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Fuel Gas Production from Animal and Agricultural Residues and Biomass

13th Quarterly Progress Report

D.E. Jantzen
Biomass Program Office

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Operated for the
U.S. Department of Energy
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FUEL GAS PRODUCTION FROM ANIMAL AND AGRICULTURAL RESIDUES AND BIOMASS

13TH QUARTERLY PROGRESS REPORT

D. E. JANTZEN
BIOMASS PROGRAM OFFICE

JANUARY 1980

PREPARED UNDER TASK NO. 3335.04

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FOREWORD

The thirteenth quarterly coordination meeting of the methane production group of the Biomass Energy Systems Branch, U.S. Department of Energy was scheduled to be held in Urbana, Illinois, October 18-19, 1979. Due to unforeseen circumstances, the meeting was cancelled. The progress reports which the contractors would have presented are included herein.

Dan Jantzen
Biomass Program Office
Solar Energy Research Institute

TABLE OF CONTENTS

LIST OF ATTENDEES
ANAEROBIC DIGESTION CONTRACTORS COORDINATION MEETING

URBANA, ILLINOIS
OCTOBER 18 - 19, 1979

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Cornell University 202 Riley - Robb Hall Ithaca, N. Y. 14853	William J. Jewell	(607) 256-4533
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ANAEROBIC FERMENTATION OF LIVESTOCK AND CROP RESIDUES

QUARTERLY PROGRESS REPORT
JULY TO SEPTEMBER, 1979

A. G. HASHIMOTO
Y. R. CHEN

ROMAN L. HRUSKA U.S. MEAT ANIMAL RESEARCH CENTER
AGRICULTURAL RESEARCH
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PREPARED FOR

U.S. DEPARTMENT OF ENERGY
DIVISION OF SOLAR TECHNOLOGY
BIOMASS ENERGY SYSTEMS BRANCH
INTERAGENCY AGREEMENT DE-AI01-79ET20638

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 during the reporting period.

PILOT-SCALE FERMENTOR

During the reporting period, the pilot-scale fermentor has been operating at 45°C and 50°C to confirm, on a pilot-scale, our laboratory results. Table 1 summarizes the operating parameters of the fermentor at 45°C and 9 days retention time, and at 55°C and 6 days retention time. The results show that between 50 and 56 percent of the volatile solids is reduced and that the other parameters closely follow the results presented previously for the pilot-scale fermentor operating at 55°C.

The methane production rates and yields are significantly lower than that predicted from our laboratory-scale fermentors, and from our kinetic model (Chen, Varel, Hashimoto, 1979). These low rates and yields prompted up to initiate an intensive leak search of the gas-handling system. This search revealed a small leak around the packed bearing of the propeller shaft and a significant leak through the secondary, gas-relief valve.

Table 2 compares the experimental methane production rate and the rate calculated using our kinetic model. The ratio of the experimental to the calculated value is also shown in Table 2. Runs 1, 2, and 3 show that the actual methane production rate was between 0.64 to 0.76 of the rate predicted by our kinetic model. Table 2 also shows the experimental yield for runs 1, 2 and 3 divided by a yield of 0.52 L CH_4/g VS utilized. The value of 0.52 L CH_4/g VS utilized is the average yield of all previous steady-state data from the methane fermentor. The ratio of methane production rates and methane yields are very close for each run indicating that we were not measuring all of the methane produced and that the kinetic model is a good predictor of methane production rate.

Run 4 shows preliminary data from the pilot-scale fermentor after all of the gas leaks were stopped. The ratio of experimental to calculated methane production rates show very good correlation and confirms our initial suspicion that the low methane production was due to leaks.

FUTURE ACTIVITIES

The pilot-scale fermentor will be operated at 50°C and at increasing influent concentration for the next few months. After the first of January, the pilot plant will be shut down and modified to accomodate manure and crop residue mixtures as substrate.

REFERENCE

1. Chen, Y. R., V. H. Varel and A. G. Hashimoto. 1979. Effects of temperature on methane fermentation kinetics. Presented at the Symposium on Biotechnology In Energy Production and Conservation. Gatlinburg, Tennessee. October 3-5, 1979.

TABLE 1. SUMMARY OF STEADY-STATE OPERATING PARAMETERS FOR THE PILOT-SCALE FERMENTOR[a]

	Temperature/Retention Time		
Parameter	45°C/9d	50°C/6d	50°C/6d
Total Solids			
Inf., g/L	74.8±9.4	70.1±3.9	85.1±11.2
Eff., g/L	38.5±6.8	39.5±0.5	42.3±5.9
Change, %	-48.5	-43.7	-50.3
Volatile Solids			
Inf., g/L	65.3±9.4	61.5±3.6	77.1±10.2
Eff., g/L	30.0±0.6	30.8±0.5	33.8±0.5
Change, %	-54.1	-49.9	-56.2
Fixed Solids			
Inf., g/L	9.5	8.6	8.0
Eff., g/L	8.5	8.7	8.5
Change, %	-10.5	+1.0	+6.2
COD			
Inf., g/L	72.4±4.8	73.9±3.3	76.5±10.4
Eff., g/L	42.7±2.7	42.8±1.6	43.6±5.7
Change, %	-41.0	-42.1	-43.0
Total Nitrogen			
Inf., g/L	2.68±0.10	2.81±0.16	—
Eff., g/L	2.80±0.06	2.98±0.10	—
Change, %	+4.5	+6.0	—
Ammonia-N			
Inf., g/L	0.58±0.04	0.62±0.05	0.72±0.06
Eff., g/L	1.21±0.02	1.33±0.03	1.37±0.01
Volatile Acids			
Inf., g/L	6.44±0.51	6.60±0.62	8.06±0.39
Eff., g/L	1.47±0.09	0.87±0.05	1.17±0.13
Alkalinity			
Inf., g/L	2.88±0.56	2.88±0.35	3.98±1.42
Eff., g/L	6.93±0.09	7.34±0.15	7.53±0.20
pH			
Inf.	4.88±0.28	4.71±0.11	4.81±0.35
Eff.	7.61±0.04	7.76±0.07	7.78±0.10
Methane, %	52.7±3.7	58.1±1.3	53.9±1.4
Methane Production			
L/L·day	1.43	2.01	2.14
L/g VS added	0.20	0.20	0.17
L/g VS utilized	0.36	0.39	0.30
L/g COD utilized	0.43	0.39	0.39

[a] Data presented as mean ± standard deviation, steady-state assumed after four retention times.

TABLE 2. COMPARISON OF EXPERIMENTAL AND PREDICTED METHANE PRODUCTION RATES AND YIELDS

Run	T °C	Θ d	S_o g VS/L	γ_V exp	γ_V[a] calc	$\frac{\gamma_V(\mathrm{exp})}{\gamma_V(\mathrm{calc})}$	$\frac{\text{Yield (exp)}}{0.52\ \text{L}\ CH_4/\text{g VS utilized}}$
1	45	9	65.3	1.43	2.02	0.71	0.69
2	50	6	61.5	2.01	2.66	0.76	0.75
3	50	6	77.1	2.14	3.33	0.64	0.58
4[b]	50	6	98.8	4.22	4.28	0.99	——

[a] $\gamma_V = (B_o S_o/\Theta)(1 - K/(\mu_m\Theta - 1 + K))$, $\mu_m = 0.46\ d^{-1}$ @ 45°C and $0.55\ d^{-1}$ @ 55°C, $K = 0.8$, $B_o = 0.35$ L CH_4/g VS added.

[b] Nonsteady-state data. Data collected after all gas leaks stopped.

HAMILTON STANDARD Division of UNITED TECHNOLOGIES™

FUEL GAS FROM AN
ENVIRONMENTAL FEEDLOT

CONTRACT NO. EG-77-C-01-4015

PROGRESS FROM MAY 1 TO SEPTEMBER 30, 1979

PREPARED FOR THE
QUARTERLY COORDINATION MEETING

OCTOBER 18-19, 1979

Summary

Since May, successful fermentations were established at both 122°F and 131°F. Due to lower than anticipated manure quantities, a result of low feedlot cattle population, the contents of the two fermentors were blended together in one tank which is presently operating at 131°F. It is evident from the data that an adaptation time of a minimum of 30 days is necessary before the onset of significant fermentation. Specific methane production of more than 3.5 cubic feet per pound of volatile solids loaded has been attained. The present limitation to increased gas production and the restart of the second fermentor is the lack of cattle in the feedlot. This situation is expected to improve slowly over the next several months.

Background

The facility was first placed in operation in February, 1979. The only fermentor operated at that time was fermentor #1. Due to equipment problems, temperature stability was poor. In addition, control of pH was not as good as desired. Proper fermentation was never established and, although temperature and pH stability were thought to contribute, investigation of the problem pointed to the presence of Rumensin in the residue as the major cause. Experiments performed by Dr. Perry McCarty indicated that Rumensin was highly inhibitory. Experiments by Dr. Richard Speece also showed this but also indicated that adaptation was possible. The following is a description of subsequent system operation starting in May. Data covering the operation is displayed in figures 1 through 9.

Fermentor Performance - #2 Fermentor

Fermentor #2 was loaded on 5/5/79 to attempt a new start-up at 122°F. Volatile solids concentration in the tank started out at 2.05%. It was thought that a more careful control of temperature and chemistry, along with sufficient time to allow for adaptation to Rumensin, would result in a successful start-up. It was also decided that the only chemical control which would be exercised would be one of pH control. This was accomplished by repeated additions of lime and sodium bicarbonate during the first few days of operation. A total of 3,400 lb sodium bicarbonate and 2,550 lb lime were added to the tank. One exception was made to restricting chemical control to pH modification. On May 29, 50 ppm iron were added in the form of $FeCl_3$ as it was suspected that the fermentor was iron deficient. On June 9, a positive indication of gas production was seen on the flare gas meter. The exact value of gas production is not known because the gas meter is not accurate below 1,500 CFH. The start of gas production was followed by a sharp drop in TVA from about 5,000 mg/l to about 1,500 mg/l. Daily loading of the fermentor was initiated on June 12. This brought the TVA back up into the 2,000 range followed by a general decline to nearly 1,000 mg/l over a period of a month. The pH reacted predictably to the changes in TVA resulting in a pH of about 7.4 by the middle of July. The lowest pH reached prior to this was 6.46 which was measured on May 7.

From 7/11/79 to 7/21/79 gas flow measurements were taken by means of timing pressure rise in the tank with the gas outflow valve. closed. The average daily gas production measured in this way was 11,500 cu ft STP (dry). During this period, retention time was constant at 20 days and the tank liquid volume was 23,400 cu ft. Specific methane production was calculated using the same data. The average of the data is 3.77 cu ft/lb.

Fermentor #1 was started in early June and by mid-July it was evident that there was not enough residue available to operate both tanks. As a result of this and the fact that the level gage in tank #2 needed modification, the contents of tank #2 were transferred to fermentor #1 on July 24. When the tank was opened, it was found that a large amount of the chemicals used for pH control never dissolved.

It is evident from the performance of fermentor #2 that the patient control of fermentation conditions is at least one way of achieving start-up. Presumably the process needed about 30 days to adapt to whatever it was that was blocking gas production. This assumption is based on the successful rapid start-up of our fermentor at Kaplan 4 years ago. The only significant difference between the residue then and now is the use of Rumensin in the present feed ration.

Fermentor Performance - #1 Fermentor

Fermentor #1 was loaded on 6/5/79 to attempt a start-up at 131°F. Start-up of this unit was to be similar to start-up of fermentor #2 except that no chemical control was attempted. Volatile solids concentration in the tank was initially 0.9%. pH started out at 6.66. It dropped to a low of 6.30 on June 16 and then began a slow rise. TVA started out at approximately 2,000 mg/l and dropped slowly. By June 28 pH had reached 6.61 and TVA was down to 1,141 mg/l. Methane concentration in the gas was up to 47.3%, although gas production was essentially undetected by the gas meter. Since this fermentor was very lightly loaded, it was felt that significant fermentation had begun but that the light loading was keeping the gas production from being large enough to measure. It was therefore decided that daily loadings of residue should be started. This was started at 0.5 ft/day which, except for the fact that daily withdrawals were not started at this time, translates to a retention time of 34 days. pH remained steady at about 6.7 and TVA rose to a high of 1,680 mg/l. Significant gas production was first recorded on July 6. As was the case with fermentor #2, the exact gas production is not known as the gas flow was far below the flow range where the gas meter is accurate. After 3 days TVA had dropped to 1,140 mg/l and pH had risen to 7.04. On July 16 the loading was doubled.

This drove the TVA to about 2,500 mg/l just prior to the mixing of the fermentors on July 24.

Specific methane production (as determined by measuring gas flow by timing pressure rise) averaged 3.89 cu ft/lb between July 11 and July 24.

After completion of adding tank #2 contents to tank #1, the conditions were as follows:

pH	7.27
TVA	2,377 mg/l
alkalinity	4,796 mg/l
volatile solids concentration	2.27%

At this point the fermentor was completely full (36.7 ft) and loading was resumed at a rate of 1 ft/day (retention time of 36.7 days). On July 30 loading was increased to 2 ft/day (retention time of 18.4 days) and kept at this level with few exceptions through August. By the end of August conditions in the fermentor were as follows:

pH	7.4
TVA	1,050 mg/l
alkalinity	5,196 mg/l
volatile solids concentration	2.23%

During the month of August the dry, air-free methane concentration averaged 60.8% (STD DEV 1.75%) and the specific methane production averaged 3.49 cu ft/lb (STD DEV 1.52 cu ft/lb).

Operation of fermentor #1 appears stable except for the wide variations of the quality and quantity of the residue. The mode of operation will be maintained until such time as more residue becomes available.

Residue Characteristics

Retention time is controlled at fixed levels on a day to day basis as shown in figure 8. The spike near the end of July occurred for a few days following the transfer of fermentor #2 contents to fermentor #1. The varying loading rate, on the other hand, has been a direct result of the wide fluctuations in the volatile solids content of the residue. Figure 9 is a plot of fermentor #1 loading rate for the month of August. During August the retention time was constant. The loading rate; however, varied from about .04 to about .22 lb vs/cf/day. The fluctuation of the volatile solids content of the residue appears to be due to four major causes:

- rainwater infiltration

- feedlot structure
- cattle population
- cattle weight

Although the feed lot is basically a roofed over structure, the roofing acutally consists of slats. In addition, there is essentially no overhang at the edges. For these reasons some amount of rain water enters the system every time it rains causing large fluctuations in the volatile matter content of the residue. Furthermore, there has been wind damage to the roofing exposing a considerable number of pens to direct rain. Due to settling of the ground there has also been a few areas where surface water has drained directly into the pen area. To a great extent these problems have been fixed over the last few months; however, there are still two other sources of water in the feed lot. First, there are several hundred waterers for the cattle. No direct water from these enters the residue collection system except when one or more malfunctions. Second, the cables which draw the scrapers in the pits under the pens are kept clean by jets of water applied during operation. The size of these jets was recently reduced to cut down on this source of dilution. The last two items, cattle population and weight, affect the residue dilution problem in the same way. Compared with operation on a pilot plant basis at the feed lot four years ago, the total quantity of residue is much lower. This is because the total cattle population and the weight of the cattle are significantly lower due to the present economics of the cattle market. The net effect is that rain water and cable wash water have a much greater impact on the solids content of the residue.

This problem has not been totally resolved at this point. It is hoped that increases in cattle population will bring improvement. Meanwhile, all possible sources of water infiltration will be monitored and corrective action taken where possible.

Product Utilization

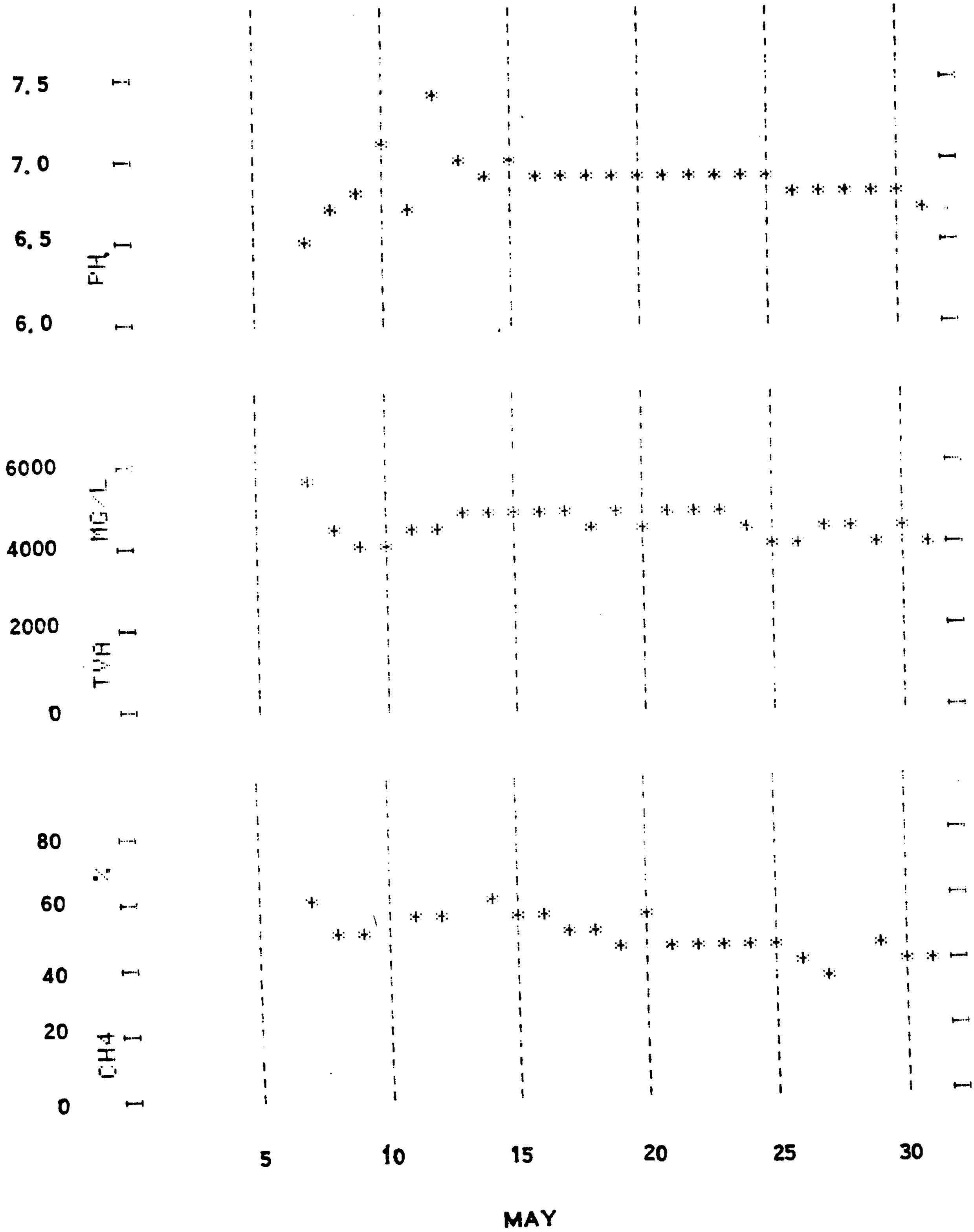
Product gas is used in the fermentation system boiler except for periods of high demand. No problems have been encountered in this application. Final preparations for utilizing the product gas in the meat packing plant boiler neared completion. In addition, the engine generator was placed on order.

Since the system is not yet operating at the ten day retention time design point, no effort has been expended on protein recovery.

Plans for Next Quarter

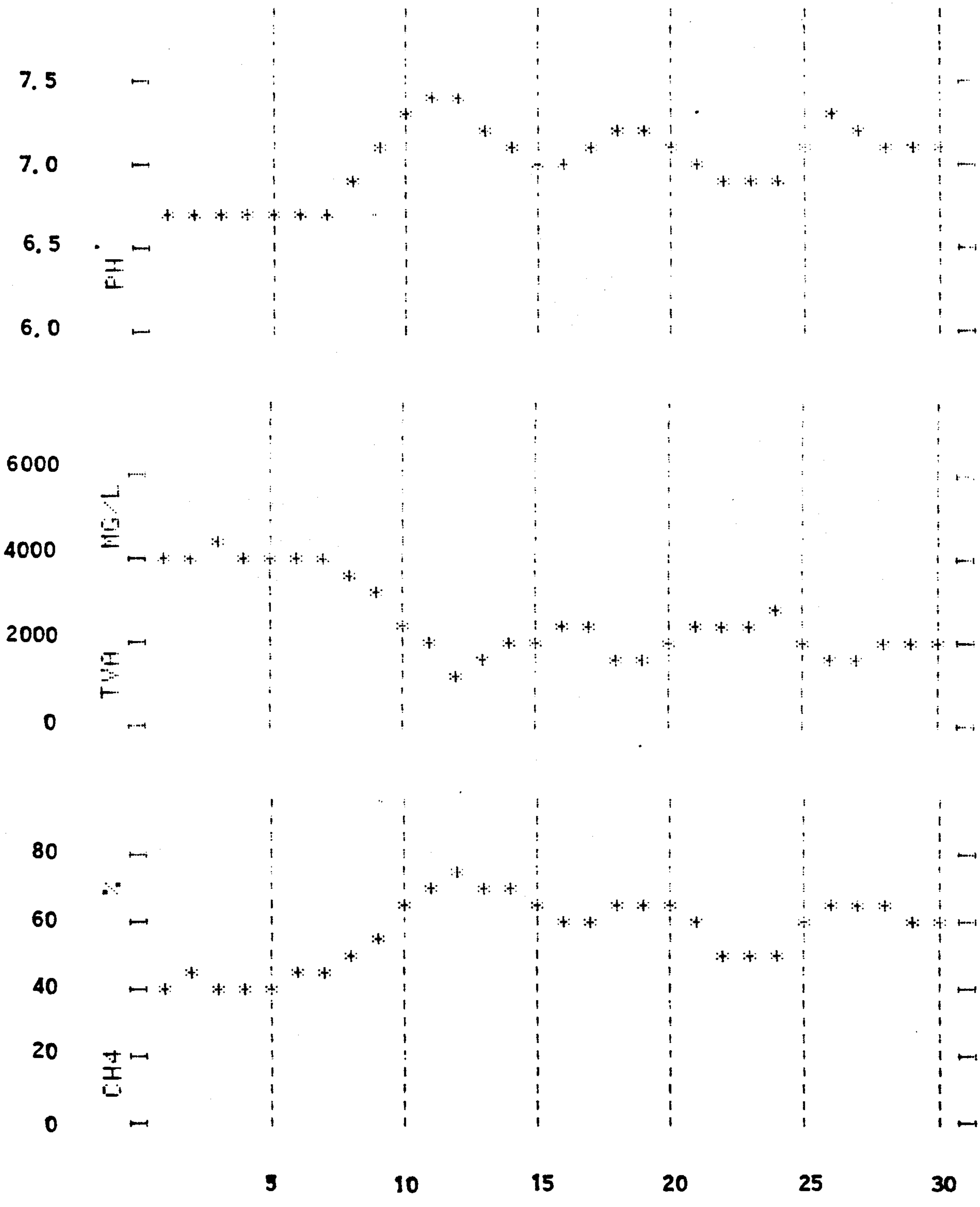
Early next quarter the packing house boiler experiments with fermentor gas will begin.

Fermentor #1 will be brought to a ten day retention time and experiments in protein recovery will commence. As the quarter proceeds, fermentor #2 will also be brought to design point. If no unforeseen problems occur, limited feeding trials will start before the end of the year.



FERMENTOR NO. 2

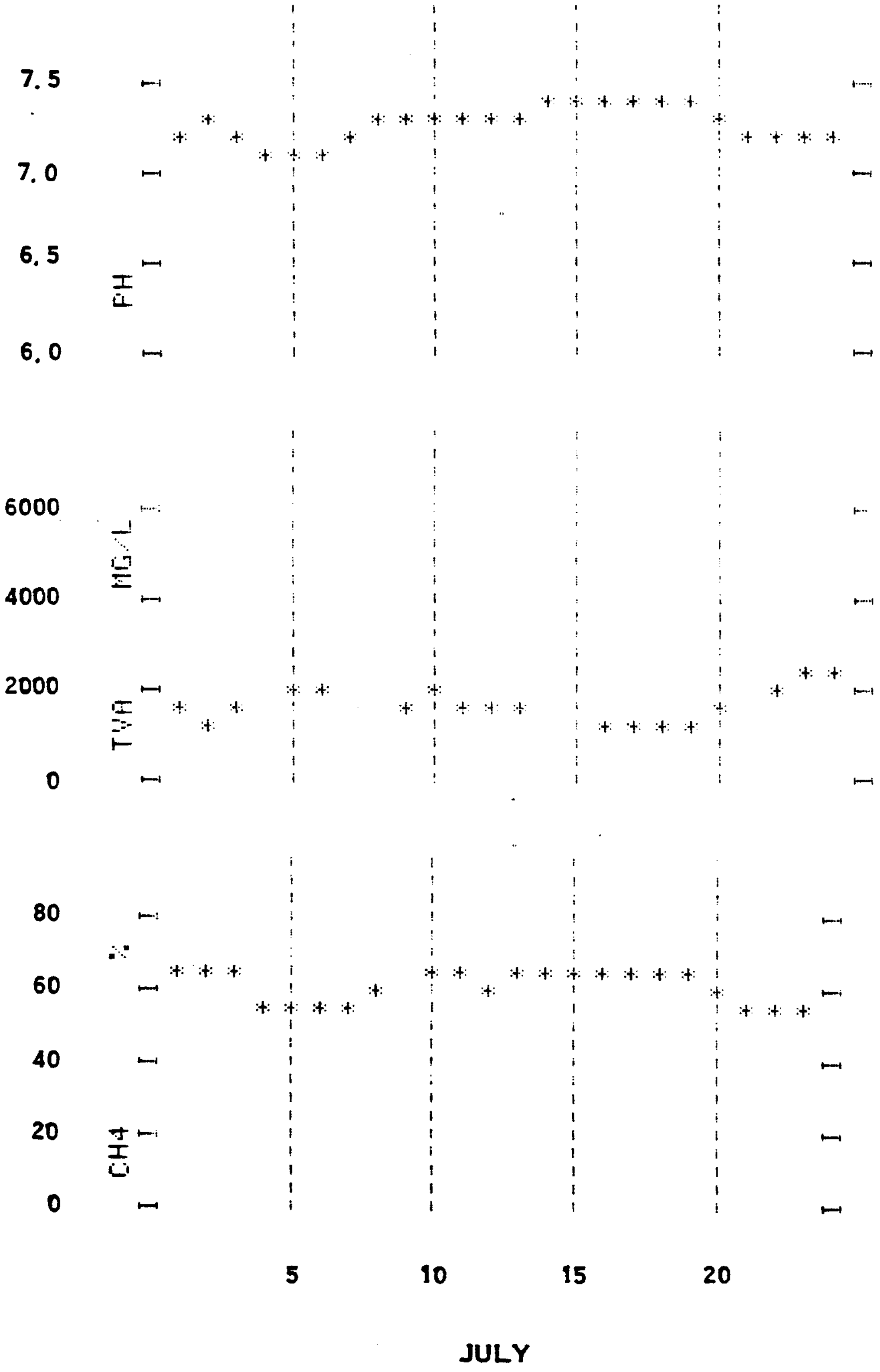
FIGURE 1



JUNE

FERMENTOR NO. 2

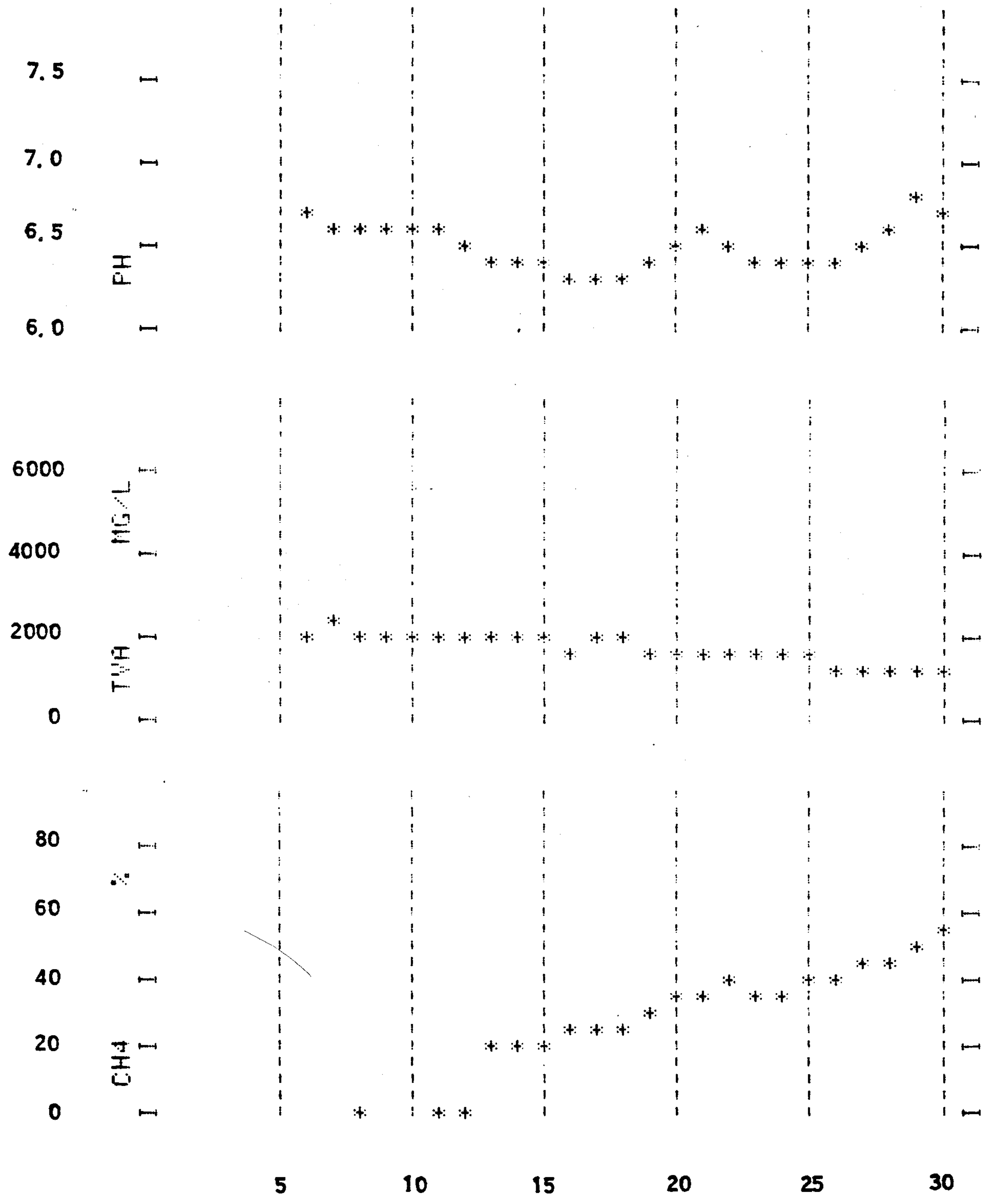
FIGURE 2



FERMENTOR NO. 2

11490 CF/DAY 3.77 CF CH_4/LB VS R.T. 20 DAYS

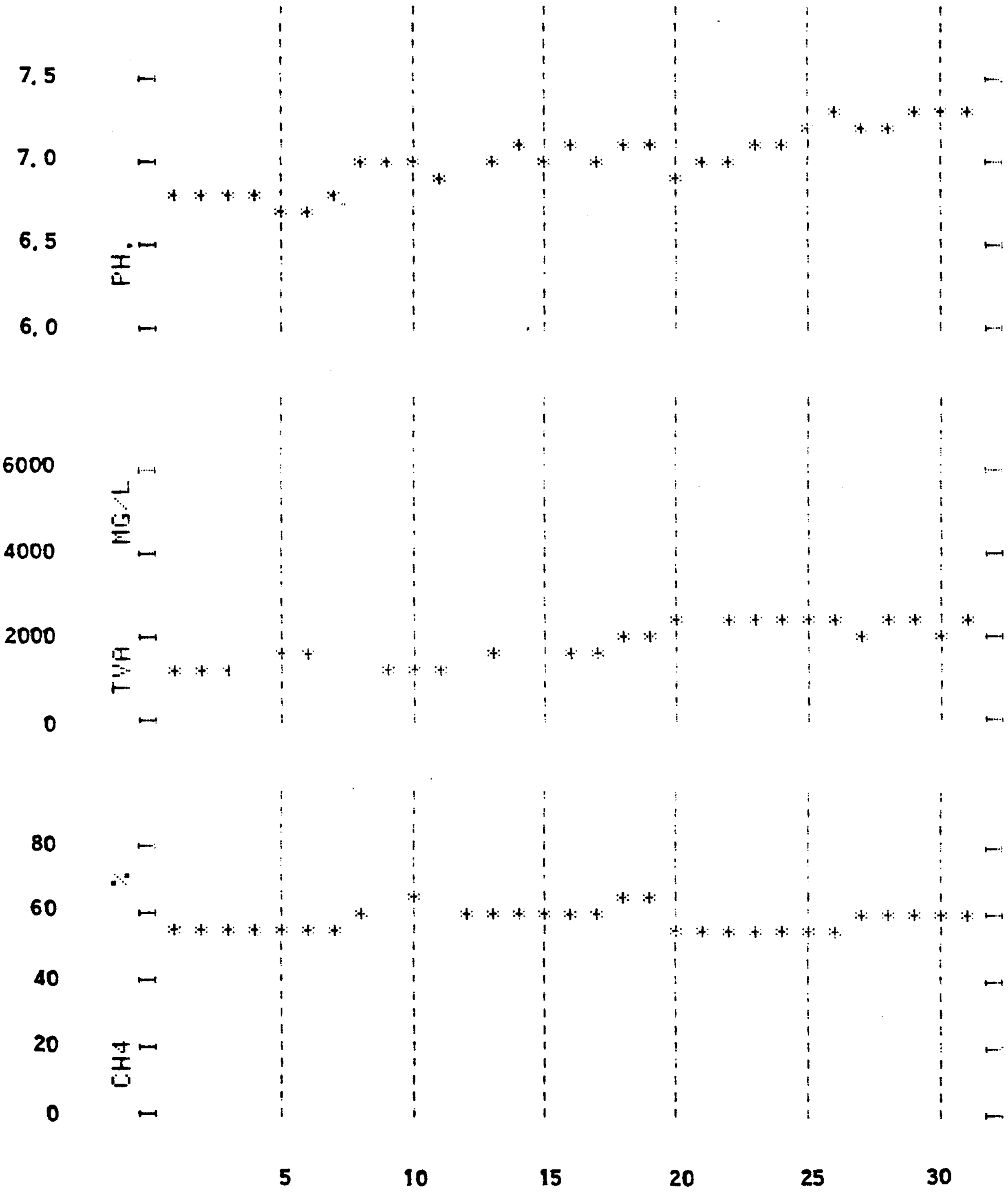
FIGURE 3



JUNE

FERMENTOR NO. 1

FIGURE 4

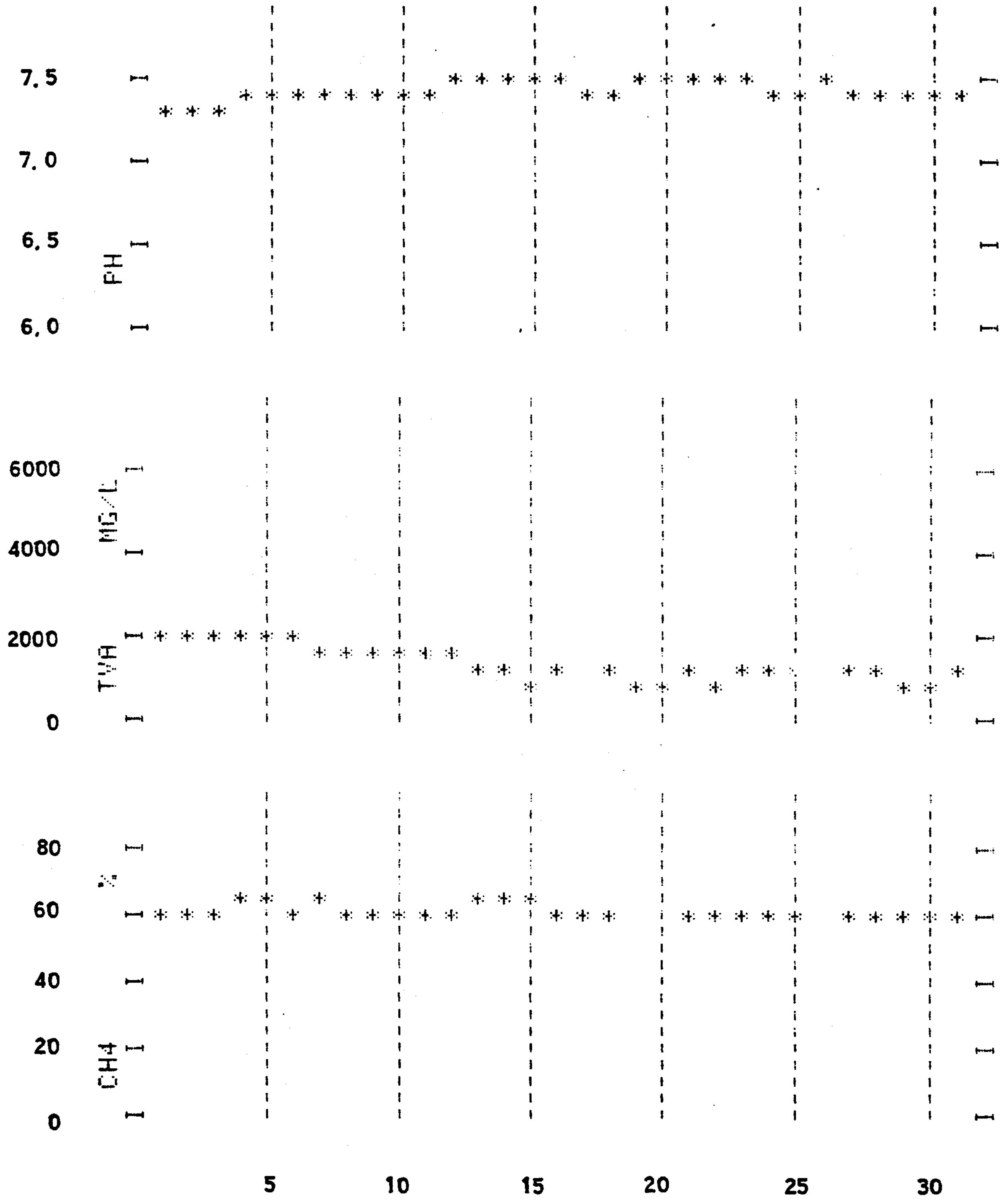


JULY

FERMENTOR NO. 1

11230 CF/DAY 3.89 CF CH4/LB VS R.T. 29 DAYS

FIGURE 5

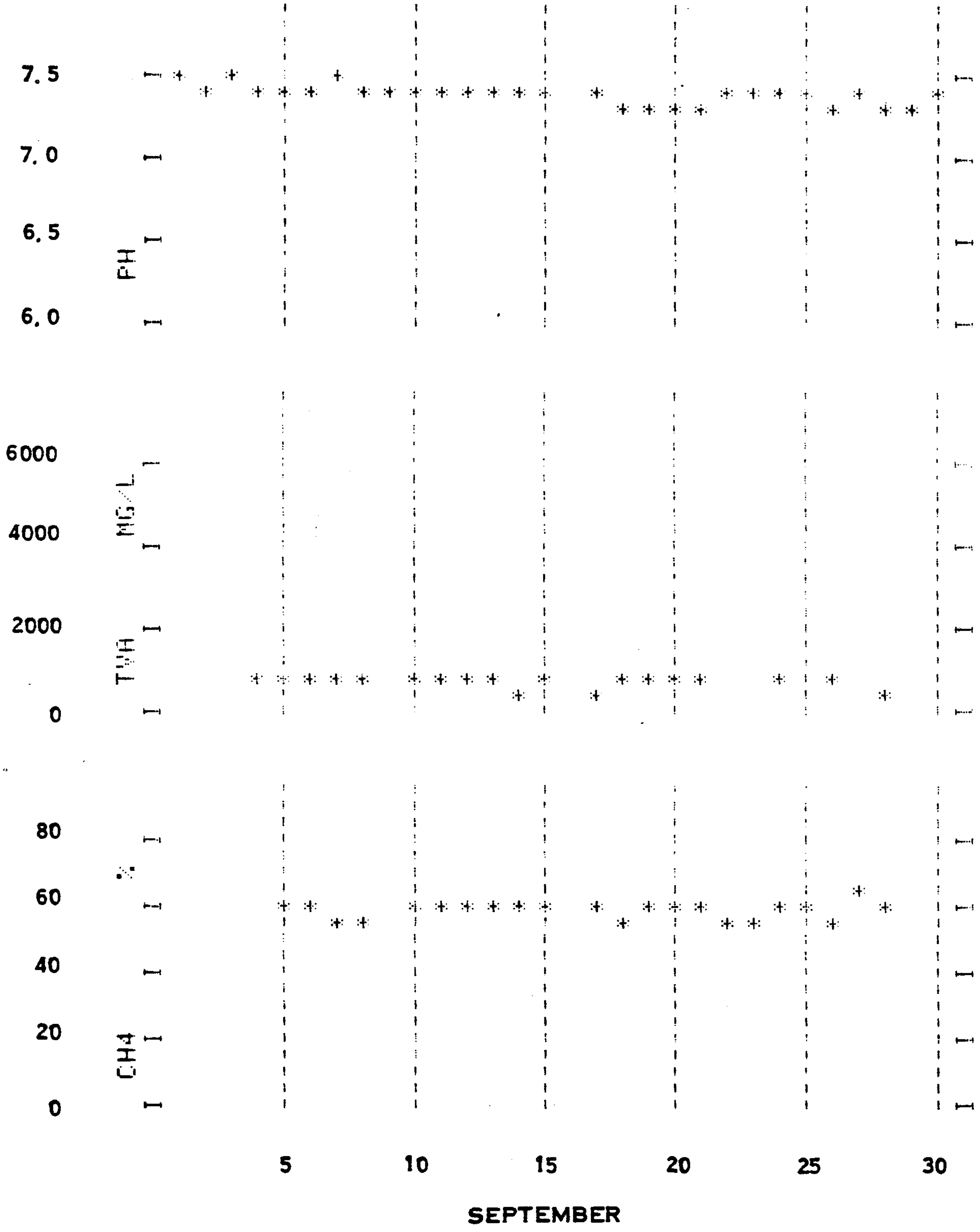


AUGUST

FERMENTOR NO. 1

28620 CF/DAY 3.49 CF CH_4/LB VS R.T. 18 DAYS

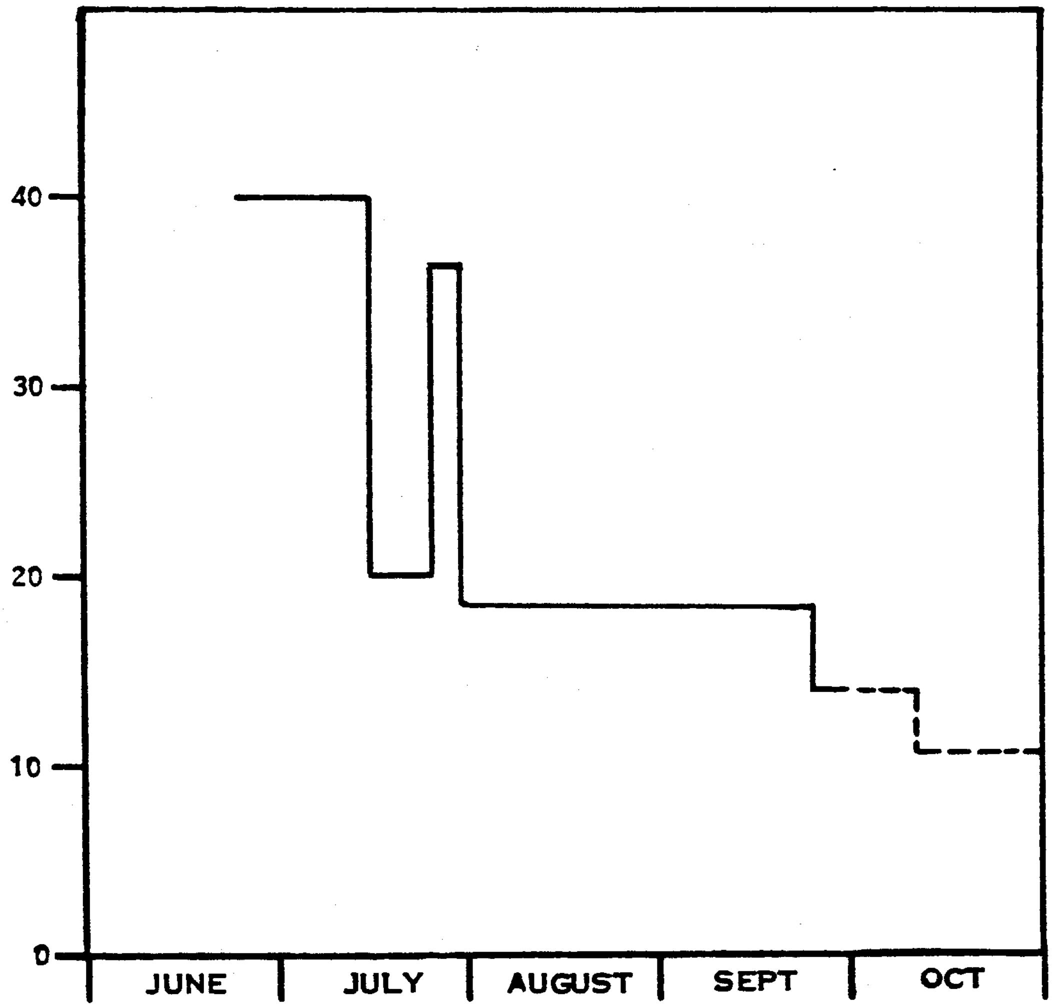
FIGURE 6



FERMENTOR NO. 1 (WITH SOME NO. 2)

26260 CF/DAY 3.76 CF CH_4/LB VS R.T. 18 DAYS

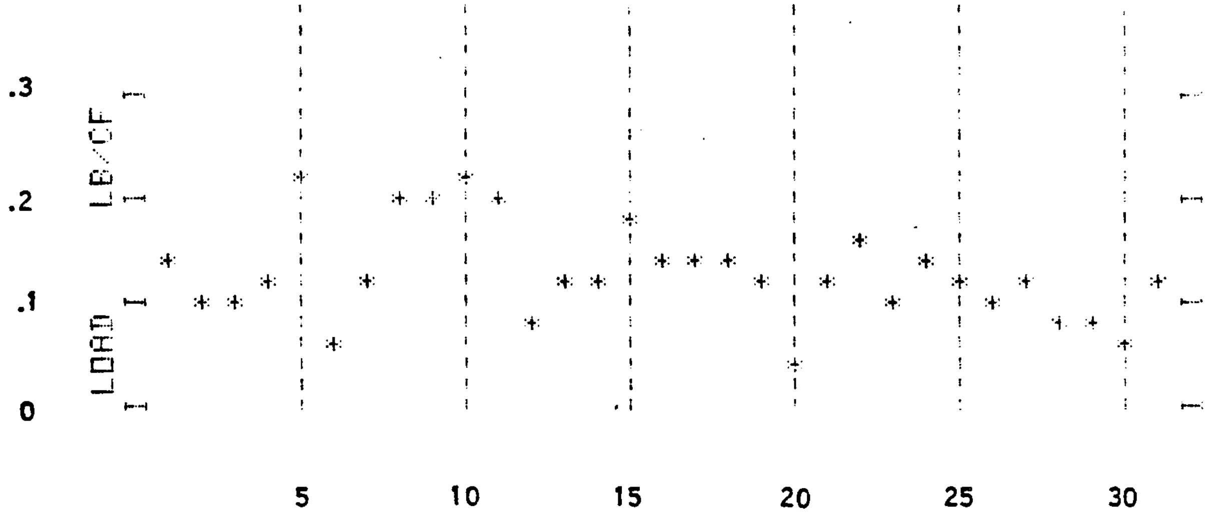
FIGURE 7



FERMENTOR NO. 1

RETENTION TIME (DAYS)

FIGURE 8



AUGUST

FERMENTOR NO. 1 LOADING RATE

POSSIBLE CAUSES OF FLUCTUATION :

- RAIN WATER INFILTRATION
- FEEDLOT STRUCTURE
- CATTLE POPULATION
- CATTLE WEIGHT

FIGURE 9

FEASIBILITY STUDY FOR ANAEROBIC DIGESTION OF AGRICULTURAL CROP RESIDUES

E. Ashare, M. G. Buivid, and E. H. Wilson

Dynatech R/D Co.

ABSTRACT

The objective of this study was to provide cost estimates for the pretreatment/digestion of crop residues to fuel gas. A review of agricultural statistics indicated that the crop residues wheat straw, corn stover, and rice straw are available in sufficient quantity to provide meaningful supplies of gas.

Engineering economic analyses were performed for digestion of wheat straw, corn stover, and rice straw for small-farm, cooperative, and industrial scales. The small-farm scale processed the residue from an average size U.S. farm (400 acres), and the other sizes were two and three orders of magnitude greater.

The results of the analyses indicate that the production of fuel gas from these residues is, at best, economically marginal, unless a credit can be obtained for digester effluent. The use of pretreatment can double the fuel gas output but will not be economically justifiable unless low chemical requirements or low-cost chemicals can be utilized. Additional development is necessary in this area. Use of low-cost "hole-in-the-ground" batch digestion results in improved economics for the small-farm-size digestion system, but not for the cooperative- and industrial-size systems.

Recommendations arising from this study are continued development of autohydrolysis and chemical pretreatment of agricultural crop residues to improve fuel gas yields in an economically feasible manner; development of a low-cost controlled landfill batch digestion process for small-farm applications; and determination of crop residue digestion by-product values for fertilizer and refeed.

COO-2917-15
(Not for reproduction
without GTR approval)

BIOLOGICAL CONVERSION OF BIOMASS TO METHANE

QUARTERLY PROGRESS REPORT

Quarter Ending September 30, 1979

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Urbana, Illinois 61801

November 1979

Prepared for

The U.S. Department of Energy
under Contract No. EY-76-S-02-2917

Introduction

Investigations into the viability of straw as a feed stock for methane production has continued with emphasis placed on the effect of thermochemical pretreatment on the conversion efficiency. Previous results of this investigation were reported in Report COO-2917-14 in March 1979. Baled wheat straw was milled prior to the pretreatment by passing it through a 3.2 mm (0.125 in) screen. This was necessary in order to handle the material in the pumping system. The particle size of the milled straw was determined by a dry sieve and a wet sieve sizing technique. Mixed results were obtained in the initial set of tests conducted in the pretreated straw. It was felt that follow up tests were necessary in order to determine the effectiveness of this technique in straw pretreatment.

Pretreatment Procedure

Because of the uniqueness of the response of the system to the pretreatment step, the procedure will be presented specifically as related to the following data. Dry milled straw, 27 kg (60 lbs), was added to a 400 liter mixed pressure 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. Granular sodium hydroxide was added to the straw at an initial rate of 1.9 kg per 27 kg of dry straw for addition to Reactors 1 and 2. The rate of caustic addition for these reactors was reduced to 1.52 kg per 27 kg on Day 29080 (March 21, 1979). This lower rate was also being used for the feed slurry for Reactor 3 and 4. After the chemical and straw were mixed for about 5 minutes, 190 kg of tap water was added to the reactor. 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 heating to 115°C, approximately 38 kg of steam condensate was added to the slurry. The pH of the paste before steam addition was above 12.0. After five hours in the heated reactor, four hours heat-up time and 1 hour at temperature, the pH was reduced to near 10.0. There appeared to be some variation in the final pH. Before the condensate accumulated, the NaOH was 0.20 molar when 1.52 kg was added. This was reduced to 0.17 molar with the addition of steam.

The treated slurry was pumped from the pressure reactor to the mix tanks. An additional 190 kg of water was added to dilute the slurry to approximately six percent solids. This was done to conserve straw since higher concentrations, i.e. 12 percent, could be pumped through the system. The resultant NaOH concentration was reduced to 0.09 molar. The pH was near neutral after the water was added. The alkalinity was only about 3000 mg/l. Clearly, most of the caustic (OH^-) had been consumed in the heat treatment step.

In addition to the sodium hydroxide, 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 in the reactor varying between 200 and 300 mg/l. This suggests that a substantial quantity of nitrogen, approximately 300 to 400 mg/l of feed volume, was converted into cell mass. Analysis for phosphorous showed levels between 50 and 100 mg/l of P in the slurry.

Results and Discussions

The primary effort was directed toward obtaining a stable and efficient operating condition in the reactors. At the end of the last reporting period, Reactors 3 and 4 were appearing to recover as a result of a reduction in caustic used in the pretreatment step. Reactors 1 and 2 were receiving the higher caustic dosage and had essentially failed due to the high total volatile acid content. The results of this period are shown in Figure 1 through 4. These data start on March 7, 1979 (Day 29077). These figures show the total gas production in liters per hour, the volatile solids loading in kg per day per m^3 and the pH.

Reactor 1 failed completely as a result of the operating conditions as reported previously (Report COO-2917-14). All feed was terminated and the pH gradually increased to 6.6. The total volatile acids (TVA) decreased from 5700 mg/l March 8, 1979 (Day 1 in Figure 1) to 3000 mg/l by Day 6. The reactor was also reseeded with 50 liters of effluent from Reactor 4. Feed of the caustic pretreated straw was initiated on Day 4. On Day 12, the contents of the reactor were diluted with 20 percent tap water and the caustic addition in pretreatment was reduced from 1.9 to 1.52 kg per 27 kg of dry straw. There was a surge in gas production during this period while the TVA continued to drop to about 1300 mg/l. The system continued to respond favorable at a loading of about 2.0 kg V.S./m^3-day. This resulted in a retention time of 13 to 15 days at a 58 to 60°C temperature. On Day 46, the loading was essentially doubled and the retention time reduced to approximately 7.5 days. After an initial surge in gas, the pH dropped as did the gas production. The TVA rapidly increased to 6000 mg/l and the system failed. A number of additions ranging from potassium sulfide to nutrient broth were tried. None of these additions worked. However, because of the short term nature of these tests no conclusions could be drawn. After several weeks of attempting to get this reactor to recover, it was shut down.

Reactor 2 was restarted in the same manner as Reactor 1. There was an initial surge in gas production. As long as the pH was maintained above 6.6, the system performance was acceptable. However, the TVA concentration was consistantly in the 2000 mg/l or greater range. It was difficult to maintain the pH. At the 13 to 15 day retention time and the lower loading rates, it was possible to operate the system. It was an unsatisfactory mode of operation that was very difficult to control. Gas production calculated during Day 40 to 60 in Figure 2 was 0.44 m^3/kg V.S. fed. This gas production is somewhat better than that obtained without caustic pretreatment. However, it is not a significant improvement, probably because of something that inhibits the fermentation process.

Reactor 3 (see Figure 3) had been receiving feed cooked at a lower caustic level (1.52 kg NaOH) for two weeks prior to the period shown in Figure 3. Gas production was good during the early part of the period. The retention time was in the 13 to 15 day range with a loading of approximately 2.0 kg of volatile solids per day. After about day 40, the gas production decreased and it was difficult to maintain the pH without addition of lime. The volatile acids were in the 2000 to 3000 mg/l range. By the end of the period, the volatile acids had increased in excess of 4000 mg/l. Control of pH was very difficult, and process failure ensued. Also, problems with the gas seal were being experienced. This could account for some of the reduction in gas production.

A number of additions were tried, including raw sewage sludge. Due to the short term nature of these additions, it should not be concluded that they were not effective. However, some immediate response could be expected with certain inhibitors. For example, if for some reason, a high concentration of heavy metals was present, the addition of 50 mg per liter of reactor of sulfide would precipitate the metals with a rapid recovery. It would appear that the problem is not toxicity, but probably a nutrient deficiency. On Day 77, the feed to Reactor 3 was diluted two-fold. There was an initial surge in gas production as shown in Figure 3 and the pH dropped to 6.5. The pH was elevated with lime to above 6.6, but the gas production continued to decrease. This high dilution rate was continued for another three weeks at which time the volatile acids were approximately 3000. It was not possible to get a stable system operating.

Reactor 4 exhibited essentially the same response. The feed for Reactor 4 was the same as Reactor 3. The high feed rate of 4.0 kg V.S. per day resulted in a retention time of 7 to 8 days. Control of pH was very difficult and the system was frequently stressed due to low pH levels. By the end of the period, the volatile acids had exceeded 5000 mg/l. It was not possible to effectively control this system under the loading and with the feed material.

Based on the problems encountered with the pretreated straw, the feasibility of this material as a feed stock is questionable. This material needs more investigation before a large scale study is undertaken. The optimum pretreatment system has not been determined. The cause of the poor operating efficiency must be determined and corrected. It will then be possible to evaluate the effectiveness of pretreatment and determine the optimum pretreatment conditions.

The Anaerobic Digestion of Corn Stillage

The energy crisis has increased the interest in producing automotive fuels from biomass and, in the United States, the production of ethanol from corn has attracted much attention.

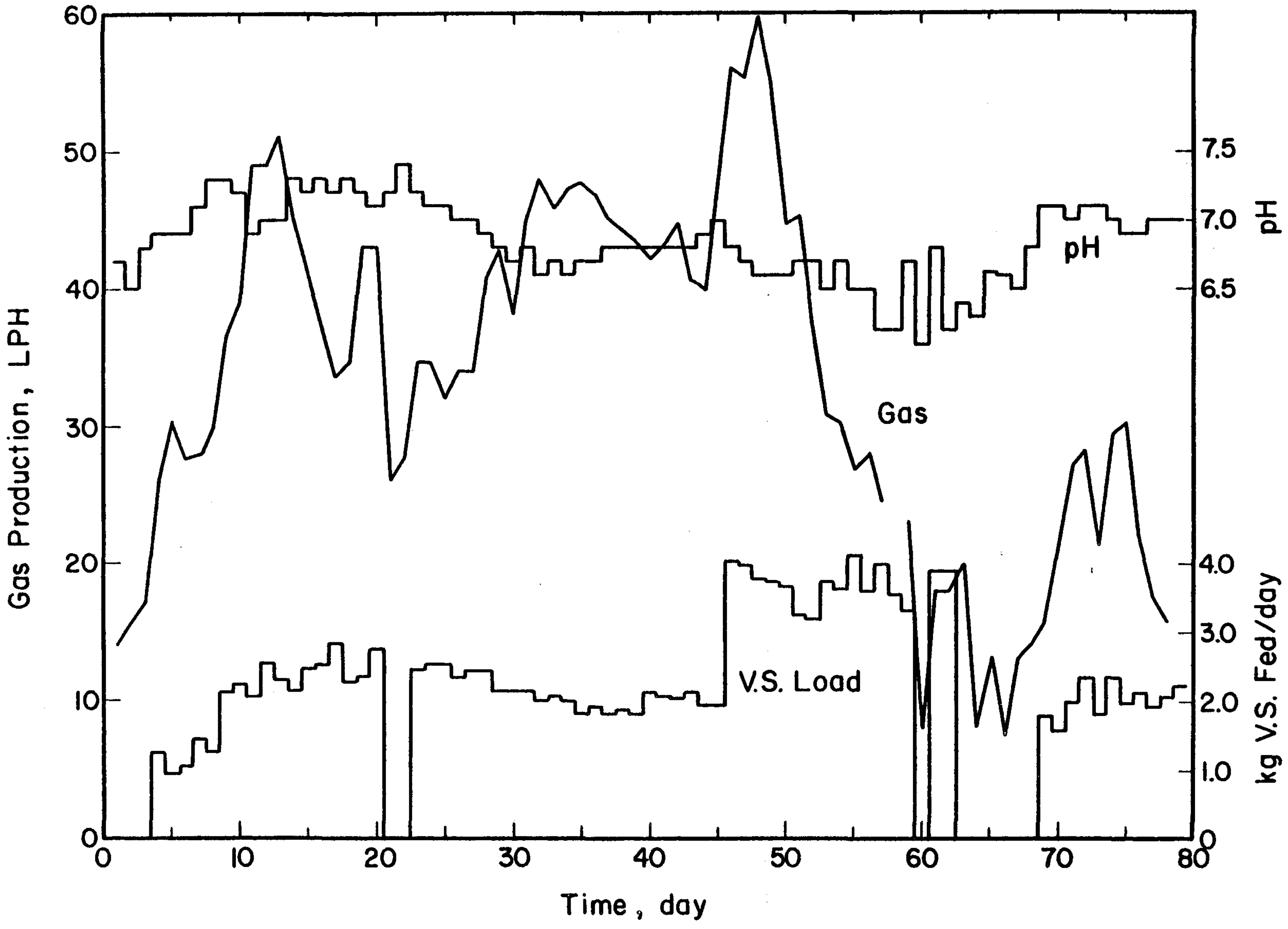

Figure 1. Performance of Reactor 1 in Pretreated Wheat Straw

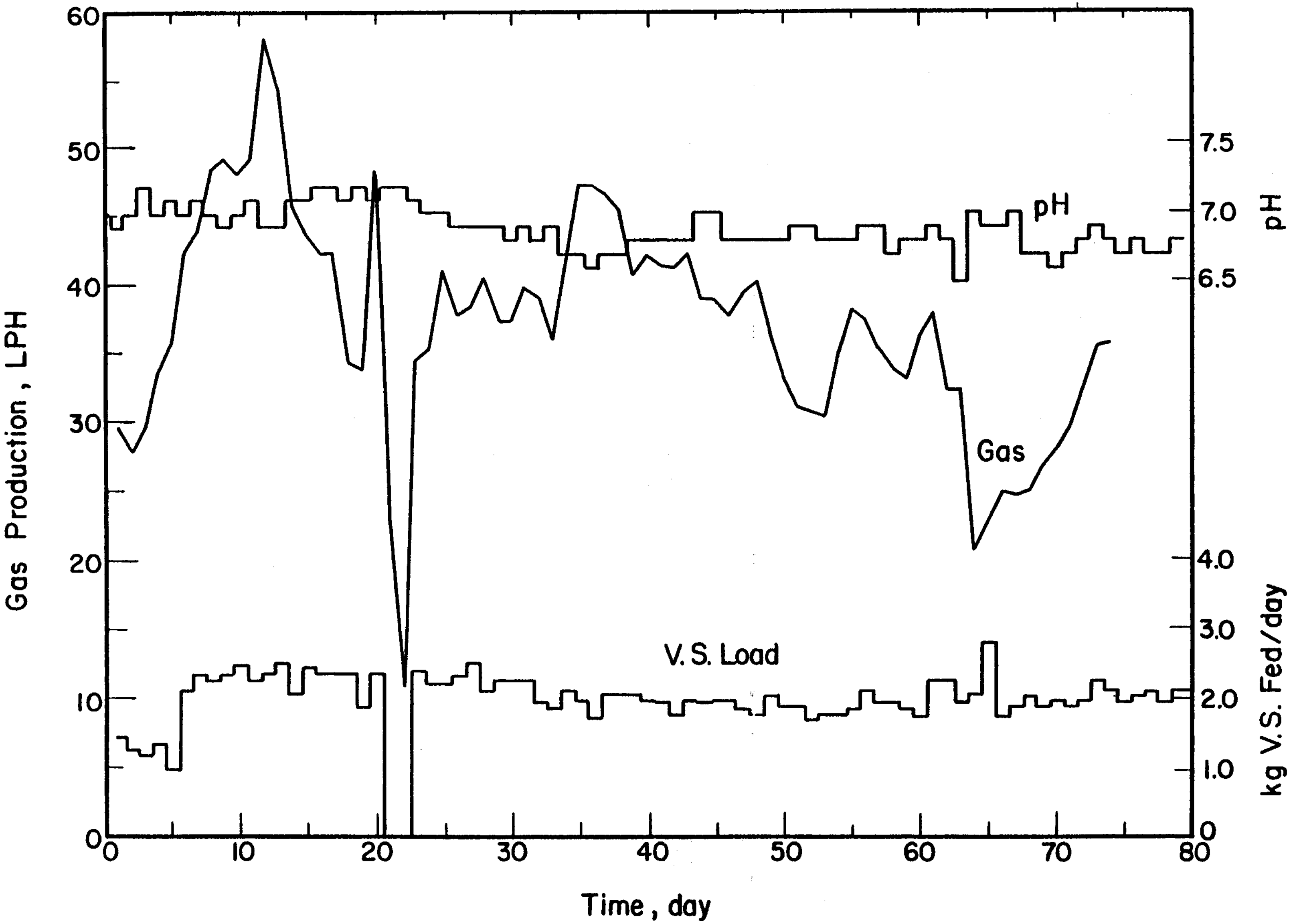

Figure 2. Performance of Reactor 2 on Pretreated Wheat Straw

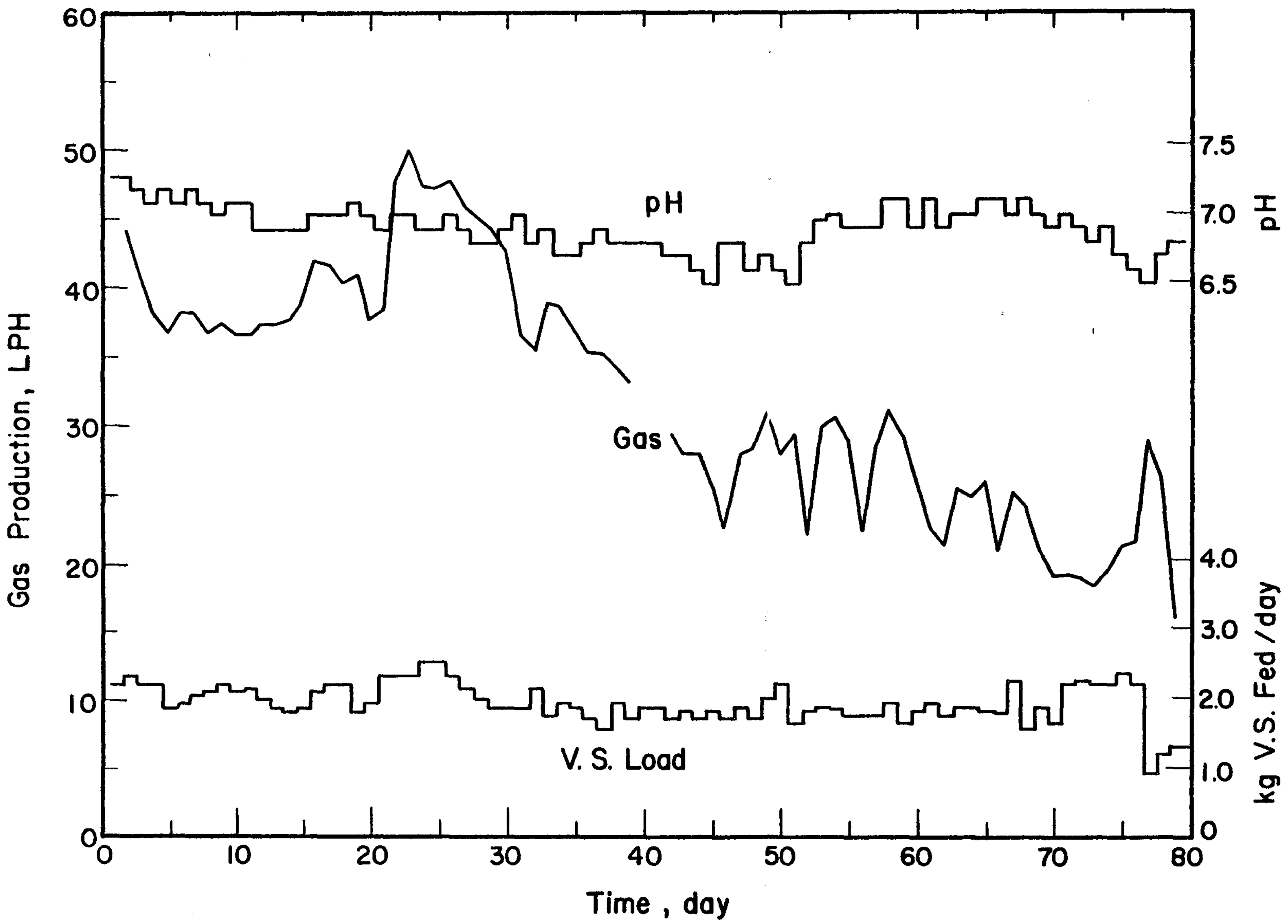

Figure 3. Performance of Reactor 3 on Pretreated Wheat Straw

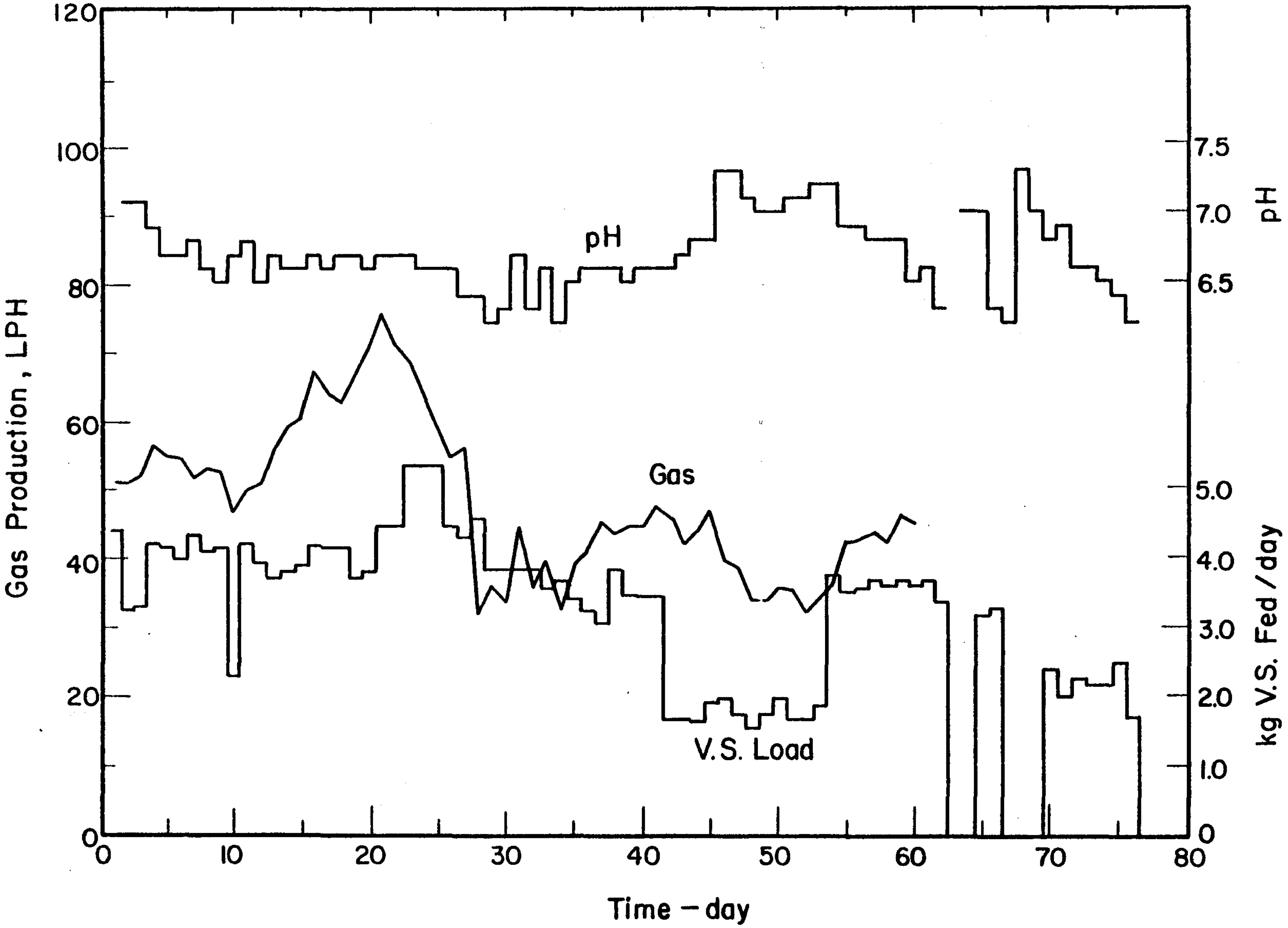

Figure 4. Performance of Reactor 4 on Pretreated Wheat Straw

To be economic and energy efficient, the conversion of corn carbohydrates to ethanol must consume as little high grade energy as possible. It is therefore important that a cheap, readily available fuel is used in the conversion process. It is generally believed that coal is the most suitable energy source. However, the anaerobic digestion of corn stillage has the potential to provide much of the necessary process energy while producing an effluent which may be suitable for use as an animal feedstock supplement.

Research into the anaerobic digestion of corn stillage is required to:

i) assess the potential of various types of digester,

ii) provide design criteria for full-scale plants,

iii) determine the net energy yield, and

iv) assess the suitability of the solids produced for use as a feedstock.

Characteristics of Corn Stillage

Currently, corn stillage is dried and sold as a livestock feed with a digestible protein content of 23% (National Academy of Sciences, 1976). As such it fetches 60-85% the price of soybeam meal (David, et al., 1978). To produce a suitable feedstock, the stillage must be centrifuged, evaporated and dried. This processing consumed 32% of the total plant energy.

With the large scale production of ethanol from corn, there is unlikely to be a continued market for all the feedstock produced. Anaerobic digestion would provide a suitable use for this material, and with reduced prodessing substantially offset the net energy consumption of the plant.

Grain distillery effluents are very amenable to anaerobic digestion with 90% BOD removals being reported (Buswell, 1949). Although information on the characteristics of stillage is sparse, the available data are summarized in

Table 1. Also, the effluent is hot, making thermophilic digestion practical (Buswell and LeBosquet, 1936).

Table 1. Characteristics of Grain Distillery Effluent (Buswell & LeBosquet, 1936).

Solids concentration	30-40,000 mg/l
Volatile solids concentration	24-32,000 mg/l
BOD	15-16,000 mg/l
Organic nitrogen	1,900 mg/l

Anaerobic Process Selection

Five types of anaerobic digestion process may be identified:

i) conventional anaerobic digester,
ii) anaerobic contact process (Schroepfer, et al., 1955),
iii) anaerobic filter (Young and McCarty, 1969),
iv) upflow anaerobic sludge blanket (UASB)(Lettings, et al., 1979,
and v) anaerobic attached film expanded bed (AAFEB) (Switzenbaum and Jewell, 1978).

This project will assess the suitability of three of these processes for treating corn stillage.

The anaerobic contact process will be studied as the concentration and recycle of the waste solids offers many advantages over the conventional process. Traditionally, there have been major difficulties in separating the solids from the digester effluent and part of this project will concentrate on finding a means of alleviating this problem.

The anaerobic filter provides a simple means of anaerobically treating wastewaters. However, it has generally been used to treat soluble effluents and its suitability for treating wastewaters containing high solids concentrations has yet to be assessed. This project will investigate this aspect and will determine the performance characteristics of this process.

The UASB is a recent development that has been used to treat relatively dilute effluents. This study will assess the suitability of this process for treating a concentrated organic effluent and determine criteria allowing its application to corn stillage.

The AAFEB has been developed to allow the anaerobic treatment of very dilute organic wastewaters. As its potential for treating effluents containing a high solids concentration is unknown, this process will not be investigated.

Conclusions

If the large scale production of ethanol from corn occurs, the continued sale of the dried stillage as a feedstock will be impractical. Anaerobic digestion of the stillage will provide an alternative, beneficial use for this material by recovering energy from the effluent. However, to assess the potential of this process, various digestion systems must be investigated to determine the most suitable type and its operating characteristics.

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

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FARM ENERGY SYSTEM

The farm energy system, shown schematically in Figure 1, has been constructed on a farm in Drury, Missouri. The purpose of this unit is to demonstrate the feasibility of producing energy for farms (heat and electricity) from methane produced by anaerobic digestion of crop residues and other crop materials.

The system consists of four 4,000 gallon digestors equipped with axial agitators. The reactors are housed in an insulated building maintained at 95°F. Crop matter is fed to the digestors on a sixty-day batch cycle. Methane produced is stored in PVC bags and used to generate electricity or for heat in the farmhouse. Waste heat from the engine-generator is used to heat the building.

The system was started in early summer by inoculating five percent hay-water mixtures with sewage sludge. Start-up went smoothly with gas production reaching a maximum within two weeks, as shown in Figure 2. Control of pH required frequent lime addition during the first week, but lime additions were not necessary after this period to maintain pH > 7. Methane concentrations were between 45 and 65 percent and averaged above 50 percent. After sixty days carbon destruction was 50 percent.

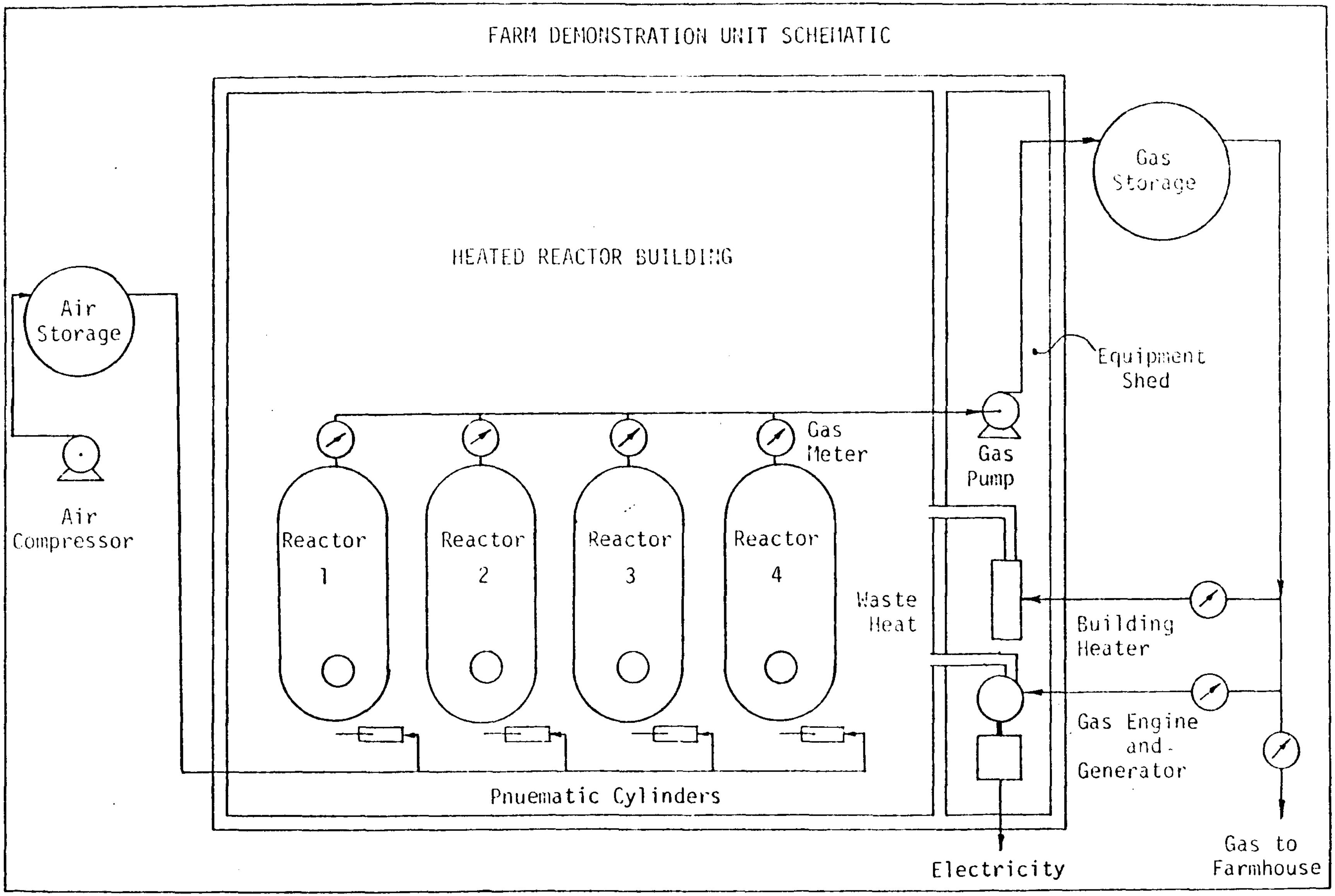
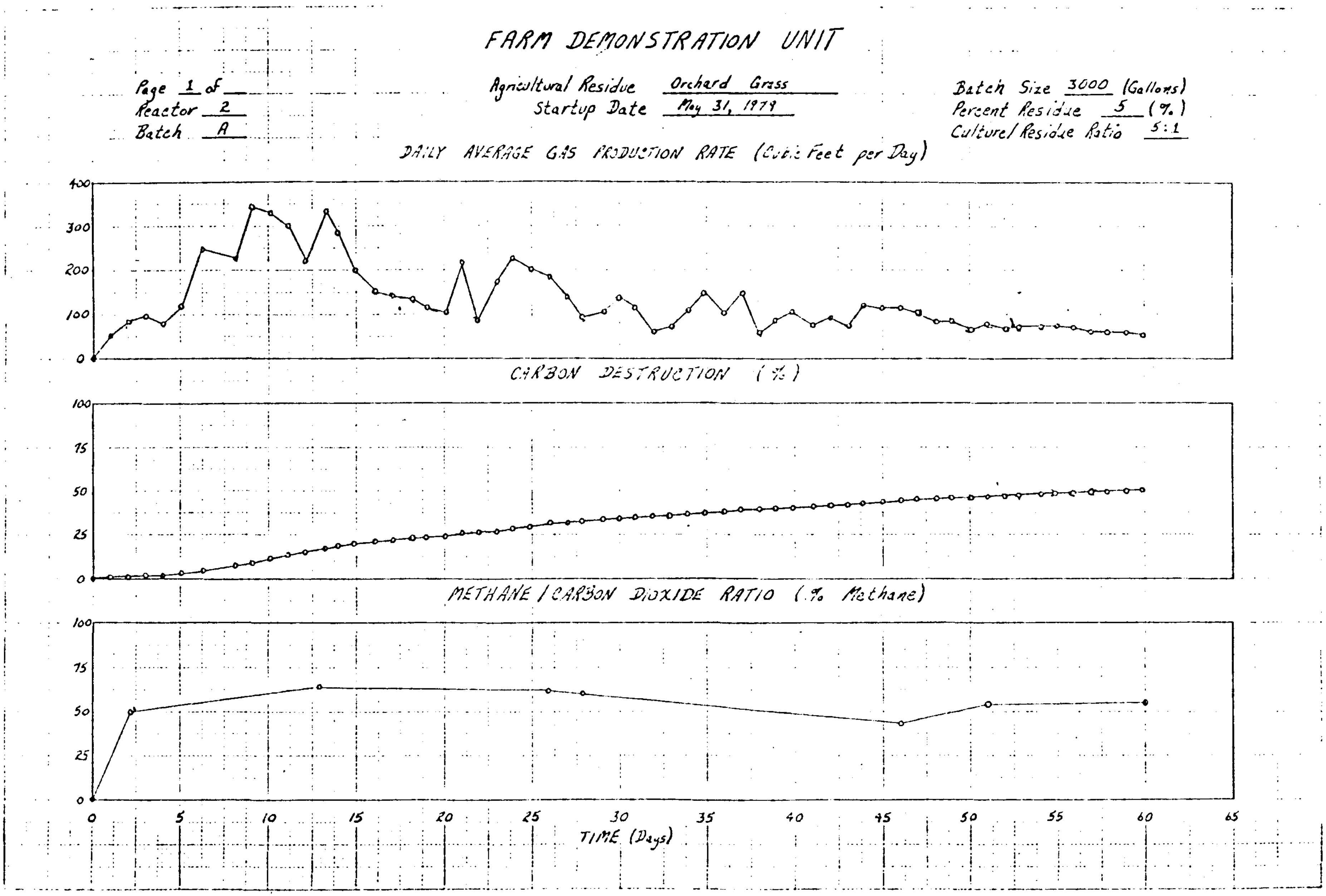


Figure 1. Schematic of Farm System



FARM DEMONSTRATION UNIT

Page 1 of ___
Reactor 2
Batch A

Agricultural Residue Orchard Grass
Startup Date May 31, 1979

Batch Size 3000 (Gallons)
Percent Residue 5 (%)
Culture/Residue Ratio 5:1

Figure 2. Farm Reactor Data

The performance of batch laboratory reactors using the same hay as the farm system is shown in Figure 3. These laboratory reactors are operating with ten percent hay initially and three cycles of several weeks duration are shown. Each cycle is re-inoculated from the previous culture. The same performance cycle as the farm reactors is apparent with maximum gas production occurring after two weeks. Carbon destructions have been poor, but improve with each cycle. Methane concentrations are consistently above 50 percent. These lab reactors are operated to determine the best inoculation sequence for the farm reactors and to study possible problems with culture nutrient deficiencies and aging.

The initial agitator drive mechanism consisted of two pneumatic cylinders driving all four agitators through a linkage shaft. This concept minimized the energy input, but introduced severe mechanical problems with proper alignment. This system is presently being modified with a pneumatic cylinder on each reactor. Since only periodic agitation will be used, the additional energy consumed will not be excessive.

The engine-generator has been installed and satisfactorily tested with biogas. A 10 hp induction motor is used as the generator. Negotiations with the local utility for the sale of electricity are underway.

Three replications of field plots were established at the Southwest Center near Mt. Vernon, Missouri, in order to evaluate cropping mixtures for biomass production. Each plot is 30 by 100 feet so that enough material will be produced for evaluation of methane production in pilot studies. Treatments include double cropping winter rye and sorghum-sudan or corn, intercropping tall fescue and red clover or alfalfa or orchardgrass, and monoculture of warm-season perennials such as caucasian bluestem and indiangrass. Plots

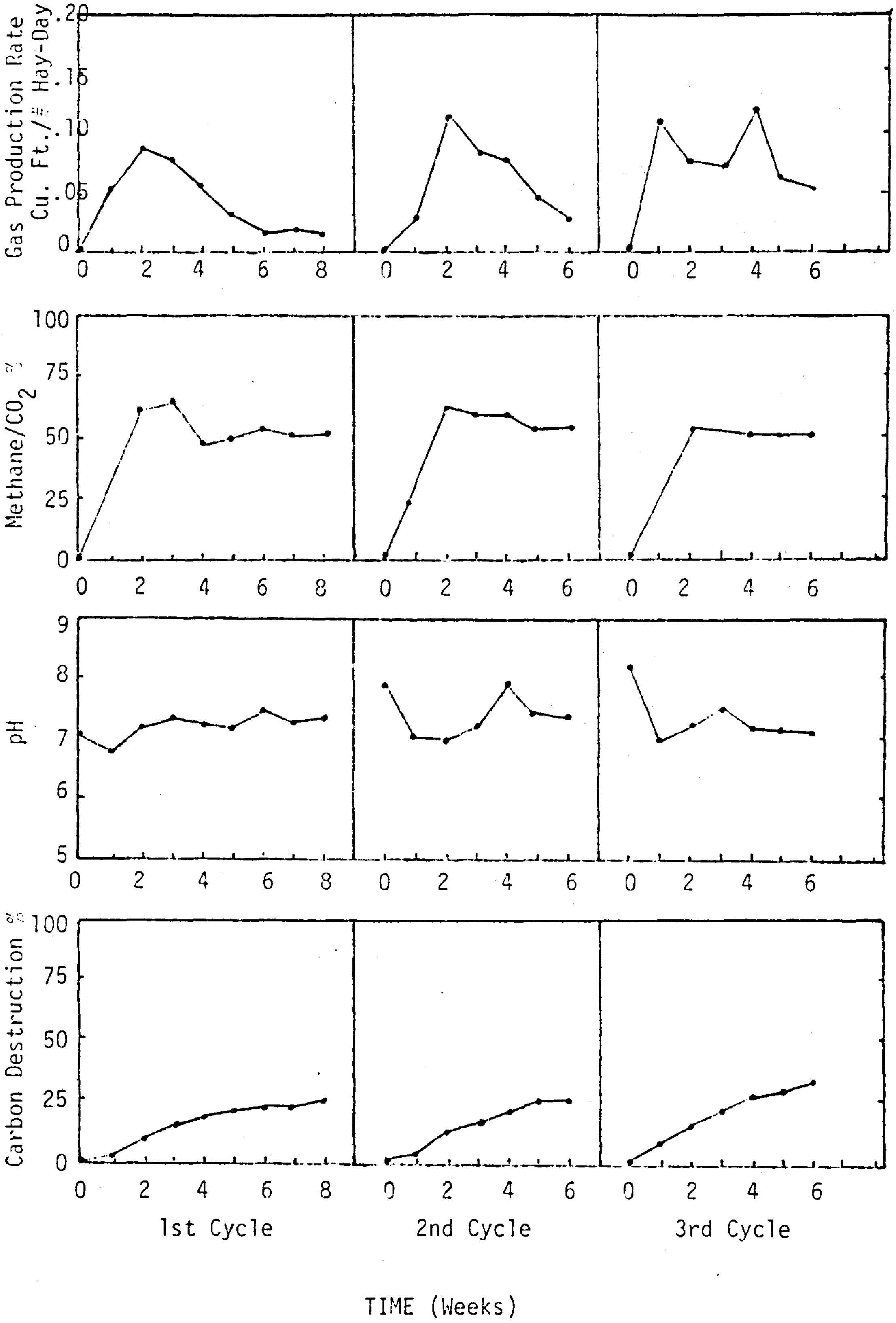


Figure 3. Laboratory Digestor Performance

of the rye component and the cool-season forage mixtures were seeded this fall. The warm-season annuals and perennials will be seeded next spring.

ACID HYDROLYSIS/FERMENTATION STUDIES

The acid hydrolysis pre-treatment of corn stover studies utilize a two stage sulfuric acid contact. In the first stage, dilute sulfuric acid is used to hydrolyze the pentosan fraction of ground biomass. The second stage uses concentrated sulfuric acid for hexosan hydrolysis. The use of the two steps give high yields, possible with concentrated acid, without the problems of pentose decomposition.

Figure 4 gives a typical concentration profile for the pre-hydrolysis step. This hydrolysis is carried out at 98°C with 4.4 percent acid. Figure 5 gives the profile for the second stage with 85 percent acid also at 98°C. As noted, only small quantities of glucose are produced in the pre-hydrolysis. No xylose is present in the hydrolyzote, indicating complete conversion of pentosans in the pre-hydrolysis.

A series of studies is being conducted to determine the optimal temperatures, acid concentrations and reaction times for both steps. Fermentation of the hydrolyzate fractions will begin when these studies are completed.

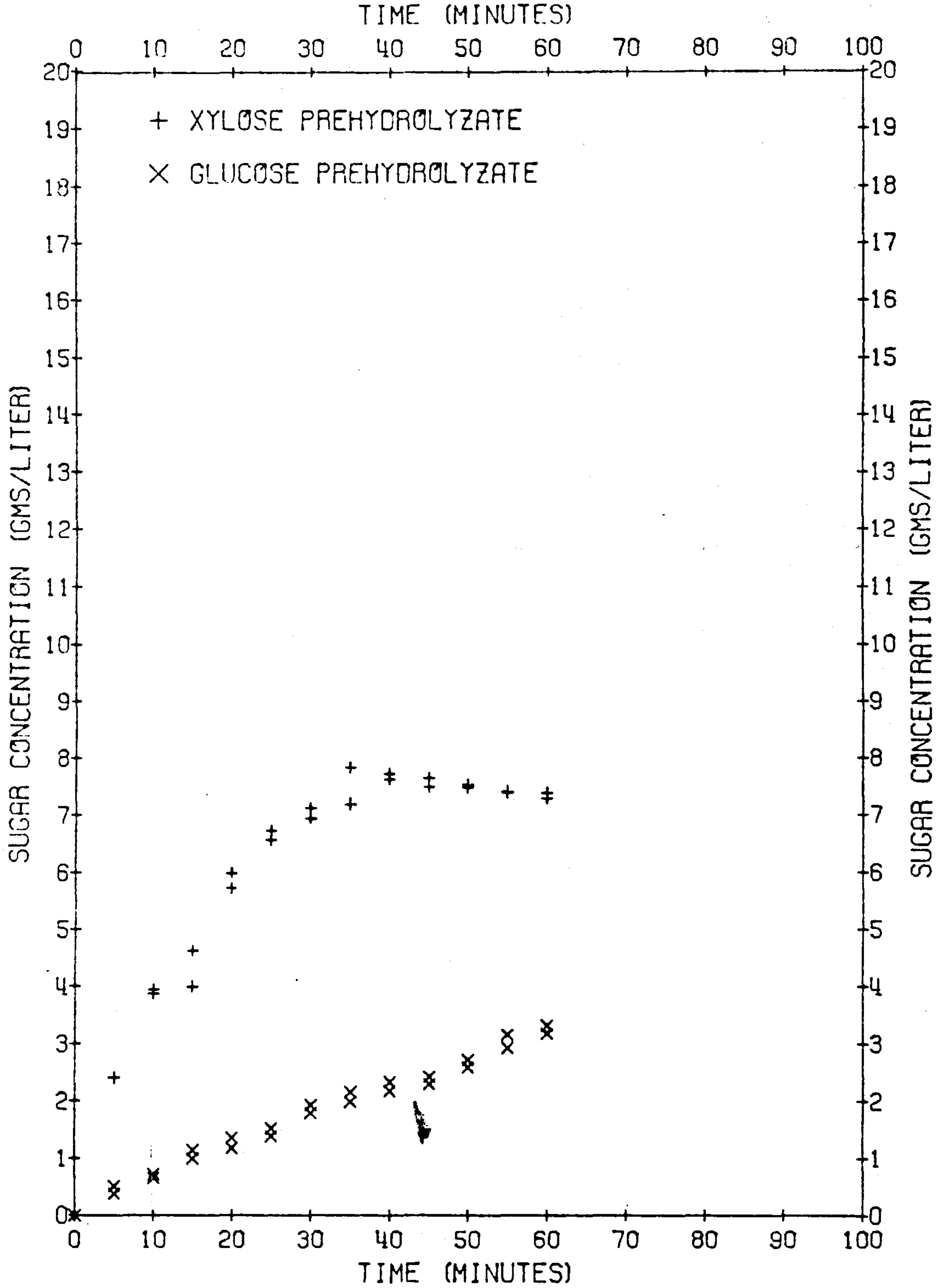


Figure 4. Sugar Formation in Prehydrolysis Step

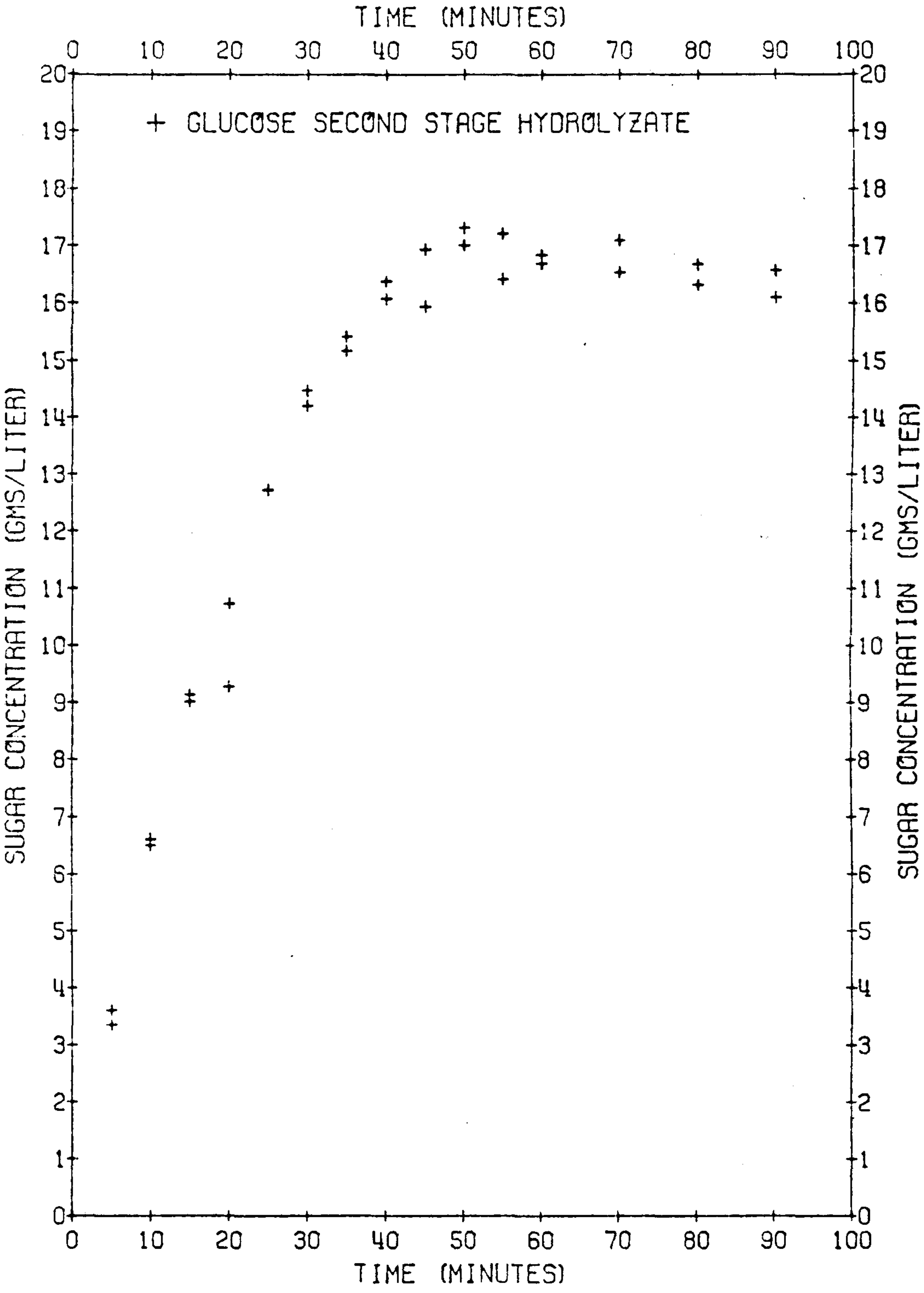


Figure 5. Sugar Formation in Second Hydrolysis

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Report Number COO-EY-S-02-2981-12

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

Twelfth Quarter Progress Report for Period From
March 16, 1979 to June 15, 1979
Plus
Addendum Describing Project Activities From
June 16, 1979 to October 15, 1979

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Prepared For
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Modification A002

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

SUMMARY

The Cornell University project on the conversion of agricultural residues to biogas has as its 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 last scheduled quarter of this study. Due to the delay of funding in the early phase of this study, however, it will be necessary to finish testing and report preparation during the summer and fall of 1979.

Five different types of anaerobic fermentor reactor designs were operated, with the majority of effort focussed on two full scale reactors (both about $35m^3$), each designed to process the manure residues from up to 65 dairy cows. Three pilot units ($5m^3$ 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 more than 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. During the twelfth quarter the full scale plug flow and conventional control reactors were tested in parallel at new conditions of 15 days and 10 days HRT, 35°C and 10-12% TS manure feed. Steady state results for the 15 day HRT condition once more indicated a more efficient solids conversion with the plug flow design (34.1 percent TVS destruction efficiency) than with the completely mixed full scale system (27.8 percent TVS destruction efficiency) when operated on dairy manure (13% TS) at 35°C. No serious operational problems have been encountered with either full scale reactor during the twelfth quarter.

Thermal data from the plug flow reactor has now been obtained for a full year cycle. The apparent overall efficiency of the boiler and reactor heating systems varied between 40 and 55 percent. In order to translate the temperature and operating data of the plug flow unit into a comprehensible energy balance, a computer model for the prediction of energy production and for the description of conducted heat losses and feed heating requirements was developed. The computer program was written in BASIC and used on a Hewlett Packard desk top calculator, model 9830.

Data analysis and the development of certain sections of the final report were given considerable attention throughout the twelfth quarter. Writing on the preparation of the farmer's feasibility manual was also initiated during this period.

Activities throughout the coming summer months will include continued operation of the full scale fermentors through conditions of 10 days HRT at 35°C and 30 days HRT at a reduced temperature, 25°C. It is anticipated that the completion of the last scheduled test runs and preparation of the final report will extend into the 13th quarter (summer, 1979).

REPORT OUTLINE

A. SUMMARY

B. INTRODUCTION

C. OBJECTIVES

D. PROJECT STATUS

1. Proposed Status
2. Present Status
3. Pilot Scale Random Mix Reactor
4. Pilot Scale Plug Flow Fermenter
5. Full-Scale Reactors—Completely Mixed and Plug Flow
6. Plug Flow Fermenter Energy Balance Computer Model
7. Final Report
8. Feasibility Manual

E. FUTURE ACTIVITIES

F. ADDENDUM-Progress Report for the Project Period from June 16 to October 15, 1979

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

INTRODUCTION

It is virtually undebatable that the continued heavy dependence of the U.S. on foreign oil has the potential of seriously aggravating a multitude of world-wide issues related to inflation, unemployment, poverty, political unrest, currency devaluation, recession, foreign policy, etc. However, the severe social and political effects of rapidly increasing energy prices may be mild compared to the potential disruptions that could occur with only modest cutbacks in Middle East oil production. There is definitely an urgent need for accelerated programs of energy conservation and alternative energy development. As new sources of energy are sought, fuels from biomas 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 twelfth 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 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 twelfth quarter, extending from March 16, 1979, to June 15, 1979, have included the following:

1. Collection of steady state data from the full scale plug flow reactor and control unit operated at 15 days HRT, 35°C and 10-12% TS manure feed.
2. Initiation of the full scale reactors into the next condition of 10 days HRT at 35°C and 10-12% TS manure feed.
3. Completion of the last run of the pilot scale plug flow fermentor with steady state data collecting at 25°C, 30 days HRT and 11-13% TS straw and manure feed.
4. Completion of the final experiment with the pilot scale random mix reactor operated at 25°C, 28 days HRT, fed every 7 days with 11-13% manure and straw.
5. Termination of both pilot units and storage of these two units for possible future use.
6. Continued operation of the pilot scale semisolid reactor.

7. Preparation and use of a computer model to predict energy balances for the Cornell plug flow digester and plug flow digesters of varied capacity operated on dairy cow manure.

8. Analysis of data collected from the demonstration phase of the project, from June 15, 1977 to present.

9. The beginning of preparation of the final report of the methane project.

10. The initiation of writing on the Farmer's Feasibility Manual.

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. During the twelfth quarter, the pilot and full scale fermentors were to complete their scheduled tests, the pilot reactors were to be terminated and full scale reactors were to be maintained for possible future studies. The pilot scale random mix reactor (5.0 m^3) was to conclude its experimental testing with manure and bedding at low temperatures and close 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 twelfth quarter was the collection of steady state data from the last operating conditions of the full scale plug flow and conventional control reactor (34 m^3) which included testing at 10 days HRT, 35°C with 10-12% manure feed and testing at a reduced temperature (25°C) at 30 days HRT.

Present Status

Long-term operation of the full scale low-cost reactor has now been ongoing continuously for more 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. Experimentation with the pilot scale reactors has been completed in accordance with the work plan. However, the full scale demonstration phase has had delays, mainly due to the adversity

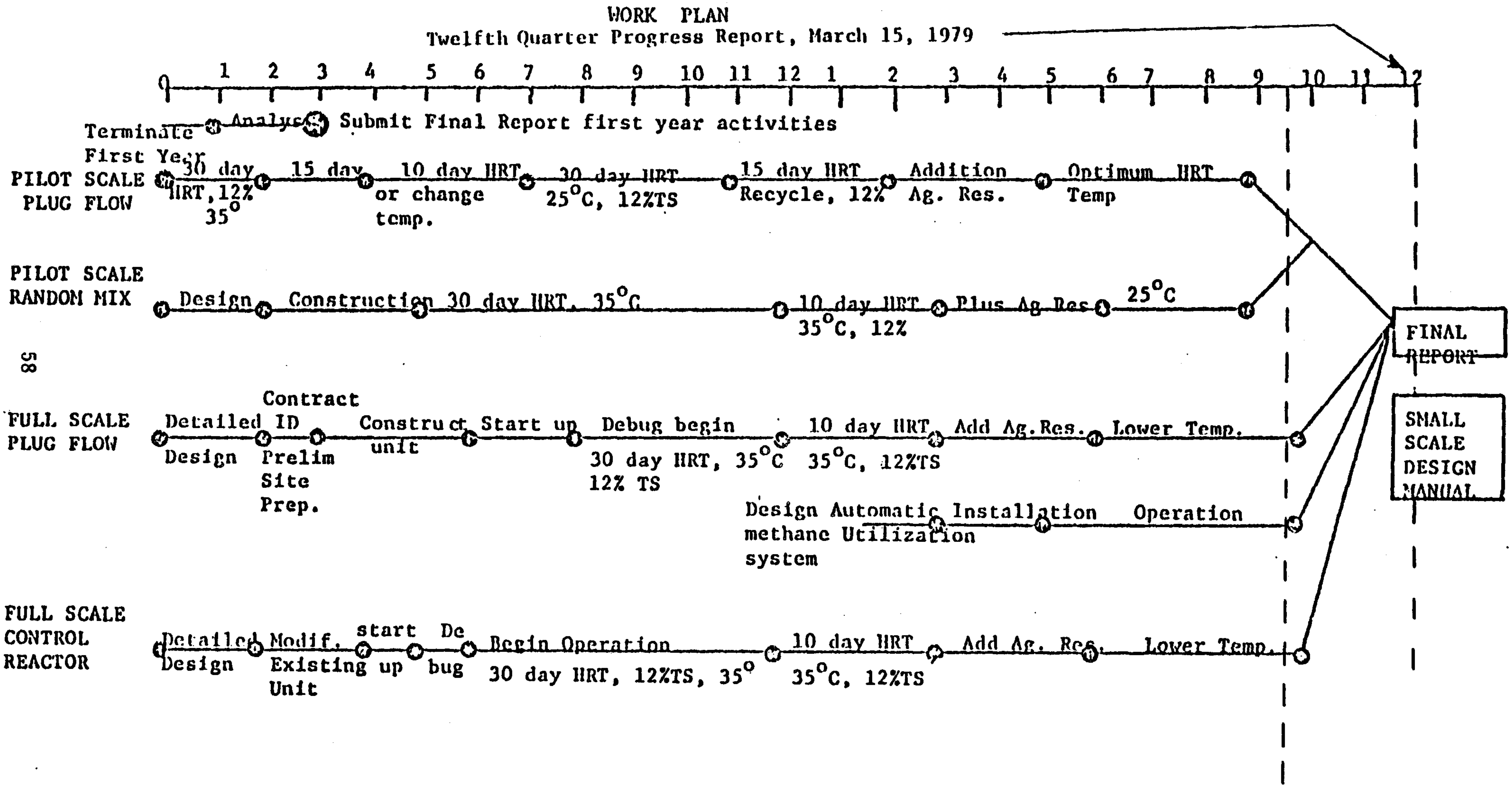
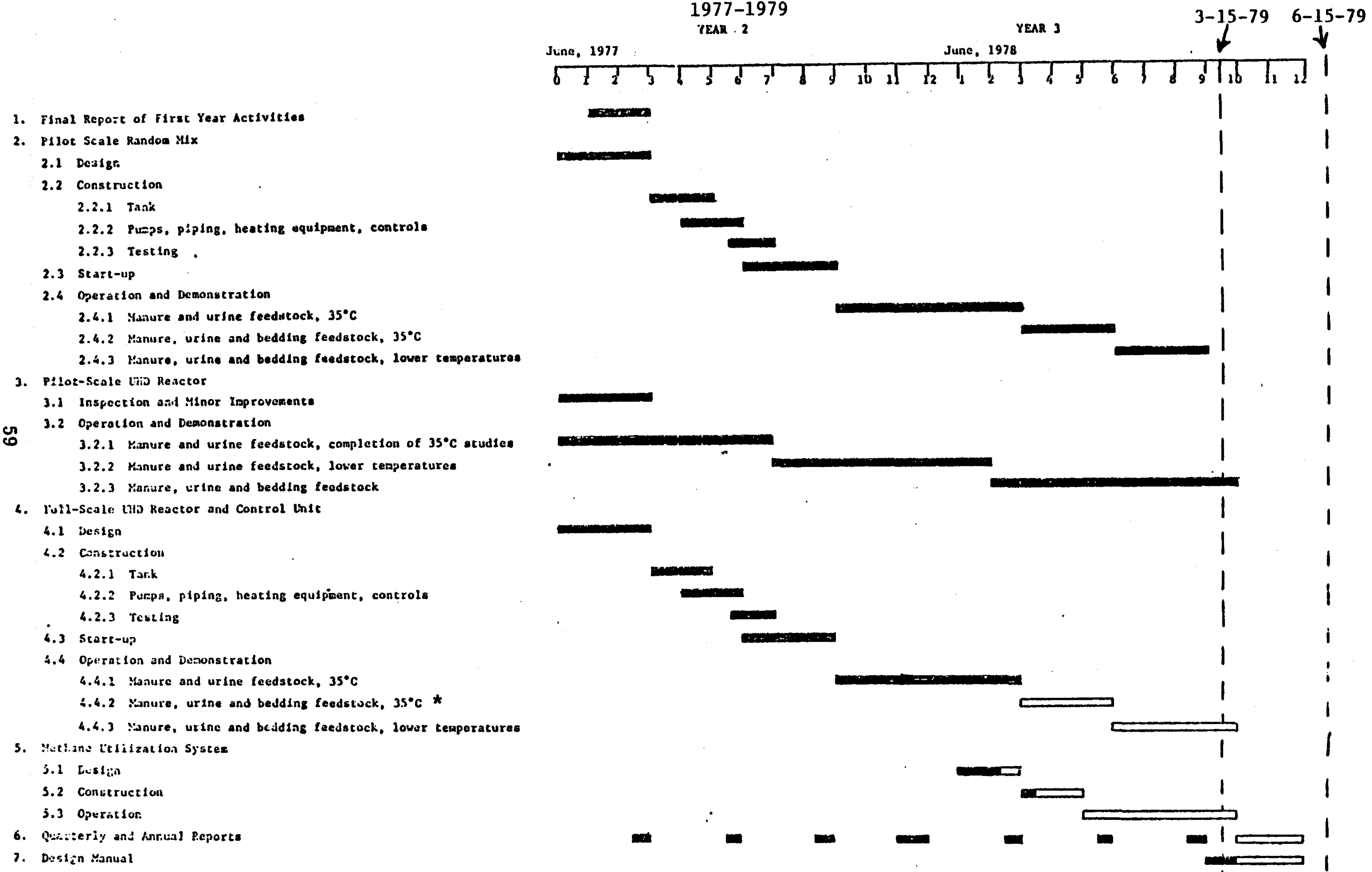


Figure 1. Detailed work plan for the development and demonstration of low cost fermentors.

FIGURE 2. CORNELL UNIVERSITY METHANE PROJECT WORK PLAN

1977-1979



* Substituted with a manure feed experiment at 35°C, 15 days HRT on the basis of observation from bedding addition tests conducted on the pilot scale plug flow fermentor. See Figure 3 comment.

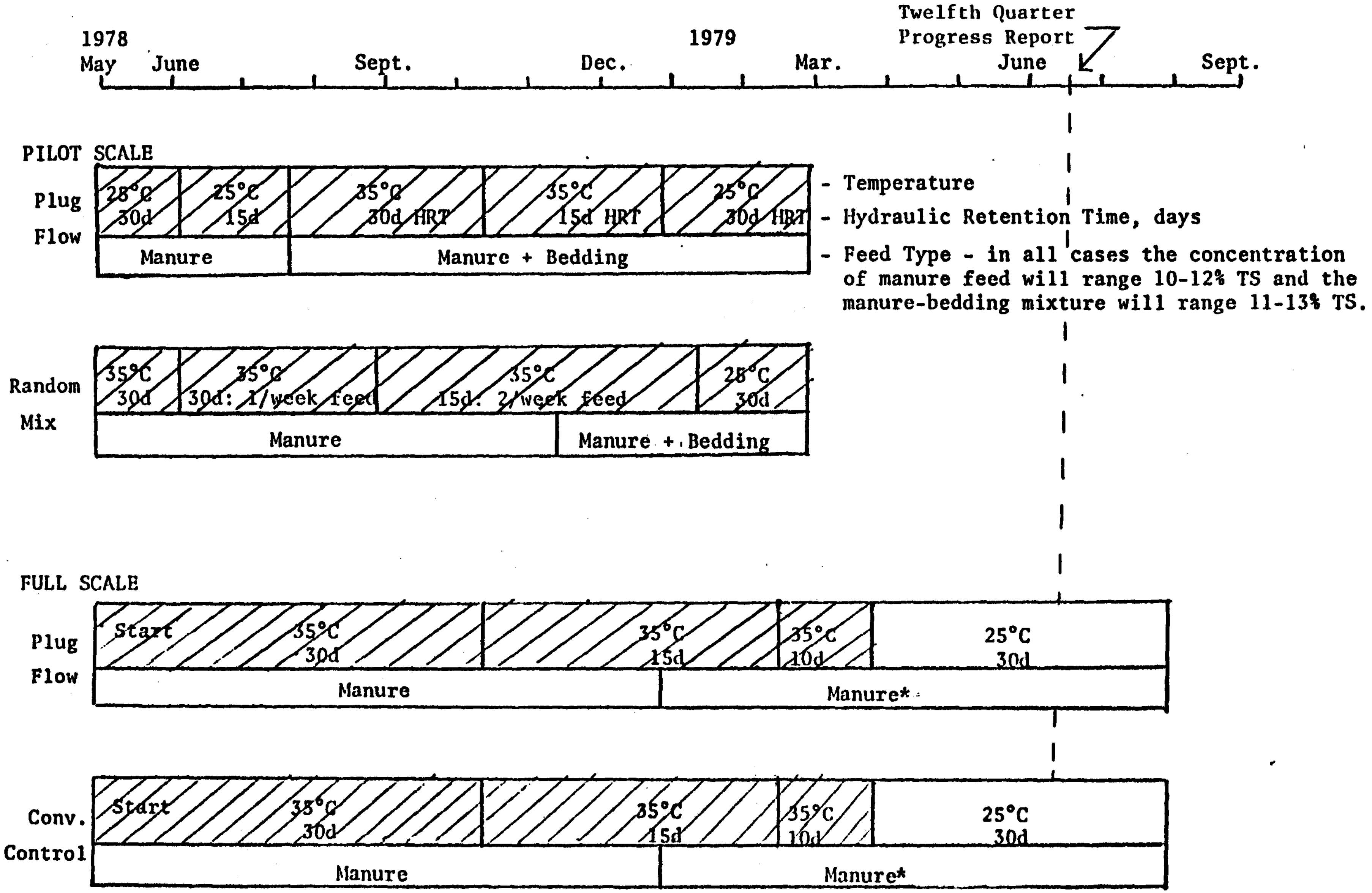
of severe winter weather during the initial construction phase (December 1977 - March 1978). The revised experimental plan was drafted to accelerate the testing program and to narrow the schedule gap, as shown in Figure 3. Progress in reference to the new schedule is indicated, showing a 2 1/2 month overall delay behind the accelerated work plan.

It should be pointed out that as soon as the time for testing the reactors on bedding (as per the work plans of Figures 1 and 2) was reached, a decision had to be made concerning the advisability of straw addition to the large scale units in light of past experience with the pilot scale plug flow reactor. As mentioned in previous progress reports, the addition of straw bedding to the influent of the pilot scale plug flow system while operating under conditions of 15 days HRT, 35°C and 30 days HRT, 25°C, had the pronounced effect of an accumulation of a straw float layer which grew to a substantial thickness, 8-12 inches within two months of operation. Hence, it was decided that the pilot-scale experience was sufficient to predict the probable result of adding certain bedding materials (straw and wood chips) to the influent feed of an unmixed plug flow reactor. It was reasoned that other operating conditions on manure at 35°C and at a low temperature (25°C) would be more useful than the potentially debilitating straw bedding experiments originally planned. These substitutions of experimental protocol are indicated on Figure 3.

Pilot Scale Random Mix Reactor

During the twelfth quarter, the final experiment with the 5.0 m^3 pilot scale random mix reactor was completed and the operation of this

Figure 3. EXPERIMENTAL TESTING PROGRAM



*Since straw bedding additions to the pilot scale plug flow reactor resulted in a substantial accumulation of a straw float layer within a month of operation it was decided that the addition of the same bedding material to the full scale plug flow reactor would have a similar disruptive effect. Consequently, it was decided that an additional test run at 35°C 10 days HRT would be more useful than the potentially debilitating bedding addition experiment.

unit was terminated. This reactor was designed to handle manure from 3 to 10 cows when operated at hydraulic retention timess (HRT) between 30 and 10 days. Throughout the twelfth quarter this unit was operated on a bedding and manure feed mixture at a reduced temperature of 25°C, and fed one quarter of the reactor's volume every seven (7) days; at this feeding mode the reactor was operated at a 28 day HRT. The contents of this limited-mix reactor were only recirculated for a brief period following every feeding. In this last experiment, 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 1.12 m^3/m^3 reactor-day (0.69 m^3/m^3 reactor-day of methane) with a concomitant total volatile solids (TVS) destruction of 26.9 percent. Steady state data from this latest operating condition are shown in Table 1. No significant accumulations of straw bedding, either as a float or settled solids, were observed during the manure-straw feed condition at 25°C for the random mix system.

Comparisons of reactor performances at this condition with data from other operating modes are also provided in Table 1. It is particularly interesting to note that at a 28 day HRT (feeding and mixing every 7 days) the random mix reactor yielded nearly as much daily methane when fed 11-13% TS manure and straw at 25°C (0.69 m^3/m^3 reactor-day) as it did when fed 10-12%TS manure with no bedding at 35°C (0.74 m^3/m^3 reactor-day).

Upon completion of the bedding addition experiment at 25°C, the

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

	Operating Conditions				
Operational and Performance Parameters	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	11-13% TS Manure & Straw 28 days HRT
Feeding Frequency	once/day	once/7 days	once/4 days	once/4 days	once/7 days
Mixing Frequency	once/10 days	once/7 days	once/4 days	once/4 days	once/7 days
Days of Operation	104	90	52	70	55
Average Gas Production					
m^3/day	10.1	6.4	8.2	10.0	6.0
m^3/m^3 reactor/day	2.0	1.3	1.6	2.0	1.12
Methane Production					
m^3/day	6.3	3.7	4.9	5.9	3.7
m^3/m^3 reactor/day	1.3	0.74	0.98	1.2	0.69
Effluent pH	7.8	7.7	7.6	7.7	7.7
TVS Destruction, Percent	37.0	31.4	28.7	22.3	24.5

random mixed reactor was discontinued in operation. The contents of this unit were pumped out and the system was placed in storage for possible dismantling in future months. Random mix reactor experimentation was completed nearly as scheduled.

Pilot Scale Plug Flow Fermentor

The pilot scale plug flow fermentor (5.6 m^3) completed its last experimental run during the twelfth quarter while operated on a feed mixture of manure and bedding. Throughout this period, this reactor system was operated at a mode of 11-13% TS influent, 30 days HRT and 25°C. Bedding was added to the feed at a blending rate equivalent to about 0.68 kg/cow/day (1.5 lbs/cow/day). At this operating condition, the pilot plug flow reactor was producing biogas at a steady rate of about 4.7 m^3 per day (0.84 m^3/m^3 reactor/day) with a total total volatile solids destruction efficiency of 18.0 percent. Steady state data obtained from this condition with bedding addition at 25°C are tabulated in Table 2; data from other previous operating conditions when bedding materials were added to the feed are also included in Table 2.

As mentioned in previous progress reports, the behavior of bedding materials when introduced into the plug flow fermentor with respect to separation from manure seemed to depend upon the type of bedding used and the operating temperature of the digester. Wood chips introduced into the feed at the 30-day HRT, 35°C operating condition did not result in separation while straw introduced at this mode and at a 15-day HRT, 35°C condition produced a fibrous float of 0.15 m (6.0 inches) to 0.76 m (30 inches) thick inside the reactor basin within two months of operation. On the other hand, operation at a reduced temperature of

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	30 days HRT Wood Chips* 35°C	30 days HRT Chopped Straw** 35°C	15 days HRT Chopped Straw** 35°C	30 days Straw 25°C
Days of Operation	44	89	32	55
Influent Solids g/ℓ TS	123	119	118	127
Effluent Solids g/ℓ TS	91.9	81.3	92.2	107.2
Solids Destruction				
TS %	25.5	31.5	21.7	20.1
TVS %	28.9	35.2	25.1	18.0
Effluent pH	7.5	7.5	7.8	7.7
Effluent Alkalinity g/ℓ	16.8	13.6	19.6	19.7
Gas Production				
m^3/day	5.50	4.67	5.85	4.67
m^3/m^3 reactor/day	0.98	0.84	1.05	0.84
Methane Production				
m^3/day	3.30	2.61	3.39	2.76
m^3/m^3 reactor/day	0.59	0.47	0.61	0.50
m^3 CH_4/Kg VS_D	0.55	0.38	0.35	0.73
Gas Composition (Percent CH_4)	60	56	58	59

* Data from the tenth quarter period.

** Data from the eleventh quarter period.

25°C at 30 days HRT allowed prolonged fermentation without straw/manure separation. Apparently, the increased viscosities produced at 25°C in 11-12% TS dairy manure are sufficient to prevent the upward movement of straw fibers caused by gas bubble attachment.

A comparison of straw bedding experiments at 30 days HRT reveals that the methane gas production at 25°C (0.50 m^3/m^3 reactor/day) was approximately equal to the methane production at 35°C (0.47 m^3/m^3 reactor/day). The expectation here, however, would be that far higher energy production should be achievable at the 35°C condition. It seems evident that straw fiber accumulations in the 35°C experiment severely reduced the effective reactor volume to the extent where gas production performance was significantly hindered. It is estimated that, at 35°C, straw fiber had occupied as much as 30 to 40 percent of the reactor; hence, the HRT of the system was effectively reduced from 30 days to about 21 days and the actual conversion efficiencies of organics to methane were substantially decreased from about 0.55 to as low as 0.38 m^3 CH_4/kg volatile solids destroyed.

Experimentation on the pilot scale plug flow reactor was concluded with the collection of steady state data from the final bedding-addition condition at 25°C. All operating conditions outlined for this unit in the work plan have been tested and the pilot study on plug flow fermentation was ended close to the proposed schedule.

Full Scale Plug Flow Fermentor and Completely Mixed Control Unit

Two operating conditions were applied to the full scale plug flow and conventional control fermentors during the twelfth quarter:

15 days and 10 days HRT at 35°C while fed about 13 percent TS dairy manure. For reasons previously given, bedding was not added to the feedstock of the full scale reactors. The experiment at 15 days HRT was completed about two months into the twelfth quarter; steady state data obtained from this condition is shown in Table 3.

Upon completion of the 15-day condition, the hydraulic retention time of the full scale units was then reduced to 10 days HRT. Some initial steady state data for this unit are given in Table 4.

For comparison purposes, the solids destruction and gas production performances of the full scale units operated at 10, 15 and 30 days HRT (35°C, 13% TS manure feed) are tabulated in Table 5; plots of solids conversion and methane yield are presented in Figure 4. The data for the full scale systems indicate that the plug flow reactor consistently maintained higher rates of solids conversion to biogas than its full scale completely mix control. The newest information from the full scale demonstration study agrees well with the results from bench and pilot reactor studies and strongly suggests that the anaerobic fermentation of manure can be greatly simplified in design, operation and cost without sacrificing performance in converting organics to biogas.

By the end of the twelfth quarter period the 10-day HRT condition was nearly completed. By the end of the twelfth quarter, the full scale demonstration effort was running about three months behind the revised schedule.

Plug Flow Fermentor Energy Balance Computer Model

One of the most important aspects of the design and construction of simplified, earthen fermentors is the careful usage of soil drainage

TABLE 3. STEADY STATE DATA FROM THE OPERATION OF THE FULL SCALE PLUG FLOW AND CONVENTIONAL CONTROL FERMENTORS AT 10 DAYS HRT, 35°C and 10-12% TOTAL SOLIDS DAIRY MANURE FEED.

	Completely Mixed Reactor	Plug Flow Reactor
Condition, HRT, days	9.8	10.4
Feed Rate, m^3/day	3.65	3.80
Days of Operation	38	38
Days of Steady State	18	18
Total Solids, gm/ℓ		
Infl.	125.8	125.8
Effl.	96.9	92.4
Red.		
Red., %	23.0	26.6
Total Volatile Solids, gm/ℓ		
Infl.	110.0	110.0
Effl.	81.2	76.8
Red.	28.8	33.2
Red., %	26.2	30.2
Total Biod. Volatile Solids, gm/ℓ		
Refr. Fraction	0.56	0.56
Refr. Solids	61.6	61.6
Infl.	48.4	48.4
Effl.	19.6	15.2
Red.	28.8	33.2
Red., %	59.5	68.6
Gas Production, STP		
m^3/day	82.4	97.3
% CH_4	60	60
m^3 CH_4/day	49.5	58.4
Ft^3 CH_4/day Predicted from BVS dest.	52.6	63.1
Ratio (predicted/observed)	1.06	1.08

TABLE 4. STEADY STATE DATA FROM THE OPERATION OF THE FULL SCALE PLUG FLOW AND CONVENTIONAL CONTROL FERMENTORS AT 15 DAYS HRT, 35°C AND 10-12 PERCENT TOTAL SOLIDS DAIRY MANURE FEED

	Completely Mixed Reactor	Plug Flow Reactor
Condition, HRT, days	14.8	16.1
Feed Rate, m^3/day	2.39	2.45
Days of Operation	57	107
Days of Steady State	26	23
Total Solids, gm/ℓ		
Infl.	129.1	129.1
Effl.	97.9	91.0
Red.	31.2	39.1
Red., %	24.2	29.5
TVS, gm/ℓ		
Infl.	112.1	112.1
Effl.	80.9	73.9
Red.	31.2	38.2
Red., %	27.8	34.1
TBVS, gm/ℓ		
Refr. Fraction	0.56	0.56
Refr. Solids	62.7	62.7
Infl.	49.4	49.4
Effl.	18.2	11.2
Red.	31.2	38.2
Red., %	61.1	75.3
Gas Production STP		
m^3/day	75.3	92.5
% CH_4	55	55
m^3 CH_4/day	41.4	50.9
m^3/CH_4/day predicted from BVS Destruction	37.3	46.8
(ratio of predicted/observed)	0.90	0.92

TABLE 5. SUMMARY OF FULL SCALE OPERATION OF DAIRY MANURE ANAEROBIC FERMENTORS WHEN FED A TS FEED OF 129 gm/ℓ.

		10-day HRT	15-day HRT	30-day HRT	
Gas Production	vol/vol	2.33	2.13	1.13	FULL SCALE COMPLETELY MIXED REACTOR (1250 ft^3)
	ℓ/gm VS_A	0.205	0.281	0.310	
	ft^3/lb VS_A	3.3	4.5	5.0	
Gas Composition	% CH_4	60	55	58	
Solids Destruction	% TVS red	26.2	27.8	31.7	
	% TBVS red	59.5	61.9	70.4	
Gas Production	vol/vol	2.52	2.33	1.26	FULL SCALE PLUG FLOW REACTOR (1360 ft^3)
	ℓ/gm VS_A	.233	0.337	0.364	
	ft^3/lb VS_A	3.7	5.4	5.8	
Gas Composition	% CH_4	60	55	57	
Solids Destruction	% TVS red	30.2	34.1	40.6	
	% TBVS red	68.6	75.8	90.1	

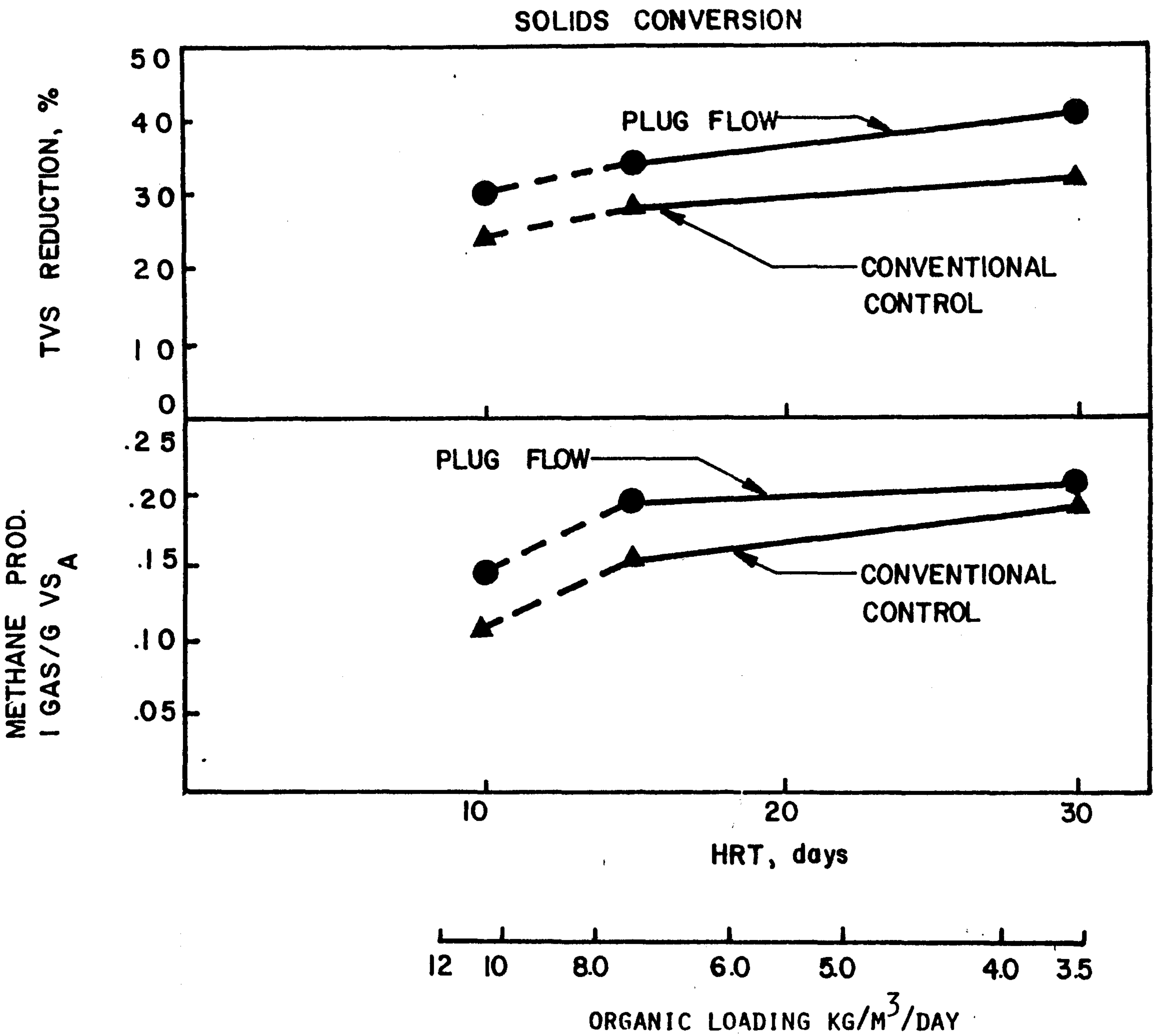


Figure 4. Comparison of solid conversion efficiency in full scale completely mixed and plug flow reactors fed about 13 percent solids dairy manure.

and insulation to conserve energy that would otherwise be lost through conduction. With the Cornell design, the soil surrounding the reactor was kept as dry as possible with the installation of an extensive underdrain system to reduce the heat conductivity of the ground. The reactor walls were lined with 10.2 cm (4.0 inches) foam glass insulation, the gas collection membrane of the unit was covered with 8.9 cm (3.5 inches) of fiberglass insulation and another impermeable rubber cover was placed over the fiberglass to keep the insulation dry. Finally, all exposed liquid surfaces of the moat and effluent section were covered with a 5.1 cm (2.0 inches) of floating polystyrene.

It is intuitive that adequate insulation for the plug flow digester would be especially important in cold climates. The temperature of northern New York often falls below minus 30°C and can average minus 20°C for several weeks. During this period, the heating demand to maintain an anaerobic fermentor at 35°C will be its highest. The digesters at Cornell are heated with their own biogas; in this case the net biogas available for farm use is equal to the total energy production minus the boiler biogas usage required to maintain reactor temperature. Since the space heating demand on most farms is likely to coincide with a period of low net biogas production, it became evident that a careful analysis of the year-round energy balance of the plug flow methane generator was needed.

In the previous progress report, both of the full scale fermentors at Cornell were characterized with respect to energy balances conducted during the coldest months of an Ithaca winter, January and February. The data clearly showed that uninsulated or poorly-insulated systems could result in a net energy demand instead of a net energy surplus during critical winter months. During one cold-weather test period, the insulated plug flow reactor at Cornell, sized for handling manure from 32 cows at a 15 day HRT, was able to produce an amount of net energy that was 44 percent of the gross biogas output at an average ambient air temperature of -18°C (one week) and at a reactor temperature of 35°C.

The calculation of an energy balance for the plug flow digester required the daily measurement of gas flows and temperatures. Using two meters it was possible to directly monitor the total biogas produced, biogas utilized by the boiler and the net biogas available for on-farm use. In addition, temperatures of the reactor, the reactor manure feed and the soil surrounding the reactor were taken daily. Average daily and monthly ambient air temperatures were obtained from the Atmospheric and Sciences Department of Cornell University. Gas flow and temperature data accumulated for almost a year have made it possible to calculate the month-by-month energy distributions associated with the Cornell plug flow system. What was needed at this point was a model to extrapolate the energy balance information obtained from the Cornell system to plug flow reactors of varied capacities and designs.

During the twelfth quarter, a computer model was developed, incorporating basic heat transfer relationships and first order kinetic information from Cornell reactors to provide predictions of energy balances for prismoidal plug flow reactors of various shapes, sizes, loading rates and designs. Heat balance components included the conducted heat loss, H_c, the feed heating requirement, H_F, the total biogas produced, H_T, and the net biogas, H_N, available for use. To complete the energy balance, the energy lost due to the overall inefficiency of the boiler and reactor heat exchanger system had to be calculated; the following equation was used to estimate the overall heating efficiency (E) of the Cornell plug flow digester:

$$E = \frac{100 \times (H_c + H_F)}{H_T - H_N}$$

The value of E was calculated from direct measurements of the total and net gas productions (H_T and H_N, respectively), the feed heating requirement (H_F) as computed from the known influent flow and feed and reactor temperatures, and from the measured conducted heat loss (H_c) obtained by turning off feed and hot water supplies to the digester and recording the reactor temperature drop during a 48-hour period. In the Cornell study, the overall heating efficiency, E, was calculated at around 55 percent. This value was employed in the energy balance model developed for the plug flow reactor, even though greater efficiencies of digester heating could conceivably be achieved through the installation of an automatic stack damper on the gas-fired water heating unit for flue heat conservation and through the use of a water heater instead of a water boiler for greater efficiency of heating recirculated water to temperatures of 60 to 65°C.

Conducted heat losses through the digester top, walls and floor were calculated in the model using the general equation for heat transfer through a flat sheet:

$$H_c = A = 24(T_1 - T_2) \cdot \left[\frac{1}{K_i} + \frac{1}{K_o} + \frac{B_1}{K_1} + \frac{B_2}{K_2} + \ldots \frac{B_n}{K_n}\right]^{-1}$$

where; A = area of section normal to the direction of heat flow (ft^2);

T_1 = temperature of the reactor (°F);

T_2 = Temperature outside the digester barrier (soil or air temperature, °F);

K_i, K_o = inside and outside unit surface conductances (Btu/hour-ft^2-°F);

K_n = coefficient of thermal conductivity of barrier "n" (Btu-inch/hour-ft^2-°F);

and B_n = thickness of barrier "n" (inch).

Feed heating demand was calculated from the straight forward equation:

$$H_F = Q(T_1 - T_2)\ S = \frac{V(T_1-T_2)S}{U}$$

where; H_F = feed heating requirement (Btu/day);

Q = feed flow to reactor (ft^3/day);

T_1 = temperature of reactor (°F);

T_2 = temperature of feed (°F);

U = hydraulic retention time (days);

V = reactor volume (ft^3);

S = density of feed (lbs/ft^3).

The total energy production was calculated from a first order kinetic expression developed for solids conversions in plug flow fermentor systems operated between 10 and 30 days HRT. The mass conversion rate of biodegradible volatile solids (BVS) was calculated by the following equations:

Influent BVS $S_o = C_o \times (1-R)$

Effluent BVS $S_1 = S_o e^{-ku}$

Biogas Production $H_T = \dfrac{f\ (S_o - S_1)\ Y\ V\ 1000}{U} = \dfrac{1000\ fYVS_o\ (1-e^{-ku})}{U}$

where C_o = influent volatile solids concentration, g/l;

S_o = influent BVS, g/l;

S_1 = effluent BVS, g/ℓ;

R = refractory volatile solids fraction = .56;

f = conversion factor = 0.0623 lbs ℓ/g u ft^3;

k = first order kinetic rate constant, 35°C, for dairy manure, $days^{-1}$;

U = hydraulic retention time, days;

Y = methane yield 8.0 ft^3/lb BVS destroyed;

V = volume of reactor, ft^3;

H_T = total energy production 10^6 Btu/day.

The components of the energy balance were then used in an energy balance equation to calculate the net energy production of the plug flow digester:

$$H_N = H_T - \frac{100(H_c + H_F)}{E}$$

where H_N = net energy production, Btu/day;

H_T = total energy production, Btu/day;

H_c = conducted heat loss, Btu/day;

H_F = digester influent heating requirements, Btu/day;

E = overall digester heating efficiency.

These energy balance equations were incorporated into a model which was written in BASIC program language to be used on a Hewlett Packard desk top computer, model 9830A. The most important input parameters and the ranges of values used for them in the program are tabulated in Table 6. Average monthly temperature data used in this analysis are shown in Table 7; temperatures of the best, base (average) and worse case scenarios are also included. Upon entering the appropriate values for design and operating parameters, an energy balance output on the plug flow

TABLE 6. ASSUMPTIONS AND PARAMETER INPUTS USED FOR THE PLUG FLOW REACTOR ENERGY BALANCE COMPUTER PROGRAM

Parameter	Range of Value(s) Used	Comment
Capacity	25 to 500 dairy cows	
Total Depth	1.5-3.0m (5-10 ft.)	Varies with capacity from 1.5 deep for a 25 cow unit to 3.0 m deep for a 500 cow digester. Shallower digester depths may be advisable for high water table areas.
Liquid Depth	1.04-2.54 m	Total Depth minus 0.46 m freeboard.
Length to Width Ratio as measured at ground surface	3.7	Cornell system L/W ratio.
Slopes of digester walls	45° Endwall 40.6° Sidewall	Walls have to be sloped to 45° or less in order to work with the earthen materials.
Insulation		
Walls	10.2 cm (4")	Foam Glass
Floor	10.2 cm (4")	Foam Glass
Liquid surface, moat and effluent end	5.1 cm (2")	Polystyrene (floating)
Gas collection bag	8.9 cm (3.5")	Fiberglass
Kinetic Information		
First Order Rate Constant, 35°C	0.083 days^{-1}	Determined from Cornell pilot and full scale plug flow fermentation studies.
Refractory TVS Fraction	0.56	Determined from bench scale batch reactors.

TABLE 7. TEMPERATURE DATA OBTAINED FROM THE CORNELL PLUG FLOW REACTOR AND USED IN THE ENERGY BALANCE MODEL.

Month	TEMPERATURES, °C				
	Ambient Air	Feed	Effluent	Earthen Wall*	Floor**
Jan	- 7.8	5.0	25.0	14.8	17.8
Feb	-11.1	5.0	25.0	10.0	16.1
Mar	- 2.8	8.0	28.0	13.0	16.1
Apr	5.0	10.0	28.0	14.2	18.3
May	12.2	15.0	29.0	18.0	23.9
June	17.2	18.0	29.0	21.2	26.7
July	19.4	20.0	30.0	19.5	26.7
Aug	19.4	20.0	30.0	19.5	26.7
Sept	13.3	18.0	30.0	20.0	23.9
Oct	7.8	14.0	29.0	20.0	21.1
Nov	3.3	12.0	28.0	17.2	20.0
Dec	- 3.9	7.0	27.0	15.8	19.4
Best Case	19.4	20.0	27.0	19.5	27.0
Worst Case	-11.1	5.0	16.1	10.0	16.1
Average Case	6.0	12.7	19.0	16.9	21.4

* Average of four temperatures taken evenly distributed along the sloping lateral wall 4" into the soil.

** Temperature of soil taken 4" below reactor floor.

fermentor could be obtained as described in Table 8. This program then became a potentially useful tool in translating the data from the 1360 ft^3 plug flow reactor operated at Cornell to other hypothetical systems of varied designs, operating conditions and capacities, exposed to different climatic conditions.

Of great interest was the effect of dairy farm size on the net amount of biogas as predicted by the model. This relationship is shown in Figure 5 for a 20-day HRT plug flow fermentor. The computer energy balance model indicated that as the volume of the plug flow reactor is increased the per animal net energy production is generally increased. Reactor scale-up from a 50-cow digester to a 500-cow unit, for example, would likely result in an increase in the normalized net energy production from 23.9 to 27.0 MJ/cow/day, a rise of 12.7 percent.

Greater per cow net biogas yields at the larger reactor capacities are mainly due to the decreased conducted heat loss per unit volume liquid contents; this effect is seen in Figure 6. The high per-volume conducted heat losses, most noticeable at capacities below 100 cows, are predisposed by higher surface area to volume ratios that increase with decreasomg reactor capacity for the prismoidal plug flow fermentor design, as shown in Figure 6.

Detailed Energy balances for the computer simulation of 100 and 500 cow reactors operated at 35°C under average case temperature conditions are presented in Table 9. This table shows that the greatest energy demands are exerted by the feed heating requirements and the heating inefficiency of the boiler itself. These demands could be substantially reduced, however, through the addition of automatic stack damping to the water heater to minimize the escape of hot flue gas

TABLE 8. OUTPUT INFORMATION FROM THE CORNELL PLUG FLOW REACTOR ENERGY BALANCE COMPUTER PROGRAM.

Information Category	Data Printout
I. Reactor Geometry	Length (ft); Width (ft.); Depth (ft.); Endwall Slope (degrees); Sidewall Slope (degrees); Reactor Volume (ft^3).
II. Kinetic Information	HRT (Days); Influent TVS g/l; Refractory Fraction; First Order Rate Constant (Days^{-1}); Methane Yield (Percent); Energy Production (Btu/day).
III. Energy Balance	
Temperatures (°C)	Reactor; Ambient Air; Influent; Effluent; Biogas; Average Soil 4" from the Reactor Walls;
Energy (Btu/day)	Walls; Floor; Moat Surface; Effluent; Gas Collection Biogas; Total Conducted Heat Loss; Feed Heating; Conducted plus Feed Heating; Water Heater Input, Gross Energy Production; Net Energy Production; Net Energy-percent of Gross Energy Production.

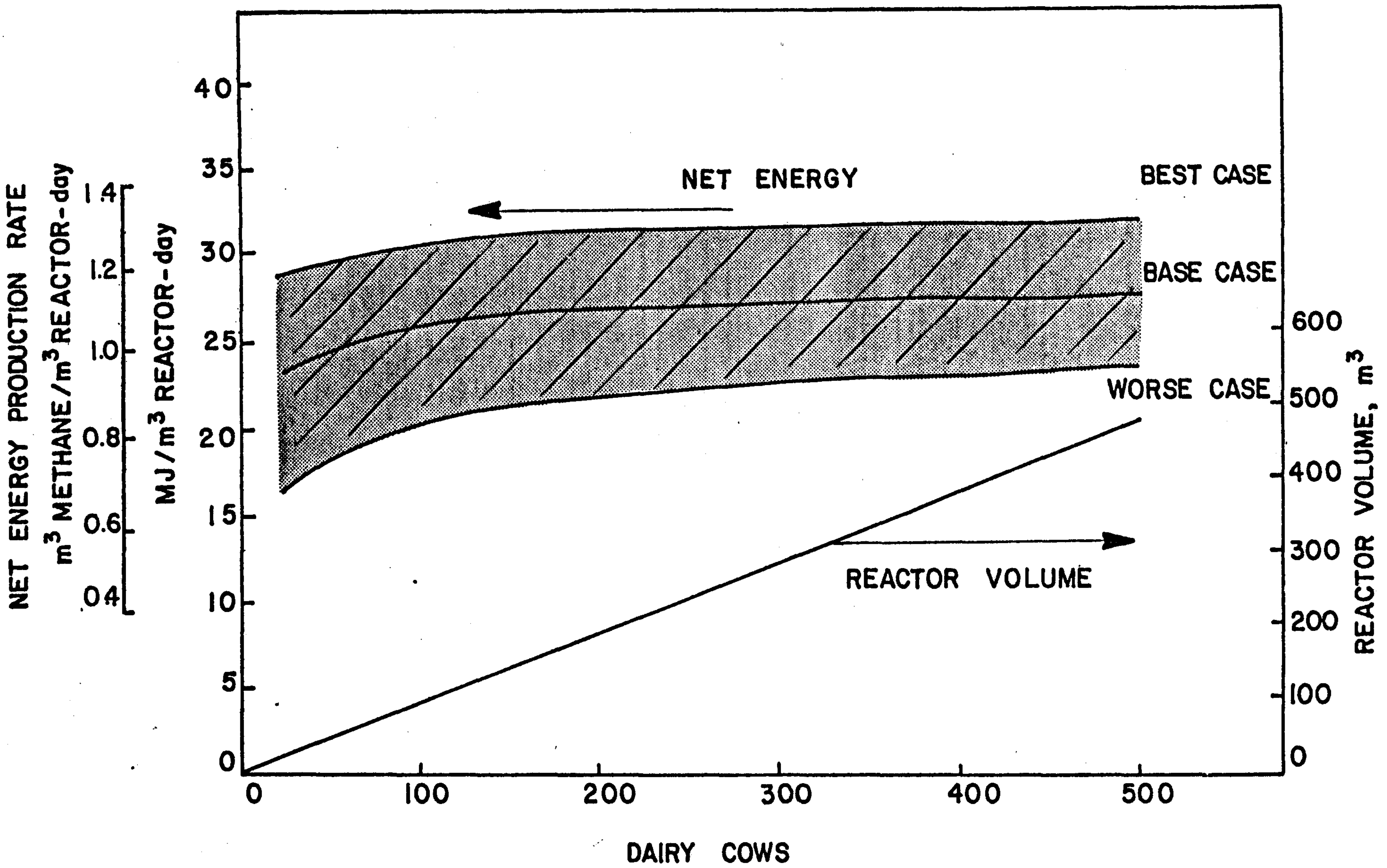


Figure 5. Net Energy Production Per Cow Versus Capacity for Plug Flow Fermentors Operated on Dairy Manure at 35°C in Climates Similar to Upstate New York as Predicted by the Cornell Reactor Energy Balance Model.

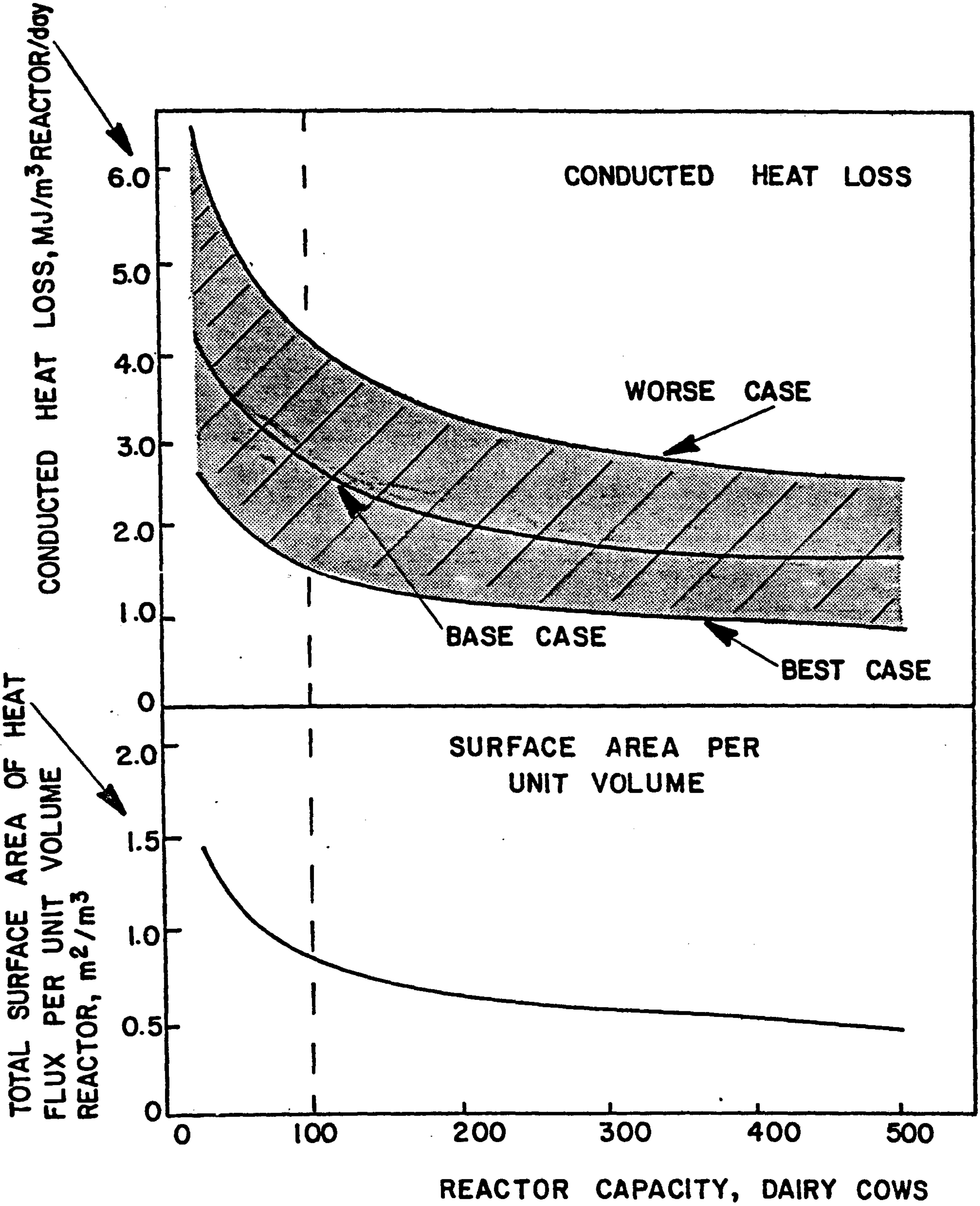


Figure 6. Conducted Heat Loss and Wall and Reactor Top Surface Area per Unit Volume Versus Capacity for Plug Flow Fermentors Operated on Dairy Manure at 35°C in Climates Similar to Upstate New York.

TABLE 9. ENERGY BALANCE ON THE PLUG FLOW REACTOR OF 100 AND 500 COW CAPACITIES OPERATED AT 35°C, 20 DAYS HRT, AVERAGE CASE TEMPERATURES.

Energy Component	100 Cows		500 Cows	
	GJ/day**	% of Total	GJ/day	% of Total
Energy Demands				
Walls	0.074	1.9	0.19	1.0
Floor	0.013	0.3	0.059	0.3
Top	0.168	4.4	0.53	2.8
Feed	0.452	11.9	2.26	11.9
Heating Inefficiency	0.578	15.3	2.49	13.1
Net Energy Prod.	2.51	66.2	13.5	70.9
Gross Energy Production	3.80		19.0	

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* Assuming an overall reactor heating efficiency of 55%.

** GJ = Giga Joule = 10^9 Joules.

during burner shutdown, and through the use of heat exchange equipment to transfer heat from the effluent at 30°C to the colder influent stream at 2 to 20°C.

The projected year-round variation of net biogas production from a 100 cow plug flow digester operated at 20 days HRT at 35°C, as affected by cold weather, is shown in Figure 7. It would be expected that any energy conservation measures, like those mentioned above, would not only have the effect of increasing the total yearly net energy production, but would tend to buffer the month to month changes in available net energy output as well.

Final Report

Data analysis and the writing of the final report received much attention in the twelfth quarter. A detailed outline of this document was prepared early in the last quarter which will serve as a basis for the general organization of the report. It is expected that the writing of the first draft of the final report will extend well into the summer. By the end of the twelfth quarter period, the preparation of the final report was 1 1/2 months behind schedule.

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. During the twelfth quarter, development of certain sections of the manual was initiated with respect to data and literature collation. This document will not be an extensive or comprehensive set of instructions on the construction of anaerobic fermentation systems, but rather a practical

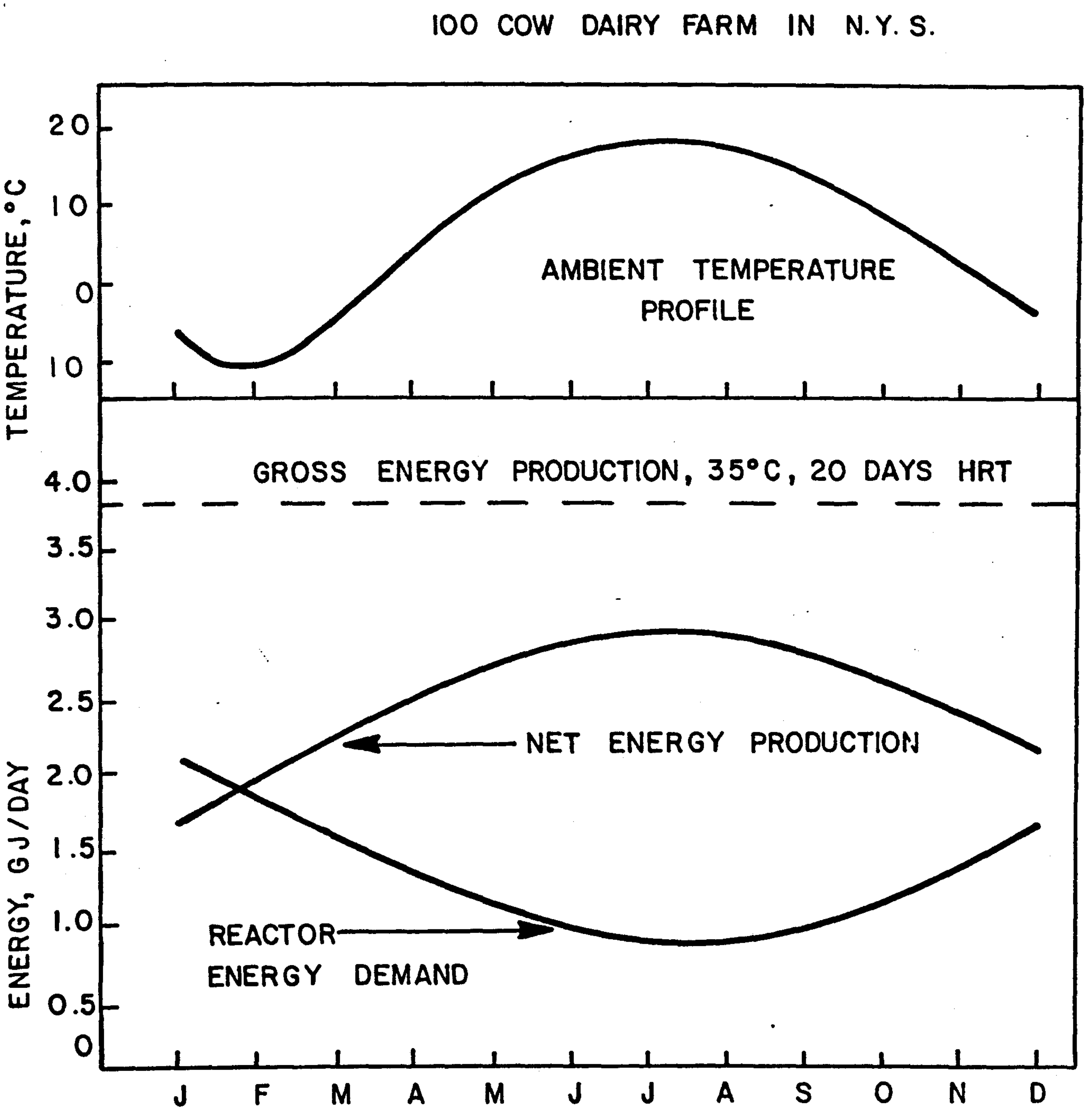

Figure 7. Predicted Annual Variation of Net Energy Production from a 100 Cow Plug Flow Anaerobic Fermentor Operated at 20 Days HRT, 35°C, fed 13 percent TS Dairy Manure.

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.

Because a great amount of attention was given to completing the pilot reactor experiments, maintaining the full scale reactors and data analysis for the final report, the farmers feasibility manual was not completed in the twelfth quarter. Thus, progress on the preparation of the manual is now behind schedule by about 1 1/2 months.

FUTURE ACTIVITIES

The Cornell Methane Project will continue its work into the summer of 1979, beyond the originally intended concluding date of June 1, 1979. However, as mentioned in previous progress reports, the present demonstration phase of the project fell behind the originally proposed schedule due to an unfortunate 3 1/2 month delay in receiving the necessary funds from DOE. Because the construction of the full scale units was forced to coincide with the winter months, adverse weather added more delays to the start-up and testing of the demonstration scale fermentors. The revised work plan of Figure 3 has helped to accelerate project activities so that the proposed experimentation might be concluded reasonably close to schedule.

Although the pilot-scale reactor testing program has already been concluded, operation of the full scale reactors will be extended into the next three-month quarter period. Within the next two weeks in June, additional steady state data will be obtained from the large plug flow and conventional control reactors while operating at 35°C, 10-12% TS and 30 days HRT. The reactors will then be shifted to low-temperature operation at 25°C while fed dairy manure at 10-12% TS, 30 days HRT.

As previously stated, experimentation at the pilot scale has made it possible to assess the probable response of unmixed plug flow and random mix (intermittant mix) fermentation systems to straw and wood chip bedding additions to dairy manure feeds. Solids accumulation data from the pilot scale plug flow fermentor operated on straw bedding and manure mixtures have shown that straw addition to an unmixed fermentor at 35°C will probably result in a substantial solids flotation problem, although the same pilot unit at 25°C experienced little problem with float formation. In light of the information already obtained at the pilot scale on bedding-manure feeding, the straw addition runs planned for the full scale units have been replaced with one more manure feed run at 35°C (15 days HRT) and one manure feed condition at 25°C (30 days HRT) to obtain more kinetic information on the full scale fermentation of dairy cow manure.

In the next three months, increased emphasis will be given to the preparation of the final report and the farmers feasibility manual. Data analysis for the next quarter will include continued definition of the full scale and pilot scale simplified reactors and a close examination of the total energy balance on the earthen, full scale, plug flow fermentor under various operating conditions. The development of computer models for fermentor costing and economic analysis will also be a part of the report preparation activities planned for the coming quarter.

Finally, during the next quarter period the Methane Project Team will be prepared to respond to comments or requests for clarification from DOE concerning the continuation proposal submitted to DOE May 18, 1979. The new proposal included a 3-year research plan for areas of continued testing of the dairy farm fermentors (plug flow and conventional control), swine manure fermentation, biogas storage and utilization and dry fermentation of crop residues. Discussions with DOE will continue over the coming months to reach an agreement on the future research directions outlined in the Cornell proposal.

Addendum Progress Report

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

June 16, 1979to October 15, 1979

Cornell University
Ithaca, NY

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

Addendum Progress Report

June 16, 1979 to October 15, 1979
Cornell University, Ithaca, NY

PROJECT STATUS

During the period between June 16 and October 15, 1979 the Cornell Methane project continued work toward the completion of the tasks outlined in the work plan. This brief addendum will outline the accomplishments contributing to the progress of the project within this period.

Pilot Scale Plug Flow and Random Mix Fermentor Units

Experiments involving these reactors were concluded in the twelfth quarter period. During the summer months these systems were cleaned out partially dismantled. Some of the components of these systems were salvaged for possible use in future fermentation research. However, some of the materials from the pilot reactors seem to be unsalvageable and will probably be discarded.

Full Scale Plug Flow and Conventional Control Fermentors

By the end of June, 1979, the full scale plug flow and conventional control reactors concluded their steady state operation at 10 days HRT, 35°C, 10-12% TS manure feed. Steady state biogas production rates averaged 2.45 m^3/m^3 reactor/day (60 percent methane) with total volatile solids (TVS) destruction efficiency of 30.2 percent for the plug flow fermentor compared to 2.33 m^3/m^3 reactor/day biogas production (60 percent methane) and a 26.2 percent TVS destruction efficiency for the conventional control. Both fermentors operated at the 10-day condition without noticeable signs of stress. But it is again apparent from the steady state data that the simplified, low cost, plug flow fermentor is capable of out-performing the completely-mixed conventional system in solids destruction and gas production, even at the higher hydraulic loadings. The 10-day HRT condition was the last experiment to be completed at 35°C.

Following this condition, both full scale systems were shifted in operation to a lower temperature, 25°C while fed 10-12% TS dairy manure (no bedding) at a 30 day HRT. The reactors were then operated at the lower temperature condition from the first week in July through October 15, 1979. As of mid-October, the 25°C reactors had just entered steady state in operation with respect to gas production. Data from the low temperature operation at 30 days HRT are presented in Table 10. Also presented in this table are steady state data from the three previous runs at the higher temperature of 35°C. In switching from 35°C to 25°C at 30 days HRT, both full-scale units experienced a decline in gas production of about 24 percent. It is interesting to note that, even at the lower reactor temperature, the full scale plug flow fermentor was able to achieve significantly higher rates of biogas production and solids destruction that the high-technology conventional control fermentor.

Cost Assessment and Economic Analysis Computer Model Development

An integral part of the final report and the farmers feasibility manual is the description of the economics of methane generation on the farm. During the summer months of 1979, two computer models were

TABLE 10. COMPARISON OF GAS PRODUCTION AND SOLIDS CONVERSION DATA FROM THE FULL SCALE PLUG FLOW AND CONVENTIONAL CONTROL FERMENTORS OPERATED ON DAIRY MANURE AT 35° AND 25°C.

		35°C			25°C	
		10-day HRT	15-day HRT	30-day HRT	30-day HRT	
Gas Production	vol/vol	2.33	2.13	1.13	0.86	Full Scale Completely Mixed Reactor
	ℓ/gm VS_A	0.205	0.281	0.310	.266	
	ft^3/lb VS_A	3.3	4.5	5.0	4.3	
Gas Composition	% CH_4	60	55	58	58	
Solids Destruction	% TVS red.	26.2	27.8	31.7	16.2	
	% TBVS red.	59.5	61.1	69.7	36.8	
Gas Production	vol/vol	2.45	2.33	1.26	0.96	Full Scale Plug Flow Reactor
	ℓ/gm VS_A	0.233	0.337	0.364	.283	
	ft^3/lb VS_A	3.7	5.4	5.8	4.5	
Gas Composition	% CH_4	60	55	57	57	
Solids Destruction	% TVS red.	30.2	34.1	40.6	23.5	
	% TBVS red.	68.6	75.3	90.0	53.4	

formulated to carry out this analysis. One program was developed for use on a desk top computer (Hewlett Packard, model 9830) to allow the rapid calculation of the capital costs of plug flow reactors of varied dimensions, designs and capacities. The costing model was formulated by first performing a detailed, cost-element accounting of the Cornell plug flow fermentor, then developing equations to extrapolate these estimates to other plug flow fermentor systems of given design and capacity. Cornell's plug flow reactor, the example for the cost analysis, had a manure-handling capacity equivalent to 22 to 65 dairy cows when operated between 30 and 10 days HRT. The cost model was made applicable for reactor capacities between 25 and 500 dairy cows.

Capital costs associated with the construction of a plug flow reactor were divided into 18 categories or components. Costing elements and the basis for scale-up used on each of these items to estimate costs of other plug flow fermentor systems are summarized in Table 11.

The general costing approach taken here was to consider the plug flow reactor as an energy generation facility to be integrated into an existing liquid manure-handling system consisting of a barn scraper system, ram pump and a holding pond. This type of system is not uncommon, since many dairy cattle operations in the U.S. (particularly the larger ones) have adopted liquid-waste handling to control labor costs.

Examples of data generated from the cost assessment program are seen in Table 12 which gives a detailed breakdown of construction costs for 100 and 500 cow digesters, operated at 20 days HRT, 35°C. The highest cost items at both digester capacities are the insulation for the earthen basin (about 20% of total cost), labor (16%), and the flexible gas collection material (10%).

TABLE 11. BASES FOR SCALE-UP OF COST COMPONENTS OF PLUG FLOW FERMENTORS CONSTRUCTED FOR ON-FARM GENERATION OF METHANE.

Cost Component	Costs Associated With Cornell's Plug Flow System (32-Cow Capacity)	Basis for Scale-Up
1. Excavation	$ 364	Earth displaced to dig the basin and to install the underdrains
2. Underdrain	576	Gravel and pipe required, f(reactor dimensions)
3. Grading	309	f (reactor volume)
4. Wall Hypalon	679	f (reactor wall & floor areas)
5. Gas Cover Material	1,209	f (top surface dimensions)
6. Gas Cover Anchoring	1,164	Placed every 2 ft, 1 1/2 ft bel liquid surface, f(reactor perimeter)
7. Basin Insulation	2,913	f (wall and floor areas, inches of foam glass insul. thickness)
8. Gas Cover Insulation	574	f (gas collection bag area)
9. Liquid Surface Insulation	105	f (moat and effluent end liquid surface areas, floating)
10. Water Heater	462	f (worse case reactor heating requirements, heating efficienc
11. Reactor Internal Heat Exchanger	472	f (worse case heating required, diameter of pipe used, pump flow rates of recirculated hot water, black steel pipe assumed 4" diam.)
12. Thermostats and Wiring	390	f (reactor volume)
13. Gas Transport Lines	200	f (reactor length)
14. Baffle	37	f (reactor width, depth)
15. Influent and Effluent Piping	1,357	Black steel, 8" diam, f (reactor length)
16. Equipment Housing	600	Floor area constant, 10 ft x 10 ft at $6.00 per ft.^{2}
17. Labor	2,208	Using the Cornell system labor requirement as the reference fo scale-up; 25% of labor - fixed at 60 man-hours 25% of labor - scaled up on basis of reactor perimeter
TOTAL	$13,619	

TABLE 12. CAPITAL COST COMPONENTS OF PLUG FLOW REACTORS OF 100 AND 500 COW CAPACITIES OPERATED ON DAIRY CATTLE MANURE AT A 20 DAY HYDRAULIC RETENTION TIME.

Cost Component	100 Cows		500 Cows	
	Dollars	% of Total	Dollars	% of Total
Excavation	786	3.5	3136	5.3
Underdrain	891	4.0	1945	3.3
Grading	668	3.0	2666	4.5
Wall Hypalon	1064	4.8	24.6	4.1
Gas Cover Material	2236	10.0	6019	10.1
Gas Cover Anchoring	1642	7.4	2857	4.8
Basin Insulation	4711	21.1	11257	18.9
Gas Cover Insulation	1366	6.1	4542	7.6
Liquid Surface Insulation	153	0.7	295	0.5
Water Heater	678	3.0	1951	3.3
Heating Pipes	1218	5.5	5500	9.2
Thermostats and Wiring	910	4.1	4550	7.7
Gas Lines	300	1.3	500	0.8
Baffle	66	0.3	169	0.3
Influent/effluent Piping	1500	6.7	1500	2.5
Equipment Housing	600	2.7	600	1.0
Labor	35.2	15.8	9560	16.1
Base Cost	22301		59463	

Total capital costs for digester systems constructed on New York State dairy farms are presented in Table 13. Capital costs for the plug flow reactor design range from about $120 per cow for 500 cow operations to about $500 per cow for a 25 cow unit. From the capital costs in Table 13 it can be seen that there is great flexibility in selecting a reactor size to match anticipated biogas demands without significantly increasing the capital cost. For farm operations less than 100 dairy cows, it appears that the basin size of an earthen fermentor is not a highly cost-sensitive design variable. Expansion of the simplified plug flow digester from 15 to 20 days (a 33% increase in volume) would result in an additional cost of less than $2,300, a 7 to 8 percent increase, for the smaller dairy farms. The modest nature of the cost increase in this case is due to the relatively low construction cost of the reactor basin itself as compared to the fixed costs of the system such as heating equipment, piping, electrical work, fixed labor, equipment housing, etc. Even at the 500-cow scale, an additional capital expenditure of only 15 percent would be required for this kind of increase in reactor volume.

The economics of methane generation from cattle waste were examined for various sizes and applications of the Cornell plug flow fermentor by estimating net energy production rates from the heat balance model, by calculating capital costs with the reactor costing model, and by inputing the data from these programs into an economics model formulated by Ecotope Group (Coppinger, et al., 1978). This model has been programmed for use on the Hewlett Packard HP 9830 desk top computer and for use on the Hewlett Packard HP 97 and Texas Instruments TI58 and TI59 programmable calculators. The major assumptions used in the economic analysis model are listed in Table 14.

TABLE 13. TOTAL CAPITAL COSTS FOR PLUG FLOW REACTORS OPERATED AT 15 AND 20 DAYS HYDRAULIC RETENTION TIME.

Dairy Cows	15 Days HRT		20 Days HRT	
	Dollars	$/Cow	Dollars	$/Cow
25	11,460	458	12,387	495
50	14,551	291	16,334	327
100	19,895	199	22,303	223
200	29,336	147	33,680	168
300	36,988	123	42,768	143
400	44,129	110	51,147	128
500	50,755	102	59,464	119

TABLE 14. ASSUMPTIONS AND INPUTS UDED IN THE ECONOMIC ANALYSIS OF SIMPLIFIED METHANE GENERATION.

Parameter	Value	Comment
Fraction of Net Biogas Utilized	>90%	
Interest Rate	10%	
Inflation Rate	7%	
Fuel Escalation Rate	15%	Average yearly price increase since 1973.
Cost of Energy Dispaced	$5.90/GJ	Fuel oil and propane prices in Upstate New York.
Life of Facility	15 years	Estimated life of expendable materials.
Life of Loan	15 years	Same as the life of the facility.
Tax Bracket	20%	Federal and State.
Capital Credits:		
Capital Investment	7% of CC*	Tax Credits.
Clean Water Act (EPA)	12% of CC	Total Credit $\leq$ $3,500.
Renewable Energy	30% of Initial @2,000 CC 20% of Balance of CC	Total renewable energy tax credit not to exceed $2,000.
Depreciation	Straight Line	Taken over 15 years.

* CC = Capital Cost of the Plug Flow Anaerobic Fermentor.

Typical results of the economics of biogas generation from 20-day HRT fermentors of varied capacities, operated on 11-13 percent dairy manure at 35°C are presented in Table 15. The economics information of Table 15 indicate that if nearly all of the biogas can be utilized, the cost of converting cattle manure to methane can be competitive with current prices for propane and fuel oil (priced at about $5.25 per GJ). Energy production costs from methane generation appear especially attractive for farms of 50 head or more. For dairy farms of 100 cows or larger it is estimated that methane can be generated with simplified anaerobic systems at a cost of about 50-60 percent of current liquid fuel prices. Payback periods on these systems range from about two years for a 500 cow unit to seven years for a 25 cow digester. It is noteworthy that the U.S. tax credits for methane generation may already be substantial, particularly if anaerobic fermentation on the farm is recognized by U.S. regulatory agencies as both an alternative energy source and an effective process for pollution control. Such credits, based on existing laws, could defray up to 20 to 30 percent of the initial capital cost.

The preliminary economic analysis of the operation of the plug flow fermentor on dairy manure indicates that biogas can be produced on dairy farms of 25 to 500 cows at stable costs lower than current prices for propane and fuel oil. As world energy prices continue to climb, the economics of on-farm methane generation will continue to look more and more attractive. It should be pointed out, however, that although the economics appear promising, the ultimate value of the biogas will depend upon the degree to which high-priced fuels can be displaced by fermentor gas on the farm. The economic analysis presented here assumes that more than 90 percent of the yearly biogas could be utilized. The specific costs of

TABLE 15. SUMMARY OF THE ECONOMIC ANALYSIS ON THE PLUG FLOW ANAEROBIC FERMENTATION OF DAIRY MANURE USING THE ECOTOPE MODEL.

Item	25 Cows	50 Cows	100 Cows	500 Cows
Inputs:				
Capital Cost, Dollars	12,974	16,900	22,300	54,000
Tax Credits, Dollars	4,839	5,069	6,050	9,053
Maintenance, Dollars	454	590	781	1,899
Operating Costs, Dollars	356	512	825	3,325
Net Energy Production, GJ/year	215	452	917	4,520
Results:				
Energy Production Cost, Dollars/GJ				
With Operating Labor	$6.80	$4.68	$3.40	$2.29
Without Operating Labor	$5.14	$3.55	$2.50	$1.55
Payback Period, Years	6.9	4.9	3.6	2.2

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* Energy Production Costs were calculated with and without the costs of farm labor involved in the operation of the fermentor. Operating labor costs may not be recognized by the farmer particularly if he is not forced to hire additional personnel and if he is able to cover the additional labor requirement through more efficient time management.

utilizing the biogas were not taken into account because such schemes may vary widely in expense and complexity: from a simple retrofit of biogas burners in existing propane space heaters and water heating units, to the outright purchase of new biogas utilizing equipment. It is intuitive that if biogas can be generated on the farm at a cost far below current energy prices, a certain degree of gas wastage can be tolerated; the data in Table 15 indicate that for dairy farms of 50 cows or greater, more than 20 to 40 percent of the net biogas would have to be unused before methane production costs would begin to appear noncompetitive with liquid fuels.

The availability of biogas utilization options should, on the whole, enhance the implementation of anaerobic fermentation on small farms. The easiest and most direct usage of biogas is through water and space heating (involving direct burning). For larger agricultural operations (> 100 cows) additional investment into other biogas utilization systems may be warranted. Electricity generation from biogas-driven internal combustion engines may be attractive, since a variety of electrical farm equipment, refrigeration units, and appliances could then be indirectly operated on fermentor gas. Gas compression and storage may involve a substantial capital investment; but such systems could allow an improved match-up between farm energy demands and biogas generation patterns. Agreements with utilities for the sale of excess biogas or farm-generated electricity may also be beneifical in the future; such arrangements could virtually insure total utilization of the biogas. More research and analysis on the utilization and storage of biogas on small farms is undoubtedly needed.

Dry Fermentation

In the Fall of 1979, some effort was placed on the planning of a bench scale study to investigate certain aspects of the proposed dry fermentation study as outlined in the new Methane Project proposal submitted to D.O.E. A preliminary testing program was develcped by mid-October. Dr. Jewell would be consulted at the beginning of every experimental test. The main topics planned for the bench scale dry fermentation study include thermophilic fermentation, $NaHCO_3$ versus $CaCO_3$ buffering, and volatile acid stripping.

After 336 days of operation, the 5.0 m^3 mesophilic, pilot-scale dry fermentor charged with wheat straw at a solids concentration of about 25 percent was producing biogas at a rate of 8 ft^3 per day with a methane content of 54 percent. This study has been described in more detail in the eleventh quarter progress report. The dry fermentor will continue in operation until one year has elapsed, at which time the unit will be opened and the contents examined. Of particular interest will be the physical appearance of the material and the presence of any large pockets of undigested material.

Final Report

During the period from June 16 to October 15, 1979, final report preparation activities continued at a steady and productive pace. Computer simulations of energy balances on anaerobic fermentors of varied capacity and design were carried out during the summer months. As previously mentioned, the cost assessment economic analysis programs that were developed were used to closely examine the effects of reactor construction, capacity and operation on the costs of producing biogas energy on the farm. Consultants David Baylon of Ecotope Group and Tom Abeles of I E. Associates provided the Cornell methane project with additional perspectives to the economic analysis and suggested various approaches of evaluation. The latest data from the operation of the full scale plug flow and conventional control reactors at Cornell were analyzed and included in the experimental write up. By mid-October, most of the major technical sections of the final report were developed to the rough-draft stage. Work is continuing on the preparation of tables, figures and graphics.

Feasibility Manual

In the months following the end of the twelfth quarter period, information gathering and literature analysis for the development of the technical sections of the farmer's feasibility manual progressed rapidly. Of the seven total chapters, four and one-half were completed in first draft form by mid-October.

Stanford University
Department of Civil Engineering

HEAT TREATMENT OF ORGANICS
FOR
INCREASING ANAEROBIC BIODEGRADABILITY

Contract XR-9-81-74-1

QUARTERLY PROGRESS REPORT
for the period
July 1, 1979 to September 30, 1979

by

D. Stuckey, P. J. Colberg, K. Baugh, L. Y. Young, and P. L. McCarty

Prepared for

Division of Solar Energy

U.S. Department of Energy

Washington, D.C. 20545

REPORT OUTLINE

A. INTRODUCTION

B. BIOLOGICAL CONVERSION OF LIGNOCELLULOSE TO METHANE

1. Background
2. Procedures and Results
3. Summary

C. BIODEGRADATION OF LIGNIN AND LIGNIN FRACTIONS

1. Preparation of Peat Lignin for Biodegradation
2. Results and Discussion
3. Future Work

D. PRETREATMENT OF NITROGENOUS ORGANICS

1. Biodegradation of Amino Acids, Sugars, and Bases
2. Toxicity of Amino Acids, Sugars, and Bases
3. Conclusions

E. REFERENCES

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 four 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.

Results are reported for phases one, two, and three. No new information is available for phases four and five at this time.

B. BIOLOGICAL CONVERSION OF LIGNOCELLULOSE TO METHANE

K. Baugh and P. L. McCarty

Background

Previous investigations at Stanford (Owen et al., 1978) have shown that staged heat treatment has the best potential for maximizing the solubilization of organics from wood products. The increased solubilization of organics by staged autohydrolysis offers a potential for increasing the bioconversion efficiency of lignocellulosic materials to methane in anaerobic digesters. Besides maximizing the yield of solubilized organic materials, staged heat treatment of wood products could also reduce the formation of toxic products present in all heat-treatment products attributable to soluble dehydration products (furan compounds) formed from heat treatment of polysaccharides.

Staged heat treatment was developed by Owen to increase the solubilization of the biodegradable fraction of wood products, the hemicellulose and cellulose. The first stage is a mild heat treatment for solubilization of the easily solubilized polysaccharides, notably hemicellulose, while minimizing condensation reactions. The two following stages require more severe conditions of temperature and heating duration to separate the more resistant polysaccharides, such as cellulose. Thus, a non-biodegradable lignocellulosic material is converted into two easily separable fractions: a soluble fraction resulting from carbohydrates, and a particulate residue consisting mainly of lignin condensation products. This report contains the results of Biochemical Methane Potential (BMP) tests of the products of a three-stage heat treatment.

The BMP results will show if increasing the solubilized organic concentration by staged autohydrolysis also increases the biodegradability of wood products.

Procedures and Results

A white fir slurry (61.5 g/l total solids) was hydrolyzed in staged, sequential reactions as reported previously (Owen et al., 1978). In Stage 1, 1 liter of white fir slurry was heated to 200°C and immediately cooled to room temperature. Stages 2 and 3 were both conducted for two hours at 225°C. After each stage, the product was assayed for total and soluble COD, and the particulate fraction was separated by filtration. The recovered particulate solids were resuspended in 0.75 liters of deionized water and treated in the subsequent stage. All chemical analyses, solids and chemical oxygen demand (COD), were performed in accordance with Standard Methods (1976). A representative sample was taken from the products (total and soluble) of each heat treatment stage to determine biodegradability by the BMP test (Owen et al., 1979).

The results from the stage heat treatment of white fir are shown in Table 1. The COD values are similar to those reported previously (Owen et al., 1978). The particulate yield (32.4%) approximates 81 percent of the COD represented by the lignin fraction, and the soluble yield (48.8%) approximates 82 percent of the carbohydrate COD. These results confirm that a three-stage scheme is effective in recovering a significant portion of the initial solids either as soluble products or insoluble residue. The BMP and anaerobic bioconversion efficiencies for the autohydrolysis products of white fir are summarized in Table 2. The biodegradability of the solubilized products was quite high, with the first stage showing almost an eighty percent bioconversion efficiency while the last two stages were slightly under sixty percent. The overall bioconversion efficiency of the solubilized organics when referenced to the initial feed total COD was 32 percent. This compares reasonably to an estimated maximum overall bioconversion efficiency of 40 percent by Owen (1979). Some improvement in the overall bioconversion efficiency should be possible when difficulty in solids recovery between stages is minimized.

Summary

In summary, staged autohydrolysis pretreatment of a relatively nonbiodegradable forest product residue can be used to maximize the production of biodegradable materials through the solubilization of the carbohydrate fraction of the residue.

Future studies will further address the potential of staged treatment. The various soluble organic compounds formed during staged autocatalytic treatment will be determined to evaluate potential for recovery and influence on the overall process.

TABLE 1

SUMMARY OF 3-STAGE AUTOHYDROLYSIS OF WHITE FIR

Stage	Reaction Conditions[a]		Initial Feed COD (g/l)	Product COD (g/l)			Percent of Initial Feed COD[b]	
	Temp. (°C)	Time (hr)		Total	Soluble	Particulate	Particulate	Soluble
1	200	0.0	77.4	62.9	17.1	45.8	59.2	22.1
2	225	2.0	50.6	50.6	13.7	36.9	43.2	16.0
3	225	2.0	20.9	20.9	5.2	15.7	32.4	10.7
Reaction Sum							32.4	48.8

[a] First stage employed 1-liter liquid volume; for stages two and three, a portion of the recovered particulates from the preceding stage was resuspended in 0.75 liter liquid volume.

[b] Respective fraction referenced to the initial feed COD of stage one, and based on percent particulate recovery of preceding stage as referenced to feed.

TABLE 2

BIOCHEMICAL METHANE POTENTIAL OF 3-STAGE AUTOHYDROLYZED WHITE FIR

	Reaction Conditions[a]		Referenced to Product				
			BMP (1 CH_4/g COD)		Bioconversion Efficiency[b] (%)		Overall Bioconversion Efficiency of Soluble COD Referenced to Initial Feed COD (%)
Stage	Temp. (°C)	Time (hr)	Total	Soluble	Total	Soluble	
1	200	0.0	0.094	0.27	26.7	77.1	17.0
2	225	2.0	0.089	0.19	25.4	54.3	8.7
3	225	2.0	0.048	0.20	13.7	57.1	6.1
Reaction Sum							31.8
Column No.	1	2	3	4	5	6	7

[a] Reaction conditions as per Table 1, note (a).

[b] Based on theoretical BMP of 0.35 1 CH_4/g COD at STP.

[c] Overall bioconversion efficiency = (Column 6, Table 2) x (Column 8, Table 1) x 100%.

C. BIODEGRADATION OF LIGNIN AND LIGNIN FRACTIONS

P. J. Colberg and L. Y. Young

Previous studies in our laboratories at Stanford have related enhanced biodegradability of lignocellulosics to the solubilization of lignin during alkaline heat treatment (Healy et al., 1977). Chemically altered lignin fractions separated according to molecular weight were examined for their biodegradability and toxicity.

Preparation of Peat Lignin for Biodegradation Studies

Preparation of peat lignin and its separation by gel filtration chromatography has been described in previous reports (Healy et al., 1978). For purposes of identification, the largest peak of MW ~ 1400^+ is designated Fraction 1 in this report; a smaller peak of MW ~ 600 is Fraction 2; and the smallest peak of MW ~ 200 is designated Fraction 3.

Individual fractions were added to pre-reduced, defined media as the sole source of carbon according to the Biochemical Methane Potential (BMP) and Anaerobic Toxicity Assay (ATA) protocols developed by Owen et al. (1979). Since the quantities of Fractions 2 and 3 eluted from the column with each passing were small, repeated fractionations were required in order to obtain sufficient quantities of substrate for biodegradation experiments. Consequently, the serum-bottle size was also reduced to a 14-ml capacity. The total liquid volume was 12 ml (medium + substrate = 10 ml; seed = 2 ml), with a void space of 2 ml. The Total Organic Carbon (TOC) concentration (mg carbon/l) tested for each fraction in the BMP and ATA tests were as follows: 100, 300, 500, 750, 1000, 1200, and 1500. The seed organisms were obtained from a laboratory digestor fed waste-activated sludge. Gas volumes were measured periodically during the 30-day incubation period and gas composition was determined by gas partitioning analysis.

Results and Discussion

A comparison of the percent total carbon converted to CO_2 and CH_4 for each of the three peat fractions tested in the BMP test resulted in the following observations (see Table 3).

1. For Fraction 1 samples, the lowest concentration (100 mg/l) had the most carbon conversion to gas. Among the other concentrations, which were all significantly lower, there were no major differences.

TABLE 3

CONVERSION OF LIGNIN FRACTIONS TO GAS

	Percent TOC Converted to CO_2 and CH_4						
	100 mgC/l	300 mgC/l	500 mgC/l	750c mgC/l	1000 mgC/l	1200 mgC/l	1500 mgC/l
Fraction 1 (MW ~ 1400)	10.8 ± 2.9	4.1 ± 4.7	2.3 ± 1.5	3.6 ± 2.4	3.7 ± 0.5	3.5 ± 0.1	4.9 ± 0.1
Fraction 2 (MW ~ 600)	5.6 ± 1.2	3.3 ± 1.2	2.8 ± 3.8	4.2 ± 3.0	4.2 ± 7.8	6.1 ± 1.6	5.9 ± 2.8
Fraction 3 (MW ~ 200)	8.1 ± 1.6	5.8 ± 2.0	1.5 ± 0.4	4.6 ± 0.5	5.4 ± 1.7	4.4 ± 1.4	5.3 ± 0.6

Values reported as mean ± standard deviation.

2. There were no apparent differences among the samples in Fraction 2; whereas, in Fraction 3, the lowest concentration (100 mg/l) tended to provide more carbon conversion than the higher concentrations.
3. When examining the conversions between the different fractions, Fraction 1 at 100 mg/l displayed greater conversion to gas than Fraction 2.
3. Although the overall conversions were small, the larger values at the lowest concentration suggests some toxicity occurred in the other samples.

If the BMP results for each of the three fractions are totalled for substrate concentrations corresponding to those reported by Owen et al. (1979) in an equivalent alkaline heat-treated peat, the results concur. Owen et al. (1979) conducted BMP tests on whole (unfractionated) peat and observed a 20 percent conversion of substrate carbon to CH_4. If the appropriate data are totaled from each of the three fractions in this study, a conversion of 17.3 percent of substrate carbon to CH_4 is realized.

It is evident from the data that all fractions tested produced CO_2 and CH_4, although the overall conversions of substrate carbon to gas were small. There does not appear to be any trend regarding molecular-weight fractions and biodegradability. However, a number of considerations in addition to molecular size complicate the interpretation of available data.

The most obvious complication may be that the seed organisms did not acclimate to the substrate in the 30-day test period. Upon longer incubation and repeated feedings, it may be possible to selectively enrich for a more active population of microorganisms.

Because of the similar percentage conversions of substrate carbon to gas observed between fractions, it might be surmised that the same types of compounds are undergoing degradation within each fraction regardless of fraction size. However, since the fractions are physically separated via gel filtration chromatography, these suspected compounds would have to be unaffected by molecular sieving and be eluted indiscriminately with each fraction. Large MW carbohydrates such as cellulose might meet this criterion, yet available evidence indicates that cellulose is solubilized during alkaline heat treatment by an end-wise degradation scheme with the production of isosaccharinic acid (MW 192), which, in turn, should be eluted with Fraction 3 based on its molecular size. If cellulose solubilization were incomplete following alkaline pretreatment, the remaining cellulose fragments might have different molecular weights and would elute with the different fractions.

Based on the observed data, it might be suspected that fractions of peat lignin exert toxic effects regardless of molecular size. ATA data for these fractions were not conclusive, since controls in this study yielded only 50 percent of expected gas production from the acetate-propionate spike. Consequently, ATA tests on peat fractions are currently being retested.

The observed degradation of peat fractions may be due, at least in part, to attack on functional groups. Although the number of available functional groups is probably greater in the larger MW fractions, steric effects may retard attack, accounting for the insignificant differences in degradation between fractions. Or it is possible that degradation of the two large fractions is limited to functional groups only, while organic acids of carbohydrate origin (Gossett, 1977) are perhaps being degraded in Fraction 3.

Future work

In addition to developing experiments to test some of the questions posed in this study, current work is focusing on development of reverse-phase High Pressure Liquid Chromatography (HPLC) for classification and identification of potential degradation products, preparation of ^{14}C-(lignin)-lignocellulose (Crawford and Crawford, 1976) for tracing the degradation of lignin-derived structures and compounds, and gas chromatographic analyses of peat BMP cultures for volatile fatty acid content (Healy, 1979).

D. PRETREATMENT OF NITROGENOUS ORGANICS

D. Stuckey and P. L. McCarty

The effect of thermochemical pretreatment on the degradability and toxicity of pure nitrogen compounds and sugars is currently being investigated.

Biodegradability of Amino Acids, Sugars and Bases

In order to more fully understand the behavior of complex nitrogenous organics under thermochemical pretreatment, the individual components were studied separately.

The percentage of each of these components converted to methane was assessed using the Biochemical Methane Potential (BMP) bioassay. Destruction of each component was assessed both before and after thermochemical pretreatment at 200°C for 1 hour and in the presence of 300 meq/l NaOH.. Data after 35 and 78 days are set out in Table 4. Also, in order to obtain some idea of the effect of pretreatment on the chemical structure of the pure components, chemical analyses were carried out for NH_3 and organic nitrogen. These data are included in Table 4 and indicate NH_3 as a percentage of the total nitrogen measured (organic N + NH_2), and the percentage of total nitrogen measured compared to the theoretical value.

With the untreated amino acids, after 35 days, approximately one-third were highly degradable, one-third were moderately degradable, and the remainder were quite refractory. This behavior seems to be related in a general sense to structure. If the functional group of the amino acid is either branched, or contains a ring compound, the acid appears to be harder to degrade.

After 78 days of degradation the degradability of only three acids had increased significantly: valine, leucine and tryptophan. Since these compounds are toxic at the concentrations tested (see Table 5), it is possible that this increase could be due to acclimation to the toxic effect.

Of the nucleic acid bases, four of them were moderately degradable, while thymine was virtually inert. After 78 days thymine was 26 percent degradable, while there was not significant increase in the other bases. Since thymine is identical to the other pyrimidines except for a methyl group on the fifth carbon, it is apparent that small structural changes can have profound effects on degradability.

TABLE 4

BMPs OF AMINO ACIDS, SUGARS AND BASES

Component		Destruction of Pure Component		Destruction of Component after Pretreatment[a]		Effect of HT on N	
		35 days	78 days	35 days	78 days	% NH_3 / total N	% Theoretical N Accounted For
Alanine	non-polar R groups	91	91	87	83	0.3	79
Valine		20	90	16	74	2	87
Leucine		18	70	16	30	1	96
Isoleucine		86	86	93	95	1	90
Proline		90	88	87	87	0.5	66
Phenylalanine		73	74	37	91	21	7
Tryptophan		59	75	59	83	3	93
Methionine		82	90	68	69	8	82
Glycine	unchanged polar	94	92	92	91	2	88
Serine		99	98	67	69	14	111
Threonine		97	97	35	35	5	86
Cysteine		94	96	12	12	83	77
Tyrosine		72	76	45	52	1	95
Asparagine		83	91	84	80	67	86
Aspartic acid	negative at pH 6	79	73	88	82	50	103
Glutamic acid		39	37	120	118	2	95
Lysine	positive at pH 6	77	78	70	74	4	44
Orginine		-		-		49	63
Histidine		58	57	60	58	4	61
Cystine		64	71	6	15	74	89
Adenine	purines	73	61	89	78	8	97
Guanine		71	50	65	69	14	79
Uracil	pyrimidines	77	77	62	69	17	91
Thymine		0	26	1	36	6	88
Cytosine		61	64	24	26	75	53
Glucose	sugars	92	95	36	39	-	-
Ribose		97	99	35	38	-	-
Deoxyribose		91	93	4	6	-	-
Glucose/leucine (20/20)		68	66	38	41		
Uracil/ribose (17.1/22.9)		95	95	52	53		

[a] 200°C for 1 hour and with 300 meq/l NaOH.

TABLE 5

ATAs OF AMINO ACIDS, SUGARS AND BASES EXPRESSED AS 7-DAY MMRR[a]
(All stock solutions 40 g/l, mesophilic condition used)

Chemical		Non-Heat Treated Controls (1/2 Dilu.)	Heat-Treated Samples, 200°C NaOH (300 meq/l)		
			1/30 Dilu.	1/5 Dilu.	1/2 Dilu.
Alanine	non-polar R groups	0.43	1.10	0.62	0.22
Valine		0.42	1.10	0.62	0.20
Leucine		0.42	1.17	0.56	0.39
Isoleucine		0.41	0.87	0.51	0.11
Proline		0.72	0.65	0.38	0.22
Phenylalanine		0.14	0.89	0.57	0.04
Tryptophan		0.02	0.71	0.04	0.01
Methionine		0.39	0.96	0.56	0.06
Glycine	unchanged polar R groups	0.20	0.52	0.26	0.15
Serine		1.09	1.13	0.85	0.18
Threomine		0.22	0.97	0.25	0.10
Cysteine		0.11	0.35	0.01	0.01
Tyrosine		0.58	0.79	0.63	0.25
Aspargine		0.61	1.11	0.76	0.39
Aspartic acid	negative at pH 6	0.61	0.92	0.58	0.16
Glutamic acid		1.10	1.17	1.03	0.58
Lysine	positive at pH 6	0.28	1.29	0.85	0.03
Arginine		0.14	1.20	0.79	0.17
Histidine		0.61	0.89	0.65	0.22
Cystine		0.16	0.48	0.0	0.0
Adenine	purines	0.39	0.59	0.16	0.15
Guanine		0.17	0.93	0.68	0.43
Uracil	pyrimidines	0.68	1.12	0.73	0.08
Thymine		0.0	1.08	0.60	0.49
Cytosine		0.37	1.10	0.49	0.05
Glucose	sugars	0.06	1.00	0.01	0.01
Ribose		0.06	0.98	0.20	0.0
Deoxyribose		0.03	0.78	0.53	0.0
Uracil/ribose (17.1/22.9)		0.06	0.96	0.42	0.03
Leucine/glucose (20/20)		0.0	0.87	0.0	0.0

[a] Maximum methane rate ratio.

All the sugars, as expected, were highly degradable. Glucose together with leucine seemed to increase leucine degradabality. Since leucine was only half as concentrated as in the pure component test, it may be that toxicity was limiting leucine degradation, and that decreasing its concentration increased its degradability. The uracil/ribose mixture was highly biodegradable.

With thermochemical pretreatment of the amino acids the overall effect was either to decrease their degradability, or to affect it very little. In only three cases did it increase degradability, and only with glutamic acid was this increase substantial. It was postulated that any significant change in chemical structure during pretreatment might be reflected in the amount of free ammonia released, and the percentage of the measurable nitrogen to the theoretical amount that should be present. A value of the latter less than 100 percent may reflect formation of complex nitrogen forms not amenable to acid hydrolysis, and hence possibly to biodegradation.

In correlating these parameters to degradability it appears generally that when the ammonia released was low, and a high percentage of nitrogen was accounted for, the degradability was either unaffected or increased. The antithesis is that when a lot of ammonia was released, the degradability tended to decrease since the structure appears to have been altered considerably.

The effect of time on amino acid degradability was in general insignificant. However, with valine, leucine, phenylalanine and tryptophan there was a considerable increase with time.

With the purine and pyrimidine bases, thermochemical treatment only increased the degradability of adenine, while thymine was unaffected. The rest had decreased degradabilities. With time only thymine increased in degradability.

Finally, as expected with the sugars, pretreatment caused caramelization and a substantial decrease in COD destruction. Again the subtle difference between ribose and deoxyribose resulted in very different behavior under treatment. Time did not appear to have any effect in increasing the degradability of the sugars.

Toxicity of Amino Acids, Sugars and Bases

The toxicity of the individual components from the first phase were also assayed for toxicity using the anaerobic toxicity assay (ATA). These data are set out in Table 5.

In previous work toxicity was assessed by taking the ratio of total gas produced over a certain time in a sample bottle, to that of a spiked control. This ratio was denoted the maximum rate ratio (MRR). However, due to high rates of CO_2 production from certain samples this figure can be misleading, and can indicate no inhibition when in fact there is significant inhibition. To overcome this problem an alternative ratio was formulated, the maximum methane rate ratio (MMRR). To calculate this ratio, gas composition and production were both monitored, and the rate of methane production over a given time period was calculated. The MMRR was then calculated as the ratio of sample methane production rate to that of the control.

From Table 5 it is apparent that at a concentration of 20 g/l all of the amino acids except serine and glutamic acid were toxic. It is outside the scope of this report to examine all the structural aspects of this toxicity; however, a few points are worth mentioning. Alanine is considerably less toxic than glycine even though the R groups are similar, with alanine having a methyl group while glycine only hydrogen. Valine and leucine have identical end groups, and behave very similarly with regard to toxicity; however, in a similar situation with aspartic and glutamic acids the behavior is not similar.

All the bases were toxic, with thymine extremely so, again the methyl substitution on thymine compared with uracil seems to make it more toxic as well as less degradable.

While the data indicate that the three sugars were toxic, problems were experienced here in maintaining the pH above 6.4 and it is felt that the data do not give a true picture. It is known from the literature that these compounds are not toxic at these levels.

The effect of thermochemical pretreatment was to increase the toxicity in all cases except with adenine and tyrosine. Even at high dilution (1/30 = 1.33 g/l), amino acids such as cysteine, cystine and glycine were still extremely toxic.

Conclusions

1. With nitrogen-containing organics very small differences in structure can lead to substantial differences in degradability.
2. Thermochemical pretreatment tends to either decrease degradability, or affect it very little.
3. The toxicity of nitrogenous organics is similar to degradability inasmuch as small changes in structure can have profound changes on toxicity.
4. Thermochemical pretreatment in almost all cases lead to increased toxicity.

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