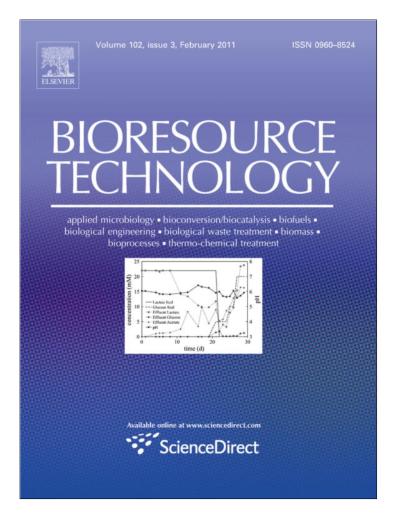
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Effect of organic loading and retention time on dairy manure fermentation

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ABSTRACT

The investigations presented and discussed herein establish an enhanced understanding on volatile fatty acid (VFA) production as a function of dairy manure fermenter organic loading (OL) and retention time (RT), first through a factorial of 64 fermentation potential (FP) batch tests, followed by analysis of a continuously operated pilot-scale fermenter. The maximum observed net FP – 0.103 mg VFA produced (as COD) (mg VS applied)⁻¹ – occurred at an OL of 40.7 g VS L⁻¹ and at a RT of 6 days. The pilot-scale fermenter exhibited an average yield of 0.09 mg VFA (as COD) synthesized (mg VS applied)⁻¹, with average effluent total VFA concentrations of 6398 mg VFA (as COD) L⁻¹. The research demonstrates that FP tests are an effective method to optimize continuously operated dairy manure fermenters, and that dairy manure fermentation can yield large quantities of organic acids at short RTs and high OL rates.

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1. Introduction

Over 9 M dairy cows generate >500B tons annually of wet manure in the US (Liebrand and Ling, 2007), and dairies are increasingly being challenged to manage this waste stream in a more environmentally effective manner. Of particular environmental concern are greenhouse gas (GHG; in particular CH₄), nitrogen, and phosphorus emissions. Nationally, dairy cows produce an estimated 6.4 M tons of CO₂ equivalents/yr (BSSC, 2008), and each ton of manure contains 4.5 kg of nitrogen and 0.8 kg of phosphorus (Church, 1993). Dairy manure biodegradation can impair air quality and cause odor issues; manure biodegradation is estimated to be the second largest source of greenhouse gas emissions associated with dairy operations (BSSC, 2008). Regarding water quality, historically raw or partially treated manure has been spread as fertilizer to arable and sometimes non-arable land as a means of disposal; however, this practice can impair ground and surface waters (Bosch et al., 2006). For example, manure land application has been shown to yield excess phosphorus in the soil (Hristov et al., 2006), which can contribute to advanced surface water eutrophication associated with storm water runoff. Soil (Hristov et al., 2006) and ground water (Wang et al., 1999) nitrate concentrations have also been found to be elevated associated with dairy manure land application. Recognizing the potential water quality risks associated with nutrient transport from confined animal feedlots (CAFOs), the US EPA has strengthened the rules associated with their operations (Federal Register/Vol. 73, No. 225). The effect of these rules will ultimately be broader scale manure treatment.

Current dairy manure management practices are treatmentcentric and include lagoon treatment, composting, aerobic digesters, and anaerobic digesters (Bowman, 2009). Lagoon systems have been historically, and to a large degree are currently, the most prevalent form of manure treatment at dairies (Van Horn et al., 1994) principally due to ease of construction and operation. In recent years anaerobic digestion has gained attention due to the ability to produce a commodity (methane gas to electricity (USEPA, 2006)). However, manure AD technology is not yet considered sufficiently economical, reliable, or stable to support widespread use at dairies (Briones and Raskin, 2003; Ghaforri and Flynn, 2007; Schink, 1997). In fact, nationally only $\sim 2\%$ of candidate facilities employ this technology while only \sim 5% of the energy potential is realized (USEPA, 2006). Beyond implementation realities, and perhaps most importantly, current AD technology does not recover all the high value organic matter (El-Mashad et al., 2008); in fact, it can be argued that no current manure management practice fully captures the real value of this raw resource.

The solids matrix in dairy manure consists of a complex array of lignocellulosic material, simple carbohydrates, and proteins. While commonly viewed as a waste, if we conversely considered converting the manure to a more readily useable form (i.e., monomeric sugars), opportunities exist to upcycle (McDonough and Braungart, 2002) the material to high value commodities. Beyond anaerobic digestion for methane production, dairy manure could be thermo-chemically pretreated to produce various precursors to a number of energy products (Huber et al., 2006). Manure could also be

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fermented to produce a liquid stream rich in volatile fatty acids (VFAs), a substrate which can be used in the microbial synthesis of polyhydroxyalkanoates (Coats et al., 2007, 2010) or potentially liquid fuels (Huber et al., 2006). Fermentation involves the sequential and bacterially mediated processes of hydrolysis and acidogenesis, with hydrolysis of the particulate organic matter commonly the rate limiting step (Banister and Pretorius, 1998). The nature of the organic matter determines the types of VFAs produced, with fermentation of carbohydrates, proteins, and lipids yielding shorter change VFAs such as acetic, propionic, butyric and iso-butyric acids; conversely, the production of longer-chain VFAs such as valeric and iso-valeric acids is the result of the fermentation of proteins (McInerney, 1988).

Regarding organic matter fermentability, Lie and Welander (1997) established the concept of fermentation potential (FP) as being the sum of the VFAs originally present in the wastewater and the amount of VFAs produced via fermentation; their protocol was based on the depletion of readily fermentable substrate, and was applied to municipal wastewater. Güngör et al. (2009) advanced the FP concept – using both municipal primary sludge and dilute dairy wastewater – by normalizing the amount of VFAs produced (initial plus synthesized) to the mass of volatile solids (VS) loaded. By expressing the fermentation potential on a VS basis, one can compare the fermentation potential of not only different waste streams but also the organic loading rate of each discrete waste stream.

We are conducting research focused on upcycling dairy manure to multiple commodities through an integrated set of bioprocesses. Manure fermentation is the cornerstone process, and maximizing VFA production (both quantity and quality) is paramount to overall success. To the best of our knowledge, the concept of fermentation potential has not been applied to dairy manure; Mason and Mulcahy (2003) conducted a single FP test on dairy manure, but did not investigate fermentability in detail, nor did Güngör et al. (2009) conduct an extensive concentrated dairy manure FP assessment. The purpose of the investigations presented and discussed herein was to establish an enhanced understanding on VFA production as a function of fermenter organic loading and retention time, first through a combination of FP batch tests, followed by analysis of a continuously operated pilot-scale fermenter designed based on extrapolated FP test results.

2. Methods

2.1. Source and characteristics of dairy manure

Dairy manure was obtained from the University of Idaho dairy farm. A single batch of fresh manure was collected for the fermentation potential factorial and stored at 4 °C until used. Manure was not frozen to avoid the reduction in VFA production rate observed by Lie and Welander (1997). For the fermentation potential tests, the total solids (TS) concentration for the raw manure was 141.8 g L⁻¹ (±18.3 g L⁻¹), while the VS concentration was 120.2 g L⁻¹ (±15.2 g L⁻¹); the TS and VS values represent the average of six tests. The wet manure exhibited a dry solids content of 14.1% (±1.8%). Several batches of fresh manure were required to support the continuously-operated pilot-scale fermenter. The manure dry solids content ranged from 15.4% to 18.2% (w/w), with a VS fraction of 86.3–88.3%.

2.2. Fermentation potential factorial

The fermentation potential test was conducted in the same manner as described by Lie and Welander (1997) and Güngör et al. (2009). The experiment was designed as a factorial, with organic loading (OL; 8 levels – 6.5, 13.8, 19.6, 27.1, 35.0, 40.7, 48.7,

and 58.1 g VS L⁻¹) and residence time (RT; 8 levels – 0, 1, 2, 4, 6, 8, 10, and 15 days) as the tested variables (64 batch tests in total). The fermentation potential tests were performed in 300-mL serum bottles filled with 100 mL of a mixture of dairy manure and tap water. For each replicate OL (i.e., the 8 RTs), the target quantity of manure was homogenized in a 1 L beaker, then portioned volumetrically into the serum bottles. The bottles were sealed using rubber stoppers, and the tests were performed at room temperature (approximately 20–21 °C). The fermentation potential results were calculated by (i) dividing gross measured VFAs (initial plus synthesized) by the mass of VS applied, and (ii) dividing the net VFA production by the mass of VS applied. Results are expressed as mg of VFA (as COD) per gram of VS.

2.3. Pilot-scale fermenter

A 20 L pilot-scale fermenter was operated to validate the results of the fermentation potential tests. The fermenter was operated at a 4 day RT and an OLR of 10.8 g VS (L-day)⁻¹. Thus, over a full operational cycle (i.e., the operational RT), the fermenter received 43.2 g VS L⁻¹. The fermenter was operated a room temperature (approximately 20–21 °C) and uncovered, and consisted of a polypropylene tank with a conical bottom. The fermenter was mixed using a 32° pitched-blade turbine mounted to a 15 W AC motor (USM315-401W/3GN36KA; Oriental Motors, San Jose, CA). The fermenter was decanted (from the bottom) and fed once per day to maintain the target RT.

2.4. Analytical techniques

Samples were collected to measure the following parameters: TS, volatile solids (VS), VFAs, and pH. For soluble constituents, samples were centrifuged at 10,000 rpm and the supernatant filtered through a 0.22 µm syringe filter (Millipore Corp., Billerica, MA, USA) prior to testing. TS and VS were measured in accordance with Standard Methods 2540G (Clesceri and Eaton, 1998). pH was measured using a Thermo Scientific Corp. (Waltham, MA, USA) Accumet AP85 waterproof pH/conductivity meter. VFA concentrations were measured using a Hewlett-Packard (Palo Alto, CA, USA) 6890 Series Gas Chromatograph with a flame-ionization detector (FID). The temperature of the column (Grace Davison Discovery Sciences, Deerfield, IL, USA, Alltech[®] Heliflex[®] AT[™]-Wax Column, length 30 m, internal diameter 0.32 mm) was held constant at 150 °C; the injector was maintained at 210 °C and the detector was operated at 210 °C. Helium was used as the carrier gas (flow rate of 1.2 mL min⁻¹). Samples were acidified to a pH of 2 with HCl prior to injection. 0.5 µL of sample was injected in 20:1 split mode for analysis. VFAs were confirmed by retention time matching with known standards (Grace Davison Discovery Sciences, Deerfield, IL, USA) and quantified using linear standard curves $(R^2 > 0.99)$. Calculation of total VFAs as total COD was made using the appropriate VFA-to-COD stoichiometric ratios (Güngör et al., 2009; Mason and Mulcahy, 2003).

2.5. Statistical methods

Paired student *t*-tests were used for the statistical comparison of all values. Differences were declared significant at p < 0.05.

3. Results and discussion

3.1. Volatile fatty acid production

Fermentation potential both broadly quantifies VFA production capacity for a given organic substrate and describes the potential ability to manipulate fermenter operations to produce target VFA species, while also taking into account influent VFA quantities and concentrations. The inherent value in conducting a batch fermentation potential test is to gain an enhanced understanding on how to design and operate a continuous fermenter to maximize VFA production from organic matter for use as precursors in downstream wastewater treatment and/or commodity production processes. Fermenter design and operation is, in part, based on the RT, which is the average length of time biomass resides in the system. Skalsky and Daigger (1995) observed significant VFA production in a municipal wastewater fermenter at RTs as short as 2 days. At RTs greater than 6 days, methanogens can begin to accumulate in fermenters (Banister and Pretorius, 1998), resulting in VFA consumption and reduced fermenter yield. To limit methanogen growth, the RT in fermenters is commonly limited to 6 days (Banister and Pretorius, 1998; Grady et al., 1999). The OL similarly impacts fermentation potential, in that sufficient organic matter is required to support the continuous and synergistic hydrolysis and fermentation processes, yielding excess VFA production. Although logic would dictate that there would be a minimum OL to support VFA accumulation in a fermenter, there are no general recommendations in this regard.

Gross and net VFA yield (calculated as mg VFA (as COD) synthesized per mg VS applied) from the fermentation potential batch tests conducted in this research are presented in Fig. 1. First considering gross fermentation potential (Fig. 1A and B), as shown all eight tests exhibited positive ratios, with maximum FP occurring at an OL of 40.7 g VS L⁻¹. Interrogating the data in this manner, which is consistent with Lie and Welander (1997), suggests that VFA accumulation occurred under all conditions. However, when only net VFA production is considered (i.e., VFAs present in the inoculum are excluded), the true effect of OL can be observed (Fig. 1C and D). As shown, observed VFA production was negative for all RTs at the lowest two OLs (Fig. 1A). Recognizing that the bovine rumen is enriched with methanogens (Whitford et al., 2001), some of which would be present in the raw manure, these results suggest that the environmental conditions at these low OLs were insufficient to shift the microbial dynamics toward bacteriallydominated hydrolysis and VFA accumulation. The pH at the lowest two OLs (Fig. 2A) was also modestly favorable for methanogens (Ward et al., 2008). However, as the OL increased, VFA production with increasing RT can be observed (Fig. 1C and D). The shift toward VFA accumulation was likely affected, in part, by the increasing VFA concentrations in the inoculum (Table 1) and the associated decrease in pH (Fig. 2); methanogens become metabolically inhibited as the pH decreases below approximately 6.6 (Ward et al., 2008). The maximum observed net fermentation potential - estimated at 0.103 mg VFA produced (as COD) per mg VS applied – occurred at an OL of 40.7 gVS L^{-1} and at an RT of 6 days. Similarly, maximum net VFA yield at the next two highest and next lowest OLs occurred at an RT of 6 days (Fig. 1C and D).

While it appears that there is a minimum RT that must be achieved before excess VFA accumulation is realized, there is also a threshold RT that, once crossed, VFA utilization commences. Mason and Mulcahy (2003) observed a similar trend using a dilute dairy wastewater, and in fact observed, as we did, that maximum VFA yield occurs at an RT in the range of 6–8 days. Using municipal primary solids, Skalsky and Daigger (1995) similarly measured increasing VFA yield with RT, observing a peak at an RT of 5 days, while Bouzas et al. (2007) - also using municipal primary solids - observed peak VFA production at an RT of 6-8 days. Primary solids and manure exhibit similar lignocellulosic characteristics, although manure can contain more readily biodegradable hemicellulose while primary solids can contain higher amounts of cellulose, which is more resistant to bio-hydrolysis (Howard et al., 2003). Regarding optimal OL, there are no comparative studies with which to contrast our results.

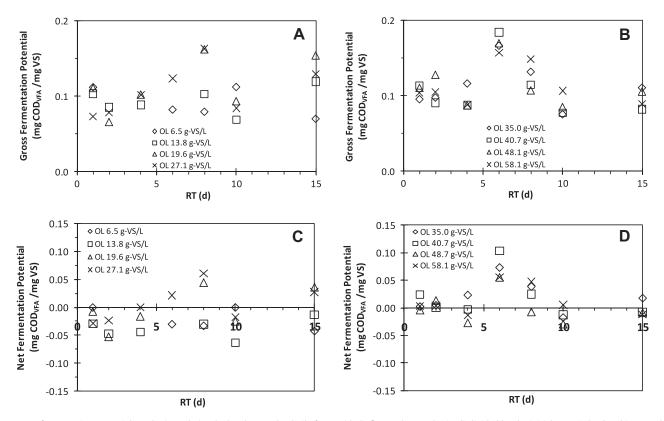


Fig. 1. Gross fermentation potential results (A and B), calculated as total volatile fatty acids (influent plus synthesized) divided by the initial organic load and in accordance with Lie and Welander (1997). Net fermentation potential results (C and D), calculated as total volatile fatty acids (synthesized) divided by the initial organic load.

E.R. Coats et al./Bioresource Technology 102 (2011) 2572-2577

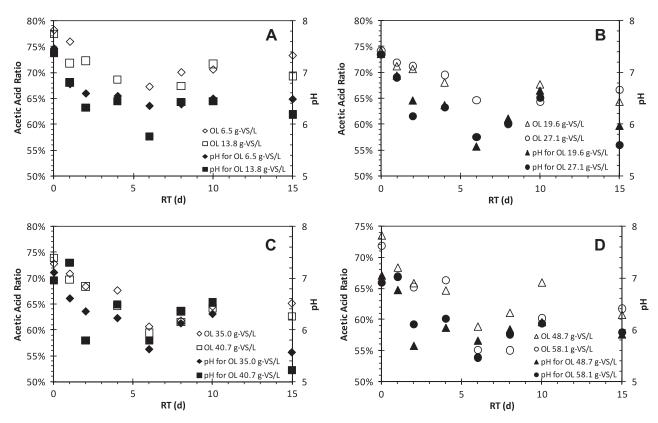


Fig. 2. Reactor pH (closed symbols) and acetic acid ratio (open symbols) for the fermentation potential tests.

Table 1
Total VFA concentrations $[mg L^{-1} as COD]$ in the dairy manure fermentation potential
tests.

RT (day)	Orgai	Organic Loading (OL) [g VS/L]						
	6.5	13.8	19.6	27.1	35.0	40.7	48.7	58.1
0	733	1830	2329	2761	3269	3657	5549	5877
1	727	1425	2184	1985	3351	4624	5369	6060
2	-	1177	1298	2117	3426	3687	6213	6089
4	-	1221	2013	2762	4076	3552	4238	5119
6	533	-	-	3344	5818	7845	8256	9117
8	515	1417	3192	4403	4614	4667	5204	8612
10	729	953	1840	2281	2656	3143	4124	6193
15	454	1645	3032	3507	3881	3337	5124	5190

To compare fermentation potential results with that of others, we must consider the gross FP data (i.e., Fig. 1A and B), since all other FP research has been presented in this manner. The maximum observed fermentation potential (estimated at 0.184 mg VFA (as COD) per mg VS) was approximately 25% of that reported by Güngör et al. (2009), who evaluated a single dilute liquid separated dairy manure stream. Contrasting the two studies, while the initial VS concentration applied in this research was nearly 190% higher than that of Güngör et al. (2009), the latter study inoculated their FP test with an anaerobic culture of microorganisms. Providing a critical mass of fermentative microorganisms would have greatly enhanced the FP results. Mason and Mulcahy (2003) observed a maximum VFA concentration at 6-8 days of 1800-2000 mg VFA (as COD) L^{-1} using dairy manure wastewater (no inoculum). No TS or VS data was provided to calculate gross FP, however, the low VFA concentrations suggest a dilute wastewater.

Regarding VFA concentrations, the largest observed increase in bulk solution VFAs was approximately 90% at the maximum observed fermentation potential (OL of 40.7 and RT of 6 days; Table 1). In contrast, the highest observed VFA concentration occurred at the largest OL (58.1) and at a 6 day RT; however, this outcome was clearly influenced by the presence of excess VFAs in the manure in the inoculum (Table 1). The inherent benefit of fermenting a concentrated dairy manure source (without a microbial inoculum) can be observed by contrasting the results from this study with one using a dilute dairy manure wastewater – at the four highest OLs we tested (and wherein maximum fermentation potential was observed), the maximum measured VFA concentrations were 200% or more higher that observed by Mason and Mulcahy (2003). Although Güngör et al. (2009) observed higher VFA concentrations with a more dilute dairy manure, as noted, their fermentation potential investigations were inoculated with an anaerobic culture of microorganisms that would have enhanced the process, as contrasted with our investigations.

The observed variability in VFA production – with OL and RT in general, and specifically for the first 24 h for many of the tests – can be in part explained by variable manure source. While the manure was homogenized prior to portioning material into each test bottle, given the inherent complexity of the substrate matrix, certainly some heterogeneity would be expected that could ultimately affect VFA production potential in a given bottle.

3.2. Acetic acid ratio

While maximizing VFA production is an important outcome in fermenting organic matter, relative VFA distribution (i.e., acetate, propionate, etc.) can also be a critical parameter in regards to ultimate use of the produced liquor. For example, the form of the biopolymer PHA, which is one candidate downstream commodity that could be synthesized using dairy manure fermenter liquor, is directly related to the carbon substrate (Madison and Huisman, 1999). Even-carbon organic acids generally yield polyhydroxybutyrate (PHB), while odd-carbon VFAs beget polyhydroxyvalerate (PHV). PHB is similar to polypropylene, but is brittle and exhibits

2575

little stress resistance, while polymer ductility and impact resistance increase with hydroxyvalerate copolymerization to form polyhydroxybutyrate-valerate (PHB-co-PHV) (Madison and Huisman, 1999). Thus a mixture of even- and odd-carbon VFAs is most desirable for PHA production. In contrast, acetate is a more favorable substrate for CH₄ production via anaerobic digestion (Ward et al., 2008). Finally, if phosphorus removal is desired, the composition of VFAs is also important for the enhanced biological phosphorus removal (EBPR) process, as propionate has been shown to enhance the enrichment of polyphosphate accumulating organisms (PAOs) (Oehmen et al., 2005).

The dairy manure inoculum in all batch tests exhibited an acetic acid ratio ranging from approximately 72% to 78%. Within the first day of fermenting, this ratio had decreased in all tests, and continued to decrease for 6-8 days (Fig. 2). For the maximum observed FP, at the optimal OL and RT (i.e., 40.7 g VS L^{-1} and 6 days) the acetic acid ratio reached a trough at approximately 59%. In fact, for the four highest OLs (Fig. 2C and D), the acetic acid ratio was consistently at a minimum for an RT of 6 days. The minimum acetic acid ratio for the OLs of 19.6 and 27.1 occurred at an RT of 8 days, concurrent with maximum FP. Table 2 provides a summary of the relative VFA distribution with RT for the optimal OL batch fermentation test and for one OL higher/lower. The observed composition of the VFAs is consistent with other research on dairy manure and municipal wastewater (Güngör et al., 2009; Lie and Welander, 1997; Mason and Mulcahy, 2003). In all batch tests, as the RT increased beyond 6-8 days, there was a slight increase in

Table 2

Relative distribution of VFAs in the fermentation potential test for the three highest results.

OL (g VS/L)	RT (d)	% Acetic	% Propionic	% Butyric	% Valeric
35.0	0	73	16	10	1
	1	71	18	10	1
	2	68	19	12	1
	4	68	19	12	1
	6	61	21	16	2
	8	62	21	16	2
	10	65	19	15	2
	15	65	17	16	2
40.7	0	74	16	10	1
	1	70	19	11	1
	2	68	19	11	1
	4	65	18	16	2
	6	59	21	17	2
	8	62	20	17	2
	10	64	18	16	2
	15	63	20	16	2
48.7	0	73	16	10	1
	1	68	20	11	1
	2	66	20	14	1
	4	65	18	15	2
	6	59	21	18	2
	8	61	19	18	2
	10	66	18	14	2
	15	61	18	19	3

the acetic acid ratio. The increase in the acetic acid ratio can be attributed to the onset of the acetogenic process, where longerchain VFAs are oxidized to acetic acid (Batstone et al., 2002).

3.3. TS/VS reduction and VFA yield

The relative fraction of total and volatile solids reduction generally increased with OL in the fermentation potential tests (Table 3), with the largest reduction occurring at the highest OL. The results presented in Table 3 are specific to the RT at which maximum fermentation potential was realized for the respective OLs. Data on the two lowest OLs was excluded from Table 3, since no net VFA yield was observed in these tests (Fig. 1C). VFA yield results as a function of actual VS utilized, for maximum organic acid production, mimicked the observation presented in Fig. 1. As shown (Table 3), the maximum VFA yield was 1.18 mg organic acids synthesized per mg VS destroyed.

3.4. Pilot-scale dairy manure fermenter

Using the fermentation potential results as a guide, a pilot-scale fermenter was designed to match the optimal conditions from the single-batch FP tests. Specifically, the pilot-scale fermenter was operated at an OLR of $10.8 \text{ g VS} (\text{L}-\text{d})^{-1}$, which correlates with an OL of 43.2 g VS L^{-1} (i.e., close to the optimal OL observed in the batch FP tests); the OL was calculated using the 4-day operational RT applied to the pilot-scale fermenter. As contrasted with the optimal FP test, which was observed at an RT of 6 days, the pilot-scale fermenter was operated at a slightly lower RT to account for the inherent enriched presence of fermentative microorganisms. Güngör et al. (2009) employed a similar approach, although they comparatively reduced the RT from 8 days in the batch FP test to 2 days in their continuous fermenter.

Performance of the pilot-scale unit was monitored over a 27 d period. As shown (Fig. 3), the influent manure exhibited a VFA concentration ranging from approximately 2000-3000 mg VFA L⁻¹, while effluent VFA concentrations ranged consistently from 5500 to over 7000 mg L⁻¹. Average effluent total VFA concentration of the pilot-scale fermenter was 6398 mg VFA (as COD) L^{-1} with a 95% confidence interval of 6078–6717 mg VFA (as COD) L^{-1} . Average influent total VFA concentration of the pilot-scale was 2549 mg VFA (as COD) L^{-1} with a 95% confidence interval of 2341–2758 mg VFA (as COD) L^{-1} . The increase in total VFA concentration between the fermenter influent and effluent was also statistically significant $(p < 2 \times 10^{-10})$. Acetic acid was the predominant VFA in the pilotscale fermenter effluent. On average, acetic acid constituted 53% of the total VFA concentration. Other notable VFAs in the fermenter effluent were propionic, butyric, iso-butyric, valeric, iso-valeric, and caproic acid.

Effluent VFA concentrations from the pilot-scale fermenter were comparable to that observed in the batch FP tests (Table 1). In contrast, Güngör et al. (2009) observed an average VFA concentration of 723 mg L^{-1} in their pilot-scale fermenter (at an RT of

Table 3

TS and VS reduction in fermentation potential tests at maximum VFA production. Table also presents VFA yield as a function of VS destroyed.

		Organic Loading (OL) [g VS/L]						
		19.6	27.1	35.0	40.7	48.7	58.1	
RT = 0	TS (mg/L)	24,130	32,870	42,160	49,600	59,230	69,300	
	VS (mg/L)	19,630	27,060	34,990	40,660	48,730	58,100	
Optimal RT	TS (mg/L)	22,500	30,020	39,520	45,520	51,990	58,980	
	% Reduction	6.8%	8.7%	6.3%	8.2%	12.2%	14.9%	
	VS (mg/L)	18,570	24,540	32,790	37,120	42,420	48,840	
	% Reduction	5.4%	9.3%	6.3%	8.7%	12.9%	15.9%	
VFA yield	mg VFA synthesized (mg VS destroyed) ⁻¹	0.81	0.65	1.16	1.18	0.43	0.35	

E.R. Coats et al./Bioresource Technology 102 (2011) 2572-2577

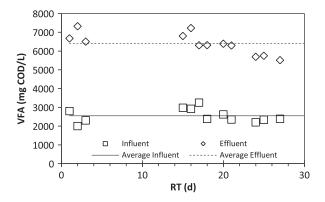


Fig. 3. Influent and effluent VFA concentrations for pilot-scale fermenter.

2 days), while Mason and Mulcahy (2003) observed peak VFA concentrations less than 2000 mg L⁻¹ (RT of 7 days in their pilot-scale system). The differences between these studies and the results presented herein reinforce the value of using batch fermentation potential tests to determine optimal OLR. Güngör et al. (2009) applied an OLR of 3 g $(L-d)^{-1}$, or 28% of our OLR; Mason and Mulcahy (2003) similarly used a dilute wastewater. Regarding VFA yield, the pilot-scale fermenter exhibited an average yield of 0.09 mg VFA (as COD) synthesized per mg VS applied, which is comparable to the maximum value observed in the optimum FP test. In contrast, Güngör et al. (2009) observed a yield of 0.13 mg VFA (as COD) synthesized per mg VS applied. Note that the yield observed by Güngör et al. (2009) was likely increased due to their pilot-scale fermenter being fed twelve times per day, as contrasted with our one. Using a dilute municipal primary solids waste stream, Cokgor et al. (2009) observed a maximum yield of 0.13-0.15 mg VFA (as COD) synthesized (mg VS applied) $^{-1}$, but measured VFAs at less than 3000 mg L^{-1} . Similarly, Bouzas et al. (2007) observed a yield of approximately 0.20-0.25 mg VFA (as COD) per mg VS applied using a very dilute municipal wastewater, with maximum effluent VFA concentrations less than 40 mg L^{-1} . Here again, yields were generally comparable to our results, but total net VFA concentrations (and inherently total VFA production) was markedly less due to the low OLRs.

4. Conclusions

The purpose of these investigations was to establish an enhanced understanding on organic acid production through dairy manure fermentation. Key findings included: (i) Fermentation potential batch tests are an efficient and effective method to optimize continuously operated fermenters; (ii) Dairy manure fermentation can yield large quantities of organic acids at short retention times and under high organic loading rates; (iii) At low organic loading rates, minimal net organic acid production may be realized in a continuously operated fermenter; and (iv) The minimum acetic acid ratio occurs concurrently with the maximum fermentation potential. A similar relationship also exists with pH.

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References

- Banister, S.S., Pretorius, W.A., 1998. Optimisation of primary sludge acidogenic fermentation for biological nutrient removal. Water SA 24, 35–41.
- Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H., Vavilin, V.A., 2002. The IWA Anaerobic Digestion Model No. 1 (ADM1). Water Sci. Technol. 45, 65–73.
- Bosch, D.J., Wolfe, M.L., Knowlton, K.F., 2006. Reducing phosphorus runoff from dairy farms. J. Environ. Qual. 35, 918–927.
- Bouzas, A., Ribes, J., Ferrer, J., Seco, A., 2007. Fermentation and elutriation of primary sludge: effect of SRT on process performance. Water Res. 41, 747–756.
- Bowman, D.D., 2009. Manure pathogens: manure management, regulations, and water quality protection. WEF, Alexandria, Virginia.
- Briones, A., Raskin, L., 2003. Diversity and dynamics of microbial communities in engineered environments and their implications for process stability. Curr. Opin. Biotechnol. 14, 270–276.
- BSSC "US Dairy Sustainability Initiative: A Roadmap to Reduce Greenhouse Gas
- Emissions and Increase Business Value", Innovation Center for US Dairy, 2008. Church, G.A., 1993. Livestock Waste Facilities Handbook, Midwest Plan Service.
- Ames, Iowa. Clesceri, L.S., Eaton, A.D., 1998. Standard Methods for Examination of Water and Wastewater, 20th ed. American Public Health Association, Washington, DC.
- Coats, E.R., Loge, F.J., Wolcott, M.P., Englund, K., McDonald, A.G., 2007. Synthesis of polyhydroxyalkanoates in municipal wastewater treatment. Water Environ. Res. 79, 2396–2403.
- Coats, E.R., VandeVoort, K.E., Darby, J.L., Loge, F.J., 2010. Toward polyhydroxyalkonate production concurrent with municipal wastewater treatment in a sequencing batch reactor system. ASCE J. Environ. Eng.
- Cokgor, E.U., Oktay, S., Tas, D.O., Zengin, G.E., Orhon, D., 2009. Influence of pH and temperature on soluble substrate generation with primary sludge fermentation. Bioresour. Technol. 100, 380–386.
- El-Mashad, H.M., McGarvey, J.A., Zhang, R., 2008. Performance and microbial analysis of anaerobic digesters treating food waste and dairy manure. Biol. Eng. 1, 235–244.
- Ghaforri, E., Flynn, P., 2007. Optimizing the size of anaerobic digesters. ASABE 50, 1029–1036.
- Grady Jr., C.P.L., Daigger, G.T., Lim, H.C., 1999. Biological Wastewater Treatment, second ed. Marcel Dekker, Inc..
- Güngör, K., Müftügil, M.B., Ogejo, J.A., Knowlton, K.F., Love, N.G., 2009. Prefermentation of liquid dairy manure to support biological nutrient removal. Bioresour. Technol. 100, 2124–2129.
- Howard, R.L., Abotsi, E., Jansen van Rensburg, E.L., Howard, S., 2003. Lignocellulose biotechnology: issues of bioconversion and enzyme production. Afr. J. Biotechnol. 2, 602–619.
- Hristov, A.N., Hazen, W., Ellsworth, J.W., 2006. Efficiency of use of imported nitrogen, phosphorus, and potassium and potential for reducing phosphorus imports on Idaho dairy farms. J. Dairy Sci. 89, 3702–3712.
- Huber, G.W., Iborra, S., Corma, A., 2006. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem. Rev. 106, 4044–4098. Lie, E., Welander, T., 1997. A method for determination of the readily fermentable
- organic fraction in municipal wastewater. Water Res. 31, 1269–1274.
- Liebrand, C.B., Ling, K.C., 2007. "Cooperative Approaches For Implementation of Dairy Manure Digesters". USDA-Rural Development.
- Madison, L.L., Huisman, G.W., 1999. Metabolic engineering of poly (3hydroxyalkanoates): from DNA to plastic. Microbiol. Mol. Biol. Rev. 63, 21–53.
- Mason, I.G., Mulcahy, J., 2003. Volatile fatty acid production from farm dairy wastewater. Trans. ASAE 46, 819–824.
- McDonough, W., Braungart, M., 2002. Cradle to cradle: remaking the way we make things. North Point Press, New York.
- McInerney, M.J., 1988. In: Zehnder, A.J.B. (Ed.), Biology of Anaerobic Microorganisms. Wiley, New York.
- Oehmen, A., Yuan, Z.G., Blackall, L.L., Keller, J., 2005. Comparison of acetate and propionate uptake by polyphosphate accumulating organisms and glycogen accumulating organisms. Biotechnol. Bioeng. 91, 162–168.
- Schink, B., 1997. Energetics of syntrophic cooperation in methanogenic degradation. Microbiol. Mol. Biol. Rev. 61, 262–280.
- Skalsky, D.S., Daigger, G.T., 1995. Wastewater solids fermentation for volatile acid production and enhanced biological phosphorus removal. Water Environ. Res. 67, 230–237.
- USEPA, 2006. "Market Opportunities for Biogas Recovery Systems Improved Performance at Competitive Costs".
- Van Horn, H.H., Wilkie, A.C., Powers, W.J., Nordstedt, R.A., 1994. Components of dairy manure management systems. J. Dairy Sci. 77, 2008–2030.
- Wang, S.J., Fox, D.G., Cherney, D.J.R., Klausner, S.D., Bouldin, D.R., 1999. Impact of dairy farming on well water nitrate level and soil content of phosphorus and potassium. J. Dairy Sci. 82, 2164–2169.
- Ward, A.J., Hobbs, P.J., Holliman, P.J., Jones, D.L., 2008. Optimisation of the anaerobic digestion of agricultural resources. Bioresour. Technol. 99, 7928–7940.
- Whitford, M., Teather, R., Forster, R., 2001. Phylogenetic analysis of methanogens from the bovine rumen. BMC Microbiol. 1, 1–5.