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FUEL GAS PRODUCTION FROM ANIMAL AND AGRICULTURAL RESIDUES AND BIOMASS

Quarterly Coordination Meeting, December 11–12, 1978, Denver, Colorado

Second Quarterly Progress Report

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

MASTER

January 5, 1979

Work Performed Under Contract ET-78-C-02-5099.A000

Dynatech R/D Company
Dynatech Corporation
Cambridge, Massachusetts

U.S. Department of Energy

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Solar Energy

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Second Quarterly Progress Report

D.L. Wise
E. Ashare
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Dynatech Project No. DOE-5
Dynatech Report No. 1845

Prepared for:

United States Department of Energy
Fuels From Biomass Systems Branch

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

to DYNATECH R/D COMPANY
A Division of Dynatech Corporation
99 Erie Street
Cambridge, Massachusetts 02139

Published:

January 5, 1979

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SUMMARY

The tenth quarterly coordination meeting of the methane production group of the Fuels from Biomass Systems Branch, U.S. Department of Energy was held at Denver, Colorado, December 11-12, 1978. Progress reports were presented by the contractors and a site visit was made to the Solar Energy Research Institute, Golden, Colorado.

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

AGENDA

Methane Coordination Group
Fuels From Biomass
U.S. Department of Energy

Meeting

December 11-12, 1978
Ramada Inn - West
Golden, Colorado

Monday, December 11, 1978

2:00 - 2:15	Introduction D.L. Wise
2:15 - 3:00	W.B. Coe/D.J. Lizdas Hamilton Standard
3:00 - 3:45	E. Coppinger Ecotope Group
3:45 - 4:15	BREAK
4:15 - 5:00	A.G. Hashimoto USDA/MARC
7:00	DINNER @ The Broker (in downtown Denver)

Tuesday, December 12, 1978

8:30 - 9:15	W.J. Jewell Cornell University
9:15 - 10:00	P.L. McCarty Stanford University
10:00 - 10:30	BREAK
10:30 - 11:15	J.T. Pfeffer University of Illinois
11:15 - 12:00	Dr. Roscoe Ward U.S. Department of Energy
12:00 - 1:30	DISCUSSION (LUNCH in Conference Room)
1:30 - 2:00	Travel: Ramada Inn - West to SERI
2:00	Clayton Smith SERI (@ SERI)
5:00	CLOSURE

LIST OF ATTENDEES

Coordination Meeting
Denver, Colorado
December 11-12, 1978

Organization	Name	Telephone
Cornell University 202 Riley-Robb Hall Ithaca, NY 14853	W.J. Jewell	(607)256-4533
Fuels From Biomass Department of Energy 600 "E" Street, N.W. Washington, D.C. 20545	Roscoe Ward	(202)376-1615
Dynatech R/D Company 99 Erie Street Cambridge, Massachusetts 02139	D.L. Wise R.L. Wentworth	(617)868-8050
Ecotope Group 2332 East Madison Seattle, WA 98112	Elizabeth Coppinger	(206)322-3753
Hamilton Standard Division United Technologies Corporation Windsor Locks, CT 06096	Warren B. Coe Daniel J. Lizdas	(203)623-1621
Solar Energy Research Institute 1536 Cole Blvd. Golden, CO 80401	Ruxton Villette Dan Jantzen	(303)234-7171
Stanford University Dept. of Civil Engineering Stanford, CA 94305	Perry L. McCarty	(415)497-3504
U.S. Dept. of Agriculture Meat Animal Research Center P.O. Box 166 Clay Center, NE 68933	A.G. Hashimoto	(402)762-3241
University of Illinois Dept. of Civil Engineering Urbana, IL 61801	John Pfeffer	(217)333-6965

PIPELINE FUEL GAS FROM AN
ENVIRONMENTAL FEEDLOT

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

PROGRESS FROM SEPTEMBER 1 TO NOVEMBER 30, 1978

PREPARED FOR THE
QUARTERLY COORDINATION MEETING
DECEMBER 11-12, 1978

HAMILTON STANDARD
Windsor Locks, Connecticut 06096
Division of
UNITED TECHNOLOGIES™

1.0 PROGRAM OBJECTIVE

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

The program is divided into three phases:

- Design
- Fabrication, Start-Up and Acceptance Test
- Operational Evaluation

The design phase was completed in February 1978. The Fabrication, Start-up and Acceptance Test phase is presently in progress, and the Operational Evaluation will begin in March, 1979.

2.0 PROGRESS DURING THE QUARTER

During September, fabrication continued on the electrical control console. Final assembly, alignment and checkout of tank mixer No. 2 were completed. Drives and motors for all pumps were received and installed. The loading subsystem was operated in the recirculating mode and found to operate satisfactorily.

During October, the gas cooler heat exchangers were installed as was the remaining piping and hardware for the gas management subsystem. Steam lines, water supply and drain line installation was completed; as a result all mechanical installation was essentially completed by the end of October. The electrical console was received on site and checkout was initiated. Due to late delivery of certain hardware, system checkout was not completed in October as planned.

Activities during November concentrated on preparation of hardware for painting, color-code painting all subsystems, electrical hookup of components to the electrical control console, and preparation for a dedication ceremony on December 8. Although some checkout activities extended into early December, precluding initiation of startup in November, it is expected that operating conditions can be achieved on schedule by the end of February.

Figure 1 depicts the layout of the system.

Figures 2 through 9 show the status of construction as of mid-November.

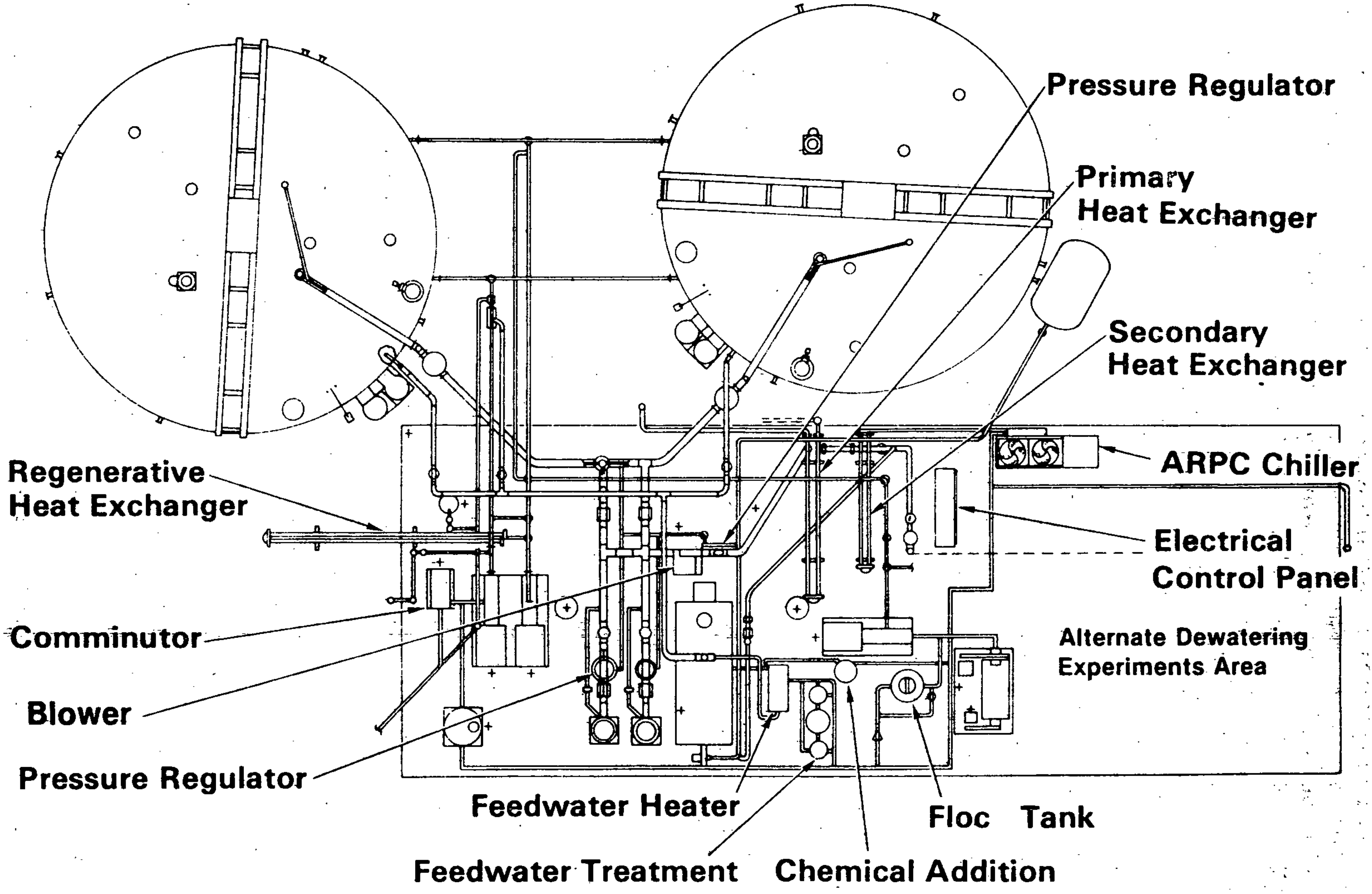


Figure 1
System Layout

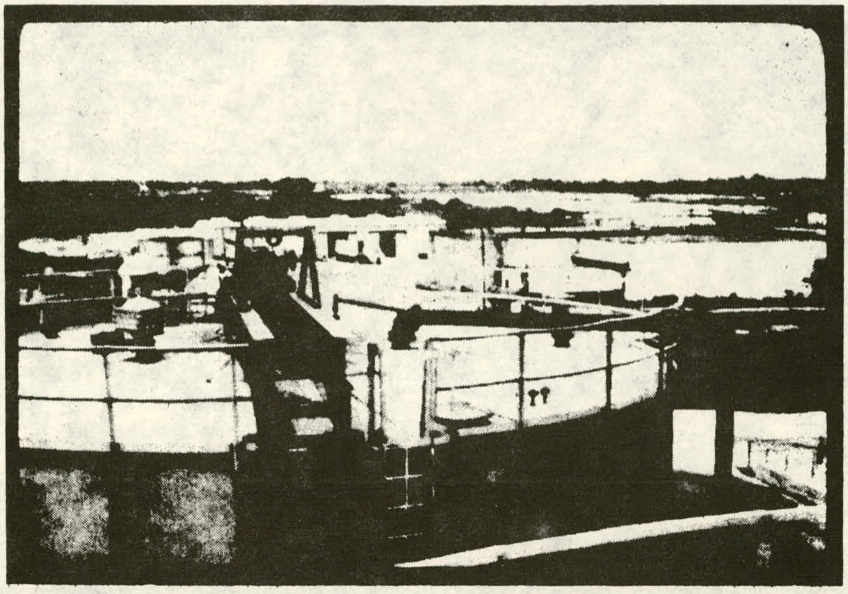


Figure 2
Fermentation Tank with Mixer, Flame Arrester/Pressure Relief/Vacuum Breaker Valve, and Main Gas Pipe Installed

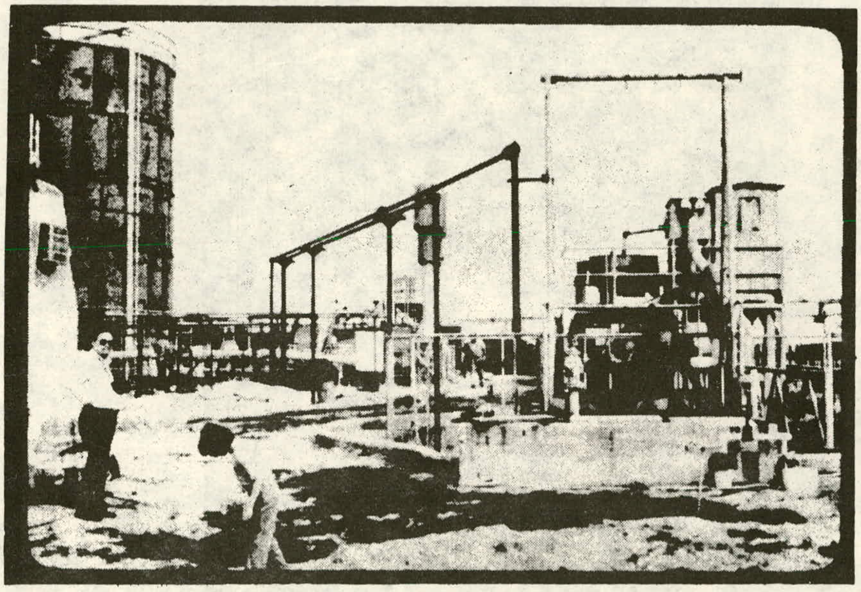


Figure 3
One Day Holding Tank and Loading Subsystem

Figure 4
Loading Subsystem

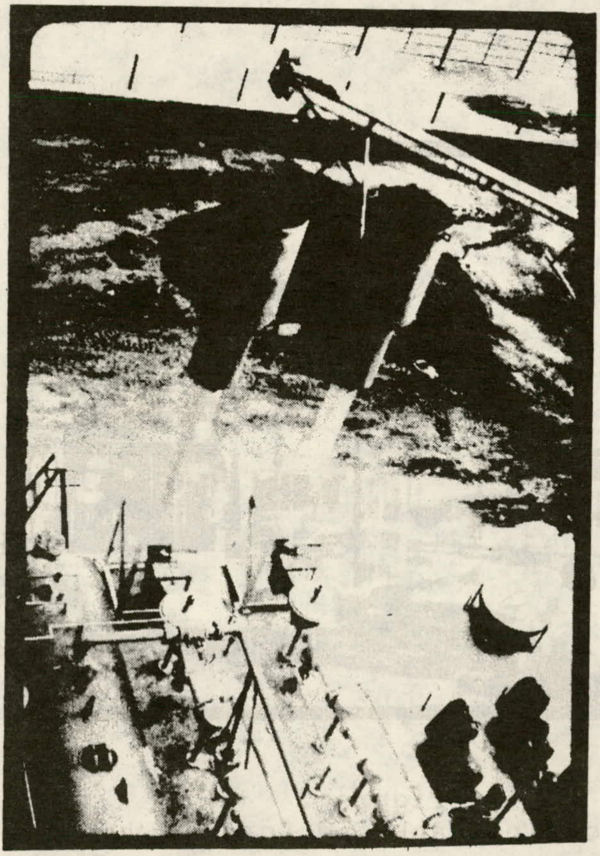


Figure 5
Flares

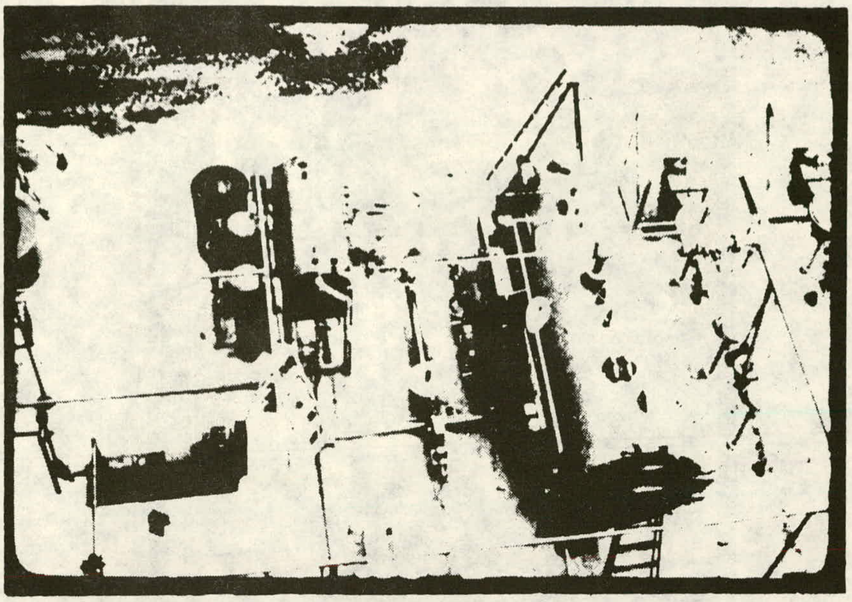


Figure 6
Boiler

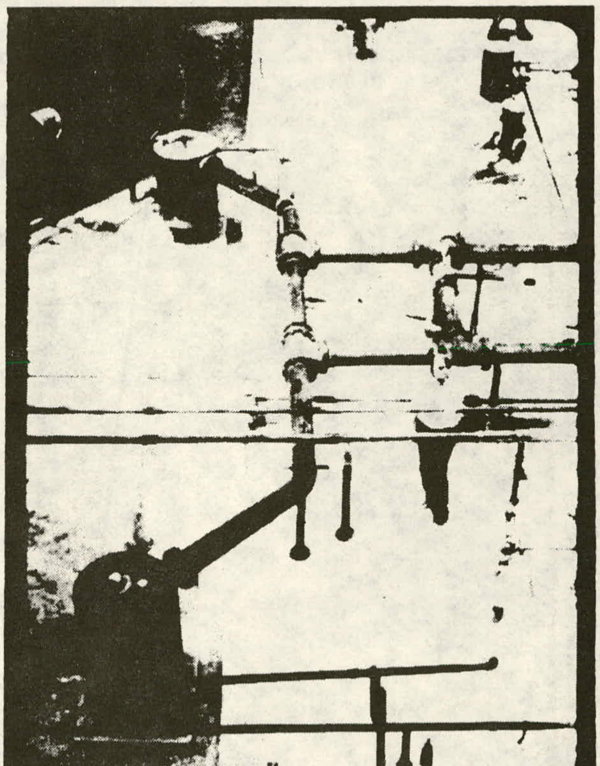


Figure 7
Gas Collection Piping

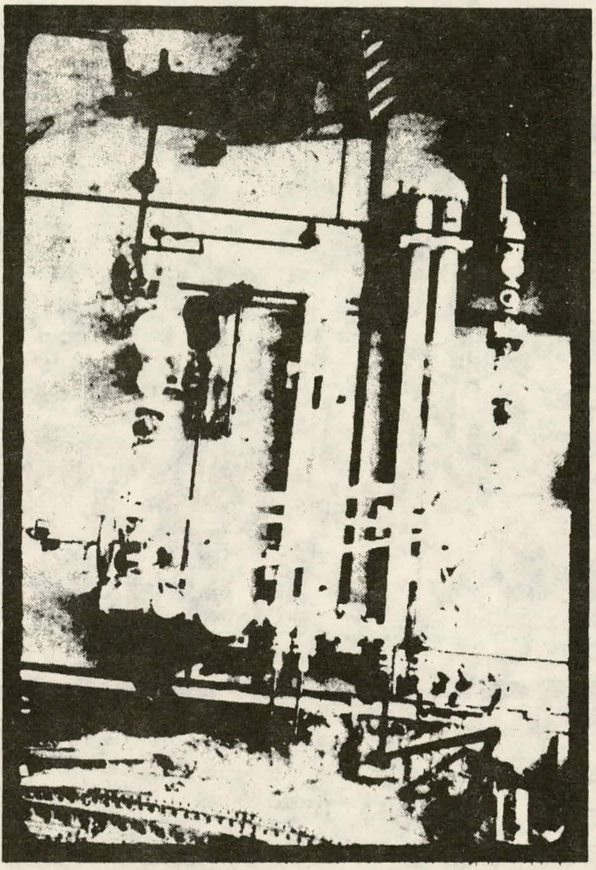


Figure 8
Gas Cooler Heat Exchangers

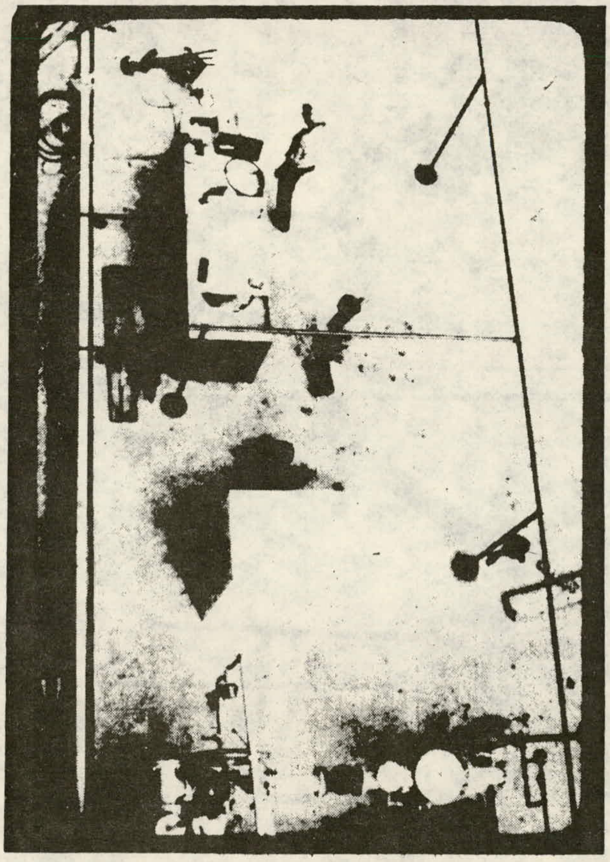


Figure 9
Control Console and Refrigeration Package

3.0 ACTIVITIES DURING NEXT QUARTER

During the next quarter, final checkout will be completed and startup will be initiated with the goal of reaching stable operating conditions by the end of February, 1979.

Ecotope Group

2332 East Madison · Seattle, WA 98112 · (206) 322-3753

SUMMARY PROGRESS REPORT

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

December 1978

Prepared for:

U.S. Department of Energy
Contract # EG-77-C-06-1016

Elizabeth Coppinger
Project Manager
Ecotope Group

Digester Operation. The Monroe digester continues to operate in a stable manner. The pH remains near 7.3. Alkalinity has remained at 8250 mg/liter and total volatile acids have stayed below 600 mg/liter. Gas production has fallen off to an average of 155.7 m^3/day. This decrease is mainly due to a decrease in herd size to 180 head. The average percent volatile solids reduction for the quarter was 27%. The average gas production was .24 m^3/kg VS-added and .95 m^3/kg VS-destroyed. The net gas energy for the quarter was 1.76 GJ/day. The percent of gas produced which was used for digester heating averaged 50% over the quarter. Daily ambient temperature varied between 15° and 0°C. Electrical consumption is approximately 20 kWh/day.

Loading. During October and early November, the digester was loaded only once every two or three days to investigate the impact of less frequent loading on the net energy and operation of the system. Operator time was decreased from 45 minutes per day to 30 m/d. Electrical demand decreased to 11 kWh/day, mainly due to less frequent digester mixing. Gas production and CO_2 content fluctuated drastically with the erratic loading schedule. In addition, the system was much more susceptible to clogging and freezing problems.

Maintenance. During the past quarter, ten to thirteen hours per week of maintenance time were required. The major time demand was dealing with the water and oil which had accumulated in the high pressure lines over the past year. Now water will be removed routinely from the lines and a bi-yearly cleaning of the lines will occur. This should reduce maintenance time by preventing the occurrence of problems. Controlling cycling of the flare was the other major maintenance task this quarter. It now appears to be solved.

While investigating options for loading through the heat exchanger, the impact of replumbing the influent lines to eliminate elbows and straight runs of pipe was examined as a possible means of reducing the total dynamic head and possibly to allow the Vaughan to load through the heat exchanger. However, pressure measurements revealed that at the flow rates at which we load (119 l/m - 380 l/m), a 17 kPa drop in pressure between the outlet pipe of the Vaughan and the inlet pipe of the digester, which suggests that replumbing would have little effect on reducing the pressure requirements of the system. As a result of these measurements, we are beginning to generate pump curves for the Vaughan which plot flow rates versus pressure for a given percent solids.

System Improvements. A Moyno pump (Model 2GOGSI, 11 kW with a vari-pully drive) has been ordered to replace the inoperative Marlow diaphragm pump. This pump can meet the pressure requirements of loading through the heat exchanger without the inherent problems of the Marlow check valves and will deliver the low flow rates needed for most efficient heat exchange. The Moyno is sized to run at low speeds to insure long life. The pump should be on line by late January.

Utility Hook-up. During this quarter, we contacted the Snohomish County Public Utility District which serves the Monroe area. The PUD is now in the process of performing an indepth study of the technical, safety and economic concerns associated with receiving energy from small dispersed producers. Out of this study will come recommendations for a utility policy and rate structure for purchasing electricity from small scale producers. The utility is very interested in our facility since it will provide an opportunity for gaining working experience with an interface between the utility and small dispersed suppliers.

Economics. Cost of energy figures using the American Gas Association routines for Utility Financing and Investor Financing were derived using the information generated for the Monroe facility. These figures are presented below along with those derived using a life cycle analysis. The three methods differ markedly in results.

	AGA (discounted cash flow method)			Utility finance	Life Cycle
rate of return:	12%	4%	0%	15%	4%
dairy size:					
400 cows					
gas	8.72	4.80	3.61	5.12	3.24
electric	.12	.066	.050	.067	.044
200 cows					
gas	13.70	7.51	5.64	7.33	5.17
electric	.21	.11	.087	.12	.079
100 cows					
gas	24.77	13.12	9.59	13.10	5.73
electric	.39	.21	.15	.22	.088

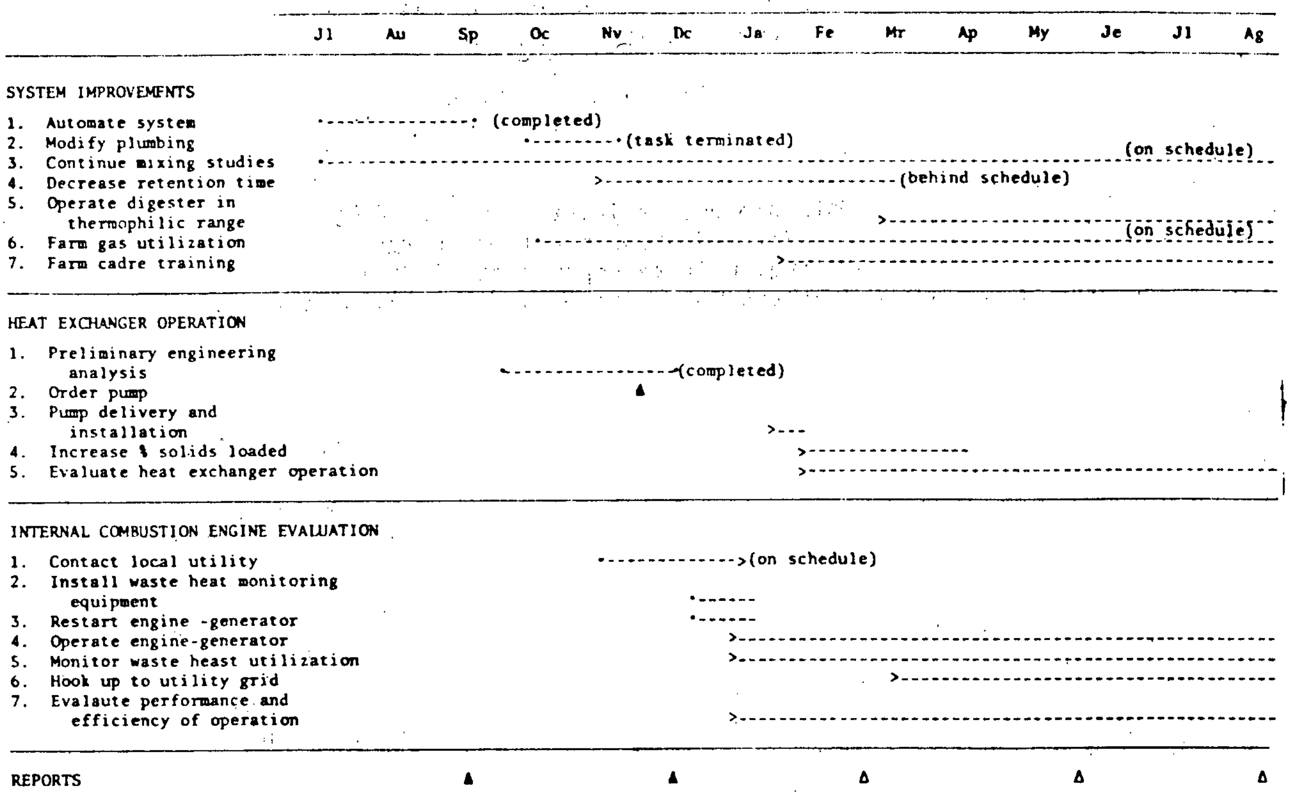
The major difference between the Investor Financing method and the life cycle cost method is that the effect of inflation is not taken into account when considering the rate of return for the capital investment for the Investor Financing Method. Consequently, the opportunity cost of the capital is overestimated, since the declining value of money has not been taken into account.

Modifying the "rate of return" assumptions and recomputing the discounted cash flow yields more comparable results. The other major difference is the presence of start-up costs in the DCF method which were not computed in the life cycle analysis. It is very difficult to alter assumptions or include factors missing in the AGA method. With anaerobic digestion, this is a very serious deficiency since the market includes farms of various sizes with widely varying capital investment possibilities.

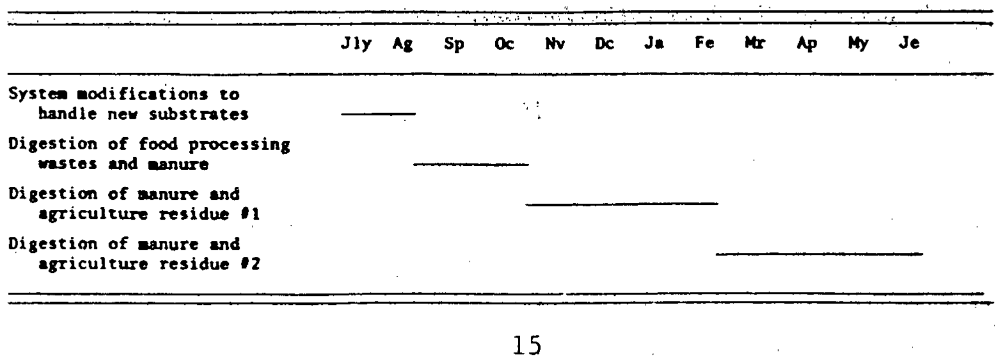
Management Report. The planned activities are all on schedule with the exception of the decrease in retention time. We are still negotiating with local farmers to contract to receive manure. The major problem is securing a dependable means of delivery. We are now working with a farmer who is the only remaining option for receiving liquid manure. If an agreement cannot be reached with him, we will investigate acquiring dry manure.

Ecotope Group
Monroe State Honor Farm
Anaerobic Digestion Project
10 Dec 78

MILESTONE AND MANAGEMENT REPORT



The following time line is an indication of how our budget could be directed towards verifying the digestion of agricultural residues. Digestion of any new substrate requires both investigation of biological performance and the mechanics of full scale digestion. Due to the large and, to this point, unused capacity of our system and its flexibility of operation, the system can easily be adapted to combine the digestion of agricultural residues with the digestion of manure. Since handling the substrate has a major impact on the economics of digestion, both in terms of operation/ maintenance costs and net energy, full scale experience is essential to an evaluation of the feasibility of a given substrate. Our system can be used to evaluate the handling characteristics and net energy of up to three substrates per year.



Ecotope Group

2332 East Madison · Seattle, WA 98112 · (206) 322-3753

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

Sixth Quarterly Technical Status Report
September 1, 1978 - November 30, 1978
and
Milestone Plan and Management Report

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

10 December 1978

Ecotope Group
Seattle, WA 98112

Project Manager: Elizabeth Coppinger
Project Liaison: David Baylon
Principal Researchers: Jack Brautigam
Bruce Lampcov
David Smith

Prepared for:

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

non-profit research, demonstration & education for conservation, renewable energy & appropriate technology

Digester Performance

Biological Performance. The Monroe digester has continued to operate in a stable manner despite changes in loading rate and loading schedule (See Figure 1). The pH has varied between 7.2 and 7.5,staying mainly at 7.35. Alkalinity has remained at over 8250 mg/liter for this quarter. Likewise, TVA has never gone above 600 mg/liter. Gas production has dropped off to an average of 155.7 m^3/day. This is due mainly to a decrease in herd size to 180 head. There has also been an apparent decrease in the amount of manure we receive per cow due to a lower metabolic rate in the winter. The erratic gas production seen in Figure 1 for October and the beginning of November is due to an experiment with less frequent loading. The overall reduction in loading and gas production during the last week in October was due to a problem in the loafing shed which prevented us from receiving manure from one of the four pens.

The average percent volatile solids reduction increased to 27% in this quarter as opposed to 23% last quarter. This is most likely caused by an increased retention time due to the reduced herd size. The cubic meters of gas produced per kilogram of volatile solids added changed little. The average for this quarter was .24, while last quarter it was .23. The gas produced per volatile solids destroyed fell from 1,04 m^3/kg VS-detroyed to .95 m^3/kg VS-destroyed.

Net Energy. Table 2 presents the weekly gas production and consumption during this quarter. Figure 2 shows how it varied daily. The percent of gas produced used for digester heating has risen from a low near 40% at the beginning of September to 60% by the end of November. The ambient temperature

Figure 1

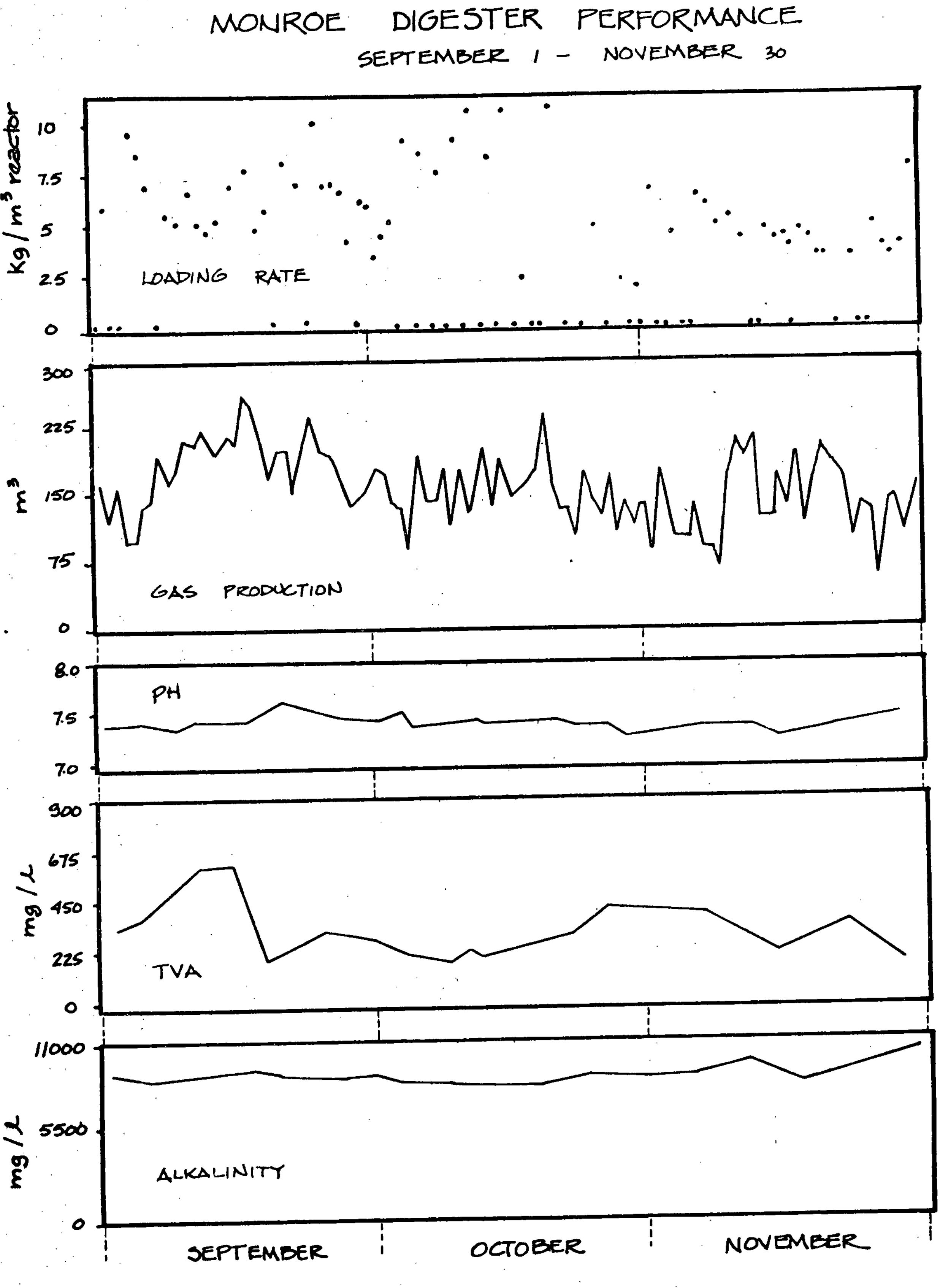

MONROE DIGESTER PERFORMANCE
SEPTEMBER 1 - NOVEMBER 30
Kg / m³ reactor
10
7.5
5
2.5
0
LOADING RATE
m³
300
225
150
75
0
GAS PRODUCTION
8.0
7.5
7.0
PH
mg / l
900
675
450
225
0
TVA
mg / l
11000
5500
0
ALKALINITY
SEPTEMBER
OCTOBER
NOVEMBER

Figure 2

MONROE DIGESTER PERFORMANCE

SEPTEMBER 1 - NOVEMBER 30

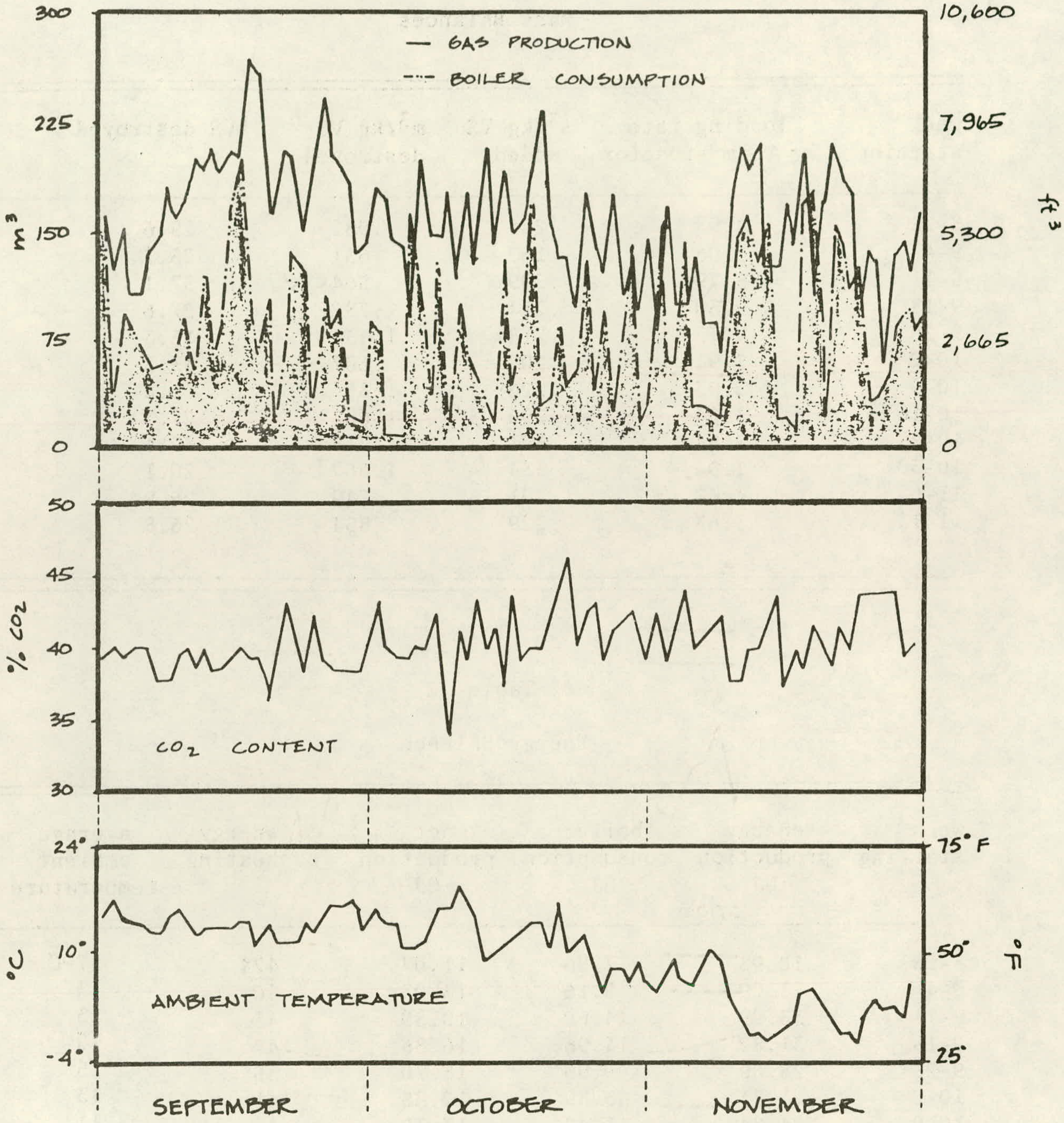


Table 1

Mass Balances

week starting	loading rate kg VS/m^3-reactor	m^3/kg VS added	m^3/kg VS destroyed	%VS destroyed
8-28	4.97	.291	.982	29.6
9-4	5.06	.162	.631	25.7
9-11	5.79	.209	.564	37.1
9-18	5.30	.214	.782	27.6
9-25	4.73	.218	1.43	15.3
10-2	3.91	.202	.607	33.3
10-9	3.93	.226	1.35	16.8
10-16	3.04	.299	1.08	27.7
10-23	2.64	.291	.735	39.6
10-30	1.94	.334	1.66	20.1
11-6	4.58	.201	.749	26.9
11-13	3.63	.229	.854	26.8

Table 2

Energy Balance

week starting	energy production GJ	boiler consumption GJ	net production GJ	% for energy heating	average ambient temperature
8-28	18.93	7.86	11.07	42%	17°C
9-4	23.09	9.16	13.93	40	13
9-11	33.99	14.60	19.39	43	13
9-18	31.82	14.96	16.86	47	12
9-25	28.69	9.99	18.70	35	15
10-2	21.74	8.89	12.85	41	13
10-9	24.84	11.49	13.35	46	11
10-16	24.47	13.17	11.30	54	13
10-23	26.76	9.84	10.92	47	9
10-30	17.55	13.08	4.46	75	8
11-6	23.39	14.61	8.78	62	5
11-13	22.71	12.84	9.87	51	2
11-20	21.58	12.95	8.63	60	0
			12.32 (avg.)	50 (avg.)	

over this period fell from about 15°C to 0°C. Net energy over the quarter averaged 1.76 GJ/day.

Electrical consumption of the system is approximately 20 kWh/day. Of this, 11 kWh are used for influent mixing and loading and 7 kWh are used for mixing the contents of the digester. The remaining 2 kW was miscellaneous use.

Decreased Loading. After 13 months of loading the digester once a day, the loading schedule was changed to investigate the impact of less frequent loading on the net energy and operation of the system.

Starting October 1, the digester was loaded once every two or three days. Manure was scraped daily, but held in the tank until loaded. The impacts of this less frequent loading routine were significant. Operator time was decreased from an average of 45 minutes per day to 30 minutes per day. Electrical demand of the system decreased from an average of 20 kWh/day to 13 kWh/day. The major reason for this decrease was that the gas recirculation blower was run only when the digester was loaded. Consequently, its energy consumption was decreased by 45%.

Gas production during this period varied with the loading. In addition, the CO_2 content of the gas fluctuated dramatically. Values ranged between 38% and 46% in noticeable contrast to its former stable value of 40%. The major problem with these fluctuations is that it severely affects gas utilization. An erratic loading schedule is unrealistic if a regular and dependable energy source is desired.

Another important impact of the change was that it made the system more susceptible to clogging and freezing. The only freezing incident which we have had occurred after a day of not loading, despite the fact that those were not the coldest two-day periods encountered. Consequently, the operator time saved could easily be offset by a single incident of freezing. Likewise, although the electrical consumption of the plant was decreased, gas production was erratic. This coupled with the wide fluctuation of CO_2 makes the regular utilization of the gas more difficult. Consequently, after one month of this loading routine, we felt that the convenience of not loading daily was greatly offset by the erratic gas production and increased system susceptibility to operating problems.

Maintenance

During this quarter, explicit documentation of maintenance work was kept in order to make a more accurate assessment of maintenance time and costs associated with the plant. During the past three-month period, 10-13 hours per week of maintenance time was required. The solution to a number of problems encountered will now be integrated into the regular maintenance schedule used to insure proper functioning of the plant.

Moisture. Moisture condensation in the gas lines has been a problem throughout the plant's operation. Many problems caused by moisture condensation such as valve freezing and corrosion were successfully solved earlier by insulating pipes and drip traps. One additional drip trap was installed in October upstream of a gas meter to cut down on water accumulation in the meter. Approximately two liters of water are removed from the drip traps each day. Water accumulation has also proved to be a problem in high pressure (1.65 MPa) lines. Since no drip traps were installed on any high pressure lines, water accumulated over the past year and led to numerous problems with pressure reducers. The solution has been to draw water off by inserting a pressure gauge needle adapter into a Pete's Plug. This allows water to be removed on a regular basis without depressurizing the lines.

Our experience with moisture condensation in the gas lines has led us to believe that a large amount of water probably has condensed in the storage tanks. However, after emptying and inspecting the storage tanks, we found only .6 cm of water at the low points of all three tanks, suggesting that water condensation in the tanks is not a problem.

Moisture condensation has proven to be our greatest maintenance problem. Careful system planning and the use of an adequate number of drip traps is imperative for smooth and low maintenance operation.

High Pressure System. An oil leak in the compressor caused oil to be sprayed into the high pressure lines where it formed an emulsion with water. This emulsion combined with small amounts of grit deposited in the diaphragms and orifices of the two pressure reducers. This caused the pressure to increase from 14 kPa to 172 kPa and caused the Varec regulator to malfunction, resulting in a significant loss of gas from storage for about one week.

This incident was more of an unanticipated problem than one which could have been avoided by improved system design. However, the incident did point out the need for regular water removal from gas lines and the need for bi-yearly cleaning of the high pressure lines to remove grit and oil. This operation will take approximately four hours in a regular maintenance schedule.

Flare Cycling. Cycling of the flare has been a recurrent problem throughout the operation of the plant. When gas production is up, the compressor cannot pull off gas as rapidly as it is produced. Pressure builds up in the line, causing the pressure switch which activates the flare to turn on while the compressor is running. This severely decreases the expected life of the solenoid in addition to increasing the wear on the control switches and valves.

One solution is to size a compressor for the maximum production rate of the digester. We solved the problem by decreasing the flow rate of gas to the flare. Elevating the flare set point is another option, but is unacceptable for safety reasons. Cycling has proven to be a difficult problem, but it can be solved by careful adjustments of valves, set points and bandwidths on controls. Consequently, it is important that a gas handing system be designed with the flexibility to handle a wide range of gas production rates.

Influent Mixing. Influent is mixed by using the Vaughan chopper pump to draw manure from the bottom of the tank and discharge it through a 5cm recycle line at the top. This recycle line is attached to a 10cm pipe line with a 5cm elbow. The operational problem most often encountered is material clogging the 5cm elbow. This elbow clogs about four times per month and can take an average of one-half hour to unclog. If the recycle line were 10cm, it would reduce the incidence of clogging, but most likely not do a good job of mixing the slurry since the velocity of the manure through the recycle lines would decrease. If recirculation is used for influent mixing, the plumbing should be designed to minimize the possibility of clogging and to allow easy access to any areas which do have the potential to clog.

System Improvements

Replumbing. While investigating options for loading through the heat exchanger, we examined the impact of replumbing influent lines to eliminate elbows and straight runs of pipe. It was hoped that this would result in a significant reduction in the total dynamic head, thus enabling the Vaughan to pump through the heat exchanger. We examined this option by monitoring total line pressure at two points in the system -- the outlet pipe of the Vaughan and the inlet pipe to the digester. Pressure measurements revealed that at the low flow rates we experience (119 l/m - 380 l/m) there is at most a 17 kPa drop in pressure between the two measured points. These findings suggested that replumbing would have little effect on the performance of the Vaughan and the replumbing project was abandoned.

Our investigation into the pressure drops caused by pipe and elbow junction stimulated a general interest in the dynamics of manure flowing through the digester system -- in particular, the relationship between fluid velocity, percent solids and functional pressure losses. We have begun to generate pump curves for the Vaughan which plot flow rate versus pressure for a given percent solids and location in the system (Figure 3). This information will be useful to those designing digesters, especially for sizing pumps.

Our technique for measuring these parameters is straightforward: Percent solids is measuring using the technique described in Standard Methods. Flow rate is measuring by timing a given decrease in influent tank volume. Pressures are measured with inexpensive pressure gauges screwed into a one-foot section of 1cm PVC pipe, then screwed into a hole tapped in the 10cm influent pipe. This method of measuring pressure alleviates the need for expensive diaphragm-oil type adapters and also allows for easy cleaning of the pressure gauges (Figure 4).

Influent Pump. A Moyno pump (Model 2G0GSI, 11 kW motor) has been ordered to replace the inoperable Marlow diaphragm pump. This pump is capable of

Figure 3

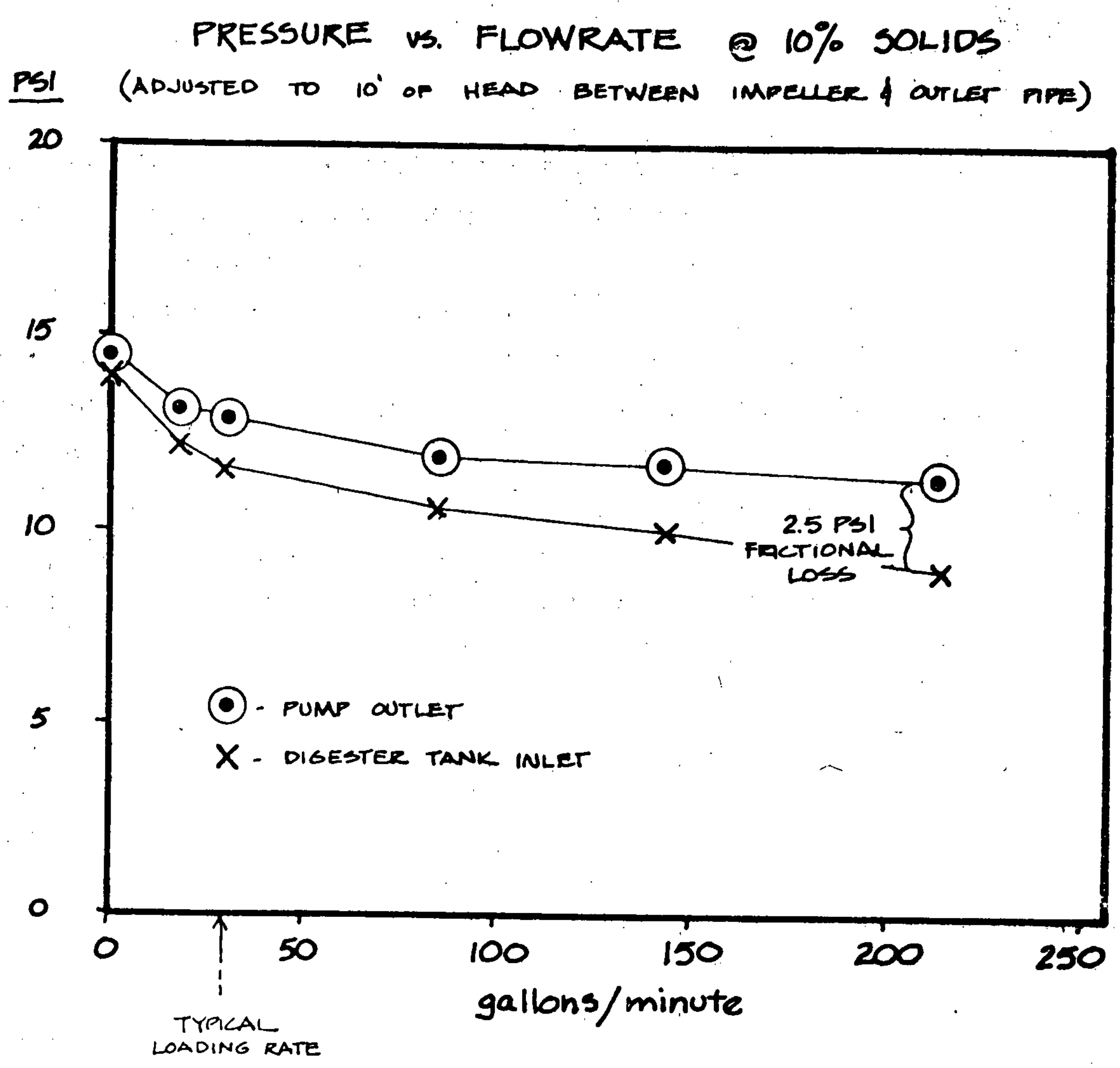
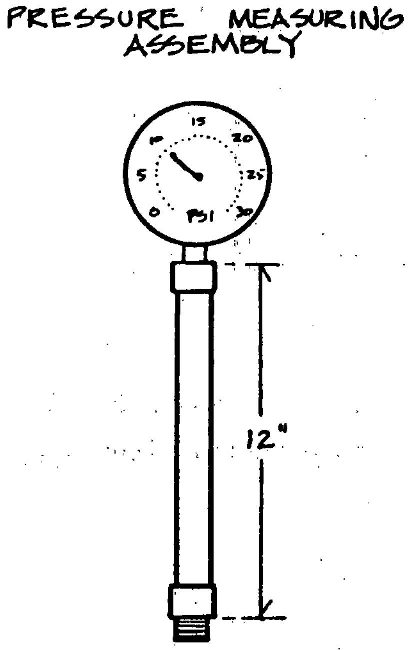


Figure 4



meeting the pressure needed to utilize the heat exchanger without the inherent difficulties of the Marlow check valves and will deliver low flow rates for more effective heat exchange. The pump design selected includes a vari-pulley drive, allowing simple adjustment of flow rates. Depending on pressure requirements and slurry characteristics, flow rates can be adjusted to between approximately 26 l/m and 75 l/m. If heat exchanger performance is not sacrificed at the higher flow rate, testing at greater flow rates may be performed with an easy modification of pully and belt sizes.

This model can also handle material up to 2.8 cm in length, such as the small stones and chips of wood normally encountered in the substrate. Material larger than this size may stall this pump or force it to run dry, a potentially damaging condition, although every attempt to prevent this situation will be made. Two solutions seem feasible: (1) A filter with large (>3 cm) openings could be attached to the pump suction. This device would probably require a high pressure water backflush on a regular timed cycle to clean the filter. (2) Another method is to minimize the amount of large deleterious objects that get into the influent tank. This would involve taking more care in scraping out the cow pens or/and switching to the use of a finer grade of cow bedding.

The Moyno is sized to run at very low speeds (<200 rpm) to insure long life and trouble free operation. The pump should be on line by late January to enable significant heat exchange testing.

Utility Hook-up. During November and December 1977, gas was burned in an internal combustion engine with a 40 kW (peak) generator. The conversion efficiency of this operation was only 11%, well below the expected 20%. The major reason for this low efficiency was that the system never ran at full load.

The engine-generator was acquired to provide emergency backup electricity for the Farm's creamery and milking operation. It was sized to meet those needs and to match the gas production of the digester. The daily electrical needs of the plant are significantly less than this. The energy and power requirements of the facility are only 50 kWh/day, 25 kW peak. Consequently, it is difficult to achieve high efficiencies for generation. An obvious solution to this problem is to hook into the utility grid to allow the engine-generator to operate at full load by providing a demand for all electricity produced.

During this quarter, we have been in contact with the utility serving the Monroe area, Snohomish Public Utility District. The PUD is very interested in the area of small scale energy production. They are now in the process of performing an indepth study of the technical, safety and economic concerns associated with receiving energy from small dispersed producers. This study is funded in part by a grant from the Ford Foundation. Out of this study will come recommendations for a utility policy and rate structure for producing electricity from small scale producers. The study is expected to be completed in two to three months. As a result of its work on this study, the utility is very interested in our facility. This will provide them with an opportunity for gaining working experience with an interface between the utility and small dispersed suppliers.

Economics

In considering the use of anaerobic digestion, it is essential that the technology be cost competitive with alternative sources of the goods it provides. Consequently, it is important that an economic analysis routine be available which acts as a decision making tool for individuals and organizations considering investment in anaerobic digestion. Ecotope Group has prepared an economic analysis based on life cycle costing methodology which was presented in our fourth quarterly report, June 1978. The American Gas Association costing routine has been proposed as the preferred methodlogy to alleviate confusions which result from the absence of a common economic analysis.

The AGA method is a series of derived formulas which are placed in an equation to compute average costs of energy production from coal gasification facilities. There are two methods of analysis presented:

(1) Utility Financed Facility. This assumes that the utility invests in a plant and places the expenses of operating and fueling the plant, the opportunity cost, and the regulated rate of return into the rate base. These costs are divided by total energy production to give an energy cost averaged over the life of the plant.

(2) Investor Financed Facility (Discounted Cash Flow -- DCF). In this analysis, an acceptable profit is computed as an expense along with operating costs, depreciation and interest, and divided by the gas production to find the necessary sale price of the gas from the given plant.

The application of these methods to the Monroe facility yields very different results from the life cycle cost methodologies used in the fourth quarterly report (Ecotope Group, 1978). The reasons for this variation are linked to assumptions which are used by the AGA method. These assumptions are not readily adapted to the agricultural situation and tend to be biased against systems with high capital costs and relatively low operation costs.

The annualized capital cost is dominated by an assumed opportunity cost of 12% that is the rate of return required on this capital in order to compete with alternative investments. Since the <u>real</u> opportunity cost is much lower than this when inflation is included, we have made several moderating assumptions.

Table 1 summarizes the gas cost from the life cycle method and the two AGA methods, using the given assumption and then modifying the assumptions to reflect current conditions that might reflect on a farmer's investment decision.

The three methods differ markedly in result. The principal distinction between the "life cycle cost" method is that the capital costs are computed on a mortgage annuity formula while in the "discounted cash flow" they are computed on a constant rate of return formula. The second difference is the effect of inflation. The opportunity cost of the capital is overestimated if declining value of money returned is not taken into account. Modifying the "rate of return" assumption and recomputing the discounted cash flow yields more comparable results. Another difference is the presence of start up costs in the DCF method. These were not computed into the life cycle analysis, resulting in somewhat lower cost cost estimates.

The Utility Financing is very sensitive to debt financing ratio as the "rate of return on rate base" is higher than the cost of debt; thus, the expenses which can be charged against the energy output fall as the percent debt rises.

If, for example, the percent debt were 25% instead of 95%, the cost of the energy output would double. Of course, a farmer would very likely not have the luxury of extensive equity financing.

Critique of AGA Methodology

There are several important considerations which are essential to usable economic analysis which are inadequately developed in the AGA methodology. These oversights make the use of this routine questionable for analyzing agricultural applications of anaerobic digestion.

1. Inflation. The method was devised in 1972. The principal difference between 1972 economic conditions and 1978 economic conditions is the persistance of high levels of inflation and an even higher level of fuel cost escalation. The constants produced for inclusion in the model allow a 3.5% fuel cost escalation and do not account for inflation. The effect of this distinction is to underestimate the values of capital invested in fixed plant capacity where the return is a good or service (energy) which has intrinsic value versus an investment where the return is in dollars.

For example, if the rate of return or the opportunity cost is 15% and the inflation rate is 7%, then the real opportunity cost is about 8%. Similarily, if the interest rate is 10% and the inflation rate is 7%, then the real interest rate becomes 3%. Even neglecting the escalating value of energy produced, the comparative cost of fixed equipment and interest become very different in the face of high inflation.

If this correction is applied to the formula, the size of the operation and maintenance costs become more important and the effect of the annualized cost of the investment capital becomes less significant. In that case, the analysis would suggest higher capital cost relative to operator costs to minimize the cost of a given energy production.

2. Comparative Economic Benefits. A function of economic analysis is to provide comparative evaluation between alternative plant investments to provide the same output or/and among design options for a given plant. In both of these contexts, the value of the AGA methodology falls short. The factors in this model are fixed and derived from a network of assumptions. This network is neither obvious nor accessible to a designer or researcher. It is very difficult to alter assumptions or include factors missing from the existing model. With anaerobic digestion, this is a very serious deficiency since the market includes farms of various sizes with widely varying capital opportunity costs, acceptable rates of return, operator time, and alternative investment possibilities. A much more flexible model is essential if economic evaluation is to be included as a criteria for research or design for anaerobic digestion.

3. Market Analysis. An economic analysis should provide a picture based on factors relevent to the market place. In this case, the farmer (a consumer of energy) is in the market as a potential energy producer. The economics of that are more complex than a simple "cost of gas" analysis. First, anaerobic digesters are waste-processing facilities which have byproducts with economic value: pollution control, reduced waste handling problems, refeed supplement, etc. These benefits must be evaluated on an individual basis. However, these are the benefits which will open the market for digestion in

animal farming. Without these benefits, anaerobic digestion simply adds an additional farming operation to produce energy which is available elsewhere.

4. Utility Financing. The impact of utility financing on an essentially agricultural operation presents some interesting institutional challenges. It is likely, however, that utility investment in agricultural applications of anaerobic digestion will be more constrained than the classic utility financing model presented in the AGA report. A more appropriate method to evaluate the utility roles in this is to set an energy cost at the market value of the output and rewrite the equation to solve for the capital cost. This equation would then give a justifiable capital cost in the context of the rate of return on equity, operation, debt ratio, tax rates and the value of the energy production. Additional capital costs (if any) would be borne by the farmer in order to achieve other benefits. While this is not the most advantageous position for the farmer, since the utility can make a profit on the energy produced rather than the farmer, it does provide a means of supplying capital to speed the implementation of anaerobic digestion as an energy production technology.

Table 3

Comparative Cost of Energy Analysis for Monroe Digester

	AGA	(D.C.F. method)		Utility finance	Life Cycle
rate of return	12%	4%	0%	15%	4%
dairy size:					
400 cows					
gas	8.72	4.80	3.61	5.12	3.24
electric	.12	.066	.050	.067	.044
200 cows					
gas	13.70	7.51	5.64	7.33	5.17
electric	.21	.11	.087	.12	.079
100 cows					
gas	24.77	13.12	9.59	13.10	5.73
electric	.39	.21	.15	.22	.088

Assumptions:

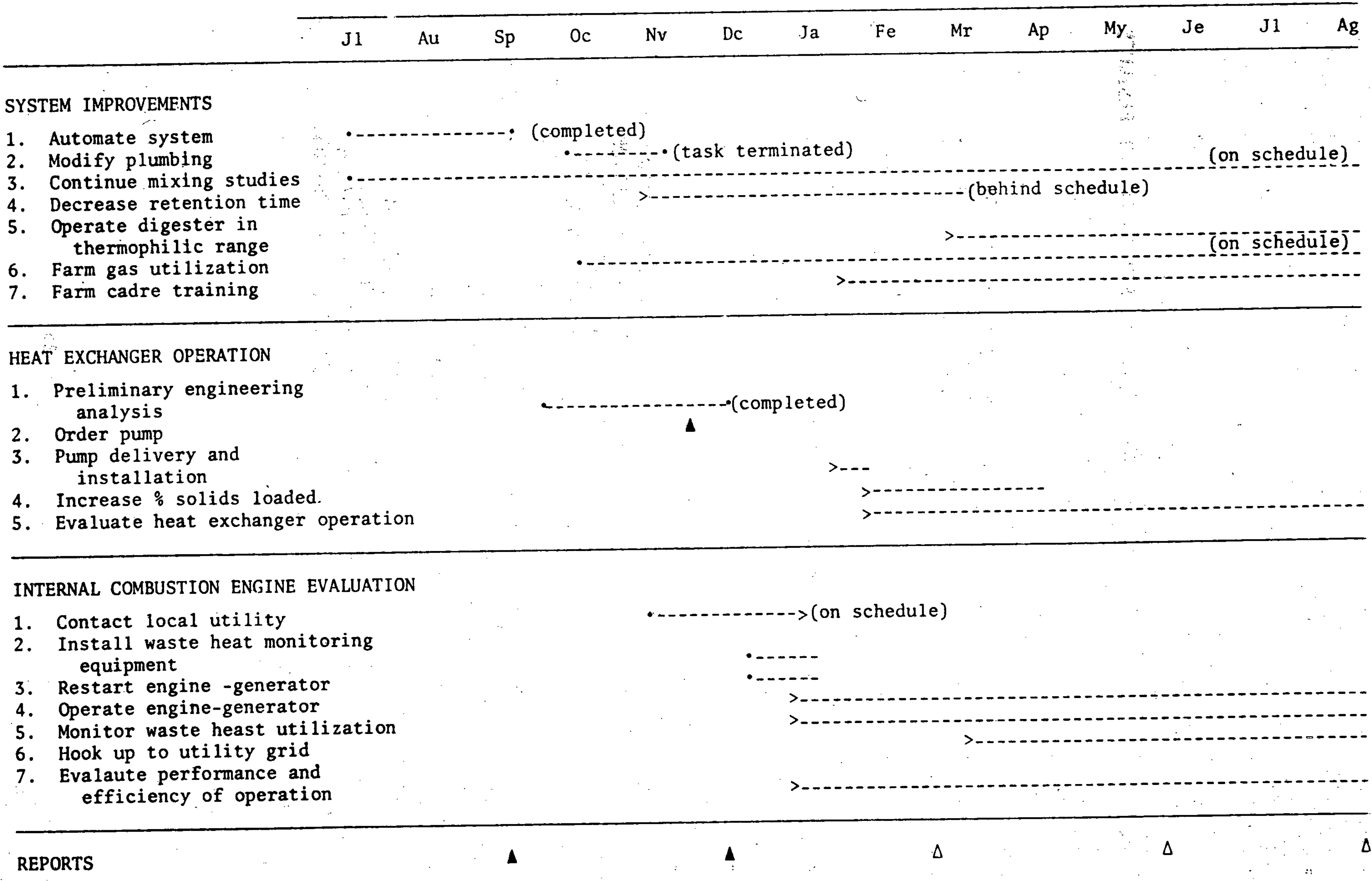
Life cycle
1. 100% financing
2. $3500 investment credit (EPA)
3. 9% interest rate
4. 6% inflation rate
5. no "working capital"
6. 30% tax rate
7. 25 year life

AGA "Discount Cash Flow"
1. no inflation
2. no "working capital"
3. 48% tax rate
4. 25 year life
5. return as noted

AGA Utility Finance Method
1. no inflation
2. no "working capital"
3. 48% tax rate
4. 15% rate of return
5. 25 year life
6. 95% debt financing

Ecotope Group
Monroe State Honor Farm
Anaerobic Digestion Project
10 Dec 78

MILESTONE AND MANAGEMENT REPORT



ANAEROBIC FERMENTATION OF LIVESTOCK AND CROP RESIDUES

QUARTERLY PROGRESS REPORT
SEPTEMBER to NOVEMBER, 1978
GOLDEN, COLORADO

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PREPARED FOR

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

INTRODUCTION

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

PILOT-SCALE FERMENTOR

The pilot-scale fermentor has been operating on an hourly withdraw-feed cycle to determine whether more stable operation can be achieved than under once per day feedings. Table 1 summarizes the operating parameters of the fermentor at 5 days retention time being fed once daily and once hourly. The effluent concentrations of the various parameters were higher when the fermentor was fed hourly. This is expected since the effluent sample was taken about 22 hours after feeding for the once-per-day feeding scheme, while the sample was taken less than one hour after feeding for the hourly withdraw-feed scheme. Thus, the daily-fed system approximated a batch operation while the hourly-fed system approximated a continuously fed system.

The volumetric methane production rate was about 10% higher during the hourly feeding (4.65 vs 4.23 L CH_4/L fermentor·d). This steady-state production rate of 4.65 L CH_4/L fermentor·d is the highest reported rate for systems fermenting animal residue. This rate is at least four times higher than any reported rate for pilot or full scale systems fermenting animal residue. We believe that one reason for the lower methane production rates of other systems may be the inhibition caused by antibiotics and growth stimulants used by commercial livestock enterprises.

FUTURE ACTIVITIES

Table 2 lists the completed and projected parametric testing program of the pilot-scale fermentor. The objective of this testing program is to maximize the volumetric methane production rate through maximum loading, and recycle of bacteria. After the conditions for maximum methane production are determined, the cattle will be fed rations containing antibiotics (Aureomycin and Rumensin) to determine the effect of these compounds on methane production. After these tests are completed, substrate containing manure and crop residue will be fed to the fermentor.

In regard to shifting the program emphasis from livestock to crop residue, we see no problems in fermenting this material once it is mechanically reduced in size to prevent clogging of pumps or pipelines. The major area needing research and development is in increasing the biodegradability of the cellulosic components of crop residues. The facilities at the U.S. Meat Animal Research Center can be used to pilot-test promising crop residue pretreatment systems prior to fermentation.

Table 1. Summary of Operating Parameters for the Pilot-Scale Fermentor Operating at Five Day Retention Time[a]

	Feeding Frequency	
Parameter	once/day	once/hr
Total Solids		
Inf., g/ℓ	92.8 ± 8.9	94.7 ± 5.9
Eff., g/ℓ	46.4 ± 1.9	51.6 ± 2.0
Change, %	-52.0	-45.5
Volatile Solids		
Inf., g/ℓ	84.9 ± 8.4	83.8 ± 5.1
Eff., g/ℓ	39.8 ± 1.7	41.5 ± 1.7
Change, %	-53.1	-50.5
Fixed Solids		
Inf., g/ℓ	7.9 ± 1.0	10.9
Eff., g/ℓ	6.6 ± 0.5	10.1
Change, %	-16.5	-7.3
COD		
Inf., g/ℓ	93.7 ± 11	96.1 ± 13.1
Eff., g/ℓ	52.9 ± 5.2	56.9 ± 9.2
Change, %	-43.5	-40.8
Total Nitrogen		
Inf., g/ℓ	3.62 ± 0.31	—
Eff., g/ℓ	3.88 ± 0.29	—
Change, %	+7.2	—
Ammonia-N		
Inf., g/ℓ	0.94 ± 0.13	1.12 ± 0.16
Eff., g/ℓ	1.44 ± 0.03	1.85 ± 0.14
Volatile Acids		
Inf., g/ℓ	6.89 ± 0.34	7.70 ± 1.14
Eff., g/ℓ	1.64 ± 0.12	2.39 ± 0.33
Alkalinity		
Inf., g/ℓ	2.95 ± 0.59	4.37 ± 0.25
Eff., g/ℓ	6.12 ± 0.32	8.63 ± 0.63
pH		
Inf.	4.61 ± 0.31	5.65 ± 0.30
Eff.	7.70 ± 0.05	7.71 ± 0.12
Methane, %	52	54.8 ± 3.9
Methane Production		
ℓ/ℓ·day	4.23	4.65 ± 0.40
ℓ/g VS added	0.25	0.28
ℓ/g VS utilized	0.47	0.55
ℓ/g COD utilized	0.52	0.59

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[a] Data presented as mean ± standard deviation.

Table 2. Parametric Testing of Pilot Scale Fermentor

Test	Feeding	Temp (°C)	Retention Time (days)	Loading Rate (g/L·day)	Influent V.S. Conc. (g/ℓ)	Status or Completion Date
A	1	55	20	3.4	68.5	Completed
B	1	55	12	5.2	61.8	Completed
C	1	55	6	11.4	68.7	Completed
D	1	55	4	14.9	59.5	Completed
E	1	55	7	11.8	82.6	Completed
F	1	55	5	17.0	84.9	Completed
G	2	55	5	16.8	83.8	Completed
H	2	55	3.5	23	80	12/31/78
I	3	55	5	16	80	2/28/79
J	3	55	3.5	23	80	4/30/79
K	4	55	12	6.7	80	6/30/79
L	4	55	9	8.9	80	8/30/79
M	4	55	5	16	80	10/31/79
N	5	55	5	16	80	12/31/79

1 - Feeding once per day

2 - Feeding once per hour

3 - Feeding once per day w/recycle

4 - Feeding once per day w/manure containing chlortetracycline and rumensin

5 - Feeding once per day w/manure and crop residues.

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Report Number COO-EY-S-02-2981-10

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

Tenth Quarter Progress Report for Period From
September 16, 1978 to December 15, 1978

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Prepared For

The U.S. Department of Energy
Under Contract No. EY-76-S-02-2981
Modification A002

REPORT OUTLINE

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

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

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

1. Pilot scale randomly fed and mixed, three-cow residue handling capacity when operated at a 30-day HRT;
2. Pilot scale plug flow reactor, three-cow residue handling capacity when operated at a 30-day HRT;
3. Full-scale plug flow reactor, 65-cow residue handling capacity when operated at a 10-day HRT; and
4. Full-scale conventional completely mixed control, same residue handling capacity as the full-scale plug flow fermentor.

The overall progress attained with the major components of the project is estimated to be about 2 1/2 months behind schedule. Scheduled activities in the next quarter should bring the tasks up to the time schedule as originally proposed.

In general, activities for the tenth quarter, extending from September 16, 1978, to December 15, 1978, have included the following:

1. Continued operation of the full-scale plug flow and conventional control fermentors at the 30-day, 35°C, 10-12% TS manure feed condition.

2. The replacement of the flexible cover on the full-scale plug flow reactor.

3. Ongoing experimentation with bedding addition to the dairy manure feedstock of the pilot scale plug flow fermentor operated at 30 days HRT, 35°C and 11-13% TS feed.

4. Completion of the manure feed studies at 35°C for the random mix reactor and the initiation of bedding addition to the manure influent (11-13% TS).

OBJECTIVES

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

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

PROJECT STATUS

Proposed Status

The work plan originally submitted with the proposal is presented in Figure 1. A bar chart schedule indicating the proposed and actual progress of certain project components is presented in Figure 2. During the tenth quarter, operation of all pilot and full-scale fermentors continued. The 5.0 m^3 pilot scale random mix reactor was to conclude its experimental testing with manure and bedding at 35°C and a new series of operating modes with the same feed type at lower temperatures was to be initiated. The 5.6 m^3 pilot scale plug flow reactor was also to continue operating with a manure and bedding feed. Also scheduled for the tenth quarter was the completion of the manure and bedding feeding modes at 35°C for the full-scale conventional and plug flow fermentors; during the latter portion of this period testing with the manure and bedding feed at the lower temperatures was to be initiated.

Present Status

The overall progress of the methane project is presently about two months behind the proposed schedule. Although the operation of the pilot scale reactors has adhered closely to the work plan, the full scale demonstration phase has lagged by about 2 1/2 months. In an effort to accelerate the testing program and to narrow this schedule gap, a revised experimental plan was drafted in August, 1978, as shown in Figure 3. Progress in reference to the new schedule is indicated showing a close adherence to the accelerated work plan.

Progress review meetings were held with the methane project group on a weekly basis throughout the tenth quarter for periodic progress review.

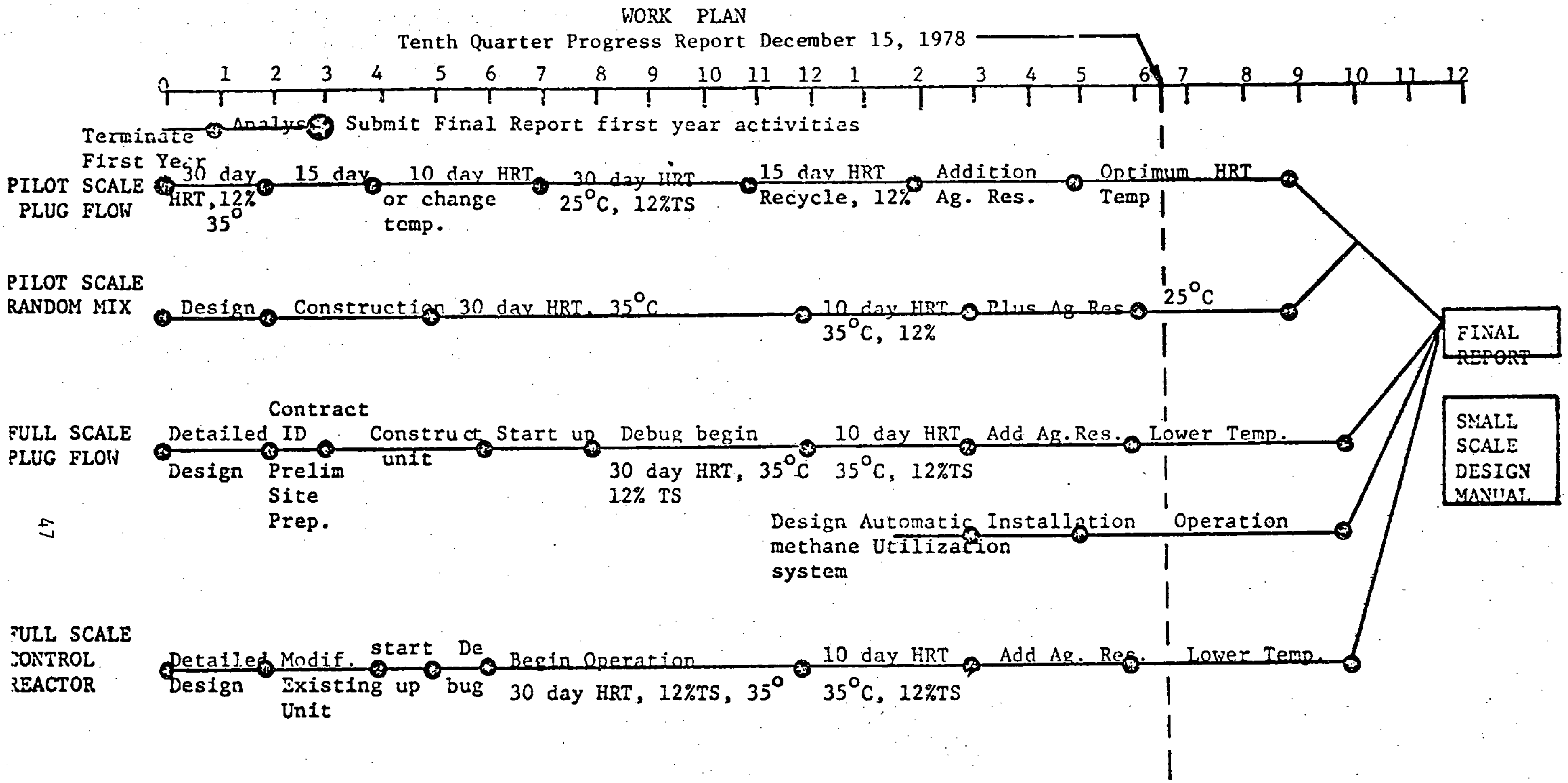


Figure 1. Detailed work plan for the development and demonstration of low cost fermentors.

FIGURE 2.

CORNELL UNIVERSITY METHANE PROJECT WORK PLAN FOR 1977-1979

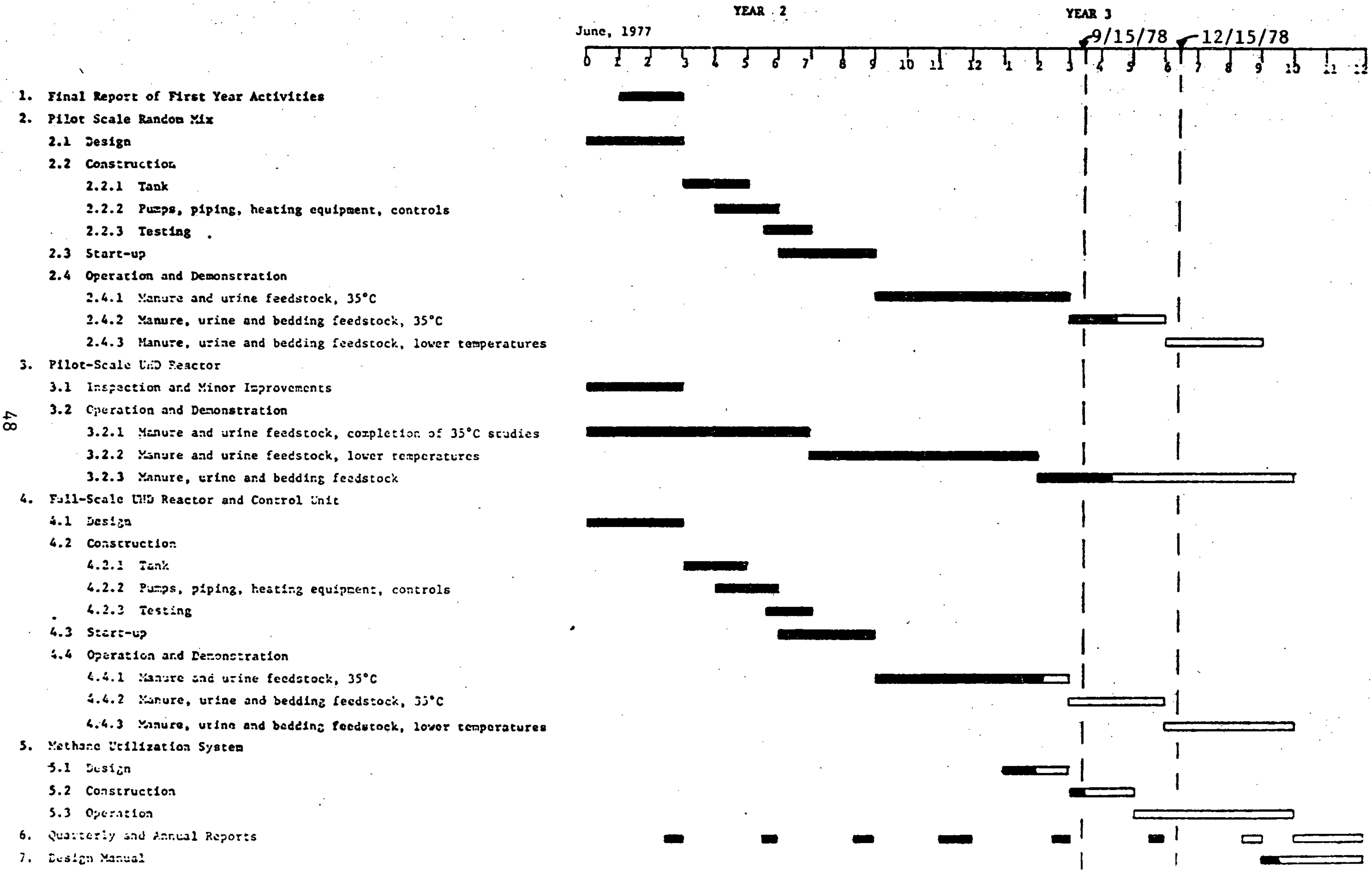
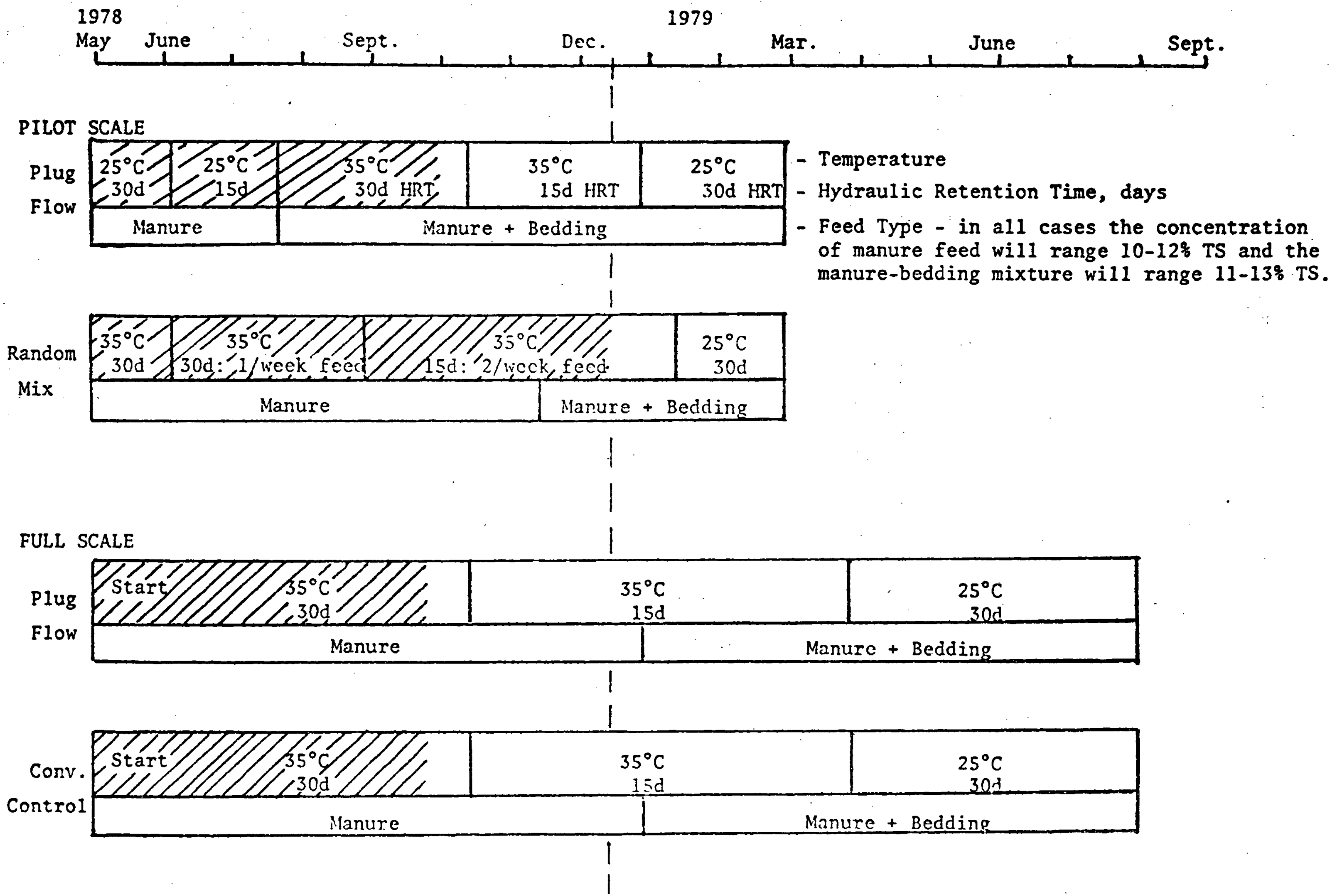


Figure 3. EXPERIMENTAL TESTING PROGRAM



- Feed Type - in all cases the concentration of manure feed will range 10-12% TS and the manure-bedding mixture will range 11-13% TS.

The notes and minutes from these sessions are presented in Appendix A.

Pilot Scale Random Mix Reactor

Steady state data was collected from this unit during the last quarter while operating at a 16-day HRT, 35°C, fed 10-12% TS dairy manure at a frequency of once every four days and mixed after every feeding. At this operating mode the random mix reactor produced biogas at an average rate of about 1.4 m^3/m^3 reactor/day (0.84 m^3/m^3/day CH_4) with a concomitant TVS destruction efficiency of about 28 percent over the 24-hour period. After feeding, gas production for this 5.0 m^3 reactor typically peaked at levels over 11.0 m^3 and decreased over the remainder of the four-day feeding cycle to values below 6.0 m^3. This condition indicated that the biological system acclimated to these wide variations in feeding.

Upon collection of steady state data from this condition, the random mix unit was fed a mixture of chopped straw bedding and manure while maintained in the same operating mode. Straw was added to the influent manure on the basis of a bedding utilization rate of 1.4 Kg/cow/day (3.0 lbs/cow/day). During the first feeding period, introduction of the manure-straw material predisposed significant foaming in the reactor, displacing about 25 percent of the volume of the reactor. Due to recent design changes in the reactor, all of the expelled contents were eventually returned to the reactor. The bedding content of the feed was subsequently reduced by 33% and the foaming problem has since subsided.

The first mechanical problem with this system occurred with a break in the pvc heat exchanges grid through which hot water is normally recirculated. After close examination and testing, it was decided that the disconnection occurring in the 2-inch pvc pipe probably resulted from the pulsating action of the diaphragm feed pump which causes large hydraulic shocks to move through the reactor. Corrective measures have consisted mainly of the installation of a steel heat grid that would be capable of holding together during mixing and feeding periods. Although metal components for the interior of the reactor are not advised for any final full scale fermentor design (due to corrosion problems), the steel heat grid is expected to yield consistent operation for the short term of experimentation with the random mix unit.

The concept of using pvc heat grids for full scale fermentor applications utilizing recirculation mixing is already under observation with the full scale conventional control fermentor now operating.

Pilot Scale Plug Flow Fermentor

Throughout the entire tenth quarter, the pilot scale plug flow fermentor has been operating on a dairy cow manure-bedding mixture at a consistency of 11-13% TS, while maintained at 35°C and 30 days HRT. Chopped straw was initially added to the feed, but when float accumulations became noticeable sawdust was substituted as the bedding additive. Midway through the last quarter, a significant float layer of 0.15-0.2m (6-8 inches) had accumulated in the reactor making accurate solids destruction determinations difficult.

Subsequent addition of water for dilution had no significant remedial effect; the float mat continued to grow to 0.2-0.3m (8-12 inches).

In November the float material was removed and feeding was resumed with a manure and wheat straw mixture. Bedding addition to the manure feed was decreased to a blending rate of 0.68 Kg/cow/day (1.5 lbs/cow/day). Straw accumulation in the float will be watched closely over the next few weeks to determine the extent of difficulties that may be expected with bedding addition to the large scale fermentors. Currently, the pilot scale plug flow reactor is producing about 1.1 m^3/m^3 reactor/day of biogas (0.65 m^3/m^3 reactor/day CH_4).

The testing program for the pilot scale reactor is about 1.5 to 2.0 months behind the proposed work plan schedule.

Full Scale Plug Flow Fermentor and Control Unit

The full scale plug flow and conventional control reactors have continued to operate at 35°C, 10-12% TS manure feed and 30 days HRT through all of the tenth quarter.

During the first half of the last quarter, gas leak problems persisted with the hypalon flexible cover originally installed on the full scale plug flow unit, accurate gas production data from this unit could not be obtained during most of this period. The special weather-resistant hypalon cover material ordered early in the summer of 1978 from Cooley Inc. was received in late October. A substitution in the liner order was then made from hypalon at $10.75/$m^2$ ($1.00/$ft^2$) to a 45 mil, 2000 denier scrim Estane (Brand) material. (polyurethane, 58630 ether, B.F. Goodrich) at $21.52/$m^2$ ($2.00/$ft^2$).

The new liner material was received in late October, but before it was installed the old liner had to be removed and discarded. In light of questions regarding the safety of flexible cover digesters relevant to fire and explosion possibilities, a carefully conducted and controlled fire test was conducted on the old, inflated gas collection cover. A burning cloth dropped on the gas collection bag resulted only in a large flare of biogas which died out as soon as the bag deflated. No explosion occurred. No significant damage was imparted to the reactor or surrounding buildings. Within two days the old hypalon cover was removed, and the Estane material was installed on the plug flow reactor.

During cover replacement it was noticed that manure had filled the pvc anchoring pipes to which the Estane liner was to be attached, thus making the pipes harder to handle due to the added weight. Design changes will be sought to alleviate this problem. The new gas collection cover has been holding biogas without leakage at pressures exceeding 1200 n/m^2 (5.0 inches of water column) since mid-November.

The conventional completely mixed control reactor also developed a leak problem that resulted in a noticeable amount of liquid escaping from under the freeboard liner and out the top of the reactor in the form of foam. This fermentor was subsequently repaired by altering the liquid level in the basin and by plugging the source of the liquid leak with concrete. Final adjustments to the liner and to the reactor caused delay in testing of about one month.

The full scale plug flow and conventional control reactors have reached stable operation at the 30-day HRT, 35°C, 10-12% TS feed mode. A summary of gas production and solids destruction data obtained from these units is presented in Table 1 as compared to performances observed from bench and pilot scale reactors operated in previous phases of the project. The data indicate that full scale plug flow and conventional control fermentors are operating at gas production and solids destruction efficiencies comparable to those obtained with their reactor types at the bench and pilot scale level. Both full scale units are presently producing biogas at rates of 1.1 to 1.2 m^3/m^3 reactor/day for the completely mixed and plug flow systems, respectively.

One of the most important aspects of any anaerobic fermentor operated in cold climates is the overall energy balance of the process. The monitoring of gas flows from the full scale reactors and biogas utilization rates of the boilers has been completed with new gas meters during the tenth quarter. Determinations of heat losses from the full scale reactors and of boiler efficiencies have also been planned. Heat and energy balances are incomplete

Table 1

Gas Production and Solids Destruction Data from Bench, Pilot and Full Scale Plug Flow and Completely Mixed Control Reactors Operated at 30 Days HRT and 35°C

Reactor Type and Scale	Biogas Production m^3/m^3 Reactor/day	Biogas Production $m^3/Kg/VS_A$	Gas Composition Percent Methane	TVS Destruction Percent
Plug Flow				
Bench[1]	0.91	0.36	56	--
Pilot[2]	1.10	0.33	61	26
Full[2]	1.16	0.38	58	39
Conventional Control				
Bench[2]	0.92	0.25	64	32
Bench[3]	0.81	0.35	63	36
Full[2]	1.08	0.37	59	31

1. Feed Consistency = 8% TS dairy manure.
2. Feed Consistency = 10-12% TS dairy manure.
3. From previous Cornell study, G. Morris thesis, using 8% TS dairy manure feed.

at this time. This will be a major focus in the next quarter.

The full scale fermentation effort is approximately three months behind schedule.

Design Manual

The initial outline for the design manual has been prepared and will be used as a guide to format and content. This portion of the study is well ahead of schedule.

FUTURE ACTIVITIES

The pilot scale random mix reactor will conclude its present operation of feeding and mixing every four days, 16-days HRT, 35°C, and 11-13% TS manure-bedding influent and will complete the next operating mode of 30 days HRT, 25°C, 11-13% TS manure-bedding feed. The pilot scale plug flow reactor operating on manure and bedding will soon be shifted from 30 days HRT at 35°C to 15 days HRT. This operating mode should end within the eleventh quarter and the last condition of 25°C, 30 days HRT and 11-13% TS manure-straw feed will be started. By the end of the eleventh quarter, both pilot reactors should be nearly complete according to their respective testing programs.

In the next quarter the full scale plug flow and conventional control fermentor will both conclude operation at 30 days HRT, 35°C and 10-12% TS manure influent; when steady state data at this condition has been completed, the HRT of these reactors will be changed from 30 to 15 days. Toward the latter portion of the next quarter both reactors will then end their test period on manure and will begin experimentation with bedding additions to manure feedstocks.

Most important, comprehensive energy balance data will be obtained from the operation of the full scale anaerobic reactors as operated at realistic dairy manure loading rates under actual environmental conditions that would be encountered on a farm in a typical northern winter. Information to be collected will include determinations of boiler efficiencies, net gas production rates and conducted heat losses from the fermentor basins. As yet, the full scale plug flow fermentor has not been insulated over its exposed liquid surfaces, nor has the uninsulated flexible cover been protected from winds and weather with any kind of shelter. Closed cell insulation blocks will be laid over every exposed liquid surface, and additional insulation will be placed over the flexible liner, if required. Heat balances on the plug flow fermentor will be conducted before and after the addition of these features to determine their actual value.

Lastly, a serious effort to initiate preparation of the design manual will be made before the close of the next quarter. It should, however, be emphasized that this document will not be a construction and service manual in a strict sense, but will instead be targeted for farmers to provide a basis for determining the applicability and economic feasibility of implementing anaerobic fermentation on any particular small scale farm.

Stanford University
Department of Civil Engineering

HEAT TREATMENT OF ORGANICS
FOR
INCREASING ANAEROBIC BIODEGRADABILITY

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

QUARTERLY PROGRESS REPORT
for the period
September 1, 1978 to November 30, 1978

by

W. Owen, P. J. Colberg, D. Stuckey, L. Y. Young, and P. L. McCarty

Prepared for
Division of Solar Energy
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TABLE OF CONTENTS

A. INTRODUCTION

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

The largest portion of this report is devoted to details of results under Phase One. During the past quarter model lignocellulose constituents were used for studying the effect of oxygen on hydrolyses. Initial results under Phase Two are also presented. Successful separation of several molecular weight fractions from heat-treated lignin have been obtained. Phase Three is progressing but with little new information at this time. Phase Four has been completed as reported in the last quarterly report and Phase Five is being initiated with no results to report at this time.

B. BIOLOGICAL CONVERSION OF LIGNOCELLULOSE TO METHANE

W. Owen and P. McCarty

Studies on pretreatment of lignocellulose by autohydrolysis were continued during this phase of the project. Preliminary studies had shown that the bioconversion efficiency of complex lignocellulosics could, indeed, be improved by oxidative or nonoxidative autohydrolysis and that solubilization of organics was the primary mechanism for improving biodegradability (Healy et al., 1978 b). Therefore, during this phase, relative yields of soluble chemical oxygen demand (COD) were employed for determining optimum autohydrolysis conditions. Initially, model lignocellulose constituents were used for studying the effect of oxygen on hydrolysis independent of pH by following soluble COD yields during various reactions. Subsequently, batch studies which simulated full-scale processing were employed for obtaining a better understanding of autohydrolysis reactions and for optimizing process sequencing.

Experimental Methods

Autohydrolysis reactions were performed in a 2-liter, bomb-type autoclave as previously described (Healy et al., 1978 a). Solubilization kinetics were studied for a representative lignocellulosic (white fir) and model components (cellulose, xylan, and peat) over a temperature range from 150 to 225°C and reaction times up to six hours. Air was employed as the feed gas and off-gas flow rate was varied from 0.0 (nonoxidative) to 0.64 m^3(STP)/hr/kg feed COD. Reaction pH was buffered at 2.5 ± 0.1 with phosphoric acid for all treatments so that the effects of oxygen and temperature could be assessed independent of hydrogen ion concentration. Reactions were monitored by periodic sampling of the liquid and off-gas. Typically, fourteen, 35-ml liquid samples were taken during a reaction; the total represents approximately one-half of the feed volume.

In order to simulate full-scale processing, a series of batch treatments was conducted over a temperature range from 175 to 225°C with reaction times up to 4 hours. Autohydrolysis was studied in detail for white fir, including a comparison of oxidative and nonoxidative processing at 225°C. A moderate off-gas flow was used for oxidative treatments (approximately

0.2 m^3(STP)/hr/kg feed COD). As a result of this comparison, all subsequent treatments were performed without oxygen. Then batch treatments of white fir at various reaction temperatures were assayed for lignin and hexosan content of the residual solids in order to better understand the mechanisms involved. Finally, sequential reactions with white fir, selected based on the previous chemical results, were studied to assess the significance of condensation reactions on yields of soluble organics.

All reaction times are referenced to a time of 0.0 when the reactor reached operating conditions. Prior to heating, the vessel was purged with helium, and it was maintained with a nonoxidative atmosphere during heat-up. At time 0.0 the reactor was immediately pressurized with helium to 10 atm above saturated steam pressure, and for nonoxidative treatments the system was maintained at this condition during the course of reaction. For oxidative treatments, the feed gas was changed to compressed air at the same operating pressure (10 atm above steam pressure) and the predetermined off-gas flow rate was immediately established. This procedure ensured that the off-gas flow rate controlled the amount of oxygen entering the vessel throughout the entire oxidative treatment.

Analytical procedures were conducted according to Standard Methods (1976) and Procedures for the Chemical Analysis of Wood and Wood Products (Moore and Johnson, 1967). Samples for analysis of soluble constituents were obtained through Whatman GF/C glass fiber filters or equivalent. Hexosan was determined colorimetrically (Gossett, 1976) using the hydrolyzate from acid-insoluble lignin assays. Acid soluble polysaccharides were defined as the difference between holocellulose and Cross and Bevan cellulose determinations.

Tables B-1 to B-4 detail the chemical characteristics of the test slurries used for kinetic studies, and Table B-5 lists characteristics of the white fir slurry employed in batch treatments. All solids were sized on the order of 50 mesh.

Results and Discussion

Effect of Oxygen on Solubilization Kinetics

Temporal variations in soluble COD yields for hydrolysis of cellulose and xylan are illustrated for representative reactions at 150°C in Figure B-1. In general, at any given reaction time and temperature, the amount of soluble

TABLE B-1. CHEMICAL CHARACTERISTICS OF CELLULOSE SLURRY USED FOR KINETIC STUDIES

Cellulose	microcrystalline, 50 micron
Total Solids (TS):	71.2 ± 0.35 g/l
Volatile Solids (VS):	71.1 ± 0.33 g/l (99.9% of TS)
Chemical Oxygen Demand (COD):	76.7 ± 1.6 g/l
Soluble COD:	0.023 g/l at test pH
COD/VS Ratio:	1.08
Ash:	0.14% of TS (exclusive of H_3PO_4)

TABLE B-2. CHEMICAL CHARACTERISTICS OF XYLAN SLURRY USED FOR KINETIC STUDIES

Xylan	extracted from larchwood
Total Solids (TS):	51.5 ± 0.5 g/l
Volatile Solids (VS):	45.6 ± 0.4 g/l (89.3% of TS)
Chemical Oxygen Demand (COD):	49.3 ± 0.9 g/l
Soluble COD:	18.8 g/l at test pH
COD/VS Ratio:	1.08
Ash:	10.7% of TS (exclusive of H_3PO_4)

TABLE B-3. CHEMICAL CHARACTERISTICS OF PEAT SLURRY USED FOR KINETIC STUDIES

Peat	from Minnesota
Total Solids (TS):	42.3 ± 0.3 g/l
Volatile Solids (VS):	35.8 ± 0.3 g/l (84.6% of TS)
Chemical Oxygen Demand (COD):	50.3 ± 1.9 g/l
Soluble COD:	0.22 g/l at test pH
COD/VS Ratio:	1.41
Total Kjeldahl Nitrogen (TKN):	1.1 g N/100 g TS
Extractives:	6.4% of TS
Lignin:	56.1% of TS
Hexosan:	9.4% of TS
Ash:	15.4% of TS (exclusive of H_3PO_4)

TABLE B-4. CHEMICAL CHARACTERISTICS OF WHITE FIR SLURRY USED FOR KINETIC STUDIES

White Fir	*Abies concolor* Lindl.
Total Solids (TS):	9.04 ± 0.1 g/l
Volatile Solids (VS):	9.03 ± 0.1 g/l (99.5% of TS)
Chemical Oxygen Demand (COD:)	11.4 ± 0.2 g/l
Soluble COD:	0.11 g/l at test pH
COD/VS Ratio:	1.27
Extractives:	1.8% of TS
Lignin (Klason):	29.1 ± 0.2% of TS
Lignin (difference):	30.2 ± 0.6% of TS
Holocellulose:	67.5 ± 0.6% of TS
Cellulose:	52.5% of TS
Acid-Soluble Polysaccharides:	15.0% of TS
Hexosan:	52.2% of TS
Ash:	0.47% of TS (exclusive of H_3PO_4)

TABLE B-5. CHEMICAL CHARACTERISTICS OF WHITE FIR SLURRY USED FOR AUTOHYDROLYSIS STUDIES

White Fir	*Abies concolor* Lindl.
Total Solids (TS):	65.6 ± 1.2 g/l
Volatile Solids (VS):	65.3 ± 0.8 g/l (99.5% of TS)
Chemical Oxygen Demand (COD):	82.6 ± 0.6 g/l
COD/VS Ratio:	1.27
Extractives:	1.8% of TS
Lignin (Klason):[a]	29.1 ± 0.2% of TS (29.6% of ETS)
Lignin (difference):	30.2 ± 0.6% of TS
Holocellulose:	67.5 ± 0.6% of TS
Cellulose:	52.5% of TS
Acid-Soluble Polysaccharides:	15.0% of TS
Hexosan:	52.2% of TS
Ash:	0.47% of TS
pH:	5.0
Total Acidity:	2.0 meq/l (0.03 meq/g VS)

[a] Acid-insoluble lignin determined for extracted sample and referenced to total solids (TS) and extracted total solids (ETS).

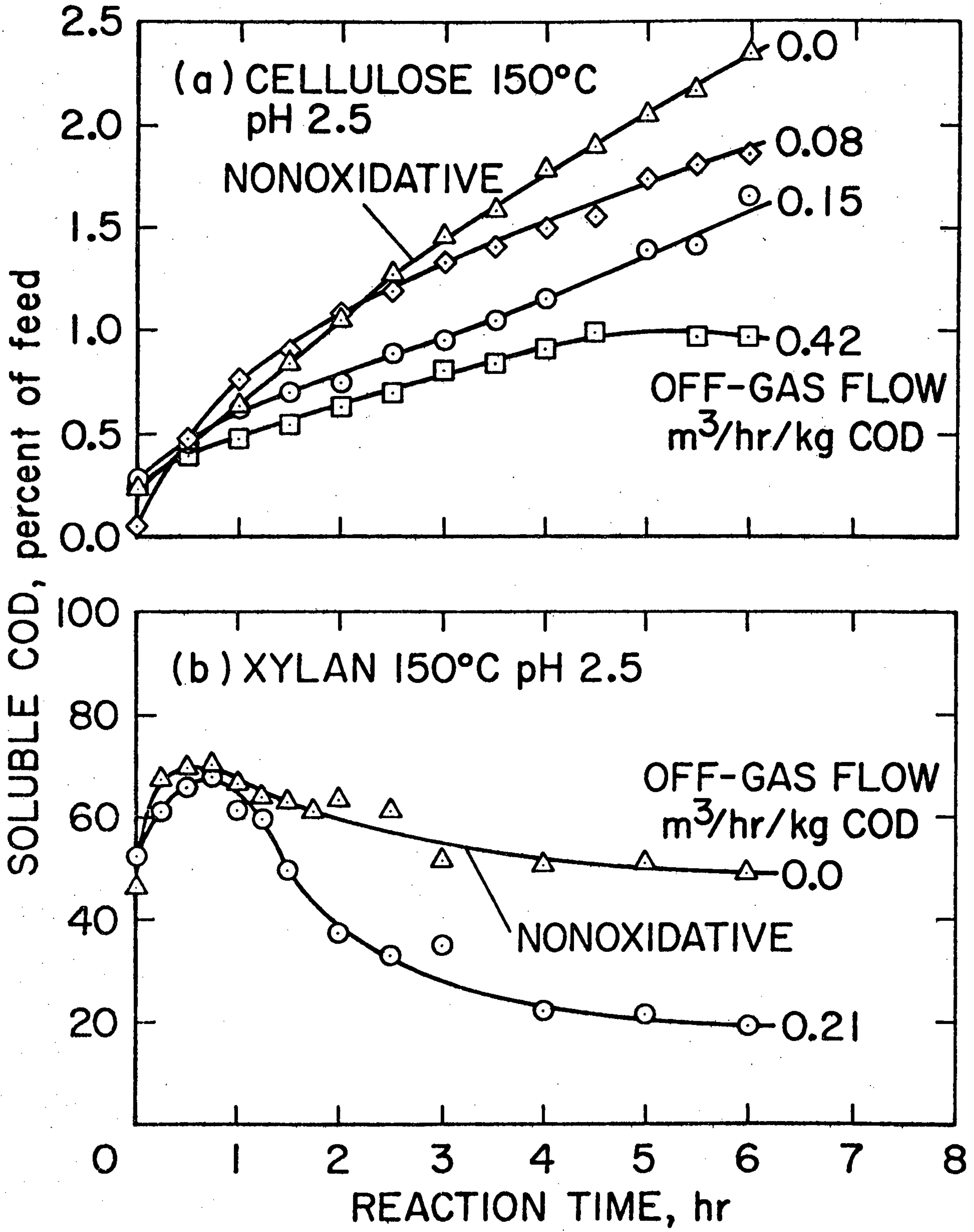

Figure B-1. Solubilization kinetics for oxidative and nonoxidative hydrolysis of (a) cellulose, and (b) xylan at 150°C, pH 2.5

COD present was proportionally less for oxidative than for nonoxidative treatment. Soluble organics were apparently oxidized under oxidative conditions, and the amount oxidized increased as the off-gas flow rate increased. These data suggest that either oxygen is not catalytic for hydrolysis of polysaccharides, as previously hypothesized (Schaleger and Brink, 1977), or the catalytic effect is small and offset by oxidative conditions. The former explanation is believed correct since off-gas flow rates were selected in a range previously reported as catalytic for cellulose hydrolysis from white fir (Schaleger and Brink, 1977). However, in agreement with previous research (Saeman, 1945), the rate of acid hydrolysis increased with increasing reaction temperature up to the maximum evaluated (225°C) as seen for the nonoxidative case in Figure B-2. In addition, for nonoxidative treatment at the two highest temperatures evaluated, 200 and 225°C, soluble COD reached a maximum and decreased slightly at longer reaction times.

Although not shown, lower yields of soluble COD associated with oxidative treatments were also exhibited at the higher temperatures evaluated: 175, 200, and 225°C. Furthermore, the results from hydrolysis of peat and white fir at pH 2.5 paralleled those depicted for cellulose and xylan hydrolysis. Therefore, a general and most important finding of this portion of the study was that oxygen is not beneficial for solubilization of polysaccharides from the lignocellulose matrix when independent of hydrogen ion concentration. These results reduce the potential advantages of oxidative hydrolysis to two possibilities: (1) oxidative conditions might increase hydrolysis rates by increasing the hydrogen ion concentration through generation of organic acids, or (2) heat generation from aqueous combustion of acid-resistant and/or refractory organics may prove economically attractive.

Autohydrolysis of White Fir

In order to test the first potential advantage of oxidative hydrolysis listed above, a comparative analysis of oxidative and nonoxidative autohydrolysis of white fir was conducted at a temperature of 225°C and solids concentrations that simulated full-scale processing. The highest temperature, 225°C, was selected from the previous kinetic studies for this evaluation since soluble organic concentrations were maximized at high temperature and short reaction times. Pretreatment performance was evaluated here with respect to organic solubilization and organic acid production (i.e., effect of pH or hydrogen ion concentration).

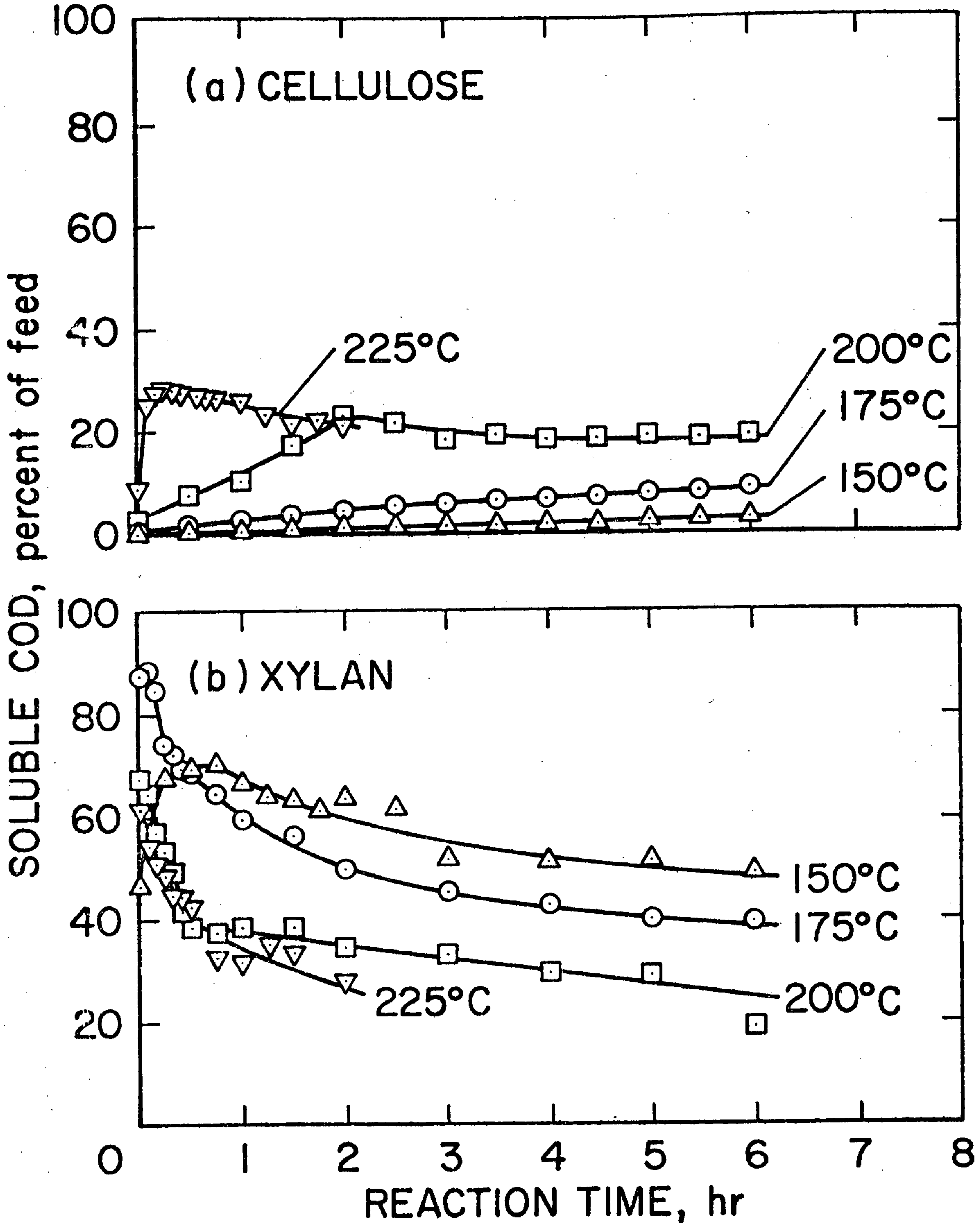

Figure B-2. Solubilization kinetics at various reaction temperatures for non-oxidative hydrolysis of (a) cellulose, and (b) xylan at pH 2.5

Results are included in Table B-6. Here again, soluble COD recoveries were proportionally less for all oxidative relative to nonoxidative treatments for reaction times from 0.5 to 4.0 hours. The effect of oxidative hydrolysis on pH, total acidity, and soluble COD can be seen in Figure B-3. Oxidative processing resulted in slightly higher product acidities, but the comparative effect on lowering pH or apparent acidity constants (pK_a, Table B-6) was insignificant, and possibly detrimental. The ultimate result was that solubilization was not increased either by acid generation or the presence of oxygen. Soluble organics were apparently oxidized, and thus soluble COD recoveries were lower under oxidative treatment. Based on these findings, only nonoxidative processing was evaluated in subsequent studies.

Additional nonoxidative autohydrolysis reactions were conducted for white fir in order to better understand the solubilization mechanisms involved and the overall pretreatment potential of this method. Organic solubilization was monitored by measurement of total acidities and CODs (Table B-6), and selected products were analyzed for lignin and hexosan content. The primary objective of these experiments was to confirm that optimum autohydrolysis conditions had been established for organic solubilization.

Figure B-4 depicts product soluble CODs and the chemical changes that occurred in the residual particulates during the course of nonoxidative hydrolysis of white fir. Acid-soluble polysaccharides constituted approximately 15 percent of the feed solids (Table B-5), or about 12 percent of the feed COD, and undoubtedly, these easily hydrolyzed hemicelluloses were initially solubilized at mild reaction conditions (175°C). As the severity of treatment increased, product soluble COD also increased, then stabilized at approximately 20 to 25 percent of the feed COD. There was only about 5 percent loss in total COD even at the most extreme conditions (225°C, Table B-6), and COD of the particulate residue stabilized at about 70 to 75 percent of the feed COD.

Substantial chemical changes occurred in the residual particulates at 225°C, and thus, are worthy of review. At time 0.0, the hexosan/lignin ratio of the product (1.68) was similar to the feed solids (1.79), and both components were of somewhat larger respective proportions to the total solids due to loss of hemicelluloses and pentosans during the heating cycle. As the reaction proceeded, lignin content increased substantially with a concomitant decrease in hexosan. Hexosan content was very low after four

TABLE B-6. CHEMICAL RESULTS FROM AUTOHYDROLYSIS OF WHITE FIR

Pretreatment Conditions					Acidity,[d] meq/g VS		Chemical Oxygen Demand				
Temp. °C	Time,[a] hr	Off-Gas Flow[b]	pH	pK_a[c]	Total	Soluble	Total g/l	Soluble g/l	Soluble % of Feed COD	Percent Loss[e]	Percent Oxidized[f]
175	0.0	He	4.0	-	0.09	0.05	79.7	6.68	8.1	3.6	-
175	2.0	He	3.3	4.1	0.45	0.42	79.0	16.6	20.0	4.4	-
175	4.0	He	3.1	4.1	0.78	0.75	77.1	15.6	18.9	6.7	-
200	0.0	He	3.6	-	0.18	0.14	77.6	14.5	17.5	6.1	-
200	2.0	He	3.1	4.1	0.86	0.82	78.3	16.8	20.3	5.3	-
200	4.0	He	2.8	4.1	1.08	1.05	76.5	15.5	18.8	7.4	-
225	0.0	He	2.9	4.0	0.70	0.70	79.9	18.4	22.3	3.3	-
225	0.5	He	3.0	4.1	1.01	0.94	79.4	17.9	21.7	3.9	-
225	1.0	He	2.7	4.1	1.10	1.12	80.6	19.1	23.1	2.5	-
225	2.0	He	2.6	4.0	1.76	2.02	79.6	21.7	26.3	3.7	-
225	3.0	He	2.5	4.0	1.47	1.74	79.1	19.9	24.1	4.2	-
225	4.0	He	2.9	4.1	1.42	1.28	78.2	18.3	22.1	5.4	-
225	0.5	0.18	2.5	4.0	1.28	1.12	75.7	14.8	17.9	8.4	2.7
225	1.0	0.18	2.5	4.0	1.32	1.16	76.9	16.4	19.9	6.9	5.1
225	2.0	0.24	2.8	4.1	1.87	1.44	69.1	12.6	15.3	16.4	12.8
225	3.0	0.17	2.9	4.0	1.58	1.17	69.7	9.22	11.2	15.7	13.7
225	4.0	0.18	2.6	4.5	1.79	1.07	60.8	7.01	8.5	26.5	14.9

[a] Reaction time at indicated temperature; 0.0 hr denotes heated to indicated temperature and immediately cooled to room temperature.

[b] Off-gas flow referenced as m^3(STP)/hr/kg feed COD; He denotes nonoxidative treatment.

[c] Apparent acidity constants for soluble fractions as estimated from titration curves. Dashes denote insufficient data for estimates.

[d] Acidity determined by titration to pH 8.3 and referenced to feed volatile solids (VS).

[e] COD loss due to oxidation and or volatilization.

[f] COD oxidized as determined by off-gas analyses for oxidative reactions.

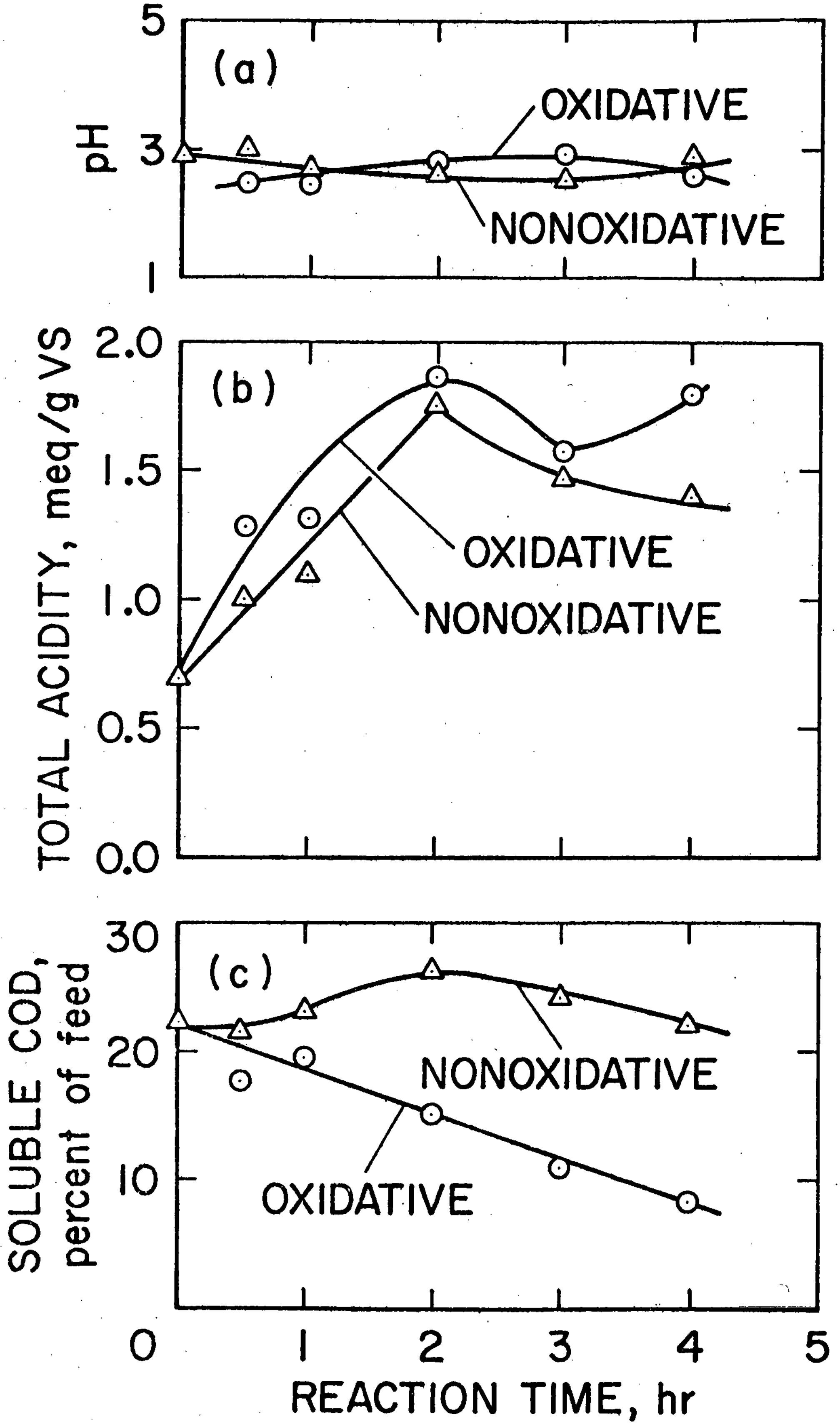

Figure B-3. Pretreatment product (a) pH, (b) total acidity, and (c) soluble COD for oxidative and nonoxidative autohydrolysis of white fir at 225°C. Apprroximate off-gas flow rate for oxidative treatments: 0.2m^3(STP)/hr/kg feed COD

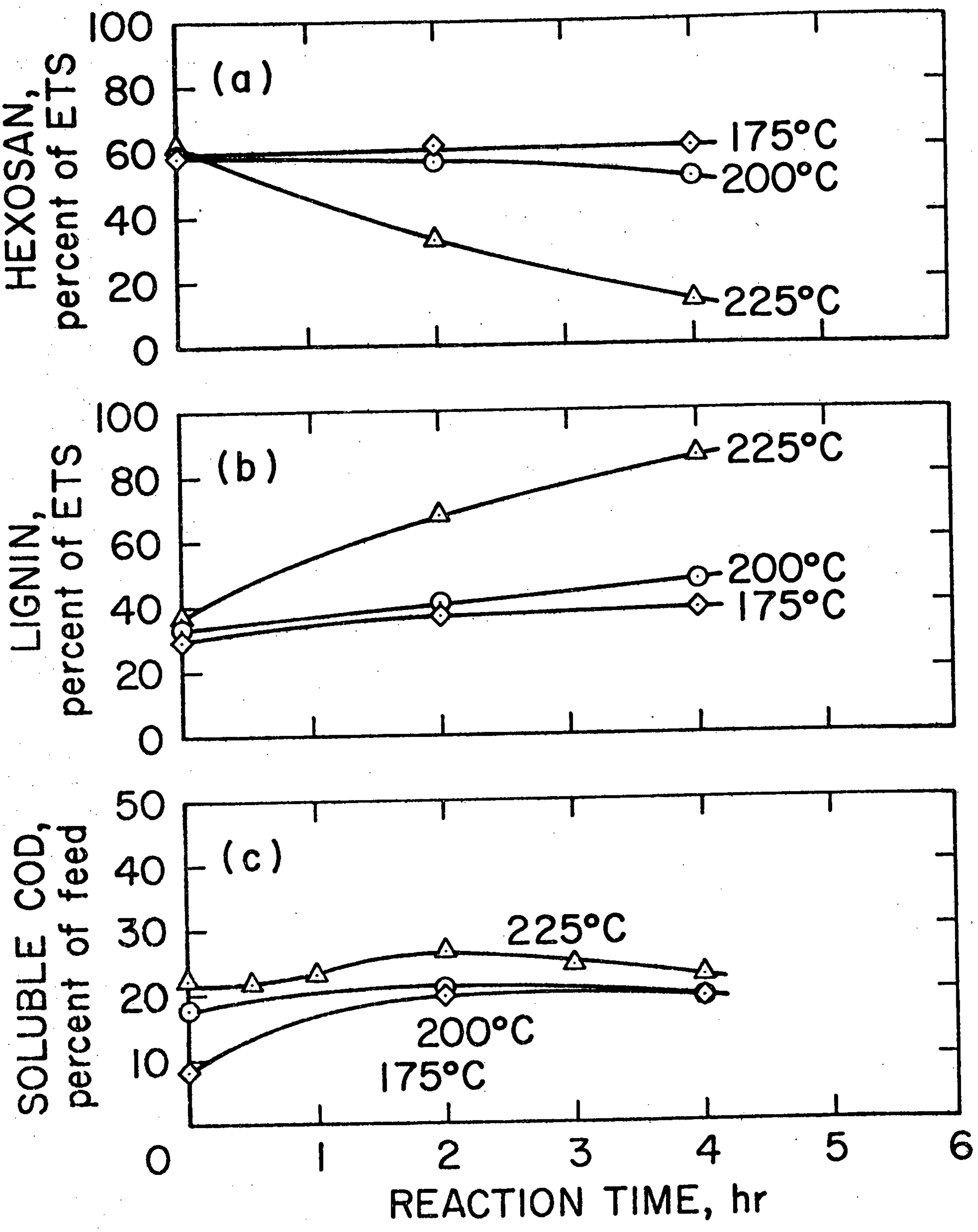

Figure B-4. Progressive change in chemical properties of the extractive-free particulate residue (ETS), (a) hexosan, and (b) lignin; and (c) product soluble COD with respect to reaction time for nonoxidative autohydrolysis of white fir at 175, 200, and 225°C hours of treatment, and the residual solids assayed as approximately 85 percent lignin (note: COD of these solids did not change significantly during treatment).

There are two possible explanations for these observations. First, hemicelluloses were initially solubilized during the heating cycle. This resulted in the lignin plus hexosan sum increasing from 81.3 percent of the particulate solids content to 99.2 percent. Then, with time of treatment, either (1) the hexosans, which were predominantly cellulose, were solubilized and then subsequently formed condensation products which were assayed as lignin; or (2) the hexosan fraction formed such condensation products directly without forming soluble intermediates.

It is important to understand which mechanism predominates for proper assessment and application of autohydrolysis pretreatment; therefore, three nonoxidative reactions were conducted to test these hypotheses. The white fir slurry (Table B-5) was hydrolyzed in staged, sequential reactions as follows: Stage 1 - heated to 200°C and immediately cooled to room temperature, and Stages 2 and 3 were performed identically as 2-hour nonoxidative treatments at 225°C. After each stage, the product was assayed for total and soluble COD, and the particulate fraction was separated by filtration. These solids were resuspended in 0.75 liter of deionized water, assayed for total COD, and treated in the subsequent stage. The overall objective was to simulate nonoxidative processing as depicted in Figure B-4 for 225°C, but with soluble product recovery at intermediate steps. If polysaccharides were being solubilized and reprecipitated as lignin-like matter, then overall soluble-product recovery would be significantly higher in staged processing due to a reduction in condensation reactions. However, if lignin-like products were formed directly, then staged processing would not result in significant improvement in soluble-product recovery.

The data, summarized in Table B-7, show rather conclusively that the former mechanism predominates. Also, the particulate yield (41 percent) closely approximates the theoretical 40 percent COD represented by the lignin fraction of the original solids, and the soluble yield (51 percent) represents approximately 85 percent of the theoretical carbohydrate COD. Thus, a complex lignocellulosic, represented by white fir, was transformed by autohydrolysis into two easily separable fractions: a soluble fraction that originated predominantly from carbohydrates, and a particulate residue comprised primarily

TABLE B-7. SUMMARY OF 3-STAGE NONOXIDATIVE AUTOHYDROLYSIS OF WHITE FIR

Stage	Reaction Conditions		Feed[a] COD, g/l	Product COD, g/l			Percent of Original COD[b]		
	Temp., °C	Time, hr		Total	Soluble	Particulate	Loss	Particulate	Soluble
1	200	0.0	82.6	82.6	14.3	68.3	0.0	82.7	17.3
2	225	2.0	63.4	61.2	18.4	42.8	3.1	55.9	24.0
3	225	2.0	49.8	45.1	8.51	36.6	5.3	41.0	9.6
Sum							8.4	41.0	50.9

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

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

of lignin condensation products. Furthermore, virtually the entire heating value was retained in each fraction. These data in conjunction with preliminary biodegradability studies from autohydrolyzed newsprint (Healy et al., 1978), suggest that staged, nonoxidative autohydrolysis pretreatment and anaerobic fermentation has potential for obtaining significant methane yields from a relatively non-biodegradable lignocellulosic, white fir.

Conclusions and Future Studies

The following conclusions can be drawn from the previous study:

1. Oxygen was found not to be beneficial for solubilization of the components of lignocellulose or for polysaccharide solubilization from the lignocellulose matrix independent of pH.
2. Oxidative treatment has the potential of increasing the amount of acids produced from autohydrolysis of lignocellulose; however, the corresponding effect on hydrolysis rate is insignificant.
3. Based on the first two conclusions, nonoxidative treatment would be preferred over oxidative hydrolysis of lignocellulose for the purpose of increasing product bioconversion efficiency by solubilization of polysaccharides.
4. The mechanism of COD solubilization can be likened to the acid-saccharification process: polysaccharides are hydrolyzed first, and soluble constituents subsequently condense forming lignin-like products. Also, for single-stage processing, soluble COD is maximized by analogous conditions for maximizing sugar yields by saccharification: high reaction temperatures and short contact times.
5. Within constraints of the test facilities employed for these studies, a three-stage nonoxidative scheme worked well for soluble COD recovery from white fir. The overall scheme recovered 85 percent of the carbohydrate heat content as a mixture of soluble products, and virtually all of the lignin fraction as insoluble residue.

Based on these findings, future studies will address the biochemical aspects of fermentation of soluble products from autohydrolysis. Products from the reactions discussed in this phase will be employed for bioassay testing using the BMP and ATA methods. In addition to determining overall system bioconversion efficiency, autohydrolysis products will also be tested for potential toxicity.

C. BIODEGRADATION OF LIGNIN AND LIGNIN FRACTIONS

P. J. Colberg and L. Y. Young

Background

Approximately half of the earth's carbon which is fixed annually via photosynthesis is incorporated into lignocellulosic cell walls (Bassham, 1975). Lignin is a structural polymer of all vascular plants that performs functions essential to survival (Sarkanen and Ludwig, 1971), by imparting rigidity and cementing plant cells together, so as to confer resistance to impact, bending, and compression. Lignified tissues also act as barriers to permeation of water across cell walls and prevent invasion by pathogenic microorganisms. Most microorganisms which are able to degrade isolated wood carbohydrates cannot attack woody tissues directly unless they are also able to decompose lignin. Thus the microbial degradation of lignin is an integral part of the carbon cycle, not only because lignin is a major repository of reduced carbon in the biosphere, but also because it physically protects wood carbohydrates from decomposition. Lignin, therefore, is perhaps one of the most serious impediments to the development of successful bioconversion processes for waste lignocellulosics.

Previous studies at Stanford have related enhanced biodegradability of lignocellulosic wastes and wood products to the solubilization of lignin during alkaline heat treatment, which has been correlated to an increase in the number of low molecular weight compounds released (Healy et al., 1977). Most investigators maintain that lignin's resistance to biodegradation is most probably related to its large molecular size and poor solubility. Since lignin is such a complex polymer, much work has centered on the degradation of model compounds of low molecular weight (Healy and Young, 1978). With the advent of radioactive-labeled natural lignocellulose, biodegradation studies with intact lignins have recently begun (Crawford and Crawford, 1976). The potential for biodegradation of the two extremes (whole lignin and model lignins), therefore, have been assessed under a variety of aerobic and anaerobic conditions. However, the potential for anaerobic degradation by bacteria of the more complex compounds produced during alkaline heat treatment of lignin is unknown at this time.

Although the phenomenon of toxicity has been reported for both anaerobic digesters, bioassay studies, and enrichment cultures in which relatively low concentrations of lignin were fed (Calder and Tader, 1976; Chmielowski et al., 1964; Scheffer and Cowling, 1966; Gossett, 1976; and Healy et al., 1977), little experimental attention has been focused on the problem. Previous work at Stanford has related lignin toxicity with the presence of aromatic compounds, though specific identification of potentially toxic substances has never been attempted.

Current Studies

The objective of the first phase of laboratory work was to adapt gel filtration chromatographic techniques for the preparative fractionation and collection of alkaline heat-treated peat lignin to be used in biodegradation and toxicity studies. The protocol employed for lignin pretreatment, fractionation by gel filtration chromatography, and preparation for feeding experiments were described in detail in the last report (Healy et al., 1978 b) and schematically in Figure C-1.

Elution Patterns of Peat Lignin

Fractionation of alkaline heat-treated peat preparations on Sephadex LH-20 (Pharmacia Fine Chemicals, Uppsala, Sweden), resulted in three major fractions: two low molecular weight peaks (mw ~ 200 and mw ~ 600), and one larger, high molecular weight fraction, the size of which approaches the exclusion limit of the gel (Fig. C-2).

It was suspected that the larger molecular weight fraction (Fraction 1) might be composed of more than one peak which were not resolvable on Sephadex LH-20. Sephadex LH-60 (Pharmacia Fine Chemicals, Uppsala, Sweden) was chosen to further elute Fraction 1 (Fig. C-3). Although LH-60 elution revealed the presence of a broad range of higher molecular weight compounds, the majority of material was still eluted in one major peak.

Mass Balance Results

Biochemical Methane Production (BMP) assays (Owen et al., 1979) were performed on the lignin fractions. Gas formation commenced after one month of incubation with data based on the mean results of duplicate bottles (Table C-1). These results should be viewed with some caution as the gas volumes produced were very small. One of the limitations of the lignin separation

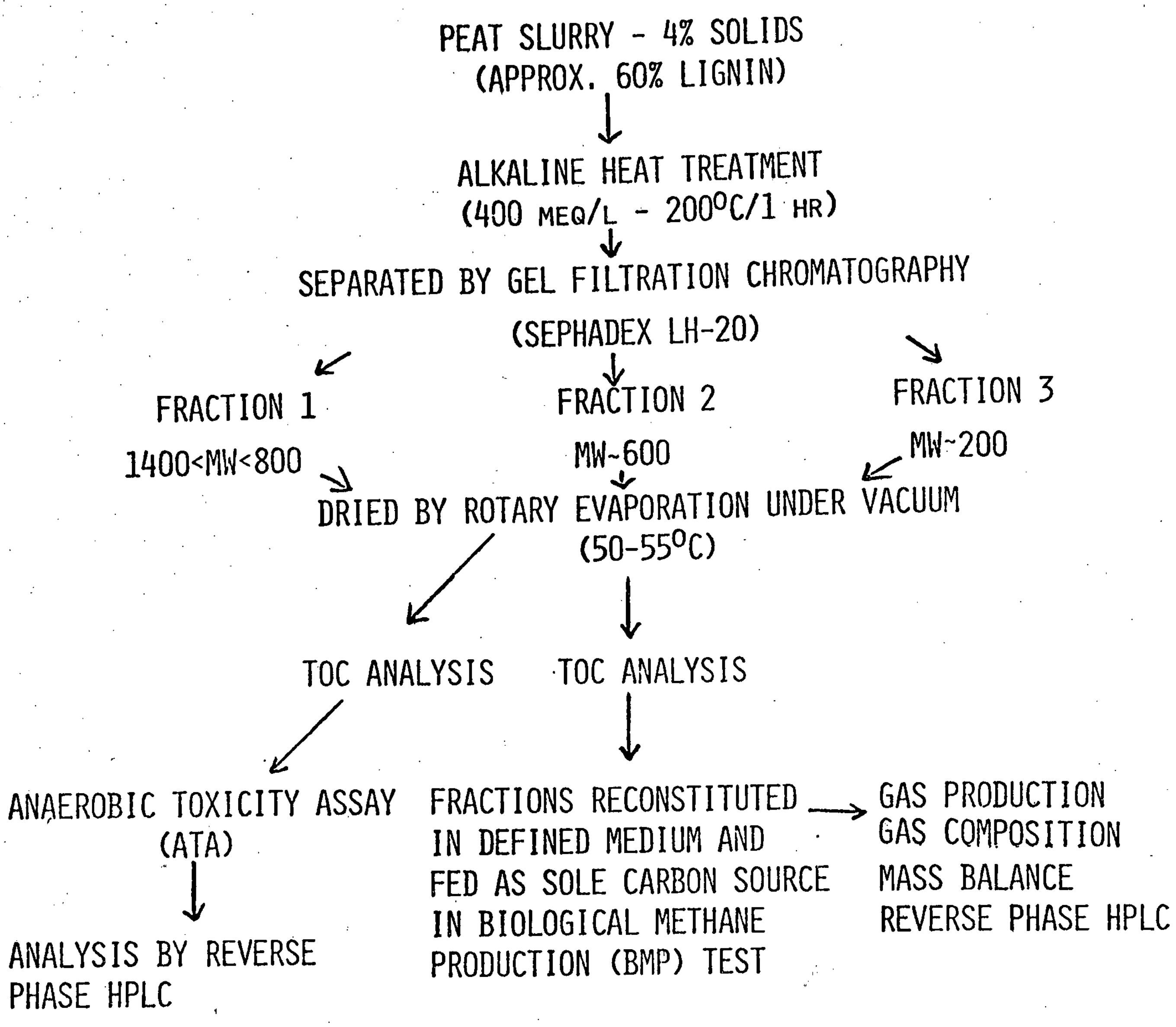

Figure C-1. Schematic representation of protocol to be followed for examining lignin fraction degradation

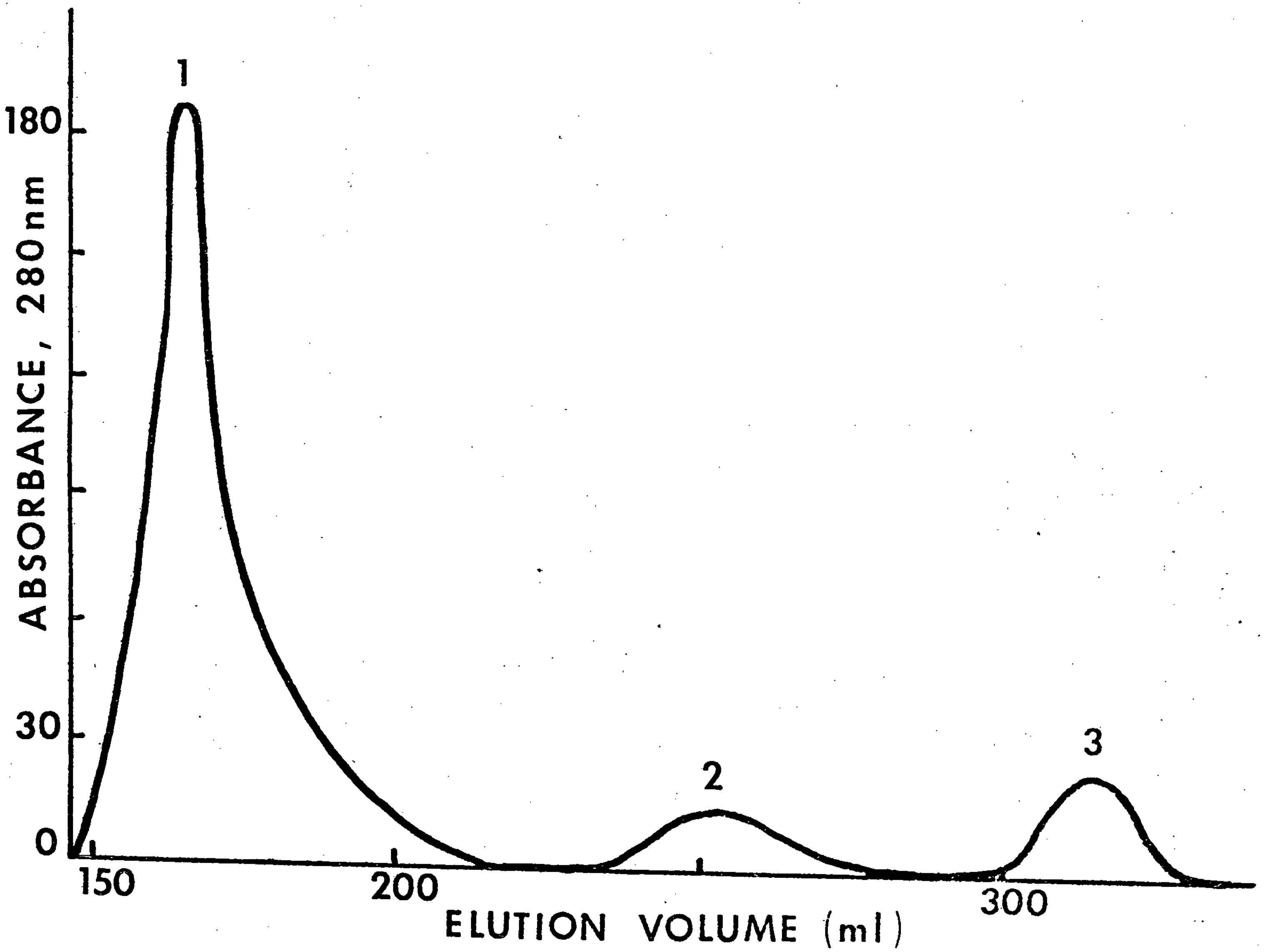

Figure C-2. Elution pattern of alkaline heat-treated peat on Sephadex LH-20 in 1:1 dioxane-water; peak 1, m.w. > 600; peak 2, m.w.~ 600; peak 3, m.w. ~ 200.

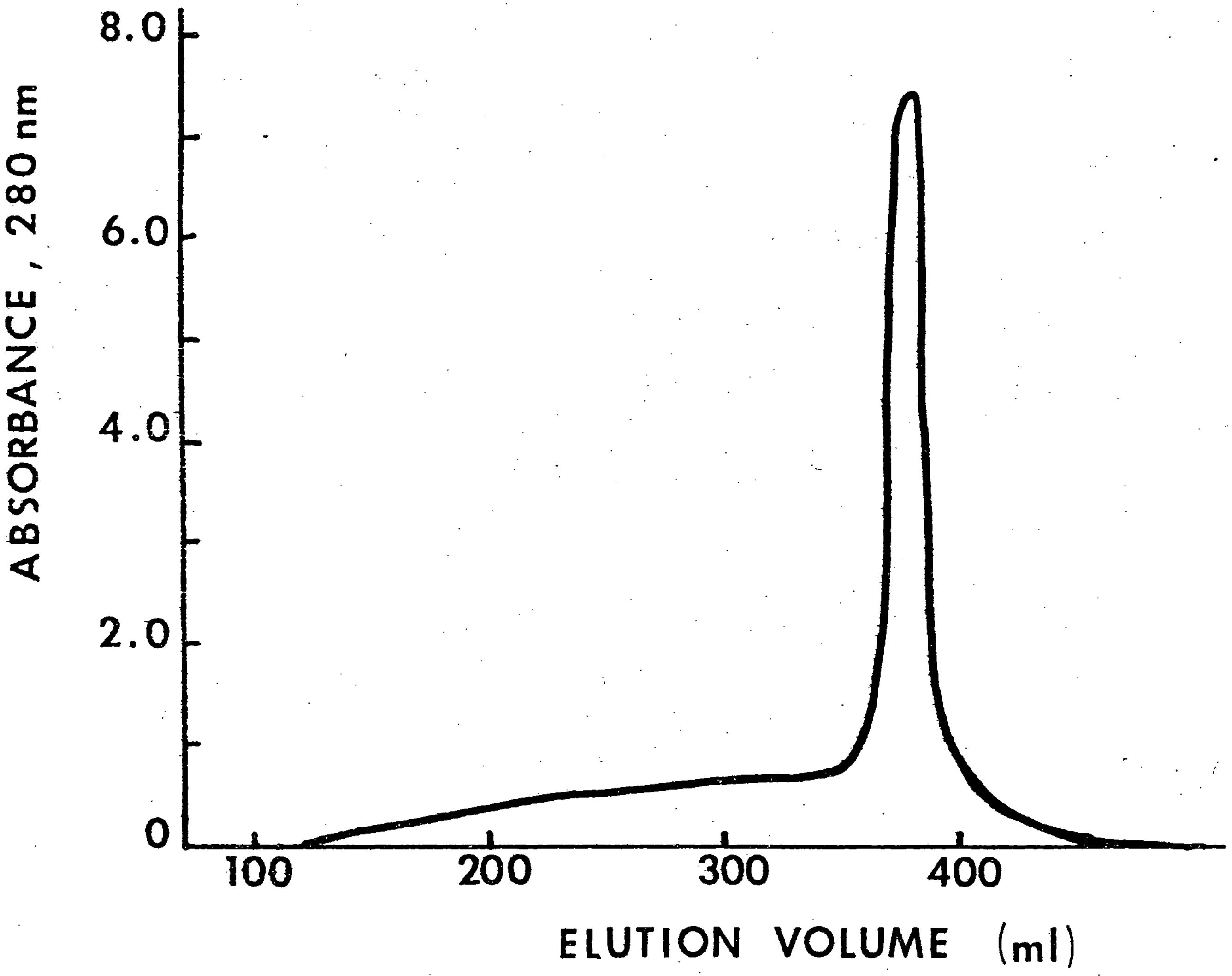

Figure C-3. Elution pattern of Fraction 1 on Sephadex LH-60

TABLE C-1. CONVERSION OF LIGNIN FRACTIONS TO GAS

	Percent Carbon Converted to CO_2 & CH_4	Percent Carbon Converted to CH_4
Fraction 1 (1000 mg C/l)	30	4
Fraction 2 (750 mg C/l)	38	23.5
Fraction 3 (1000 mg C/l)	7	3

is that repeated fractionations are necessary in order to yield sufficient quantities of Fractions 2 and 3. In addition to re-feeding acclimated cultures, assays employing larger bottles have recently been set up in order to minimize errors in calculation of mass balance data.

Future Work

In addition to continuation of biodegradation studies, Anaerobic Toxicity Assays (Owen et al., 1979) will be conducted on the lignin fractions. In order to delineate the presence of a specific toxic compound or compounds, more refined analytical procedures will be required. Methodology testing and development is now in progress to adapt High-Pressure Liquid Chromatography (HPLC) techniques for assessment of biodegradation and potential toxicity. Structural changes in lignin fractions fed in BMP assays may be followed by HPLC reverse-phase analysis, separating the molecular size peaks into individual components according to molecular weight. Since the column is run at low pressures (100-200 psi), the fractions and individual compounds should remain intact during analysis. This technique affords the ability to follow degradation of specific compounds during anaerobic decomposition. In addition, it allows for identification of compounds which are either non-biodegradable, i.e., their peaks do not disappear during anaerobic incubation, and/or potentially toxic, their peaks likewise persisting during incubation. HPLC reverse-phase analysis also allows compounds of interest to be collected during analysis--a major advantage over other chromatographic techniques in which the sample is destroyed during analysis (i.e., gas chromatography). Identification of compounds suspected to be toxic may subsequently be identified by Gas Chromatography-Mass Spectroscopy (GC/MS).

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COO-2917-12

BIOLOGICAL CONVERSION OF BIOMASS TO METHANE

QUARTERLY PROGRESS REPORT
for Period September 1 - November 30, 1978

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December 1978

Prepared for

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

1. Particle Size Distribution

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

When the material was wetted, the particles swelled substantially as a result of the absorbed moisture. Using a wet sieving technique, over 65 percent of the total solids were retained on the #10 sieve. At the same time, 30 percent of the total solids passed the #200 sieve. Essentially all of this 30 percent was soluble solids. Upon fermentation, the total solids passing the #200 sieve increased to 41 percent. However, only 48 percent of the total solids passed the #10 sieve. These data are also shown in Figure 1. This size distribution certainly facilitates dewatering of the fermented slurry by simple passage over a 10 mesh screen.

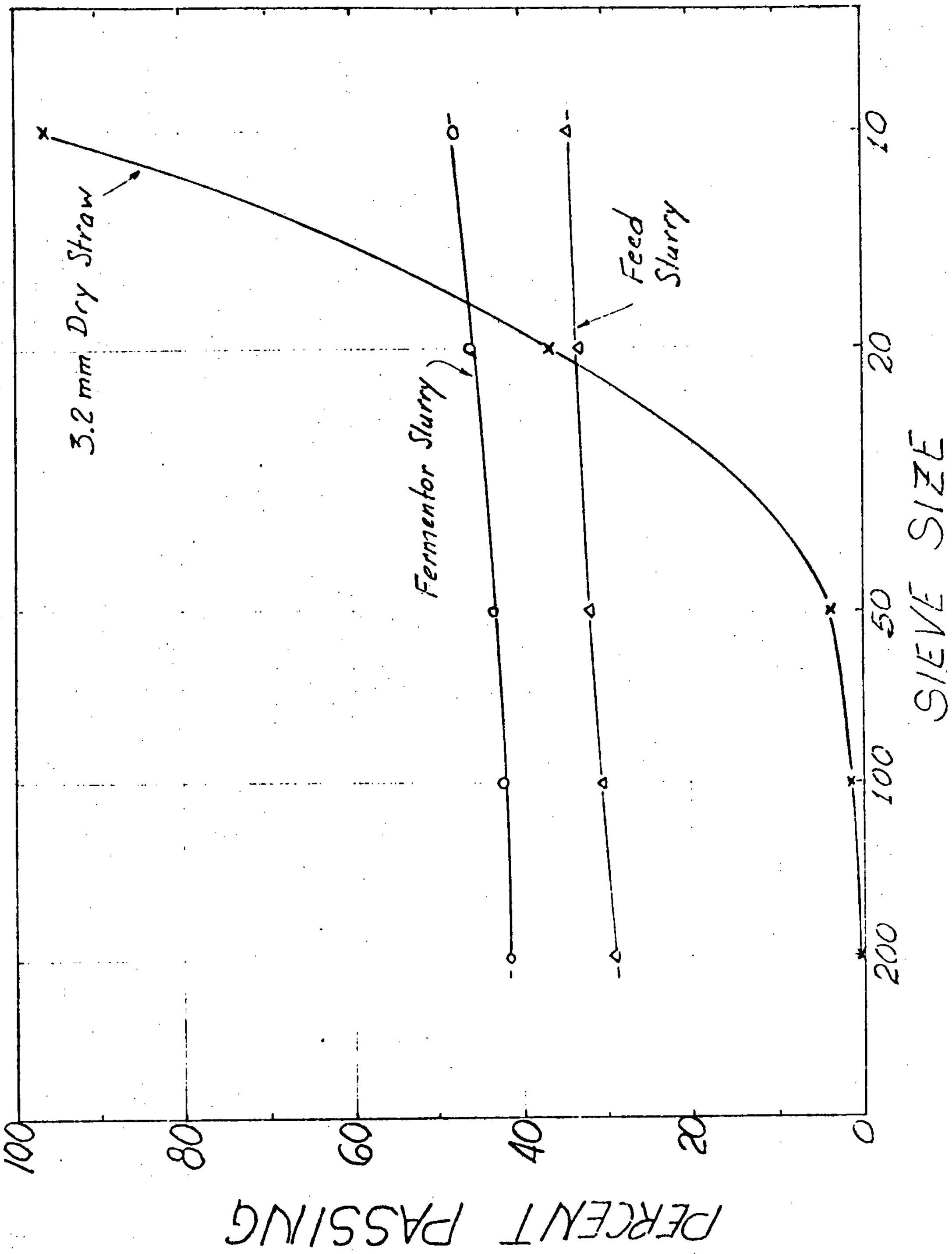

Figure 1. Particle Size Distribution of Chopped Straw

Better than 90 percent of the solids of a size greater than 74 μm can be recovered. The moisture content of the screened solids will be approximately 85 to 90 percent. Additional dewatering can be obtained by appropriate presses.

2. Straw Slurry Characteristics

This straw slurry has unique characteristics. With a solids content of 12 to 13 percent, the straw and water mixture has absolutely no fluid properties. It has an angle of repose that approaches 90 degrees. Mixing by conventional fluid mixers is impossible. The power required by a ribbon mixer designed to mix concentrated slurries exceeded 2 KW/m^3 (75 HP per 1000 cu ft). This slurry could only be mixed at significantly lower solids concentrations.

Pumping of a slurry containing 10 percent solids was impossible. It was necessary to dilute the solids to about 3 percent. Even at these concentrations, it was extremely difficult to pump the slurry. To facilitate pumping, the Moyno pump speeds were increased to 300 rpm. Various other procedures were tried in hopes that it would be possible to operate the pumping system with the time clocks to approximate continuous operation. Steam heating of the straw-water mixture at 115°C (240°F) did improve the water absorption. It was possible to wet the straw more easily with the heat treatment It also appeared to ease the pumping problems slightly. However, the feeding had to be accomplished manually. The pumps would not start without flushing with water prior to turning on the pumps.

After completing a run with straw pretreated as above, a thermochemical pretreatment was initiated. Water containing 0.25 normal sodium hydroxide was added to the straw to produce a 12.5 percent solids concentration. The resultant pH of the slurry was 12.2 to 12.3. This slurry was heated at 115°C (240°F) for a total time of 4 hours. The physical characteristics of this slurry drastically changed. Mixing and pumping with a solids concentration of 12.5 percent was possible. Dilution of the slurry with tap water to 6.3 percent solids yielded a slurry having the appearance of cooked oatmeal. The pH of this dilution is approximately 10. Pumping was easy and feed to the fermentation system was possible with the pumps operating on the time clocks. As with the corn stover, the slurry characteristics of the straw suspension is unique. Special considerations must be given to handling of these slurries in any system.

3. Gas Production Data

The data presented in Table 1 show the gas production obtained at various retention times. Each reactor was operated at the specified condition for at least 3 retention times before these data were collected. These data are for a fermentation temperature of 59 ± 1°C (138 ± 2°F). The straw slurry had been heat treated prior to addition to the slurry holding tanks. As discussed previously, this treatment was necessary to alter the characteristics of slurry so that it was possible to pump it.

Problems in pumping of this slurry were encountered. It was not possible to start pumping without first flushing the pipes with water. The time cycle pump activation system could not be used. Approximately 50 liters of slurry were added each time the pumps were activated. At the short retention time (3.8 days), four such pump periods were used daily. Unfortunately, this resulted in adding a substantial feed volume (200 liters into 750 liters) over a period of 4 to 6 hours. This mode of feeding resulted in an unstable system.

Table 1. Gas Production Data for Wheat Straw

Week	θ	Gas		Vol. Solids	CH_4 Produced[1]
		Lph	% CH_4	kg/day	m^3/kg Vol. Solids
1	3.8	23.5	57.5	3.73	0.087
2	3.8	25.7	56.7	3.90	0.090
3	3.8	21.1	57.0	4.06	0.071
4[2]	5.0	17.8	60.8	3.39	0.077
1	5.0	18.4	56.6	2.97	0.084
2	5.0	19.2	57.3	3.02	0.087
3	4.9	22.1	56.1	2.93	0.101
4	5.1	17.1	58.0	2.86	0.083
1	7.5	16.6	56.6	1.96	0.115
2	7.4	16.2	58.7	2.02	0.113
3	7.3	16.7	54.5	2.00	0.109
4	7.5	14.2	57.5	1.94	0.101
1	13.1	10.7	58.6	1.12	0.134
2	13.2	12.6	58.7	1.18	0.150
3[3]	13.2	9.7	54.1	1.20	0.104
4	14.2	9.7	59.5	1.06	0.131
5	14.3	10.0	(58.9)	1.04	0.136

[1] To obtain scf/lb multiply by 16

[2] pH drop to 5.9 due to drop in alkalinity and volatile acid increase

[3] Gas leak in reactor

Wheat straw does not produce adequate natural alkalinity when fermented. Consequently, additional alkalinity must be added with the feed. As a result of the instability in the short retention time reactor, the volatile acids increased. With an alkalinity in the 900 mg/l as $CaCO_3$ range, the pH dropped as the volatile acids increased. During Week 4, the pH in the short retention time reactor dropped to less than 6.0. The feed was stopped for two days and lime added to the reactor for pH control. A rapid recovery was experienced. The gas data for this week were not used in subsequent calculations.

During Week 3, the reactor with the longest retention time experienced a gas leak in the feed piping. This resulted in incorrect gas readings. Consequently, the gas data for this week were excluded in the subsequent data analyses.

The gas production in Table 1 is expressed in terms of the gas (methane) generated per unit of volatile solids added. When processing straw, a liquid recycle stream is employed. The fermented slurry is passed over a screen to remove most of the suspended solids. The total solids of this stream was reduced from approximately 20 g/ℓ to 6 g/ℓ by this simple screening process. The liquid fraction is used as make-up water for the new feed slurry. Consequently, a measurable quantity of solids is recycled with this system. The gas production in Table 2 is the average for the data shown in Table 1 and is expressed in terms of the total volatile solids fed (including recycle solids) and in terms of the volatile solids added with the straw only, the latter being the data in the adjusted CH_4 production column.

Table 2. Gas Production Data for Straw

θ Days	CH_4 Production m^3/kg V.S. Fed	Adjusted CH_4 Production m^3/kg V.S. Fed
3.8	0.083 (1.31)*	0.100 (1.58)
5.0	0.089 (1.41)	0.109 (1.72)
7.4	0.110 (1.74)	0.134 (2.12)
13.7	0.138 (2.18)	0.167 (2.64)

*( ) Data expressed as SCF/lb V.S. fed

The adjusted methane production was used to determine the percentage of volatile solids that are degradable. This is accomplished by extrapolating the gas production data to an infinite retention time. A semi-log plot of methane production against the reciprocal of the retention time (Figure 2) yields a straight line. The y-intercept is the methane production at an infinite retention time, or the biodegradability of the organic material. Based on the data in Figure 2 the maximum possible methane production would be 0.22 m^3/kg volatile solids added (3.52 scf/lb). If one assumes that the organic material being fermented is cellulose, the methane production per kg of cellulose fermented would be 0.44 m^3 at a gas temperature of 15°C. Based on this maximum gas production, the volatile solids in the straw would be 50 percent biodegradable.

The rate of conversion is determined from a simple first order kinetic relationship in which the substrate removal rate (dS/dt) is a function of the biodegradable substrate remaining.

$$\frac{dS}{dt} = KS \qquad (1)$$

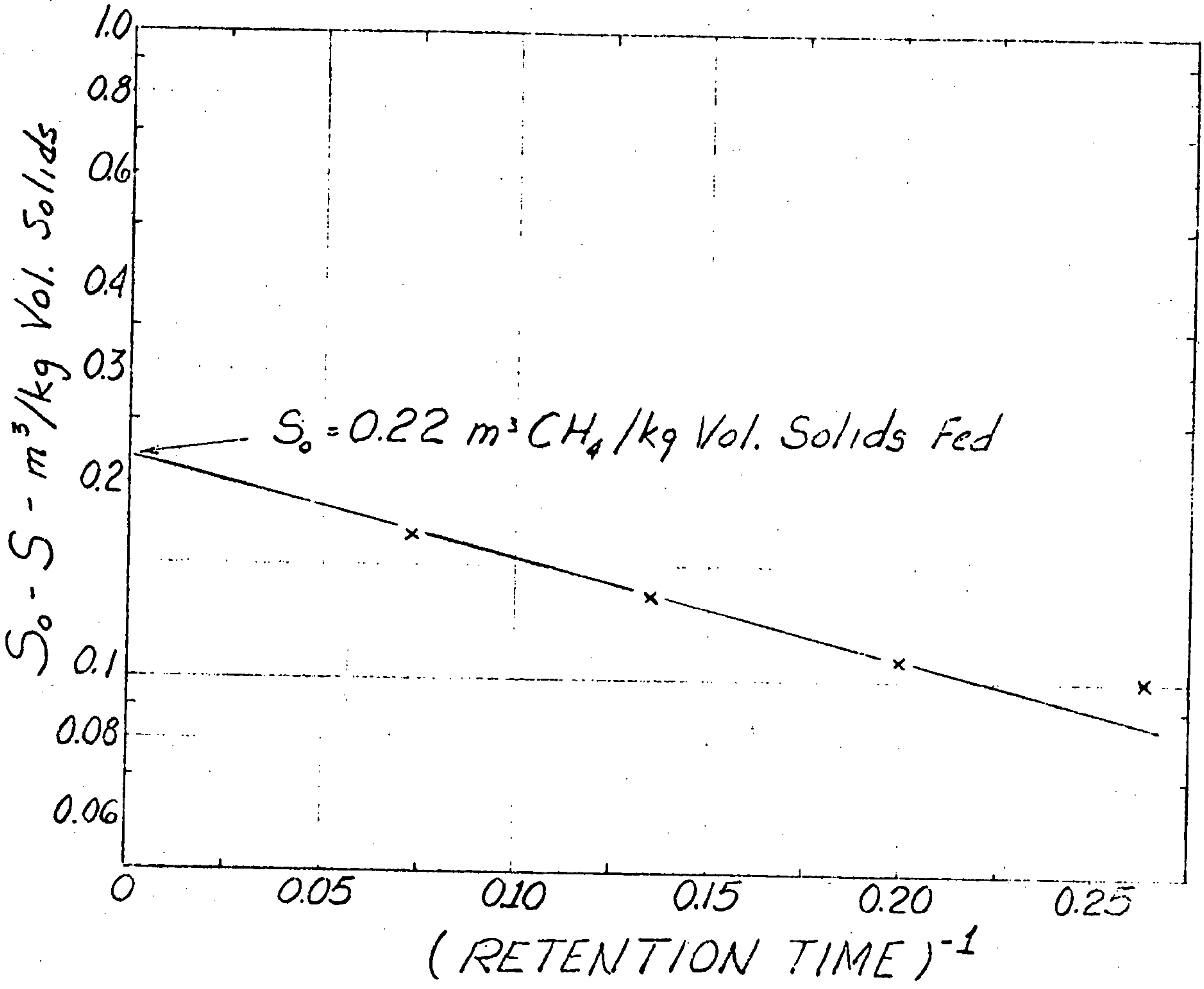

Figure 2. Determination of the Fraction of Volatile Solids that are Biodegradable

A mass balance on a complete-mix reactor without sludge recycle yields the following equation:

$$S = S_0 \left(\frac{1}{1 + K\theta}\right) \qquad (2)$$

where:

S = biodegradable substrate remaining

S_0 = initial biodegradable substrate

θ = reactor retention time - days

K = rate constant - day^{-1}

Using a value for S_0 as determined from Figure 2, and the values of $S_0 - S$ (methane produced per kg of volatile solids) from Table 2, Figure 3 can be constructed. This is a linear form for Equation 2. A least squares fit, including the y-intercept value (0,1), yields a line with a slope of 0.23 day^{-1}. This is the rate constant, K, in Equation 2.

This rate constant (temperature of 59 $\pm$ 1°C) corresponds closely with the values found for manure (0.25 day^{-1}) and corn stover (0.25 day^{-1}).

4. Discussion

Review of the data obtained for wheat straw and corn stover can be used to identify the major limitation of these materials as substrate for methane production. The poor conversion efficiency results in extreme penalties for residue disposal. A thermophilic system (58-60°C) operating at a 10-day residence would generate the results shown in Table 3. The corn stover and straw would be harvested with a moisture content of less than 25 percent. After fermentation, 71.4 and 62.9 percent of the corn stover and straw volatile solids (dry weight), respectively, would

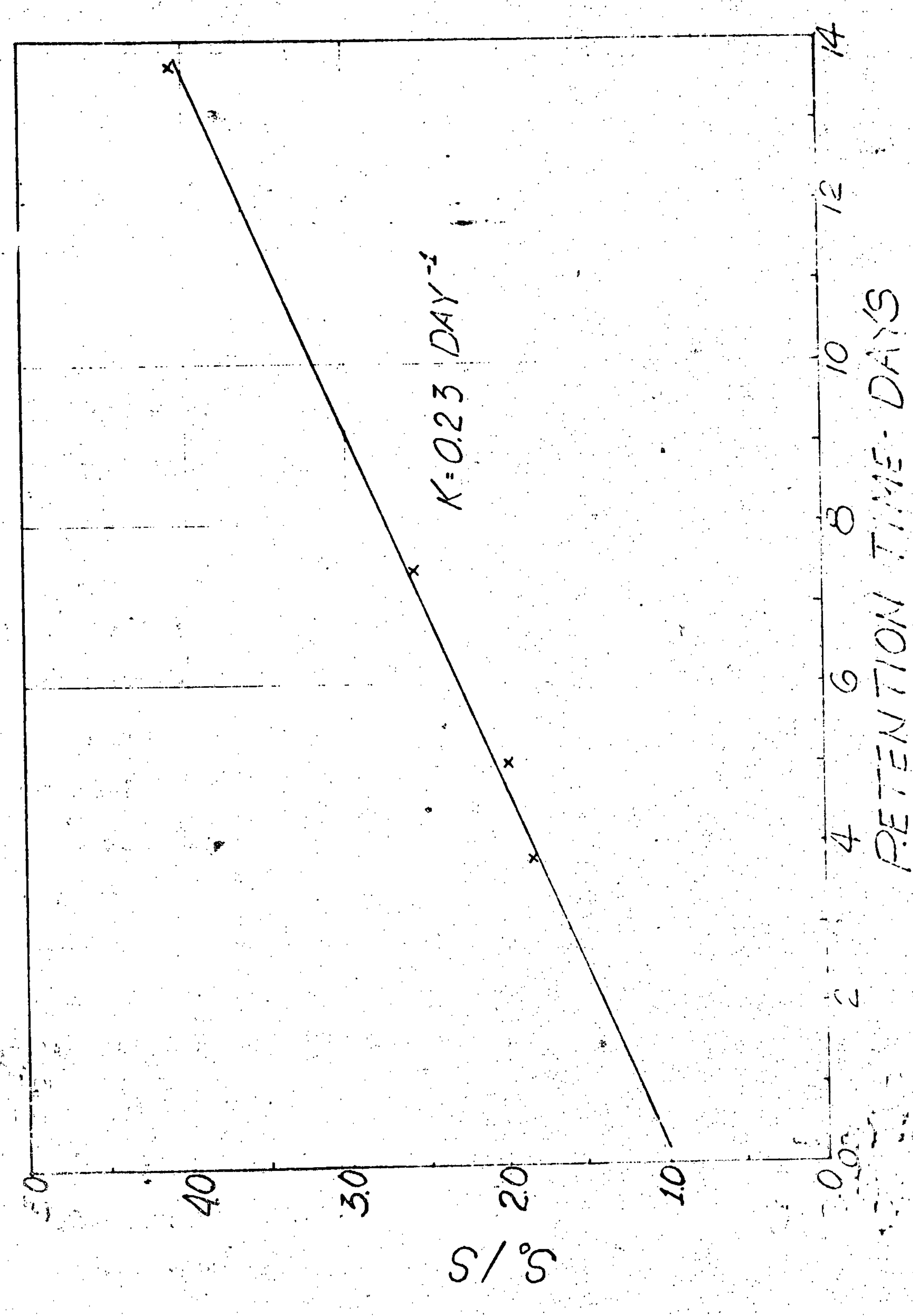

Figure 3. Determination of the Rate Constant for Straw Fermentation

Table 3. Fate of the Volatile Solids During Fermentation - Initial Weight = 100 kg

	S_o	S_{nb}*	S	Cells	Protein	S_{nb} + S
Corn Stover	40	60	11.4	2.9	2.0	71.4
Corn Stover (Pretreated)	77	23	22.0	5.5	3.8	45.0
Wheat Straw	53	47	15.9	3.7	2.6	62.9

*S_{nb} denotes the nonbiodegradable volatile solids

remain as residue. Mechanical dewatering processes can reduce the moisture content in this residue to about 70 percent. Therefore, for each ton of material harvested from the field (25 percent moisture), approximately 1.8 and 1.6 tons, respectively, of corn stover and straw residue would have to be adequately disposed.

This residue does not have any value as an animal feed. Using a cell growth ratio for the above system equal to 10 percent of the carbohydrate fermented, the cell yield can be calculated. The cell yield data have been extrapolated from Speece and McCarty (1964). The results are shown in Table 3. Clearly, the resulting protein production is low. The quality of the residue (dry solids) as an animal feed is shown in Table 4. For corn stover, 84 percent of the volatile solids in the residue are refractory, or unavailable in the rumen. At most, some 13 percent might be considered to be digestible. The protein content of this residue would be about 2.8 percent. This is hardly a quality feed.

The composition of the residual volatile solids from wheat straw is slightly better. The straw was more biodegradable than stover. Consequently, the proportion of refractory solids was less. Also, the protein content of the residue was calculated to be 4.1 percent.

Table 4. Composition of Residual Volatile Solids - % by Dry Weight

	Corn Stover		Wheat Straw	
	No Pretreat	Pretreat	No Pretreat	Pretreat
Nonfermentable Volatile Solids	84.0%	51.1%	74.7%	-
Fermentable Volatile Solids	13.2%	40.5%	21.2%	-
Protein	2.8%	8.4%	4.1%	-

A mild thermochemical pretreatment of the corn prior to fermentation substantially improved the conversion efficiency of the system. As shown in Table 3, only 45 percent of the volatile solids remained in the residue. The wet weight of the residue would be approximately 1.1 times the weight of the corn stover as harvested from the fields. The value of this residue as an animial feed is also improved. Only 51.1 percent of the residual volatile solids are refractory. About 40 percent of these residual solids are digestible carbohydrates. The protein content increases to 8.4 percent.

From this discussion, it is quite clear that pretreatment of both stover and straw is essential if this system is to have any chance to be economically feasible. Improvement of this pretreatment process can be expected to substantially increase the probability of success.

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