MASTER

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BIOLOGICAL CONVERSION OF BIOMASS TO METHANE

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1. Introduction

After completion of the fermentation studies using manure as the substrate, a series of tests was 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. Stover was collected from the corn fields adjacent to 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.

The particle size of the collected stover was large, with corn stalks up to approximately 30 cm in length. Prior to feeding to the fermenters, the corn stover was milled so that it would pass through a 6.3 mm screen initially and at a later date, through a 3.2 mm screen.

Figure 1 shows the particle size distribution of corn milled on both the 3.2 mm and 6.3 mm screen. The manure milled on the 6.3 mm screen is included as a comparison. The dry corn milled on the 6.3 mm screen is retained to a greater degree on the three largest mesh sizes. The majority of the wetted feed and digested effluent solids are either retained on the 10 mesh screen or pass the 200 mesh screen. Approximately 65 percent of the fermented corn stover slurry "suspended" solids can be removed by 2.0 mm screen. This particle size increase results from swelling of the corn stover by absorption of water. All of the results contained in the report were obtained with stover that passed the 3.2 mm screen.

Figure 1. Corn-Particle Size Distribution at Various Process Stages

2. 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 1. The corn stover feed to the system was milled through the 3.2 mm screen. These data cover the period from January 21, 1978 through August 15, 1978.

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 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.

TABLE 1. CONTROL REACTOR PERFORMANCE

WEEK ENDING	Θ DAYS	GAS LPH	FEED Kg V.S./D	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
199	13.3	13.4	2.02	58.7	0.09
206	13.8	11.6	1.69	55.9	0.09
213	14.1	10.3	1.45	57.5	0.10
220	13.8	11.7	1.63	57.4	0.10
227	14.8	10.7	1.47	55.1	0.10

The effect of retention time on conversion efficiency is shown in Table 2. The four reactors were operated at various retention times as shown in this table. The corn stover slurry was

Table 2. 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	0.047	1.48	0.070
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

fed to the reactor at a continuous rate over a period of 12 to 16 hours daily (4 to 16 liters per hour). Reactor 3 had been operating for approximately 15 weeks at this retention time prior to collecting the data shown in Table 2 (see Table 1). 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 2 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 2. 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 2 were collected from 78109 to 78122.

During this period, the reactor effluents were screened to remove 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, including 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. This allowed for the calculation of the correction factor shown in Table 2. 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 $0.132 \text{ m}^3/\text{Kg vol. solids fed}$ with an average retention time of 14.6 days (see Table 1). The adjusted CH_4

production in Table 2 for Reactor 3 operating at a 13.7 day retention time in 0.129 m³/Kg vol. 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 $S_0 - S$ (m³ CH₄/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 1 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 0.165 m³ CH₄/kg vol. 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 0.415 m³/kg. Based on this maximum possible methane production and the observed S_0 value of 0.165 m³/kg, the corn stover appears to be only 40 percent biodegradable for the test conditions employed (58°C fermentation temperature).

Using the above biodegradability factor and the adjusted gas production in Table 2, a rate constant can be determined on the basis that the gas production rate is first order with respect to biodegradable substrate. The following equation applies:

$$S = \frac{S_0}{1 + K\theta}$$

This equation can be linearized in the following form:

Figure 2. Determination of biodegradability of corn stover.

$$\frac{S_0}{S} = K\theta + 1$$

The slope of the line will be K. A least square computation for the data in Table 2, 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. The corn stover was also found to be 40 percent biodegradable.

3. 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 has shown that sodium hydroxide can be an effective agent in the enhancement of the biodegradability of the organics. A series of tests was 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 3. 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 0.25 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 110°C. After the heat treatment, the pH decreased to approximately 9.5. This paste was then diluted to about 6 percent solids and pumped to the mixing tank for feed to the reactors.

The results of this pretreatment are given in Table 3. 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 retention time in the fermenters of 13.7 days. This pretreatment was repeated again in Reactor 1 during the period from 78197 through 78224. 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:

$$S_0 - S = 0.25 \frac{\text{m}^3}{\text{kg}} = S_0 \left(\frac{K\theta}{1 + K\theta} \right)$$

The calculated value for S_0 is $0.32 \text{ m}^3 \text{ CH}_4$ per kg volatile solids fed. Based on an ultimate gas production of $0.415 \text{ m}^3 \text{ CH}_4$ per kg volatile solids destroyed, the biodegradability of the corn stover was increased from 40 percent to 77 percent.

The above calculation applied to the data collected from Reactor 2 during the period from 78197 through 78224 yield an S_0 value of $0.30 \text{ m}^3 \text{ CH}_4$ per kg volatile solids fed. This would result in a 72 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 Reactor 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

TABLE 3. EFFECT OF NaOH PRETREATMENT OF CORN STOVER

WEEK ENDING	Ø DAYS	GAS PROD. LPH	%CH ₄	CH ₄ PROD m ³ /Kg V.S.	LOADING Kg V.S./m ³ -D	NaOH % DRY SOLIDS
<u>REACTOR 1</u>						
136	8.3	23.7	51.8	0.07	5.2	0
143	12.9	48.4	54.8	0.24	3.4	5.0
150	14.1	41.4	58.2	0.26	2.9	5.0
157	14.2	35.2	61.0	0.25	2.6	5.0
164	14.2	24.4	58.1	0.17	2.6	3.0
171	13.5	22.8	56.2	0.15	2.6	3.0
178	14.4	22.8	56.3	0.18	2.3	3.0
185	13.9	15.9	57.5	0.14	2.0	3.0*
192	14.2	11.6	55.6	0.11	1.8	3.0*
203	14.2	26.8	55.8	0.23	2.0	5.0
210	13.9	26.0	60.0	0.28	1.7	5.0
217	14.0	23.2	58.6	0.24	1.8	5.0
224	14.8	26.3	57.1	0.25	1.9	5.0
<u>REACTOR 2</u>						
164	14.4	19.7	57.7	0.11	3.1	3.0
171	8.5	33.3	-	0.14	4.2	3.0
178	8.2	34.5	57.5	0.15	4.0	3.0
185	7.5	34.8	57.7	0.18	3.4	3.0*
192	7.8	20.0	54.9	0.10	3.4	3.0*
203	7.2	49.1	60.3	0.23	4.0	5.0
210	8.1	41.6	58.9	0.24	3.1	5.0
217	7.3	34.2	55.9	0.18	3.4	5.0
224	7.6	36.7	53.6	0.16	3.7	5.0

* NaOH + Ca(OCl)₂ added to pretreatment step.

pH, 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 m³ CH₄ per kg volatile solids fed. Reactor 2, operating at a retention time of 8.4 days, had a methane production rate of 0.145 m³ 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 indicate 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 decreased.

3. Additional Studies of Corn Stover

The corn stover feed has been terminated. Additional data on the dewatering properties have been collected. Also, data on the chemical characteristics of the stover, before and after fermentation, have been collected. These data are being analyzed and will be included in the study report on corn stover that is in preparation.

4. Current Substrate Investigations

On August 15, 1978, wheat straw became the substrate under investigation. Numerous problems have been encountered in handling the straw, especially in the slurry feed system. However, preliminary data suggest that methane yields will be comparable to corn stover.