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IN SITU METHANE ENRICHMENT IN METHANOGENIC ENERGY CROP DIGESTERS

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Abstract—A simple *in situ* technique to enrich digester offgas, which normally contains 30–50% carbon dioxide (CO_2) by volume, was developed to take advantage of the differing solubilities of CO_2 and methane (CH_4). Dissolved CO_2 was removed from the digester in a recycled leachate stream and gas stripped in an external stripper. Bench-scale systems easily enriched the remaining digester offgas to over 95% CH_4, and CH_4 purities in excess of 98% were achieved. Quantitative evaluation of system variables defined the effects of leachate recycle rates and alkalinity on the resulting offgas methane contents. Offgas CH_4 contents correlated well with the ratio of CO_2 transport capacity to CO_2 production. This ratio was termed the alkalinity/CO_2 ratio, a variable representing the cumulative effects of leachate recycle, leachate alkalinity and digester gas production. Operation at alkalinities of 2 and 4 g l^{-1} (as $CaCO_3$) was more effective than 8 g l^{-1} for the specific mode of operation used in this study, as elevated alkalinities required extensive lag times between feeding and initiation of stripping, resulting in blow-by of CO_2 into the digester offgas, lowering the offgas CH_4 content. Excessively high recycle rates led to digester pH levels above 8.1, resulting in volatile fatty acid accumulation and lowered CH_4 production rates.

Keywords—Anaerobic digestion; substitute natural gas; methane; gas quality; energy crops; biogas; enrichment.

1. INTRODUCTION

Much progress has been made in the development of technology for the cost-effective production of methane (CH_4) as a substitute natural gas via fermentation of energy crops. Systems analyses have been conducted to determine the key areas where improvements in economics are necessary.[1,2] One of the most significant cost factors is the purification of digester offgas (biogas) to meet pipeline quality (95% CH_4). Biogas generally contains 50–60% CH_4, with the balance being carbon dioxide (CO_2) and small quantities of hydrogen sulphide. In place of costly gas treatment processes (physical–chemical processes such as a molecular sieve are estimated to cost $1.50–2.50 per GJ), *in situ* purification has been proposed, which takes advantage of the differential solubility of CO_2 and CH_4.

Ferguson *et al.*[3] proposed a system whereby CO_2 was removed from a recycle stream by air stripping. The goal was not methane enrichment but stabilization of digester pH to allow stable digestion of acidic waste streams.

A concept first described by Hayes and Isaacson[4] employs phase separation, with a first-phase leaching bed at a gauge pressure of 0 atm and a temperature of 35°C, and a second-phase packed bed at a pressure of 2 atm. The combination of low pressure and low pH in the acetogenic first-phase reactor decreases CO_2 solubility, encouraging CO_2 offgassing in this stage. Conversely, the high pH and increased pressure of the methanogenic phase result in high CO_2 solubility and low CO_2 offgassing, resulting in higher CH_4 contents. Their model predicted methanogenic phase CH_4 contents of 92%, assuming an alkalinity of 500 mg l^{-1}. Hayes *et al.*[5] subsequently showed that the creation of such a separated phase digestion, differential pressure system combined with liquid recycle resulted in CH_4 contents of up to 93%.

Experiments described in this paper were begun in 1987[6–8] to test and optimize a simpler *in situ* process. This process was based solely on the differential solubilities of CH_4 and CO_2 under ambient pressure throughout the system,

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and with no attempt to separate acidogenic and methanogenic fermentation phases. For water at 55°C at ambient pressure, the saturation solubility of CH_4 will equal 0.16% of the saturation solubility of CO_2. The hypothesized process used continuously recycled leachate from a semicontinuously fed and mixed reactor (SCFMR) through an external gas-stripping chamber. The stripper was operated using a sweep gas to decrease the partial pressure of CO_2 in the liquid, thus stripping the CO_2 from the liquid (with correspondingly negligible CH_4 losses, as so little is in solution). This removal of CO_2 in the stripper resulted in high CH_4 purities in the SCFMR offgas. Removal of CO_2 would also increase pH in the liquid and, due to recycle, in the SCFMR as well.

The CH_4 content of digester offgas in such a system will be affected by variables such as pH, alkalinity, gas production rate and recycle flow rate. In order to model and optimize the operation, an understanding of the relationships between key variables and digester performance is critical. The objective of this study was to investigate key variables affecting methane enrichment in order to identify critical operating parameters between which a digester can be successfully operated and to observe the effects of operation with those parameters.

2. EXPERIMENTAL

2.1. *Reactor system*

The system (Fig. 1) was designed to recycle CO_2-rich leachate from the digester to an external gas-stripping column. The digester used consisted of a 12 l clear Plexiglas™ cylinder (15 cm internal diameter (ID)), with net digester contents of 8–10 kg. Digester offgas was accumulated in a 60 l Tedlar™ gas bag. A screened intake manifold in the bottom of the digester allowed liquid to drain from the digester and flow into the gas stripper. The stripper consisted of a 1.5 m tall column (10 cm ID) with a liquid volume of 2 l. Leachate was pumped from the base of the stripper back to the top of the digester using a peristaltic pump. Sweep gas (compressed nitrogen) was first humidified by bubbling through water and then introduced into the bottom of the stripper through a stone gas diffuser at a rate of 0.7 l min^{-1}. The open top of the stripper allowed the sweep gas and CO_2 to be vented to the atmosphere. Stripper liquid retention times were inversely proportional to recycle rates, varying from nearly 10 h (0.5 l kg^{-1} day^{-1} recycle rate) to 1.1 h (4 l kg^{-1} day^{-1} recycle rate).

For conditions in which the recycle was pH controlled, a pH controller (Cole-Parmer Model 5656-00) and an additional recycle loop were added (Fig. 2), which enabled cycling of leachate from the bottom to the top of the digester. Whenever leachate pH exceeded a pH setpoint, recycle to the stripper was discontinued and the added internal recycle loop was activated.

2.2. *Substrate*

Sorghum, a candidate 'energy crop', was the feedstock used throughout the study. Analysis and composition are given in detail elsewhere.[7–9] Whole plants (including grain) were field chopped and ensiled. Prior to use, they were rapidly air dried to prevent spoilage, and were hammer milled to fracture seeds. The sorghum

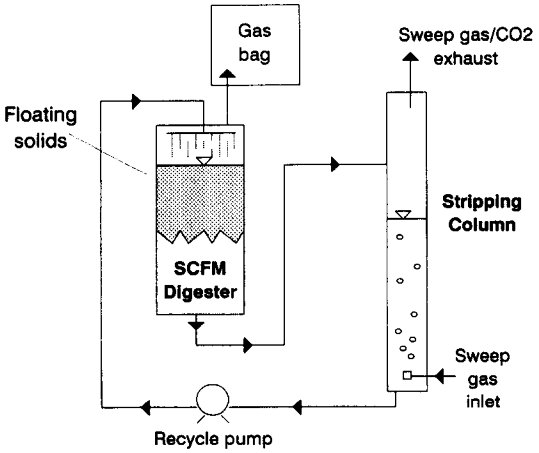

Fig. 1. Methane enrichment system configuration: constant recycle.

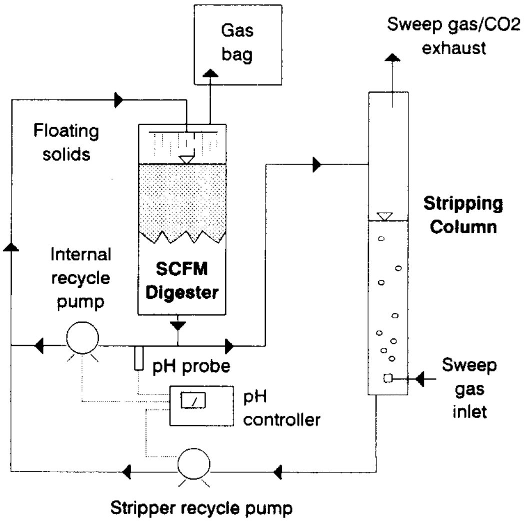

Fig. 2. Methane enrichment system configuration: pH-controlled recycle.

had a significant soluble organic fraction that was rapidly biodegradable, which characteristically led to rapid gas production rates following feeding, with rates peaking approximately 6 hours after start up.[9] Typical offgas contents from digestion of this crop were 52–56% CH_4, with volatile solids (VS) removals commonly in excess of 70%.

2.3. *Conditions examined*

A range of leachate alkalinities and recycle rates as well as digester loading rates and total solids concentrations were examined. Leachate total alkalinities examined were 2, 4 and 8 $g\ l^{-1}$ as $CaCO_3$. Conditions ME-4 to ME-14 in 1988 were operated at a loading rate of 2 $gVS\ kg^{-1}\ day^{-1}$ at a controlled effluent solids concentration of 9% total solids (TS). Solids contents were lowered to 5–6% TS for conditions ME-15 to ME-23, with the loading rate lowered to 1.25 $gVS\ kg^{-1}\ day^{-1}$. During pH-controlled operation (ME-25 to ME-31) the loading rate was 4 $gVS\ kg^{-1}\ day^{-1}$ at 8% TS. Digester alkalinities were controlled by dilution (replacing a portion of the leachate with water to lower alkalinity) or by K_2CO_3 additions (to raise alkalinity). All digesters were allowed to equilibrate for as long as required to adjust to changes in control variables between conditions.

The digester was operated as a SCFMR, fed from three to seven times per week. Liquid addition rates (and therefore digester retention times) were varied as needed to maintain constant digester solids contents at the various VS loading rates. At each feeding, the digester was thoroughly hand mixed before effluent removal and again after addition of feed and water. After each feeding, a lag time of several hours (up to 6 h for 8 $g\ l^{-1}$ alkalinity conditions) was required for the digester solids to form a floating layer before recycle could be reinitiated.

Concurrent SCFMR control digesters were operated at similar loading rates and effluent TS concentrations. Correspondence of control reactors to CH_4 enhancement conditions was as follows: control C-1: ME-4 to 14, control C-3: ME-15 to 23, control C-6: ME-25, control C-7: ME-27 to 30, control C-8: ME 31.

2.4. *Analytical methods*

Accumulated digester offgas volumes were measured with a wet-gas meter. Gas volumes were standardized as dry gas at 0°C and 1 atm.[10] Loading and gas production rates were expressed on a digester wet mass basis.[10] CH_4 and CO_2 contents of the digester offgas were determined with a Gow-Mac Series 550 thermal conductivity detector equipped with a 1.8 m stainless steel 6.35 mm ID column packed with 60/80 Porapak Q, with helium carrier gas. Stripper offgases were not analysed for several reasons. First, offgas concentrations would vary during a given feeding cycle due to the variable rates of gas production typically resulting from semicontinuous feedings,[9] requiring either constant on-line gas analysis or that all offgas for a given cycle be accumulated, mixed and sampled, with neither being feasible within the scope of the present study. Secondly, the offgas concentrations of stripped gases, particularly CH_4, would have been at or below the detection limits of this study's equipment. Thus, removal of CO_2 and CH_4 in the stripper were not directly quantified.

Volatile fatty acid (VFA) analysis was performed with a Gow-Mac 740-P flame ionization detector, equipped with a Supelco 15 m Nukol™ capillary column. VFA samples were extracted from the effluent material by diluting with water, acidifying with H_3PO_4 to below pH 2, agitating for 10 min, and centrifuging and filtering. Total alkalinity was determined by potentiometric titrations with 0.15 N H_2SO_4 to a pH 4.3 endpoint.

Leachate recycle rates were expressed in three ways. The first was based on the volume of leachate recycled per unit digester wet mass per day (LRR, $l\ kg^{-1}\ day^{-1}$). The second basis of expression was found by dividing the rate of leachate recycle (LRR) by the rate of digester CO_2 production, yielding a 'recycle ratio' (l leachate l^{-1} CO_2 produced). The third basis was calculated by multiplying the recycle ratio by the leachate alkalinity concentration, yielding a ratio of relative CO_2 transport capacity to the production rate, termed the 'alkalinity/CO_2 ratio':

$$ACR = LRR^{*}\ TAlk/V_{Ci},$$

where: ACR = alkalinity/CO_2 ratio (g alkalinity recycled l^{-1} CO_2 produced); LRR = leachate recycle rate ($l\ kg^{-1}\ day^{-1}$); TAlk = leachate total alkalinity (g $CaCO_3$ equivalent l^{-1}); and V_{Ci} = calculated initial CO_2 production rate ($l\ kg^{-1}\ day^{-1}$).

Initial digester CO_2 production rates (V_{Ci}) were calculated from measured CH_4 production rates and associated control digester mean CH_4 contents:

$$V_{Ci} = V_{Mo}(100 - M_i)/M_i$$

Table 1. Summary of constant recycle, pH-controlled recycle and control digester steady performance operation. Numbers in parentheses represent standard deviations

						Offgas CH_4						Effluent analysis		
Condition no.	Days of data	No. data points	Total alkalinity ($g\,l^{-1}$)	Leachate recycle rate ($l\,kg^{-1}\,day^{-1}$)	VS loading rate ($g\,kg^{-1}\,day^{-1}$)	CH_4 Conc. %	CH_4 rate ($l\,kg^{-1}\,day^{-1}$)	Rate as % of control	Calc. CO_2 rate ($l\,kg^{-1}\,day^{-1}$)	Recycle ratio ($l\,l^{-1}$ CO_2)	Alkalinity ratio ($g\,l^{-1}$ CO_2)	TS (%)	Mean pH	Mean VFA (as C2) ($g\,kg^{-1}$)
Constant recycle														
ME-4	20	18	8.0	3.0	2.05	94.6 (1.3)	0.62 (0.20)	90 (29)	0.55	5.42	43.4	9.0	8.3	2.97 (0.62)
ME-5	4	3	8.2	2.0	2.03	94.9 (1.7)	0.76 (0.12)	109 (17)	0.68	2.96	24.1	9.0	8.4	2.53 (0.14)
ME-6	3	3	8.6	1.0	2.04	88.8 (3.3)	0.79 (0.10)	114 (14)	0.71	1.41	12.1	9.0	8.0	1.45 (0.16)
ME-7	3	3	8.1	0.5	2.03	76.0 (5.3)	0.87 (0.05)	125 (7)	0.77	0.65	5.2	9.0	7.4	1.19 (0.10)
ME-10	18	9	4.1	2.0	1.98	97.7 (1.1)	0.55 (0.10)	79 (14)	0.49	4.11	16.8	9.0	8.2	0.19 (0.07)
ME-11	5	2	4.3	1.0	1.94	87.1 (1.0)	0.66 (0.11)	95 (16)	0.59	1.70	7.2	9.0	7.2	0.02 NA
ME-14	10	4	2.3	1.0	2.02	74.9 (3.4)	0.63 (0.04)	91 (6)	0.56	1.77	4.0	9.0	6.7	0.08 (0.03)
ME-15	14	6	2.2	3.0	1.25	98.2 (0.7)	0.30 (0.04)	77 (10)	0.25	12.17	27.1	5.5	8.4	0.44 (0.16)
ME-16	24	9	2.1	2.0	1.25	96.4 (1.8)	0.46 (0.05)	119 (13)	0.38	5.29	10.9	5.3	7.8	0.19 (0.08)
ME-17	11	5	2.3	1.0	1.25	89.7 (3.1)	0.44 (0.05)	113 (13)	0.36	2.77	6.4	5.6	7.2	NA NA
ME-18	5	2	2.2	0.5	1.22	68.0 (1.8)	0.48 (0.01)	124 (3)	0.39	1.27	2.8	5.5	6.9	NA NA
ME-19	5	2	4.1	0.5	1.25	71.3 (0.2)	0.56 (0.01)	144 (3)	0.46	1.09	4.5	5.9	7.2	NA NA
ME-22	9	4	4.1	0.75	1.25	97.6 (0.6)	0.42 (0.02)	108 (5)	0.35	2.17	9.0	5.9	8.1	0.28 NA
ME-23	6	3	4.2	0.68	1.25	94.6 (0.6)	0.45 (0.05)	116 (13)	0.37	1.84	7.6	5.1	7.8	NA NA
pH-*controlled recycle*														
ME-25	8	3	8.1	1.4	3.95	82.8 (3.1)	1.12 (0.10)	88 (8)	0.89	1.57	12.7	8.3	8.1	0.33 (0.15)
ME-27	19	8	8.1	3.4	3.99	95.4 (2.4)	1.16 (0.19)	90 (15)	0.95	3.54	28.5	8.5	8.3	2.13 (0.59)
ME-28	7	3	8.0	3.5	3.98	95.9 (1.1)	1.13 (0.18)	88 (14)	0.92	3.75	29.9	8.4	8.6	0.94 (0.12)
ME-29	7	3	7.8	3.6	3.99	96.4 (0.6)	1.07 (0.10)	83 (8)	0.87	4.11	32.0	8.0	8.7	1.56 (0.35)
ME-30	12	5	8.0	4.3	4.03	96.7 (1.0)	1.02 (0.13)	79 (10)	0.83	5.14	40.9	8.3	8.7	2.02 (0.94)
ME-31	21	8	8.1	3.1	1.99	97.7 (0.7)	0.52 (0.16)	69 (21)	0.43	7.33	59.7	8.2	8.6	4.64 (0.73)
Control reactors														
C-1	182		7.4	—	2.00	52.9 (0.7)	0.69 (0.11)		0.62			9.0	7.5	
C-3	77		NA	—	1.25	54.9 (1.3)	0.39 (0.04)		0.32			5.8	7.4	
C-6	33		NA	—	3.97	55.7 (2.0)	1.27 (0.10)		1.01			9.1	7.6	
C-7	49		9.0	—	3.98	55.1 (1.5)	1.29 (0.07)		1.05			8.4	7.7	
C-8	16		10.7	—	1.97	54.8 (0.9)	0.75 (0.05)		0.62			8.8	7.7	

NA, not available; TS, total solids; VFA, volatile fatty acids; VS, volatile solids.

where: V_{Ci} = calculated initial CO_2 production rate ($l\ kg^{-1}\ day^{-1}$); V_{Mo} = measured offgas CH_4 production rate ($l\ kg^{-1} day^{-1}$); and M_i = measured control digester CH_4 content (% CH).

3. RESULTS

Results are summarized in Table 1. Cumulative days of steady performance data and the number of actual data points (feeding intervals) represented are given for each condition. The data shown characterize the condition once stable performance was achieved. Variability of several key indices of operation (CH_4 content and production rate, CH_4 production rate as percent of control rate, and VFA content) is indicated by standard deviations in parentheses.

The use of semicontinuous feeding in order to provide constant gas production rates (i.e. as opposed to batch digestion) led to operational problems such as plugging of recycle lines, particularly at higher recycle rates. This resulted in several conditions being discarded due to unsteady physical operation (data not shown).

The use of the recycle ratio basis (l leachate recycled l^{-1} CO_2 produced) for expressing recycle rates served well to remove VS loading and gas production rates as separate variables. As can be seen in Fig. 3, offgas CH_4 contents for 2, 4 and 8 g l^{-1} alkalinity fell into distinct curves. As would be expected, recycling requirements were lower for 4 g l^{-1} alkalinity conditions than for those at 2 g l^{-1} due to the higher CO_2-carrying capacity resulting from higher alkalinity. Recycle ratios necessary to achieve 95% offgas CH_4 contents were approximately 4.5 and 1.8 l l^{-1} CO_2 at alkalinities of 2 and 4 g l^{-1}, respectively.

An expected additional enhancement of offgas CH_4 resulting from operating at 8 g l^{-1} alkalinity was realized only at low rates of recycle, i.e. under 1.5 l l^{-1} CO_2. However, this enhancement of performance did not hold at higher recycle rates due to physical problems. As noted earlier, the formation of the layer of floating solids was a necessary prerequisite to initiation of recycle after feeding. At 8 g l^{-1} alkalinity, the required delay was unusually long, averaging 6 h in several conditions, as opposed to 2–3 h at lower alkalinities. The reason why float layer formation was so slow at 8 g l^{-1} alkalinity is not known. During this delay, an irretrievable 'blow-by' of CO_2 from the digester into the offgas occurred, thereby limiting the cumulative gas-stripping ability of the system. This limitation occurred in both the continuous and pH-controlled conditions.

The use of the 'alkalinity/CO_2 ratio', the ratio of relative CO_2 transport capacity to the production rate, expressed as g alkalinity recycled l^{-1} CO_2 produced, allowed the collective effects of leachate recycle rate, leachate alkalinity and digester gas production rate to be expressed in

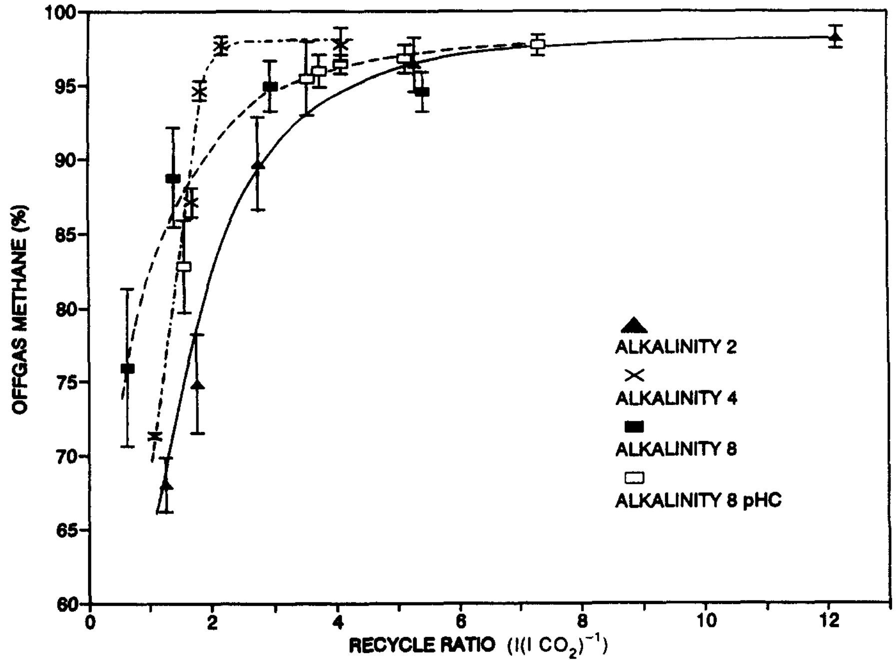

Fig. 3. Effect of recycle ratio (l leachate recycled l^{-1} CO_2 produced) on offgas CH_4 concentration at alkalinities of 2, 4 and 8 g l^{-1}. 'pHC' refers to pH-controlled conditions. Error bars represent standard deviations.

a single variable. There was excellent agreement between the offgas CH_4 contents from 2 and 4 g l^{-1} alkalinity conditions when recycle rates were expressed on this basis (Fig. 4). An alkalinity/CO_2 ratio of approximately 7.5 g alkalinity l^{-1} CO_2 was required to reach CH_4 contents of 95%. As before, the physical limitations encountered in 8 g l^{-1} alkalinity operating conditions led to less effective CH_4 enhancement, with alkalinity/CO_2 ratios of over 20 required to reach 95% CH_4.

The correlation between the degree of gas stripping and digester pH is shown in Fig. 5. At low levels of recycle (alkalinity/CO_2 ratios of less than 7.5 g l^{-1} CO_2), pH values were comparable to control digesters. Exceptions to this were the 2 g l^{-1} alkalinity conditions at the two lowest recycle rates, which had pHs of under 7.0. For these conditions there was substantial CO_2 remaining in the system (offgas CH_4 contents were under 75%), with relatively little alkalinity to counteract it. For all alkalinity concentrations, alkalinity/CO_2 ratios of greater than approximately 12 g l^{-1} CO_2 resulted in mean pH values in excess of 8.0, with pHs as high as 8.7 observed at high alkalinity/CO_2 ratios.

As shown in Fig. 6, pH values much in excess of 8.1 correlated with depressed CH_4 production rates. To compensate for varied loading rates, CH_4 production rates were expressed as a percentage of associated control digester rates. CH_4 production rates for conditions below pH 8.1 appeared to be somewhat enhanced over control rates, possibly due to a beneficial mixing effect afforded by moderate recycle rates. Associated with the reduction in CH_4 production rates at high pHs was the fact that VFA concentrations tended to be higher and more variable (Fig. 7). This effect of pH on CH_4 production and VFA concentrations was reflected in additional conditions (not presented here because they were unstable), where operation at high recycle rates led to offgas CH_4 contents of nearly 100%, but CH_4 production rates dropped rapidly and VFA concentrations increased as the pH approached 9.

4. DISCUSSION

Operation of a simple ambient pressure digester system utilizing leachate recycle to an external stripper can achieve high-quality CH_4. However, the particular digester configuration chosen for examination in this study had a number of limitations. For practical purposes, the application for SCFMR or CSTR (continuously stirred) digesters is limited to relatively low-solids systems, with solids that are easily separated via flotation from the leachate stream. Due to liquid flow limitations, CH_4 production rates are limited to the vicinity of 1 l kg^{-1} day^{-1}. Although not investigated in this study because of the desire to maintain steady gas production

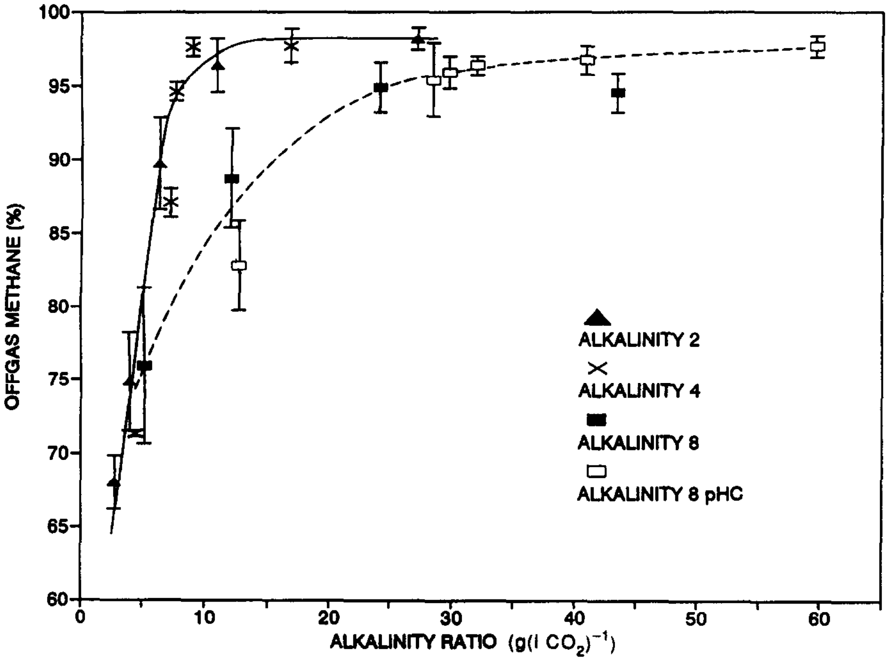

Fig. 4. Effect of alkalinity/CO_2 ratio (g alkalinity recycled l^{-1} CO_2 produced) on offgas CH_4 concentration.

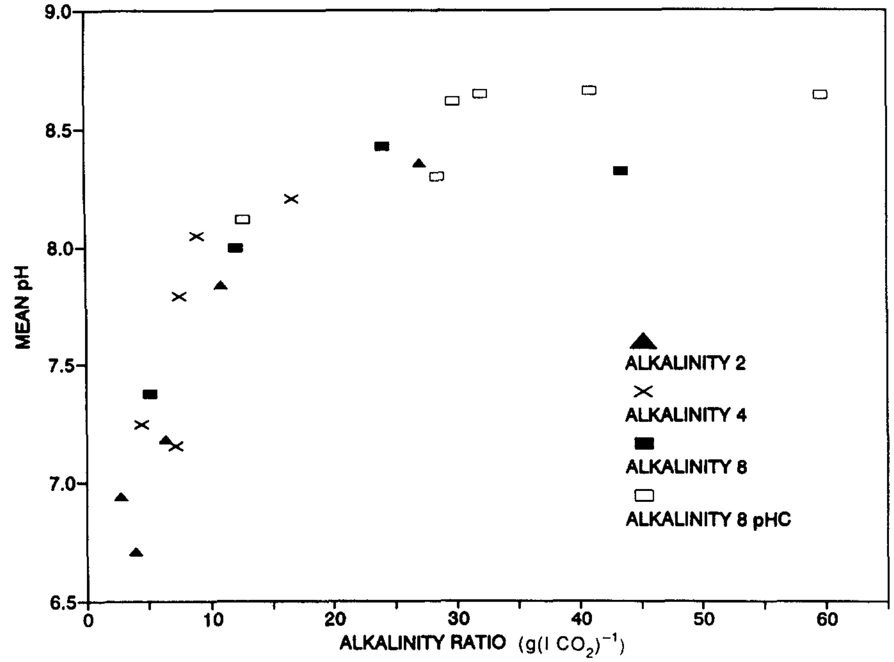

Fig. 5. Effect of alkalinity/CO_2 ratio (g alkalinity recycled l^{-1} CO_2 produced) on mean digester pH.

rates, the use of leachate recycle in other types of digesters such as packed beds has been suggested.

However, irrespective of the digester configuration, the need to balance maximization of CH_4 content with pH constraints is evident. For the conditions at alkalinities of 2–4 g l^{-1}, it appears that the optimum recycle rate (expressed as alkalinity/CO_2 ratio) was 10 g l^{-1} CO_2, which resulted in offgas CH_4 contents of over 95% CH_4 and digester pH values between 7.8 and 8.1. These pH values were low enough to avoid reduction of CH_4 production and VFA accumulations. While a pH of 7.5 has been suggested as the normal upper limit for anaerobic digestion,[11] pH values up to 8.1 were tolerated under these systems with minimal reduction in conversion efficiencies. Note that even in this pH range, care must be taken to ensure that ammonia nitrogen contents do not

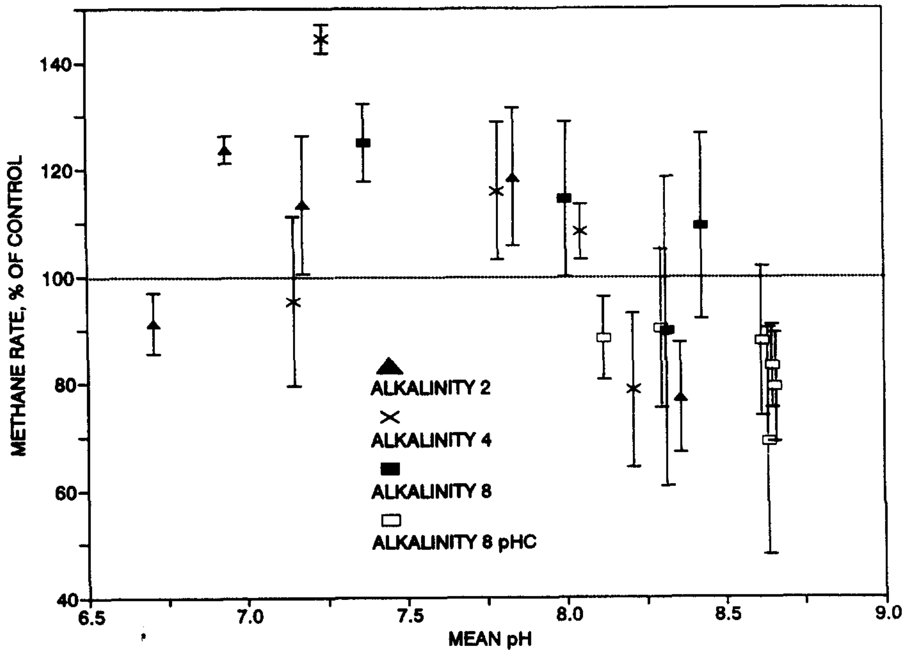

Fig. 6. Relationship of the mean digester pH to relative CH_4 production rate (as % of control CH_4 production rate).

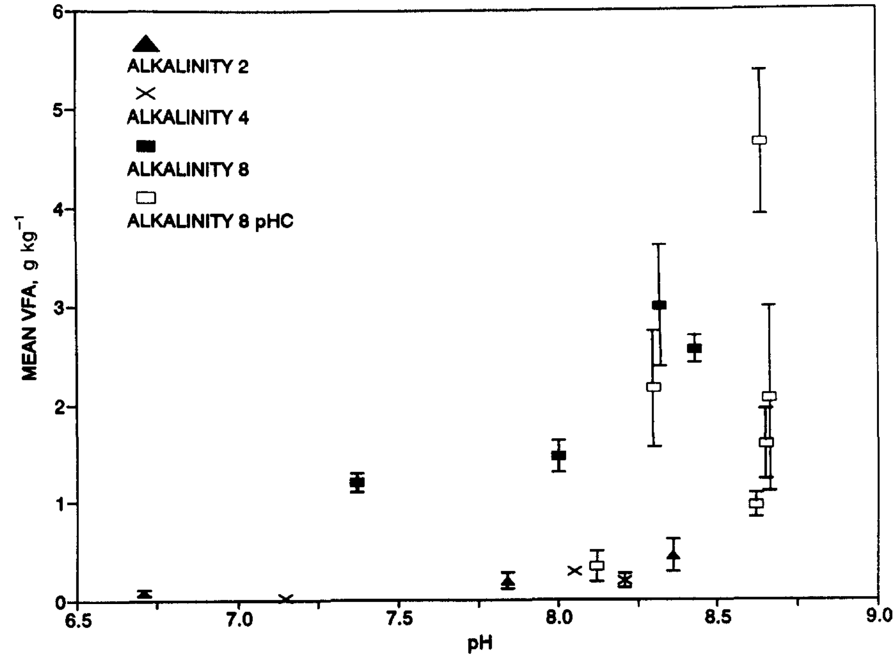

Fig. 7. Relationship of the mean digester pH to digester VFA concentrations (g kg^{-1} as C2).

become excessive, as at elevated pH the relative concentration of the free NH_3 form increases, which may cause toxicity[12] at levels greater than 100 mg l^{-1}.

Larger-scale testing will be necessary to determine practical designs and operating requirements for *in situ* methane enrichment. Initial pilot-scale testing of methane enrichment was carried out at the Experimental Test Unit in Florida.[13]

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REFERENCES

1. R. Legrand, T. M. Masters, C. S. Warren and T. D. Hayes, Analysis of biological gasification of terrestrial biomass using the ECSA model. In D. L. Klass (Ed.), *Energy from Biomass and Waste XII*. Institute for Gas Technology, Chicago, IL (1988).
2. J. R. Frank and W. H. Smith, Perspectives on biomass research. In W. H. Smith and J. R. Frank (Eds), *Methane from Biomass: A Systems Approach*. Elsevier Applied Science, London (1987).
3. J. F. Ferguson, B. J. Eis and M. M. Benjamin, Neutralization in anaerobic treatment of an acidic waste. *Water Res.* **18**(5), 573–580 (1984).
4. T. D. Hayes and H. R. Isaacson, Bioengineering concepts for methane enrichment in anaerobic digestion, pp. 496–510. In *Proceedings of the* 1984 *International Gas Research Conference*, Chicago, IL (1984).
5. T. D. Hayes, H. R. Isaacson, J. T. Pfeffer and Y. M. Liu, *In situ* methane enrichment in anaerobic digestion. *Biotechnology and Bioengineering* **35**, 73–86 (1990).
6. W. J. Jewell, H. Kang, F. G. Herndon, B. K. Richards and T. E. White, Engineering design considerations for methane fermentation of energy crops. Cornell University Annual Report, Fourth Year, for the Gas Research Institute, Report Number GRI-88/0263, Chicago, IL (January 1988).
7. W. J. Jewell, R. J. Cummings, B. K. Richards, F. G. Herndon, T. E. White, C. C. Nicholson, W. A. Chrusciel and K. G. Lindenauer, Engineering design considerations for methane fermentation of energy crops—fundamental considerations. Cornell University Annual Report, First Year, for the Gas Research Institute Report Number GRI-91/0010, Chicago, IL (December 1989).
8. W. J. Jewell, R. J. Cummings, F. G. Herndon, T. D. Nock, B. K. Richards, T. E. White, W. Chrusciel and C. C. Nicholson, Engineering design considerations for methane fermentation of energy crops—fundamental considerations. Cornell University Annual Report, Second Year, for the Gas Research Institute, Report Number GRI-91/0275, Chicago, IL (September 1991).
9. B. K. Richards, R. J. Cummings and W. J. Jewell, High rate low solids anaerobic methane fermentation of sorghum, corn and cellulose. *Biomass and Bioenergy* **1**, 249–260 (1991).
10. B. K. Richards, R. J. Cummings, W. J. Jewell and T. E. White, Methods for kinetic analysis of methane fermentation in high solids biomass digesters. *Biomass and Bioenergy* **1**, 65–73 (1991).
11. P. L. McCarty, Anaerobic waste treatment fundamentals: part 2: environmental requirements and control. *Public Works* 123–126 (October 1964).
12. G. Parkin and W. F. Owen, Fundamentals of anaerobic digestion of wastewater sludges. *ASCE-JEED* **112**(5), 867–920 (1986).
13. V. Srivastava and A. Hill, *Methane Enrichment Digestion Experiments at the Anaerobic Experimental Test Unit at Walt Disney World.* Insitute for Gas Technology Annual Report for the Gas Research Insitute, Report No. GRI-92/0498 (June 1993).