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HIGH RATE LOW SOLIDS METHANE FERMENTATION OF SORGHUM, CORN AND CELLULOSE

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Abstract—Sorghum, sorghum/alpha-cellulose mixture, and corn were anaerobically digested at 55°C at effluent solids contents of 8–12% total solids (TS), using trace nutrient supplementation. Volatile solids (VS) loading rates at much higher levels than conventional maxima were maintained without volatile fatty acid (VFA) accumulation. Semi-continuously fed digesters with organic loading rates (OLR) up to 12 gVS kg^{-1} d^{-1} produced methane at rates up to 3.3 L kg^{-1} d^{-1}. Continuous feeding of corn at an OLR of 18 gVS kg^{-1} d^{-1} resulted in a methane production rate of 5.4 L kg^{-1} d^{-1}. VS removal efficiencies at maximum OLRs were 60% (sorghum) and 67% (corn). At an OLR of 4 gVS kg^{-1} d^{-1}, sorghum alone as a feedstock led to excess ammonia-N accumulation. Excess ammonia did not accumulate at sorghum loading rates of 8 and 12 gVS kg^{-1} d^{-1}, nor with a sorghum/alpha-cellulose mix loaded at 8 gVS kg^{-1} d^{-1}. Instantaneous gas production rates were directly related to feedstock cell soluble content, with peak instantaneous biogas production rates from corn (OLR of 8 gVS kg^{-1} d^{-1}) approaching 25 L kg^{-1} d^{-1} following a three-day feeding.

Keywords—Anaerobic digestion, methane, biogas, biomass, trace nutrients, sorghum, corn, fiber analysis, C:N ratio.

1. INTRODUCTION

Methane fermentation of biomass produces a clean fuel that is renewable, but economic feasibility of the process is limited by, among other factors, relatively low rates of methane production.[1] While extremely high conversion and production rates have been reported from pH-controlled systems fed acetate with carefully balanced trace nutrient additions,[2] methane productivities from naturally-occurring particulate biomass are generally under 2 vCH_4 v^{-1} d^{-1}. Semi-continuously fed-and-mixed (SCFM) slurry digesters fed sorghum had maximum volumetric methane production rates of 1.5 to 1.8 v v^{-1} d^{-1} (VS loading rates of 4.8 to 6 g kg^{-1} d^{-1}).[3,4] Attempts to increase loading rates resulted in digester failure. A non-mixed vertical flow digester fed sorghum at a VS loading rate of 7.5 gVS L^{-1} d^{-1} produced 2.0 v v^{-1} d^{-1} of methane.[5]

Operation at higher digester solids contents concentrates digesting biomass and allows higher loading rates, increasing volumetric methane productivity. Rates approaching 5 vCH_4 v^{-1} d^{-1} have been reported from digestion of the organic fraction of municipal solid waste.[6,7] Digestion of a 1:1 sorghum/alpha-cellulose mix yielded methane productivities of up to 7.5 L kg^{-1} d^{-1} at 28–29% effluent total solids.[8] Trace nutrient supplementation was required for stable operation.

The experiments described here were run to determine the potential for high rate operation of low solids (8–12% effluent TS) systems at methane productivities higher than 2 L kg^{-1} d^{-1} with trace nutrient supplementation. ("Low solids" is here defined as a digesting slurry that has free drainable liquid.) It has been suggested that trace nutrient additions are likely to be required for stable digestion of biomass.[9] Four napiergrass digesters operated at a low loading rate saw a marked reduction in volatile fatty acid (VFA) concentrations and a corresponding increase in biogas production when trace quantities of nickel, cobalt, molybdenum, selenium and sulfur were added.[10]

Sorghum (*Sorghum bicolor* L. Moench) has been identified as a potential "energy crop" due to high yields and biodegradability.[11] Field corn (*Zea mays* L.) has comparable cultural requirements and dry matter yields[3] in New York State, but yields of corn are somewhat more reliable, since sorghum is sensitive to the state's relatively cool climate.[12]

2. MATERIALS AND METHODS

2.1. *Substrate analysis*

Sorghum (commercial hybrid silage variety X9204, Stanford Seeds) was grown at Cornell

University in 1987. The entire above-ground250portion of the plant was field-chopped after maturity and ensiled at 30–40% TS by sealing it in a large plastic bale bag at room temperature. Corn (an unknown commercial field corn variety with 85–105 days maturity) was grown at Cornell University in 1989. As with sorghum, the entire plant (including grain) was field-chopped after maturity and ensiled in a large bunker silo. Both crops were grown and harvested using conventional cultural practices. The resulting ensiled materials were later air-dried at 55°C to over 90% TS to prevent spoilage during handling, and were hammermilled to fracture seeds and to reduce particle sizes to less than 0.5 cm. All solids analysis and kinetics were based on the composition of the materials after drying and milling. For one condition, sorghum and alpha-cellulose (Sigma Chemical) were mixed 1:1 on a VS basis to adjust the C:N ratio.

Fiber and *in vitro* analyses were conducted using the methods of Van Soest and Robertson[13] and Robertson and Van Soest.[14] The standard 48 h *in vitro* digestibility test was extended to 96 h to better approximate ultimate biodegradabilities. Biochemical methane potential (BMP) assays were carried out using a modified procedure of Owen *et al.*[15] Elemental analysis was carried out by inductively-coupled plasma (ICP) emission spectroscopy, and carbon/hydrogen/oxygen analysis was performed by Galbraith Laboratories (Knoxville, TN).

2.2. *Digester operation*

Digesters were operated as thermophilic (55°C) semi-continuously fed-and-mixed systems, with feed added and effluent removed three times per week. Digesters were 10 L wide-mouth polypropylene carboys, operated with constant net contents of 5 kg (sorghum digesters, Conditions 1 through 4) or 3 kg (corn digesters, Conditions 5 and 6). Digester solids contents were maintained between 8 and 12% TS throughout the study.

A dry material feeder (AccuRate Inc. Model 300 with custom 1″ helix) was used for the highest loading rate corn condition (Condition 6). Its purpose was to ameliorate the shock that results from the instantaneous addition of several days' feed, rather than to achieve a true continuous feeding regime. As such, the feeder was operated 1 min h^{-1} (concurrent with mixing) at a rate such that all feed for a two or three day interval was added by 18–24 h before the next sampling. This was done to optimize conversion efficiency by ensuring that all feed particles had at least an 18 h residence time.

A nitrogen gas purge was used to prevent air from entering the reactors during feeding and wasting. (It is unlikely that this technique totally excluded oxygen from the reactor headspace.) Digesters were mounted on a shaker table and mixed (approximately 100 rpm, 1 inch orbit) for 5 min h^{-1} (10 min for the highest loading rate corn condition), as well as manually before effluent removal and after addition of feed. This mixing regime was observed to result in complete mixing of digester contents. Tap water was added as part of the influent to control digester solids concentration. For the corn conditions, screened (#16 sieve, 1.2 mm openings) liquid separated from stored digester effluents was used in place of tap water. This was done to reduce the need for supplementation of ammonia-N and other nutrients. Trace nutrients (from soluble salts) were supplemented at rates shown in Table 1. No attempt was made to optimize these addition rates other than to ensure that reactor concentrations of added elements remained in the general ranges which accompanied stable performance in previous high solids digesters.[8] Addition rates were generally proportional to the OLR, with rates

Table 1. Trace nutrient elemental addition rates (mg kg^{-1} d^{-1}) and source compounds

Element	Conditions 1	2 and 3	4	5	6	Source
Ni	—	1.50	2.10	0.90	3.50	$NiSO_4 \cdot 6H_2O$
Co	—	1.00	1.40	0.50	1.95	$CoCl_2 \cdot 6H_2O$
Mo	—	1.25	1.75	0.63	2.44	$NaMoO_2 \cdot 2H_2O$
W	—	0.20	0.30	0.10	0.39	$Na_2WO_4 \cdot 2H_2O$
S	—	5.0	7.0	2.4	9.5	K_2SO_4
Cu	—	—	—	0.001	0.004	$CuSO_4 \cdot 5H_2O$
V	—	—	—	0.002	0.006	NH_4VO_3
Zn	—	—	—	0.12	0.45	$ZnSO_4 \cdot 7H_2O$
B	—	—	—	0.003	0.013	H_3BO_3
Mn	—	—	—	0.005	0.020	$MnSO_4 \cdot H_2O$

lowered somewhat for corn (Conditions 5 and 6) due to the recycling of screened liquid. Due to the low VS loading rate and high background concentrations of trace elements resulting from the initial inoculum (well-digested sorghum), no trace nutrient additions were required for Condition 1. No base or buffer additions were made to any condition. In general, operating conditions were chosen to provide, if possible, a "safe excess" of environmental factors to allow maximum reaction rates.

2.3. *Analysis procedures*

Laboratory procedures and methods for kinetic analysis are detailed elsehwere.[8,16] Trace metal analysis was performed on acid extracts (using HCl, extract pH < 2) of the effluent using ICP spectroscopy. The measured trace nutrient concentrations were thus viewed as a "minimum labile pool", including not only trace nutrients normally in solution but also those easily acid-solubilized. Concentrations and rates were expressed on a mass basis. Mass removals were determined both on the basis of reactor mass loss (corrected for evaporation) and by the mass of biogas produced. VS removals were determined by VS mass balance and by comparison with total mass removals corrected for water removed by hydrolysis. Retention times are reported as solids retention time (SRT, reactor mass divided by effluent rate). Also reported is the influent-based "hydraulic retention time", HRT_i (reactor mass divided by the total inflow rate), which defines the total wet mass loading rate, not the actual residence time of material in the reactor.[16]

Gas volumes were measured with a wet gas meter. The pattern of biogas production during feeding intervals was recorded by connecting an event recorder (Esterline-Angus EventGraph) to the wet gas meter. Biogas volumes were standardized as dry biogas at 0°C and one atmosphere pressure. Effluent from several conditions was subjected to fiber analysis, as detailed above.

3. RESULTS

3.1. *Substrate composition*

Results of elemental analysis are presented in Table 2. The values for the sorghum/alpha-cellulose mix are calculated from component results (alpha-cellulose analysis is presented elsewhere[8]). Empirical formulae were calculated from the respective CHON contents, using a common carbon coefficient of 6. Fiber and digestibility analyses are shown in Table 3. Data shown for the sorghum/alpha-cellulose mix

Table 2. Solids and elemental analysis of sorghum, sorghum/alpha-cellulose mix (calculated from components, solids confirmed by analysis) and corn

	Sorghum	Mix	Corn
Total solids, %	94.5	95.0	95.1
Ash, % of TS	5.80	2.99	2.51
VS, % of TS	94.2	97.0	97.5
Per cent of TS:			
C	46.3	45.3	47.2
H	6.17	6.36	6.40
O	38.1	43.2	41.4
N	1.32	0.68	1.16
K	2.10	1.08	0.72
P	0.272	0.140	0.23
Ca	0.297	0.164	0.17
Mg	0.235	0.121	0.23
S	0.124	0.066	0.11
C/N ratio	35.1	66.6	40.6
C/P ratio	170	324	205
Empirical formulae	$C_6H_{9.6}O_{3.7}N_{0.15}$	$C_6H_{10.1}O_{4.3}N_{0.08}$	$C_6H_{9.8}O_{4.0}N_{0.13}$
Parts per million (PPM) of TS:			
Fe	244	130	133
Na	18.0	230	16.4
Zn	29.8	15.6	18.7
Mn	18.9	9.82	10.5
Cu	5.68	2.99	11.6
B	4.71	2.46	1.95
Mo	0.66	0.34	0.13
Co	0.16	0.08	0.15
Cd	0.12	0.06	0.00
Cr	0.73	0.38	0.00
Ni	0.44	0.31	0.10
V	0.17	0.12	0.01

Table 3. Substrate fiber and digestibility analysis

Substrate	Sorghum	Mix	Corn
Neutral detergent fiber analysis, % of VS:			
Cell solubles	45.9	24.8	54.2
Hemicellulose	18.8	10.0	21.0
Cellulose	27.3	60.8	22.0
Crude Lignin	7.95	4.36	2.74
Lignin	3.57	1.69	1.48
Cutin	4.38	2.67	1.25
In vitro digestibility, % of VS	79.1	87.6	87.4
BMP Assay			
Methane potential, L g^{-1} VS	0.36	0.38	NA
VS destruction, %	82.0	90.7	91.8

were the results of direct analysis, except as noted below. Sorghum had a large cell soluble component (46% of VS), and a crude lignin content of nearly 8%, divided equally between lignin (as determined by permanganate) and cutin. The cellulose content of the sorghum/alpha-cellulose mix was 60%, with nearly 25% cell solubles. Corn had the highest cell soluble content (54.2%) and the lowest crude lignin content (2.7%) of any of the feedstocks. *In vitro* digestibilities (96 h) were uniformly lower than the digestibilities determined by the much longer BMP analysis. Volatile solids destruction as measured during BMP analysis were 82% for sorghum and 91.8% for corn. Due to an abnormally large variability in replicates, the measured 90.5% VS destruction for the sorghum/alpha-cellulose mix was not used. Instead, values were calculated from mix component data, resulting in a methane potential of 0.38 L gVS^{-1} and a nearly-identical VS destruction of 90.7%.

3.2. *Sorghum and sorghum/alpha-cellulose digester operation*

Steady performance results for sorghum and sorghum/alpha-cellulose mix digester conditions are shown in Tables 4 and 5. Sorghum alone as a feedstock operated in a stable manner at a conventional organic loading rate (OLR) of 3.9 gVS kg^{-1} d^{-1} (Condition 1, Fig. 1), with a 70.2 day SRT. Methane production was stable at 1.33 L kg^{-1} d^{-1}, with a methane yield of 0.34 L gVS^{-1}, which was 93.7% of sorghum's BMP. The mean mass removal rate was 3.19 g kg^{-1} d^{-1}, with a VS removal rate of 2.85 gVS kg^{-1} d^{-1}, indicating 0.109 g water consumed by hydrolysis per gram mass removed. The efficiency of VS conversion and removal was 72.4%. Despite stability of all other indices,

Table 4. Steady performance period results for sorghum (Conditions 1, 3 and 4) and sorghum/alpha-cellulose mix (Condition 2) (standard deviation in parentheses)

Condition	1	2	3	4
Days operated continuously at OLR	97	72	86	72
Number of SRTs operated	1.4	2.0	3.2	4.3
Analysis period, day #s	78–97	37–72	135–158	54–79
Length of analysis period, days	19	35	23	25
VS OLR (gVS kg^{-1} d^{-1})	3.93	7.76	7.93	12.2
HRT_i (influent-based, days)	57.6	28.9	23.4	14.8
SRT (days)	70.2	35.9	26.6	16.7
Biogas production (L kg^{-1} d^{-1})	2.48 (0.17)	5.26 (0.53)	4.17 (0.13)	6.15 (0.26)
Methane production (L kg^{-1} d^{-1})	1.33 (0.09)	2.73 (0.27)	2.25 (0.07)	3.26 (0.14)
Methane content (%)	53.4	52.0	54.0	53.0
Methane yield (L gVS^{-1})	0.34	0.35	0.28	0.27
Methane yield (% of BMP)	93.7	92.7	77.5	74.1
Mass removal rate				
Mass loss basis (g kg^{-1} d^{-1})	3.21 (0.21)	6.85 (0.64)	5.49 (0.17)	7.98 (0.32)
Biogas basis (g kg^{-1} d^{-1})	3.18 (0.19)	6.90 (0.58)	5.37 (0.17)	8.00 (0.34)
Mean (g kg^{-1} d^{-1})	3.19	6.88	5.43	7.99
VS removal rate (gVS kg^{-1} d^{-1})	2.85 (0.10)	5.93 (0.67)	4.98 (0.20)	7.27 (0.41)
VS removal efficiency (%)	72.4	76.4	62.8	59.5
Hydrolysis (gwater g mass $removed^{-1}$)	0.109	0.137	0.083	0.090
BVS OLR (g BVS kg^{-1} d^{-1})	3.23	7.04	6.50	10.0
So (g BVS g $influent^{-1}$)	0.186	0.204	0.152	0.148
Se (g BVS g $effluent^{-1}$)	0.027	0.040	0.041	0.046
First order k (d^{-1})	0.11	0.15	0.12	0.16

Table 5. Steady performance period effluent analysis for sorghum (Conditions 1, 3 and 4) and sorghum/alpha-cellulose mix (Condition 2)

Condition	1	2	3	4
Total solids (%)	9.76	7.91	9.54	9.41
Volatile solids (% of TS)	82.4	84.3	84.5	84.5
pH	7.85	7.34	7.62	7.66
Total Kjeldahl N (TKN, mg kg^{-1})	NA	NA	3,590	3,310
Total ammonia-N (TAN, mg kg^{-1})	1474*	537	729	742
Free NH3-N (mg kg^{-1})	316*	42	99	109
Ammonia-N supplementation rate (mg N kg^{-1} d^{-1})	0	16	0	0
Net influent C:N ratio	40.6	51.5	40.6	40.6
Alkalinity (g kg^{-1} as $CaCO_3$):				
Total	10.2	5.37	8.28	7.95
Bicarbonate	8.33	4.96	7.93	7.46
Total VFA (mg kg^{-1})	156	51	91	110
Acetic acid (mg kg^{-1})	109	31	68	68
Propionic acid (mg kg^{-1})	11	3	15	30
Acid-extractable trace metals (mg kg^{-1})				
K	4270	3840	4280	4050
P	NA	NA	630	650
Ca	1232	763	678	645
Mg	733	504	511	477
Na	146	133	38	46
Fe	363	138	61	61
S	49	63	53	54
Zn	25	19	10	10
Mn	10	4	4	4
Ni	2	28	28	23
Co	1	14	13	11
Mo	2	3.5	5.5	7.1
B	2	1.1	1.3	1.8
Cu	0	0.5	0.01	0.1

*Ammonia-N increasing, final values shown.

total ammonia-N (TAN) continually accumulated, reaching 1,500 mg kg^{-1} (Fig. 1). The rate of accumulation during steady performance was 8.4 mgTAN kg^{-1} d^{-1}. The condition was terminated to preclude further accumulation and possible ammonia toxicity. Trace nutrient concentrations steadily declined from their high initial levels, but remained at detectable levels throughout the analysis period (Table 5).

To prevent TAN accumulations in condition 2, sorghum/alpha-cellulose mix was used as the feedstock, and the OLR was increased to 7.76 gVS kg^{-1} d^{-1}. Trace nutrient additions were begun. Operation was again stable: the noticeable period-to-period variation in removals (Fig. 2) tended to reflect the thrice-weekly feeding pattern, as was observed in high solids systems fed the same feedstock.[8]

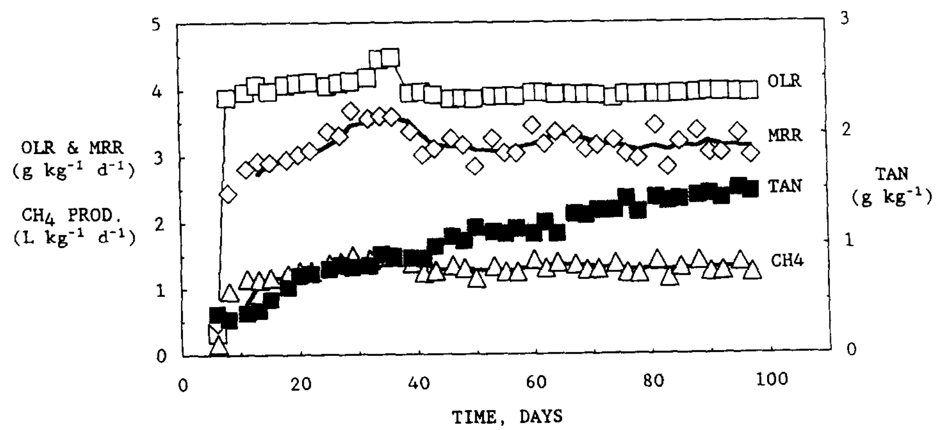

Fig. 1. Condition 1 (sorghum) operation. Organic loading rate (OLR), mass removal rate (MRR), methane production rate (CH_4), and effluent total ammonia-N concentration (TAN). Bold lines indicate weekly running means.

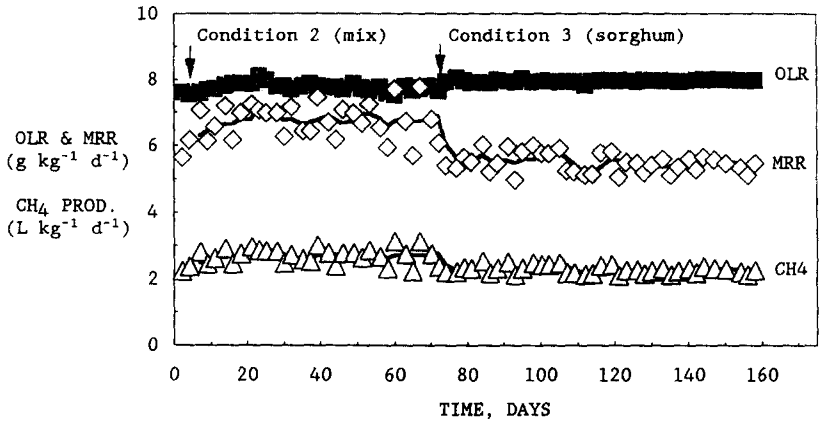

Fig. 2. Condition 2 (mix) and 3 (sorghum) operation. Same key as Fig. 1.

One-week running means show that the overall operation was stable. The mean methane production rate was 2.73 L kg^{-1} d^{-1}, with a methane yield of 0.35 L gVS^{-1}. The mean mass removal rate was 6.88 g kg^{-1} d^{-1}. The VS removal rate was 5.93 gVS kg^{-1} d^{-1}, yielding a VS removal efficiency of 76.4%. Mean total VFAs were only 51 mg kg^{-1}, indicating very stable operation. Ammonia-N (as NH_4Cl) eventually had to be supplemented at a constant rate of 16 mgN kg^{-1} d^{-1} to maintain an average effluent TAN concentration of 537 mg kg^{-1}. The *N* addition resulted in a net influent C:N ratio of 51.5.

Pure sorghum feedstock was then used at an OLR of 7.93 gVS kg^{-1} d^{-1} for Condition 3 (Fig. 2). The shorter SRT (26.6 days) resulted in acceptable equilibrium TAN concentrations of 729 mgN kg^{-1}. The mass removal rate stabilized at 5.43 g kg^{-1} d^{-1}, lower than in Condition 2 due to the lower biodegradability of the sorghum alone. Similarly, the VS removal efficiency of 62.8% was also lower. Mean total VFAs were 91 mg kg^{-1}.

Due to the stability of Condition 2, a second digester was started to operate concurrently using sorghum loaded at a rate of 12.2 gVS kg^{-1} d^{-1} and an SRT of 16.7 days (Condition 4). This digester also operated in an extremely stable manner (Fig. 3), producing methane at 3.26 L kg^{-1} d^{-1}, with a methane yield of 0.27 L gVS^{-1}. The mean mass removal was 7.99 g kg^{-1} d^{-1}, with a VS removal rate of 7.27 gVS kg^{-1} d^{-1}. The VS removal efficiency was 59.5%. Mean VFAs were 110 mg kg^{-1}, and TAN concentrations averaged 742 mgN kg^{-1}.

For Conditions 1 through 4 conventionally-defined "retention times", HRT_i (reactor mass divided by the total mass inflow rate), were shorter than the actual retention times (SRT) due to the removal of a significant fraction of the total influent mass of biogass. SRT/HRT_i ratios ranged from 1.13 to 1.22 (sorghum conditions) to 1.24 (sorghum/alpha/cellulose mix).

3.3. *Corn digester operation*

Condition 5 (Fig. 4) was operated with corn at an OLR of 8.25 gVS kg^{-1} d^{-1} with a SRT of

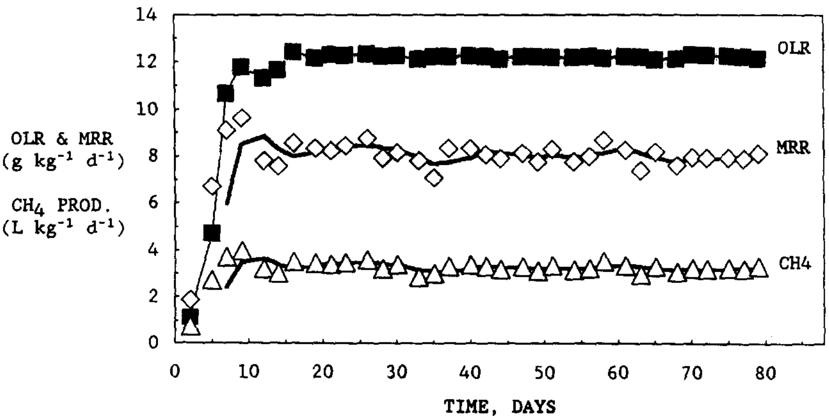

Fig. 3. Condition 4 (sorghum) operation. Same key as Fig. 1.

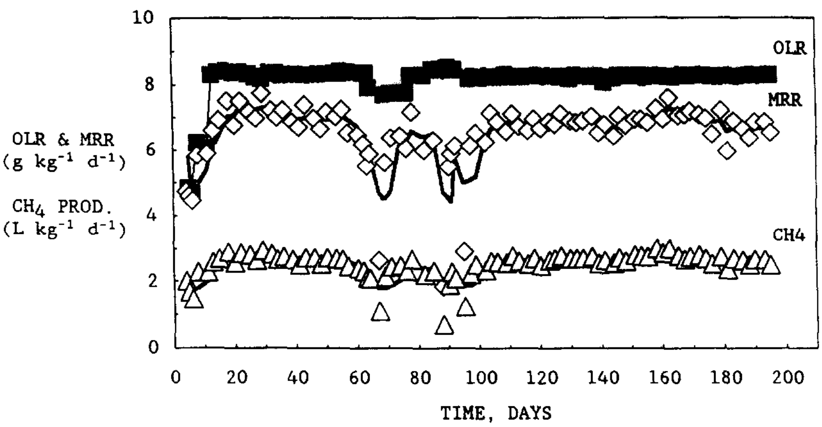

Fig. 4. Condition 5 (corn) operation. Same key as Fig. 1.

30.9 days, and appeared stable until day 60, when VFA (primarily propionic acid) began to rapidly accumulate, reaching 2 g kg^{-1} total VFA. Additions of recycled liquids were begun at the rate of 10 mL kg^{-1} d^{-1} to help prevent possible shortages of limiting nutrients as well as to increase TAN concentrations. The system recovered, consuming all excess VFA in a single feeding interval. An attempts on day 78 to extend the feeding interval to 4 days (thereby increasing the instantaneous loading rate) triggered a second period of VFA accumulation, again primarily propionate. Excess VFAs were only gradually removed as feedings were resumed. Operation thereafter was stable, with a mean methane production rate of 2.69 L kg^{-1} d^{-1} and a methane yield of 0.326 L gVS^{-1} (Tables 6 and 7). The mass removal rate was 6.87 g kg^{-1} d^{-1}, and the VS removal rate was 5.87 gVS kg^{-1} d^{-1}, yielding a hydrolysis coefficient of 0.146 g H_2O hydrolytically consumed per gram mass removed. The VS removal efficiency was 71.2%. Mean VFAs were 167 mg kg^{-1}.

A range of higher loading rates were attempted with the continuous feeder. Operation

Table 6. Corn semicontinuous (Condition 5) and continuous (Condition 6) steady performance period results (standard deviation in parentheses)

Condition	5	6
Days operated continuously at OLR	195	67
Number of SRTs operated	6.3	5.0
Analysis period, days	111–195	39–67
Length of analysis period, days	84	28
Recycle rate (mL kg^{-1} d^{-1})	10.0	50.9
Recycled TS (gTS kg^{-1} d^{-1})	0.39	1.19
Recycled VS (gVS kg^{-1} d^{-1})	0.29	0.92
Recycled TAN (mgN kg^{-1} d^{-1})	9.8	48.6
Recycled TKN (mgN kg^{-1} d^{-1})	NA	154
VS OLR (gVS kg^{-1} d^{-1})	8.25	18.1
HRT_i (influent-based, days)	25.5	11.1
SRT (days)	30.9	13.2
Biogas production (L kg^{-1} d^{-1})	5.20 (0.23)	10.0 (0.41)
Biogas calculated from mass loss (L kg^{-1} d^{-1})	—	10.6 (0.38)
Methane production (L kg^{-1} d^{-1})	2.69 (0.78)	5.43 (0.19)
Methane content (%)	51.8	51.8
Methane yield (L gVS^{-1})	0.326	0.300
Mass removal rate		
Mass loss basis (g kg^{-1} d^{-1})	6.90 (0.28)	14.1 (0.52)
Biogas basis (g kg^{-1} d^{-1})	6.84 (0.31)	13.3 (0.56)
Mean (g kg^{-1} d^{-1})	6.87	—
VS removal rate (gVS kg^{-1} d^{-1})	5.87 (0.80)	12.2 (0.58)
Hydrolysis (g water g mass removed^{-1})	0.146	0.136
VS removal efficiency (%)	71.2	67.4
BVS OLR (gBVS kg^{-1} d^{-1})	7.57	16.6
So (g BVS g influent^{-1})	0.193	0.184
Se (g BVS g effluent^{-1})	0.053	0.058
First order k (d^{-1})	0.11	0.21

Table 7. Corn semicontinuous (Condition 5) and continuous (Condition 6) steady performance period effluent analysis

Condition	5	6
Total solids	9.58	11.0
Volatile solids (% of TS)	88.4	87.7
pH	7.32	7.44
Total Kjeldahl N (TKN, mg kg^{-1})	3880	4900
Total ammonia-N (TAN, mg kg^{-1})	418	735
Free NH3-N (mg kg^{-1})	31	70
Total VFA (mg kg^{-1})	167	1250
Acetic acid (mg kg^{-1})	88	67
Propionic acid (mg kg^{-1})	28	1167
Acid-extractable trace nutrients (mg kg^{-1})		
K	3167	3670
P	798	700
Ca	721	845
Mg	939	959
Na	128	80
Fe	38.6	31
S	77	88
Zn	14.2	13
Mn	3.6	4.7
Ni	26.4	33
Co	7.9	14
Mo	3.3	4.1
B	1.2	1.2
Cu	0.5	0.6

at an OLR of 21 gVS kg^{-1} d^{-1} with a SRT of 11 days resulted in a gradual reactor failure (data not shown). At a reduced loading rate of 18 gVS kg^{-1} d^{-1} with a 13.2 day SRT (Condition 6) the system operated in a stable manner (Fig. 5). Power was interrupted and feeder control stopped during days 33–35, drastically lowering the OLR for that interval. The VFA content fluctuated throughout the condition, but appeared to be self-controlling, with no outside intervention required. (The first decline in VFA content, accelerated by the drop in feed additions during days 33–35, began spontaneously 2 feedings earlier.) The mean VFA content for the period was 1,250 mg/kg, predominantly propionate (1,167 mg/kg). The recycle rate of screened liquids for this condition was 50.9 mL kg^{-1} d^{-1}, resulting in solids loading rates of 1.19 gTS kg^{-1} d^{-1} and 0.92 gVS kg^{-1} d^{-1}. Nitrogen loading rates from the recycle were 48.6 mg kg^{-1} d^{-1} TAN and 154 mg kg^{-1} d^{-1} TKN.

A slow but consistent gas leak, eventually traced to the feeder system, was present during Condition 6, as evidenced by the approximately 6% disparity in Table 6 between mass removal rates calculated from mass losses (14.1 g kg^{-1} d^{-1}) and from measured biogas production (13.3 g kg^{-1} d^{-1}). Total gas production, estimated by back-calculating from the mass-loss-based removal rate, was 10.6 L kg^{-1} d^{-1}, resulting in a methane pro-

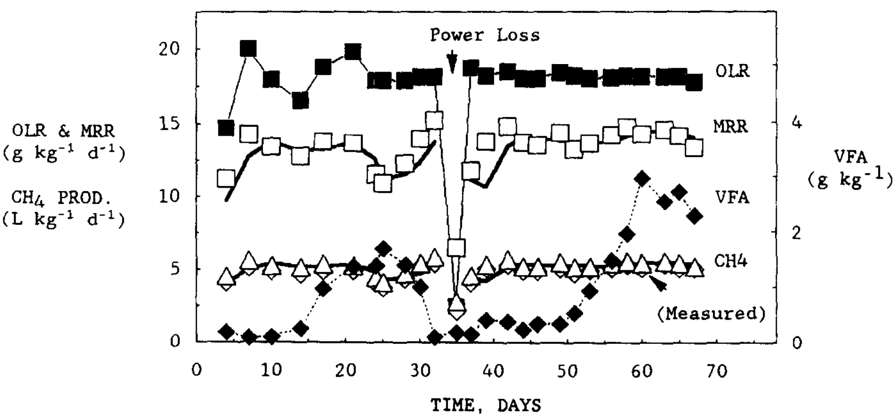

Fig. 5. Condition 6 (continuously-fed corn). Same key as Fig. 1, with measured (uncorrected) methane and total VFA.

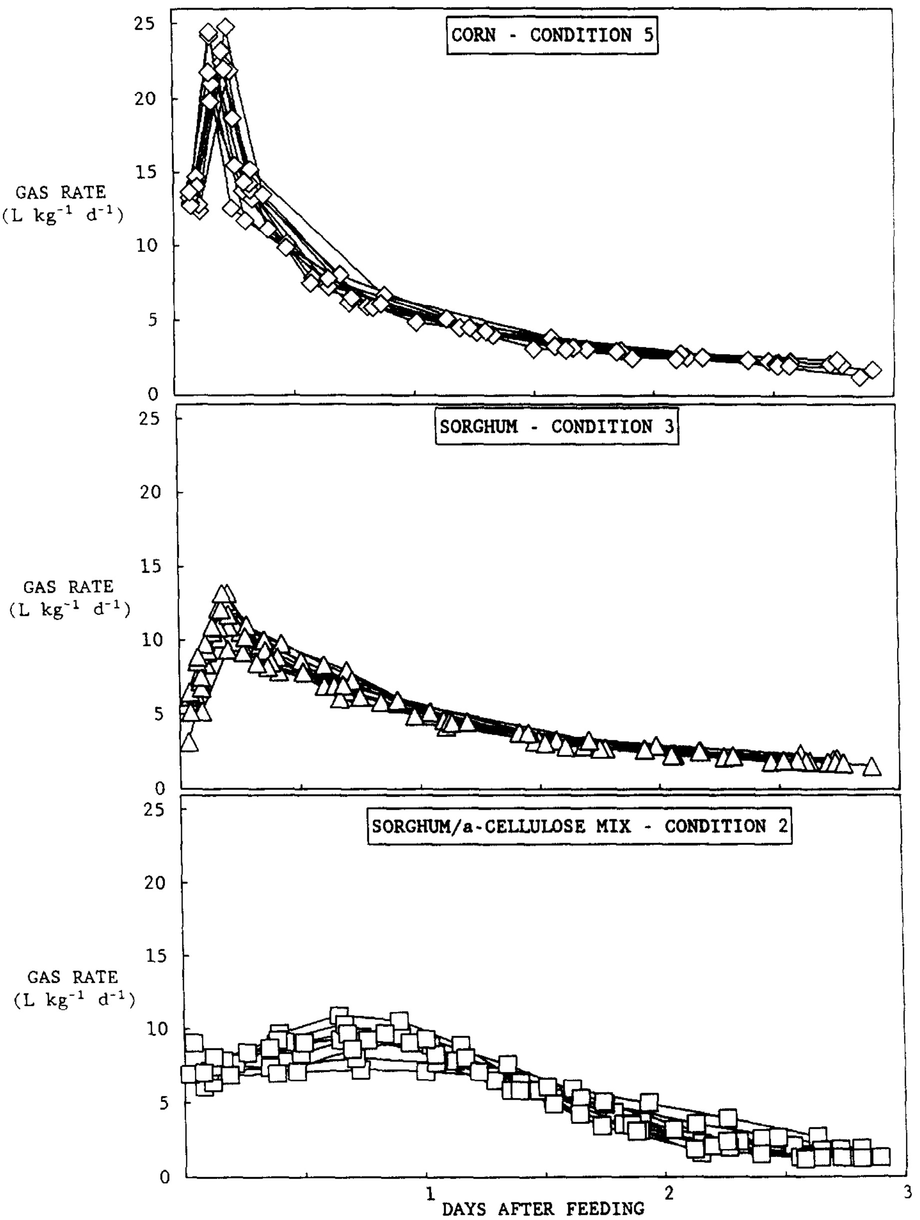

Fig. 6. Instantaneous biogas production rates following three-day feedings for corn, sorghum and sorghum/alpha-cellulose mix at similar OLRs.

duction rate of 5.43 L kg^{-1} d^{-1} and a methane yield of 0.30 L gVS^{-1}. Both measured and calculated methane production rates are shown in Fig. 5. The VS removal rate was stable at 12.2 gVS kg^{-1} d^{-1}, resulting in a VS removal efficiency of 67.4% and a hydrolysis coefficient of 0.136 g H_2O per g mass removed. The agreement between the hydrolysis coefficients in Conditions 5 and 6 confirms the validity of the mass-loss based removal rate and the corrected gas production rate.

The mean solids content for the period (11.0%) was affected by the accidental feeding rate reduction mentioned above, which occurred a week before steady performance began. By the end of the steady performance period the digester solids contents stabilized at 11.5% TS, more representative of the condition. The mean effluent TAN content was 735 mgN kg^{-1}.

As with sorghum, conventionally-defined "retention times" (HRT_i) were shorter than the actual SRTs. SRT/HRT_i ratios were 1.21 for Conditions 5 and 1.18 for Condition 6.

3.4. *First-order kinetics*

BMP VS destruction values were used as estimates of ultimate biodegradability, allowing calculation of influent (So) and effluent (Se)

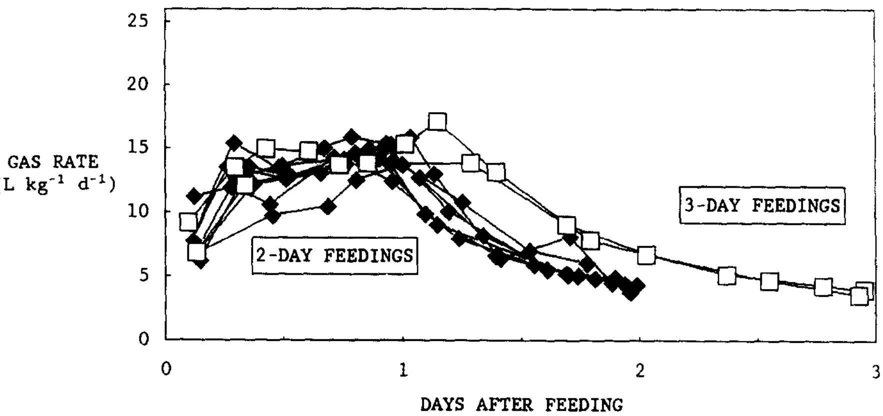

Fig. 7. Condition 6 instantaneous gas production rates for two-day and three-day continuous feeding intervals. (Three intervals not shown due to erratic feeder operation.)

biodegradable VS (BVS) concentrations and loading rates. BVS-based first order reaction rate coefficients (Tables 4 and 6) for semi-continuously fed conditions (all substrates) fell within a fairly narrow range of 0.11 to 0.16 d^{-1}, with a rate coefficient of 0.21 d^{-1} for continuously-fed Condition 6.

3.5. *Instantaneous gas production rates*

Figure 6 compares instantaneous biogas production rates during 3-day feeding intervals for corn, sorghum and sorghum/alpha-cellulose mix feedstocks at similar loading rates of 7.76 to 8.25 g VS kg^{-1} d^{-1} (Conditions 2, 3 and 5). Rates peaked at approximately 5 h after feeding for corn and sorghum, with peak corn rates double those of sorghum. The mixed feedstock peak was lower, occurring approximately 16–20 h after feeding. Despite a much higher overall loading rate, the continuous feeding regime for condition 6 (Fig. 7) kept peak rates at or below about 15 L kg^{-1} d^{-1}.

3.6. *Fiber component degradation*

Fiber component mass balances based on effluent fiber analysis were performed for Conditions 3, 4 and 5. Destruction efficiencies (Table 8) were expressed as % of initial cellulose and hemicellulose VS degraded. For sorghum, 67.9–70.8% of hemicellulose and 56.9%–61.6% of cellulose were destroyed. For corn, 77.3% of hemicellulose and 67.1% of cellulose were destroyed.

Table 8. Fiber component destruction efficiencies for Conditions 3, 4 and 5. Expressed as % of initial fiber VS destroyed

Condition	Cellulose (%)	Hemicellulose (%)
3—Sorghum	70.8	61.6
4—Sorghum	67.9	56.9
5—Corn	77.3	67.1

4. DISCUSSION

The methane production rates presented here are among the highest reported for slurry digestion of naturally-occurring particulate biomass, and are significantly higher than those achievable under conventional operation (Fig. 8). The mode of reactor operation was extremely simple: Trace nutrients (as direct supplements alone or in concert with recycled liquids) plus hourly mixing allowed operation with sorghum at loading rates up to 12 gVS kg^{-1} d^{-1}, resulting in methane production rates up to 3.3 L kg^{-1} d^{-1}. Process stability was attested to by constant gas production rates and by low, stable VFA concentrations in all semicontinuously fed conditions. The inclusion of continuous feeding for Condition 6 allowed loading rates up to 18 gVS kg^{-1} d^{-1}, with a methane production rate of 5.4 L kg^{-1} d^{-1}. VFA concentrations were higher and more variable with the heavily-fed continuous-feed condition, but appeared to be self-regulating.

Methane production rates were directly related to loading rate (Fig. 8), with rates in the continuous corn unit (Condition 6) approaching those of high solids systems.[8] VS conversion was efficient, reflecting high feedstock biodegradabilities. Removal efficiency was inversely related to SRT (Fig. 9), with, as expected, the more biodegradable feedstocks resulting in higher removal efficiencies at a given SRT. Even at the shortest SRTs and highest OLRs, the removal efficiency on a biodegradable (BVS) basis was over 73%.

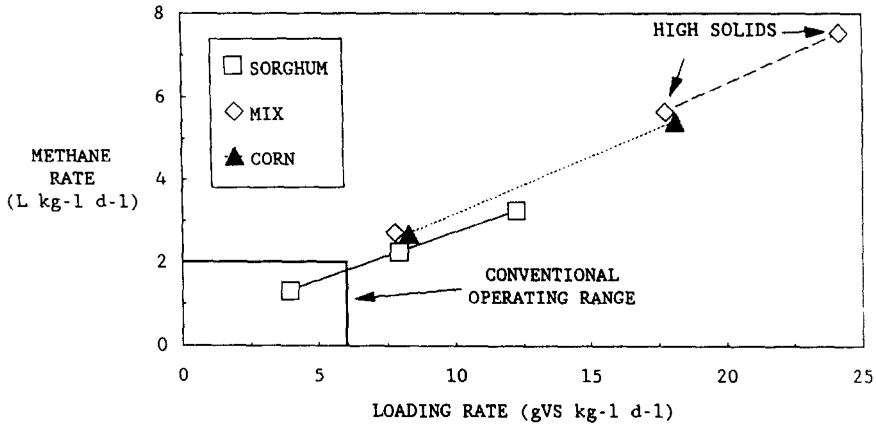

Fig. 8. Steady-performance methane production rate vs. organic loading rate (OLR). High solids data from Ref. 8.

The impact of feedstock milling on observed reaction rates and efficiencies was not quantified. However, it has been noted that, as a minimum measure, seed coats of grain contained in the feedstock should be fractured. Grain (in field-chopped silage) with intact seed coats has been observed to emerge from digestion unscathed,[17] which creates the potential for significant reductions in both rates and efficiencies, since up to half of silage dry matter can be present in the grain fraction.

Peak instantaneous biogas production rates appeared directly related to substrate cell soluble content for semicontinuously-fed conditions. Corn, with a cell soluble content of nearly 55% of VS, had the highest peak rate. Instantaneous rates varied up to twelvefold over the course of a 3-day feeding interval for corn, nearly tenfold for sorghum and fivefold for the sorghum/alpha-cellulose mix. For both corn and sorghum, the bulk of conversion appeared to be completed two days after feeding, with instantaneous biogas production rates dropping below 2.5 L kg^{-1} d^{-1}. Variation was greatly reduced under continuous feeding, with only a fivefold change in instantaneous rates for corn-fed Condition 6.

TAN concentrations over 2 to 3 g kg^{-1} are considered inhibitory to non-adapted systems, especially where the pH is high enough to cause a significant fraction to be in the associated NH_3 form.[18] Sorghum's C:N ratio of 35 appeared to be too low for operation at extremely long SRTs (i.e. 70 days for condition 1), where cell die-off and accumulation of mineralized ammonia-N is favored. There was no accumulation problem at higher loading rates, where cycling is less efficient. Recycling of liquids met the N requirement posed by the higher C:N ratio of corn.

The lowered VS removal efficiency at high loading rates (i.e. 67.4% for Condition 6, 73.5% on a BVS basis) indicates potential for multi-stage operation, with second-stage digesters used to increase overall VS removals. Testing of

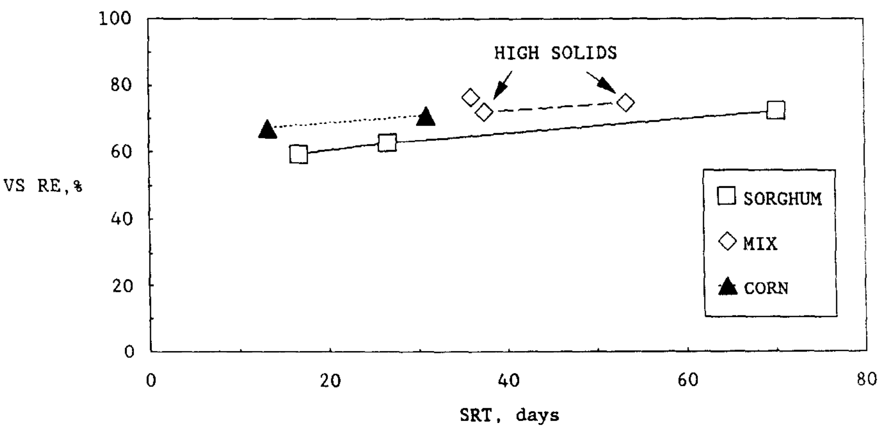

Fig. 9. Steady-performance VS removal efficiency (VS RE) vs. solids retention time (SRT). High solids data from Ref. 8.

a second-stage solids-concentrating digester following the Condition 6 digester (data not shown) resulted in a net system methane production rate of 4.53 L kg^{-1} d^{-1}, a slight decrease from the first stage alone. However, the overall VS removal efficiency was significantly enhanced, reaching 75.7% (82.5% on a BVS basis).[19]

This data indicates significant potential for simple, high rate slurry digestion of biomass. Further study is needed to optimize the form and degree of trace nutrient additions, and to define the effects of operating variables such as increased recycling of liquids, mixing, feedstock particle size, multi-stage operation and optimum timing of feed additions. Operation of semi-solid digesters at intermediate solids contents (i.e. between 12 and 20% TS) also warrants investigation.

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