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BIOLOGICAL CONVERSION OF BIOMASS TO METHANE
FINAL REPORT

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DISCLAIMER

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ABSTRACT

An experimental methane fermentation system was constructed for the purpose of evaluating the processing requirements and conversion efficiencies associated with production of methane from various organic feed stocks. The fermentation reactors had an operating volume 0.775 m^3. This permitted operation with an approximate continuous feed of milled organics including beef feedlot manure, corn stover, wheat straw and alfalfa hay. A thermochemical pretreatment was applied to the corn stover and wheat straw in order to increase the biodegradability of these substrates. Working with these large units provided sufficient volumes of fermented slurry for evaluation of the dewatering properties of these slurries.

Kinetic data were obtained by operating four reactors at different retention times. These data were used to calculate a first order rate constant and the percent of substrate volatile solids that were biodegradable. These data were obtained on beef feed lot manure at 40°C and 60°C nominal fermentation temperatures. This manure was found to be highly variable in its characteristic. At 40°C, the estimated biodegradable solids ranged from 30.1 to 48.2 percent of the volatile feed solids. The first order rate constant was found to be 0.08 day^{-1} for this temperature. At the 60°C fermentation temperature, volatile feed solids biodegradability ranged from 33.1 to 78.3 percent. The value of the first order rate constant was found to be 0.25 day^{-1}.

Data from the fermentation of corn stover showed that the biodegradability of the stover volatile solids was only 36 percent at the thermophilic fermentation temperature. The first order rate constant was found to be 0.25 day^{-1}. Thermochemical pretreatment increased the biodegradability of stover volatile solids to 71 percent. Milled wheat straw that had been steam heated to 115°C was found to contain volatile solids that were 50 per cent biodegradable. The first order rate constant for the straw was 0.23 day^{-1}. It was not possible to obtain successful operation of the fermentors when thermochemically pretreated straw was used. The cause of this failure was not determined.

The final substrate tested was a green crop that was field dried, alfalfa. Significant foaming problems were encountered with this material. The volatile solids were found to be 74 percent biodegradable at a fermentation temperature of 60°C. The first order rate constant as determined from methane production was 0.27 day^{-1}. Because of the higher nitrogen content of this material, it would serve as an excellent source of supplemental nitrogen for the nitrogen deficient residues such as corn stover and wheat straw.

The cake produced by dewatering the fermented slurry with a centrifuge was relatively dry, 30 to 33 percent solids, for the manure and corn stovers. The solids capture without chemical addition was between 85 and 90 percent of the suspended solids. Wheat straw slurries did not yield as dry a cake. The percentage solids was in the range of 21 to 25 percent. Solids capture for the untreated straw was about 85 percent of the suspended solids. Thermochemical pretreatment reduced this figure to about 65 percent. Dewatering of the alfalfa slurry was rather inefficient, achieving cake solids of only 15 percent with a suspended solids capture of 57 percent.

Vacuum filtration of these slurries is possible under two conditions. If a low solids capture is permissible, then a course filter medium will yield a cake containing approximately 20 percent solids. A high solids capture can be obtained only by chemically conditioning the slurry prior

to filtration. Without this conditioning, the filter medium as well as the filter cake may blind before any volume of filtrate can be produced. A number of chemical conditioners was evaluated. Cationic organic polymers were generally effective. Ferric chloride, at massive dosage, was also effective.

The residual solids did not exhibit any characteristics that would make by-product recovery attractive. Manure slurries contained significant quantities of nitrogen, phosphorous and potassium. Recovery of plant nutrients by land application would be a possible end use for the slurry. The crude protein of the centrifuge cake obtained from this slurry ranged from 10 to 30 percent, depending upon the quality of the raw manure. The protein content of the residual solids from the corn stover and wheat straw would be expected to be less than 4 percent. Because nitrogen and phosphorous were added to the fermentation process for microbial nutrition, the quantity of these nutrients remaining will be a function of the amount added.

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INTRODUCTION

Recovery of energy from residual organic materials and from crops grown specifically for their energy content is part of the Fuels from Biomass Program. One of the processes for energy recovery is the methane fermentation system. In order to evaluate the methane yields from various organic materials a small pilot scale experimental system has been established. Construction of this facility was initiated in June of 1976, and it became operational in October 1976.

After the initial shakedown period, tests were conducted on the methane yields from beef feedlot manure. This initial substrate was selected to complement the work being conducted on other related projects. After completion of the manure studies, the substrate evaluated was corn stover collected from the University farms after the grain had been harvested. Following the corn stover studies, another residue, wheat straw was used as a substrate. The final substrate selected was alfalfa hay. This material was selected as representative of a green crop that is field dried for storage.

One objective of the proposed research is to provide data on the methane yield for various operating conditions. These data will provide the necessary base from which economic feasibility studies can be conducted. Since a major factor in the economic evaluation is the yield of methane per unit of material processed, these data are essential for the above studies. Additional objectives include the evaluation of the benefits of substrate pretreatment and the evaluation of potential systems for processing and disposing of the fermentor slurry.

DESCRIPTION OF EXPERIMENTAL SYSTEM

Continuous Fermentation System

This methane fermentation system is housed in the Department of Civil Engineering's Dynamic Testing Lab. This building is located on the south campus of the University of Illinois at Urbana-Champaign. A floor plan of this facility is shown in Figure 1. In addition to a large test bay in which the test reactors were housed, this facility contained adequate laboratory, office and related space for the research staff.

The fermentation reactors consisted of four completely mixed stainless steel reactors with a total volume of 235 gal (0.89 m^3) each. The operating level in each reactor was 205 gal (0.775 m^3). Heating was provided by circulating hot water from a water heater through external jackets on each tank. A temperature controller (TC) opened a solenoid valve (SV) to allow the hot water to circulate through the jacket when the temperature dropped below the set point. Figure 2 shows a schematic of one set of reactors. A second set operated in parallel.

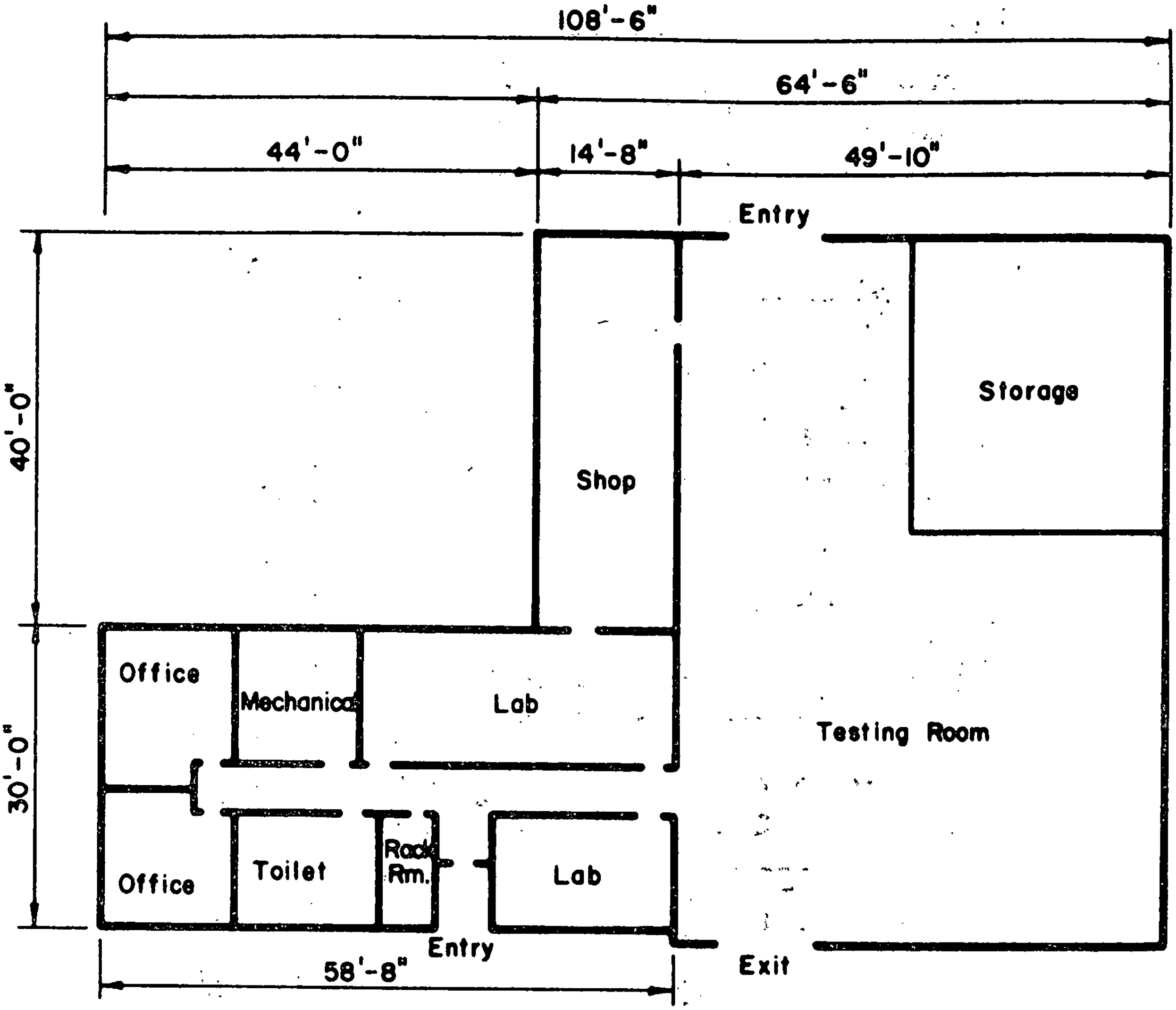
The reactors were initially equipped with variable speed turbine mixers. The mixing speed could be varied from 20 to 120 rpm. Recording watt meters measured the power consumption on each mixer. The mixing power input could be varied from 0.05 to 1.3 HP (0.1 kw to 1.0 kw). This is equivalent to mixing power input ranging from 0.25 to 6.3 HP per 1000 gal (0.04 to 1.3 kw per m^3) of slurry. Because of repeated failure of the variable speed drives, they were removed from the system in April 1977. The mixer speed was fixed at 75 rpm. The dimensions of the reactor and the associated mixer are shown in Figure 3.

The feed slurry was pumped into the fermenters with a progressing cavity pump (P1). This pump was connected to a time switch (TS) to allow for the approximation of a continuous feed system by pumping a percentage of each hour. Effluent from the reactors was pumped by a similar type pump (P2) that was actuated by a level controller (LC). The effluent was collected in a holding tank (T1) for additional processing. Gas from the reactors was passed through wet test gas meters (M) for determining gas flow rate. The gas was sampled for gas analysis with a Fisher Gas Partitioner.

Feed Preparation

The organic materials used in this process have to be prepared for feed into the system. The initial step was one of size reduction. This was accomplished by a "granulator" manufactured by H. C. Davis Sons, Inc. This unit was equipped with four screens, 3.2 mm, 6.3 mm, 19 mm, and 39 mm. The organic material could be milled to either of these four desired sizes. In order to effectively process this material it had to be relatively dry. This also assisted in storage of significant quantities of feed material. The dry material did not decompose.

After size reduction, a predetermined weight of the feed material was added to the slurry tanks (ST). The dry feed was slurried with the desired amount of water. Either recycled liquor or fresh water could be



Dynamic Test Laboratory Plan

Figure 1. Floor Plan of Building for Housing the Experimental System

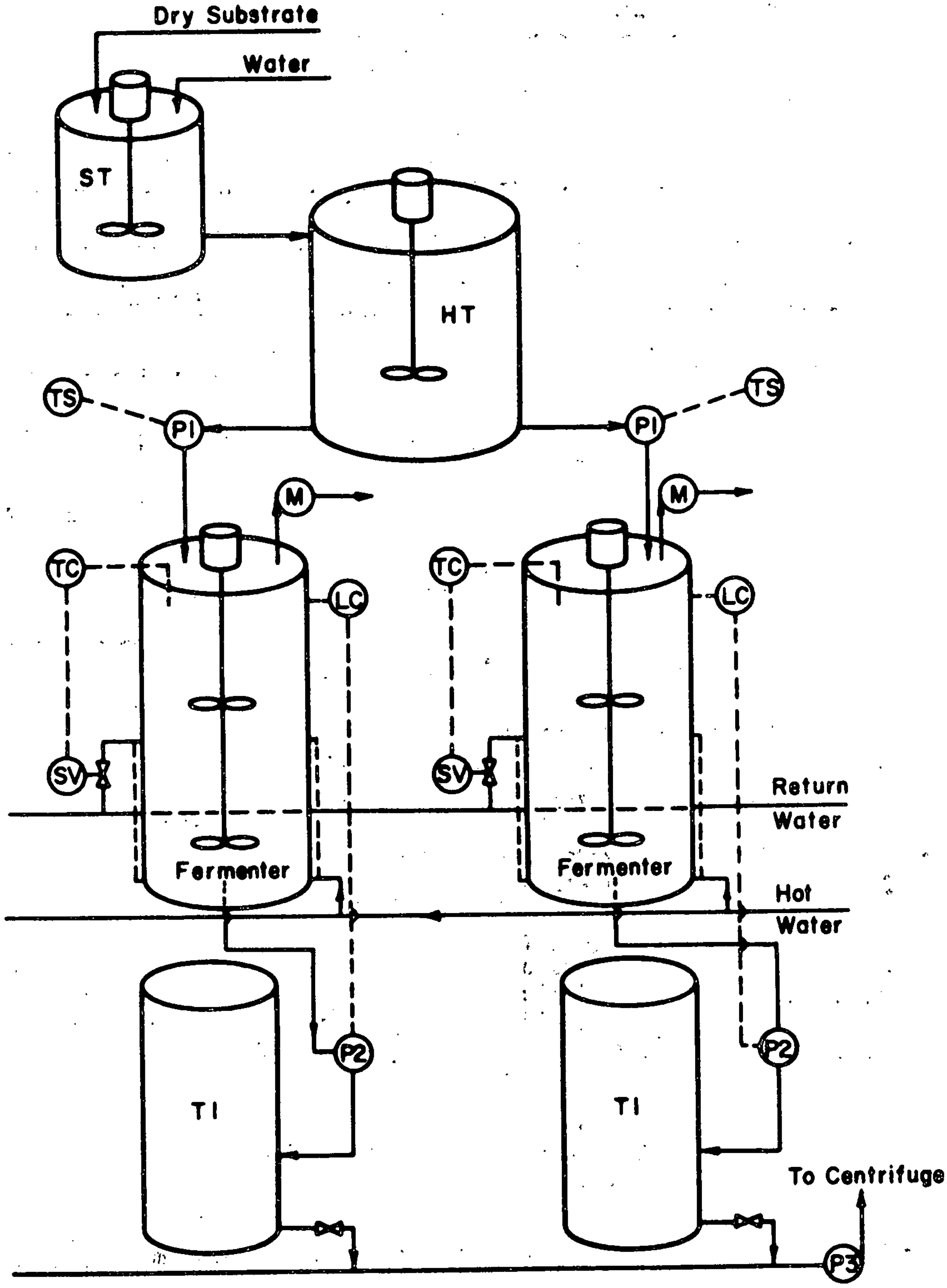


Figure 2. Schematic of One Set of Fermentors

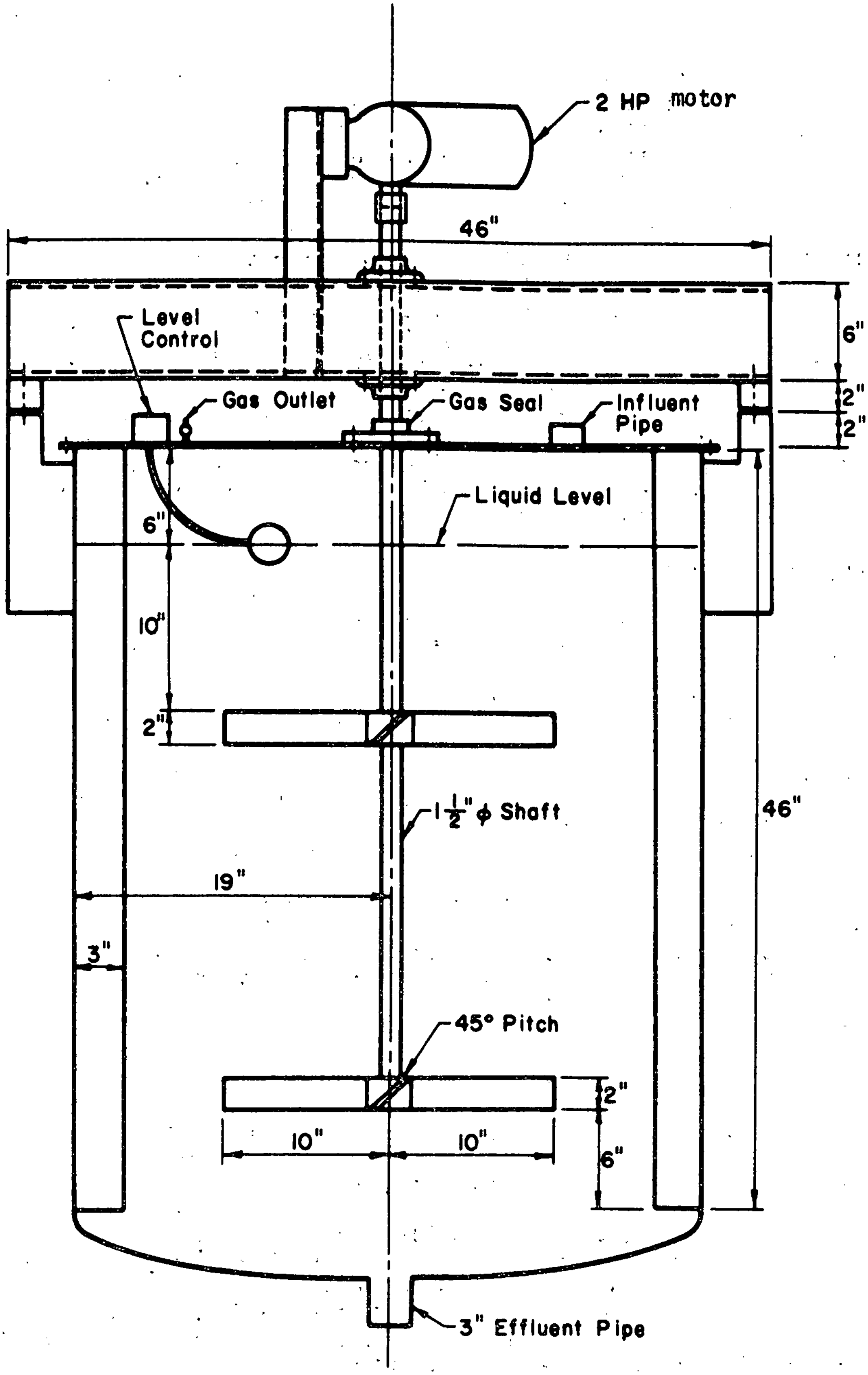


Figure 3. Details of Reactor and Mixer

used in the slurry tanks. After completely wetting the organic material, it was then discharged into mixed holding tanks (HT). This provided for storage of the slurry prior to pumping into the reactors. These mixed tanks also provided for a relative uniform feeding of material into the reactors since they contained approximately two days supply of feed slurry. These tanks were covered primarily for odor control.

The manure was relatively easy to slurry in the slurry tanks. It easily accepted the water and did not exhibit any resistance to wetting. Corn stover was more resistant to wetting and had to be mixed for an extended period in the slurry tanks in order to obtain a good slurry. In order to assist in preparing the slurry, the straw was soaked for 24 to 48 hours with a mix of one part dry stover and two parts water. This soaking greatly assisted in slurry preparation. Because of the uniqueness of the water absorption characteristics of the straw and alfalfa, presoaking did not significantly improve the wetting properties of these two substrates. It was necessary to steam the dry solids for 1 to 2 hours at 240°F (115°C). After this treatment, it was possible to effectively slurry the substrate and pump it through the system.

Fermenter Operation

The loading rate on the reactors was determined by the concentration of organic solids in the feed slurry and the volume of slurry pumped per unit time. The predetermined loading rates were set by controlling the feed slurry concentration and varying the pumping time.

The performance of the fermentation system was analyzed on the basis of gas production. This was augmented with analysis of the reactor contents for total and volatile total solids, pH, alkalinity, and volatile acids. These data provided the basis for calculating the conversion efficiencies and methane yields. Each reactor was on an independent temperature control system so that the fermentation temperature could be varied as desired.

There were only two feed slurry holding tanks so two reactors were fed from each tank. However, by varying the throughput, the loading rate and retention time of each reactor could be varied. This arrangement essentially allowed each reactor to operate independent of the others. Therefore, it was possible to evaluate four operating conditions at one time.

Residue Processing and Disposal

The effluent from the reactors was collected in an effluent storage tank (T1). These storage tanks were connected to a progressing cavity pump (P3) that fed the centrifuge. The resulting centrifuge cake was collected for either further processing or disposal by landfill. The centrate was discharged into a holding tank. When centrate recycle was employed this liquor was used to make up the feed slurry. Without recycle this material was allowed to flow to the drain.

Two centrifuges were used. One was a Fletcher Mark III. This was a solid bowl basket centrifuge. This unit had a variable speed drive so that it is possible to evaluate the effect of centrifugal force on solids capture and cake moisture. This unit was augmented with a horizontal solid bowl conveyor centrifuge (Sharples P-600) that could be operated continuously. Larger quantities of slurry could be processed with the continuous unit than with the basket unit.

Provisions were made for applying a thermochemical treatment process for either the residue or the feed material. A mixed reactor capable of withstanding an internal gage pressure of 1 atm was connected to a steam generator. By adding the fibers to this reactor along with an appropriate amount of caustic and water it was possible to heat treat this material prior to fermentation. This permitted evaluation of the effect of thermochemical treatment of the solids on the fermentation characteristics.

In addition to the dewatering by centrifugation, the effluent was available for additional tests. This slurry can be dewatered by vacuum filtration and filter leaf tests were available to evaluate the slurry filtration characteristics. Also, the quality of the effluent liquid and solids was evaluated with respect to its nutrient value both as a possible animal feed material or as a soil additive. These evaluations were made with laboratory analyses rather than having actual field tests.

Fermentor Feed Stock

The original proposal specified the application of the methane fermentation process to various crop residues and crops grown specifically for biomass production. The actual substrate to be tested was to be selected in consultation with the research sponsor. After discussion of the Fuels from Biomass Program's activities, it was decided that additional information was needed to complement the research on cattle feed lot manure fermentation. Therefore, manure from the College of Agriculture beef cattle feed lots was obtained for the initial substrate investigation.

The manure, which contained some small quantity of bedding, was scraped from the lots with a front end loader and hauled by truck to the laboratory. The moisture content of the manure varied, being dependent upon the temperature and precipitation. In general, the moisture content was too high to permit passage through the 0.25 in. (6.3 mm) screen on the mill. A fraction of the pile was spread on the floor to allow for some drying. This was passed through the mill without any screen simply to break up the lumps. This material was respread and additional drying allowed passage through the 0.25 in. (6.3 mm) screen. Figure 4 shows the particle size distribution obtained by this processing.

Because of the way in which manure was collected and handled, the large piles were relatively compact. The exposed surface dried quickly. Until the surface dried, there was some aerobic decomposition. However, the bulk of the pile was anaerobic. With the relatively dry nature of the manure and the high ammonia content, biological activity in the pile was limited. However, repeated handling of the manure did allow for stabilization to occur as will be discussed later.

After completion of the fermentation studies using manure as the substrate, a series of tests were designed to evaluate the gas yield from corn stover. Corn stover is the residue remaining in the fields after the grain has been harvested. Because the grain is shelled from the cob, stover contains the cob, stalk and leaves of the mature corn plant as well as a quantity of soil. Stover was collected from the corn fields adjacent to

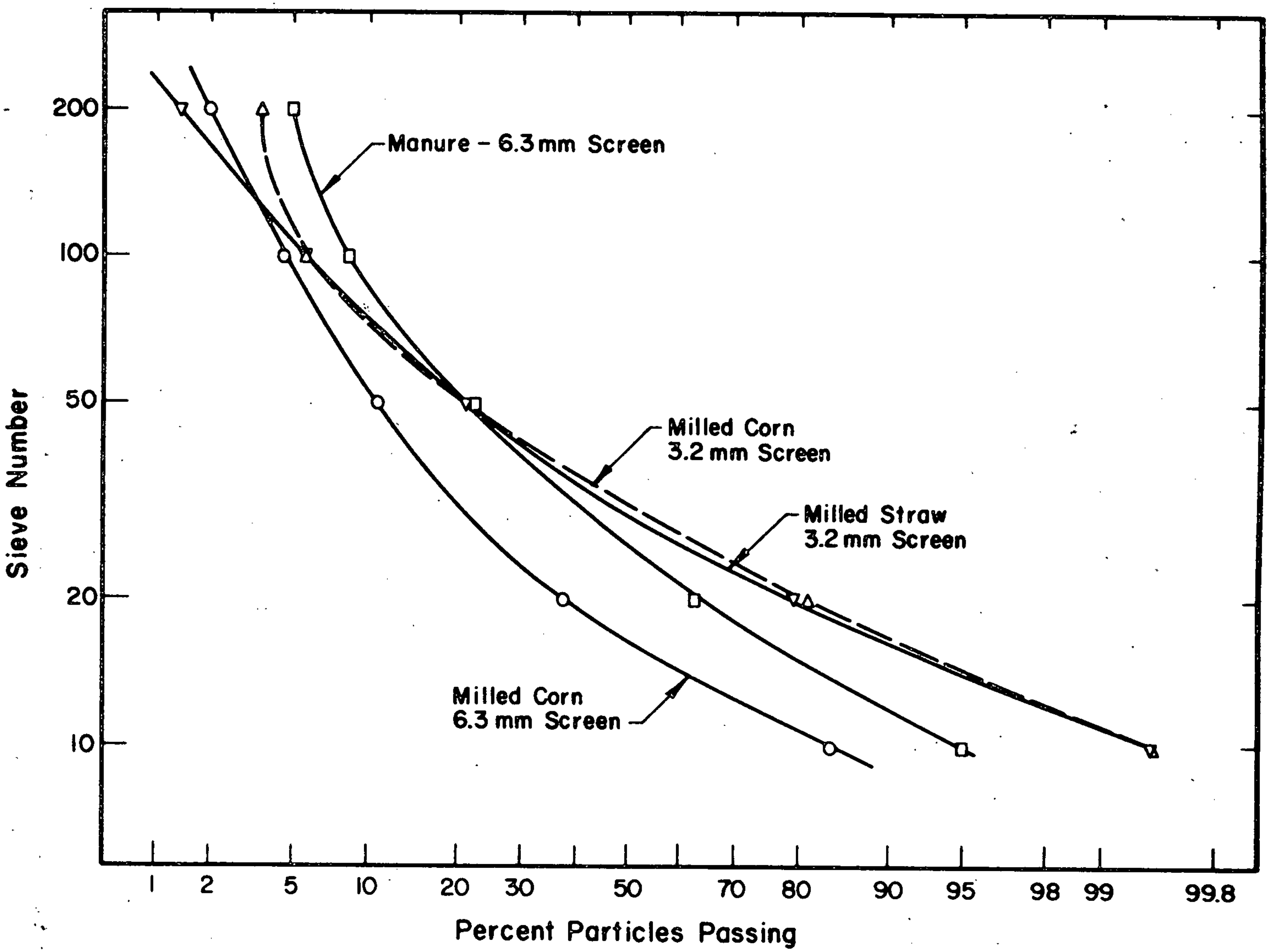


Figure 4.. Particle Size Distribution of Milled Substrates

the laboratory. The material was collected mechanically and consisted of the above ground plant material that had either been cut or broken from the stem during grain harvest. Several wagon loads of stover were collected and stored in a covered storage area. Since the stover was not chopped during harvest, the particle size of the collected stover was large, with corn stalks up to approximately 20 cm in length. Prior to feeding to the fermenters, the corn stover was milled so that it would pass through a 6.3 mm (0.25 in.) screen initially and at a later date through a 3.2 mm (0.125 in.) screen.

Figure 4 shows the particle size distribution of corn stover milled on both the 3.2 mm and the 5.3 mm screen. The manure milled on the 6.3 mm screen is included as a comparison. Less than 5 percent of these samples passed through the 200 mesh sieve. Milling of the corn stover actually resulted in particle size reduction as evidenced bv the significant difference in the particle size distribution for two different screen sizes. However, the manure clumps were simply broken apart in the mill and were not influenced significantly by the screen size in this small size range.

The third substrate investigated in this study consisted of wheat straw. Baled straw was obtained from a commercial supplier who had a 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 and was stored under cover until used. Since the straw was not chopped during harvest, it was necessary to mill it prior to slurry preparation. The straw was passed through the 3.2 mm (0.125 in.) screen in order to facilitate pumping of this material into the fermentation system. The resultant particle size is shown in Figure 4. As can be seen from these data, the milled straw exhibited essentially the same particle size distribution as did the corn stover. The stover did have a slightly higher percentage passing the 200 mesh screen. This may have resulted from a relatively high proportion of field dirt that was carried with the stover.

The final substrate investigated in this study was alfalfa. This material was used because of its availability and the manner in which it is harvested. The green crop is cut and field dried prior to harvest. Consequently, the digestibility of the plant is relatively good. The green alfalfa was selected in lieu of silage for two reasons. First, the timing was bad for obtaining silage in time to finish the work. Second, the processing system is not equipped with size reduction equipment that can mill wet fibers. The particle size of the silage was too large to permit processing through the system. Therefore, the alfalfa forage was selected as a substitute for the corn silage.

Beef manure contained adequate nitrogen and phosphorus for bacterial nutrition. Adequate natural alkalinity was found to maintain the fermentation pH well in excess of 7.0. Corn stover and straw were both found to be deficient in nitrogen and phosphorus. Natural alkalinity did not form in sufficient quantity to maintain the pH in excess of 6.6. Consequently, it was necessary to add nitrogen and phosphorus for nutrients as well as lime for pH control. Sufficient lime was added to maintain the pH in the 6.7 to 6.8 range. Nitrogen addition was based on the need to maintain an ammonia nitrogen content of 200 mg/l in the fermentation tanks. Phosphorus addition was equal to 20 percent of the nitrogen addition.

BEEF FEEDLOT MANURE FERMENTATION

Reactor Startup

Installation of the fermentation system was completed by October 15, 1976. The reactors were filled with tap water and allowed to reach the 58°C ± 2° operating temperature prior to October 22, 1976 (Day 76296). On this date, 0.115 m^3 of manure feed slurry at approximately 1.5 percent solids was added to Reactors 1 through 3. This quantity of feed was added daily. As can be seen in Table 1, the pH of all three units dropped below 6.0. The alkalinity of the reactor slurry was very low. On Day 76304, lime was added to the feed tanks to elevate the pH of the feed slurry to 8.5. The pH of the feed slurry was maintained at this level until the reactor pH increased to 6.6.

On Day 76306 (Nov. 1, 1976) the seal on Reactor 2 was damaged. The air leaking by this seal resulted in a low partial pressure of carbon dioxide which resulted in a higher pH in this unit. The seal on this unit was replaced and by Day 76316 the pH in all reactors was in an acceptable range. The alkalinity was approximately 900 mg/ℓ and the gas production was increasing. It appeared that a reasonable population of methane bacteria was established since the volatile acids measured less than 400 mg/ℓ in all units.

On Day 76315 the manure was increased to 45 kg per 0.2 m^3 of slurry resulting in an increase in the feed slurry solids concentration. The feed rate was set for 0.06 m^3 per day to produce a 13.3-day retention time. The actual feed volume varied between .06 to .08 m^3 resulting in a retention time between 9.7 and 13 days. Wigh an operating volume of 0.775 m^3, the initial solids loading was approximately 0.64 kg VS/m^3 day.

The reactors reached an apparent operating equilibrium in mid-November (Day 76320). Because of the variable nature of the feed slurry quantity and concentration, a true equilibrium was not established. It was not possible to obtain representative solids data on the reactor contents due to the difficulty in sampling. This was a continuing problem throughout the study. Several sampling techniques were tried, but none was totally satisfactory until the procedure instituted in May 1977.

The sampling technique used consisted of withdrawing approximately one liter of slurry directly from the reactor. This technique provided a representative sample of the reactor contents. However, it was still not possible to obtain a solids balance on the system. A check on the technique employed in sampling the feed slurry storage tank showed that the solids concentration measured at the bottom of the tank was as much as 20 to 30 percent greater than at the top of the tank. Because of the inability to obtain representative samples from the top of the tank, a sampling port was inserted at one-third the tank depth. Solids loading and gas production data have been adjusted to account for this sampling error.

The volatile solids loading and gas production during start-up are shown in Table 2. Gas leaks in Reactors 3 and 4 made it impossible

Table 1. Variations in pH, Alkalinity and Volatile Acids

	Reactor #1			Reactor #2			Reactor #3			Reactor #4		
Date	pH	Alk[1]	V.A.[2]	pH	Alk	V.A.	pH	Alk	V.A.	pH	Alk	V.A.
76 296	7.05	129	-	7.37	129	-	7.35	124	-	-	-	-
300	6.32	-	-	6.49	-	-	6.58	-	-	-	-	-
301	5.80	-	-	5.90	-	-	6.30	-	-	-	-	-
302	5.80	319	-	5.90	520	-	6.10	263	-	-	-	-
303	6.72	376	228	6.54	551	192	6.30	324	216	-	-	-
305	5.90	-	-	6.35	-	-	5.90	-	-	-	-	-
306	6.45	-	-	6.90	-	-	6.30	-	-	-	-	-
307	6.30	530	204	6.80	716	264	6.05	592	360	-	-	-
308	6.60	-	-	7.15	-	-	6.20	-	-	-	-	-
309	6.85	422	96	7.35	566	72	6.25	644	192	-	-	-
311	6.70	-	-	6.90	-	-	6.65	-	-	-	-	-
313	6.90	876	192	6.95	1063	288	6.85	891	204	-	-	-
314	6.92	-	-	6.97	-	-	6.79	-	-	-	-	-
316	6.86	1452	-	6.95	1401	-	6.82	1045	-	-	-	-
317	6.95	1421	-	-	-	-	6.90	1164	-	-	-	-
321	6.97	1700	288	6.89	1694	216	6.89	1617	216	-	-	-
323	7.05	2173	336	7.05	2070	240	7.00	2045	197	-	-	-
324	7.00	2070	-	6.95	2199	-	7.10	2366	-	6.95	1931	-
327	7.15	2938	120	7.20	2910	192	7.10	2706	168	7.20	2434	144
328	7.20	3182	-	7.10	3142	-	7.10	3006	-	6.95	2557	-
329	7.22	-	264	7.22	-	144	7.27	-	144	7.18	-	144
330	7.25	-	-	7.22	-	-	7.36	-	-	7.14	-	-
331	7.30	3903	-	7.30	3917	-	7.30	3495	-	7.30	3373	-
332	7.27	4053	120	7.23	4066	216	7.26	3563	216	7.20	3468	264
334	7.20	-	-	7.25	-	-	7.35	-	-	7.40	-	-
335	7.40	4855	-	7.20	4746	-	7.35	4720	-	7.32	4610	-
337	7.20	4869	-	7.25	4896	-	7.25	4461	-	7.25	4502	-
338	7.30	4836	120	7.25	4876	144	7.20	4243	192	7.25	4420	216
339	7.25	-	-	7.20	-	-	7.30	-	-	7.20	-	-

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[1] mg/l as $CaCO_3$

[2] mg/l as acetic acid

to obtain consistent gas readings. However, Reactors 1 and 2 were gas tight and the gas data show a significant conversion of organics to gas. For the period shown in Table 2, Reactors 1 and 2, respectively, produced 0.346 and 0.389 m^3 of gas per kg of volatile solids fed. One set of gas analyses showed that the gas from each reactor was 58 percent methane and 42 percent carbon dioxide.

Gas Production Rates

After the initial shakedown-period, the loading rate, temperature and retention time was specified for each reactor. In general, Reactor 1 served as a control. It was operated at 58°C, a nominal retention time of 9 days, a moderate solids loading.

This operational pattern was continued until Day 77268. All reactors were operated successfully until the end of December 1976. The manure obtained prior to this time was completely free of bedding. During wet periods, some bedding was added to the pens to reduce the effect of the wet conditions on the animals in each pen. An unusually dry fall accounted for the total absence of bedding in the manure obtained during this period. Since it was unnecessary to reduce the particle size of the manure, a mill was not initially purchased.

When additional manure was obtained in November 1976, it contained a small quantity of straw. It was necessary to chop this manure before it could be used. A mill was ordered, but it did not arrive until mid January 1977. During the interim, frozen dairy manure was used as feedstock. Starting on Day 76348, this was the feed for all four reactors. This manure was exhausted by the beginning of January 1977. At this time feed was discontinued in all units. Extreme weather conditions delayed installation of the mill until the first week of February 1977 (77035). At this time the reactors were restarted and were in equilibrium by 77060.

After about five weeks of operation, severe problems developed with the slurry withdrawal system. Due to the nature of the slurry, it was not possible to obtain gravity flow from the reactors. As soon as flow stopped, the effluent pipe clogged completely. Semi-continuous feeding was impossible. It was necessary to install effluent pumps on the reactors to remove the slurry. Also during this period, excessive foaming developed in the higher loaded reactors. This was a result of the batch feeding necessary since the slurry would not drain from the reactors by gravity. The effluent pumps were installed during this shut down period and the reactors restarted, reaching equilibrium conditions by Day 77140.

Operation was reasonably successful for the balance of the test period. A frequent problem was encountered with grit in the pumps and pipes. When the manure was scraped from the lot, crushed limestone was also picked up with the manure. When passed through the mill, the majority of this rock was broken into small particles that were not effectively removed in the slurry tank. On occassion, the quantity of grit was sufficient to plug the feed lines. This disrupted the feeding schedule and resulted in fluctuations in the data.

In order to reduce the fluctuations in the data, gas composition and gas production data are presented as the average of seven days.

Table 2. Gas Production Rates
(Nov. 16 through Dec. 3, 1976)

	Reactor #1			Reactor #2			Reactor #3			Reactor #4		
	kg VS	Gas Prod.		kg VS	Gas Prod.		kg VS	Gas Prod.		kg VS	Gas Prod.	
Date	day	ℓ/d	m^3/kg VS	day	ℓ/d	m^3/kg VS	day	ℓ/d	m^3/kg VS	day	ℓ/d	m^3/kg VS
76321	-	-	-	-	-	-	-	-	-	-	-	-
322	1.52	515	0.339	1.14	665	0.583	2.06	480	-	-	-	-
323	1.36	462	0.339	1.70	780	0.459	1.82	*	-	-	10[1]	-
324	1.82	775	0.426	1.21	747	0.617	3.90	*	-	-	193	-
325	1.29	938	0.727	1.14	676	0.593	1.82	*	-	1.82	482	0.265
326	1.29	516	0.400	0.83	431	0.519	0	*	-	0	390	-
327	0.99	587	0.592	1.44	621	0.431	2.42	*	-	2.42	501	0.207
328	3.00	1001	0.334	3.00	1138	0.379	2.06	*	-	1.82	559	0.307
329	4.94	1195	0.242	6.52	1836	0.282	2.26	*	-	2.11	622	0.314
330	3.50	881	0.252	3.18	1094	0.344	2.86	730		2.56	713	0.279
331	2.57	713	0.277	2.28	898	0.394	1.63	*	-	3.25	653	0.201
332	2.85	936	0.328	2.85	1066	0.374	2.00	730		1.88	662	0.352
333	3.26	926	0.284	3.26	1082	0.332	2.07	*	-	2.00	542	0.271
334	3.45	1121	0.325	3.45	994	0.288	2.40	*	-	2.27	590	0.260
335	3.05	497	0.163	4.27	998	0.234	2.00	*	-	2.13	621	0.292
336	2.41	620	0.257	3.00	597	0.199	2.56	*	-	2.94	*	-
337	0	739	-	0	1063	-	0	*	-	0	*	-
338	4.76	797	0.167	6.00	1190	0.198	2.76	*	-	2.76	873	0.316

*Gas leak due to mixer seal problems.

[1] Started operation of #4.

The data collected on a daily basis was entered into a data storage program. This program was used to calculate the loading rates and gas production rates. The gas volume is measured at room temperature and atmospheric pressure. Corrections to standard conditions have not been applied.

The gas production data, loading rates and retention time data for Reactor 1 are given in Table 3. This reactor operated at 58 ± 2°C throughout the test period. This reactor initially had a moderate loading rate of 3 to 4 kg of volatile solids per m^3 per day (0.19 to 0.25 lb/cu ft day). This rate was doubled about halfway through the test period.

The average gas production data for 7 day periods was relatively consistant for a given manure. There was significant variation in the gas production resulting from variations in manure characteristics. For example, the addition of the frozen fresh dairy manure on Day 76248 resulted in a two fold increase in gas production over the previous manure. When fresh manure was fed on Day 77156, gas production again increased substantially. However, there was a steady decrease in gas production during the following weeks. By the time a new batch of manure was obtained on Day 77190, the gas production decreased from approximately 0.4 m^3/kg V.S. fed to about 0.22 m^3/kg V.S. fed. The same pattern was exhibited when fresh manure was fed on Day 77197.

This reduction in gas yield is closely correlated with the quality of the manure. The manure was exposed to aerobic stabilization while on the feed lot. Precipitation not only accelerates the biological activity, but also can result in the leaching of organics from the manure. In addition, the handling, storage and preparation of the manure prior to adding to the fermentation system resulted in a loss of biodegradable organics.

The range of operating parameters for Reactor 1 for each week is given in Table 4. The pH was always greater than 7.0. The total volatile acids were generally less than 500 mg/ℓ as acetic acid. The only exception was during the period of Day 76246 to about Day 76274. Prior to this period, the pH was 7.9 to 8.1 with alkalinities of approximately 5.0 g/ℓ. The volatile acids reach a high of 1,670 mg/ℓ.

The initial methane composition was set at 60 percent. The gas chromatograph did not become operational until the week ending with Day 77162. Prior to that date, one set of gas analysis was conducted on the gas from each reactor. This analysis showed that the gas from each reactor contained 58 percent methane and 42 percent carbon dioxide. The values of 60 percent given in Table 3 are simply so the computer program had a number to use when calculating the methane production.

In order to evaluate the effect, if any, of a mild thermochemical treatment step on increased gas yield, a series of tests employing both dewatered fermentor residue and raw manure was undertaken. On Day 77268, the feed to Reactor 1 was the dewatered residual solids. With a retention time of 5 days, gas production dropped to very low levels. On Day 77289, raw manure was again used in the feed for Reactor 1. There was a significant increase in gas production. During the week ending with Day 77316, the manure supply was exhausted. Reactor 1 did not receive any feed for 5 days. An additional load of manure was obtained in order to collect some additional data on the thermochemical pretreatment.

Table 3. Average Weekly Gas Production Data - Reactor 1

Week Ending	Θ Days	Gas LPH	CH_4 %	Gas Production m^3/kg V.S. Fed	Loading Kg V.S./m^3-Day
76326	11.5	21.6	(60)	0.387	1.73
333	10.8	28.6	(60)	0.191	4.63
340	12.0	30.3	(60)	0.281	3.34
347	7.8	33.8	(60)	0.220	4.76
354	8.0	65.9	(60)	0.450	4.53
361	7.3	59.2	(60)	0.419	4.37
77066	9.3	41.5	(60)	0.327	3.94
073	11.6	32.2	(60)	0.312	3.20
080	9.9	(19.9)	(60)	-	3.51
087	9.4	29.4	(60)	0.268	3.39
094	9.4	27.6	(60)	0.261	3.28
148	9.3	20.9	(60)	0.204	3.17
155	9.2	22.2	(60)	0.223	3.08
162	9.3	42.8	60.1	0.411	3.23
169	9.4	53.7	65.4	0.398	4.18
176	9.2	53.4	62.0	0.400	4.13
183	8.6	53.8	62.0	0.247	4.75
190	9.1	36.8	61.3	0.216	6.25
197	9.3	56.4	62.7	0.289	5.05
204	9.3	55.8	62.2	0.270	6.40
211	9.2	50.9	61.2	2.256	6.15
218	10.9	48.2	56.9	0.240	6.21
225	9.1	43.1	61.1	0.214	6.25
232	8.9	47.9	66.1	0.206	7.19
239	8.8	49.9	63.8	0.213	7.26
246	8.7	37.3	63.0	0.171	6.74
253	8.8	(14.1)	56.9	-	5.43
260	8.8	(13.3)	53.1	-	5.08
267	5.0	34.8	63.7	0.196	5.50
274[1]	4.6	21.6	61.4	0.092	7.26
281	4.7	12.8	63.5	0.031	6.36
288	4.6	7.6	66.0	0.061	7.48
295[2]	7.9	11.4	61.4	0.084	4.19
302	7.5	16.9	59.7	0.095	5.48
309	7.3	19.1	55.8	0.102	5.81
316	(7.0)	22.8	54.2	0.119	5.95
323	8.4	26.7	50.6	0.198	4.18
330	7.5	59.5	51.7	0.231	7.96

[1] Start feed of digested residue

[2] Start feed of raw manure

Table 4. Operating Parameters - Reactor 1

Week Ending	θ Days	pH Range	Alkalinity Range - g/l	Volatile Acid - g/l
76326	11.5	7.0-7.1	1.7-2.2	0.29-0.34
333	10.8	7.2-7.3	2.9-4.1	0.12-0.26
340	12.0	7.2-7.4	4.8-4.9	0.12
349	7.8	7.2-7.3	5.4-5.8	0.17-0.29
354	8.0	7.2-7.3	6.5-7.0	0.29
361	7.3	7.2-7.3	6.8	0.14
77066	9.3	7.1-7.4	4.7-5.2	0.17-0.31
073	11.6	7.3-7.4	7.1-5.8	0.19-0.22
080	9.9	7.1-7.3	4.0-4.7	0.22-0.67
087	9.4	7.2-7.4	3.9-4.3	0.29-0.38
094	9.4	7.3-7.4	4.0-4.1	0.34=0.60
148	9.3	7.1-7.2	2.2-2.5	0.14-0.22
155	9.2	7.2-7.3	2.3-2.5	0.07-0.17
162	9.3	7.0-7.3	2.3-3.0	0.29-0.53
169	9.4	7.0-7.5	3.0-3.7	0.17-0.62
176	9.2	7.5-7.7	3.6-4.5	0.17-0.41
183	8.6	7.3-7.7	4.3-4.6	0.24-0.50
190	9.1	7.6-7.7	4.2-5.0	0.14-0.29
197	9.3	7.6-7.7	4.3-5.0	0.14-0.53
204	9.3	7.6-7.8	4.4-5.0	0.26-0.29
211	9.2	7.6-7.7	4.6-5.5	0.17-0.26
218	10.9	7.5-7.9	4.5-4.8	0.24-0.53
225	9.1	7.5-7.9	4.8-5.1	0.17-0.53
232	8.0	7.9-8.0	4.4-5.3	0.10-0.38
239	8.8	7.9-8.1	4.4-4.8	0.05-0.29
246	8.7	7.9-8.1	4.6-5.2	0.07-0.31
253	8.8	7.5-7.9	3.7-4.3	0.36-1.34
260	8.8	7.4-7.6	3.3-4.0	0.36-1.05
267	5.0	7.2-7.5	2.6-2.8	0.22-1.33
274	4.6	7.2-7.5	2.2-2.7	0.22-1.67
281	4.7	7.2-7.6	1.3-1.9	0.02-0.10
288	4.7	7.2-7.3	1.2-1.4	0.05-0.12
295	4.9	7.2-7.3	1.5-2.1	0.02-0.10
302	7.5	7.2-7.4	2.3-3.2	0.05-0.12
309	7.3	7.4-7.6	3.0-3.4	0.05-0.12
316	7.0	7.4-7.5	3.0-3.1	0.05-0.10
323	8.4	7.4-7.5	2.7-3.0	0.07-0.14
330	7.5	7.4-7.4	2.9-3.4	0.12-0.48

The summary of the gas production data and loading rates for Reactor 2 is given in Table 5. The operating parameters are shown in Table 6. This reactor was subjected to various loading rates and retention times. The same manure used for Reactor 1 was also fed to Reactor 2. This reactor responded normally even at retention times as low as 3.0 days and loadings 16.65 kg V.S./m^3-day (1.0 lb/ft^3-day). This high loading rate was not maintained due to temperature control problems during the period from Day 77184 to 77190. The temperature dropped to 50°C two days in succession. As shown in Table 6, the volatile acids increased to greater than 4000 mg/ℓ with the pH decreasing to 6.5. During this period, excessive foaming was experienced. The foam filled the gas handling system, voiding any gas readings obtained.

A reduction in loading during the week ending with Day 77197 did not result in system recovery. The volatile acids increased to 7.26 g/ℓ and the pH decreased to 6.2. At the end of this week, the temperature control malfunctioned again. The temperature in Reactor 2 reached 71°C and the gas production dropped to 0ℓ/hr. The reactor was reseeded with effluent from Reactor 3 and brought back on line.

This reactor continued to operate at the thermophilic temperature until Day 77219 when the temperature was reduced to 40°C. Data were collected on mesophilic digestion until Day 77261. The temperature was increased to 58°C and dewatered fermented residue that was thermochemically treated was the feed. This residue was mixed with 3 g of lime per 100 g dry solids and heated to 110°C for two hours. The gas production decreased to exceptionally low levels. On Day 77289, raw manure was subjected to this pretreatment and used as feed for Reactor 2.

The gas production data and loading rates for Reactor 3 are given in Table 8. Reactor 3 received the same manure as Reactor 1 except during the thermochemical treatment tests when raw manure was fed to Reactor 3.

This reactor responded normally until an attempt was made to apply a high loading rate. On Day 77177, the feed solids concentration was increased to 10 percent. With an initial retention time of 6 to 7 days, the volatile acids increased to almost 6.0 g/ℓ. Excessive foaming developed and the gas handling equipment was frequently filled with foam. During the week ending on Day 77204, the foaming was so intense that it was not possible to obtain any gas readings. Because of this problem with foam, the feed solids concentration was reduced to 5 percent and the loading reduced. On Day 77219 the temperature was reduced to 40°C for the balance of the study.

The system functioned normally during this period. A gas leak developed during the week ending with Day 77267, resulting in excessively low gas production rates for this week.

The gas production data and loading rates for Reactor 4 are given in Table 9. The operating parameters for this reactor are given in Table 10. Reactor 4 was subjected to the same feed slurry as Reactor 3. Gas leaks were encountered during the period from 77177 to 77190. The gas production data are in error. This reactor responded reasonably well to high loadings of 20 kg V.S./m^3-day (1.25 lb/ft^3-day). Gas production was good. The pH and volatile acids were within acceptable ranges. On Day 77219, the temperature was reduced to 40°C for the balance of the study.

Gas production data from Day 77240 to 274 were in error due to gas leaks. The source of the leak could not be found for several weeks. It was finally corrected by adjusting the mixer seal.

Table 5. Average Weekly Gas Production Data - Reactor 2

Week Ending	Θ Days	Gas LPH	CH_4 %	Gas Production m^3/kg V.S. Fed	Loading Kg V.S./m^3-Day
76326	12.7	16.0	(60)	0.312	1.59
333	11.3	23.1	(60)	0.195	3.68
340	10.2	23.4	(60)	0.198	3.66
347	7.9	32.7	(60)	0.213	4.76
354	8.3	55.2	(60)	0.366	4.67
361	7.7	59.1	(60)	0.404	4.53
77002	8.8	71.1	(60)	0.511	4.31
066	7.0	43.3	(60)	0.271	4.95
073	6.2	40.1	(60)	0.261	4.76
080	6.9	39.7	(60)	0.239	5.15
087	6.3	32.0	(60)	0.226	5.07
094	6.0	29.6	(60)	0.188	4.88
148	3.7	30.9	(60)	0.120	7.94
155	3.7	35.5	(60)	0.145	7.59
162	3.8	73.4	61.4	0.287	7.91
169	3.8	98.2	63.3	0.293	10.36
176	3.7	98.8	60.8	0.302	10.14
183	3.0	109.0	62.0	0.203	16.65
190	3.8	(59.5)	55.0	-	16.74
197	7.4	(17.9)	53.1	-	5.06
204	11.1	54.8	61.3	0.295	5.75
211	8.9	47.3	60.0	0.254	5.77
218	9.2	43.1	60.2	0.218	6.13
225	7.6	41.5	60.7	0.153	8.41
232	5.0	36.8	62.4	0.096	11.85
239	8.7	29.2	62.2	0.153	5.90
246	4.9	37.5	61.2	0.102	11.42
253	4.7	28.5	64.7	0.087	10.12
260	4.5	37.3	62.5	0.108	10.70
267	5.6	-	59.2	-	8.04
274[1]	4.7	16.4	70.3	0.074	6.86
281	4.9	4.1	77.4	0.023	5.55
288	4.6	3.9	84.6	0.020	6.19
295[2]	12.2	15.8	78.9	0.083	5.88
302	7.5	23.0	61.8	0.112	6.62
309	6.9	35.2	56.9	0.144	7.59
316	(7.5)	32.1	55.2	0.166	3.60
323	10.5	22.8	52.6	0.185	3.82
330	7.6	58.0	53.0	0.244	7.36

[1] Start feed of digested residue - caustic pretreatment

[2] Start feed of raw manure - caustic pretreatment

Table 6 Operating Parameters - Reactor 2

Week Ending	Θ Days	pH Range	Alkalinity Range - g/l	Volatile Acid Range - g/l
76326	12.7	6.9-7.1	1.7 - 2.2	0.22 - 0.24
333	11.3	7.1-7.3	2.9 - 4.1	0.14 - 0.22
340	10.2	7.2-7.3	4.7 0 4.9	0.14
347	7.9	7.2-7.3	5.4 - 6.5	0.12
354	8.3	7.2-7.3	5.9 - 6.2	0.31
361	7.7	7.2-7.5	5.1 - 6.5	0.14
77002	8.8	7.3-7.4	6.4 - 6.5	0.12
066	7.0	7.1-7.3	4.8 - 5.3	0.34 - 0.50
073	6.2	7.1-7.4	3.9 - 5.4	0.17 - 0.55
080	6.9	7.1-7.2	4.0 - 4.5	0.17 - 0.50
087	6.3	7.2-7.3	3.8 - 4.2	0.29 - 0.70
094	6.0	7.2-7.3	3.6	0.86
148	3.7	7.0-7.1	2.1 - 2.3	0.14 - 0.22
155	3.7	7.1-7.2	2.2 - 2.5	0.07 - 0.19
162	3.8	6.8-7.2	2.4 - 3.0	0.50 - 1.08
169	3.8	6.9-7.5	3.0 - 3.7	0.38 - 1.32
176	3.7	7.4-7.7	3.8 - 5.1	0.31 - 1.15
183	3.0	7.2-7.7	4.1 - 4.4	0.22 - 1.32
190	3.8	6.5-7.7	3.1 - 3.8	0.89 - 4.03
197	7.4	6.2-6.5	3.0 - 3.4	1.86 - 7.26
204	11.1	7.5-7.8	4.3 - 4.9	0.30 - 1.56
211	8.9	7.6-7.8	4.8 - 5.5	0.19 - 0.46
218	9.2	7.5-7.8	4.4 - 4.7	0.26 - 0.78
225	7.6	7.4-8.0	4.1 - 4.6	0.34 - 1.15
232	5.0	7.6-7.8	4.5 - 4.8	0.48 - 1.26
246	8.7	7.3-7.7	3.8 - 4.1	0.96 - 1.32
253	4.9	7.2-7.2	3.5 - 4.5	0.22 - 0.54
260	4.7	7.4-7.6	2.9 - 3.1	0.07 - 0.34
267	4.5	7.4-7.7	2.5 - 3.0	0.22 - 0.48
274	5.6	7.7-7.9	1.8 - 2.1	0.02 - 0.22
281	4.7	7.5-7.9	1.6 - 1.9	0.05 - 0.07
288	4.9	7.5-7.9	1.7 - 2.0	0.02 - 0.14
295	12.2	7.5-7.8	1.8 - 3.2	0.05 - 0.22
302	7.5	7.5-7.7	4.0 - 4.2	0.12 - 0.38
309	6.9	7.5-7.7	3.7 - 5.0	0.10 - 0.34
316	7.5	7.5-7.6	3.8 - 4.4	0.05 - 0.34
323	10.5	7.4-7.6	3.7 - 4.3	0.26 - 0.74
330	7.6	7.4-7.5	3.9 4.1	---

Table 7 Average Weekly Gas Production Data - Reactor 3

Week Ending	Θ Days	Gas LPH	CH_4 %	Gas Production m^3/kg V.S. Fed	Loading kg V.S./m^3-Day
76326	12.7	----	(60)	----	2.55
333	12.7	----	(60)	----	2.55
340	12.6	----	(60)	----	2.79
347	7.7	32.6	(60)	0.232	4.35
354	8.5	50.9	(60)	0.385	4.09
361	7.8	61.1	(60)	0.443	4.27
77002	9.3	48.0	(60)	0.346	4.30
066	7.0	47.6	(60)	0.291	5.06
073	6.3	41.2	(60)	0.254	5.02
080	6.1	48.3	(60)	0.307	4.86
087	6.1	31.5	(60)	0.192	5.07
148	4.6	28.5	(60)	0.133	6.62
155	4.7	31.8	(60)	0.165	5.97
162	4.7	60.9	62.9	0.311	6.06
169	4.7	81.0	64.7	0.316	7.94
176	4.7	93.6	63.9	0.357	8.06
183	6.5	70.5	55.0	0.161	13.5
190	7.5	63.1	58.9	0.162	12.1
197	4.9	99.3	61.9	0.163	18.8
204	4.9	----	59.2	----	19.3
211	5.9	71.6	55.6	0.150	14.8
218	6.1	80.2	55.7	0.169	14.7
225	9.0	62.1	60.4	0.223	8.6
232	9.4	35.0	63.2	0.166	6 52
239	8.9	37.0	62.2	0.170	5.72
246	8.8	42.6	64.0	0.172	7.63
253	9.2	48.4	64.0	0.178	8.36
260	9.3	57.3	54.1	0.251	7.08
267	9.3	(14.6)	68.7	----	4.62
274	9.7	22.6	67.3	0.166	4.19
281	9.3	20.9	57.1	0.158	4.12
288	9.3	16.1	62.8	0.110	4.68
295	9.0	17.3	59.3	0.116	4.61
302	13.1	13.9	57.1	0.135	3.16
309	14.3	10.9	56.3	0.137	2.48
316	14.2	12.0	53.0	0.143	2.57

Table 8 Operating Parameters - Reactor 3

Week Ending	Θ Days	pH Range	Alkalinity Range- g/l	Volatile Acid Range - g/l
76326	12.7	6.9 - 7.1	1.6 - 2.4	0.20 - 0.22
333	12.7	7.1 - 7.4	2.7 - 3.6	0.14 - 0.22
340	12.6	7.2 - 7.4	4.3 - 4.5	0.19
347	7.7	7.2 - 7.4	5.0 - 5.2	0.14 - 0.22
354	8.5	7.2 - 7.5	5.8 - 6.0	0.38
361	7.8	7.2 - 7.5	5.8 - 6.3	0.14
77002	9.3	7.1 - 7.4	5.7 - 5.8	0.29
066	7.0	7.1 - 7.4	5.1 - 5.9	0.17 - 0.26
073	6.3	7.2 - 7.4	4.2 - 5.1	0.24 - 0.53
080	6.1	7.1 - 7.2	3.9 - 4.0	0.31 - 0.38
087	6.1	7.3 - 7.4	3.6 - 3.8	0.32 - 0.46
148	4.6	7.1 - 7.2	2.0 - 2.7	0.17 - 0.22
155	4.7	7.2 - 7.3	2.0 - 2.3	0.17 - 0.26
162	4.7	6.8 - 7.3	2.4 - 2.8	0.17 - 0.91
169	4.7	7.1 - 7.6	3.0 - 4.0	0.29 - 0.77
176	4.7	7.6 - 7.8	4.1 - 4.7	0.31 - 1.01
183	6.5	7.3 - 7.9	4.8 - 5.4	0.53 - 5.94
190	7.5	7.6 - 7.9	6.3 = 6.9	0.66 - 3.90
197	4.9	7.6 - 7.8	6.3 - 6.9	2.40 - 2.76
204	4.9	7.7 - 7.9	6.8 - 7.9	0.78 - 1.98
211	5.9	7.7 - 7.9	6.5 - 9.1	0.72 - 3.36
218	6.1	7.5 - 8.0	6.7 - 7.1	0.60 - 1.68
225	9.0	7.8 - 7.9	6.9 - 7.0	0.12 - 0.67
232	9.4	7.6 - 7.8	5.2 - 6.1	0.89 - 1.32
239	8.9	7.4 - 7.6	4.3 - 5.2	1.62 - 3.65
246	8.8	7.6 - 7.8	4.3 - 4.9	0.34 - 1.32
253	9.2	7.7 - 7.8	4.2 - 5.2	0.10 - 0.26
260	9.3	7.3 - 7.6	3.5 - 4.4	0.05 - 0.19
267	9.3	7.4 - 7.5	3.3 - 4.0	0.24 - 0.41
274	9.7	7.4 - 7.5	3.1 - 3.3	0.05 - 0.22
281	9.3	7.3 - 7.6	3.3 - 3.5	0.05 - 0.26
288	9.3	7.4 - 7.5	3.2 - 3.6	0.05 - 0.12
295	9.0	7.2 - 7.3	3.3 - 3.5	0.07 - 0.12
302	13.1	7.2 - 7.3	2.7 - 2.9	0.05 - 0.12
309	14.3	7.2 - 7.3	2.7 - 2.9	0.05 = 0.16
316	14.2	7.0 - 7.3	2.4 - 2.8	0.02 - 0.07

Table 9 Average Weekly Gas Production Data - Reactor 4

Week Ending	Θ Days	Gas LPH	CH_4 %	Gas Production m^3/kg V.S. Fed	Loading kg V.S./m^3-Day
76333	12.1	39.2	(60)	0.384	3.16
340	12.2	23.4	(60)	0.246	2.94
347	7.6	35.2	(60)	0.251	4.35
354	7.9	49.8	(60)	0.346	4.45
361	6.9	60.2	(60)	0.348	5.35
77002	8.5	70.7	(60)	0.471	4.65
006	6.8	41.8	(60)	0.253	5.10
073	---	----	(60)	-----	----
148	6.3	27.5	(60)	0.175	4.88
155	6.2	27.2	(60)	0.185	4.55
162	6.2	55.4	60.4	0.368	4.66
169	6.2	74.6	56.6	0.386	5.99
176	6.2	78.0	62.7	0.400	6.04
183	5.9	(79.7)	61.0	-----	14.90
190	8.2	(34.1)	60.7	-----	9.78
197	5.1	100.7	61.2	0.176	17.70
204	4.8	95.0	58.7	0.162	18.10
211	4.5	123.7	58.8	0.190	20.10
218	5.4	78.8	57.6	0.153	15.90
225	11.9	48.6	63.8	0.187	8.10
232	14.0	31.6	64.7	0.220	4.44
239	14.6	30.9	63.3	0.225	4.25
246	14.1	(20.1)	61.1	-----	4.86
253	14.3	(14.1)	61.4	-----	5.60
260	14.0	(16.0)	55.3	-----	4.37
267	13.0	(17.7)	57.7	-----	4.14
274	4.6	22.2	65.0	0.109	6.31
281	4.7	25.7	61.6	0.113	7.05
288	6.2	19.8	64.0	0.109	5.64
295	14.6	12.2	58.7	0.143	2.63
302	10.0	15.0	57.9	0.181	2.55

Fermentation Kinetics - Beef Feedlot Manure

The gas production data collected at the various retention times can be used to determine the fermentation kinetics at 58°C and 40°C. The gas production data expressed as m^3 per kg volatile solids added are shown in Figures 5 and 6 as a function of retention time. The square symbols represent the data obtained from beef manure while the circle symbols represent data generated from fermentation of fresh dairy manure void

Table 10 Operating Parameters - Reactor 4

Week Ending	Θ Days	pH Range	Alkalinity Range - g/l	Volatile Acid Range - g/l
76333	12.1	7.0 - 7.3	2.4 - 3.5	0.14 - 0.26
340	12.2	7.2 - 7.4	4.4 - 4.6	0.22
347	7.6	7.2 - 7.3	4.9 - 5.6	0.12 - 0.14
354	7.9	7.2 - 7.3	6.1 - 6.3	0.35
361	6.9	7.2 - 7.5	6.1 - 6.2	0.12
77002	8.5	7.3 - 7.4	6.2 - 6.4	0.12
066	6.8	6.9 - 7.4	3.9 - 6.3	0.67 - 3.00
073	---	6.8 - 6.9	4.5 - 4.7	3.30 - 3.70
148	6.3	7.0 - 7.2	2.0 - 2.4	0.12 - 0.22
155	6.2	7.2 - 7.5	2.4 - 2.5	0.17 - 0.26
162	6.2	6.9 - 7.2	2.5 - 2.8	0.24 - 0.79
169	6.2	7.0 - 7.5	3.0 - 3.0	0.34 - 0.70
176	6.2	7.5 - 7.7	4.2 - 4.9	0.26 - 0.72
183	5.9	7.8 - 8.0	4.7 - 6.3	0.40 - 0.70
190	8.2	7.7 - 7.8	6.3 - 8.1	0.36 - 2.76
197	5.1	7.8 - 8.0	7.0 = 8.6	0.18 - 1.08
204	4.8	7.8 - 8.0	7.0 - 8.5	0.24 - 0.72
211	4.5	7.6 - 8.0	6.8 - 9.9	0.43 - 0.96
218	5.4	7.6 - 8.0	6.7 - 7.8	0.35 - 1.10
225	11.9	7.8 - 7.9	6.3 - 8.1	0.31 - 0.62
232	14.0	7.7 - 7.9	5.7 - 6.3	0.48 - 0.84
239	14.6	7.7 - 7.8	5.1 - 6.0	0.19 - 0.60
246	14.1	7.7 - 7.0	4.6 - 5.8	0.10 - 0.26
253	14.3	7.7 - 7.8	5.1 - 6.0	0.07 - 0.26
260	14.0	7.3 - 7.5	3.8 - 4.8	0.02 - 0.10
267	13.0	7.3 - 7.5	3.5 - 3.9	0.07 - 0.10
274	4.6	7.2 - 7.4	2.5 - 3.8	0.02 - 0.36
281	4.7	7.3 - 7.5	3.2 - 3.5	0.02 - 0.19
288	6.2	7.2 - 7.2	3.1 - 3.2	0.12 - 0.17
295	14.6	7.2 - 7.3	3.0 - 3.4	0.07 - 0.19
302	10.0	7.2 - 7.3	2.7 - 3.1	0.07 - 0.10

of any beeding. These data show an extremely wide variation in gas production for given retention times, especially for the 58°C fermentation temperature. This wide variation was caused by changes in the quality of the manure fed to the reactors.

In order to obtain a rate constant for this fermentation, it is necessary to obtain an estimate of the original biodegradable substrate level. The volatile solids as such do not reflect the level of biodegradable organics. The initial substrate level can be estimated by plotting

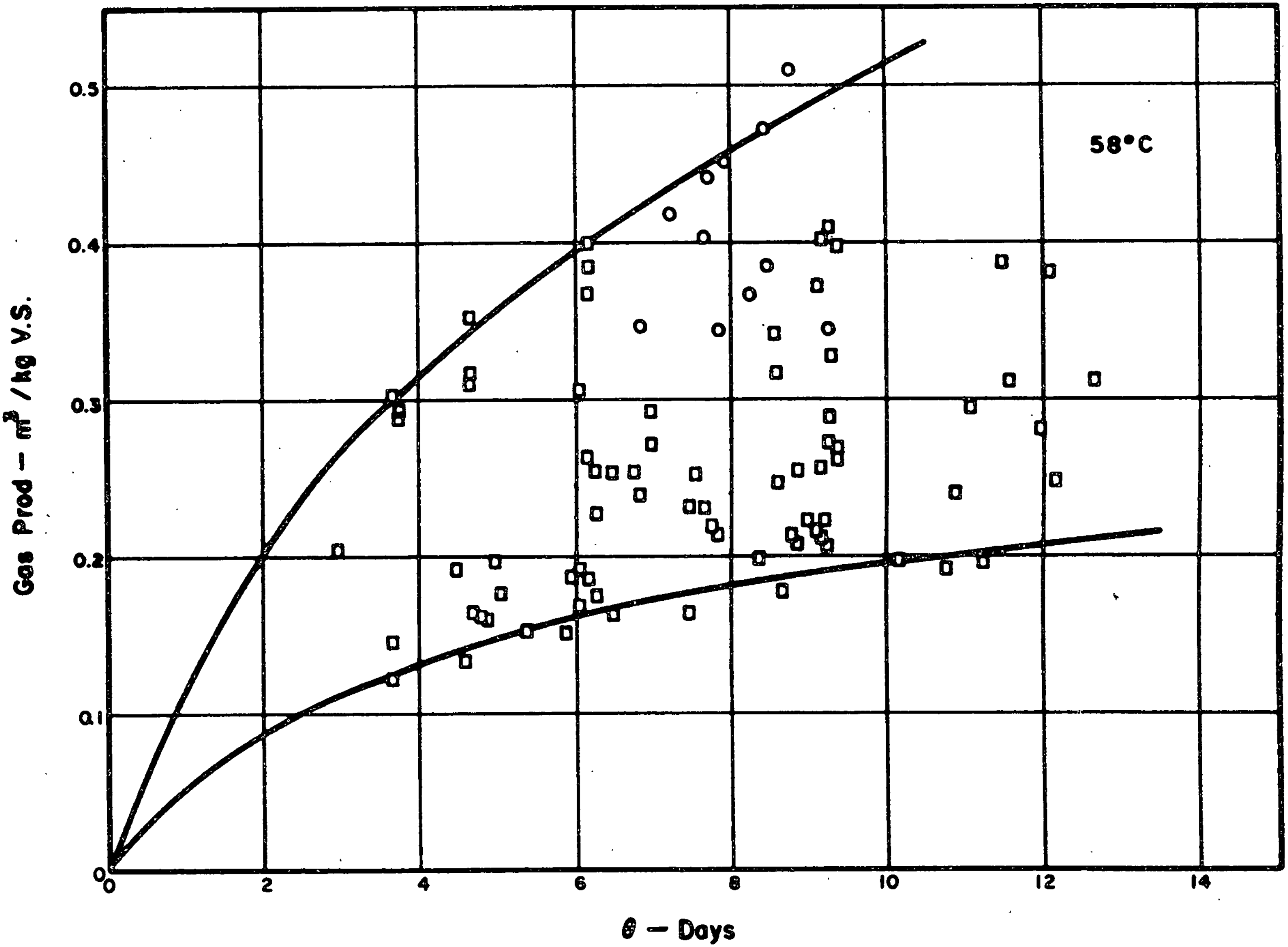

Figure 5. Thermophilic Gas Production - Manure Fermentation

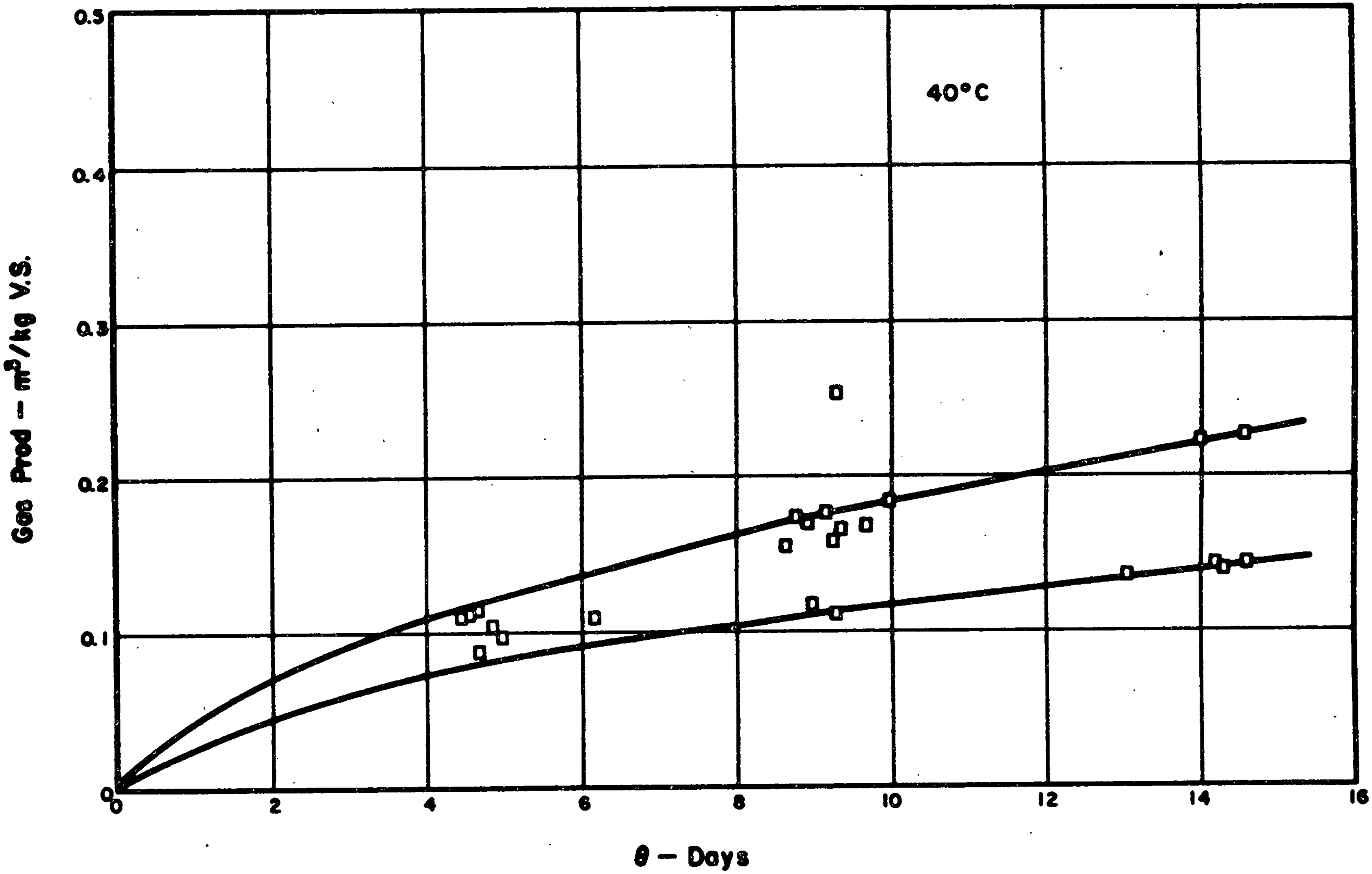

Figure 6. Mesophilic Gas Production - Manure Fermentation

the log of the gas production against the reciprocal of the retention time. The y-axis intercept represents the level of gas production at infinite retention time.

The data shown in Table 11 were used to estimate the initial level of biodegradable organics. These data were taken from Figures 5 and 6 and represent the maximum and minimum gas production levels. After the above graphical analysis was completed, the value for the initial substrate level was then slightly adjusted so the following equation plotted as a straight line was an intercept of 1.0.

$$\frac{S_o}{S_e} = K\theta + 1 \qquad (1)$$

where S_o = Initial substrate level

S_e = Final substrate level

Θ = Fermenter retention time

K = Rate constant

This equation is derived from a mass balance on a CSRT without solids recycle in which the gas production rate is first order with respect to the biodegradable substrate remaining.

Table 11. Evaluation of the Rate Constant

Θ Days	$\frac{1}{\Theta}$	40°C Gas - m^3/kg V.S. Fed Min	Max	58°C Gas - m^3/kg V.S. Fed Min	Max
3	0.33	0.059	0.090	0.111	0.260
4	0.25	0.070	0.107	0.130	0.320
6	0.17	0.090	0.137	0.160	0.390
8	0.125	0.105	0.162	0.180	0.437
10	0.10	0.119	0.182	0.195	0.437
12	0.083	-----	-----	0.208	0.500
15	0.067	0.145	0.230	-----	-----
S_o (est.)		0.250	0.400	0.275	0.650
K (Day^{-1})		0.081	0.079	0.240	0.250

This analysis produced the estimated initial substrate levels and rate constants shown in Table 11. The estimated biodegradability of this manure ranged from 33.1 percent to 78.3 percent for the thermophilic data. This is based on a miximum gas production of 0.83 m^3 per kg volatile solids if these solids were 100 percent biodegradable. The calculated rate constants were 0.240 and 0.250 day^{-1} for the minimum and maximum biodegradability respectively. In a similar manner, the biodegradability for the mesophilic studies ranged from 30.1 to 48.2 percent. The calculated rate constants were 0.081 and 0.079 day^{-1}.

This analysis suggests that thermophilic fermentation results in a higher level of biodegradability. However, this conclusion is not necessarily valid since the mesophilic and thermophilic studies were not conducted concurrently, using the same manure feed. However, this analysis does show that the rate constant is three fold higher at the thermophilic temperature than at the mesophilic temperature. These data show that the rate constant determined by this technique did not vary with the biodegradability of the manure.

Reactor Stability

One of the concerns with the methane fermentation process is stability of operation. Changes in temperature, loading rate, etc. are thought to cause perturbations in the system that may result in process failure. An unplanned example of reactor stability developed when the hot weather conditions caused repeated thermal overload of the hot water heater used to heat the reactors. As shown in Figure 7, reactor temperature reductions occurred three times, with the temperature dropping to 40°C. In addition to the temperature drop, the manure feed was changed to a fresh manure that was more biodegradable.

As a result of this temperature drop and increased loading of biodegradable organics, the volatile acids increased from approximately 200 mg/ℓ to 800 mg/ℓ. When the temperature was increased to 60°C, the acids decreased to less than 400 mg/ℓ. Each time the temperature dropped, this was repeated. Gas production also followed a similar pattern with a net increase resulting from the change in the manure characteristics. Therefore, at a retention time of 9.2 days, the system was extremely stable.

In the reactor operating at a 3.7 day retention time, the same pattern was observed as shown in Figure 8. The response was more extreme with the volatile acids reaching a maximum of 1300 mg/ℓ. Since the system is well buffered, the pH did not drop below 6.8 with the high volatile acids. Therefore, the system was able to recover rapidly when the temperature was increased to the operating level. Very high gas production rates were observed. Gas analysis showed that the methane content was 60 percent or greater, reaching a high of 68 percent.

Nitrogen Level Variations

Nitrogen is an important parameter in the anaerobic fermentation process. Adequate nitrogen must be maintained in the system to meet the nutritional requirements of the microorganisms. Conversely, excess ammonia (NH_3) levels may be inhibitory to the microorganisms. Therefore, the ammonia nitrogen was monitored in the system. Each week, two to five

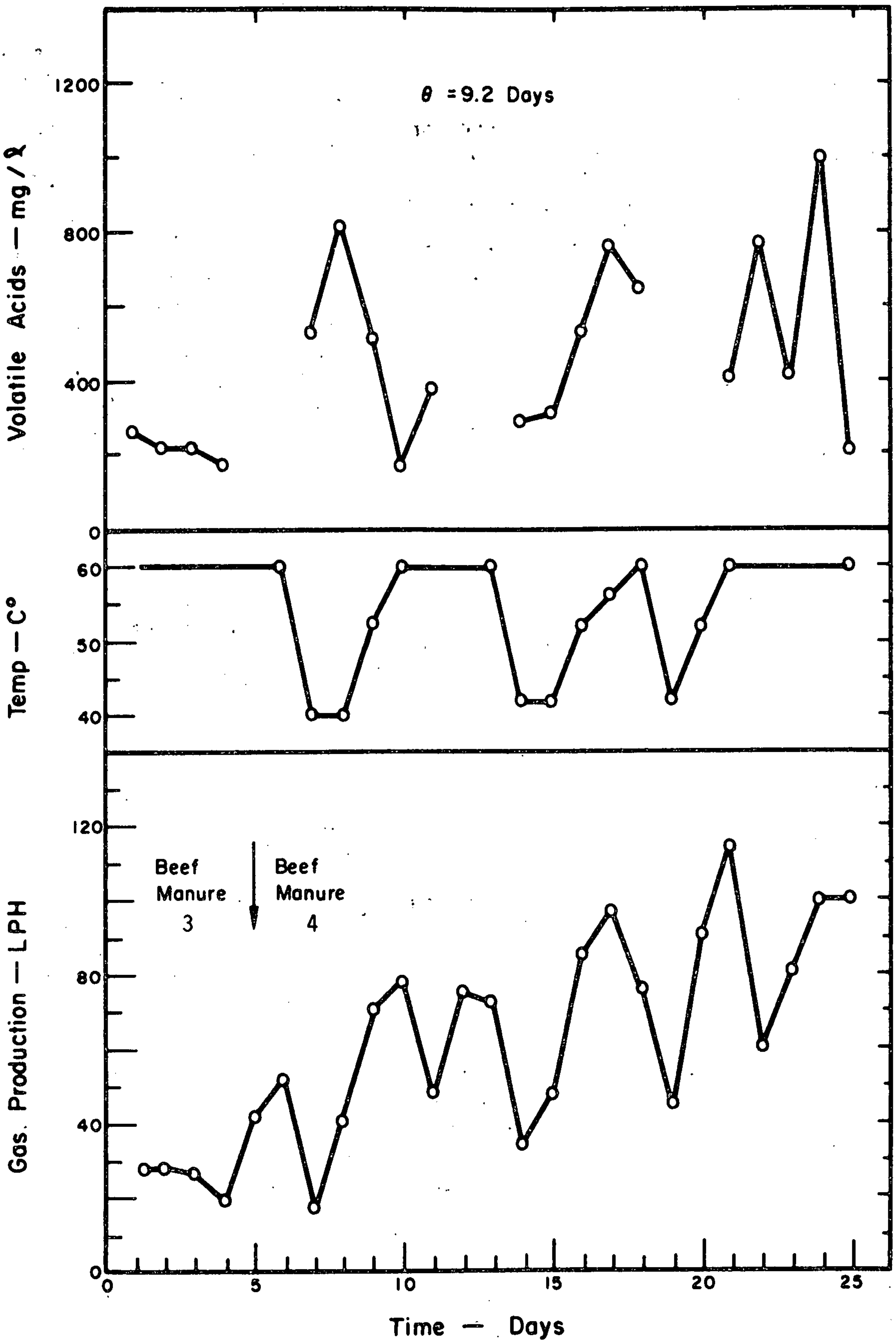

Figure 7. Reactor Stability with Temperature Fluctuations

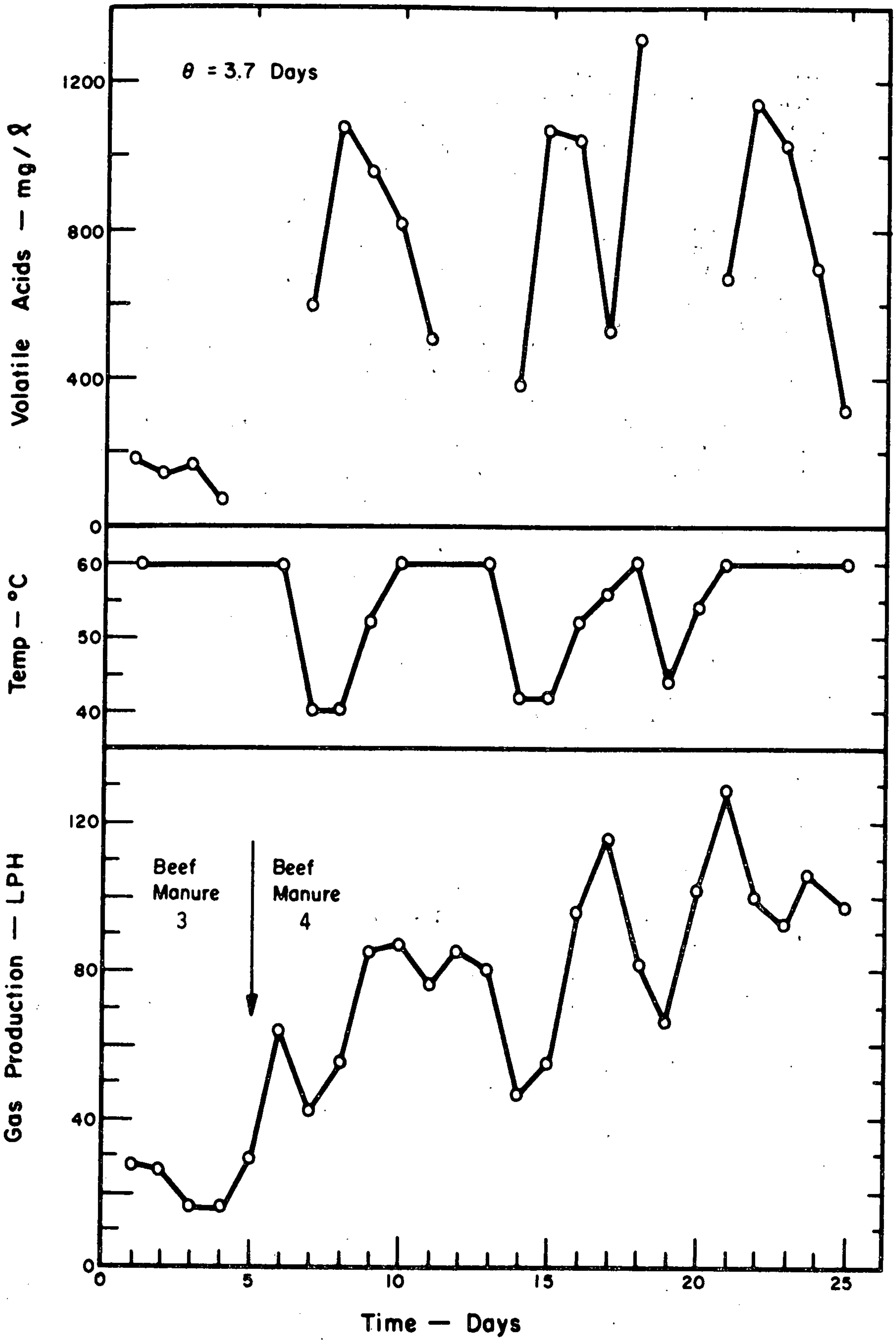

Figure 8. Reactor Stability with Temperature Fluctuations at High Loadings.

samples from the feed slurries and each reactor were analyzed for ammonia content. Less frequent measurements of the total Kjeldahl nitrogen were also made. These data are shown in Table 12 as the average value for the seven-day period.

The specific ion probe technique was used for the ammonia determinations. TKN analyses were obtained by the micro-kjeldahl digestion technique. However, with the large number of samples being tested, distillation facilities were not available to recover the ammonia. Instead, the digested liquor from the micro-kjeldahl digestion was subjected to ammonia analysis using the ammonia probe. These analytical procedures are discussed in Appendix A.

The feed slurry samples were taken from the mixing tanks. Feed sample 1 was fed to Reactors 1 and 2 while feed sample 2 was fed to Reactors 3 and 4. These data clearly reflect the quality of the manure and the operating conditions. In general, the TKN values for the reactors were significantly higher than the corresponding feed slurry. This is probably a result of the inability to obtain a representative sample from the feed mixing tanks. Due to the mixing pattern in these tanks, samples taken from the top of the tank contained significantly fewer suspended solids than samples taken from near the tank bottom. The ammonia samples should be accurate since this nitrogen form is soluble and not subject to mixing problems.

Two periods shown in Table 12 show extreme variations in nitrogen levels. From Day 77179 through 77218, the solids concentration in feed slurry 2 was increased to the 10 percent range. The organic and ammonia nitrogen present in the feed slurry increased accordingly. There was also a significant increase in the organic and ammonia nitrogen level in Reactors 3 and 4. This increase in the reactors did lag the feed slurry increase.

During this period, the ammonia nitrogen reached levels of 1200 mg/l. With a fermentation temperature of 58°C, the unionized ammonia can reach relatively high levels, especially when the associated pH is 8.0 to 8.1. When the effect of the temperature on the ammonium ion dissociation is considered, a pH of 8.0 and a temperature of 58°C will result in a (NH_3/NH_4^+) ratio of 0.32. Therefore, a total ammonia concentration of 1200 mg/l will produce an NH_3 concentration of 290 mg/l. This level is generally considered to inhibit methane fermentation at mesophilic fermentation temperatures. Of course, the reactors were experiencing significant operational problems during this period as shown in Tables 8 and 10.

During the period 77268 to 281, feed slurry 1 consisted of the previously digested residue. This was the period when Reactor 1 was receiving only this residue while Reactor 2 was receiving this residue after a mild thermochemical pretreatment. The ammonia levels in feed slurry 1 and Reactors 1 and 2 dropped significantly during this period. Most of the nitrogen had been washed from the solids during the previous fermentation. Consequently, very little nitrogen remained.

Feed slurry 2 also had a very low ammonia nitrogen level. However, the ammonia nitrogen in the reactors remained at a satisfactory level. The low nitrogen in the feed slurry was a result of the poor quality manure being processed at this time.

Table 12. Average Nitrogen Contents of Feed and Effluent Slurries - mg/l

	Feed Slurry				Reactor Effluent							
	TKN		NH_3-N		TKN				NH_3-N			
Week Ending	1	2	1	2	1	2	3	4	1	2	3	4
77162	--	1030	182	174			1880	1660	205	202	195	195
169	1410	1385	207	216	1980	1920	1920	1990	250	240	243	240
176	--	--	275	300	2200	1830	1670	1360	300	325	370	400
183	1515	3070	320	482	3070	3070	3260	2600	463	402	595	530
190	--	--	215	450	--	--	--	--	450	340	800	610
197	1350	2906	--	--	--	--	--	--	--	--	--	--
204	--	--	405	570	--	--	--	--	460	460	--	--
211	1350	3220	415	450	3490	2310	3310	2630	580	560	960	730
218	1850	4800	410	620	2780	2450	5620	5630	750	670	1215	1110
225	2150	--	350	430	2800	2360	5410	3540	600	460	650	620
232	--	--	--	--	3560	2380	3690	3420	550	570	710	720
239	1400	1440	250	310	2700	2700	2830	2640	590	650	620	615
246	1200	2150	230	245	3810	3340	3300	3200	740	560	505	610
253	1350	1350	230	--	2200	2100	2360	2700	663	373	485	520
260	--	1190	69	105	2480	1900	1850	2000	385	160	257	324
267	1334	1940	111	150	--	--	1780	1415	232	197	216	246
274	--	--	74	100	1600	1360	1530	1530	230	133	235	176
281	--	1580	22	95	--	--	--	1650	122	78	239	188
288	--	--	76	111	--	--	--	--	113	89	177	182
295	--	--	--	82	--	--	--	--	134	102	149	140
302	--	--	51	38	--	--	--	--	173	199	165	159
309	--	--	88	57	--	--	--	--	430	442	273	236
316	--	--	111	81	--	--	--	--	912	820	327	640
323	--	--	170	31	--	--	--	--	--	--	407	640
330	--	--	325	440	--	--	--	--	797	547	342	543

In general, sufficient nitrogen was present in the reactors to maintain adequate levels of nutrients for the microorganism population. Under certain operating conditions, the ammonia reached levels that have been considered inhibitory.

Thermochemical Pretreatment

A short test of the effect of thermochemical pretreatment on the gas yield was undertaken. From day 77268 until 289, Reactor 1 was being fed a slurry containing only solids centrifuged from the effluent from Reactors 3 and 4. These same solids, after being mixed with 3 g of lime per 100 g dry solids and heated at 110°C for two hours, were fed to Reactor 2. The gas production in both reactors was exceptionally low. These data are shown in Tables 3 and 6. The methane production from Reactor 1 was greater than Reactor 2 during this period. However, the gas production rates dropped to such low levels that the cost of such gas production would be excessive.

On Day 77289, the previously fermented solids were replaced with raw manure. The thermochemical treatment was continued. Gas production in both reactors increased significantly. A break in the test run occurred during the week ending with day 77316, when the manure supply was exhausted. The reactors were not fed for 5 days. Allowing for equilibrium to be established during the weeks ending with day 77295 and 77323, three weeks of gas production data can be used to compare the effectiveness of this treatment. The methane production in Reactor 1, the control, was 0.080 m^3/kg volatile solids added. The methane production from Reactor 2, the test reactor, was 0.095 m^3/kg volatile solids added. This mild treatment appeared to increase the methane yield by 19 percent. However, the quality of this manure was very poor. This percentage is magnified by the low gas production from the control. Using gas production rates from biodegradable manure of 0.20 m^3 of methane per kg volatile solids fed, the percentage increase is due to this mild thermochemical pretreatment would only be 7.5 percent. However, if this gas is priced at $7/100 m^3 ($2/MCF) of methane, it will pay the lime cost at $53/metric ton ($48/ton). In addition to lime, caustic soda may be much more effective, especially on the solid remaining after the initial fermentation. A considerable amount of research in the effect of thermochemical treatment of organic on biodegradability has been conducted at Stanford University (McCarty et al, 1979). Therefore, a more careful evaluation of this processing step may be warranted, especially if the price of this gas continues to increase.

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CORN STOVER FERMENTATION

After completion of the manure fermentation studies at the end of November 1977, the substrate was changed to corn stover. During December of 1977, different techniques of processing and pumping of the stover were investigated. Significant problems were encountered in trying to pump the slurry of stover. Pumping of this slurry with total solids concentration of 5 to 6 percent was not possible. Examination of the Moyno pump showed extensive wear on the stators and rotors. The grit in the manure and small pieces of metal incorporated in the manure either from the feed lot or while in storage, did significant damage to these pumps. It was necessary to replace the rotors and stators.

The minimum size screen purchased with the mill was 6.3 mm (0.25 in.). After a few attempts at pumping this slurry milled through the above screen, it was clear that a smaller size particle would be necessary for ease of processing with the existing equipment. In addition to pumping problems, it was not possible to dewater the fermented slurry in the conveyor centrifuge. The small openings in the center feed mechanism and the cake discharge ports plugged frequently with the larger particles. A decision was made to mill through a 3.2 mm (0.125 in.) screen.

During the period of December 1, 1977 to January 14, 1978, the major effort was directed toward developing techniques for handling of the slurry and in modification of the pumping system so that the slurry could be handled. The fermenters received varying quantities of slurry and the microbial culture allowed to acclimate to the corn stover substrate. It should be mentioned that the size and capacity constraints required low flow velocities in the pipes and frequent on-off pump cycles. This slurry handling problem could be significantly reduced by continuous pumping at higher fluid velocities.

Gas Production Rates

One of the primary objectives of these tests was to determine the efficiency of the methane fermentation system in converting the corn stover into methane. The four fermenters were operated under various conditions in order to obtain gas production data. Reactor 3 was operated as a control, with the retention time maintained in the 13 to 15 day range throughout the study. The average weekly loading rates and gas production data for this reactor are given in Table 13. The gas production is measured at room temperature and atmospheric pressure. Correction to standard conditions has not been applied. The corn stover feed to the system after 78035 was milled through the 3.2 mm screen. These data cover the period from January 21, 1978 (78021) through August 15, 1978 (78231).

These data show variations in gas production. The relatively low gas production after the week ending on 78084 was a result of the recycle of significant quantities of inert organic solids. Prior to Day 78021, the effluent from the fermenters was dewatered with the

Table 13. Control Reactor Performance

Week Ending	θ Days	Gas LPH	Feed Kg V.S./D	CH_4 %	CH_4 M^3/Kg V.S. Fed
78021	14.5	11.4	1.26	55.3	0.12
28	15.2	12.5	1.50	53.4	0.11
35	14.4	17.1	1.87	53.8	0.12
42	14.6	17.8	1.79	54.9	0.13
49	13.4	20.2	2.00	50.9	0.12
56	14.6	20.1	2.08	51.0	0.12
63	14.3	21.6	2.21	52.6	0.12
70	13.9	24.1	2.16	53.1	0.14
77	15.0	24.5	2.40	53.9	0.13
84	15.0	27.6	2.33	53.0	0.15
92	13.2	15.1	2.24	53.4	0.09
99	13.8	16.1	1.81	52.9	0.11
106	14.2	13.1	1.83	52.8	0.10
113	14.0	12.0	2.01	52.8	0.07
120	13.2	15.7	2.00	54.8	0.10
127	14.0	13.9	2.09	56.5	0.09
134	14.9	15.8	1.86	49.4	0.10
141	13.6	15.1	2.12	54.6	0.09
148	12.0	15.1	2.08	57.4	0.10
155	13.4	13.4	1.95	61.4	0.10
162	14.6	12.9	2.10	59.8	0.09
169	14.9	11.9	2.07	59.0	0.08
176	13.9	15.3	1.93	58.7	0.11
183	12.8	15.1	1.98	55.1	0.10
190	14.7	11.9	1.63	59.4	0.10
203	13.3	13.4	2.02	58.7	0.09
210	13.8	11.6	1.69	55.9	0.09
217	14.1	10.3	1.45	57.5	0.10
224	13.8	11.7	1.63	57.4	0.10
231	14.8	10.7	1.47	55.1	0.10

Sharples conveyor centrifuge, and the centrate recycled. Because of problems of plugging with the centrifuge, the reactor effluents were dewatered on a screen, and the liquid was then centrifuged prior to recycle. This practice was continued until Day 78083. At this time, the screened effluent was recycled directly to the mix tanks. A significant quantity of small organic solids was recycled, resulting in a higher volatile solids feed rate. These recycled solids were very stable, having been passed through the anaerobic fermentation process at least once. Consequently, the gas production per unit of volatile solids fed decreased. The effect of these recycle solids will be discussed in more detail.

The weather presented some major problems with operation and may be responsible for some of the data variation. A blizzard on Day 78026 (January 26, 1978) and again on Day 78043 (February 12, 1978) isolated the lab for 3 and 2 days, respectively. Of course, during this period, the reactors did not receive any substrate. From Day 78083 through Day 78086 (March 25-28, 1978), an ice storm disrupted the power to the lab. Fortunately, the ambient temperature did not drop much below freezing. Therefore, even though the heat in the building was off, no freezing problems were caused by the low temperatures.

The gas production from Reactor 1 is shown in Table 14. After an initial period of acclimation to corn stover, a thermochemical pretreatment step was introduced. Starting on Day 78014, milled corn stover was mixed with $Ca(OH)_2$ (3 percent by weight of lime) and added to a pressure reactor. Water, generally recycled liquid, was added to this tank to increase the moisture to approximately 75 percent. Steam was then added to maintain a temperature of 110°C for approximately 4 hours. On Day 78058, the lime was increased to 6 percent by weight and on Day 78079 to 10 percent by weight. There is no apparent improvement in gas production as a result of this pretreatment. After heating for a 4-hour period, the pH of the 10 percent lime treatment was in the range of 9.1 to 9.3. Additional water was added to this tank to obtain the desired slurry concentration before transfer to the holding tank.

Reactor 2 received the same treatment as Reactor 1 (see Table 15). The only variable was a reduced retention time during part of the period. The feed particle size for these reactors was the same as that fed to the control. The thermochemical pretreatment was terminated on Day 78098. The feed to all reactors was the untreated corn stover and the retention times were changed in preparation for obtaining some rate data.

The data for Reactor 4 are shown in Table 16. This reactor was initially intended to duplicate Reactor 3. However, excessive variations in the temperature caused erratic data. It was necessary to shut this reactor down and correct the temperature control problem. This reactor was reseeded and started again for the rate studies.

The methane production data for Reactors 1 through 3 during the period when lime was used in the thermochemical pretreatment of the feed slurry for Reactor 1 and 2 are summarized in Table 17. The effects of any pretreatments employed were insufficient to show any trends. There was some variation in the data. This variation was due to a number of factors, some of which have been previously discussed. However, any significant improvement in biodegradability would have been obvious. Approximately 30 percent of the volatile solids were being fermented. An increase in the biodegradability to 50 percent would have resulted in methane produc-

Table 14. Gas Production from Reactor 1

Week Ending	θ Days	Gas LPH	Feed Kg V.S./D	CH_4 %	CH_4 M^3/Kg V.S. Fed
78021	14.7	12.8	1.24	56.4	0.139
28	13.9	13.7	1.24	53.8	0.143
35	13.7	11.1	1.10	54.6	0.132
42	13.7	12.8	1.28	54.5	0.131
49	13.1	13.8	1.62	53.4	0.109
56	13.7	11.5	1.62	53.2	0.091
63	14.4	14.0	1.56	53.2	0.115
70	14.3	17.4	2.12	51.7	0.102
77	14.6	19.5	2.23	55.3	0.116
84	14.0	20.7	2.64	55.7	0.105
92	14.5	26.9	2.88	52.9	0.118
99	13.9	30.0	2.54	54.2	0.154
106	7.2	17.4	3.93	53.3	0.057
111	7.2	18.4	4.02	52.7	0.058
120	7.1	17.1	3.82	55.4	0.071
127	7.4	23.7	3.99	52.5	0.075
134	8.3	23.7	4.00	51.8	0.074
141	12.9	48.4	2.67	54.8	0.238
148	14.1	41.4	2.25	58.2	0.257
155	14.2	35.2	2.04	61.0	0.253
162	14.2	24.4	2.02	58.1	0.168
169	13.5	22.8	2.05	56.2	0.150
176	14.4	22.8	1.69	56.3	0.182
183	13.9	15.9	1.52	57.5	0.144
190	14.2	11.6	1.41	55.6	0.110
203	14.2	26.8	1.56	55.8	0.230
210	13.9	26.0	1.34	60.0	0.279
217	14.0	23.2	1.36	58.6	0.240
224	14.8	26.3	1.47	57.1	0.245
231	14.5	22.7	1.22	57.7	0.258

Table 15. Gas Production from Reactor 2

Week Ending	θ Days	Gas LPH	Feed Kg V.S./D	CH_4	
				%	M^3/Kg V.S. Fed
78021	14.7	13.9	1.24	54.6	0.147
28	14.6	13.5	1.17	53.0	0.147
35	13.7	10.9	1.10	54.4	0.129
42	14.2	15.2	1.23	53.9	0.159
49	13.6	14.9	1.66	53.6	0.115
56	13.2	14.1	1.68	52.8	0.106
63	13.9	14.1	1.81	53.7	0.100
70	10.6	21.8	3.00	52.6	0.092
77	8.5	28.8	3.91	54.0	0.096
84	8.8	30.3	4.09	54.4	0.097
92	10.7	37.7	4.40	52.9	0.109
99	9.0	38.1	3.88	53.8	0.127
106	4.9	23.3	5.70	53.1	0.052
113	5.0	25.8	5.88	53.5	0.057
120	5.1	24.4	5.32	53.7	0.059
127	5.1	24.6	6.02	52.3	0.051
169	8.5	33.3	3.24	-	0.141
176	8.2	34.5	3.10	57.5	0.154
183	7.5	34.8	2.61	57.7	0.185
190	7.8	20.0	2.64	54.9	0.100
197	7.7	23.1	2.96	57.4	0.108
203	7.2	49.0	3.07	60.3	0.231
210	8.1	41.6	2.41	58.9	0.244
217	7.3	35.3	2.60	55.7	0.176
224	7.6	36.8	2.90	53.6	0.163
231	7.6	38.5	2.81	55.7	0.183

tions of approximately 0.2 m^3 per kg volatile solids added. Clearly no such increase occurred.

In order to determine the effect of retention time on the gas production rates, a run was made using retention times ranging from 3.8 to 13.7 days. Although the reactors were designed to be fed continuously, it was not possible to do so with this corn stover. Continuous feed requires the feed pumps to operate on a time switch, pumping at short intervals during the day. Unfortunately, the stover slurry would not pump without an initial flush with water. Once the slurry was pumping, there were no problems. Therefore, it was necessary to manually operate the feed pumps. The reactors were fed approximately 50, 100, 150,

Table 16. Gas Production From Reactor 4

Week Ending	θ Days	Gas LPH	Feed Kg V.S./D	CH_4 %	CH_4 M^3/Kg V.S. Fed
78021	14.6	12.5	1.26	53.6	0.132
28	14.8	13.0	1.53	52.6	0.107
35	14.3	16.9	1.88	53.5	0.115
42	13.9	16.3	1.90	54.5	0.112
49	13.3	22.4	2.08	51.1	0.132
56	13.4	20.3	2.30	51.4	0.108
63	13.0	19.6	2.51	51.9	0.097
70	13.7	17.2	2.27	50.1	0.091
77	13.9	24.8	2.56	53.7	0.125
106	3.7	21.2	7.25	50.9	0.036
113	3.9	25.4	7.45	54.3	0.044
120	3.9	30.2	6.76	54.6	0.059
Daily Performance Data at Short Retention Time					
78114					
115	3.9	28.3	7.29	54.6	0.052
116	3.8	28.7	7.91	54.0	0.049
117	3.8	29.9	6.69	56.7	0.060
118	4.0	31.2	5.84	53.1	0.071
119	3.8	32.5	6.00	-	0.072
120	3.8	30.7	6.83	-	0.060

and 200 liters per day. The appropriate volume was fed in 50 liter quantities in order to reduce the surge effect at the high feed rate.

The effect of retention time on conversion efficiency is shown in Table 18. The four reactors were operated at various retention times as shown in this table. Reactor 3 had been operating for approximately 15 weeks at this retention time prior to collecting the data shown in Table 18 (see Table 13). These data were collected during the period from 78101 to 78129.

Reactor 1 was operated at approximately 7.8 day retention time from 78101 to 78136. The data in Table 18 were taken only from 78116 to 78136. This would represent a period when the reactor could be expected to have reached equilibrium. The retention time for Reactor 2 was set at 5 days on 78101 and continued until 78129. The data collected during the period from 78109 to 78129 were used in Table 18. Reactor 4 was operated at 200 liter per day feed rate, resulting in 3.8 day retention time. This feed rate was initiated on 78101 and the data shown in Table 18 were collected from 78109 to 78120.

During this period, the reactor effluents were screened to remove

Table 17. Methane Production Rates

Control (3)		Reactor 1		Reactor 2	
θ (days)	m^3/kg V.S.	θ (days)	m^3/kg V.S.	θ (days)	m^3/kg V.S.
		Lime - 3%			
14.7	0.117	14.1	0.138	14.3	0.141
14.2*	0.123	13.5	0.110	13.7	0.127
		Lime - 6%			
14.4	0.132	14.4	0.110	11.0	0.096
		Lime - 10%			
14.0	0.117	14.1	0.126	9.5	0.111

*Size of milled stover reduced from 6.3 to 3.2 mm

the coarse solids. Fine suspended solids passed through the screen and were incorporated in the recycle liquor used to slurry the corn stover being fed to the fermenters. The organic solids contained in this liquor had been fermented and were essentially biologically inert. These solids added to the quantity of volatile solids fed to the fermentation tanks, resulting in lower methane production rates as shown by the column labeled Measured CH_4. This methane production was calculated from the total volatile solids fed to the fermenters.

In order to determine the impact of the recycle of these solids on gas production, sampling of the recycle liquor was initiated. The total volatile solids of the recycle liquor varied significantly, ranging from low values of 5 g/ℓ to high values of 15 g/ℓ. This variation was due to a number of factors, incluinq how well the recycle storage tank was mixed prior to using the recycle liquor to slurry more corn stover. By measuring the recycle solids concentration and the volume of recycle added, the mass of the recycle solids added to the feed was calculated. Thes allowed for the calculation of the correction factor shown in Table 18. When this factor is applied to the measured methane production, an adjusted methane production rate is calculated. This is the gas production rate based on the volatile solids added as new corn stover.

This adjustment is valid as can be seen by comparing the gas production from the control reactor. During the period from 78050 through 78084, all of the recycle liquor was passed through the Sharples centrifuge. The recycle liquor contained approximately 6.0 g/ℓ of volatile total solids. The soluble solids, fixed and volatile, were about 4.5 g/ℓ. The measured CH_4 production during this period averaged 0.132 m^3/kg volatile solids fed with an average retention time of 14.6 days (See Table 13). The adjusted CH_4 production in Table 18 for Reactor 3 operating at a 13.7 day retention

Table 18. Effect of Retention Time on Gas Production

Reactor No.	θ Days	Measured CH_4 m^3/kg V.S. Fed	Correction Factor	Adj. CH_4 m^3/kg V.S. Fed
4	3.8	0.046	1.48	0.068
2	5.0	0.056	1.48	0.083
1	7.8	0.073	1.38	0.101
3	13.7	0.090	1.43	0.129

time is 0.129 m^3/kg volatile solids fed. These data show that the mass of recycle volatile solids can significantly alter the measured gas production rate.

The adjusted gas data can be used to determine the kinetics of the fermentation. The first step is to determine the biodegradability of the substrate. This must be done in order to establish the S_0, the initial substrate level. S_0 can be determined graphically by linearizing a plot of S_0 - S (m^3CH_4/kg V.S. fed) against the reciprocal of the retention time, θ. When θ approaches infinity, θ^{-1} approaches zero. Also, the substrate remaining, S will also approach zero. Consequently, S_0-S will approach S_0.

Figure 9 shows a plot of the log of S_0-S, expressed as methane production, vs. the reciprocal of the retention time. The four points provide a reasonably good fit to a straight line, with a y intercept of 0.16 m^3 CH_4/kg volatile solids fed. If one assumes that corn stover is a carbohydrate composed primarily of hexoses, the methane production at 100 percent conversion of substrate would be 0.45 m^3/kg. Based on this maximum possible methane production and the observed S_0 value of 0.16 m^3/kg, the corn stover appears to be only 36 percent biodegradable for the test conditions employed (59 ± 1°C fermentation temperature).

Using the above biodegradability factor and the adjusted gas production in Table 18, a rate constant can be determined on the basis that the gas production rate is first order with respect to biodegradable substrate (see Equation 1). A least square computation for the data in Table 18, including a value of $S_0/S = 1$ when $\theta = 0$, yield a slope of 0.25 day^{-1}. Therefore, K is equal to 0.25 day^{-1} This constant can be used to predict gas production rates and solids destruction at various retention times. This constant applies for 58-60°C fermentation temperatures. A plot of S_0/S vs. θ is shown in Figure 10.

Effect of Thermochemical Pretreatment

As reported previously, the use of lime in the thermochemical pretreatment process was ineffective in improving the methane production. The research at Stanford University (Gossett et al., 1976, McCarty et al.. 1979) has shown that sodium hydroxide can be an effective agent in the enhancement of the biodegradability of the organics. A series of tests was

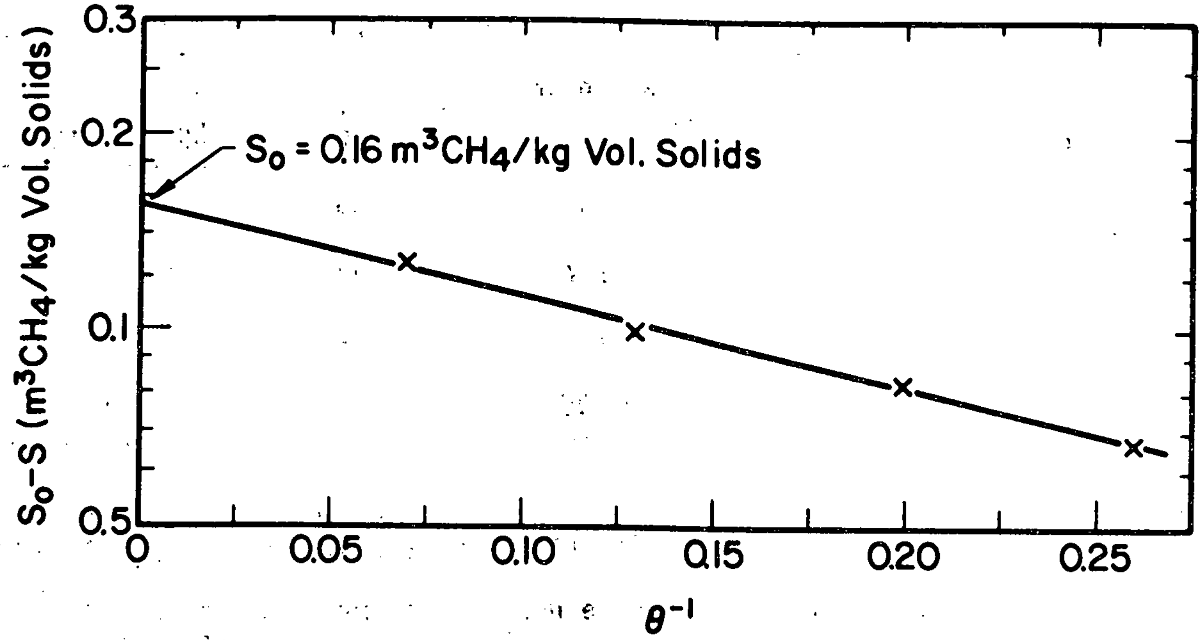

Figure 9. Biodegradability of Corn Stover

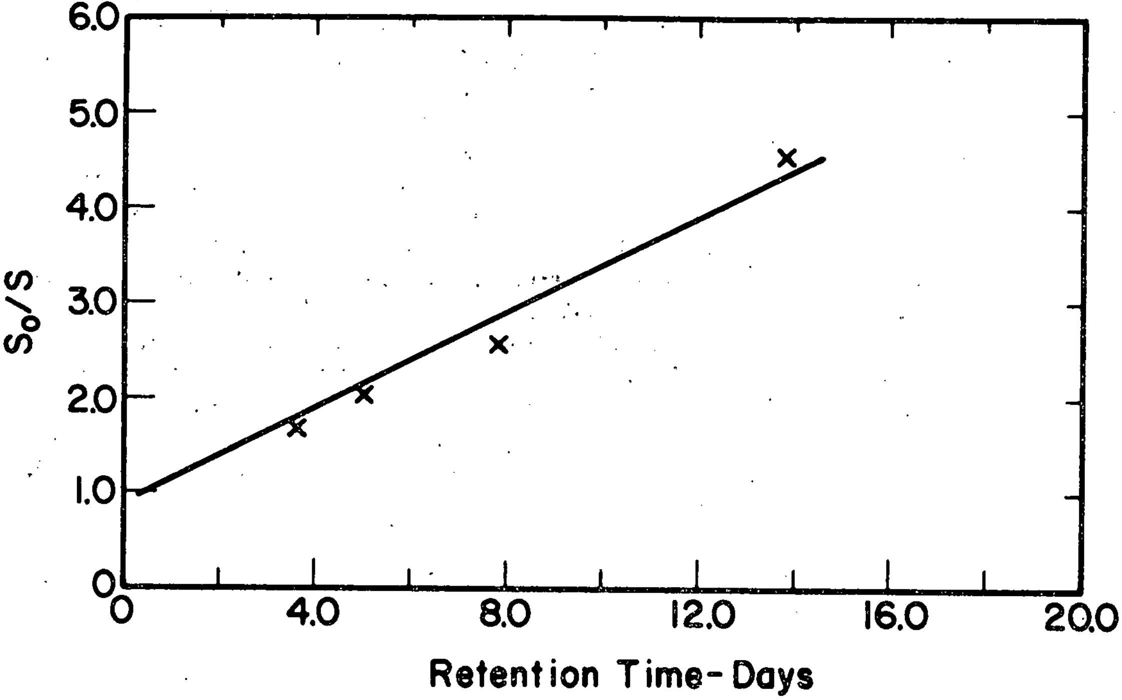

Figure 10. First Order Rate Constant for Corn Stover

undertaken to evaluate this pretreatment technique in a larger scale system.

The milled dry corn stover was mixed with sodium hydroxide at the rate shown in Table 19. Tap water was added at the rate of 4 kg per kg of dry stover. With a caustic addition of 5 g/100 g of dry stover, the caustic concentration in this mixture was approximately 0.30 molar. After thorough mixing of this paste in the pressure reactor, the pH at the above caustic addition was 12.1 to 12.2. This mixture was heated for 4 hours at 115°C. After the heat treatment, the pH decreased to approximately 9.5. This paste was then diluted with recycled water to about 6 percent solids and pumped to the mixing tank for feed to the reactors.

Table 19. Effect of NaOH Pretreatment of Corn Stover

Week Ending	θ Days	Gas LPH	Feed Kg V.S./m^3-D	CH_4 %	CH_4 M^3/Kg V.S. Fed	NaOH % Dry Solids
			REACTOR 1			
134	8.3	23.7	5.2	51.8	0.07	0
141	12.9	48.4	3.4	54.8	0.24	5.0
148	14.1	41.4	2.9	58.2	0.26	5.0
155	14.2	35.2	2.6	61.0	0.25	5.0
162	14.2	24.4	2.6	58.1	0.17	3.0
169	13.5	22.8	2.6	56.2	0.15	3.0
176	14.4	22.8	2.3	56.3	0.18	3.0
183	13.9	15.9	2.0	57.5	0.14	3.0*
190	14.2	11.6	1.8	55.6	0.11	3.0*
203	14.2	26.8	2.0	55.8	0.23	5.0
210	13.9	26.0	1.7	60.0	0.28	5.0
217	14.0	23.2	1.8	58.6	0.24	5.0
224	14.8	26.3	1.9	57.1	0.25	5.0
231	14.5	22.7	1.6	57.7	0.26	5.0
			REACTOR 2			
162	14.4	19.7	3.1	57.7	0.11	3.0
169	8.5	33.3	4.2	-	0.14	3.0
176	8.2	34.5	4.0	57.5	0.15	3.0
183	7.5	34.8	3.4	57.7	0.18	3.0*
190	7.8	20.0	3.4	54.9	0.10	3.0*
203	7.2	49.1	4.0	60.3	0.23	5.0
210	8.1	41.6	3.1	58.9	0.24	5.0
217	7.3	34.2	3.4	55.9	0.18	5.0
224	7.6	36.7	3.7	53.6	0.16	5.0
231	7.6	38.5	3.6	55.7	0.18	5.0

*NaOH + $Ca(OCl)_2$ added to pretreatment step

The results of this pretreatment are given in Table 19. A caustic dosage of 5 g/100 g dry solids resulted in a significant increase in methane production. The data for 78137 through 78157 for Reactor 1 show a methane production rate of 0.25 m^3 per kg of volatile solids fed with an average retenrion time in the fermenters of 13.7 days. This pretreatment was repeated again in Reactor 1 during the period from 78197 through 78231. With an average retention time of 14.2 days, the methane production was 0.25 m^3 per kg of volatile solids fed. If the rate constant for treated and untreated stover remains the same, the increase in biodegradability can be estimated from these data and the following equation:

$$S_o - S = 0.25 \frac{m^3}{kg} = S_o \left(\frac{K\theta}{1 + K\theta}\right) \qquad (2)$$

The calculated value for S_o is 0.32 m^3 CH_4 per kg volatile solids fed.

Based on an ultimate gas production of 0.45 m^3 CH_4 per kg volatile solids destroyed, the biodegradability of the corn stover was increased from 36 percent to 71 percent. The gas production in the control reactor is given in Table 13.

The above calculation applied to the data collected from Reactor 2 during the period from 78197 through 78231 yield an S_o value of 0.30 m^3 CH_4 per kg volatile solids fed. This would result in a 67 percent biodegradability. There was substantial variation in the four weeks of gas production. Therefore, one should not place too much confidence in these latter numbers.

Lower caustic dosages were investigated. The pretreatment for Reactors 1 and 2 during the period 78158 through 78178 was 3 g NaOH per 100 g dry solids. The initial pH of the mixed stover paste was in the range of 11.8 to 12.0. After the 4 hour heating period, the pH was approximately 9.0. While there did not appear to be a major change in the initial and final pH at this level of NaOH, there was a substantial reduction in the gas production. The methane production in Reactor 1 operating at a 14.0 day retention time was 0.17 m^3 CH_4 per kg volatile solids fed. Reactor 2, operating at a retention time of 8.4 days, had a methane production rate of 0.145 m^3 per kg volatile solids fed. These data clearly show that significant caustic dosages are required to enhance the biodegradability of the corn stover.

An attempt was made to see if an oxidant such as chlorine would have any effect on the conversion efficiency. Calcium hypochlorite and sodium hydroxide were added to the dry stover each at the rate of 3 g per 100 g. The two week period shown in Table 3 indicates a substantial reduction in gas production. No attempt was made to determine what caused this reduction. The experiment was not continued as it was obvious that under these test conditions, gas production severely decreased.

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WHEAT STRAW FERMENTATION

The milled straw provided a unique experience in handling a slurry through a pumping system. When the milled particles were wetted, they swelled substantially. In a dry state, 99 percent of the particles passed the 10 mesh sieve. However, when subjected to a wet sieve analysis, 65 percent of the total solids in the slurry were retained in the 10 mesh sieve. At the same time, 30 percent of the total solids passed through the 200 mesh sieve. Essentially all of these solids were dissolved. Even though the straw was milled to a small size, it behaved as a much larger particle once it was slurried.

Mixing of the wetted straw was very difficult. With a solids content of 12 to 13 percent, the straw and water mixture had absolutely no fluid properties. It had an angle of repose that approached 90 degrees. Mixing by conventional fluid mixers was impossible. The power required by a ribbon mixer designed to mix concentrated slurries exceeded 2 kw/m^3 (75 HP per 1000 cu ft). The slurry could be mixed with conventional mixing equipment only at significantly lower solids concentrations.

Pumping of a slurry containing 10 percent solids was impossible. It was necessary to dilute the solids to about 3 percent. Even at these concentrations, it was extremely difficult to pump the slurry. 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. Consequently, reactor loading was accomplished in 50 liter quantities, spread over an eight hour period to ease the shock at the higher through put rates.

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

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

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

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

The slurry used in Reactors #3 and #4 received this treatment from December 2, 1978 to February 12, 1979. At this date, the amount of NaOH added to the dry straw was reduced from 1.9 kg to 1.52 kg. This resulted in a NaOH concentration in the pretreatment step of 0.166 molar and 0.091 molar in the feed slurry. Feed slurry for Reactors #1 and #2 was pretreated with 1.9 kg of NaOH from January 4, 1979 to March 21, 1979. At this date, the NaOH was reduced to 1.52 kg.

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

Gas Production Rates

The data presented in Table 20 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 a relatively unstable system.

Table 20. Gas Production Data for Wheat Straw

Week	θ Days	Gas Lph	 % CH_4	Vol. Solids kg/day	CH_4 Produced[1] 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 20 is expressed in terms of the gas (methane) generated per unit of volatile solids added. When processing straw, a liquid recycle stream was employed. The fermented slurry was 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 was used as make-up water for the new feed slurry. Consequently, a measurable quantity of solids was recycled within the system. The gas production in Table 21 is the average for the data shown in Table 20 and is expressed in terms of the total volatile solids fed (including recycle solids) and in terms of the volatile solids addid with the straw only, the latter being the data in the adjusted CH_4 production column.

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 (Figure 11) 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 11 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

Table 21. Adjusted Gas Production Data for Straw

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

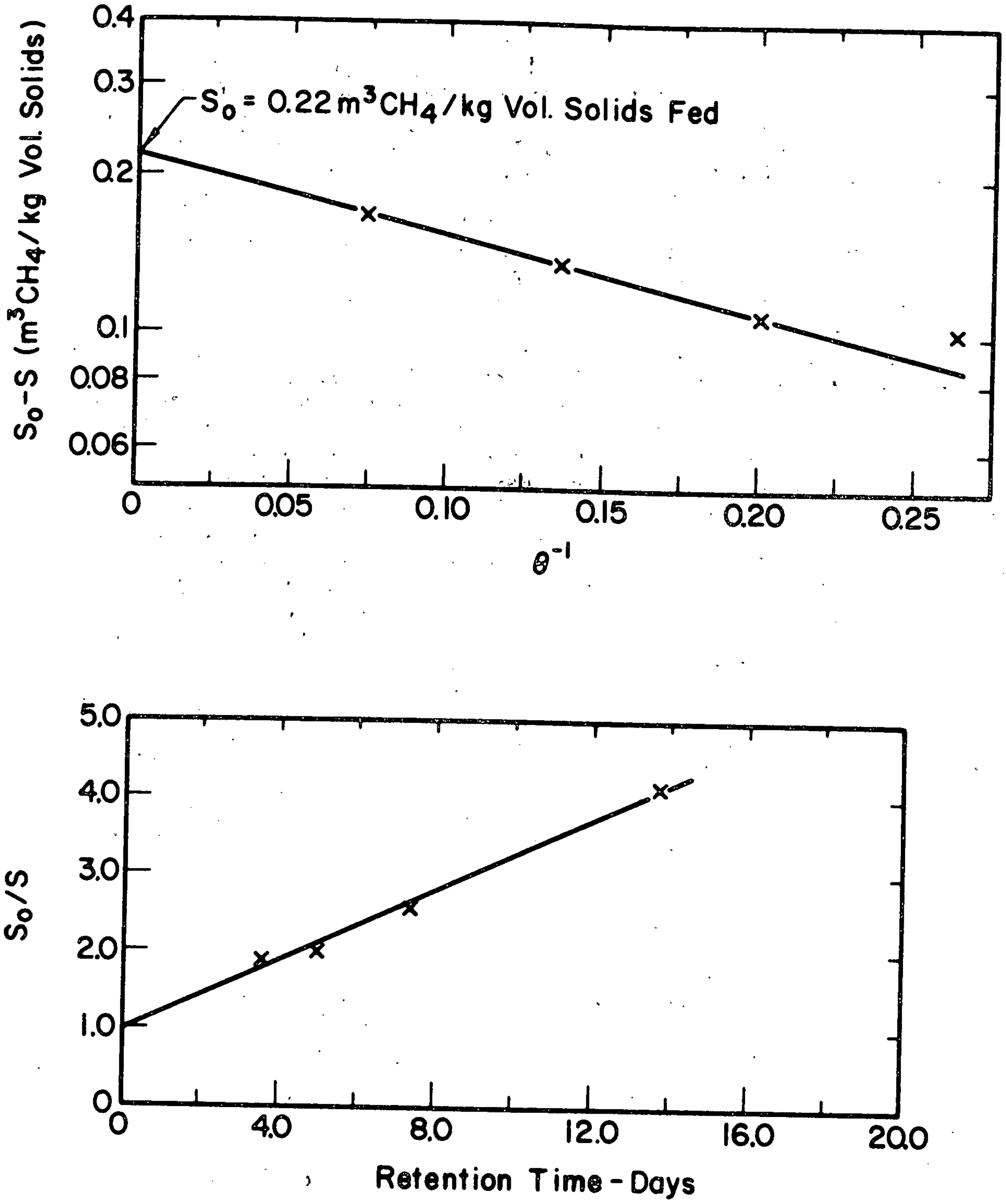

Figure 11. Biodegradability and First Order Rate Constant for Wheat Straw

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 was determined from a simple first order kinetic relationship in which the substrate removal rate (dS/dt) is a function of the biodegradable substrate remaining (see Equation 1)

Using a value for S_0 as determined previously, and the values of $S_0 - S$ (methane produced per kg of volatile solids) from Table 20, a plot of $S_0 - S$ vs. retention time (θ) can be constructed (See Figure 11). A least squares fit of the data 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 1. This rate constant (temperature of 59 ± 1°C) corresponds closely with the values found for manure (0.25 day^{-1}) and corn stover (0.25 day^{-1}).

Effect of Thermochemical Pretreatment

The feed of thermochemical pretreated slurry to Reactors #3 and #4 was initiated on December 2, 1978. Prior to this change, these reactors were receiving untreated straw with Reactor 3 operating at a retention time of 7.5 days and a volatile solids loading of 1.9 kg/day. The retention time in Reactor 4 was 5.0 days with a volatile solids loading of 2.9 kg/day. On the assumption that a significantly higher availability of volatile solids would result from the pretreatment, the loading on the reactors was initially low. Also, the fermentation temperature in Reactor 4 was reduced to 40°C on November 26, 1978.

During the first week, significant pH drops were encountered. With intermittent feed and lime addition, a stable pH was achieved. These start-up data are shown in Figure 12. Day 0 corresponds to December 9, 1978. Reactor 4 was operated at a retention time of approximately 30 days until Day 12 when the retention time was decreased to about 15 days. The pH remained in an acceptable range during this period, even though the total volatile acids gradually increased to 2500 mg/l by Day 20. A stable operation was obtained from Day 16 to 26. The gas production during this period was 0.11 m^3/kg volatile solids feed. This was a relatively poor gas production when one considers that untreated straw produced 0.167 m^3/kg volatile solids fed at 58°C and a 13.7 day retention time. The gas production from Reactor #3 during this period was 0.15 m^3/kg of volatile solids fed with a 7.7 day retention time and 60°C fermentation temperature.

Reactor 3 exhibited a very good acclimation to the new feed during the first two weeks. The loading was increased to about 4 kg per day of volatile solids with the retention time decreased to 7.5 days. After about Day 15, the gas began to decrease, as did the pH, while the volatile acids increased to about 4000 mg/l. Because of the

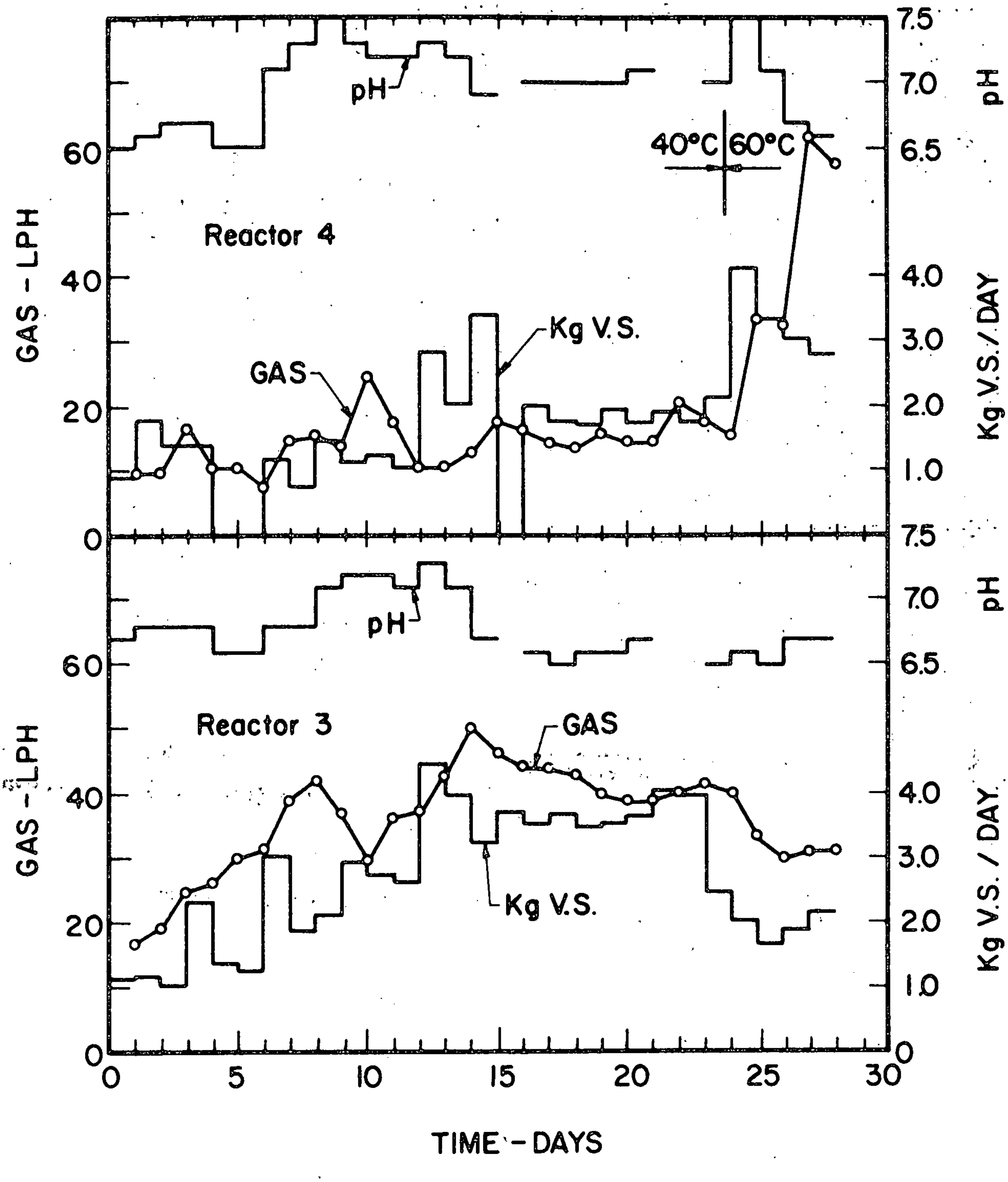

Figure 12. Response of Reactors to Thermochemically Pretreated Straw

decreasing pH, the loading was reduced. However, the system did not recover.

Figure 13 shows the response of Reactor 3 during the next two months. Day 0 corresponds to January 6, 1979. The gas production continued to decrease while the loading was maintained to approximately 2.0 to 2.5 kg per day and a 13 to 15 day retention time. The pH also decreased to inhibitory levels of 6.4. Lime was added to maintain the pH at 6.6 or greater. The system did not receive any feed on January 18, 1979 because of severe weather that prevented access to the laboratory. An excessive feeding on Day 26 so overloaded the system that failure resulted. The pH dropped to 6.1 and the feed was terminated on Day 32.

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

The cause of the inhibition of the methanogens was not known, but it appeared to be associated with the level of NaOH employed in the thermochemical pretreatment. The characteristics of this straw required that a higher moisture be utilized in the pretreatment step. Consequently, the amount of dilution applied to the feed was reduced. The sodium concentration, as well as any products of the pretreatment step, were significantly higher than the previous tests using this pretreatment. Acting on the premise that the concentration of some inhibitory material was high, the reactor contents were diluted to 80 percent of the original concentration by adding tap water to the reactors. This was done on February 12, 1979 (Day 37 on Figure 13). Also the caustic used in the pretreatment was reduced from 1.9 to 1.52 kg. Recovery was almost immediate. Feed was again initiated. The pH increased to acceptable levels while the volatile acids decreased. The gas production also increased to significant levels. An analysis for the individual short chain organic acids was undertaken on Day 38 and 45. The results are shown in Table 22. Clearly, the methanogens using acetic acid were being inhibited. Acetic and propionic acids were the primary acids found in these samples. As can be seen, the acid concentrations decreased significantly by Day 45. This supports the conclusion that a rapid recovery was occurring. However, it has not been demonstrated that total recovery has occurred since the total volatile acids did not drop below 2000 mg/l.

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

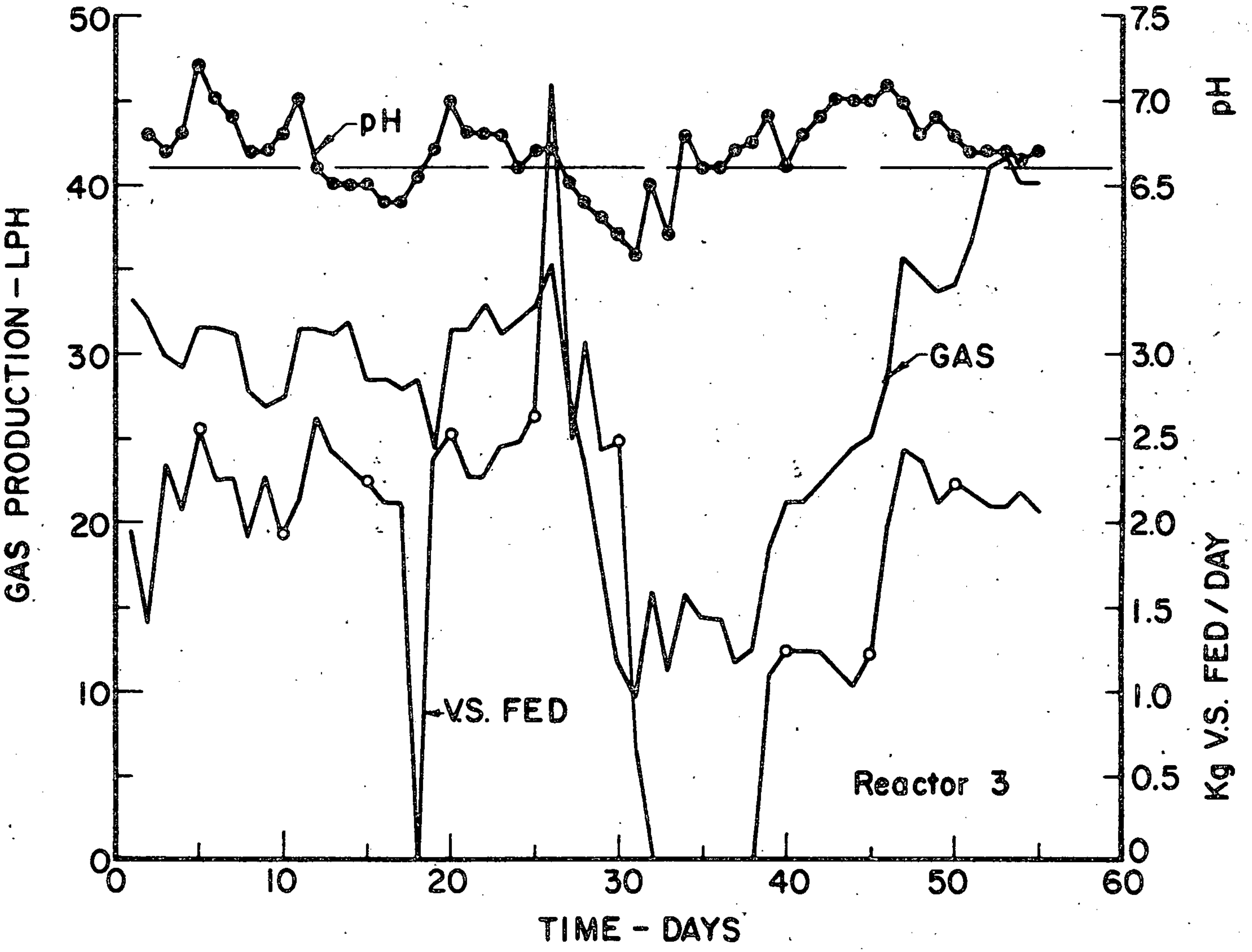

Figure 13. Reactor 3 Performance with Thermochemically Pretreated Straw

Table 22. Volatile acid distribution during recovery at the lower NaOH dosage

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

Table 23. Volatile acids distribution during inhibition at higher NaOH dosage

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

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

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

The response in Reactor 2 was essentially the same as Reactor 1. Failure occurred more rapidly because the fermentation temperature was lowered to 50°C February 10, 1979 and maintained at this temperature for 10 days. This temperature reduction was undertaken to ascertain if the inhibition was temperature related. Clearly it was not as gas production and pH dropped significantly. The total volatile acids increased to more than 6000 mg/l by the time the temperature was increased again.

Individual volatile acid analysis showed that the primary acids were acetic and propionic. These data are shown in Table 23. The variation of the volatile acids in the mix tank was a result of the length of time the slurry had been stored in the tank. Since this tank was not sterile, fermentative bacteria were quite active. Reactor 2 exhibited extremely high volatile acids as a result of operation at 50°C. An increase in temperature back to 60°C on February 20, 1979 did not result in a significant improvement in the reactor performance.

The poor performance of these units when using thermochemical pretreated straw was quite perplexing. Reactor 3 (Figure 13) as well as Reactor 4 appeared to respond favorably to the reduced level of caustic in the pretreatment.

Reactor 3 had been receiving feed cooked at a lower caustic level (1.52 kg NaOH) for two weeks prior to the period shown in Figure 14. The time period for Figure 14 started on March 7, 1979. Gas production was good during the early part of the period. The retention time was in the 13 to 15 day range with a loading of approximately 2.0 kg of volatile solids per day. After about day 40, the gas production decreased and it was difficult to maintain the pH without addition of lime. The volatile acids were in the 2000 to 3000 mg/l range. By the end of the period, the volatile acids had increased in excess of 4000 mg/l. Control of pH was very difficult, and process failure ensued. Also, problems with the gas seal were being experienced. This could account for some of the reduction in gas production.

A number of additions were tried, including raw sewage sludge. Due to the short term nature of these additions, it should not be concluded that they were not effective. However, some immediate response could be expected with certain inhibitors. For example, if for some reason, a high concentration of heavy metals was present, the addition of 50 mg per liter of reactor of sulfide would precipitate the metals with a rapid recovery. It would appear that the problem is not toxicity, but probably a nutrient deficiency. On Day 77, the feed to Reactor 3 was diluted two-fold. There was an initial surge in gas production as shown in Figure 14 and the pH dropped to 6.5. The pH was elevated with lime to above 6.6, but the gas production continued to decrease. This high dilution rate was continued for another three weeks at which time the volatile acids were approximately 3000. It was not possible to get a stable system operating.

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

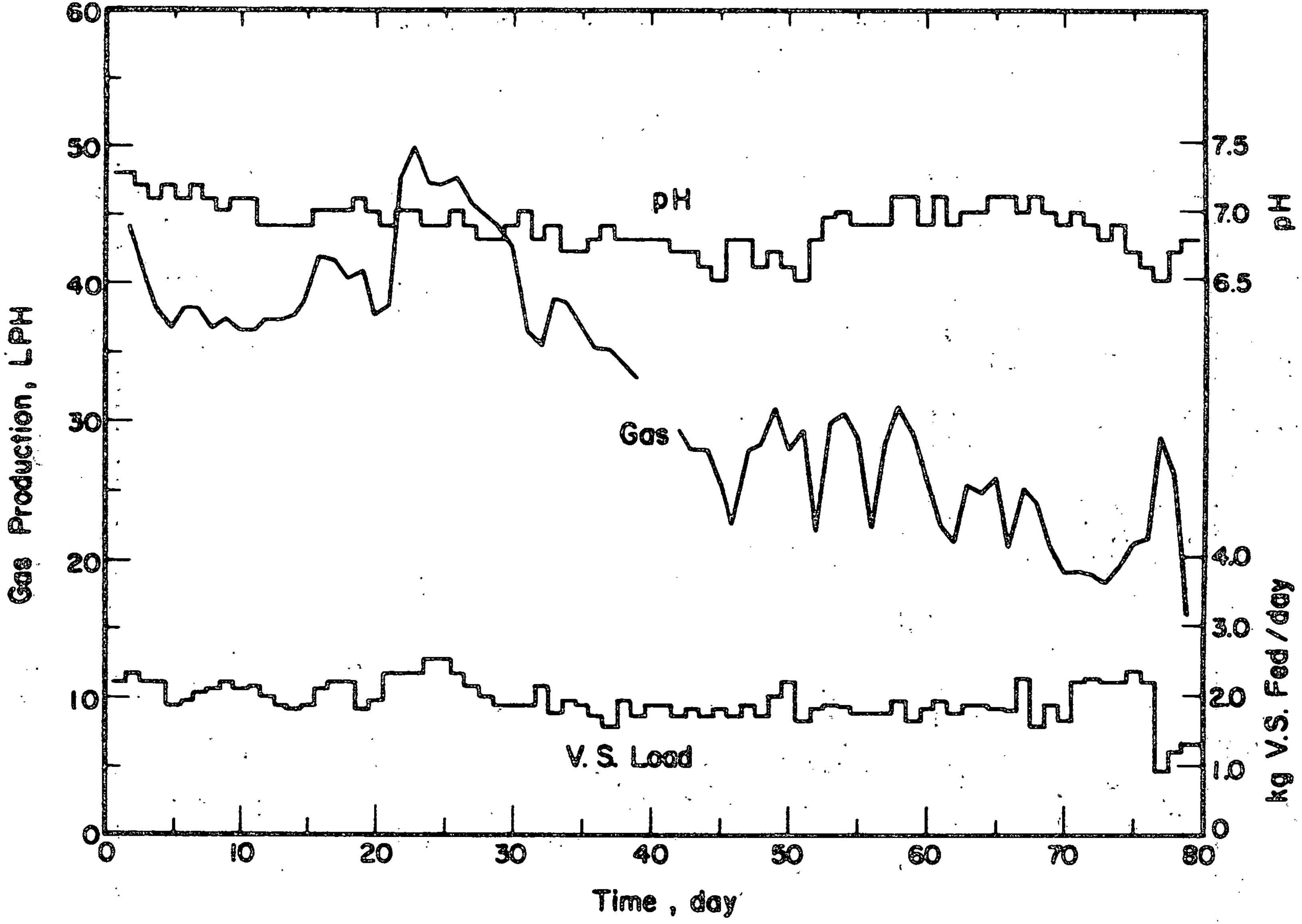

Figure 14. Performance of Reactor 3 on Pretreated Wheat Straw

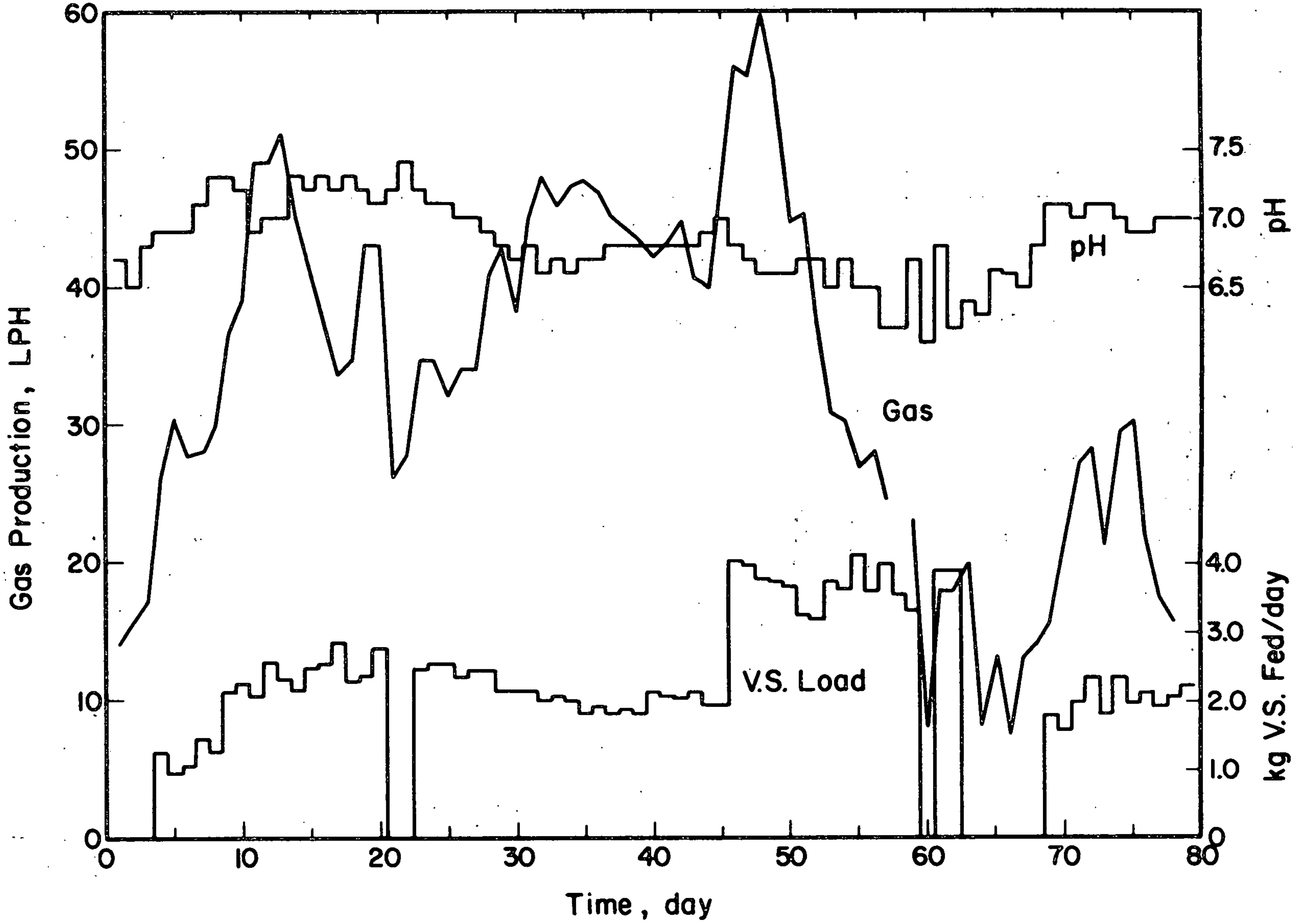

Figure 15. Performance of Reactor 1 in Pretreated Wheat Straw

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

Reactor 2 was restarted in the same manner as Reactor 1. There was an initial surge in gas production. As long as the pH was maintained above 6.6, the system performance was acceptable. However, the TVA concentration was consistantly in the 2000 mg/l or greater range. It was difficult to maintain the pH. At the 13 to 15 day retention time and the lower loading rates, it was possible to operate the system. It was an unsatisfactory mode of operation that was very difficult to control. Gas production calculated during Day 40 to 60 in Figure 16 was 0.44 m^3/kg V.S. fed. This gas production is somewhat better than that obtained without caustic pretreatment. However, it is not a significant improvement, probably because of something that inhibits the fermentation process.

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

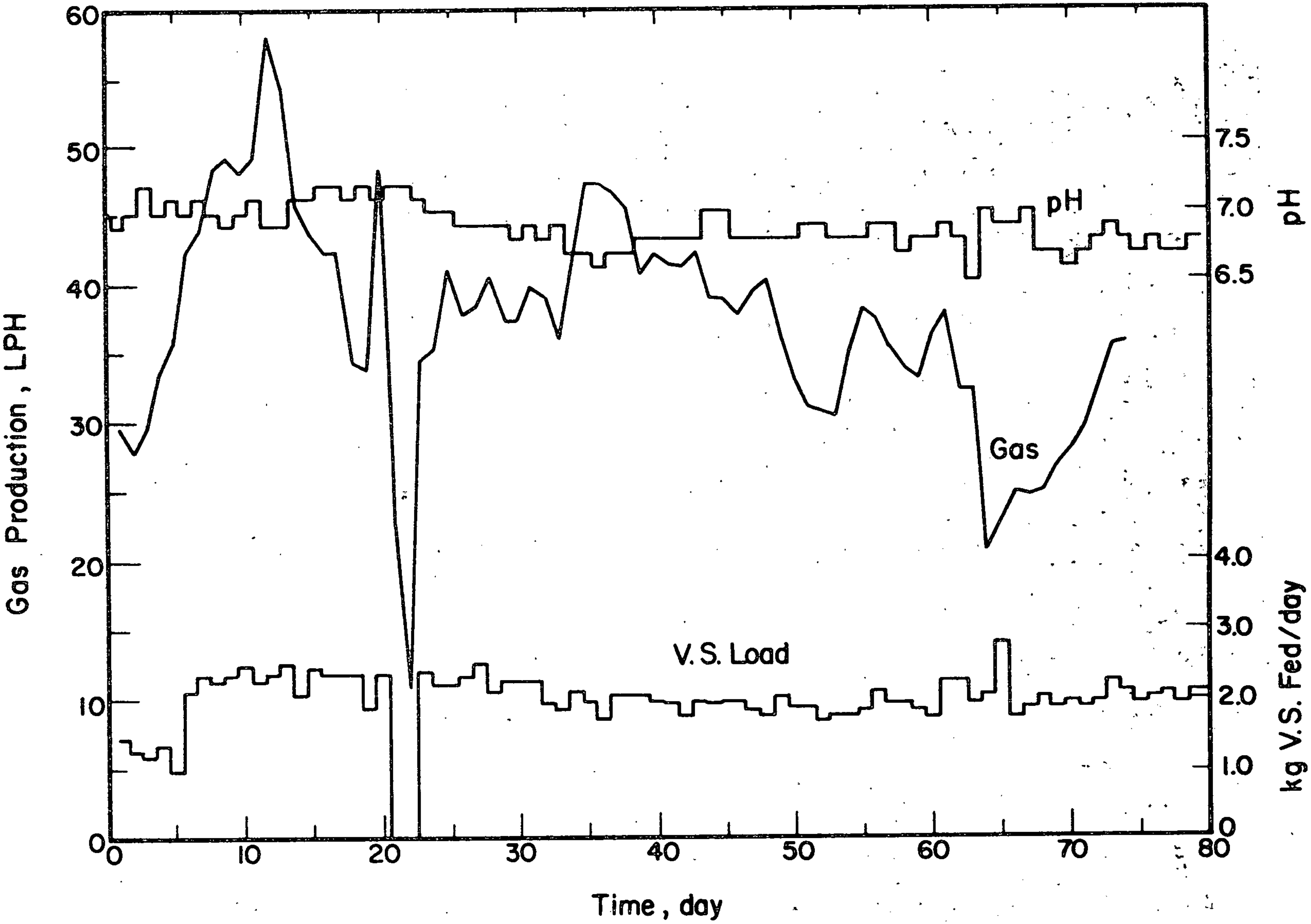

Figure 16. Performance of Reactor 2 on Pretreated Wheat Straw

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GAS PRODUCTION FROM GREEN CROP (ALFALFA)

When the supply of straw was exhausted without resolving the cause of the failure of the process receiving thermochemical pretreated straw, it was decided to evaluate the performance of the system on a green crop. The only green crop available during the period was alfalfa. A quantity of baled alfalfa was obtained from a local supplier. The hay was fresh cut and field dried prior to baling. The bales were stored in the crane bay to protect them from rain. The alfalfa was milled through the 3.2 mm (0.125 in) screen prior to slurry preparation. A dry sieve analysis of the milled alfalfa was not conducted. It was assumed that the particle size distribution was the same as milled straw. The milled alfalfa presented essentially the same problem as the straw in the preparation and handling of the feed slurry. It was difficult to wet, and when in slurry form, its pumping characteristics were very poor. The pumps could not be operated on the time cycle because of pipe plugging problems. It was observed that steaming of the alfalfa assisted in wetting the solids and markedly changed the properties of the particles in the slurry. It was possible to pump the slurry when the alfalfa was heat treated at 115°C for one hour.

Gas Production Rates

A series of experiments was undertaken to establish the rate of methane production as well as the biodegradability of the feed stock. Since chemical pretreatment was not employed in these tests, it was possible to recycle the liquor extracted from the fermented slurry dewatering step. Because of the nitrogen present in the alfalfa, it was not necessary to add nitrogen for nutrients. In fact, the ammonia nitrogen level in the reactors was in the 800 to 1000 mg/ℓ range. Supplemental phosphorus was added to insure excess phosphorus.

Alfalfa fermentation created some problems, especially an excessive amount of foaming. The problem was so acute in Reactor 3 that it was not possible to obtain a period when the loading and gas production were near steady-state. Because of the limited head space in the reactors, 15 cm (6 in), foam commonly entered the gas line and filled a 30 liter foam trap before plugging the gas meter. At other times, the solids in the foam would plug the 1 cm (0.375 in) diameter gas line. When this happened, the reactor overflow discharged liquid away from the effluent holding tank as well as allowed gas to escape from the reactor. Consequently, it was impossible to obtain an accurate measure of the gas production. This problem was experienced to some degree in all reactors. However, there were periods when the foaming was not excessive and reasonably constant data were obtained.

The data used in this evaluation are presented in Figures 17, 18 and 19. All reactors were operated at 59 ±1°C on a semi-continuous feed over a 20 hour day. Feed was pumped to the reactors for one or more 30 second periods each hour. The volatile solids loading shown in these figures contain both the solids from the alfalfa as well as the solids in the recycle liquor. The data will be analysed with a correction factor

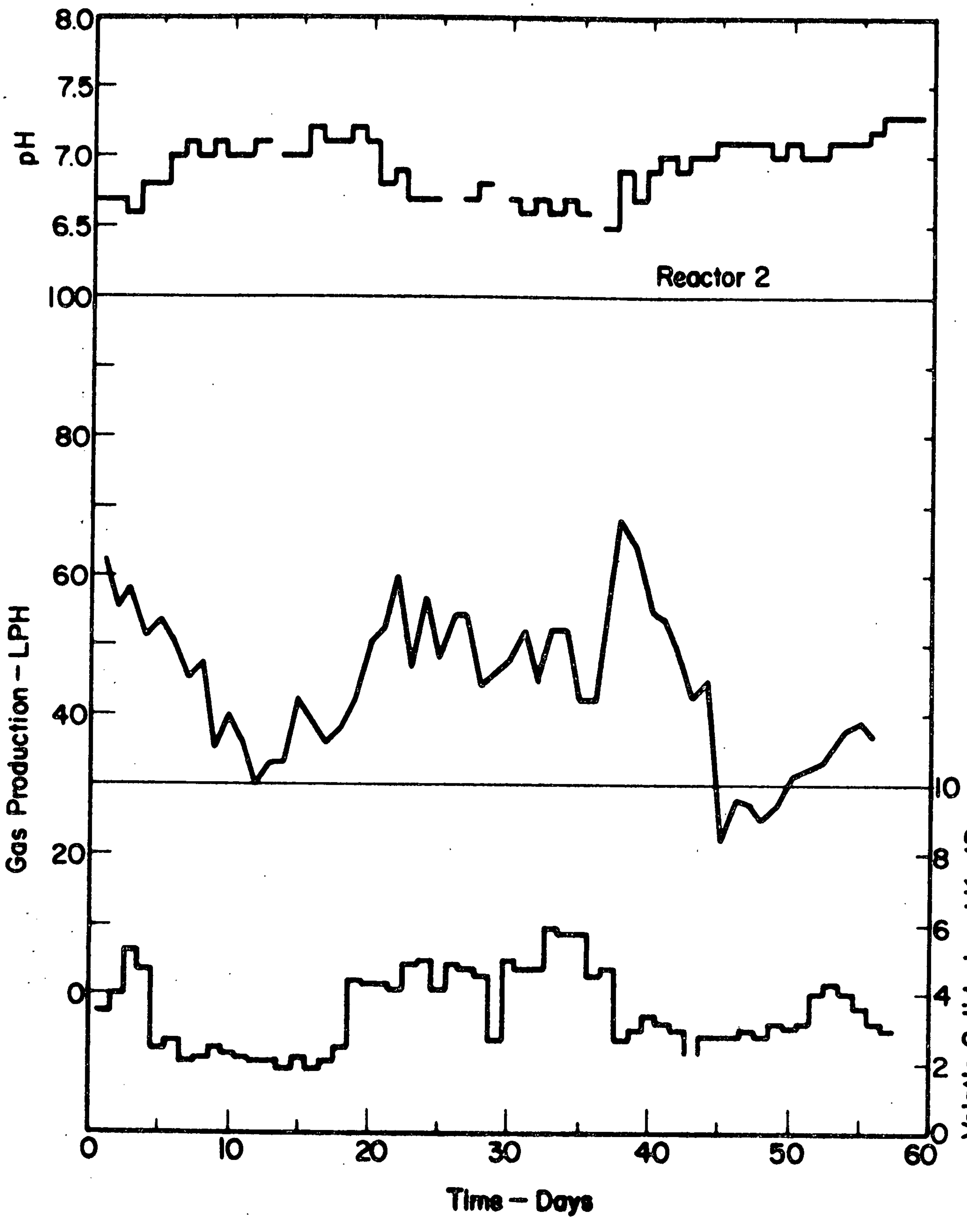


Figure 17. Gas Production and Loading on Reactor 2 (Alfalfa)

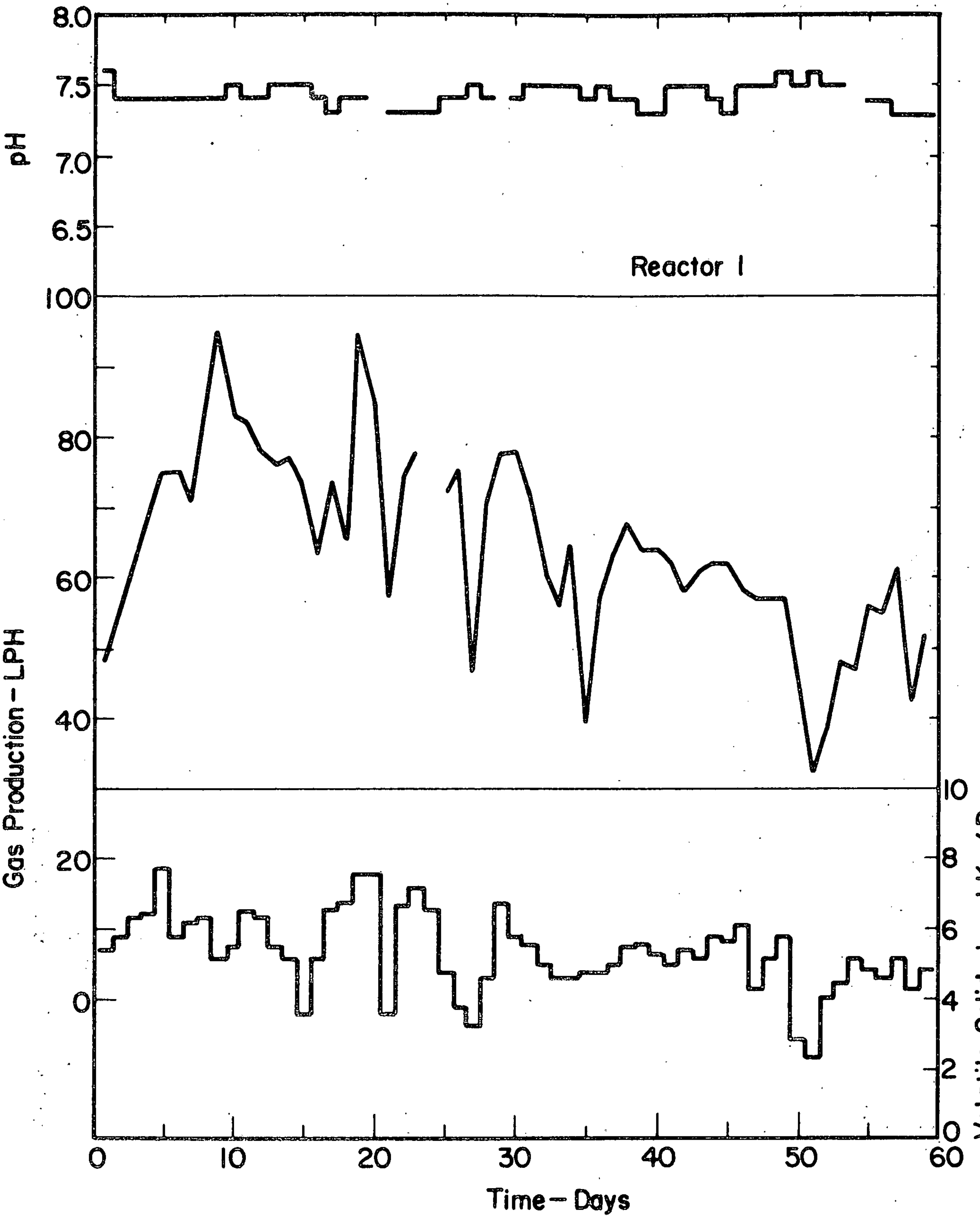


Figure 18. Gas Production and Loading on Reactor 1 (Alfalfa)

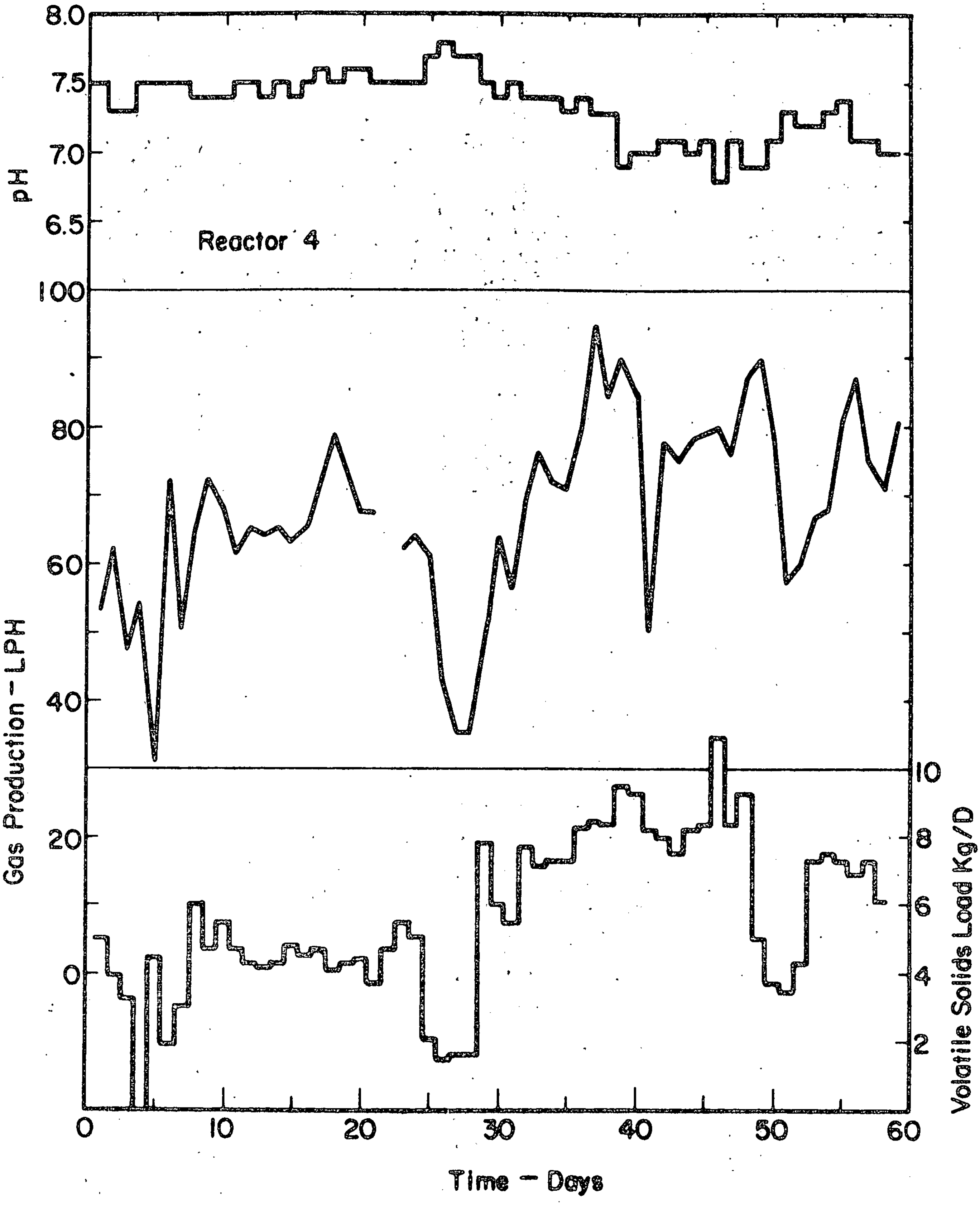


Figure 19. Gas Production and Loading in Reactor 4 (Alfalfa)

applied to compensate for the mass of essentially nonbiodegradable solids that were recycled.

In general, the pH remained above 7.0 except for Figure 17. This unit was converted from straw feed to alfalfa shortly before the data in this figure were collected. It took time to purge the straw slurry which had a low alkalinity with the alfalfa feed. At the low loading rate and long retention time, the pH increased rapidly. However, the increase in loading on Day 19 caused a sharp drop in pH as the volatile organic acids increased from less than 1000 mg/ℓ to over 3000 mg/ℓ. When the loading was again lowered on Day 37, the pH began to increase and the volatile acids dropped to less than 2000 mg/ℓ.

The data in Figures 18 and 19 were collected after the reactors had been receiving alfalfa feed for approximately 60 days. Reactor 1 (Figure 19) was receiving a low loading prior to this test period and had a total volatile acid concentration of less than 1000 mg/ℓ. When the loading was increased to 4 kg per day, the acids increased to about 2000 mg/ℓ. When the loading was 8 kg per day the volatile acids exceeded 5000 mg/ℓ with a concomitant pH drop.

The data shown in Table 24 were taken from periods when the loading and gas production were relatively stable. These data are based on the total volatile solids fed to the fermentation tanks. Because the feed slurry contained a quantity of volatile solids that were present in the recycel water, it was necessary to adjust the data in Table 24 to allow for the fact that the recycle solids were essentially nonbiodegradable. This was done for Table 25 and the gas production is expressed in terms of volatile solid of alfalfa fed.

Table 24. Kinetic Data for Alfalfa Fermentation

Reactor	Time Period	Gas		kg Vol. Sol.	Gas Prod. m^3/kg V.S.	
		(lph)	(day)	Day	Total	CH_4
1	5 - 20	80.0	7.9	5.96	0.322	0.179
	36 - 49	60.9	7.2	5.18	0.282	0.153
2	9 - 18	36.2	14.2	2.17	0.400	0.217
	19 - 32	49.9	6.6	4.43	0.270	0.141
4	8 - 24	66.9	9.2	4.66	0.345	0.194
	32 - 48	79.6	4.5	8.35	0.229	0.121

Table 25. Adjusted Gas Production Data

Reactor	θ	Gas	kg Vol Solids/Day			Gas Prod. m^3/kg V.S.	
	(Day)	(lph)	Total	Recycle	Alfalfa	Total	CH_4
1	7.9	80.0	5.96	0.96	5.00	0.384	0.214
	7.2	60.9	5.18	1.14	4.04	0.362	0.196
2	14.2	36.2	2.17	0.33	1.84	0.472	0.256
	6.6	49.9	4.43	0.82	3.61	0.331	0.176
4	9.2	66.9	4.66	0.83	3.83	0.419	0.236
	4.5	79.6	8.35	1.82	6.53	0.293	0.155

A least square fit of the data in Table 25 yielded the lines shown in Figure 20. This figure is used to estimate the biodegradability of the feed material. The value of S_0 obtained from the total gas data is 0.58 m^3 per kg volatile solids. These gas data were measured at approximately 15°C (ambient temperature). If the feed material was a pure carbohydrate such as cellulose, the maximum gas production would be 0.88 m^3 per kg volatile solids destroyed if the gas was measured at 15°C and one atmosphere pressure. Consequently, the total gas data show that the volatile solids are only 66 percent biodegradable.

A better estimate of the biodegradability of this material is obtained from the methane production data. Because of the relatively high nitrogen content in the alfalfa, a substantial amount of bicarbonate alkalinity was formed and the carbon dioside content of the gas was lower than the 50 percent expected. When using the methane production data, the maximum expected methane production (S_0) was found to be 0.327 m^3 per kg volatile solids. At a 15°C gas temperature, the theoretical methane production is 0.44 m^3 per kg volatile solids destroyed. Based on these data, the volatile solids in the alfalfa were found to be 74 percent biodegradable.

Once the initial value for S_0 has been determined, Equation 1 can be used to determine a first order rate constant for the methane production. Figure 21 is a plot of this relationship. This is a least square fit of the data, including the (0.1) point, or the fact that S_0 equals S when the retention time is zero. With this process, it is probable that the minimum retention time is greater than 0. However, this model is not sufficiently sophistocated to allow for making such determinations. The slope of these lines represent the rate constant, K.

When using the methane production data, the rate constant is 0.27 day^{-1}. This rate is somewhat greater than the values found for manure, corn stover and wheat straw. The total gas data yield a higher value. However, this value is not as accurate as the one obtained with the methane production rate as a result of the lower S_0 value used for the total gas. Because of the carbon dioxide lost from the fermenter in the liquid phase, a higher S_0 value than measured would be expected. This higher value would reduce the slope of the line, yielding a smaller rate constant.

The methane production rate is good relative to the other substrates. However, the inability to operate with volatile acids less than 2000 mg/ℓ raises some concern as to the possible inhibition of the methanogins. It may be that pH is a cause of the higher volatile acids, or the high level of ammonia may be exerting an inhibition. Some improvement in the conversion efficiency could be expected if one could reduce the organic acids to more common levels of a few hundred rather than a few thousand mg/ℓ.

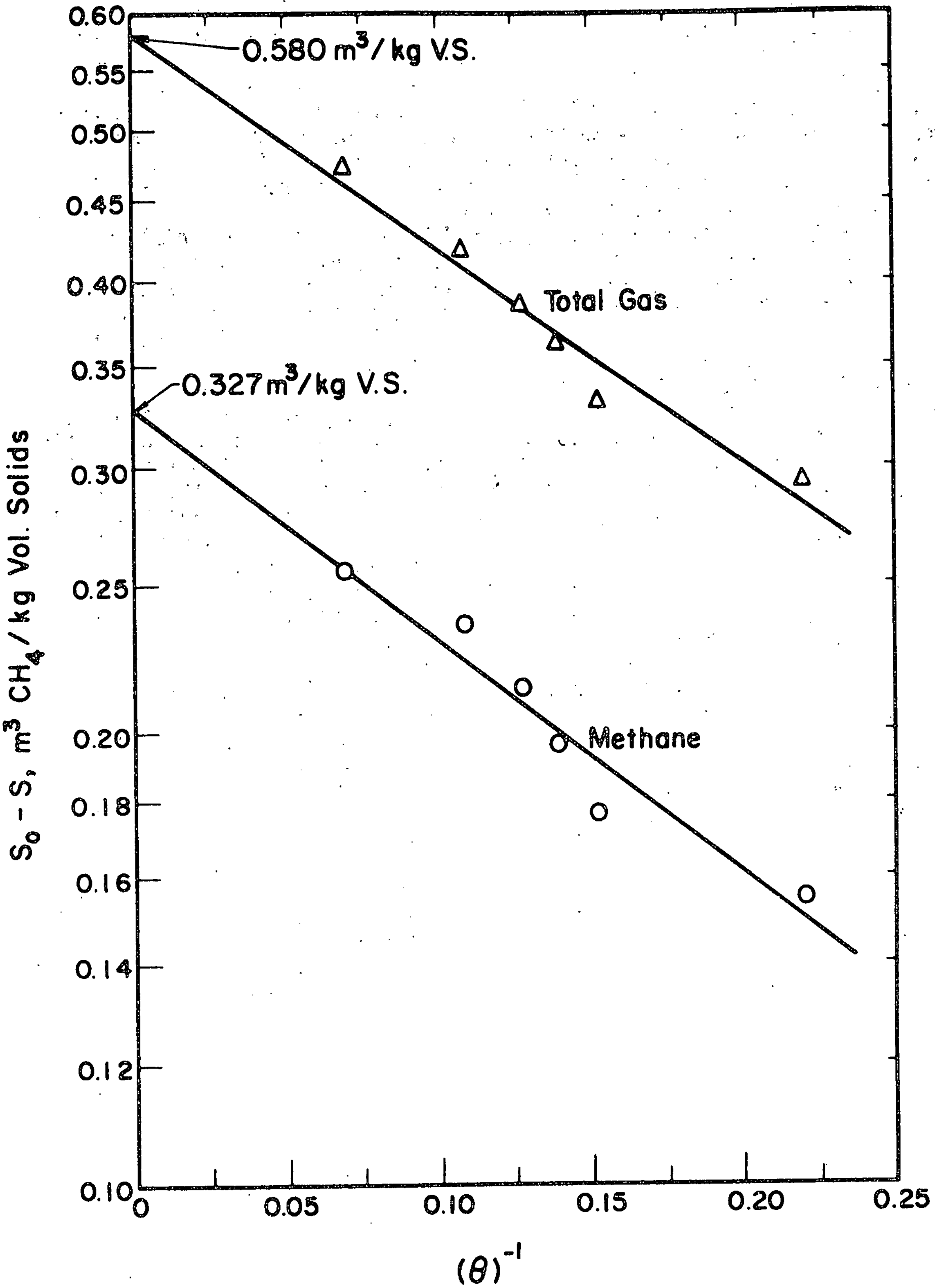


Figure 20. Determination of Biodegradability of Alfalfa

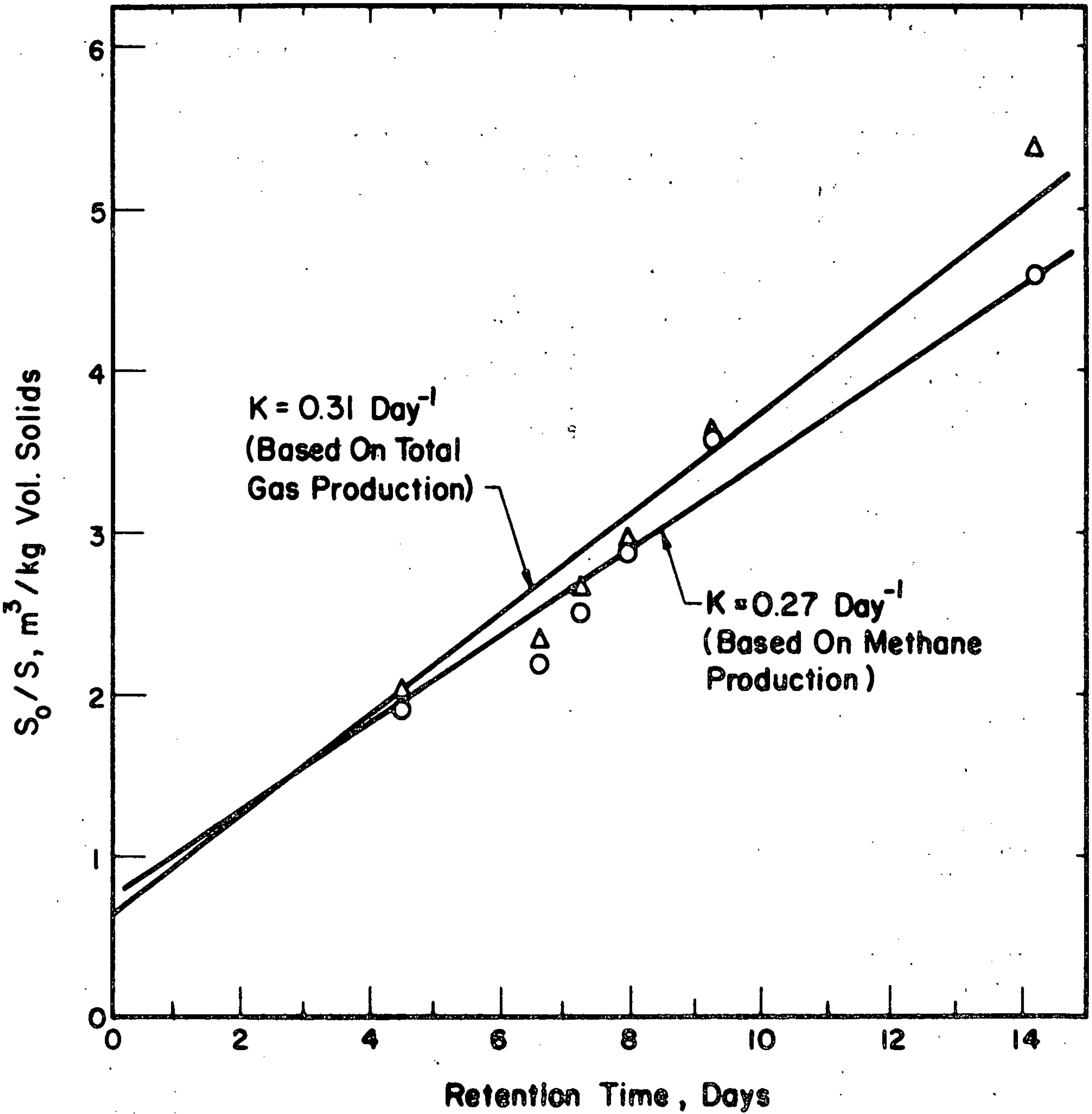


Figure 21. First Order Rate Constant Determination (Alfalfa)

FERMENTED SLURRY CHARACTERISTICS

The fermented slurry presents a major management problem when withdrawn from the reactors. This material must be processed in an acceptable environmental manner. The only viable technique for handling this material is to store it until it can be applied to the land. The solids remaining after fermentation may have some by-product recovery value. In order to better understand the properties of this slurry, various tests were conducted to determine dewatering characteristics of the slurry, particle size distribution and the characteristics of the various size fractions.

Slurry Particle Size Distribution - Manure

The particle size distribution of the solids in the fermented slurry plays a major role in determining the solids recovery potential. The composition of these solids will determine their value in any by-product recovery system. A wet sieve analysis technique (see Appendix A) was used to obtain the particle size distribution.

A sample volume of 2 liters was obtained for each test. These samples were withdrawn from the appropriate slurry holding tanks while the tanks were being vigorously mixed to insure a representative sample. The 2 liter sample was separated into six different size fractions. Samples for this analysis were obtained from reactors operating under different conditions.

The results of the wet sieving of manure slurries are shown in Figure 22. These data provide some interesting information regarding the size distribution of the feed solids and the fermented solids. A significant portion of the total solids and volatile total solids passed the 200 mesh sieve. These solids represented the small suspended and colloidal solids as well as the dissolved solids. Solids from reactors operating at long retention times generally had more solids passing the 200 mesh screen than the reactors operating at short retention times. The total solids passing the 200 mesh screen ranged from 40 to 55 percent for the fermented slurries. In the raw manure slurry, the percent of total solids passing the 200 mesh screen was 34 and 43 percent for the samples tested.

The distribution of suspended solids as defined for this study is of more importance. Removal of insoluble solids passing the 200 mesh screen (74 m) will generally require chemical treatment. This will greatly increase the cost of processing these solids. The distribution of suspended solids shows that the majority of the solids can be recovered as a relatively large particle. In all fermented slurries tested 90 percent of the solids retained on the 200 mesh screen were retained on the 100 mesh (149 μm) screen. With the exception of the reactors operated at long retention times, 90 percent of the solids retained on the 200 mesh screen were retained on the 50 mesh screen (297 μm). Therefore, a major portion of these solids can be recovered without the use of expensive dewatering systems.

This relationship is shown graphically in Figure 22 where the percent of solids passing a given size screen is plotted against screen size. The dry manure, after passage through the mill with a 6.3 mm screen, was subjected to a dry sieve analysis resulting in the size distribution shown in Figure 22. When the manure was slurried with water, the size distribution changed substantially as shown by the curve for the feed slurry. This curve is for only those solids that are equal to or greater than the 200 mesh size. This substantial change in size distribution can be attributed in part to an increase in particle size due to absorption of water, but more likely to the adhesion of the small particles to the larger particles. Washing removed additional fine solids.

This figure also illustrates the variation in size distribution resulting from increased stabilization. More organics were fermented to gas at the longer retention times resulting in smaller particles. Of the two curves marked as 10-day retention time, the upper curve was for a 58°C fermentation temperature, while the lower curve was for a 40°C temperature. A highly loaded system as evidenced by the curve marked as a 2.5-day retention time shows a particle size distribution only slightly different from the feed slurry.

This analysis suggests that a manure fermentation system operated to obtain maximum gas production will produce a slurry containing solids that are more difficult to recover. Conversely, a system with a reduced conversion efficiency may be expected to produce a slurry containing solids that are more easily recovered.

Composition of Fermented Manure Residual Solids

The potential for by-product recovery depends upon the composition of the residue from the fermentors. In particular, the composition of the various particle sizes will be of significance in establishment of the type of solids recovery system required. Samples for fiber analysis and nitrogen analyses were taken from the various size sieves after the particle size distribution had been completed. (See Appendix A for analytical techniques.)

The results of the fiber analysis shown in Table 26 are the average of 8 sets of analyses conducted on the reactor effluents. The extractable material as measured by an alcohol-benzene extraction was approximately 1 percent in the reactor effluents. The composition of the remaining solids is generally considered to be holocellulose, lignin and ash. In any sample containing nitrogeneous compounds, a correction for the protein content is applied. There are several techniques for protein determination. However, for this correction, protein was calculated as 6.25 times the organic nitrogen. The protein level of these solids was considerably lower than expected. During the washing process, it is probable that some of the bacterial biomass was dislodged and passed through to the pan. Therefore, these protein values were used only in correcting the fiber composition.

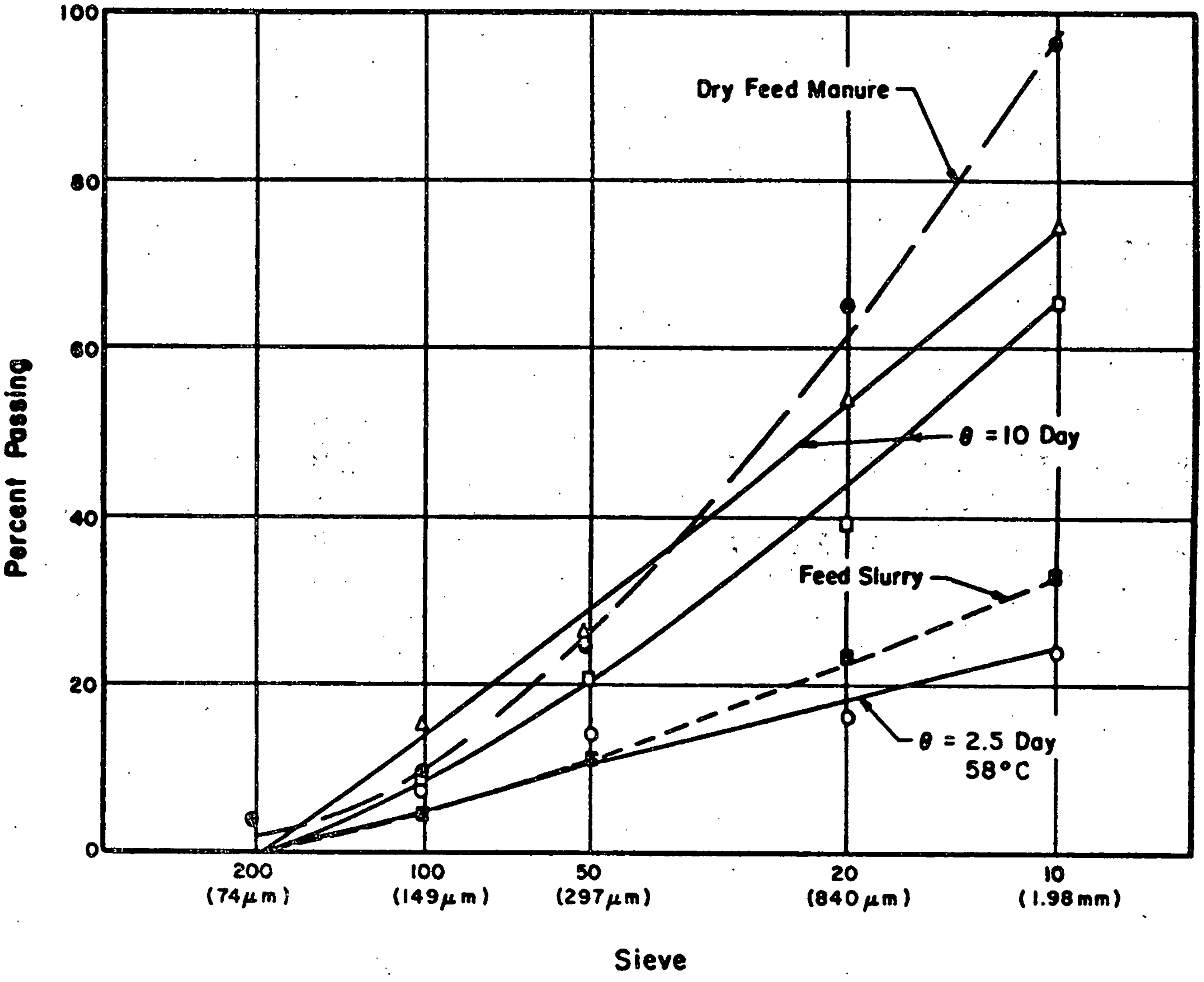


Figure 22. Manure Particle Size Distribution at Various Process Stages.

Table 26. Fiber Analysis - Reactor Effluent

Sieve Size	Tot. Solids Retained on Sieve - %	Percent of Solids Retained on Sieve				
		Ext.	Cellulose	Lignin	Protein	Fixed Solids
10	27.2	1.1	52.7	14.8	1.4	30.0
20	8.6	1.4	50.7	11.7	1.8	34.7
50	8.8	1.3	44.3	5.7	2.6	46.1
100	4.7	1.1	38.1	3.3	2.1	55.4
200	4.5	1.0	37.0	9.4	1.5	51.1
Pan	46.4	---	----	---	---	----

These data clearly show that essentially all of the recoverable solids exist as particles greater than 0.3 mm (50 mesh sieve). The ash content of these solids varied from 30 to 46.1 percent. The cellulose and lignin content decreased as the ash content increased with the smaller particles. In general, the protein content was less than 3 percent. It was, however, relatively uniform with particle size distribution. Based on these analyses, the most practical system for solids recovery appears to be a mechanical screen sized to capture 0.25 mm particles. The screened solids can then be pressed to remove additional water if desired.

Corn Stover Slurry Particle Size Distribution

The particle size distribution for corn stover depended upon the degree of size reduction obtained during the milling step as shown in Figure 4. Milling through the 3.2 mm screen resulted in a much smaller particle than that obtained with the 6.3 mm screen. The importance of particle size reduction in the processing of corn stover has not been defined to date. It is probable that the stover will need to be chopped prior to fermentation to assist in material handling.

When the stover that had been milled through the 3.2 mm screen was slurried with water, the particle size distribution as determined by the wet sieve analysis changed significantly. The data in Table 27 show that the total solids were either large or small. In the feed slurry, 76.1 percent of the total solids were larger than 1.98 mm. For the remaining 23.9 percent, 21.1 percent were smaller than 74 μm. This fraction includes the soluble solids as well as small colloidal particles.

The action of the microorganisms during fermentation tended to reduce the particle size. As can be seen in Table 27, there was a significant decrease in the solids retained by the 10 mesh sieve, decreasing from 76.1 percent in the feed slurry to 63.2 percent in the reactor slurry. This effect is also shown in the "suspended" solids. In the feed slurry,

Table 27. Slurry Particle Size Distribution - No Thermochemical Pretreatment

Sieve Size	Percentage of Slurry Solids Retained		
	Total Solids	Volatile Total Solids	Suspended* Solids
	Feed Slurry		
10	76.1	76.5	96.3
20	76.8	--	97.4
50	77.8	--	98.4
100	78.4	--	99.4
200	78.9	79.4	100.0
Pan	100.0	100.0	--
	Reactor Effluent, θ = 14.7 days, Temp = 58°C		
10	63.2	65.2	89.9
20	65.6	--	93.3
50	67.3	--	95.6
100	68.7	--	97.6
200	70.3	72.6	100.0
Pan	100.0	100.0	--

*Suspended solids are considered to be those solids retained on the 200 mesh sieve

96.3 percent of this fraction was retained by the 10 mesh sieve. In the reactor slurry, the percentage was only 89.9. These data show that the fermentation increases both the soluble solids and the weight of solids found in the smaller size range.

Thermochemical pretreatment of the corn stover would also be expected to shift the particle size distribution. As shown by the data in Table 28, there was a relatively minor shift in the solids distribution when the low NaOH dosage (3 g/100 g) was used. This pretreatment step resulted in a marginal increase in gas production. When a higher dosage of NaOH (5 g/100 g) was employed, there appeared to be a significant shift in the particle size distribution as shown in Table 29. The solids passing the 200 mesh sieve (74 μm) increased from 21.1 percent with no thermochemical pretreatment to 34.1 percent at the higher NaOH level. The solids retained on the 10 mesh screen decreased because of the above, but also because the solids in the size range between the 10 and 200 mesh sieve increased. Based on these analyses, it would appear that the particle size was changed by the thermochemical pretreatment.

The soluble solids in the reactor slurries accounted for about one-half of the solids passing the 200 mesh sieve. When feeding untreated stover, a reactor effluent containing 36.0 g/ℓ of total solids contained 4.8 g/ℓ of soluble solids. The soluble solids accounted for approximately

Table 28. Slurry Particle Size Distribution - 3 Percent NaOH Pretreatment

Sieve Size	Percentage of Slurry Solids Retained: Total Solids	Volatile Total Solids	Suspended* Solids
		Feed Slurry	
10	73.7	74.5	96.3
20	74.7	75.8	97.8
50	75.8	77.2	99.1
100	76.2	77.8	99.5
200	76.5	78.3	100
Pan	100	100	
	Reactor Effluent,	= 7.75 days, Temp = 58°C	
10	63.7	67.3	91.7
20	66.3	--	95.4
50	67.5	--	97.2
100	68.4	--	98.5
200	69.4	73.4	100.0
Pan	100.0	100.0	--

*Suspended solids are considered to be those solids retained on the 200 mesh sieve

14 percent of the total solids. As can be seen from the data in Table 27, approximately 30 percent of the total solids passed the 200 mesh sieve. This is a significant quantity of very small insoluble solids that will be difficult to remove from the filtrate/centrate.

The caustic pretreatment (3 percent NaOH) did not greatly alter the feed slurry particle size distribution. However, as shown by the data in Table 28, the microorganisms do change this size distribution. The reactor effluent did show a reduction in the larger size particles. However, the "suspended" solids distribution was not substantially different from the feed slurry.

An increase in the NaOH dosage used in the pretreatment only increased the particle size reduction. The feed slurry at the 5 percent NaOH dosage exhibits a smaller particle size, with 34.1 percent of the total solids passing the 200 mesh sieve. Processing at a 5.2 day retention time changes the total solids only a little. More of the solids are retained on the intermediate sieves. Therefore, the "suspended" solids capture obtained with a 10 mesh screen would be less than obtained in the effluents shown in the previous tables. Solids recovery from the effluent from reactors processing thermochemical pretreated stover will be more expensive. For untreated stover, screening with a 10 mesh screen would recover 63 percent of the total solids and 90 percent of the solids greater than 74 μm size. As shown in Table 29, only 56 percent of the total solids

Table 29. Slurry Particle Size Distribution - 5 Percent NaOH Pretreatment

Sieve Size	Percentage of Slurry Solids Retained: Total Solids	Volatile Total Solids	Suspended* Solids
	Feed Slurry		
10	60.0	59.5	91.1
20	62.1	--	94.4
50	64.6	--	98.0
100	65.3	--	99.1
200	65.9	65.4	100.0
Pan	100.0	100.0	--
	Reactor Effluent, θ = 5.2 days, Temp = 58°C		
10	56.3	59.1	84.0
20	58.8	--	87.9
50	63.6	--	95.2
100	65.2	--	97.5
200	66.8	70.1	100.0
Pan	100.0	100.0	--

*Suspended solids are considered to be those solids retained on the 200 mesh sieve

and 84 % of the "suspended" solids can be captured by the 10 mesh screen.

Composition of Stover and Residual Solids

Analysis of the corn stover was conducted to determine the nutrient level and the cellulose content. The analysis of six separate samples of corn stover yielded the results shown in Table 30. If only the carbon in the total cellulose is considered to be available, the carbon to nitrogen ratio is 33 to 1. This should be adequate to support microbial activity. However, it was necessary to add nitrogen in order to maintain approximately 200 mg/ℓ of ammonia nitrogen in the reactor. While significant nitrogen appeared to be present in the stover, it apparently was not available. The additional nitrogen requirements depended upon the amount of centrate recycle employed. Phosphorus was added, as K_2HPO_4, to supplement the phosphorus available. This also resulted in an increase in the potassium level of the slurries. Consequently, the quantity of N, P and K in the slurries will be a function of the amount of chemicals added. However, the distribution of these plant nutrients in the slurry may be of significance.

Analysis of the slurry solids to determine the composition of various fractions and changes associated with different treatment schemes were conducted. The solids collected on the sieves during the particle size distribution tests were used to determine the composition of these

Table 30. Composition of Corn Stover

Constituent	% Total Solids	% Volatile Solids
TKN	0.63	0.83
Phosphorus	0.11	0.15
Potassium	0.81	1.07
Total Cellulose	46.6	58.4
Lignin	23.5	29.4
Ash	20.2	--

solids. The solids retained by sieves other than the 10 mesh were of insufficient quantity to use in the analyses. Therefore, only those solids retained on the 10 mesh sieve and those captured in the pan were used for analysis. The results are shown in Table 31.

From these data, one can see that the phosphorus content is very low in both size fractions. The phosphorus added to the system was soluble and, except for that utilized by the microorganisms, would be expected to be found in the soluble solids fraction. In general, the phosphorus content of larger size fractions of these slurries was about the same as the original corn stover (see Table 30). While a significant portion of the phosphorus is associated with the larger particles, it is probably unavailable. Certainly the soluble phosphorus in the liquid fraction would be more available for plant nutrients. A similar observation can be made for the potassium except that a much greater proportion of this ion was present in the liquid fraction.

The nitrogen data also show that most of the nitrogen is found in the fraction passing the 200 mesh sieve. The ammonia added for microbial nutrition is soluble and accounts for approximately one-half of the nitrogen found in this size fraction. The organic nitrogen content of those small size particles is significantly higher than that found in the larger size fraction. This would suggest that much of the bacterial mass is present in the particle size fraction passing the 200 mesh sieve. Any protein recovery scheme would necessarily concentrate on this size fraction.

The change in the total cellulose compostion of the solids in the different slurries reflects the conversion efficiency achieved. For those reactors receiving untreated stover, the cellulose content of the various size fractions did not change significantly. As the conversion efficiency increased, as was the case for the reactor receiving stover pretreated with 5 percent NaOH and operated at a retention time of 14.7 days, the cellulose content of the solids decreased substantially. This was especially true for the large size fraction.

5. Wheat Straw Slurries

Only limited data were obtained on the wheat straw slurries. Gas

Table 31. Composition of Various Size Fractions

Particle Size	% Total Slurry Solids	Composition - % of Size Fraction					
		Holo-Cellulose	Nitrogen		K	P	Ash
			TKN	Organic			
Feed Slurry, No Pretreatment							
>1.98 mm	76.1	50.3	0.61	0.37	0.78	0.12	18.5
< 74 μm	21.1	36.1	2.07	1.02	5.40	0.48	20.8
Reactor Effluent, No Pretreatment, $\theta = 14.7$ Days							
>1.98 mm	63.2	53.0	0.65	0.39	0.26	0.10	23.6
< 74 μm	29.7	31.3	1.76	0.83	5.04	0.48	31.5
Feed Slurry, 3% NaOH Pretreatment							
>1.98 mm	73.7	49.6	0.55	0.47	1.20	0.13	37.2
< 74 μm	23.5	22.5	2.01	1.51	4.84	0.48	7.2
Reactor Effluent, 3% NaOH Preatment, $\theta = 7.75$ Days							
>1.98 mm	63.7	49.2	0.61	0.37	0.26	0.09	19.4
< 74 μm	30.6	24.8	2.08	1.14	4.53	0.41	33.7
Reactor Effluent, 3% NaOH Preatment, $\theta = 14.7$ Days							
>1.98 mm	36.3	40.6	0.49	0.27	0.29	0.13	32.6
< 74 μm	52.4	21.0	2.42	1.72	5.61	0.45	25.3
Feed Slurry, 5% NaOH Preatment							
>1.98 mm	60.0	52.5	0.37	0.28	0.54	0.10	20.0
< 74 μm	34.1	29.7	1.25	0.83	5.07	0.42	18.3
Reactor Effluent, 5% NaOH Preatment, $\theta = 5.2$ Days							
>1.98 mm	56.3	45.2	0.36	0.39	0.12	0.05	26.2
< 74 μm	33.2	23.9	1.75	0.59	3.91	0.32	36.9
Effluent, 5% NaOH Preatment, $\theta = 14.7$ Days							
>1.98 mm	27.8	23.5	1.05	0.94	0.18	0.15	52.8
< 74 μm	62.2	32.0	2.46	1.06	4.01	0.19	52.9

production data were not good and it appeared that straw was not a likely candidate feed stock. Milled straw exhibited essentially the same particle size distribution as stover (see Figure 4). However, in slurry form, a smaller percentage of the straw slurry was retained on the 10 mesh screen. There appeared to be a higher percentage of solids in the 74 m to 2 mm range than found with the stover as shown in Table 32. Upon fermentation, the particle size of the straw was further reduced. From these data, one could expect that solids recovery from the fermenter effluent will be more difficult and expensive. Because of the low percentage retained in the 10 mesh screen, chemical conditioning may be necessary to obtain an efficient recovery of these solids. Analysis of the fiber content of the individual size categories was not undertaken on these slurries.

Table 32. Particle Size Distribution for Wheat Straw Slurries

Sieve Size	Percentage of Slurry Solids Retained	
	Feed Slurry	Fermented Slurry
10	59.4	50.1
200	65.3	55.1
Pan	100	100.0

SLURRY DEWATERING BY CENTRIFUGATION

The objective of this study was to evaluate the efficiency of the centrifuge on solids capture and solids dewatering. A Sharples/Fletcher Mark III solid bowl basket centrifuge was used for most of the centrifuge analysis. This unit had a variable speed drive with a maximum speed of 3400 rpm (2200 x g). Since this unit did not provide for a continuous cake discharge, a predetermined volume of slurry was used in each test so that the solids did not overload the bowl.

A Sharples P-600 Super-D-Canter continuous discharge centrifuge was also used for part of the study. This unit operated at a constant speed of 2400 rpm. Analysis with this unit was limited to the wheat straw slurry subjected to a caustic heat pretreatment. It was found that the unit could not handle the solids loading even at the lowest permissable pumping of the corn stover slurry or regularly treated wheat straw slurry. Due to the solids characteristics, the unit plugged with solids and shut down at these feed rates. It was not available for testing when the manure fermentation studies were underway.

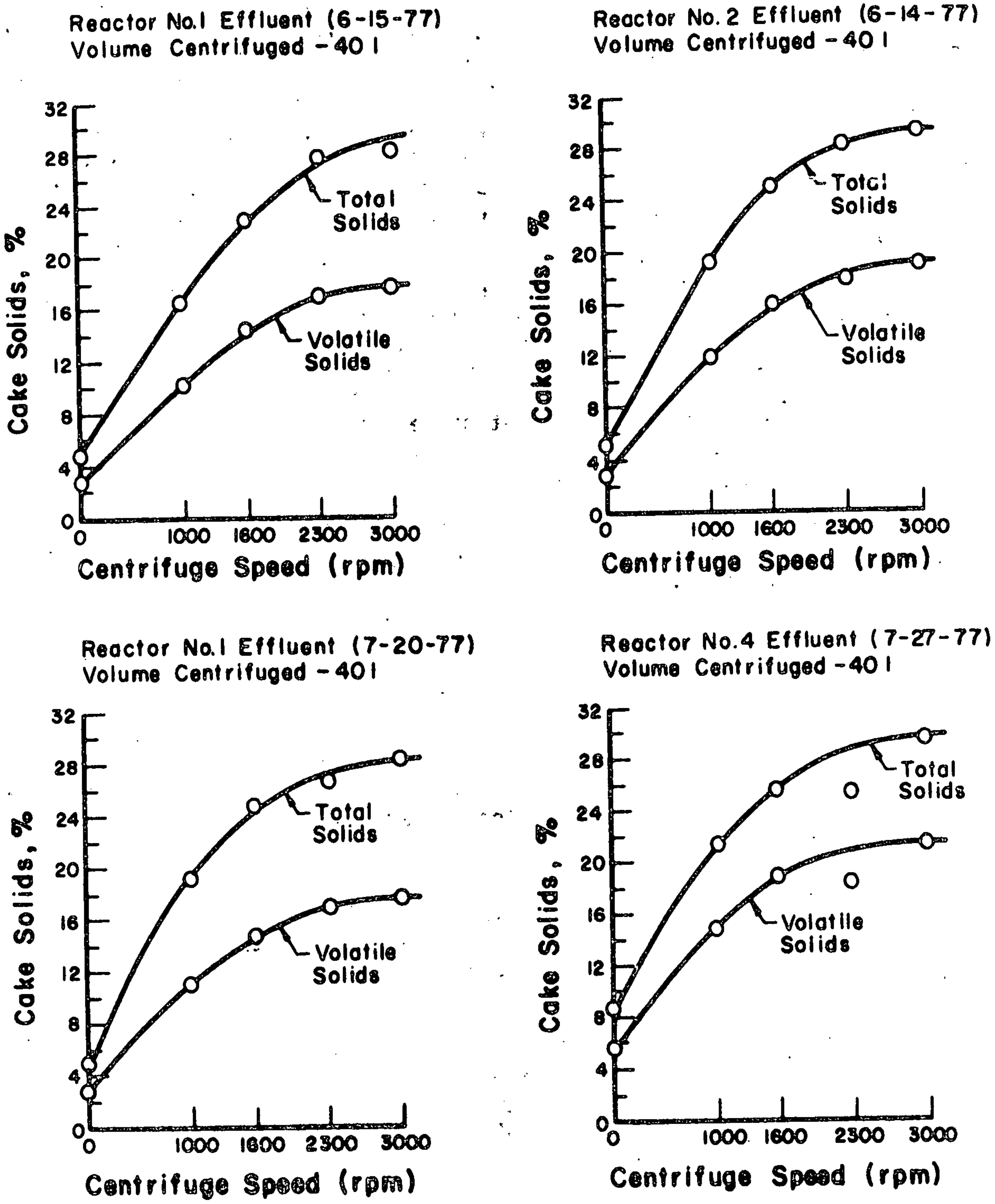
Manure Slurry Dewatering

The digested manure slurries were pumped to the Mark III centrifuge at a fixed rate of 8 liters per minute. This pumping was continued until approximately 40 liters was passed through the centrifuge. The centrate samples were taken from the unit discharge line after approximately 20 liters had been pumped through the unit. After the run was complete, the centrate remaining in the bowl was decanted. Representative samples of the cake were obtained by thoroughly mixing the entire contents of the bowl by hand. Samples of the feed slurry were also obtained from the reactor effluent holding tanks. Duplicate tests were run on all samples and the results averaged.

After completion of one run, the centrifuge speed was readjusted and another run initiated. Speeds of 1000 (200 x g), 1600 (510 x g), 2300 (1050 x g) and 3000 rpm (1790 x g) were used for the tests. The percent solids of the cake are plotted against the centrifuge speed (rpm) and are shown in Figure 23. A curve for both total and volatile solids is presented in this figure. In each case, the ratio of volatile solids to total solids was relatively constant at 60 to 65 percent. At low speeds and g forces, the cake contained a considerable amount of water. At a rotational speed of 1000 rpm, the cake solids were found to be only 16 to 19 percent with a feed solids concentration of approximately 5.0 percent. Increasing the speed to 2300 rpm resulted in cake solids which varied from 22 to 27 percent.

The maximum cake solids were obtained at 3000 rpm with a high value of 30 percent. The curves show that very little additional solids capture was gained after approximately 2300 rpm. At the higher speeds the cake was very dry and was not easily removed from the bowl. The fermentor retention time apparently was not a factor in the dewatering tests since Reactor 1 was operating at a 10-day retention time while Reactors 2 and 4 were operating at a 3.8 day retention time.

The results for a reactor receiving a feed slurry of approximately 9.0 percent solids are shown for Reactor #4. As one might expect, the cake



Reactor No.1 Effluent (6-15-77)
Volume Centrifuged - 40 l

Reactor No. 2 Effluent (6-14-77)
Volume Centrifuged - 40 l

Reactor No.1 Effluent (7-20-77)
Volume Centrifuged - 40 l

Reactor No.4 Effluent (7-27-77)
Volume Centrifuged - 40 l

Figure 23. Cake Solids Produced During Centrifuge Tests

solids increased with increasing speed. From inspection of this curve, it would appear that the optimum speed was again 3000 rpm or less, as with the 5.0 percent feed slurry used in the other reactors.

The centrate percent solids are plotted against rotational speed for the same runs and are shown in Figure 24. Again, both total and volatile solids are plotted. The ratio of volatile solids to total solids was found to be between 65 to 70 percent. This is higher than the ratio for the cake solids.

With a 5.0 percent feed slurry, the lowest centrate solid percentage of 1.5 to 1.8 percent was obtained at the highest speeds. There was virtually no improvement in centrate solids capture after 2300 rpm. As with the cake solids, the fermentor retention time did not seem to influence centrate solids capture.

However, the concentration of the feed slurry had a pronounced effect upon the capture, as illustrated by Reactor #4 in Figure 24. Doubling the feed concentration has the effect of more than doubling the solids concentration at the lowest speeds, and increasing the values at the higher speeds by at least one half. Inspection of Figure 24 would indicate that the optimum speed was not obtained. The maximum speed of the Mark III unit is 3400 rpm; therefore, tests at higher speeds were not possible.

Corn Stover Slurries

During the initial testing of the digested corn stover effluent, some operational procedures had to be modified in order to produce reliable results. It was found that the maximum centrifuge speed that could be obtained varied from 2600 rpm (1344 x g) to 2800 rpm (1559 x g). The chosen range of centrifuge speeds investigated varied from 1000 rpm to the maximum allowable speed of either 2600 or 2800 rpm. This reduction in maximum speed resulted from replacement of bearings and supports that had experienced excessive wear.

The first set of results illustrate the effect of digester detention time (θ) and centrifuge speed on the cake solids concentration and percent solids capture. Table 33 lists the digester operating conditions for this portion of the study. Feed rates are approximate. Actual feed volumes were recorded and used to calculate the digester detention time.

Table 33. Digester Operating Conditions for Detention Time Study (Corn Stover Slurry).

Digester No.	Test Date	(C°) Temp	(l/day) Feed Rate	(%) Effluent TS	(%) Effluent VS
4	4-27-78	60	200	4.66	2.52
2	5-04-78	60	150	4.66	2.56
1	5-10-78	57	100	4.24	2.16
3	4-10-78	58	50	3.14	1.82

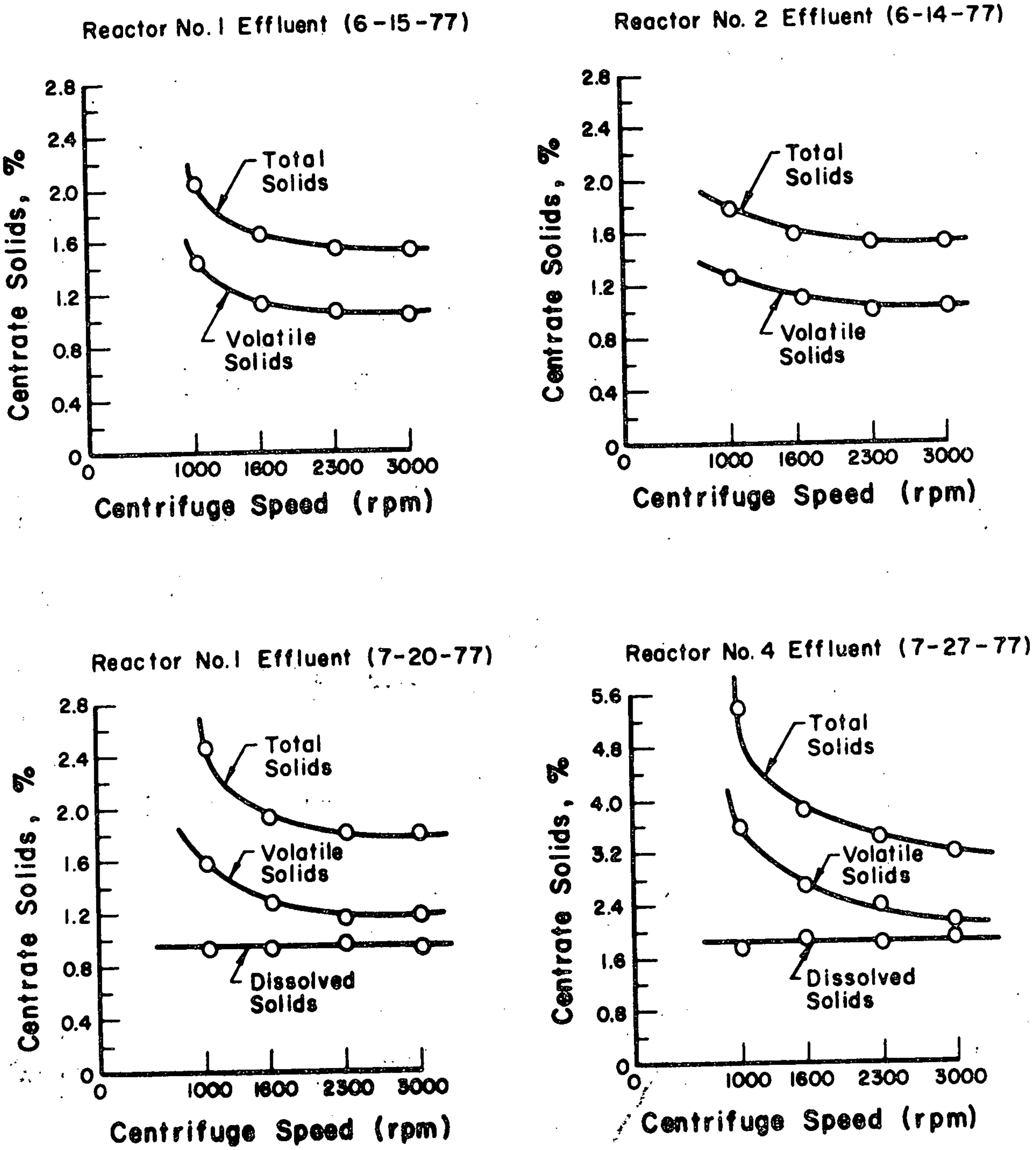


Figure 24. Centrate Solids Produced During Centrifuge Tests

Figure 25 shows how the cake solids varied for the various different digester detention times. Both total solids and volatile solids concentrations are represented. After observing these plots, it is apparent that both the total solids and volatile solids increase with increasing centrifuge speed. This rate is initially steep, but begins to level off somewhat at higher speeds. In order of increasing digester detention time, the maximum total solids concentration are 31%, 33%, 33%, and 31% at a centrifuge speed of 2600 rpm.

The corresponding volatile solids concentrations are 18%, 20%, 19%, and 17%. Table 34 summarizes these results below. There appears to be little variation in cake dryness in relationship to digester detention time based on these results.

Table 34. Maximum Cake Solids Concentration for Various Digester Detention Times. (Corn Stover Study)

Digester No.	(days) θ	Maximum Cake Solids*, %	
		TS	VS
4	3.75	30.9	18.0
2	5.0	33.4	19.6
1	7.5	33.0	18.5
3	15.0	31.0	17.4

*Centrifuge Speed of 2600 rpm (1344 x g)

The percent solids capture is a parameter reflecting the percent solids removal from the slurry effluent. This parameter is represented by the following equation:

$$\% \text{ Capture} = \frac{C_c(C_o - C_e)}{C_o(C_c - C_e)} \times 100 \qquad (3)$$

where C_o = initial slurry concentration,

C_c = cake concentration,

C_e = centrate concentration.

One can regard the objective of the cake solids analysis as trying to remove water from the solids residue fraction. Similarly, the objective behind a percent solids capture analysis is to try to remove the solids from the remaining water fraction. Both a dry cake and clean centrate are desired.

The maximum percent solids removal are summarized in Table 35 for each of the digester effluents. The maximum suspended solids capture ranges from 76% to 87%, while the maximum total solids capture ranges from 66% to 80%, at centrifuge speeds of 2600 rpm. Even at a low centrifuge speed, the percent capture was only slightly less than at the high speeds. At 1000 rpm the suspended solids capture ranged from 66% to 83%, while the total solids capture ranged from 58% to 76%.

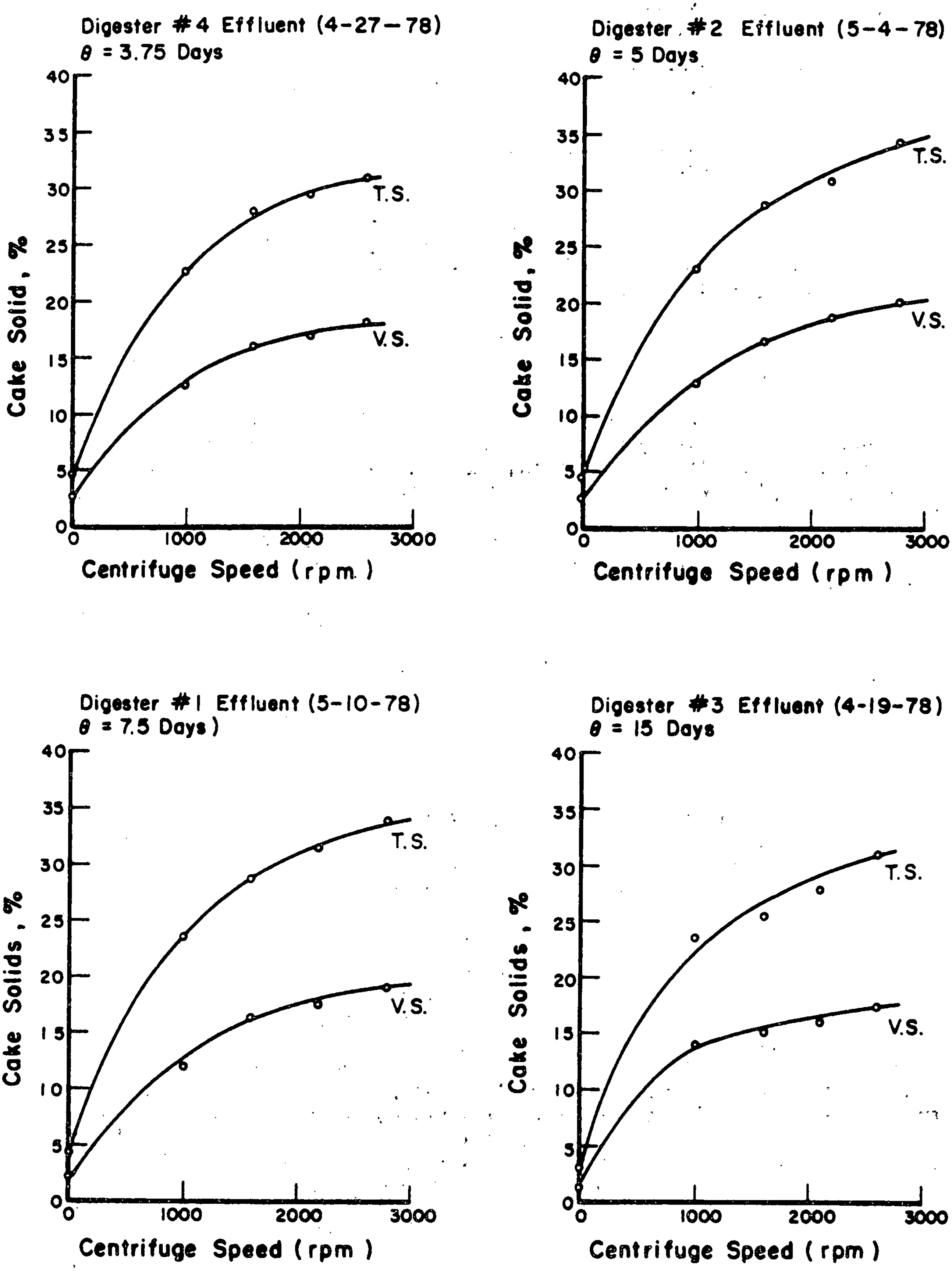


Figure 25. Cake Solids for Various Digester Detention Times Using Corn Stover Slurry

Table 35. Maximum Percent Capture for Various Digester Detention Times. (Corn Stover Study)

Digester No.	(days) θ	Maximum Percent Capture* TS	TVS	SS	VSS
4	3.75	80.0	79.5	87.4	84.9
2	5.0	77.0	76.5	85.0	82.2
1	7.5	74.0	72.5	83.0	80.0
3	15.0	65.5	66.8	76.4	74.1

* Centrifuge Speed of 2600 rpm

Wheat Straw Slurries

When the feed material was changed to wheat straw, it became evident that the straw slurry did not pump as well as the corn stover slurry. A routine procedure for steam heating the straw was instituted to improve the slurry pumping characteristics. The following set of results were performed using digester effluents to which the feed solids had been heat treated. The effects of digester detention time and centrifuge speed were investigated. Table 36 lists the digester operating conditions for this portion of the study.

Table 36. Digester Operating Conditions for Detention Time Study. (Wheat Straw Slurry)

Digester No.	Test Date	(°C) Temp	(1/day) Feed Rate	(%) Effluent TS	(%) Effluent VS
2	11-20-78	58	200	2.14	1.70
4	11-07-78	60	150	2.02	1.64
3	10-31-78	58	100	2.26	1.86
1	12-18-78	59	50	2.04	1.61

Figure 26 shows how the cake solids concentration varied with centrifuge speed at these various loading rates. As with the previous effluents, both total solids and volatile solids concentrations increase with increasing centrifuge speed for each of the digester effluents. The maximum solids concentrations, however, were lower than was achieved with the manure and stover effluents. Table 37 summarizes these results. At a centrifuge speed of 2800 rpm (1559 x g), the maximum total solids concentration varied from 21% to 25%, while the volatile solids concentration varied from 17% to 20%. Again, there appears to be little variation in cake dryness in relationship to digester detention time. It does appear, however, that the cake solids concentration decreases slightly with increasing digester de-

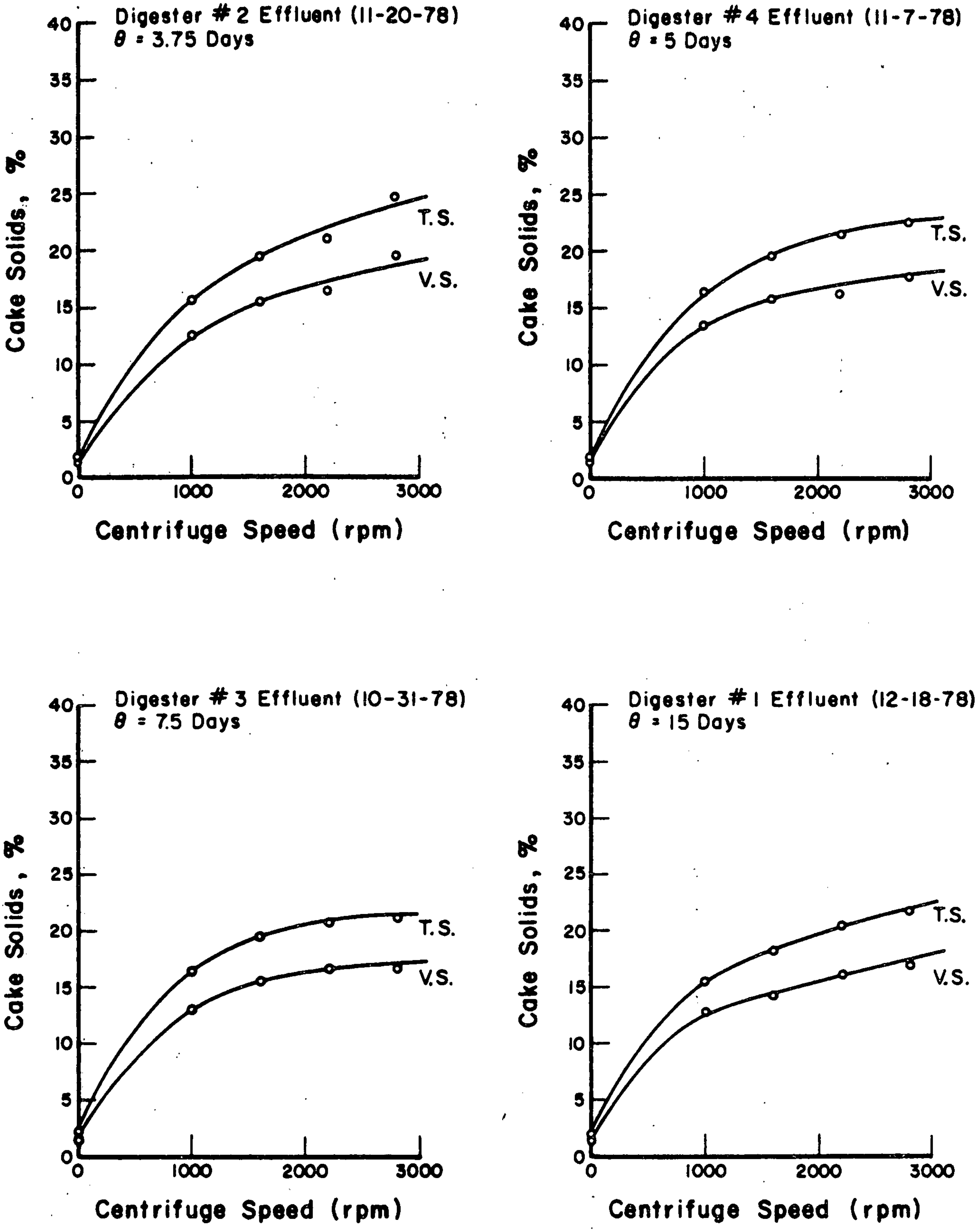


Figure 26. Cake Solids for Various Digester Detention Times Using Wheat Straw Slurry

tention time.

It should be noted that the slurry solids concentration when using wheat straw was about half that found with the corn stover and manure. Because of the lower solids loading on the centrifuge, the volume of the bowl occupied by the solids was less. This fact made it more difficult to extract the last bit of centrate. This may have increased the final cake moisture. However, one should also recognize that straw has a tendency to absorb more water than stover.

Table 37. Maximum Cake Solids Concentration for Various Digester Detention Times. (Wheat Straw Study)

Digester No.	(days) θ	Maximum Cake Solids*,% TS	VS
M2**	0.0	23.5	18.6
2	3.75	24.8	19.6
4	5.0	22.5	17.8
3	7.5	21.2	16.8
1	15.0	21.8	17.0

*Centrifuge Speed of 2800 rpm
**Mixing Tank with undigested straw slurry

The maximum percent solids capture for each of the digester effluents and for the mixing tank effluent are summarized in Table 38. At a centrifuge speed of 2800 rpm, the maximum suspended solids capture ranges from 83% to 90%, while the maximum total solids capture ranges from 70% to 74%.

Table 38. Maximum Percent Capture for Various Digester Detention Times. (Wheat Straw Study)

Digester No.	(days) θ	Maximum Percent Capture* TS	TVS	SS	VSS
M2**	0.0	74.2	83.6	90.0	91.3
2	3.75	70.1	79.7	83.5	85.5
4	5.0	70.8	79.6	84.8	86.4
3	7.5	75.2	83.9	87.0	88.6
1	15.0	68.8	78.7	83.1	85.5

*Centrifuge Speed of 2800 rpm
**Mixing Tank with undigested straw slurry

The following portion of the wheat straw study involved a thermochemical pretreatment of the straw slurry prior to digestion. Sodium hydroxide and straw were mixed together and added to a pressure reactor. Water was then added to produce a slurry. Live steam was injected into the reactor to maintain a temperature of 115°C for approximately 4 hours. The NaOH concentration in this mixture was tested initially at 0.25 M. This was later decreased to 0.166 M, then later raised again to 0.30 M. Table

39 lists the reactor operating conditions for this part of the study.

Table 39. Digester Operating Conditions for NaOH Pretreatment Study. (Wheat Straw Slurry)

Digester No.	Test Date	(°C) Temp	(Molar) NaOH	(1/day) Feed Rate	(%) Effluent TS	(%) Effluent VS
3	3-14-79	60	0.166	50	3.12	2.12
4	4-11-79	60	0.300	100	4.01	2.83

The maximum cake solids obtained are shown in Table 40. The 0.166 molar NaOH pretreated effluent produced a maximum total solids concentration of only 19%, as compared to the untreated effluent cake of 22%. The higher concentrated NaOH effluent, however, produced a maximum total solids concentration of 26%, as compared to the untreated effluent cake of 21%. It appears that this high sodium hydroxide pretreatment, therefore, improves the dewatering characteristics of the digested straw effluent.

Table 40. Maximum Cake Solids Concentration for NaOH Pretreatment Study. (Wheat Straw)

Digester	(Molar)	(1/day)	Maximum Cake Solids*,%	
No.	NaOH	Feed Rate	TS	VS
3	0.166	50	18.8	13.7
4	0.300	100	25.6	18.2

*Centrifuge Speed of 2800 rpm

The maximum percent capture data are summarized below in Table 41. Greater solids capture was obtained for the untreated digested effluents than for the NaOH treated effluents. This may be due, in part, to the higher initial effluents solids concentration of the effluent slurry (see Table 39).

Table 41. Maximum Percent Capture for NaOH Pretreatment Study. (Wheat Straw)

Digester	(Molar)	(1/day)	Maximum Percent Capture*			
No.	NaOH	Feed Rate	TS	TVS	SS	VSS
3	0.166	50	37.8	42.7	59.9	60.5
4	0.300	100	42.0	48.4	66.6	67.0

*Centrifuge Speed of 2800 rpm

The continuous conveyor discharge centrifuge was also used on the treated straw effluent. This unit operated at a constant rotational speed of 2400 rpm (bowl radius of 3.25 inches). The corresponding centrifugal force was 530 x g. In order to produce the equivalent force with the Mark III bowl centrifuge, a rotational speed of about 1600 rpm would be necessary.

Two tests were performed using the continuous centrifuge. The digester operating conditions for these tests are listed below in Table 42.

Table 42. Digester Operating Conditions for Continuous Discharge Centrifuge Study. (Wheat Straw)

Digester No.	Test Date	(°C) Temp.	(Molar) NaOH	(1/day) Feed Rates	% Effluent TS	% Effluent VS
3	3-19-79	60	0.166	50	3.02	2.21
4	4-11-79	60	0.300	100	4.01	2.83

For comparison, the Mark III bowl centrifuge was run at a rotational speed of 1600 rpm. Table 43 summarizes the results of these tests. A flowrate of 8 liters/minute was used through both centrifuge units in these tests.

Table 43. Cake Solids and Percent Capture for Continuous Conveyor Centrifuge and Mark III Centrifuge. (Wheat Straw)

Test		Cake Solids, %		Percent Capture			
Date	Unit	TS	VS	TS	TVS	SS	VSS
3-19-79	Continuous	23.6	18.4	28.5	36.9	46.7	52.1
"	Mark III	14.2	10.2	32.4	36.8	52.6	53.2
4-11-79	Continuous	22.8	17.1	36.0	40.7	56.5	56.1
"	Mark III	20.0	14.6	40.4	46.3	62.7	63.2

Both units operated at a centrifugal force of 530 x g. Despite the equivalent g force, the continuous centrifuge was able to produce a drier cake in both instances. A higher solids capture was obtained, however, using the Mark III unit. It is important to consider the detention time within each unit in order to understand why perhaps a better solids removal was attained using the Mark III centrifuge. The feed rate through each was 8 liters/minute. The volume occupied by the slurry in the Mark III unit was 10ℓ, while the corresponding volume for the conveyor unit was only 3.2ℓ. The respective detention times in each unit were therefore 1.3 minutes and 0.4 minutes.

Fermented Alfalfa Slurries

Because of the short test period employed with alfalfa as a substrate and the extreme operational (foaming) problems experienced with this substrate, only a limited number of centrifuge runs were made. Pumping of the slurry was considerably more difficult than previously encountered. Because of clogging problems, test runs were frequently aborted. The results of the test runs completed on the fermented alfalfa slurry are given in Table 44. These data suggest that it will not be possible to obtain a very dry cake when dewatering this slurry with a centrifuge. Clearly a 15 percent cake solids is not good. A considerable quantity of water remains in this cake. Solids capture is also very poor. The feed slurry for the centrifuge contained 3.09 percent total solids and 2.14 percent suspended solids. Using Equation 3, one calculates the maximum total solids capture to be 41 percent while the maximum suspended solids capture is only 57.3 percent. This is an unacceptable solids capture. One would be required to chemically condition the slurry in order to effect an acceptable solids capture either for solids recovery or to allow recycle of the liquid. This will impose a substantial cost on the processing system.

Table 44. Centrifugal Dewatering of Fermented Alfalfa Slurry

Speed	Centrate				Cake	
rpm	Tot. Solid %	Vol. Tot. Solids %	Sus. Solids %	Vol. Sus. Solids %	Tot. Solids %	Vol. Tot. Solids %
1300	2.24	1.73	1.31	1.08	12.32	11.49
1600	2.19	1.71	1.30	1.07	12.12	11.30
1900	2.05	1.56	1.11	0.92	12.76	11.58
2200	2.01	1.50	1.01	0.80	13.82	12.91
2500	1.98	1.45	1.00	0.84	15.20	14.24

SLURRY DEWATERING BY VACUUM FILTRATION

The objective of the vacuum filtration tests was twofold. The first objective was to develop a set of design parameters which will allow for sizing an efficient vacuum filtration unit to dewater the various slurries under investigation. The second objective was the development of several cause and effect relationships to aid in selecting and altering experimentation in order to achieve the most useful results. The experimental parameters can be divided into three categories: control variables, independent variables, and dependent variables. The control variables involve the condition or state of the sludge being investigated. Due to the dynamic test conditions of the total fermentation system, the incoming sludge was monitored to insure that the battery of tests was being conducted on a sludge of constant nature. The independent variables are those which can be systematically varied to ascertain the filtration characteristics of the slurries. The dependent variables are those which reflect the result of changing the independent variables. Table 45 outlines the three variable types.

Table 45. Deliniation of Control, Independent and Dependent Variables

Control	Independent	Dependent
Slurry Total Solids	Coagulant Type	Filtrate Total Solids
Slurry Particle Distribution	Coagulant Dose	Filtrate Dissolved Solids
	Polymer Type	Filtrate Suspended Solids
Slurry pH	Polymer Dose	Solids Capture
Slurry Temperature	Form Time	Filter Loading Rate
	Dry Time	
	Form Pressure	
	Drying Pressure	
	Filter Media Type	

The dependent variables are a measure of the process performance. This will determine the utility of this unit process for slurry dewatering. The cake solids, which defines the ratio of dry solids and water in the cake, are important should incineration of the cake be desired. It the cake contains 30+ percent solids by weight, combustion usually may proceed without the aid of auxiliary fuel. Or if the sludge is for land application, the higher the cake solids, the lower the weight of wet cake required to be transported to the application site.

The solids capture is the ratio of the suspended solids retained on the filter to those fed to the filter. If recovery in the solid phase is the primary interest a high solids capture value is necessary. If the main purpose is to recycle the liquid fraction, a high solids capture value might be desired to avoid a build up of refractory solids in the fermenter.

The three filtrate related variables, total solids, suspended solids, and dissolved solids, are also needed for evaluation of liquid recycle possibilities. These parameters, along with chemical analysis of these solid fractions, determine the amount of nutrients and alkalinity available for recycle.

The filter loading rate is a design parameter derived from the information revealed in the filter leaf test. It integrates the information into a loading parameter for the continuous vacuum filter system. Loadings are expressed as weight of solids processed per area of filter per time.

A laboratory filter leaf test procedure was used for the evaluation of the filtration characteristics of the reactor effluent slurries. This procedure employs a section of filter cloth that is commercially available for installation on a vacuum filter. The test cloth is subjected to the same sequence of operations encountered in an operating vacuum filter. A detailed discussion of this experimental procedure is presented in Appendix A.

The dewatering characteristics of the slurry can be changed by chemical conditioning. Various chemicals can be used to improve the filtration characteristics. Iron Salts, especially ferric chloride, are effective in this chemical conditioning. The addition of organic polymers has also been found to be of assistance.

A series of tests using the filter leaf test procedure was undertaken using three different media as follows. These media were provided by Eimco. In all experiments the iron dosage is expressed as g/l of $FeCl_3 \cdot 6H_2O$.

PO-808 - Polyethelene monofilament yarn, 1/1 plain weave, 40 x 23 thread count at 10.5 oz/yd^2

NY-415 - Nylon monofilament yarn, 1/1 plain weave, 40 x 40 thread count at 5.7 oz/yd^2

POPR-859- Polypropylene monofilament yarn, 2/2 twill weave, 68 x 30 thread count at 8.5 oz/yd^2

The NY 415 was the most porous of the three media used, while POPR-859 had the tightest weave. As would be expected, the media plays a key role in determining the response of the slurry to this dewatering technique.

Vacuum Filtration of Fermented Manure Slurries

Sludge conditioners used for these studies included lump form ferric chloride with six waters of hydration and two anionic polymers, Dow Purifloc A-22 and A-23. The stock solution of ferric chloride had a concentration of 100 g/l. The stock solutions of polymers had a concentration of 1 g/l. The concentrations of the stock solutions are expressed as weight of chemical per final volume of solution. It is important to note that all concentrations of chemical conditioners are expressed as grams of conditioner per initial volume of slurry rather than final volume after the conditioner has been added.

The success of sludge conditioning is dependent on the initial pH of the sludge and the final pH of the sludge after chemical conditioning. These pH levels were a function of the sludge's alkalinity. Table 46 depicts the initial and final sludge pH along with the associated chemical dosage. The pH depression by ferric addition is small because of the high alkalinity of digester effluent. The alkalinity averaged around 5000 mg/l as $CaCO_3$ during the period of investigation.

Table 46. Depression of pH as a Function of $FeCl_3 \cdot 6\ H_2O$ Dosage

Initial pH	g/l $FeCl_3 \cdot 6\ H_2O$	Final pH
7.7	1.6	7.1
8.0	1.7	7.3
7.9	1.9	7.2
8.1	2.1	7.1
7.9	2.5	6.9
7.9	3.0	6.8
7.9	7.0	6.5

The data shown in Table 47 provide some interesting information on the filtrability of this slurry. The slurry solids concentration varied somewhat, but in general, was in the 40 to 60 g/ℓ range. For the media tested, POPR - 859 produced an exceptional filtrate quality, about 150 mg/ℓ of suspended solids.

Table 47. Filter Leaf Test Results[1]

Filter Media	$FeCl_3$ g/l	Polyelec.[2] mg/l	Cake Solids %	Filtrate Sus. Solids - g/l
POPR-859	7.0	10(A22)	14.6	0.149
PO-808	7.0	10(A22)	21.1	0.694
PO-808	2.1	0	29.2	1.007
PO-808	2.1	5(A23)	21.2	0.884
PO-808	2.1	10(A23)	18.0	0.443
NY-415	1.7	0	24.0	0.920

[1] Form time - 30 sec., drying time - 120 sec.

[2] Polyelectrolyte - Dow Purifloc A22 and A23.

Unfortunately, this required a massive chemical dose and the resulting filter cake had a very high moisture level. The chemical flocculation of the fine particles results in a large quantity of water that is retained by the cake when removed by this media. The same chemical treatment resulted in a cake of 21.1 percent moisture for the PO-808 medium. However, the filtrate suspended solids concentration was significantly higher. The cake solids content for the PO-808 medium was 29.2 percent with lower chemical addition, but again, the filtrate suspended solids concentration was 1007 mg/l.

These data show that higher cake solids can be obtained with limited chemical addition when using a coarse weave media. The data also show that higher cake solids are produced at the expense of the solids capture. The filtrate suspended solids are significantly higher when a drier cake is produced. Attempts to use fine media such as the POPR-859 without chemical conditioning were a total failure. The media clogged immediately and it was not possible to pull any liquid through the test leaf.

As a result of several tests, it became apparent that the most effective filter media for solids recovery would be a course medium like NY415. The effect of ferric chloride dosage on this slurry filterability was determined. A cake solids of 20 percent was obtained without any chemical addition. A dosage of 1.7 g/l of $FeCl_3$ (68 lbs per ton of dry solids) produced the maximum filter cake solids of 25 to 26 percent. The filtrate suspended solids were reduced from 1250 mg/l at 0 mg/l $FeCl_3$ to 800 mg/l at $FeCl_3$ dosage of 1.7 g/l.

A series of tests was conducted using the above medium and chemical dosage. Variables were form time and dry time. The results are shown in Figure 27. As can be seen from the figure, cake dryness increased with a longer form time. Also, the solids capture was higher and the filtrate solids lower at the longer form time. Initial solids capture was simple screening by the filter cloth. As the cake thickness increased with form time, the solids capture resulted from deep bed filtration. Consequently, the percentage of smaller solids captured increased.

The expected vacuum filter performance based on the filter leaf test analysis is shown in Table 48. The finer medium, PO-808, provided a higher solids capture when a massive dosage of chemical was added.

Table 48. Expected Vacuum Filter Performance

Form Time Sec.	Dry Time Sec.	Cake Solids %	Filter Loading kg/m^2-hr*	Solids Capture %
NY-415, $FeCl_3$ - 1.7 g/l				
15	90	17.6	21.5	78.6
	105	17.0	17.6	77.4
	120	22.2	28.3	83.5
30	90	22.0	32.7	86.1
	105	21.9	28.8	90.2
	120	24.0	24.4	85.5
PO-808, $FeCL_3$ - 7 g/l, A 23-10 mg/l				
15	90	19.5	24.4	83.0
	105	21.3	18.1	82.0
30	90	19.4	25.9	93.5
	105	21.9	22.4	97.0
	120	22.3	18.5	96.0
	135	21.0	15.6	85.0

*Multiply kg/m^2-hr by 0.205 to obtain lb/ft^2-hr

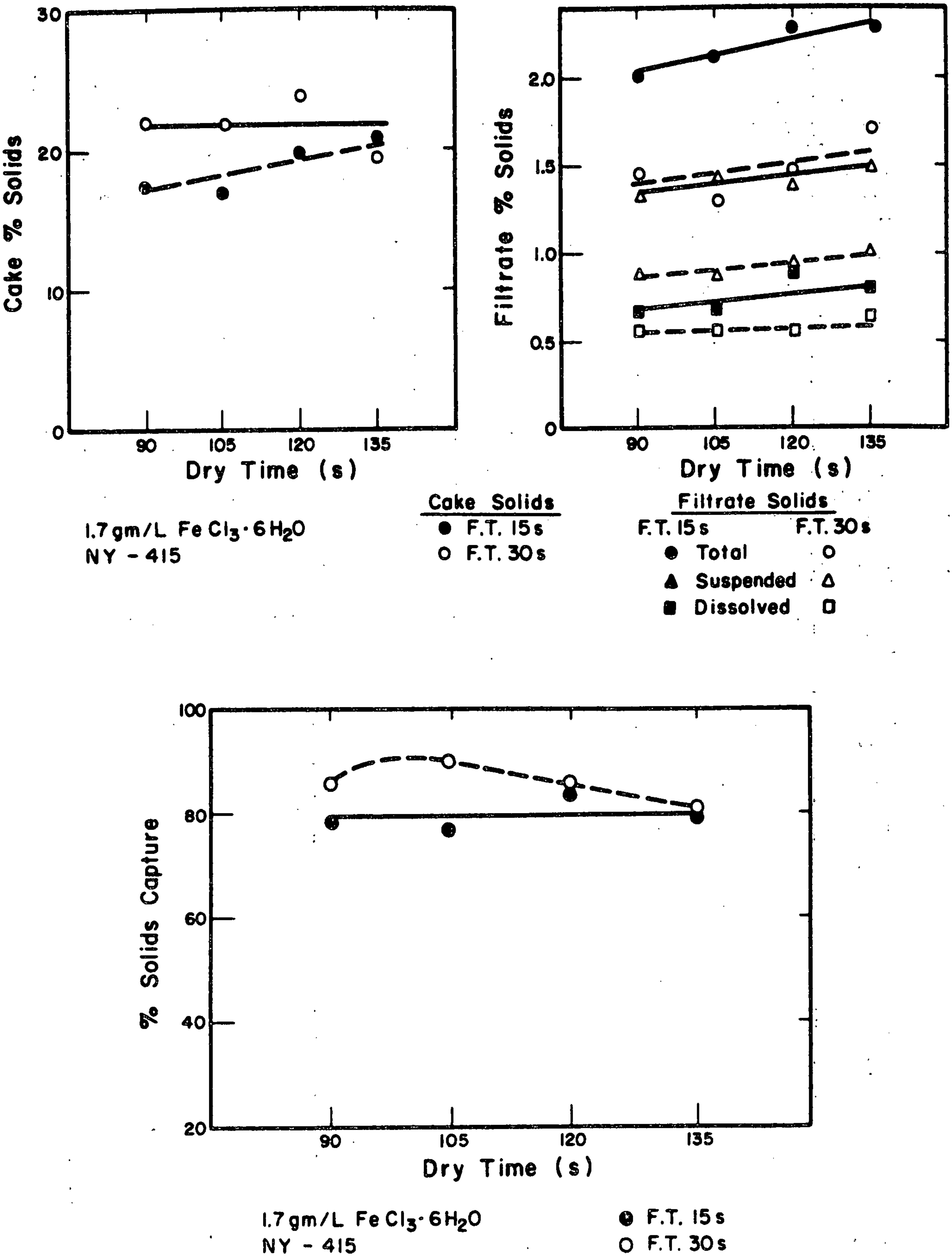


Figure 27. Vacuum Filtration of Manure Slurries.

Filtration rates were low and the cake moisture was low. The coarse medium NY-415 did not yield as high a solids capture, but the cake solids were somewhat higher. The filtration rate was also better than for the finer medium.

Based on the results of this study, it appears that vacuum filtration is a questionable option for dewatering of the fermented slurry. Filtration rates are low even when substantial quantities of chemicals are added to condition the sludge. The most effective solids removal system may well be a course mesh filter cloth that captures only the larger particles. The applied vacuum may assist in removing some of the excess water so that the cake is reasonable dry.

Vacuum Filtration of Fermented Corn Stover Slurries

Vacuum filtration studies were conducted on digested corn stover during the period which started February 2, 1978, and ended July 26, 1978. Effluent slurries were taken from Reactor 3 and were used in all studies in which the stover was not pretreated. This unit served as a control, operating with a retention time of 14.7 days. The average total solids concentration of the effluent slurries for the thirty-seven days of testing was 4.59 percent.

Chemical conditioners employed in these studies included $FeCl_3 \cdot 6H_2O$ and Dow Purifloc animic polymers, A-22 and A-23, plus two cationic polymers, C-31 and C-43. The chemical dosages are all expressed as grams of conditioner per initial volume of slurry.

The alkalinity of the fermented corn stover slurry averaged about 1300 mg/ℓ as $CaCO_3$ during the period of study. This value was much lower than the alkalinity encountered during the studies on cow manure. Consequently, the pH of the corn stover slurry was easier to depress with ferric salt addition. The relationship between pH depression of the corn slurry and ferric chloride addition is given in Table 49.

Filter leaf tests conducted on corn stover utilized the Eimco NY-415 medium. This selection was made for a number of reasons. Firstly, this medium can produce filter cakes without the aid of any chemical conditioning. Secondly, plugging does not appear to be a problem for this filter leaf. In addition, the mass of solids captured per cycle is large. This implies that high solids loading rates will be possible.

Table 49. Depression of pH as a Function of $FeCl_3 \cdot 6H_2O$ Dosage

Initial pH	g/l $FeCl_3 \cdot 6H_2O$	Final pH
7.6	0.467	6.9
7.6	0.667	6.8
7.6	1.0	6.7
7.7	4.67	4.2
7.7	6.67	2.8
7.4	8.67	2.6
7.4	10.0	2.5
7.4	11.67	2.4

The first tests run on the fermented corn stover did not involve chemical conditioning. The effects of varying form and dry time for this experimental mode were studied. Figure 28 shows that drier cakes were produced with longer form and dry times. The driest cake produced without chemical conditioning had a solids content of 20 percent. Increasing the form time beyond the range studied does not appear to substantially increase the cake dryness. A limiting factor in this experimental procedure is the weight of filter cake that can be suspended from the filter leaf upon withdrawal from the slurry. The filter cakes produced in the above tests were in excess of one inch thick. When a cake of this nature is removed from the slurry, it is saturated with fluid and is heavy. When using form times longer than 30 seconds, the cake usually falls from the filter leaf as it is withdrawn from the slurry. Increasing the drying time beyond 135 seconds increased the filter cake solids due to air drying of the cake. Since the cake releases water very quickly, thus allowing the movement of large volumes of air through the filter cake, extended dry times could tend to be expensive.

The limiting factor in attaining dry cakes with no chemical conditioning was the amount of water present in the large particles (those retained on a 10 mesh sieve). These particles had the ability to absorb large quantities of water. Since the fermented corn stover slurry had two distinct particle size distributions, it is likely that the vast majority of the particles retained by the filter leaf, when no chemical conditioners were used, was in the 10 mesh size category. Therefore, even if the interparticle spaces were completely drained of liquid, a large amount of water was still absorbed by the particles.

Figure 28 shows the response of the filtrate solids concentration to the test conditions. There was slight variation in the filtrate suspended solids concentration with respect to the form time.

Figure 28 also depicts trends which are peculiar to the filterability of fluid and of small particles through this filter cake and medium. A higher solids capture might be expected to occur at longer form times. This was not the case in this instance. The reason for the difference is that as the medium emerges from the slurry tank, the mass of particles retained by the filter medium and removed from the slurry tank was limited. Therefore, at long form times a disproportionate amount of filtrate was collected in the filtrate reservoir. Since some of the cake associated with this filtrate was not retained on the test leaf, the solids capture at the longer form times would be lower.

In an attempt to achieve higher cake solids, chemical conditioning with ferric chloride was investigated. For these tests and those to follow, standard form and dry times of 30 seconds and 120 seconds, respectively, were used in order to facilitate data comparison. The results are depicted as the solid symbols in Figure 29. As the dosage of ferric chloride increased, more of the smaller particles were retained by the filter cake. In the case of corn stover, the smaller particles contain less moisture than the larger particles. Therefore, the dryness of the filter cake increased with the dosage of ferric chloride. However, addition of ferric chloride introduced a gelatinous nature to the filter cake. For this reason, the increase in cake solids was small with respect to the massive amounts of ferric chloride added.

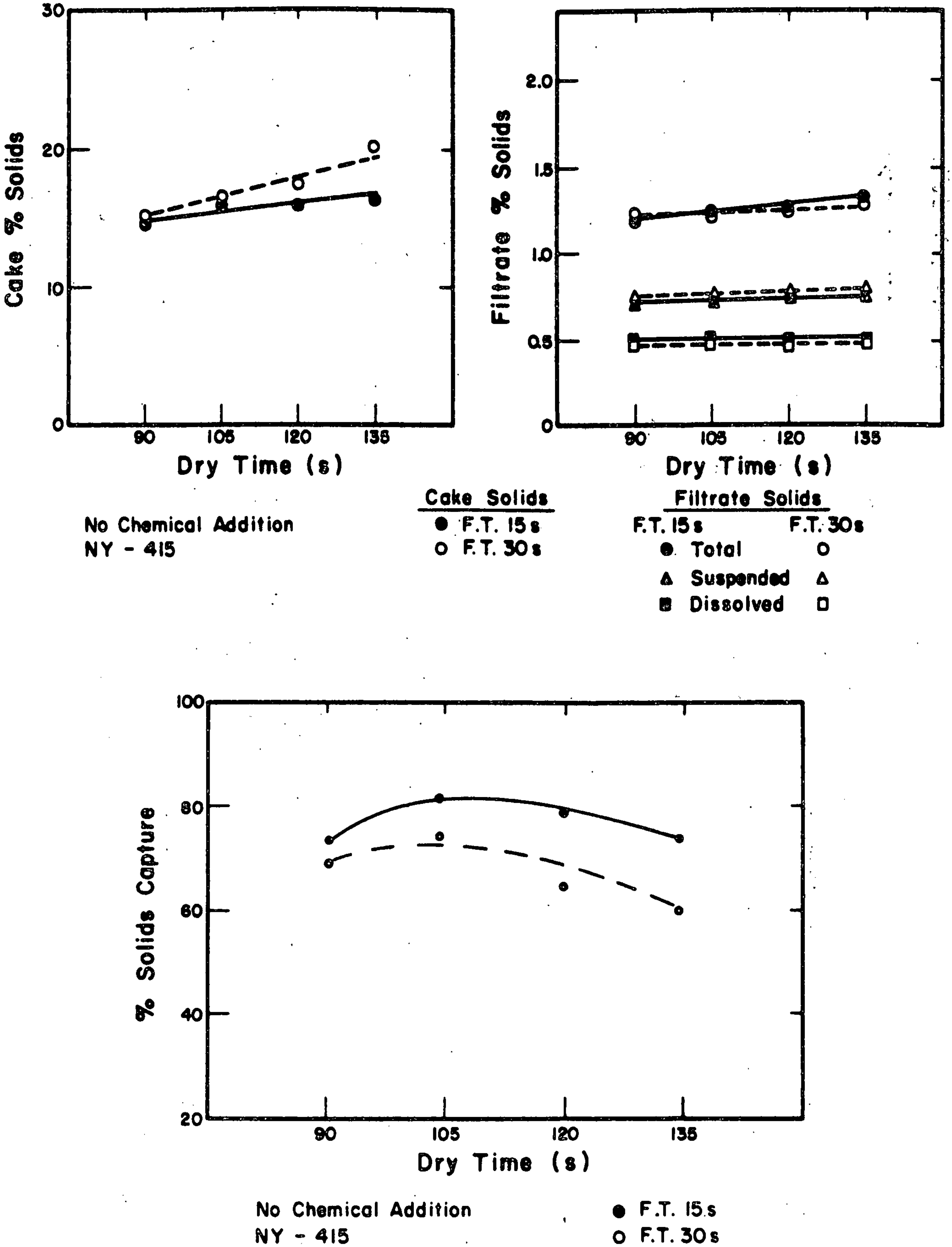


Figure 28. The Effects of Form Time and Dry Time on the Filter Performance

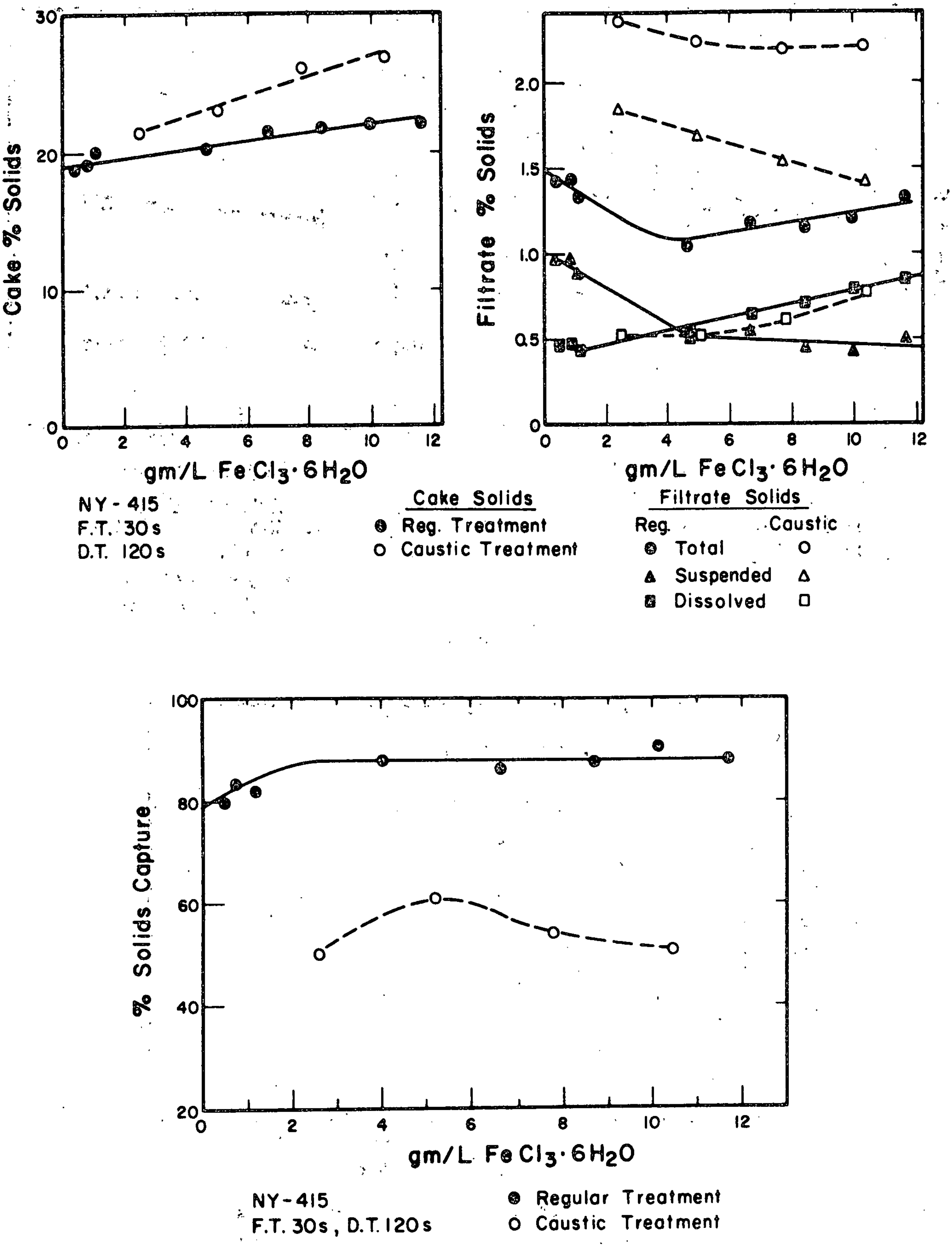


Figure 29. The Effect of $FeCl_3$ Conditioning on the Filter Performance

Examination of Figure 29 reveals that the fine suspended material was indeed being coagulated and incorporated into the filter cake. The increase in the dissolved solids concentration reflected the addition of ferric chloride to the slurry. Figure 29 also shows that approximately 90 percent of the suspended solids can be captured with the use of ferric chloride as a conditioner on the slurries that had not received the thermochemical pretreatment.

Similar tests were run on a slurry which had undergone caustic pretreatment prior to digestion (see Figure 29). This pretreatment consisted of dosing the corn slurry with NaOH (3 percent NaOH) and cooking it at a temperature of 115°C for four hours. The caustic treatment generally broke down the structure of the corn particles making them more supple. This slurry formed a drier filter cake than the untreated feed slurry. However, a much lower solids capture was obtained.

The filtrate suspended solids obtained with stover slurry that was not subjected to the caustic pretreatment decreased with iron dosages up to about 5 g/ℓ. Additional iron dosage appeared to marginally increase the cake solids. This additional cake solids may have been the result of more iron precipitate in the cake or because of the lower pH resulting from the higher iron dosage. To determine the extent of this dilemma, pH adjustment with acid prior to ferric chloride addition was investigated. It was hoped that smaller iron dosages could be used once an optimum pH was attained through the addition of the acid. For these experiments concentrated sulfuric acid (18 molar) was used in order to avoid dilution of the test slurry. The iron dosage used in this test was 1.67 g/ℓ $FeCl_3 \cdot 6H_2O$. Table 50 shows the extent of pH adjustment through the addition of sulfuric acid while the experimental results are shown in Figure 30.

As illustrated in Figure 30, the depression of the pH by the addition of acid did not affect the dryness of the filter cake. The filtrate suspended solids concentration illustrates that an optimum pH for particle destabilization did exist. This optimum pH was approximately 3.5.

Table 50. pH Depression Through the Addition of Sulfuric Acid and Ferric Chloride

Initial pH	mℓ* 18 Molar H_2SO_4 Added	Intermediate pH	Final pH After Ferric Salt Addition
8.0	1.0	6.1	5.3
7.8	1.4	5.5	4.0
7.8	1.7	4.6	3.5
8.0	2.2	3.4	2.9
7.8	2.9	2.4	2.4

*1.5 liter slurry test volume

The cake solids appeared to be a function of iron dosage rather than pH. An increase in solids capture did not influence the cake solids. The optimum pH for solids capture appeared to be about 3.0.

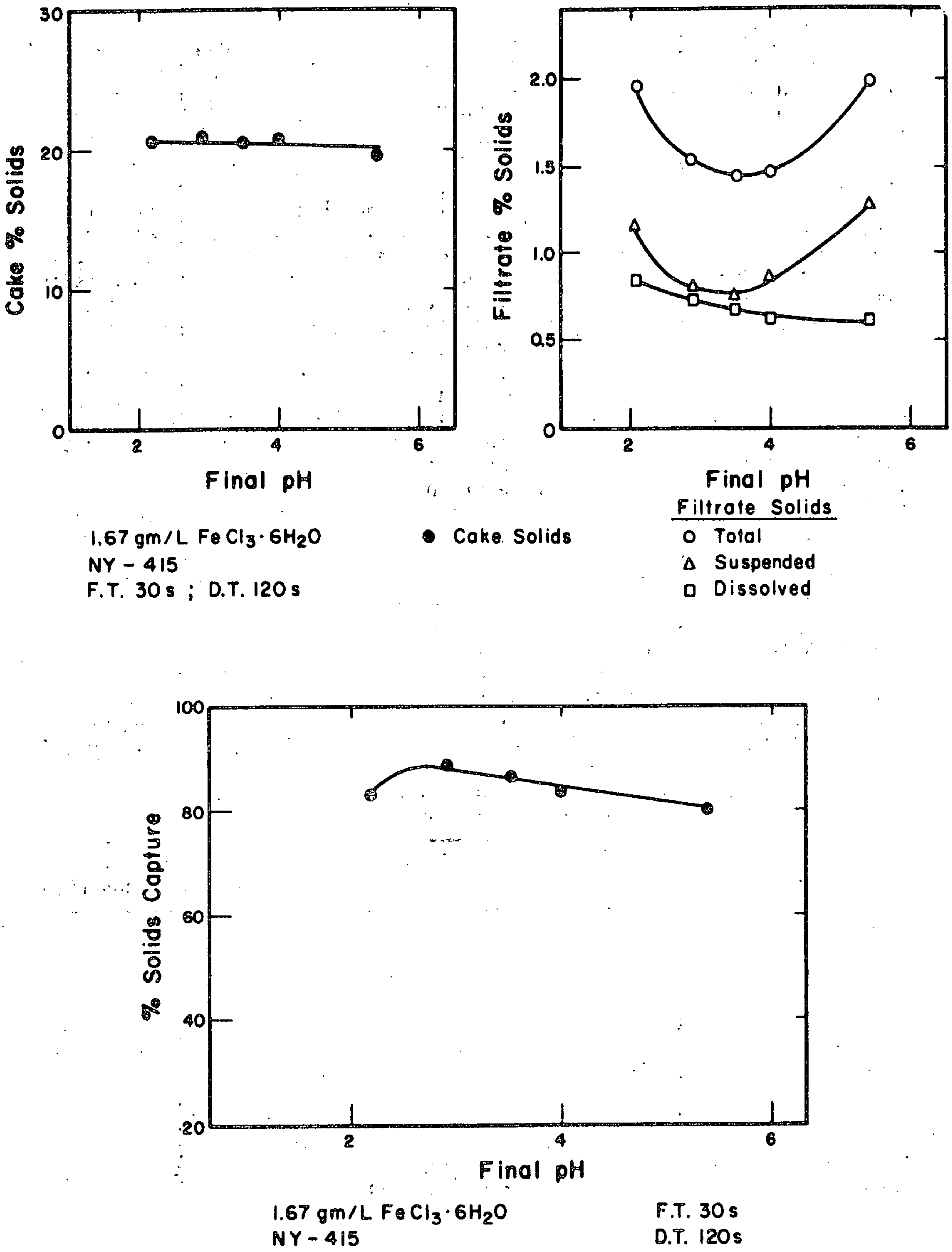


Figure 30. The Effect of pH on Filter Performance

The anionic polymers, A-22 and A-23, did produce a cake that had a higher solids content than that produced with no chemical additive. The cake solids was independent of polymer dosage. Solids capture was very poor, between 60 to 70 percent. It appeared that the polymer was stabilizing the fine solids and assisting their passage through the filter cake.

Another investigation was made using two cationic polymers, Dow Purifloc C-31 and C-43. Figure 31 shows that C-31 did not produce significantly drier cakes than any of the other conditioners that were investigated. However, C-43 did produce filter cakes of appreciable dryness. The filtrate suspended solids concentrations for the two polymers were similar within the bounds of experimental error. Increasing the polymer dosage of C-43 increased the percentage of mass retained by the filter leaf. Experimental records show that as the polymer dosages increased, the volume of filtrate decreased. This caused an increase in the solid capture percentage since less fluid was drawn through the cake. With C-31, the filtrate volume increased with polymer dosage. Consequently, the solids capture decreased with a larger volume of filtrate.

The solids loading rate is a very important design parameter with respect to equipment selection and sizing. This parameter describes the weight of solids (on a dry basis) which is retained per square foot of filter media per hour. Reviewing the objectives of this dewatering process, it is appropriate to cite the solids loading rate for a number of pertinent system conditions such as: obtaining the driest filter cake, minimum chemical addition, lowest effluent solids concentration, and highest solids capture. The results are listed in Table 51.

The parameters listed in Table 51-A for production of the driest filter cake relation to a polymer dosage of 160 mg/ℓ. Review of Figure 31 shows that a slightly drier cake can be formed with a dosage of 200 mg/ℓ. The difference is insignificant when considering experimental error. Therefore, the lower dosage, namely 160 mg/ℓ, was cited in this table.

Values given in Table 51-B relate to a form time of 30 seconds and a dry time of 135 seconds since these conditions yield the driest filter cake when no chemicals are used. Table 51-C relates to test conditions which produce the lowest filtrate total solids concentration. There were tests which yielded lower suspended solids concentration. However, the filtrate dissolved solids concentration were excessive due to large chemical additions.

When one considers the amount of nutrients that must be added to the corn stover slurry in order to maintain the digestion process, re-use of the effluent liquid fraction becomes an interesting prospect. The influent digester slurry is generated by incorporating the freshly ground substrate into the reclaimed liquor. Not only does this effluent utilization method reduce the cost of supplemental nutrient addition, but also eliminates the transportation costs which are generally associated with the alternative utilization plans.

Vacuum Filtration of Fermented Wheat Straw Slurries

As discussed previously, the fermented wheat straw exhibited particle size distributions similar to the fermented corn stover. Vacuum fil-

Table 51. Solids Loading Rates

(A) DRIEST FILTER CAKE

Cake Solids = 28.7%
Filtrate Suspended Solids = 1.0%
Filtrate Dissolved Solids = 0.33%
Solids Capture = 65%

Form Time = 30 seconds
Dry Time = 120 seconds
Conditioner: Dow Purifloc C-43
Dosage: 160 mg/l

Solids Loading Rate = 1.64 lb/ft^2 - hr

(B) MINIMUM CHEMICAL DOSAGE

Cake Solids = 20.2%
Filtrate Suspended Solids = 0.81%
Filtrate Dissolved Solids = 0.47%
Solids Capture = 60.1%

Form Time = 30 seconds
Dry Time = 135 seconds
Conditioner: None
Dosage: None

Solids Loading Rate = 5.67 lb/ft^2 - hr

(C) LOWEST FILTRATE SOLIDS CONCENTRATION

Cake Solids = 20.2%
Filtrate Suspended Solids = 0.5%
Filtrate Dissolved Solids = 0.54%
Solids Capture = 87.4%

Form Time = 30 seconds
Dry Time = 120 seconds
Conditioner: $FeCl_3 \cdot 6H_2O$
Dosage: 4.67 g/l

Solids Loading Rate = 3.79 lb/ft^2 - hr

(D) HIGHEST SOLIDS CAPTURE

Cake Solids = 21.9%
Filtrate Suspended Solids = 0.41%
Filtrate Dissolved Solids = 0.79%
Solids Capture = 90.6%

Form Time = 30 seconds
Dry Time = 120 seconds
Conditioner: $FeCl_3 \cdot 6H_2O$
Dosage: 10.0 g/l

Solids Loading Rate = 5.31 lb/ft^2 - hr

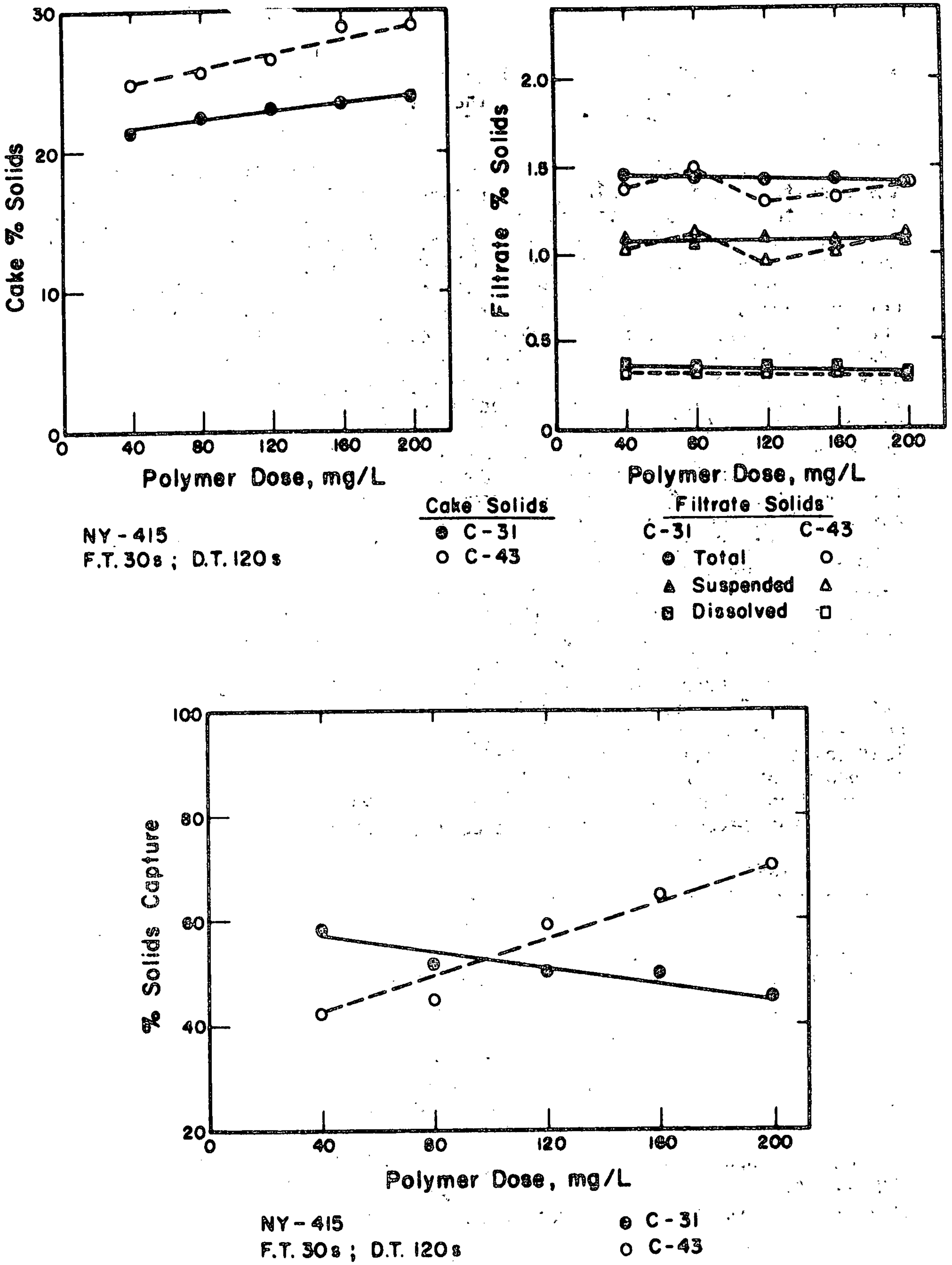


Figure 31. The Effect of Cationic Polymer on Filter Performance

tration of the straw slurry would be expected to respond in the same manner as straw. Certainly, the most effective dewatering system would involve a screening unit process to remove the large particles followed by chemically conditioning of the fine solids if it was necessary or desirable to recover these solids.

When the straw was subjected to a thermochemical pretreatment, the resultant fermented slurry was rather unusual relative to the other slurries tested. For this reason, an in depth analysis of the requirements for chemical condition of this slurry was indertaken to determine chemical dosages necessary to achieve acceptable dewatering.

During the initial period of investigation, filter leaf tests were performed on unconditioned slurries. Before long it became obvious that this slurry could not be dewatered by vacuum filtration without some type of conditioning. Several filter media types were used. The tightly woven filter medium would blind almost immediately, with essentially no cake formation. The most porous medium (like the screen on a screen door) was not subject to blinding but after a very thin cake formed the cake would blind and no further filtration could occur.

The most important point demonstrated in the early filter leaf tests was the need to carefully determine what part of the filtering system was rate-limiting; i.e. whether the medium or cake, or both, were responsible for poor filter performance. Because future filter leaf tests would be done on conditioned slurry to compare conditioner effectiveness, it was decided to choose one fairly open or porous medium as a base for comparison purposes. The tightest weave to demonstrate consistent non-blinding characteristics was Eimco Envirotech NY 415. This medium was used throughout the filter leaf testing program, except where noted otherwise.

Initially, the effectiveness of the conditioners was characterized by the filter test leaf procedure. The first conditioner used was $FeCL_3\text{-}6H_2O$, with a stock solution concentration of 100 g/l. Many filter leaf tests were run with varying ferric chloride dosage. The results were disappointing. Only thin cakes (2.0 mm) would form before cake blinding prevented any more filtrate to be drawn through the filter leaf. Table 52 shows the test results for three dosage levels:

Table 52. Filter Leaf Performance with Ferric Chloride

Dosage (% Dry Solids)	Cake Solids (%)	Filtrate Suspended Solids (%)	Solids Capture (%)	Yield ($lb/ft^2/hr$)
0	16.6	1.0	34	0.36
10.3	17.7	1.4	32	0.47
26.6	18.2	1.1	46	0.72

These tests were conducted with a form time of 30 seconds, a dry time of 120 seconds and a slurry solids of 3.1 percent. Even at a chemical dosage of 26.6 percent, the filter loading rate was far from acceptable. The ferric chloride was not an effective conditioner for this slurry.

Because the filter leaf test is time-consuming and becomes tedious, the capillary suction time was introduced into the program to facilitate a more rapid and complete evaluation of slurry conditioning agents. From now on in this report, that process will be called the CST test. The CST test instrument and its theory are described by Baskerville and Gale (1968). In the CST test, a sample of slurry is placed in contact with the center of a piece of filter paper. The capillary attraction of the absorbent filter paper causes filtrate to spread outward from the sludge. The CST is defined as the time it takes the filtrate front to spread a given distance on the filter paper.

The factors affecting the CST are:

1. properties of the filter paper
    a. capillary suction pressure
    b. filtrate-absorbing capacity per unit area
2. surface tension of the filtrate
3. temperature (viscosity of filtrate)
4. suspended solids content
5. the specific resistance of the given sludge to filtration

By holding factors 1-4 constant, a comparison of sludge conditioners can be made on the basis of CST for a given sludge.

The CST can be correlated empirically to the specific resistance as described by Baskerville and Gale (1968) but it is a good measure of sludge filterability on its own.

The CST test is a more convenient method than the filter test leaf procedure when it comes to estimating slurry filterability. The advantages of the CST test are that 1) it is a quicker test, 2) there is no need of a vacuum pump, and 3) it is an easily performed test.

Evaluation of Sludge Conditioners: CST and Jar Tests

Table 53 shows the 16 different sludge conditioners evaluated in an effort to find the most effective. Briefly--six 400-ml sludge samples were placed in six one-liter beakers and set up on a standard jar test apparatus. Stirring and chemical addition were done coincidentally for each beaker, but this step was time-staggered between beakers to allow for time-staggered CST testing. After the specified time for rapid mixing and flocculation, the sample of conditioned slurry was placed in the CST apparatus.

Of the two inorganic conditioners tested, ferric chloride was only slightly superior to ferric sulfate on a weight basis, as shown in Figure 32. Two things to note about Figure 32 are the slurry concentration and temperature differences between the two tests. A lower slurry concentration and higher temperature would lower the relative CST, and therefore the ferric chloride would maintain a slightly greater edge on ferric sulfate than indicated by Figure 32 if the CST values were corrected for solids concentration and temperature. The ferric sulfate was tried to see whether the sulfate ion would aid in the conditioning. No such effects were seen.

Table 53 Sludge Conditioners Tested

Organic Polymers	Ionic Type	Form
Percol 728*	medium cationic	solid
Percol 722*	medium cationic	micro-bead
Percol 776	high cationic	micro-bead
Percol 763	high cationic	micro-bead
Percol 757	high cationic	micro-bead
Percol 751	very high cationic	liquid (15% active)
Percol 744	very high cationic	liquid (20% active)
Percol 725	medium anionic	solid
Percol 726	high anionic	solid
Percol 727	medium high anionic	solid
Percol 730	low anionic	solid
Percol 720	non-ionic	solid
Dow C31	cationic	liquid
Dow C43	cationic	liquid
Inorganic Polymers		
$FeCl_3$-$6H_2O$	cationic	lump
$Fe_2(SO_4)3$-XH_2O	cationic	lump

*Most effective

Another parameter, mixing or shear effects, can be seen in Figure 32 by comparing curves for 10 and 58 minutes mixing time. The unconditioned sludge was most sensitive to shear forces as shown by increased CST. As the conditioner dosage increased, so did the sludge's ability to resist shearing forces. At high conditioner dosages, there was little difference between the CST value for 10 and 58 minutes mixing time.

Practically, the difference in conditioner performance between ferric chloride and ferric sulfate is insignificant. The choice between them would depend upon cost and availability.

A very high dose of either iron conditioner was necessary before the CST was reduced into the good filtering range (a CST of 3-15 seconds).

The effectiveness of metal ion conditioners was strongly affected by pH. The optimum pH for ferric chloride was found to be near 3.0 as shown in Figure 33. The pH was lowered by the addition of sulfuric acid. A coagulant dosage of 6 percent was added to a slurry containing 2.5 percent solids.

Some problems with the iron conditioners are:

1. High dosages are required.
2. pH adjustment may be necessary
3. Corrosion by acidic filtrates is possible.
4. There is an increase in the amount of solids, due to conditioners alone.
5. There is an increased ash content of solids.
6. The iron conditioners may have low effectiveness.

A good organic polyelectrolyte could eliminate all of the above problems.

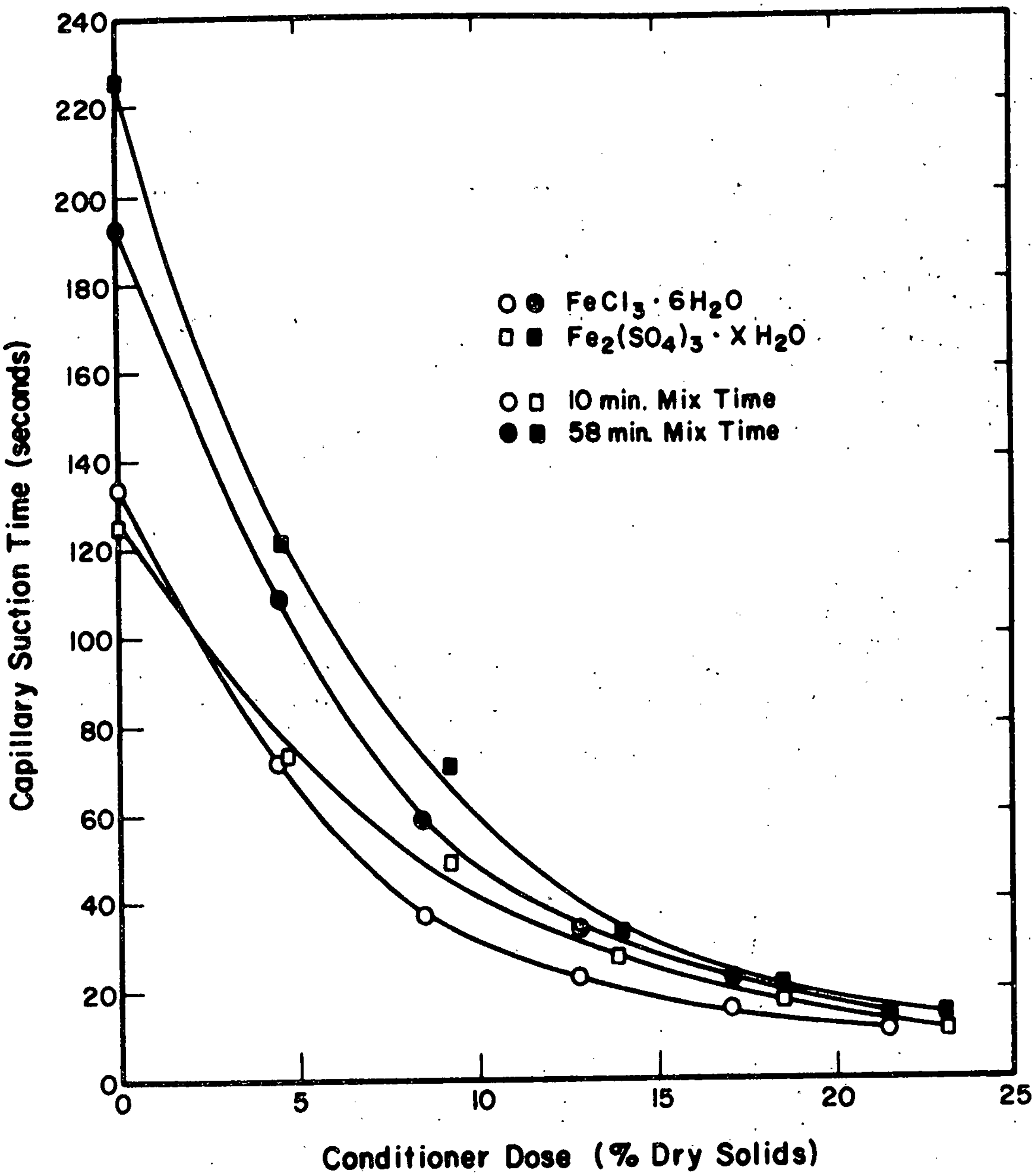


Figure 3'. Capillary Suction Time vs. Inorganic Conditioner Dosage.

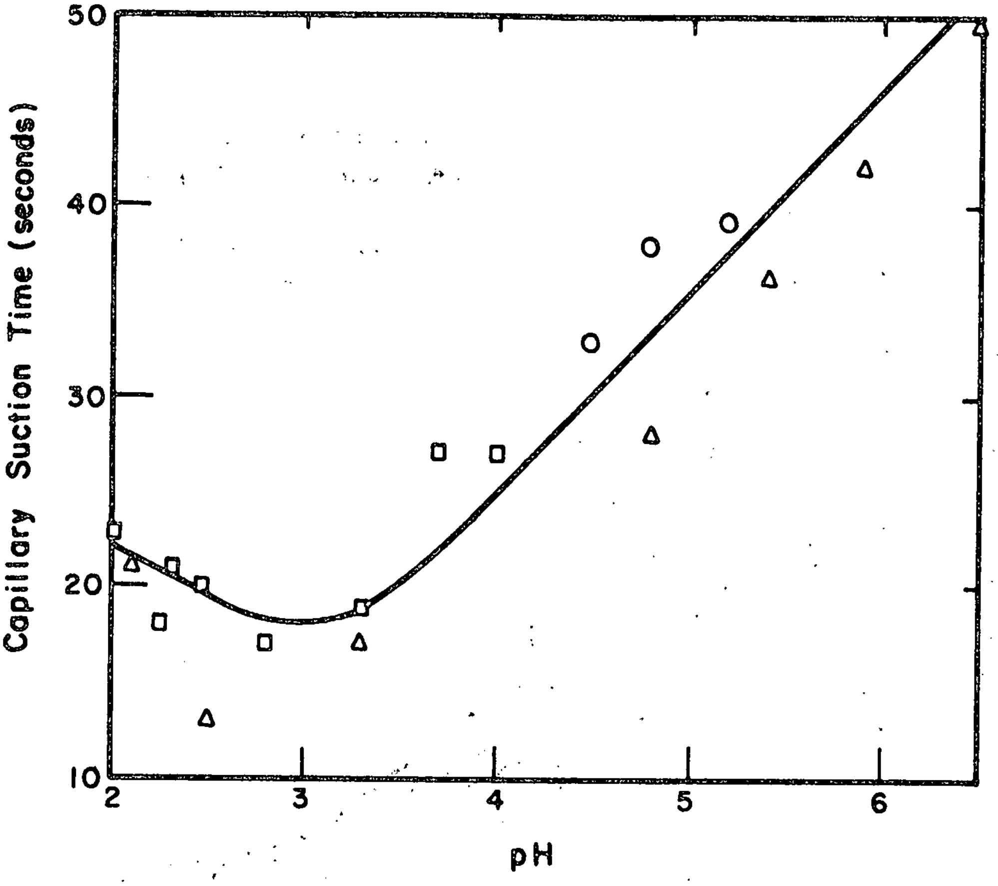


Figure 33. Capillary Suction Time vs. pH

After some preliminary screening of polymers it was found that the most effective ones could be identified, usually by using the jar test apparatus alone. Evidence of a good polymer was visible aggregation of the solids into larger and larger clumps, with increasing dosage. Two polymers exhibited aggregation in the jar test at lower dosages than any of the others (Table 53). These polymers were Percol 722 and Percol 728, both classified as medium cationic with very high molecular weights. Polymers classified as high cationic worked fairly well and very high cationic polymers werked poorly. Nonionic and anionic forms did not work at all.

Figure 34 shows the performance of Percol 722 and 728. Both polymers show very low CST relative to iron salts, even at minimum dosage. Percol 728 was effective at a lower dosage than 722. It also produced a floc that was much more resistant to shearing as evidenced by its independence of mixing time.

A series of tests using the filter test leaf procedure was conducted to evaluate the filtrability of the slurry conditioned with these polymers. These tests were conducted on a slurry that was thickened to 3.5 percent solids. The form time was 60 seconds followed by a dry time of 120 seconds.

Percol 728 was shown to be about equal in performance to Percol 722, but at a lower dosage as predicted by the CST tests. Figure 35 shows that 728 reached a maximum percent solids capture and filtrate solids removal at a dose of 0.2% of dry solids. Percol 722 reached the same point at a dose of 0.4% of dry solids, twice the dose of 728. Figure 36 shows little difference in cake solids for the two polymers but a significant difference in filter yield. Percol 728 at a dose of 0.2% of dry solids has a yield of 2.0 lb/ft^2/hr. It takes a 75% higher dosage of Percol 722 for the same yield. In this case the CST test-jar test combination accurately predicted the superior performance per unit dose of Percol 728.

Based on the above findings, Percol 728 was chosen for the last group of filter leaf tests to optimize and predict vacuum filter performance.

In an effort to increase the efficiency of Percol 728 and determine whether polymer solution concentration is a significant factor in polymer conditioning efficiency, polymer solution concentration was lowered from 0.5% to 0.1% dry polymer (in distilled water). Comparing data from Figures 35 and 37 under like conditions it can be seen that the percent capture and yield values were much higher when using lower-concentration polymer solution. These results might be explained in two ways:

1) The difference is due only to the increased feed slurry solids concentration used in the latter filter leaf tests, or

2) The polymer is more effective when applied as a more dilute solution. (Allied Colloids, Incorporated, maker of Percol polymers, recommends a polymer solution concentration of 0.25% to 0.5% maximum for full-scale use and a 0.05% solution for laboratory studies.

Polymer solution concentrations lower than 0.1% were avoided during the testing program to keep any possible dilution effects to a minimum.

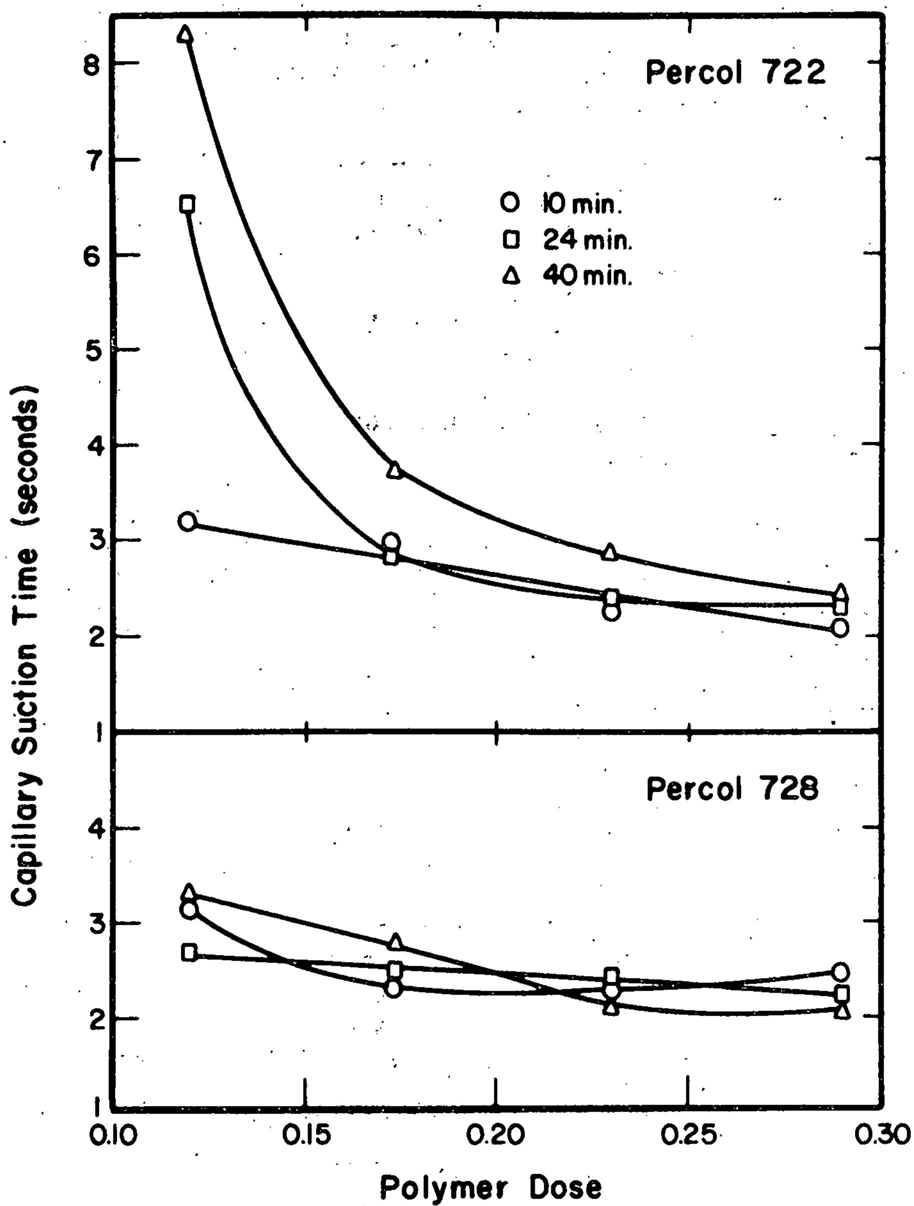


Figure 34. Capillary Suction Time vs. Polymer Dosage.

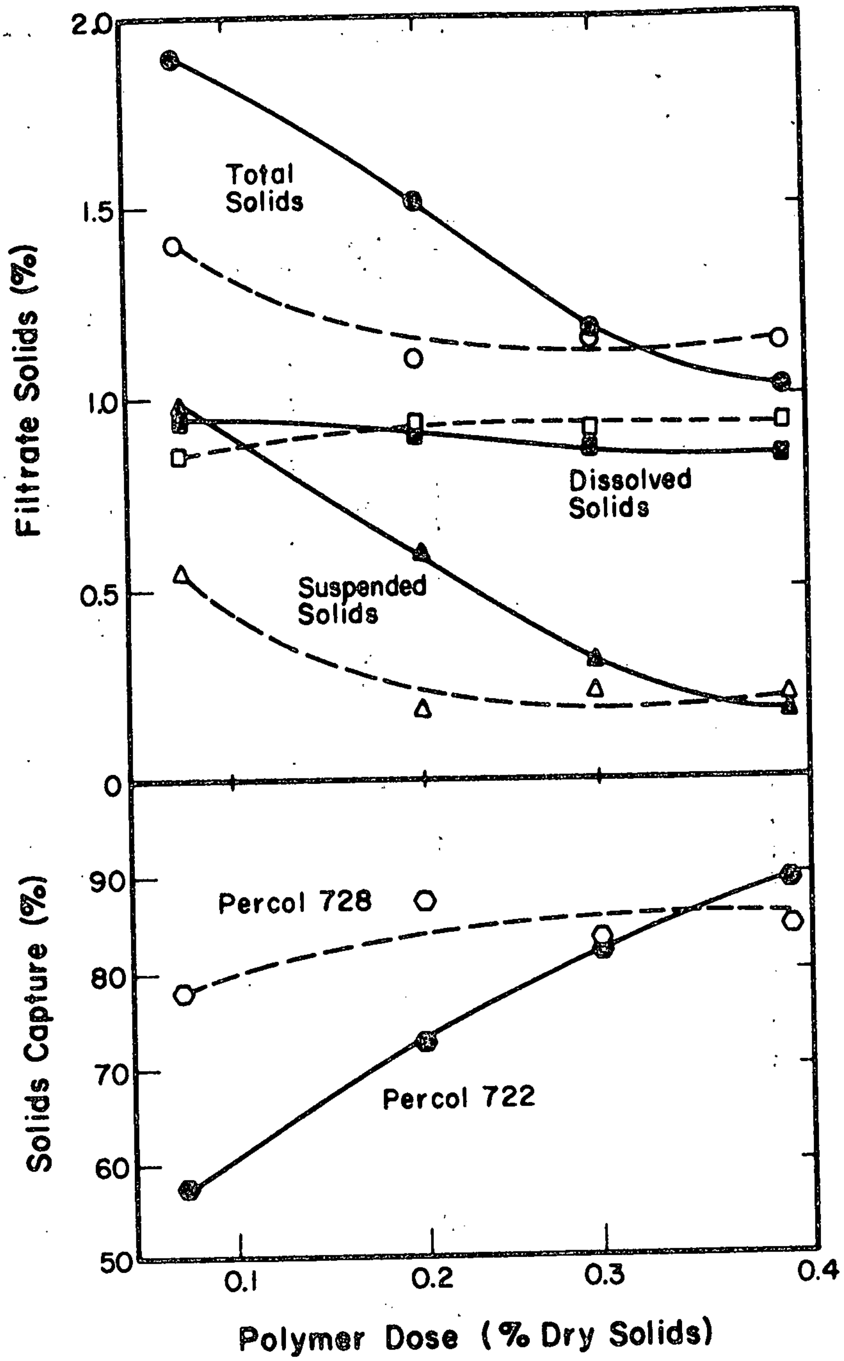


Figure 35. Percent Capture and Filtrate Solids vs. Polymer Dosage.

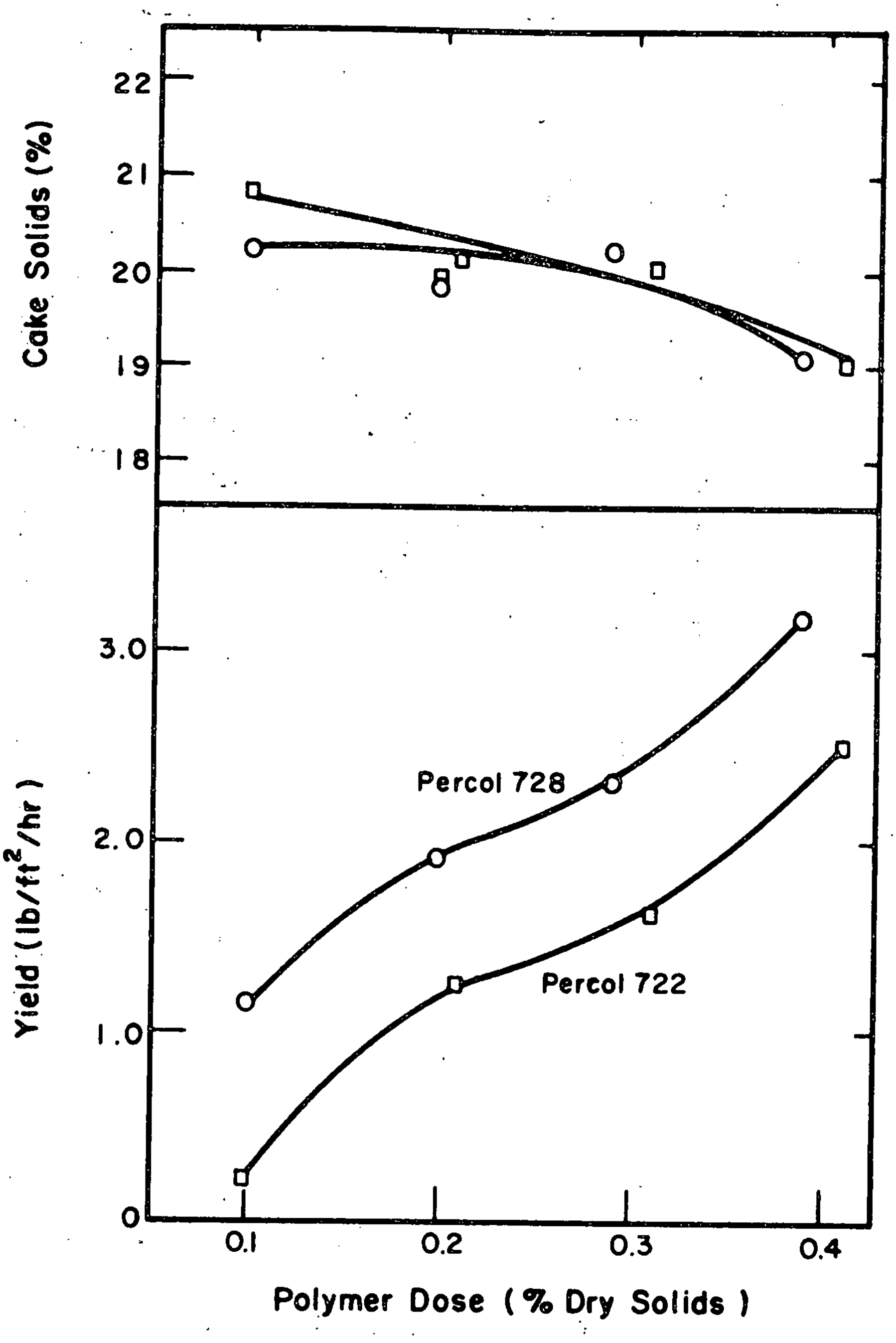


Figure 36. Yield and Cake Solids vs. Polymer Dosage.

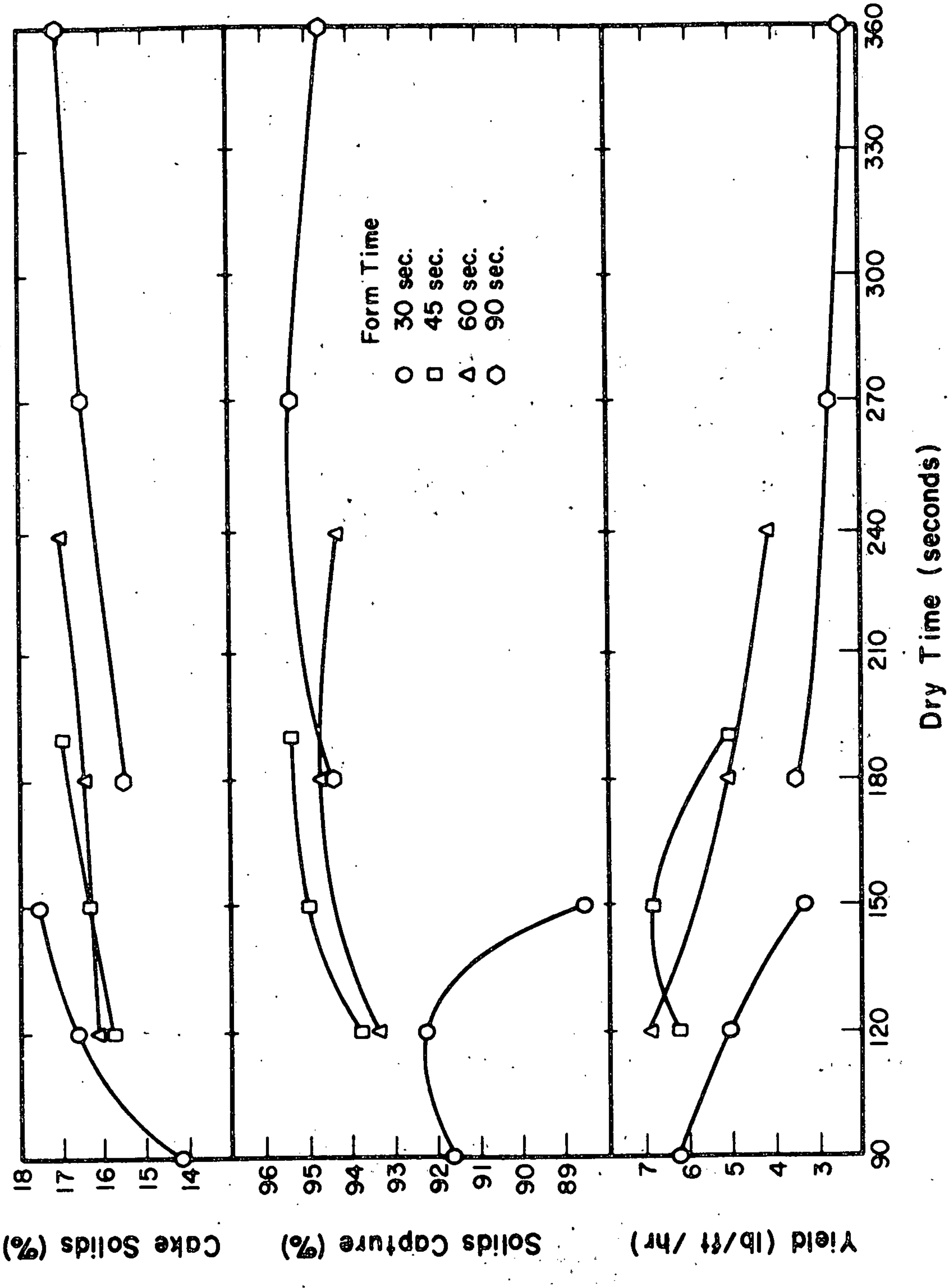


Figure 37. Cake Solids, Capture and Yield vs. Dry Time

For the data shown in Figure 37 the polymer dosage based on dry slurry solids was 0.2 percent. The slurry solids concentration was 4.2 percent after thickening. For form times of 45, 60 and 90 seconds, the filtrate suspended solids concentration remained at about 0.2 percent regardless of dry time. At a form time of 30 seconds, the filtrate suspended solids were higher (0.3 to 0.4 percent) for 90 and 150 seconds dry time, respectively.

The most significant design parameters as a function of dry time for four form times are presented in Figure 37. In choosing values for these machine variables, one must consider which parameters are most important for the designer's particular application. For example, would one want to optimize cake solids, percent solids capture, filtrate suspended solids, or yield? In general, long form times and short dry times will raise the solids capture, yield and lower filtrate suspended solids at the expense of cake moisture. To produce drier cakes would require shorter form times and longer dry times at the expense of lower yields, solids capture and higher filtrate suspended solids.

Performance of vacuum filtration on the slurries produced by fermentation of thermochemically pretreated straw was poor. With dosages of organic polymers of 0.2 percent of slurry solids, a cake solids of about 16 percent could be expected at a yield of 5.0 lb per ft^2/hr. The solids capture was 93 percent or better. The cost of disposal of such a wet cake may be significant. Based on the information obtained to date on the system employing thermochemical pretreatment of the substrate, dewatering of the fermented slurry will impose a significant operating cost on these systems. The chemical cost for slurry dewatering would be about $2.60 per ton of wheat straw processed if 75 percent of the volatile solids are converted to gas. When one adds the haul cost of returning 1.95 tons of wet cake to the fields for each ton of straw processed, it becomes clear that the cost of management of the fermenter residue will be a significant cost factor in these systems.

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UTILIZATION OF RESIDUAL SOLIDS

Fermented Beef Feedlot Manure

The fermentation process removes only carbon, hydrogen and oxygen from the substrate being utilized. All other elements are conserved by this process. The microorganism growth will require certain elements for the synthesis of new cellular protoplasm. As a result of this protoplasm production, the value of the residue may be enhanced. A portion of the ammonia nitrogen present in the manure is synthesized into protein. This protein has potential for recovery as an animal feed supplement. Therefore, not only are all forms of plant nutrients (nitrogen, phosphorus, potassium and minerals) conserved, but the nitrogen is partially upgraded to protein nitrogen in the form of bacterial cells, i.e. single cell protein.

In order to develop information required to evaluate the recovery potential of the residue from the system, one must know if these materials are soluble or insoluble and the associated concentrations. Therefore, a series of tests was conducted to determine the nitrogen, phosphorus and potassium content of the feed and effluent slurries and the centrifuge cake. Also, the nitrogen forms found in these fractions were determined.

1. Nitrogen Analysis

A summary of the results of the nitrogen analysis is shown in Table 54. These numbers are the average of four separate samples. The effect of temperature and retention time on the nitrogen distribution does not appear to be significant. As expected, the degradation of organics increases the ammonia content in the effluent. This is the only

Table 54. Nitrogen Distribution, mg N per g Total Solids

Temp °C	θ Days	Organic Nitrogen Feed	Organic Nitrogen Eff.	Organic Nitrogen Cake	Ammonia Nitrogen Feed	Ammonia Nitrogen Eff.	Ammonia Nitrogen Cake
40	4.8	15.1	20.7	40.1	0.9	2	0.3
	9.5	18.1	16.9	39.7	1.5	3	0.2
	13.7	28.4	32.7	39.2	1.3	2.3	0.4
	3.9	29.2	21.8	19.1	2.3	2.4	0.02
	4.7*	54.8	53.8	48.6	3.9	4.0	2.2
	4.9	26.8	21.3	21.3	1.6	2.2	0.01
	5.7*	44.4	53.9	-	4.5	5.5	4.0
	6.4	26.8	19.4	19.3	1.6	2.0	0.02
	9.5	29.2	28.8	22.1	2.3	2.0	0.03

observation that can be made regarding the effect of the processing on the nitrogen distribution. However, the organic nitrogen content of these streams is significantly affected by the nitrogen content of the feed manure. The two retention times marked with an asterisk in Table 54 recieved feed manure of different quality than that used for the other four retention times at the 58°C temperature. The high level of organic nitrogen in the feed slurry is reflected in the effluent as well as the centrifuge cake.

The cake contained a reasonable quantity of organic nitrogen, ranging from 1.91 to 4.86 percent of the total solids. The crude protein content of this cake would range from 12.0 to 30.3 percent. Based on the results of the centrifuge tests, approximately 75 percent of the suspended solids was captured in the cake. A mass balance on the organic nitrogen shows that on the average, approximately 60 percent of the input organic nitrogen was present in the centrifuge cake. A similar balance on the total kjeldahl nitrogen (TKN) shows that 55 percent of the TKN was captured in the centrifuge cake. Essentially all of the ammonia nitrogen was present in the liquid portion of the effluent stream. Consequently, the ammonia nitrogen in the cake was present as a result of water being retained by the cake.

The total nitrogen in the effluent ranged from 1.99 to 5.94 percent of the total solids. The effluent from the reactors contained between 4 and 10 percent total solids. The total nitrogen in the effluent could range between 0.08 to 0.6 percent, depending upon the fermentor operating conditions and the quality of the feed manure. The organic nitrogen was approximately 90 percent of the effluent nitrogen. Ammonia nitrogen contributed only 10 percent to the total nitrogen. This liquor will have an ammonia concentration between 200 and 1000 mg/l, depending upon the feed manure and the feed solids concentration.

2. Phosphorus Analysis

A summary of the phosphorus analysis is shown in Table 55. As with the nitrogen data, these values represent the average of four separate samples. Soluble phosphorus was higher in the raw feed than in the effluent from the reactors. It appeared that the phosphorus was precipitating in the

Table 55. Phosphorus Distribution, mg P per g Total Solids

Temp °C	θ Days	Total Phosphorus			Soluble Phosphorus		
		Feed	Eff.	Cake	Feed	Eff.	Cake
40	4.8	8.9	9.4	6.0	1.4	0.8	2.0
	9.5	8.5	9.2	5.8	2.1	0.7	1.4
	13.7	7.8	9.7	6.6	2.0	0.9	2.1
58	3.9	8.6	7.1	5.1	4.8	1.0	1.0
	4.7*	8.8	8.7	6.8	8.4	0.9	3.2
	4.9	7.3	8.0	5.1	2.8	1.5	1.3
	5.7*	9.0	8.0	8.3	7.3	1.0	4.7
	6.4	7.3	7.4	4.4	2.8	1.1	1.4
	9.5	8.6	8.4	4.8	4.8	1.1	0.6

in the fermentation step. This phosphorus may have been precipitated, but it was not of sufficient size particles to be removed by the centrifuge. In fact, the total phosphorus content of the solids in the cnetrifuge cake was significantly lower than the solids in the reactor effluents.

Phosphorus recovery will be greatest if the total effluent stream is utilized. Considering a 75 percent recovery of suspended solids in the centrifuge cake, the phosphorus recovery in this cake will be approximately 53 percent. The balance will be retained with the centrate.

3. Potassium Distribution

A summary of the potassium analysis is given in Table 56. These values are the average of four separate samples. Most of the potassium in these samples was in the soluble form. In the feed slurry, the potassium was 72.3 percent soluble. There appeared to be some effect of temperature on the potassium solubility. At the 40°C fermentation temperature, the soluble potassium accounted for 86.9 percent of the total potassium. At 58°C, the soluble potassium was reduced to 72.6 percent of the total K in the effluent slurry.

As a result of the solubility of this element, the potassium content of the centrifuge cake was low. A balance of the potassium in the feed stream shows that with a 75 percent recovery of suspended solids in the centrifuge step, the potassium recovery was 20 percent at 40°C and 23 percent at 58°C fermentation temperature. These variations with temperature probably are not significant. However, it is clear that the potassium recovery with the solids is very low. Effective recovery of the potassium will require use of the entire stream.

Table 56. Potassium Distribution, mg K per g Total Solids

		Total Potassium			Soluble Potassium		
Temp °C	θ Days	Feed	Eff.	Cake	Feed	Eff.	Cake
40	4.8	31.8	32.6	8.5	23.6	32.9	3.6
	9.5	29.4	34.8	8.9	32.7	34.4	3.9
	13.7	30.7	39.7	6.7	29.5	25.8	5.1
	3.9	23.0	18.6	7.0	12.0	8.0	5.9
	4.7*	34.7	32.8	10.4	23.9	21.3	6.3
	4.9	25.1	21.1	6.4	10.3	8.2	2.4
	5.7*	38.5	33.7	15.0	34.4	27.4	5.3
	6.4	25.1	22.3	6.2	10.3	12.9	2.6
	9.5	23.0	20.7	5.9	12.0	12.5	8.0

Fermented Corn Stover and Wheat Straw

The nutrient content of both of these crop residues was not sufficient to support an active microbial fermentation system. It was necessary to add nitrogen and phosphorus to the fermenters to maintain the culture. Since K_2HPO_4 was the source of phosphorus, the slurries contained a significant quantity of potassium. The data presented in Table 31 show that 80 to 90 percent of the phosphorus and potassium in the fermented corn stover was present in the slurry fraction passing the 200 mesh sieve. These nutrients are primary soluble and therefore can be recovered if one uses the liquid portion of the fermented slurry.

Recovery of the solids from the fermented slurry to use as an animal feed supplement has been proposed. As shown in Table 31, the organic nitrogen content of the particle size fraction retained on the 10 mesh sieve is low. The data in Table 57 show the nitrogen and phosphorus content of cake from the centrifuge. The maximum protein that can be obtained from the material is limited. The stover residue as well as the straw contain less than one percent nitrogen. Therefore, this residue will contain less than 6 percent protein. This is not a valuable feed material.

Table 57. Nitrogen and Phosphorus Levels in Fermented Solids (% Dry Solids)

	Total Nitrogen	Total Phosphorus
Corn Stover	0.42	0.13
Wheat Straw	0.81	0.28

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 58.

Table 58. 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

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 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 58. Clearly, the resulting protein production is low. The quality of the residue (dry solids) as an animal feed is shown in Table 59. 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 59. 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 58, 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 animal 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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APPENDIX A

ANALYTICAL TECHNIQUES

1. Wet Sieve Analysis

The wet sieve analysis was used to separate a sample of slurry into various size fractions.

Apparatus:

Standard sieves - sizes:

#10 - 1.981 mm
#20 - 0.840 mm
#50 - 0.297 mm
#100 - 0.149 mm
#200 - 0.074 mm

Procedure:

1. Dry and tare sieves to within ± .5 grams.
2. Collect and measure 2 liters of slurry.
3. Allow slurry to settle for at least 10 minutes.
4. Pass supernatant through #10 and #20 mesh sieves. Rotate sieves to encourage passage of solids. Transfer settled solids to screen and allow to drain.
5. Set liquid aside and allow solids to settle for 15 to 20 minutes.
6. Wash solids on first 2 screens with small quantities of water. Wash until clean water passes screen (less than 4 liters). Collect wash water.
7. Pass wash water through the remaining screens. Collect wash water and use to wash accumulated solids on the remaining sieves.
8. Pour supernatant from step 5 through the next 2 finer screens. Collect liquid. Transfer settled solids to screens and allow to drain.
9. Using wash water from step 7, wash accumulated solids.
10. Pour remaining liquid to other screens and repeat steps 8 and 9.
11. After above steps have been performed for all sieves, collect and measure volume of passed liquid and wash water.
12. Allow solids on screens to dry in 103°C oven and weigh when dry.

2. Fiber Analysis

This test measures the hemicellulose and cellulose as holocellulose. The fats, oils, waxes, etc., are extracted with an organic solvent. Acid hydrolysis removes the holocellulose and the remaining solids are ignited at 600°C to measure the inorganic solids.

Apparatus:

Soxhlet extraction apparatus

- 250 ml soxhlet extraction flask
- 100 ml soxhlet extraction tube
- Cool water condensers
- 25 x 80 mm cellulose crucibles, hot plate
- 1 liter side arm erlenmeyer flasks
- 25 ml Gooch crucibles w/asbestos pads
- 32 mm filtration holders for Gooch crucibles
- 125 ml erlenmeyer flasks

Reagents:

Alcohol-benzene solution (1 volume ethyl alcohol to 2 volumes of c.p. benzene), sulfuric acid (72 percent)

Procedure:

1. Grind test samples to a size of less than 1 mm by passing it through a Wiley Mill.

2. Determine percent fixed solids of sample material. Dry and weigh a crucible without lid on it. Place dry sample in crucible and reweigh. The difference gives the weight of the sample. Combust the sample at 600°C for 2-3 hours with the lid on. Remove the lid from the crucible and let stand at 600°C for 4-5 hours for complete combustion. Cool the crucible in a desiccator and weigh it without the lid. Substract the weight of the crucible to obtain the fixed solids remaining. Divide this remaining weight by the initial weight of the sample to obtain the percentage fixed solids in the sample.

3. Place 120 ml of alcohol-benzene solution in extraction flask. Connect flask, tube with cellulose crucibles, and condensor and

place in water bath. Extract empty crucibles for 4 hours to remove any extractables in the crucible.

4. Dry and weigh empty crucibles. Fill crucibles with sample and dry and weigh. Difference gives the weight of the sample. Follow extraction procedure as given for empty crucibles.

5. Dry and weigh crucibles and extracted sample. Weight loss is the weight of the extractable material.

6. Dry and weigh 125 ml flasks. Add approximately 1 g of extracted sample of flask; dry and weigh again. Add 15 ml of cold sulfuric acid to flask while stirring. Place flask in cool water bath (20°C) for 2 hours and stir frequently. Wash material from flask into 1 liter beaker with distilled water. Add 500 ml of distilled water to beaker and boil for 4 hours keeping volume constant.

7. Dry and weigh Gooch crucibles with asbestos pad. Filter beaker contents through Gooch crucibles. Dry and weigh crucibles. Material in crucible is lignin and fixed solids.

8. Subtract percent of fixed solids from percent of lignin and fixed solids.

    As in step 7, the material not only contains lignin and fixed solids, but protein present in the residue precipitates and is measured as part of the residue which is designated as lignin. Total nitrogen of the residue is determined to correct for protein which is 6.25 times total nitrogen. Therefore, net lignin = (weight in step 7) - fixed solids - protein.

3. Filter Leaf Test Procedure

The test procedure discussed below has, for the most part, been followed for the entire testing period. Slight variations have been made to accommodate various peculiarities of the sludge in question and to ease the operation of the test. Deviations from this method of testing have been mentioned previously. These deviations are minor and were designed in such a way that their effect on the continuity of the data is minimal.

The tests were run on actual fresh digested material. In no instance was the digester effluent older than 5 hours. A 5 gallon sample was obtained from the digester effluent tanks while the effluent was subjected to compressed air agitation. For each test run a known volume of sample (1 to 3 liter depending on the substrate) was obtained under vigorous mechanical mixing from the larger volume.

Much of testing procedure involves determining the percentage of solids by weight of a given material. Since evaporative loss of weight techniques were used, the handling and weighing of crucibles was necessary. Therefore, a consistent and theoretically sound method of crucible weighing and handling had to be determined. First this technique is enumerated and then the actual filter leaf test will be described.

Crucible Handling Technique:

1. Wash crucible with soap and water using spatulas and brushes to remove foreign objects. Rinse with distilled water.
2. Crucibles are placed in muffle furnace (600°C) to oxidize any organic matter remaining.
3. Crucibles are moved to drying oven (103°C) to cool.
4. Cooled crucibles are dry brushed out to remove ash formed in step 2.
5. Crucibles are stored in drying oven in order to avoid the additional weight of adsorbed water.
6. When a crucible is to be weighed, it is placed in a desiccator for about 45 minutes. (Crucibles must be cool to avoid convection currents during weighing. The crucibles are stored in desiccator to keep water from adsorbing on them.)
7. Crucibles are weighed to 10^{-3} grams.
8. Crucibles that are used in a weight added mode are stored in atmospheric conditions.
9. Crucibles used where the total weight of crucible and added material is determined are stored in a drying oven until use.

Crucibles are not touched by hand before or after weighing.* An exception to this is where the tare weight is known and a known weight is

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*Since oils and moisture transferred from hand to crucible add an unaccounted foreign weight to crucibles.

added to the crucible. Any oils transferred to the crucible after taring will be volatized off in the oven before the next weighing.

Filter Leaf Test Procedure:

A step by step procedure is listed below. This procedure is for one run. However, step 4 and step 5 are needed only once every 4 runs.

1. Wash test equipment
2. Rinse test equipment (except hoses and filter support) with distilled water.
3. Select 1 Gooch crucible and 4 tared crucibles.
4. Agitate anaerobic effluent tank with compressed air mixer.
5. Immerse clean 5 gallon bucket in mixed effluent tank to obtain representative sample.
6. Set up mechanical mixer in 5 gallon bucket and turn mixer on.
7. Take representative 150 ml sample from well mixed 5 gallon bucket.
8. While stirring 150 ml sample, pour 60 g of liquor into crucible #1. (Determine weight to 0.25 g and record.) Place in drying oven.
9. Take the remainder of the 150 ml sample and record its pH to 10^{-1} accuracy.
10. Withdraw 3 liters from the well mixed 5 gallon bucket and transfer to the clean 4 liter beaker.
11. Turn off rapid mix. (Continuous mixing causes CO_2 release, thus raising pH.)
12. Turn on vacuum pump to preset pressure. (Usually 16 inches of mercury.)
13. Turn off vacuum actuate and vacuum release valve allowing pressure to build up in 5 gallon vacuum reservoir.
14. Measure out coagulant or polymer dose (if any).
15. Place mechanical mixer in 4 liter beaker.
16. Turn on mixer (go to next step without delay).
17. At time = 0 minutes turn on stopwatch, dump coagulant or polymer into 4 liter beaker.

18. At time = 0.5 minutes, turn off rapid mix.

19. Transfer 4 liter beaker to magnetic stirrer.

20. Record pH.

21. At time = 6.5 minutes, turn on magnetic stirrer to low setting (#2).

22. At time = 7.75 minutes, place filter leaf holder in a 4 liter beaker.

23. At time = 7.0 minutes, open vacuum actuate valve (form time begins).

24. Record form pressure 15 seconds into the form time.

25. At the end of the form time remove the filter leaf from the 4 liter beaker and place it upright in the holder (dry time begins).

26. Turn off magnetic stirrer.

27. 15 seconds into the dry time record the drying pressure.

28. At the end of dry time turn off the vacuum pump and open the vacuum reservoir release valve.

29. Remove cake from test leaf with spatula.

30. Record thickness of cake.

31. Place cake in crucible number 2, weigh cake and crucible, place in drying oven.

32. Empty filtrate in vacuum flask into 1 liter graduated cylinder.

33. Record volume.

34. Pour known weight of filtrate into crucible number 3 and determine weight to 0.25 g. Place in drying oven.

35. Pour 70 g of filtrate into centrifuge tube using balance (determine weight to 0.25 g).

36. Centrifuge sample at 4500 rpm for 40 minutes.

37. Turn on second vacuum pump.

38. Wet glass filter in Gooch crucible with distilled water.

39. Subject Gooch crucible to vacuum.

40. Pour centrate into Gooch crucible.

41. Rinse remains in centrifuge tube in Gooch crucible with distilled water.

42. When glass filter is dry turn off vacuum.

43. Disassemble Gooch crucible and stopper, rinse surfaces of these components with distilled water into vacuum flask associated with Gooch crucible.

44. Pour contents of vacuum flask into crucible number 4.

45. Rinse vacuum flask with distilled water into crucible number 4 and place in drying oven.

46. After at least 24 hours, remove crucibles 1 to 4 from oven.

47. Reweigh crucibles.

Calculations and Discussion of Procedure:

In many instances the calculations and procedures are standard as they are dictated by logic. However, in some cases various peculiarities of the sludge make standard evaluations difficult. In such instances procedures were designed which allowed for the properties of the sludge to arrive at the designed dependent variables. A discussion of the calculations and procedures is given in the following paragraphs. The calculations will be outlined with respect to the enumerated experimental steps.

Total Solids of Digester Effluent -

This is a standard method of evaluating percent solids. It necessitates the removal of the liquid fraction of the sample by drying the sample in an oven at 103°C. The ratio of the dry weight to the wet weight of the sample yields percent total solids.

T_1 = tare weight of crucible #1

W_1 = weight added to crucible #1

C_1 = weight of crucible #1 and dried solids

$$\text{Sludge total solids (\%)} = \frac{C_1 - T_1}{W_1} \times 100$$

--Possible sources of error --

1. Obtaining representative sample
2. Determining weight added (accuracy of scale used)

Filter Cake Percent Total Solids -

This method is also fairly standard except for the fact that the entire cake is used in the sample. This is done in order to be able to compute a filter capture ratio with a minimum number of assumptions. Using the entire cake is probably a better method as it eliminates the concern about removing a representative sample from the cake.

T_2 = tare weight of crucible #2

W_2 = weight of crucible #2 plus wet cake

C_2 = weight of crucible #2 plus dry cake

$$\text{Cake solids (\%)} = \frac{C_2 - T_2}{W_2 - T_2} \times 100$$

-- Possible sources of error --

1. Ability to remove all the cake from filter
2. Cake dries out in the period between testing and weighing
3. Since entire cake is used the weight of a large cake (corn stover) forces one to use a less accurate balance which has a larger capacity

Filtrate Total Solids -

This test is very standard and identical to the sludge total solids. Obtaining a representative sample is easy since the particles are small and settle slowly.

T_3 = tare weight of crucible #3

W_3 = weight of filtrate added to crucible #3

C_3 = weight of crucible #3 and dry solids

$$\text{Filtrate total solids (\%)} = \frac{C_3 - T_3}{W_3} \times 100$$

-- Possible sources of error --

1. Determining weight added (accuracy of balance used)

Filtrate Dissolved Solids -

This test is one that had to be designed to fit the sludge. This test is usually performed by passing the filtrate through a fiberglass micropore filter thus filtering out the suspended solids. However, because of the concentration and nature of suspended solids, the glass filter was subject to rapid plugging. To eliminate this problem, a known weight of filtrate was centrifuged first to remove the majority of suspended solids. The centrate was passed through the filter and the filtrate analyzed for dissolved solids. The original weight of the sample is used in the denominator of the ratio since theoretically this is correct. An operational error does exist since the water within the pore volume of the settled suspended solids also contains dissolved solids and is not accounted for. This error is believed to be small and smaller than the error associated with other techniques.

T_4 = tare weight of crucible #4

W_4 = weight filtrate placed in centrifuge tube

C_4 = weight of crucible #4 and dried solids

$$\text{Filtrate dissolved solids (\%)} = \frac{C_4 - T_4}{W_4} \times 100$$

-- Possible sources of error --

1. Dissolved solids in water retained by suspended solids centrifuge pellet
2. Determination of weight added to centrifuge tube (accuracy of scale)

Filtrate Suspended Solids -

This value was determined as the difference between the total solids and the dissolved solids.

Filtrate suspended solids (%) = TS - DS

-- Possible sources of error --

1. Errors associated with filtrate total and dissolved solids

Solids Capture -

The percent solids capture is the ratio of the weight of solids caught on the filter media to the weight of suspended solids entering the system. Although there are formulas which allow the use of a sample of the filter cake in the calculation, they are subject to error due to assumptions made in the derivations. The method used below eliminates those errors since the whole cake is used in the ratio determination.

T_2 = tare weight of crucible #2

W_2 = weight of crucible #2 and wet cake

$W = W_2 - T_2$ = weight of wet cake

X_1 = cake solids (%)

V = volume of filtrate

X_2 = filtrate suspended solids (%)

ρ = density of filtrate $\approx \rho_{H_2O}$

$$\text{Solids capture (\%)} = \frac{\text{weight of solids caught on filter}}{\text{weight of suspended solids entering system}}$$

$$\text{Solids capture (\%)} = \frac{WX_1}{WX_1 + \rho_{H_2O} X_2 V}$$

-- Possible sources of error --

1. Assumption $\rho = \rho_{H_2O}$

2. Errors in terms X_1 and X_2 disclosed previously

Solids Loading Rate -

The solids loading rate is an important design parameter used in sizing vacuum filtration facilities. The units of the solids loading rate is commonly lb dry solids/ft^2-hr. The relationship will be derived below:

T_2 = tare weight of crucible #2

W_2 = weight of crucible #2 and wet cake

$W = W_2 - T_2$ = weight of wet cake

A = area of test leaf = 0.1 ft^2

FT = form time (s)

DT = dry time (s)

T = FT + DT (s)

X_1 = % cake solids

$$\text{Solids loading rate} = \frac{WX_1}{0.1\ \text{ft}^2 T} \times \frac{\text{LB}}{453.9\ \text{g}} \times \frac{3600\ \text{S}}{\text{hr}} = 79.3\ \frac{WX_1}{T}$$

To account to dead time the above figure is usually multiplied by a factor of 0.8 (Eimco, 1975).

$$\text{Solids loading rate} = 63.44\ \frac{WX_1}{T}\ \frac{\text{LB}}{\text{ft}^2\text{-hr}}$$

4. Routine Analyses

Routine tests for control of the fermentation process and for evaluation of the performance were conducted as outlined by Standard Methods (1976).

APPENDIX B

PUBLICATIONS

The following major progress reports have been issued under this contract.

Biological Conversion of Organic Refuse to Methane Final Report NSF Grant NSF/AER 73-07872 (Formerly NSF GI-39191) Vol. I & II, Nov. 1976	C00/2917-3
Biological Conversion of Biomass to Methane, The Effect of Reactor Design on Kinetics Report for DOE Contract No. EY-76-S-02-2917, Dec. 1977	C00/2917-8
Biological Conversion of Biomass to Methane, Beef Lot Manure Studies Report for DOE Contract No. EY-76-S-02-2917, July 1978	C00/2917-9
Biological Conversion of Biomass to Methane, Corn Stover Studies Report for DOE Contract No. EY-76-S-02-2917, June 1979	C00/2917-13

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