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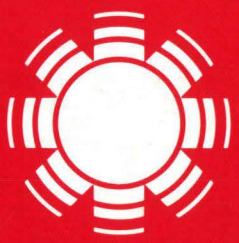
June 1980

Fuel Gas Production from Animal and Agricultural Residues and Biomass

16th Quarterly Coordination Meeting June 23-24, 1980 Denver, Colorado

D. E. Jantzen
Biomass Program Office



SERI

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A Division of Midwest Research Institute

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SERI/PR-624-537-4
JUNE 1980

FUEL GAS PRODUCTION FROM ANIMAL AND AGRICULTURAL RESIDUES AND BIOMASS

16TH QUARTERLY COORDINATION MEETING
JUNE 23-24, 1980
DENVER, COLORADO

D. E. JANTZEN
BIOMASS PROGRAM OFFICE

PREPARED UNDER TASK NO. 3335.01

Solar Energy Research Institute
A Division of Midwest Research Institute

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Golden, Colorado 80401

Prepared for the
U.S. Department of Energy
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FOREWORD

The 16th Quarterly Coordination Meeting of the Anaerobic Digestion Group of contractors working for the Biomass Energy Systems Division, U.S. Department of Energy, was held June 23-24, 1980 in Denver, Colorado. The meeting included presentations of progress reports by the subcontractors and a discussion of revised administrative arrangements in which the USDA will manage a program of demonstration and commercialization of digestive systems, and SERI will manage the R&D program.

Dan Jantzen
Biomass Program Office

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LIST OF ATTENDEES

ANAEROBIC DIGESTION CONTRACTORS COORDINATION MEETING

Denver, Colorado

June 23-24, 1980

Organization	Name	Telephone
Cornell University 202 Riley - Robb Hall Ithaca, NY 14853	Randy Kabrick	(607) 256-2173
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AGENDA

ANAEROBIC DIGESTION CONTRACTORS COORDINATION MEETING

June 23 - 24, 1980
Stapleton Plaza
Denver, Colorado

Monday, June 23

1:00 - 1:15 p.m.	Dan Jantzen	SERI
1:15 - 2:00 p.m.	Kent Baugh	Stanford University
2:00 - 2:45 p.m.	Don Wise	Dynatech (Biomethanation)
2:45 - 3:00 p.m.	Coffee	
3:00 - 3:45 p.m.	John Pfeffer	University of Illinois
3:45 - 4:30 p.m.	Don Lizdas	Hamilton Standard
7:00	Dinner	To be announced

Tuesday, June 24

8:30 - 9:15 a.m.	Andy Hashimoto	USDA MARC
9:15 - 10:00 a.m.	Jim Gaddy	University of Missouri
10:00 - 10:15 a.m.	Coffee	
10:15 - 11:00 a.m.	Randy Kabrick	Cornell University
11:00 - 11:45 a.m.	Gerald Ward	Colorado State University
12:00 - 2:00 p.m.	Lunch	
2:00 - 2:45 p.m.	Randy Kabrick	Cornell University (Algae Digestion)
2:45 - 3:30 p.m.	Ed Ashare	Dynatech (Secondary Residues)
3:30 - 3:45 p.m.	Coffee	
3:45 - 4:30 p.m.	Dan Jantzen	SERI (Policy/Contracts Update)

BIOLOGICAL CONVERSION OF BIOMASS TO METHANE

QUARTERLY PROGRESS REPORT

For Period April 1 to June 31, 1980

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and
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University of Illinois
Urbana, Illinois 61801

June 23, 1980

Prepared for

THE U.S. DEPARTMENT OF ENERGY
Under Contract No. SBC SERI XB-9-8357-1

1. INTRODUCTION

During this quarter further research into the thermochemical pretreatment of corn stover was conducted. Currently this research is approximately 50% complete. However, a depleted stock of corn stover has resulted in only one digester being able to ferment corn stover during the next quarter. All digesters will resume treating stover when more becomes available in October.

In the interim, a study will be made of the thermochemical pretreatment of wheat straw. This research will serve two purposes. Firstly, it will determine if the difficulties previously observed in fermenting thermochemically pretreated straw (Pfeffer, 1980) can be resolved and, secondly, the efficiency of the pretreatment process can be compared to that observed with corn stover.

Recently a new pretreatment vessel capable of withstanding 100 psig was delivered and installed. This vessel will be used for all subsequent pretreatment studies.

2. CORN STOVER STUDY

2.1 Experimental Procedure

The experimental procedure and experimental design used for this study have been described previously (McFarlane and Pfeffer, 1980).

2.2 Results and Discussion

During pretreatment, the degree of COD solubilization achieved is most dependent upon the amount of hydroxide added. This is clearly demonstrated from a study of Table 1 which summarizes the pretreatment data.

Trial 23 was conducted using a 1.0% w/w NaOH concentration which resulted in a pH prior to pretreatment in the range of 8.5-8.7. When compared to the 5.5% w/w NaOH trials (Trials 19 and 25-28) a substantial decrease in COD solubilization was observed. The final pH and alkalinity were also lower. This decreased pretreatment effect was also visibly apparent with the fibers generally remaining intact and the aqueous extract appearing a pale yellow instead of the dark brown color observed at the higher alkali dosage. Because the fibers separated very readily from the water, the stover pretreated under these conditions proved impossible to pump with the existing apparatus and had to be manually transferred to the digester. The fiber separation created major problems in obtaining representative samples and resulted in the very poor 95% confidence interval observed with the total COD data.

Trial 11 was performed using a 3.25% w/w NaOH concentration and resulted in a final pH, alkalinity and COD solubilization intermediate to those observed using 1% and 5.5% w/w NaOH doses. However, a more complete treatment of the fibers occurred than in trial 23 and there was no difficulty in pumping this material into the digester using the automated timing system.

Table 1: Summary of Thermochemical Pretreatment Date

Parameter	Trial 11	Trial 19	Trial 23
pH	9.6	10.4	7.1
95% CI	9.4-9.9	10.2-10.6	7.0-7.3
Alkalinity (mg/l as $CaCO_3$)	1,750	2,720	728
95% CI	1,410-2,100	2,290-3,160	290-1,160
Total COD (mg/l)	62,700	62,700	53,500
95% CI	50,900-74,500	57,400-68,000	-2,920-110,000
Soluble COD (mg/l)	15,700	20,700	7,820
95% CI	13,800-17,600	19,300-22,100	5,520-10,000
COD Solubilization (%)	25	33	14.6

Parameter	Trial 25	Trial 26	Trial 27
pH	10.4	10.6	10.7
95% CI	10.0-10.8	10.5-10.7	10.5-10.8
Alkalinity (mg/l as $CaCO_3$)	3,290	3,350	2,790
95% CI	2,860-3,720	2,730-3,960	2,420-3,170
Total COD (mg/l)	59,100	58,700	61,800
95% CI	55,500-62,700	52,200-65,200	57,600-66,000
Soluble COD (mg/l)	22,300	18,700	19,900
95% CI	18,800-25,700	13,400-24,100	18,000-21,900
COD Solubilization (%)	37.7	31.9	32.2

Parameter	Trial 28
pH	10.0
95% CI	9.9-10.2
Alkalinity (mg/l as $CaCO_3$)	2,840
95% CI	2,600-3,010
Total COD (mg/l)	61,000
95% CI	54,700-67,400
Soluble COD (mg/l)	22,600
95% CI	21,700-23,500
COD Solubilization (%)	37.0

95% CI = 95% Confidence Interval

The remaining trials presented in Table 1 were all conducted using a 5.5% w/w NaOH concentration and similar final pHs, alkalinities and COD solubilizations were observed in all cases. This demonstrates that the hydroxide concentration is the major factor determining the extent of pretreatment as measured by the COD solubilization. Using this criterion, the other independent variables investigated (pretreatment temperature, time and solids concentration) were of secondary importance.

With the exception of Trial 23, good agreement is observed between the total COD data. These values also agree well with those reported for the previous quarter (McFarlane and Pfeffer, 1980).

A summary of the results obtained for the slurry in the holding tanks is presented in Table 2. As previously observed, a substantial decrease in pH occurs while the pretreated stover is in the holding tanks. Also an increase in alkalinity and COD solubilization was observed in all instances except Trial 23. A preliminary analysis of the data indicates that the increase in COD solubilization observed within the holding tanks is related to the amount of NaOH used in the thermochemical pretreatment process. Presumably, the increased lignin solubilization obtained at the higher alkali concentrations increases the availability of the cellulose to the microorganisms present in the holding tank. These microbes are then able to ferment a portion of the cellulose to acidic end-products thereby increasing the soluble COD and, in conjunction with atmospheric carbonation, decreasing the pH. This may explain the negligible change in soluble COD observed in Trial 23 (1% w/w NaOH). The other trials showed increased in soluble COD ranging from 4.64% (Trial 28) to 15.3% (Trial 26).

Table 2: Summary of Holding Tank Data Analysis

Parameter	Trial 11	Trial 19	Trial 23
pH	6.0	6.7	5.8
95% CI	5.9-6.1	6.5-6.9	5.7-6.0
Alkalinity (mg/l as $CaCO_3$)	2,670	3,850	1,310
95% CI	2,600-2,750	3,670-4,020	1,170-1,450
Total COD (mg/l)	59,700	61,100	59,300
95% CI	54,500-65,000	56,800-65,400	47,000-71,500
Soluble COD (mg/l)	16,700	22,100	8,780
95% CI	15,900-17,500	21,600-22,600	7,400-8,160
COD Solubilization (%)	28.0	36.2	13.1
Δ Soluble COD (mg/l)	1,000	1,400	-40

Parameter	Trial 25	Trial 26	Trial 27
pH	7.4	7.4	6.7
95% CI	6.9-7.9	7.0-7.8	6.6-6.8
Alkalinity (mg/l as $CaCO_3$)	3,630	3,770	3,780
95% CI	3,300-3,970	3,440-4,100	3,640-3,920
Total COD (mg/l)	66,300	60,800	57,700
95% CI	55,500-77,200	55,500-66,000	54,700-60,700
Soluble COD (mg/l)	24,700	22,100	22,100
95% CI	23,900-25,500	21,600-22,600	23,000-24,300
COD Solubilization (%)	37.2	36.3	38.3
Δ Soluble COD (mg/l)	2,400	3,400	2,200

Parameter	Trial 28
pH	6.9
95% CI	6.6-7.2
Alkalinity (mg/l as $CaCO_3$)	3,870
95% CI	3,680-4,060
Total COD (mg/l)	58,100
95% CI	55,400-60,900
Soluble COD (mg/l)	23,700
95% CI	23,000-24,300
COD Solubilization (%)	40.8
Δ Soluble COD (mg/l)	1,100

Δ Soluble COD = Holding Tank Soluble COD - Pretreatment Soluble COD

As previously mentioned, the difficulty in obtaining a representative sample for Trial 23 has resulted in the observed variability in the total COD data and the lack of agreement between the pretreatment and holding tank total COD data.

A summary of the steady-state operation of the digesters is presented in Table 3. This table demonstrates that good control was obtained over the retention time and volatile solids loading rate. This is essential if a meaningful comparison of the results is to be made.

No data are included for Trial 28 as it did not attain steady-state. This digester was unable to maintain a pH greater than 6.8 even with the batch-wise addition of substantial quantities of lime. On several occasions up to 20 l/d of effluent from stable digesters were recycled to this fermenter in an attempt to revive it. These efforts were only temporarily successful with increased gas production occurring for a maximum of three days.

In addition, 1.0 g/l of lime was added to the holding tank and although an increase in alkalinity in the digester was apparent a continued increase in total volatile acids (TVA) and a decrease in gas production was observed. When this trial was terminated the total volatile acids were 6,350 mg/l and the total gas production was approximately 650 l/d, equivalent to 0.073 m^3 CH_4/kg VS fed.

Trial 28 was the longest pretreatment time (3.16 hr) investigated. Thus, the preliminary indications are that such extended pretreatment times lead to the formation of compounds inhibitory to the methane bacteria. However, conclusive proof of the deleterious effect of extended pretreatment times must await the completion of this study.

Table 3: Summary of Digester Data Analysis

Parameter	Trial 11	Trial 19	Trial 23	Trial 25	Trial 26	Trial 27	Trial 28	Trial 29
Hydraulic Retention Time (d)	7.60	7.77	7.52	7.76	7.75	7.76		7.52
Temperature (°C)	58.4	59.1	59.1	58.8	58.3	58.9		58.2
Volatile Solids Load (kg VS/m^3·d)	4.09	4.31	4.16	3.97	3.99	4.12	unable to attain steady-state operation	4.36
COD Load (kg COD/m^3·d)	7.89	7.58	8.12	8.33	7.92	7.15		8.44
pH	7.0	7.0	6.9	7.3	6.9	7.2		7.0
Alkalinity (mg/l as $CaCO_3$)	2,940	4,150	1,690	4,210	4,260	4,100		3,900
Feed Total Solids (mg/l)	49,200	53,900	47,600	49,900	49,900	51,000		53,300
Feed Volatile Solids (mg/l)	40,100	43,300	40,400	39,800	39,800	41,200		42,600
Effluent Total Solids (mg/l)	33,300	34,700	25,400	31,100	33,900	32,100		34,900
Effluent Volatile Solids (mg/l)	22,100	22,500	17,260	19,500	22,200	20,400		23,200
Total Volatile Acids (mg/l as acetate)	1,630	2,710	377	1,710	2,760	1,940		2,930
Methane Content of Gas (%)	55.1	53.8	53.1	54.0	51.9	54.2		53.3
Volatile Solids Destruction (%)	45.7	48.9	56.2	51.6	45.6	52.4		45.9
Gas Production (m^3 CH_4/kg VS loaded)	.247	.237	.188	.295	.189	.229		.230
Gas Production (m^3 CH_4/kg COD loaded)	.168	.182	.128	.183	.128	.174		.158

Satisfactory operation of the digesters for the remaining trials was obtained and a range of gas production from 0.188 to 0.295 m^3 CH_4/kg VS loaded was observed.

Trial 23 demonstrated the lowest gas production and operated at the lowest steady-state TVA level yet observed. As the volatile solids loading and the retention time was comparable to the other trials, this may indicate that slightly inhibitory products are formed by thermochemical pretreatment at elevated NaOH dosages. This may explain the unusually high steady-state TVA levels observed in all the other trials. Gossett et al. (1976) reported a similar finding in their semi-continuous feed evaluation of the digestibility of alkali/heat pretreated refuse. Their study concluded that such inhibition was probably caused by some of the soluble organics formed by the heat treatment of lignin.

Trial 23 also achieved a satisfactory volatile solids destruction of 56.2%. However, the gas production, based on both a volatile solids basis and a COD basis, was very poor. This was disconcerting as a similar effect was observed with trial 16 described in the previous quarterly report (McFarlane and Pfeffer, 1980).

Trial 11 was conducted using a 3.25% w/w NaOH dosage. The gas production data demonstrate the improved degradability of this material when compared to Trial 23, although a much poorer volatile solids destruction occurred.

Trials 19 and 20 are replicate center point runs and although the gas production data on a volatile solids basis show good agreement, those based on the total COD do not. The significance of this cannot be assessed until all the center point trials have been performed and the inherent variability of the data assessed. The relationship between the gas production

based on the VS loading and that determined from the COD loading can then be determined.

Trials 25 and 26 respectively represent the lowest (16.8% w/w) and highest (33.2% w/w) pretreatment solids concentrations investigated. A comparison of the two trials clearly indicates the benefits of performing pretreatment under the more dilute conditions. Trial 25 demonstrated a 35.9% greater gas production on a VS basis and a 30.0% increase on a COD basis over Trial 26.

Trial 27 underwent the shortest pretreatment time investigated (19 minutes). This trial was conducted using a 5.5% w/w NaOH dose and a comparison with the center-point runs (Trials 19 and 29), which used a pretreatment time of one hour, demonstrates that no significant variation in biodegradability occurred. It is possible that even shorter pretreatment times may be utilized with success.

3. WHEAT STRAW STUDY

3.1 Experimental Procedure

As only a short time is available for a study of the thermochemical pretreatment of wheat straw, the effect of only two independent variables, pretreatment temperature and NaOH dose, will be investigated. These will be studied in a full 3^2 factorial design with replicated center points (Table 4).

To allow a comparison to be made between this study and the corn stover investigation, the uncoded levels of the indepdent variables have been selected to be compatible with those used in the stover experimental design (Table 5) (McFarlane and Pfeffer, 1980). For all trials a pretreatment time of one hour at temperature and a solids concentration of 25% w/w will be used. These values correspond to the center point values used in the corn stover experimental design.

The dependent variables studied will be identical to those used in the corn stover investigation. These are presented in Table 6.

3.2 Results and Discussion

No performance data are available for inclusion in this report as Trial 5, which is currently underway, has not been completed. However, some of the preliminary problems experienced may be described.

Initially, there was considerable difficulty pumping a 5% TS slurry of freshly pretreated straw. The digester could not be loaded using the pump operated from a time clock. It was necessary to prime the pump with water and manually control its operation during feeding.

The fresh 5% TS straw slurry had the appearance of cooked oatmeal, was much more viscous than a comparable corn stover slurry and contained much of the yellow color originally present in the straw. By contrast, the

Table 4: Experimental Design Used for the Wheat Straw Study

Trial Number	Coded Independent Variables x_1 Temperature	x_2 NaOH Dose
1	-1	-1
2	0	-1
3	1	-1
4	-1	0
5	0	0
6	1	0
7	-1	1
8	0	1
9	1	1
10	0	0
11	0	0

Table 5: Definition and Levels of Independent Variables Used in the Wheat Straw Experimental Design

Independent Variable	Coded Symbol	Coded Level -1	0	1
Pretreatment Temperature (°C)	x_1	106	133	160
NaOH dose (w/w%)	x_2	3.25	5.50	7.75

Table 6: Dependent Variables Studied

A. Pretreatment Variables (all data collected following pretreatment)

1. pH
2. Alkalinity
3. Total COD
4. Soluble COD

B. Holding Tank Variables

1. pH
2. Total Solids
3. Volatile Solids
4. Alkalinity
5. Total COD
6. Soluble COD

C. Digester Variables

1. pH
2. Total Solids
3. Volatile Solids
4. Alkalinity
5. Gas Production
6. Gas Composition
7. Total Volatile Acids

corn stover slurries were dark brown. However, after being in the holding tank for one week, the appearance of this slurry changed dramatically. It was far less viscous, with a dark green-brown color and could readily be pumped using the automated feeding system.

Some problems acclimating this digester to the new feedstock have been encountered and current efforts are being directed towards resolving these problems.

4. SUMMARY

1. The current investigation into the thermochemical pretreatment of corn stover is approximately 50% complete. A lack of stover has resulted in a reduced experimental program until October when more will become available.
2. A study of the thermochemical pretreatment of wheat straw will be undertaken during the next quarter.
3. Gas yields ranging from 0.188 to 0.295 m^3 CH_4/kg VS loaded were obtained under a wide variety of pretreatment conditions.
4. Trial 28 using a pretreatment time of 3.16 hours did not achieve steady-state. Extended pretreatment times appear to cause the formation of products inhibitory to the methanogenic bacteria.

5. REFERENCES

Gossett, J. M., J. B. Healy, Jr., W. F. Owen, D. C. Stuckey, L. Y. Young and P. L. McCarty (1976): Heat Treatment of Refuse for Increasing Anaerobic Biodegradability. Report No. NSF/RANN/SE/AER-74-17940-A01/PR/76/2, ERDA/NSF/7940-76/2. Dept. of Civil Engineering, Stanford University, Stanford, CA.

McFarlane, P. N. and J. T. Pfeffer (1980): Biological Conversion of Biomass to Methane. Quarterly Progress Report for Period January 1 to March 31, 1980. Prepared for Solar Energy Research Institute, Golden, CO.

Pfeffer, J. T. (1980): Biological Conversion of Biomass to Methane - Final Report. Prepared for the U.S. Dept. of Energy under contract No. EY-76-S-02-2917. Report No. UILU-ENG-80-2009.

ANAEROBIC FERMENTATION OF LIVESTOCK AND CROP RESIDUES

Quarterly Progress Report
April to June, 1980

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Prepared for

Solar Energy Research Institute
Biomass Program Office

SUMMARY

The effects of mixing duration and vacuum on methane production rates from anaerobically-fermented beef cattle wastes were discussed. The results showed that continuously-mixed fermentors produced significantly ($P<0.05$) higher methane production rates than fermentors mixed two hours per day. However, the rates from the continuously-mixed fermentors were only 8 to 11% higher than the intermittently-mixed fermentors at 6 and 4 days hydraulic retention time (HRT), respectively. There was no significant difference between the vacuum and conventional fermentors at 6 days HRT, but there was a significant difference at 4 days HRT. The CH_4 production rate of the vacuum fermentors was 5% higher than the conventional fermentors at 4 days HRT. The results of these experiments compared well with predicted CH_4 production rates. These results suggest that there is little potential for increasing the fermentation rates of livestock wastes by increased mixing or vacuum.

INTRODUCTION

Finney and Evans [1] hypothesized that the rate limiting step in the biological production of CH_4 is the phase transfer of products, and that the product gases (CH_4 and CO_2) inhibit methanogenic bacteria. They suggested that vigorous agitation, low pressure (vacuum), and elevated temperatures would increase the rate of phase transfer, and result in high CH_4 production rates.

However, Coppinger et al. [2] reported no decrease in gas production from a full-scale dairy manure fermentor when mixing was discontinued. They reported that gas bubbling and thermal-convection currents provided sufficient mixing. Others [3, 4] have recommended intermittent mixing for livestock waste fermentors operating under mesophilic conditions and loading rates of 6 kg volatile solids (VS)/m^3 fermentor·d or less. Under these conditions, CH_4 production rates of 1 L CH_4/L fermentor·d was expected. High-rate, thermophilic fermentations of beef cattle manure have produced over 4.5 L CH_4/L

fermentor•d under continuously-mixed conditions [5, 6]. This study was undertaken to determine whether continuous mixing was necessary to maintain high CH_4 production rates under thermophilic conditions, and whether vacuum fermentation would yield even higher CH_4 production rates.

METHODS

Experiment Design

Two sets of experiments were conducted to examine the hypotheses presented above:

Experiment 1: Effect of mixing duration on CH_4 production rate (temperature of 55°C, mixing speed of 220 revolutions per minute).

a. Four fermentors at 6 d HRT and mixed for either 1, 2, 3 or 24 h/d.
b. Four fermentors at 3 d HRT and mixed for either 1, 2, 3 or 24 h/d.
c. Duplicate fermentors at 6 d HRT and mixed for either 2 or 24 h/d.
d. Duplicate fermentors at 4 d HRT and mixed for either 2 or 24 h/d.

Experiment 2: Effect of vacuum (0.96 atm., -38 cm of water column) on CH_4 production rate (temperature of 55°C, continuous mixing).

a. Two vacuum fermentors and two conventional fermentors at 6 d HRT.
b. Two vacuum fermentors and two conventional fermentors at 4 d HRT.

Fermentors

Figure 1 illustrates the anaerobic fermentors used in Experiment 1. The

fermentors were 4 L Pyrex reaction kettles (Corning 6947) modified with an outlet fused to the bottom of each kettle. The feed-tube outlet was placed below the 3-L working-volume level to minimize the introduction of air during feeding. Mixing was accomplished by two, 5.5 cm diameter, 3-bladed propellers spaced 14 cm apart on the shaft. The intermittently-mixed fermentors were mixed while samples were withdrawn and the fermentors were fed. The mixer was a 20 watt variable speed motor operating at 220 revolutions per minute. The fermentor temperature (55°C±1°C) was maintained by a heating mantle controlled by a variable transformer. The fermentors were housed in a walk-in, constant-temperature chamber maintained at 25°C.

Figure 2 illustrates the experimental anaerobic fermentors used in Experiment 2. The fermentors were 4-L aspirator bottles with approximate working volumes of 3 L. The fermentors were similar to those described by Varel et al. [5] except that two 6 cm x 2 cm plexiglas baffles were glued to the side of the fermentor (one baffle near the liquid surface and one near the bottom) to aid mixing. The fermentors were placed on a reciprocating platform shaker, reciprocating 140 times per minute, and housed in a constant-temperature chamber. Fermentor temperatures were maintained by heating tapes wrapped around the aspirator bottles, and adjusted by variable transformers. The fermentors were maintained at the desired temperature with a variation of 1°C.

The biogas produced by the fermentors in Experiment 1 and the conventional fermentors in Experiment 2 was collected in Tedlar bags (Pollution Control Corp., Chicago, IL). The vacuum fermentation gas collection system (Figure 3) consisted of two carboys with a 1.7 m difference in elevation. A transducer measured the vacuum on the fermentor head-space, and opened a solenoid valve when the transducer measured a pressure greater than 0.96 atm. The opened solenoid valve allowed the collection solution (20% NaCl and 0.5%

citric acid) in the elevated carboy to flow to the lower carboy and maintain the designated vacuum. The biogas collected in the elevated carboy was displaced into gas collection bags by opening the 2-way stopcock and pumping the collection solution back to the elevated carboy.

Substrate

Beef cattle manure (feces and urine) was the substrate used in these experiments. The manure for Experiments 1a and 1b was collected from young steers (weighing about 300 kg) confined to indoor, metabolism stalls on concrete floors. The manure was collected daily and frozen until about 200 kg was accumulated. The ration for these steers consisted of 87.6% corn, 7% corn silage, 3.3% soybean meal, 1.6% limestone, 0.5% salt and trace mineral and vitamin A, D and E supplements.

The manure for Experiments 1c and 1d was collected from steers (weighing over 400 kg) fed a ration consisting of 85% corn, 13% corn silage and 2% soybean meal-mineral supplement (80.5% soybean meal, 11.5% limestone, 3% dicalcium phosphate, 0.8% vitamin A, D and E, 0.2% beef trace minerals, and 3.75% salt). The manure was less than three days old and scraped off concrete-floored pens. The manure for Experiments 2a and 2b was from the same group of cattle as Experiment 1c and 1d, but was collected about one month later.

The manures for Experiments 1 and 2 were diluted with tap water to a total solids content of about 14%. The slurry was then poured into 1-L polyethylene bottles and stored at -20°C until used. Before use, the bottles were placed in a refrigerator to thaw overnight, and the slurry was diluted with hot tap water to 6 to 7% total solids.

Experimental Procedures

The fermentors in Experiment 1a were started by placing 3 L of slurry from our pilot-scale, thermophilic (55°C) fermentor into each fermentor. The

temperature was adjusted to 55°C, and all four fermentors were mixed continously. After two days of acclimation, the mixers were connected to time clocks which allowed mixing periods of 1, 2, 3 or 24 h/d. The fermentors were operated at each retention time for 4 volume turnovers before steady-state gas production rates were measured and effluent quality were analyzed for 5 consecutive days. The HRT was then reduced to 3 days (Experiment 1b) and operated at this HRT for 4 volume turnovers before steady-state gas production rates were measured and effluent quality were analyzed.

The same start-up procedure used in Experiment 1a was used in starting Experiments 1c and 2a, except that duplicate fermentors were mixed at either 2 h/d or 24 h/d for Experiment 1c, and duplicate fermentors were either vacuum or conventional fermentors in Experiment 2a. After steady-state data at 6 d HRT were obtained, the HRT was reduced to 4 days (Experiments 1d and 2b).

After steady-state data at 4 d HRT were obtained for Experiment 2b, the 4 fermentors (2 vacuum and 2 conventional) were not fed and the CH_4 production was measured periodically until negligible gas was produced (102 to 126 days). The ultimate CH_4 yield was calculated by the following formula:

$$B_o = (\bar{V}_d \cdot \theta + V_b)/S_o \cdot V_f \qquad (1)$$

where: B_o = ultimate CH_4 yield, L CH_4/g VS fed (VS_f)

$\bar{V}_d$ = average steady-state CH_4 production rate, L CH_4/d

θ = hydraulic retention time, d

V_b = total volume of CH_4 produced under batch conditions, L CH_4

S_o = influent VS concentration, g VS/L

V_f = liquid volume of fermentor, L

Analytical Methods

The slurry fed to the fermentors and the fermentor effluent during steady-state were analyzed for total solids (TS), volatile solids (VS), fixed

solids (FS), ammonia (distillation method), chemical oxygen demand (COD), alkalinity (to pH 3.7), pH, and total volatile acids (TVA, silicic acid method) using the standard methods for wastewater analysis [7]. Total Kjeldahl nitrogen was determined by the method described by Wael and Gehrke [8].

Samples for TVA analysis were prepared by diluting 25 mL of sample to 100 mL, adjusting the pH to 1.0 - 1.2 with 80% H_3PO_4, and centrifuging at a relative centrifugal force of 12,062 x G for 30 minutes. Aliquots of the supernatant were used in the TVA analysis.

The volume of gas produced was measured using the apparatus shown in Figure 4. Before gas-volume measurement, the top carboy (18 L) was filled with a solution containing 20% NaCl and 0.5% citric acid by pumping the solution from the bottom carboy. The electronic balance (Mettler Model PS 30) was then tared to zero and the gas collection bag was attached to the apparatus. The stopcocks from the gas bag, manometer and bottom carboy were then opened to allow the solution to siphon from the top carboy and evacuate the gas bag. While the gas bags were being evacuated, 0.5 mL gas samples were withdrawn with a syringe and analyzed for CH_4 and CO_2. When the gas bags were completely evacuated (i.e., solution displacement ceased), the weight of the solution displaced, the manometer reading and the gas temperature were recorded. The total gas volume was then calculated using the solution density (1.028 kg/L) and corrected to standard pressure (1 atm.), and temperature (0°C), and zero water vapor.

CH_4 and CO_2 concentrations were measured using a Packard Model 428 gas chromatograph with dual thermal conductivity detectors. The stainless steel column (0.64 by 183 cm) was packed with 60/80 mesh Chromosorb 102. Injector, oven detector and filament temperatures were 100, 130, 70 and 350°C, respectively. The helium carrier gas flow was 40 mL/min.

RESULTS

Effect of Mixing

Table 1 summarizes the influent and effluent concentrations and CH_4 production of the fermentors operated at 6 days HRT, 55°C, loading rate of 9.6 g VS/L·d and mixed for 1, 2, 3 or 24 h/d. The concentration and percent reduction in TS, VS and COD were similar for the four fermentors. The influent and effluent FS concentrations were the same in three of the fermentors and only about 5% less in the other fermentor, indicating that the fermentor contents were being completely mixed. The low total volatile acids concentrations (less than 0.4 g/L as acetic acid), high alkalinity (over 5 g/L as $CaCO_3$) and stable pH (about 7.4) indicate that all of the fermentors were operating well and not stressed. The CH_4 production rates and yields show that the fermentors mixed for 1, 2 and 3 h/d produced slightly more CH_4 than the fermentor mixed 24 h/d.

The fermentors were then operated at the same temperature (55°C) and mixing periods (1, 2, 3 and 24 h/d) as the previous study, but at 3 days HRT and loading rate of 20.4 g VS/L fermentor·d. This high loading rate was imposed to determine whether continuous mixing is necessary when fermentors are heavily loaded or stressed. Two of the four fermentors failed in this experiment; therefore, meaningful conclusions could not be drawn.

Based on the previous results, a more detailed experiment was initiated to determine whether intermittent mixing was signficantly different from continuous mixing. Two thermophilic (55°C) fermentors were mixed 2 h/d and two fermentors were mixed continuously. These fermentors were first operated at 6 days HRT then at 4 days HRT. Table 2 summarizes the mean steady-state results of this experiment. Analyses-of-variance showed no significant difference in effluent characteristics between the 2 and 24 h/d fermentors operated at 6 days HRT; however, significant ($P<0.05$) differences were noted in fixed

solids, total nitrogen, ammonia and pH between the fermentors at 4 days HRT. Table 2 also shows that the continuously-mixed fermentors produced CH_4 at significantly ($P<0.05$) higher rates than the fermentors mixed 2 h/d. The CH_4 production rates (L CH4/L fermentor.d) of the continuously-mixed fermentors were 8% (6 day HRT) and 11% (4 day HRT) higher than the fermentor mixed 2 h/d.

Effect of Vacuum

Table 3 summarizes the mean steady-state conditions of the vacuum (0.96 atm.) and conventional fermentors operated at 55°C and 6 and 4 days HRT. At 6 days HRT, there were significant ($P<0.05$) differences between the vacuum and conventional fermentors in TS, VS, COD, total nitrogen and methane concentration, but no significant difference in CH_4 production rate. At 4 days HRT, there were significant ($P<0.05$) differences between the vacuum and conventional fermentors in FS, COD, ammonia, alkalinity, pH, CH_4 production rate and CH_4 yield (L CH_4/g VS_u). The CH_4 production rate for the vacuum fermentors was 5% higher than the conventional fermentors at 4 days HRT.

After steady-state at 4 days HRT was completed, the fermentors were not fed and the CH_4 production was measured. Using Equation 1 to estimate B_o, the mean B_o was calculated to be 0.36 ± 0.02 L CH_4/g VS_f.

DISCUSSION

Effect of Mixing

The preliminary mixing experiments (1a and 1b) indicated that intermittent mixing may produce more rapid CH_4 production rates than continuously mixed fermentors. However, the more controlled experiments (1c and 1d) showed that statistically higher CH_4 production rates were achieved when fermentors were mixed continuously. The increased CH_4 production rates for the continuously mixed fermentors were, however, only 8 to 11% higher than the intermittently mixed fermentors.

To investigate further the effect of intermittent mixing on anaerobic

fermentation, our pilot-scale (5.7 m^3), thermophilic (50°C) fermentor [9] was operated at 5 d HRT and mixed continuously for 5 volume turnovers (25 days, steady-state at days 20 to 25), then mixed 2 h/d for 25 days. The steady-state operating parameters of the fermentor (Table 4) indicates similar performance when mixed continuously and 2 h/d. Based upon the results presented here, it is difficult to justify the increased energy needed to continuously mix the fermentor when the CH_4 production rate is increased, at the most, only about 10%. Thus, the recommendations for intermittent mixing of farm-scale fermentors is justified.

This study, however, only evaluated the effect of mixing on CH_4 production rate, and did not address the materials handling function that mixing also provides. If insufficient mixing causes solids deposition in the fermentor, the effective fermentor volume decreases. This decrease in effective volume affects important operational parameters such as HRT and loading rate. Thus, the minimum mixing requirement for fermentation systems may be based on the materials handling and fermentor design aspects rather than maximum CH_4 production rates. More research is needed in understanding the materials handling function of mixing systems in anaerobic fermentors.

Effect of Vacuum

This study showed that vacuum (0.96 atm.) did not increase the rate of CH_4 production over conventional fermentation systems at 6 days HRT, but did increase the rate about 5% at 4 days HRT. It is possible that a higher vacuum would have increased the CH_4 production rate even more than was measured in this study. The vacuum used in this study was only about 10% of the vacuum (0.33 atm.) reported by Finney et al. [10]. However, the higher capital cost and operational problems associated with maintaining anaerobic conditions at high vacuum precludes the use of farm-scale, vacuum fermentation in the near future.

Comparison of Experimental to Predicted CH_4 Production Rates

Because the differences in CH_4 production rates between conventional, continuously-mixed fermentors and intermittently-mixed or vacuum fermentors were only 11% or less, these rates were compared to rates predicted by the kinetic model developed by Chen and Hashimoto [11]:

$$\gamma_V = (B_o\ S_o/\theta)/(1 - K/(\theta\ \mu_m - 1 + K)) \qquad (2)$$

where: γ_V = volumetric CH_4 production rate, L CH_4/L fermentor·d,

B_o = ultimate CH_4 yield, L CH_4/g VS_f as $\theta \longrightarrow \infty$,

S_o = influent VS concentration, g/L,

θ = hydraulic retention time, d,

μ_m = maximum specific growth rate, d^{-1},

K = kinetic parameter, dimensionless.

Values for B_o were determined by long-term batch fermentations for Experiments 1a and 1b (B_o = 0.29 L CH_4/g VS_f) and as described in this study for Experiments 1c, 1d, 2a and 2b. The values for μ_m (0.586 at 55°C) and K were taken from the relations for μ_m vs temperature and K vs S_o presented previously [12].

Table 5 and Figure 5 show the experimental and predicted γ_V for all the fermentations conducted in this study. The results show good correlation between the experimental and predicted γ_V, with a mean ratio of experimental to predicted γ_V of 0.96 and a standard deviation of ± 0.06. These results show that the γ_V obtained in these studies are comparable to those predicted for conventional fermentors.

A general conclusion from this study is that phase-transfer controlling mechanisms (i.e., mixing, vacuum) have minimal effect on the CH_4 production rate from fermentation of beef cattle waste, even for high-rate anaerobic fermentation systems. Thus, these results suggest that intermittently-mixed, conventional fermentors can produce high CH_4 production rates while minimizing

energy and capital inputs. This study also shows that good prediction of CH_4 production rates can be achieved using a previously published kinetic model.

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TABLE 1. SUMMARY OF STEADY-STATE OPERATING PARAMETERS FOR THERMOPHILIC (55°C) FERMENTORS OPERATED AT SIX DAYS HYDRAULIC RETENTION TIME AND MIXED FOR VARIOUS PERIODS PER DAY[a]

Parameter	Influent	1h	2h	3h	24h
Total Solids					
g/L	63.9±1.5	34.7±0.9	33.5±0.09	34.6±1.3	34.9±0.8
Change, %	---	-45.7	-47.5	-45.9	-45.4
Volatile Solids					
g/L	57.5±1.2	28.3±0.7	27.1±0.9	28.5±0.6	28.5±0.8
Change, %	---	-50.8	-52.9	-50.4	-50.4
Fixed Solids					
g/L	6.4	6.4	6.4	6.1	6.4
Change, %	---	0	0	-4.7	0
Volatile Acids					
g HOAc/L	2.28±0.47	0.29±0.03	0.37±0.05	0.30±0.05	0.33±0.08
pH					
Unit	---	7.38±0.07	7.37±0.08	7.46±0.06	7.45±0.07
Methane					
%	---	49.7±3.3	49.5±2.9	49.2±3.4	49.4±3.0
Methane Production					
L/L·d	---	2.38±0.19	2.51±0.20	2.37±0.18	2.15±0.11
L/g VS fed	---	0.25	0.26	0.25	0.22
L/g VS used	---	0.49	0.50	0.49	0.45

[a]Mixed at 220 revolutions per minute

TABLE 2. SUMMARY OF STEADY-STATE OPERATING PARAMETERS FOR THERMOPHILIC (55°C) FERMENTORS OPERATED AT 4 AND 6 DAYS HYDRAULIC RETENTION TIMES AND MIXED[a] FOR 2 OR 24 HOURS PER DAY

Parameter	Influent[b]	Hydraulic Retention Time[c]			
		6 days		4 days	
		2 h/d	24 h/d	2 h/d	24 h/d
Total Solids, g/L	65.0±2.3	34.2±0.6	33.8±0.4	34.8±0.8	35.6±0.8
Volatile Solids, g/L	56.1±2.2	25.8±0.7	25.9±1.0	26.8±1.2	27.0±0.6
Fixed Solids, g/L	8.9	8.4±0.1	7.9±0.6	8.0±0.3[f]	8.6±0.2[g]
Chemical Oxygen Demand, g/L	60.8±5.9	35.0±0.8	34.2±1.4	30.8±0.1	30.5±0.5
Nitrogen					
Total, g/L	2.75±0.12	2.80±0.02	2.80±0.02	2.68±0.04[f]	2.77±0.01[g]
Ammonia, g/L	0.99±0.13	1.54±0.03	1.56±0.01	1.38±0.01[f]	1.28±0.03[g]
Total Volatile Acids, g/L	6.48±1.00	0.77±0.09	0.70±0.08	1.60±0.34	1.14±0.04
Alkalinity, g/L	3.56±0.88	7.94±0.16	7.95±0.08	7.40±0.16	7.18±0.14
pH					
Unit	5.23±0.52	7.54±0.01	7.52±0.01	7.44±0.01[f]	7.26±0.02[g]
Methane, %	---	56.1±0.5	56.2±0.2	55.6±0.2[f]	56.4±0.4[g]
Methane Production					
L/L·d	---	2.62±0[d]	2.84±0.06[e]	3.57±0.23[f]	3.96±0.6[g]
L/g VS fed	---	0.28±0[d]	0.30±0.01[e]	0.26±0.02[f]	0.28±0.01[g]
L/g VS used	---	0.52±0.01	0.56±0.04	0.49±0.01[f]	0.54±0.02[g]

[a]Mixed at 220 revolutions per minute

[b]Data presented as mean ± one standard deviation of 15 determinations

[c]Data presented as mean ± one mean standard deviation of 2 fermentors per treatment (5 obs./ferm.)

[d,e,f,g]Means bearing different superscripts in the same row are significantly different ($P < 0.05$)

TABLE 3. SUMMARY OF STEADY-STATE OPERATING PARAMETERS FOR VACUUM[a] AND CONVENTIONAL[b] THERMOPHILIC (55°C) FERMENTORS OPERATED AT 4 AND 6 DAYS HYDRAULIC RETENTION TIMES

Parameter	Influent[c]	Hydraulic Retention Time[d] 6 days Vacuum	6 days Conventional	4 days Vacuum	4 days Conventional
Total Solids, g/L	76.6±4.6	31.8±1.2[e]	34.0±0.1[f]	37.4±0.8	36.4±0.8
Volatile Solids, g/L	68.4±4.0	25.2±1.0[e]	27.2±0.2[f]	29.8±0.6	29.5±1.0
Fixed Solids, g/L	8.2	6.6±0.1	6.8±0.2	7.6±0.2[g]	6.9±0.2[h]
Chemical Oxygen Demand, g/L	71.7±9.8	38.2±0.6[e]	39.9±0[f]	43.2±1.0[g]	46.8±0.4[h]
Nitrogen					
Total, g/L	3.01±0.20	2.84±0.01[e]	2.95±0.02[f]	2.84±0.01	2.82±0.04
Ammonia, g/L	0.73±0.09	1.48±0.04	1.42±0.04	1.38±0.03[g]	1.30±0.02[h]
Total Volatile Acids, g/L	7.61±0.56	1.48±0.20	1.25±0.01	2.04±0.02	2.02±0.01
Alkalinity, g/L	2.23±0.44	7.10±0.12	6.88±0.52	6.86±0.06[g]	6.24±0.36[h]
pH					
Unit	4.58±0.51	7.62±0.01	7.63±0.04	7.44±0.01[g]	7.22±0.02[h]
Methane, %	---	52.2±0.02[e]	54.6±0.6[f]	53.8±1.0	53.9±0.6
Methane Production					
L/L·d	---	3.45±0.07	3.54±0.01	4.28±0.10[g]	4.08±0.05[h]
L/g VS fed	---	0.30±0.01	0.31±0.0	0.25±0.01	0.24±0
L/g VS used	---	0.48±0.02	0.52±0.01	0.44±0.01[g]	0.42±0.01[h]

[a]Vacuum of 0.96 atm.

[b]Atmospheric pressure

[c]Data presented as mean ± one standard deviation of 16 determinations

[d]Data presented as mean ± one mean standard deviation of 2 fermentors per treatment (5 obs./ferm.)

[e,f,g,h]Means bearing different superscripts in the same row are significantly different ($P < 0.05$)

TABLE 4. SUMMARY OF STEADY-STATE OPERATING PARAMETERS FOR THERMOPHILIC (55°C), PILOT-SCALE FERMENTOR OPERATED AT SIX DAYS HYDRAULIC RETENTION TIME AND MIXED CONTINUOUSLY AND TWO HOURS PER DAY[a]

Parameter	Mixing Duration, h/d	
	24	2
Total Solids		
Inf., g/L	67.7±3.3	69.6±4.1
Eff., g/L	34.4±0.4	33.1±0.8
Volatile Solids		
Inf., g/L	59.8±3.0	61.4±3.6
Eff., g/L	26.5±0.3	25.1±0.8
Change, %	-55.7	-59.1
Fixed Solids		
Inf., g/L	7.9	8.2
Eff.,	7.9	8.0
COD		
Inf., g/L	68.9±3.5	70.2±6.9
Eff., g/L	34.0±4.3	34.8±5.1
Total Nitrogen		
Inf., g/L	2.42±0.17	2.61±0.24
Eff., g/L	2.65±0.06	2.54±0.03
Ammonia-N		
Inf., g/L	0.73±0.02	0.78±0.04
Eff., g/L	1.24±0.06	1.29±0.02
Volatile Acids		
Inf., g/L	5.07±0.70	6.72±0.82
Eff., g/L	0.62±0.10	0.92±0.35
Alkalinity		
Inf., g/L	3.33±0.15	3.19±0.26
Eff., g/L	6.57±0.22	6.79±0.27
pH		
Inf.	5.45±0.37	4.80±0.04
Eff.	7.50±0.04	7.51±0.05
Methane, %	52.5±0.8	53.9±4.7
Methane Production		
L/L·d	2.59±0.06	2.60±0.19
L/g VS_f	0.26	0.25
L/g VS_u	0.47	0.43

[a]Mixed at 160 revolutions per minute.

TABLE 5. EXPERIMENTAL AND PREDICTED VOLUMETRIC METHANE PRODUCTION RATES[a]

Fermentation Conditions	Mixing h/d	B_o L CH_4/g VS_f	θ d	S_o g VS_f/L	K	γ_v, L CH_4/L·d		Ratio Pred./Exp.
						Exp.	Pred.	
Conventional	1	0.29	6	57.5	0.60	2.38	2.24	0.94
Conventional	2	0.29	6	57.5	0.60	2.51	2.24	0.89
Conventional	3	0.29	6	57.5	0.60	2.37	2.24	0.95
Conventional	24	0.29	6	57.5	0.60	2.15	2.24	1.05
Conventional	2	0.36	6	56.1	0.60	2.62	2.72	1.04
Conventional	2	0.36	6	56.1	0.60	2.62	2.72	1.04
Conventional	24	0.36	6	56.1	0.60	2.78	2.72	0.98
Conventional	24	0.36	6	56.1	0.60	2.91	2.72	0.93
Conventional	2	0.36	4	56.1	0.60	3.80	3.49	0.92
Conventional	2	0.36	4	56.1	0.60	3.34	3.49	1.04
Conventional	24	0.36	4	56.1	0.60	3.90	3.49	0.89
Conventional	24	0.36	4	56.1	0.60	4.01	3.49	0.87
Vacuum	24	0.36	6	68.4	0.60	3.42	3.26	0.95
Vacuum	24	0.36	6	68.4	0.60	3.56	3.26	0.92
Conventional	24	0.36	6	68.4	0.65	3.55	3.26	0.92
Conventional	24	0.36	6	68.4	0.65	3.54	3.26	0.92
Vacuum	24	0.36	4	68.4	0.65	4.39	4.15	0.95
Vacuum	24	0.36	4	68.4	0.65	4.18	4.15	0.99
Conventional	24	0.36	4	68.4	0.65	4.13	4.15	1.00
Conventional	24	0.36	4	68.4	0.65	4.03	4.15	1.03

[a]Fermentation temperature = 55°C, μ_m = 0.586 d^{-1}

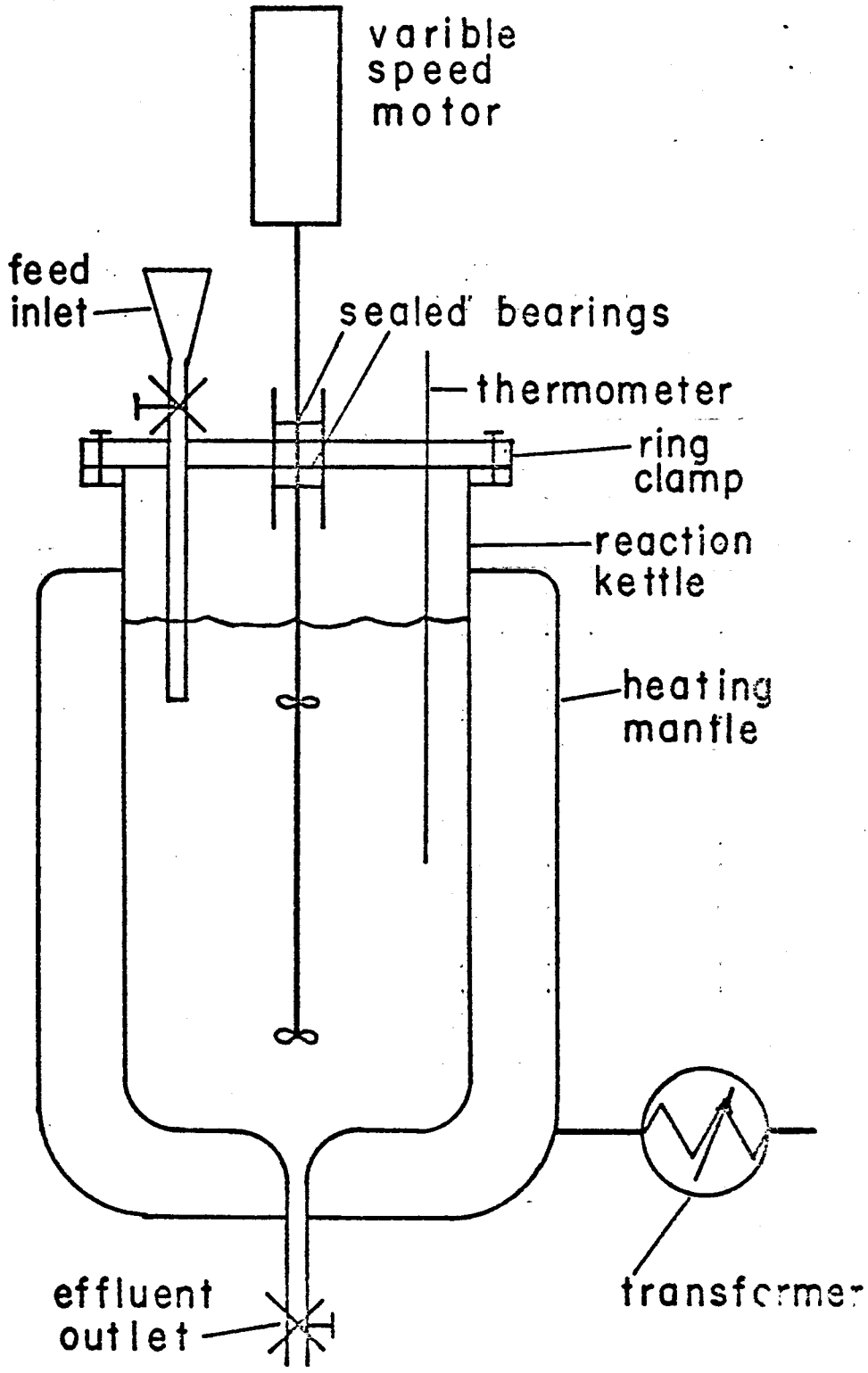

Figure 1. Anaerobic Fermentor Used in Mixing Experiments.

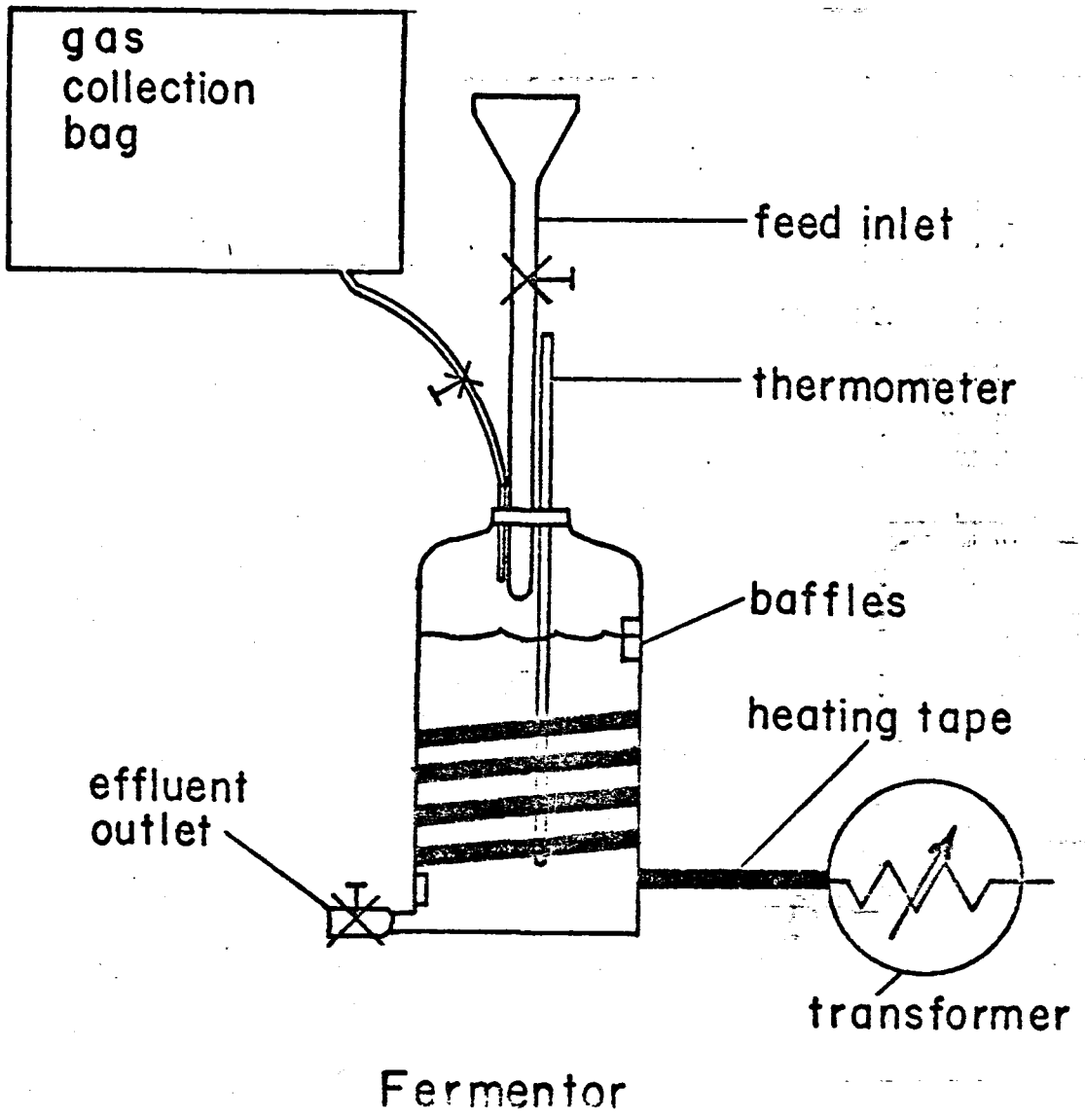

Figure 2. Anaerobic Fermentors Used in Experiment 2.

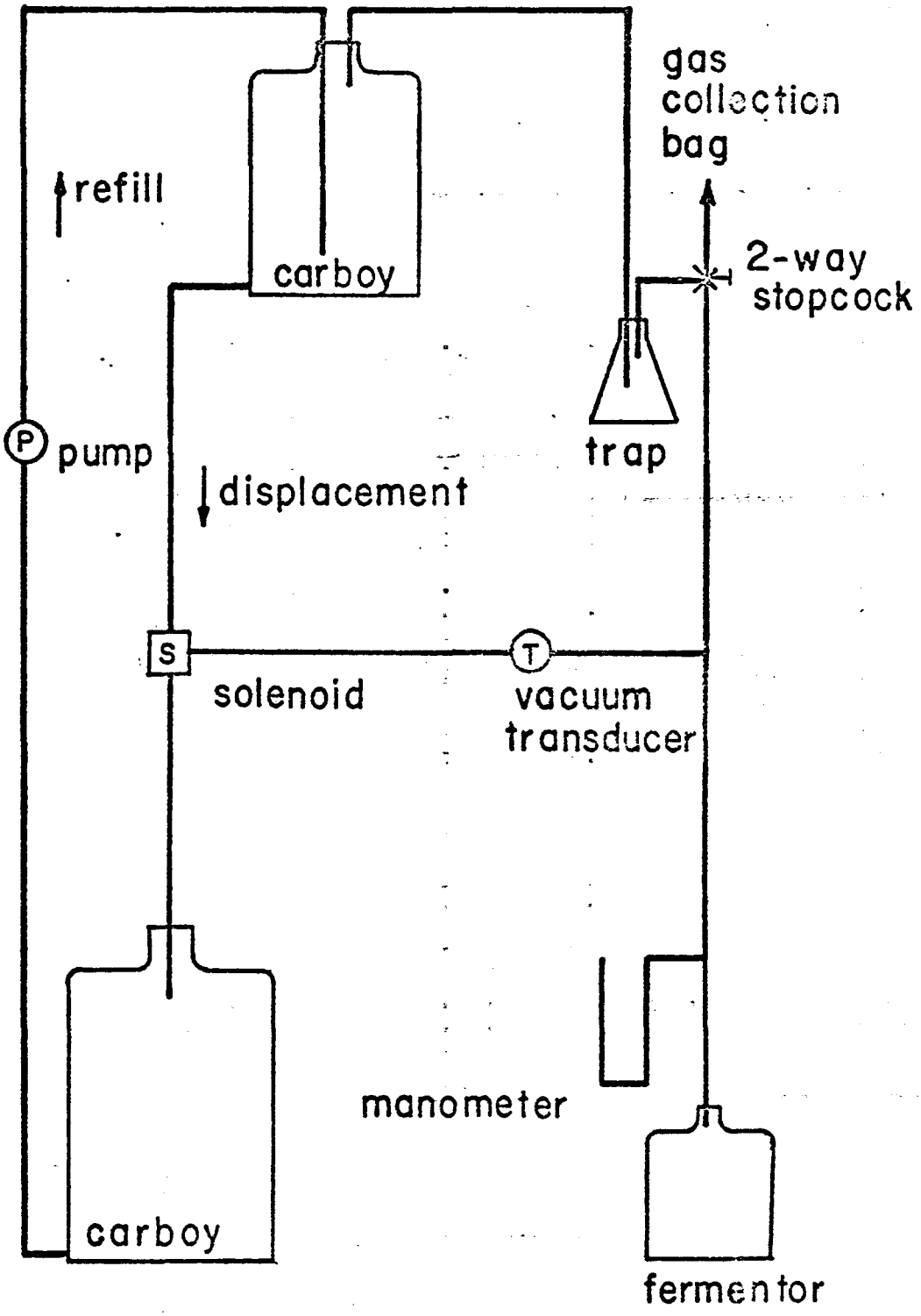

Figure 3. Schematic Diagram of Vacuum Fermentation Apparatus.

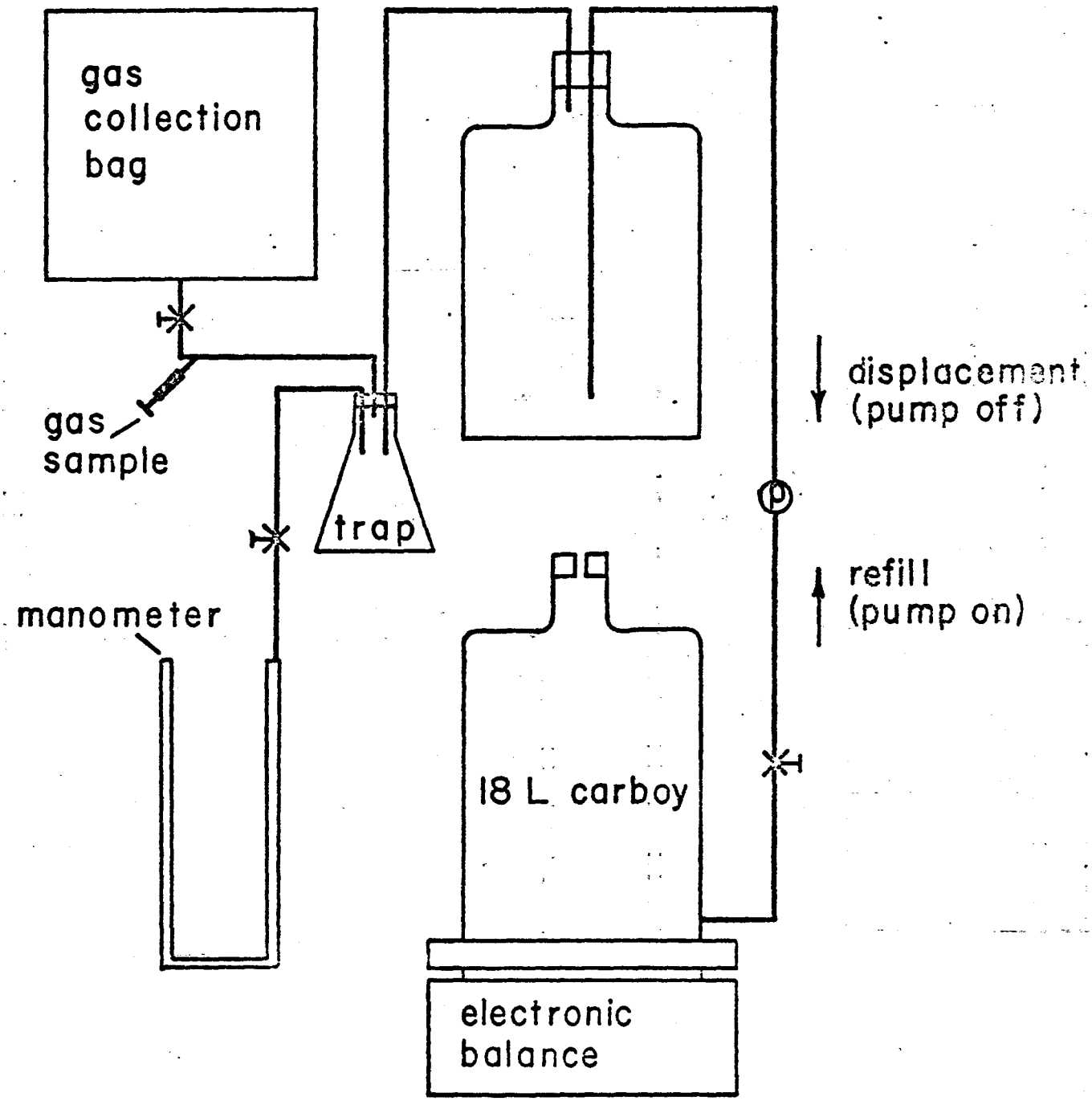

Figure 4. Apparatus for Measuring Gas Volume.

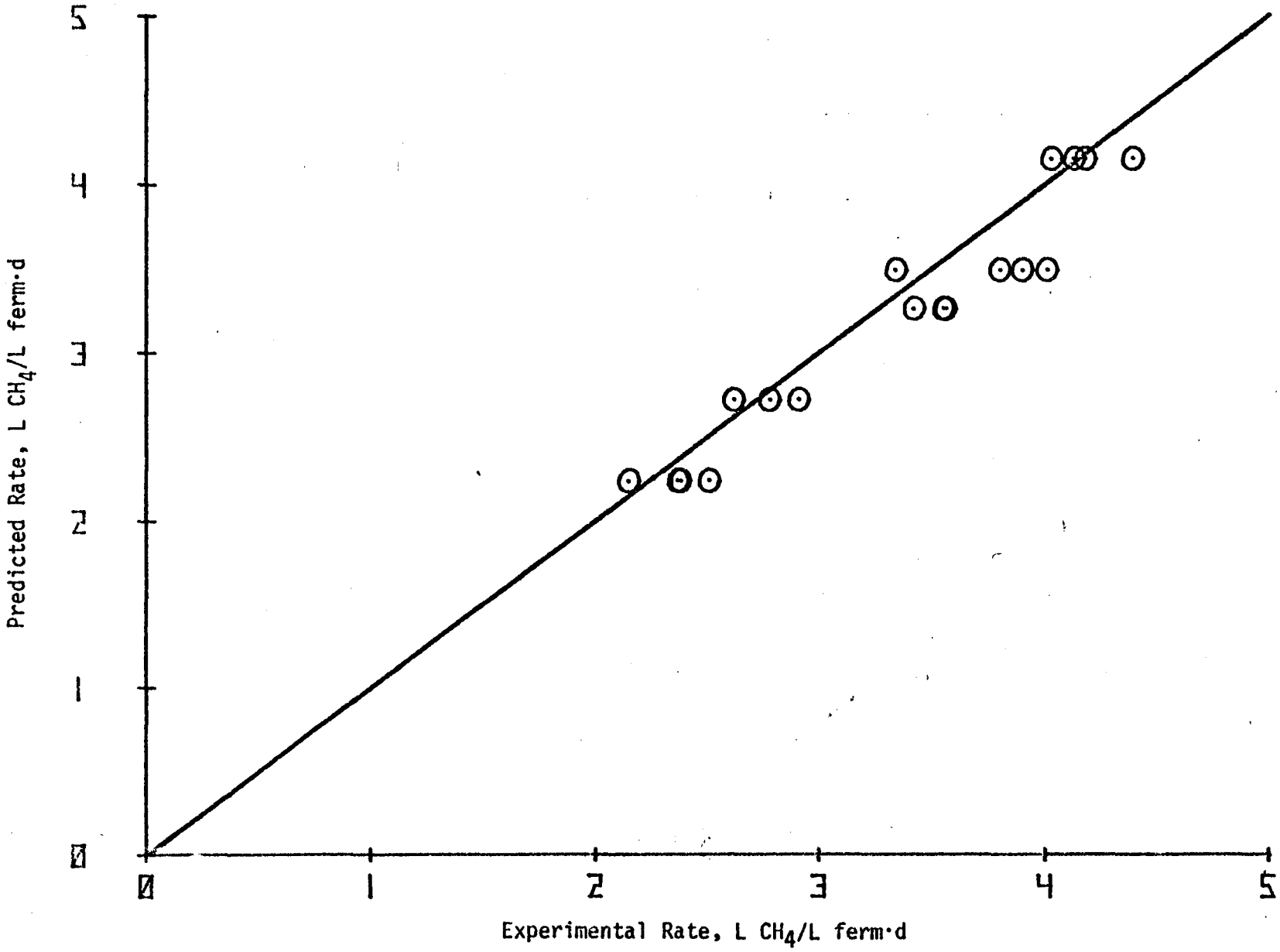

Figure 5. Comparison of Predicted and Experimental Methane Production Rates

HAMILTON STANDARD Division of UNITED TECHNOLOGIES

FUEL GAS FROM AN ENVIRONMENTAL FEEDLOT

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

PROGRESS FROM APRIL 1 TO JUNE 15, 1980

PREPARED FOR THE
QUARTERLY COORDINATION MEETING

JUNE 23-24, 1980

SUMMARY

The experimental anaerobic fermentation facility in Bartow, Florida has been operated during the second quarter of 1980 at retention times of 15 and 40 days at an operating temperature of 55°C (131°F).

The centrifuge subsystem has undergone parametric evaluation in preparation for the feeding trials scheduled to start in July.

The engine/generator subsystem installation is essentially complete. Utilization of the fermentor gas in Kaplan Industries boiler has continued.

Overall system operational status is good.

FERMENTOR PERFORMANCE

Methane concentration in the fermentor gas remains high (60+%); however, due to the low cattle population, total gas flow has been below the point where it can be reliably measured. Cattle population started to increase in early June. Fermentor chemistry remains stable with pH in the range of 7.4 to 7.6 and TVA around 1,000 ppm.

CENTRIFUGE OPERATION

Nineteen centrifuge runs were made utilizing Fermentor #2 effluent. The centrifuge parameters which can be varied are:

1 - Input flow
2 - Flocculant quantity
3 - Dilution water flow
4 - Bowl/scroll differential speed
5 - Bowl liquid depth

During the May testing, items 1, 2 and 4 were varied.

Simple data correlations have been attempted with reference to percent capture. Correlation coefficients have generally been quite low (.3 or lower) except for percent capture versus flocculant quantity where the correlation coefficient is approximately .8. The test results are shown in Figure 1. Evaluations run on-site by Hercules Inc. who supplies the flocculant (Hercofloc 815 polymer) have confirmed that our choice of 815 for this service was proper.

PRODUCT GAS UTILIZATION

The engine/generator installation is essentially complete. Start-up is scheduled for mid June.

The Kaplan Industries boiler has been utilizing fermentor gas on low fire in conjunction with oil since mid April.

SYSTEM STATUS

The system kilowatt-hour meter as well as the new flare pilots have been installed.

In order to have the least impact on the program, it was decided that a new withdrawal pump would be ordered from a different manufacturer. This has been done and delivery is expected sometime in June.

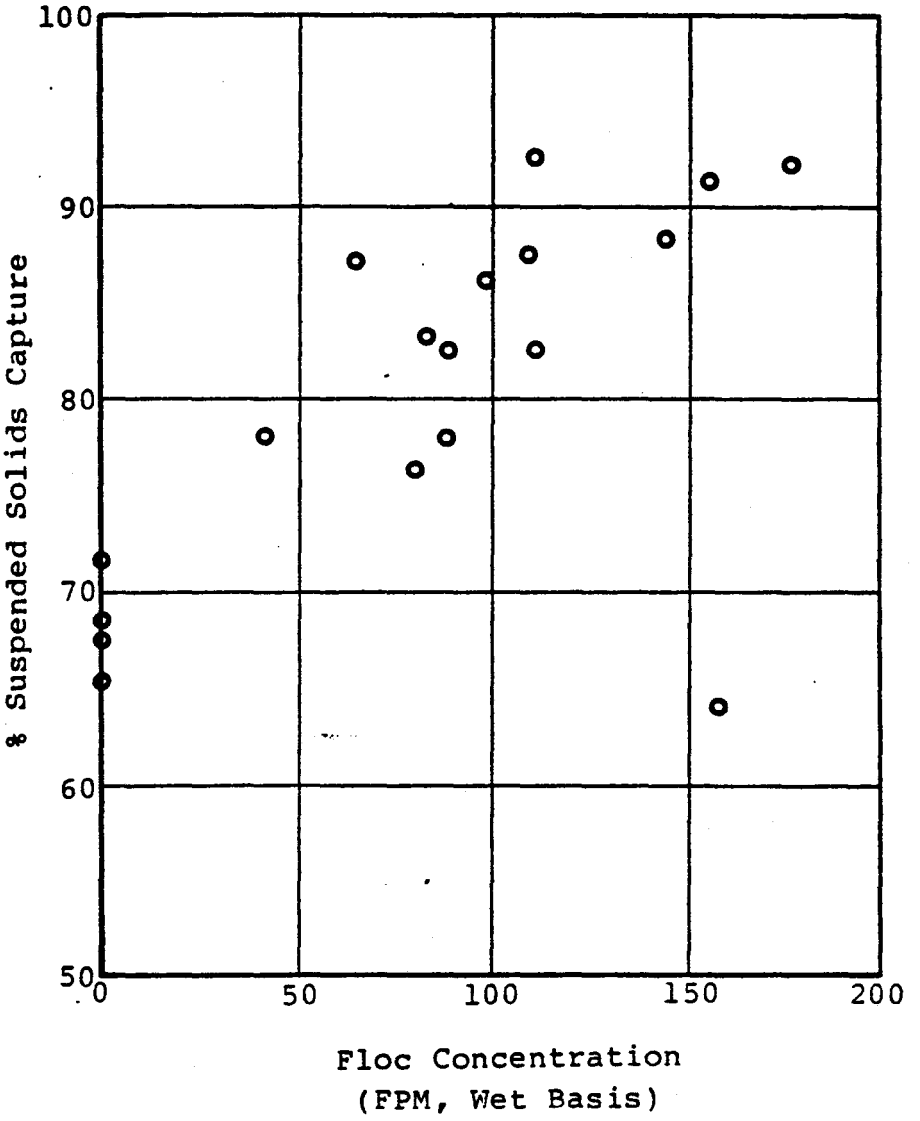
100
90
80
70
60
50
% Suspended Solids Capture
0
50
100
150
200
Floc Concentration
(FPM, Wet Basis)

FIGURE 1

BIOMETHANATION OF BIOMASS PYROLYSIS GASES

PROGRESS REPORT FOR

16th QUARTERLY COORDINATION MEETING
June 23-24, 1980

Subcontract No. XB-9-8356-1
Dynatech Project No. SLR-5

Submitted to:

Dan Jantzen
Biomass Program Office
Solar Energy Research Institute
1536 Cole Boulevard
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Prepared by

E. Ashare
C.A. Tracy
A.P. Leuschner

June 20, 1980

BIOMETHANATION OF BIOMASS PYROLYSIS GASES

Summary

Progress since the last meeting has been in completion of the laboratory set-up with associated safety design and the start-up of viable bacterial cultures for both methanation and shift conversion reactions. A mixed culture of methanogens was established utilizing sewage digester effluent and methane production of 15 VVD was attained without cell recycle or high pressure. A pure culture of Rhodopseudomonas gelatinosa sp. was obtained and this culture is converting CO to H_2 and CO_2 at a rate of 0.4 VVD.

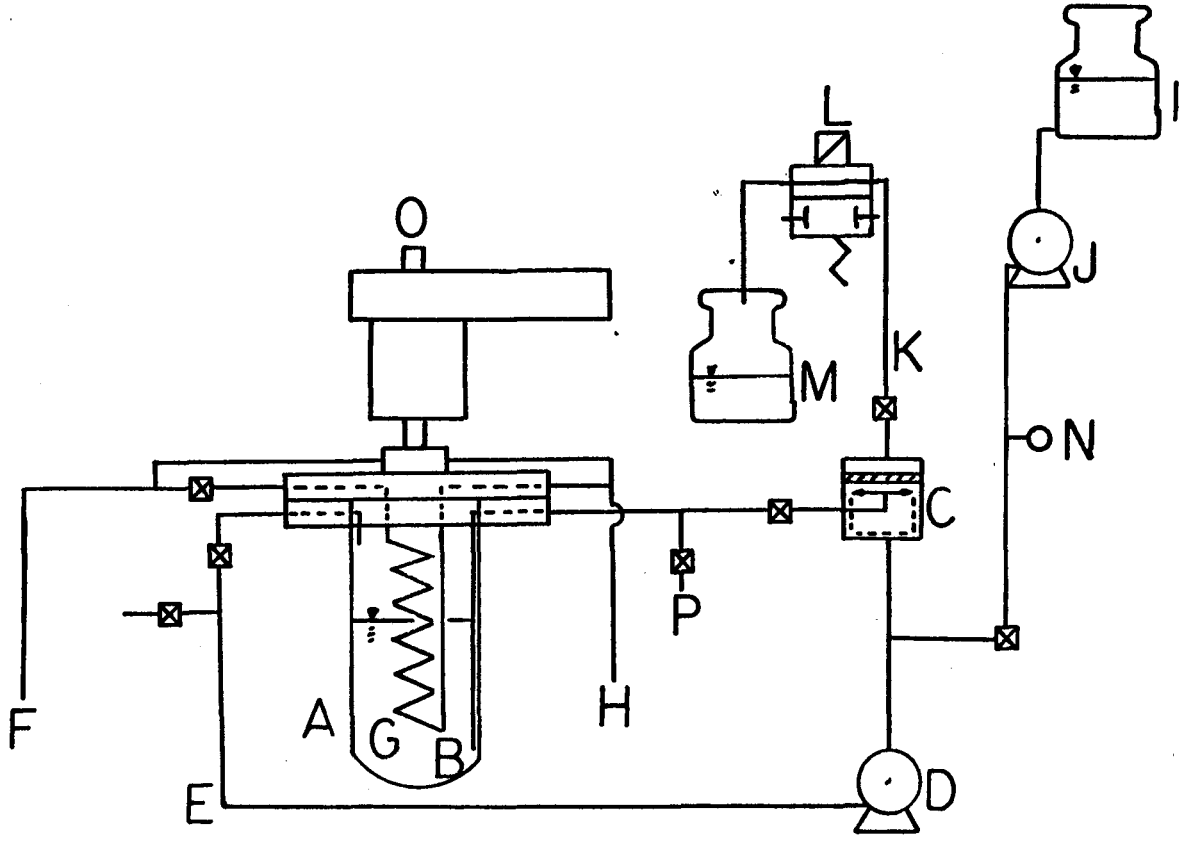
Laboratory Design

High pressure reactors, purchased from Pressure Products Industries, will be used for optimization of methanation and shift conversion reactions. The reactors are two liters in volume which allows a one liter active volume to be used for these experiments. The reactors, constructed with 316ss have a working pressure of 5,000 psig, are stirred with a magnetic couple, air-driven motor combination, and have an impeller that draws headspace gas back into the liquid. Specific alterations made to the reactors for this program include:

1. Dip tubes into both the liquid and the headspace for reactor input and output.
2. Dual thermistor sensors for liquid level control.
3. A continuous filtration system capable of separating liquid from the culture broth and recycling the cell biomass back to the reactor at pressure.

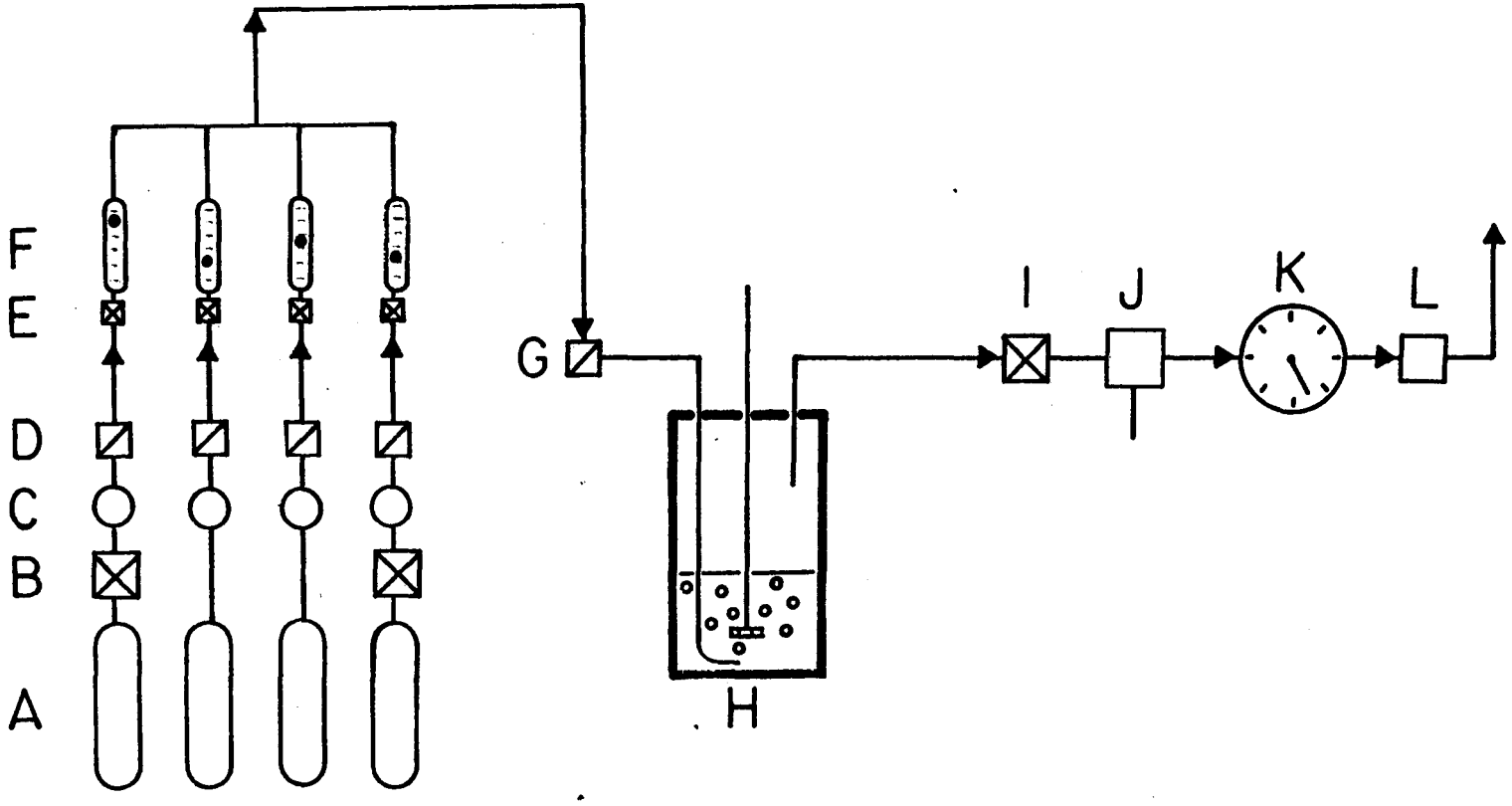
Reactor pressure is controlled by back-pressure regulating valves which drop the product gas pressure to atmospheric. The product gas flow is then quantified by a wet-test meter and passed through another sample point where it can be drawn for analysis. The product gas then flows through a flash arrestor and exits the building where an electronic igniter flares it.

A diagram of the experimental process and equipment is presented in Figures 1 and 2. Gas is regulated down to a pressure of 50 to 150 psig before entering a flow meter. The flow meters are adjusted to produce the desired gas mixture and the gases are then manifolded together. A reactant gas sample point is used to confirm that the mixture is correct. For high pressure reactors, the gas mixture is boosted by a pressure booster.



A Reactor	E Liquid Recycle Line	I Nutrient Feed	M Liquid Overflow
B Liquid Effluent Line	F Cooling Water Source	J Nutrient Pump	N Pressure Gage
C Filter	G Cooling Coil	K Filtrate Overflow Line	O Mixer
D Pump (liquid Recycle)	H Cooling Water Discharge	L Solenoid Valve	P Sample Port

FIGURE 1 HIGH PRESSURE REACTOR - LIQUID LINES



A	Gas Cylinders	E	Metering Valves	I	Shut Off Valve
B	Solenoid Valves	F	Rotameters	J	Back Pressure Regulator
C	Regulators	G	Check Valve	K	Wet Test Meter
D	Check Valves	H	P.P.I. Reactor	L	Flash Arrestor

Figure 2 Gas Distribution System

Experimental Results

The establishment of viable bacterial cultures for both the methanation and shift reactions was accomplished. For the mesophilic methanogen culture, sewage digester effluent was acquired locally from the Nut Island Sewage Treatment Facility, Quincy, Massachusetts. A medium based on yeast extract was made up and combined with the digester effluent in a New Brunswick Fermenter. The composition, 75% nutrient media-25% effluent, was reinforced with about 15% more effluent every two days for a week. Supply gases of CO_2 and H_2 were constantly bubbled into the well stirred fermenter at rates that ensured that the gas supply was always in excess. Methane production of 15 VVD has been maintained for three weeks. Part of this culture has been diluted by 80% with fresh media and transferred to the high pressure reactor. After 2 days of fermentation at atmospheric pressure in batch mode, the rate has increased to 11 VVD. Growth is presently being monitored spectrophotometrically at A_{640}. After cell density peaks, this information will be used to determine dilution rates for fresh media addition in conjunction with cell recycle.

The CO shift reaction requires a pure strain of bacteria that has the capability for utilizing CO. A culture of Rhodopseudomonas Gelatinosa sp. was obtained from Dr. Uffen of Michigan State University. This is presently growing as batch cultures in closed erlenmeyer flasks on a trypticase based media. Preliminary CO_2 production rates of 0.4 VVD have been reached. These cultures will be used to start a continuous, CO, atmospheric fermentor.

Future Work

Work will continue on optimization of the methanation and shift reactions. This will include:

(1) Increasing culture levels by cell recycle.
(2) Increasing reactor pressure and reactant gas flow rates.
(3) Optimizing nutrient levels and stabilizing pH.

Development of the combined shift/methanation reaction cultures will be initiated in atmospheric reactors.

SERI/PR-8174-3
UC Category, UC-

HEAT TREATMENT OF ORGANICS FOR INCREASING ANAEROBIC BIODEGRADABILITY

QUARTERLY PROGRESS REPORT
March 16, 1980 to June 15, 1980

June 16, 1980

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Prepared Under Subcontract
No. XR-9-8174-1
For the

Solar Energy Research Institute
A Division of Midwest Research Institute
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SECTION 1.0

INTRODUCTION

The objective of this study is to evaluate thermochemical pretreatment as a method for increasing the anaerobic biodegradability of organic materials so that they can be more completely fermented to methane gas, a potential source of fuel. The current study has five specific phases: (1) biological conversion of lignocellulose to methane, (2) biodegradation of lignin and lignin fractions, (3) pretreatment of nitrogenous organics for increasing biodegradability, (4) biodegradation of lignin aromatic compounds, and (5) biochemical methane potential and toxicity testing.

Phases 3 and 4 have been completed, and results have been summarized in previous progress reports. This report contains further results on phase 1, and in particular the effect of number of stages of autohydrolysis treatment on the solubilization and biodegradability of milled white fir. Also included under this phase are further results from continuous anaerobic fermentation of these soluble products. The phase 2 studies on biodegradation of lignin fractions are continuing, and the initial results obtained from studies with ^{14}C-labeled Douglas fir lignin are contained in this report. Under phase 5, a comparative study has been made of the biodegradability of fine and coarse corn stover obtained from two different sources.

SECTION 2.0

BIOLOGICAL CONVERSION OF LIGNOCELLULOSE TO METHANE

2.1 BACKGROUND

A process termed "autohydrolysis" has been developed for pretreatment of lignocellulosic biomass in order to increase its biodegradability to methane. This process, which operates without chemical addition, results in the hydrolysis of cellulose and hemicellulose to produce soluble sugars and their dehydration products. These materials can then be separated from the non-biodegradable lignaceous residue, and fermented to methane.

One difficulty with this process is that if the solubilized materials remain in the autohydrolysis reactor for too long a period, they can be converted to a non-biodegradable residue. This problem is significantly reduced by staged treatment. Current efforts are being directed towards determining the optimum time, temperature, and number of stages in order to obtain a maximum amount of biodegradable product. Also, analyses are being conducted in order to determine the soluble organic products produced during each stage with the possibility that some may have commercial potential. Results in these areas since the last progress report are contained in the following. Also included are results from continuous anaerobic fermentation of the soluble hydrolysis products in order to better evaluate overall biodegradability and to assess potential treatment problems such as toxicity.

2.2 AUTOHYDROLYSIS TREATMENT VARIABLES (K. Baugh and P. L. McCarty)

In staged autohydrolysis, time and temperature at each stage of treatment have been found to affect the degree of organic solubilization and the biodegradability of the soluble products. In past studies, only three stages were evaluated, and mass balances suggested that a significant proportion of the carbohydrate fraction of the white fir tested was not hydrolyzed by this many stages. In the following study, eight stages were evaluated in an effort to determine how much additional solubilization could be obtained. The relative biodegradability of the products was also determined.

Each stage of the autohydrolysis consists of (1) non-oxidative (helium atmosphere) heat treatment of a lignocellulosic (white fir) slurry at a selected temperature and duration, (2) following heat treatment, separation of the soluble and particulate fractions by filtration, (3) resuspension of the recovered particulate solids in deionized water for the subsequent heat treatment stage (step 1), and (4) analysis for biochemical methane potential (BMP) (Owen et al., 1979) on the soluble fraction to determine biodegradability. A summary of the staged autohydrolysis conditions and product characteristics is presented in Table 2-1.

Table 2-1. STAGED AUTOHYDROLYSIS OF WHITE FIR

Stage	Heat Treatment		Input Characteristics		Output Characteristics	
	Temp. (°C)	Time (min)	Solids (g/l)	COD (g/l)	pH	Soluble COD (g/l)
Input (1)	-	-	66.0	88.8	-	-
Output						
1	175	0	-	-	3.5	10.4
2	175	30	-	-	3.1	12.1
3	200	15	-	-	3.0	7.7
4	200	60	-	-	2.9	5.5
5	225	15	-	-	2.8	6.8
6	225	60	-	-	2.7	7.7
7	225	120	-	-	2.7	10.9
8	225	120	-	-	2.7	5.5
Residue (2)	-	-	-	-	-	18.9

(1) Initial untreated white fir slurry, 1 liter

(2) Residual particulate solids from stage 8 output diluted to 2 liters with deionized water.

An analysis of carbohydrate hydrolysis and the soluble product biodegradability is shown in Table 2-2. The autohydrolysis of white fir removes a significant portion of the hydrolyzable carbohydrate fraction (approximately 50 percent) at the milder heat treatment conditions (175-200°C, 0-30 minutes). To hydrolyze the more resistant carbohydrates, much harsher heat treatments are required (225°C, 60-120 minutes), but the use of more severe autohydrolysis conditions reduces the bioconversion efficiency of the solubilized products. The maximum potential for bioconversion to methane of the carbohydrate fraction of white fir is around 60 percent (Table 2-2), based upon 8 stages of treatment.

Based on the total wood organic content, the maximum biodegradation potential from autohydrolysis of white fir is between 30 and 40 percent (62% carbohydrate COD x 75% solubilization x 77% average bioconvertibility). This compares with a maximum soluble product biodegradation of 16 percent for a single stage autohydrolysis

Table 2-2. SUMMARY OF STAGED AUTOHYDROLYSIS RESULTS, COD MASS BALANCE AND BIODEGRADABILITY

Stage (1)	Heat Treatment Temp. (°C) (2)	Heat Treatment Time (min) (3)	Soluble COD Mass (g) (4)	Percent of Initial Carbohydrate COD (a) (5)	BMP ($\frac{m^3CH_4 \text{ @ STP}}{kg \text{ COD}}$) (6)	Bioconversion Efficiency (%) Based on Product (b) (7)	Bioconversion Efficiency (%) Based on Total Feed Carbohydrate (c) (8)
Input	-	-	88.8 (d)	-	0.008	2	-
Output							
1	175	0	5.22	9.5	0.29	83	7.9
2	175	30	7.74	14.1	0.30	85	12.0
3	200	15	5.61	10.3	0.30	85	8.8
4	200	60	2.93	5.4	0.27	77	4.2
5	225	15	3.78	6.9	0.25	71	4.9
6	225	60	6.39	11.7	0.26	73	8.5
7	225	120	5.28	9.7	0.24	70	6.8
8	225	120	3.25	5.9	0.23	65	3.8
Residue	-	-	37.8	-	0.005	1	-
Output Total			78.0	73.5			56.9

Notes:
(a) Based on 70% by weight (66.0 g/1 x 0.7 = 46.2 g/1) of initial feed is carbohydrate (Owen, 1979). COD of polysaccharide $(CH_{1.67}O_{0.83})_n$ is 1.184 g COD/g TS. Therefore the initial feed carbohydrate COD is 54.7 g/1 (46.2 g/1 TS x 1.184).
(b) Theoretical BMP of 0.35 m^3CH_4 @ STP/kg COD.
(c) Column (8) = Column (5) x Column (7)/100.
(d) Total COD

(Owen, 1979). The use of staged sequential autohydrolysis improves the total bioconvertible to methane fraction of the wood, but is still below the theoretically obtainable volume of 56 percent (62% carbohydrate x 90% bioconvertibility). Future work will use semi-continuously fed autohydrolysis reactors in an attempt to further improve the bioconvertibility of lignocellulosics.

2.3 ANAEROBIC TREATMENT OF AUTOHYDROLYSIS LIQUOR (A. Bachmann and P. L. McCarty)

The objective of this study is to evaluate the biodegradability of liquid from 3-stage autohydrolysis treatment of white fir under continuous anaerobic treatment. Three anaerobic biological reactors with short liquid but long biomass detention times are being evaluated at 35°C for possible use in treatment of autohydrolysis liquor: the anaerobic filter (AF), the anaerobic rotating biological contactor (ARBC) and the anaerobic contact process (AC). For a more detailed description, see Stuckey et al. (1980) and P. J. Colberg et al. (1980).

The AF reactor is the only one which has received autohydrolysis liquor, which was diluted to a COD of 8 g/l. Presently, the AF reactor is operating with 100 percent autohydrolysis liquor under steady-state conditions at a three-day hydraulic detention time, but previously was operated under steady state conditions at a one-day hydraulic detention time (Figure 2-1).

The autohydrolysis liquor was obtained by taking 91 g (115.7 g of COD) of milled white fir, clarified to pass a 42-mesh screen, and mixing it with 1.3 l of tap water to a concentration of 70 g/l, which yields a COD concentration of 89 g/l. The autohydrolysis treatment, described earlier (P. J. Colberg et al., 1980), resulted in about 3 liters of combined solubilized organic phase with a COD of about 12.7 g/l, representing approximately 34 percent of the initial wood COD. This is less than the 40-44 percent previously obtained (P. J. Colberg et al., 1980) because less rigid heat treatment conditions have been used and a higher alkalinity dilution water (about 400 mg/l as $CaCO_3$) led to a smaller drop in pH during treatment, and in turn to less autohydrolysis.

With a detention time of one day, the total effluent COD was approximately 1.7 g/l (Table 2-3). The biodegradability of the autohydrolysis liquor was then 78 percent [100(1-1.7/7.7)]. This represents an overall biodegradability of (0.78)(0.34)(100) or 27 percent. With carbohydrate as a food source, approximately 20 percent of the consumed material would be converted to cells, and the remainder into methane. This means that 0.8 x 27% or 21% of the heat content of the milled white fir was converted into methane by autohydrolysis and anaerobic treatment.

The above calculations can be compared with the actual methane production from the reactor (Figure 2-1) of about 0.24 m^3CH_4/kg COD fed, which represents a convertibility to methane of 0.24 (100)/0.395 or 61 percent based upon 0.395 m^3/kg COD for 100 percent convertibility at 35°C. This suggests that approximately 0.61 (0.34)100 or 21 percent of the heat content was converted to methane. This agrees with the estimate made from COD reduction.

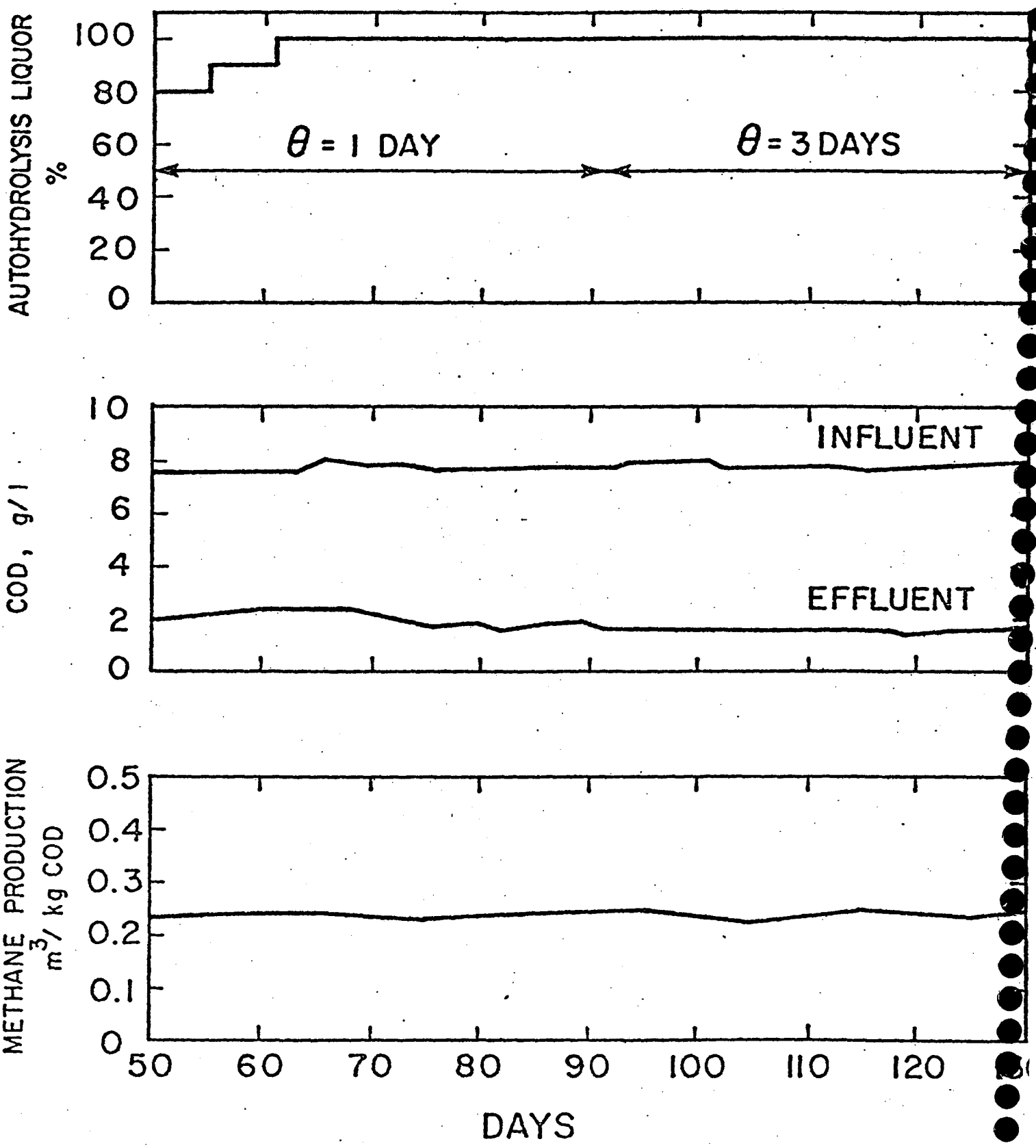

Figure 2-1. Performance of Anaerobic Filter on the Treatment of Autohydrolysis Liquor from 3-stage Treatment of White Fir.

Table 2-3. OPERATIONAL CHARACTERISTICS OF ANAEROBIC FILTER REACTOR WITH 100% AUTOHYDROLYSIS LIQUOR AT STEADY STATE

Parameter	1 day hydraulic Detention Time (θ)		3 days hydraulic Detention Time (θ)	
	Average	Range	Average	Range
θ, days	0.98	0.94-1.02	2.9	2.2-4.0
COD, kg/m^3				
Influent total	7730	7640-7800	7840	8010-7690
Effluent total[a]	1700	1440-1890	1520	1395-1720
Effluent soluble[a]	1115	960-1320	930	800-1500
pH	7.2	7.0-7.3	7.35	7.25-7.5
Alkalinity, mg/l				
Influent	4590	4500-5000	5000	-
Effluent	4100	4000-4200	4550	4400-4900
Volatile acids, mg/l	660	290-1130	540	250-1365
CH_4 Production, m^3/m^3 reactor-day				
based on void volume	2.9	2.75-3.2	0.86	0.75-1.1
based on total volume	1.2	1.1-1.27	0.34	0.3-0.44

[a]Reactor effluent COD was mostly soluble, but acidification of effluent samples resulted in some organic precipitation which is reflected in these analyses.

With a detention time of 3 days, the effluent COD was approximately 1.5 g/l (Table 2-3), representing a biodegradability of 81 percent for the autohydrolysis liquor and 27.5 percent based upon initial white fir COD. A comparison with the one-day detention time results indicates increasing the detention time results in an insignficant increase in biodegradation but increases the reactor volume by a factor of three.

An evaluation is also being made of the potential of the ARBC for short detention time digestion of wastewater. This reactor is currently operating

under a high stress situation at a COD feed of 12 g/l and a detention time of one day. This seems to be a maximum loading for this reactor. The overall study with this reactor shows that it is a very reliable and stable operation, and is advantageous over the filter in that it has a high void volume (about 90%) and is less subject to clogging.

The AC reactor has been shut down after repeated washout of the contact mass by rising gas bubbles at a liquid detention time below about 1.2 days which led to low reactor reliability. There are no further plans for operation of this system.

SECTION 3.0

BIODEGRADATION OF LIGNIN AND LIGNIN FRACTIONS

(P. J. Colberg and L. Y. Young)

3.1 INTRODUCTION

The last quarterly report (Colberg et al., 1980) detailed the procedure for preparation of ^{14}C-(LIGNIN)-lignocellulose (Crawford and Crawford, 1976) from Douglas fir. This section includes the preliminary results of anaerobic enrichment cultures, fed thermochemically-treated ^{14}C-(LIGNIN)-lignocellulose as the sole source of carbon, after 30 days' incubation.

3.2 MATERIALS AND METHODS

Thermochemical pretreatment conditions, preparation of labeled substrate, separation of molecular size fractions, composition of enrichment media, and gas measurement methods are identical to procedures described previously (Healy et al., 1977; Healy et al., 1978; Colberg et al., 1980). Liquid scintillation determinations of $^{14}CO_2$ and $^{14}CH_4$ were according to procedures developed by Zehnder et al. (1979, 1980). Total methane was quantified with a Poropak QS (100/120 mesh) column in a gas chromatograph (Hewlett Packard Model 5730A) equipped with a flame ionization detector. Gas samples were removed using a Pressure-Lok syringe (Precision Sampling Co., Baton Rouge, LA).

3.3 RESULTS AND DISCUSSION

A comparison of gel filtration chromatography (GFC) elution profiles (Figure 3-1) both before and after anaerobic degradation of thermochemically-treated ^{14}C-labeled Douglas fir indicates that the higher molecular weight compounds were degraded to smaller molecular weight substances as evidenced by peaks for 30 days' incubation that eluted later than the original peaks. Since the elution profiles were determined by monitoring ^{14}C-activity, these changes reflect alterations in molecules of lignin origin, which were labeled specifically in the preparation.

A range of 25-37 percent of original ^{14}C-activity (specific activity = 1.5×10^7 dpm/mole C) was recovered as $^{14}CO_2$ and $^{14}CH_4$ in a relatively constant ratio of 2:3. These data, plotted in Figure 3-2, suggest that molecules of lignin-origin are degraded under anaerobic conditions and released as labeled end products of methanogenesis.

Significant percentages of the total CH_4 evolved were released as $^{14}CH_4$, as shown in Figure 3-3. In the case of the 500 mgC/l enrichments, the ^{14}C-labeled lignin-related substrates were degraded to yield 61 percent of the total methane yield. In addition, since the ^{14}C-labeled Douglas fir had a lignin content of approximately 30 percent, it appears that these enrichment cultures were effecting a significant attack on the lignin-derived molecules.

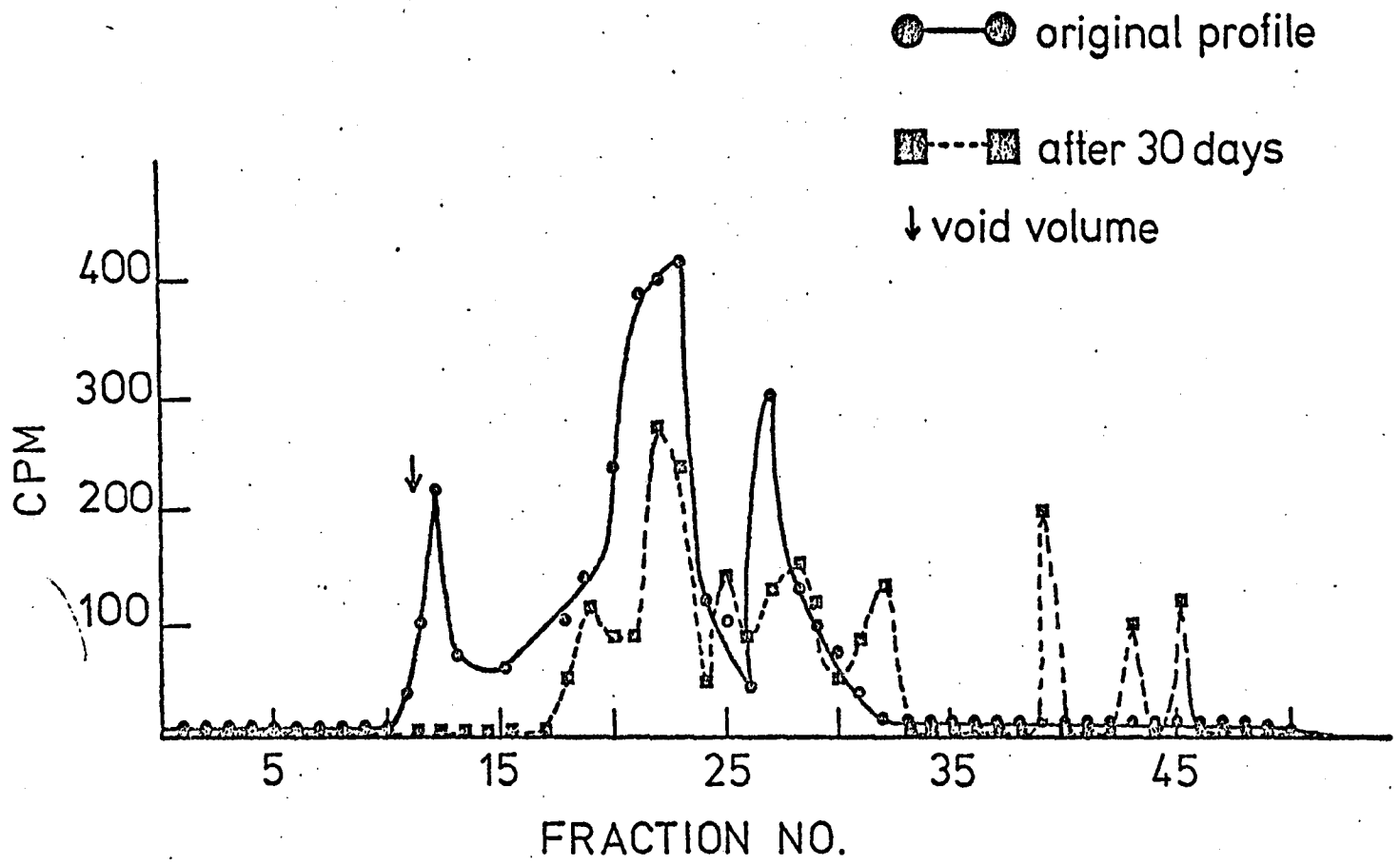

Figure 3-1. Counts per Minute for Various Gel Filtration Fractions of Treated Douglas Fir Before and After Anaerobic Biodegradation.

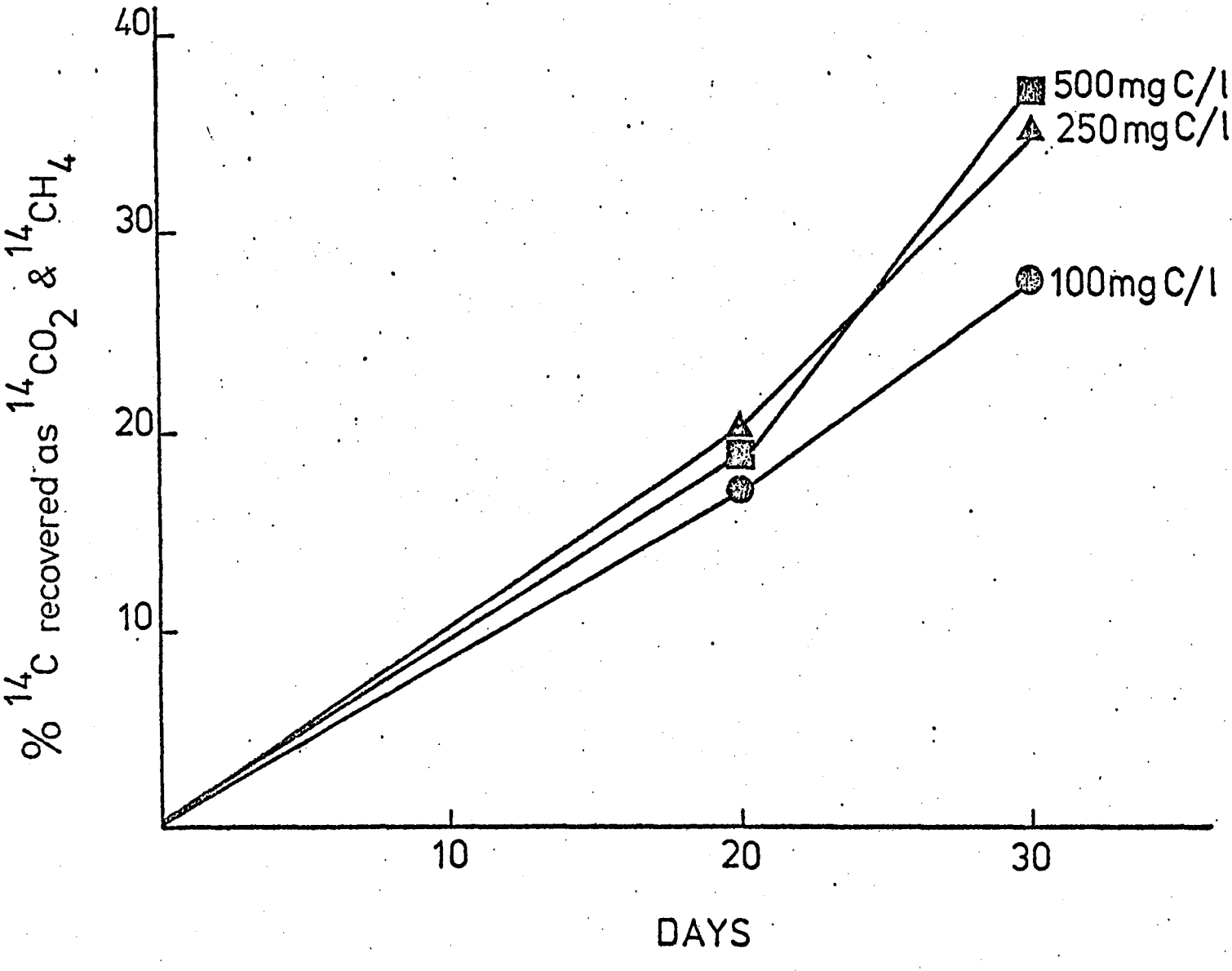

Figure 3-2. Percent of Sample Activity Recovered in Carbon Dioxide and Methane as a Function of Incubation Time under Anaerobic Conditions.

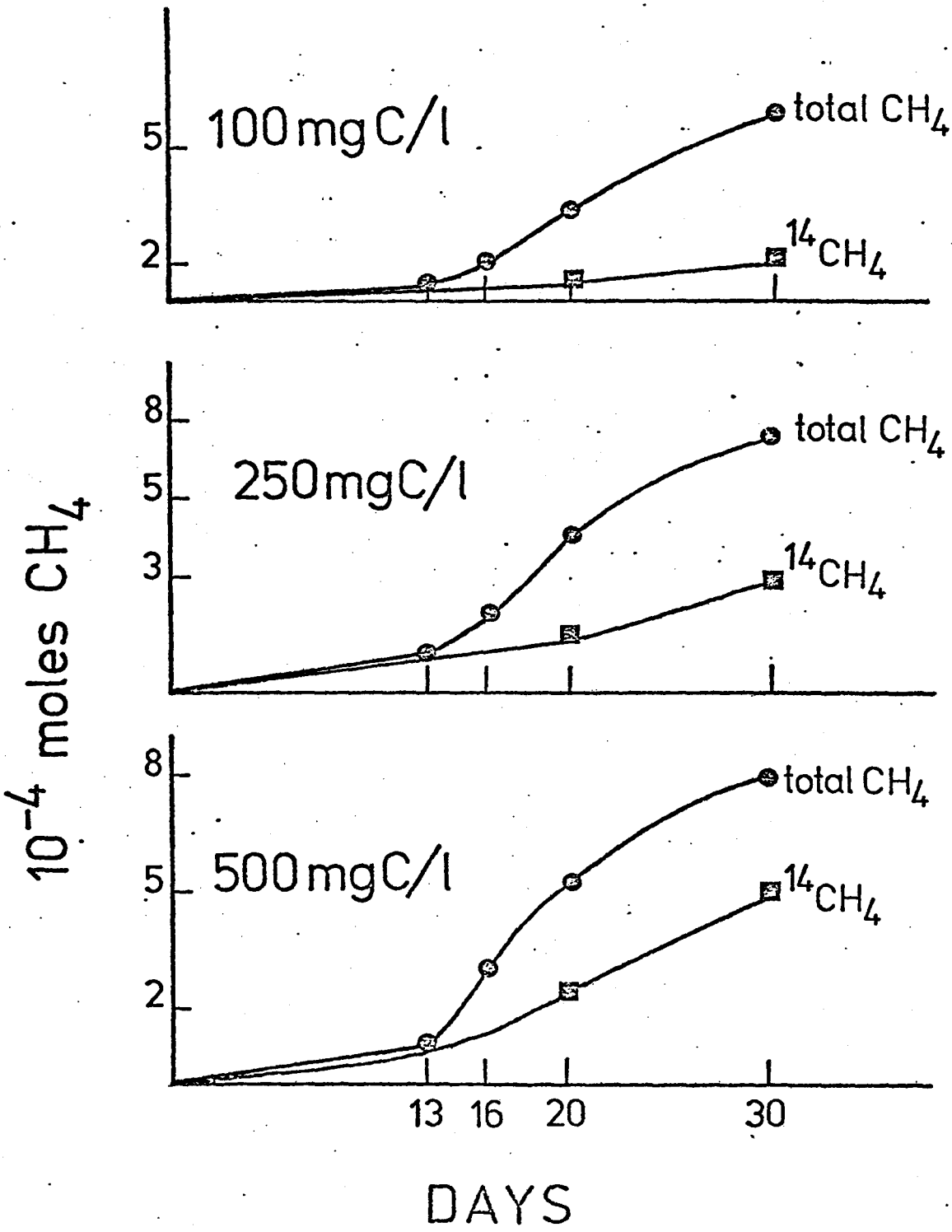

Figure 3-3. Comparison Between ^{14}C-tracer Methane and Total Methane as Functions of Sample Organic Carbon Concentrations and Anaerobic Incubation Time.

SECTION 4.0

BIODEGRADABILITY OF CORN STOVER

(D. Harrison and P. L. McCarty)

4.1 BACKGROUND

At the quarterly meeting, a question arose as to reasons for the difference in methane production from Corn Stover reported from studies at the University of Illinois and the University of Missouri. Some studies using BMP analysis were conducted previously at Stanford on corn stover. It was requested that these studies be reviewed, and also that Stanford conduct additional BMP analyses of corn stover samples from the universities in Illinois and Missouri in order to determine if there were any significant differences between the materials.

4.2 SUMMARY OF PREVIOUS STUDIES

Table 4-1 contains a summary of results from reports from the University of Illinois, the University of Missouri, and Stanford University. The former two universities conducted pilot studies with digesters operated at different detention times. The Missouri studies were at mesophilic and the Illinois at thermophilic temperatures. The Stanford studies were batch tests using the BMP analysis, a temperature of 35°C, and a 30-day incubation time.

The Stanford data was for two different corn stover samples, and was obtained by two different researchers. In general, the Stanford data previously obtained is at the high end of the Illinois data and the low to intermediate end of the Missouri data.

4.3 SUMMARY OF NEW DATA

Samples of corn stover were received from the Universities of Illinois and Missouri. The Illinois material was finely ground, while the Missouri material came both finely ground and coarsely ground. The previous Stanford studies are questionable because of difficulties in transferring small quantities of material contained in slurries. Also, an insufficient number of tests were conducted per sample to be certain of analytical precision. In order to get around this problem, the materials for the current study were weighed dry and transferred directly to BMP bottles. Two weights, 150 mg and 450 mg, were evaluated in order to determine effects of sample concentration. For each weight four samples were analyzed in order to determine analytical precision. The samples were seeded with sludge from mesophilic digestion of municipal waste activated sludge, and incubated at 35°C.

Methane production data as a function of incubation time for all samples are listed in Table 4-2. Precision of analysis was excellent, resulting in a standard deviation in methane production of about 3 percent for the sample 40-day values.

Table 4-1. COMPARISON OF RESULTS FOR DIGESTION OF CORN STOVER

Results from	Detention Time - days	cu. meters methane per kg vol. solids added	Percent bioconvertibility of volatile solids	
			based upon methane prod.	based upon C destruction
Univ. of Illinois	3.8	0.063	14	
	5.0	0.077	18	
	7.8	0.094	22	
	14	0.120	27	
Univ. of Missouri	20	0.19	46	43
	20	0.20	48	46
	30	0.23	56	53
	40	0.24	57	55
	40	0.27	64	62
Stanford				
Illinois stover				
Owen studies	BMP	0.161	37	
Willey studies	BMP	0.26	59	
	BMP	0.18	41	
Indiana stover				
Willey studies	BMP	0.22	50	

Table 4-2. CUMULATIVE METHANE PRODUCTION DURING BMP ANALYSIS OF CORN STOVER SAMPLES

Sample	Size mg	Methane Production - ml					
		Day 3	Day 6	Day 13	Day 20	Day 27	Day 40
Ill. - Fine	150	7.7	18.9	33.2	45.2	50.7	57.3
		7.7	19.6	34.5	45.4	52.5	59.8
		7.1	19.2	35.4	48.3	53.5	60.9
		5.6	19.6	35.3	46.7	52.6	60.5
Avg. & S.d.		7.0±1.0	19.3±0.3	34.6±1.0	46.4±1.4	52.3±1.2	59.6±1.6
	450	18.1	50.6	85.7	110.1	118.9	131.2
		22.1	55.0	91.5	117.0	127.2	139.1
		21.6	51.8	88.1	112.4	122.3	132.8
		20.2	51.9	88.6	111.6	119.4	132.9
Avg. & S.d.		20.5±1.8	52.3±1.9	88.5±2.4	112.8±3.0	122.0±3.8	134.0±3.5
Miss. - Fine	150	6.5	12.5	25.4	38.0	45.6	58.0
		7.0	13.7	26.0	38.5	48.3	59.6
		6.9	14.9	26.8	41.6	48.6	61.9
		6.1	11.7	24.6	39.6	47.8	56.3
Avg. & S.d.		6.6±0.4	13.2±1.4	25.7±0.9	39.4±1.6	47.6±1.4	59.0±2.4
	450	21.7	38.5	67.8	96.7	111.9	133.1
		17.9	35.6	65.6	94.0	107.3	128.1
		16.9	34.5	53.2	90.1	103.8	125.1
		16.6	34.8	64.3	91.2	104.4	123.7
Avg. & S.d.		18.3±2.4	35.9±1.8	62.7±6.5	93.0±3.0	106.9±3.7	127.5±4.2
Miss. - Coarse	150	4.8	16.9	32.9	45.9	54.0	64.4
		4.0	17.5	32.7	47.4	53.6	61.7
		4.1	18.9	36.2	48.5	56.1	63.9
		4.9	17.9	35.9	52.0	58.4	66.6
Avg. & S.d.		4.5±0.5	17.8±0.8	34.4±1.9	48.5±2.6	55.5±2.2	64.2±2.0
	450	14.4	46.8	85.0	110.2	125.7	145.6
		12.7	48.6	92.6	123.1	135.9	151.8
		13.8	47.2	89.2	119.4	131.3	147.3
		17.2	51.7	90.9	118.8	130.5	147.4
Avg. & S.d.		14.5±1.9	48.6±2.2	89.4±3.3	117.9±5.5	130.9±4.2	148.0±2.6
Seed Blank		2.4	2.4	6.9	10.9	15.6	19.8
		1.6	1.6	3.4	4.1	9.0	13.1
		1.6	1.6	6.7	11.6	16.8	21.3
Avg. & S.d.		1.9±0.5	1.9±0.5	5.7±2.0	8.9±4.1	13.8±4.2	18.1±4.4

From these results, the bioconvertibility to methane was calculated and the results are summarized in Table 4-3. The calculation made use of the formula at the bottom of the Table. The COD/volatile solids ratio for these samples was found to be 1.2, and this value was used in the calculations.

A summary of the bioconvertibility data for the 450 mg samples is given in Figure 4-1. This illustrates that the biodegradability of all materials was quite similar. Surprisingly, the Missouri coarse material appeared more biodegradable than the fine material. The bioconvertibility of Missouri coarse material and the Illinois fine material was identical. A similar comparison indicated the results for the 150 mg samples were the same. However, as indicated by the data in Table 4-2, the low concentration samples all exhibited about 5 percent higher bioconvertibility after 40 days incubation than the high concentration samples. Reasons for this are not known.

The results from the current studies are similar to those from the previous Stanford studies, if consideration is given to the different incubation times. The bioconvertibilities measured with a 40-day incubation time are in general all higher than obtained at the University of Illinois and perhaps similar to that obtained at the University of Missouri with a 40-day detention time.

A comparison of data for percent bioconvertibility in Figure 4-1 with the Illinois and Missouri data in Table 4-1 indicates good correspondence between results as a function of detention time in digesters, and incubation time in the BMP analysis. This is not what would be expected based upon the usual kinetic considerations. It is also interesting to note that in the BMP analysis, bioconvertibility still appeared to be increasing after 40 days of incubation.

These results indicate that the bioconvertibility of corn stover to methane is indeed greater than 50 percent, and appears to be independent of particle size, at least over the range tested. Differences between results obtained at the University of Illinois and the University of Missouri might be attributable to differences in digester detention time rather than to differences in the nature of the corn stover being digested. Further studies on corn stover appear desirable.

Table 4-3. SAMPLE CHARACTERISTICS AND PERCENT BIOCONVERTED TO METHANE AS FUNCTIONS OF INCUBATION TIMES AT 35°C

Sample	Size mg	Volat. Solids %	Percent Bioconverted to Methane					
			Day 3	Day 6	Day 13	Day 20	Day 27	Day 40
Ill-Fine	150	87	8.2	28.1	46.7	60.6	62.6	67.1
	450	87	10.0	27.2	44.6	56.0	58.3	62.5
Miss-Fine	150	92	7.2	17.3	30.6	46.6	51.7	62.5
	450	92	8.4	17.3	29.0	42.9	47.4	55.7
Miss-Coarse	150	93	3.9	24.0	43.4	59.9	63.1	69.7
	450	93	6.4	23.5	42.2	54.9	59.0	65.5

$$\% \text{ Bioconvertibility} = \frac{(\text{Sample } CH_4 \text{ Prod., ml}) - (\text{seed } CH_4 \text{ Prod., ml})100}{(\text{Sample size, Mg}/1000)(1.2)(\% \text{ Vol. Solids}/100)(0.395)}$$

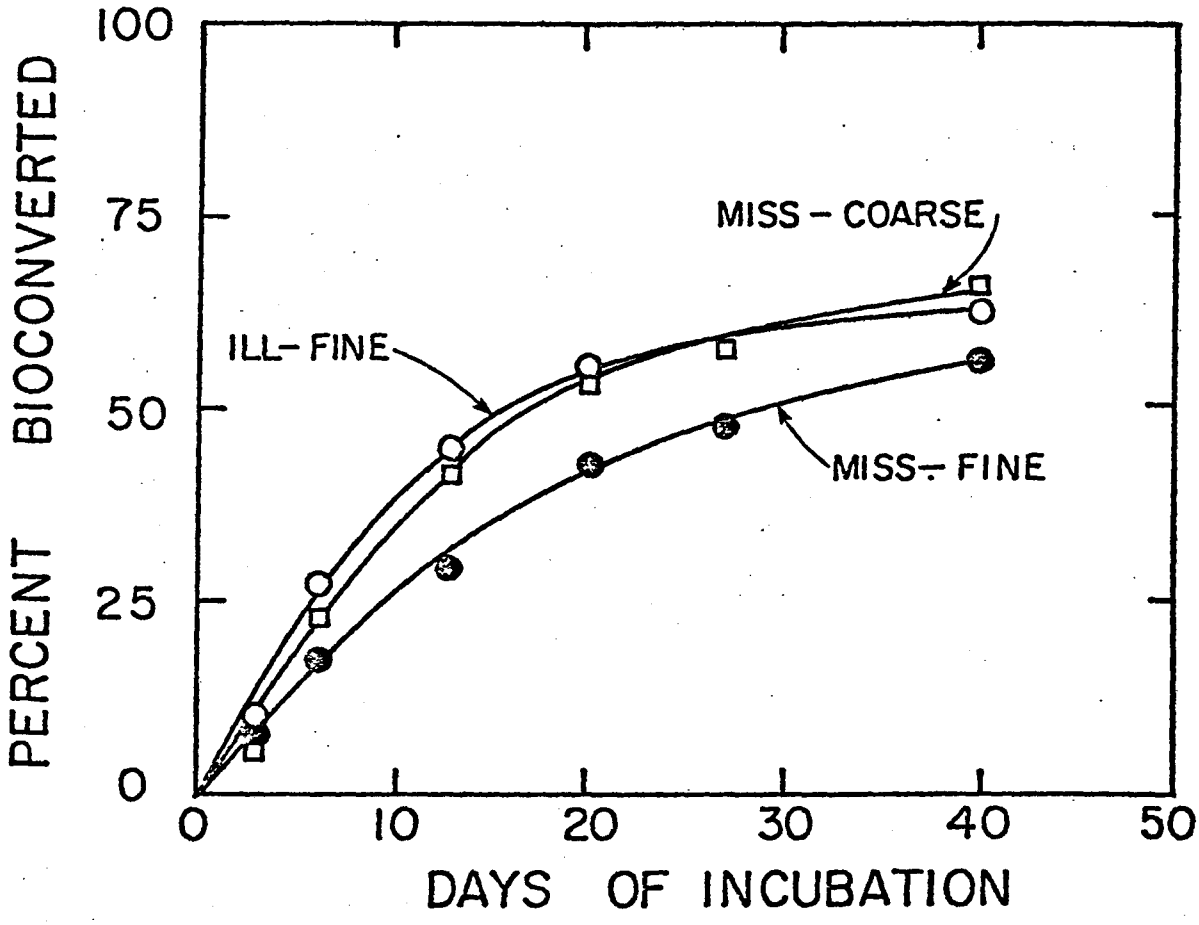

Figure 4-1. Percent Bioconversion to Methane as Function of BMP Inoculation Time for 450 mg of Three Different Corn Stover Samples.

SECTION 5.0

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

SERI Contract No. XJ-9-8020-1

Quarterly Report for Period 4/1/80-7/1/80

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Rolla, Missouri

INTRODUCTION

The objectives of this project are to: (1) Demonstrate the technical and economic feasibility of producing methane by anaerobic digestion of native grasses in a farm demonstration unit, and (2) Investigate improvements in the kinetics or yield in the anaerobic digestion process by use of an acid hydrolysis pre-treatment followed by fermentation to methane or other chemicals.

FARM ENERGY SYSTEM

All four farm reactors are now in service and operation has been satisfactory during the quarter. The pneumatic agitators are working properly and no operating problems have been experienced to date.

The performance of all reactors has been normal with peak gas production of about .25 CF gas/pound hay/day occurring during the first two weeks of the batch cycle. No pH problems have been experienced and methane concentrations are slightly above 50 percent.

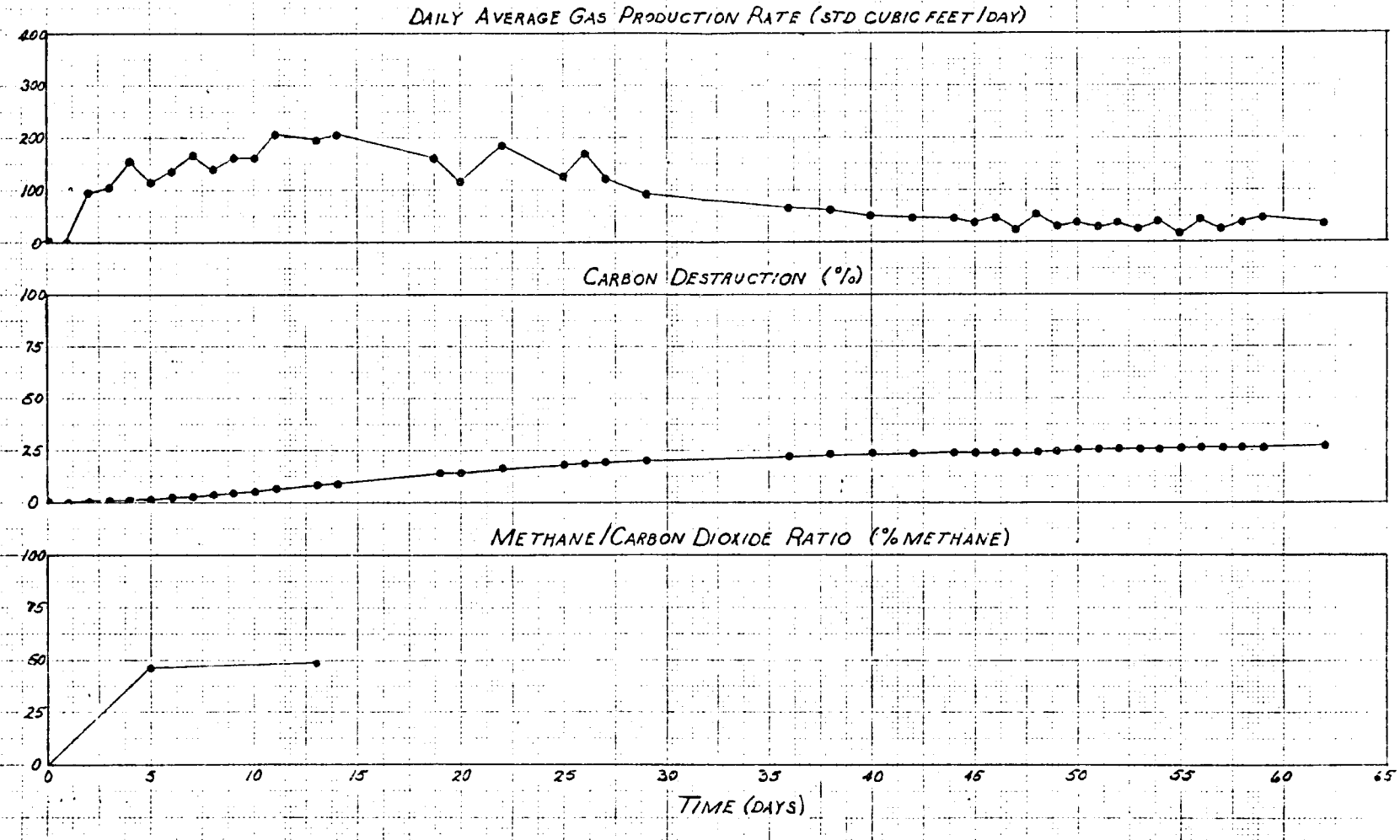
An experiment has been conducted to determine the affect of agitation on reactor performance. Figure 1 shows the gas production and yield for a full 60 day cycle without agitation. Gas production reached a peak of only

FIG. 1 FARM DEMONSTRATION UNIT

REACTOR 4
BATCH 2
START UP DATE : MARCH 21, 1980

AGRICULTURAL RESIDUE : ORCHARD GRASS
AGITATION CYCLE : NONE

BATCH SIZE : 3500 GALLONS
PERCENT RESIDUE : 6.4 %
CULTURE/RESIDUE RATIO : 3.5 : 1



.1 CF gas/pound-day with a conversion of about 26 percent after 62 days. Normal agitation has been for a period of 5-10 minutes once a day. With this agitation frequency, peak production is normally .25 CF gas/pound-day with conversions of around 40 percent.

Figure 2 shows the performance of a reactor agitated more frequently for a total of 1 1/2 hours per day. Peak production reached .3 CF gas/pound-day and conversion was 40 percent after 50 days. Therefore, agitation frequency has a definite affect upon the gas yield and the gas production cycle.

Figure 3 compares the cumulative gas production for reactors with no agitation, normal agitation and frequent agitation. The normal cycle shows a much steeper slope initially than the cycle without agitation. However, after about 35 days, the production rate is about the same with or without agitation. After a short delay of about 5 days, probably due to a less active culture, the reactor with frequent agitation produced gas at a faster rate than the cycle with normal agitation. However, after about 20 days, the rates were about the same. The ultimate yield from each cycle was also about the same.

The amount of energy required for agitation on the normal cycle is 7000 BTU/day, or about 7 CF CH_4/day, allowing a 20 percent conversion efficiency. Methane production with normal agitation ranges from 350 CF/day down to 50 CF/day at the end of the 60 day cycle. Therefore, agitation energy is only a small part of production initially and increases to 14 percent of production at the end of the cycle.

Agitation for 1 1/2 hours/day requires 84 CF CH_4/day and production ranges from 370 down to 50 CF CH_4/day. Consequently, agitation at this rate cannot be justified during the latter stages of the cycle.

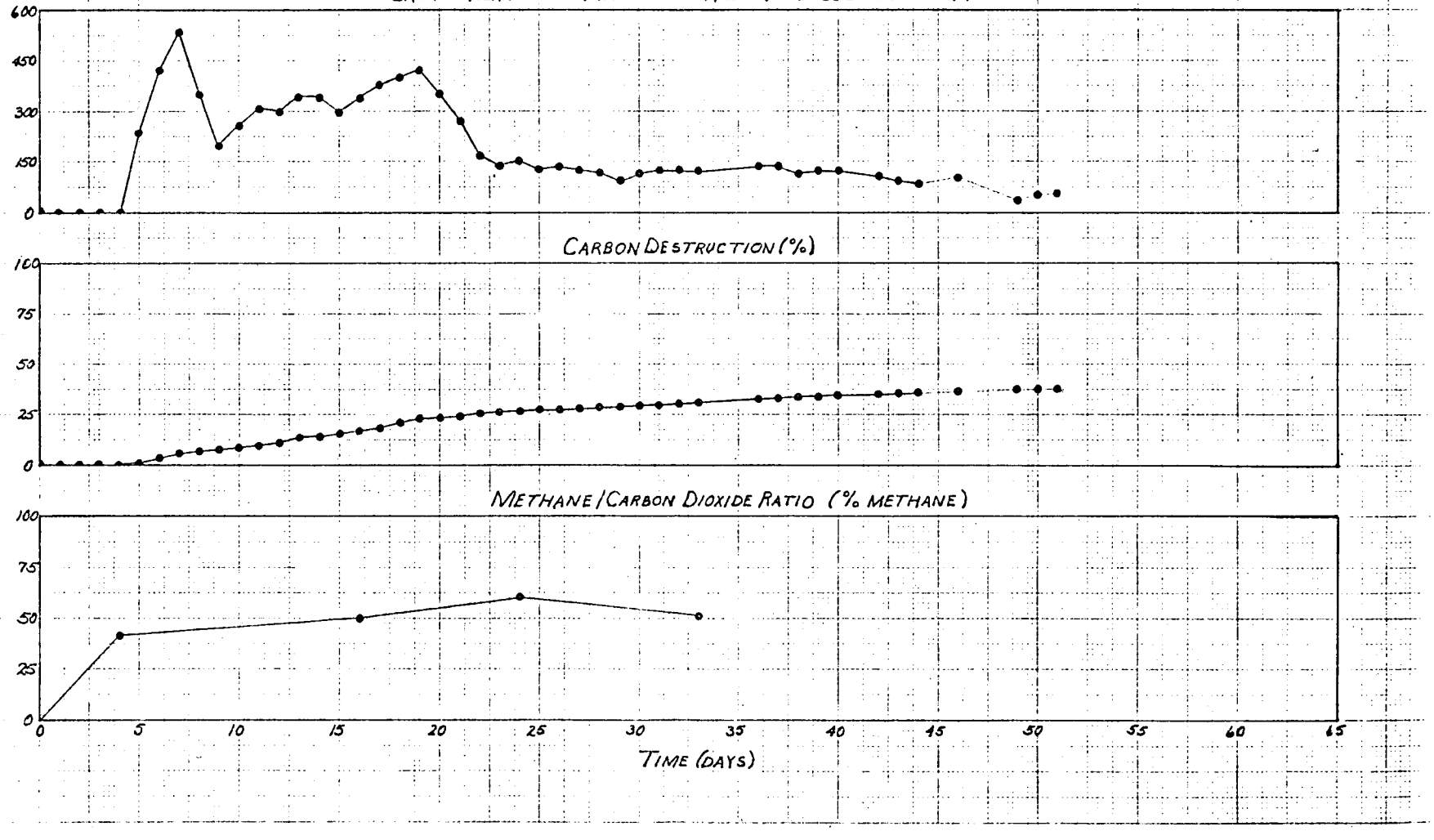
Table 1 gives the energy required for these agitation levels and the

FIG. 2 FARM DEMONSTRATION UNIT

REACTOR 2
BATCH 2
STARTUP DATE: APRIL 28, 1980

AGRICULTURAL RESIDUE: ORCHARD GRASS
AGITATION CYCLE: 1.5 HOURS/DAY

BATCH SIZE: 2600 GALLONS
PERCENT RESIDUE: 8.5%
CULTURE/RESIDUE RATIO: 3:1



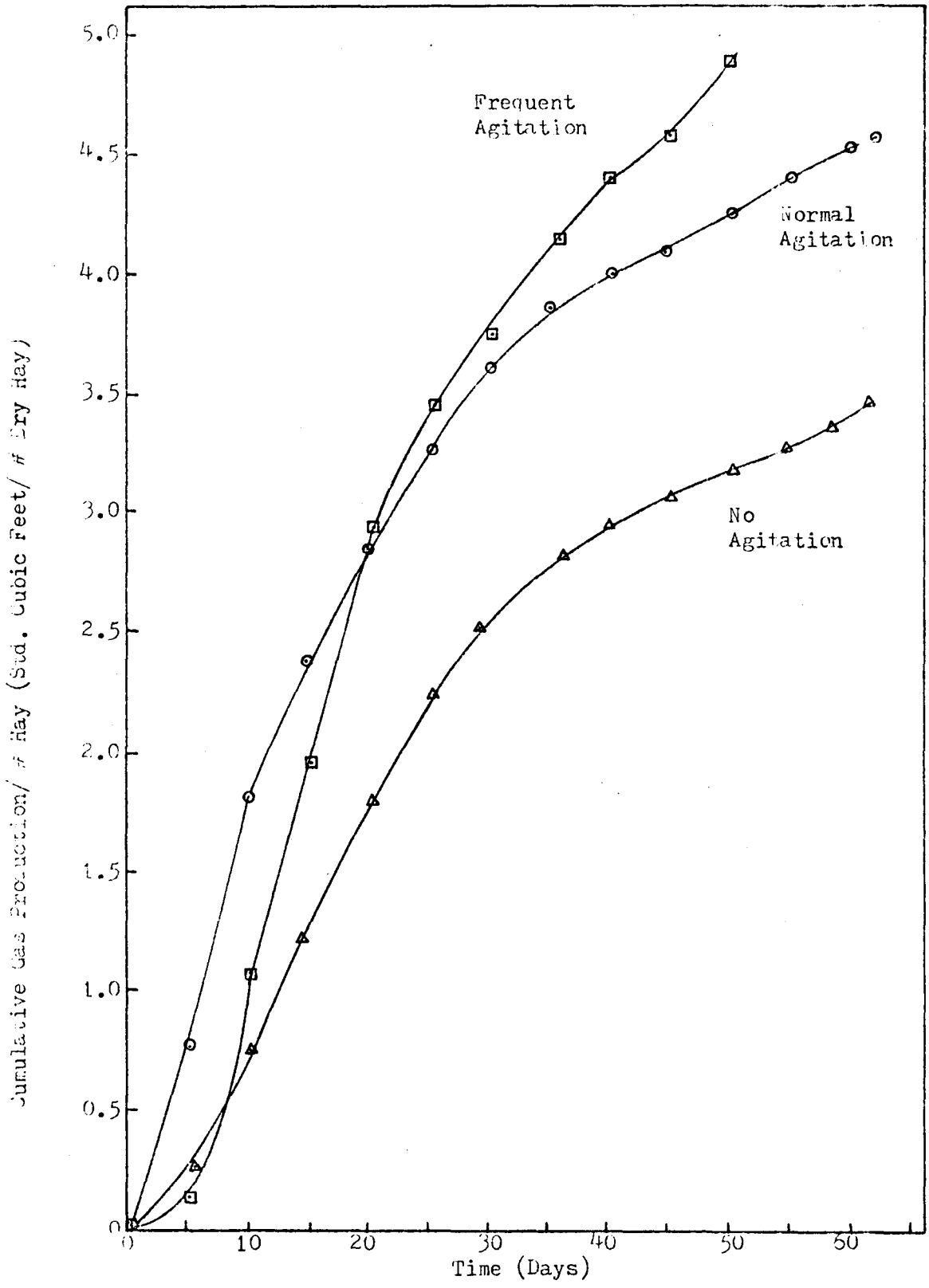


Figure 3. Comparison of Batch Digestor Performance with Agitation

TABLE 1. ENERGY BALANCE FOR VARIOUS AGITATION LEVELS

Level of Agitation	Energy Required		Energy Balance (CF CH_4) Energy Produced		Net Production	
	20 days	60 days	20 days	60 days	20 days	60 days
No agitation	0	0	2,330	5,100	2,330	5,100
Normal agitation	140	420	4,050	6,750	3,910	6,330
Frequent agitation	1,680	5,040	4,950	7,200	3,270	2,160

energy production at 20 days and 60 days. The difference, or net energy production is also given. The energy production figures are based on 10 percent solids concentrations. It is apparent that agitation for 1 1/2 hours during the full 60 day cycle cannot be justified; since the net production is less than with no agitation. Frequent agitation during only the first 20 days is also not justified, since a lower net production results than for normal agitation. Perhaps a less frequent level of agitation, possibly 30 minutes/day, would give equally fast rates and could be justified.

When comparing the normally mixed cycle with the unmixed cycle, it is apparent that agitation is justified on the basis of net energy production. This may not be true when capital costs are included, although agitation would likely be required for unloading. It appears that a combination of agitation levels may be optimal. During the last 20-30 days of the cycle, no agitation may be desirable. Further studies varying the frequency of agitation are planned to arrive at the proper level.

ACID HYDROLYSIS/FERMENTATION STUDIES

A series of runs has been made to optimize the prehydrolysis of corn stover with sulfuric acid. Acid concentration was varied from 4.4 percent to 12 percent. Temperature was varied from 90 to 110°C. Glucose and xylose concentrations were monitored with reaction time up to 1 1/2 hours.

Figures 4,5 and 6 show the concentration profiles with time for temperatures of 90, 100, 110°C. Glucose concentration is only slightly affected by temperature and acid concentration. Maximum glucose concentration of about 5 g/l occurs after 1 hour.

Xylose yield improves with acid concentration and temperature, although 100°C gives comparable results with 110°C. Yields are improved about 1/3

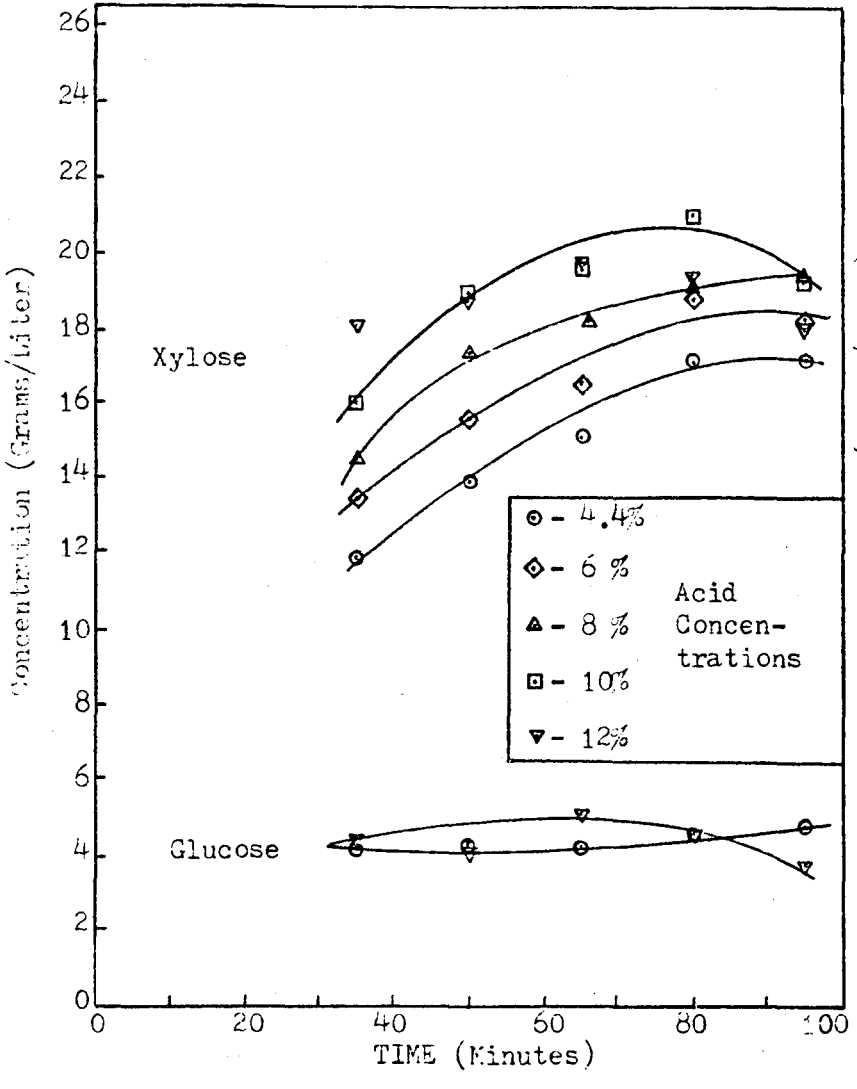


Figure 4. Results of Prehydrolysis at 90°C

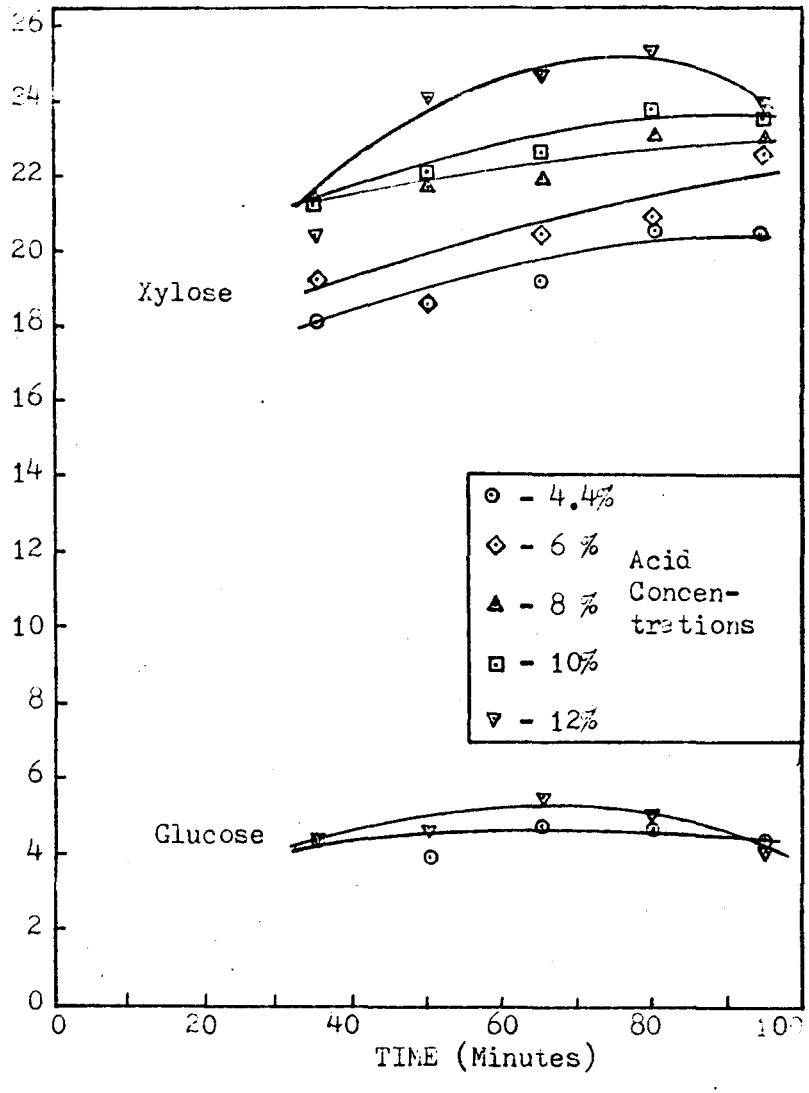


Figure 5. Results of Prehydrolysis at 100°C

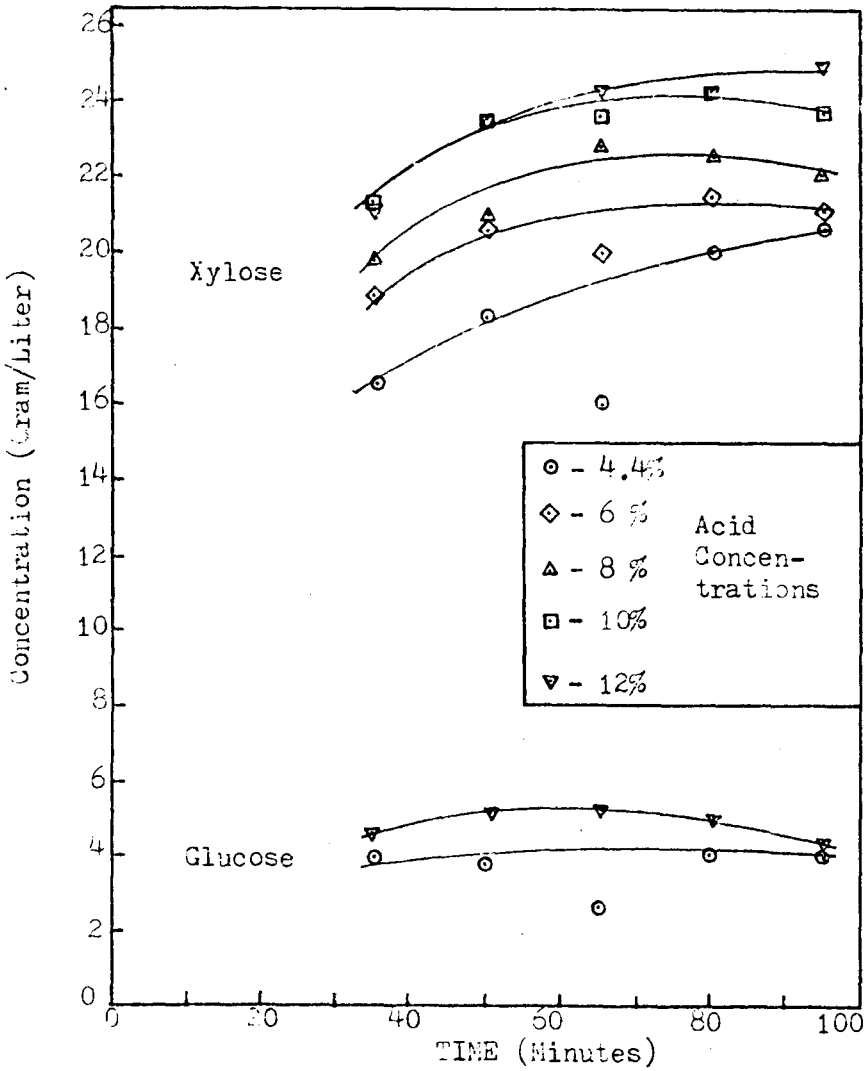


Figure 6. Results of Prehydrolysis at 110°C

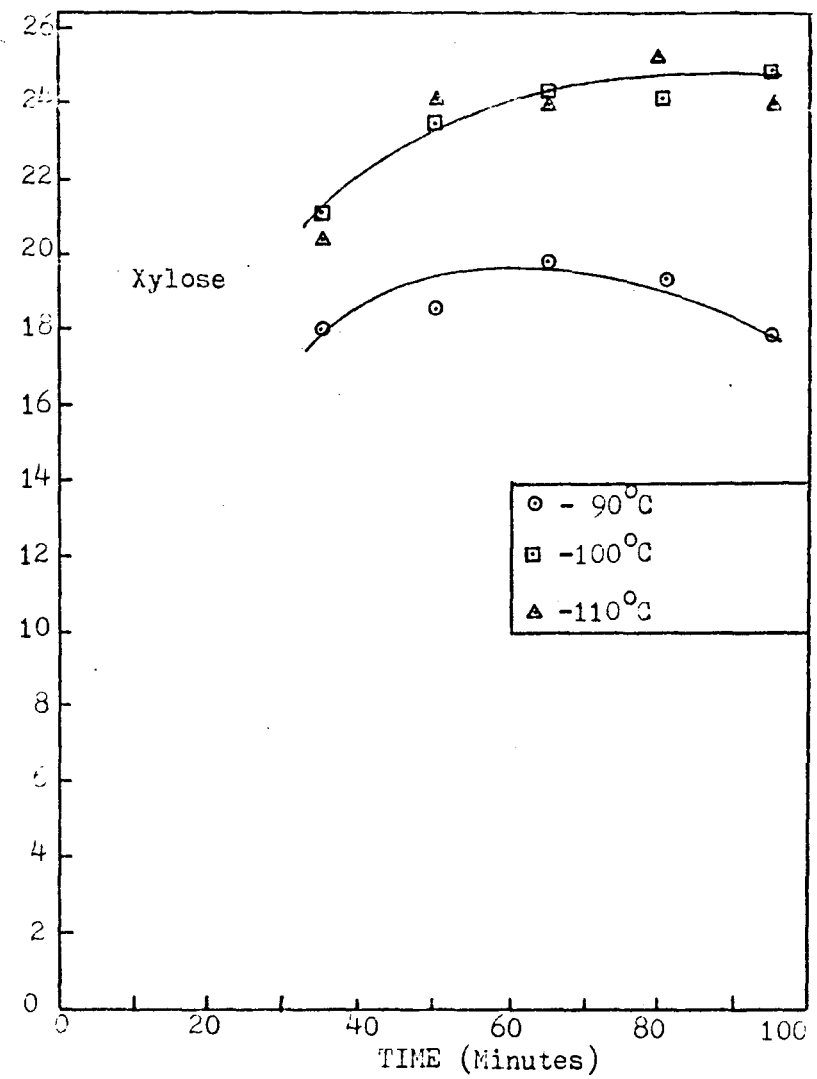


Figure 7. Results of Prehydrolysis with 12 % H_2SO_4

with 12% acid compared with 4.4% acid. Little improvement is observed with a 12% concentration over the 10% acid, especially at higher temperatures. As expected, the xylose concentration drops due to repolymerization as the reaction time is extended. Maximum concentrations occur at 80 min. for most acid strengths and temperatures.

Figure 7 shows the influence of temperature on xylose yield with 12% acid. A significant improvement is apparent when the temperature is increased to 100°C, but only marginal improvement at 110°C. Maximum xylose yields of about 25 g/l occurs at 110°C after 80 min. A few additional runs at slightly higher concentrations and temperatures are being made to define the optimal conditions.

Cornell University
College of Agriculture and Life Sciences
A Statutory College of the State University of New York

Report Number XB-Ø-9038-1-2

LOW COST APPROACH TO METHANE GENERATION, STORAGE, AND UTILIZATION FROM CROP AND ANIMAL RESIDUES

Second Quarter Progress Report for Period From
April 1, 1980 to June 30, 1980

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Prepared For
Solar Energy Research Institute
Under Contract No. XB-Ø-9038-1

LOW COST APPROACH TO METHANE GENERATION, STORAGE, AND UTILIZATION FROM CROP AND ANIMAL RESIDUES

Summary

The Cornell University project on the conversion of crop and animal residues to methane has successfully developed a low cost reactor that promises to be capable of producing a significant amount of biogas from agricultural residues at a cost competitive with existing fuels. The goal of the latest phase of research will be to further develop the understanding of low cost anaerobic fermentation designs for animal and crop residues. This progress report covers the activities included in the second scheduled quarter of this study.

The preparation of the final report (D.O.E. Contract No. DE-AS02-76ET20051) entitled "Anaerobic Fermentation of Agricultural Residues: Potential for Improvement and Implementation" and the Feasibility Manual (D.O.E. Contract No. DE-AS0276ET20051) entitled "Anaerobic Fermentation of Agricultural Residues: A Feasibility Manual" was continued during the last quarter. The final report is now in press and will be distributed in July 1980.

Both full scale (plug flow and completely mixed) dairy cow digesters at ASTARC have been operated at a 20-day HRT, 35°C. This condition was found to be optimal in terms of net energy production and capital investment. The full scale plug flow dairy manuer reactor was found to have a torn gas collection bag. The bag was repaired and the anchoring system for the bag was reinforced to minimize the possibility of further bag damage. These units

are being operated and will continue to be operated for the express purpose of gathering long term operational and maintenance data, and information on materials reliability.

The central focus of the first year of this project is the dry fermentation study. During the second quarter of this project the following accomplishments were achieved in support of the dry fermentation research:

1. Preliminary experiments were concluded which provided information on the important variables in dry fermentation, thereby allowing the initiation of comprehensive experiments to further define dry fermentation;

2. Approximately one hundred reactors (1 ℓ volume) were operated (operation is continuing) in a comprehensive study of variables important for the biological optimization of dry fermentation. Preliminary data indicate that initial seed requirements may be reduced with higher initial solids contents, and that compaction, free moisture, and seed distribution and source are important variables for scale-up;

3. One set of experiments on buffer sources was completed and has shown that there are some differences in buffering capacity for reagent grade $CaCO_3$ and pulverized limestone; differences between $NaHCO_3$ and $CaCO_3$ were found to be significant;

4. Computer data retrieval, storage, and graphical analysis systems were debugged.

Activities for the next quarter include continued operation of both full scale dairy manure reactors, further definition of process variables important to dry fermentation (bench scale), and the construction and start-up of several 200 ℓ pilot scale fermentors to study scale-up variables important in dry fermentation.

OBJECTIVES

The general approach of this new three-year study will be to further develop the understanding of low cost anaerobic fermentation designs for animal and crop residues. Specific objectives of this study will be to:

1. develop long-term cold weather operational reliability of dairy manure digestion in full scale completely mixed and plug flow reactors;

2. develop a feasibility analysis of crop residue digestion to confirm the potential for anaerobic fermentation with untreated dry crop residues;

3. using pilot plant analysis, determine the kinetics of dry or semi-solid digestion of three major crop residues, and the influence of temperature of operation, nutrient availability, and start-up requirements in terms of bacterial seed innoculum and alkalinity requirements;

4. develop a minimum cost full scale dry crop residue fermentor design; and,

5. construct and operate a full scale dry reactor system at a scale that will enable rapid scale-up to community-size systems. This will involve a gas production rate design goal of between 10,000 ft^3/day to 100,000 ft^3/day.

REPORT OUTLINE

Topic

Summary

Objectives

Project Status

- Final Report
- Feasibility Manual
- Full Scale Plug Flow and Completely Mixed Dairy Manure Reactors
  - Plug Flow Reactor Repair and Observations
- Gas Utilization Study
- Dry Fermentation Study: Background and Rationale
- Dry Fermentation Research
  - Introduction
  - Moisture Content, Seed Quantity, Substrate Type, and Temperature as Process Variables (Phase BII)
  - The Use of $CaCO_3$ and $NaHCO_3$ as Buffering Agents
  - Other Experiments in Progress

Future Activities

- Dry Fermentation Study
  - General Overview
  - Bench Scale Research
  - Pilot Scale Research
  - Feasibility and Conceptualization Study
- Full Scale Plug Flow and Completely Mixed Dairy Manure Reactors

References

Low Cost Approach to Methane Generation, Storage, and Utilization from Crop and Animal Residues

Quarterly Progress Report No. 2

April 1, 1980 to June 30, 1980
Cornell University, Ithaca, NY

PROJECT STATUS

During the period April 1, 1980 to June 30, 1980 the Cornell Methane Project continued work toward the completion of the tasks outlined in the work plan, as shown by the shaded areas in Figures 1 and 2. This quarter of research was marked by the realization that funding of the gas utilization study for the full scale digesters would not be forthcoming unless year-end money was available, or a decision to fund in FY '81 was made. The comprehensive dry fermentation study was placed in full operation while the full scale plug flow and completely mixed dairy manure reactors were operated in an effort to gather long-term operational and maintenance information. This report outlines the progress of this project in all areas of research within the aforementioned time period.

FINAL REPORT (D.O.E. Contract No. DE-AS02-76ET20051)

The final report from "Anaerobic Fermentation of Agricultural Residues: Potential for Improvement and Implementation" is now being printed by Cornell Media Services. Six copies of this report will be submitted to D.O.E.'s Chicago Operations and Regional Office prior to August 1, 1980. S.E.R.I. will receive a number of copies for distribution at the same time. Submission of this report will fulfill Cornell's obligations under this contract.

FEASIBILITY MANUAL (D.O.E. Contract No. DE-AS02-76ET20051)

Work has continued, albeit slowly, on this report. S.E.R.I. has indicated that they do not have the time to provide input to this document; therefore,

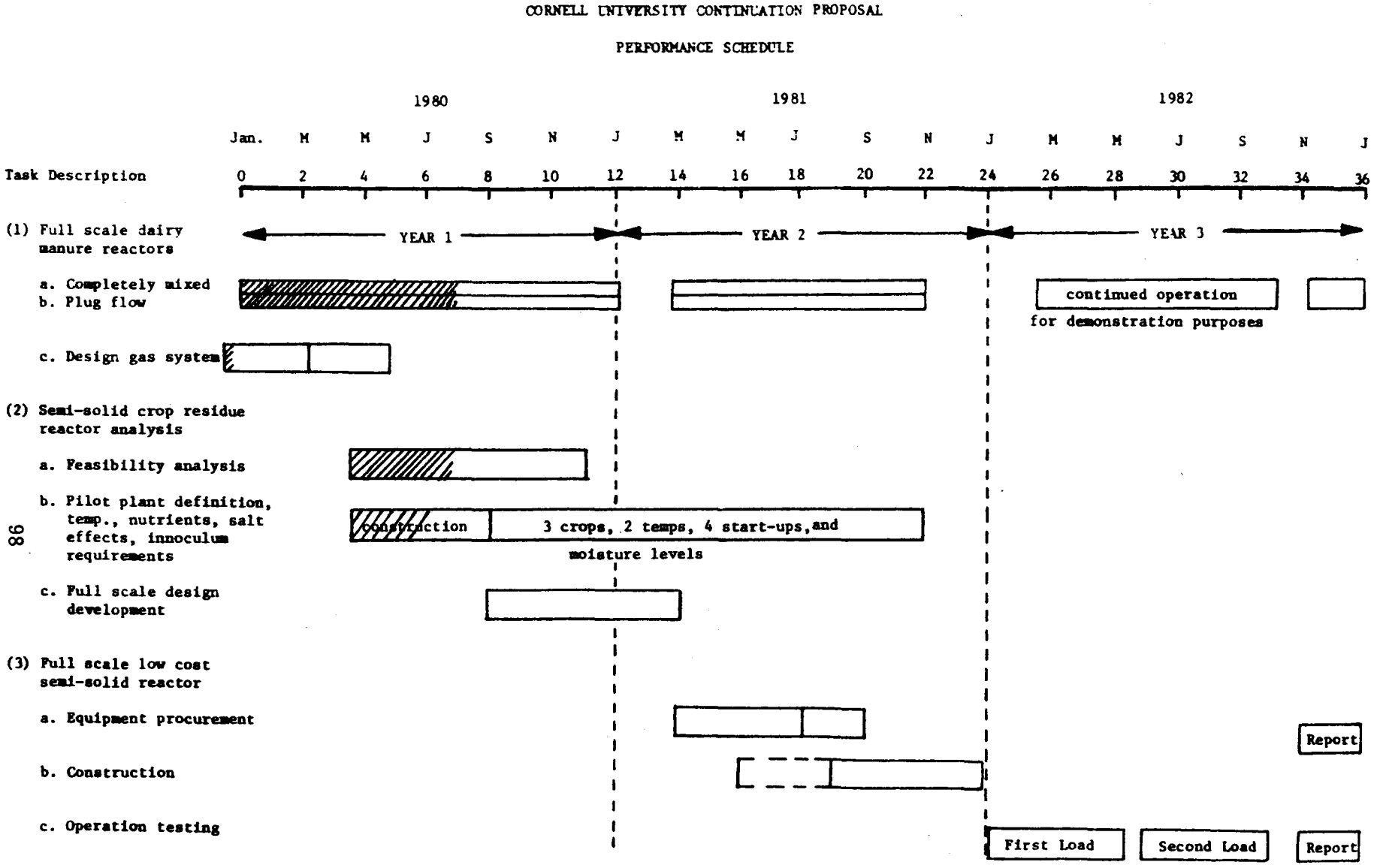


Figure 1. Schedule of tasks, events, and output of research and development program.

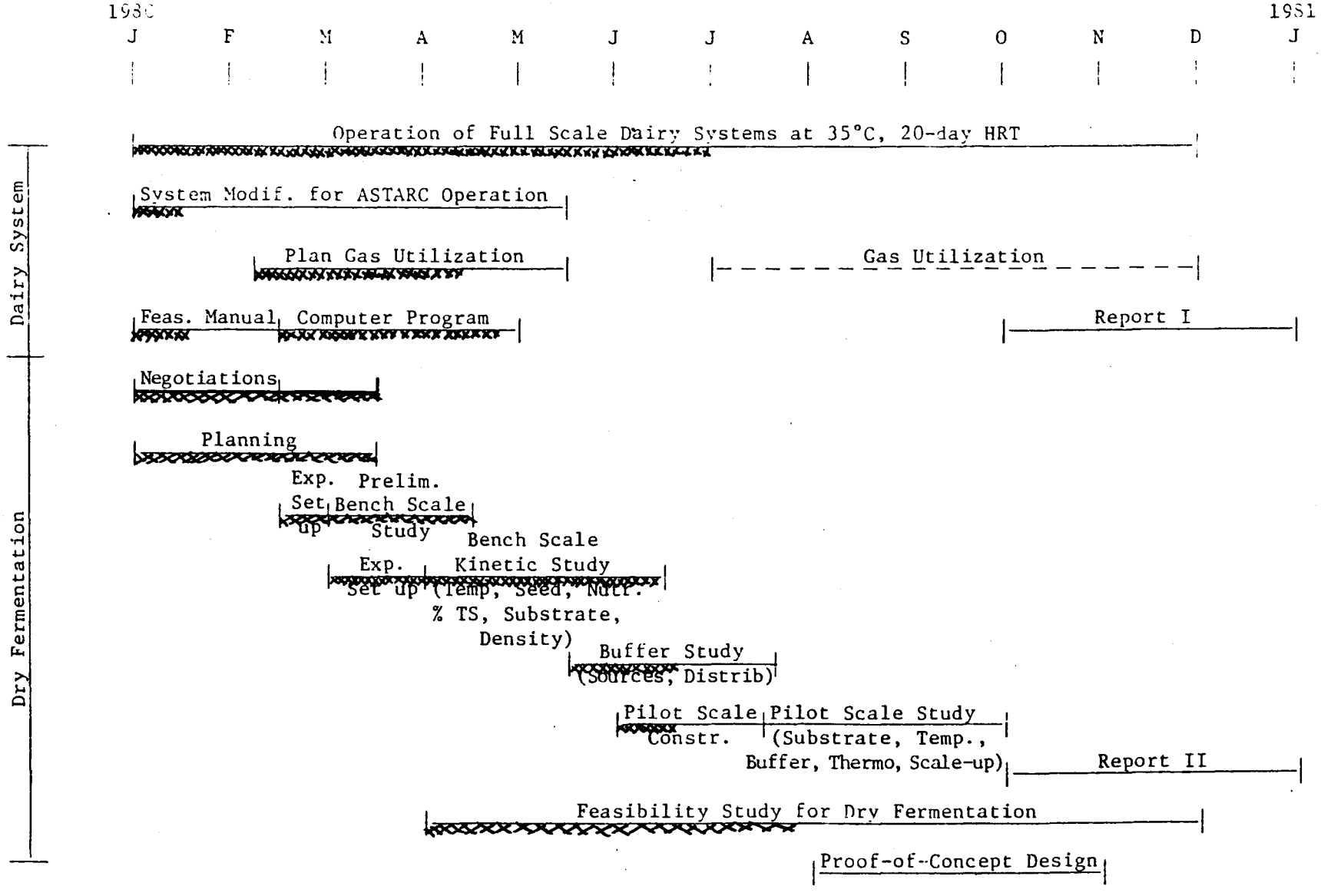


Figure 2. Projected schedule of tasks, events, and output of research and development program for the first year.

finalization of this document will not be complete until September 1980.

The complementary computer programs for assessment of energy and economics criteria for specific farm operations are continually being modified and upgraded. They will be included in the Feasibility Manual.

FULL SCALE PLUG FLOW AND COMPLETELY MIXED DAIRY MANURE REACTORS

The full scale plug flow and completely mixed dairy manure reactors have been operating since January 2, 1980 at 35°C and 20-day HRT. This was the condition which was found to be optimal in terms of net energy production and capital investment. The reactors have been maintained at an alternate-day feeding and monitoring schedule since January so as to provide increased manpower to the dry fermentation study.

The problems associated with the dual-fuel boilers have been corrected, thereby allowing firm control of the reactor temperature. Both reactors operated without problems through mid-May 1980 with the completely mixed reactor producing 56.6 m^3 (2000 ft^3) of biogas per day and the plug flow reactor producing 67.9 m^3 (2400 ft^3) of biogas per day. However, while gas production continued at this level in the completely mixed reactor, gas production in the plug flow reactor dropped drastically, eventually reaching zero. At this point, repair of the plug flow reactor was initiated.

Plug Flow Reactor Repair and Observations

The blue weather shield and cover insulation were removed from the plug flow reactor and the digester contents were pumped to a holding tank for storage, as biological seed. The cover insulation (fiberglass batting) was matted and much of it was wet from condensation. The moat areas on the east and west side consisted of a very thick manure. It was apparent that this material had been stagnant for a long period of time. This thick material was washed back into the digester

The inside of the reactor showed no indication whatsoever of a floating or settled layer; in fact, the entire reactor contents looked very homogeneous. All interior piping was in place and showed no signs of wear.

After the reactor material was pumped down to the one foot depth, the reason for the gas leak was apparent. Of the 14, 1/2-inch diameter steel pipe anchors, 7 had broken or had been bent vertical. The liner was ripped by as much as one foot at each of these anchors. Two years ago the same problem had occurred on the east side of the digester. The broken anchors were repositioned and welded; then as was done on the east side, a 3-inch diameter black steel pipe was horizontally positioned below the pipe such that all anchors would share an equal load. The tears in the liner were repaired with glue.

When the estane cover was first put into use two years ago, some holes developed immediately at the 3 pipe cover clamping assembly on the west side. When the reactor contents were removed, it was apparent that this clamping method had allowed the cover to slip by two to three inches. Wherever there was a bolt to clamp the pipes, the cover was ripped. The cover material itself had not failed; the clamping assembly had. The whole clamping assembly was loosened and the cover was pulled back through the assembly, then a thick layer of glue was put on the inside of the cover material so that the cover was glued back to itself. The 3-pipe assembly was then retightened to hold the cover.

The stored seed from the holding tank was pumped back to the digester and raw manure was also pumped to the reactor to make-up the operating volume. By the next day the digester was operating and producing enough methane to run the boiler. All repairs seemed successful. Current gas production is in excess of 67.9 m^3 (2400 ft^3) per day. Approximately 40 man-hours were required to disassemble, repair, and reassemble the plug flow reactor.

GAS UTILIZATION STUDY

A separate sub-proposal for a gas utilization and storage study, using the two full scale dairy manure digesters (complete mix and plug flow), was submitted to, and at the request of, S.E.R.I. on April 21, 1980. Recent funding developments within D.O.E. make the funding of that portion of research very unlikely, even in FY '81. However, operations of the two full scale units will continue so that long term operational and maintenance requirements can be determined. Excess gas from these units, as in the past six months, will be vented to the atmosphere.

DRY FERMENTATION STUDY: BACKGROUND AND RATIONALE

In the preceeding three years of methane fermentation research, Cornell University has conducted extensive laboratory bench scale, pilot scale, and full scale studies in order to define dairy farm fermentor designs which are cost effective. These three years of research culminated in the development of an earthen-wall fermentor using flexible rubber-like materials that can be constructed at half to one-third the cost of rigid tank designs. Due to this successful outcome, Cornell University is now ready to engage in a new area of methane fermentation research which, hopefully, will broaden and accelerate further implementation of this process. Using the same low-cost approach, Cornell now hopes to develop fermentor designs which are capable of efficient and cost effective biogas and by-product production from agricultural crop residues.

The potential of utilizing agricultural crop residues for biogas production is not new. Buswell and Hatfield (1936) over 40 years ago speculated on the potential benefits of crop residue fermentation.

> A ton of cornstalks will yield 10,000 to 20,000 ft^3 of (substitute natural) gas. Taking the lower figure, a ton of cornstalks would

> furnish gas for 400 people for one day, allowing 50 cubic feet per capita per day . . . where 30% of the land is planted to corn, a circle with an 8 mile radius would produce enough cornstalks to supply a city of 80,000 inhabitants with gas. The residue would be suitable for paper making . . . The cost of producing gas is seen to be approximately ten cents per 1000 cubic feet (or $0.19 per million Btu).

There are approximately 900 million tons of organic solids produced in the U.S. annually. A major obstacle found in previous attempts at producing biogas from biomass such as crop residues has been in attempting to apply practices traditionally used for digestion and stabilization of sewage and industrial sludges. The requirement that substrates be in a slurry form that is suitable for liquid-solids handling prior to fermentation is a great deterrent. Most agricultural residues are found in the field and conventionally transported at moisture contents that may be less than 10 percent (90 percent TS). Traditional sludge digestion practice would dictate that the solids content should not exceed 10 percent TS with 4 to 7 percent being a preferred range. These and other problems have discouraged Cornell from using this approach for fermentation of agricultural crop residues.

The potential benefits of fermentation at solids contents in excess of 10 percent TS has been recognized for some time (Schulze, 1958; Wong-Chong, 1975), but until recently little comprehensive research has been performed. Recently Jewell (1979) outlined several of the potential advantages and disadvantages of dry fermentation as shown in Table 1. At Cornell University Wujcik and Jewell (1979) investigated several variables of interest in biogas production at minimal moisture content, which they called dry fermentation. These investigations showed that quite rapid and complete fermentation of dairy cow manure is possible at initial dry matter contents approaching 33 percent TS. In a follow-up effort by Jewell et al. (1980) at Cornell, a 5000 ℓ pilot scale fermentor using wheat straw as a substrate at an initial total

TABLE 1. SUMMARY OF ADVANTAGES AND DISADVANTAGES OF USING A DRY REACTOR APPROACH FOR THE CONVERSION OF AGRICULTURAL CROPS AND RESIDUES TO METHANE

Advantages	Disadvantages
1. Minimizes handling and pretreatment requirements of agricultural products using in-place production and collection techniques	1. Large reactor required
2. Exceptionally simple design and operation	2. Two large storage areas required for liquid or wet residues and solid residues
3. Low labor requirements	3. Process limitations are poorly defined
4. Indiscriminate in type of organic input that could be used	
5. Little or no water requirement	
6. Potential energy production could satisfy up to 100 percent of the total energy needs for many communities	
7. Appears to be a self-sustaining reaction, which further simplifies the reactor design	
8. Has major pollution control side benefits--eliminates liquid waste on farms and from cities, and uses a low nutrient feed which could result in control of highly volatile nitrogen products while producing a slow-release organic fertilizer as an end-product	
9. Appears to be capable of producing a final organic residue with moisture less than 50 percent	
10. Project overall economics indicate that such a system may be presently economically feasible	

solids content of 22 percent was started. The results from that pilot scale effort were reported previously (Jewell et al., 1980a).

DRY FERMENTATION RESEARCH

Introduction

Several sets of dry fermentation experiments are in progress which address some of the important process variables identified in our preliminary experiments (Jewell et al., 1980a). Only two of these experiments have been underway for a sufficient period of time to justify presentation of preliminary data.

Moisture Content, Seed Quantity, Substrate Type, and Temperature as Process Variables (Phase BII)

The ideal dry fermentor will be required to meet many rigorous performance standards including the following:

1. Operate at a high dry matter content
2. Achieve nearly 100% destruction of the biodegradable organic matter over a time interval compatible with substrate availability
3. Use a minimal quantity of seed in order to achieve successful fermentation

These criteria are the focus of this phase of the study. Using 96, 1 ℓ-capacity fermentors, this phase of the study will define the seed, moisture content, and temperature requirements for successful fermentation of corn stover and wheat straw substrates.

Method and Materials--

Ninety-six 1 ℓ-capacity canning jars were used as fermentors in this study. This large number prohibits the use of conventional gas measurement devices (i.e., wet test meters or acidified salt solution displacement gas tubes); thus an alternative performance monitoring technique was developed (Jewell et al.,

1980a). Organic matter undergoing methane fermentation is ultimately converted to methane and carbon dioxide. Both gases, being relatively insoluble in water, escape from the fermenting mass and are lost from the system. Performance of a fermentor can then be monitored by measuring reactor weight change throughout the fermentation period.

The laboratory apparatus used in this study is shown in Figure 3. Five 1 ℓ dry fermentors are engaged to a single water trap. Each fermentor is equipped with its own gas line, quick disconnect, and septum for gas composition analysis. When weighing of fermentor contents is required, the fermentor's quick disconnect is detached from the water trap and quickly placed on the inverted cork stopper attached to the #13 rubber stopper of each fermentor. This is done to minimize possible contact of fermentor contents with air during weighing.

Digested dairy cow manure effluent from completely mixed bench scale reactors was used as seed in this study. Seed reactors were established approximately two months in advance of the study at both 25°C and 35°C. Seed fermentor operation and performance at start-up of the 96 1 ℓ fermentors is shown in Table 2.

The wheat straw substrate used in this study was obtained from the Animal Science Teaching and Research Center (ASTARC) in Harford, New York where it was stored under cover. Corn stover was donated by a local farmer who had baled it in late November 1979.

The variable combinations examined for corn stover at 25 and 35°C and wheat straw at 35°C are shown in Table 3. Fermentors were also placed in operation at 55°C, but one week after start-up a malfunctioning relay caused the chamber to overheat and all 55°C units were terminated. The seed/feed (S/F) presents the ratio of digested dairy cow manure TS to substrate TS placed into each fermentor. At each TS content, this range of S/F examined

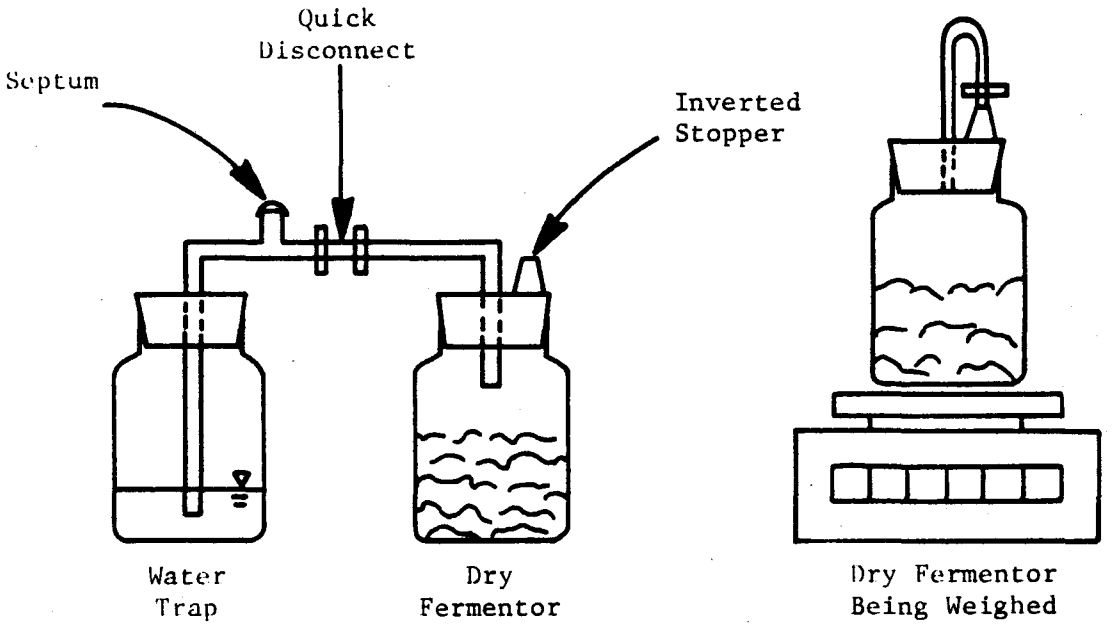


Figure 3. Experimental apparatus.

TABLE 2

SEED FERMENTOR OPERATION AND PERFORMANCE

PARAMETERS	25°C SEED FERMENTOR	35°C SEED FERMENTOR
Volume (ℓ)	12	12
HRT (days)	30	15
EFFLUENT:		
%TS	10.1	9.7
%VS	83.2	82.4
Total Alk (mg/ℓ as $CaCO_3$)	18,042	18,042
VFA (mg/ℓ as HAC)	3,480	1,260
Bicarb ALK (mg/ℓ as $CaCO_3$)	15,578	17,150
GAS PRODUCTION:		
Daily Biogas		
ℓ/day	9.6	28.1
V/VD	0.64	1.88
Daily CH_4		
ℓ/day	5.2	17.7
V/VD	0.35	1.18
CH_4/CO_2	54/46	63/37

TABLE 3

VARIABLE COMBINATIONS EXAMINED USING
WHEAT STRAW AND CORN STOVER

%TS	SEED/FEED (S/F)									
	.10	.20	.30	.40	.50	.60	.70	.80	.90	1.0
15	-	-	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-			
22.5	-	-	-	-	-					
25	-	-	-	-						
30	-	-	-							
35	-	-								
40	-									

was extended to the maximum point where the seed material supplied all the moisture for the seed-substrate mixture.

The initial fermentor contents for corn stover at 25°C and 35°C and wheat straw at 35°C are shown in Tables 4 and 5. For each substrate type the quantity of substrate TS was maintained constant, while the quantity of seed was adjusted to the desired level. Tap water was used to adjust reactor contents to the desired moisture content.

All fermentors used in this study were weighed every 3 days. This was continued for a total of 60 days. Gas composition was first performed on day 6 and every 15 days thereafter.

Results to Date--

Although the data are incomplete, this study has revealed some interesting differences between fermentation of corn stover and wheat straw at 35°C. Figures 4 and 5 show the cumulative weight loss for all reactors at 20% initial TS for wheat straw and corn stover. Wheat straw performance during start-up shows a uniform response to increasing seed quantity. All fermentors with S/F > 0.10 have biogas methane contents of greater than 50% by day 21. A distinct break in performance, however, is evident with corn stover fermentors between an S/F = .30 and .40. Biogas methane content at S/F = .30 is only 29%, while at S/F = .40 it is 58% by day 21.

Figures 6 and 7 show cumulative weight loss for wheat straw and corn stover at 22.5% initial TS. Again response is uniform with increasing S/F for wheat straw. Although a distinct break is again evident for corn stover, it appears at a lower S/F than was apparent at 20% initial TS. Biogas methane content was 64% at a S/F of .30 and only 35% at a S/F of .20 on day 21.

Wheat straw and corn stover performance at 25% initial TS is shown in Figures 8 and 9. Wheat straw is again consistent with the results at lower

TABLE 4

INITIAL CORN STOVER REACTOR CONTENTS AT 25 AND 35°C

S/F	CORN STOVER			DIGESTED DAIRY COW MANURE					$NaHCO_3$	TOTAL TS	TOTAL VS
	WET	TS	VS	WET	TS	VS	TKN	NH_4-N			
.10	40.0	37.0	33.3	38.0	3.7	3.1	0.175	0.097	3.0	43.7	36.4
.20	40.0	37.0	33.3	76.0	7.4	6.1	0.351	0.194	3.0	47.4	39.4
.30	40.0	37.0	33.3	114.0	11.1	9.2	0.526	0.291	3.9	51.1	42.5
.40	40.0	37.0	33.3	153.0	14.8	12.3	0.702	0.388	3.0	54.8	45.6
.50	40.0	37.0	33.3	191.0	18.5	15.3	0.877	0.485	3.0	58.5	48.6
.60	40.0	37.0	33.3	229.0	22.2	18.4	1.052	0.582	3.0	62.2	51.7
.70	40.0	37.0	33.3	267.0	25.9	21.5	1.228	0.679	3.0	65.9	54.8
.80	40.0	37.0	33.3	305.0	29.6	24.5	1.403	0.776	3.0	69.6	[illegible].8
.90	40.0	37.0	33.3	343.0	33.3	27.6	1.578	0.872	3.0	73.3	[illegible]0.9
1.00	40.0	37.0	33.3	381.0	37.0	30.7	1.754	0.969	3.0	77.0	64.0

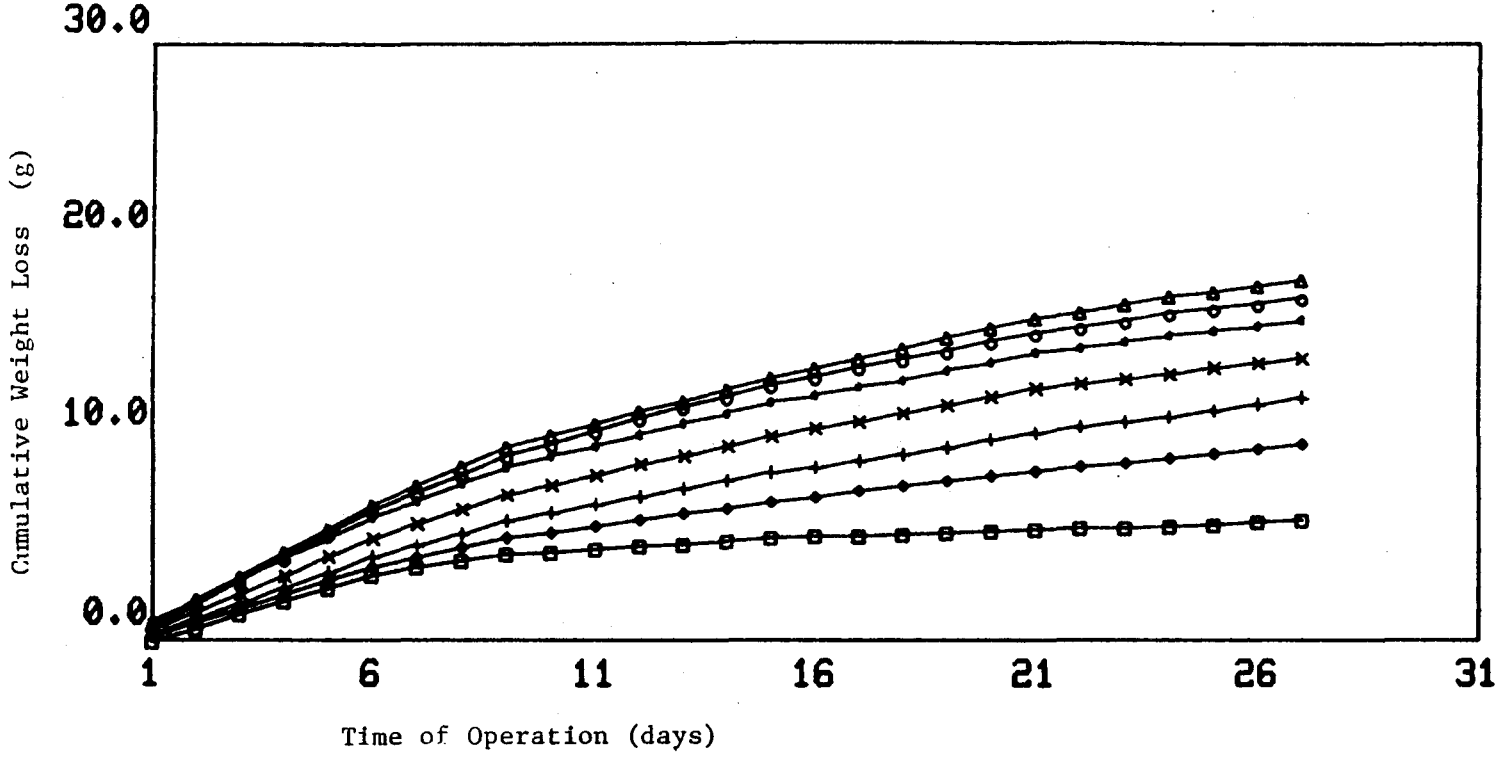
ALL MASS VALUES IN GRAMS (g)

TABLE 5

INITIAL WHEAT STRAW REACTOR CONTENTS AT 35°C

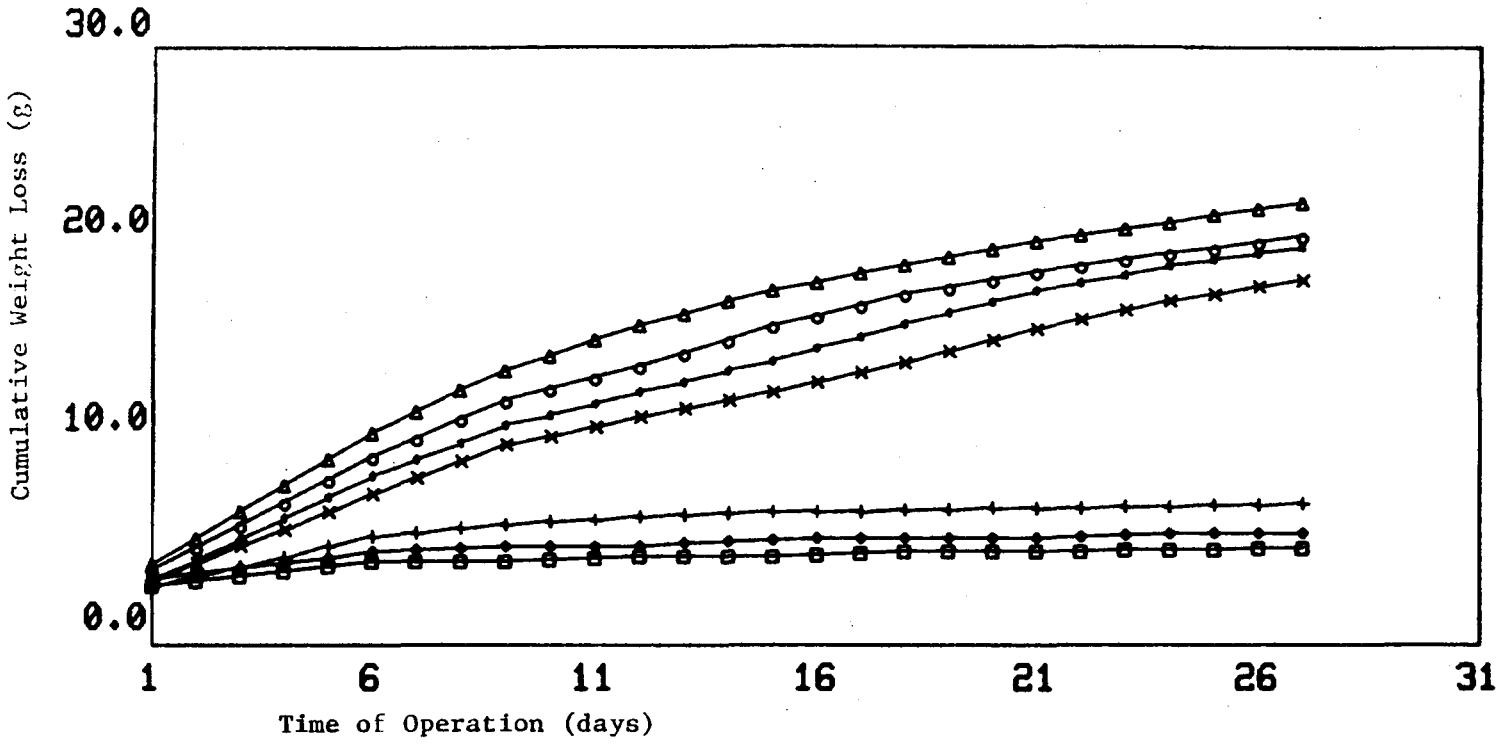
S/F	WHEAT STRAW			DIGESTED DAIRY COW MANURE					$NaHCO_3$	TOTAL TS	TOTAL VS
	WET	TS	VS	WET	TS	VS	TKN	NH_4-N			
.10	40.0	33.4	31.2	34.0	3.3	2.7	0.156	0.086	3.0	39.7	33.9
.20	40.0	33.4	31.2	68.0	6.6	5.5	0.313	0.173	3.0	43.1	36.7
.30	40.0	33.4	31.2	102.0	9.9	8.2	0.469	0.259	3.0	46.3	39.4
.40	40.0	33.4	31.2	136.0	13.2	10.9	0.626	0.346	3.0	49.6	42.1
.50	40.0	33.4	31.2	170.0	16.5	13.7	0.782	0.432	3.0	52.9	44.9
.60	40.0	33.4	31.2	204.0	19.8	16.4	0.939	0.519	3.0	56.4	47.6
.70	40.0	33.4	31.2	272.0	26.4	21.9	1.094	0.605	3.0	59.5	50.3
.80	40.0	33.4	31.2	306.0	29.7	24.6	1.251	0.692	3.0	62.8	53.1
.90	40.0	33.4	31.2	306.0	29.7	24.6	1.408	0.778	3.0	66.1	55.8
1.00	40.0	33.4	31.2	344.0	33.4	27.7	1.583	0.875	3.0	69.8	58.9

ALL MASS VALUES IN GRAMS (g)



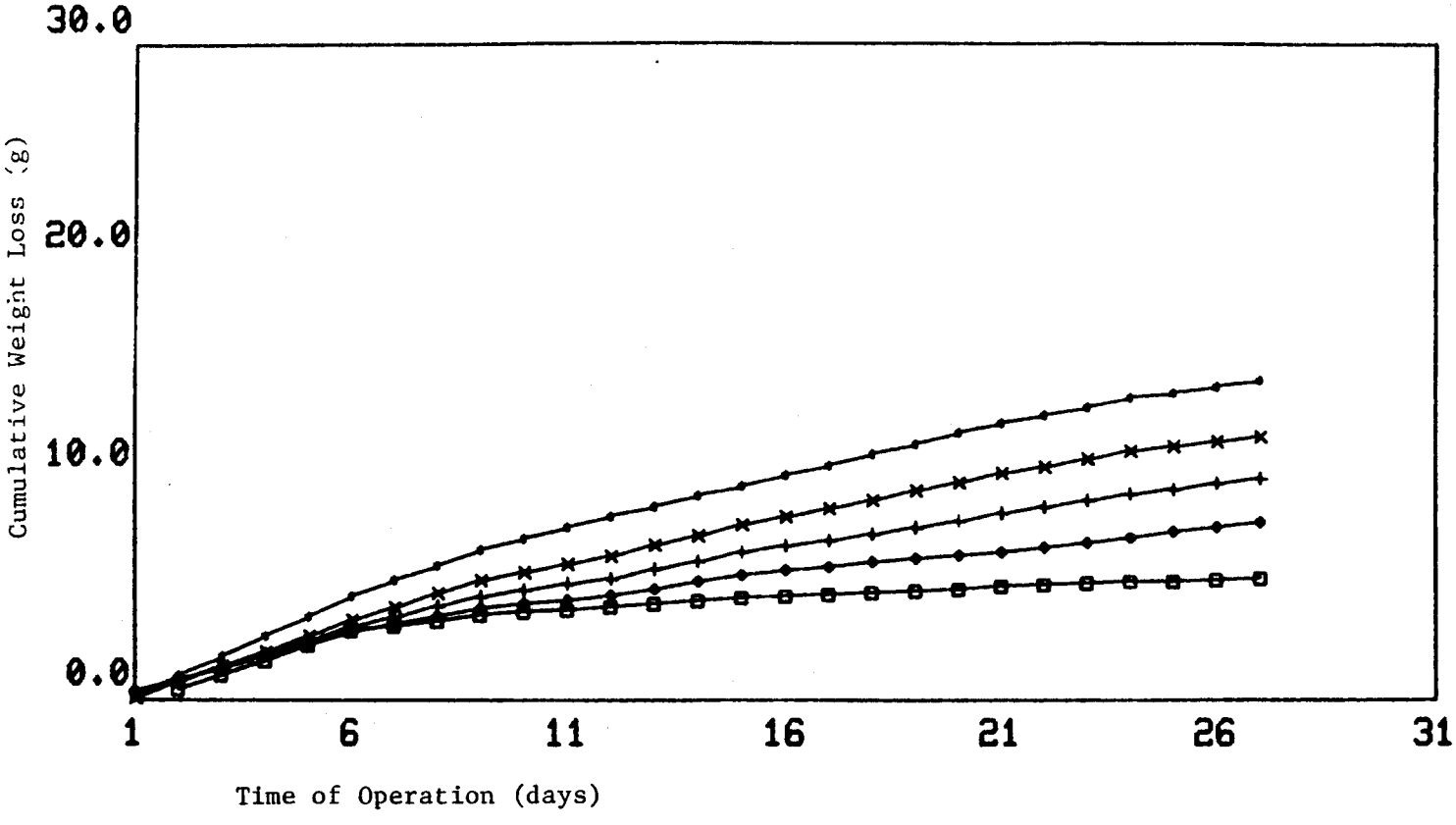
Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30
×		.40
✳		.50
○		.60
△		.70

Figure 4. Cumulative Weight Loss for Wheat Straw at 20% TS, 35°C.



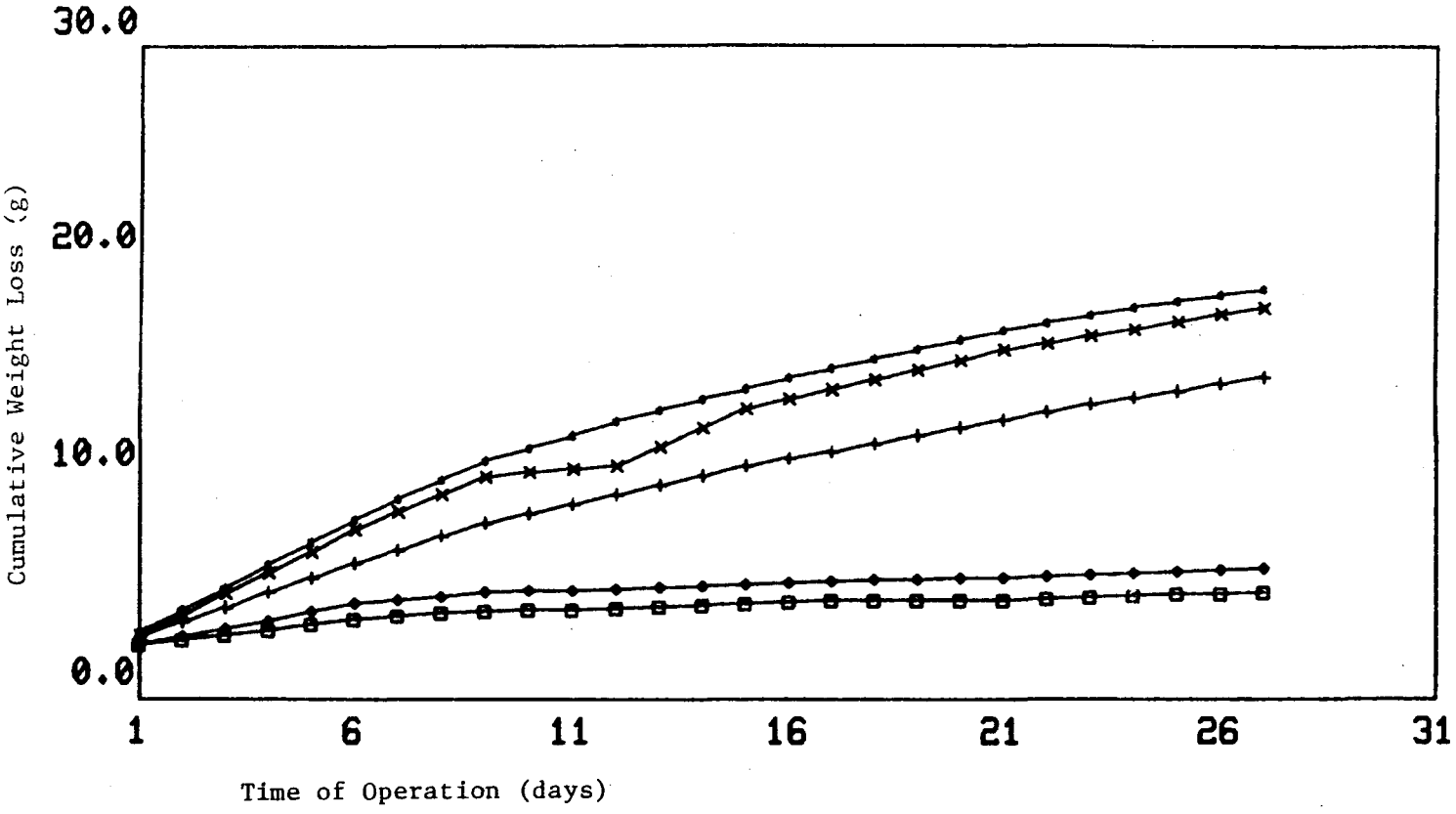
Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30
×		.40
✳		.50
○		.60
△		.70

Figure 5. Cumulative Weight Loss for Corn Stover at 20% TS, 35°C.



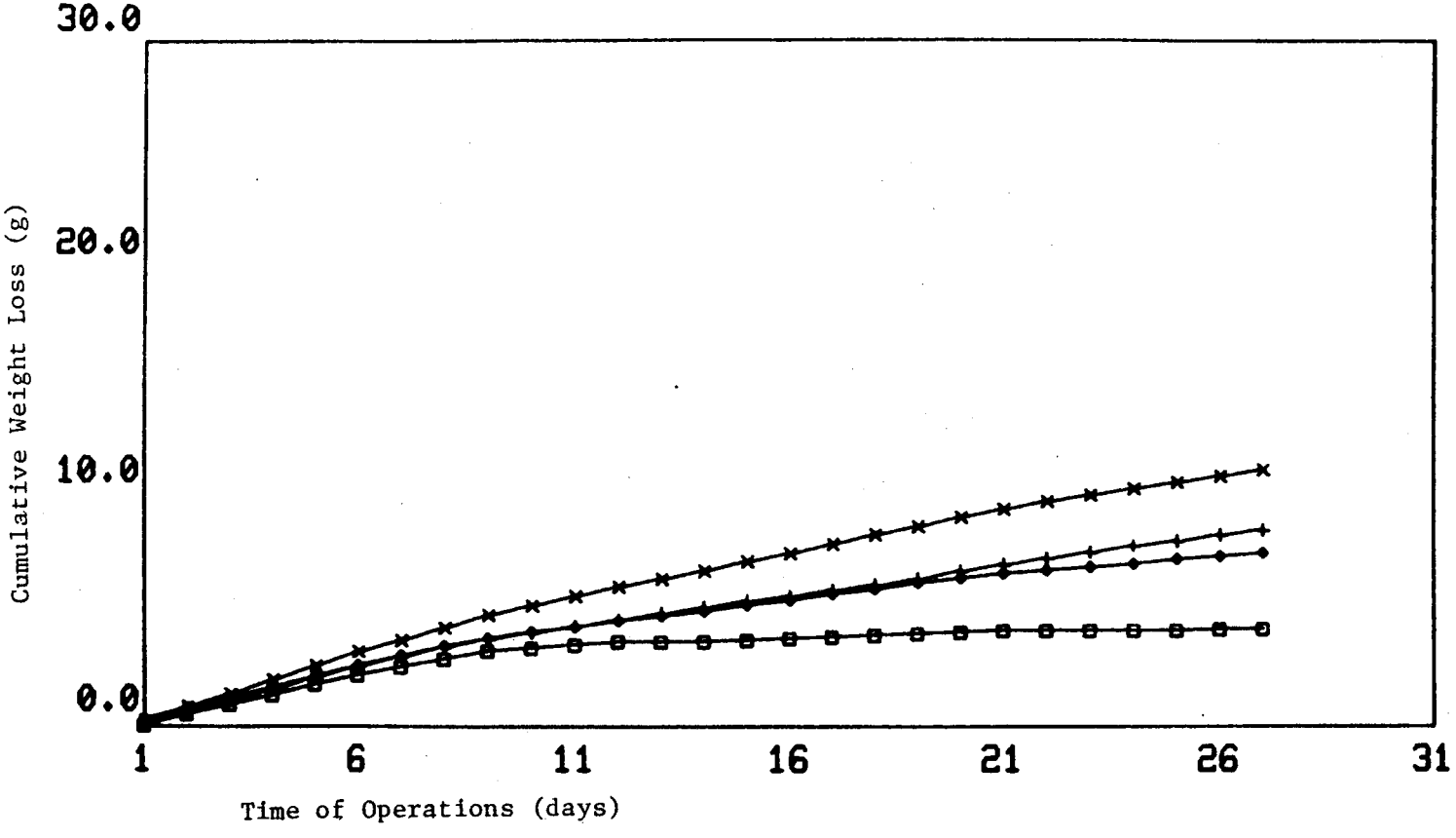
Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30
×		.40
✳		.50

Figure 6. Cumulative Weight Loss for Wheat Straw at 22.5% TS, 35°C.



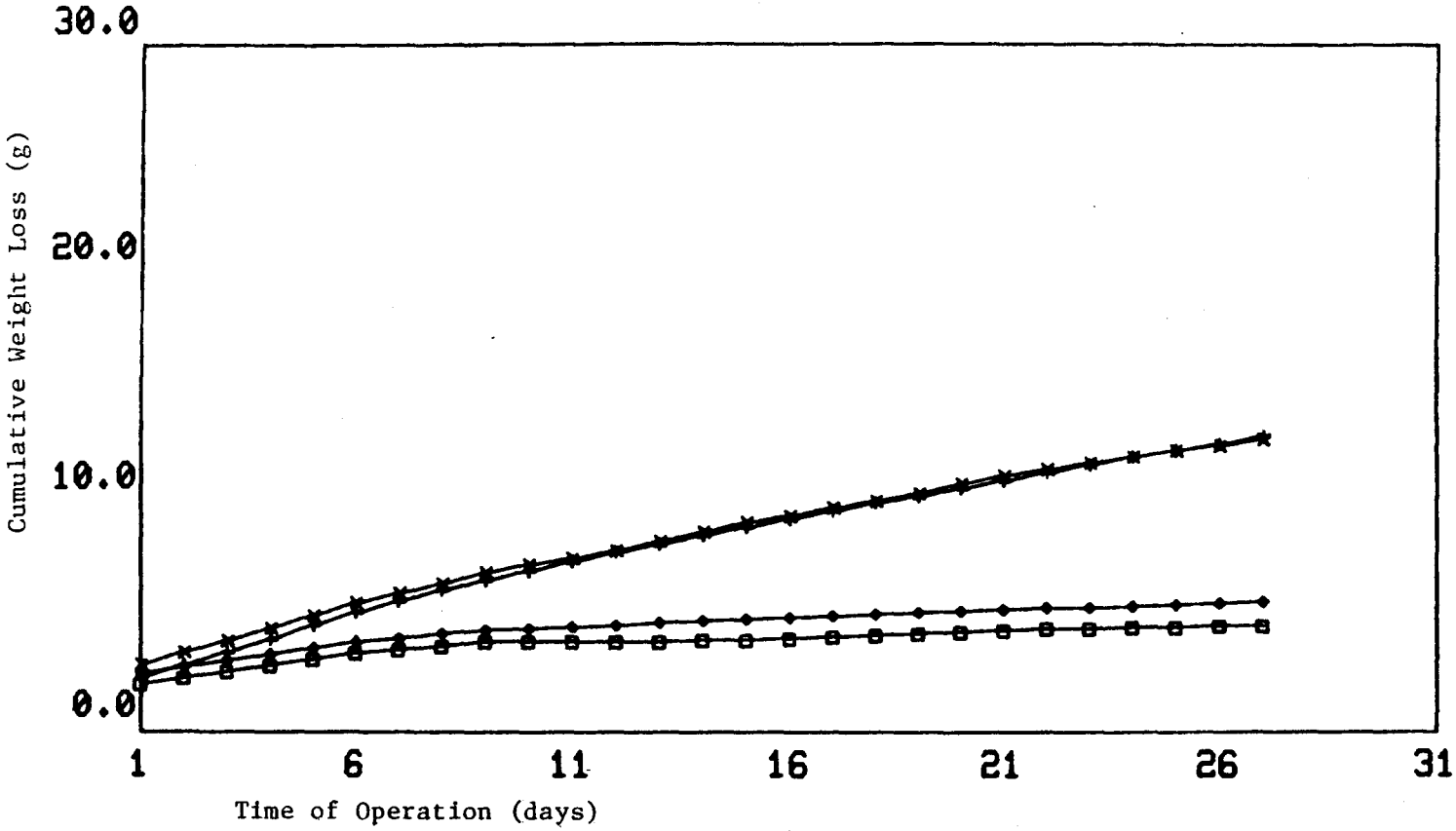
Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30
×		.40
✳		.50

Figure 7. Cumulative Weight Loss for Corn Stover at 22.5% TS, 35°C.



Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30
×		.40

Figure 8. Cumulative Weight Loss for Wheat Straw at 25% TS, 35°C.



Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30
×		.40

Figure 9. Cumulative Weight Loss for Corn Stover at 25% TS, 35°C.

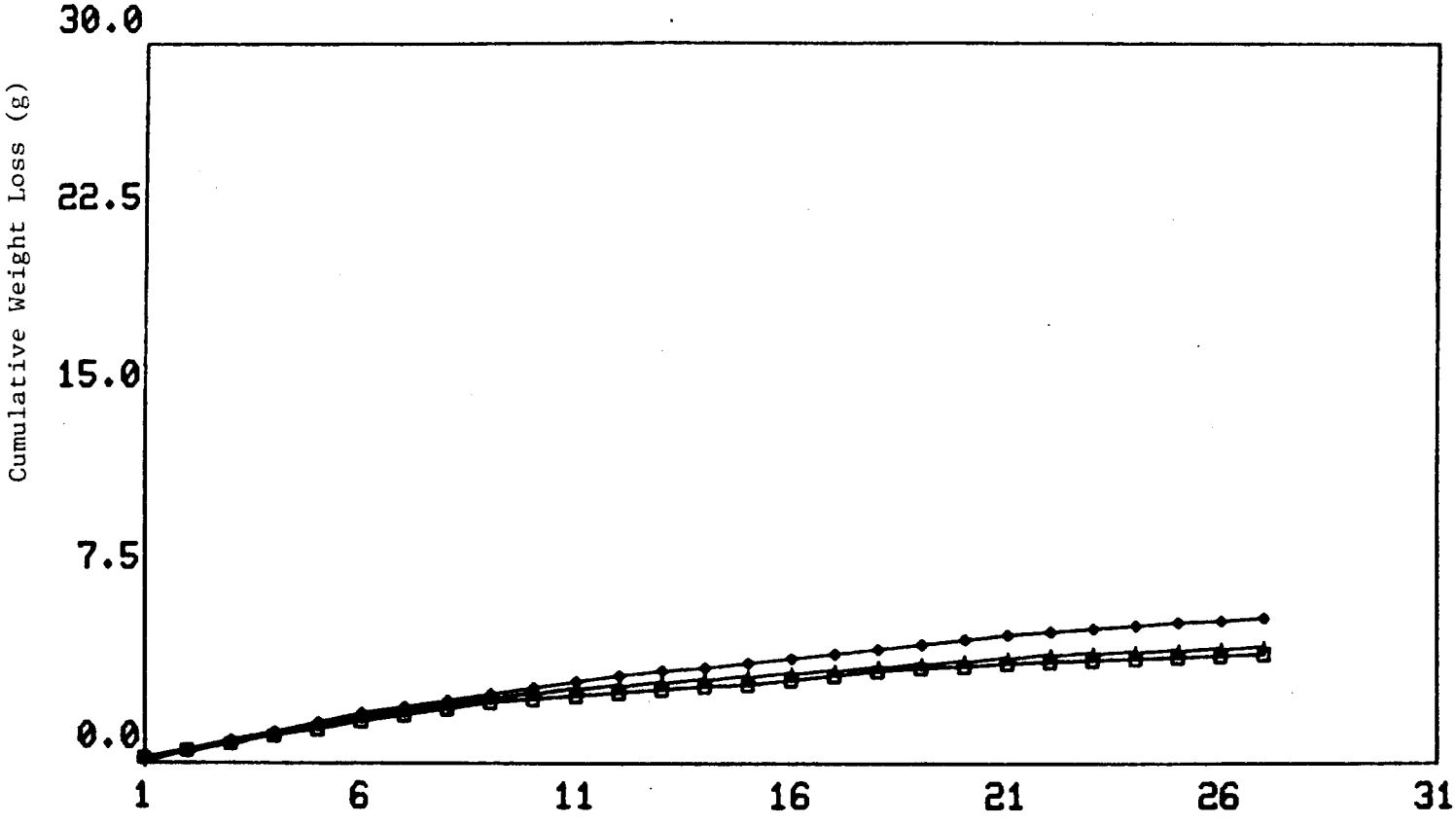
solids contents. Corn stover again shows a distinct break between S/F of .30 and .20. Corn stover's performance at S/F of .30 and .40 appears identical at this time.

The performance to date for wheat straw and corn stover at 30% initial TS is presented in Figures 10 and 11. Cumulative weight loss for wheat straw is uniform, but the rate of weight loss appears to have been dramatically reduced due to low moisture content. Although affected by low moisture content, the higher initial TS content again appears to have reduced seed requirements for corn stover. Corn stover at a S/F of .20 had a biogas methane content of 54% on day 21, while only a 20% value was observed at a S/F of 0.10. Wheat straw biogas methane content at a S/F = 0.20 was 47% on day 21. At this time then it appears that seed requirements may be reduced at higher initial solids contents for a corn stover substrate.

Performance as a function of substrate moisture content is best shown in Figure 12 for wheat straw at a S/F of .40. As would be expected, the rate of fermentation is depressed with increasing initial solids content. Fermentation of corn stover at 25°C deviates greatly from that observed at 35°C. Figure 13 shows cumulative weight loss at 22.5% initial TS. This is the highest solids content at which biogas methane content exceeds 50% by day 21. This unit is operating at a high S/F = 0.50.

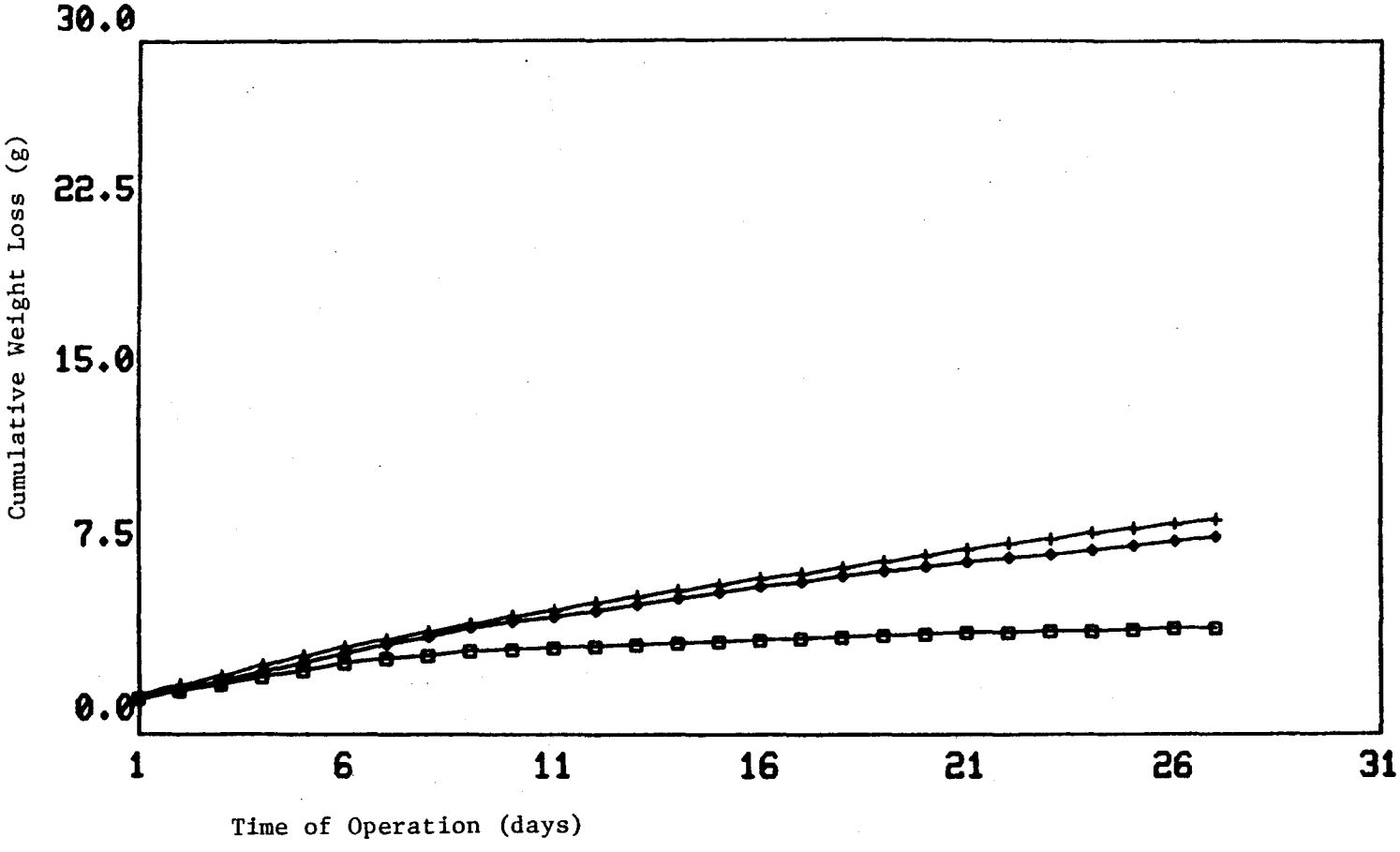
The Use of $CaCO_3$ and $NaHCO_3$ as Buffering Agents

During methane fermentation it is desirable to have chemical agents, such as bicarbonate (HCO_3^-), that act as safeguards against pH depression due to microbial imbalances that might occur. Unlike dairy cow manure, field crop residues have negligible buffering capacity of their own. Furthermore, dry fermentation, presently conceived as a batch or semi-batch process, places



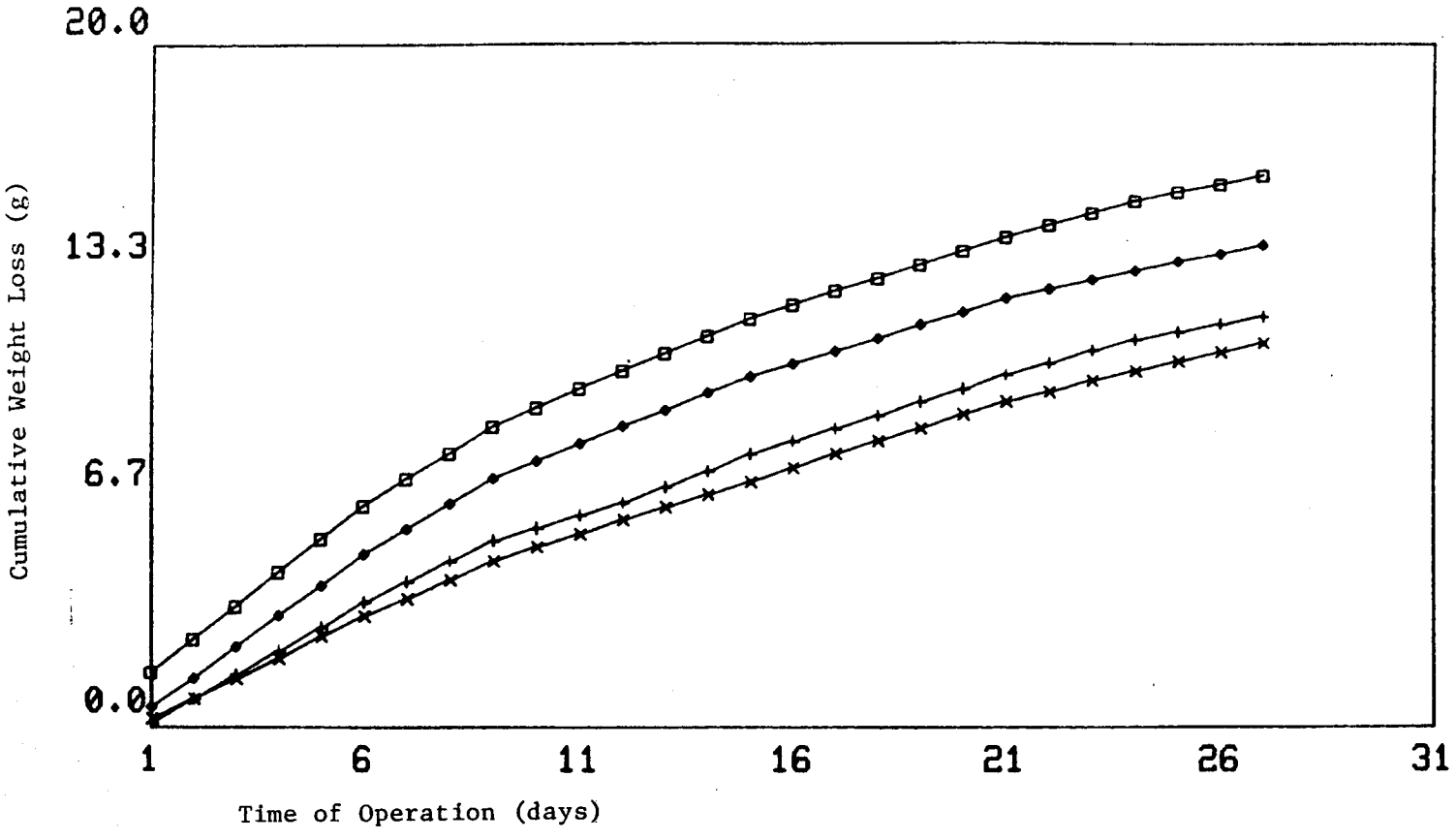
Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30

Figure 10. Cumulative Weight Loss for Wheat Straw at 30% TS, 35°C.



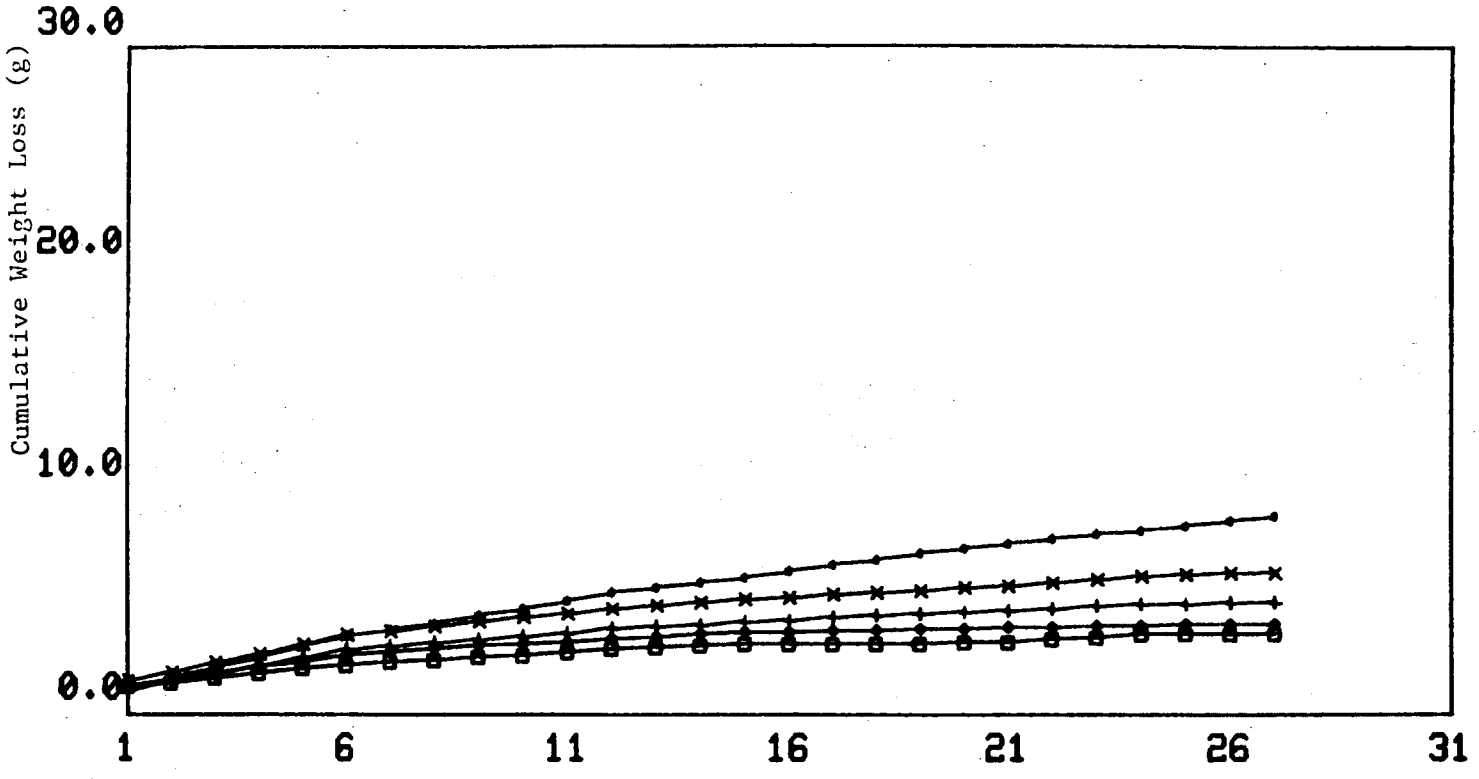
Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30

Figure 11. Cumulative Weight Loss for Corn Stover at 30% TS, 35°C.



Symbol	Scale Name	%TS
□		15
◇		20
+		22.5
×		25

Figure 12. Cumulative Weight Loss for Wheat Straw at Seed/Feed = 0.40, 35°C.



Symbol	Scale Name	Seed/Feed
□		.10
◇		.20
+		.30
×		.40
✳		.50

Figure 13. Cumulative Weight Loss for Corn Stover at 22.5% TS, 25°C.

an additional buffer demand in order to maintain a suitable pH during start-up. Thus, a supplemental source of buffer is needed.

When supplemental buffering is needed to maintain digester pH, $NaHCO_3$ is most often used. $NaHCO_3$ is fast acting, readily available, and safe for most research needs in methane fermentation. However, $NaHCO_3$ can become quite expensive when used in excess at full scale installations and may contribute significantly to the cost of gas produced by the process. Thus $NaHCO_3$ must be minimized if not replaced as a buffering agent in full scale dry fermentors.

The successful use of $CaCO_3$ as a buffer, in order to enhance conditions for methane fermentation from controlled landfilling of municipal wastes, has been reported (Augenstein et al., 1976). Using fine (300 mesh), high purity reagent grade $CaCO_3$, municipal waste digesters were successfully operated. In the study reported here, pulverized limestone, commonly used as a farm soil ammendment, was used as a source of $CaCO_3$ buffer. The $CaCO_3$ was distributed to the reactors in a variety of regimes and compared to fermentors using $NaHCO_3$ as buffer.

Methods and Materials--

With the exception of one modification, 10, 1 ℓ fermentors, identical to those previously described, were used in this study. A 1.25 cm diameter glass tube was inserted into each reacter through the #13 rubber stopper for use as a pH probe port. Each glass tube was made gas-tight by use of a #00 rubber stopper.

Digested dairy cow manure from the full scale plug flow fermentor and digested sewage sludge from Binghamton, New York were used to seed reactors in this study.

Wheat straw was the only crop residue used in this experiment. In addition to wheat straw, several fermentors contained other biodegradable solids.

Pulverized limestone ($CaCO_3$) was added directly to raw sewage sludge and cow manure in order to disperse and solubilize some of this particulate buffer, as well as to neutralize these acidic materials prior to fermentation. Two liters of unseeded raw cow manure were placed in an air-tight container at 35°C one week prior to start-up. At that time the pH of the manure was 6.4. Sixty grams of pulverized limestone ($CaCO_3$) were added to 1 ℓ of the acid cow manure, stirred manually, and allowed to sit overnight. The next morning the pH of the slurry was 6.7. An additional 30 g of pulverized limestone ($CaCO_3$) were added and vigorously stirred by means of a pneumatic mixer. After 5 minutes the pH jumped to 6.9. It was then that the slurry containing the pulverized limestone ($CaCO_3$) was added to the other fermentor contents.

Raw sewage sludge was obtained from the Cayuga Heights, New York Sewage Treatment Plant. At the time of acquisition, the pH of the sludge was 6.0. Two liters of sludge were placed in a sealed container at 35°C for 2 days. The pH at that time was 5.3. Thirty grams of pulverized limestone ($CaCO_3$) were added to 1 ℓ of raw sludge, stirred manually, and allowed to sit overnight. The next morning the pH was 5.9. An additional 30 grams of pulverized limestone ($CaCO_3$) were added and vigorously stirred by a pneumatic mixer. After 5 minutes the pH was found to be 6.1. This raw sludge was then added to the rest of the fermentor contents.

The contents of the fermentors used in this study are shown in Table 5. All $NaHCO_3$-buffered fermentors were buffered directly. Acid cow manure and raw sludge that had been incubated at 35°C, but had not been treated with pulverized limestone ($CaCO_3$), were added to $NaHCO_3$-buffered fermentors. Units numbered 2 and 5 had pulverized limestone ($CaCO_3$) added directly. All units operated at a S/F of 0.10.

TABLE 5.

BUFFER STUDY INITIAL REACTOR CONTENTS

UNIT	WHEAT STRAW			DIGESTED SLUDGE			DIGESTED C.M.			RAW SLUDGE			ACID C. M.			$CaCO_3$	$NaHCO_3$	H_2O ADD.	TOTAL TS	TOTAL VS	%TS
	WET g	TS g	VS g	WET g	TS g	VS g	WET g	TS g	VS g	WET g	TS g	VS g	WET g	TS g	VS g				g	g	
1	40	33.4	31.2	80	3.1	1.5	-	-	-	90	5.4	1.9	-	-	-	3.1[1]	-	35	42.9	34.6	17.5
2	40	33.4	31.2	80	3.1	1.5	-	-	-	-	-	-	-	-	-	6.0[3]	-	100	42.5	32.7	18.8
3	40	33.4	31.2	-	-	-	40	3.7	3.0	90	5.4	1.9	-	-	-	3.1[1]	-	75	42.5	36.1	17.3
4	40	33.4	31.2	-	-	-	40	3.7	3.0	-	-	-	-	16.5	6.9	6.5[2]	-	100	53.6	41.1	20.6
5	40	33.4	31.2	-	-	-	40	3.7	3.0	-	-	-	-	-	-	6.0[3]	-	140	43.1	342	19.6
6	40	33.4	31.2	80	3.1	1.5	-	-	-	90	2.1	1.7	-	-	-	-	3.3	30	41.9	34.2	17.2
7	40	33.4	31.2	80	3.1	1.5	-	-	-	-	-	-	-	-	-	-	3.3	90	39.8	32.7	18.7
8	40	33.4	31.2	-	-	-	40	3.7	3.0	90	2.1	1.7	-	-	-	-	3.3	70	42.5	35.9	17.5
9	40	33.4	31.2	-	-	-	40	3.2	3.0	-	-	-	-	10.2	7.1	-	3.3	90	50.6	41.3	20.0
10	40	33.4	31.2	-	-	-	40	3.7	3.0	-	-	-	-	-	-	-	3.3	130	40.4	34.2	18.9

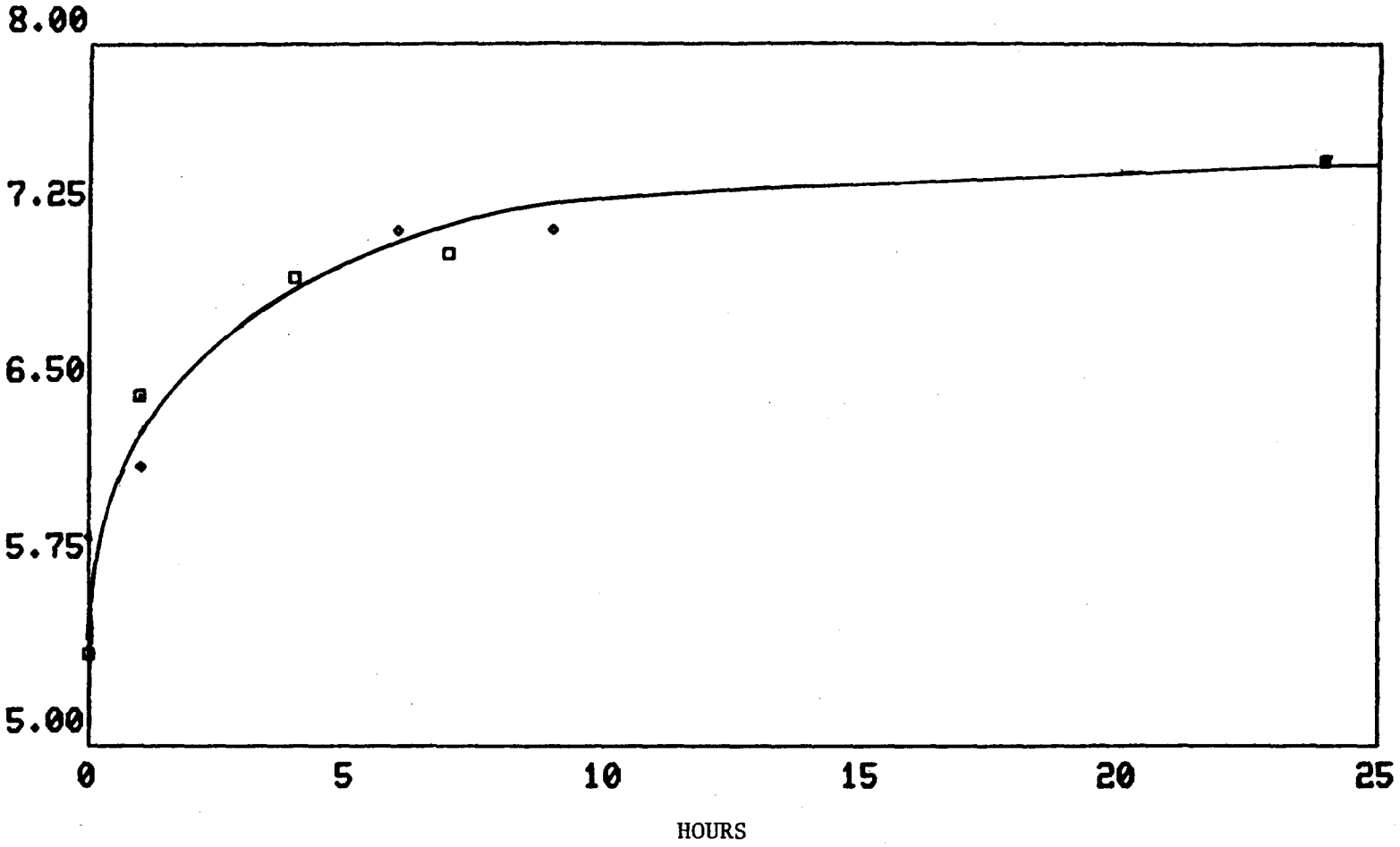
1: Dispersed in Raw Sewage Sludge
2: Dispersed in Acid Cow Manure
3: Added Directly to Fermentor

Results to Date--

In order to compare the performance of the pulverized limestone ($CaCO_3$) used as a source of buffer, to reagent grade $CaCO_3$, an equilibrium test was performed. Two beakers of distilled water with acetic acid concentrations of 10,000 mg/ℓ were used. To one, twice the quantity of pulverized limestone ($CaCO_3$) needed to neutralize the acetic acid was added. To the other, twice the equivalent of reagent grade $CaCO_3$ was added. Both beakers were continuously stirred at the same moderate speed. The results of this experiment are shown in Figure 14. Data from this experiment suggest that the pulverized limestone ($CaCO_3$) and reagent grade $CaCO_3$ have similar chemical reaction kinetics in aqueous solution.

Figures 15 and 16 show the pH profiles for reactors buffered with pulverized limestone ($CaCO_3$) and $NaHCO_3$, respectively. The pH of fermentors buffered with pulverized limestone ($CaCO_3$) dropped rapidly from time, t = 0, and never recovered. Units 4 and 5, having the highest pH of those buffered with pulverized limestone ($CaCO_3$), were allowed to continue for 47 days, while units 1 through 3 were terminated on day 25. Fermentors 6 through 10, using $NaHCO_3$ as buffer, also showed a drop in reactor pH initially. However, unlike the $CaCO_3$ fermentors, pH recovery was evident from day 7 to day 25.

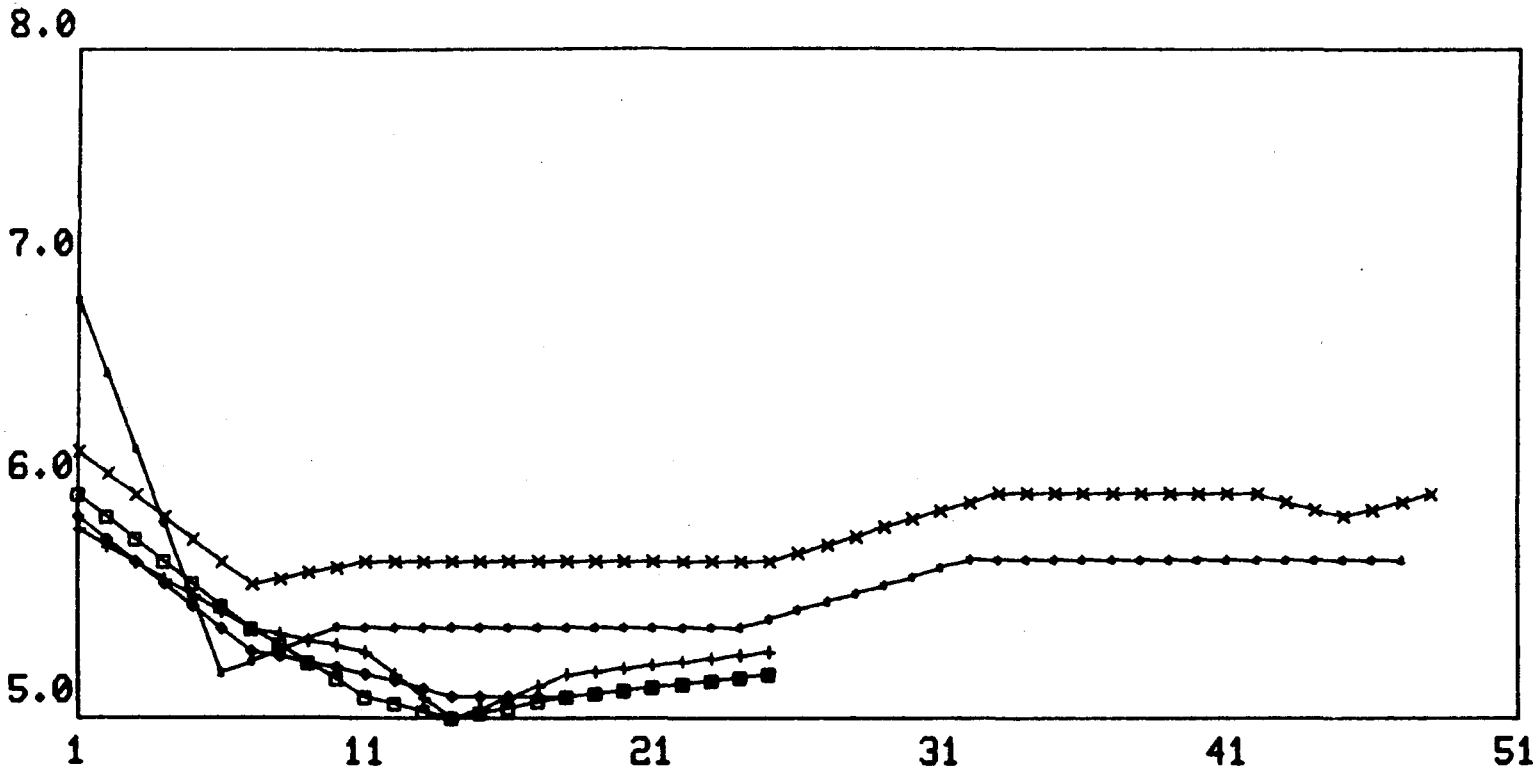
Figures 17 and 18 show cumulative weight loss and methane gas composition for the pulverized limestone ($CaCO_3$)-buffered fermentors. Figures 19 and 20 show the same two curves for those fermentors using $NaHCO_3$. Figures 17 and 18 confirm that little degradation of biodegradable matter was occurring in the pulverized limestone ($CaCO_3$)-buffered fermentors. Figure 20 shows the recovery evident in $NaHCO_3$-buffered fermentors. It is interesting to note in Figure 18 that relatively high methane content gas can be obtained from fermentors operating in what is normally considered an undesirable pH range for methane



Symbol Scale Name

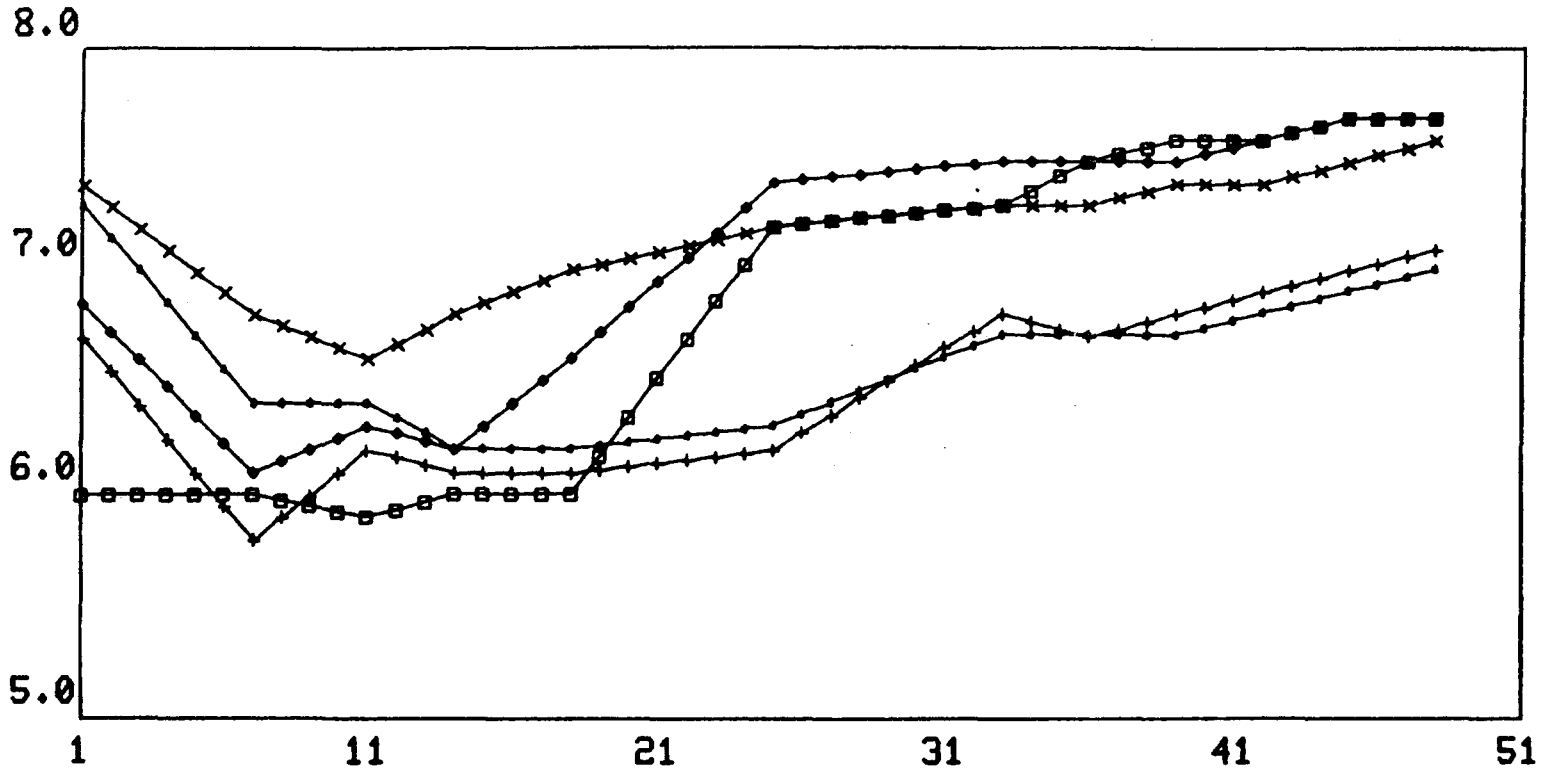
□ Pulverized Limestone
◇ Reagent Grade $CaCO_3$

Figure 14. pH Equilibrium for Pulverized Limestone ($CaCO_3$) and Reagent Grade $CaCO_3$ in 10,000 mg/ℓ Acetic Acid Solution.



Symbol	Scale Name	Unit
□		1
◇		2
+		3
×		4
✳		5

Figure 15. ph for Units 1-5, Buffered with Pulverized Limestone ($CaCO_3$).



Symbol	Scale Name	Unit
□		6
◇		7
+		8
×		9
✳		10

Figure 16. pH for Units 6 - 10, Buffered with $NaHCO_3$.

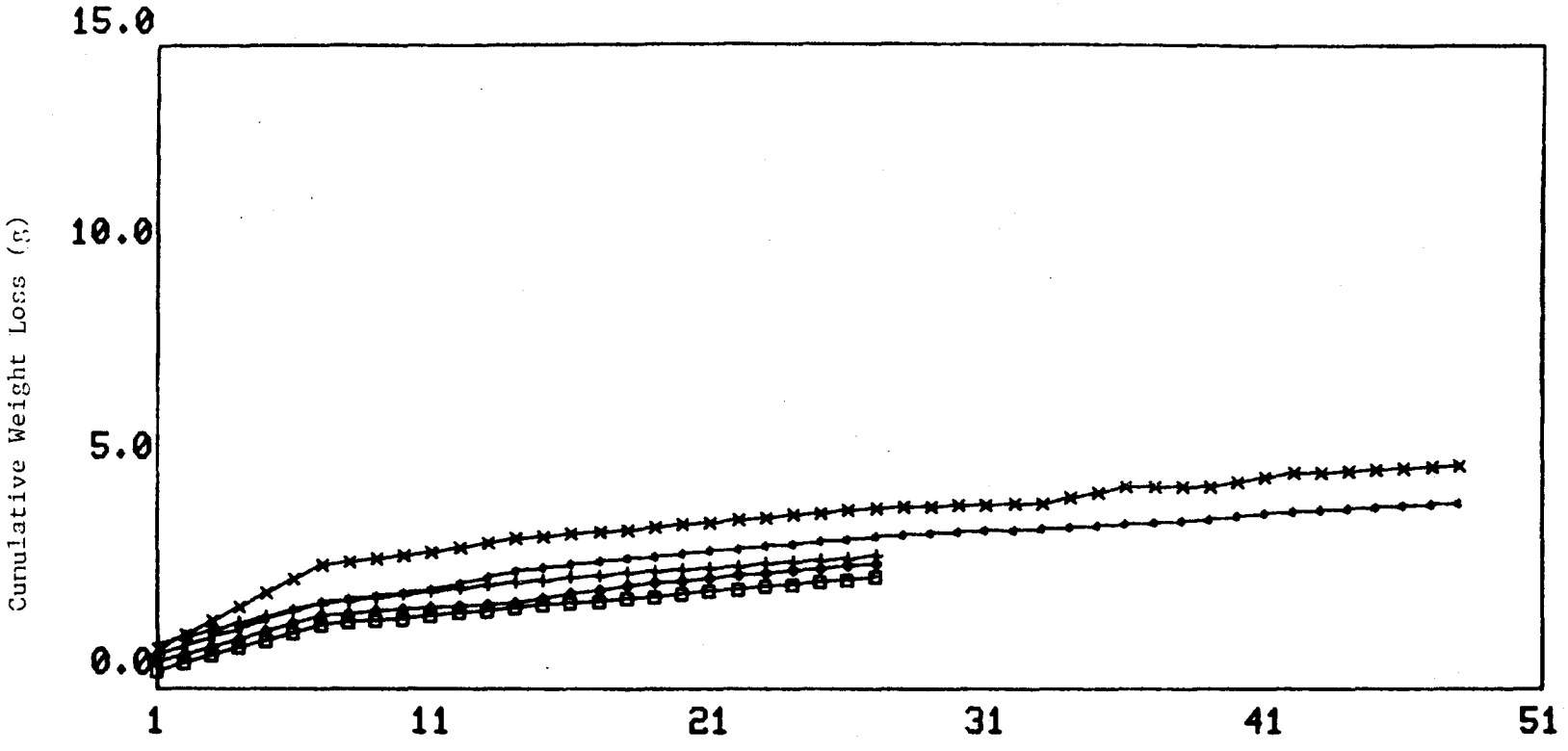
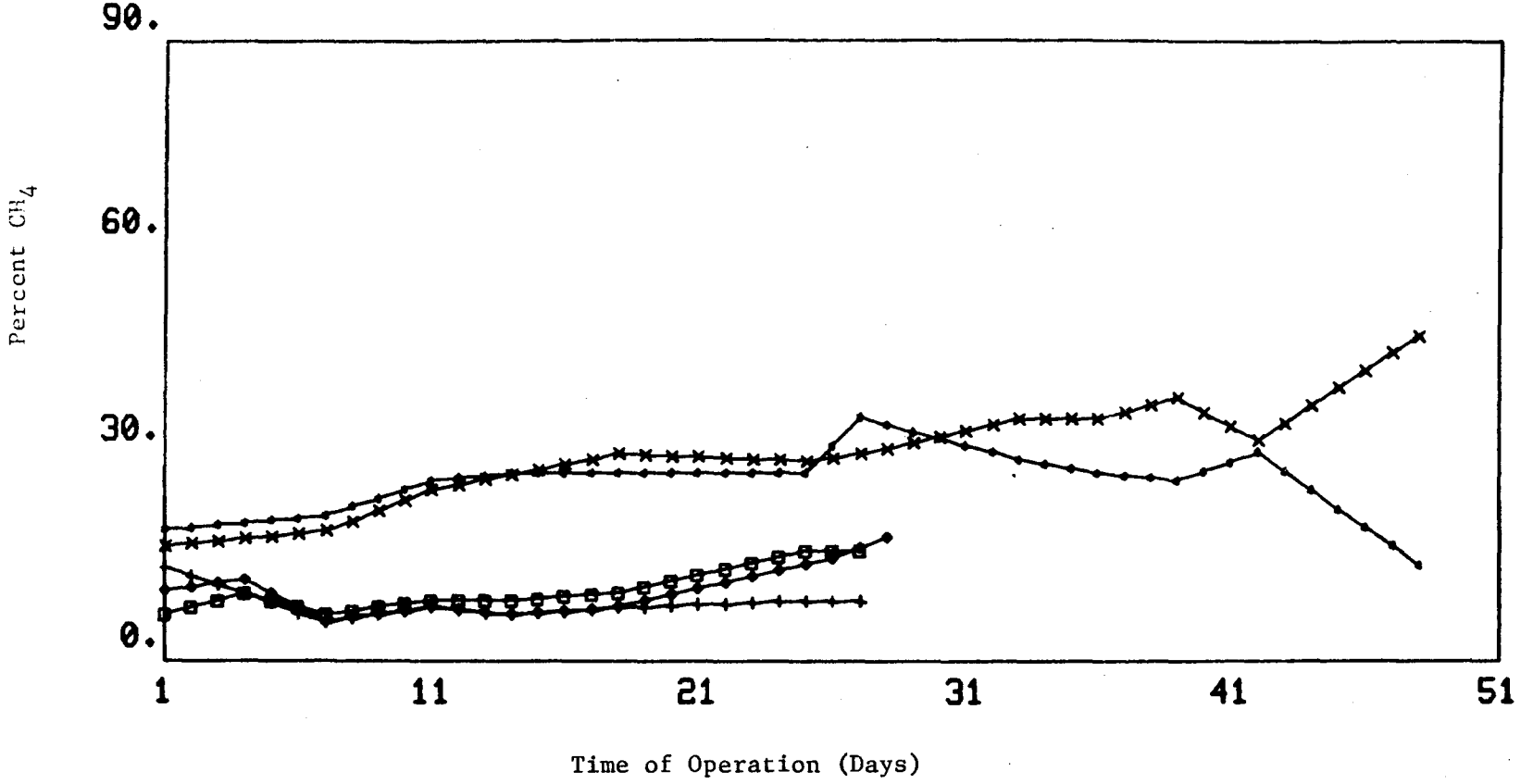
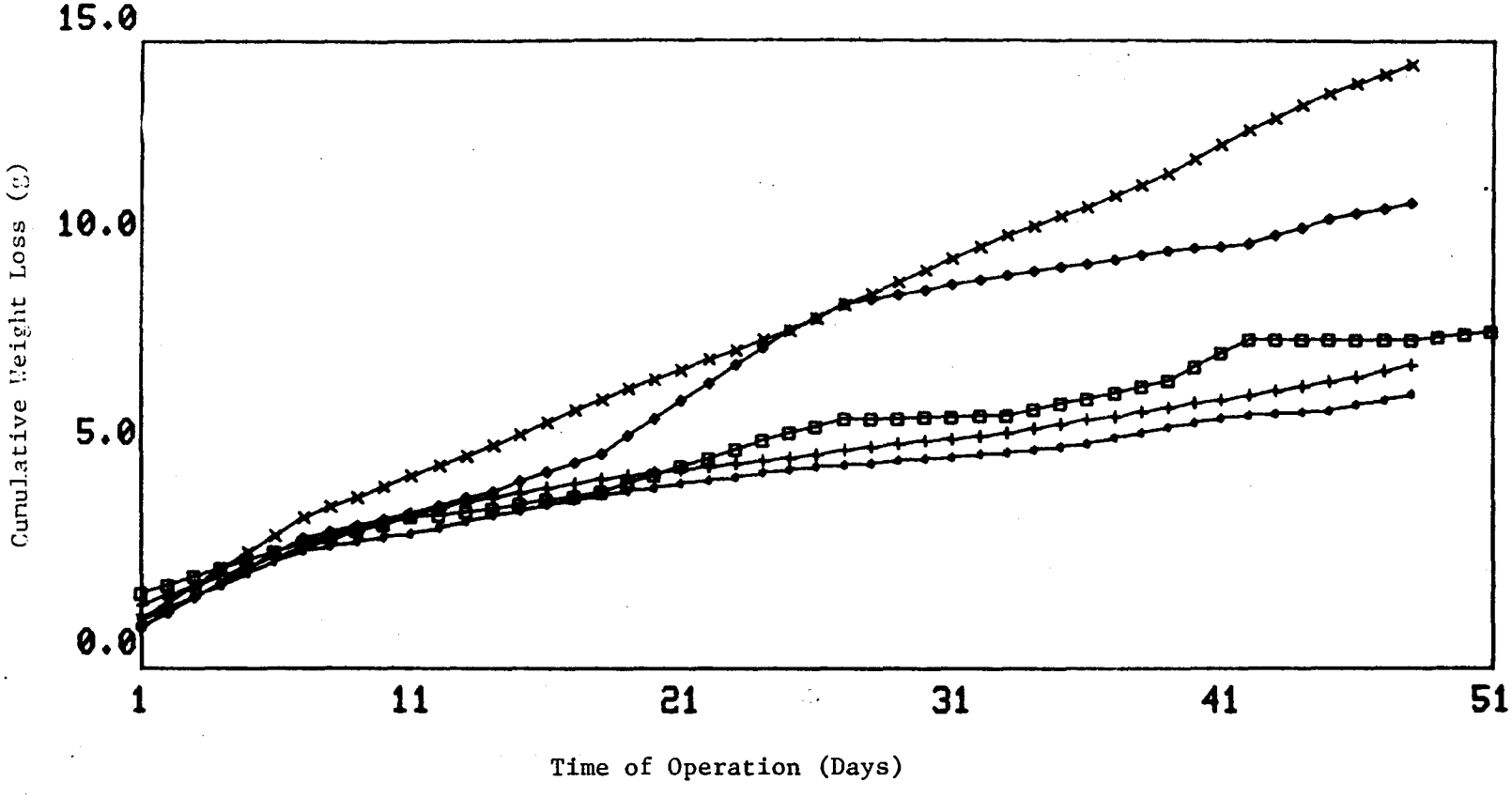


Figure 17. Cumulative Weight Loss for Units 1 - 5, Buffered with Pulverized Limestone ($CaCO_3$).



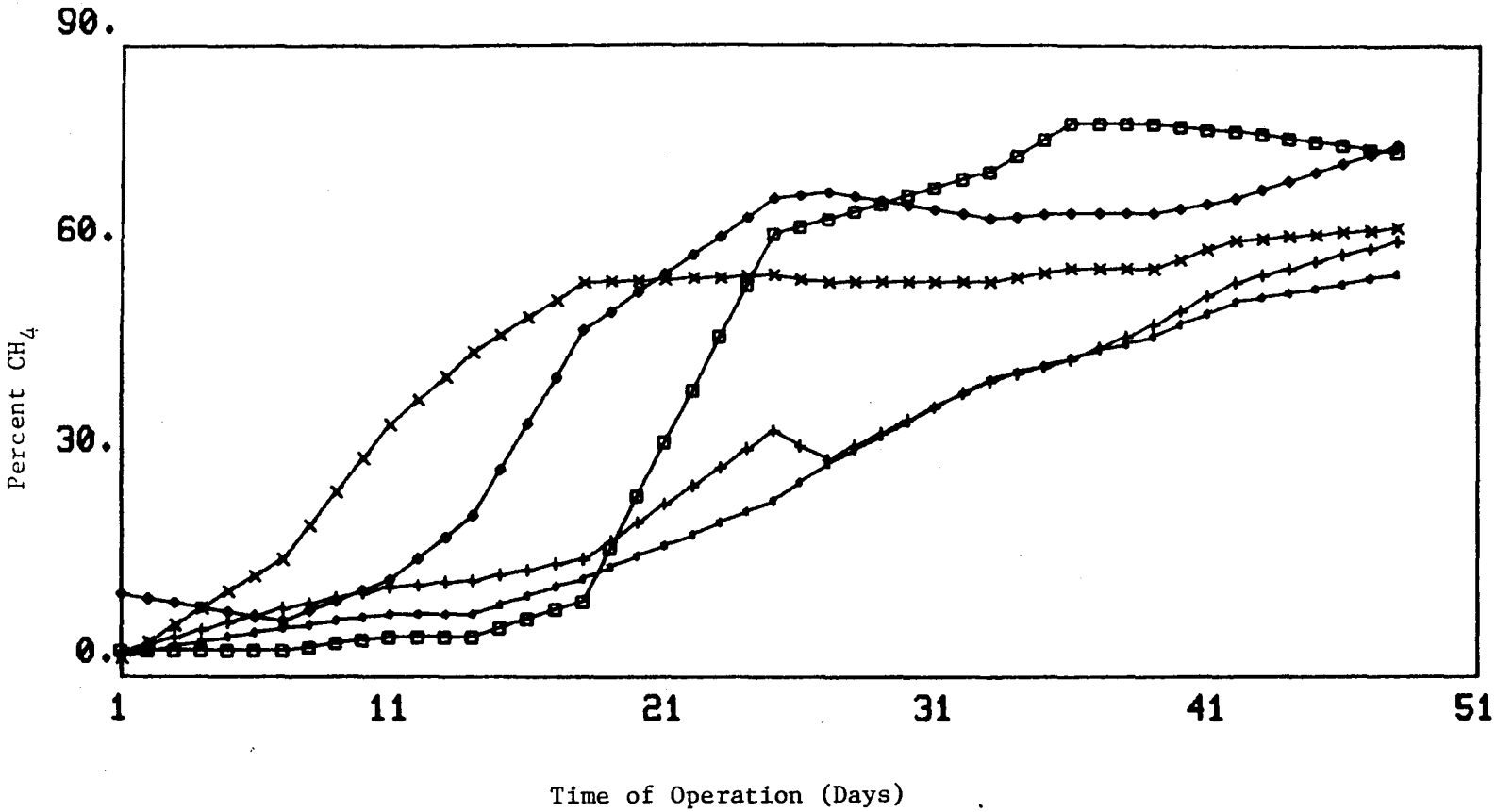
Symbol	Scale Name	Unit
□		1
◇		2
+		3
×		4
✳		5

Figure 18. Biogas Methane Content for Units 1 - 5, Buffered with Pulverized Limestone ($CaCO_3$).



Symbol	Scale Name	Unit
□		6
◇		7
+		8
×		9
✳		10

Figure 19. Cumulative Weight Loss for Units 6 - 10, Buffered with $NaHCO_3$.



Symbol	Scale Name	Unit
□		6
◇		7
+		8
×		9
✳		10

Figure 20. Biogas Methane Content for Units 6 - 10, Buffered with $NaHCO_3$.

fermentation. It is also important to note that initially all pulverized limestone ($CaCO_3$) fermentors contained a higher methane content that those fermentors buffered with $NaHCO_3$. Furthermore, it appears that prior addition of pulverized limestone ($CaCO_3$) to raw sewage sludge or acid cow manure was no more effective than adding this buffer directly to fermentor contents at start-up.

The results from this experiment are not conclusive. Particle size differences between fine mesh reagent grade $CaCO_3$ and pulverized limestone ($CaCO_3$) may be significant under limited free moisture conditions in a dry fermentor. Secondly, all fermentors were operated at a S/F of 0.10, and from the previously described experiment it was shown that with a S/F = 0.10 sluggish start-up and failure can occur. It should be further noted that substrate differences between municipal solid waste and wheat straw may be a contributing factor to differences between observed fermentor performance and that reported in the literature.

Other Experiments in Progress

Two sets of experiments have just recently been started; therefore, insufficient data have been gathered for presentation at this time. Compaction experiments (Phase BIII) are being performed using a soil compaction press in order to determine the water holding and field saturation capacities for wheat straw and corn stover residues. Five fermentors using wheat straw have been placed in operation to study how compaction might affect volumetric gas production, as well as utilization of available moisture by the bacteria. Acid stripping and free moisture recirculating experiments (Phase BIII) have also been initiated.

The thermophilic constant temperature chamber was repaired with an overheat protection switch. The unit was then returned to operation. A dairy

cow manure seed fermentor was started and is now ready for upcoming experiments.

FUTURE ACTIVITIES

DRY FERMENTATION STUDY

General Overview

The projected chronology of dry fermentation research is shown in Figure 21 with the shaded areas representing completed experiments. Phase B1 was a preliminary study to aid in identifying important variables in dry fermentation, develop new analytical techniques, and acquaint new personnel to facilities and procedures; results from Phase B1 were reported in an earlier progress report (Jewell et al., 1980a). Phase BII, a comprehensive study of important variables of dry fermentation for optimization of the biology of the process, will continue through the next quarter. The important parameters of this phase are seed quantity and source, substrate moisture content, nutrients, temperature, and source and quantity of supplemental buffer on fermentation. The results of several sets of experiments from Phase BII were presented earlier in this report. Phase BIII will conclude the initial bench scale study by examining kinetics of acid and CH_4 formation, and stripping and free moisture neutralization as a pH control technique, the effects of substrate field age on fermentation, and substrate density and compaction.

Pilot scale studies will be initiated in Phase PI. Using 200 ℓ reactors, important scale-up variables will be examined, such as substrate density-moisture and seed contact relationships, free moisture recirculation, pH control, and process thermodynamics. Phase PII will allow examination of scale-up variables using 4000 ℓ reactors. In culmination of the first year of research, PIII will test, using 4000 ℓ reactors, process designs shown to have potential from the previous studies.

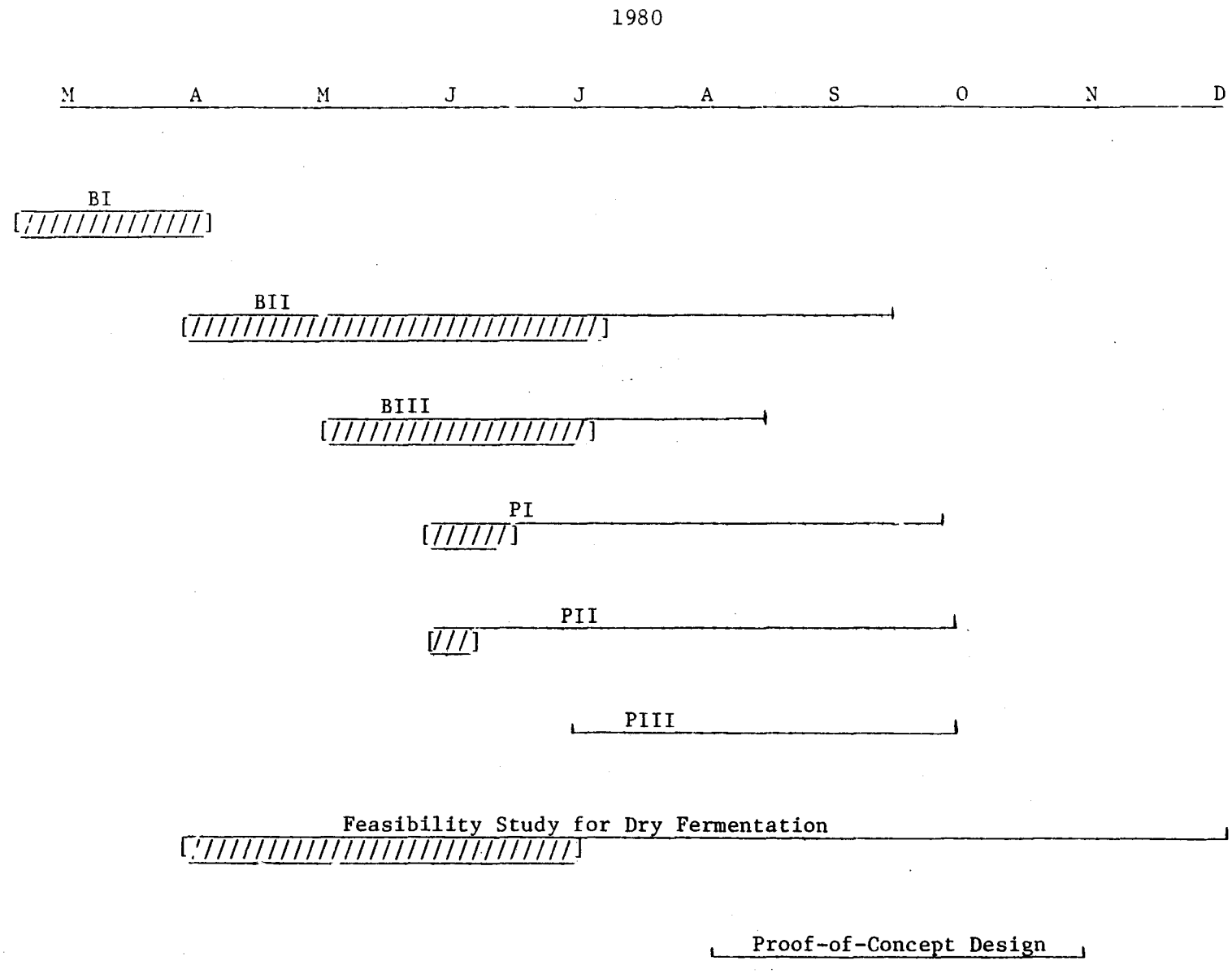


FIGURE 21. Dry Fermentation Experimental Schedule.

Bench Scale Research

In the next quarter, a large number of experiments will be conducted in an effort to further define the biological, chemical, and physical parameters necessary for successful fermentation of crop residues. These experiments will include the following:

1. Varying the quantity of buffer, seed, and raw and lagoon-stabilized cow manure as a nutrient and buffer supplement in an effort to decrease seed and buffer requirements.
2. Using previously digested residues as seed.
3. Kinetics of hydrolysis and acid digestion.
4. Moisture permeability of compacted residues.
5. Further experiments using alternative buffers.
6. Removal of acids from dry fermentors.
7. Fermentation of compacted residues vs. loose fill in reactors at comparable moisture levels.
8. Distribution of seed, moisture, residue, and nutrients in a fermentor to achieve optimal contact, hence optimal fermentation.

Pilot Scale Research

The time lines presented in Figures 1, 2, and 21 indicate that pilot scale reactors are to be constructed and in operation around July 1, 1980. Although several 200 ℓ reactors have been designed and constructed, start-up has been delayed. It was felt that more information from the bench scale activities was needed in order to achieve successful start-up of pilot scale units, thereby optimizing manpower, resources, and the amount of useful information generated at the pilot scale level. At this time, it is anticipated that start-up of the pilot scale phase(s) will be delayed for approximately two to four weeks.

Feasibility and Conceptualization Study

A summer task force has been assembled and has begun to assess the potential of dry fermentation technology at the community scale and farm scale. As was stated in the first progress report, this task force will develop the following topics during summer 1980:

1. Feasibility of fermentor operation modes.
2. Material handling and transportation.
3. Effluent utilization and cooperative industrial development.
4. Fermentor management.
5. Environmental and social considerations.
6. Identification of optimum community and farm fermentor system design.

The information generated by the task force will be used in conjunction with the experimental data to develop a full scale, proof-of-concept, detailed engineering design for a dry fermentation system.

FULL SCALE PLUG FLOW AND COMPLETELY MIXED DAIRY MANURE REACTORS

These units will continue to be operated to gather long term operational and maintenance information as well as to develop information on materials life expectancy. A minimum input of manpower will be used to run these systems with performance data taken only as necessary to ensure that the systems are operating at expected levels of performance.

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ASSESSMENT OF SECONDARY RESIDUES

Progress Report for

16th Quarterly Coordination Meeting
June 23-24, 1980

Subcontract NR-9-8175-1
Dynatech Contract No. SLR-4
Dynatech Report No. 2025

Submitted to:

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Objective

The objective of this program is to perform a technological assessment of the potential of methane and/or alcohol fermentation of secondary agricultural residues. Secondary agricultural residues are defined as the residues resulting from biomass processing to produce primary products: e.g. whey from cheese processing, vegetable processing wastes, residues from paper pulping, etc.

Program Plan

The program plan for this project consists of four tasks. Tasks I and II will be the collection and evaluation of the resource data base. Data to be collected include information on types, amounts, concentrations, biodegradability, seasonality, and locations of these resources. The data base will include waste streams and by-product streams which could be potential energy sources. Information will be obtained from the literature, trade associations, and industrial processors. The data will be presented to provide a broad understanding of the characteristics of the resource in terms of its methane and/or alcohol fermentation potential.

The third task will be to carry out an engineering analysis and preliminary economics for methane and/or alcohol fermentation of the secondary residues. The final task will be an assessment of the institutional barriers which could limit full implementation of methane and/or alcohol fermentation. In particular, electric and gas utilities and trade associations will be consulted for information.

Results

Preliminary results to date have been a collection and compilation of literature data on the food processing industry. A primary literature source has been a census of the food processing industry taken

in 1968 by the Food Canners Association (Katsuyama 1973). The census included the production and management of food products and residues from the processing of canned and frozen fruits and vegetables, seafoods, pickles, dehydrated fruits and specialty items (soups, baby foods, health foods, ethnic foods, prepared dinners). Data applicable to this study have been summarized in Tables 1 through 7.

The tonnages of 38 selected foods used by the food processing industry are shown in Table 1. The largest tonnages for the vegetables are tomatoes, white potatoes and corn; for the fruits - citrus, apples and peaches; and for the seafoods - tuna (and miscellaneous seafoods), shrimp and salmon. Table 1 also shows the percentages of these foods that are canned, frozen and processed by other methods such as pickling and dehydration. Data is not available for the seafoods, some fruits and specialty items. The regional distribution of types of food products and processing methods are shown in Table 2. The data is presented as a percentage of processing plants surveyed in each of nine regions, i.e., 7 percent of the New England plants processed vegetables (excluding tomatoes) and 93 percent of the processing plants in New England canned foods. Some of the columns in this table add to more than 100 percent because some plants handled more than one type of product and employed more than one process. Where data was lacking from plants, the total is less than 100 percent.

The seasonality of food processing is reflected in Tables 3 and 4. Expressed as a percentage of plants surveyed, the number of months the plant is in operation per year is shown for products, processing methods and regions in Table 3. The average number of operating months is 6 overall, with peaks at both 3 - 4 and 11 - 12 months. Alaska, Mountain, and North Central plants averaged the shortest seasons, South Central and Mid and South Atlantic plants, the longest. New England hand relatively high percentages of plants with 1 - 2 and with 11 - 12 operating months. Tomato processing plants had the shortest average seasons among product types (the figures for tomato plants with long seasons do not mean that tomatoes were canned for this many months but only that some tomato processing plants were

processing some product for the indicated times; similarly for other products and processes). Other specific commodity plants (such as peaches or corn) would also have had short seasons. Specialty plants had by far the longest seasons, as expected. Seafoods also averaged fairly long seasons in spite of the very short season in Alaska. Freezing operations lasted longer than canning operations, and plants that had both, averaged even longer seasons, about the same as dehydration plants.

The 1968 census showed that the number of operating months per year varied some with plant size (as measured by the total tons of food input received). The smallest plants (1000 tons or less) had either very short or very long operating seasons and the largest plants (over 200,000 tons) mostly had long seasons. However, the only trend across all six of the plant size categories was a decrease in 1- or 2-month seasons with increasing plant size; 21, 5, 3, 1, 0, and 0 percent of the plants of successively larger size operated for one or two months per year.

The seasonal production of solid residues from food processing, residue totals for the year, and total food input are shown in Table 4. Non-food wastes are also shown separately. This table reflects the highly seasonal operations on such products as corn, tomatoes, and peaches in contrast to the nearly continuous operation on specialties and minor month-to-month fluctuations in processing potatoes, some seafoods and other products. In 1968, more than 33 million tons of raw food products were used by the industry, and more than 9 million tons of solid residues were generated. Relatively few products accounted for the bulk of the residuals from citrus, tomatoes, white potatoes, corn, and specialties combined, and more than half were from the first three of these products. Non-food residues were only a small fraction of the total.

Table 5 lists the same total residues and food input as the previous table, but distributes the residues according to disposal method and utilization. Three columns break down the tonnages handled as solid (sometimes wet solid) wastes, and are summed in the column "total handled as solid waste". "Fill" does not imply frequent covering and compacting; practices varied from these to simple dumping. "Spread" disposal is

usually on agricultural land and may or may not include disking. "Burn" refers to the materials, mostly non-food, burned at the site of the food processing plant. Tonnages of solid residues disposed of in a liquid medium are listed in four columns and as a total. "Body of water", means a stream, lake, bay or ocean; "holding pond" is that or treatment pond; "sewer", a public treatment system; and "irrigation", disposal by irrigation. Small percentages of all products are leached or comminuted and disposed of in the plant liquid waste stream aside from the tonnages listed; these quantities were not available in the project data. By far the largest proportion of by-products from food processing residues went into animal feed. The column headed "other use" includes smaller amounts for charcoal, alcohol, oil, vinegar, and some other products. Non-food by-products have separate headings - "metal" and "other"; the latter is mostly recovery of paper and cardboard.

Of the million tons not accounted for, 630,000 tons were from citrus, tomatoes and white potatoes, and only 4, 2, and 5 percent, respectively, of the total raw tons of these products were unaccounted for. Shrinkage after weighing the raw product and before processing is expected at least for tomatoes and potatoes. The large quantity of pumpkin and squash lost, 97,000 tons, probably came from discrepancies in the methods of reporting the data; these products lose a large proportion of their weight as water during processing. The relatively large residual tonnages of some seafoods not accounted for may also have arisen from reporting errors; the 65,000 tons from clams and scallops must be shell. Some of the unaccounted for tonnages were negative, probably from errors of estimate of the percent yields or of the residual tons disposed of. Data on peach tonnages were possibly inaccurate because of a complex system of diverting fruit at various stages of processing in California.

Table 5 illustrates wide variations in disposal practices from product to product. More than three-fourths of the total food residues were used in by-products. About 5.6 of the total 7.1 million tons of residues used as feeds were from only three products; citrus, corn, and white potatoes. These are all large crops, producing large percentages of

residues, and generally processed in regions where there are livestock to consume the residues. Citrus and potatoes are processed the year around and corn residues are made into silage which can be stored; the feed by-products are therefore available over long periods. Some of the tonnages reported as fed to animals were spread on the land for livestock to eat. No doubt, portions were trampled in and wasted. On the other hand, some of the tonnages summarized as waste spread on land were probably handled in the same way. Only 3 percent of the food by-products were for uses other than animal feed. These included oil from olives, charcoal, and other by-products from peach and apricot pits, vinegar from apples, alcohol from various fruits, oil and fertilizer from some seafood, and oil and other by-products from citrus. Fill and spread methods were about equally utilized for solid waste disposal, but the proportions to each of these methods varied widely among products. Only small quantities of residues were burned at the plant site; some disposal operations away from the plant included burning. Very few of the industry's food waste products would burn without prior dehydration (cull dry beans, onion skins, and a few others), but much of the non-food waste is paper, cardboard, and wood.

Disposal of residues to "body of water" (stream, lake, bay, ocean) was mainly by seafood plants returning fish and shellfish remains to the medium from which they came. Small percentages of the residues from several fruits and vegetables were barged to the open ocean for disposal. Small quantities of solid waste were disposed of in company-operated treatment ponds and irrigation systems or municipal plants.

Data on processing plant sizes is presented in Table 6. Food input tonnages are the weights of foods as delivered to the plant, i.e., corn in the husk and peas removed from the pod. Plants packing two or more types of products were tallied according to the tonnage of each product type. Southwest processing plants averaged by far the largest in the survey, followed by South Atlantic, North Central, and Northwest plants. Tomato processing plants were twice the average size and seafood plants were much smaller than average.

Table 7 shows the location of food processing plants. All values are expressedas a percentage of the plants surveyed, i.e., 32 percent of the vegetable (excluding tomatoes) processing plants occurred in an agricultural area and 35 percent were 0.1 to 0.3 miles from the nearest residence. Of all the food processing plants, only 28 percent were located in agricultural settings. The percentage of agricultural settings varied widely among regions and among food types. Almost two-thirds of the plants were located within 0.3 miles of a residential development. The proportion of plants so located was particularly high in the Mountain, New England and North Central regions.

Future Work

Additional information for the resource data base will be obtained by continued literature search and direct contact with industrial processors and trade associations. These data will be compiled, and a report will be prepared presenting the resource data base.

The engineering analysis and preliminary economics task will be initiated by developing a mathematical computer model. This will be used to assess the potential for methane and/or alcohol fermentation from secondary residue biomass.

Reference

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Table 1

TONNAGE OF FOOD PROCESSED AND PROCESSING METHODS
(based on a 1968 census of food processing in the U. S.)

Product	Total Food input/yr (1000 tons wet weight)	Processing Method		
		% Canned	% Frozen	% Other
Vegetables:				
Asparagus	120	71	29	0
Bean, lima	120	28	72	0
Bean, snap	630	77	23	0
Beet	270	100	0	0
Broccoli, sprouts, cauliflower	260	0	100	0
Cabbage	230	100	0	0
Carrot	280	36	64	0
Corn	2,480	72	28	0
Greens, spinach	240	52	48	0
Mushroom	67	100	0	0
Pea	580	61	39	0
Potato, white	3,570	6	62	32
Pumpkin, squash	220	80	20	0
Tomato	7,000	100	0	0
Vegetable, misc.	1,220			
Fruits:				
Apple	1,050	56	11	33
Apricot	120	92	7	0
Berry	200			
Cherry	190	32	45	23
Citrus	7,800			
Fruit, misc.	150			
Olive	85			
Peach	1,100	92	5	2
Pear	410	100	0	0
Pineapple	900			
Plum, Prune	27	96	4	0
Other Processed Foods:				
Bean, dry	230	100	0	0
Pickle	560	0	0	100
Specialty	2,500			
Seafoods:				
Clam, Scallop	90			
Oyster	20			
Crab	30			
Shrimp	120			
Salmon	120			
Sardine	26			
Tuna, misc. seafood	520			

Table 2

FOOD PRODUCTS AND PROCESSING METHODS IN NINE REGIONS OF THE U. S.
(Percentages of plants surveyed in each region from a 1968 census)

Region	Food Products					Processing Methods					
	Vegetable	Tomato	Fruit	Specialty	Seafood	Can	Freeze	Dehydrate	Raw or Fresh	Salt or Smoke	Pickle
New England	7	0	21	21	50	93	43	0	7	0	0
Mid Atlantic	65	23	19	21	2	86	21	2	2	0	0
South Atlantic	31	6	25	33	6	75	47	11	0	0	6
North Central	62	16	14	25	0	87	25	0	0	0	1
South Central	32	0	11	42	32	84	3	5	0	0	0
Mountain	64	45	9	18	0	100	18	0	0	0	9
Northwest	69	0	45	6	18	55	68	8	3	1	0
Southwest	43	28	62	13	2	72	30	7	0	0	1
Alaska	0	0	0	0	100	82	32	0	0	5	0
Total	50	15	30	18	13	77	36	4	1	<1	1

Note: The columns may add up to more than 100 percent because some plants handled more than one type of product or used more than one processing method.

Table 3

SEASONALTY OF FOOD PROCESSING PLANT OPERATIONS

(Percentages of Plants surveyed in a 1968 census)

	Number of Months in Operation Per Year					
	1 - 2	3 - 4	5 - 6	7 - 8	9 - 10	11 - 12
PRODUCT:						
Vegetable	2	24	30	13	12	19
Tomato	7	52	18	8	8	7
Fruit	5	21	32	16	11	15
Seafood	11	16	7	20	13	33
Specialty Item	0	0	9	7	4	80
PROCESSING METHOD:						
Can Only	6	37	23	9	7	18
Can & Freeze	6	12	14	14	14	41
Freeze Only	1	12	21	22	12	31
Dehydrate	0	0	21	29	7	43
REGION:						
New England	23	0	8	23	0	46
Mid Atlantic	0	16	24	8	24	27
South Atlantic	11	4	15	18	15	37
North Central	5	41	24	10	1	19
South Central	0	6	0	18	12	65
Mountain	0	64	36	0	0	0
Northwest	3	20	32	14	15	17
Southwest	2	33	16	17	8	23
Alaska	28	39	11	6	6	11
Total	5	28	21	13	9	24

Table 4

MONTHLY FOOD PROCESSING SOLID RESIDUE PRODUCTION
(based on a 1968 Census)

Residue	Residue Production (1,000 Tons)													Total Food Input/yr (1,000 tons wet weight
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Total	
Vegetables:														
Asparagus			4	14	14	9	2	x					42	120
Bean, lima						x	x	5	8	5	x	x	19	120
Bean, snap				2	2	7	37	41	35	9	1		130	630
Beet	2			2	1	1	9	16	18	22	11	3	90	270
Broccoli, sprouts, cauliflower	7	6	7	7	6	7	5	13	13	16	16	10	110	260
Cabbage	4	4	4	3	2	1		8	14	16	14	7	76	230
Carrot	6	3	4	5	4	5	9	10	23	33	26	12	140	280
Corn						8	70	620	590	280	48		1620	2480
Greens, spinach	2	2	8	7	3	1		x	2	2	3	2	33	210
Mushroom	3	3	3	3	3	3	2	2	2	3	3	3	32	67
Pea				1	5	25	28	11	1	x	x	x	74	580
Potato, white	99	90	92	86	90	62	69	100	110	130	130	120	1170	3570
Pumpkin, squash							1	12	10	22	10		55	220
Tomato	7	7	6	6	10	70	140	150	110	6	6		520	6970
Vegetable, misc.	11	12	12	11	17	19	30	38	36	38	32	16	270	1220
Fruits:														
Apple	28	21	15	5	4			2	33	53	61	56	290	1050
Apricot	x	x	x	x		6	7						16	120
Berry	x	x	x	x	x	3	3	4	2	x			14	200
Cherry					x	1	13	11					26	190
Citrus	330	330	330	330	330	330	210	100	100	160	210	330	3080	7800
Fruit, misc.	x	x	x	x	1	3	4	8	9	8	2	1	36	150
Olive	1	1	x		x	x	x		2	3	3	x	11	85
Peach						23	81	100	83	3			290	1100
Pear							14	33	39	25	6		120	410
Pineapple	25	25	30	50	55	55	55	55	30	25			400	900
Plum, Prune	1	1	1	x		1	x	x	1	1	x	x	7	27
Other Processed Foods:														
Bean, dry	1	1	1	1	x	x	x	x	x	1	1	1	7	230
Pickle	x	x	x	x	x	8	9	8	8	6	x	x	41	560
Specialty	26	26	26	26	25	24	23	24	24	25	25	26	300	2500
Seafoods:														
Clam, Scallop	1	1	1	1	1	1	1	1	1	1	1	1	13	90
Oyster	3	3	2	2	x					2	2	3	18	20
Crab	2	2	2	2	1	2	1	2	2	2	2	2	22	30
Shrimp	5	7	7	6	8	5	5	5	5	5	5	5	66	120
Salmon	x	x	x	x	x	8	12	10	8	2	x		40	124
Sardine	x	x	1	1	x	1	1	1	1	x	x	x	6	26
Tuna, misc. seafood	7	7	7	7	8	8	9	10	10	9	9	7	99	520
TOTALS	570	550	560	580	590	700	860	1400	1330	920	640	600	9310	33500
Non-Food	39	38	40	43	43	55	69	76	78	73	49	43	650	

X = 500 tons or less

Table 5

UTILIZATION AND DISPOSAL OF FOOD PROCESSING RESIDUES
based on a 1968 census (1,000 tons)

Product	Total Food Input	Disposal of Solids Waste			Total Handled As Solid Waste	Disposal of Liquid Waste				Total Handled As Liquid Waste	By-product Use		Total By-Product	Total Residue	Not Acc't For
		Fill	Spread	Burn		Body of Water	Holding Pond	Sewer	Irrig.		Feed	Other			
Vegetables:															
Asparagus	120	8	16		24					0	19		19	42	3
Bean, lima	120	1	8		10					0	10		10	19	(-3)
Bean, snap	630	35	32		67		x	3		3	64		64	130	0
Beet	270	18	46		65			6		6	18		18	90	21
Broccoli, sprouts, cauliflower	260	12	9		21			1		1	91		91	110	x
Cabbage	230	19	44		64		6			6	6		6	76	(-1)
Carrot	280	6	30	x	36			2		2	100	x	100	140	10
Corn	2,480	3	86	x	89			2	1	3	1,530		1,530	1,620	42
Greens, spinach	240	5	3		8		x	x		x	24		24	33	4
Mushroom	67	4	28		32	x				x			0	32	(-2)
Pea	580	3	22	x	24					0	49	x	49	74	4
Potato, white	3,570	57	28		85	42	2	4		48	1,040		1,040	1,170	170
Pumpkin, squash	220	8	13		22		x	9		9	24	2	25	55	97
Tomato	6,970	250	130	x	380	21	7	x	1	30	120		120	520	150
Vegetable, misc.	1,220	38	71	4	110		1	52		52	110		110	270	
Fruits:															
Apple	1,050	35	54		90	x	x		x	x	110	87	200	290	30
Apricot	120	4	2		6	x				x	7	2	9	16	5
Berry	200	4	5	1	10	2	x	x		2	1		1	14	2
Cherry	190	15	5	x	20				1	1	4	x	4	26	1
Citrus	7,800	4	76		80				1	1	3,000	3	3,000	3,080	310
Fruit, misc.	150	13	13		25			x		x	8	2	10	36	3
Olive	85		1	x	2		x			x		10	10	11	x
Peach	1,100	130	56		180	13	x	1	x	14	50	44	94	290	(-19)
Pear	410	40	32		72	10		x		10	36		36	120	
Pineapple	900	30			30	5		5		10	360		360	400	0
Plum, Prune	27	4	2		6	1				1	x		0	7	1
Specialty Items:															
Dry Bean	230	3	2	x	6			x		x	2		2	7	(-1)
Pickle	560	37	3		40			1		1			0	41	(-15)
Specialty	2,500	37	3	8	48		7	18	x	24	210	17	230	300	0
Seafood:															
Clam, Scallop	90	8	4		12	x				x			0	13	65
Oyster	20				0	2				2		16	16	18	x
Crab	30	5	1		6	16				16			0	22	1
Shrimp	120		4	3	7	29		12		41	16	x	17	66	20
Salmon	120				0	35				35	4	2	6	40	3
Sardine	26				0					0		6	6	6	x
Tuna, Misc. Seafood	520				0	x				x	69	30	99	99	91
Total	33,500	830	830	18	1,680	180	24	120	5	320	7,080	220	7,300	9,310	1,010
Non-Food		300	17	97	410	x	32			32	Metal 130	Other 67	200	650	

x = 500 tons or less

Table 6

FOOD PROCESSING PLANT SIZE
(based on a 1968 census)

Product	Annual Production Tonnage (Percentages of plants surveyed)						Average Production per plant (tons/year)
	0-1000	1000-5000	5000-25,000	25,000-100,000	100,000-200,000	over 200,000	
PRODUCT:							
Vegetables (excluding tomato)	1	12	52	30	3	1	9,000
Tomatoes	2	14	24	31	22	7	64,000
Fruits	2	17	39	26	10	6	13,000
Seafood	24	67	7	2	0	0	3,000
Speciality Items	10	18	37	30	2	3	31,000
REGION:							
New England	15	62	15	8	0	0	7,000
Mid Atlantic	8	26	44	23	0	0	12,000
South Atlantic	10	20	37	10	13	10	39,000
North Central	3	11	50	32	1	2	28,000
South Central	26	26	32	16	0	0	14,000
Mountain	0	64	36	0	0	0	9,000
Northwest	2	15	51	28	3	2	27,000
Southwest	2	18	22	33	18	6	59,000
Alaska	30	65	5	0	0	0	3,000
Total	7	22	38	25	6	3	31,000

Table 7

FOOD PROCESSING PLANT LOCATIONS

(Percentages of Plants surveyed in a 1968 census)

	Type of Location				Miles to the Nearest Residence				
	Agricultural	Industrial	Commercial	Residential	0	0.1-0.3	0.4-0.9	1-4	over 5
PRODUCT:									
Vegetable (excl. Tomato)	32	35	18	43	35	35	12	17	1
Tomato	33	29	28	42	35	38	5	20	2
Fruit	24	35	27	37	36	33	10	18	3
Seafood	4	32	36	38	36	29	4	29	2
Specialty Items	16	44	27	47	28	32	7	32	1
REGION:									
New England	0	50	14	50	15	69	0	15	0
Mid Atlantic	42	28	21	49	35	27	11	24	3
South Atlantic	31	31	33	53	29	29	13	23	6
North Central	37	38	16	54	40	36	9	14	1
South Central	11	26	42	58	41	24	6	29	0
Mountain	27	45	18	36	56	33	0	11	0
Northwest	27	39	28	38	29	29	12	27	3
Southwest	25	46	30	36	29	25	11	34	0
Alaska	5*	27	41	27	37	26	5	26	5
Total	28	38	16	45	34	31	10	24	2

* Forest

Cornell University
College of Agriculture and Life Sciences
A Statutory College of the State University of New York

Report Number XB-9-8263-1-1

PROOF OF CONCEPT STUDY OF AN ANAEROBIC ATTACHED FILM EXPANDED BED DIGESTER FOR SEPARATION AND DIGESTION OF ALGAL BIOMASS

First and Second Quarter Technical Progress Report for Period From October 1, 1979 to March 31, 1980

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PROOF OF CONCEPT STUDY OF AN ANAEROBIC ATTACHED FILM EXPANDED BED DIGESTER FOR SEPARATION AND DIGESTION OF ALGAL BIOMASS

Summary

A high rate methane production system known as the Anaerobic Microbial Attached Film Expanded Bed (AAFEB), developed by Jewell et al (1978) at Cornell University for application to soluble organics and complex substrates is now being applied to the separation and subsequent digestion of algal biomass. The general goal of this study is to test the applicability of the AAFEB reactor for the separation, concentration, and digestion of algal biomass and to estimate the conversion efficiency of the algae to methane. This progress report covers the activities included in the first and second scheduled quarters of this study.

The focus of the first six months of this study has been the design, construction and startup of the Attached Film Expanded Bed Reactors (AFEB), as well as the development of algal resources. Progress to date includes the startup and operation of six AFEB reactors with 4 reactors operated as anaerobic units and 2 reactors kept under aerobic conditions. Results have indicated that while attachment and development of a substantial anaerobic film on the bed particles is slow, it is continuing to develop. Pilot scale oxidation ponds have been started to provide an initial source of algae for use in the acclimation of the AAFEB reactors to an algae substrate. Efforts are being directed towards the procurement of an algae concentrate (1% total solids) that will be used during the comprehensive testing phase.

Activities for the next quarter include the continued development of algal resources, the operation of all six AFEB reactors for adequate stabilization and attachment prior to testing, and the initiation of experiments for determining the feasibility of using the AAFEB reactor for the separation and concentration of algal biomass.

OBJECTIVES

The general goal of this study is to determine the feasibility of microscopic algae harvesting and converting to methane, utilizing laboratory anaerobic attached film expanded bed reactors. Specific objectives of this study will be to:

1. design, construct, and operate several anaerobic attached film expanded bed reactors under various conditions, thereby developing information on the conversion efficiency of algal cells to methane and on the kinetics of the process;

2. determine the feasibility of separating and digesting heterogeneous microscopic algal cells produced under rapid growing conditions similar to those that exist in aerobic stabilization ponds, using the anaerobic attached film expanded bed process;

3. determine the feasibility of scaling up the optimized system, found in this study, to harvest and convert microscopic algae to methane.

REPORT OUTLINE

Topic

Summary

Objectives

Introduction and Background

Project Status

- Attached Film Expanded Bed Reactors
- Source of algae

Future Activities

References

Proof of Concept Study of an Anaerobic Attached Film Expanded Bed Digester for Separation and Digestion of Algal Biomass

Quarterly Progress Report Nos. 1 and 2

October 1, 1979 to March 31, 1980
Cornell University, Ithaca, NY

INTRODUCTION AND BACKGROUND

Of the various waste treatment systems in use today, oxidation ponds, and aerobic and facultiative lagoons are perhaps the simplest. Stabilization of organic matter in these systems is accomplished generally by bacteria while nutrient removal (nitrogen and phosphorous) is achieved by algae. Figure 1 illustrates the possible biological interactions in an oxidation pond. In these systems, solar energy is converted to algal biomass at a relatively high rate of efficiency, $\sim$ 2%. Because algae grow rapidly and have a high productivity rate, a number of schemes have been proposed to use algae as solar energy collectors to produce food and/or fertilizer and energy.

Recent studies have indicated that oxidation ponds have the capability of generating large amounts of algal biomass, and with subsequent concentration, then converting the biomass to methane via conventional anaerobic digestion (Benemann et al.,1978). In fact, these studies have indicated that the algal ponds that have the capability of generating 20 to 40 tons per acre per year are potentially economically feasible, but the harvesting and processing costs are significant (Benemann et al., 1977; Goldman, 1978). A breakthrough in decreasing the cost of harvesting and processing algae could significantly influence the energy and pollution control situations.

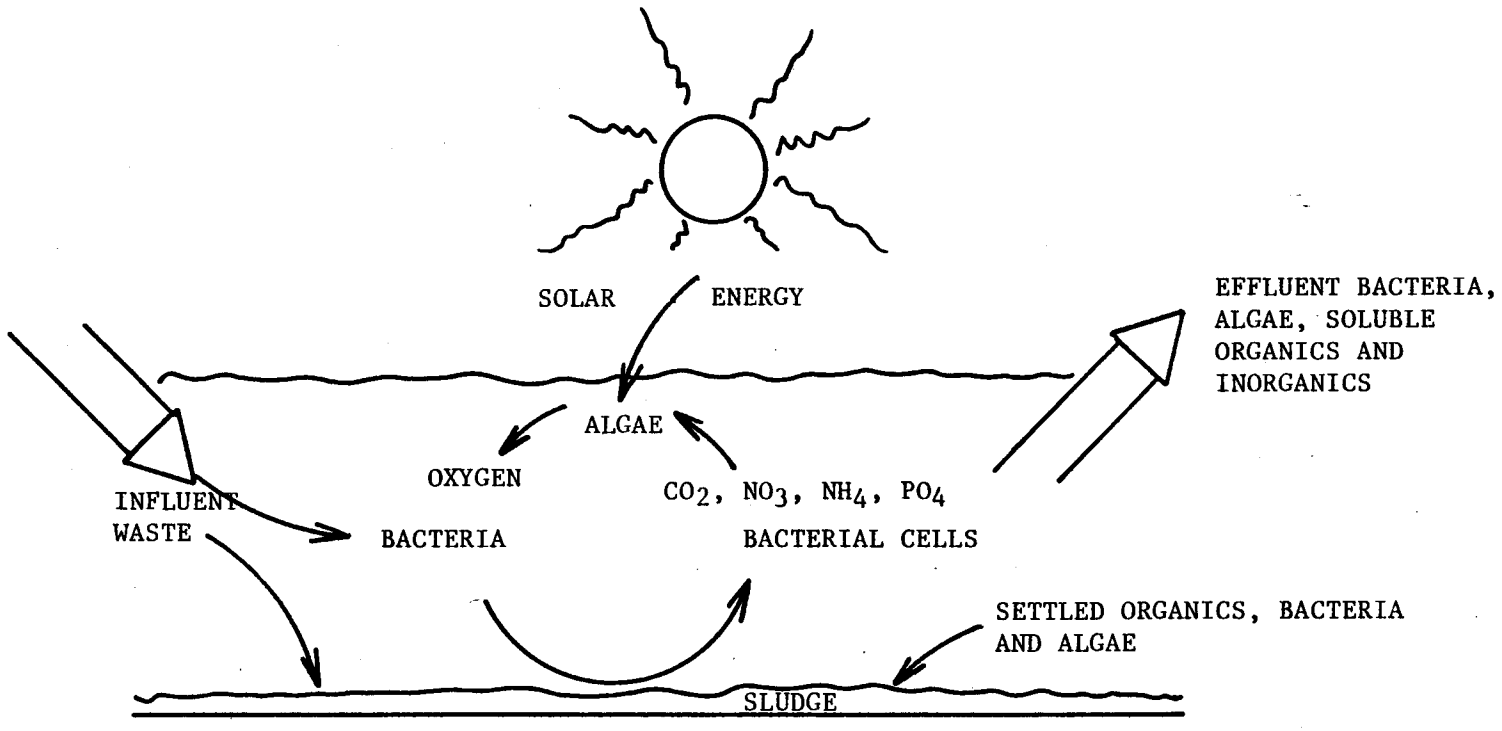

FIGURE 1. Biological interactions in an oxidation pond.

Energy from existing sewage lagoons could generate several hundred million dollars' worth of energy per year. It is interesting to note that the total U.S. nitrogen fertilizer production (8×10^6 tons/yr) could be produced using 4 million acres of algal ponds (Benemann et al., 1977). Energy production from these ponds would equal one quad. The energy saved from the manufacture of the nitrogen fertilizer would equal about one quad also (Sherff, 1975). Thus, there are significant potentials for contribution to the U.S. energy picture. However, major limitations of this concept appear to include costs and difficulties of harvesting/concentrating the microalgae and providing a nutrient environment capable of supporting maximum growth rates. Existing data indicate that a new methane generation process may be able to drastically reduce these restrictions.

The new system, a high rate methane production system, was developed for application to soluble organics and then applied to a complex substrate in an earlier DOE sponsored study (Jewell et al., 1978). This study indicated that an anaerobic microbial attached film expanded bed (AAFEB) such as that shown in Figure 2 could process high solids streams (2 percent TS) at hydraulic retention times as short as three hours, as compared to a minimum of about five days with the highest rate conventional process.

Earlier unpublished data on sewage treated with the AAFEB is shown in Figure 3. These data were obtained at ambient air temperatures at 19°C with primary raw domestic sewage. The very high treatment efficiencies were achieved because of the large attached microbial biomass. Obviously, since bacterial concentrations were removed to below 10 mg/ℓ at hydraulic retention times as short as 30 minutes, similar removal efficiencies would probably be achieved with algae substrate.

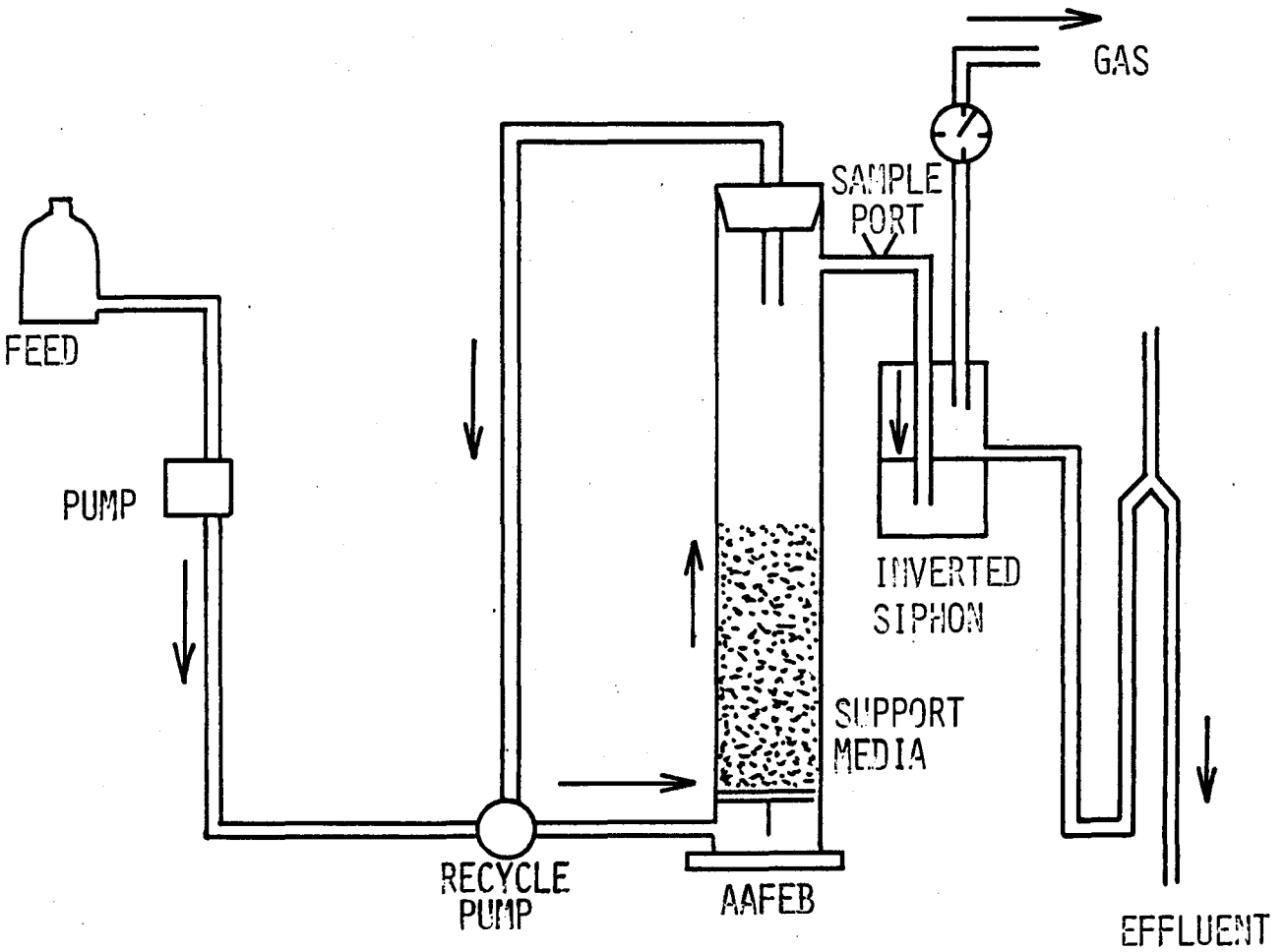

FIGURE 2. Schematic diagram of AAFEB system.

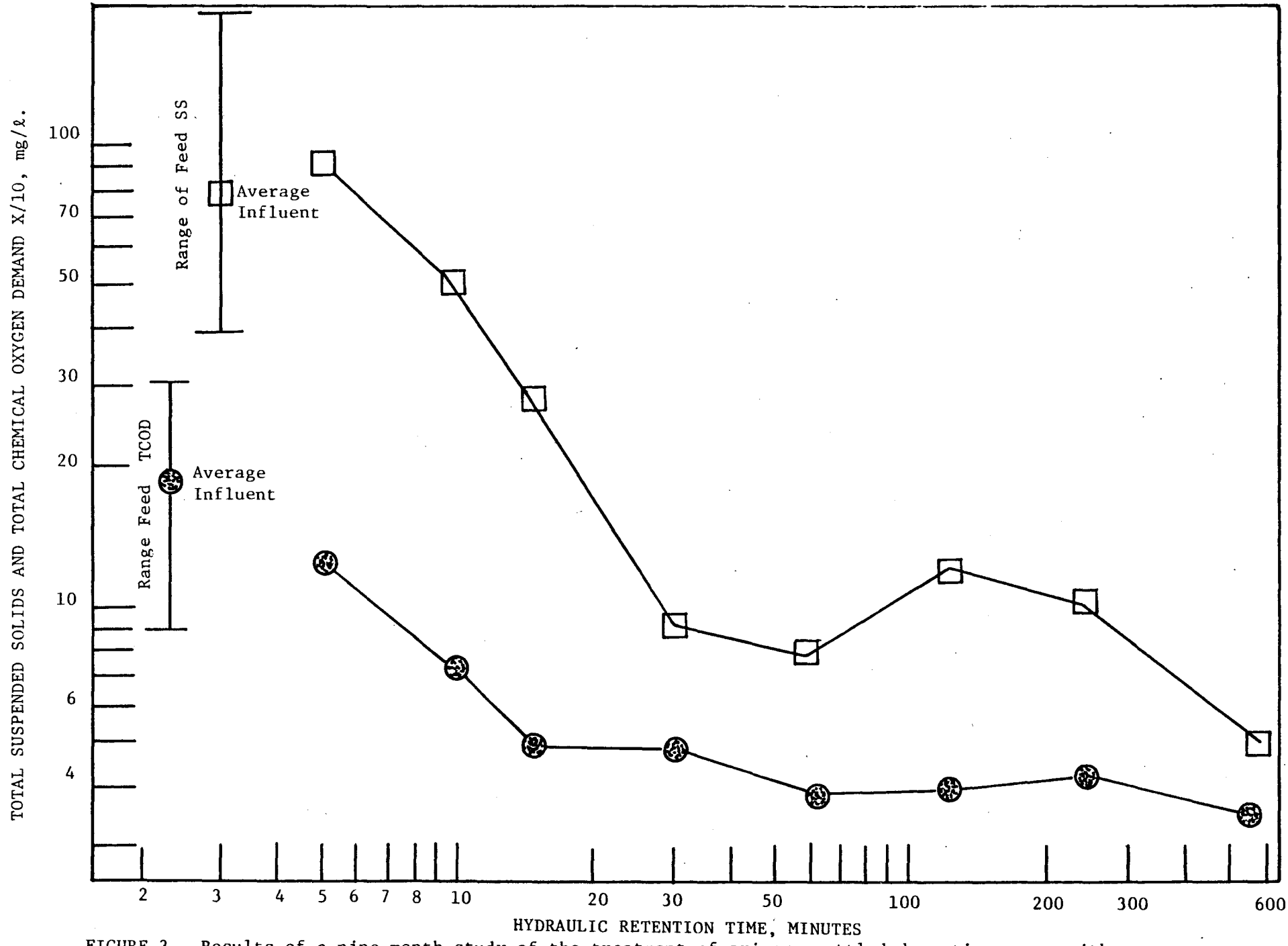

FIGURE 3. Results of a nine-month study of the treatment of primary settled domestic sewage with an anaerobic attached film expanded bed reactor at 19°C showing the impact of decreasing hydraulic retention times (empty bed [illegible]) on the effluent suspended solids and [illegible]

PROJECT STATUS

During the period October 1, 1979 and March 31, 1980 work was conducted towards the completion of the tasks outlined in Figure 4. This report outlines the progress of this project within the aforementioned time period.

ATTACHED FILM EXPANDED BED REACTORS

The reactor design of choice which is being used has a tapered design. It consists of a plastic cone which is 40 cm long and has a diameter that increases from 2 cm at the bottom of the reactor to 9 cm at the top where the effluent line starts (Figure 5). The total volume is 1 ℓ. It was felt that this design reduced the chance of 'short-circuiting' in the reactor to a minimum. In columns with a constant cross section area, it was found in previous studies that the flow distribution throughout the column cross section sometimes was not equal ('short-circuiting').

The solid particles used for the support bed are diatomaceous earth (AIROX, Diatomite product produced by AIROX EARTH RESOURCES, Santa Maria, Ca.) in the size range of 0.297 to 0.595mm. The bulk density of the dry particles is 0.54g/cm^3 and 1 g of the particles replaces 0.6 cm^3 of water. The particles are very light and provide, because of the roughness of their surface, a large surface area for the microorganisms to attach. Another reason for choosing this medium was that it is rather cheap, which makes it suitable for scale-up.

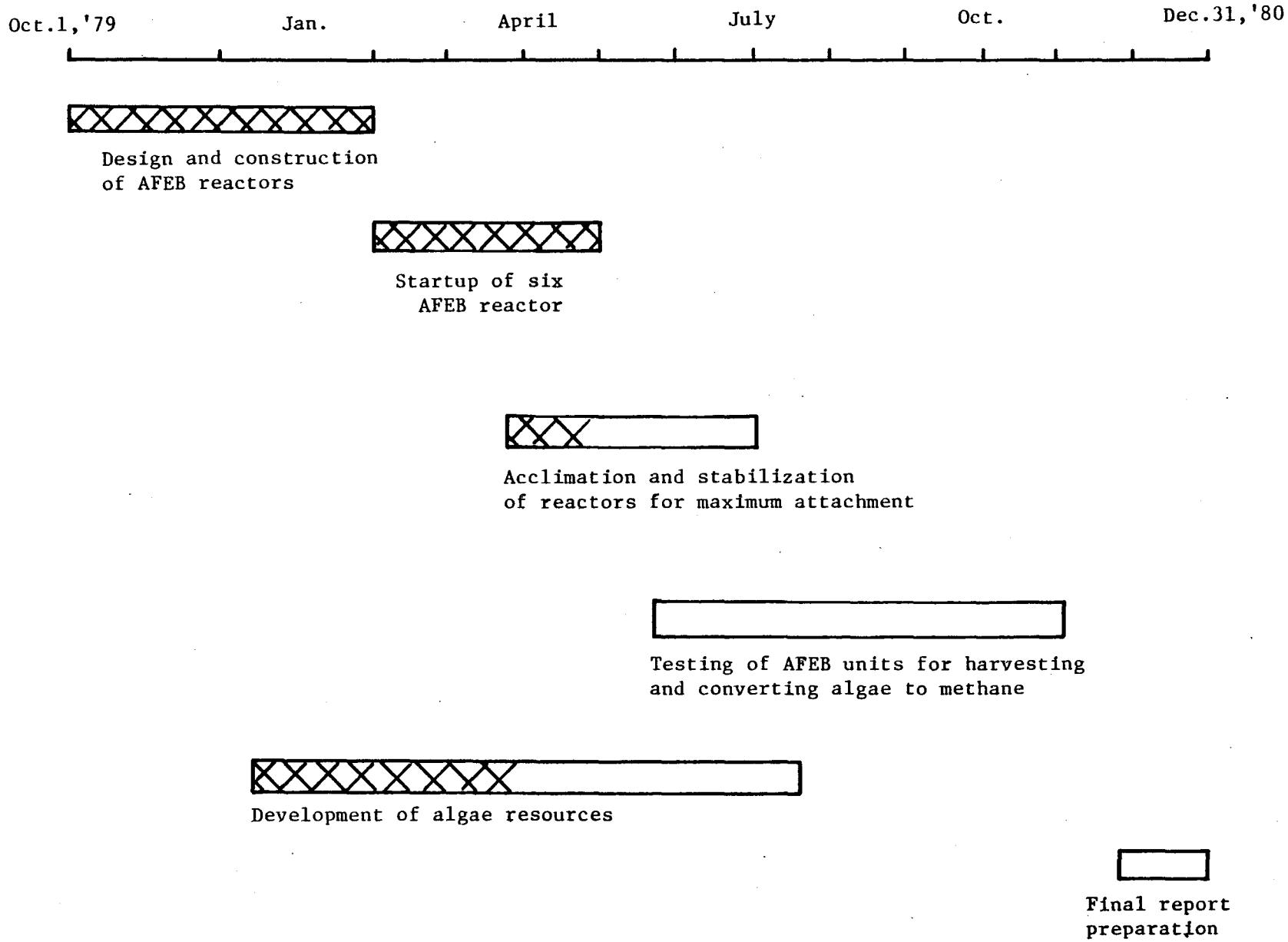

FIGURE 4. Projected schedule of tasks, events, and output of research and development program for the 15-month study period.

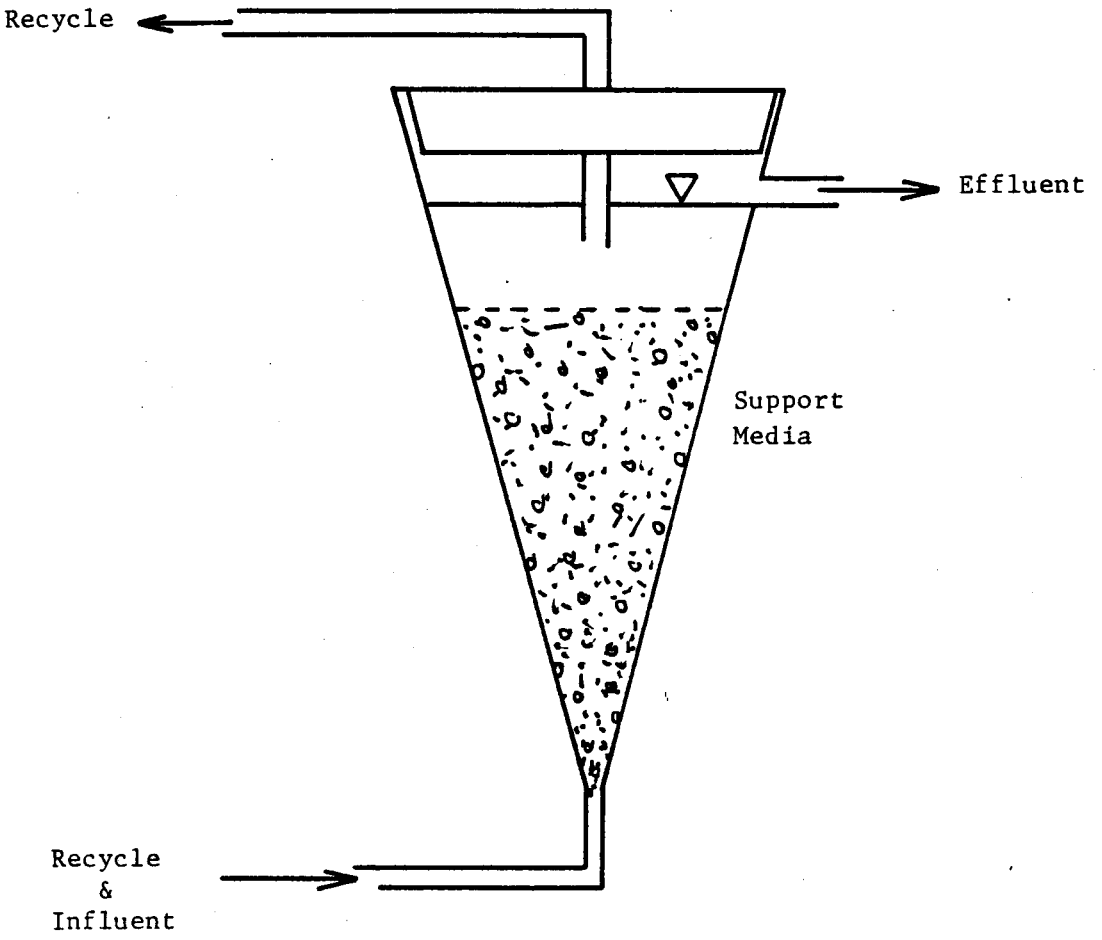

Figure 5. Diagram of a Tapered Reactor (Not to Scale).

To develop an attached film of anaerobic microorganisms and to study the behavior of the expanded bed (10-20%) in the column, one tapered reactor with 500 ml diatomaceous earth was placed in a controlled temperature room (30°C). Two more columns with a constant cross-sectional area (diameter=8.5cm) and with approximately 1250 ml of diatomaceous earth were also placed in this temperature room. A fourth column, also with a constant cross-sectional area and 1250ml diatomaceous earth, was kept at room temperature (19°C). These 4 columns had an approximate 10% expansion of the bed created by the introduction of a liquid to the bottom of the column. This liquid consisted of reactor effluent, and a mixture of primary sewage effluent, sucrose-solution and cellulose solution. The liquid feed was regularly replenished and also regularly seeded with the supernatant from an anaerobic digester, rumen fluid of a cow and anaerobically digested cow manure.

Two tapered reactors, each with 500ml diatomaceous earth were kept at room temperature under aerobic conditions. Expansion of the bed (10-20%) was created by recycling reactor effluent combined with liquid feed which consisted of primary effluent sewage and sucrose solution and which was kept aerobic by injection of air. In this way a film of aerobic and facultative microorganisms was allowed to develop on the particles. These particles might eventually be used to decrease the oxygen level in the oxidation pond effluent before it is used in the anaerobic columns as well as to separate and concentrate the algae. This can be achieved by putting an aerobic column with a short hydraulic retention time before the anaerobic reactor.

SOURCE OF ALGAE

For the acclimation to an algal substrate of the microorganisms on the diatomaceous earth particles, a small oxidation pond (± 300ℓ) was established in an environmental chamber. It was diurnally illuminated and fed regularly with fresh cow manure. The effluent contained different types of green algae among which were: Chlorella, Scenedesmus, Chlamydomonas and Closteriopsis. However, it is not intended that this effluent be used for the comprehensive testing phase. Attempts are being made to find a source of algae concentrate (1% solids) from oxidation ponds. The reason that attention has been focused on an algae concentrate is that it is easy to dilute to a certain influent concentration of solids for the reactor. If no algae concentrate can be found, an outdoor pond at the Cornell facilities will be used this summer to produce the desired pond effluent.

FUTURE ACTIVITIES

Acclimation and stabilization of the anaerobic attached film expanded bed (AAFEB) reactors to maximize attachment will continue during the next quarter. Upon the establishment of an adequate film of anaerobes on the bed, testing will begin utilizing oxidation pond effluent, at various solids concentrations, as feed for the AAFEB units. Data from this comprehensive testing phase will allow the development of the kinetics of the anaerobic conversion of microscopic algae to methane via the AAFEB process.

The two aerobic attached film expanded bed reactors will be tested to determine the rates of oxygen removal. These units will also be used

to test the AFEB process for the separation and concentration of the microscopic algae. The testing of these aerobic units will begin during the next quarter and continue to the end of the testing phase.

The development of algae resources will also continue during the next quarter of the study.

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Quarterly Report - June 1980

NUTRITIONAL STIMULATION OF METHANE BACTERIA

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STIMULATORY COMBINATION

A study was performed to examine the effects of various vitamins in combination with nickel and/or coenzyme M (2-mercaptoethane sulfonic acid). Coenzyne M is a required growth factor for many species of methanogens and has been identified in Methanosarcina barkeri, a species which can utilize acetate as a substrate. The serum bottles were gassed and injected with 50 ml of innoculum, 5000 mg/l KAc as Ac, and 2000 mg/l HAc as Ac. Methane production was measured Monday through Friday. Each bottle was compensated with an equivalent amount of HAc in proportion to the gas production to restore the acetate concentration to 7000 mg/l. Three replicates were used for each combination of compounds, along with seven controls. The experiment ran for one month. Stimulation was defined as gas production, which exceeded 2 standard deviations above that of the controls. All of the combinations which were stimulatory included the following compounds, known as combination A: 0.1 mg/l coenzyme M, 0.1 mg/l vitamin B_{12}, 1.0 mg/l Benzimidazole, and 10 mg/l Proline. The five stimulatory combinations were:

1) Combination A + 1.0 mg/l Folic Acid + 1.0 mg/l Nickel

2) Combination A + 1.0 mg/l PABA

3) Combination A + 1.0 mg/l PABA + 1.0 mg/l Nickel

4) Combination A + 1.0 mg/l Pantothenic Acid + 1.0 mg/l Nickel

5) Combination A + 1.0 mg/l Folic Acid

Combinations which did not quite reach the level defined as stimulatory, but which showed gas productions much higher than the controls include:

1) Combination A + 1.0 mg/l Thiamine

2) Combination A + 1.0 mg/l Vitamin B_6

3) Combination A + 1.0 mg/l Pantothenic acid

4) 0.1 mg/l Coenzyme M + 0.1 mg/l Vitamin B_{12}

5) 0.1 mg/l Coenzyme M + 1.0 mg/l Benzimidazole + 1.0 mg/l Nickel

When these compounds were tried individually, the gas production rates were not as high as occured with the above mixtures.

As shown in the results, when combination A was used with other vitamins, the mixture resulted in consistent stimulation. Consequently, combination A will be added in further studies as part of the background media to which other stimulants may be added. Essentially, combination A will act as the first building block in the determination of the optimum nutrient requirements for our enriched culture.

ACETATE SALT & COMPENSATION STUDY

In the previously described serum bottle techniques, either a single dose of substrate was injected into each bottle or an initial dose was injected with subsequent additions after the substrate was utilized. Both methods allow for the study of many compounds with relative ease and are hence valid screening techniques. Now that several compounds have been shown to frequently cause stimulation of the methanogens, however, a more fundamental serum bottle tech-

nique was required. Both of the earlier methods allow substrate limitations to occur during certain portions of the experiment - a condition which might mask stimulation. An experiment was designed to see if these substrate limited periods could be reduced. The decision was made that an acetate level of 7000 mg/l would allow for high stimulation over a 24 hour period without the substrate level becoming rate limiting. Such a level could be maintained if the methane production was measured each day and an equivalent amount of acetate was re-injected back into the bottle. Four methods for obtaining the initial concentration and compensating were studied and are shown below. They utilize mixtures of potassium acetate, calcium acetate and acetic acid to prevent pH and ion toxicity.

METHOD	1	2	3	4
Initial	5000 mg/l KAc as Ac	4000 mg/l KAc as Ac	7000 mg/l $CaAc_2$ as Ac	7000 mg/l CaAc as Ac
Injection	2000 mg/l HAc as Ac	3000 mg/l HAc as Ac		
Compensated with	HAc	HAc	HAc	$CaAc_2$

Ten replicates in each group were prepared with 50 ml innoculum using the gassing and transfer technique described elsewhere. The study continued for a period of one month and compensation took place Monday through Friday. Monday's gas production was not included in the analysis because the bottles were conceivably substrate limited after not being fed on the weekend. The accumulated weekly gas production for each group was analyzed using a two way analysis of variance (F test) and a Student-Newman-Keuls test to rank the groups at a 95% confidence interval. Method 4 - initially using calcium acetate and compensating with calcium acetate - consistently showed the highest methane production. Method 1 was the next highest. Methods 3 & 4 showed lower gas productions with no significant

difference between the two. All the gas production rates decreased with time. This same study was duplicated by another technician to check for replicability. The results were the same in both experiments although the absolute numbers were not comparable. The decision was made to use both Methods 1 & 4 in further studies to examine their effects upon stimulants. These techniques should allow for a fundamental examination of stimulation rates using serum bottles.

NUTRISTATS

Data presented in the last quarterly report indicated that one-time additions of combinations of several compounds resulted in gas production up to about four times that of background levels. Based on these results, continuous addition of selected compounds was under taken. Selection of compounds and combinations was based on results from serum bottle screening tests and the one-time addition studies mentioned above.

Before tests could be started, the six nutristats had to be emptied, cleaned, and reinocculated with acetate enrichment culture. Routine maintenance of feed pumps, seals, and gas measuring devices was also conducted during this time. Prior to addition of potential stimulants, background gas production data was collected for three to four weeks. Once background gas production leveled off, candidate compounds and combinations were added as described below.

Nutristat 1.	Vitamin B_{12}; starting at 0.001 mg/l and increasing until gas production peaks.
Nutristat 2.	0.1 mg/l B_{12} + 1 mg/l Bnezimidazole + 10 mg/l Proline
Nutristat 3.	Control (no additions)
Nutristat 4.	0.1 mg/l B_{12} + 0.1 mg/l Biotin + 1 mg/l Benzimidazole + 1 mg/l para-amino benzoic acid + 10 mg/l Thiamine

Nutristat 5. Used to make one-time additions of new candidate compounds and combinations. The first addition was 0.1 mg/l Coenzyme M.

Nutristat 6. 0.1 mg/l B_6 + 0.1 mg/l Riboflavin + 0.1 mg/l Folic Acid + 0.1 mg/l Pantothenic Acid

Systems have been operating only for a short time and data collected so far permit no firm conclusions. During the coming quarter, these systems will be monitored and additional compounds and combinations will be added once gas production levels off.

pH STATS

For these nutritional stimulation studies, there is the need to maintain the acetate concentration sufficiently high to prevent substrate limitation. In the serum bottle assay technique, occasionally acetate becomes limiting over the weekend when the systems are not fed. The nutristats are able to automatically maintain unlimiting acetate levels for extended periods of time, but there are only six.

In order to increase the number of stimulation assay systems which are able to automatically maintain acetate concentrations above limiting levels, twenty additional units were constructed with pH feedback control. These systems are referred to as pH STATS according to Bungay. These twenty stimulation assay systems operate in the following sequence:

1. A 20 position stepper switch actuates a solenoid which allows the contents of a digester to flow into a pH electrode chamber.
2. After the pH has stabilized, it is read.
3. If the pH exceeds 6.8, a time delayed acetic acid feed pump injects a sufficient amount of a stock solution to increase the acetate concentration by 500 mg/l.

4. Whenever the acetic acid feed pump is actuated, a counter is ticked for that respective digester so that the accumulative acetate addition can be determined for any time interval.
5. Next a solenoid opens to allow a low pressure source of 50% CO_2 and 50% N_2 gas to force the sample out of the pH chamber back into the respective reactor.
6. The stepper switch then advances, allowing the above sampling sequence to be administered to the next reactor.

For the alkalinity levels present in our system, by maintaining the pH below 6.8, the acetate level is maintained in excess of 2000 mg/l which is considered non-limiting. Each sampling and feed cycle requires 2 minutes so that every 40 minutes all 20 reactors are sampled and fed if necessary.

The Nutristats are based upon stoichiometrically injecting acetic acid in proportion to the gas production and the feed pump calibration must be adjusted to prevent over or under feeding. This is not a problem with the pH STATS.

The pH STATS have been operated with a dye in one reactor to determine carryover to the following reactor. Some leakage of the solenoids has been observed and needs correction before the system is operational.

EVALUATION OF METHANE PRODUCTION FROM WET STILLAGE AND THE NUTRITIONAL VALUE OF THE RESIDUE

Progress Report for

Quarterly Coordination Meeting
June 23-24, 1980
Denver, Colorado

Prepared by

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Objectives

This project is designed to determine the value of wet stillage from small-scale alcohol plants as a source of methane. The fermentation characteristics of various stillage residues are being investigated. The potential feed value of stillage and of the residue remaining after methane fermentation is being estimated by means of *in vitro* dry matter digestibility (IVDMD). This technique is widely used in animal nutrition to estimate feed value and consists of anaerobic fermentation for 48 hours with ground feed samples, rumen fluid inoculum and buffers to maintain pH at about 7.0.

Research Plan

Samples of stillage are obtained from a still designed and operated on the Schroeder farm near Campo, Colorado, the only operating still in Colorado to our knowledge.

The entire cooked mash is passed through the distillation column. The stillage as it leaves the column is run through a screw press which separates it into two fractions; a solid fibrous fraction of about 30 percent dry matter and a liquid fraction containing only about 5 percent solids. This is the fraction commercially sold as distillers solubles. So far methane production has been determined only on the more solid fraction.

The nutrient composition of the first three samples are shown in table 1 as well as the composition of one sample from the liquid phase. The protein content, on a dry basis, of samples 2 and 3 at 34 percent and 36 percent is higher than usually reported from distillers grains and we are not sure why it should be higher.

Table 1. Composition of Stillage From Alcohol Fermentation
(% of dry matter in the sample)

	Sample 1		Sample 2	Sample 3
	Solids	Liquid	Solids	Solids
Dry matter	36.3	5.8	38.1	37.7
Crude protein[1/]	30.1	19.9	34.3	36.3
Ether extract	10.4	8.2		
ADF[1/]	32.8	30.5	50.4	38.3
NDF[2/]	36.3	37.5	31.6	34.8
Lignin	3.8	----		
Ash	2.3			

[1/] Acid detergent fiber.
[2/] Neutral detergent fiber.

Fermentors of the type shown in figure 1 were charged with 18 grams of solids from the wet stillage. The methane culture was grown on feedlot cattle manure. The combined fluid was about 800 ml in the one-liter flasks. Figures 2 and 4 illustrate the daily cumulative gas production while figures 3 and 5 indicate daily methane production for Samples 1 and 2, respectively. The figures indicate a lag period of about six days before methane production is hardly detectable. From that time to about 16 days, all fermentor flasks behaved in a uniform manner. Differences between 16 and 26 days probably represent small differences between flasks in fermentable carbohydrate added. The pH of each flask was determined each morning and then adjusted to pH 7.0. The daily pH is plotted in figures 6 and 7 for Sample 1 and 2, respectively.

The early lag phase in gas and methane production was probably due to acid buildup at the start of fermentation. To determine the acids responsible for the higher acidity, samples were collected daily and short-chain fatty acids

determined by gas chromatography by methods used in our laboratory for short-chain fatty acids produced by rumen fermentation. Acid production for the first four days of fermentation for all flasks containing Sample 1 are indicated in figure 8. Acetic acid (C_2) is the predominant acid and the concentration increased for the four-day period. Butyric acid (C_4) was about one-half the acetic acid levels and propionic (C_3) was much lower. Isobutyric (iC_4), isovaleric (iC_5) and valeric acids (C_5) were present in negligible amounts.

Stillage with its relatively high protein content is higher in protein and contains more soluble protein and non-protein nitrogen than most methane substrates. We plan to analyze the fermentation fluid for ammonia; a product that may be inhibiting methanogenic bacteria. Because so much of the organic matter is protein the question arises as to whether protein is converted to methane. Isovaleric acid is considered an indicator of protein degradation at least in rumen fermentations. The low isovaleric concentrations perhaps indicate this not occurring. Ammonia levels, however, will provide a more definitive answer.

Methane yields were 7 to 9 liters in 26 days from 18 grams of dry matter in the form of stillage or about 400 to 500 ml per gram of solids.

One <u>in vitro</u> digestion study (Sample 1) has been completed that compares the IVDMD of the stillage as used in the fermentors with the IVDMD of the residue removed from the fermentor after the 26-day digestion. The results as presented in table 2 indicate a considerable decline in digestibility after the stillage solids have been fermented in the methane digestor. The results are not surprising since methane fermentation and rumen digestion are both anaerobic fermentation processes. The IVDMD method provides an estimate of the feed energy available from a substrate, but it does not indicate the potential value of the protein component. It can be assumed that the protein residue would be

Table 2. *In Vitro* Dry Matter Digestion (IVDMD) of Wet Stillage and Residue From Methane Digester

	Pressed Stillage	Residue from Methane Digester
Dry matter %	36.3	2.5
Crude protein	30.1	21.5
ADF	32.8	30.5
NDF	36.3	37.5
IVDMD	54.4	11.4

available to animals. The true protein and the non-protein-nitrogen distribution in the crude protein will be determined.

Although conclusions drawn from one sample are tentative, it does appear that the feed value of the residue from methane digestion would have limited feed value considering the relatively low protein, the low feed energy value as indicated by the IVDMD method and perhaps most important that is present in liquid form with only 2.5 percent solids.

FERMENTATION FLASK AND GAS COLLECTION APPARATUS

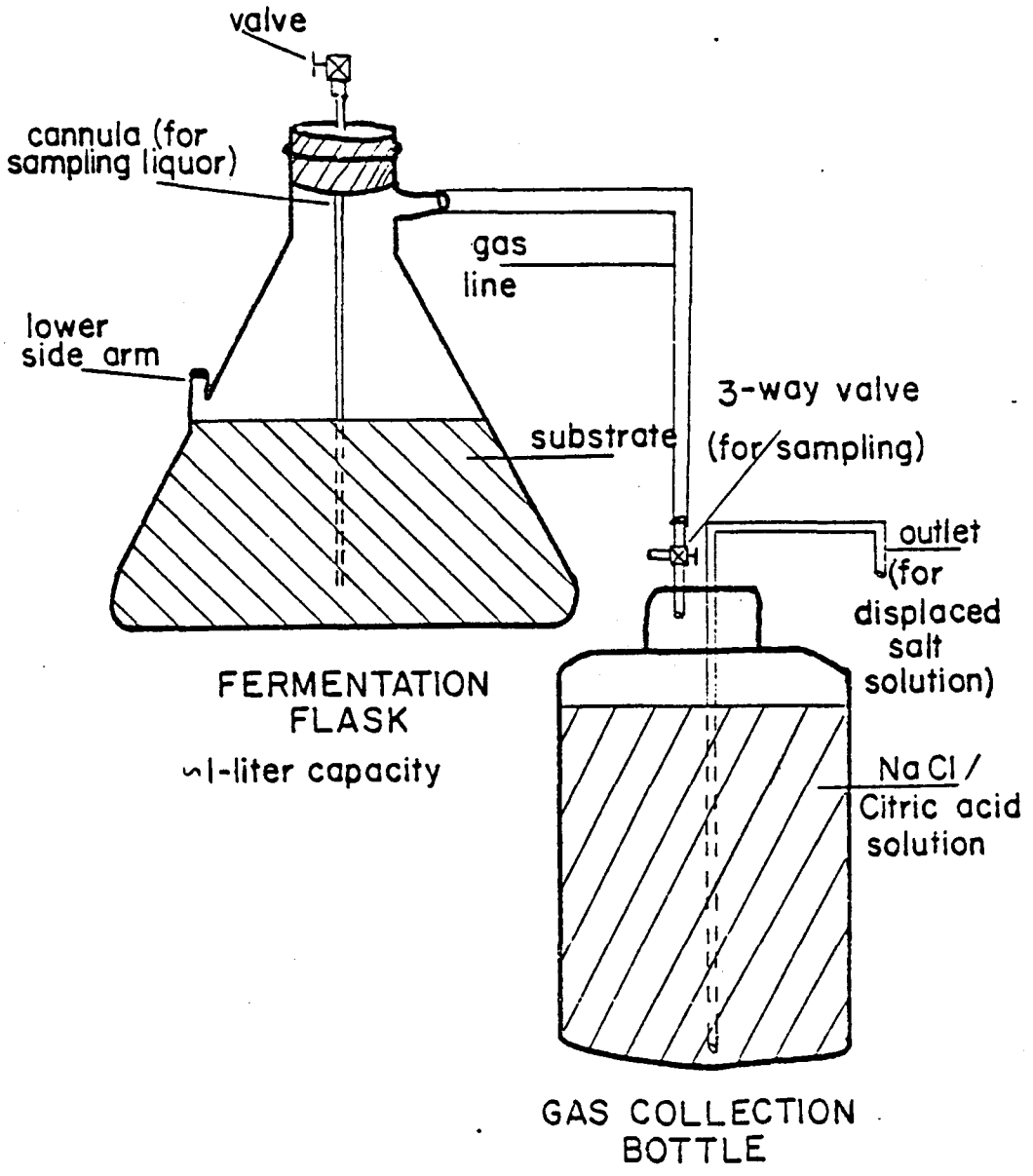
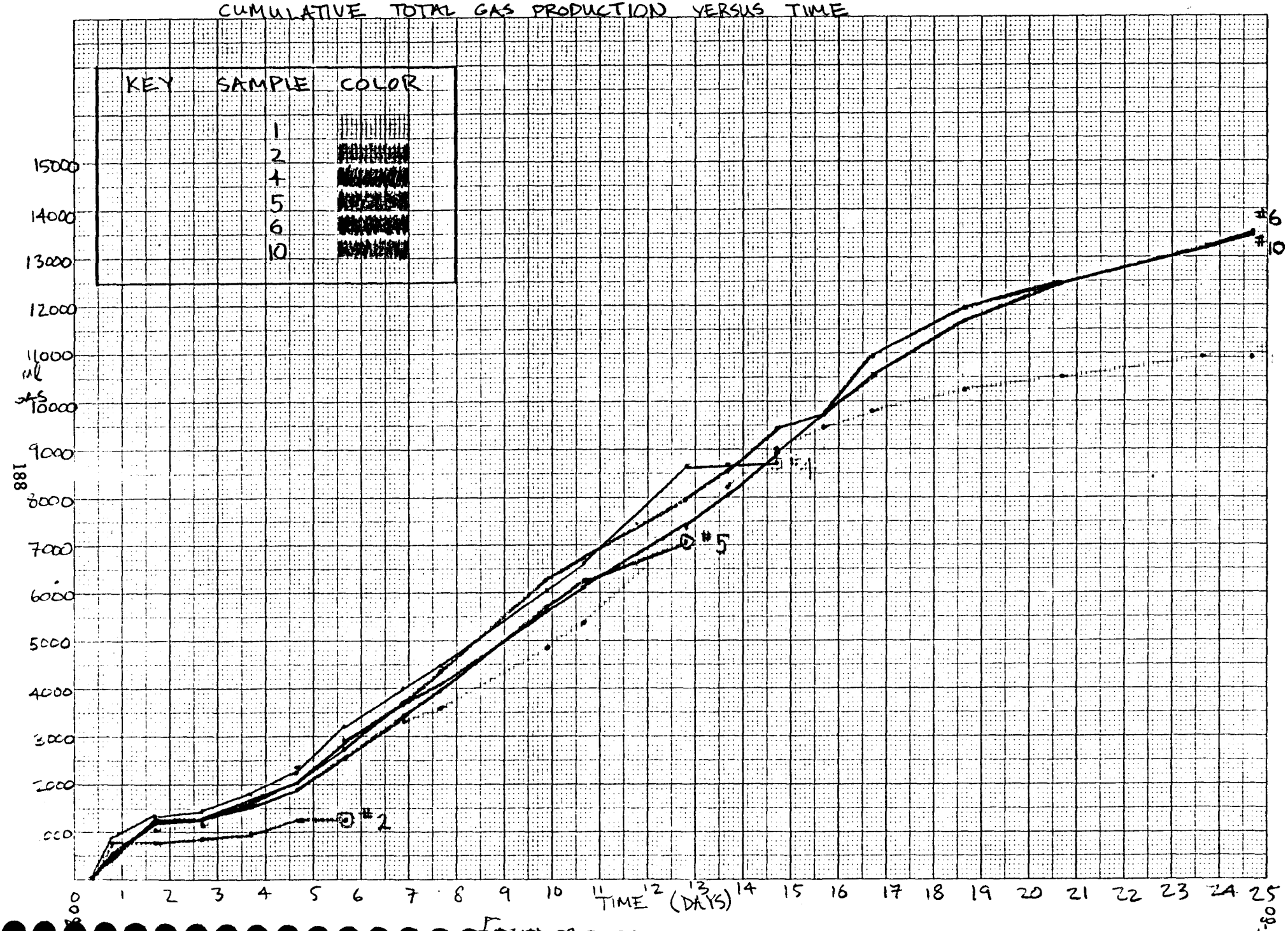
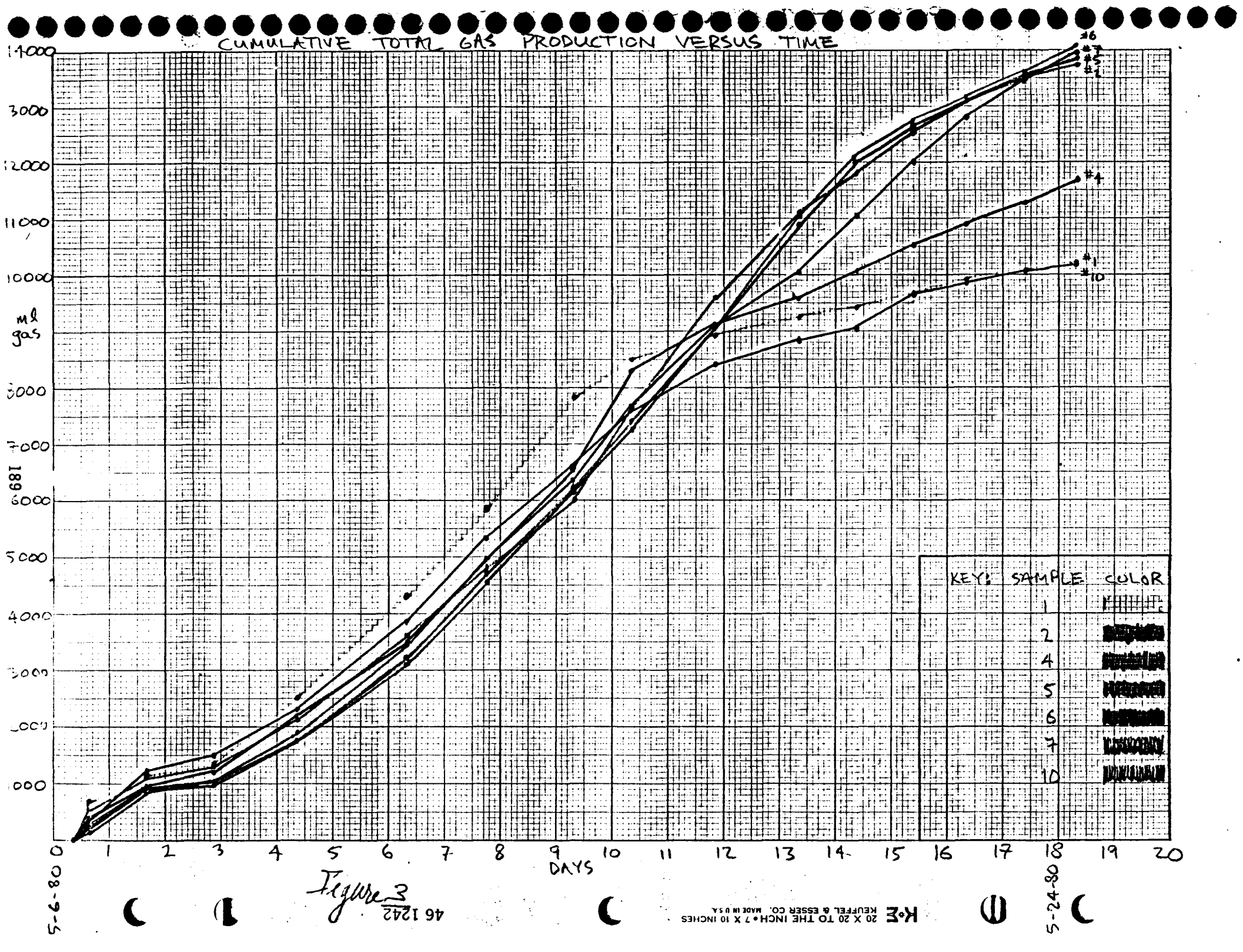


Figure 1

ANAEROBIC DIGESTION OF DISTILLERS GRAIN BY S. C. [illegible]

CUMULATIVE TOTAL GAS PRODUCTION VERSUS TIME





5-6-80

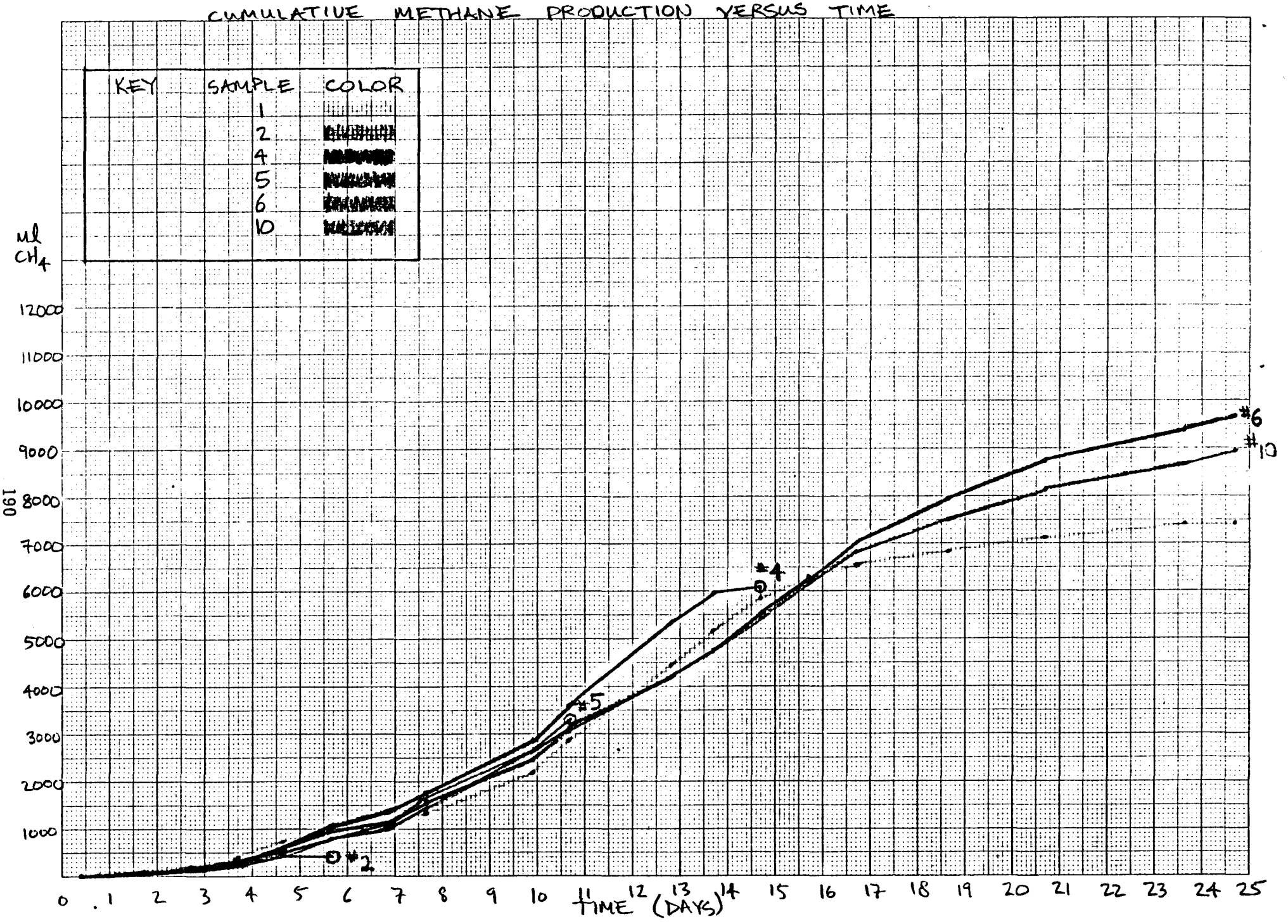
Figure 3

46 1242

K&E 20 X 20 TO THE INCH • 7 X 10 INCHES KEUFFEL & ESSER CO. MADE IN U.S.A.

5-24-80

ANAEROBIC DIGESTION OF DISTILLERS GRAINS, ETC.



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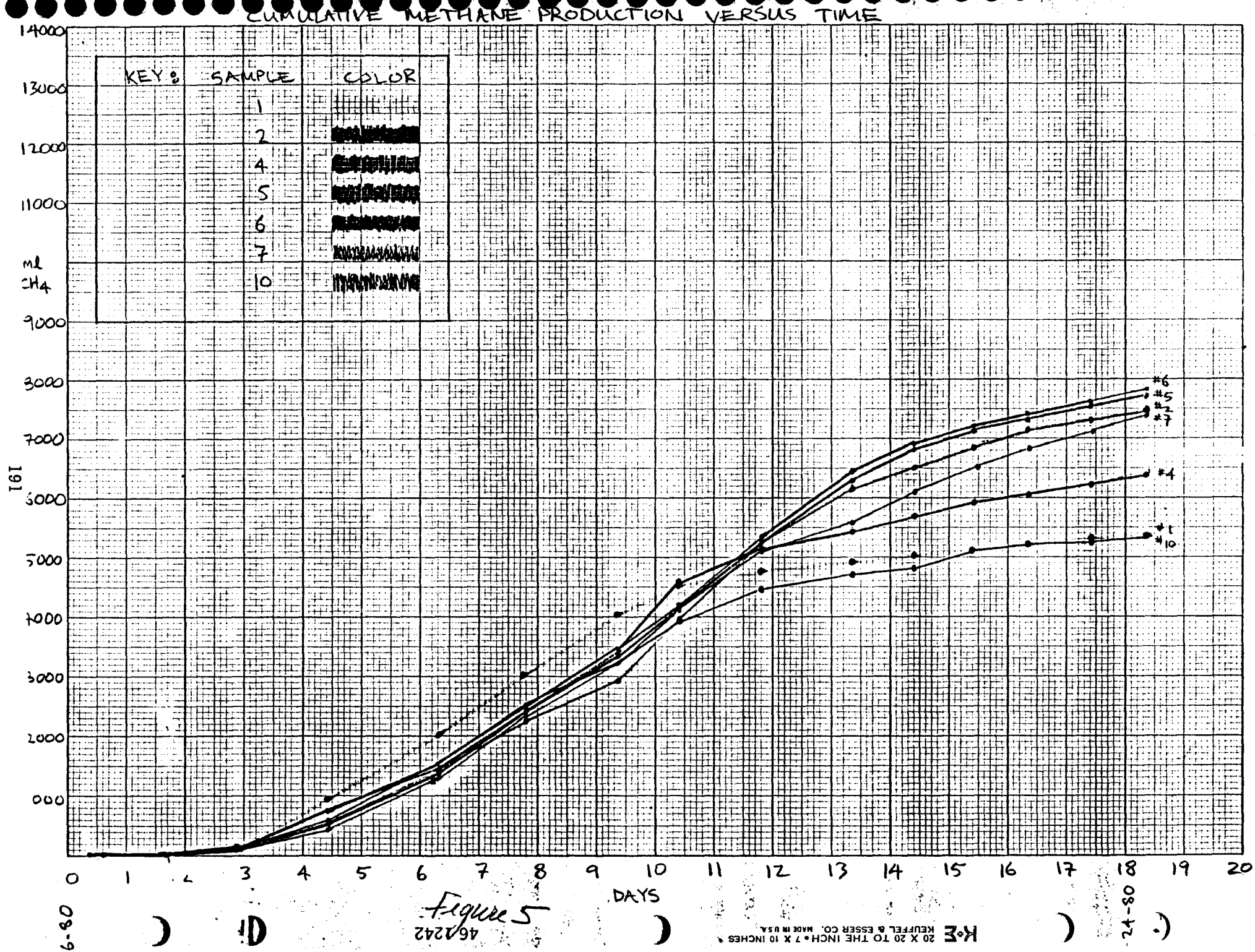

Figure 5

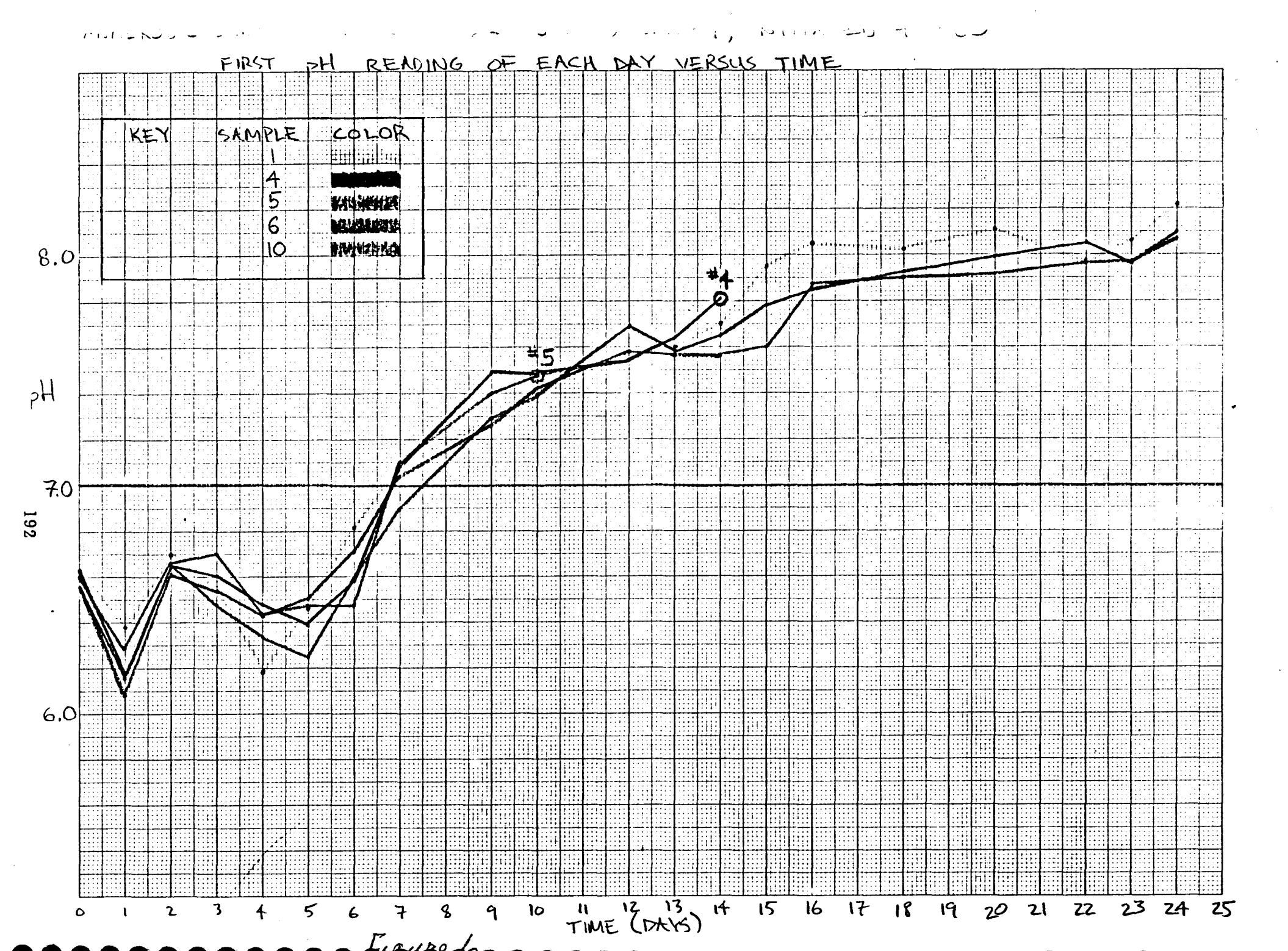
FIRST pH READING OF EACH DAY VERSUS TIME
KEY
SAMPLE
COLOR
1
4
5
6
10
#4
#5
8.0
7.0
6.0
pH
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
TIME (DAYS)

Figure 6

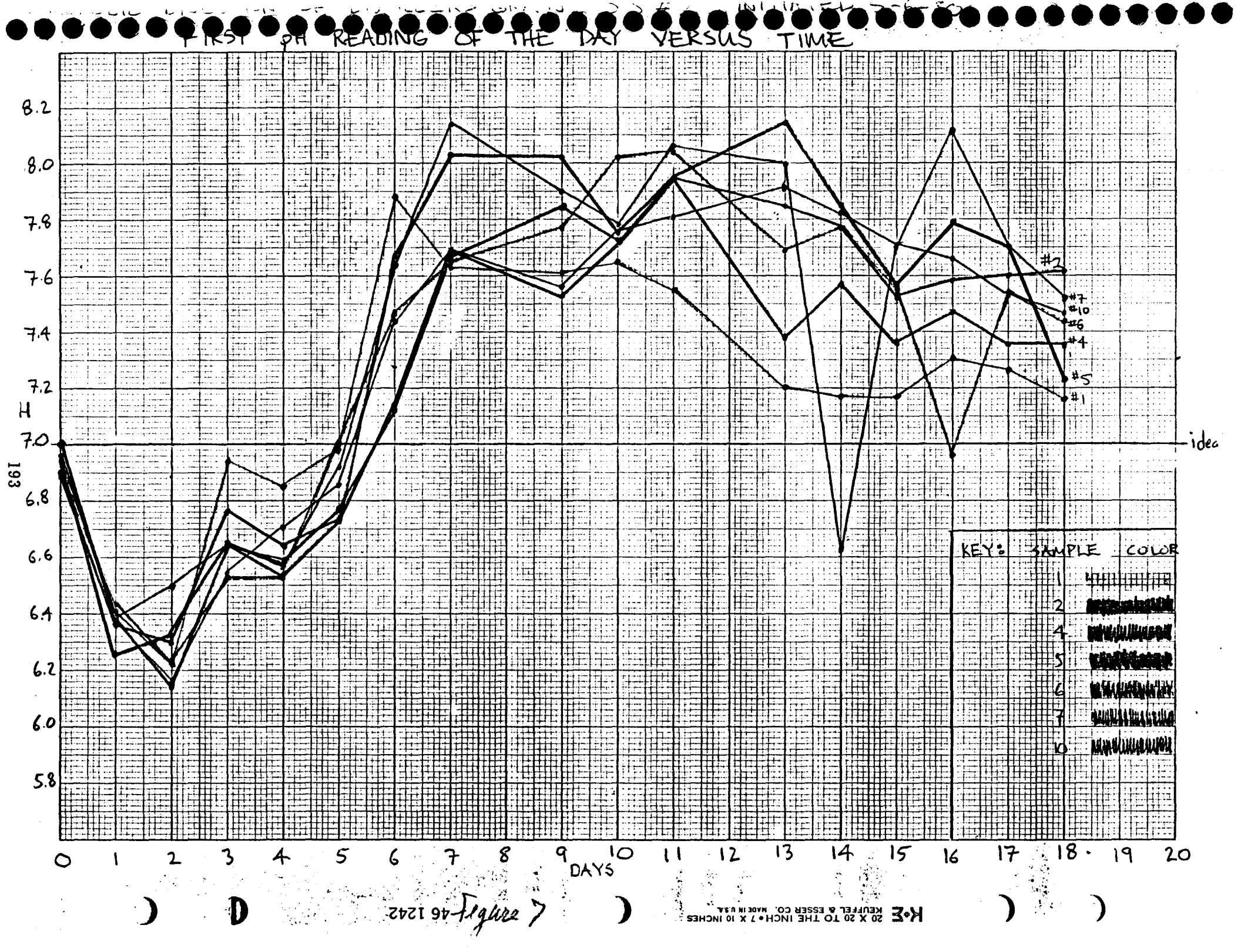
FIRST pH READING OF THE DAY VERSUS TIME
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
pH
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
DAYS
#2
#7
#10
#6
#4
#5
#1
KEY: SAMPLE COLOR
1
2
4
5
6
7
10

Figure 7

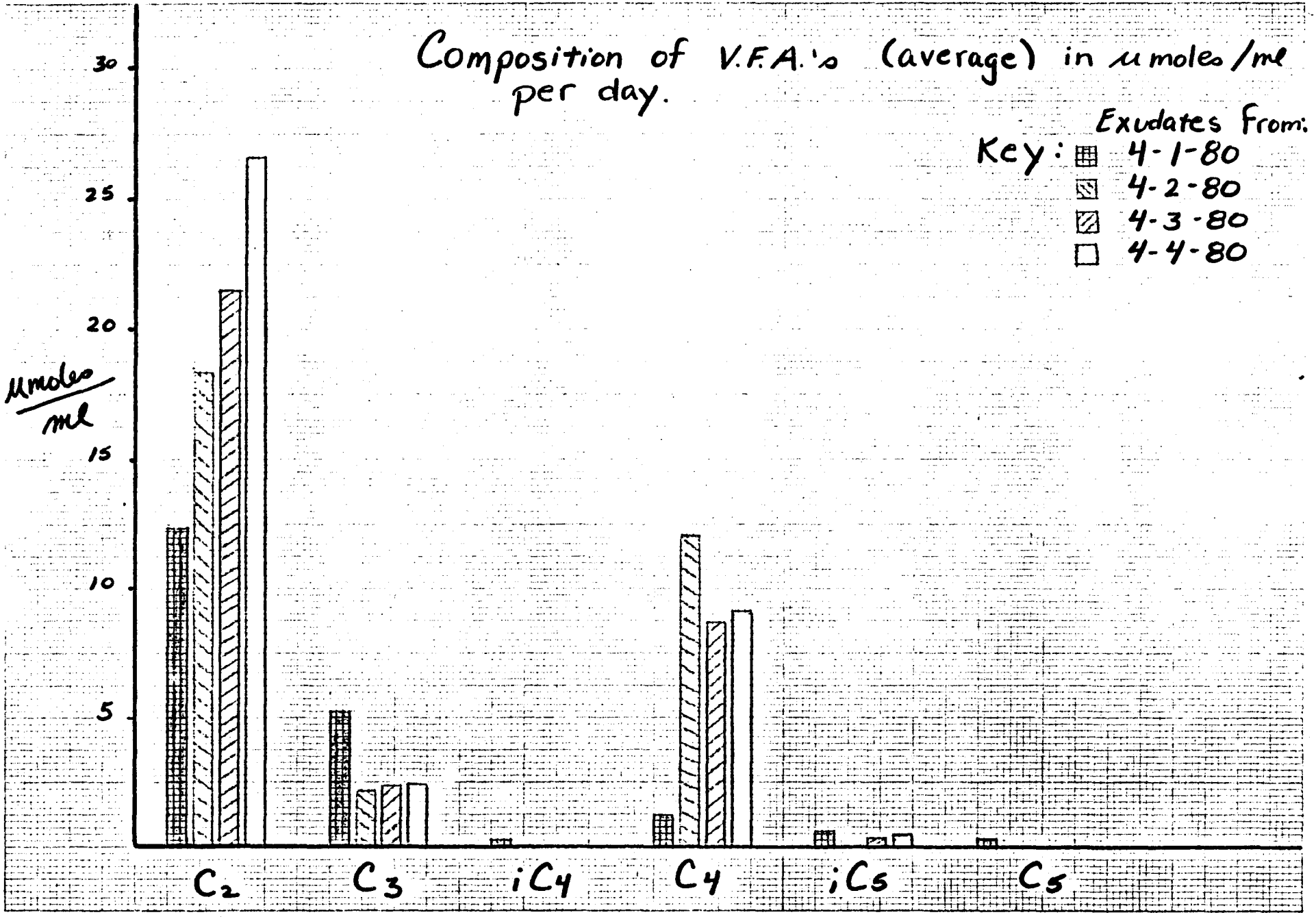

Figure 8