SIMILARITY OF FIRST-ORDER RATE CONSTANTS FOR METHANE FROM FOOD WASTES IN BATCH AND CONTINUOUS FEED SYSTEMS

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SUMMARY: Evaluation of the suitability of food wastes for anaerobic digestion is made difficult because of variable and uncertain degradation parameters. Simpler tests that can estimate degradation kinetics can make it quicker and less expensive to assess suitability. The purpose of the research was to examine the correspondence of first-order rate constants between laboratory testing of batch and continuous-feed systems. The feedstock for the experiments was a food waste developed to simulate residential collection. Batch tests were conducted using 120 g of food waste with 1.5 L of digested sewage sludge as inoculum. Continuous feed tests were conducted in 30 L digesters with daily feed/wasting and a hydraulic retention time of 30 days. Methane production was fit to a first-order rate equation with a resulting 0.22 d^{-1} rate over 13 reactors. The overall fitted methane yield for batch tests varied greatly from 0.15 to 0.56 L CH_4/g VS, although no signs of souring were seen. The inferred rate constant for the continuous tests were 0.09 d^{-1} when using only the yield data from the 8 of 13 tests above 0.35, and 0.3 when using all data. The influence of inclusion of a lag time term is explored, but not found to greatly impact on results. The results indicate broad similarity in rate constants between the two systems. They also indicate that a large number of batch tests are needed, and researchers should be reluctant to remove non-souring batch test results when fitting parameters.

1. INTRODUCTION

Evaluation of the suitability of food wastes for anaerobic digestion is made difficult because of variable and uncertain degradation parameters. Simpler tests that can estimate degradation kinetics can make it quicker and less expensive to assess suitability. A common sequence of testing would be: batch laboratory testing, bench-scale continuous reactor testing, pilot-scale continuous reactor testing, full-scale application. The purpose of the research was to examine the correspondence of first-order rate constants between laboratory testing of batch and continuous-feed systems.

Caffaz et al. (2007) observed that, for digested sludge, the gas production rate (GPR) data of a pilot plant agrees well with the GPR of a laboratory batch test. Brunn et al. (2007) instead observed higher yield and more rapid gas production in 80 L continuous-feed laboratory reactors than in a biogas plant, based on differences in VS, total organic carbon (TOC), ammonia (NH_3-N), organic acids, and gas yields between the two scales. Their study used a feed of 70% sewage sludge, 20% biowaste, and 10% fat. They suggest that the small sample amount that was used in

their lab tests may have been a contributing factor in the divergent results.

2. METHODOLOGY

2.1 Feedstock and Inoculum

The feedstock for the experiments was a food waste developed to simulate domestic collection. The composition is summarised in Tables 1 and 2. The food waste was coarsely shredded and blended with a food processor (without water addition), and then frozen at -20 °C. When required for use, subsamples were thawed overnight at 35 °C.

2.2 Experimental procedure

For the batch system, a 100 mm diameter polyvinyl chloride tube with a maximum capacity of 3.6 L was used. After preliminary tests of loading rates and inoculum needs, all tests reported here were conducted at an organic loading rate of 18.8 g VS/L-d, and 1.5 L of DSS. Further details on the batch reactors are reported in Qamaruz-Zaman and Milke (2008).

For the continuous system, two 30 L stainless steel digesters were employed. The digesters were manually wasted/fed daily. The digesters were designed to minimise oxygen ingress during feeding/wasting. The reactors were rotated daily for mixing. These digesters were loaded at 3.0 and 1.5 g VS/L-d organic loading rate. The hydraulic retention time (HRT) was 30 days. About

Table 1. Composition of the food waste feedstock.

Categories	Items	Wet weight (g)
Fruit and Vegetables	Potato skin	47
	Stir fried mixed vegetable	47
	Carrot skin	12
	Apple skin	22
	Apple seed	22
	Orange peel	77
	Broccoli stalk	72.5
	Pumpkin skin	42
	Pumpkin seed	27
	Salad	132
	Banana skin	92
Leftover food	Rice	77
	Spaghetti leftover	57
	Mashed potato	57
	Bread	37
	Boiled pumpkin	61.5
Teabags/coffee	Coffee ground & filter	45
	Teabags	33
Eggshells		40
	TOTAL	1000

Table 2. The chemical characteristics of the food waste feedstock.

Total nitrogen	0.41% of wet wt.
Total carbon	8.2 % of wet wt.
Phosphorus	0.039 % of wet wt.
Moisture	72% of wet wt.
Volatile Solids	84% of dry wt.
Protein	17.9 % of VS
Fat	12.6 % of VS
Carbohydrate	43.7 % of VS
Lignin	8.4 % of VS
Cellulose	8.9 % of VS
Hemi cellulose	8.4 % of VS

50 ml of phosphate buffers (100 mg/L) were added with the feedstock daily until Day 7 to counter acidification during start-up. A small amount of trace element solution was added to avoid washout of initial nutrients in the microbial seed.

2.3 Analyses

Biogas was collected in Tedlar bags (SKC, USA) of varying sizes and in large foil balloons designed for long-term helium containment. Gas volume was measured by squeezing the bags into a water displacement cylinder. Biogas composition was determined with a calibrated GA 2000 Plus (Geotechnical Instruments, UK). pH was measured, after daily calibration, with an EDT RE357 meter (UK), and is reported to one decimal point. VFA, ammonia, and COD were measured after centrifugation and filtration to 1.2 µm. After appropriate dilution, soluble COD (SCOD) was measured using the Hach Dichromate Reactor Digestion method, and ammonia using the salicylate method given as Hach Method 10031. Alkalinity was measured via titration as per Standard Methods (1989). For VFA analysis, further filtation to 0.22 µm was conducted prior to analysis on a HP6980 gas chromatograph with a HP19091N-133 column with various standards and calibration checks.

2.4 Evaluation of kinetic parameters

Experimental data were fit to a first-order kinetic model. For a batch system, cumulative methane production data was analysed using first order kinetics as given in (1) (Prashanth et al., 2006):

$$B = B_0*(1-e^{-k(t-tlag)}) \qquad (1)$$

where B is cumulative methane at time t (L CH_4/g VS); B_0 is ultimate methane yield (L CH_4/g VS), k is first order rate constant (d^{-1}), t is time of incubation (d) and t lag (d). All tests were run at least 20 days. Previous tests with this substrate in batch conditions had shown that over 95% (??what % here??) of methane production had occurred within 20 days. The best fit curves with respect to the experimental data were obtained using non-linear regression with the function Solver in Microsoft Excel. This function estimates values of model parameters by minimizing the sum of squared differences (SSR) between observed and predicted values.

Under steady state conditions for continuous reactors, first-order kinetics can be described as

per equation (2) (Mata Alvarez, 2003):

$$B = B_0 * k * HRT/(1 + k * HRT) \qquad (2)$$

where B is the specific methane production (L CH_4/g VS), k is the first-order rate constant (d^{-1}) and HRT is the hydraulic retention time (d). When fitting k given values of B, Bo and HRT, equation (2) takes the form:

$$k = (1/HRT) * B/(B_0 - B) \qquad (3)$$

3. RESULTS

3.1 Batch tests

Table 3 shows the first-order kinetic parameters that were estimated for batch food waste digestion. The estimated ultimate methane yield (B_0) varied greatly, and the results in Table 3 have been sorted in ascending order of the B_0. Based on the SSR values, it can be said that the parameters can be estimated reasonably accurately using the non-linear regression method. This is because the SSR values were satisfactorily very small (the highest being 0.0086).

Table 3. Kinetic parameters of batch food waste tests. Tests with the same number, but different letters, are replicates. (SSR: sum of squared residuals. C.V: coefficient of variation)

Test	B_0 (L CH_4/ g VS)	k (d^{-1})	t lag (d)	SSR	Comment
4b	0.1455	0.1448	0.0000	0.0003	
3a	0.1705	0.2423	0.3483	0.0009	
3b	0.2308	0.4228	1.0471	0.0007	*Unacceptable values*
3c	0.2519	0.2608	1.1991	0.0015	
4c	0.3136	0.0386	1.0415	0.0009	
3d	0.3503	0.1917	0.6519	0.0007	
3e	0.3699	0.2923	0.6256	0.0008	
3f	0.3948	0.2804	0.6305	0.0010	
2b	0.4134	0.1566	0.6134	0.0039	
4a	0.4312	0.1170	0.0000	0.0049	
1a	0.4434	0.4745	0.6320	0.0010	*Acceptable values*
2c	0.5129	0.1481	0.7155	0.0086	
2a	0.5595	0.1318	0.4883	0.0035	
Average	*0.4344*	*0.2241*			
Std. Dev.	*0.07*	*0.12*			
C.V. (%)	*16.3*	*53.8*			
Average	*0.3529*	*0.2232*			
Std. Dev.	*0.13*	*0.12*			*All 13 samples*
C.V. (%)	*35.8*	*55.4*			

Based on the results reported in Table 3, along with unreported tests, the authors conclude that the theoretical value for methane yield of this food waste is 0.40 – 0.50 L CH_4/g VS. Even with

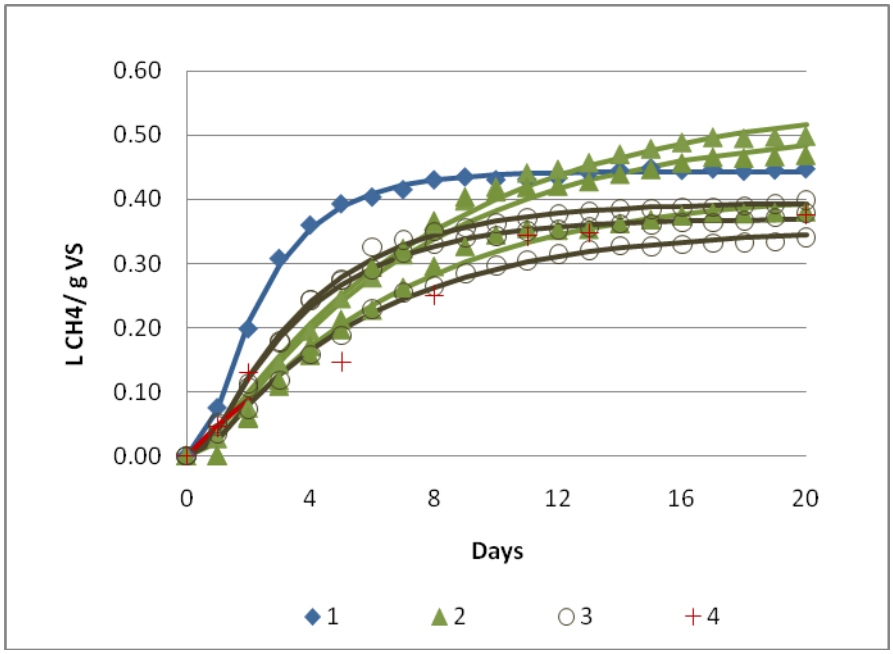

Figure 1. Methane yield of food waste in 'acceptable' batch tests. Symbols represent yields from experiments, while lines are yields fitted using first-order kinetics. Numbers give the set of the batch tests.

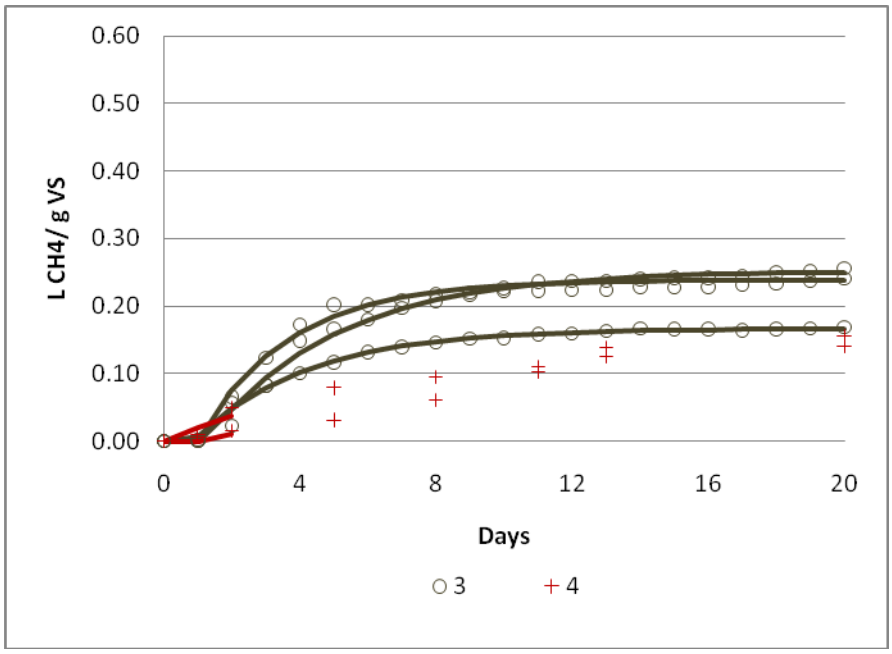

Figure 2. Methane yield of food waste in 'unacceptable' batch tests. Symbols represent yields from experiments, while lines are yields fitted using first-order kinetics. Numbers give the set of the batch tests.

various controls to ensure high reproducibility and high yield, a number of the batch reactors didnot successfully degrade. In order to allow comparison of values between batch and continuous digestion, the tests were divided into 'acceptable' and 'unacceptable' batch test results. For this study, we assume that values in the range 0.35-0.56 are acceptable. Figures 1 and 2 show the cumulative gas yield for the two types of batch tests. For the 'acceptable' values, the average yield was 0.43 L CH4/g VS, and the average first-order rate constant was 0.22 d^{-1}.

No strong correlation is seen between estimated B_0, k, and t lag for these data. Figure 3 indicates that excluding t lag in the first order equation leads to larger estimated values of B_0 and smaller estimated values of k. This effect is more pronounced for the rate constant.

No full explanation can be offered to as why methane production was limiting for some of the tests even though the reactor operating and substrate conditions were the same. The amount of organic matter reduced and the volume of methane produced for all the Test conditions appears to be balanced, so a loss of gas is not suspected. When the reactor effluent was tested, no apparent pattern could be seen between the 'acceptable' and 'unacceptable' tests in terms of their chemical composition (refer Table 4). Ammonia is quite high where levels between 1000 – 2000 mg/l have been reported to be indicative of an unstable system. When compared with their pH values, no distinct pattern can be seen to suggest the inhibiting effect of an ammonia and pH combination.

3.2 Continuous reactor

The methane yield at loading rates of 1.5 and 3.0 g VS/L-d were relatively similar (Figures 4 and 5). After removing the start-up data of the first 10 days, the average yields were 0.313 and 0.321 L CH_4/g VS. The methane composition after day 10 was consistently near 60%.

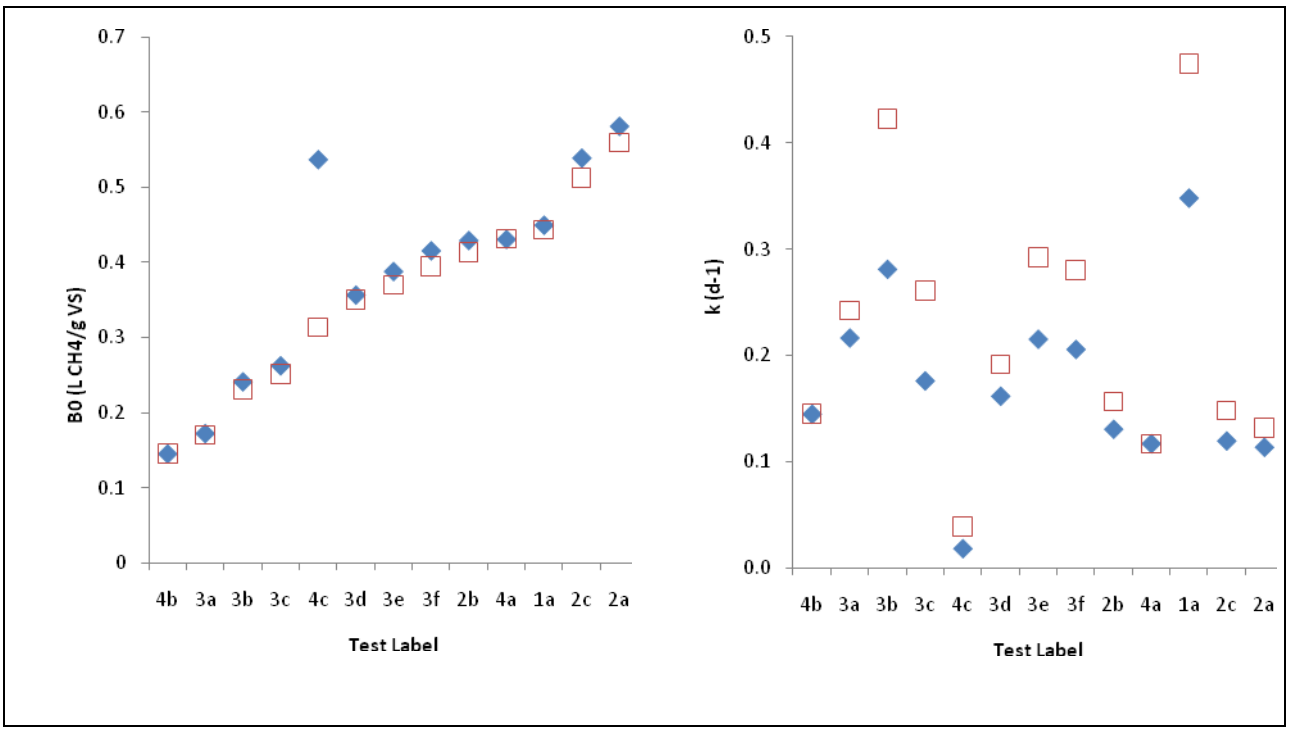

Figure 3. Effect of inclusion of a t lag term on the estimate of B_0 and k values for batch digestion of food waste. The square symbol represents the condition if t lag is added to the first order equation, while the diamond symbol omits t lag.

Table 4. Chemical analyses at end of batch food waste tests. Notes: [a] Similar tubes that were tested at Day 2 had 2635 mg/l TVFA, at Day 5 = 1059 mg/l and at Day 13 had VFA < 696 mg/l. [b] Indicates the time reactor incubation is completed and samples taken for the ammonia, SCOD, alkalinity and VFA tests. Highlighted cells represent tests that are outside of acceptable range for B_0 and k.

Test	SNH_3-N (mg/l)	SCOD (mg/l)	Alkalinity (mg/l)	TVFA[a] (mg/l)	pH	Day[b]
1a	1650	1450	5700	n/a	7.5	20
3a	1105	0	6700	n/a	7.3	20
3b	1343	325	5700	< 696	7.4	40
3c	1160	1550	4800	n/a	7.5	27
3d	1368	1325	4500	< 696	7.4	62
3e	1220	1750	6000	< 696	7.0	56
3f	1313	1725	4800	< 696	7.4	62

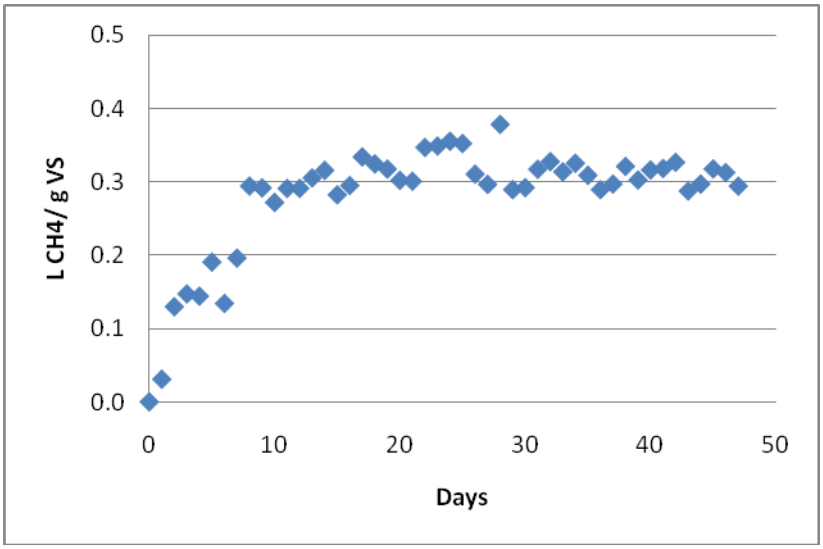

Figure 4. CH_4 yield of a continuous reactor fed food waste at 3.0 g VS/L-d with 30 day HRT.

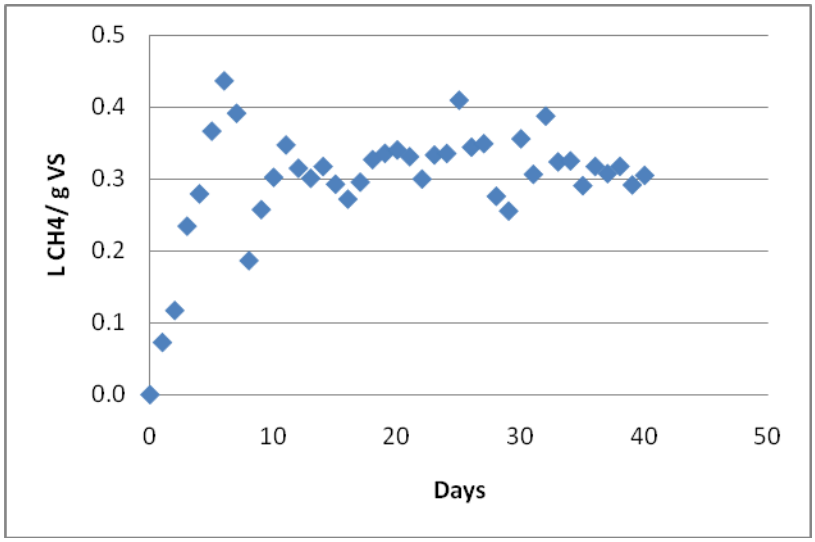

Figure 5. CH_4 yield of continuous reactor fed food waste at 1.5 g VS/L-d with 30 day HRT.

For B of 0.313 and 0.321 L CH_4/g VS, and applying B_0 of 0.434 L CH_4/g VS from the batch tests, the first-order constants for the 3.0 and 1.5 OLR reactors, respectively, are 0.086 and 0.094 d^{-1}. The estimation of k in this way is sensitive to the assumption of B_0. For the 3.0 OLR reactor, a B_0 of 0.35 would give a k of 0.37, while a B_0 of 0.5 would give a k of 0.056 d^{-1}.

4. DISCUSSION

4.1 Comparison of kinetics between various systems

Table 5 provides a summary of the fitted parameters for the two tests. The estimation of k for the continuous reactors is sensitive to the assumption of a B_0 value. The assumed B_0 value must be greater than the measured B value, and the fitted value of k will be greater the closer B_0 is to B. Using the 'acceptable' batch tests, the fitted k value for the continuous reactors is lower than for the batch tests, while using all of the batch tests, it is higher. Interestingly, the average best fit k value is similar independent of whether certain batch tests with low total yields are removed or not.

The average first-order rate constant of 0.22 d^{-1}determined in the batch tests is in agreement with the k values obtained by other researchers. Neves et al. (2008) obtained hydrolysis rate constants, assuming first order kinetics, between 0.12 d^{-1} and 0.32 d^{-1}, for restaurant waste with an excess of lipids and carbohydrates, respectively. A hydrolysis rate constant of 0.1 to 0.8 d^{-1} was recorded by Garcia-Heras (2002) when digesting proteins, lipids and carbohydrates. Cellulose digestion has been found to occur at a first-order rate constant of 0.18 d^{-1} (Gunaseelan, 2009). Sewage sludge and organic fraction of municipal solid waste (OFMSW) co-digestion in a batch system reported a hydrolysis rate constant of 0.17 d^{-1} (Sosnowski et al., 2008), while fruits and vegetable had a first order rate constant of 0.12 d^{-1} and 0.13 d^{-1} (Gunaseelan, 2004), respectively. Kinetic studies by researchers like Bolzonella et al. (2005) as well as Vavilin and Angelidaki (2005) showed that the first order reaction for hydrolysis, k was 0.24 – 0.4 d^{-1} and 0.10 d^{-1}, respectively when treating municipal solid waste (MSW). Any comparison to the results of this study are hampered by the fact that some sources give first-order rate values for

Table 5. Fitted parameters for food waste digestion. Units – B, B_0: (L CH_4/g VS); k (d^{-1}); OLR [1]: (g VS/L); OLR [2]: (g VS/L. d).

Test Conditions		Measured B	B_0	k	OLR
'Acceptable' batch tests	(average ± std.dev.)	-	0.434 ± 0.07	0.22 ± 0.12	18.8[1]
All batch tests		-	0.353 ± 0.13	0.22 ± 0.12	18.8[1]
Continuous reactor—B_0 from 'acceptable batch tests		0.321 0.312	0.434 0.434	0.094 0.086	1.5[2] 3.0[2]
Continuous reactor—B_0 from all batch tests		0.321 0.313	0.353 0.353	0.33 0.26	1.5[2] 3.0[2]

hydrolysis rather than the overall methane production rate. In addition, much of the literature values are for differing feedstocks, which limits our ability to compare.

Martin et al. (1997) observed that scale effects seem to be significant for laboratory reactors without leachate recirculation and pH control. Their analysis suggests that a high hydrolysis rate and low pH can limit methane production in certain regions of a batch reactor, which in turn could lead to larger variability in batch degradation yields as sample size decreases. Although our batch tests did not have pH control or leachate recirculation, chemical analysis did not indicate pH inhibition or VFA accumulation as a cause for the lower yield in some reactors.

The volatile solids reduction on one instance (Test 1a, Table 3) only achieved 70% volatile solids reduction, much lower than the 94 % (± 3) VS reduction average obtained by the other tests. It is suspected that in this occasion, the volatile solids measurement may not have been accurate; this is supported by the disagreement between volatile solids lost and methane production. A COD measurement would have been a more suitable indicator of organic matter in the substrate. However, because this research deals with food waste that is semi-solid, obtaining a homogeneous, representative and analysable sample is difficult. Thus, volatile solids measurement has been used.

Fitting a value of k for continuous reactors from 'acceptable' batch test results, while excluding 'unacceptable' batch test results, could lead to a mis-representation of how continuous reactors operate. It is possible that continuous reactors operate with lower yields than the best batch reactors tested on the same substrates. Angelidaki and Sanders (2004) observed that the practical yield obtained in a continuous reactor was lower than the theoretical methane potential. The difference might be due to inhibition from a trace chemical not measured by us (coffee ground leachate?) and which varies greatly from batch to batch of 120 g food waste. The difference could also be due to variability in the inherent anaerobic degradability of the food waste between 120 g batches. The difference could also be due to poor contact between substrate and degrading communities. Any of these three scenarios would lead to a situation where the continuous reactor evens out the variable methane production potential. This scenario would indicate that all batch test results should be used to estimate yield in continuous reactors (after removing test results with obvious failure due to souring). Assuming, for the moment, that the k values for the two reactors are equal, the best fit value of B_0 for these continuous reactors (with k = 0.22) would be 0.37 L CH_4/g VS—less than the batch maximum of 0.5, and close to the value of 0.353 found when averaging all batch test yields. Although in need of confirmatory tests, these results indicate that the kinetic constants can be interchanged between laboratory

batch and continuous systems as long as a large number of non-souring batch tests are conducted.

4.2 Suitability of first-order rate function

This analysis started with the assumption that a first-order methane production function was suitable for both the continuous and batch systems. The data collected in this work tend to support that assumption. The SSR values of 0.0003-0.0086 in Table 3 for first-order fits to batch food waste digestion data give a NRSME (normalised root squared mean error) of 0.07 – 0.12. The NRSME values of the batch tests are similar to the NRSME values of 0.05 found by Gavala and Lyberatos (2001) when estimating lactose and glucose degradation using first order kinetics. The ease of parameter fitting, and the common use of first-order kinetics for methane production in anaerobic systems, identify the first-order gas production model as a first-choice model.

The suitability of a first-order model can depend greatly on the inoculums. Neves et al. (2008) and Jensen et al. (2007) both attributed the variability in their kinetic constants to the choice of inoculums. A more active or acclimitised inoculum can be expected to lead to quicker establishment of rapid methane production. Although models can be fit to describe the growth in anaerobic populations during batch digestion, a simpler parameterisation involves the addition of a lag term to the first-order model. Used in this way, the fitted t lag can represent how suitable the inoculum was with larger lag times representing longer time before first-order behaviour is seen. The fit lag times in this study were relatively short with an average of 0.6 days. Still, they were significant enough to affect the fitting of B_0, and particularly k, values. For the purpose of estimating k values for continuous reactors, it is not clear whether it would be better to use the k values found from batch tests where t lag is included or where it is excluded. Excluding the t lag term leads to a fitted k of 0.172 d^{-1} for the 'acceptable' batch tests, and 0.171 for all batch tests. Conducting the same exercise as at the end of Section 4.1, but using a k of 0.172, gives a best fit B_0 value of 0.383, again much closer to the 0.353 found from averaging all test results, than to the 0.5 maximum methane yield. Because of the strong influence that k has on reactor sizing, it would be inappropriate to extrapolate a k value from batch tests to design of a full-scale continuous system, and a pilot-scale plant would be needed to confirm kinetics; however, this research indicates that a proper batch test of food waste (with or without a lag time fit) would provide enough assurance to size a pilot-scale continuous system without the need for a bench-scale continuous system. Until further work is done to assess how the inclusion of a t lag term can impact on the estimation of k for a continuous system, it would be prudent to find fitted parameters both with and without the t lag term.

REFERENCES

Angelidaki, I., and Sanders, W. (2004). Assessment of the anaerobic biodegradability of macropollutants. Reviews in Environmental Science and Bio/Technology, 3(2), 117-129.

Bolzonella, D., Fatone, F., Pavan, P. and Cecchi, F. (2005). Anaerobic fermentation of organic municipal solid wastes for the production of soluble organic compounds. Industrial and Engineering Chemistry Research, 44(10), 3412 – 3418.

Brunn, L., Dornack, C., and Bilitewski, B. (2007). Application of laboratory scale experiments to industrial scale in case of anaerobic waste treatment. Proceedings Sardinia 2007, 11th International Waste Management and Landfill Symposium, Cagliari, Italy, 1-5 October, 2007.

Caffaz, S., Lombardi, L., Ficara, E., Bettazi, E., and Lubello, C. (2007). Characterization of anaerobic co-digestion processes using lab-scale batch tests. Proceedings Sardinia 2007, 11th

International Waste Management and Landfill Symposium, Cagliari, Italy, 1-5 October, 2007.

Garcia-Heras, J. L. (2002). Reactor sizing process kineitics and modelling of anaerobic digestion of complex wastes, in *Biomethanisation of the organic fraction of municipal solid wastes*. IWA Publishing, London.

Gavala, H. N., and Lyberatos, G. (2001). Influence of anaerobic culture acclimation on the degradation kinetics of various substrates. Biotechnology and Bioengineering, 74(3), 181-195.

Gunaseelan, V. N. (2004). Biochemical methane potential of fruits and vegetable solid waste feedstocks. Biomass and Bioenergy, 26(4), 389-399.

Gunaseelan, V. N. (2009). Predicting ultimate methane yield of Jatropha curcus and Morus indica from their chemical composition. Bioresource Technology, 100 (13), 3426-3429.

Jensen, P. D., Hardin, M. T., and Clarke, W. P. (2007). Measurement and quantification of sessile and planktonic microbial populations during the anaerobic digestion of cellulose. 11th IWA World Congress on Anaerobic Digestion, 23-27 September 2007, Brisbane, Australia.

Mata-Alvarez, J. (2003). *Biomethanization of the organic fraction of municipal solid wastes*. IWA Publishing. Cornwall, UK.

Martin, D. J., Plotts, L. G. A., and Reeves, A. (1997). Small-scale simulation of waste degradation in landfills. Biotechnology Letters, 19(7), 683-68.

Neves, L., Goncala, E., Oliveira, R., and Alves, M. M. (2008). Influence of composition on the biomethanation potential of restaurant waste at mesophilic temperatures. Waste Management, 28(6), 965-972.

Prashanth, S., Kumar, P., and Mehrotra, I. (2006). Anaerobic degradability: effect of particulate COD. Journal of Environmental Engineering, 132(4), 488-496.

Qamaruz-Zaman, N., and Milke, M.W. (2008). Digested sewage sludge as seed for batch test of anaerobic biodegradability. Global Waste Management Symposium, Colorado, September, published as CD, 11 p.

Sosnowski, P. Klepacz-Smolka, A., Kaczorek, K. and Ledakowicz, S. (2008). Kinetic investigations of methane co-fermentation of sewage sludge and organic fraction of municipal solid wastes. Bioresource Technology, 99 (13), 5731-5737.

Vavilin, V. A., and Angelidaki, I. (2005). Anaerobic degradation of solid material: importance of initiation centers for methanogenesis, mixing intensity, and 2D distributed model. Biotechnology and Bioengineering, 89(1), 113-122.