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BIOLOGICAL CONVERSION OF BIOMASS TO METHANE

QUARTERLY PROGRESS REPORT
for Period December 1 - February 28, 1979

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REA

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Introduction

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

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

When the material was wetted, the particles swelled substantially as a result of the absorbed moisture. Using a wet sieving technique, over 65 percent of the total solids were retained on the #10 sieve. At the same time, 30 percent of the total solids passed the #200 sieve. Essentially all of this 30 percent was soluble solids. This straw slurry has unique characteristics. With a solids content of 12 to 13 percent, the straw and water mixture has absolutely no fluid properties. It has an angle of repose that approaches 90 degrees. Mixing by conventional fluid mixers is impossible. The power required by a ribbon mixer designed to mix concentrated slurries exceeded 2 KW/m^3 (75 HP per 1000 cu ft). This slurry could 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. 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 (12 percent solids) 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.

The conversion efficiency of the straw was somewhat better than with the corn stover. Part of this improvement may have been a result of the need for heat treating the straw so it could be processed. Analysis of the gas data showed that approximately 53 percent of the volatile solids in the straw were biodegradable for a fermentation temperature of $59 \pm 1°C$. 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. This rate constant was found to be 0.23 day^{-1}.

Experimental Procedure

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 following data.

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 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 decreases 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 1, 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.

Results and Discussion

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. Reactor #3 was operating at a retention time of 7.5 days at 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 was reduced to 40°C on November 26, 1978. This was done to allow an initial comparison of the effect of temperature of the conversion efficiency. If it was observed that 40°C temperature was significantly less effective than 60°C, mesophilic temperature would not be further studied.

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 1. Day 0 corresponds to December 9, 1978. Reactor

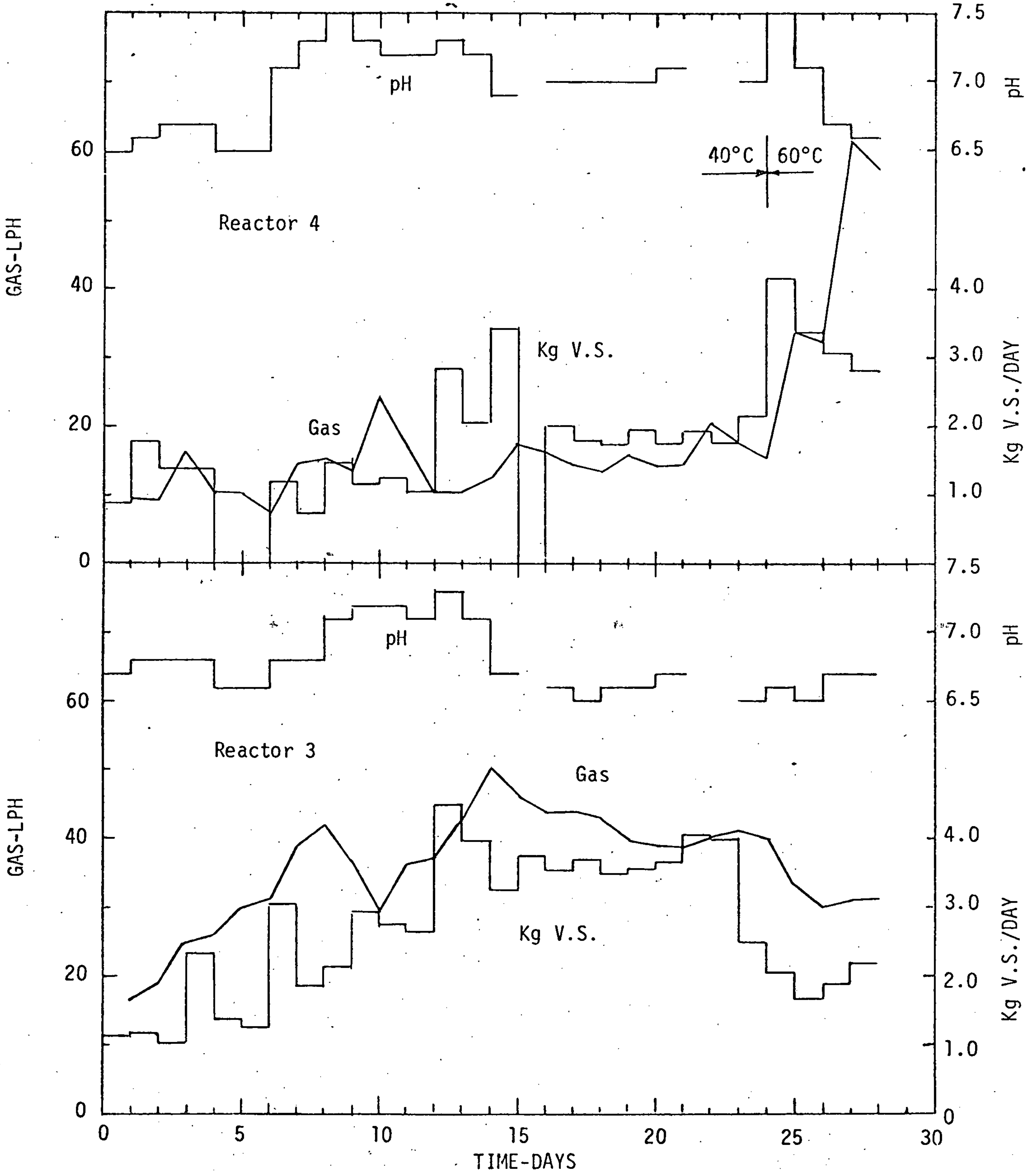

Figure 1. Response of reactors to thermochemical pretreatment.

4 was operated at a retention time of approximately 30 days until December 21, 1978 (Day 12). At this time, the feed rate was increased such that the retention 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 December 29, 1978 (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. The volatile acids were increasing to about 4000 mg/l. Because of the decreasing pH, the loading was reduced. However, the system did not recover. Because of the higher feed rate in #3, the inhibition was observed sooner. It appeared that Reactor 4 was reaching the same end. Therefore, the temperature was raised to 60°C. The loading was also increased, with a resultant increase in gas production. However, the pH decreased substantially.

Figure 2 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

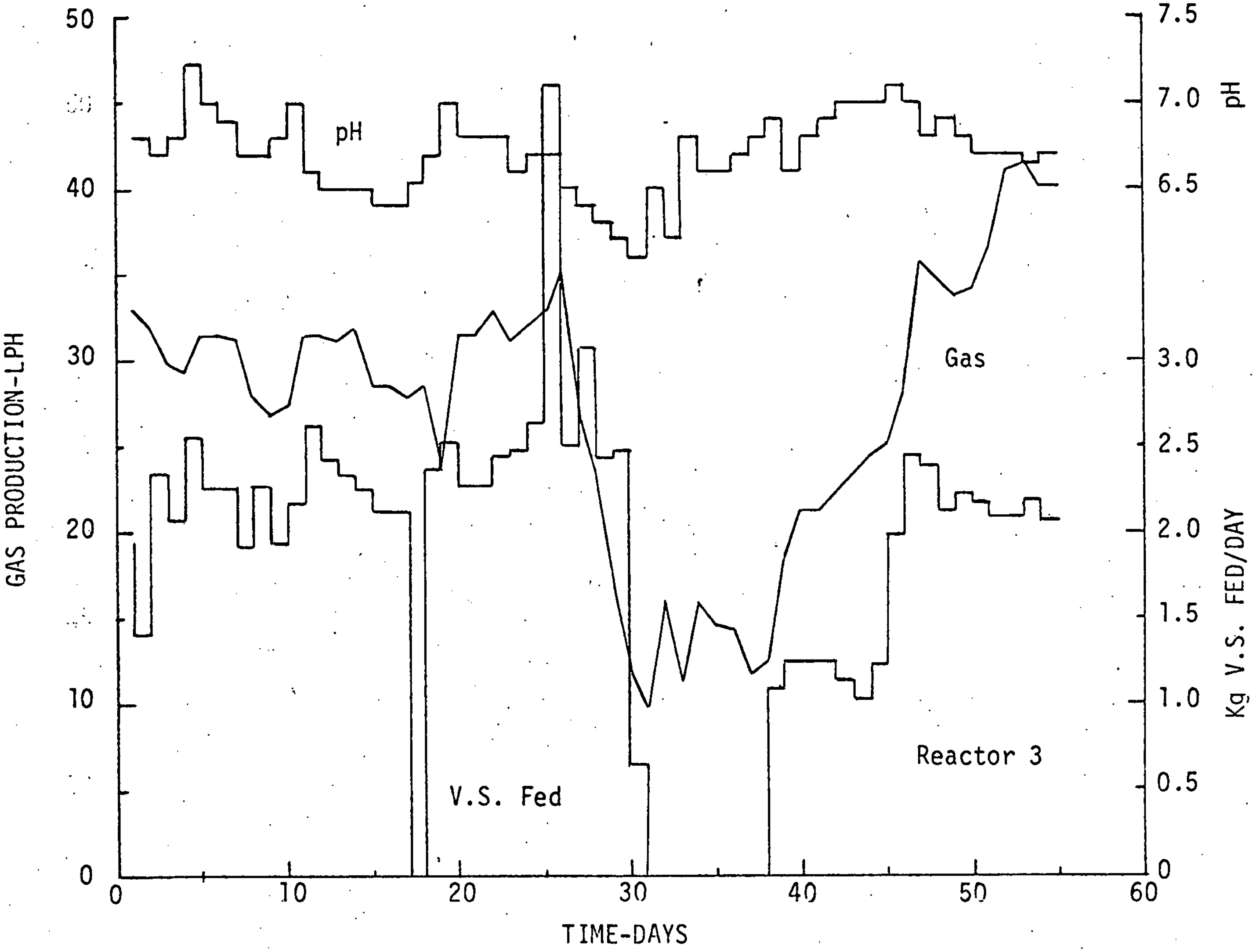

Figure 2. Reactor performance with thermochemical pretreatment.

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.

As shown in Figure 3, 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. Feeding was stopped for two days. 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 was not known, but is 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 2 and 3). 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

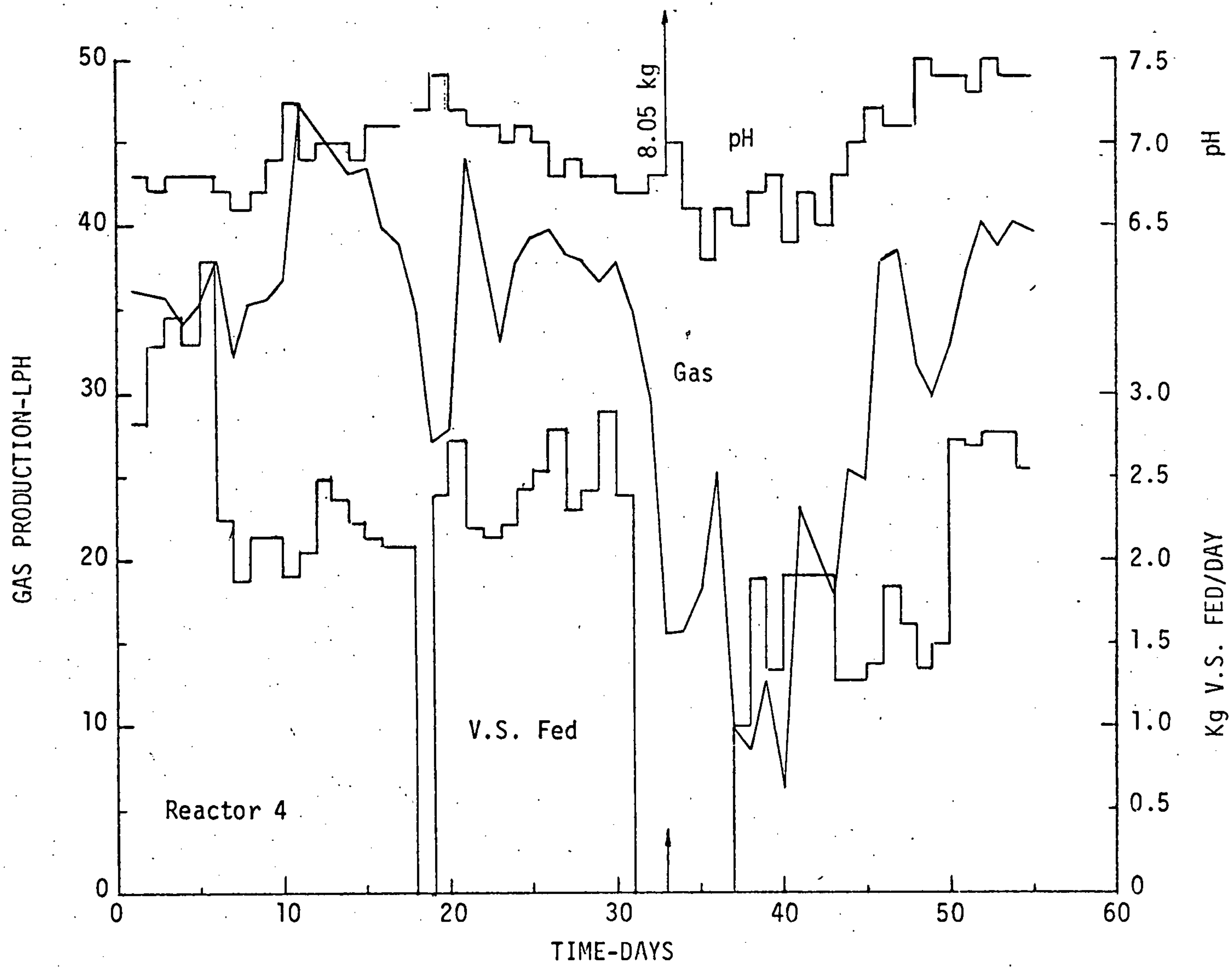

Figure 3. Reactor performance with thermochemical pretreatment.

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 1. 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.

Table 1. 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

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 in which the higher NaOH dosage was used was initiated at this time. Both reactors responded poorly as shown in Figure 4 and 5. 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 droped 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. As shown in Figure 4, the pH in Reactor 1 began to decrease on Day 40 (2-15-79). 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 day 54 (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.

As shown by Figure 5, the response in Reactor 2 was essentially the same as Reactor 1. Failure occurred more rapid because the fermentation temperature was lowered to 50°C on Day 35 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 2. The extreme variation of the volatile acids in the mix tank are 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 Day 45 did not result in a significant improvement in the reactor performance.

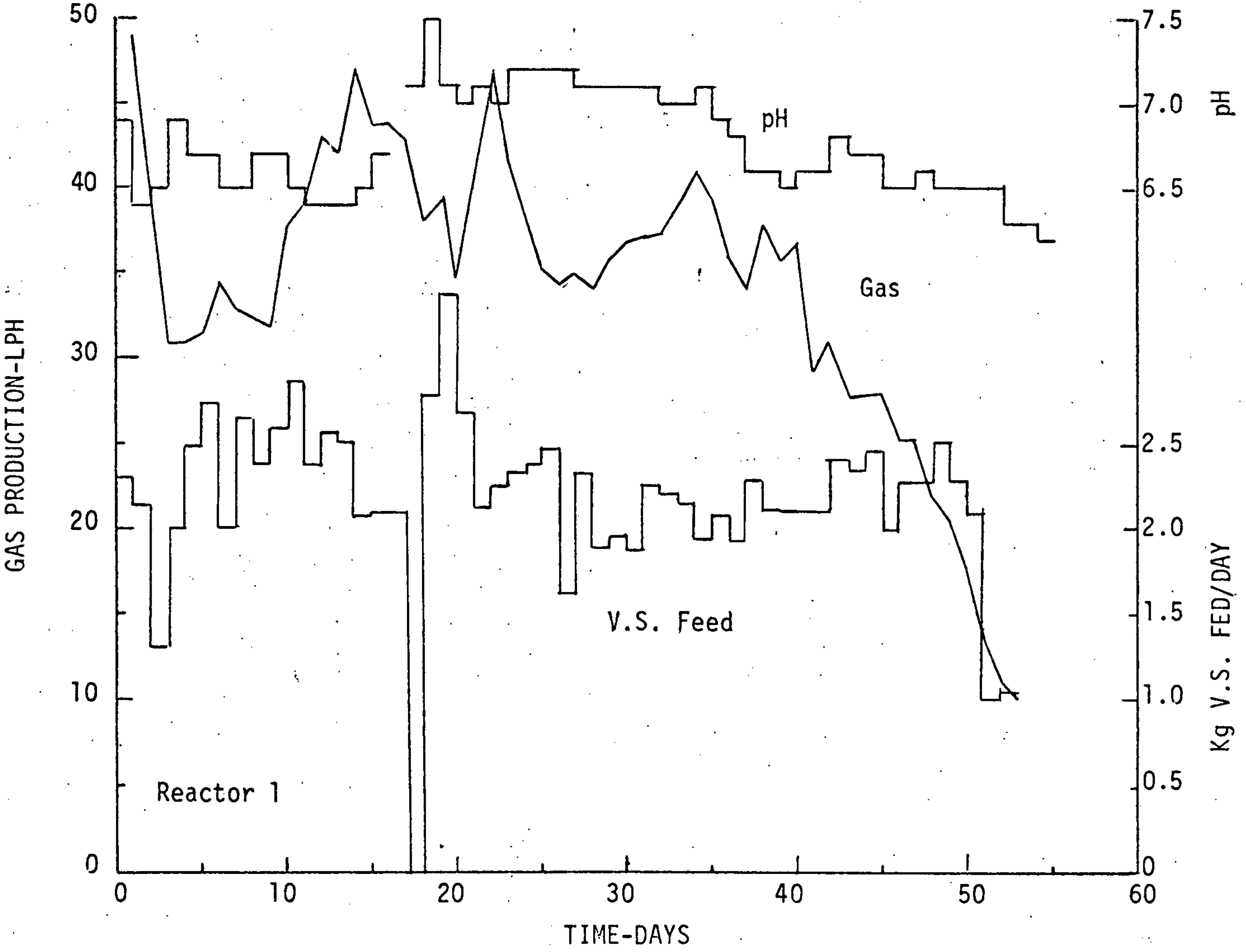

Figure 4. Reactor performance with thermochemical pretreatment.

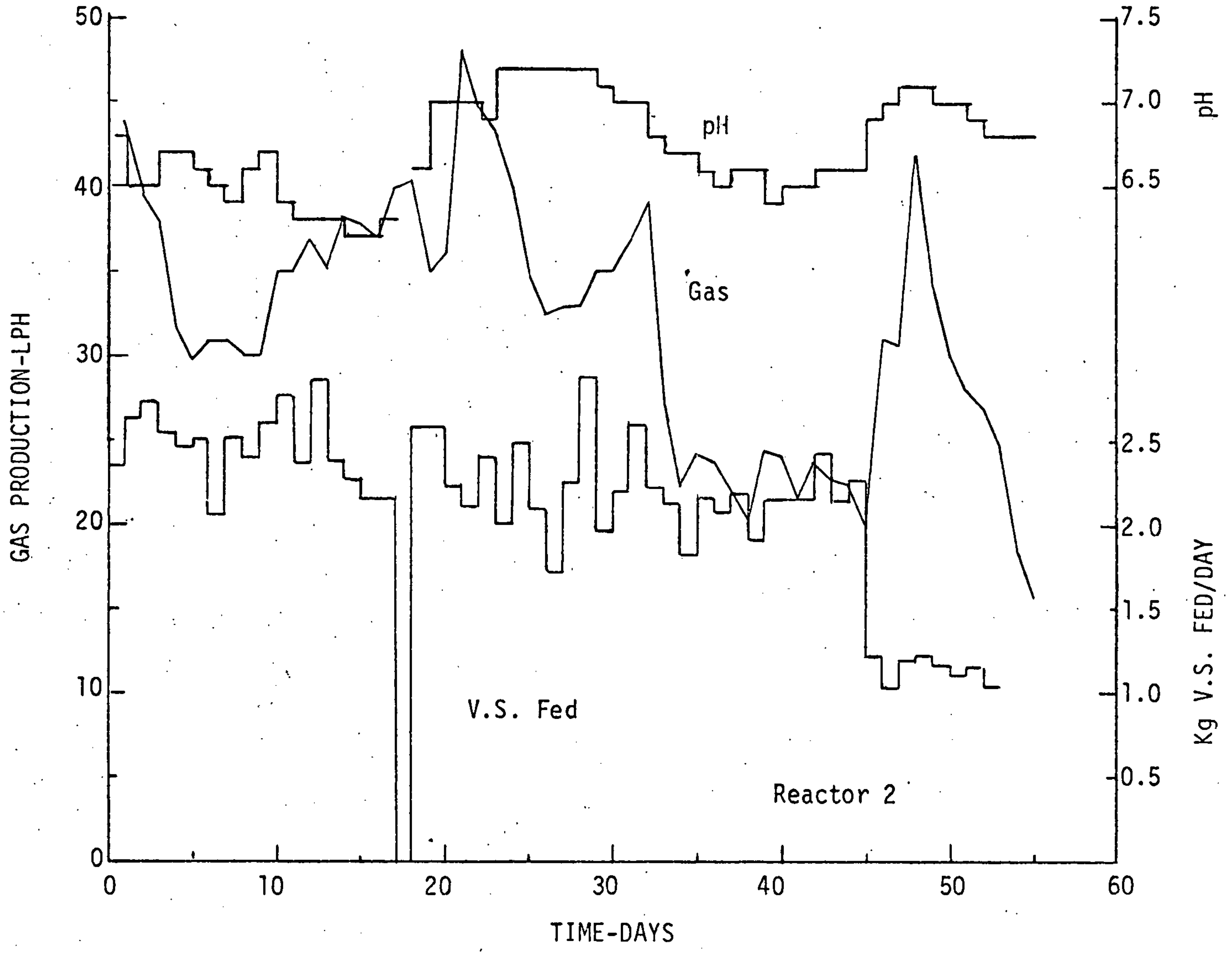

Figure 5. Reactor performance with thermochemical pretreatment.

Table 2. 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

Summary

Experience to date clearly show significant inhibition of methane production as a result of the mild thermochemical pretreatment. Extreme care must be exercised in any application of this process. Additional studies are underway in an attempt to determine an acceptable level of caustic pretreatment and required dilution to eliminate inhibitory effects.