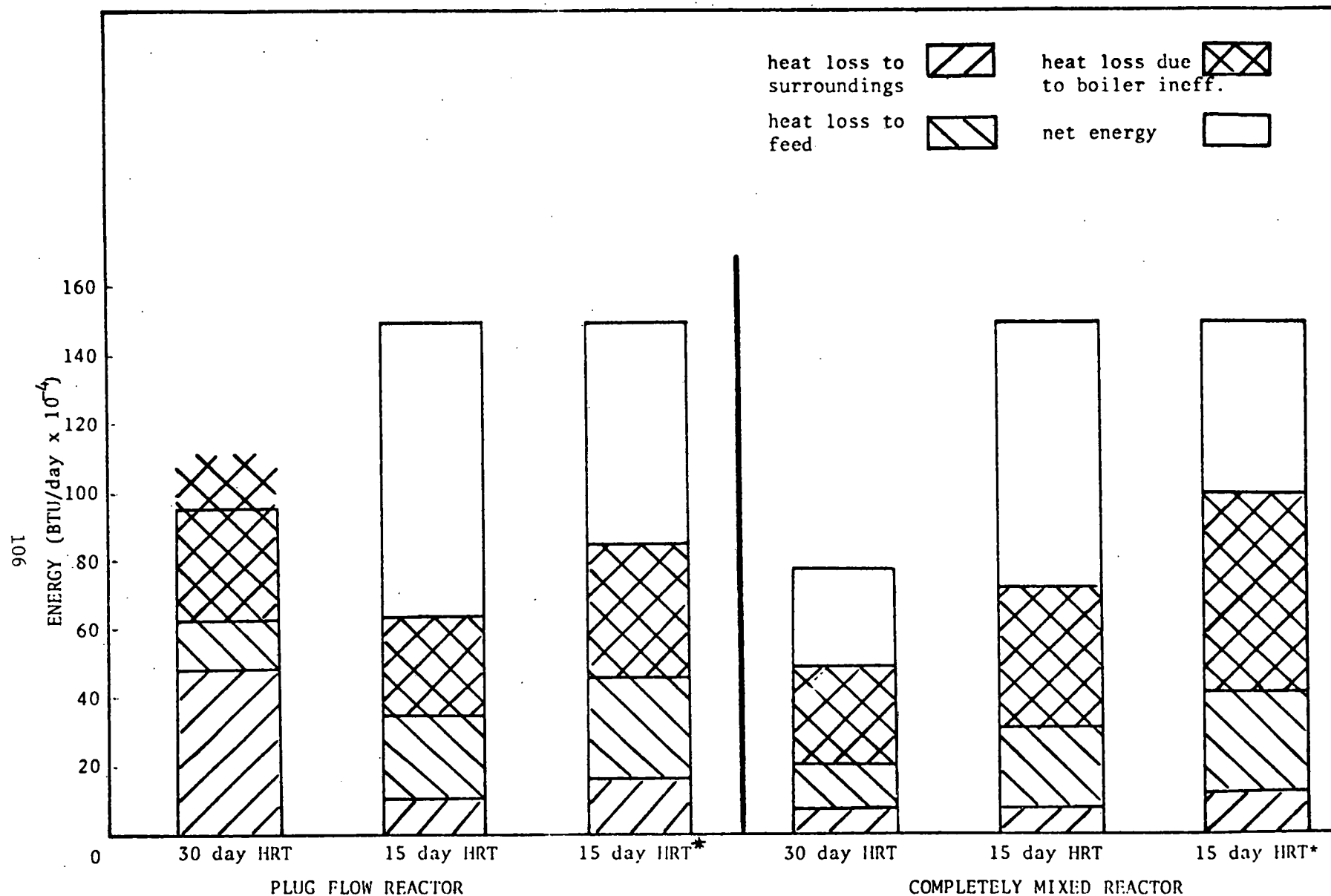


Figure 4. Observed gross biogas energy generation and resulting system total energy demands. All values based on measured thermal losses; losses correlated to 0°C in all cases except for two measured at minus 18°C. Note that the 30 day HRT plug flow reactor tests conducted without an insulated top resulted in an energy demand greater than the gross production.

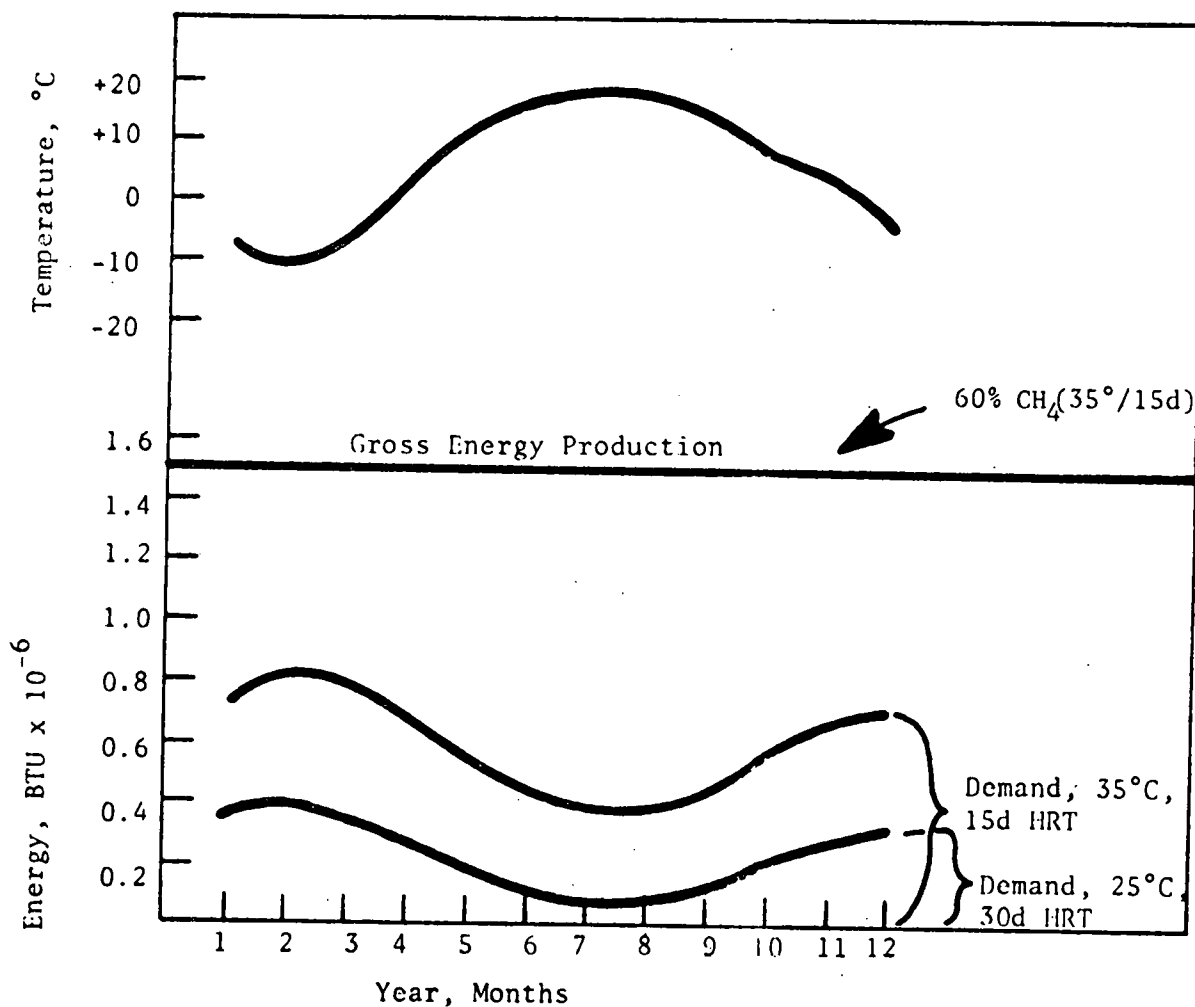


Figure 5. Annual temperature variations in New York and its influence on the net energy produced as calculated from thermal loss characteristics with a fermentor system operating on a 50 cow dairy residue feed. Two systems are illustrated operating at 35°C and 25°C.

the initiation of repair the reactor was back into operation. Startup consisted of filling the plug flow reactor up with manure and heating. The unit attained a temperature of 35°C in about three days, indicating a well-functioning heat exchanger. The speed with which this major repair task was completed, under arctic-like winter weather conditions, demonstrated a high degree of flexibility and serviceability of the Cornell plug flow design.

The full scale conventional control fermentor also required major repairs during this quarter. During a shift of conditions from 30 days to 15 days HRT, this unit experienced excessive foaming to the extent that large quantities of liquid were displaced from the reactor. More importantly, the foam that was produced apparently worked its way between the rubber-like liner and the reactor walls. A buildup of pressure occurred which apparently collapsed the liner. This reverse pressure collapsed the steel gas collection pipes and broke the PVC heat grid in several areas. When this occurred, plans were made to clean the reactor out and repair the gas collection liner and to replace the PVC heat pipes with steel.

Unfortunately, the onset of extremely low temperatures coincided with the operational problems, and the lack of operation caused a number of the effluent valves and pipes to freeze, significantly adding to the workload and difficulties of getting the units back into operation. It is anticipated that this unit will be back in operation at a 15-day, 35°C condition by mid-March.

Currently, the plug flow reactor is operating at a 15-day HRT, 35°C and 10-12% TS manure feedstock. The full scale demonstration effort is running about three months behind the revised testing schedule.

SEMI-SOLID ANAEROBIC FERMENTATION OF AGRICULTURAL RESIDUES

An ongoing Ph.D. research study by Wujcik is presently focussing on the role of water in methane production. Using information developed in this study, a 5.0m³ mesophilic pilot scale reactor using wheat straw was started to review the potential of generating methane from solids with small amounts of water.

The straw reactor was originally started at about 30 percent solids, and this was too dry, as noted by the rapid decline of gas production after initial startup. Water was added to decrease the solids content to about 25 percent, which was the target level of moisture. Gas production started at this point and has been producing between 450 and 1200 liters of gas with 50+ percent methane for nearly four months. This corresponds to a gas production rate of 0.10 to 0.25 volumes per volume of reactor per day.

In addition to this pilot scale digester, two small bench scale control reactors were also placed into operation to analyze the effect of semi-solid fermentation under a more closely controlled environment. Both reactors were 2.5 liters in volume and were kept in a 35°C environmental chamber. The first reactor was a small duplicate of the pilot scale digester. It was started at 30% T.S. It also experienced a rapid decline in gas production after initial startup, at which time water was added to decrease the total percent solid to 25%. A second 2.5 liter bench scale digester was also started at this time; this reactor had an initial concentration of 10% T.S. A summary of data from all three reactors appears in Table 7. As is shown, the bench scale 25% T.S. reactor has performed slightly better than its pilot scale counterpart. At the time of this writing it has experienced a T.V.S. reduction of 42.9%, as compared to 24.6% reduction in the pilot scale digester. In addition, the biogas

TABLE 7.
SEMI-SOLID REACTOR PERFORMANCE--COMPARISON OF
PILOT AND BENCH SCALE DIGESTER PERFORMANCE

Parameter			Pilot Scale Semi-Solid Digester 50 = 25% TS	Bench Scale Semi-Solid Digester 50 = 25% TS	Bench Scale Semi-Solid Digester 50 = 10% TS
Days of Operation			119	112	118
Reactor Volume (ℓ)			4,955	2.5	2.5
Total Biogas Produced (ℓ)			82,643	82.08	80.33
Total CH ₄ Produced (ℓ)			38,175	34.46	46.68
Avg. % CH ₄ (After Startup)			54.0	57.0	58.1
% TVS Destruction Pred. From CH ₄ Produced*			24.6	42.9	52.9
Initial Feed Comp.	Straw	gms	365,470	180	180
		T.S. (gms)	328,923	162	162
		T.V.S. (gms)	302,609	149	149
		% T.V.S./TS	92	92	92
	Manure	gms	419,768	210	450
		T.S. (gms)	33,687	16.8	36
		T.V.S. (gms)	27,337	13.6	44
		% T.V.S./TS	81.2	81.2	81.2
	H ₂ O	gms	764,570	460	1350
	NaHCO ₃	gms	25,424	10.8	27.0

*Calculations on Following Basis: $1.25 \frac{\text{gms COD}}{\text{gm VS}}$ and $5.62 \frac{\text{ft}^3 \text{CH}_4}{\text{lb COD destroyed}}$

produced from this reactor after startup contains slightly more methane than the pilot scale reactor--57% as opposed to 54%. It is hypothesized that the superior performance of the bench scale reactor is due to the fact that this reactor is shaken daily, which has allowed the free water in the reactor to come in intimate contact with the rest of the reactor contents. Because of the size of the pilot scale reactor, intimate contact between the free water and the straw solids is difficult to maintain. In this reactor the free water will drain to the bottom of the reactor and is periodically recycled back to the top of the digester. However, because of the size and limited recycle capabilities, the liquid has probably not reached all of the reactor contents. Therefore, it would be expected that degradation in the pilot unit would be slower than in the bench scale system.

Data from the 10 percent T.S. bench scale reactor is also shown in Table 7. The straw solids in this reactor are completely immersed in the liquid. Thus as would be expected, the gas production rates for this reactor are higher than for others. At the time of this writing this reactor has experienced a 52.9 percent TVS destruction. It is, for all practical purposes, biologically inactive since little gas is being produced.

FEASIBILITY MANUAL

The initial outline for the feasibility manual has been prepared and will be used as a guide to the format and content of this document. This document will not be an extensive or comprehensive set of instructions on the construction of anaerobic fermentation systems, but rather a decision aid to guide farmers through a process of rational decision-making to determine the applicability and economic feasibility of selected low-cost anaerobic fermentation systems to certain farm situations. Currently, the Methane Project does not have sufficient manpower to give adequate attention to the manual and yet conclude the remaining experimentation, analyze the data, and write the final report. Some thought, however, has been given to using certain consultants to assist in the preparation of certain sections of the design manual. Thus far, progress on the preparation of the manual is ahead of schedule.

FUTURE ACTIVITIES

In the early part of the next quarter, the pilot scale plug flow and random mix fermentors will complete the bedding addition studies, thus fulfilling all test conditions covered under the existing contract to D.O.E. By the end of the twelfth quarter both pilot units will be discontinued in operation, pumped out and cleaned.

During the first few weeks of the next quarter, the conventional completely mixed control reactor will be operating at a 15-day HRT at 35°C. For most of the twelfth quarter, both full scale reactors will progress through the accelerated testing program. The next condition of 10-12% TS manure feed, 35°C, and 15 days HRT should be completed about midway through the quarter. At that time the solids accumulation data from the pilot scale plug flow reactor will have been thoroughly analyzed, providing the basis for determining whether bedding should be added to the full scale, unmixed, plug flow fermentor while operated at 35°C. In light of the plugging problems encountered with the pilot and bench scale unmixed systems operated at this temperature, it may be advisable to postpone or eliminate this testing condition in lieu of demonstrating the long-term suitability of bedding addition with this unit operated at 25°C.

Laboratory experience with the pilot units have indicated little problem with float formation at the lower temperatures.

In the next three months there will be a major shift of manpower from experimentation and demonstration to the preparation of the final reports. Upon conclusion of the operation of the pilot reactors, minimum manpower will be operating the two full scale systems while the majority of the project personnel will be involved with the data analysis and the preparation of the final report. The detailed outline already prepared for this report will serve as a guide to content and format. Data analysis for the next quarter will include continued definition of the performance characteristics of the full scale and pilot scale

simplified reactors and close examination of the total energy balance on the full scale plug flow anaerobic fermentor under various operating conditions.

Finally, the feasibility of a continuation of this project will be reviewed. Any expansion or continuation of this project will continue to focus on the validity of considering low-cost reactor systems for the generation of biogas from animal manures and crop residues.

APPENDIX A

Minutes and Notes From the Methane Project Meetings
of the Eleventh Quarter Period--Distribution Limited

December 16, 1978 - March 15, 1979

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Stanford University
Department of Civil Engineering

HEAT TREATMENT OF ORGANICS

FOR

INCREASING ANAEROBIC BIODEGRADABILITY

Contract DOE-EY-76-S-03-PA-44

QUARTERLY PROGRESS REPORT

for the period

December 1, 1978, to February 28, 1979

by

W. Owen, D. Stuckey, P. J. Colberg, K. Baugh, B. Willey, D. Early,
L. Y. Young, and P. L. McCarty

Prepared for
Division of Solar Energy
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Washington, D.C. 20545

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A. INTRODUCTION

The objective of this study is to evaluate thermochemical pretreatment as a method for increasing the anaerobic biodegradability of organic materials so that they can be more completely fermented to methane gas, a potential source of fuel. The current study has five specific phases:

(1) biological conversion of lignocellulose to methane, (2) biodegradation of lignin and lignin fractions, (3) pretreatment of nitrogenous organics for increasing biodegradability, (4) biodegradation of lignin aromatic compounds, and (5) biochemical methane potential and toxicity testing.

This report contains results under Phases One, Two, Three, and Five. Phase Four has been completed.

B. BIOLOGICAL CONVERSION OF LIGNOCELLULOSE TO METHANE

W. Owen and P. McCarty

Current studies are attempting to increase the biodegradability of lignocellulose by autohydrolysis. In this process, a lignocellulose slurry is heat treated with no chemical additions. Thermal hydrolysis leads to acid production, a lowered pH, and increased rates of hydrolysis of the cellulose fraction to soluble end products. The influence of operating conditions on the fractional conversion to soluble products was presented in the previous quarterly report (Owen et al., 1978). This report contains the results of Biochemical Methane Potential (BMP) and Anaerobic Toxicity Assay (ATA) of the products of autohydrolysis to determine their biodegradability and potential toxicity.

Bioconversion Efficiency

Anaerobic bioconversion efficiencies for white fir and respective autohydrolysis products are summarized in Table 1. The biodegradability of untreated white fir was low (2.6%) and comparable to other softwoods. Single-stage autohydrolysis pretreatment resulted in significant improvement in bioconversion efficiency, but was less than desirable from a practical standpoint when referenced to feed conditions. However, since staged processing showed promise with respect to separating and recovering the components of lignocellulose, it is important to review the data of Table 1 concerning the general principles of autohydrolysis pretreatment for improving bioconversion efficiency of white fir.

It is clear from these data that oxidative treatment did not demonstrate any significant advantage over nonoxidative processing for improving biodegradability.

Previous studies indicated that the mechanism for improving biodegradability of lignocellulose by autohydrolysis was solubilization of organics as the digestible products. The biodegradability of the particulate fraction was not significantly affected by such treatment. This observation, which would be important in a consideration of a complete pretreatment and digestion scheme, is similar for white fir, as indicated by a comparison of product total and soluble bioconversion efficiencies when referenced to feed conditions (Table 1).

TABLE 1
BIOCHEMICAL METHANE POTENTIAL OF AUTOHYDROLYZED WHITE FIR

Pretreatment Conditions			Referenced to Product				Referenced to Feed			
			BMP ^c m ³ CH ₄ /kg COD		Bioconversion Efficiency, %		BMP m ³ CH ₄ /kg COD		Bioconversion Efficiency, %	
			Total	Soluble	Total	Soluble	Total	Soluble	Total	Soluble
Untreated Control			-	-	-	-	9.1	-	2.6	-
175	0.0	He	37.8	287	10.8	82.1	36.4	23.2	10.4	6.6
175	2.0	He	61.0	274	17.4	78.2	58.3	55.0	16.7	15.7
175	4.0	He	51.3	223	14.7	63.8	47.8	42.1	13.7	12.0
200	0.0	He	60.5	278	17.3	78.7	56.8	48.4	16.2	13.8
200	2.0	He	44.3	207	12.7	59.1	42.0	42.0	12.0	12.0
200	4.0	He	41.6	216	11.9	61.8	38.5	40.7	11.0	11.6
225	0.0	He	52.4	255	15.0	72.8	50.7	56.8	14.5	15.2
225	0.5	He	46.7	221	13.3	63.2	44.8	48.1	12.8	13.7
225	1.0	He	45.5	208	13.0	59.3	44.4	47.9	12.7	13.7
225	2.0	He	44.1	191	12.6	54.6	42.5	50.2	12.1	14.4
225	3.0	He	39.3	202	11.2	57.7	37.6	48.7	10.8	13.9
225	4.0	He	39.2	217	11.2	62.0	37.0	47.9	10.6	13.7
225	0.5	0.18	43.1	179	12.3	51.2	39.5	32.1	11.3	9.2
225	1.0	0.18	51.5	204	14.7	58.4	47.9	40.5	13.7	11.6
225	2.0	0.24	-	278	-	79.4	-	42.4	-	12.1
225	3.0	0.17	50.7	310	14.5	88.6	42.7	34.6	12.2	9.9
225	4.0	0.18	38.0	312	10.9	89.1	28.0	26.5	8.0	7.6

^aReaction time at indicated temperature; 0.0 hr denotes heated to indicated temperature and immediately cooled to room temperature.

^bOff-gas flow referenced as m³(STP)/hr/kg feed COD; He denotes nonoxidative treatments.

^cTotal BMP and respective bioconversion efficiency referenced to product total COD, and soluble BMP and respective bioconversion efficiency referenced to product soluble COD.

Reviewing the data in Table 1, there is a trend between biodegradability of soluble products and severity of treatment. Initially, the bioconversion efficiency of the soluble product was quite high (ca. 80%), but as the severity of treatment increased, bioconversion efficiency decreased somewhat and appeared to stabilize at approximately 60 percent.

Toxicity

Three pure compounds and 14 filtered reaction products were tested for relative toxicity. A summary of these results is presented in Table 2. Maximum rate ratios (MRRs) were used as a measure of toxicity, a value of less than 1.0 is indicative of substrate inhibition except where noted. All data are referenced to respective soluble CODs; and theoretical CODs were used for pure compounds. In addition, significant inhibition is noted by an asterisk, and associated lag times for culture acclimation are recorded where appropriate.

In general, the more severe treatments exhibited greater toxicity. These results are consistent with the concepts for a dehydration-reaction scenario. Many of the degradable compounds at mild treatments were probably free mono- and oligosaccharides, and dehydration products no doubt became increasingly more significant as the severity of treatment increased. It is interesting that the products from 2-hour treatment at 225°C, both oxidative and nonoxidative, were the most toxic (these were the only products where acclimation was not noted at the highest assay concentration), and that corresponding treatment for 4 hours was slightly less toxic. Likewise, soluble product BMP was somewhat higher for the 4-hour treatment compared with 2 hours at 225°C. These observations may have been the result of a shift toward levulinic acid as the primary reaction product, which is highly degradable and less toxic than 5-(hydroxymethyl)-2-furaldehyde.

A comparison of products from oxidative and nonoxidative treatments shows no significant advantage of either technique with respect to toxicity.

Summary

The mechanism for increase in biodegradability for white fir samples, due to autohydrolysis pretreatment, has been confirmed to be the solubilization of organics (polysaccharides) as the digestible product. In this regard, the soluble product is most degradable for mild treatments, and degradability decreases slightly at more severe conditions. With respect

TABLE 2
ANAEROBIC TOXICITY ASSAY SUMMARY

Sample	COD ^a Conc., g/l	MRR ^b	I ^c	Acclimation Time, days ^d
Levulinic Acid	0.15 0.38 0.76 3.0 12.2	1.02 1.04 1.01 1.27 0.62	*	14
2-furaldehyde	0.17 0.42 0.83 2.77 8.3	1.11 1.25 1.38 0.55 0.17	* *	6 two: 9, 22
5-(hydroxymethyl)- 2-furaldehyde	0.15 0.38 0.76 2.54 7.6	0.94 0.92 0.92 0.48 0.13	* *	two: 6, 12 30
WO-S-91 White Fir 175°C, 2 hr nonoxidative	0.09 0.23 0.47 1.93 7.45	1.00 1.05 1.12 0.95 1.01	(e) (e)	
WO-S-90 White Fir 200PC, 2 hr nonoxidative	0.10 0.24 0.48 1.96 7.56	1.00 1.04 1.10 0.45 0.20	* *	7 25
WO-S-82 White Fir 225°C, 0.0 hr nonoxidative	0.10 0.26 0.52 2.15 8.28	0.98 1.03 0.79 0.35 0.80	(f) * *	6 20
WO-S-80 White Fir 225°C, 1 hr nonoxidative	0.11 0.27 0.54 2.23 8.60	1.00 0.99 1.11 0.42 0.15	* *	8 30

(Table continued)

TABLE 2 continued

Sample	COD ^a Conc., g/l	MRR ^b	I ^c	Acclimation Time, days ^d
WO-S-86	0.09	1.01		
White Fir	0.23	1.00		
225°C, 1 hr	0.47	1.01		
Off-Gas = 0.18 m ³ /	1.92	0.40	*	7
hr/kg feed COD	7.39	0.23	*	25
WO-S-76	0.12	1.00		
White Fir	0.30	1.03		
225°C, 2 hr	0.61	1.09		
nonoxidative	2.53	0.50	*	6
	9.76	0.08	*	None
WO-S-77	0.10	1.04		
White Fir	0.24	1.04		
225°C, 2 hr	0.50	1.11		
Off-Gas = 0.24 m ³ /	1.98	0.58	*	two: 6, 12
hr/kg feed COD	7.99	0.04	*	None
WO-S-81	0.10	1.00		
White Fir	0.26	1.00		
225°C, 4 hr	0.52	1.05		
nonoxidative	2.13	0.62	*	two: 7, 12
	8.21	0.28	*	20

^aSample assay concentration as COD, all samples are filtrates.

^bMRR denotes Maximum Rate Ratio = $\frac{\text{Sample Maximum Rate}}{\text{Fed Control Maximum Rate}}$; measured between days 2 and 6.

^cInhibited samples denoted by asterisk.

^dEstimated time for acclimation in inhibited samples.

^eInhibition apparently due to acid generation in excess of buffering capacity.

^fApparent sampling error, no inhibition.

to softwoods, for extended treatment at severe temperatures (225°C) the soluble product bioconversion efficiency remains quite constant at 60 percent; therefore, this value represents a good, conservative estimate of product biodegradability.

The major soluble dehydration products from acid-hydrolysis of ligno-cellulosics are biodegradable and potentially toxic in anaerobic fermentation systems.

All of the soluble products from autohydrolysis of representative ligno-cellulosics demonstrated some toxicity; however, anaerobic cultures were able to acclimate to toxic compounds provided soluble COD concentrations were kept sufficiently low, less than 3 g/l. Furan derivatives were found to be a major contributor to biodegradability and toxicity in these products. Most likely, the changes in product biodegradability and toxicity with respect to change in severity of treatment, are due to shifts in relative concentrations of the different dehydration products.

Future work will evaluate the effect of autohydrolysis on agricultural residues (corn stover and bagasse). Also, staged treatment has been shown to have the best potential for maximizing biodegradable products from wood products. This will be explored in more detail in the future.

C. BIODEGRADATION OF LIGNIN AND LIGNIN FRACTIONS

P. J. Colberg and L. Y. Young

A number of lignin-related questions have been posed as a result of our heat-treatment studies at Stanford. We have shown that the aromatic subunits of lignin are fermentable to methane (Healy and Young, 1978). Murry (1974), however, found that the lower molecular size fractions are more resistant to anaerobic attack than the higher molecular weight fractions. Other investigators employing aerobic systems (Crawford et al., 1977a and 1977b), likewise report differences in the potential degradation of lignin fractions. What remains to be understood, then, is the potential for methanogenic degradation of the more complex molecules present following pretreatment of lignin.

A related problem which has received little experimental attention is the question of lignin toxicity. Our laboratory studies have shown inhibition of methane production in digesters fed heat-treated lignin in concentrations greater than 1-2 g/l. Early Warburg studies also suggested some toxicity was produced with heat-treated lignocellulosics (Gossett, 1976). More recently (Healy et al., 1977), rates of methane production monitored by the anaerobic serum-bottle-assay technique were, likewise, found to be inhibited at higher lignin concentrations (750 mg/l).

Available data suggest that the refractory nature of some aromatics could be due to toxicity. Calder and Tader (1976) described effects of aromatics as decreasing growth rate and cell densities, and reported toxicity to be a function of both concentration and decreased solubility. Chmielowski et al. (1964) found that additions of 500-1000 ppm of phenol into unadapted cultures strongly inhibited or destroyed the methane fermentation process in a few days. Other hydroxyaromatics are also believed to be among the toxic-extractible substances in wood (Scheffer and Cowling, 1966). In some instances, since it was not suspected, the observed resistance of lignin fractions to biodegradation may have been due to toxicity (Murry, 1974).

Previous work at Stanford has also related lignin toxicity with the presence of aromatic compounds, though specific identification of potentially toxic substances has never been attempted. The toxicity issue, therefore, needs to be examined in order to fully assess the biodegradation potential of the lignin polymer, particularly if toxicity is a phenomenon not limited to alkaline heat-treatment processes only.

We have adapted Gel Filtration Chromatography (GFC) techniques for the preparative fraction of heat-treated peat lignin to be used in ongoing biodegradation and toxicity studies. The protocol employed for lignin pretreatment, fractionation by GFC, and preparation for feeding experiments were described in detail in two previous progress reports (Healy et al., 1978; Owen et al., 1978). Elution patterns for peat lignin were also described. Preliminary mass-balance data from Biochemical Methane Production (BMP) assays yielded percent conversions of carbon to CO_2 and CH_4 of 7-38 percent, depending on the fraction tested.

Methodology testing and development is now in progress to adapt High-Pressure Liquid Chromatography (HPLC) techniques for assessment of biodegradation and potential toxicity. Structural changes in lignin fractions fed in BMP assays may be followed by HPLC reverse-phase analysis, separating the molecular size peaks into individual components according to molecular weight. Since the column is run at low pressures (100-200 psi), the fractions and individual compounds should remain intact during analysis. This technique affords the ability to follow degradation of specific compounds during anaerobic decomposition. In addition, it allows for identification of compounds which are either nonbiodegradable, i.e., their peaks do not disappear during anaerobic incubation, and/or potentially toxic; their peaks likewise persisting during incubation. HPLC reverse-phase analysis also allows compounds of interest to be collected during analysis--a major advantage over other chromatographic techniques in which the sample is destroyed during analysis (i.e., gas chromatography). Identification of compounds suspected to be toxic may subsequently be identified by Gas Chromatography-Mass Spectroscopy (GC/MS).

D. PRETREATMENT OF NITROGENOUS ORGANICS

D. Stuckey and P. McCarty

The effect of thermochemical pretreatment on the degradability and toxicity of bacterial cells (Waste Activated Sludge, or WAS) and pure nitrogen components is currently being investigated.

Biodegradability of WAS under Mesophilic and Thermophilic Conditions

There has been some evidence to suggest that under thermophilic conditions organics are more completely degraded than under mesophilic conditions. Experiments were carried out on thermochemically pretreated WAS to determine if there is a difference. Biochemical Methane Production (BMP) assays were conducted using seed from separate mesophilic (35°C) and thermophilic (55°C) digesters fed waste activated sludge.

Data obtained over a period of 34 days (Table 3) revealed the previously determined trends with temperature of treatment and NaOH addition. The difference in degradability under mesophilic and thermophilic conditions was usually significant, and in all cases resulted in less degradability. Even after 81 days, while overall degradability had increased slightly, mesophilic conditions led to higher degradabilities. However, it is felt that these data should be interpreted with some degree of caution since it is possible that the thermophilic seed used may not have been a "balanced" population. This point will be discussed further in the light of other data obtained.

In another experiment, a different flow scheme was tried to improve biodegradability. The effluent from both mesophilic and thermophilic digesters was heat treated and BMPs were determined over a 44-day period to increase in degradability. This flow scheme would prevent the conversion of easily degradable organics to refractory compounds by heat treatment. The data obtained indicated an overall degradability of the two-stage process of 75 percent, an increase from 62 percent without heat treatment.

Biodegradability and Toxicity of Thermochemically Pretreated Nitrogen Components

Thermal treatment of WAS leads to an increase in degradability, followed by a precipitous decline with time. In order to understand this phenomenon, the degradability of bacterial cell components after thermal treatment was

TABLE 3
PERCENT BIODEGRADABILITY OF BACTERIAL CELLS UNDER MESOPHILIC AND
THERMOPHILIC TEMPERATURES AS A FUNCTION OF PRETREATMENT CONDITIONS

Heat-Treatment Temperature (°C)	No Chemical Addition		300 meq/l NaOH	
	Mesophilic	Thermophilic	Mesophilic	Thermophilic
	<u>34 Days</u>			
Control	48	42		
150	-	-	55	49
175	61	51	58	50
200	57	48	59	54
250	48	35	60	51
275	42	19	59	42
	<u>81 Days</u>			
Control	54	45	-	-
150	-	-	65	52
175	68	52	66	53
200	61	49	67	55
225	57	41	65	55
250	55	41	61	51
275	48	35	63	50
Seeded with 27.6 ml of meso/thermo per 2-1 flask. Seed washed twice with deoxygenated buffer.				

studied. The general groups evaluated were proteins, amino acids, RNA, and DNA. The toxicity of these general groups was also assessed to try to isolate and understand the causes and source of the toxic material generally produced during thermochemical pretreatment.

Two proteins, collagen and albumin, were evaluated for toxic effects, while only the former was used in degradability tests. The concentrations used were approximately the same as the concentration of WAS, i.e., a COD of 40 g/l. However, since collagen is a fibrous protein and very gelatinous, a solution of only 20 g/l was used. The albumin used was 34.5 g/l.

The amino acid solution treated contained 2 g/l of each of the twenty common amino acids. The DNA used was extracted from salmon sperm and contained 42.1 g/l. The RNA was extracted from yeast and contained 57.15 g/l.

The percent of COD destroyed is set out in Table 4 for both mesophilic and thermophilic conditions. Mesophilic controls (i.e., non-heat-treated)

TABLE 4
BMPs OF PURE COMPONENTS IN PERCENT BIODEGRADABILITY (34 Days)

Component	Control		Heat Treatment			
			No Chemical Added 200°C		300 meq/l NaOH Added 200°C	
	Mesoph.	Thermoph.	Mesoph.	Thermoph.	Mesoph.	Thermoph.
Amino acids	92	72	70	54	67	52
RNA	92	78	56	39	60	53
DNA	91	81	36	28	41	31
Collagen	115	97	106	86	115	91

indicated that all the basic components are highly degradable as expected. The high values for collagen are probably indicative of low initial COD figures due to incomplete oxidation of the highly bound protein.

Pretreatment in all cases but one lowered the BMP. It is hypothesized that this was due to a thermally catalyzed complexation and polymerization reaction where the simple components form more complex compounds, which are less amenable to degradation. The exception to this is collagen where there appeared to be no significant decreases with pretreatment.

The difference in destructions between mesophilic and thermophilic temperatures is apparent under all the conditions studied. The difference with the controls raises the question as to whether the thermophilic seed used was a "balanced" population, since it would be expected that the destructions would be similar in both cases. The thermophilic seed digester contained approximately 1000 mg/l of propionic acid, which is suggestive of some operational problems.

An anaerobic toxicity assay (ASA) on the heat-treated basic components is set out in Table 5. Given are the maximum rate ratio (MRR) as a function of dilution. MRR values less than 1.0 indicate inhibition. Under mesophilic conditions only the amino acid mixture was toxic at a thirtieth dilution, while at a fifth dilution most compounds were toxic, except for the proteins. At the highest concentration, the proteins were still considerably less toxic than the other components.

TABLE 5
ATAs OF HEAT-TREATED NITROGENOUS COMPONENTS*

Compound	Heat Treatment	Mesophilic - MRR (3 Days)			Thermophilic - MRR (3 Days)		
		1/30	1/5	1/2	1/30	1/5	1/2
Amino acids	Control	-	-	1.7	-	-	2.28
	200°C	1.2	1.0	0.6 (4)	1.38	2.31	1.99
	200°C NaOH	0.85 (3)	0.6 (5)	0.6 (3)	1.26	1.04	0.72 (3)
DNA	Control	-	-	2.0	-	-	1.96
	200°C	1.1	0.42 (4)	0.2 (7)	1.13	0.31 (11)	0.31 (11)
	200°C NaOH	0.95 (3)	0.55 (4)	0.15	1.06	0.40 (13)	0.34
RNA	Control	-	-	3.7	-	-	3.41
	200°C	1.0 (3)	0.49 (6)	0.29 (6)	1.33	1.43	0.64
	200°C NaOH	1.0 (3)	0.69 (4)	0.37 (6)	1.20	0.75 (7)	0.59 (7)
Collagen	Control	-	-	1.98	-	-	4.23
	200°C	1.18	1.5	1.49	1.22	1.86	2.73
	200°C NaOH	1.19	1.02	0.44 (4)	1.25	2.12	1.43
Albumin	Control	-	-	1.76	-	-	-
	200°C	1.23	1.17	0.73 (21)	-	-	-
	200°C NaOH	1.17	1.19	0.90 (6)	-	-	-

* Figures in parentheses indicate time in days to acclimate.

With thermophilic temperatures the compounds appeared to be less toxic, and collagen was not toxic under any of the conditions studied.

Toxicity of Thermochemically Pretreated Pure Nitrogen Components

From the previous work described it became obvious that to fully understand the effect of pretreatment on nitrogen compounds, separate compounds would have to be treated individually, and in defined mixtures to see if there was any interaction.

The twenty common amino acids which were used previously in the mixture were made up individually in solutions at 40 g/l. The five common bases present in nucleic acids were also used at the same concentration, together with the sugars, glucose, deoxyribose, and ribose.

Table 6 sets out the data obtained to date. In a large number of cases the actual controls (20 g/l) were toxic indicating that even without heat treatment, some compounds are toxic at high concentrations. With the sugars

TABLE 6

ATAs OF AMINO ACIDS, SUGARS AND BASES*

(All stock solutions 40 g/l, mesophilic condition used)

Sample	Control (1/2 Dilu.)	Heat-Treated Sample 7-Day MRR, 200°C NaOH (300 meq/l)		
		1/30 Dilu.	1/5 Dilu.	1/2 Dilu.
Glucose	1.69	1.02	0.2	0.37
Deoxyribose	0.45	0.77 (8)	0.54 (8)	0.08
Ribose	1.58	0.98 (7)	0.34	0.33
Glycine	} uncharged polar R	0.30 (8)	0.54 (8)	0.36 (9)
Asparagine		0.96 (7)	1.15	0.86 (8)
Proline	} nonpolar R	0.79 (7)	0.74 (7)	0.47 (8)
Valine		0.54 (9)	0.17	0.77 (7)
Alanine		0.99	1.06	0.77 (8)
Leucine	} acidic	0.57 (8)	1.23	0.65 (8)
Aspartic acid		0.92 (7)	0.96 (9)	0.71 (9)
Lysine	} basic	0.91	1.36	1.10
Arginine		0.12 (10)	1.26	0.90 (7)
Cytosine	} bases	0.31	1.15	0.63 (8)
Adenine		0.33	0.55 (8)	0.13
Guanine		0.14	0.92 (7)	0.67 (8)
Uracil		0.69 (7)	1.19	1.00 (6)
Thymine		0.07	1.15	0.81 (6)
Uracil/Ribose (17.1/22.9)	1.01	0.99 (7)	0.62 (10)	0.21
Leucine/Glucose (20/20)	1.57	0.89 (7)	0.12	0.18

* Figures in parentheses indicate time in days to acclimate.

the controls appear to be non-inhibitory from the gas production; however, the gas produced was predominantly carbon dioxide with some H_2 , i.e., carbohydrate fermentation. This probably led to a sharp drop in pH, and an inhibition of methanogenesis, and hence was not a true indication of a toxic effect.

Even at a thirtyfold dilution (≈ 1.33 g/l) some compounds were toxic in all the groups tested, especially glycine. At a fifth dilution (8.0 g/l), only lysine and uracil were not toxic, while at a half-strength (20 g/l), all the compounds were toxic, although alanine and thymine were not strongly so. At this point there does not seem to be any strong correlation between the structure of the compound and its toxicity.

With the mixtures between uracil and ribose and leucine and glucose, the toxicity data indicate that there is a significant interaction leading to more toxic products being formed. Further work is proceeding on evaluating the toxicity of the other pure components and possible interactions. Also BMPs are being carried out to evaluate the effect of pretreatment on the degradability of the pure components.

E. BIOCHEMICAL METHANE POTENTIAL AND TOXICITY TESTING

D. Early, B. Willey, D. Stuckey, and P. McCarty

Under this phase of the study, the biodegradability of a variety of agricultural residues is being investigated. Biodegradability of the untreated materials and materials which received mild heat treatment with low concentrations of caustic are under study. Materials under study are cotton gin trash, corn stover, rice straw, wheat straw, barley straw, and sorghum straw. These studies will soon be completed and will be reported upon in the next quarterly report.

Another phase of this study is the evaluation of residues and digested materials for toxicity in cooperation with other DOE contractors. Professor John Pfeffer at the University of Illinois has found that digestion of wheat straw pretreated under mildly alkaline conditions and at low temperature was proceeding with difficulty. Evaluation of this material by the anaerobic toxicity assay procedure is now under way. Problems are also being experienced by Hamilton Standard in starting thermophilic digesters on cattle manure. Studies on this and on a cattle feed supplement which may become part of cattle manure are also underway to determine whether the problems being experienced may result from toxicity. The results of these studies will also be covered in the next quarterly report.

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BIOLOGICAL CONVERSION OF BIOMASS TO METHANE

QUARTERLY PROGRESS REPORT
for Period December 1 - February 28, 1979

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Introduction

As specified by this contract, investigations into the viability of wheat straw as a feed stock for methane production have been undertaken. Baled straw was obtained from a commercial supplier who has the contract to supply the University of Illinois with this material. Approximately five tons was obtained in August 1978. This straw was harvested from the 1978 wheat crop. The straw was stored inside to protect it from the weather. Since it was dry, it can be stored indefinitely without decomposition.

The straw is not chopped during harvest. Therefore, it was necessary to mill it prior to slurry preparation. The particles were milled through a 3.2 mm (1/8 in.) screen in order to facilitate feeding of this material to the fermentation system. A sieve analysis of the dry milled straw showed that 97 percent passed the #10 sieve (1.98 mm) with essentially 0 percent passing the #200 sieve (74 μ m). In fact, only approximately 5 percent of the milled straw passed the #50 screen (297 μ m). This milling resulted in a rather narrow size range.

When the material was wetted, the particles swelled substantially as a result of the absorbed moisture. Using a wet sieving technique, over 65 percent of the total solids were retained on the #10 sieve. At the same time, 30 percent of the total solids passed the #200 sieve. Essentially all of this 30 percent was soluble solids. This straw slurry has unique characteristics. With a solids content of 12 to 13 percent, the straw and water mixture has absolutely no fluid properties. It has an angle of repose that approaches 90 degrees. Mixing by conventional fluid mixers is impossible. The power required by a ribbon mixer designed to mix concentrated slurries exceeded 2 KW/m³ (75 HP per 1000 cu ft). This slurry could be mixed with conventional mixing equipment only at significantly lower solids concentrations.

Pumping of a slurry containing 10 percent solids was impossible. It was necessary to dilute the solids to about 3 percent. Even at these concentrations, it was extremely difficult to pump the slurry. Various other procedures were tried in hopes that it would be possible to operate the pumping system with the time clocks to approximate continuous operation. Steam heating of the straw-water (12 percent solids) mixture at 115°C (240°F) did improve the water absorption. It was possible to wet the straw more easily with the heat treatment. It also appeared to ease the pumping problems slightly. However, the feeding had to be accomplished manually. The pumps would not start without flushing with water prior to turning on the pumps.

The conversion efficiency of the straw was somewhat better than with the corn stover. Part of this improvement may have been a result of the need for heat treating the straw so it could be processed. Analysis of the gas data showed that approximately 53 percent of the volatile solids in the straw were biodegradable for a fermentation temperature of $59 \pm 1^\circ\text{C}$. The rate of conversion was determined from a simple first order kinetic relationship in which the substrate removal rate (dS/dt) is a function of the biodegradable substrate remaining. This rate constant was found to be 0.23 day^{-1} .

Experimental Procedure

After completion of the investigation of the conversion efficiency of the untreated straw, a thermochemical pretreatment step was initiated in order to investigate the potential for improvement of the conversion efficiency. Because of the uniqueness of the response of the system to this pretreatment step, the procedure will be presented specifically as related to the following data.

A 400 liter mixed pressure reactor was used for this treatment. Dry milled straw, 27 kg (60 lbs), was added to this reactor. This quantity of uncompacted dry straw occupied approximately 50 percent of the reactor volume. The specific gravity of this dry milled substrate was only approximately 0.12. The ribbon mixer in the reactor was operational during the entire processing. Gradular sodium hydroxide was added to the straw at the rate of 1.9 kg per 27 kg of dry straw. After the chemical and straw were mixed for about 5 minutes, 190 kg of tap water was added. An attempt was made to insure that all of the straw was wetted during this step.

The reactor was closed and the steam injection started. Live steam was added directly to the reactor. During the process of raising the temperature to 115°C, approximately 38 kg of steam condensate was added to the slurry. The pH of the paste before the steam was added was approximately 12.2. After steam treatment for 4 hours, the pH decreases to near 10.0. There appeared to be some variation in this final pH. Before the condensate accumulated, the concentration of NaOH was 0.25 molar. This was decreased to 0.21 molar by the addition of steam.

The treated slurry was pumped from the pressure reactor to the mix tanks. An addition of 190 kg of water was added to dilute the slurry to approximately 6 percent solids. This was done to conserve the straw. Higher slurry concentrations could be processed through the system. The resultant NaOH concentration was 0.114 molar.

The slurry used in Reactors #3 and #4 received this treatment from December 2, 1978 to February 12, 1979. At this date, the amount of NaOH added to the dry straw was reduced from 1.9 kg to 1.52 kg. This resulted in a NaOH concentration in the pretreatment step of 0.166 molar and 0.091

molar in the feed slurry. Feed slurry for Reactors #1 and #2 was pretreated with 1.9 kg of NaOH from January 4, 1979 to March 1, 1979. At this date, the NaOH was reduced to 1.52 kg.

In addition to the sodium hydroxide, the 1.35 kg NH_4Cl and 0.4 kg of K_2HPO_4 were added for each 27 kg of straw processed. This supplied the nutrients for the microorganisms and resulted in a residual ammonia nitrogen varying from 200 to 300 mg/l. This suggests that a substantial quantity of ammonia was converted to cell mass. Analysis for phosphorus showed levels between 50 and 100 mg/l of P in the slurry.

Results and Discussion

The feed of thermochemical pretreated slurry to Reactors #3 and #4 was initiated on December 2, 1978. Prior to this change, these reactors were receiving untreated straw. Reactor #3 was operating at a retention time of 7.5 days at a volatile solids loading of 1.9 kg/day. The retention time in Reactor 4 was 5.0 days with a volatile solids loading of 2.9 kg/day. On the assumption that a significantly higher availability of volatile solids would result from the pretreatment, the loading on the reactors was initially low. Also, the fermentation temperature was reduced to 40°C on November 26, 1978. This was done to allow an initial comparison of the effect of temperature of the conversion efficiency. If it was observed that 40°C temperature was significantly less effective than 60°C, mesophilic temperature would not be further studied.

During the first week, significant pH drops were encountered. With intermittent feed and lime addition, a stable pH was achieved. These start-up data are shown in Figure 1. Day 0 corresponds to December 9, 1978. Reactor

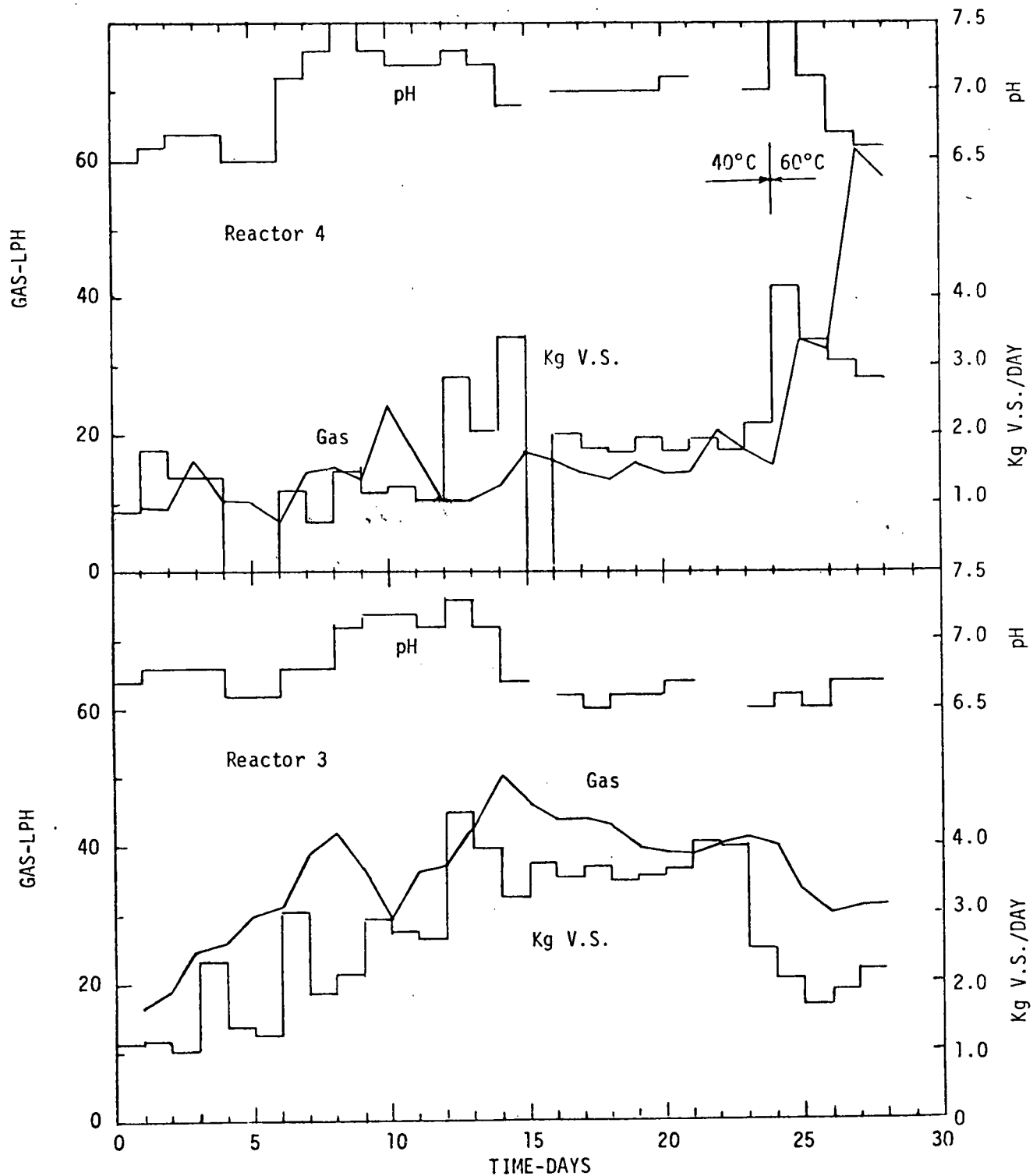


Figure 1. Response of reactors to thermochemical pretreatment.

4 was operated at a retention time of approximately 30 days until December 21, 1978 (Day 12). At this time, the feed rate was increased such that the retention was decreased to about 15 days. The pH remained in an acceptable range during this period, even though the total volatile acids gradually increased to 2500 mg/l by December 29, 1978 (Day 20). A stable operation was obtained from Day 16 to 26. The gas production during this period was $0.11 \text{ m}^3/\text{kg}$ volatile solids feed. This was a relatively poor gas production when one considers that untreated straw produced $0.167 \text{ m}^3/\text{kg}$ volatile solids fed at 58°C and a 13.7 day retention time. The gas production from Reactor #3 during this period was $0.15 \text{ m}^3/\text{kg}$ of volatile solids fed with a 7.7 day retention time and 60°C fermentation temperature.

Reactor 3 exhibited a very good acclimation to the new feed during the first two weeks. The loading was increased to about 4 kg per day of volatile solids with the retention time decreased to 7.5 days. After about Day 15, the gas began to decrease, as did the pH. The volatile acids were increasing to about 4000 mg/l. Because of the decreasing pH, the loading was reduced. However, the system did not recover. Because of the higher feed rate in #3, the inhibition was observed sooner. It appeared that Reactor 4 was reaching the same end. Therefore, the temperature was raised to 60°C . The loading was also increased, with a resultant increase in gas production. However, the pH decreased substantially.

Figure 2 shows the response of Reactor 3 during the next two months. Day 0 corresponds to January 6, 1979. The gas production continued to decrease while the loading was maintained to approximately 2.0 to 2.5 kg per day and a 13 to 15 day retention time. The pH also decreased to inhibitory levels of 6.4. Lime was added to maintain the pH at 6.6 or greater. The

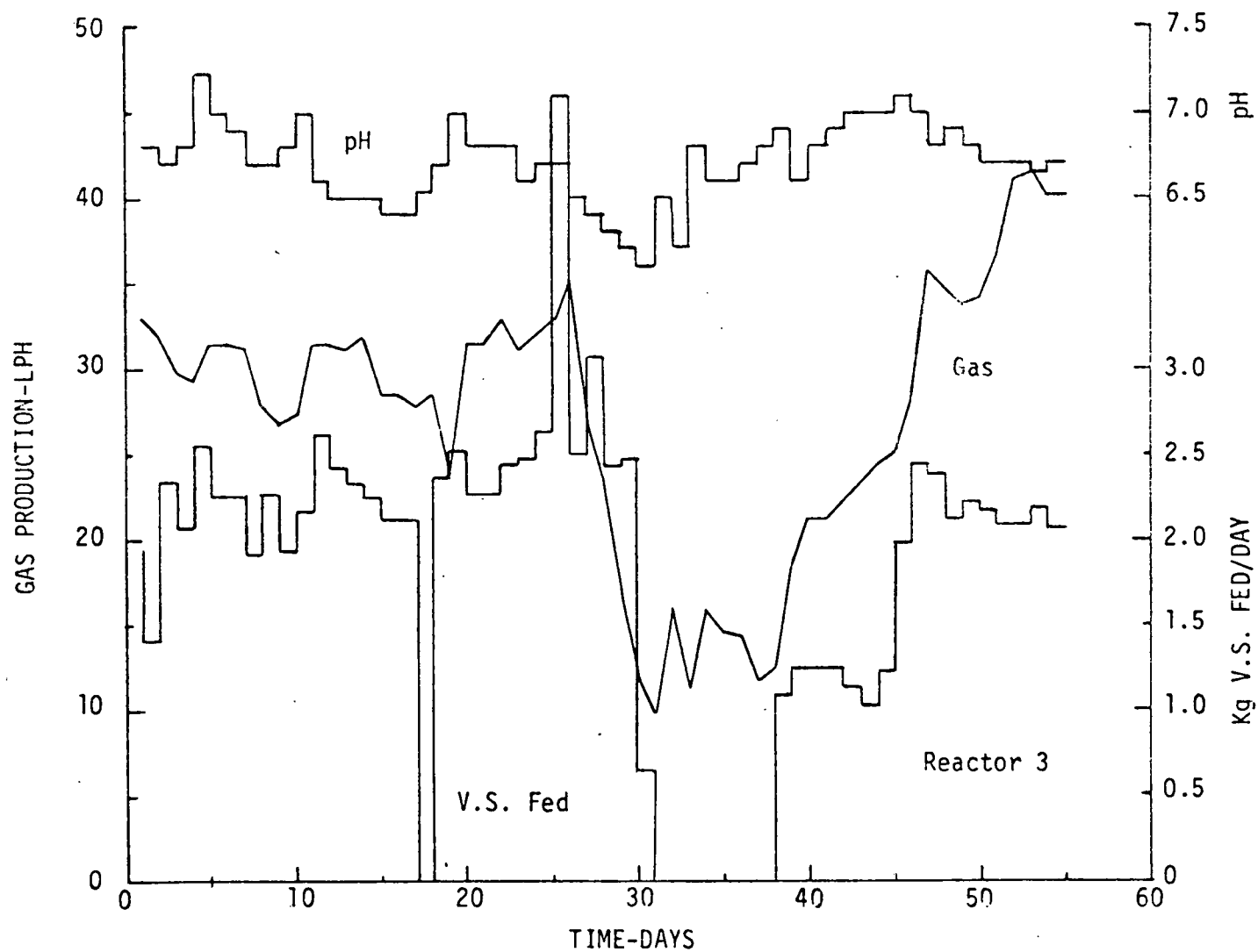


Figure 2. Reactor performance with thermochemical pretreatment.

system did not receive any feed on January 18, 1979 because of severe weather that prevented access to the laboratory. An excessive feeding on Day 26 so overloaded the system that failure resulted. The pH dropped to 6.1 and the feed was terminated on Day 32.

As shown in Figure 3, Reactor 4 responded in essentially the same way as Reactor 3. The response was delayed to a degree because of the longer initial retention time in Reactor 4. As a result, the time required to reach an inhibitory level was increased. Gas production remained at a moderately high level and pH remained above 6.6. However, the total volatile acids continued to increase and eventually reached levels of excess of 4000 mg/l. By Day 31, the pH had dropped to 6.7 and the total volatile acids were 6800 mg/l. Feeding was stopped for two days. An inadvertent overfeed of 8 kg of volatile solids caused the pH to drop to 6.3. Feeding was stopped and lime was added to return the pH to 6.6 or greater.

The cause of the inhibition was not known, but it appeared to be associated with the level of NaOH employed in the thermochemical pretreatment. The characteristics of this straw required that a higher moisture be utilized in the pretreatment step. Consequently, the amount of dilution applied to the feed was reduced. The sodium concentration, as well as any products of the pretreatment step, were significantly higher than the previous tests using this pretreatment. Acting on the premise that the concentration of some inhibitory material was high, the reactor contents were diluted to 80 percent of the original concentration by adding tap water to the reactors. This was done on February 12, 1979 (Day 37 on Figure 2 and 3). Also the caustic used in the pretreatment was reduced from 1.9 to 1.52 kg. Recovery was almost immediate. Feed was again initiated. The pH increased to acceptable

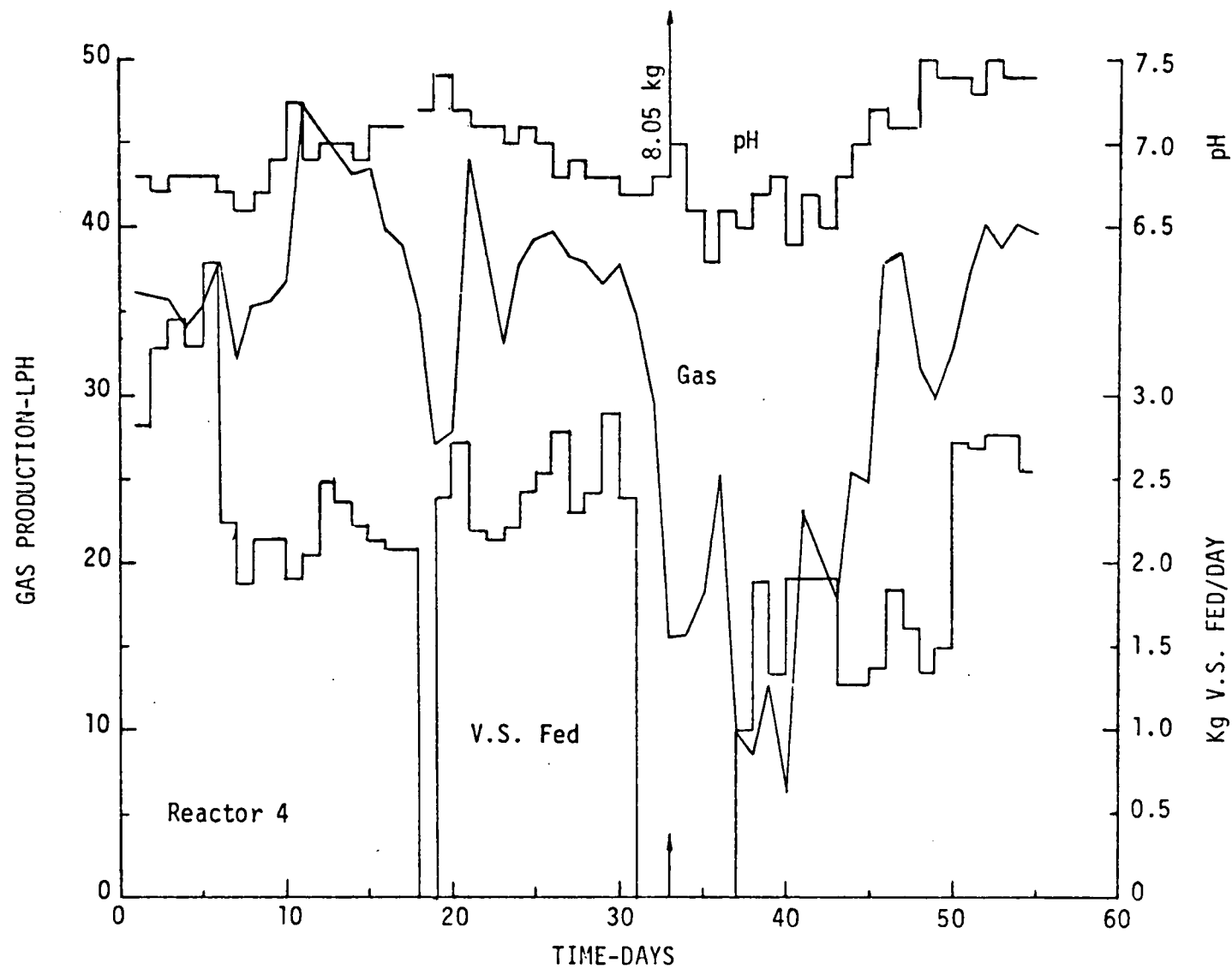


Figure 3. Reactor performance with thermochemical pretreatment.

levels while the volatile acids decreased. The gas production also increased to significant levels. An analysis for the individual short chain organic acids was undertaken on Day 38 and 45. The results are shown in Table 1. Clearly, the methanogens using acetic acid were being inhibited. Acetic and propionic acids were the primary acids found in these samples. As can be seen, the acid concentrations decreased significantly by Day 45. This supports the conclusion that a rapid recovery was occurring. However, it has not been demonstrated that total recovery has occurred since the total volatile acids did not drop below 2000 mg/l.

Table 1. Volatile acid distribution during recovery at the lower NaOH dosage

Organic Acids	Day 38 (2-13-79)			Day 45 (2-20-79)		
	Mix Tank	React. 3	React. 4	Mix Tank	React. 3	React. 4
Acetic	1530	2500	1380	1430	1370	890
Propionic	1470	1670	1520	1320	1140	730
i-Butyric	50	280	195	100	380	130
Butyric	130	660	430	240	455	280
i-Valeric	40	330	295	105	180	195
Valeric	70	270	310	55	105	80

Reactors 1 and 2 had been idle since late November 1978. Problems in starting Reactors 3 and 4 suggested that start-up problems should be resolved before activating all four reactors. By the end of December, it appeared that Reactors 3 and 4 were responding even though the volatile acids were high. Plans were made to activate Reactors 1 and 2. On January 4, 1979, both reactors were seeded with the effluent from Reactor 3. Feed consisting

of thermochemical pretreated material in which the higher NaOH dosage was used was initiated at this time. Both reactors responded poorly as shown in Figure 4 and 5. With a 15-day retention time and a loading between 2.0 and 2.5 kg of volatile solids per day, the pH in both reactors dropped substantially. Lime additions were required to keep the pH in an acceptable range. An adequate buffer was developed and the pH stabilized at a value above 6.6.

The volatile acid concentrations continued to increase. As shown in Figure 4, the pH in Reactor 1 began to decrease on Day 40 (2-15-79). The total volatile acids were approximately 3000 mg/l. Gas production declined and the system essentially failed as excessive amounts of lime were required to maintain pH. A reduction in the loading rate did not improve the operation. On day 54 (March 1, 1979) the reactor contents were diluted to 80 percent of the original level and feed pretreated at a lower NaOH dosage was initiated.

As shown by Figure 5, the response in Reactor 2 was essentially the same as Reactor 1. Failure occurred more rapid because the fermentation temperature was lowered to 50°C on Day 35 and maintained at this temperature for 10 days. This temperature reduction was undertaken to ascertain if the inhibition was temperature related. Clearly it was not as gas production and pH dropped significantly. The total volatile acids increased to more than 6000 mg/l by the time the temperature was increased again.

Individual volatile acid analysis showed that the primary acids were acetic and propionic. These data are shown in Table 2. The extreme variation of the volatile acids in the mix tank are a result of the length of time the slurry had been stored in the tank. Since this tank was not sterile, fermentative bacteria were quite active. Reactor 2 exhibited extremely high volatile acids as a result of operation at 50°C. An increase in temperature back to 60°C on Day 45 did not result in a significant improvement in the reactor performance.

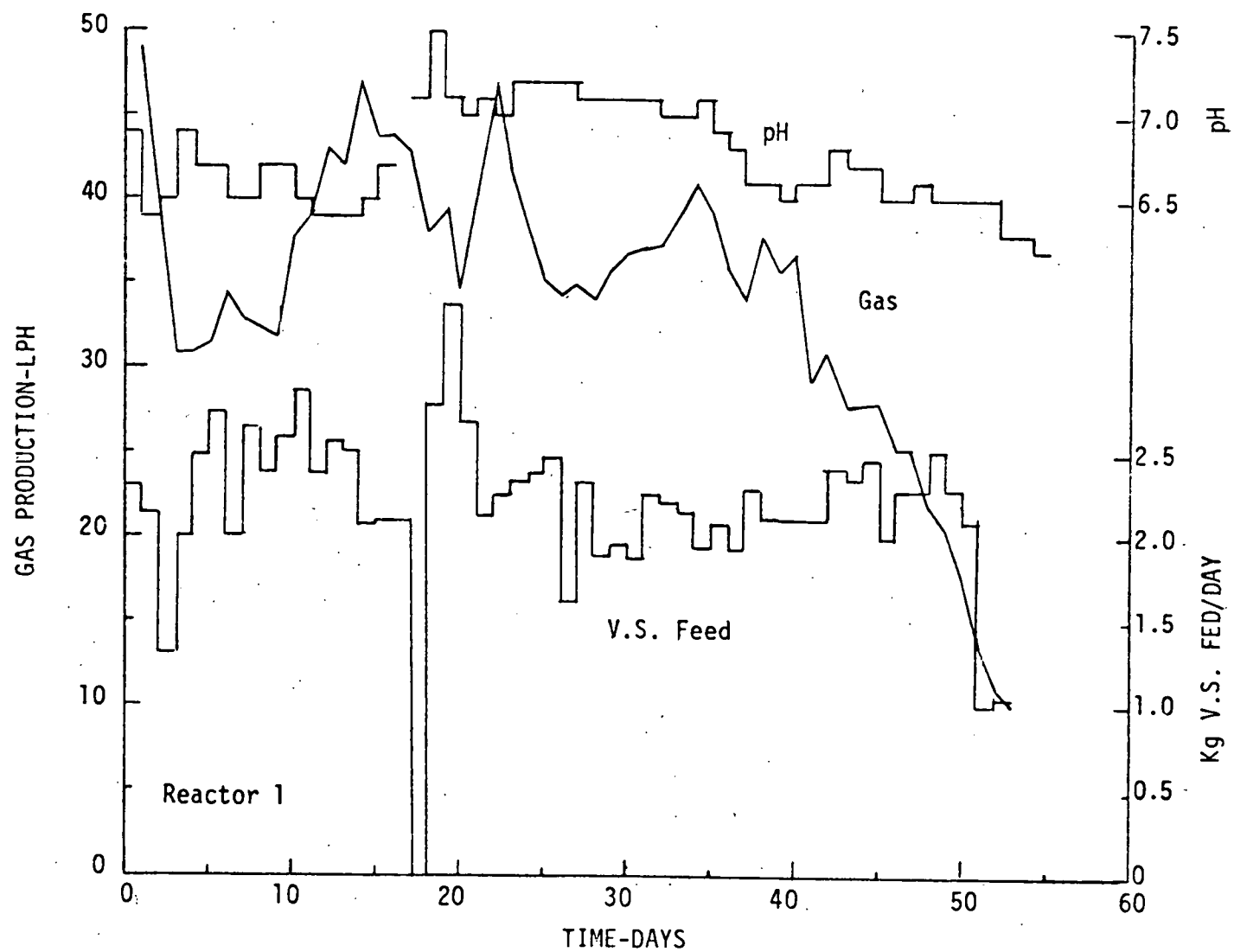


Figure 4. Reactor performance with thermochemical pretreatment.

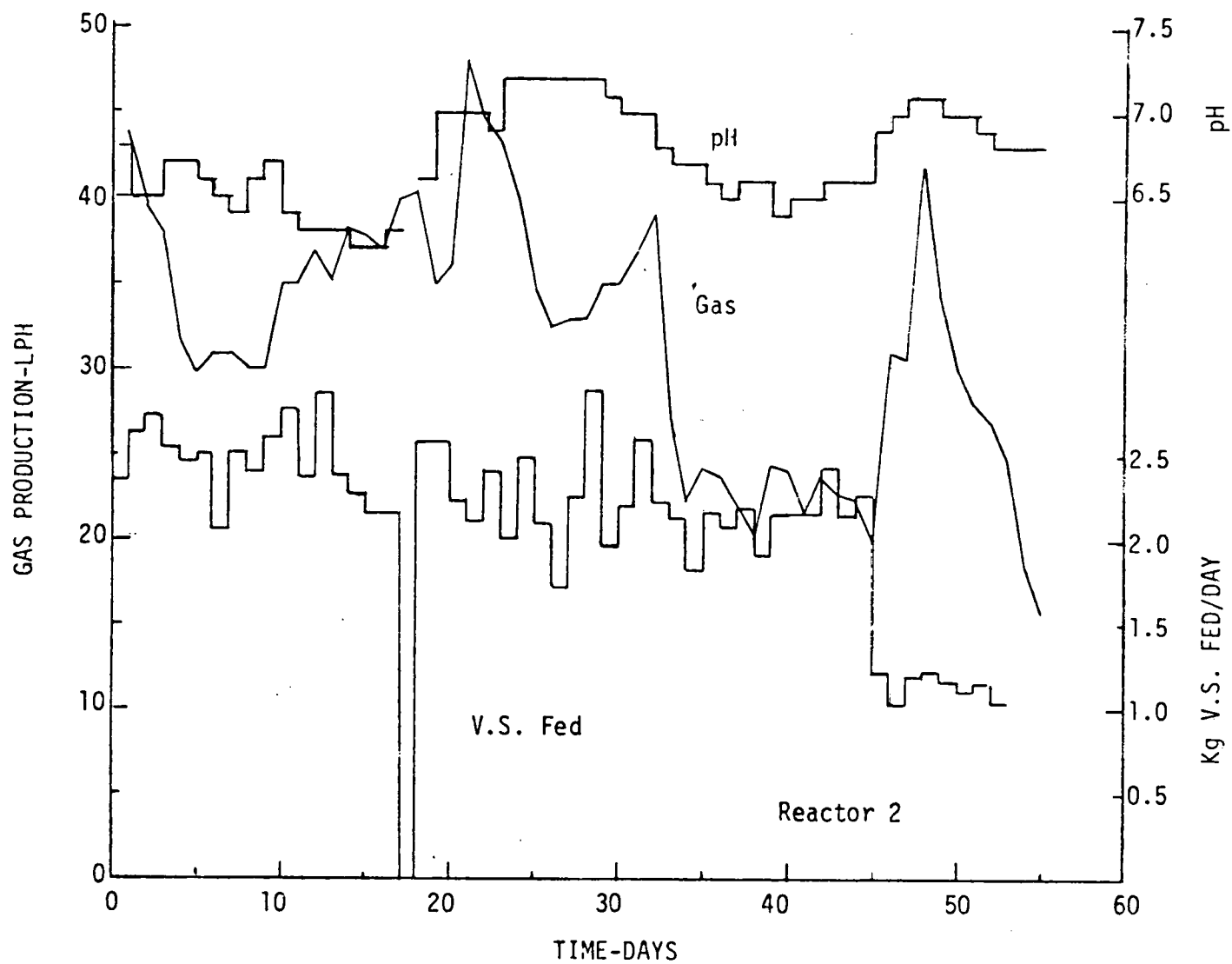


Figure 5. Reactor performance with thermochemical pretreatment.

Table 2. Volatile acids distribution during inhibition at higher NaOH dosage

Organic Acids	Day 38 (2-13-79)			Day 45 (2-20-79)			Day 51 (2-26-79)		
	Mix Tank	React. 1	React. 2	Mix Tank	React. 1	React. 2	Mix Tank	React. 1	React. 2
Acetic	360	1400	2760	1630	1910	3400	1800	1740	3960
Propionic	1070	1340	2820	2210	1500	1910	1790	2230	2230
i-Butyric	30	90	295	60	130	225	30	150	220
Butyric	100	160	330	210	405	380	70	410	530
i-Valeric	50	95	110	60	220	140	-	130	170
Valeric	30	110	120	40	260	195	-	105	40

Summary

Experience to date clearly show significant inhibition of methane production as a result of the mild thermochemical pretreatment. Extreme care must be exercised in any application of this process. Additional studies are underway in an attempt to determine an acceptable level of caustic pretreatment and required dilution to eliminate inhibitory effects.

RECOVERY AND ACCLIMATION OF METHANOGENIC BACTERIA TO TOXICANTS

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It is well known that various substances found in wastewater are toxic to the methanogenic bacteria. However, the recovery pattern after exposure to toxicants is not well documented, nor are the acclimation characteristics. The purpose of this study was to observe the recovery of methane production in an acetate enriched culture after being subjected to various concentrations of toxicants.

The toxicants investigated were:

- Chloroform
- Cyanide
- Acrolein
- Monensin
- Acrylonitrile
- Formaldehyde
- Vinyl Acetate
- Sulfide
- Ammonium
- Nickel
- Acrylic Acid

In some of the studies, the toxicants were administered as both slug and continuous doses along with nutrient salts and acetic acid substrate to anaerobic filters. The hydraulic retention time in the filters was one day. In the remainder of the studies, the toxicant was injected as a slug into a suspended, completely mixed culture of acetate enriched methanogens. The solids (and hydraulic) retention times were maintained at specified levels.

In order to observe the response of the methanogens after the toxicant was removed, slug additions were added to anaerobic filters. Concentrations were increased for each slug until the methane production was unable to recover after the toxicant was washed out of the filter. Figures 1 through 4 illustrate the filter response to representative toxicant slugs. Basically, the toxicants are shown to be bacteriostatic and not bacteriocidal. The filters demonstrated the capacity to recover from exceptionally high concentrations of toxicants.

Next, the long term acclimation of toxicants was observed by continuously adding increasing concentrations in the feed to anaerobic filters. The initial concentration of toxicant was below the unacclimated threshold level. Figures 5 through 11 show the filter response to increasing levels of various toxicants. With acclimation, production was maintained at normal rates even through the concentration of toxicant was in excess of 10 to 50 times the concentration which showed toxicity to unacclimated systems.

The complete mix nature of suspended growth methanogenic systems causes the washout rate of slug additions of toxicants to be quite prolonged when compared to the 1 day hydraulic retention time plug flow anaerobic filters. Various concentrations of toxicants were added as slugs in suspended cultures operated over a range of solids (and hydraulic) retention

times. Figures 12 to 17 show the prolonged response of the suspended, complete mix cultures. Gas production would cease for prolonged periods and then rather suddenly return to normal. The resumption of gas production in some cases was so rapid that it could not be attributed to synthesis of new cells. It had to be related to an acclimation phenomena.

In summary, it has been shown that the hydraulic flow characteristics of methanogenic bacterial treatment systems play a key role in determining their response to toxicants. Likewise, with proper acclimation, stable methane production can be maintained in the presence of unusually high concentrations of toxicants. There is a demonstrated need for ample biological safety factors to maintain process stability in the presence of intermittent or continuous doses of toxicants.

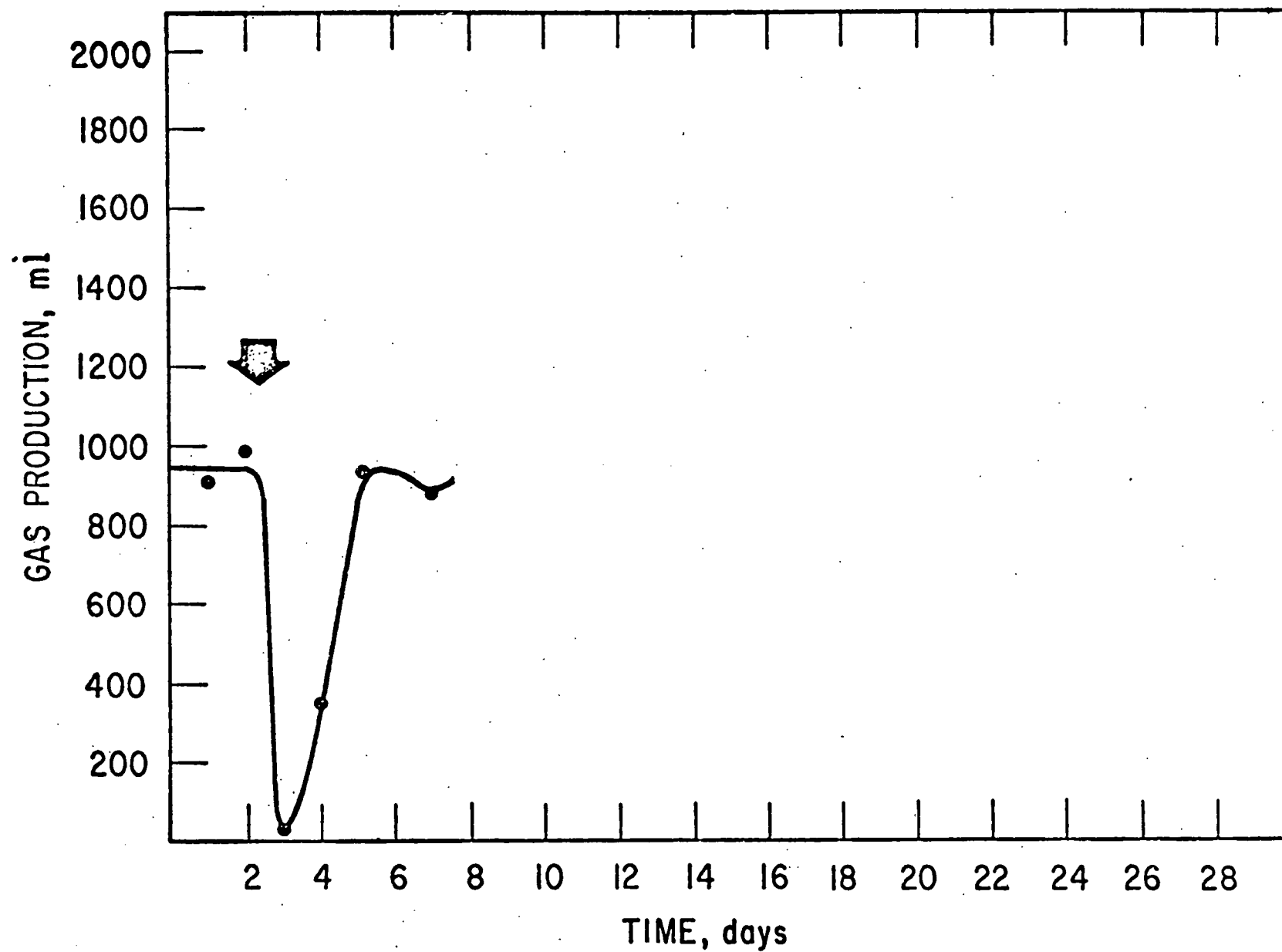


Figure 1 750mg/l KCN - 500ml - 1 hr

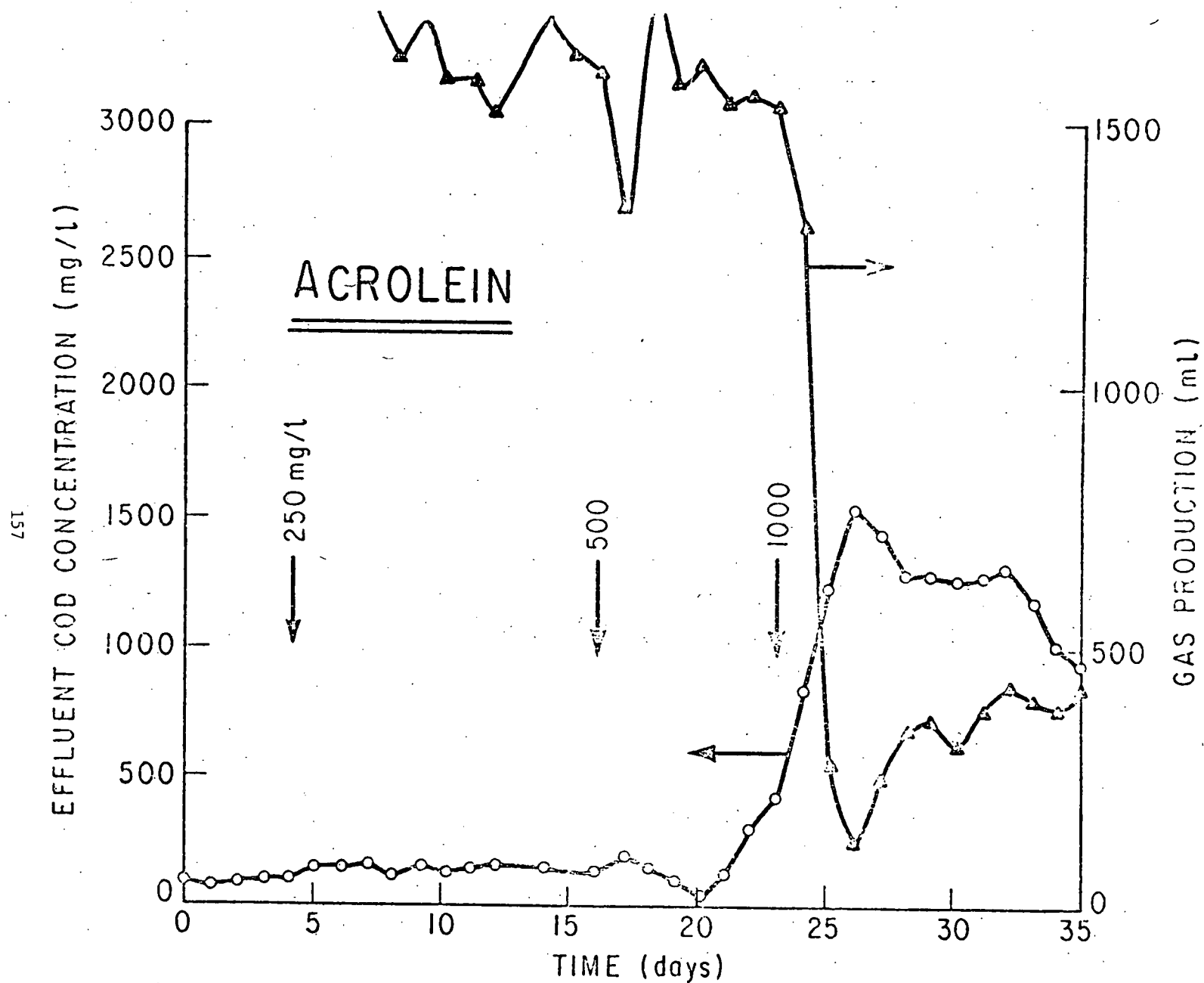


FIG. 2 RESPONSE OF ANAEROBIC FILTER TO TOXICANT

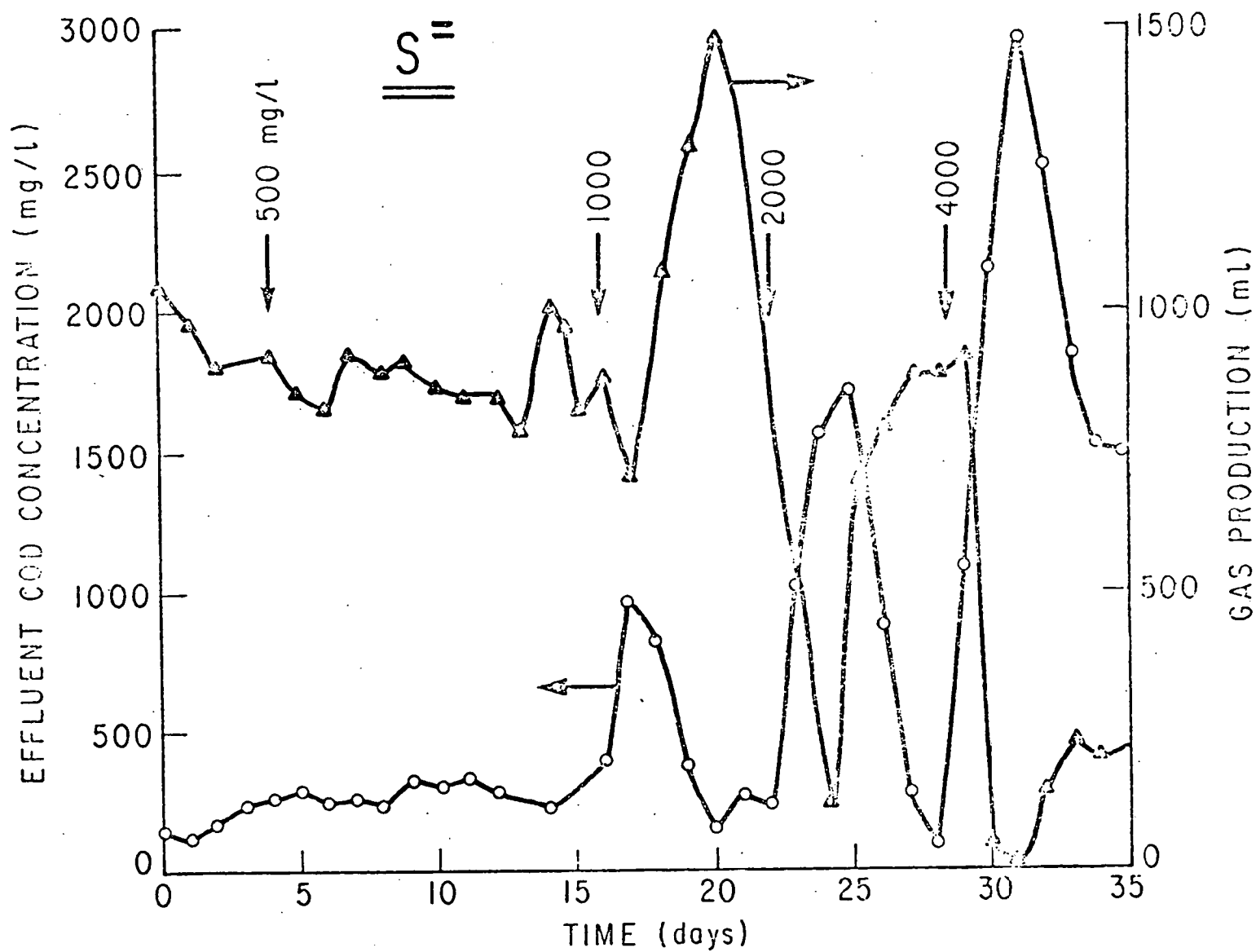


FIG. 3 RESPONSE OF ANAEROBIC FILTER TO TOXICANT

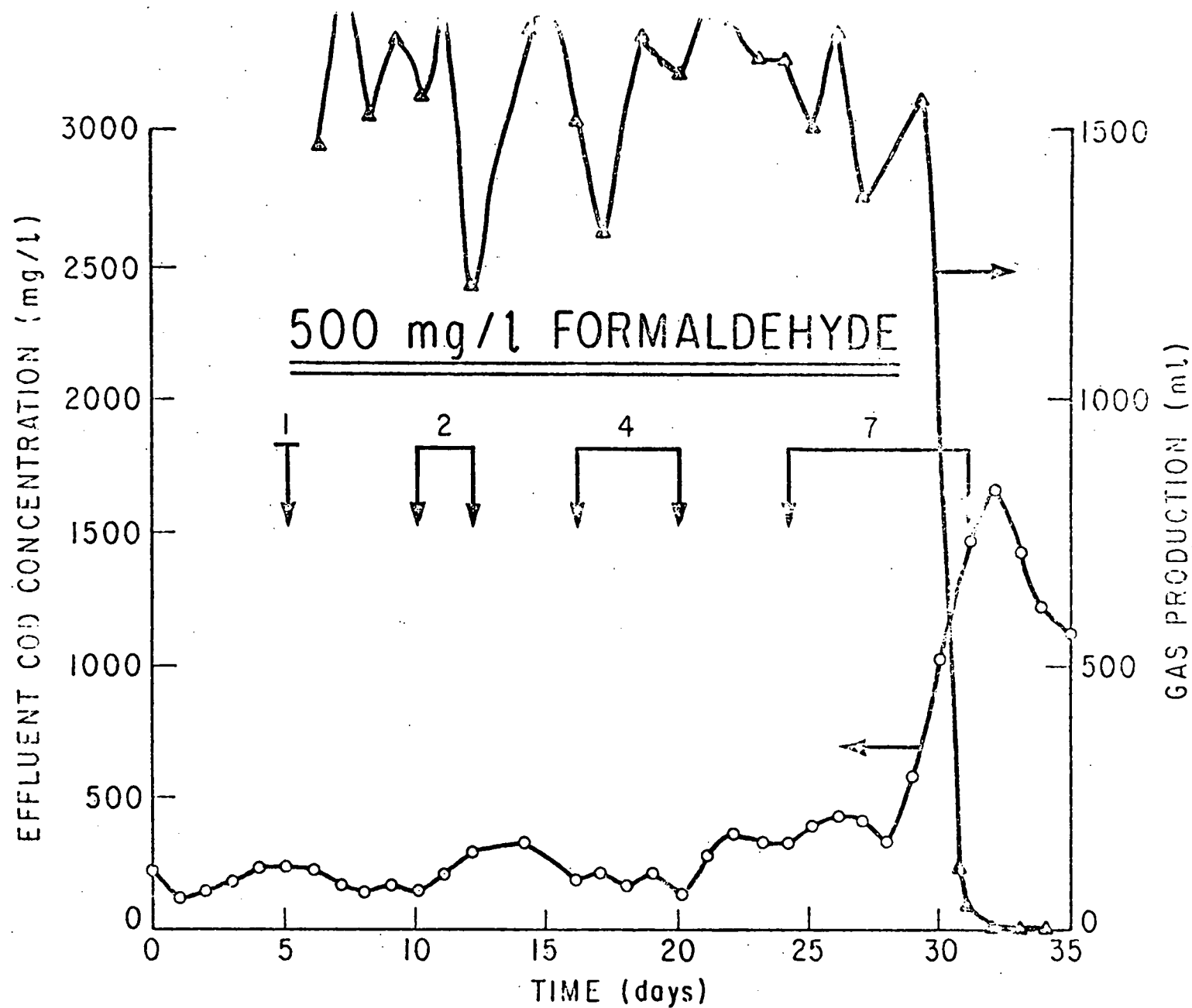


FIG. 4 RESPONSE OF ANAEROBIC FILTER TO TOXICANT

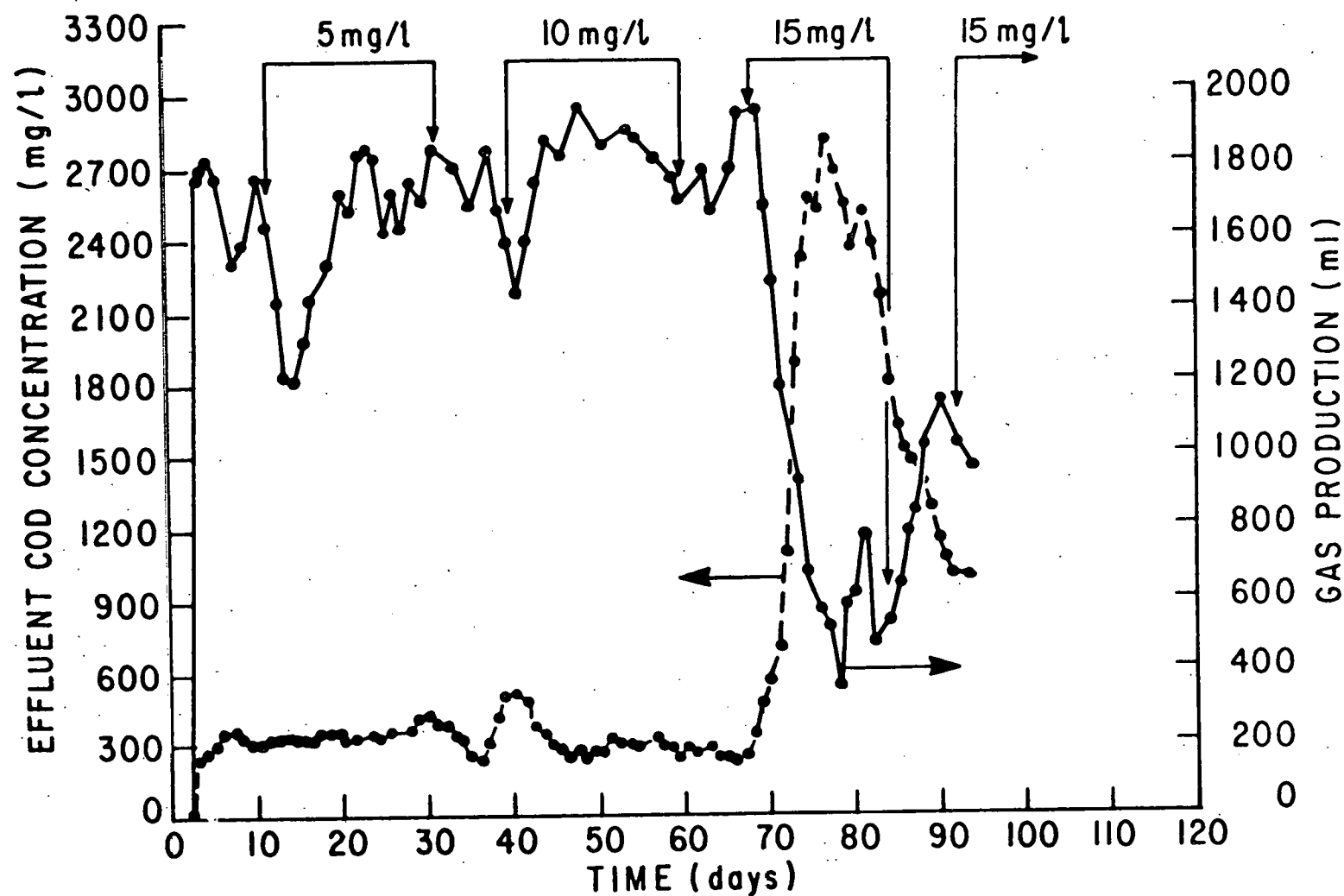


Fig. 5 Response of Anaerobic Filter to Toxicant KCN (asCN^-)

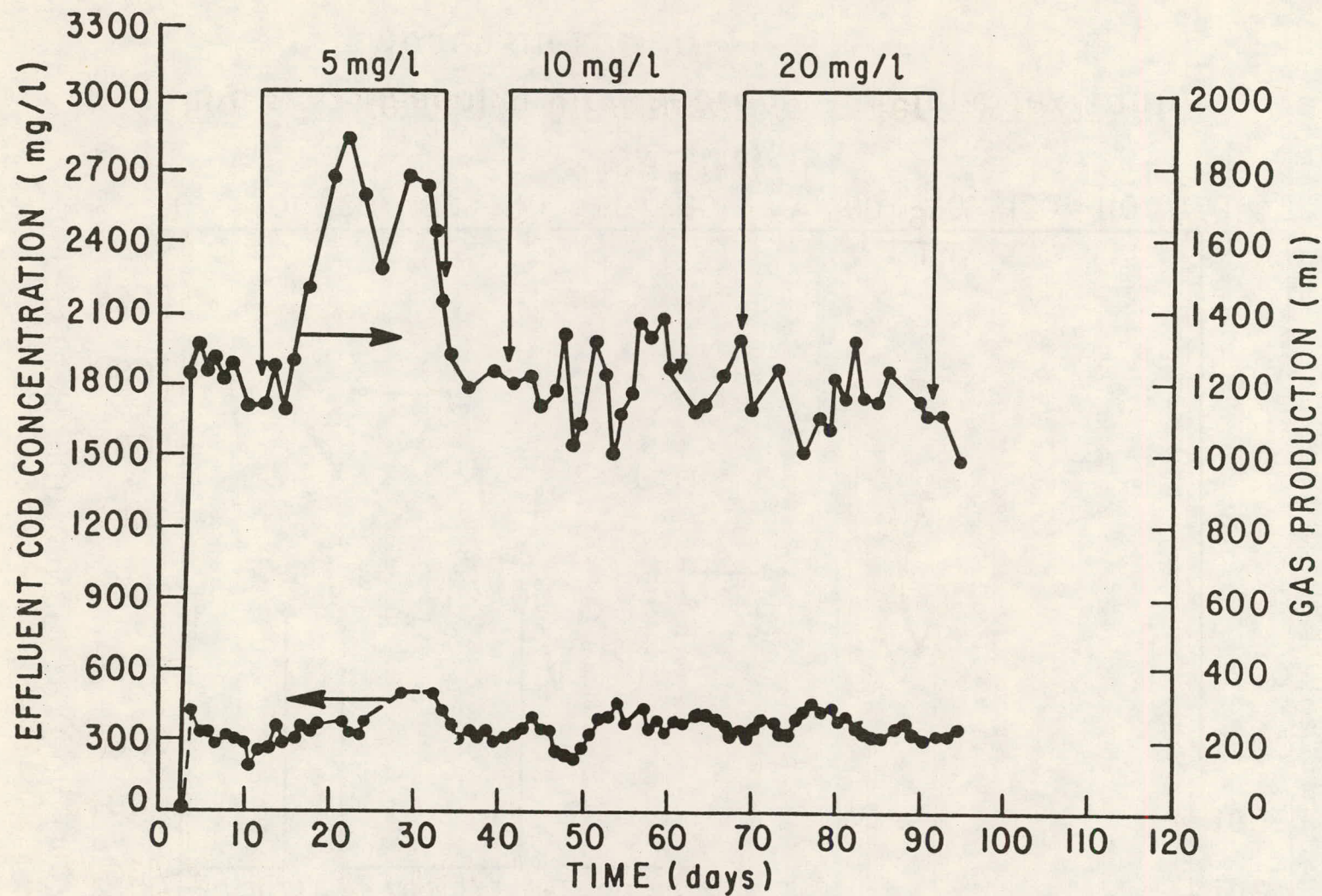


Fig. 6 Response of Anaerobic Filter to Toxicant Chloroform

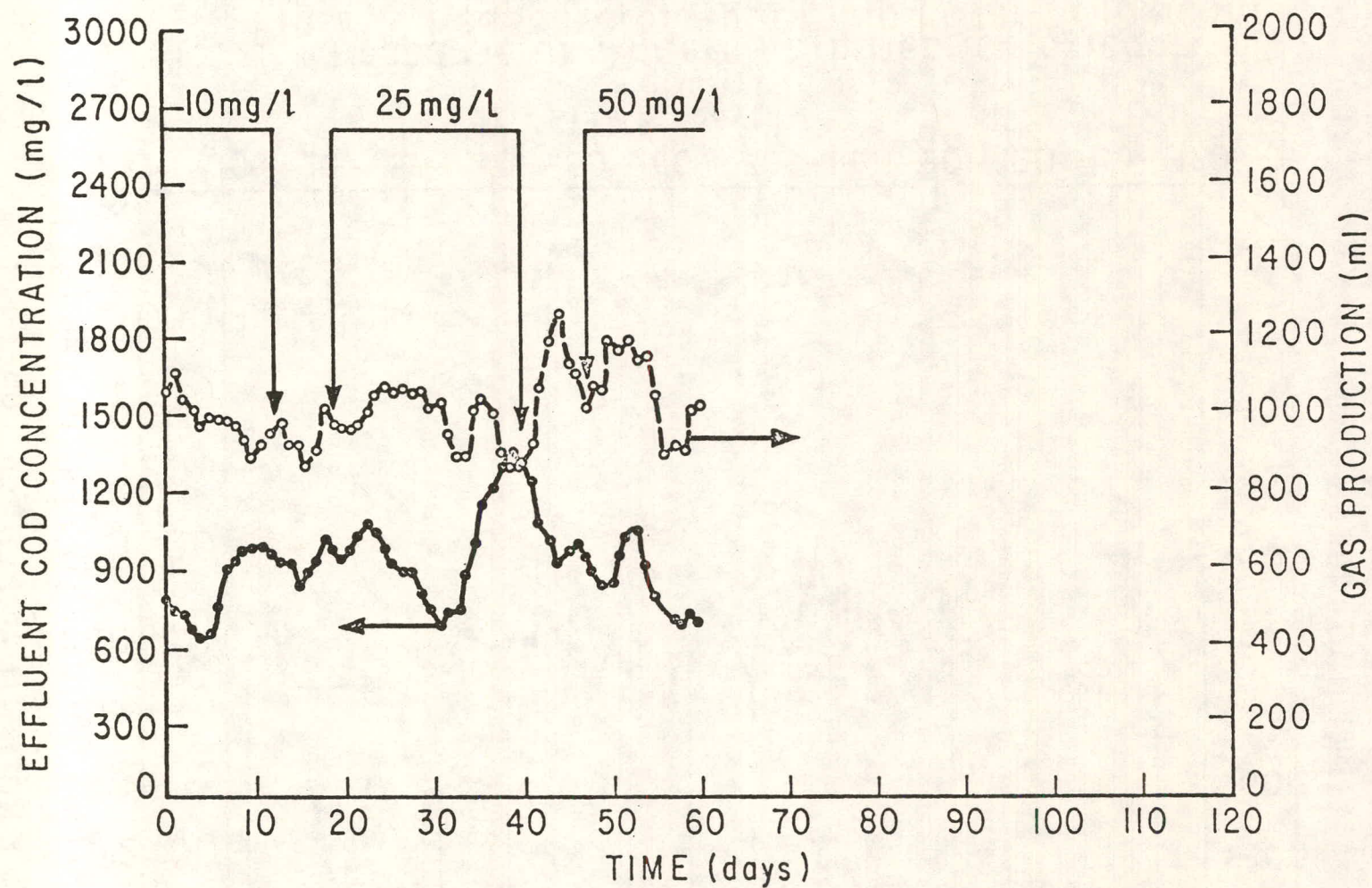


Fig. 7 Response of Anaerobic Filter to Toxicant - Monensin

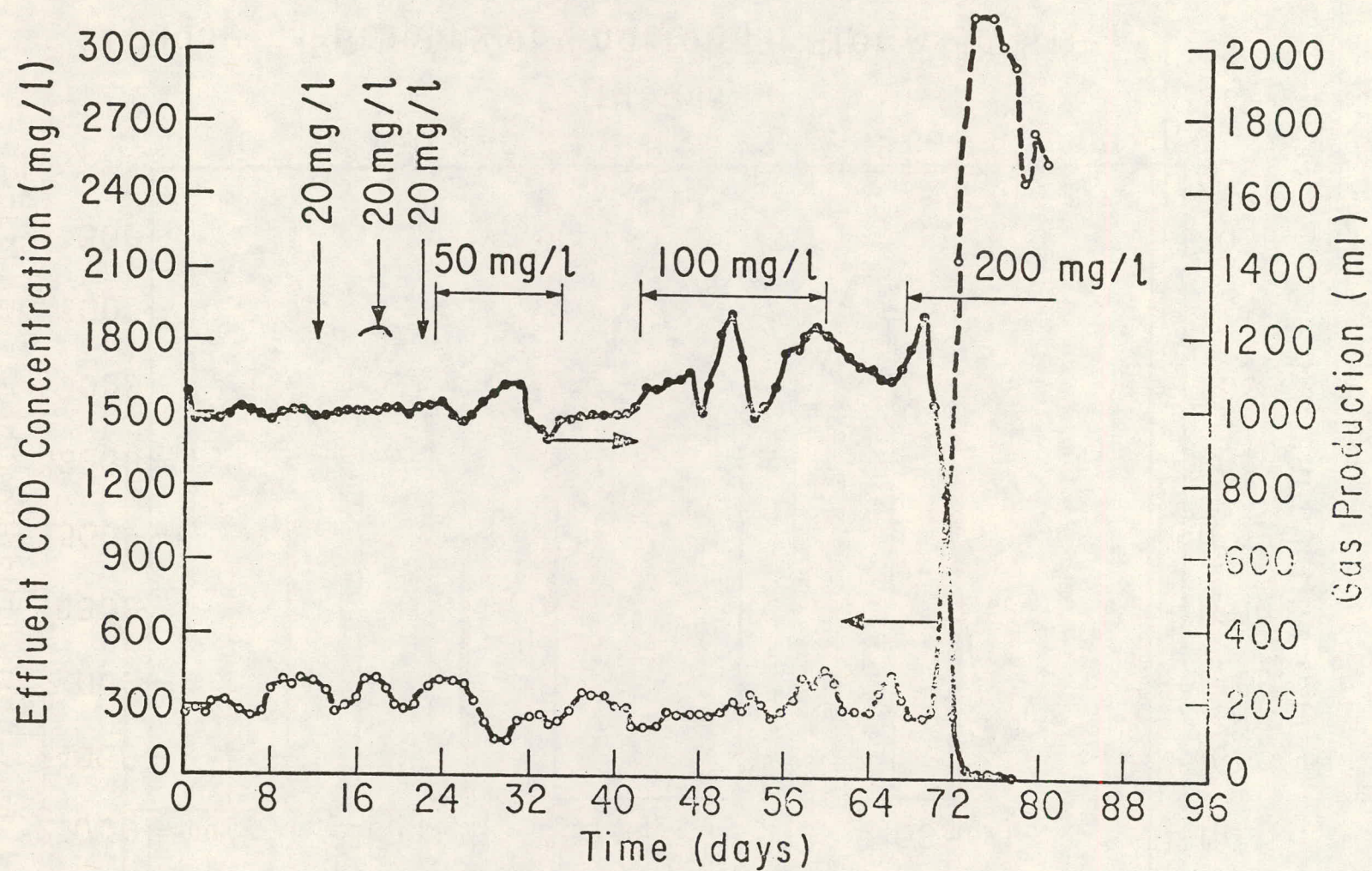


Fig. 8 Response of Anaerobic Filter to Toxicant-Acrolein

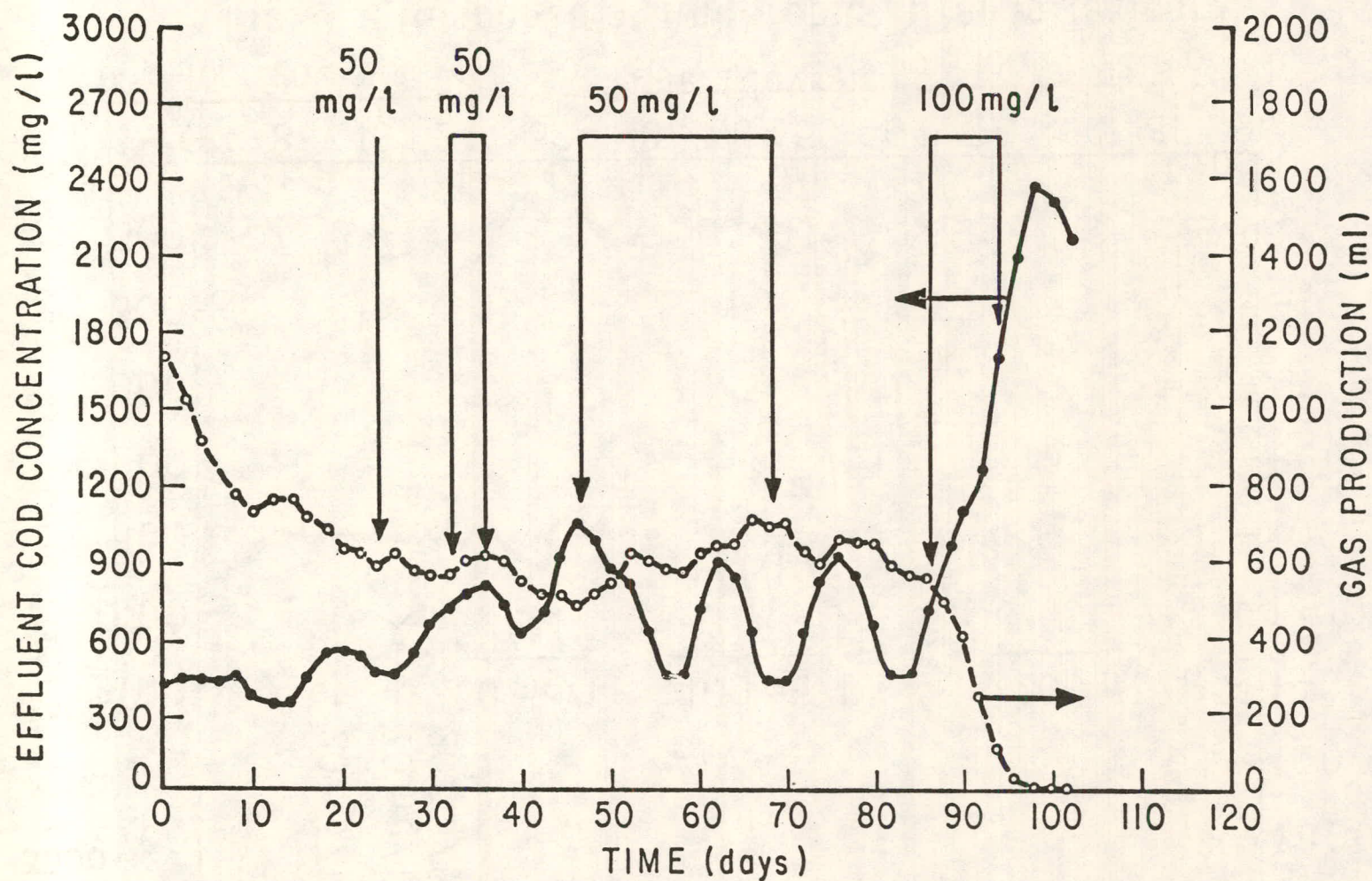


Fig. 9 Response of Anaerobic Filter to Toxicant - Acrylonitrile

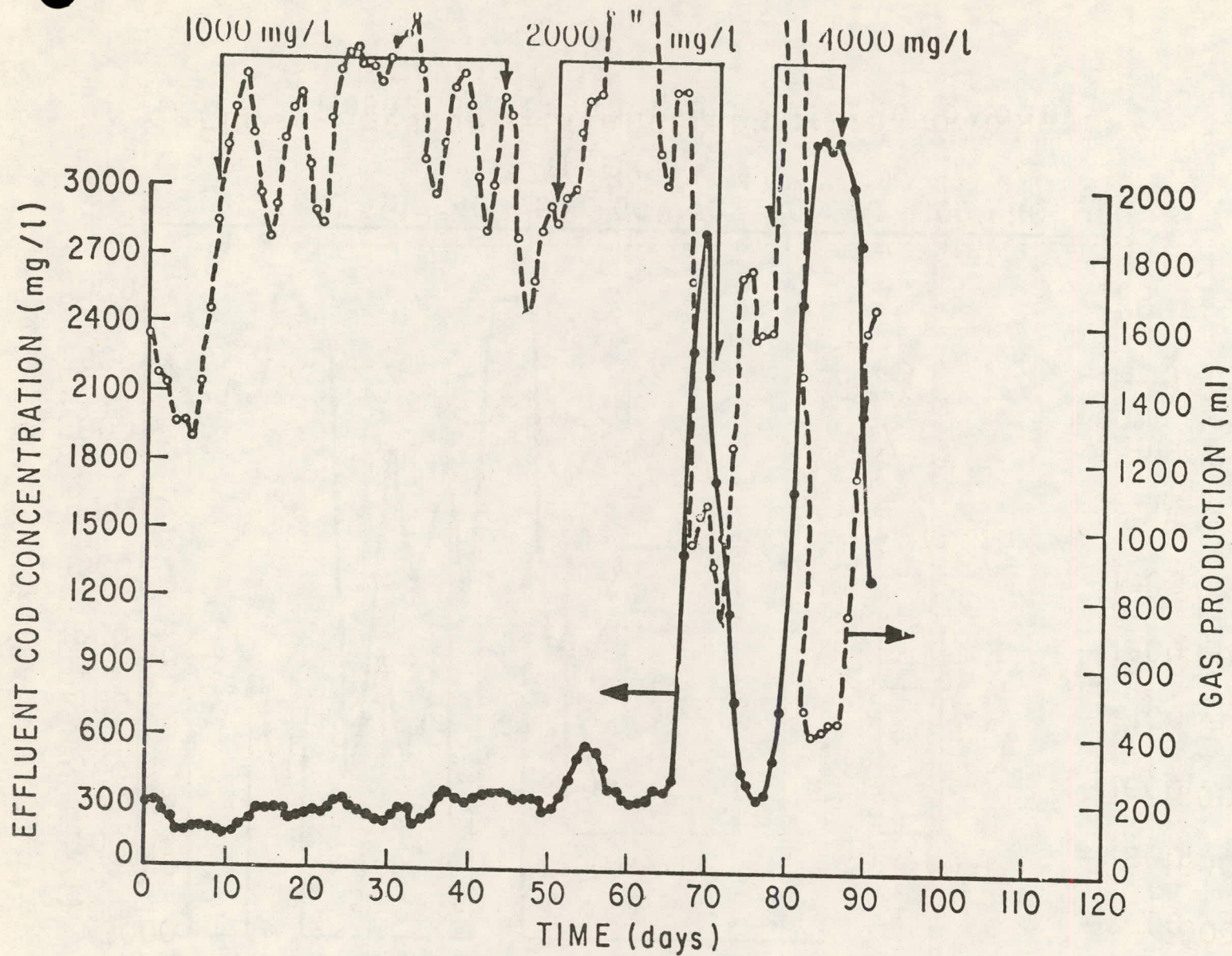


Fig. 10 Response of Anaerobic Filter to Toxicant-Vinyl Acetate

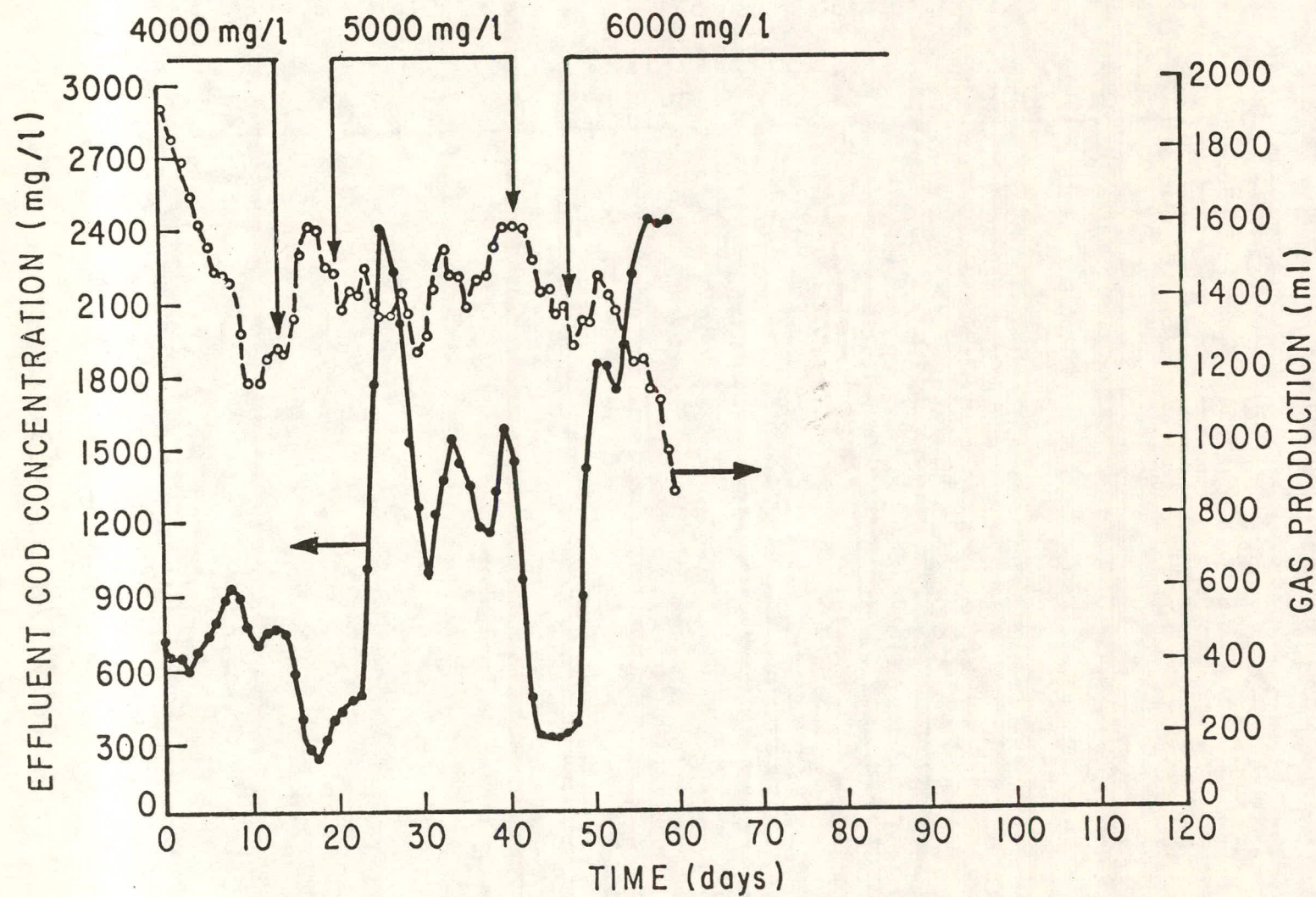


Fig. 11 Response of Anaerobic Filter to Toxicant-
 NH_4^+

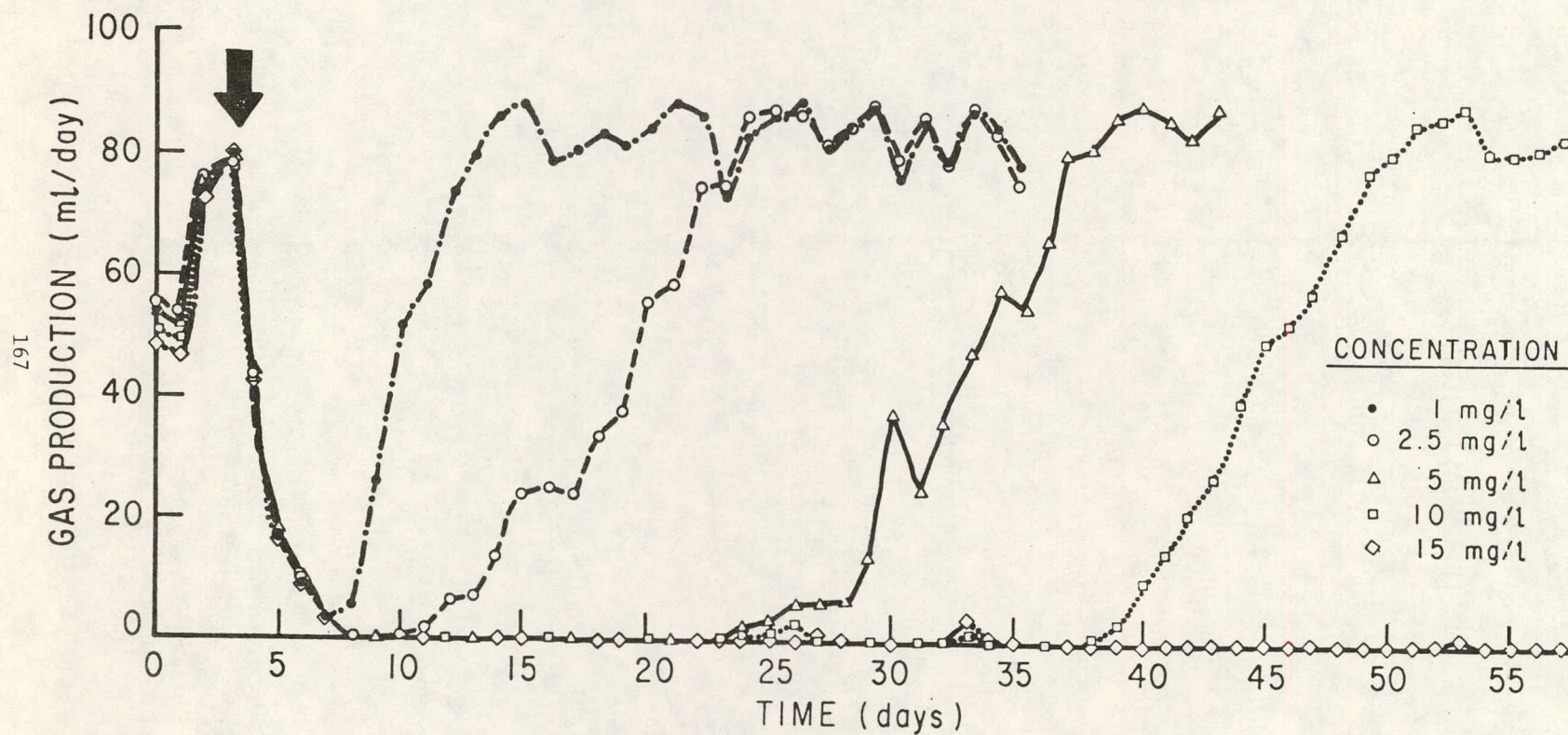


Fig.12 S.R.T. Response to Toxicant - Cyanide
50 days S.R.T., 35°C

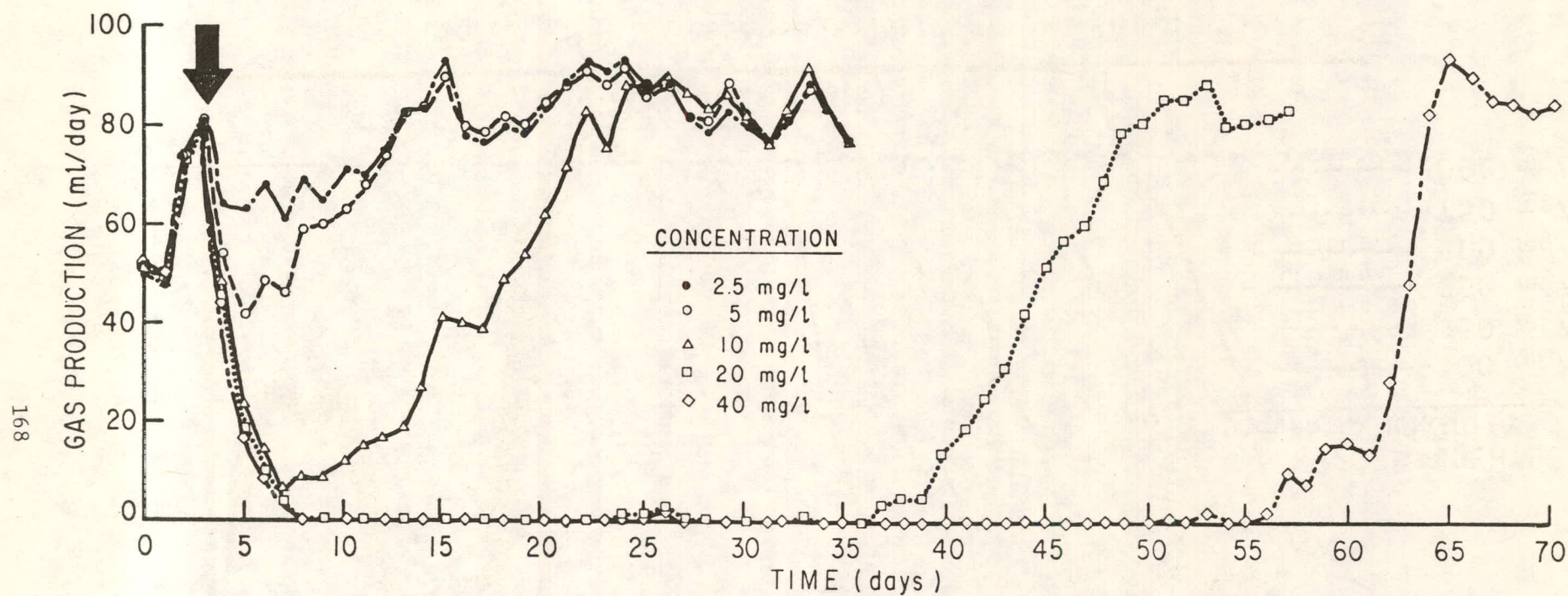


Fig. 13 S.R.T. Response to Toxicant – Chloroform
50 days S.R.T., 35°C

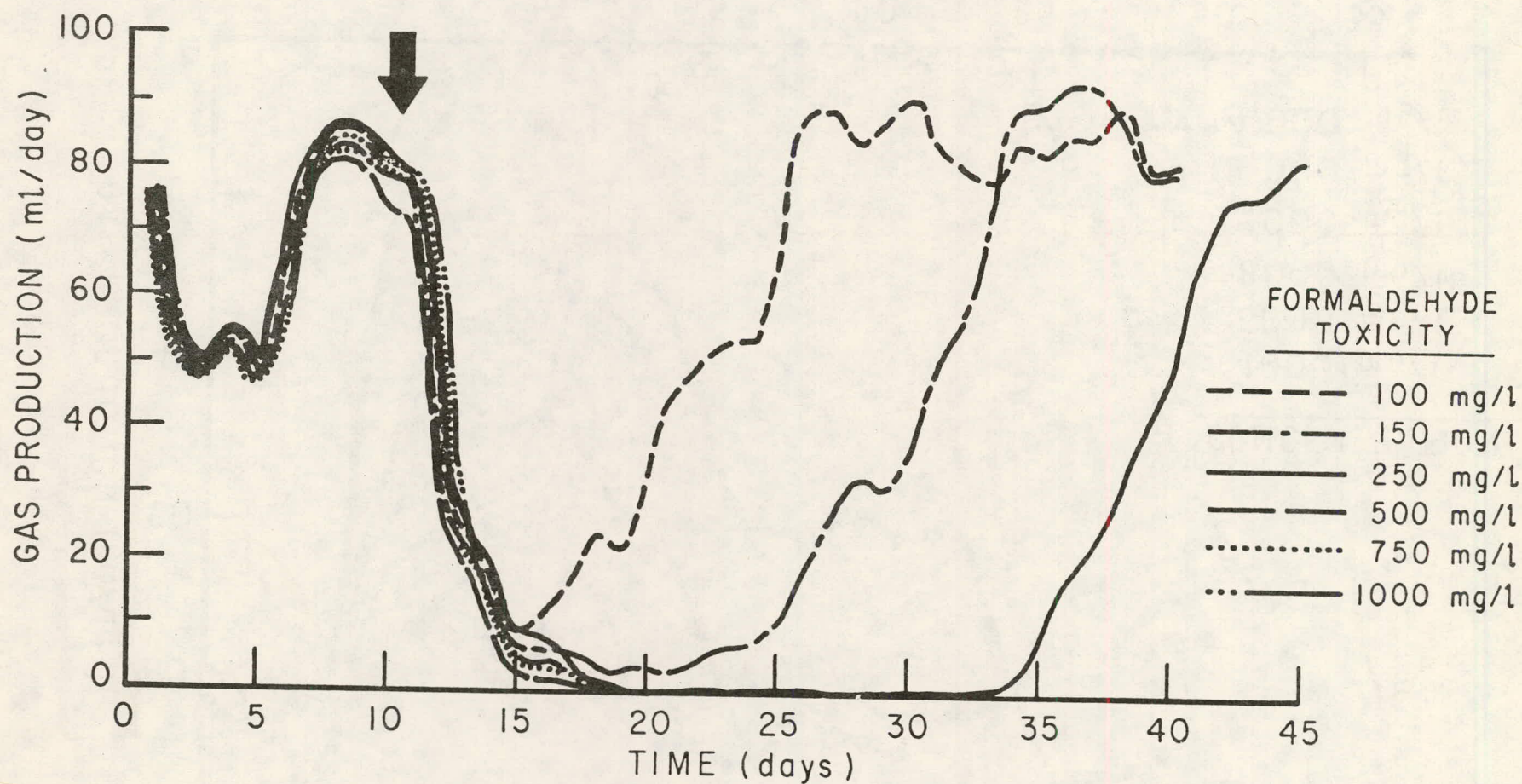


Fig. 14 S.R.T. Response to Toxicant — Formaldehyde
50 days S.R.T., 35°C

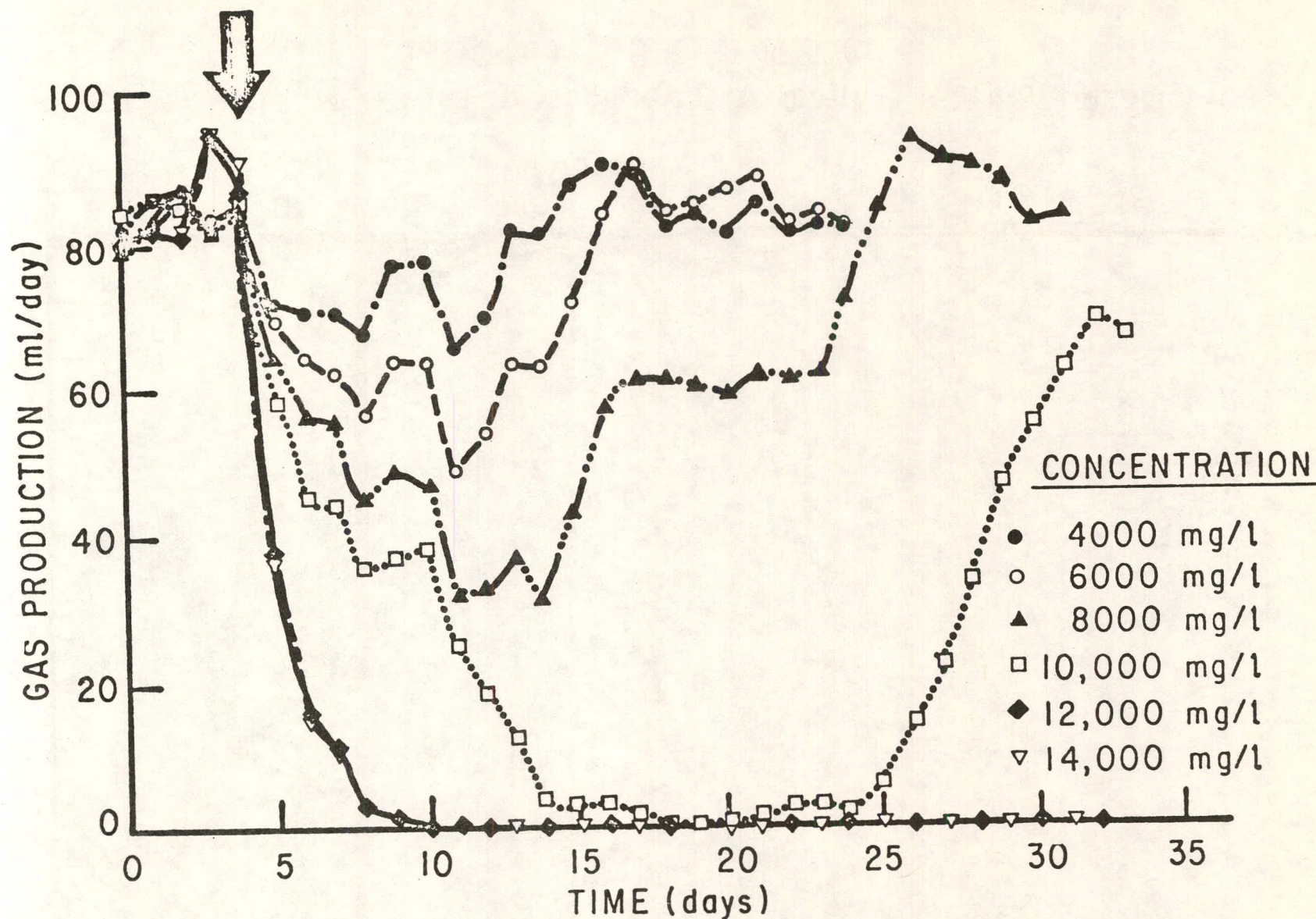


Fig. 15 S.R.T. Response to Toxicant - NH_4^+
50 days S.R.T., 35°C

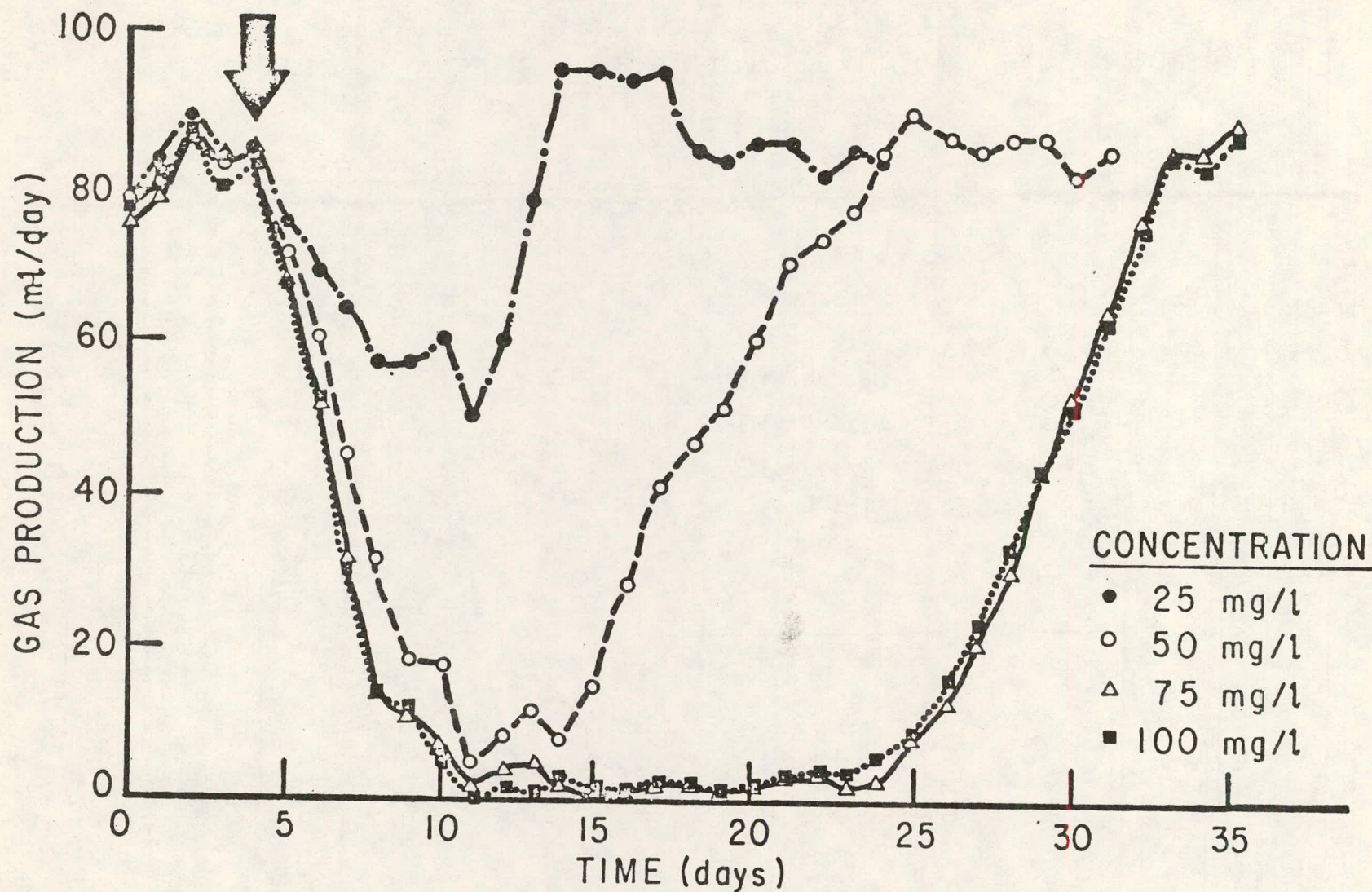


Fig. 16 S.R.T. Response to Toxicant - Acrylic Acid
50 days S.R.T., 35°C

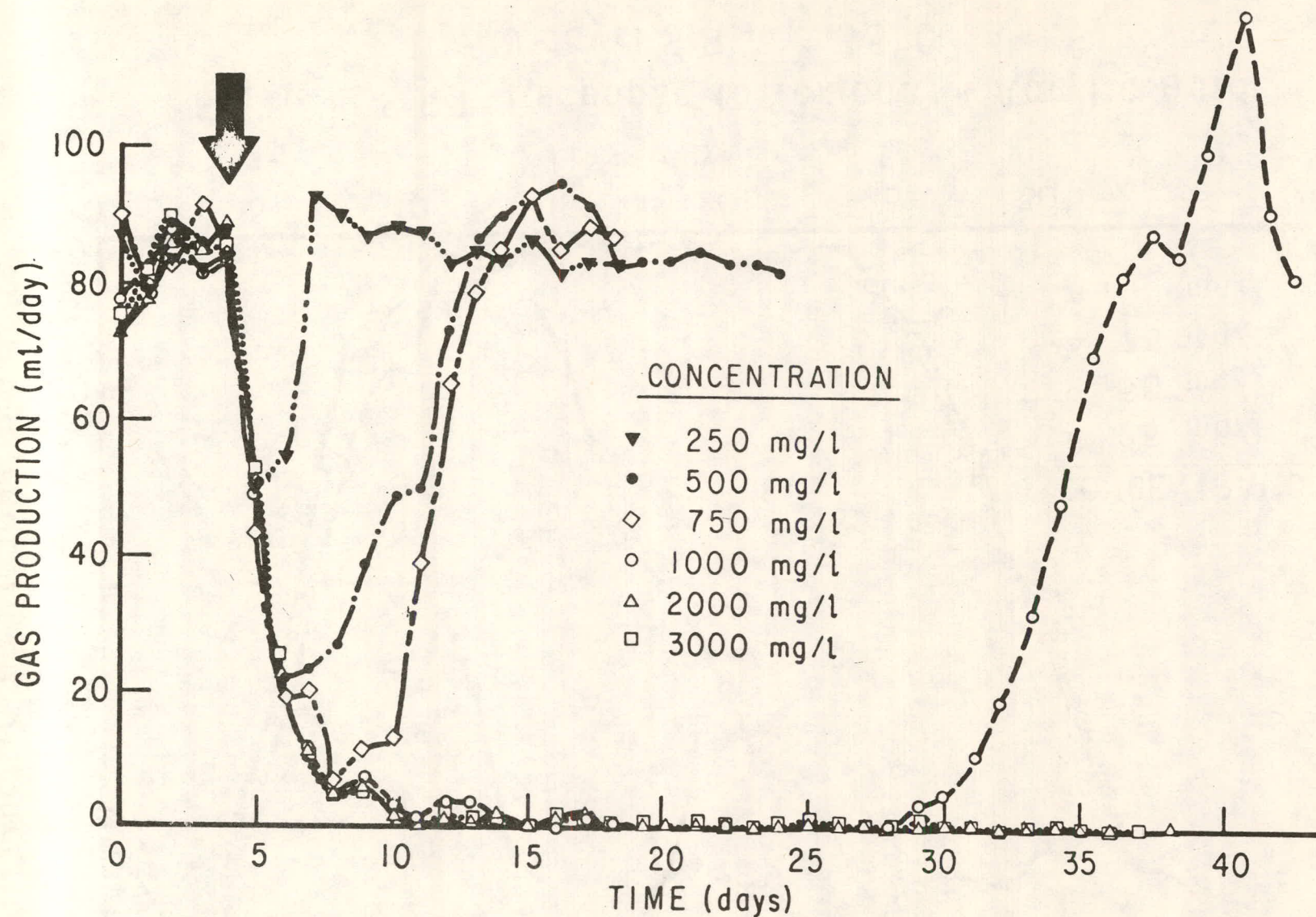


Fig. 17 S.R.T. Response to Toxicant - Vinyl Acetate
50 days S.R.T., 35°C