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BIOLOGICAL CONVERSION OF BIOMASS TO METHANE

QUARTERLY PROGRESS REPORT
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DISCLAIMER

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

1. Particle Size Distribution

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

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

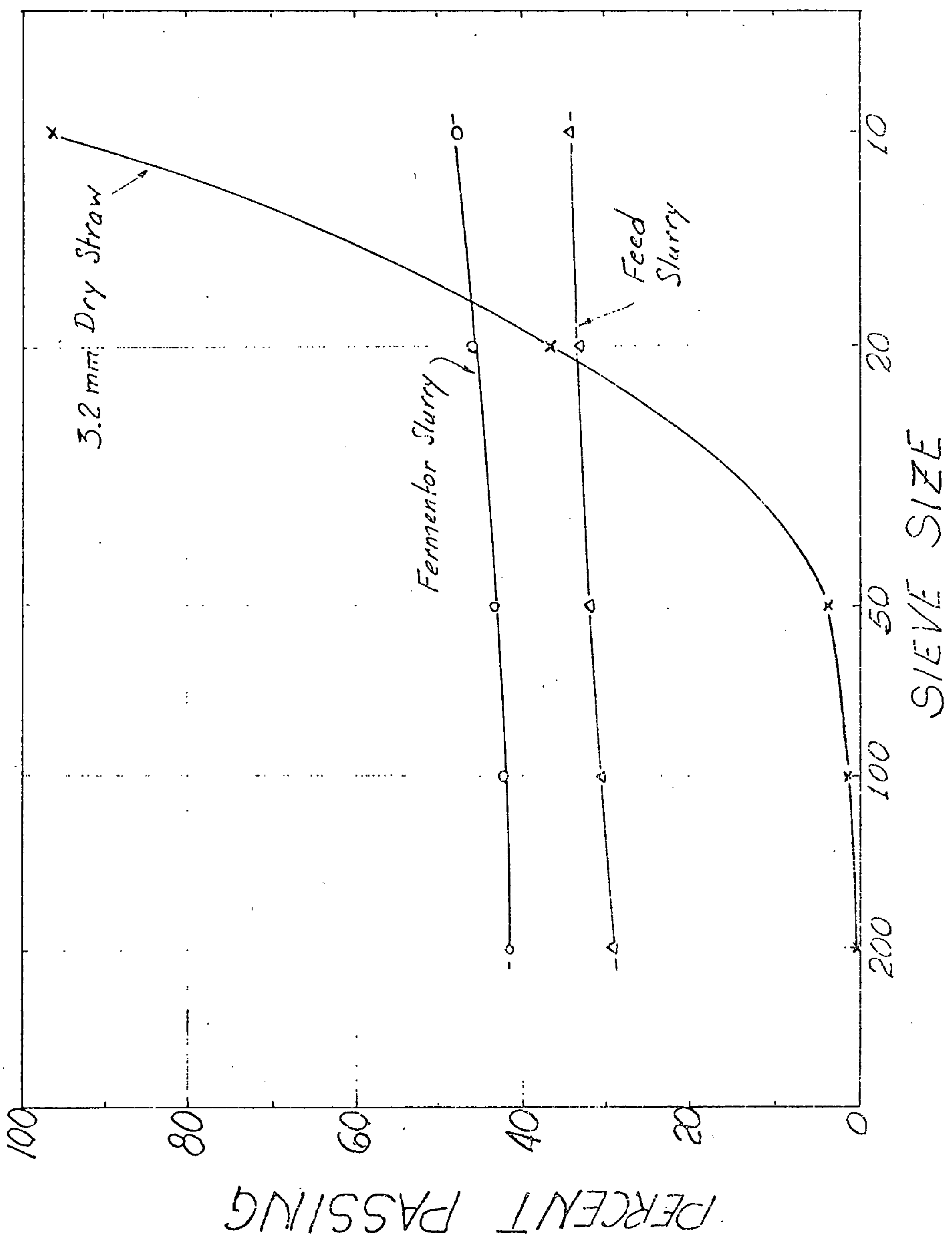

Figure 1. Particle Size Distribution of Chopped Straw

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

2. Straw Slurry Characteristics

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

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

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

3. Gas Production Data

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

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

Table 1. Gas Production Data for Wheat Straw

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

Table 2. Gas Production Data for Straw

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

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

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

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

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

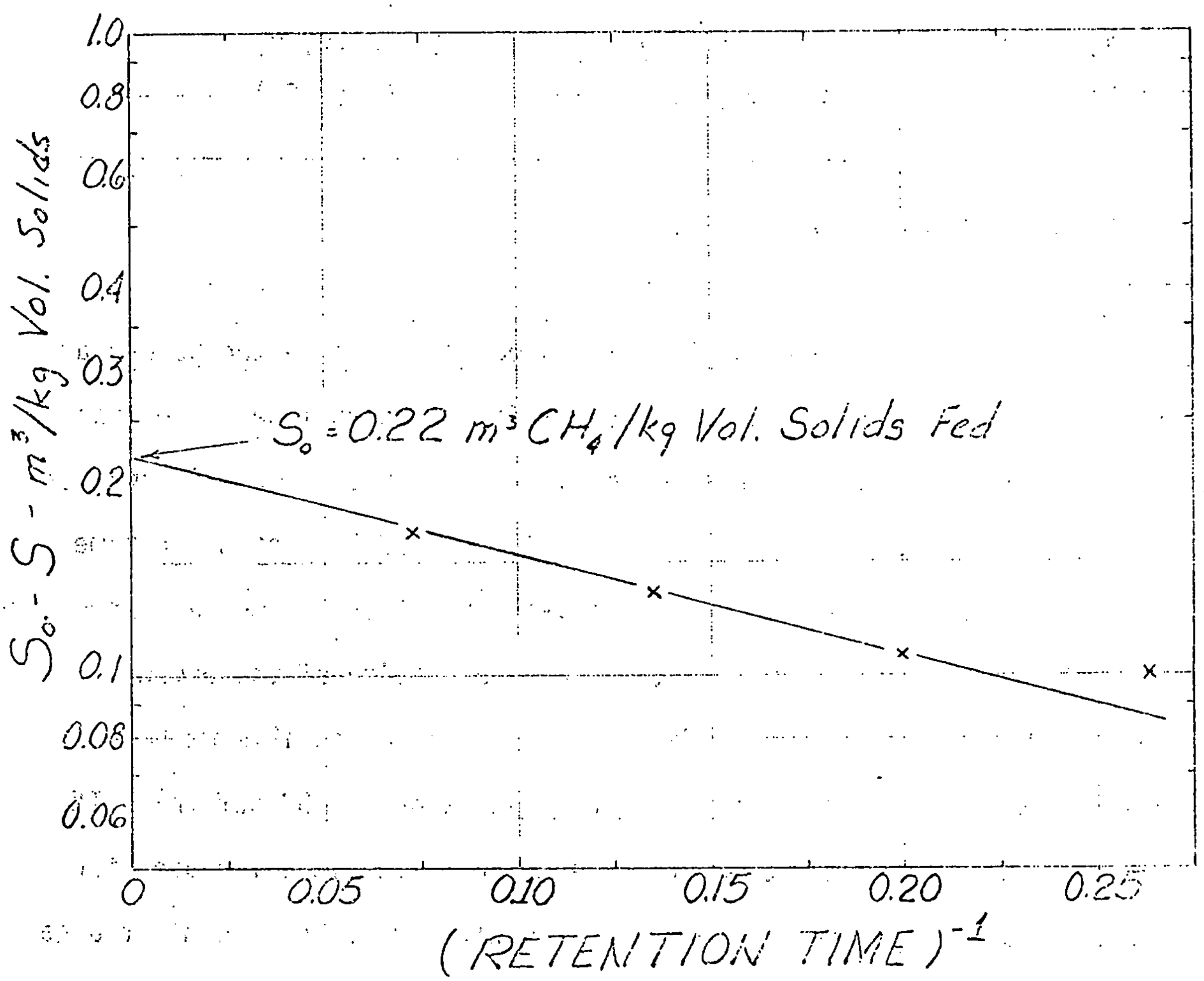

Figure 2. Determination of the Fraction of Volatile Solids that are Biodegradable

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

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

where:

S = biodegradable substrate remaining

S_0 = initial biodegradable substrate

θ = reactor retention time - days

K = rate constant - day^{-1}

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

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

4. Discussion

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

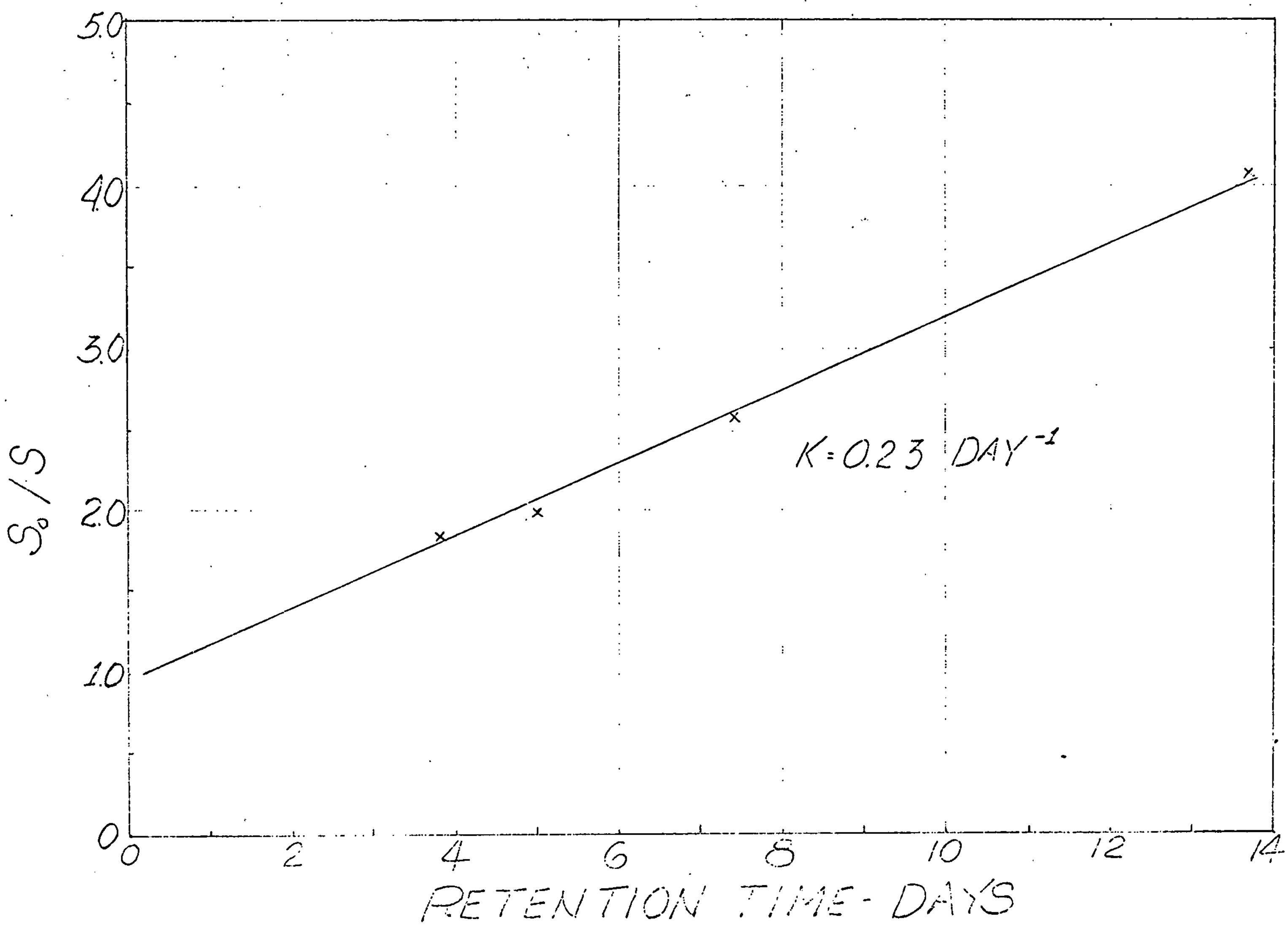

Figure 3. Determination of the Rate Constant for Straw Fermentation

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

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

*S_{nb} denotes the nonbiodegradable volatile solids

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

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

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

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

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

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

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

Reference

Speece, R. E. and McCarty, P. C., "Nutrient Requirements and Biological Solids Accumulation in Anaerobic Digestion," Advances in Water Pollution Research, 2, 305-322, W. W. Eckenfelder (ed.), Pergamon Press, New York, 1964.

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