SERI/PR-624-537-8 July 1981

Fuel Gas Production from Animal and Agricultural Residues and Biomass

20th Quarterly Coordination Meeting
June 25, 1981
Ithaca, New York

D. E. Jantzen
Biomass Program Office

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Operated for the
U.S. Department of Energy
under Contract No. EG-77-C-01-4042

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Prepared Under Task 3335.01

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FOREWARD

The 20th Quarterly Coordination Meeting of the Anaerobic Digestion group of contractors working for the Biomass Energy Systems Division, U.S. Department of Energy, was held on June 28, 1981 in Ithaca, NY. Each contractor presented a brief report on progress achieved during the last quarter. The group also toured the Cornell University labs and facilities to see the equipment used in the Cornell studies.

Dan Jantzen
Biomass Program Office

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LIST OF INVITEES

ANAEROBIC DIGESTION CONTRACTORS COORDINATION MEETING

Ithaca, NY

June 25, 1981

Organization	Name	Telephone
Cornell University 202 Riley - Rob Hall Ithaca, NY 14853	William J. Jewell	(607) 256-2173
Dynatech R/D Company 99 Erie Street Cambridge, MA 02139	Don L. Wise Edward Ashare	(617) 868-8050
University of Arkansas Department of Chemical Engr. Fayetteville, Arkansas 72701	James L. Gaddy	(501) 575-4951
Solar Energy Research Inst. 1617 Cole Blvd. Golden, CO 80401	Dan Jantzen Clay Smith	(303) 321-1469 (303) 321-1200
Stanford University Department of Civil Engr. Stanford, CA 94305	Perry L. Mc Carty	(415) 497-3921
U.S. Dept. of Agriculture Meat Animal Research Center P.O. Box 166 Clay Center, NE 68923	Andy Hashimoto	(402) 762-3241
Drexel University 32nd and Chestnut Street Philadelphia, PA 19104	Richard Speece	(215) 895-2267
SEA Southern Agricultural Energy Center Coastal Plain Experiment Station Tifton, GA 31793	Ralph Prince	(912) 386-3585
Department of Energy Biomass Energy Systems Division 600 E. Street, NW Washington, D.C. 20585	Ray Costello David Lombard	(202) 376-9739 (202) 376-9311

AGENDA

ANAEROBIC DIGESTION CONTRACTORS REVIEW MEETING

Sheraton Inn; Ithaca, New York

June 25, 1981

8:00 - 8:10	Welcome and Annoucements
8:10 - 8:50	Meat Animal Research Center: Manure and Crop Residuals
8:50 - 9:30	University of Arkansas: Biomass Fermentation Studies
9:30 - 10:10	Drexel University: Nutritional Stimulation
10:10 - 10:20	Coffee Break
10:20 - 11:00	Cornell University: Low Cost Methane
11:00 - 11:40	D. Jantzen: Contractual Affairs
11:40 - 1:00	Lunch
1:00 - 1:40	Dynatech R/D Co: Ethanol-Methane Comparative Study
1:40 - 2:20	Stanford University: Autohydrolysis
2:20 - 3:00	Dynatech R/D Co: Digestion of Peat
3:00 - 3:10	Coffee Break
3:10 - 5:30	Tour of Cornell Labs and Facilities
7:00	Dinner (Old Port Harbour Restaurant)

ANAEROBIC FERMENTATION OF BEEF CATTLE MANURE AND CROP RESIDUES

Quarterly Progress Report
April to June, 1981

Andrew G. Hashimoto and Steven A. Robinson

Roman L. Hruska U.S. Meat Animal Research Center
Agricutural Research
Science and Education Administration
U.S. Department of Agriculture
Clay Center, Nebraska 68933

Prepared for

Solar Energy Research Institute
Biomass Program Office
Subcontract No. DB-9-8372-1

PILOT-SCALE CONVERSION OF MANURE-STRAW MIXTURES TO METHANE

Andrew G. Hashimoto and Steven A. Robinson
Roman L. Hruska U.S. Meat Animal Research Center
Science and Education Administration
Agricultural Research
U.S. Department of Agriculture
Clay Center, Nebraska 68933

ABSTRACT

The pilot plant was modified into a two-stage fermentation system to accomodate manure-straw mixtures. Inputs to the system were 50% beef cattle manure and 50% wheat straw based on volatile solids (VS) content. The manure-straw mixture was mixed into a slurry and fermented in a hydrolysis tank for 1 day. The slurry in the hydrolysis tank was observed to autoheat from 40°C up to about 60°C; and, this autoheating was determined to result from aerobic hydrolysis of substrate and mixing energy dissipation. Slurry from the hydrolysis tank either passsed through a vibrating-screen solids separator or went directly to the anaerobic fermentor. When the solids were separated, approximately 37% of the screened solids were returned to the hydrolysis tank. The screened liquid, which accounted for 35% of the VS in the manure and straw, was pumped to the anaerobic fermentor for conversion to CH_4. The fermentor, operated at 8-day HRT, 44 to 47°C, and influent concentration of 47.3 kg VS/m^3, produced 1.81 m^3 CH_4/m^3 fermentor·day and 0.31 m^3 CH_4/kg VS fed. When accounting for the solids wasted from the system, the overall yield from the solids separation system was 0.11 m^3 CH_4/kg VS fed. When solids were not removed, the fermentor was operated at 5-day HRT, 52 to 54°C and influent concentrations of 70.3 kg VS/m^3·day and 68.1 kg VS/m^3·day. The CH_4 production rates and yield were 2.49 and 2.96 m^3 CH_4/m^3 fermentor·day, and 0.18 and 0.22 m^3 CH_4/kg VS fed. Thus, the system without solids separation was determined to be more efficient because it produced higher overall CH_4 yields.

INTRODUCTION

A two-stage fermentation system that converts manure-crop residue mixtures to methane (CH_4) is being evaluated at the Roman L. Hruska U.S. Meat Animal Research Center. The first stage is a completely-mixed, heated, well-insulated tank in which manure, crop residue and water are mixed to optimize cellulase and other hydrolytic activity. In order to prevent methanogenesis in the first stage, volatile solids (VS) loading rate is kept high (in excess of 30 kg $VS/m^3 \cdot day$) and solids retention time is kept short (less than 4 days).

Effluent from the hydrolysis tank is screened to remove coarse particles, and the solubles and fines pass to the second-stage fermentor for conversion to CH_4. The coarse particles (hair, undigested feed, residue particles, etc.) are either recycled back to the hydrolysis tank, wasted (this could be used as roughage in ruminant rations or as bedding) and/or thermochemically treated and then returned to the hydrolysis tank.

Potential advantages of this two-stage system are: easily hydrolyzable material is hydrolyzed in the first stage and fermented to CH_4 and CO_2 in the second stage; more resistant substrate is hydrolyzed for longer periods; only resistant substrate is exposed to alkaline treatment (reducing the amount of residue to be treated and, therefore, the chemical energy needed to treat the residue); the alkaline added to the system helps to maintain the pH in the first stage at optimum levels; neutralization of the treated material is not necessary; increased methane production rates may be achieved since the substrate to the second stage would presumably be more biodegradable; and problems associated with mixing and pumping the fermentor contents are minimized with the removal of the coarse material.

This report focuses on the pilot-scale performance of the two-stage fermentation system with and without solids separation. Effects of thermochemical pretreatment of the separated solids are not described in this report.

EQUIPMENT AND PROCEDURES

Figure 1 is a schematic diagram of the pilot-scale fermentation system. Manure (1 to 10 days old) was gathered daily from steers housed on partially roofed, concrete-floored pens. The steers weighed from 340 to 570 kg. Their feed ration consisted of 85% yellow corn, 13% corn silage, 1.6% soybean meal, 0.2% limestone, 0.1% each of dicalcium phosphate and salt, and trace minerals and vitamins A, D and E. The manure was transported to the pilot plant by a small front-end loader and dumped into the slurry tank. Water was added to form a slurry of 10 to 12% total solids (TS), and mixed with a 1-kW variable speed mixer.

Wheat straw, from hard-winter wheat grown in Clay County, Nebraska, was baled in large round bales (approximately 400 kg) and stored in an open front barn. The straw was first ground in a tub grinder equipped with a 1.9 cm screen then in a rotary hammer-mill equipped with 0.64 cm screen.

Based upon the volatile solids analysis of both the manure and ground wheat straw, the two were mixed in a 50:50 ratio (1 kg manure VS with 1 kg straw VS). This combination was mixed and water added to form a slurry of 10 to 12% TS. The slurry was then pumped by a diaphram pump to the hydrolysis tank. The hydrolysis tank (0.94-m diameter by 1.83-m high, with liquid volume of 1 m^3) was an insulated, covered tank, equipped with a hot-water heat exchanger. The hydrolysis tank was made of fiber-glass and was insulated with 7.6 cm of polyurethane foam. The insulation was protected with galvanized sheet metal. The heat exchanger consisted of 1.9-cm diameter by 27.7-m long coiled soft-copper tubing mounted on an aluminum pipe frame. Hot water in the heat exchanger was maintained between 77 to 70°C. The tank was equipped with a 3-phase, 2.2 kW variable-speed mixer with two 0.305-m diameter marine propellers. The mixer speed was 475 revolutions per minute. The mixture remained on the hydrolysis tank for 1 day.

When solids separation was used, the manure-straw mixture was pumped, at a flow rate of 433 cm^3/s, to a 0.61-m diameter vibrating screen (1.9 mm (10 mesh) opening) separator. Solids removed from the slurry were weighed and approximately 180 kg, or 37%, of the screened solid were recycled to the slurry tank and mixed with fresh straw-manure slurry. The remaining solids were disposed of on land. The screened liquid was pumped into another 1-m^3 tank (identical to the hydrolysis tank) mounted on a platform scale. This screened liquid was heated to 65°C overnight, then diluted to the desired VS concentration, and pumped into the fermentor the next day.

When solids separation was not used, the mixture in the hydrolysis tank was pumped directly to the weight tank. The mixture was also heated to 65°C overnight, then diluted to the desired VS concentration, and pumped into the fermentor the next day.

Figure 2 shows a schematic diagram of the fermentor and mixer. The fermentor volume was 5.7 m^3 with a working volume of 5 m^3. The fermentor was insulated with 3 cm of polyurethane foam. Four baffles were equally spaced around the tank and the mixer consisted of a 1.5 kW variable-speed motor and two, 3-blade, stainless steel, marine propellers on a stainless steel shaft. The mixer was not used when the solids were separated, and was used continuously at 144 revolutions per minute when the solids were not removed.

The gas produced during fermentation passed through two condensate foam traps, a temperature compensated gas meter and a pressure relief valve. The condensate-foam traps consisted of cylindrical tanks, 0.53-m in diameter and 1.73-m high, with a siphon calibrated to discharge when the pressure exceeded 0.25 m of water column.

Samples of slurries, before and after screening, screened solids and fermentor influent and effluent were routinely analyzed for various constituents. Total, volatile and fixed solids, ammonia (distillation method), chemical oxygen demand, alkalinity (to pH 3.7), pH and total volatile acids (silicic acid method) were determined by standard methods (APHA, 1975). Individual VFA's were determined by gas chromatography and Kjeldahl nitrogen was determined using technicon block digesters and Auto-Analyzer II as described by Wael and Gehrke (1975). Gas volume was measured by an American AL-175 gas meter with temperature compensation to 15.6°C. Methane concentration was determined by a Beckman 864 infra-red gas analyzer.

A Macsym II (Analog Devices) process-controller microprocessor was used to control operating temperatures and calculate total gas and methane volumes. The microprocessor adjusted the gas volume to 0°C, one atmosphere and zero water vapor pressure.

SYSTEM OPERATION

Start-up

Modification of the pilot-plant began in July, 1980. The existing heat exhanger was dismantled and the fermentor temperature decreased from 55°C to 24°C in 21 days. The slurry was left in the fermentor until early September, while the rest of the plant was modified. Then the slurry was removed and stored in open tanks while the fermentor was modified. After one week, the slurry was pumped back to the fermentor. On September 19 the slurry was again removed from the fermentor and heated to 62°C before being returned to the fermentor. The rest of the start-up procedure was as follows:

Sept. 22-26	Slurry was removed from fermentor and heated to 62°C, TVA = 3.3/kg m^3
Sept. 29-Oct. 3	Slurry was removed from fermentor and heated, by this time fermentor temperature had stabilized at 55°C

Oct. 6-9	Fed fermentor at 15-day HRT and influent concentration 60 kg VS/m^3, TVA = 2 kg/m^3
Oct. 10-13	12-day HRT, TVA = 1.25 kg/m^3, pH 7.9
Oct. 14-20	10-day HRT, TVA = 1.5 kg/m^3, pH 7.9 temperature maintained at 52-55°C
Oct. 21	8-day HRT, TVA = 1.4 kg/m^3, pH 8.0
Nov. 10	TVA gradually increased to 3.5 kg/m^3 Hot water was fed instead of manure for two days at 8-day HRT.

The 8-day HRT was continued and the TVA steadily decreased to about 0.3 kg/m^3. The influent was then changed from beef cattle manure to the beef cattle manure-ground wheat straw mixture. Throughout the duration of the experiment the fermentor temperature fluctuated 3°C over 24 hours. When the hot influent was introduced into the fermentor, the temperature increased to 47°C then cooled down to 44°C overnight. There was no apparent temperature stratification in the fermentor.

Hydrolysis Tank Operation

An interesting phenomena was observed in the operation of the hydrolysis tank. When the hydrolysis tank was heated to 40°C and mixed continuously, the temperature invariably rose to over 60°C during the night. In order to investigate the reason for this temperature rise, the hydrolysis tank was operated under two additional modes: tank covered and continuously mixed; and tank covered but not mixed after reaching 40°C. During all these modes, the heat exchanger was monitored to be certain that it was not contributing to the heating phenomena.

Figure 2 shows typical temperature profiles during the three modes of operation. When the tank was covered and mixed continuously, the temperature rose much slower than when the tank was not covered. When the tank was covered and not mixed, the temperature remained constant.

There are two apparent reasons for the observed autoheating in the hydrolysis tank: mixing energy dissipated as heat; and by heat generated during the aerobic hydrolysis of organic matter. The net power transferred to the slurry can be calculated by the procedures presented by Chen (1981). Assuming a power number of 0.4 at a Reynolds number of 6,600, slurry density of 1050 kg/m^3 and a power factor of 1.5 for two propellers spaced 1.5D apart on a shaft (Bates et al., 1966), the power input to the slurry was calculated to be 3 MJ/hour. Assuming that all the power is dissipated as heat, then a temperature rise of 0.7°C/hour would be expected. Figure 2 shows a temperature rise of 8°C over the first 10 hours when the hydrolysis tank was covered and mixed. Thus, it appears that the autoheating observed in the mixed and uncovered hydrolysis tank resulted from both mixing energy dissipation and biological oxidation since the tank volume was calculated to turnover 7 times per minute.

Steady-State Operation

The fermentor was operated at 44 to 47°C and 8-day HRT for 32 days before steady-state conditions were assumed. Table 1 shows the concentrations of various constituents in the system's flow streams during steady-state. Removing the coarse particles from the manure-straw mixture increased the COD/VS ratio from 0.89 to 1.36, for a 153% increase. This higher COD/VS ratio indicates a more biodegradable substrate for fermentation. Batch fermentations are in progress to determine whether the screened liquid is more biodegradable than the hydrolyzed manure-straw mixture. The CH_4 production rate was 1.81 m^3 CH_4/m^3 fermentor·day and yields of 0.31 m^3 CH_4/kg VS fed and 0.48 m^3 CH_4/kg VS used. These rate and yields are comparable to those expected from beef cattle manure fermented at the same conditions (8-day HRT, 45.5°C).

After the steady-state with solids seperation was completed, the fermentor was operated at 52 to 54°C and 5-day HRT for 17 days. The fermentor temperature was higher because more heat was added each day at 5-day HRT than at 8-day HRT. Steady-state data were obtained on days 34 to 38 (Trial 1) and 62 to 67 (Trial 2) and summarized in Table 2. The CH_4 yield and production rates were about 20% higher in Trial 2 than in Trial 1. We do not know the reason for this except that the influent VS concentration was less variable and the COD and TVA concentrations were higher in Trial 2 than in Trial 1.

DISCUSSION

The autoheating phenomena observed in this study shows potential for providing much of the heating requirements for thermophilic anaerobic fermentation. However, an assessment of the relative energy requirements of the autoheating and heat exchanger processes must be conducted to determine which process is the most energetically efficient. The energy required to heat 1 m^3 of slurry from 40°C to 60°C is 88 MJ. Assuming a boiler and heat exchange efficiency of 75%, the gross energy required to heat the slurry is 156 MJ. Figure 2 shows that autoheating in the uncovered hydrolysis tank raised the temperature from 40°C to 60°C within 10 hours. The energy needed to mix the slurry for 10 hours is 38 MJ, assuming an 80% efficient mixer. Assuming a fuel to electricity conversion efficiency of 25% the gross energy requirement for autoheating is 152 MJ. Thus, if the two processes are compared in the basis of the same fuel imput, there is little difference in the energy requirement of the two processes. However, it must be emphasized that the autoheating process was not optimized, so improvement in its energetic efficiency is probable with additional research and development of the process.

The two-stage fermentation system with solids seperation produced high CH_4 production rate (1.81 m^3 CH_4/m^3 fermentor·day) and yield (0.31 m^3 CH_4/kg VS fed) from the screened liquid. However, there were several problems with the system. First, only about 35% of the VS in the raw manure and straw passed to the CH_4 fermentor. Thus the effective or overall CH_4 yield for the two-stage system was only 0.11 m^3 CH_4/kg VS fed. Secondly, the maximum VS concentration in the screened liquid (fermentor influent) was about 50 kg VS/m^3, while a more optimum concentration would be between 80 to 90 kg VS/m^3. In comparison, when the solids seperation was not used, the overall CH_4 yield was about twice the overall yield when solids were seperated. Also, higher VS loading rates could be used (14 kg VS/m^3·day vs. 6 kg VS/m^3·day) when solids were not seperated. Thus, this study shows that manure-crop residue solids should not be removed before anaerobic fermentation unless the seperated solids can be used for more profitable purposes than methane, or if treatment of the separated solids can significantly increase its biodegradability.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the technical assistance of Jim Chapman, Lynn Niemann and Dale Schendt.

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TABLE 1. COMPOSITION OF PRODUCT STREAMS AT VARIOUS STAGES OF THE TWO-STAGE FERMENTATION SYSTEM

Constituent[a]	Hydrolysis Tank	Screened Solids	Fermentor Influent	Fermentor Effluent
Total Solids	108.3±9.5	175.1±10.5	60.8±8.9	25.8±5.3
Volatile Solids	88.3±6.0	152.0±10.5	47.3±7.2	16.8±3.6
Fixed Solids	20.0	23.1	13.5	9.0
COD	78.7±9.2	81.7±19.3	64.4±7.3	24.7±3.4
Total Nitrogen	2.63±0.32	2.71±0.35	2.27±0.31	2.21±0.18
Ammonia - N	0.63±0.08	0.58±0.10	0.62±0.10	1.07±0.03
Volatile Acids	6.09±2.43	6.45±1.32	9.26±1.11	0.28±0.16
Alkalinity	--	--	2.02±0.52	6.70±0.38
pH	--	--	4.19±0.13	7.62±0.52

[a] Expressed as kg/m^3 except for pH

TABLE 2. STEADY-STATE PERFORMANCE OF TWO-STAGE FERMENTATION SYSTEM OPERATED AT 53°C and 5-DAY HYDRAULIC RETENTION TIME[a]

Parameter[b]	Trial 1	Trial 2
Total Solids		
Influent	86.1 ± 21.5	77.1 ± 6.0
Effluent	51.0 ± 4.7	46.4 ± 3.1
Volatile Solids		
Influent	70.3 ± 16.1	68.1 ± 5.2
Effluent	38.6 ± 3.7	39.9 ± 3.4
Fixed Solids		
Influent	15.8	9.0
Effluent	12.4	6.5
COD		
Influent	44.7 ± 2.1	50.9 ± 5.6
Effluent	26.2 ± 1.9	29.0 ± 1.7
Total Nitrogen		
Influent	1.71 ± 0.17	--
Effluent	1.46 ± 0.11	--
Ammonia - N		
Influent	0.26 ± 0.04	0.37 ± 0.02
Effluent	0.34 ± 0.02	0.50 ± 0.04
Volatile Acids		
Influent	5.47 ± 0.66	8.12 ± 0.49
Effluent	0.29 ± 0.10	0.26 ± 0.02
Alkalinity		
Influent	1.17 ± 0.36	1.57 ± 0.20
Effluent	3.34 ± 0.05	4.20 ± 0.12
pH, unit		
Influent	4.12 ± 0.14	4.06 ± 0.05
Effluent	7.10 ± 0.08	7.43 ± 0.08
Methane, %	54.8 ± 1.6	52.1 ± 1.9
Methane Production		
m^3/m^3 day	2.49 ± 0.21	2.96 ± 0.11
m^3/kg VS fed	0.18	0.22
m^3/kg VS used	0.39	0.52

[a] Data presented as mean ± 1 standard deviation.
[b] Parameters expressed as kg/m^3 except for CH_4 percent and production.

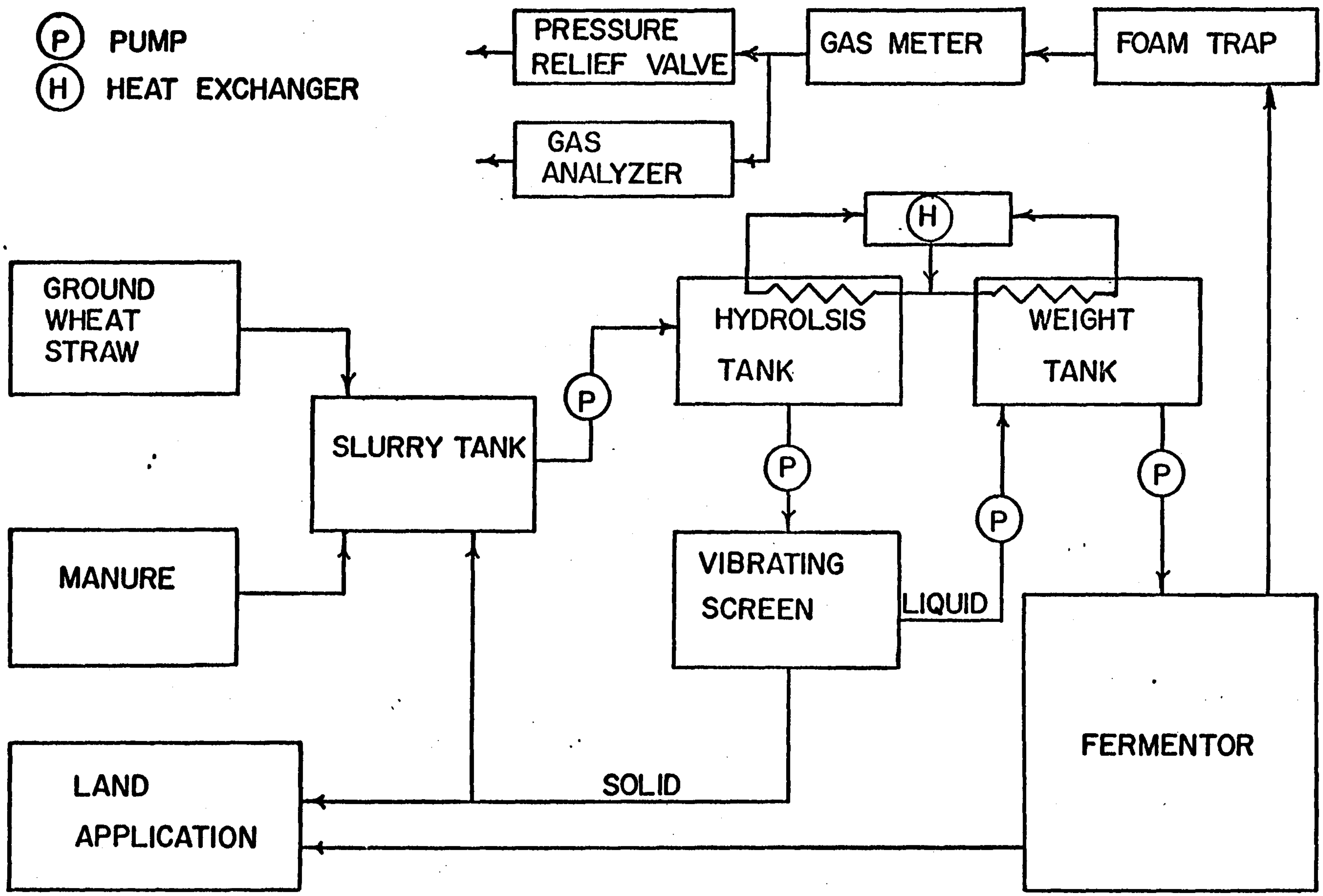


Figure 1. Schematic Diagram of Two-Stage Fermentation System

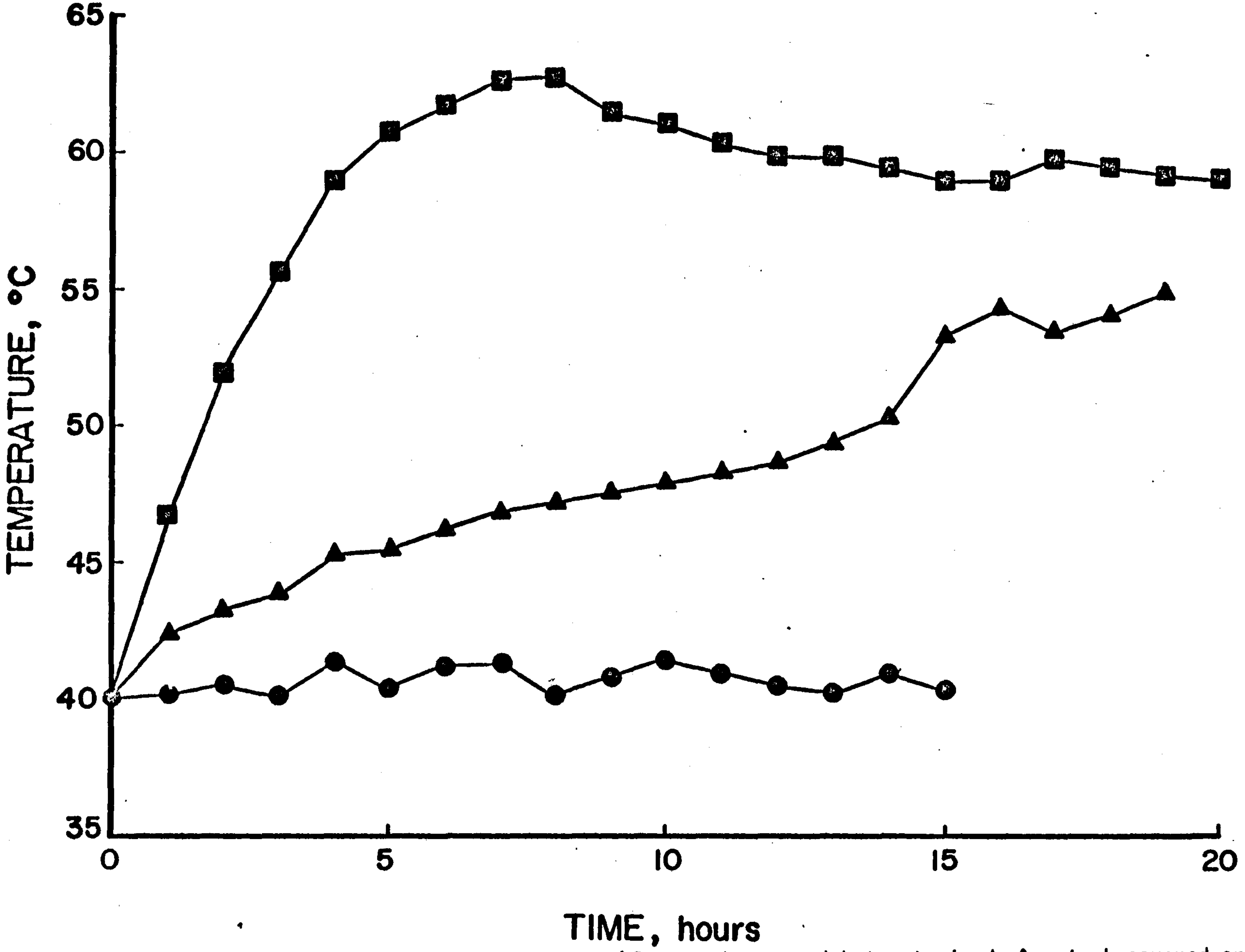


Figure 2. Temperature Profile of Hydrolysis Tank (● - tank covered but not mixed; ▲ - tank covered and mixed; [illegible])

FARM- AND INDUSTRIAL-SCALE
BIOMASS FERMENTATION STUDIES

Quarterly Progress Report for Period 3/15/81-6/15/81

Subcontract XB-1-9397-1

University of Arkansas

Submitted to

Dan Jantzen
Biomass Program Office
Solar Energy Research Institute
1536 Cole Boulevard
Golden, CO 80401

By

J. L. Gaddy
Professor and Head
Department of Chemical Engineering
227 Engineering Building
University of Arkansas
Fayetteville, AR 72701

FARM- AND INDUSTRIAL-SCALE BIOMASS FERMENTATION STUDIES

INTRODUCTION:

The objectives of this project are: (1) Demonstrate the technical and economic feasibility of producing methane by anaerobic digestion of corn stover in farm-scale equipment, and to determine the proper inoculation and agitation procedures for batch fermentation of corn stover; (2) Measure the kinetics and yields of the anaerobic digestion of corn stover in semicontinuous reactors with standard and enhanced cultures.

FARM-SCALE BIOMASS FERMENTATION STUDIES:

Drury Energy and Economic Analysis. The original design was based upon a conversion of 60 percent and was to produce 730 CF methane per day. Operation of the Drury system has demonstrated that a conversion of only 50 percent can be expected when digesting poor quality grasses with standard anaerobic cultures. A yield of 3 CF CH_4 per pound of biomass can reasonably be expected. Utilizing four 4,000 gallon reactors operating on a 60-day cycle, production of 660 CF CH_4 per day or 240 x 10^6 BTU/yr would be expected. Added gas production could be obtained by operation on shorter cycles or by periodic biomass addition during the latter stages of a cycle.

Table 1 provides a summary of the energy balance. Building heating consumes 12.5 percent of the methane produced. Exhaust heat from the engine generator provides the needed heat except during the winter months. Reactor agitation, biomass grinding and lighting requires another 12.5 percent. The net energy production is 180 x 10^6 BTU per year or 75 percent of the total.

Table 2 gives the capital cost for equipment to produce a net quantity of 180,000 CF CH_4 per year. The cost of the Drury system is shown as well as the

Table 1. SUMMARY OF ENERGY BALANCE

ITEM	AMOUNT	
	10^6BTU/yr	Percent of Total Production
Production (CH_4)	240	100
Consumption		
Building Heating (CH_4)	30	12.5
Agitation (Elec.)	10	4
Grinding (Elec.)	7	3
Lighting (Elec.)	13	5.5
Total	60	25.0
Net Production	180	75

Table 2. CAPITAL COSTS OF FARM ENERGY SYSTEM

Equipment/Materials/Labor	Drury System	New System
4 steel tanks (8'x12')	$ 100	$4,300
4 pneumatic cylinders	2,100	2,100
Air compressor, 5 hp	1,200	1,200
7.5 kw generator/engine	1,600	2,800
Gas storage bags	1,000	1,000
Biomass grinder/motor	available	1,200
Building materials (24'x40')	2,000	2,500
Building heater	300	300
Piping, valves, agitators	1,000	1,800
Labor (specialized)	800	1,000
	$13,100	$18,200

1981 cost for new facilities. The total cost for a new installation is $18,200, or about $5,100 more than the cost at Drury.

The operating costs of the farm energy system include capital charges, maintenance, supplies and biomass. Labor for the operation is assumed to be furnished by the farmer. Maintenance should be minimal and only maintenance materials are included. Lime for neutralization is included with supplies.

Table 3 provides a summary of the system operating costs. A new system is assumed, with a capital cost of $18,200. The costs for methane and electricity are shown separately so that comparisons with present energy prices can be made. Investments of $15,200 and $3,000 are used for the methane and electricit systems, respectively. The economics for this case assume that the biomass raw material is available on the farm and can be collected at no charge. Interest is charged at 8 percent, and tax credits include depreciation (10 years, straigh line), tax deductions on interest and the 40 percent energy equipment tax refund. With an income tax rate of 25 percent, the tax credit for depreciation is 2.5 percent per year and the tax credit for interest payments is 25 percent of the interest rate. If the tax refund is assumed to be spread over 10 years, the annual credit is 4 percent, making a total credit of 8.5 percent, with an 8 percent interest rate.

The annual cost of methane is $340 or $1.89 per million BTU. Electricity costs are $420 per year or $0.04 per kwh. The present price of propane is $8.11 per million BTU, and today's cost of electricity in the quantities used is about $0.10 per kwh.

Table 4 presents a more conservative economic analysis. Biomass is charged at $10 per ton, or the cost of baling in large round bales. Capital charges are based on 12 percent per year, and tax credits increase to 9.5 percent per year. Other costs are the same as for Case I. The gas cost for this case is $6.67 per million BTU and the cost of electricity is $0.13 per kwh.

Table 3. OPERATING COST ANALYSIS

Case I: Biomass - No Charge, 8 Percent Interest

Cost Item	Annual Cost $/yr
A. Methane (180 MCF/YR)	
Biomass (40 T)	-
Supplies	120
Maintenance	300
Capital Charges (8%)	1,220
Tax Credits (8.5%)	-1,300
Total	340
Methane Cost	$1.89/10^{6}BTU
B. Electricity (10,540 KWH/YR)	
Methane ($1.89/MCF)	340
Maintenance	100
Capital Charges (8%)	240
Tax Credits (8.5%)	-260
Total	420
Electricity Cost	$0.04/kwh

Table 4. OPERATING COST ANALYSIS

Case II: Biomass - $10/Ton, 12 Percent Interest

Cost Item		Annual Cost $/yr
A. Methane (180 MCF/YR)		
Biomass (40 T)		400
Supplies		120
Maintenance		300
Capital Charges (12%)		1,820
Tax Credits (9.5%)		-1,440
	Total	1,200
Methane Cost		$6.67/10^{6}BTU
B. Electricity (10,540 kwh/yr)		
Methane ($6.67/MCF)		1,200
Maintenance		100
Capital Charges (12%)		360
Tax Credits (9.5%)		290
	Total	1,370
Electricity Cost		$0.13/kwh

The energy system could be operated at a significant profit ($1,100 per year for methane) based upon no charges for the biomass and with low interest rates. Even with a more conservative approach, the system would operate at a nominal profit. These economics are especially promising when considering escalating energy costs.

Reduction of the capital costs could be achieved by utilizing shorter batch cycle times. The data of this study indicate that cycle times of thirty days may be optimal and would reduce the required reactor volume by about one-half. The biomass utilization would increase, but only slightly, since conversion is improved only marginally during the last 30 days of the cycle. Only two reactors would be needed to realize a steady gas production rate. The use of two reactors would reduce the investment in Table 2 to $12,000 (34 percent reduction) and would have an attendant influence on the cost of gas and electricity.

Farm Energy System Design. The design for a new farm energy system has been completed. This facility is to be located at the University of Arkansas Engineering Experiment Station on the Fayetteville campus. A portion of an existing concrete block building will be utilized.

The system will consist of four 3,000 gallon reactors, as shown in Figure 1. Two reactors will be agitated mechanically and two will be agitated with liquid recirculation. Biomass will be ground and fed to the reactors with a screw auger. Gas will be stored in PVC bags located on a second level.

The system is designed to produce 500 CF CH_4 per day. A 7.5 kw generator will be provided to operate on biogas. Exhaust gases from the engine will be used to maintain the 24' x 43' room at 95°F. This facility is expected to cost about $20,000.

Laboratory Agitation and Inoculation Studies. Laboratory batch reactors to study agitation requirements and inoculation procedures for corn stover digestion have been operated through the second 60-day cycle. First-cycle cultures

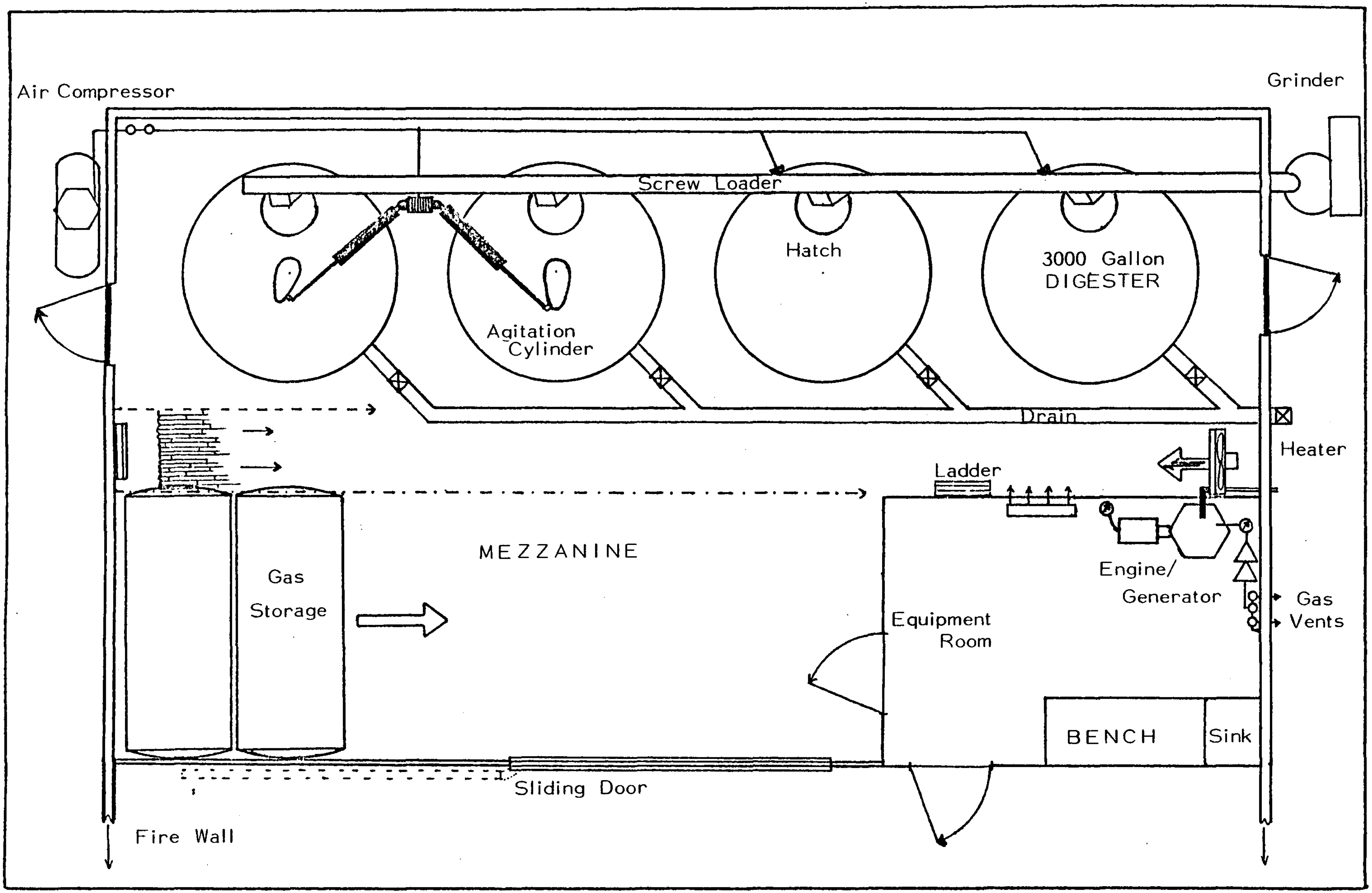


Figure 1. SCHEMATIC OF EXPERIMENTAL DIGESTER FACILITY

were agitated mechanically for periods varying between 10 and 90 minutes per day. Conversions were 25-30 percent and no advantage was apparent with frequent agitation.

The performance of second-cycle cultures is shown in Figures 2-5. These cultures utilize a 5 percent mixture of corn stover and were inoculated with slurry from the first cycle in a ratio of 4:1. Figure 2 shows a culture without agitation. Peak gas production is .007 l/g-d occurring after two weeks. Conversion was 27 percent after eight weeks.

Figure 3 shows the performance of a culture agitated 10 minutes per day continuously. Peak gas production was .013 l/g-d and the conversion reached 32 percent. Figure 4 represents a culture agitated continuously. Peak gas production and conversion were identical to the frequently agitated reactor. Although there is considerable variation in the performance of the cultures, infrequent agitation (10 min/day) appears to be the proper agitation level.

The data for a culture enhanced with *Clostridium butyricum* are shown in Figure 5. This reactor was agitated 30 minutes per day. Peak gas production of .17 l/g-d occurred during the first week and conversion was 56 percent after 8 weeks. Considerable enhancement of the performance of batch cultures appears possible, which agrees with the prior results with continuous cultures.

Difficulties have been experienced with air leakage in the liquid and gas recirculation agitation systems. Suitable cultures have not been established utilizing these methods of agitation.

INDUSTRIAL-SCALE FERMENTATION STUDIES:

It has been shown that the standard continuous cultures could be enhanced by the introduction of certain microorganisms. *Clostridium butyricum* was found to increase the first-order reaction rate constant by 20 percent.

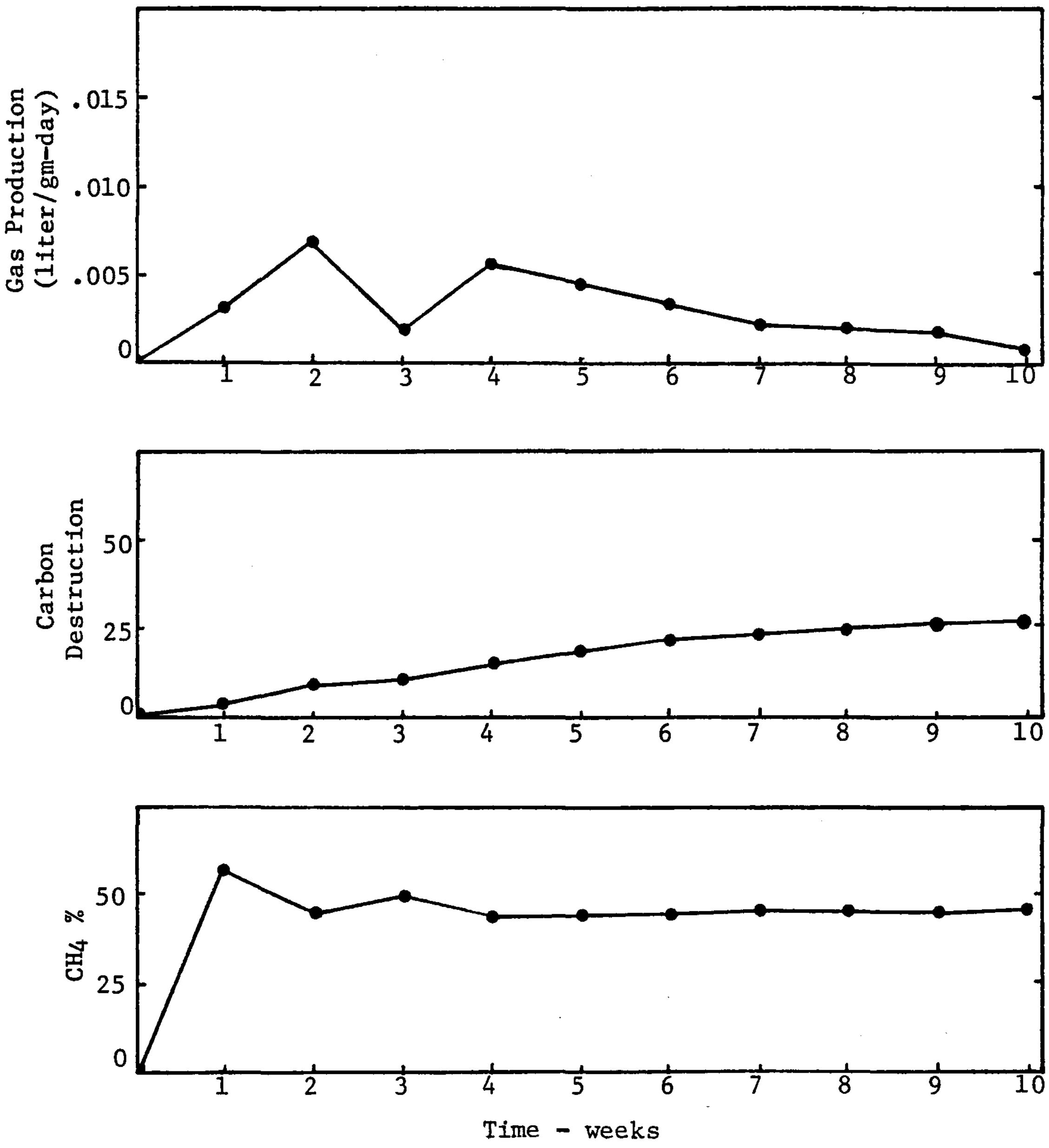
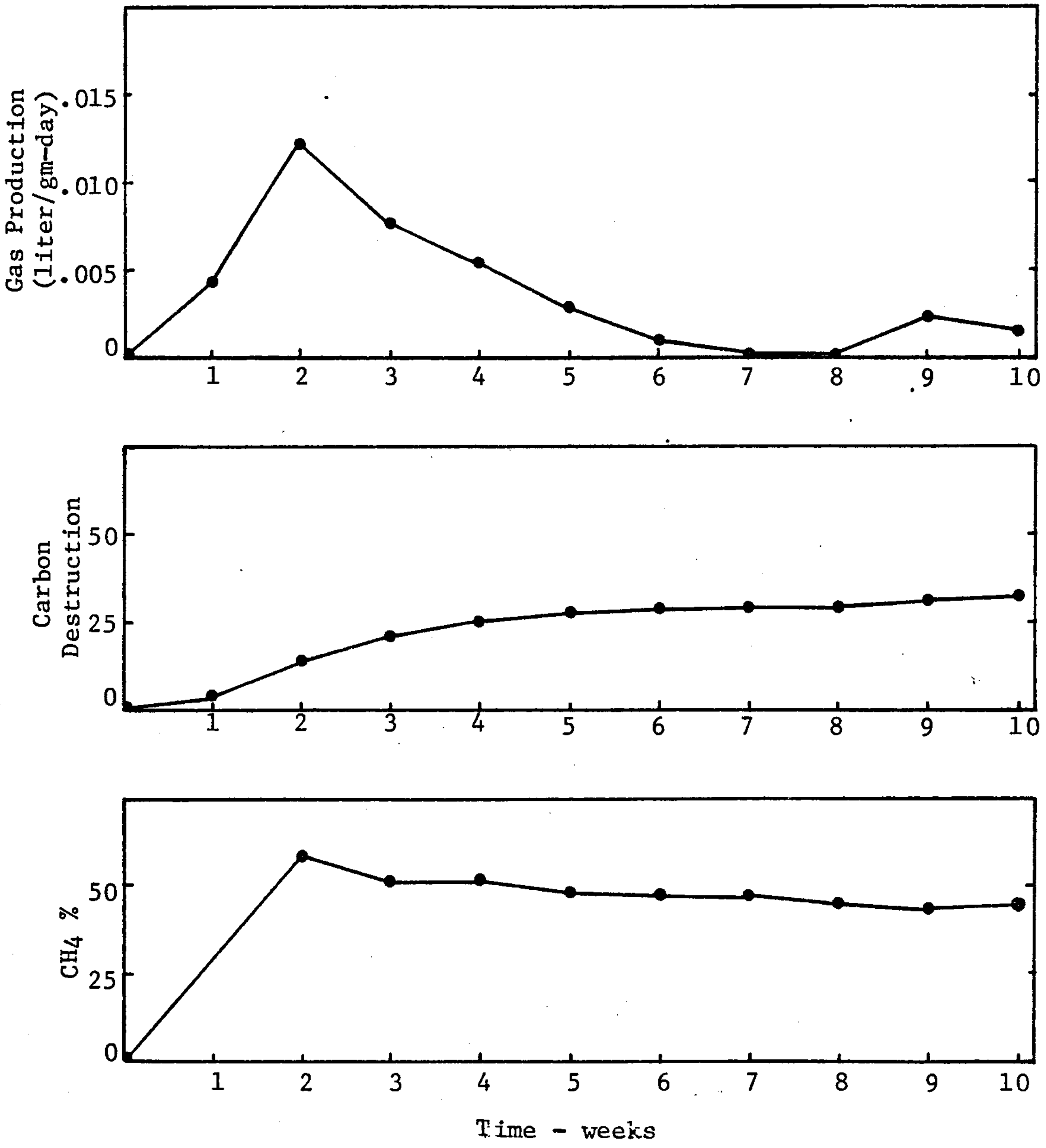


Figure 2. BATCH CORN STOVER CULTURE
Without Agitation



Ficure 3. BATCH CORN STOVER CULTURE
Agitated 10 min per day

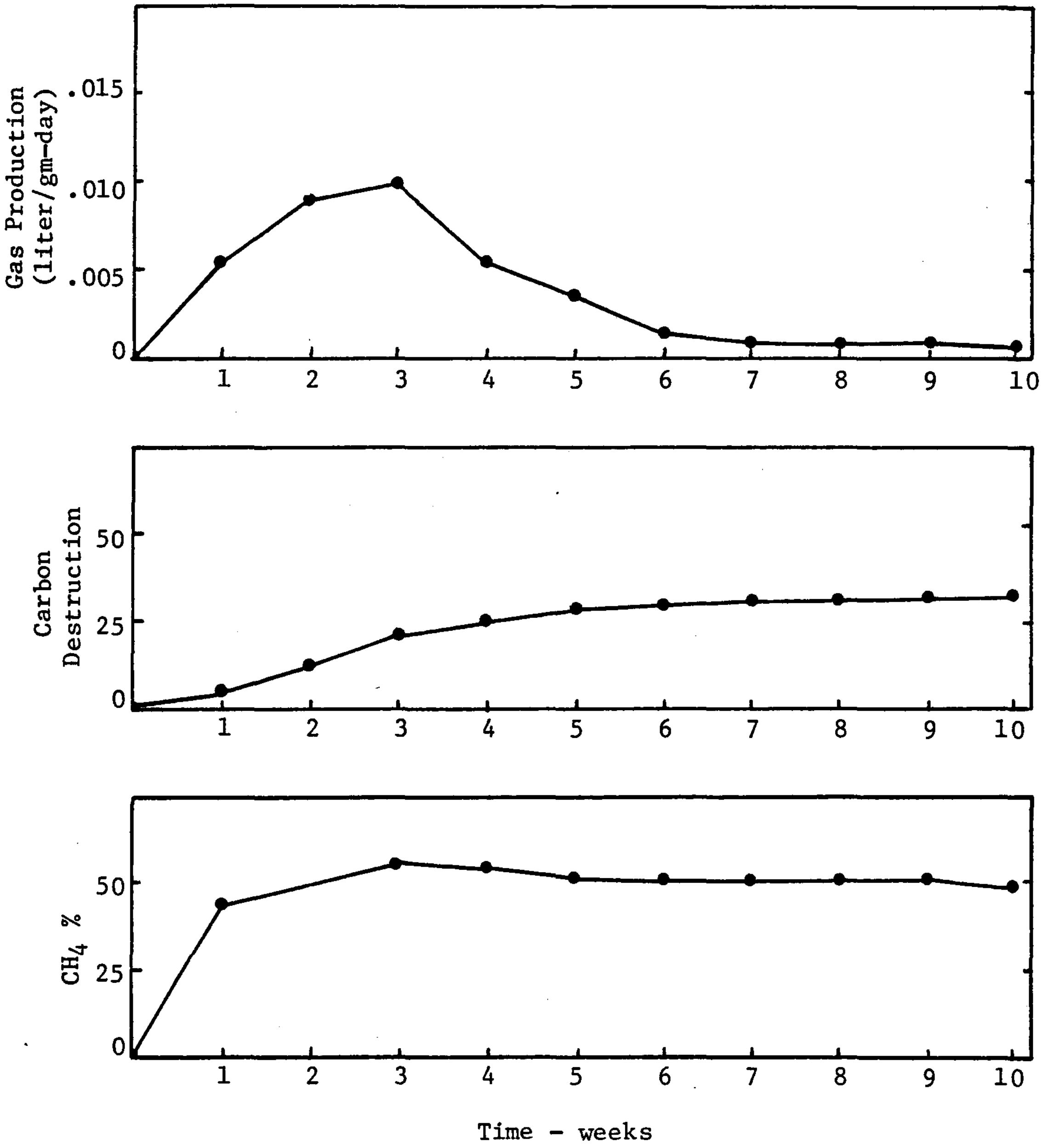


Figure 4. BATCH CORN STOVER CULTURE
Agitated Continuously

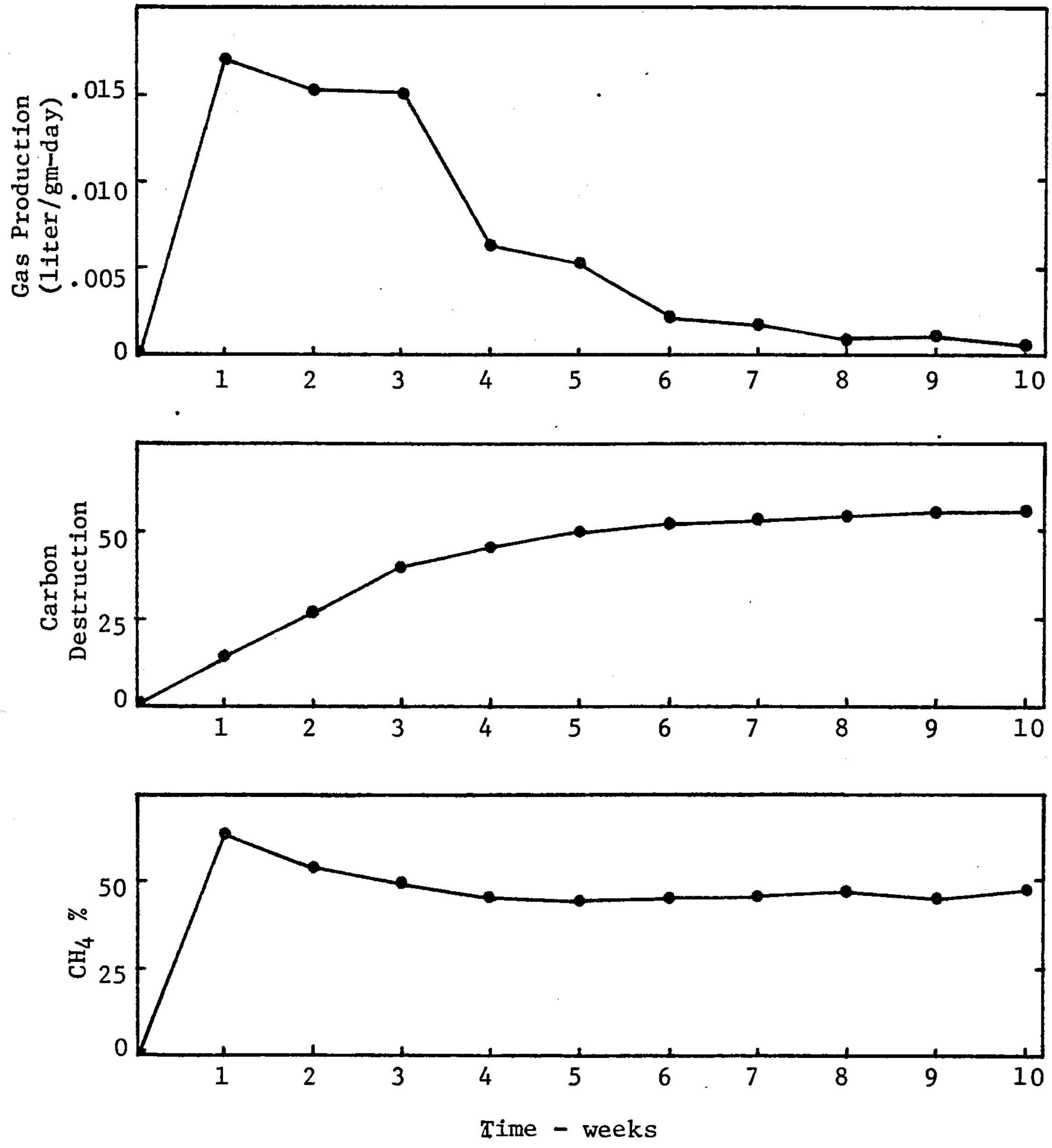


Figure 5. BATCH CORN STOVER CULTURE
Enhanced with C. butyricum

A further series of batch experiments has been made with other microorganisms. These microorganisms are summarized in Table 5. This group of microorganisms all utilize sugars to produce acetic acid, CO_2 and H_2. Culture bottles containing 190 ml of 5 percent corn stover were inoculated with 2.5 ml of the slant grown cultures suspended in saline and 10 ml of effluent from a standard anaerobic culture. Gas production rates and concentrations were measured.

Table 5 compares the final volumes of methane produced after 5 weeks with the standard containing no pure culture. Figure 6 shows the weekly methane production rates. In all cases, the gas production was enhanced. Production rates of the enhanced cultures were faster than the standard during the first three weeks. The *Enterobacter aerogenes* and *Bacillus cereus* var. *mycoides* continued at the same accelerated rate through 5 weeks and resulted in 26 percent (5 percent/week) more methane production. Further batch and continuous culture experiments will be conducted with these and cellulolytic microorganisms.

Table 5. RESULTS OF BATCH FERMENTATION OF CORN STOVER WITH ENHANCED CULTURES

MICROORGANISM	METHANE PRODUCTION % of Standard
None	100
Bacillus cereus	117
Escherichia coli	119
Enterobacter aerogenes	126
Bacillus cereus var. *mycoides*	126

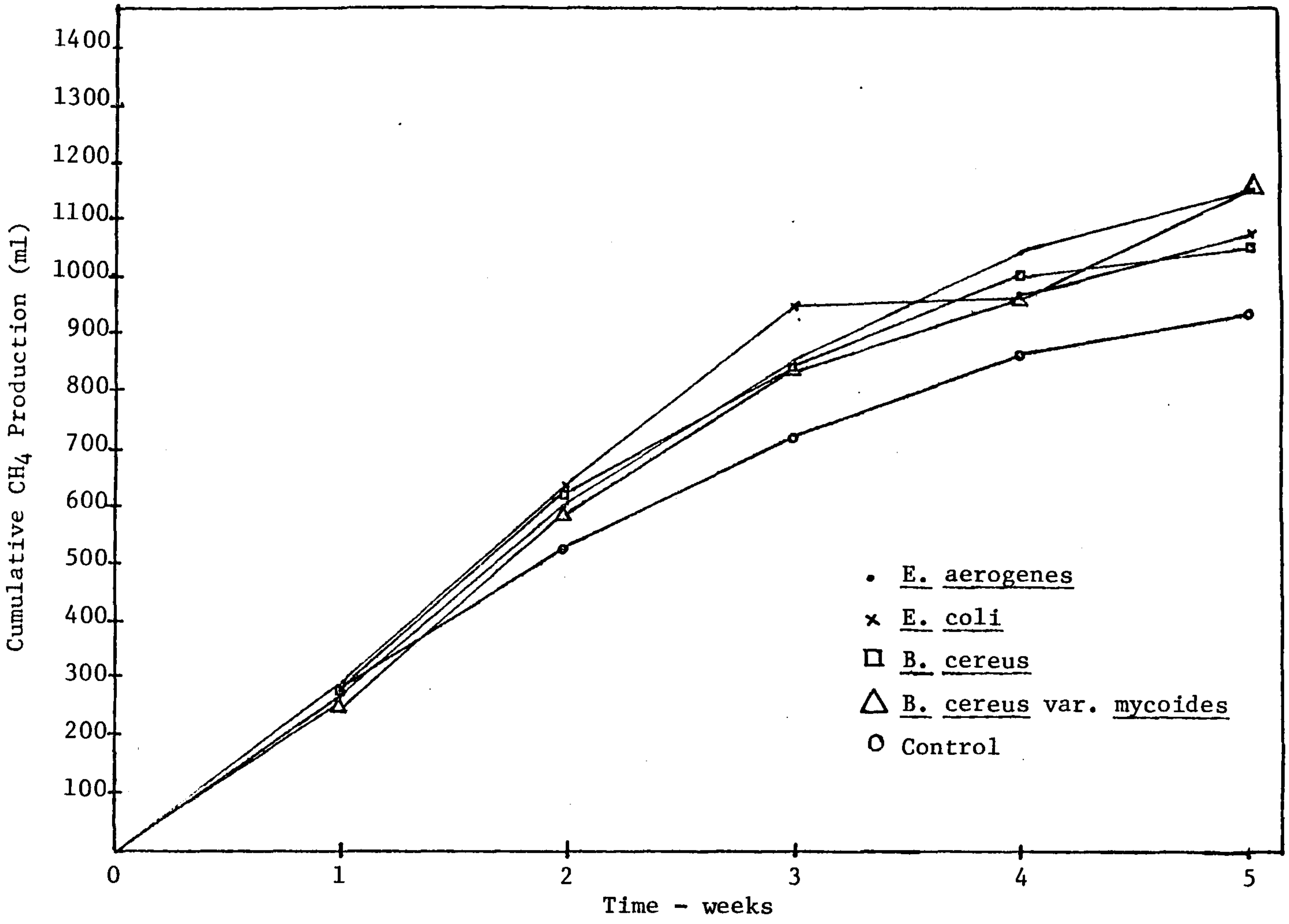


Figure 6. PERFORMANCE OF BATCH CORN STOVER REACTORS

ETHANOL-METHANE COMPARATIVE STUDY

Progress Report for
20th Quarterly Coordination Meeting

Subcontract NR-9-8175-1
Dynatech Project No. SLR-4-5
Dynatech Report No. 2150

Submitted to:

Dan Jantzen
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

Submitted by:

E. Ashare
A.P. Leuschner
C.E. West

June 23, 1981

Dynatech R/D Company
Dynatech Corporation
99 Erie Street
Cambridge, MA 02139

617-868-8050

Objective

There are a number of biological processes for conversion of crop residues to energy. The better known processes are anaerobic digestion to produce methane and fermentation to produce ethanol. There are significant differences between these processes in terms of net energy production capital and operating costs, and values of products and by-products. The objective of this analysis is to assess the relative merits of the various bioconversion processes for energy production from crop residues, including both a technical and an economic evaluation

Results

This technological assessment of energy from crop residue is divided into two distinct areas. One area includes anaerobic digestion to . methane and the other area includes fermentation to alcohol. In each area, two typical processes were chosen as representative of the current state of the technology.

Biomass

The biomass source for this analysis will be agricultural crop residues. The primary residue to be considered will be corn stover. Other residues which will be considered in the analysis are wheat straw and rice straw. The compositions of these biomass sources are presented in Table 1. The quantity of biomass to be considered is that which would be available from 100 small farms (of 400 acre average size). This would give sufficient residue to provide 200 tons per day of corn stover for the process.

Anaerobic Digestion

The two anaerobic digestion processes for methane production are a batch and a continuous process. The batch process is based on the recent high solids digestion results of Jewell. A flow sheet for this process, as described by Jewell, is presented in Figure 1. The process consists of premixing crop residue, inoculum, and buffer and placing this substrate in a batch digester at high solids loading. Three cycles per year (i.e., three batches) could be run, depending on the digestion conditions and desired conversion. Jewell's process also includes means for intitial heating of the biomass, gas collection and purification, CO_2 by-product recovery, and residue drying.

The second anaerobic digestion process which is included in this analysis is a continuous process based on Gaddy's work. Gaddy has shown that mesophilic digestion of corn stover can give high yields when operated at long retention times. His proposed process, Figure 2, consists of four anaerobic digesters operating in series. This type of process approaches a plug flow design in performance. Also included in the design are means for heating, buffer addition, gas purification, and solids dewatering.

The next phase of this study will include development of detailed designs of these anaerobic digestion processes inlcuding material and energy balances and estimates of capital and operating costs.

Ethanol Fermentation

The two ethanol fermentation processes considered in this analysis differ primarily in the method of hydrolysis. One approach is the MIT process which uses enzyme hydrolysis. The other process incorporates acid hydrolysis.

A flow sheet for the MIT process is shown in Figure 3. The primary feature of this process is that hydrolysis and fermentation occur simultaneously in the same fermenter at 140°F by using a mixed culture of Clostridium thermocellum and C. thermosaccharolyticum. This bacterial process has the advantage that it can convert both the pentoses and hexoses to ethanol whereas a yeast fermentation can convert only the hexoses. The process also includes feed preparation (milling and screening), distillation, methane production from the stillage by anaerobic digestion, and filtration to recover solids which can be used as boiler fuel.

The acid hydrolysis ethanol fermentation process is presented in Figure 4. This is based on a design proposed by Chem Systems. It consists of acid hydrolysis (5% H_2SO_4) in a plug flow reactor followed by a second milder (1% H_2SO_4) acid hydrolysis. The solubles are fermented to alcohol with S. cerevisiae for one hour in a batch operation. (Three fermenters are used in the design, with two always in operation, while the third is down for sterilization.) The dilute beer from fermentation is distilled to the azeotropic mixture, which is followed by an azeotropic distillation with benzene. The process also includes filtration steps, acid neutralization, and CO_2 and yeast by-product recovery.

The next phase of the analysis will include development of detailed process flow sheets, including material and energy balances, and an economic analysis of each of these ethanol fermentation technologies.

Process Output

Preliminary material balances have been performed to determine the potential energy output from each process. These results are presented in Table 2.

Table 1

Characteristics of Selected Residues (all data expressed as percent of dry weight)(a)

RESIDUE	TOTAL SOLIDS (%)	VOLATILE SOLIDS	ASH	CELLULOSE	HEMI-CELLULOSE	LIGNIN	LIPIDS	PROTEIN	C	H	N	O
CORN STOVER	53.0	95	4.3 - 4.88	32.0 - 40.0	28.34	8.71 - 15.1	1.41	3.77				
WHEAT STRAW	72.0	89 - 96	4.3 - 11.0	50.0		8.02 - 18.0	1.25	2.71	43.0 - 53.4	4.2	0.988 - 4.5	44.0
BARLEY STRAW	91.0	89 - 95	5.5 - 10.8	52.7	29.2	13.8 - 15.5			43.0	6.0	0.5	45.0
RICE STRAW	80.0	80 - 85	15.5 - 19.1	32.1 - 38.0		3.7 - 12.5	2.41	4.5 - 5.1	38.5	5.7	0.5	39.8
BAGASSE	51.0	98.0	2.0	47.8	29.2	19.3			48.2	6.7		45.1

(a) Several sources used in development of this table:

Lipinski, et. al., 1977
Stephens and Heichel, 1975
Gikis, et.al., 1978
Wilke, et. al., 1979
Callihan and Dunlap, 1971
Fonnesbeck and Harris, 1972
Sarma, 1976
Fong, 1978
Virkola, 1975
Dobie and Garrett, 1972
Walker, 1972
Garrett, et. al.
Han, 1975

Table 2

POTENTIAL ENERGY OUTPUT

Process	Energy Output	
		MM Btu/Yr
Anaerobic Digestion to Methane		
Batch (based on Jewell's results)	426,000 MCF/yr	426,000
Continuous (based on Gaddy's results)	528,000 MCF/yr	528,000
Ethanol Fermentation		
Acid Hydrolysis (Chem Systems design)	3.7×10^6 gal EtOH/yr	311,000
Enzyme Hydrolysis (MIT process)	5.1×10^6 gal EtOH/yr	437,000

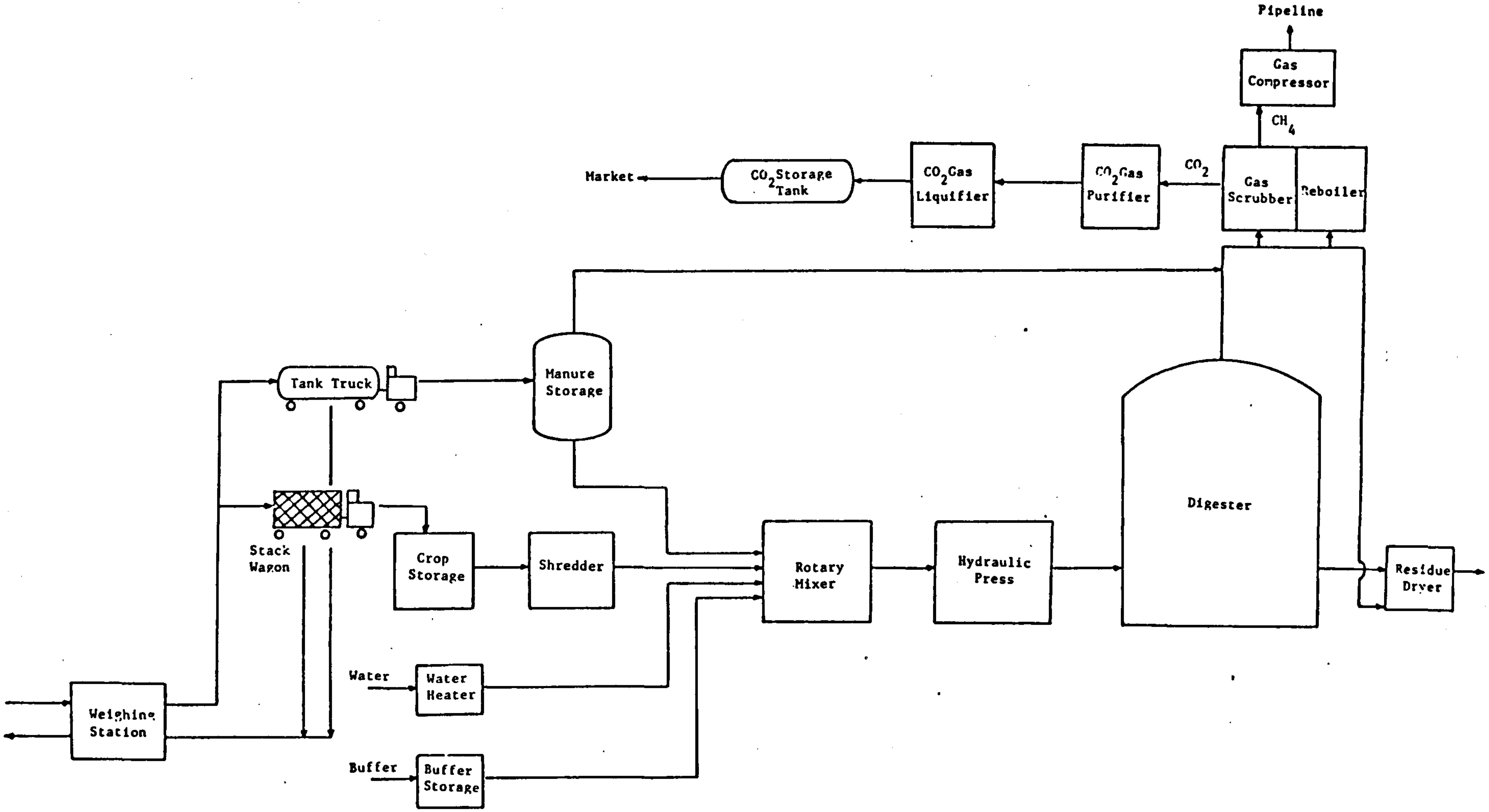


Figure 1

PROCESS FLOW SHEET FOR AN ANAEROBIC BATCH DIGESTION SYSTEM FOR METHANE PRODUCTION FROM CROP RESIDUES

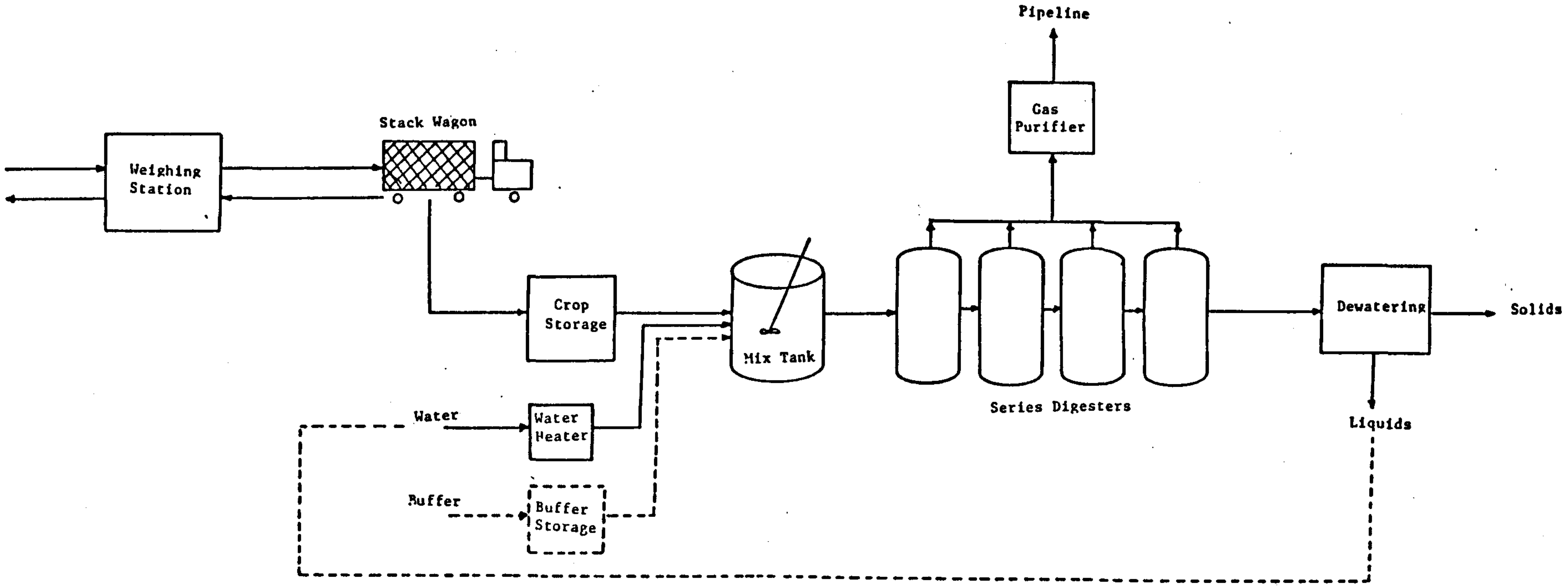


Figure 2

PROCESS FLOW SHEET FOR AN ANAEROBIC CSTR SERIES DIGESTION SYSTEM FOR METHANE PRODUCTION FROM CROP RESIDUES

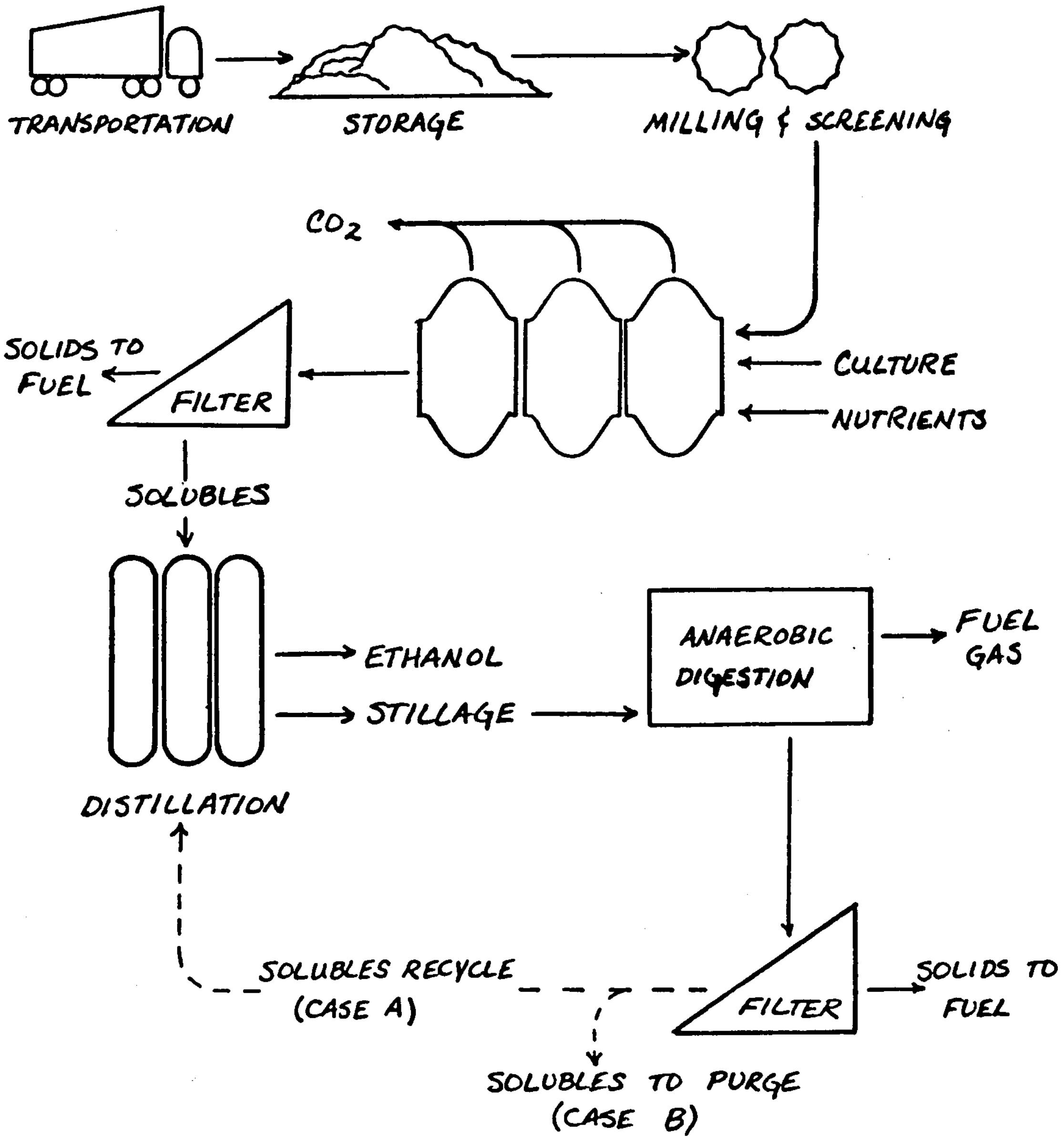


Figure 3

PROCESS FLOW SHEET FOR MIT ETHANOL FROM CORN STOVER PROCESS

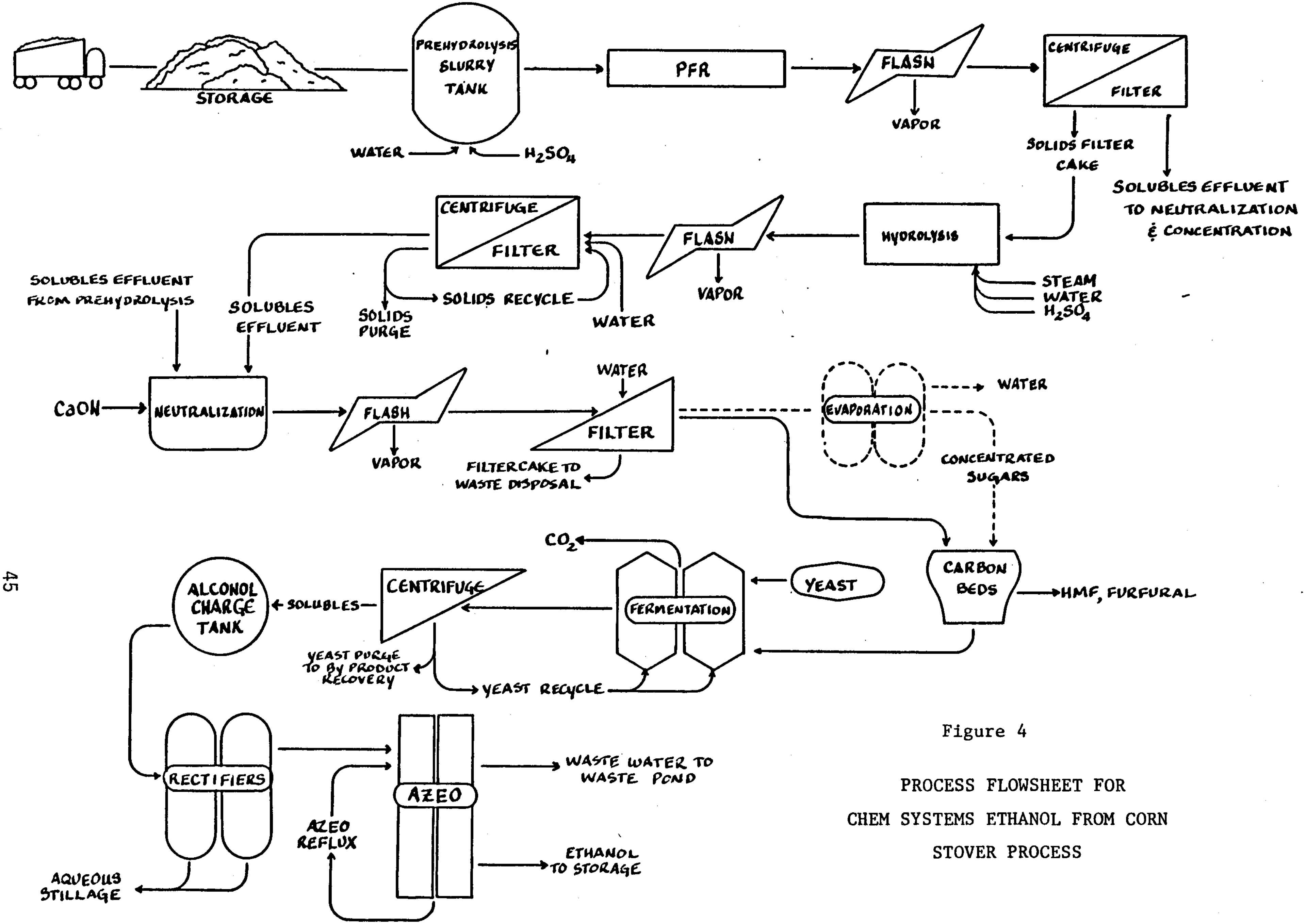


Figure 4

PROCESS FLOWSHEET FOR
CHEM SYSTEMS ETHANOL FROM CORN
STOVER PROCESS

JUNE 1981

Quarterly Progress Report

NUTRITIONAL STIMULATION OF METHANE BACTERIA

Drexel University

R. E. Speece
Gene F. Parkin
Daniel Gallagher

S.E.R.I. Subcontract XB-9-8334-1

NUTRITIONAL STIMULATION OF METHANE BACTERIA

In the last progress report, reference was made to a change in procedure, whereby Supplemented Acetic Acid was fed instead of straight glacial acetic acid. The Supplemented Acetic Acid has the following composition:

500 ml	HAc
15 gm	NH_4Cl
2 gm	$MgSO_4 \cdot 7\ H_2O$
10 mg	$NiCl_2$
250 mg	$FeCl_2$
10 mg	$CoCl_2$

This was then diluted to one liter with the standard Drexel Nutrient Media.

The rationale for use of the Supplemented Acetic Acid was to overcome the previously noted deficiencies in nitrogen, sulfur and nickel. It is realized that phosphorus should be included, but precipitation problems forced us to add phosphorus directly to the digesters rather than include it in the Supplemented Acetic Acid.

The 20 gang-automated pH Stats utilize a common feedstock of Supplemented Acetic Acid to maintain the appropriate volatile acids concentration. This is not the case with all of the seven individual pH Stats (1A-7A). Results of studies using these pH stats will be described in this report.

As reported in the last quarterly report, an individual pH Stat was set up with 100% inoculum seed. The background acetate utilization rate was approximately 2500 mg/ℓ-day. However, after about 3 weeks, the acetate utilization rate rapidly increased to 10,000 mg/ℓ-day in a period of one week. At this point the volatile suspended solids (VSS) was 1250 mg/ℓ, resulting in a k of 8 day^{-1}. Unfortunately a feed tube in the reactor broke causing overfeeding and resulting in the pH dropping to less than 4.

At this point, the contents of that pH Stat were dumped and reseeded with 100% inoculum with 3 gm/ℓ of $(NH_4)HCO_3$ added to increase the alkalinity so that the volatile acids concentration could be maintained near 2000 mg/ℓ without the pH dropping below 6.6.

The acetate utilization rate for this pH stat is plotted in Fig. 1. Here again the acetate utilization rate started off at about 2500 mg/ℓ-day. Since the VSS was approximately 800 mg/ℓ, k was approximately 3 day^{-1}. Then, after approximately 2 weeks, the acetate utilization rose to above 10,000 mg/ℓ-day within a week. At this point in time the VSS had risen to about 3600 mg/ℓ, resulting in a k = 2.8 day^{-1}. In this 21 day interval the accumulative acetate utilization was about 120 gm/ℓ (Fig. 2). The increase in VSS was (3600-800) 2800 mg/ℓ, yielding a net synthesis of 2.3%. It would be expected that 42 mg/ℓ of P (VSS/66) would be incorporated in 2800 mg/ℓ VSS. However, the system had no more than 20 mg/ℓ present in the inoculum and only 6 mg/ℓ was added on Day 19. The acetate utilization rate held at about 10,000 to 12,000 mg/ℓ-day for 16 days, then declined progressively to the background rate. Another slug addition of 12 mg/ℓ of P on Day 57 was followed by a temporary peak of about 8500 mg/ℓ-day acetate utilization. For a second time, we were able to take the inoculum from a background acetate utilization rate of about 2500 mg/ℓ-day and show an increase to over 10,000 mg/ℓ-day by feeding Supplemented Acetic Acid.

A third attempt was made to duplicate this rapid increase in acetate utilization after about two weeks in an individual pH Stat being fed Supplemented Acetic Acid. A reactor was seeded with 100% inoculum plus 3 gm/ℓ $(NH_4)HCO_3$ for additional alkalinity. Once again, after about two weeks,

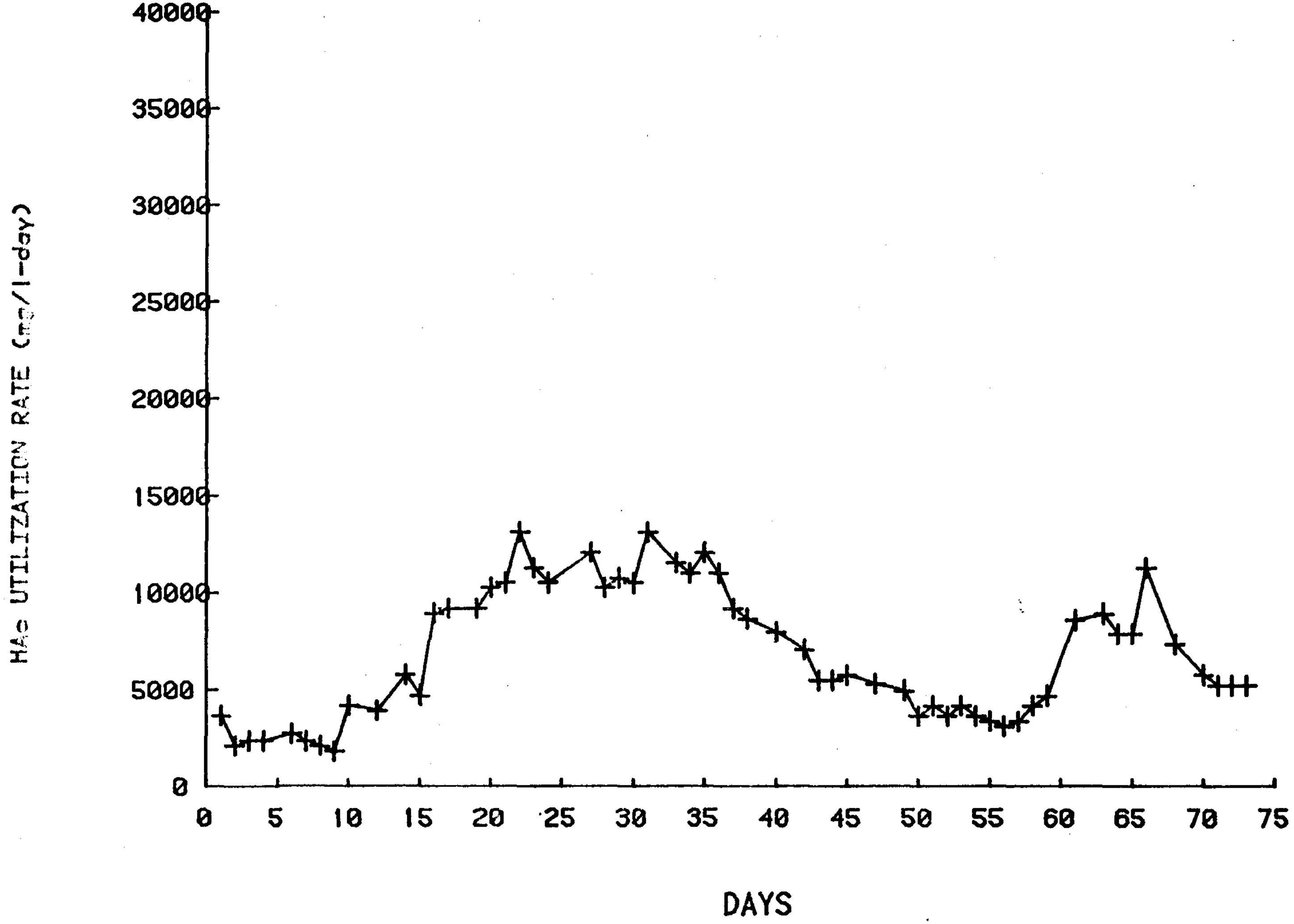


FIG. 1 Acetate Utilization Rate Using Supplemented Acetic Acid - 7A

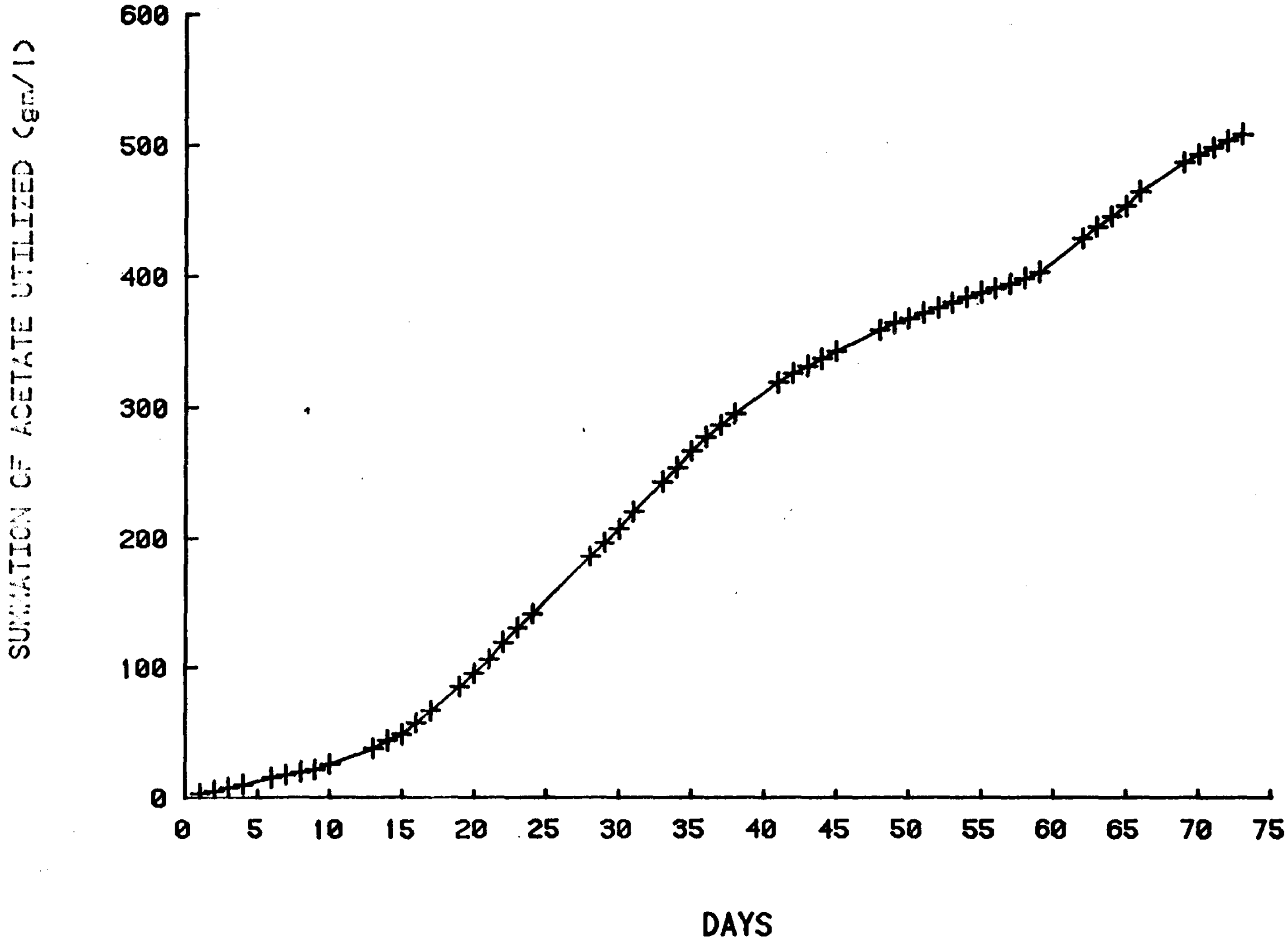


FIG. 2 Cumulative Acetate Utilization - 7A

the acetate utilization rate rapidly increased from a background rate of about 3000 mg/ℓ-day to 18,000 mg/ℓ-day over a week's period of time as shown in Fig. 3. At this point, acetate utilization abruptly decreased to zero due to biofouling of the pH electrode. In the process of cleaning the pH electrode, the volatile acids were accidentally increased to over 4000 mg/ℓ. The pH dropped to 5.8 and gas production did not resume. There was a preliminary indication that the alkalinity was being consumed because the equilibrium volatile acids concentration decreased without a change in the pH setting.

Accumulative acetate utilization by Day 21 was 85.5 gm/ℓ (Fig. 4) with VSS of 2400 mg/ℓ. The net synthesis rate was 1.9% and the maximum k was 6.2 day^{-1}. Predicted phosphorus uptake would have been 24 mg/ℓ.

A fourth attempt was made to confirm the three previous cases in which the acetate utilization rate abruptly increased after about two weeks in an individual pH Stat being fed Supplemented Acetic Acid. These results are shown in Fig. 5. The acetate utilization rate hovered around 4000 mg/ℓ-day for a month but never showed the thrice replicated rapid increase in acetate utilization rate.

The stimulatory effect of adding 100 mg/ℓ-day of yeast extract to an individual pH Stat being fed Supplemented Acetic Acid was also assayed. The yeast extract was added daily as a slug. The results are shown in Fig. 6. The initial acetate utilization rate was about 4000 mg/ℓ-day. From the very beginning, this rate increased gradually until it temporarily peaked at 10,000 mg/ℓ-day by Day 15. For some unknown reason the rate abruptly dropped to 3400 mg/ℓ-day, but then exponentially increased to 28,000 mg/ℓ-day after 9 days. Once again the rate temporarily dropped to 11,000 mg/ℓ-day due to acetate limitation. Apparently the alkalinity was being consumed so

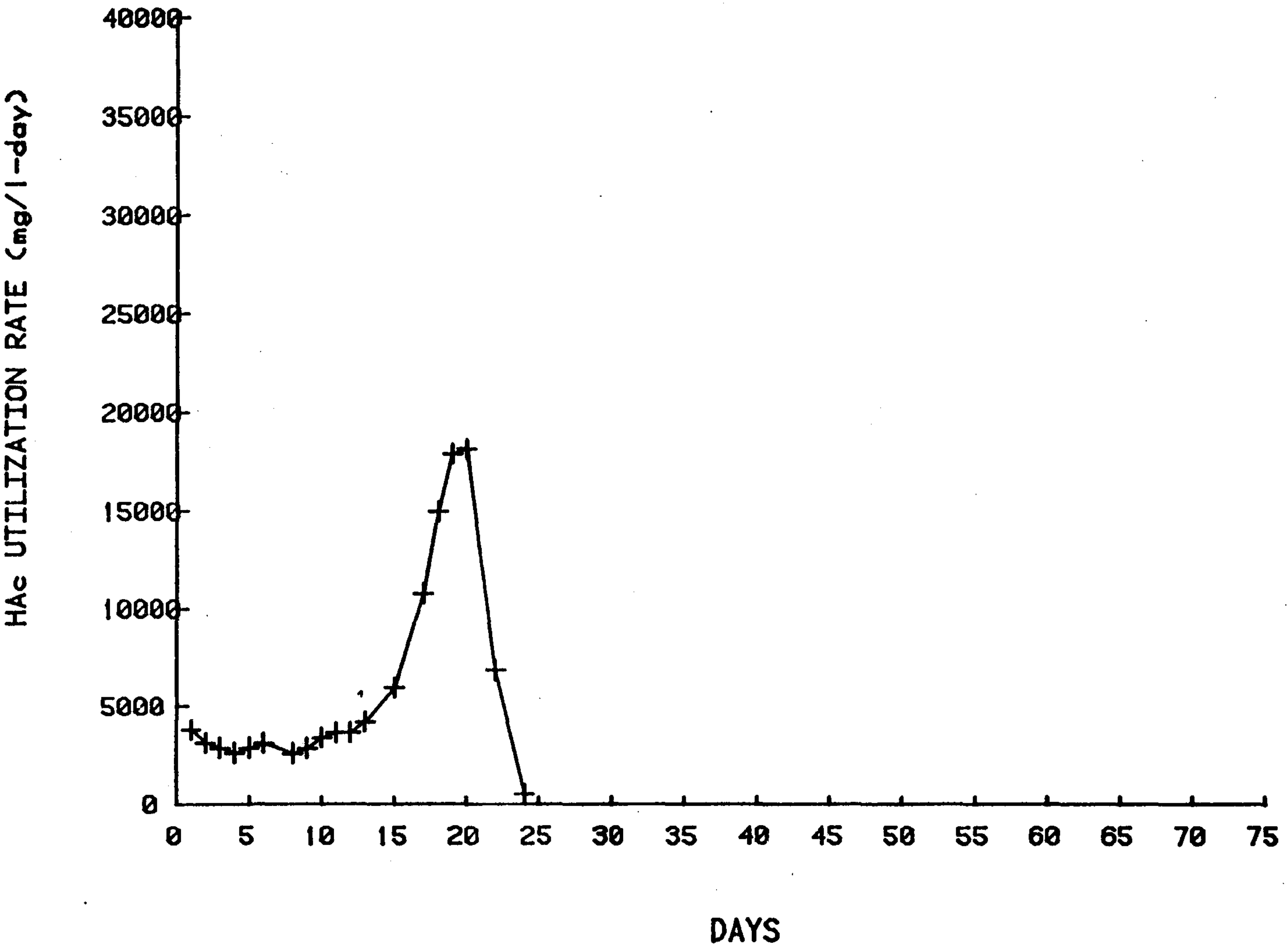


FIG. 3 Acetate Utilization Rate Using Supplemented Acetic Acid - 1A

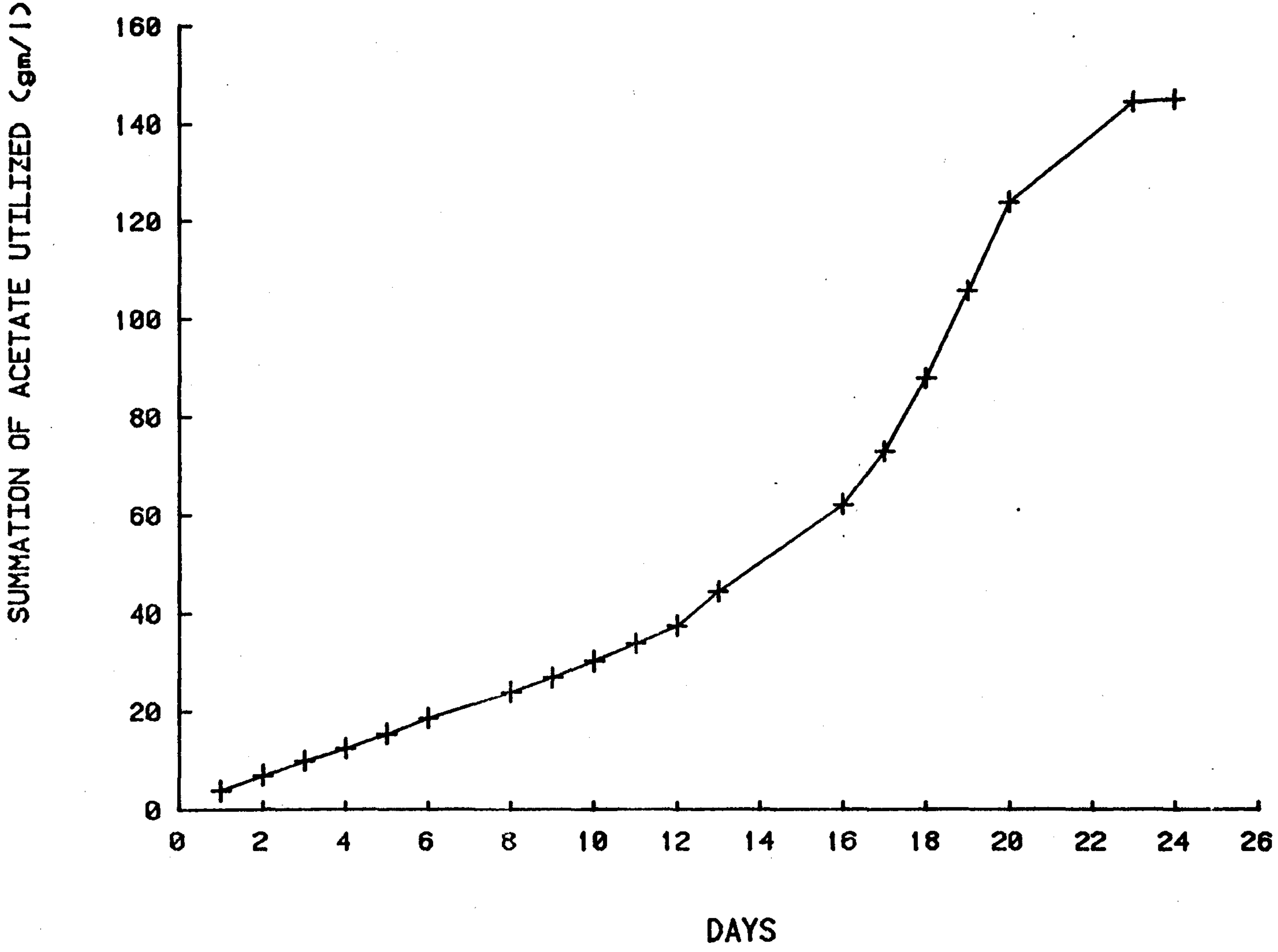


FIG. 4 Cumulative Acetate Utilization - 1A

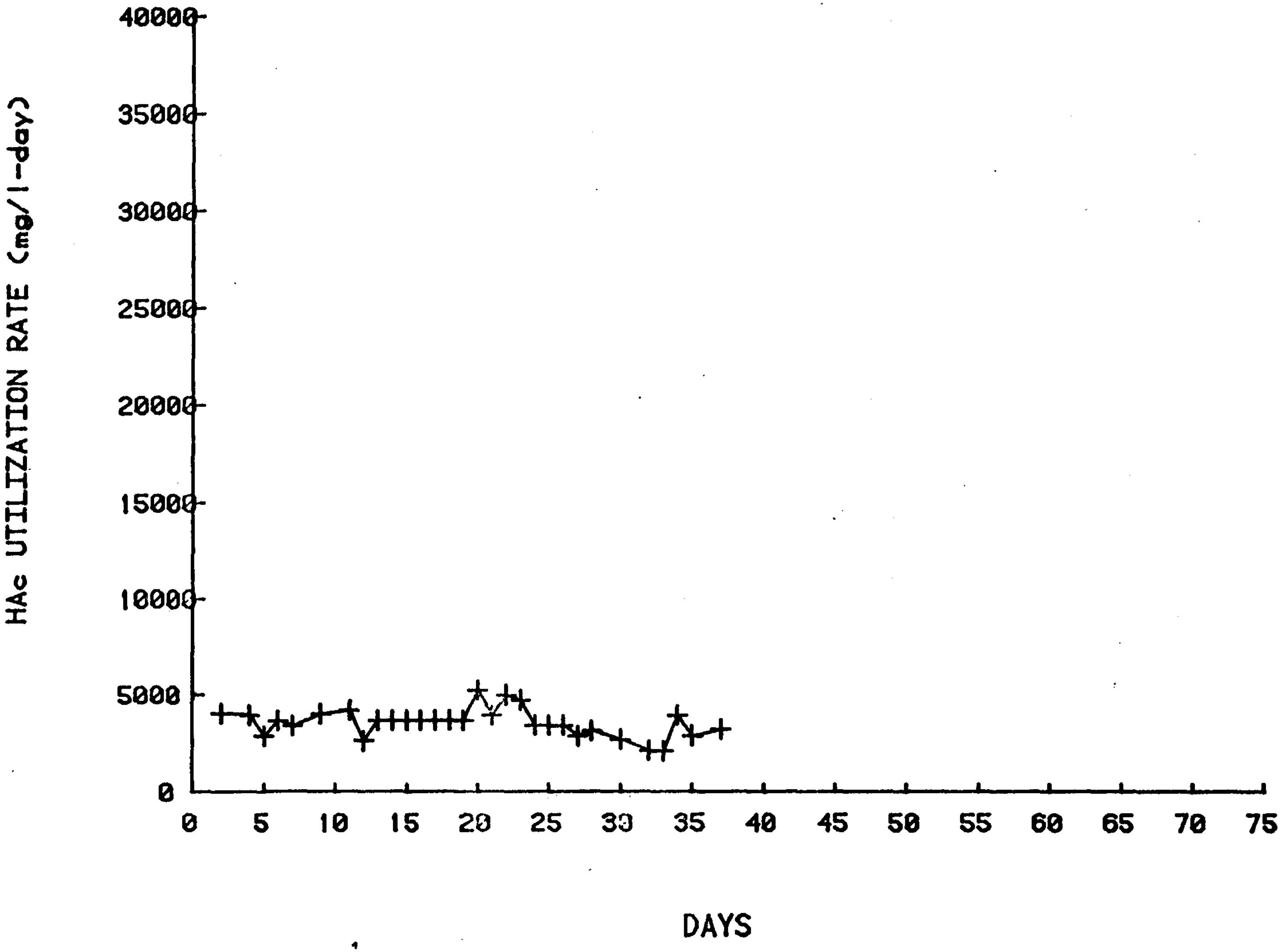


FIG. 5 Acetate Utilization Rate Using Supplemented Acetic Acid - 6A

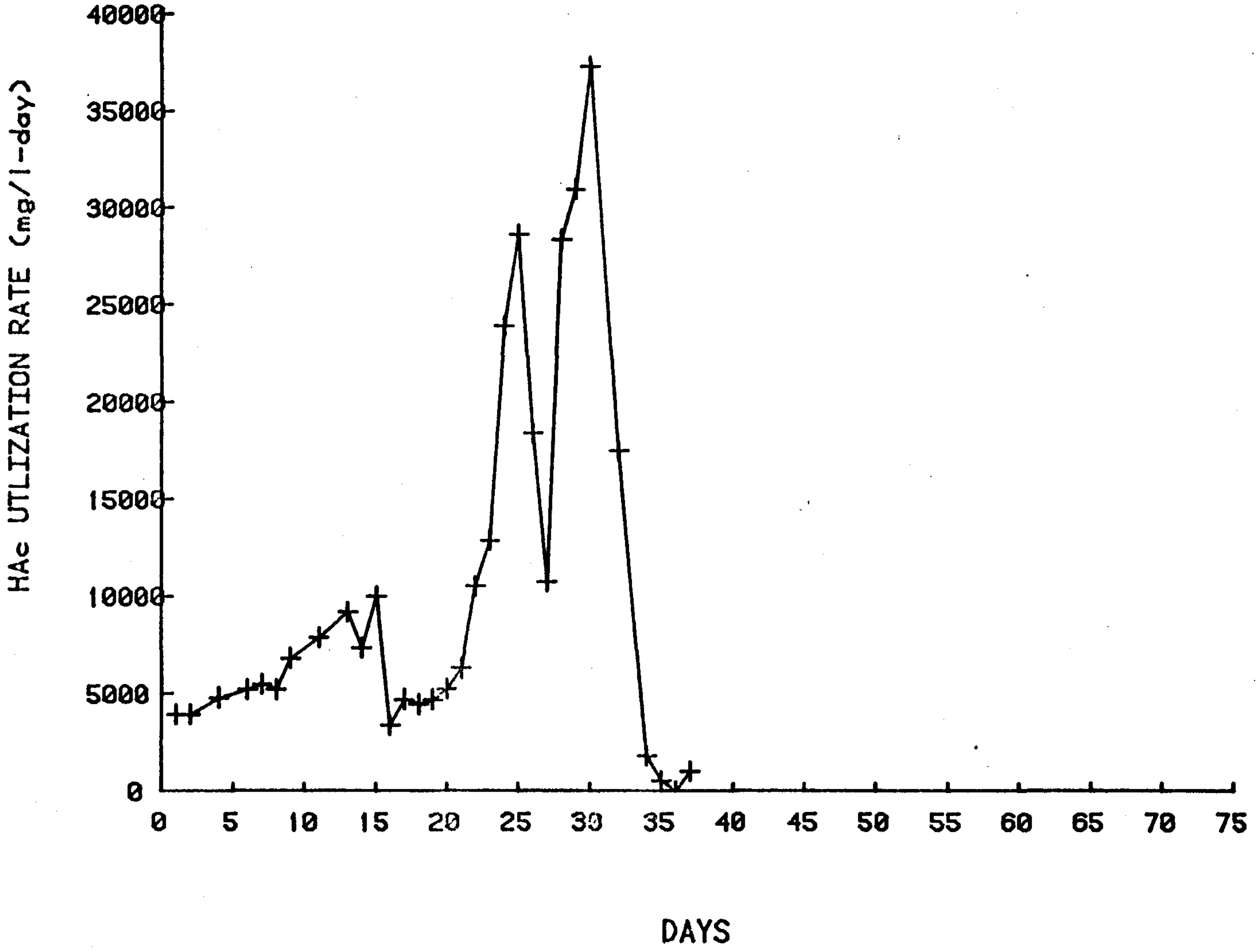


FIG. 6 Acetate Utilization Rate Using Supplemented Acetic Acid Plus 100 mg/l-day YE - 5A

that the volatile acids concentration being maintained by the pH Stat dropped gradually from over 2000 mg/ℓ to approximately 1000 mg/ℓ and then abruptly dropped to 200 and then 0 mg/ℓ. At this point 1 gm/ℓ of $(NH_4)HCO_3$ was added. This resulted in raising the acetate concentration to 400 mg/ℓ.

Subsequently, the next day, the acetate utilization reached the highest level we have yet achieved - 37,000 mg/ℓ-day. This is approximately 10 times higher than what is conventionally considered to be high rate digestion (200 lbs/1000 ft^3-day or 3300 mg/ℓ-day). At this point, the acetate utilization rate abruptly dropped to almost zero within 2 days for some unknown reason. Microscopic observation of the culture taken at the time of this highest acetate utilization rate indicated almost a complete shift in predominance from the rods typical of M. soehngenii to clumps typical of M. barkeri.

By Day 28, the accumulative acetate utilization was 260 gm/ℓ (Fig. 7) and the increase in VSS was about (4600-800) 3800 mg/ℓ for a net yield of 1.5%. The theoretical P requirement would have been about 58 mg/ℓ. Phosphorus additions were made along with the yeast extract starting on Day 26. The yeast extract also provided about 1 mg/ℓ-day of P, which seems inconsequential. Of particular note is the fact that in a 2 day interval between Days 23-25, the VSS doubled from 1700 to 3400 mg/ℓ. In this 2 day interval, the acetate consumption was 52 gm/ℓ for a net synthesis rate of 3.3%. In a one day interval between Day 23-24, the acetate utilization rate also doubled from about 12,000 to 24,000 mg/ℓ-day.

The specific utilization rate, k, of the biomass is plotted in Fig. 8. This rate varies from less than 3 to more than 8.

In an attempt to define the relative stimulatory significance of the components of Supplemented Acetic Acid four individual pH Stats were set

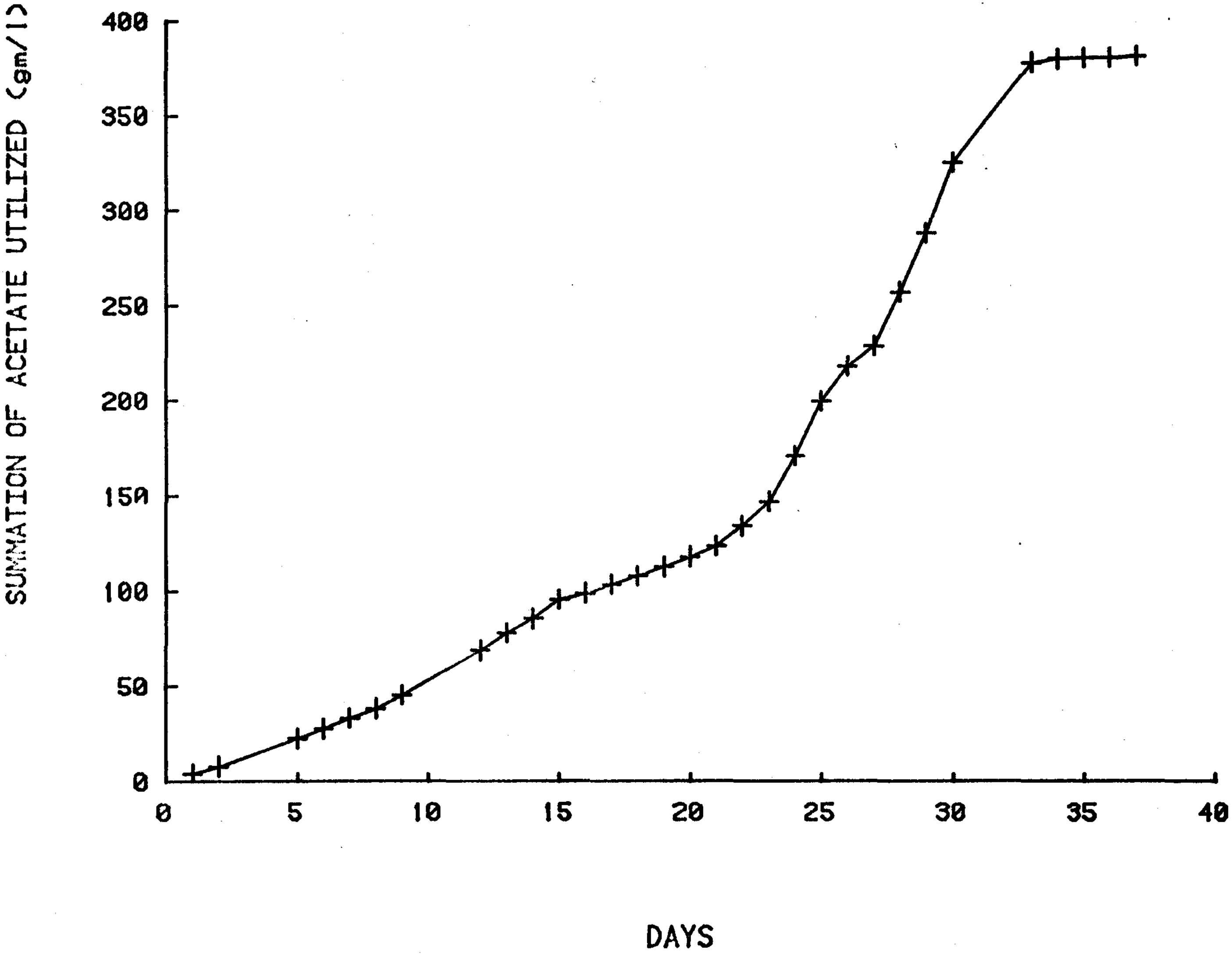


FIG. 7 Cumulative Acetate Utilization - 5A

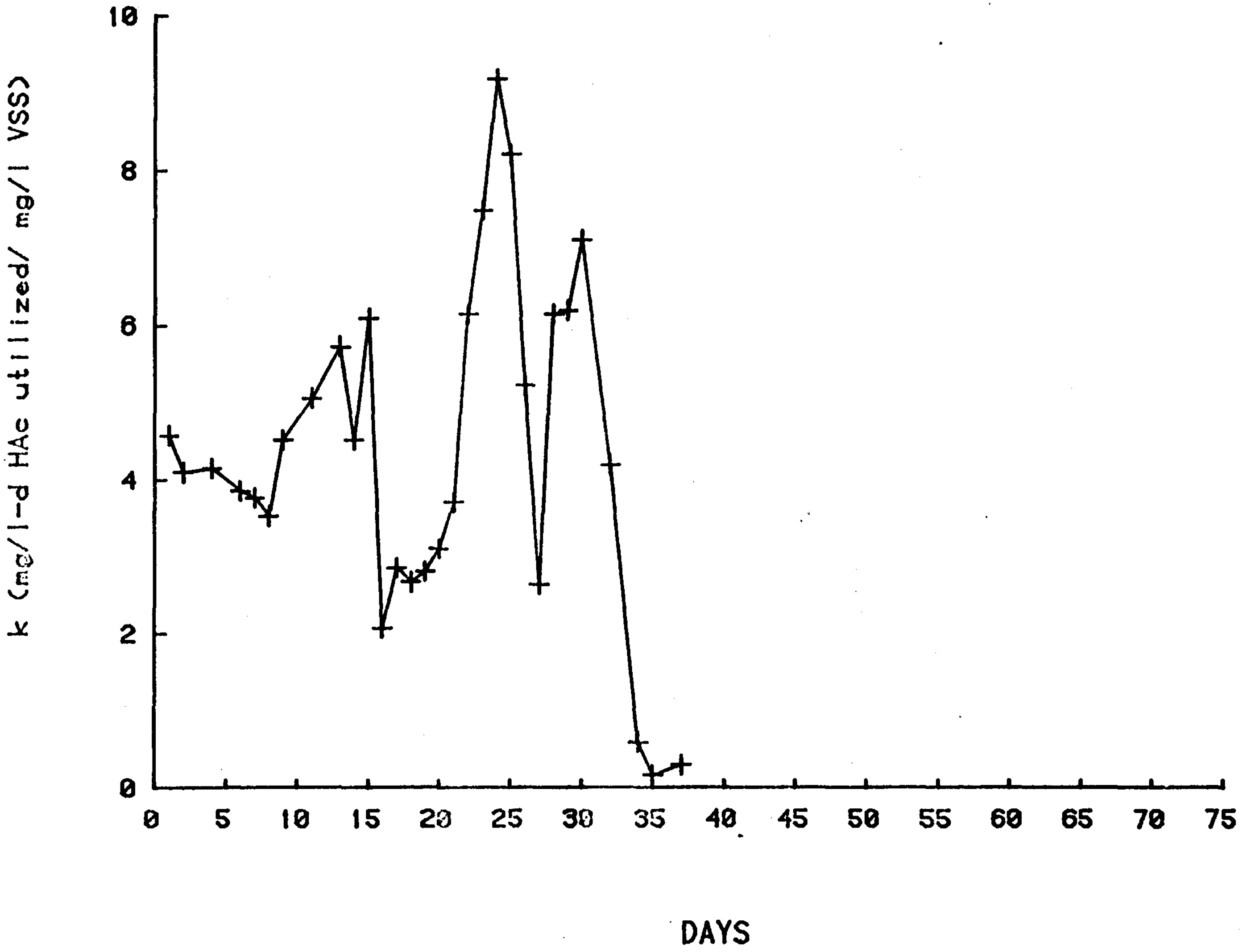


FIG. 8 k for Unit 5A

up with 100% inoculum plus 3 gm/ℓ of $(NH_4)HCO_3$. The feeds were as follows:

1. Straight Supplemented Acetic Acid
2. 50% HAc + 50% Tap Water
3. 50% HAc + 15 gm/ℓ NH_4Cl + 2 gm/ℓ $MgSO_4 \cdot 7H_2O$
4. 50% HAc + 15 gm/ℓ NH_4Cl + 2 gm/ℓ $MgSO_4 \cdot 7H_2O$ + 250 mg/ℓ $FeCl_2$ + 10 mg/ℓ $CoCl_2$

Fig. 9 shows the respective acetate utilization rates vs time for these four feed compositions.

The gradual decrease in acetate utilization in the pH Stat receiving 50% HAc plus tap water demonstrates the sulfur limitation. (It had initially been supplemented with 3 gm/ℓ NH_4HCO_3.) A slug addition of 100 mg/ℓ of $S^=$ resulted in a rise in utilization rate within 3 to 4 days.

The iron and/or cobalt limitation did not manifest itself for about a month. Thereafter, the acetate utilization curves show a definite departure. There is a slight trend toward increased acetate utilization in the system receiving N, S, Fe and Co and a definite decrease in the system receiving only N and S.

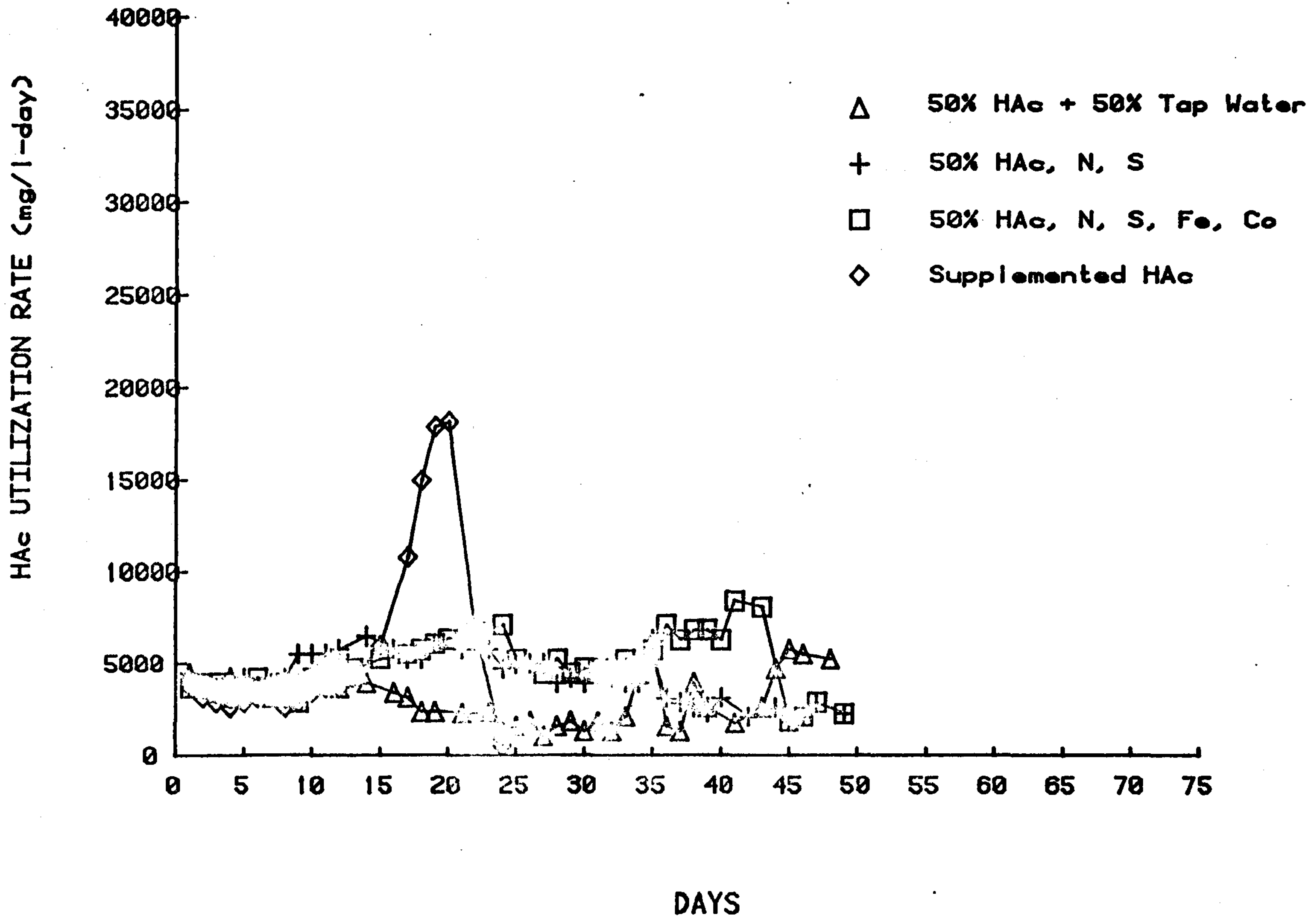


FIG. 9 Effect of Nutrients on Acetate Utilization Rate

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

Report Number XB-0-9038-1-6

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

Sixth Quarter Progress Report for Period From
April 1, 1981 to June 30, 1981

Principal Investigator

W. J. Jewell, Associate Professor
Department of Agricultural Engineering
202 Riley-Robb Hall
Cornell University
Ithaca, New York 14853

Full-Time Researchers

R. J. Cummings, S. Dell'Orto, K. J. Fanfoni, S. J. Fast,
E. J. Gottung, D. A. Jackson, R. M. Kabrick, J. Metzger

Graduate Students

J. W. Morris and G. Schraa

Cooperators

P. J. Van Soest
Department of Animal Science
Cornell University

Prepared For
Solar Energy Research Institute
Under Contract No. XB-0-9038-1

SUMMARY

Quarterly Progress Report

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

The Cornell University project on the conversion of crop and animal residues to methane has defined a low-cost reactor concept that promises to be capable of producing a significant amount of biogas from agricultural residues at a cost competitive with existing fuels. A new concept called "dry fermentation" of mixtures of crop and animal manures (with water content less than 80% of the total weight) is the main emphasis of this project. Other aspects of this effort include continued operation of the two full scale 65-cow dairy units, and design and installation of a biogas storage and utilization system.

The main emphasis of the second quarter of the second year of this three year project has been on bench scale experimentation directed at startup of farm scale systems and reduction of buffer requirements. Also during this quarter, studies were conducted on high moisture residue systems and physical densification characteristics of crop residues. Specifically, the following information on dry fermentation was developed during the sixth quarter of research:

- Compaction of wheat straw allowed startup of reactor at high initial solids contents of 30 and 35% (density = 15 lb/ft^3) with low S/F ratios of 0.05.

- Batch hydrolysis of corn stover and wheat straw may reduce buffer requirements for fermentation startup.

- Aerobic pretreatment provides some benefit for pH control but may be too costly in terms of potential methane lost by volatilization.

The two full scale dairy fermentors (plug flow and completely mixed) were fed intermittently for two months to devote full attention to construction of the biogas utilization system. Operation resumed on June 11, 1981 and the units rapidly resumed normal operation at 14 days HRT and 35°C. Most of the biogas utilization components have been delivered, including the gas purification unit, low and medium pressure compressors, and medium pressure storage tanks. Shipment is expected shortly on the low pressure storage tank and the cogeneration unit.

Future activities in the next quarter include: further definition of limited parameters of dry fermentation at bench scale (with scale-up to 200 liters and 5 m^3), startup of two pilot scale dry fermentors and completion of the biogas utilization system.

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

Quarterly Progress Report No. 5

April 1, 1981 to June 30, 1981
Cornell University, Ithaca, New York

INTRODUCTION

Previous studies at Cornell University defined modifications of anaerobic fermentation of dairy manure that appeared to be economically feasible for use on small farms. Full scale units were built and have been operated since the spring of 1978. These units continue to operate in a relatively trouble-free manner. The success of this study emphasizes that simplification of the fermentation technology may enable its application to a wide variety of substrates to produce economically competitive alternative energies.

In many farming operations the manure is available as relatively dry material, since it is mixed with varying quantities of bedding. Also, large quantities of crop residues, such as cornstalks and wheat straw, are left unused in the field. The energy value of biogas produced from dairy manure only on a 100-cow dairy may be $5000 per year; inclusion of the crop residues on this farm could increase the biogas value to ten-fold or more. Also, collection of the dryer crop residues to provide large scale alternative energy generation centers may be considered. However, the problems associated with application of any slurry fermentation technology are questionable due to the high cost of handling the residue and the large quantities of water. This study introduces a major alternative for conversion of dry mixtures of crop residues and manure to biogas using the "dry fermentation" process. The goal of this alternative is to use a low-cost, simple system that does little to the material as harvested, achieves good conversion efficiency, and results in an easy-to-handle, relatively dry and solid by-product.

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 information on biogas utilization systems for the dairy manure fermentors;
3. develop a feasibility analysis of crop residue digestion to confirm the potential for anaerobic fermentation with untreated dry crop residues;
4. using pilot plant analysis, determine the kinetics of dry fermentation of three major crop residues, and the influence of termperature on operation, nutrient availability, and start-up requirements in terms of bacterial seed inoculum and alkalinity requirements;

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

6. 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 280 m^3/d to 3000 m^3/d (10,000 ft^3/d to 100,000 ft^3/d).

PROJECT STATUS

The proposed status and present degree of completion achieved during the period April 1, 1981 - June 30, 1981 are shown in Figures 1 and 2. Due to increasing complexity of the dry fermentation process, the decision to move to full scale has been delayed six months (until the end of 1981). Additional bench scale and pilot scale testing will need to be completed prior to scale-up.

All equipment for the gas utilization study has been received with the exception of the co-generator and a complete plan of gas utilization implementation and integration has been completed and approved. The full scale plug flow and completely mixed dairy manure reactors were operated with minimal attention during this quarter in preparation for the gas utilization system hookup. The first year report on dry fermentaton was completed and is now being readied for distribution. Progress continued towards defining optimum conditions for dry fermentation and subsequent scale-up. This report outlines the progress of this project in 11 areas of research within the aforementioned time period.

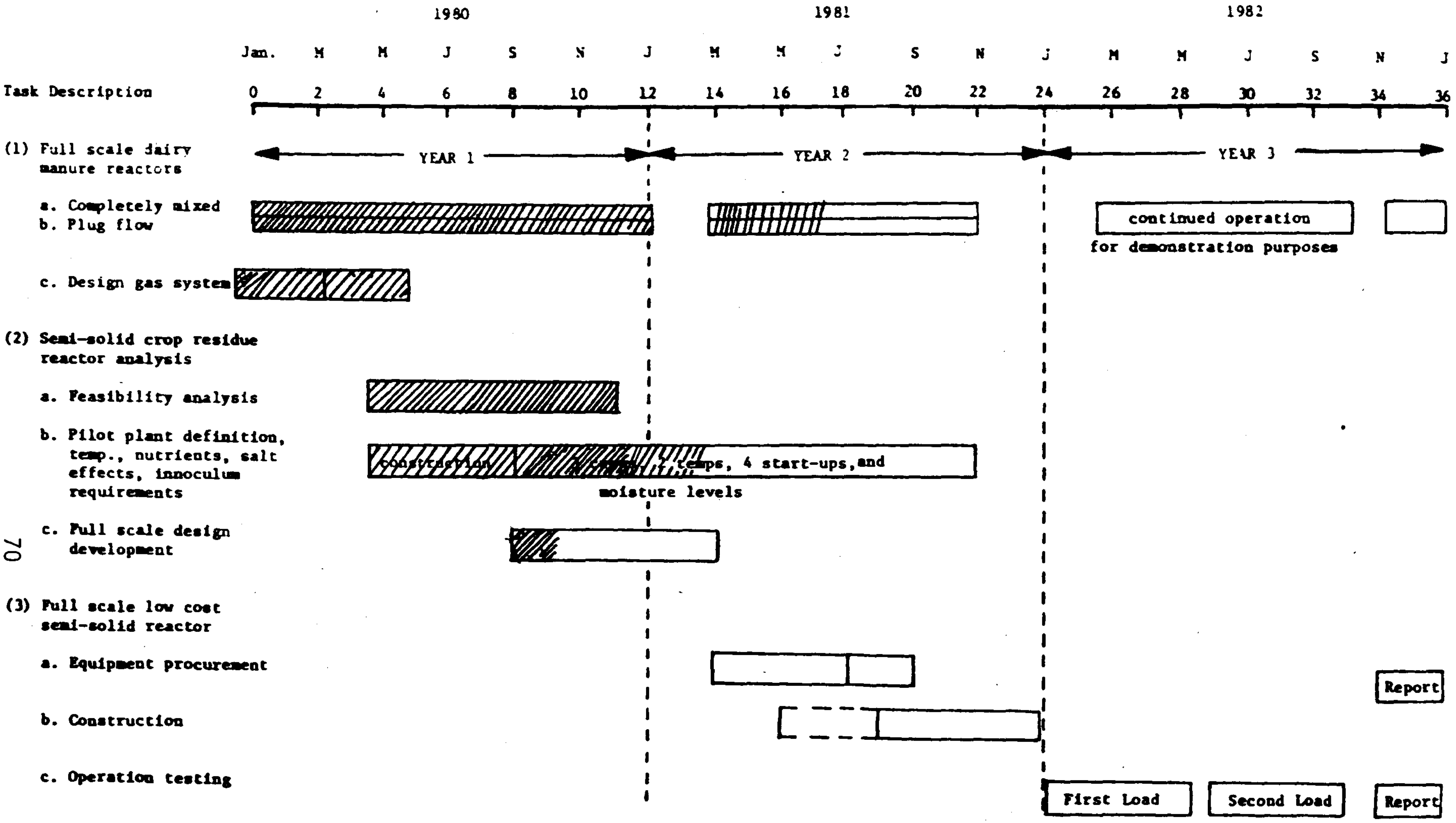


Figure 1. Schedule of tasks, events, and output of research and development program.

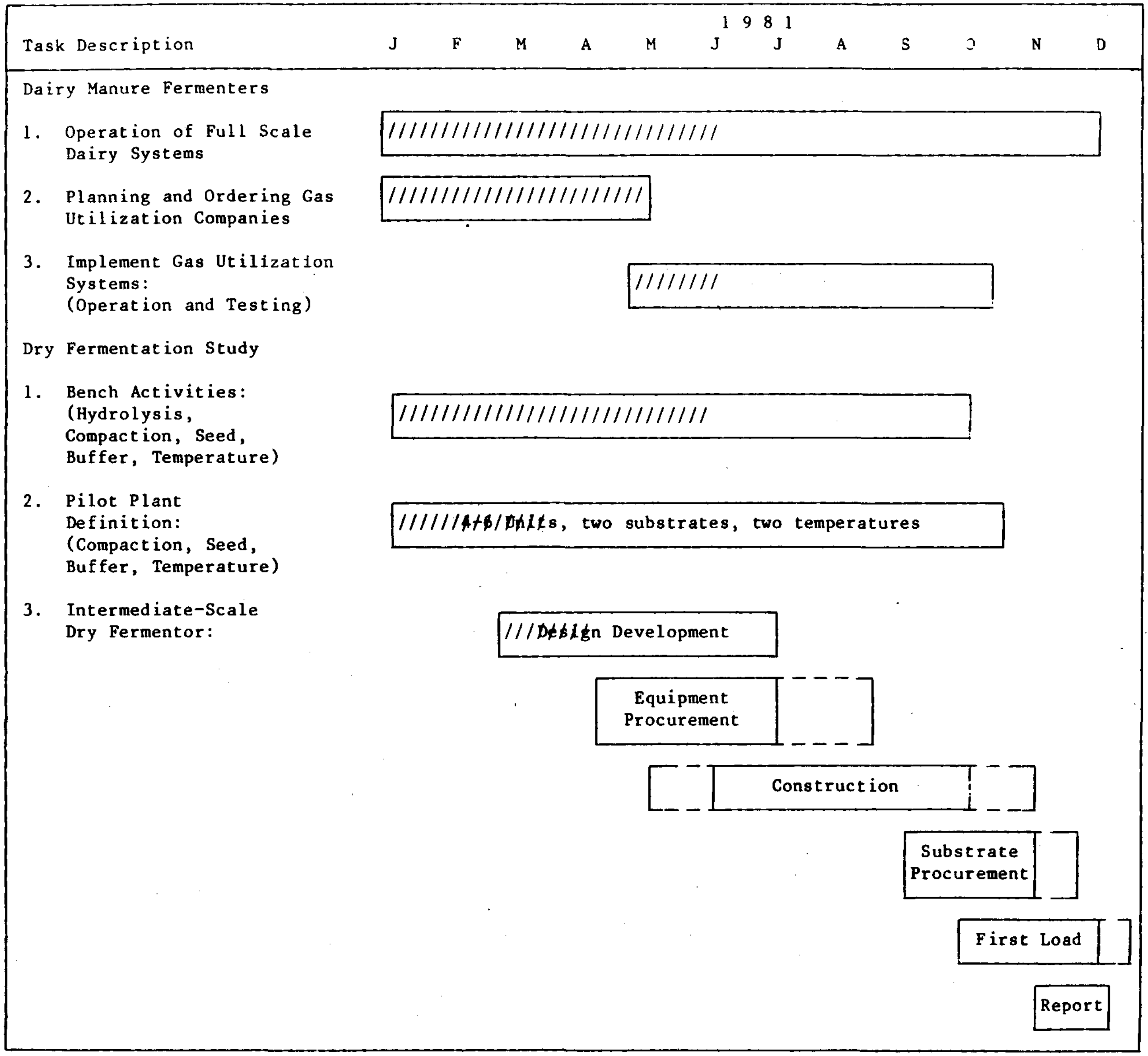


Figure 2. Schedule of tasks, events, and output of research and development program for the second year.

FULL SCALE PLUG FLOW AND COMPLETELY MIXED DAIRY MANURE REACTORS: OPERATIONAL AND GAS UTILIZATION STATUS

On April 1, 1981 continuous operation of the two full scale dairy manure anaerobic digesters at ASTARC was temporarily suspended and construction of the biogas utilization study was initiated.

Continuous operation of the two digesters was resumed June 11, 1981. Both units were back up to temperature and producing biogas at significant rates by June 15, however, steady state operation cannot be expected for at least two weeks. It was interesting that the digesters could be totally unattended for over two months (unheated, fed intermittently, and unmonitored) and then restarted by merely heating the digesters up to temperature (from 15°C at ambient temperature to 35°C reactor temperature) and resuming the five times per week feeding schedule. The digesters will be operated at a hydraulic retention time of 14 days and temperature of 35°C throughout the remainder of the study.

Construction of the biogas utilization project began April 1 and has continued on schedule according to the time line presented in Figure 3. The time line was divided into eight construction phases. A brief description and status report of each phase is presented below.

A) Digester Interconnect Piping

This was the main reason for interrupting the digester's operation. The biogas and hot water pipelines to the digesters were connected and extended to the centrally located ENGINE ROOM 6 shown in Figure 4. This task was completed June 1.

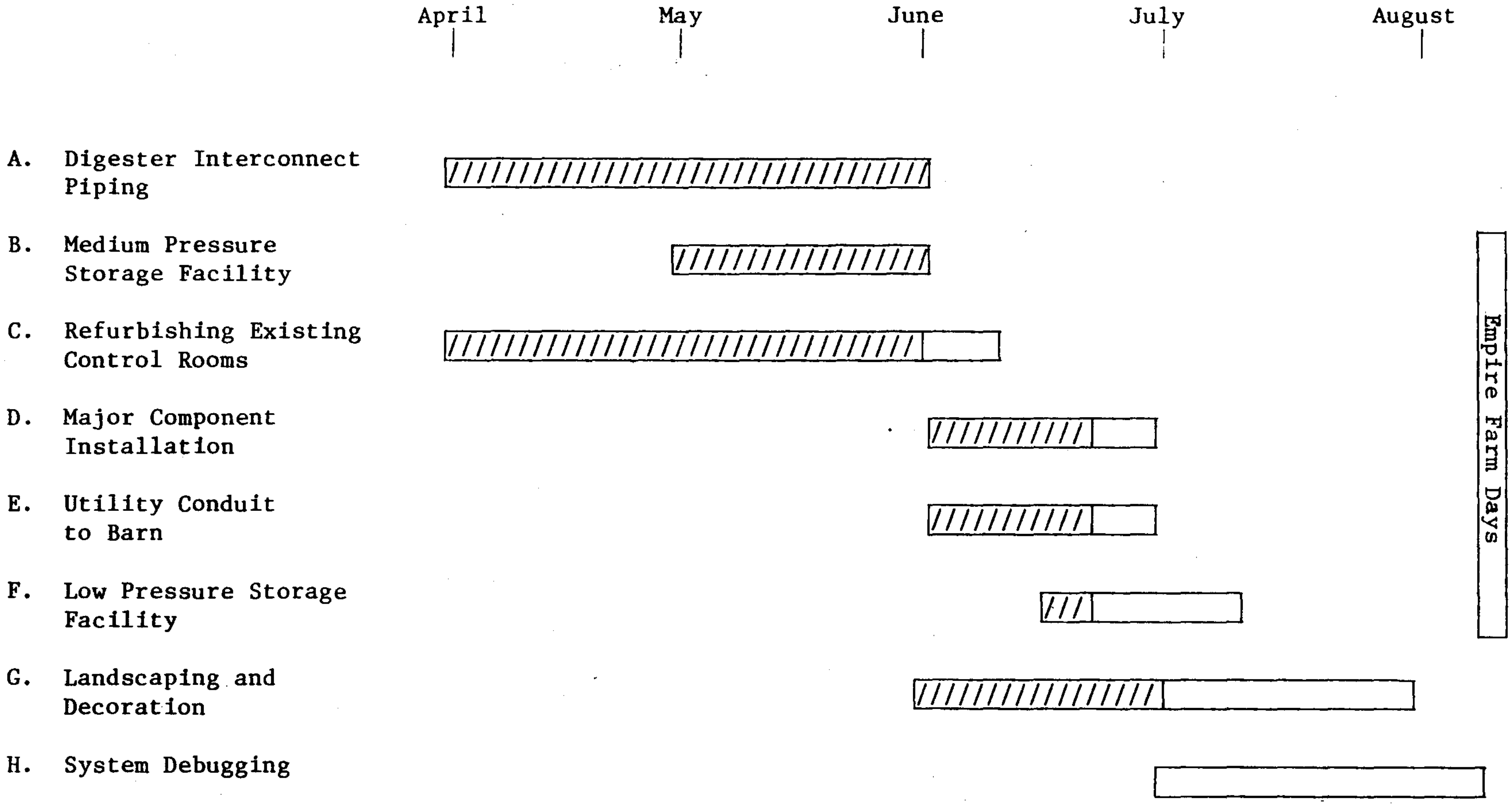


Figure 3. Construction timeline for biogas utilization project.

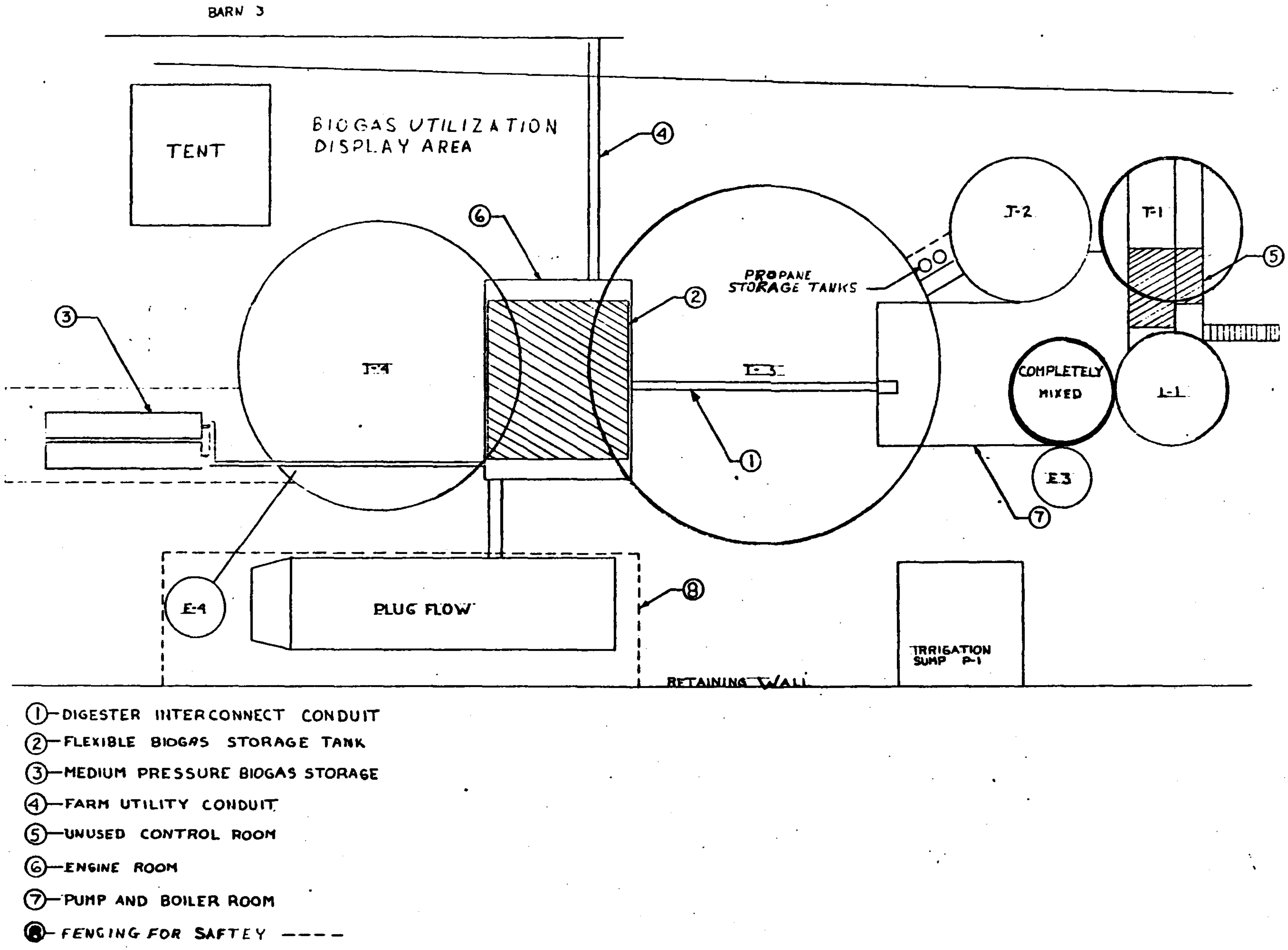


Figure 4. Plan View of Biogas Utilization Site.

B) Medium Pressure Storage Facility

This phase has also been completed. Two 1800 gallon steel tanks were positioned as shown in Figure 4 to hold slightly over 1 day's production of biogas at a pressure of 200 psi.

C) Refurbishing Existing Control Rooms

The digester control rooms were converted to serve as an engine room and pump room. General repair was necessary to both areas to upgrade the appearance and for further weatherization. Only minor touch up tasks remain to be completed.

D) Major Component Installation

The major components of the study as outlined in the last quarterly report were:

1) Low Pressure Storage Facility (Goodyear Aerospace)
2) Gas Purification Unit (iron sponge)
3) Low Pressure Compressor (Waukee)
4) Medium Pressure Compressor (Pro Chem)
5) Medium Pressure Storage Facility (Suburban Propane)
6) Cogenerator (Cummins-Mohawk)

We have accepted shipment of everything except the cogenerator and low pressure storage tank, both of which are expected by the end of June.

E) Utility Conduit to Barn

As shown in Figure 4 a main conduit line was excavated from the engine room to barn 3 at ASTARC. This conduit line conducts the electric hot water, and biogas lines from one to the other. This phase will be completed June 19, 1981.

F) Low Pressure Storage Facility

The low pressure storage site will be the roof of the engine control room. This flexible bag will collect the biogas from both digesters and serve as the sump tank from which the low pressure compressor will compress the biogas for use. Construction at this site will take two weeks and will begin June 22.

G) Landscaping and Decoration

The month of July will be devoted to site security, safety and beautification for the upcoming Empire Farm Days scheduled for August 11, 12 and 13 at ASTARC.

H) System Debugging and Operation

Construction is scheduled for completion by mid July at which time operation of the total system will begin with a two week period of system debugging and fine tuning. A schematic flow diagram of the total system is illustrated in Figure 5.

DRY FERMENTATION STUDY: BACKGROUND AND RATIONALE

In the preceding three years of methane fermentation research, Cornell Unviersity has conducted extensive laboratory, bench scale, pilot scale, and full scale studies in order to define dairy farm fermentor designs which are cost-effective. It is appropriate to review new areas of methane fermentation research which, hopefully, will broaden and accelerate further implementation of this process. Using the same low-cost approach, the Cornell team 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 25 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

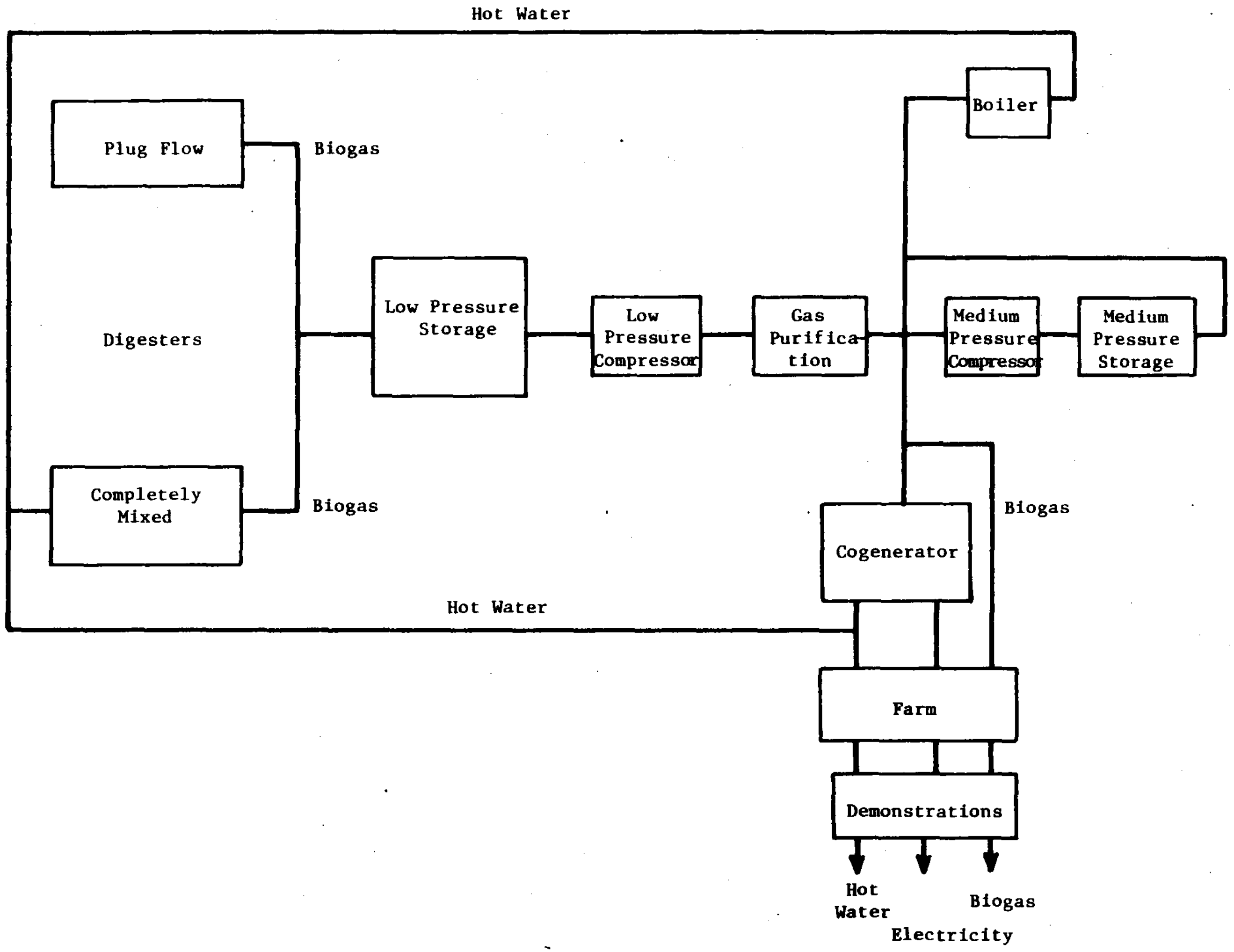


Figure 5. Schematic flow diagram of biogas, hot water, and electricity for the Biogas Utilization Study.

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 the use of conventional technology for fermentation of agricultural crop residues.

The potential benefits of fermentation at solids contents in excess of 10 percent TS have 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), a 5000-liter pilot scale fermentor using wheat straw as a substrate at an initial total solids content of 22 percent was started. The results from that pilot scale effort were reported previously (Jewell _et al_., 1980a).

DRY FERMENTATION RESEARCH: RESULTS TO DATE

Compaction Experiments - Biological Effects

Set-up of a compaction experiment relating to increased initial solids content and lower seed to feed ratios (S/F) was mentioned in the last quarterly progress report (Jewell, _et al_. Jan. 1, '81-Mar. 31, '81). The experiment consisted of duplicate 30% and 35% initial total

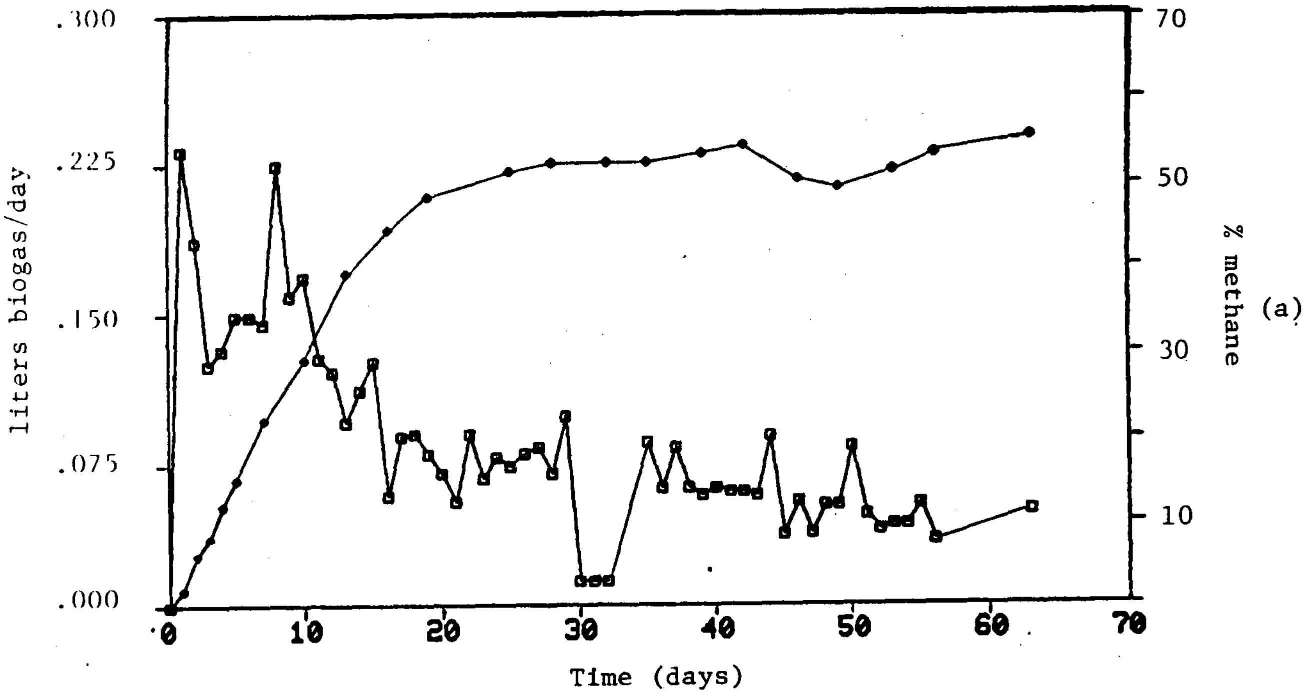
TABLE 1. Summary of Advantages and Disadvantages of Using a Dry Reactor Approach for the Conversion of Agricultural Crops and Residues to Methane.

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 or 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 (I.T.S.) wheat straw reactors with 0.05 S/F's operated at 35°C. The ratio of buffer to feed was 0.08 for all reactors. One set of 30 percent and 35 percent I.T.S. units were compacted to 15 lbs/ft^3 (dry weight) and the other set served as controls at loose-fill densities (4-6 lbs/ft^3, dry weight). These units were monitored for 63 days.

The 30 percent I.T.S. compacted unit was producing biogas of 50 percent methane content by day 25 with an average rate of 0.55 l/day (0.32 v/v-d) and average methane content of 52 percent, thereafter. The other units did not produce as much biogas and took from 35 to 40 days to begin producing 50 percent methane quality biogas (averaged less than 0.05 l/day with average percent methane between 52 and 59). Figure 6 shows the biogas production and percent methane for these units. Total volatile solids destruction (TVS_D) at 63 days was 21.4 percent and 14.3 percent for the 30 percent and 35 percent ITS compacted units and 14.8 percent and 12.6 percent for the duplicate loose-fill units, respectively.

Other 30 percent and 35 percent I.T.S. wheat straw units from a previous study (Jewell, et al. 1981b) at 35°C achieved 11.5 percent and 6.5 percent TVS_D, respectively after 69 days. These reactors were set up at loose-fill densities and had a higher S/F of 0.10. Although the units in this latest compaction experiment also achieved relatively poor solids conversions, they show that some degree of fermentation can occur at low S/F, such as 0.05 at 35°C. It also supports substrate compaction as a positive factor in the methane production process at the higher solids concentrations.



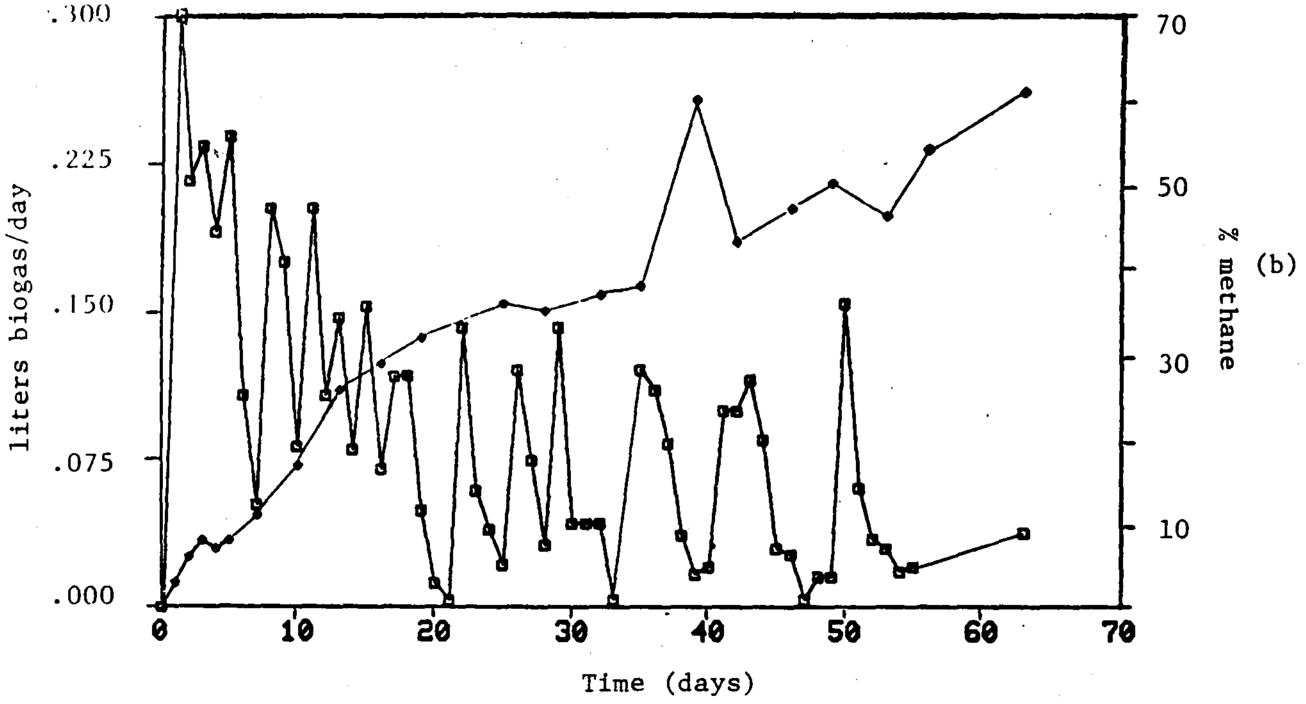


Figure 6. Gas production for units in the biological effects of compaction experiment: (a) 30% ITS, .05 S/F, 15 lbs/ft^3 unit; (b) 35% ITS, .05 S/F, 15 lbs/ft^3 unit. □ = biogas; ◆ = % methane.

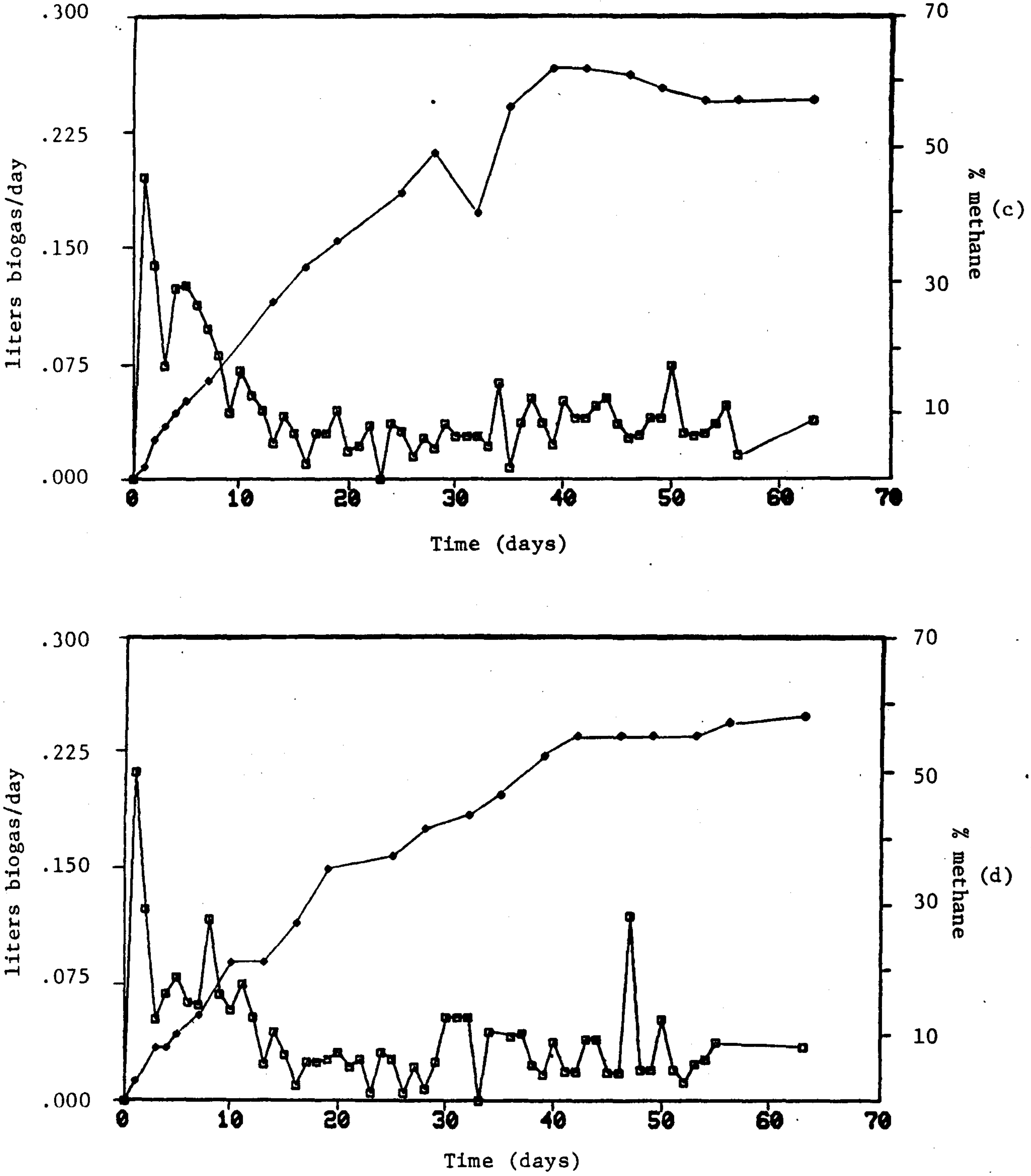


Figure 6 (continued). (c) 30% I.T.S., .05 S/F loose-fill unit;
(d) 35% I.T.S., .05 S/F loose-fill unit.

Substrate Compaction - Physical Relationships

Previous studies have indicated beneficial effects of compaction on dry anaerobic fermentation. Knowledge of the relationships between substrate density, moisture content, and compaction pressure is desirable. Construction and calibration of a constant force compaction apparatus was completed and substrate testing begun.

Some compaction test results for corn stover and wheat straw are exemplified in Figures 7 and 8. Compaction pressures up to 17 psi produced dry densities of approximately 13 lb/ft^3 for substrates with 30-40 percent total solids. Dry densities of approximately 22 lbs/ft^3 for substrates with initial total solids of approximately 20 percent were observed. The moisture content of corn stover and wheat straw at 30 percent or greater total solids was unaffected by compaction pressures up to 17 psi. Moisture was pressed from the substrates with 25 or less percent total solids in this pressure range.

Further studies will continue to quantify the effects of substrate, substrate treatment (hydrolysis, digestion) and particle size on density, moisture content, and compaction pressure relationships.

Long Term Batch Hydrolysis Study

The long term batch hydrolysis study began during the last quarter and is summarized in Table 2. The emphasis of this study was to gain additional information in the following areas:

1) use of additional substrates;
2) effect of moisture content;
3) potential benefits of pH control.

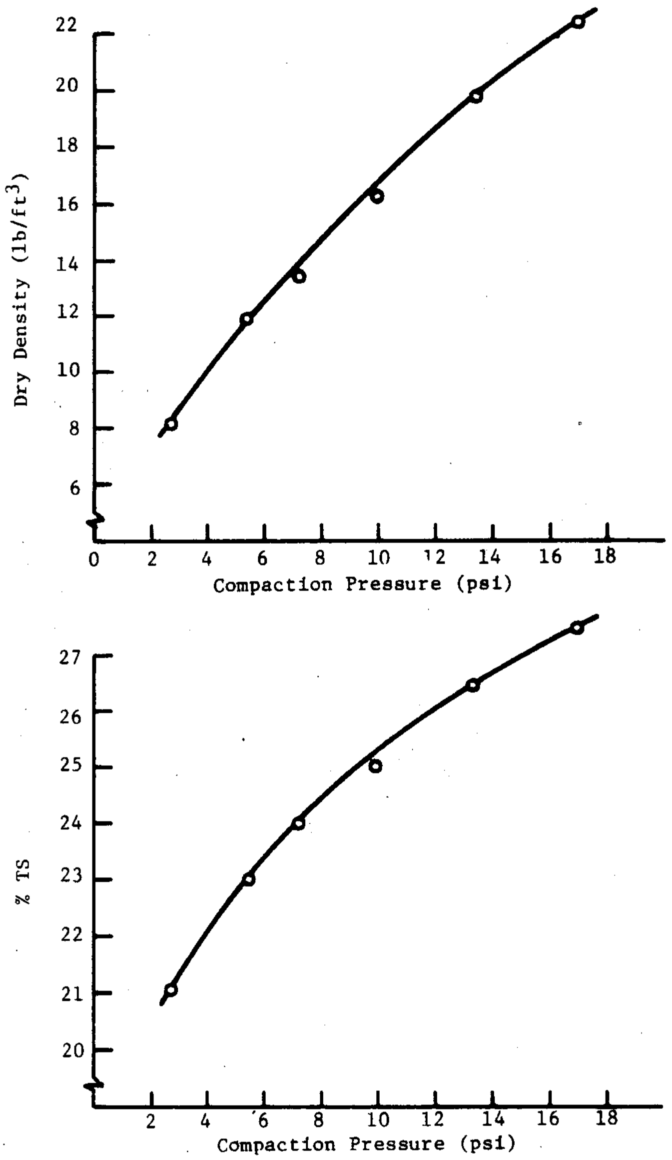


Figure 7. Compaction of corn stover @ 21.5% TS.

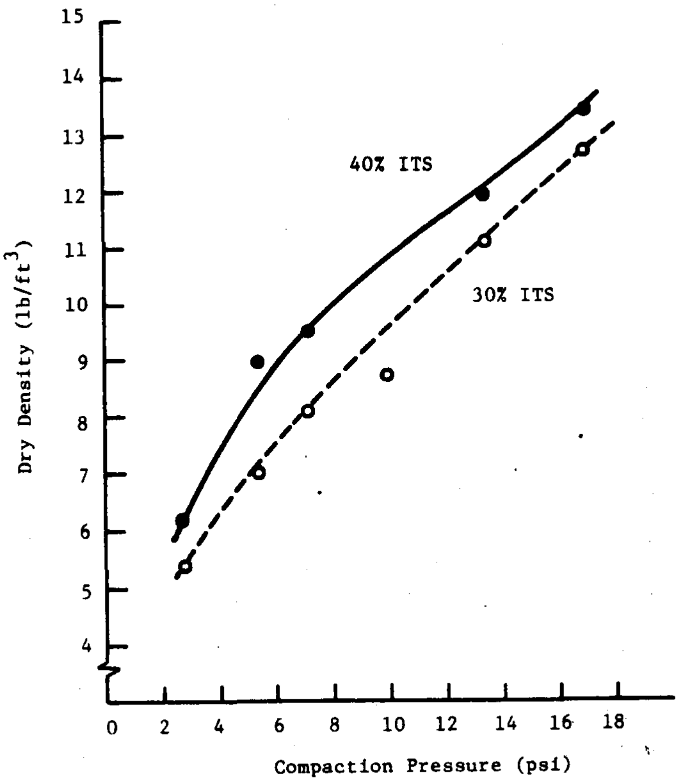


Figure 8. Compaction of wheat straw @ 30% and 40% ITS.

All new studies were started at 25°C. Corn stover was the main substrate used, as compared with wheat straw in the previous studies.

TABLE 2. LONG TERM BATCH HYDROLYSIS STUDY

Temperature	Substrate	% Initial T.S.	pH Control[1]	Seed[2]
25°C	Wheat Straw	45	No	Yes
25°C	Corn Stover	45	No	Yes
25°C	Wheat Straw	15	No	Yes
25°C	Corn Stover	15	No	Yes
25°C	Corn Stover	15	Yes	Yes
25°C	Corn Stover	45	Yes	Yes
25°C	Corn Stover	45	No	No
25°C	Corn Stover	45	No	Yes[3]

[1] pH maintained ≥ 6

[2] Seed used is 5% S/F as digested cow manure

[3] Raw manure used as seed

Figures 9 and 10 illustrate the impact of pH control on batch hydrolysis of corn stover. The pH was adjusted to approximately 6.0 whenever samples were withdrawn. Figure 9 compares two reactors at low moisture content (45 percent T.S.). It can be seen that the pH-controlled unit obtained higher solubilization rates than the non-controlled unit. The pH was adjusted only twice in this reactor, since it maintained a high pH naturally after day 35. Figure 10 shows the reactors at high moisture content (15 percent T.S.). Again, the pH-controlled reactor did not need adjustment after day 35. The difference is that the volatile acid COD in the controlled reactor is lower than the uncontrolled reactor after day 35. This is explained by the fact that this reactor began methane production after 30 days and its biogas had reached 50 percent methane after 60 days. The pH in this reactor is currently maintaining 6.3 and methane production is continuing.

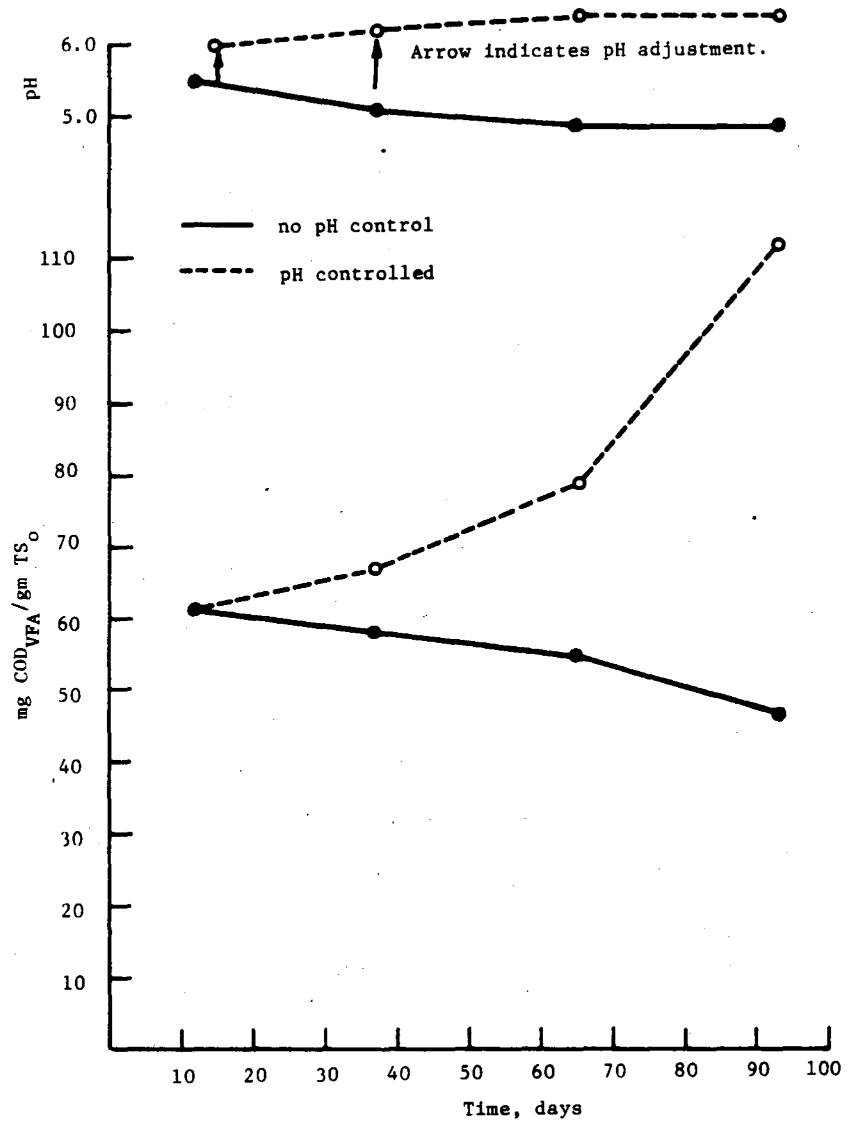


Figure 9. Effect of pH control on batch hydrolysis of corn stover at 25°C and 45% TS.

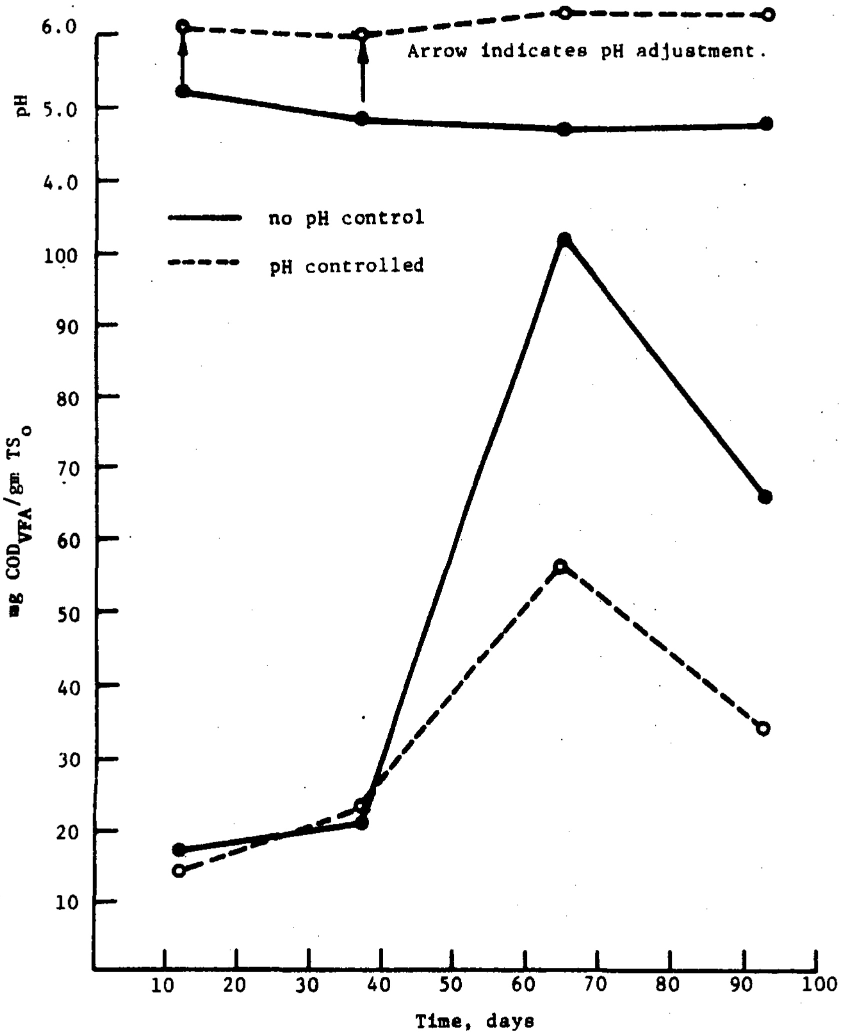


Figure 10. Effect of pH control on batch hydrolysis of corn stover at 25°C and 15% TS.

Figure 11 compares high versus low moisture content hydrolysis reactors. Both reactors rapidly dropped in pH and maintained levels below 5.0. The volatile acid COD in the high moisture reactor started at lower levels but readily increased to higher levels than the low moisture reactor. The low moisture reactor has been steadily decreasing, indicating a possible moisture deficiency which is inhibiting bacterial action.

A comparison of different substrates is shown in Figure 12. Both reactors operated at 25°C, 45 percent T.S., and without pH control. The corn stover reactor went into acid hydrolysis more rapidly than the wheat straw, but did not show any long term improvement. The wheat straw unit began at a slower rate, but reached the same level as the corn after 66 days, Figure 13 shows the two substrates again, but at 15 percent total solids. In this comparison, little difference was observed between the substrates over 100 days, although the corn stover had slightly higher yields.

Figure 14 compares hydrolysis yields from corn stover reactors with no seed, new manure seed, and digested manure seed. Overall, there was little significant variation, although the seeded reactors were generally higher.

Short-Term Hydrolysis Studies

The long term batch hydrolysis study mentioned previously was directed at maximizing the solubilized fraction of organic material to allow for more complete fermentation. The aim of the short term

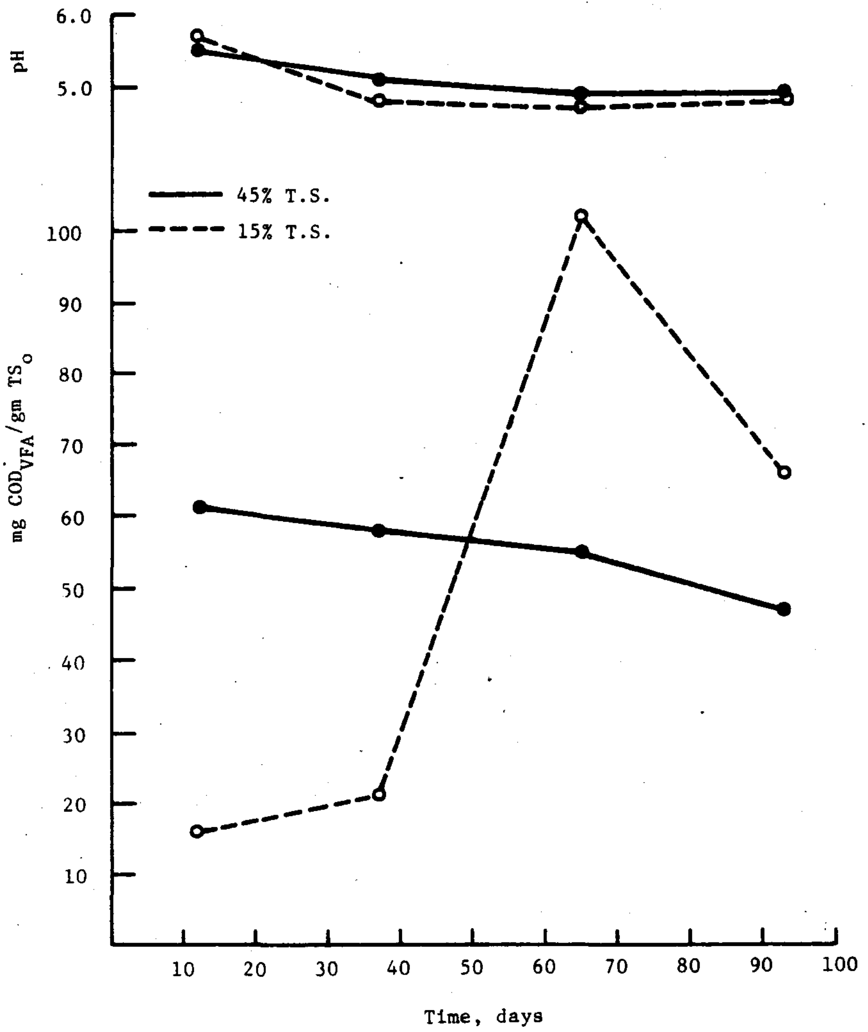


Figure 11. Effect of moisture content on batch hydrolysis of corn stover at 25°C.

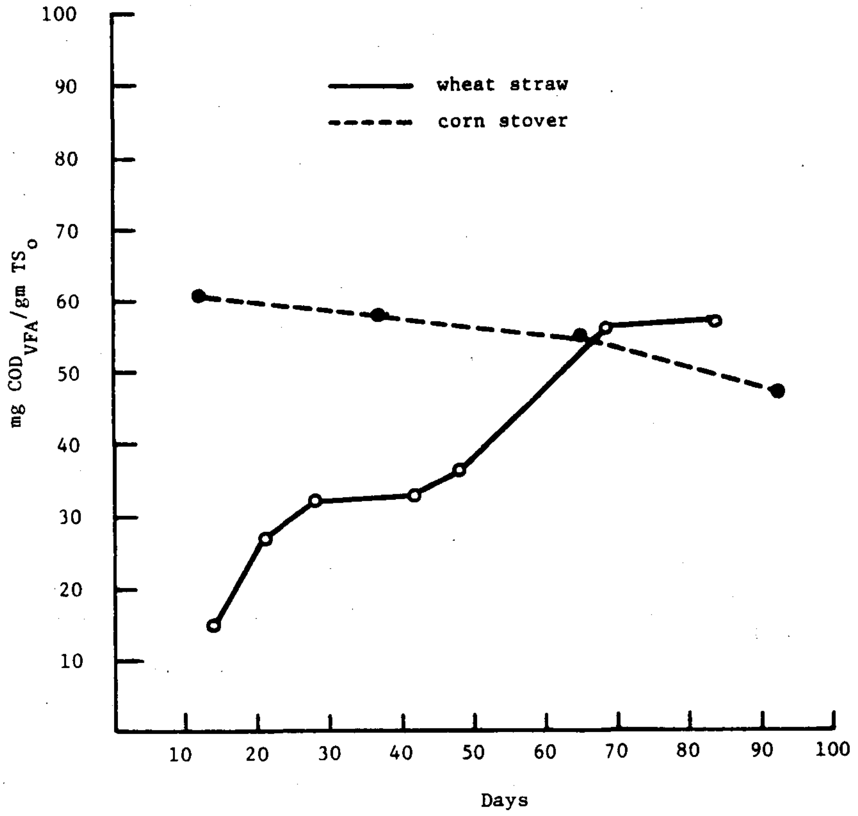


Figure 12. Batch hydrolysis of corn stover versus wheat straw at 25°C and 45% T.S.

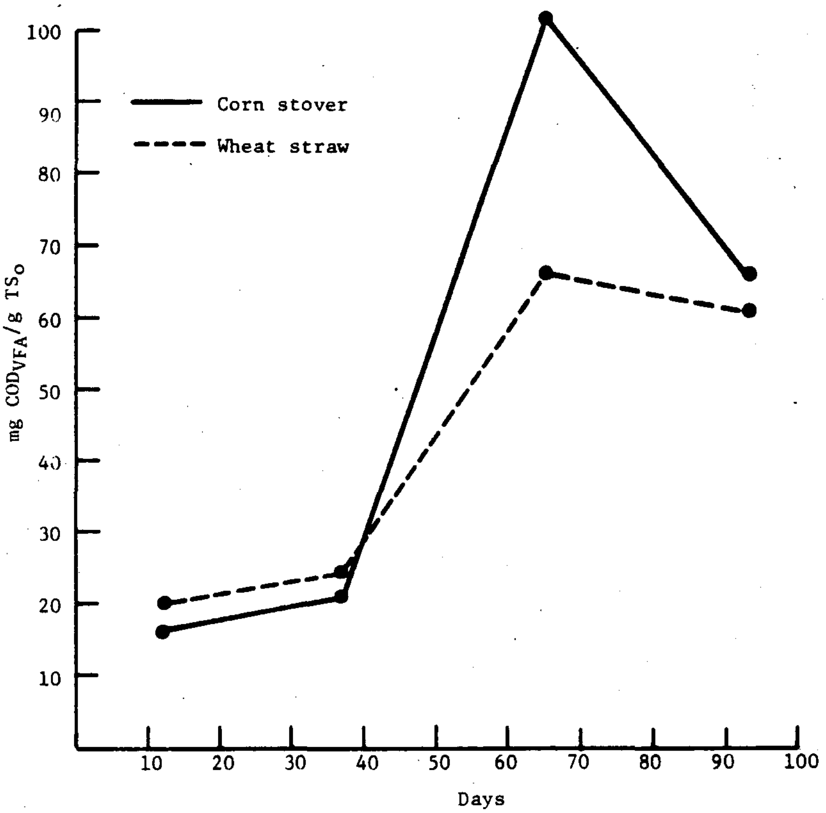


Figure 13. Batch hydrolysis of corn stover versus wheat straw at 25°C and 15% TS.

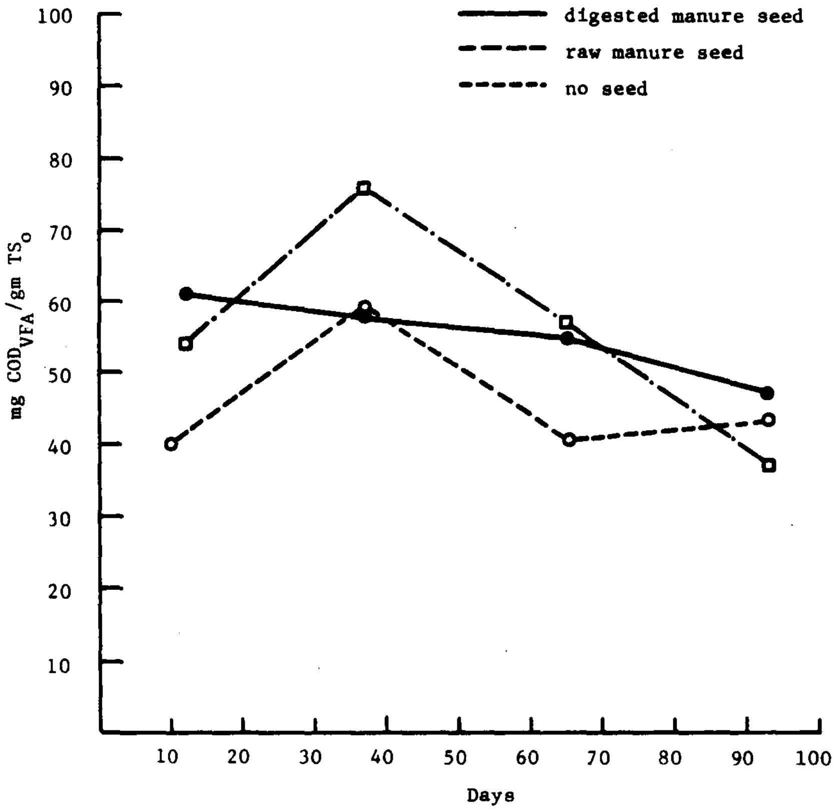


Figure 14. Batch hydrolysis of corn stover at 25°C with no seed, raw manure seed, and digested seed at 45% T.S.

hydrolysis studies is to solubilize and remove the readily biodegradable organics from the system to minimize the necessity for expensive buffer additions.

The first series of short term studies are outlined in Table 3. After batch hydrolysis at 17°C for 0 to 12 days, subsamples of corn stover and wheat straw were used to start methane fermentation reactors at either 35°C or 55°C. Each reactor was seeded with stable digested cow manure from seed reactors at the same temperature. Buffer additions were varied from 0 to 8 percent.

Figures 15a and 15b illustrate the pH and soluble fractions of the leachate from the hydrolysis reactors. The soluble COD represents potential methane which is lost to the system as it is removed for pH control purposes. The leachate from the corn stover reactor dropped to a pH of 5.2 and reached soluble COD levels of 5300 mg/ℓ. The wheat straw leachate dropped to a pH of 5.0 and only reached 4500 mg/ℓ of soluble COD. These levels of leachate COD removed from the reactors represent potential losses of nearly 10 percent of the biodegradable organic material in the leachate.

Figure 16 shows the pH, percent methane, and change in soluble COD for the corn stover after fermentation at 55°C. Each progressive point represents a substrate sample which was initially hydrolyzed for 0 to 12 days, as indicated on the abscissa. The days of fermentation after hydrolysis are also shown on the figure. Reactors with no buffer and with 0.08 B/F are depicted in the figure. The effect of buffer is shown to result in an increase in pH, but insignificant differences in percent methane of the biogas. There was also little difference measured in the

TABLE 3. EXPERIMENTAL PROGRAM FOR SHORT TERM HYDROLYSIS STUDY.

Time of Hydrolysis	0 to 12 days in 2 day increments
Temperature of Hydrolysis	17°C
Temperature of Fermentation	35°C, 55°C
Substrates	Corn Stover, Wheat Straw
Initial % T.S. for Fermentation	Approximately 15% after 1 hour free drain
S/F	.025 (55°C) .30 (35°C, wheat) .40 (35°C, corn)
B/F	0, .02, .04, .08

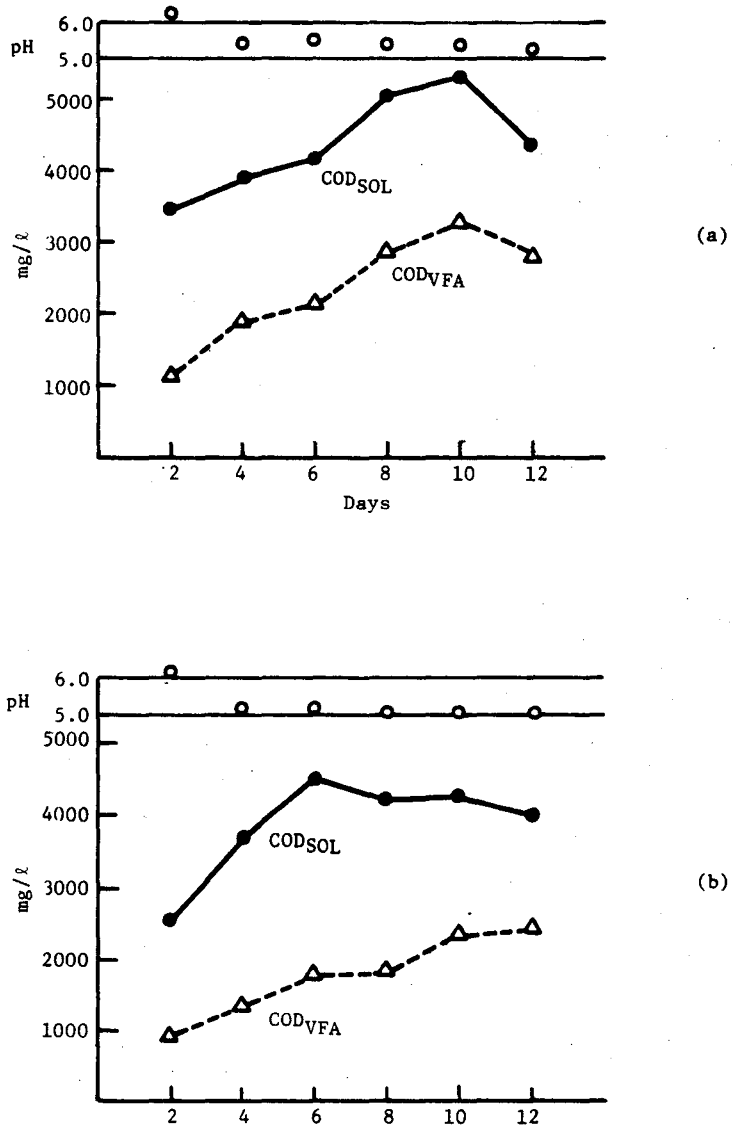


Figure 15. Leachate characteristics for corn stover (a) and wheat straw (b) in the short term acid hydrolysis study.

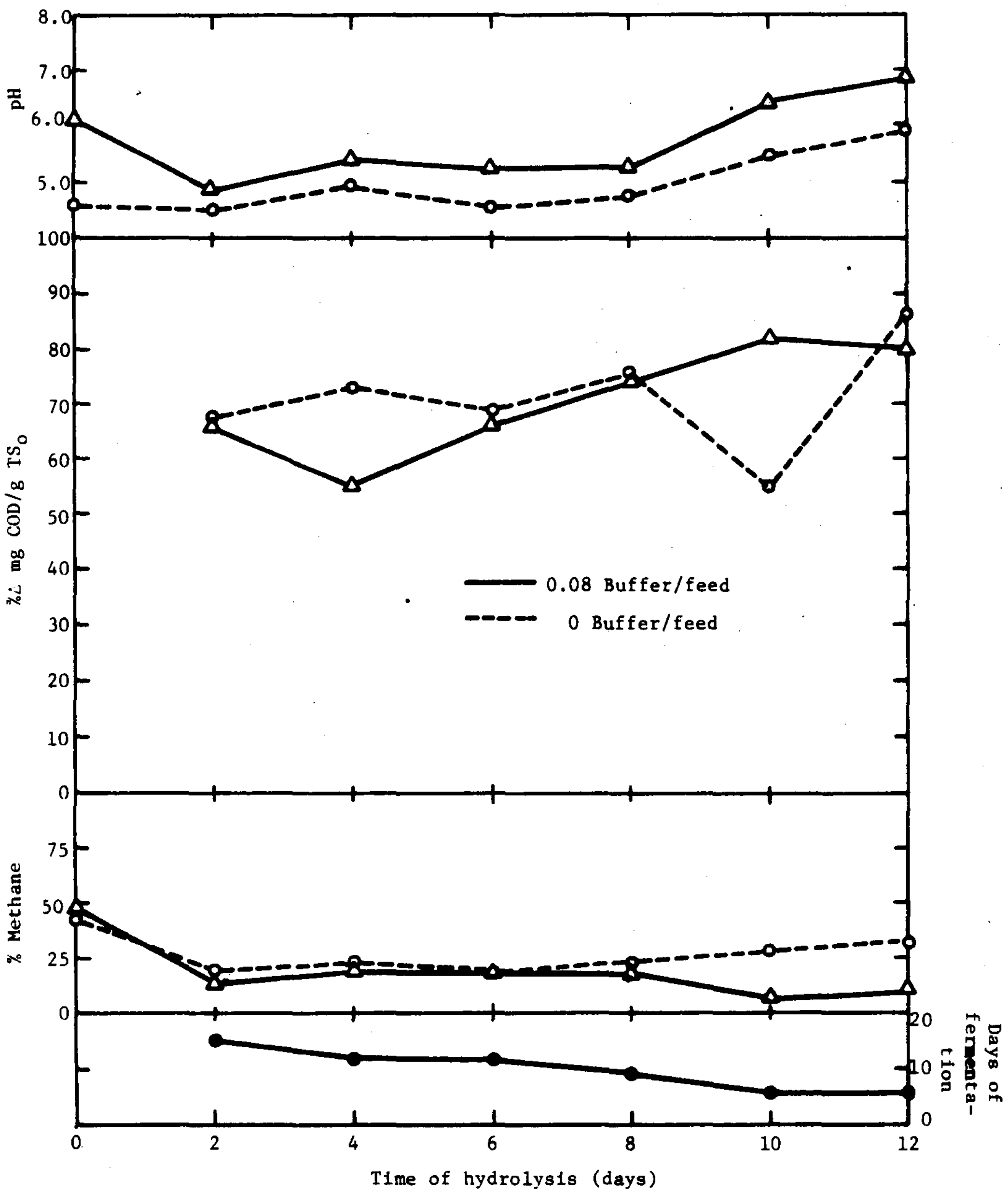


Figure 16. Post fermentation data for corn stover 55°C for the short term acid hydrolysis study.

soluble COD reduction. Soluble COD reduction increased with longer hydrolysis times. Also, the reactor pH was significantly improved after 10 or 12 days hydrolysis, even without any buffer addition.

Similar information is presented in Figure 17 for the wheat straw reactors at 55°C. Again, the effect of buffer additions was generally small, except for an overall increase in reactor pH. It is interesting to observe that reactor pH showed a dramatic rise following hydrolysis of 10 or 12 days.

It should be stated that all reactors started at 35°C performed well. Even the reactors with no supplemental buffer and no hydrolysis achieved stable methane production. This is most likely related to the impact of high S/F ratios, where the large amounts of digested seed will initiate methane production. Figure 18 compares wheat straw reactors, without supplemental buffer, after fermentation at 35°C and 55°C. Reactor pH is seen to be stable at all times at 35°C, while the 55°C reactors do not approach satisfactory levels until long hydrolysis periods have passed. The 55°C units also have lower methane percentages throughout the study. The reduction in soluble COD did not show any large differences, however. The reasons for this are not fully understood at this time. It should be noted that fermentation was initiated at high moisture contents, unlike most of our previous experiments. The performance of these residue systems at low solids concentrations is presently an area that has not been thoroughly investigated in this study.

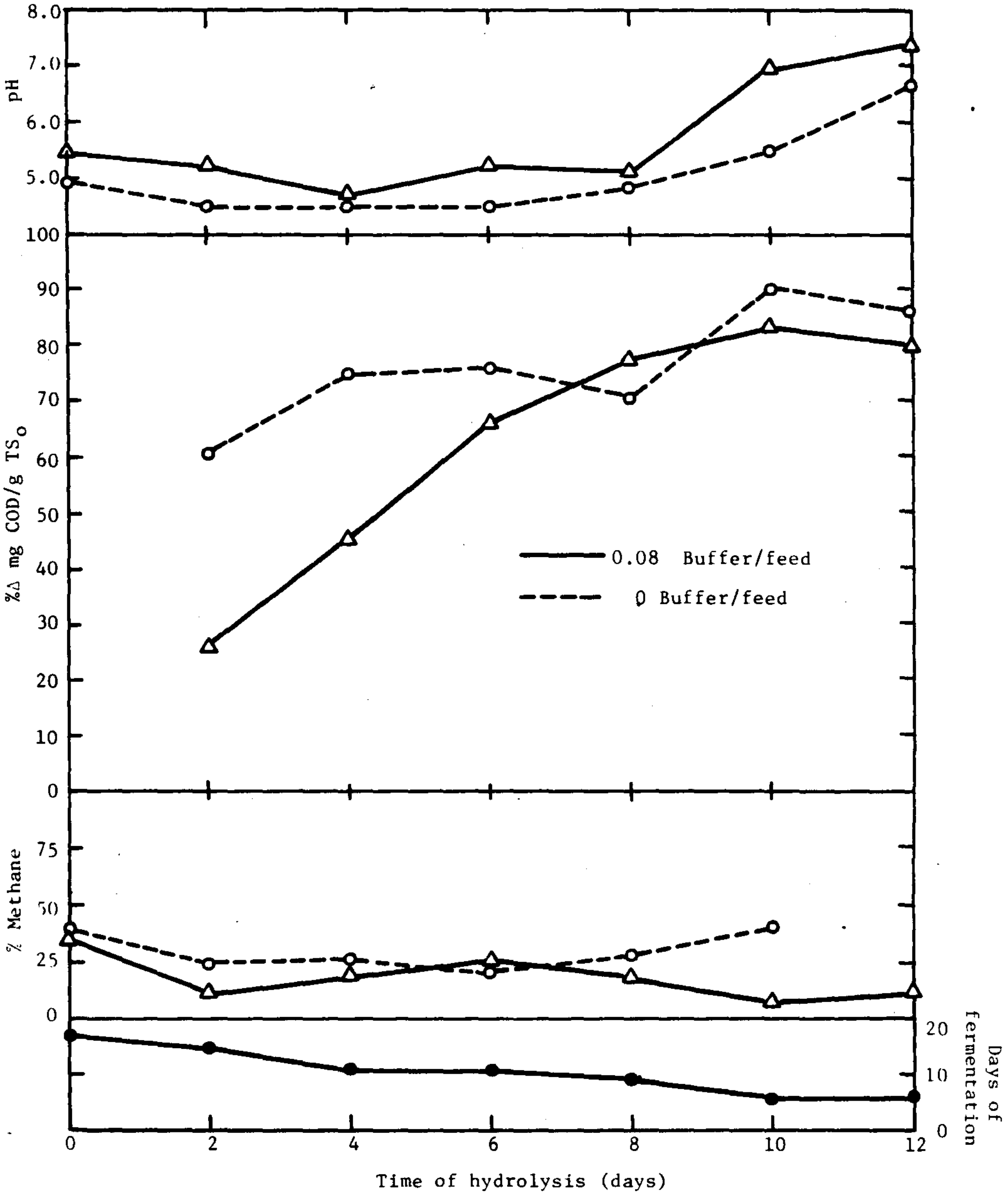


Figure 17. Post fermentation data for wheat straw, 55°C in the short term acid hydrolysis study.

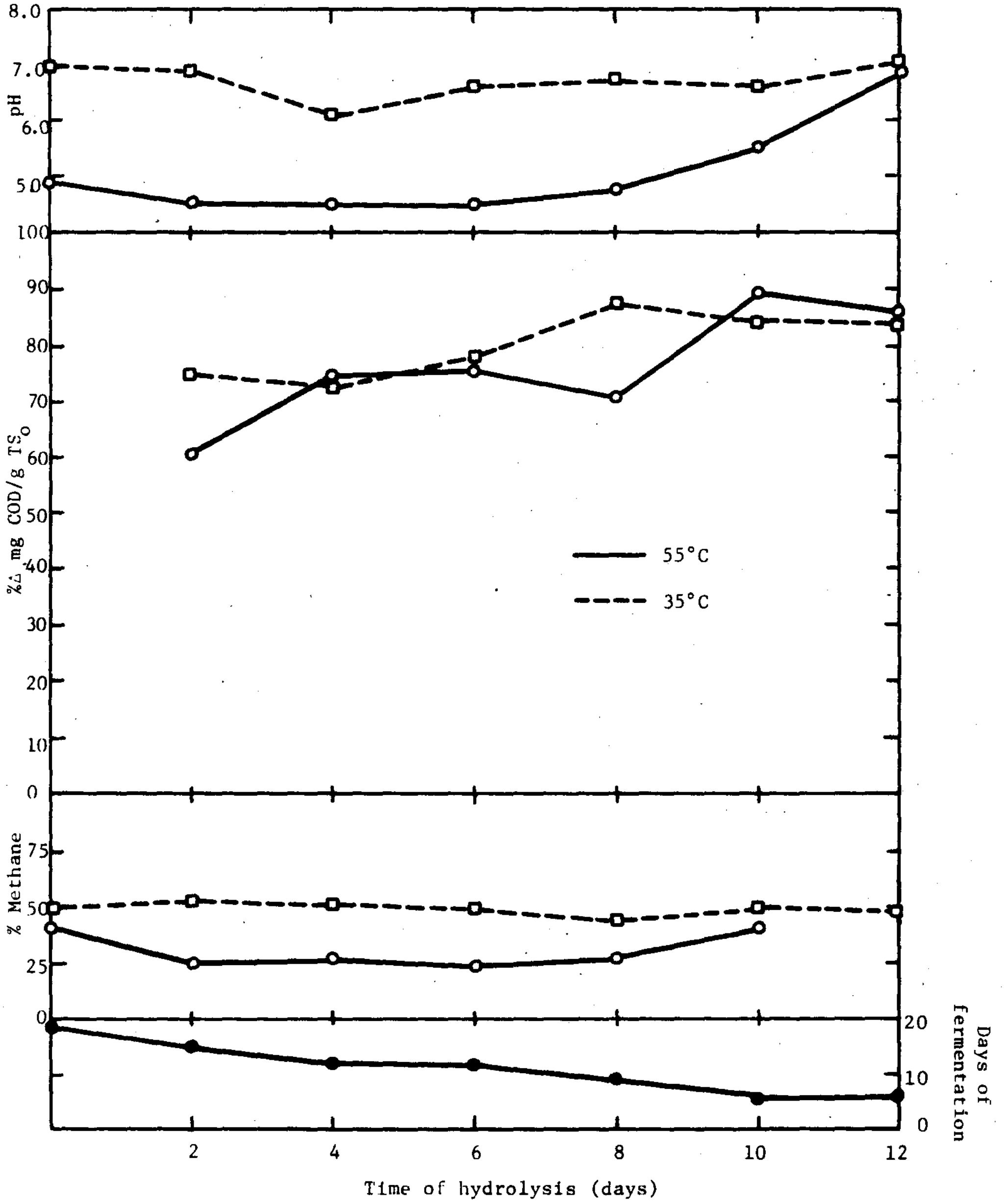


Figure 18. Post fermentation data comparing wheat straw at 35° and 55°C for the short term acid hydrolysis study.

Aerobic Pretreatment Studies

The option of using short term aerobic pretreatment for pH control and temperature increase was examined during this quarter. Four preliminary aerobic treatment studies (PATS) were completed. Additional studies are presently being conducted.

Three preliminary studies (PATS I, II, III) used simple aeration of corn stover, wheat straw, and old field grass. The variables examined are shown in Table 4. These studies employed 1 liter uncovered mason jars. Aeration was ensured through daily stirring of reactor contents. Temperature, pH, weight loss, and solids were monitored. In study I, moisture was not controlled following the initial water addition. The units were therefore extremely dry after three days. In study II daily moisture addition to selected reactors enabled the comparison of moisture and non-moisture controlled three-day aerobic pretreatment. Daily water addition brought the reactors to their initial moisture content. Temperature rise and pH were monitored for moisture and non-moisture controlled aerobic pretreatment in study III.

There were not any observable trends in the effects of a variable S/F ratio, percent total solids, temperature or substrate on percent TVS_D after 6 days of non-moisture controlled aeration. Estimated volatile solids loss (based on mass balance) ranged from 1 to 40 percent. Three days of moisture controlled aeration also showed no apparent trend in effects of a variable S/F ratio or temperature on percent TVS_D. Corn stover had consistently higher percent TVS_D than

TABLE 4. BENCH SCALE PRELIMINARY AEROBIC TREATMENT STUDY (I, II, III) REACTOR SETUP.

	PATS I	PATS II	PATS III
Substrate	Wheat, Corn, Grass	Wheat, Corn	Corn
Temperature	35, 55°C	35, 55°C	25, 35, 55°C
% Total Solids	35, 45	35	25, 35
Seed/Feed Ratio	0.2, 0.1, 0.025	0, 0.20	0
Seed Type	Raw Manure	Raw Manure	Raw Manure
Reactor Size	1ℓ	1ℓ	1ℓ
Moisture Add.	No	Yes, No	Yes, No

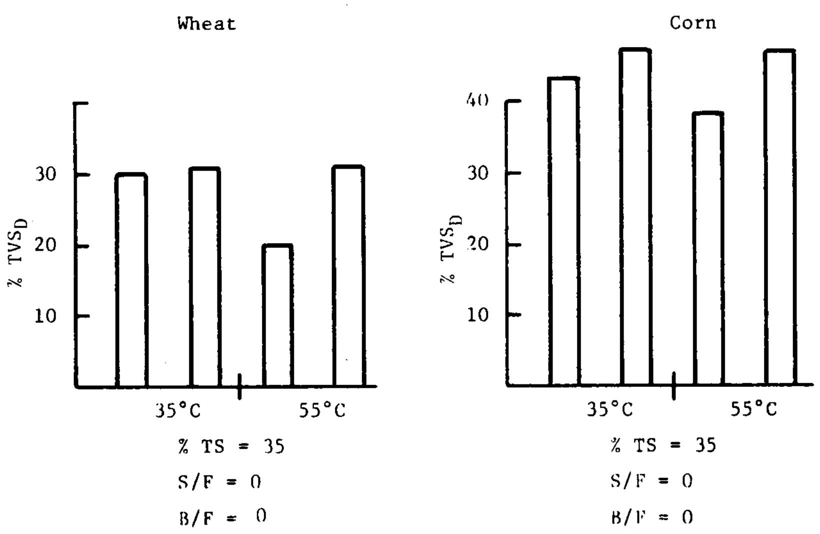


Figure 19. Effect of substrate on moisture controlled aerobic pretreatment TVS_D.

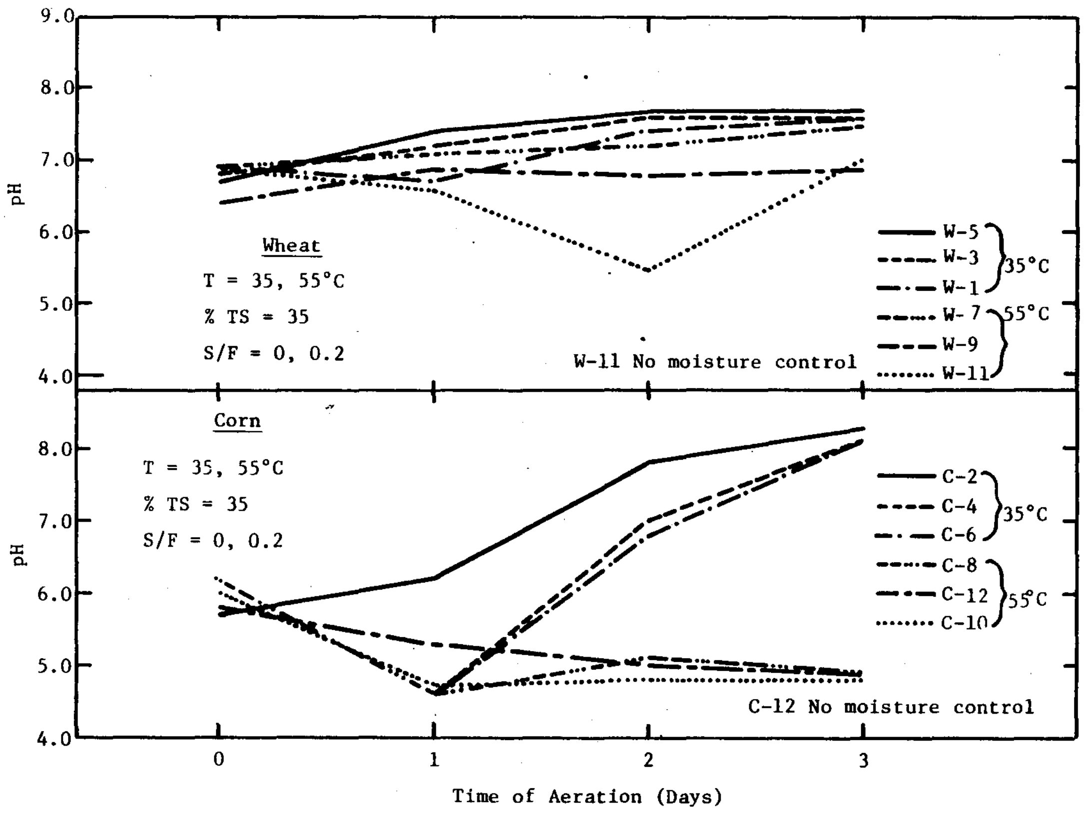


Figure 20. Variation of pH during moisture controlled aerobic pretreatment.

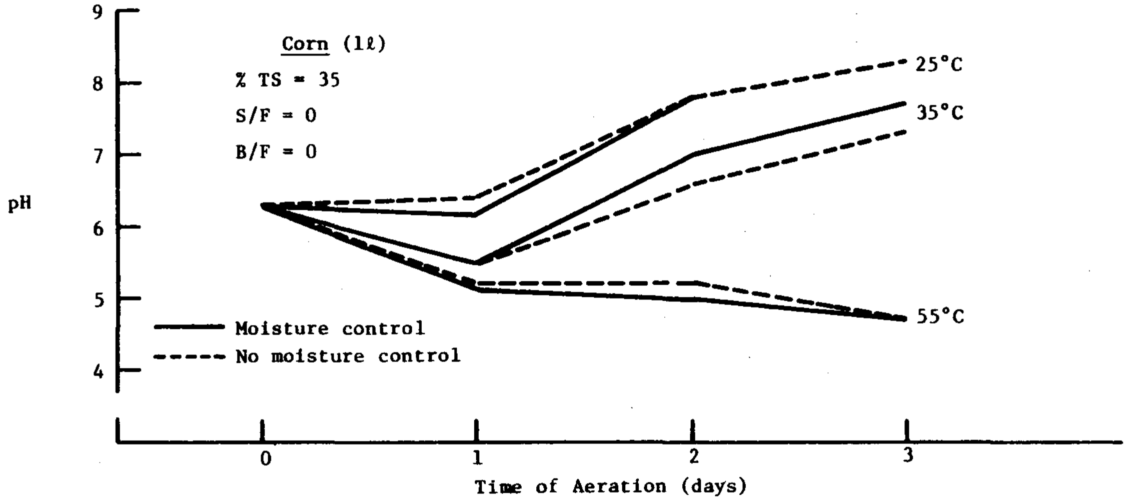


Figure 21 (a). Variation of pH during aerobic pretreatment of corn stover (PATS III)

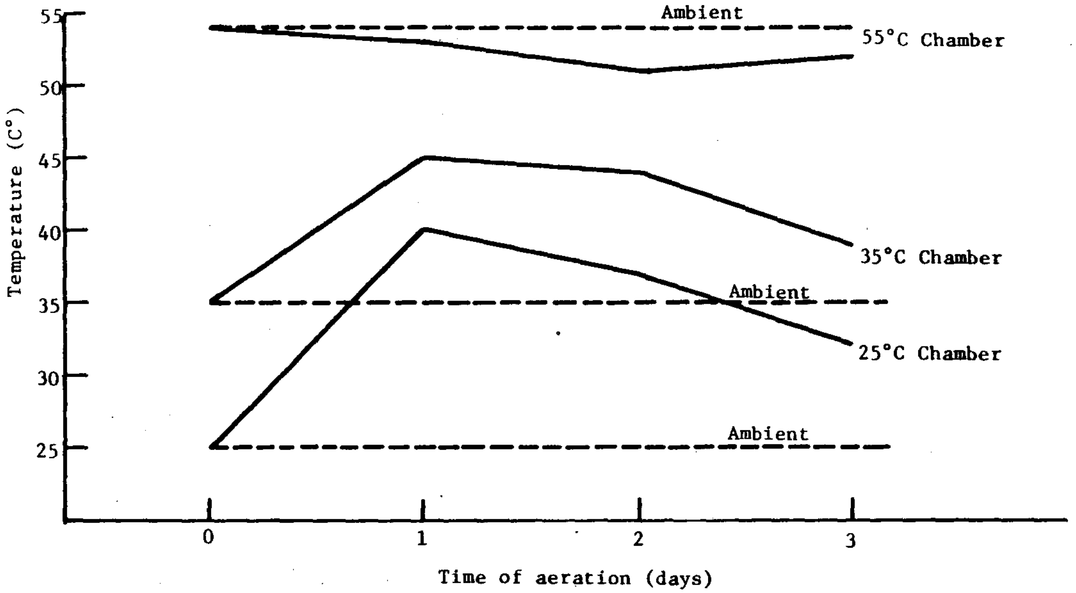


Figure 21 (b). Variations of temperature during aerobic pretreatment of corn stover (PATS III) wheat straw as seen in Figure 19. Corn stover at 35°C demonstrated a pH recovery after an initial drop. The 55°C units remained at a low pH as seen in Figure 20. Wheat straw did not demonstrate this temperature related divergence in pH, remaining at or climbing above the original pH of approximately 6.5. Figure 21 further demonstrates a difference between mesophilic and thermophilic aeration. Both the 25°C and 35°C reactors showed large temperature rises while the 55°C reactors recorded an apparent slight temperature depression. Again, a substantial rise in pH was observed in the mesophilic units while the thermophilic reactors dropped below 5.0.

The mesophilic pH recovery within 2-3 days prompted the decision to employ a standard three-day aerobic pretreatment in subsequent studies. The impact of initial TVS loss on the extent of fermentation is not fully known, and any benefits of pH control may be outweighed by an excessive loss of potential methane.

The fourth preliminary aerobic treatment study investigated viable conditions for farm scale post-aeration fermentation with raw manure seed. The post-aeration conditions of both portions of this study are described in Table 5.

After two weeks of post-aerobic fermentation the 35°C units of PATS IV A (15ℓ) showed signs of fermentation activity. Methane content approached 20% with pH's ranging between 5.5 and 6.0. The thermophilic units showed negligible methane contents with pH's at or below 5.5. Twenty days after aerobic pretreatment, the one liter reactor of PATS IV B at mesophilic and thermophilic temperatures showed negligible methane contents with most pH's below 5.5.

TABLE 5. BENCH SCALE PRELIMINARY AEROBIC TREATMENT STUDY (IV A, B) ANAEROBIC REACTOR SETUP.

	PATS IV A	PATS IV B
Substrate	Corn, Wheat	Corn, Wheat
Temperature, °C	35, 55	35, 55
% Total Solids	35	35
Seed/Feed Ratio	0.20	0.20
Buffer/Feed Ratio	0, 0.08	0, 0.04, 0.08
Reactor Size	15ℓ	1ℓ
Particle Size	Coarse (4-8 cm)	Fine (2mm)

The apparent discrepancy in results for different substrate and particle sizes prompted the initiation of an additional study described below.

Follow-up studies being initiated at the time of this writing were designed to determine viable conditions for farm scale fermentation with and without aerobic pretreatment. The anaerobic conditions for these studies at two reactor sizes are presented in Table 6. Compaction and seed type were two variables of interest in this study.

Previous studies had used only raw manure for seed. This study included digested manure as well as raw manure to examine the effects of seed stability. Compacted dry densities of 10 lb/ft^3 were set up to compare with the typical loose density of 4-6 lb/ft^3.

Reactor-Particle Size Study

A reactor-particle size study was initiated during this quarter to investigate reactor performance based on size of the reactor (1 liter vs. 20 liter), particle size of the substrate used (0.2 cm vs. 4.8 cm) and manure used as the seed source (raw manure versus digested manure).

Eight one liter reactors and four 20 liter reactors were constructed for this study; see Table 7 for reactor constituents. Initial total solids, volatile solids and pH were taken for all reactors. The analysis schedule for the one-liter reactors included weight loss and gas analysis every three days. The 20 liter reactors are monitored every three days for gas analysis and gas production. This study is ongoing.

TABLE 6. BENCH SCALE PRELIMINARY AEROBIC TREATMENT STUDY (V A,B,C) FARM SCALE ANAEROBIC REACTOR SETUP.

	PATS V A	PATS V B	PATS V C
Substrate	Corn, Wheat, Grass	Corn, Wheat, Grass	Corn, Wheat Grass
Temperature	35°C	35, 55°C	35°C
% Total Solids	25	25	25
Seed/Feed Ratio	0.35	0.35	0.35
Seed Type	Raw, Digested	Raw, Digested	Raw, Digested
Buffer/Feed	0	0, 0.04	0
Reactor Size	1ℓ	1ℓ	1ℓ
Density (lb/ft^3)	Loose Fill	Loose Fill	Loose Fill

TABLE 7. REACTOR PARTICLE SIZE STUDY CONSTITUENTS

UNIT	SIZE	TEMP	SUBSTRATE AND PARTICLE SIZE	%ITS	SEED/ FEED	SEED TYPE	BUFFER/ FEED
RC1	1 liter	35°C	Corn - fine chop[1]	25%	.20	Raw Manure	.08
RC2	1 liter	35°C	Corn - fine chop	25%	.20	Digested[3]	.08
RC3	1 liter	35°C	Corn - coarse chop[2]	25%	.20	Raw	.08
RC4	1 liter	35°C	Corn - coarse chop	25%	.20	Digested	.08
RW1	1 liter	35°C	Wheat - fine chop	25%	.20	Raw	.08
RW2	1 liter	35°C	Wheat - fine chop	25%	.20	Digested	.08
RW3	1 liter	35°C	Wheat - coarse chop	25%	.20	Raw	.08
RW4	1 liter	35°C	Wheat - coarse chop	25%	.20	Digested	.08
RS1	20 liter	35°C	Corn - coarse	25%	.20	Digested	.08
RS2	20 liter	35°C	Wheat - coarse	25%	.20	Digested	.08
RS3	20 liter	35°C	Corn - coarse	25%	.20	Raw	.08
RS4	20 liter	35°C	Wheat - coarse	25%	.20	Raw	.08

[1] fine chop = 0.2 cm [2] coarse chop = 4-8 cm [3] digested manure = 35°C seed with 15 day HRT

Reactor size compares the performance of 20 liter reactors to 1 liter bench scale reactors. A previous study in which 20 liter reactors out performed 1 liter reactors indicated a need to investigate the size question in more detail. Figures 22 through 25 show the comparison of methane percent between 1 liter and 20 liter reactors. Figures 23 and 24 indicate little difference in reactor size. Figure 22 shows the 20 liter reactor out performing the 1 liter reactor, whereas Figure 25 shows the 1 liter reactor out performing the 20 liter reactor. More data analysis is necessary before any conclusions are drawn.

Particle size of the substrate used in this study compare fine chopped (0.2 cm) corn and wheat straw and coarse chopped (4-8 cm) corn and wheat straw, on the one liter scale. Figures 26 and 27 show the comparison between the coarse and fine chopped corn and wheat straw. In Figure 26 the corn coarse chopped substrate out performed the fine chopped substrate. Through subsequent analysis (protein and fiber analysis) it was found that the biodegradable fraction is higher in the fine chopped corn encouraging rapid volatile acid formation thus dropping the pH and inhibiting the methanogens. The coarse chopped corn, having a lower biodegradable fraction allows for a progression from volatile acid formation to methanation. Figure 27 indicates that for wheat straw there is no significant difference between fine and coarse chopped.

Differences in the manure (raw vs. digested) as the seed source was also investigated. In both the 20 liter and 1 liter reactor sizes, the digested manure out performed raw manure in percent methane, see Figure 28.

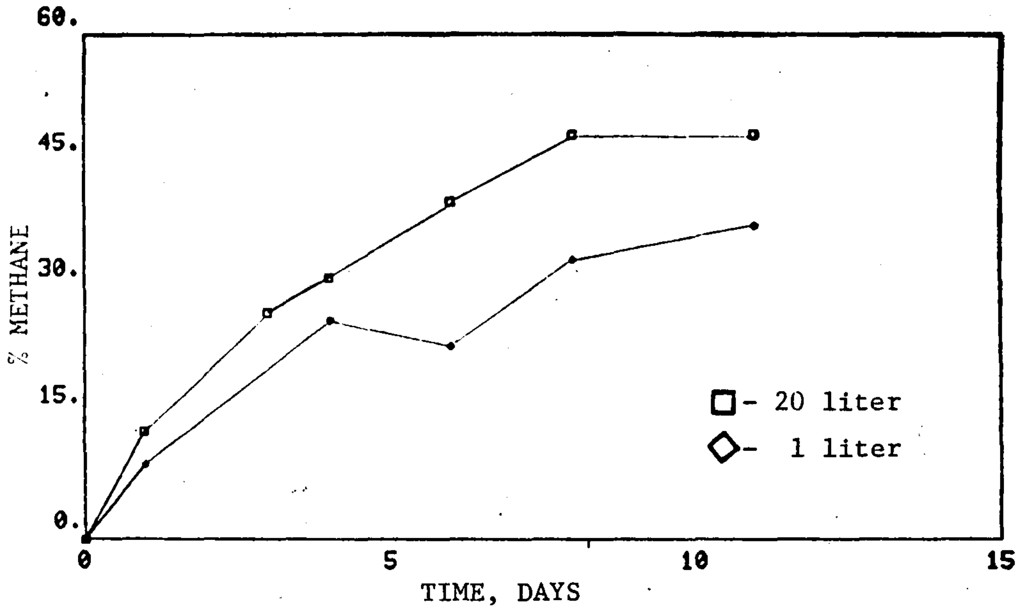


Figure 22. Comparison of % methane between 20 liter and 1 liter corn stover reactor with digested manure. (25% I.T.S.)

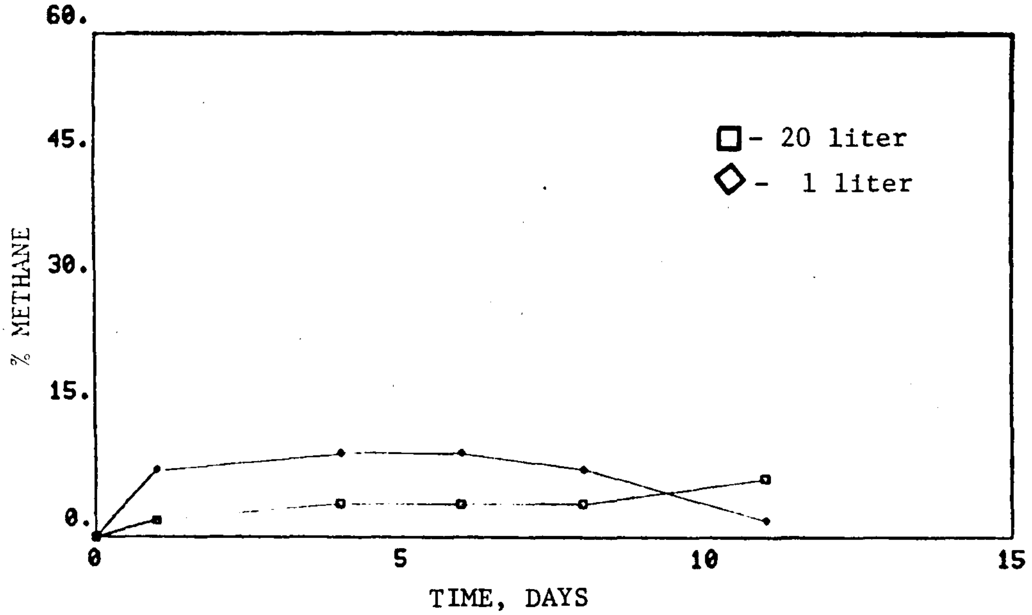


Figure 23. Comparison of % methane between 20 liter and 1 liter corn stover reactors with raw manure. (25% I.T.S.)

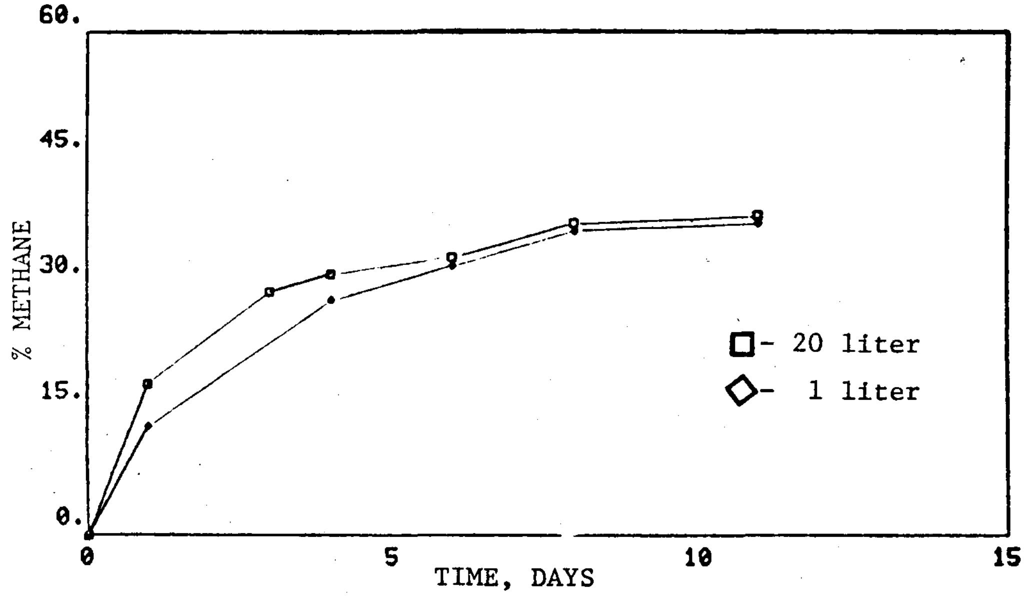


Figure 24. Comparison of % methane between 20 liter and 1 liter wheat straw reactor with digested manure. (25% I.T.S.)

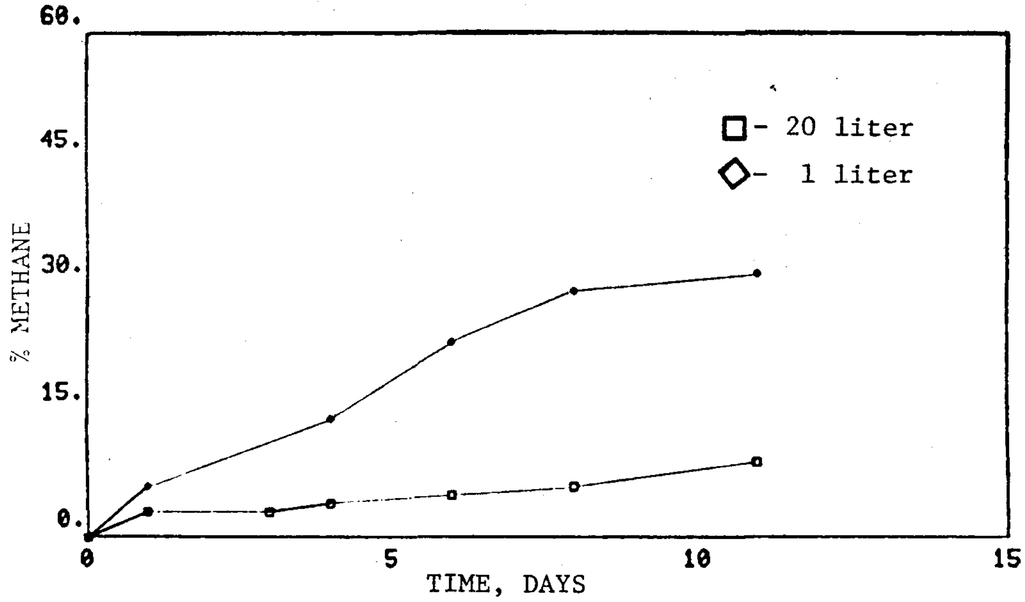


Figure 25. Comparison of % methane between 20 liter and 1 liter wheat straw reactors with raw manure. (25% I.T.S.)

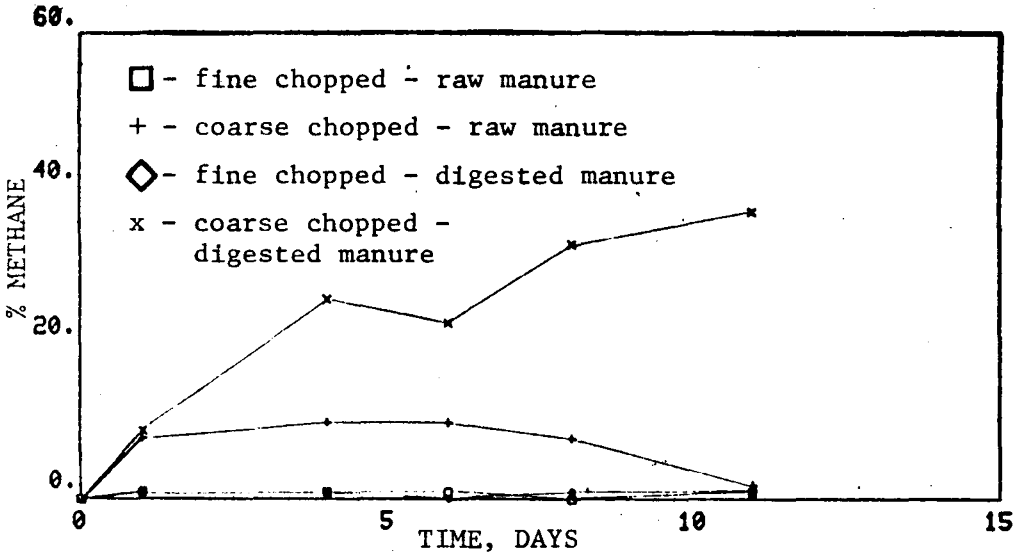


Figure 26. Percent methane of corn stover 1 liter reactors comparing: fine chopped and coarse chopped reactors with raw manure and fine and coarse chopped reactors with digested manure. (25% I.T.S.)

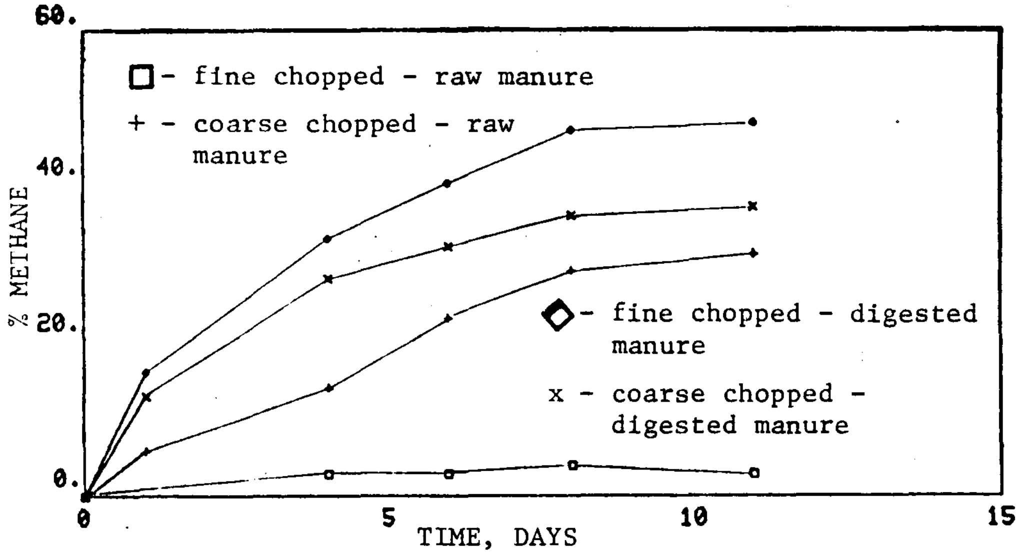


Figure 27. Percent methane of wheat straw 1 liter reactors comparing: fine chopped and coarse chopped reactors with raw manure and fine chopped and coarse chopped reactors with digested manure. (25% I.T.S.)

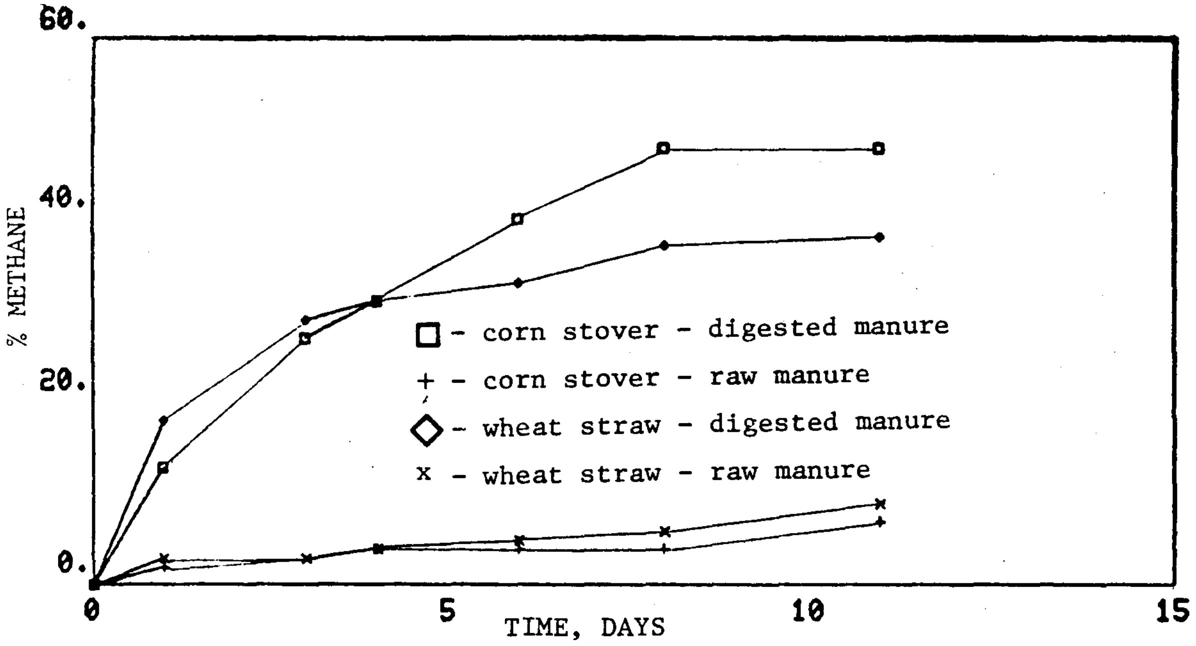


Figure 28. Performance comparison (in % methane) between 20 liter corn stover reactors with raw and digested manure; and 20 liter wheat straw reactors with raw and digested manure. (25% I.T.S.)

Tables 8a and 8b compares the cumulative biogas and methane production on 20 liter and 1 liter reactors respectively. This also shows digested manure out performing raw manure. This is an ongoing study to investigate if size is a factor in reactor performance with raw manure as a seed source.

Progressive Fiber Analysis

A study was initiated this quarter to examine the change in substrate characterization over time at thermophilic and mesophilic temperatures. Reactors were set up at 25 percent T.S., 0.08 B/F, and S/F ratios which were found to be optimal from previous studies. Substrates used were corn stover, wheat straw, and grass. Following the problems in the pilot scale digesters (Jewell _et_ _al_. 1981a) with the conversion of hemicellulose to artifact lignin, it was desired to trace the fiber conversions in these new units. Fiber samples are taken every two weeks and analyzed by the Department of Animal Science. Methane production was monitored to estimate the extent of fermentation. Figures 29 and 30 illustrate the first 28 days of fiber data for the wheat straw and grass digesters at 55°C. The figures illustrate the change in relative content of lignin, crude protein, hemicellulose, and cellulose. The hemicellulose, which is most rapidly degradable, is seen to decrease steadily for both substrates. The cellulose is relatively constant, indicative of the longer time needed for its biodegradability. The lignin and crude protein, however, both show an increase. An increase in crude protein may be indicative of bacterial protein synthesis which offsets the degradation of substrate crude protein. The increase in

TABLE 8(a). REACTOR PARTICLE SIZE STUDY COMPARING RAW MANURE AND DIGESTED MANURE IN 20 LITER REACTORS THROUGH DAY 15.

UNIT	SEED TYPE	% METHANE	CUMULATIVE BIOGAS -ℓ-	CUMULATIVE METHANE-ℓ-	pH
RSI	digested	49	163.63	58.24	6.8
RS2	digested	48	130.49	43.70	6.4
RS3	raw	9	39.35	1.93	5.3
RS4	raw	7	39.45	1.58	5.2

(b). REACTOR PARTICLE SIZE STUDY COMPARING RAW MANURE AND DIGESTED MANURE IN 1 LITER REACTORS THROUGH DAY 15.

UNIT	SEED TYPE	% METHANE	pH
RC1	raw	1	4.9
RC2	digested	3	5.1
RC3	raw	33	6.8
RC4	digested	50	6.85
RW1	raw	9	5.0
RW2	digested	55	5.4
RW3	raw	44	6.7
RW4	digested	47	6.5

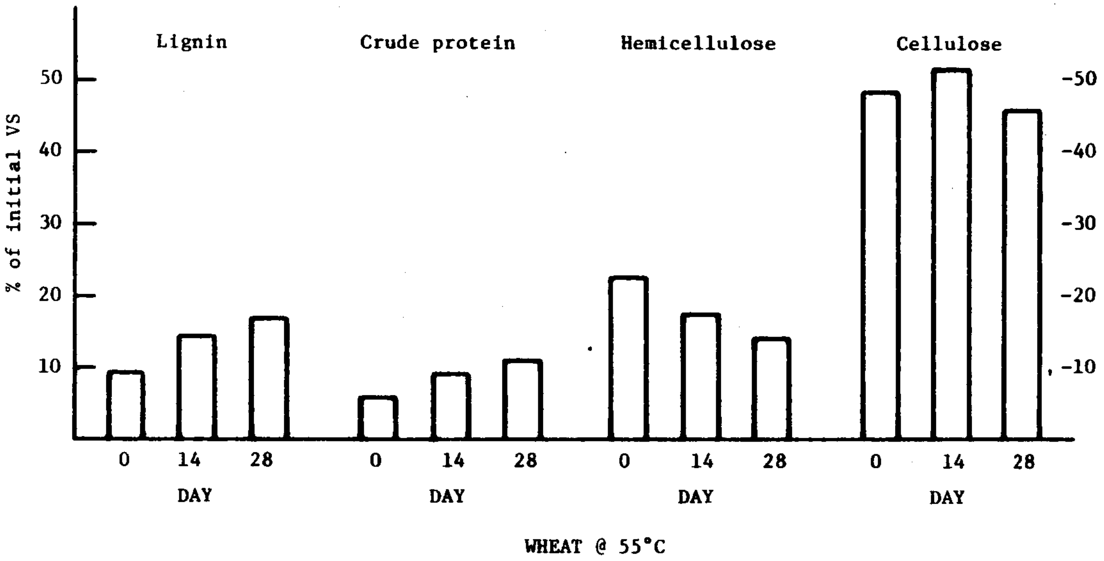


Figure 29. Fiber data from wheat straw fermentor at 55°C.

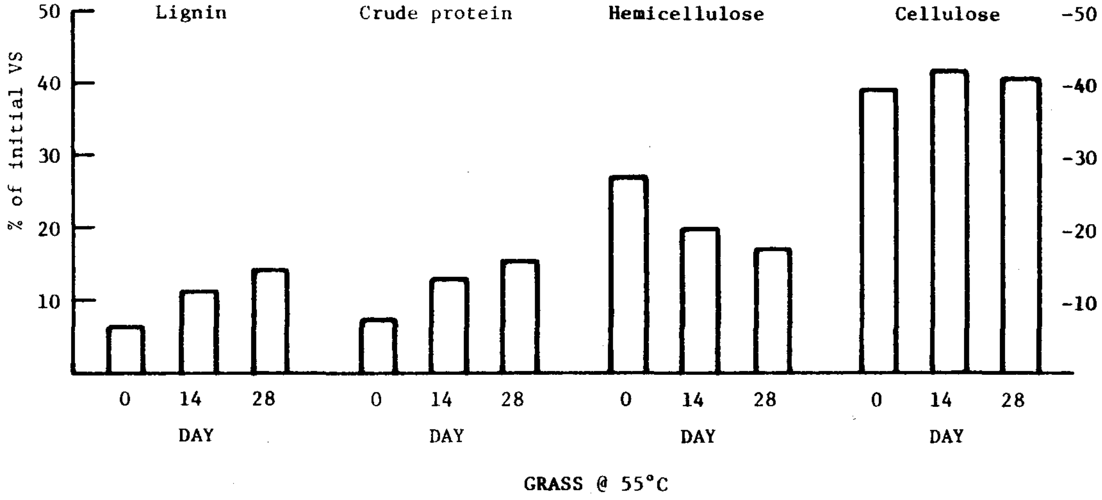


Figure 30. Fiber data from grass reactor at 55°C.

lignin may be directly related to the loss of hemicellulose, which is measured as part of the lignin content after it undergoes a browning reaction. Thus, the degradable hemicellulose, rather than becoming a food source for the bacteria, may be converted to a nondegradable compound. This is an on-going experiment (at 55°C and 35°C) which should be completed in the next quarter.

An auxiliary study which was started this quarter was a reseed study, where fermented crop residues would be used to seed fresh substrates in a dry system. The fermentors to provide this seed were started up with identical parameters for those in the fiber study. The reseeding portion of the study has not yet begun but some interesting results have been observed which may relate to the fiber study. Table 9 summarizes the estimated percent TVS destruction in the reactors set up for the fiber and the reseed study. While corn and grass did poorly in all cases at 55°C (in contrast to previous studies) the wheat did well in one case and failed in the other. Aside from a two day time period between their start up, all factors were identical. The fiber samples from thses units, currently undergoing analysis, may help to explain these types of discrepancies.

Pilot Scale Reseed/Recovery Studies

The initial study examining the feasibility of pilot scale fermented corn stover as a seed source for fermenting fresh corn residue was terminated after 14 days. A follow up study extended the seed/feed and buffer/feed ratios. The scope of these studies is shown in Table 10. The pilot scale wheat straw reactor restart study was conducted as shown in Table 11, and terminated after 26 days.

TABLE 9. ESTIMATED % TVS DESTRUCTION FROM REACTORS IN FIBER AND RESEED STUDIES AT 35°C AND 55°C.

					% TVS DESTROYED		
SUBSTRATE	TEMP °C	%TS	S/F	B/F	FIBER STUDY	RESEED STUDY	PREVIOUS DATA
Wheat Straw	55	25	.10		26.5[1]	8.8[1]	32.7[2]
	35	25	.40		40.3[2]	34.8[3]	30.4[1]
Corn Stover	55	25	.05	.08	3.6[1]	-	52.3[2]
	35	25	.40	.08	40.1[2]	36.0[3]	38.6[1]
Grass	55	25	.10	.08	5.6[1]	-	-
	35	25	.40	.08	47.0[2]	-	-

Notes:

Days of fermentation:
1. 70 days
2. 60 days
3. 50 days

TABLE 10. BENCH SCALE EXPERIMENTS TO INVESTIGATE THE USE OF FERMENTED CORN STOVER RESIDUE AS SEED SOURCE.

VARIABLE	STUDY I	STUDY II
Temperature (°C)	55	55
Seed/Feed Ratio	0.05, .10, .20, .25	.05, .10, .20, .30, .40
% Total Solids	25, 30, 35	25
Reactor Size	1ℓ	1ℓ

TABLE 11. BENCH SCALE EXPERIMENTS TO INVESTIGATE RECOVERY TECHNIQUES FOR PILOT SCALE WHEAT STRAW REACTOR.

TEMPERATURE	TIME OF AERATION	STRIPPING MEDIUM	DIGESTED EFFLUENT RESIDUE (S/F RATIO)
55°C	-	Water	-
55°C	-	Dilute Effluent	-
55°C	-	Water and Buffer	-
55°C	-	-	.05
55°C	6 hrs.	-	-
55°C	6 hrs.	-	.05

After fermentation the initial corn stover reseed reactors showed negligible methane content, low rates of reactor weight loss, and final pH's in the range of 4.7 to 5.2. It appeared evident that insufficient alkalinity was present even with a S/F ratio of 0.25. The failure of these reactors prompted the follow up study increasing the maximum S/F ratio from 0.25 to 0.40, and maximum B/F ratio from 0.04 to 0.08. After 21 days, all methane contents remained below 30%. Low rates of reactor weight loss were observed at all S/F ratios. Final pH's were between 5.0 and 5.2. Further reseeding studies with pilot scale corn stover effluent were not considered based on the reactor failures and the damaged nature of the effluent (see Progressive Fiber Analysis, above).

Each technique for wheat straw restart failed to produce an actively fermenting reactor. Stripping with dilute manure seed showed the greatest promise with a methane content reaching 50 percent. This technique produced noticeably higher weight loss than the low rates of the others. However this technique did not appear viable as the gas production remained below the level necessary even to purge the reactors.

High Moisture Control Reactors

Introduction. Twelve reactors have been started at a low total solids concentration for two reasons. First, the previous work of this group has focused on fermentation at high (15% to 65%) total solids concentrations. While good anaerobic fermentation efficiencies have been achieved at these high solids concentrations, it was realized that some comparative basis for high versus low solids conversion efficiencies

TABLE 12. INITIAL REACTOR CONSTITUENTS FOR HIGH MOISTURE CONTROL REACTORS.[a,b]

TEMP. °C	SUBSTRATE	SUBSTRATE TS	SUBSTRATE VS	SEED TS	SEED VS	WATER ADDED	TOTAL TS	TOTAL VS	$NaHCO_3$ (BUFFER)
25	Wheat	500	472	50.0	36.5	10664	590	508.5	40
25	Corn	500	461	50.0	36.5	10696	590	497.5	40
25	Grass	500	470	45.8	36.5	10686	585.8	516.0	40
35	Wheat	500	472	50.0	46.0	10575	590	518.0	40
35	Corn	500	461	50.0	46.0	10607	590	507.0	40
35	Grass	500	470	49.7	46.0	10597	589.7	506.5	40

a. All mass units in grams.

b. Does not include later additions.

reactors started up have been operating in batch mode, meaning they have received no additional food and have been opened only for pH measurements. The other half have been operated at semi-continuous feed mode. Initially the 25°C reactors were on a 30-day HRT; those at 35°C on a 15-day HRT. Feeding procedure was to vigorously shake the reactor, pour off a measured amount of waste and add measured quantities of dry substrate and a dilute nutrient solution containing 0.79 g/l NH_4Cl and 0.09 g/l K_2HPO_4 dibasic. Measurements of pH were taken on the waste.

Problems at Start-up and During First Week

By day 2 after start-up, all reactors showed a large drop in pH (1.0 to 1.5 pH units on the average) and most were producing no methane. On days 3, 4, and 7 quantities of sodium bicarbonate were added to all reactors increasing the B/F ratio from 0.08 to 0.22. At the end of the first week, wasting and feeding was temporarily halted on all semi-continuous feed units. During the second week, additional digested manure seed was added bring the S/F ratio up to 0.32 for the 25°C units and 0.20 for the 35°C units. Wasting and feeding was resumed on the semi--continuous feed units only when the pH in a particular unit measured 7.0.

After wasting and feeding began again, we tried to maintain the pH level at 6.7-6.9. Whenever the pH dropped below this level, wasting and feeding was suspended for several days until the pH recovered. This led at first to sporadic wasting and feeding. The temporary suspensions in feeding allowed both the pH and the percent methane to increase somewhat with no apparent effects on total biogas production. Also during this period, occasional small additions of buffer or digested manure seed were made to selected reactors. Such additions caused only a momentary (1 to 3 day) increase in pH and biogas production. Further, the units at 35°C were changed to a 30-day HRT with feeding every other day. This substantially improved the accuracy of the gas analysis as the reactors were opened less often. The 25°C units remained on a 30-day HRT with daily wasting and feeding.

About day 65 it was decided to waste and feed on a regular basis and allow the unit to naturally stabilize at a lower pH than we had attempted to maintain.

Results

While there was variation in individual reactor performance, certain trends and similarities can be seen along with several interesting observations. Table 13 gives current reaction rates and a data summary to day 74.

25°C Batch Units

Figure 31 shows cumulative biogas production and percent methane for the three batch reactors at 25°C. The wheat and corn reactors are very similar in reaction characteristics. The grass reactor shows an unexplained "dormant" period from days 15 to 55 when the pH rose suddenly from 6.45 to 7.1 in ten days. It is now operating as the two other 25°C batch reactors did earlier. Estimated percent total volatile solid destruction (% TVS_D) for these units is shown in Table 13.

TABLE 13. SUMMARY OF DATA FOR HIGH MOISTURE CONTROL REACTORS AT 74 DAYS.

BATCH UNITS

TEMP °C	SUBSTRATE	CUMULATIVE BIOGAS (ℓ)	CUMULATIVE METHANE (ℓ)	pH	METHANE %	ESTIMATED % TVS$_D$
25	Wheat	156.44	76.79	7.0	53	30
25	Corn	165.63	85.85	7.2	63	34
25	Grass	77.81	24.13	7.2	79	9
35	Wheat	240.16	121.95	7.3	62	50
35	Corn	241.13	128.51	7.3	57	53
35	Grass	267.34	142.74	7.3	61	58

SEMI-CONTINUOUS FEED UNITS

TEMP, °C	SUBSTRATE	BIOGAS (ℓ/day)	METHANE (ℓ/day)	pH	METHANE %
25	Wheat	3.25	1.50	6.6	46
25	Corn	2.25	0.61	6.4	27
25	Grass	3.55	2.09	7.0	59
35	Wheat	5.39	2.64	6.5	49
35	Corn	5.29	2.49	6.5	47
35	Grass	4.17	1.92	6.6	46

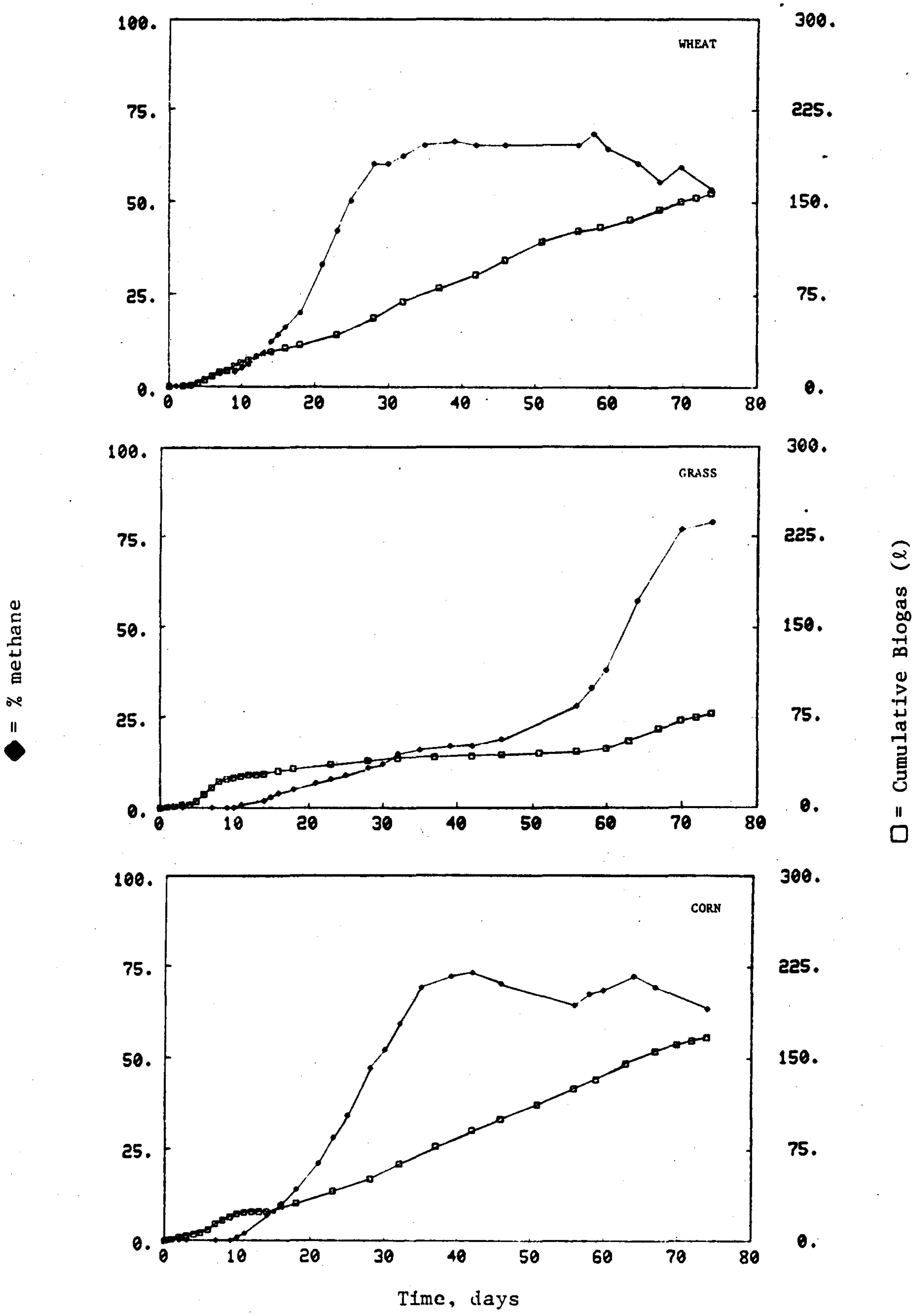


Figure 31. Cumulative biogas and % CH_4 for 3 20ℓ batch reactors at 5% TS and 25°C. Substrates are wheat straw, corn stover, and old grass.

35°C Batch Units

At 35°C, as can be seen in Figure 32 and Table 13, the batch reactors (including grass) show almost identical reaction characteristics. The problems of the first two weeks, exemplified by poor percent methane and reduced biogas production, can easily be seen here. It can also be seen that the methane content stabilized at about 60 percent and that the reactors are rapidly approaching the exhaustion of their food resources.

The upper portion of Figure 33 shows the more rapid rate of gas production at 35°C as compared to 25°C. The wheat reactors were chosen for this example, but corn and grass show the same pattern. The percent TVS_D for these units is greater than that for the 25°C units.

25°C Semi-continuous Feed Units

The start-up problems of the first two weeks are again evident in Figure 34 which shows biogas production in liters per day and percent methane for the 25°C semi-continuous feed units. All showed increases in biogas production and percent methane, but at different times and at different rates. The wheat reactor started off the quickest, followed by the corn, then grass. The wheat reactor shows the only indication of a steady-state level of production, the others not having undergone continuous wasting and feeding long enough for any trend to appear. Table 13 gives the current biogas and methane production rates, percent methane, and pH for all semi-continuous feed units.

35°C Semi-continuous Feed Units

Figure 35 shows biogas production and percent methane for the three 35°C semi-continuous feed reactors. After initial start-up problems and

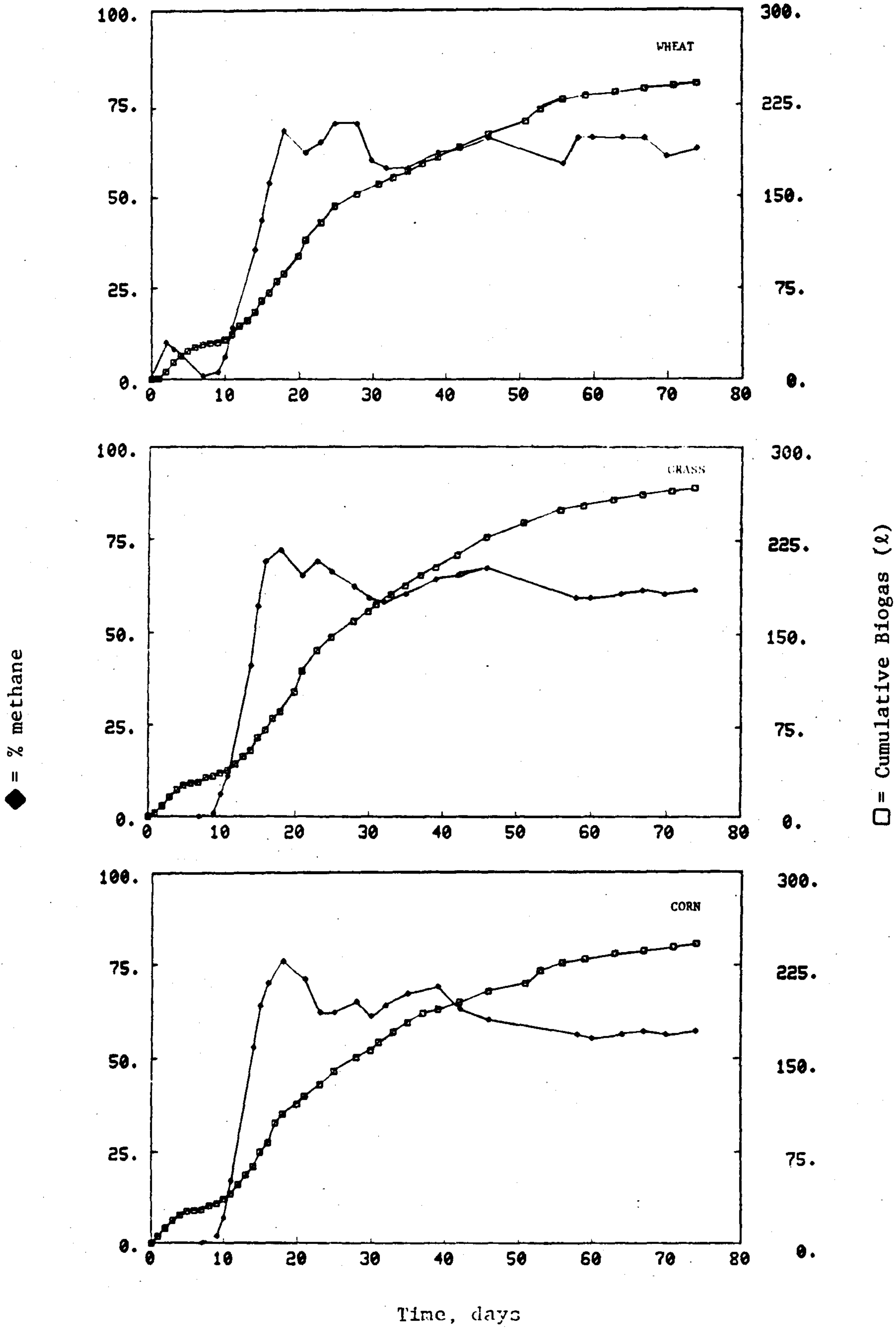
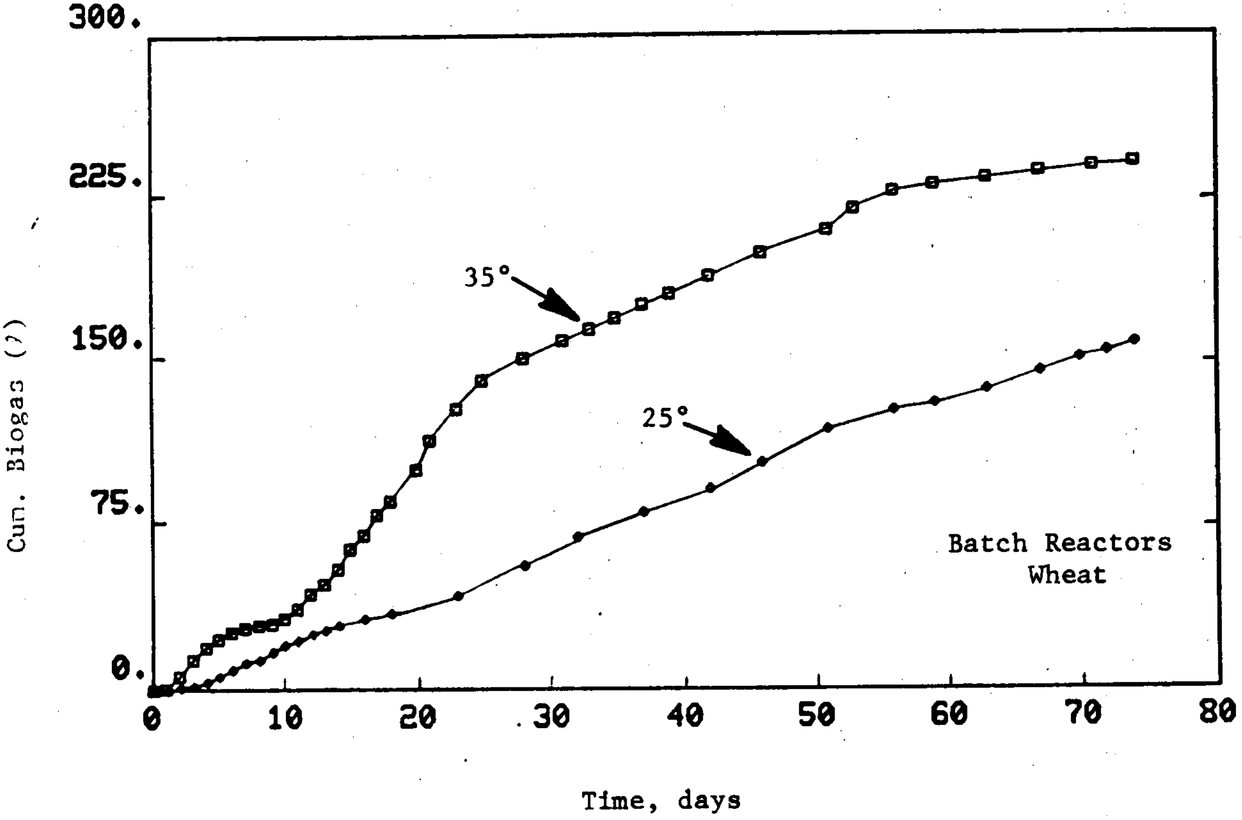


Figure 32. Cumulative biogas and % CH_4 for 3 20ℓ batch reactors at 5% TS and 35°C. Substrates are wheat straw, corn stover, and old grass.



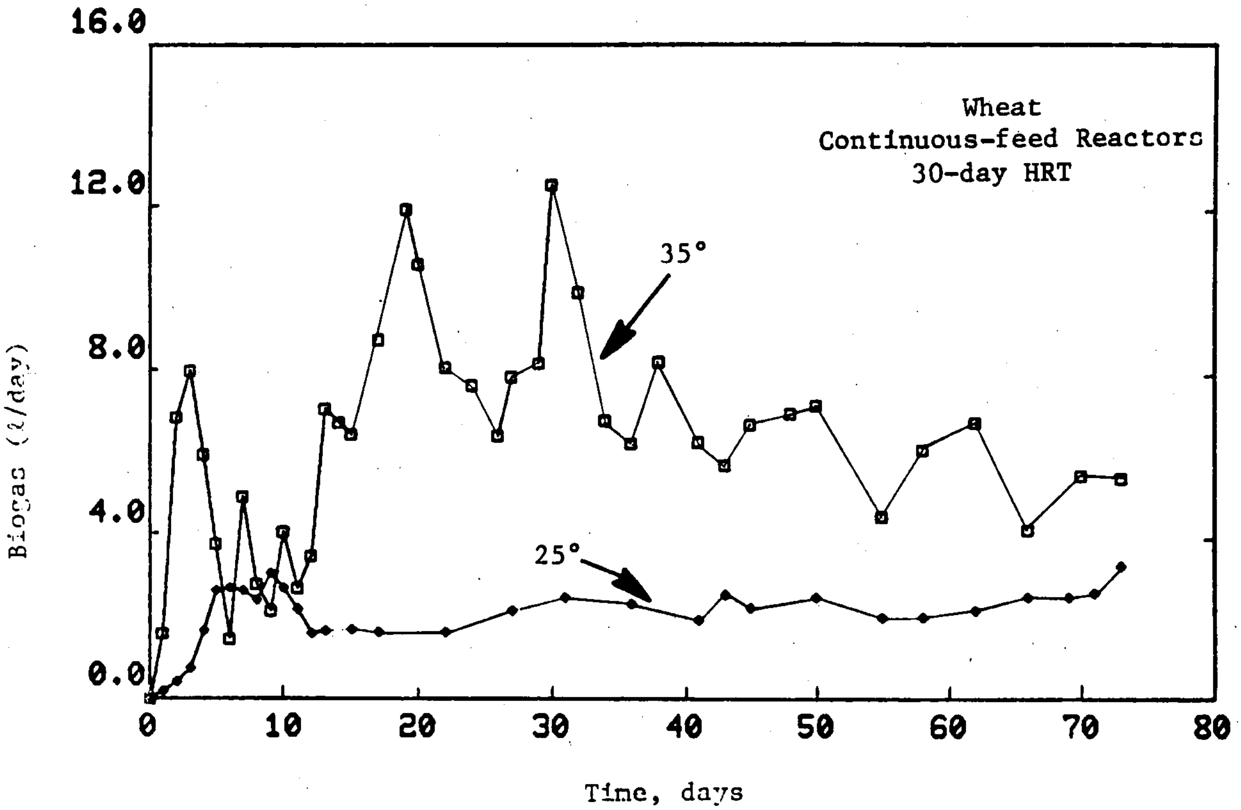


Figure 33. Comparison of biogas production from 5% TS reactors containing wheat straw at 25°C and 35°C.

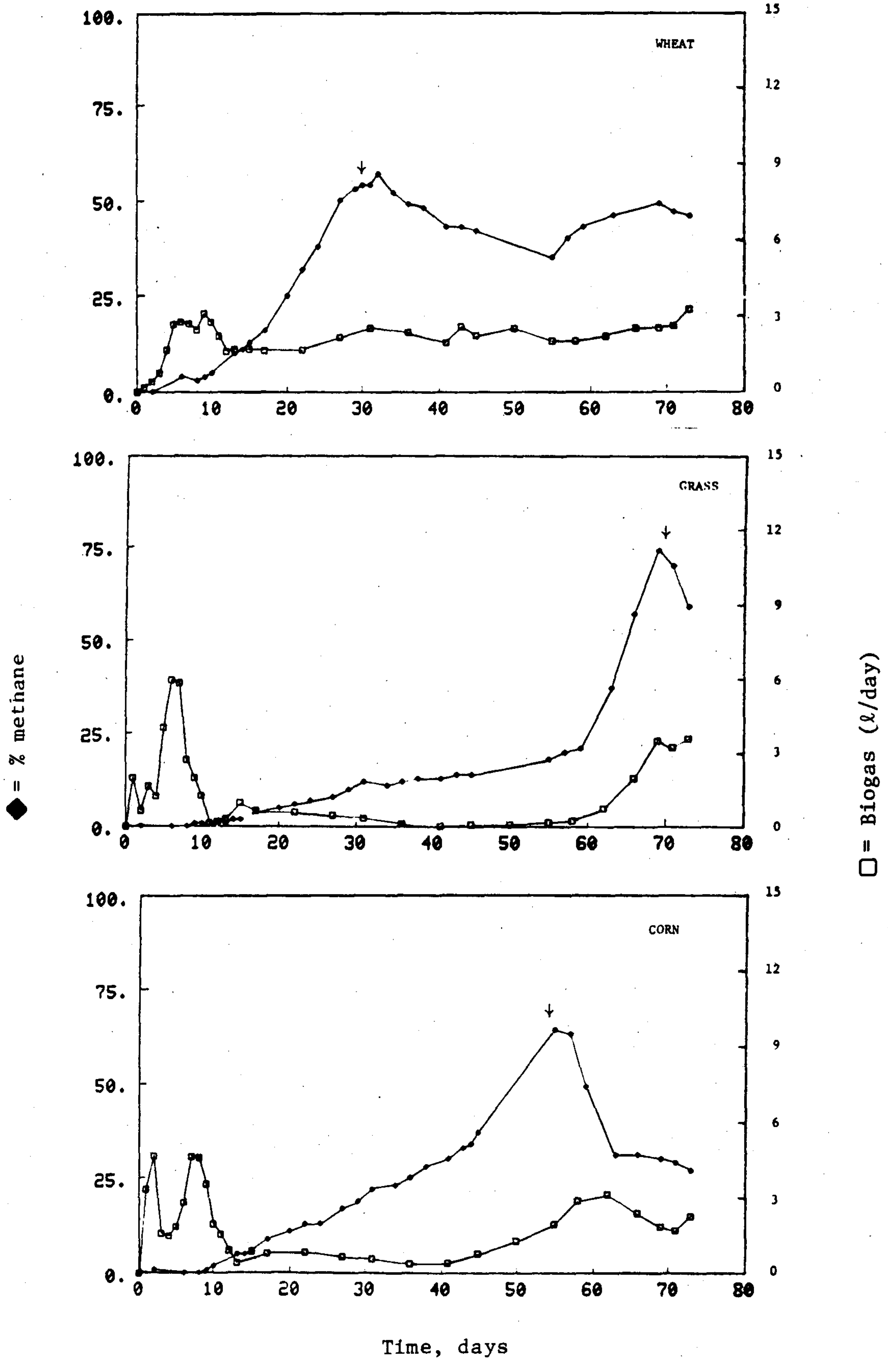


Figure 34. Biogas production and % CH_4 for 3 20ℓ continuous-feed reactors at 5% TS and 25°C. Substrates are wheat straw, corn stover, and old grass. Arrows indicate where waste and feed procedure resumed. (30-day HRT)

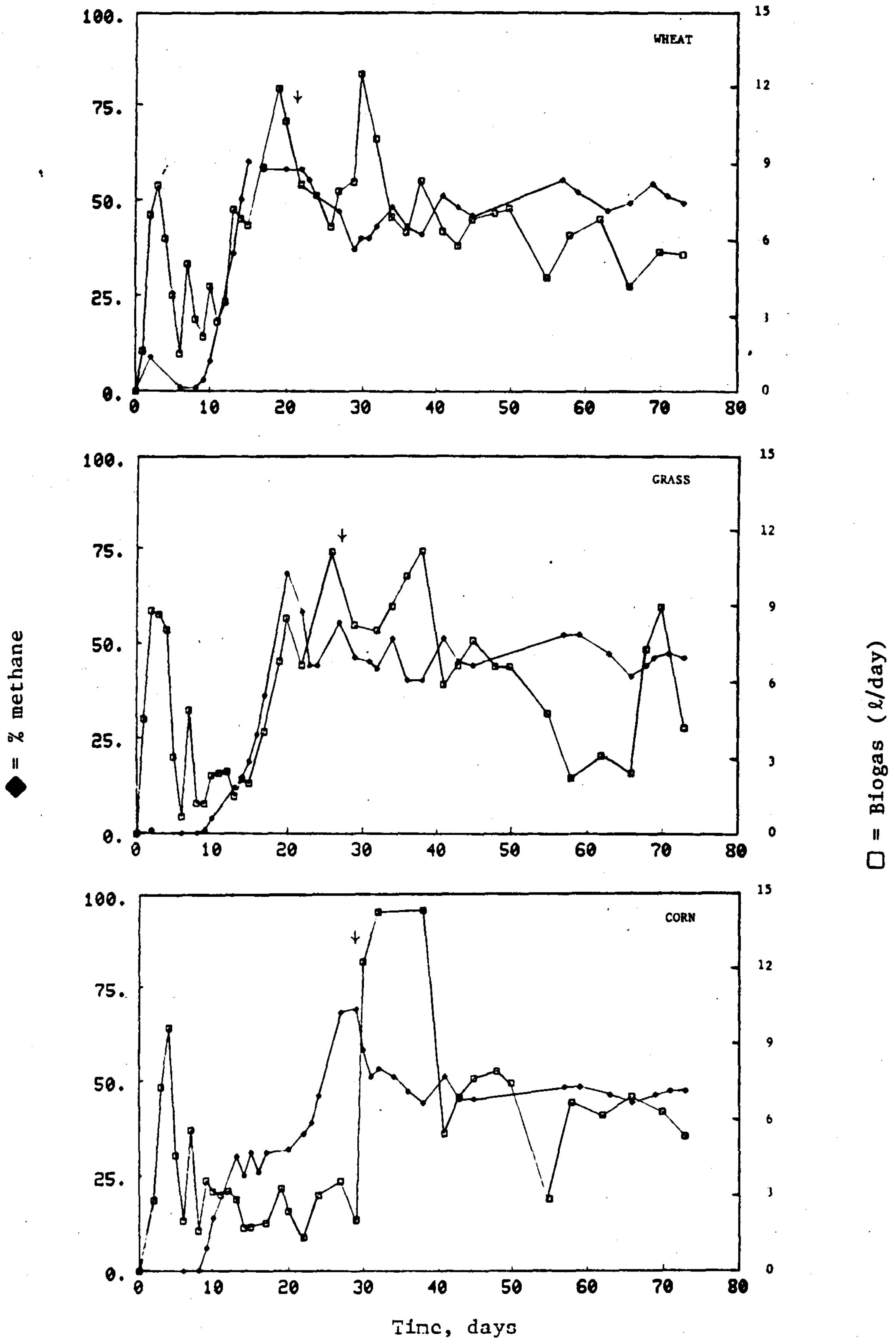


Figure 35. Biogas production and % CH_4 for 3 20ℓ continuous-feed reactors at 5% TS and 35°C. Substrates are wheat straw, corn stover, and old grass. Arrows indicate where waste and feed procedure resumed. (30-day HRT)

the resumption of wasting and feeding, a large variability in biogas rate and percent methane occurred. This is in large part due to the efforts to maintain a higher pH level (see Table 13 for current pH levels) with small buffer and digested manure seed additions and an erratic waste and feed schedule. The daily fluctuations appear less at 25°C due primarily to the smaller quantity of gas produced at 25°C and to the fact that wasting and feeding of two of the three units at 25°C began only recently. At 35°C, one can see indications of a relatively steady rate of gas production, but whether such a rate is real or due to our frequent manipulations is unknown at this time and these reactors will continue to operate until this question is resolved.

DISCUSSION

Percent total volatile solid destruction (% TVS_D) for the batch units, presented in Table 13, is estimated from methane composition of the biogas production. Results achieved last year (Jewell et al, 1981) on one-liter units at 22.5% to 25% initial total solids show that these high moisture 20 liter reactors are achieving a rate of volatile solids destruction 2 to 2-1/2 times that of the low moisture units. However, high moisture substrates are essentially incompressible and limited to dry densities (solid density) of approximately 3 lb/ft^3, compared with the 15 lb/ft^3 dry densities obtained with low moisture substrates. This indicates five times as many solids can be available for conversion under low moisture fermentation. In other words, twice as many volatile solids could be destroyed per unit volume of reactor under low moisture fermentation.

Except for the 35°C batch reactors which are near termination, the reactors will be continued for another month or two. In addition, six reactors will be started soon at 55°C, and they will be conducted for a minimum of three months.

FUTURE ACTIVITIES

The first 18 months of comprehensive efforts to develop the dry anaerobic fermentation process have resulted in improvements that enable this technology to be considered as a major option to conventional biogas-producing technology. Process requirements to initiate the reaction, and to achieve an acceptable conversion rate and efficiency have been defined for wheat straw and corn stalks. Many questions remain such as the reliability, controllability, economic feasibility and scale-up. Activities during this past quarter have raised new questions regarding particle size, reliability of operation, and start-up effectiveness. Activities during the following quarter are intended to:

1) provide additional information on the parameters that control the dry fermentation pocess; and
2) confirm the feasibility of scale-up using 200 liter and $5m^3$ units.

DRY FERMENTATION: EXPERIMENTAL DESIGN AND PLANNING

The comprehensive experimental plan was updated with a new outline (Figure 36) and summary provided below.

Fundamental Studies

These studies are broken down into three areas where basic information is needed. These are long term studies which will be conducted throughout the second year.

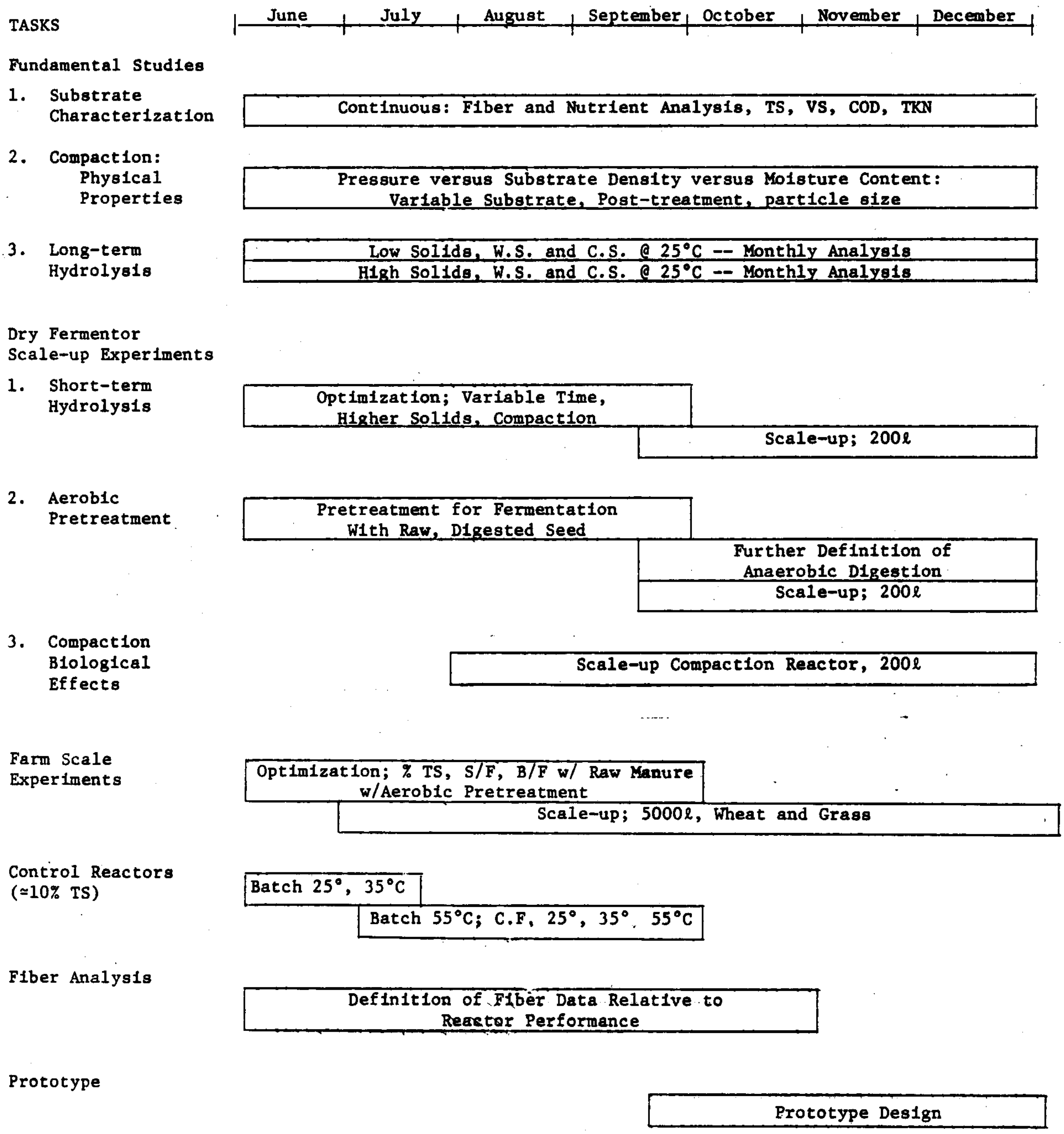


Figure 36. Experimental plan for second year of dry fermentation research.

Substrate Characterization. This includes intitial characterization of the crop residues, as well as characterization of the residues after digestion, after long term storage, and after hydrolysis. Characterization will be an integral part of all experiments.

Compaction. Studies continue to identify the physical relationships between compaction pressure, substrate density, and substrate moisture content. Variable substrates (wheat, corn, grass), effect of substrate treatments (hydrolysis, digestion, age) and particle size all are variables to be examined.

Long Term Hydrolysis. The percent of substrate solubilization will be observed over a 12 month period, and subsequently the biodegradability of the solubilized products will be assessed.

Dry Fermentor Scale-Up Experiments

These experiments are designed to enable rapid progression from initial screening experiments to optimization experiments increasing in scale from one to 5000 liters and subsequently to the design of a prototype dry fermentor. These experiments overlap with a constant flow of feedback needed to allow the program to progress rapidly. This means in many cases only start-up (2-4 weeks) will be evaluated with the small reactors. The duration of experiments will increase with the increase in scale.

Short Term Hydrolysis. pH and toxicity control

Aerobic Pretreatment. For pH and toxicity control, as well as possible temperature increases.

Compaction. Reduced seed and buffer requirements, as well as reduced reactor volume.

Farm-Scale Experiments

These experiments are designed to define viable combinations of dry substrate with raw manure seed allowing effective start-up with minimal buffer and long term operation.

Control Reactors

These units will provide a baseline of data for the comparison of new fermentation techniques to conventional fermentation technology.

All units will be slurry reactors at about 5 percent initial total solids. Two sets of reactors, batch and continuous, will be operated at 25°C, 35°C, and 55°C. All reactors will have a volume of 12 liters. Batch units will be operated for 100 days and continuous units operated at a 30 day HRT.

Fiber Analysis

These studies will determine the formation or breakdown of various cell fractions during digestion, including cell soluble, crude protein, cellulose, hemicellulose and lignin.

Prototype

The present large scale design concepts will be incorporated in the specification of a prototype dry fermentor detailed design.

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AUTOHYDROLYSIS OF ORGANIC RESIDUES TO INCREASE BIODEGRADABILITY TO METHANE

QUARTERLY PROGRESS REPORT
March 16, 1981 to June 15, 1981

June 16, 1981

P. J. Colberg
K. Baugh
A. Bachmann
V. Beard
L. Y. Young
P. L. McCarty

Environmental Engineering and Science
Department of Civil Engineering
Stanford University
Stanford, California 94305

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Solar Energy Research Institute
A Division of Midwest Research Institute

1536 Cole Boulevard
Golden, Colorado 80401

NOTICE

SECTION 1.0

INTRODUCTION

The objective of this overall 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 present study has five specific phases: (1) semi-continuous autohydrolysis system operation, (2) autohydrolysis process optimization, (3) anaerobic treatment optimization, (4) autohydrolysis of agricultural residues, and (5) biodegradation of lignin and lignin fractions.

Studies under the first phase will begin during the next year of study once a semi-continuous treatment system is built.

This report covers progress made under phases 2, 3, 4, and 5.

SECTION 2.0

AUTOHYDROLYSIS TREATMENT VARIABLES

(K.D. Baugh and P.L. McCarty)

2.1 INTRODUCTION

Staged autohydrolysis pretreatment has been shown to increase the bioconvertibility of wood products by solubilizing the carbohydrate fraction without producing refractory, inhibitory and/or toxic concentrations of sugar decomposition products. (Baugh et al., 1981). An autohydrolysis reaction model has been proposed to account for the formation and decomposition of products from staged autohydrolysis (Colberg et al., 1980b). Owen (1979) reported the bioconvertibility and toxicity of three sugar decomposition products as shown in Table 2.1. Herein are reported the results from further testing of the bioconvertibility, inhibition, and/or toxicity of the sugar decomposition products.

2.2 MATERIAL AND METHODS

Bioconvertibility, inhibition, and/or toxicity analyses were performed by modifying the anaerobic toxicity assay (ATA)(Owen et al, 1979). The modification to the ATA consisted of monitoring gas composition along with gas volume monitoring to maintain a detailed methane balance. Under conditions which inhibit methane production, large quantities of carbon dioxide can still be produced, making the rate of methane gas production a better indicator of inhibition than total gas production (Stuckey, 1980). ATA was conducted with 125 ml serum bottles.

2.3 RESULTS AND DISCUSSION

Methane production results from the ATA for glucose (GLU), 2-furfural (2-F), 5-hydroxymethyl-2-furfural (HMF), and levulinic acid (LEVA) are shown in Figure 2.1. Possible inhibition or toxicity, as indicated by the maximum methane rate ratio (MMRR)(Stuckey, 1980), is summarized in Table 2.2. The results shown in Figure 2.1 and Table 2.2 indicate that the sugar decomposition products are inhibitory to methanogenesis at higher concentrations, but acclimation usually occurs. The concentrations at which inhibition occurs for the sugar decomposition products are, in general, lower than reported previously (Owen, 1979).

The bioconvertibility to methane of the model compounds is shown in Figure 2.2. All compounds were greater than 80% bioconvertible if concentrations were below the toxic level and suitable acclimation time was provided. The bioconversion efficiencies for HMF and LEVA were greater than reported previously, while 2-F was less (Owen, 1979).

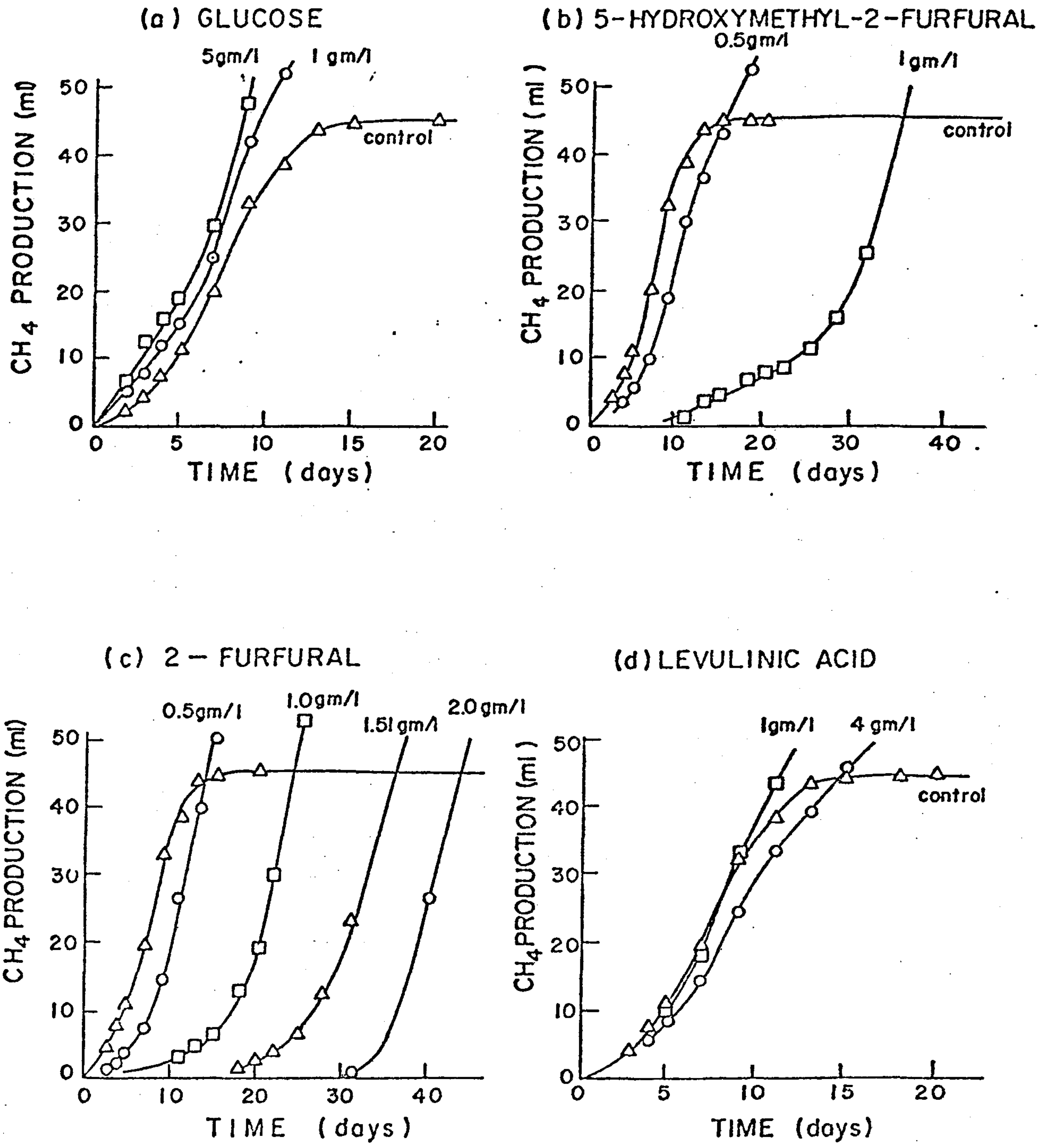

Figure 2.1. Anaerobic toxicity results for (a) Glucose, (b) 5-hydroxymethyl-2-furfural, (c) 2-furfural, and (d) Levulinic acid. Incubation temperature: 35°C, control: 1.5 gm/l acetate and 0.53 gm/l propionate.

TABLE 2.1

Anaerobic Bioconvertibility and Toxicity of Autohydrolysis Products Reported by Owen (1979)

Compound	Percent Bioconvertibility	Concentration (g/l) Inhibitory	Concentration (g/l) Toxic
2-Furfural	94.3	3	8
5-hydroxymethyl 2-furfural	72.3	2.5	7.6
Levulinic acid	74.7	12	--

TABLE 2.2

Anaerobic Toxicity Assay Summary This Study

Compound	Concentration[a] (g/l)		MMRR[a]	I[c]	Acclimation time (day)
Glucose	1	(1.07)	1.30		
	5	(5.33)	1.40		
5-hydroxymethyl 2-furfural	0.5	(0.76)	0.66	*	11
	1.0	(1.52)	0.03	*	31
	2.0	(3.05)	0.01	**	None
	3.0	(4.57)	0	**	None
2-furfural	0.5	(0.83)	0.57	*	11
	1.0	(1.67)	0.09	*	22
	1.5	(2.50)	0.01	*	31
	2.0	(3.33)	0.01	*	40
Levulinic acid	1.0	(1.52)	1.12		
	2.0	(3.03)	0.99		
	3.0	(4.55)	0.89	*	11
	4.0	(6.06)	0.75	*	11

---

[a] The theoretical COD (in parenthesis) is calculated from:
Glucose -- 1.065 gm COD/gm GLU
2-Furfural -- 1.665 gm COD/gm 2-F
5-Hydroxymethyl --
2-furfural -- 1.523 gm COD/gm HMF
Levulinic acid -- 1.516 gm COD/gm LEVA

[b] MMRR denotes the Maximum Methane Rate Ratio

$$= \frac{\text{Sample } CH_4 \text{ Production Rate}}{\text{Control Maximum } CH_4 \text{ Production Rate}}$$

[c] Inhibited samples indicated by single asterisk. Toxic concentration designated by double asterisk.

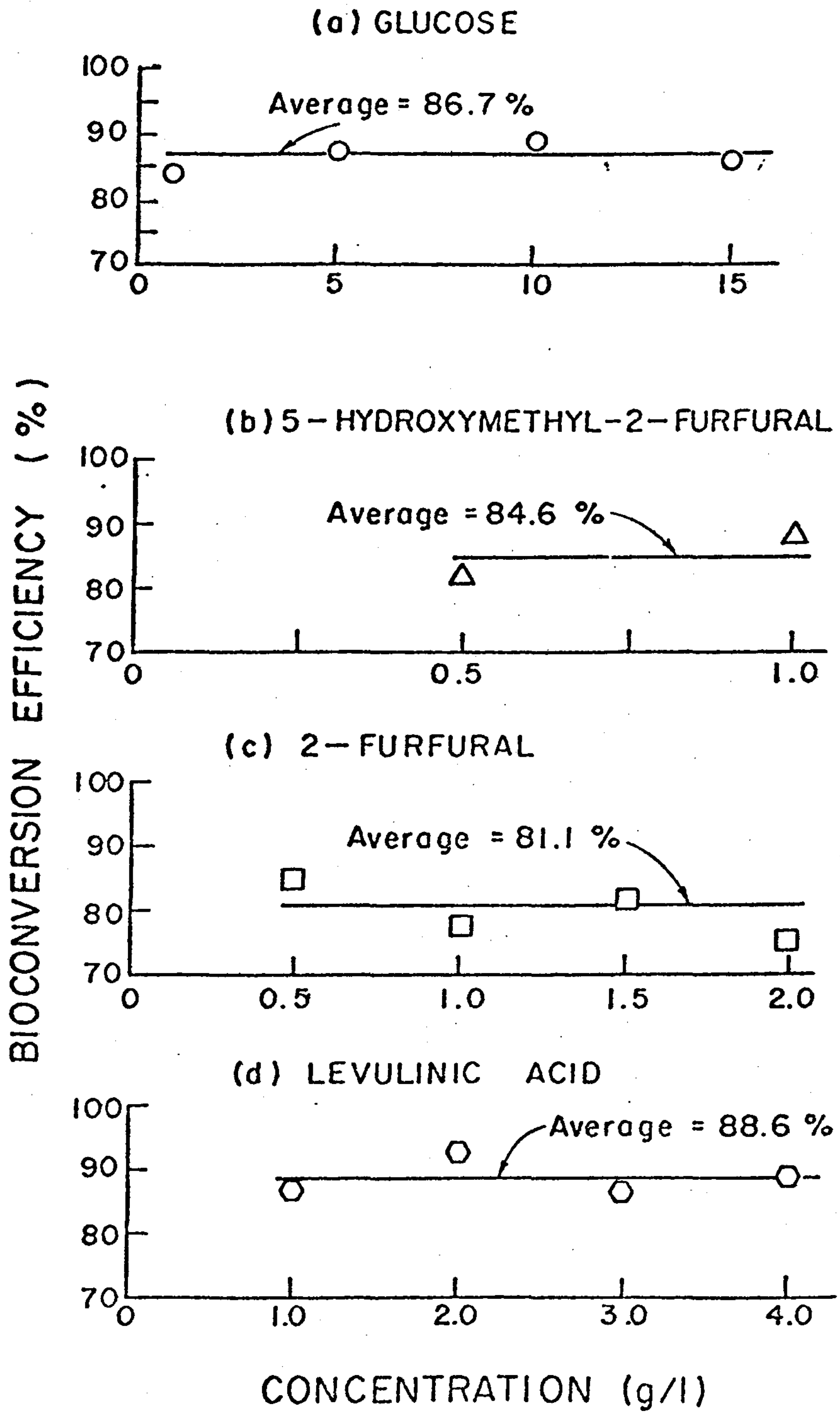

Figure 2.2. Bioconversion efficiency at 30°C of Autohydrolysis Model Compounds

2.4 CONCLUSIONS

1. Inhibiting concentrations of sugar decomposition products were:

5-hydroxymethyl-2-furfural	-- 0.5 g/l
2-furfural	-- 0.5 g/l
Levulinic acid	-- 3 g/l

2. The sugar decomposition products assayed were highly bioconvertible to methane.

3. The furan compounds are a potential cause of inhibition and even toxicity if their concentrations are sufficiently high or suitable acclimation time is not provided.

2.5 FUTURE WORK

A comparison will be made between the following intermediate compounds and their autohydrolysis products after heat treatment at 225°C for one hour and a pH of 2.5:

Cellulose
Xylan
Glucose
Xylose
5-hydroxymethyl-2-furfural
2-furfural
Levulinic acid

SECTION 3.0

AUTOHYDROLYSIS OF AGRICULTURAL RESIDUES

(A. Bachmann and P. L. McCarty)

3.1 INTRODUCTION

Initial operational characteristics of the baffled reactor using a synthetic waste were described in the previous quarterly report (Colberg et al., 1981). Steady-state data for a load of 7.9 kg COD/m^{3}d were reported followed by results obtained during a start-up period over a time frame of 28 days. Further data, especially in the increased organic loading range, are described in this report.

3.2 CHARACTERIZATION OF THE BAFFLED REACTOR

Operational characteristics of the baffled reactor up to day 28 were given in the last quarterly report (Colberg et al., 1981). The data for the reactor up to day 120 are described in this report (Figure 3.1).

At day 28, the organic loading was 9.8 gm COD/m^3 reactor day. The COD removal efficiency was 70% at an influent COD of 8.4 g/l. The organic load was further increased up to a value of 20 gm COD/m^{3}d at day 58. During this increase in organic loading, the COD removal rate peaked at day 55, reaching a value of 11.2 kg COD/m^{3}d at an organic loading of 16.6 kg COD/m^{3}d which corresponds to a removal efficiency of 68%. At day 58, when the organic load reached 20 kg COD/m^{3}d, the removal rate decreased to 10.5 kg COD/m^{3}d corresponding to a removal efficiency of 53%. The methane percentage of the produced gas remained constant at 70% up to an organic load of 7 kg COD/m^{3}d, with increasing the load from 7 to 20 kg COD/m^{3}d, the methane percentage decreased from 70% to 55% at day 58.

The organic load then was kept constant over a time period of 15 days at 20 kg/m^{3}d, at 15 kg COD/m^{3}d over a time period of 27 days up to day 100 and at 10 kg COD/m^{3}d up to day 120. Table 3.1 shows some steady-state data for these three organic loadings. Efficiencies in treatment remained constant with a decrease in organic loading in the decreasing loading range. (Table 3.1). The system behaved differently in the increasing loading range, where the efficiencies decreased with an increase in organic loading. (Figure 3.1). The total volatile acids, an indicator for the microbiological balance of the system, were essentially constant for loadings of 20 and 15 kg COD/m^{3}d and were only slightly lower at an organic load of 10 kg COD/m^{3}d. It appeared that the system was not able to overcome the stress induced by the highest organic loading. During high loading, the microorganism concentration within the reactor increased markedly and this prevented free movement of the microbial mass. It is likely that this problem was the cause of the subsequent lower efficiencies.

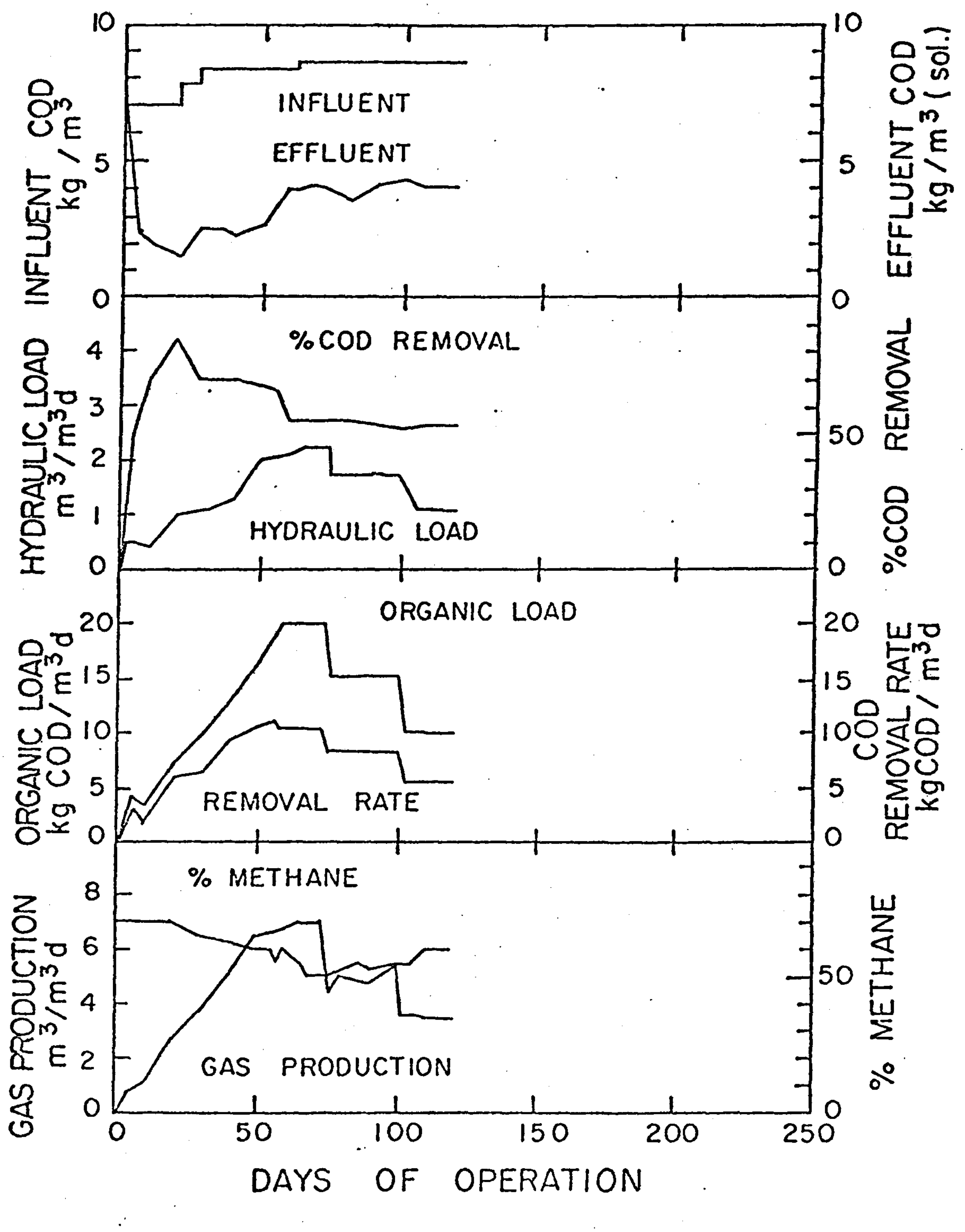

Figure 3.1. Operational characteristics of baffled reactor.

TABLE 3.1

Steady State Data for Different Organic Loadings

Theoretical Organic Loadings kg COD/m^{3}d	Time of Steady State Operation days	Theoretical Hydraulic Time hrs	Theoretical Influent COD kg/m^3	Percent COD Removed	Percent Methane	Effluent Total Volatile Acid Contamination mg/l
20	11	10	8.6	53	51	2350
15	22	15	8.6	53	54	2440
10	13	20	8.6	53	59	2160

3.3 FUTURE WORK

Further data will be abtained in the lower organic loading range to better establish the reactor's ability to recover from initial stress. Reduction of reactor suspended solids content will be obtained to help increase the contact between waste and bacteria. Also, the capacity of the reactor under increased hydraulic loading will be evaluated. On another topic under this phase, and one not reported on at this time, further significant effort is being invested into the development of a kinetic model for enzymatic hydrolysis of lignocellulosic materials.

SECTION 4.0

BIODEGRADATION OF LIGNIN-DERIVED COMPOUNDS

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

4.1 INTRODUCTION

In previous reports, we have detailed results of studies in which ^{14}C-labeled lignin-derived compounds were subjected to anaerobic degradation in the laboratory. Three molecular size fractions (MW 1400; MW 700; MW 300), collected by preparative gel permeation chromatography, were fed as the sole sources of carbon in anaerobic enrichment cultures. The data indicate that production of CH_4 and CO_2 appear to be inversely related to molecular size of the substrate, with the observed release of $^{14}CH_4$ and $^{14}CO_2$ from all three fractions. Because of the specificity of the ^{14}C-labeling procedure, release of labeled methane and carbon dioxide indicates their source to be from degradation of compounds of lignin origin.

4.2 WORK IN PROGRESS

Current work, utilizing high pressure liquid chromatography (HPLC) and gas capillary chromatography, is in an effort to characterize and quantify some of the structural changes in lignin-derived materials during anaerobic attack.

Capillary GC procedures were modified after Pereira et al. (1980) and Hedges (personal communication), and are currently being evaluated for analyses of enrichment culture extracts. One method utilizes an SE-30 fused-silica capillary column. Samples are methylated with the derivatizing agent Regisil (Regis Chemical Co). The second procedure requires derivatization with diazomethane and injection onto an SE-52 glass capillary column. These procedures should be useful in resolution of higher molecular weight compounds (MW 150) and more polar compounds, such as carboxylic acids and phenolic compounds. A previous report (Stuckey et al., 1979) detailed results of similar analyses of autohydrolyzed lignocellulose. A number of lignin-derived compounds of interest, including vanillin, guaiacol, and methoxyphenones, were resolved.

Preliminary examination of data from extraction both before and after anaerobic degradation indicates that capillary GC has the potential to quantitively characterize some of the profile changes which occur during anaerobic attack, without time-consuming sample concentration steps prior to analyses. These data will be presented in the next report.

4.3 FUTURE WORK

Subcultures have successfully been obtained from all original enrichments. HPLC analyses were recently delayed due to an instrument failure, so analyses on degraded culture extracts with this instrument are continuing.

SECTION 5.0

AUTOHYDROLYSIS OF PREDIGESTED WHEAT STRAW

(V. Beard and P.L. McCarty)

5.1 BACKGROUND

Previous work (Colberg et al, 1980) has demonstrated that autohydrolysis of wheat straw results in solubilization of the organic material and that such treatment at 150°C for one hour increases the biodegradability as assayed by the biochemical methane potential (BMP) test (Owen et al, 1979). At higher temperatures, the biodegradability decreases, suggesting that autohydrolysis products may be condensing into non-biodegradable residues. One potential way to increase the methane yield from a substrate such as wheat straw consists of three steps: (1) preliminary anaerobic digestion of the wheat straw; (2) autohydrolysis of the degraded residue; and (3) a second anaerobic digestion of the autohydrolysis products.

5.2 SAMPLE PREPARATION AND PRELIMINARY CHARACTERIZATION

A sample of anaerobically digested wheat straw (40% total solids) was obtained from the pilot scale dry fermentor at Cornell University (W.J. Jewell, Department of Agricultural Engineering). To facilitate uniform sampling by weight, the straw was cut into 1 cm lengths and dried overnight at 103°C. To allow direct comparison with previous work on undigested wheat straw (Colberg et al, 1980), 45 g/l slurries of digested straw were prepared and autohydrolyzed for one hour at temperatures of 100°C, 150°C, 175°C, and 200°C. The heat treatment apparatus consisted of a helium compressed gas cylinder, heat treatment reactor with stirrer, and an automatic constant-temperature control system (Parr Instrument Co., Pressure Reactor No. 4522). A total chemical oxygen demand (COD) determination was made on the autohydrolysis mixture (solids and supernatant liquid) and a soluble COD determination was made on the filtered supernatant liquid. (Table 4.1)

5.3 DISCUSSION

The results indicate that significant solubilization was achieved during autohydrolysis at temperatures between 100°C and 175°C. The greatly reduced soluble COD of the 200°C sample may have resulted from formation of insoluble products of the condensation reactions which can occur at this higher temperature.

The difference between total COD values is probably a consequence of the difficulty in obtaining uniform samples from the mixtures. Future COD analyses will be performed based on soluble and suspended fractions to avoid this problem.

Work is now in progress to further determine the effect of autohydrolysis on solubilization of predigested wheat straw and the anaerobic biodegradability of both soluble and suspended fractions as determined by the BMP test (Owen et al, 1979).

TABLE 5.1

Effect of Autohydrolysis Temperature on Solubilization of Digested Wheat Straw

Autohydrolysis Temperature, °C	Final pH	Soluble COD, g/l	Total COD, g/l
100	7.0	21.3	57.4
150	6.7	24.9	70.0
175	6.4	23.0	70.2
200	6.1	13.4	59.3

SECTION 6.0

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