Modeling anaerobic digestion of dairy manure using the IWA Anaerobic Digestion Model no. 1 (ADM1)

D. I. Page, K. L. Hickey, R. Narula, A. L. Main and S. J. Grimberg

ABSTRACT

The Anaerobic Digestion Model No. 1 (ADM1) can be used to describe treatment of dairy manure once manure characteristics have been incorporated in the model. In this paper a parameter set is presented that can be used with ADM1 for simulation of dairy manure digester performance. Model results have been verified with bench-scale experiments and reported data from full-scale systems. Model predictions fit experimental data best for biogas composition and digester effluent COD. Simulated biogas productions were inconsistent with measurements from three different digesters. The model overpredicted acetogenesis, resulting in higher simulated than observed acetate concentrations. However, total volatile acid concentrations were simulated reasonably well. The model consistently predicted higher inorganic nitrogen than measured or reported results, indicating a need for further research in that area. The presented model and associated parameter set can be used to simulate and optimize the performance of full-scale dairy manure digesters.

Key words | acetogen, ADM1, biogas, dairy manure, methanogen, VFA

D. I. Page (corresponding author)
K. L. Hickey
R. Narula
A. L. Main
S. J. Grimberg
Department Civil Environmental Engineering,
Clarkson University,
8 Clarkson Avenue,
Potsdam, NY 13699,
USA
E-mail: *pagedi@clarkson.edu*

INTRODUCTION

Dairy farm owners are increasingly considering the application of anaerobic processes as a component of manure management. Anaerobic digestion (AD) on farms provides waste stabilization through the reduction of effluent chemical oxygen demand (COD), volatile solids (VS), and volatile fatty acids (VFA). Furthermore, mesophilic anaerobic digestion of dairy manure has been shown to substantially reduce fecal coliforms and pathogenic microorganisms, including fecal streptococcus and *Mycobacterium avium paratuberculosis* (U.S. EPA 2004, 2005). Additionally, biogas utilization through heat recovery and electricity generation provides economic incentive for implementation of AD technologies on farms.

The development of dynamic models can lead to automated digester control, resulting in more efficient process performance and reduced reliance on skilled operators (Blanchard & Gill 1987). Additionally, predictive models can help to evaluate the economics of AD applications by giving insight to biogas production. Fundamental dynamic models of various complexities describing anaerobic degradation of organic material have been developed over the years (Hill 1982; Vavilin *et al.* 1994; Angelidaki *et al.* 1999; Siegrist *et al.* 2002). Other models have been developed to describe digestion of cattle manure under non-ideal mixing conditions (Keshtkar *et al.* 2003) and biogas production for plug-flow digesters (Kifle & Inglis 2006; Wu *et al.* 2006). In 2002, the International Water Association (IWA) task group for mathematical modeling of anaerobic digestion processes developed Anaerobic Digestion Model No. 1 (ADM1), with the objective of simulating anaerobic degradation of any organic material in a continuously stirred tank reactor (CSTR) (Batstone *et al.* 2002).

ADM1 can be used by researchers and practitioners to aid in design, operation, and optimization of full-scale systems (Batstone *et al.* 2002). However, use of the model requires knowledge of the concentrations of many substrate

doi: 10.2166/wst.2008.678

components fed to the anaerobic digestion system, when often the concentrations of only a limited number of components are known. A default parameter set is given in Batstone *et al.* (2002) for use with municipal wastewater, and slight modifications in parameter values have recently been suggested (Batstone *et al.* 2006). However, it is unlikely that this parameter set would suffice to describe anaerobic degradation of dairy manure. The goal of the research presented here is to develop a parameter set for the simulation of dairy manure and to verify ADM1 results with laboratory experiments and full-scale systems. Initial experimental results indicated that small changes in input parameters such as carbohydrate, monosaccharide, protein, and lipid contents, as well as biomass concentrations, significantly influence predictions of digester performance. In this paper we have characterized many of the required input parameters to ADM1. We also show that using these parameters with the model provides reasonable predictions for most components, when compared to data from real systems.

METHODS

Bench-scale digesters

Four bench scale anaerobic digesters ($V = 6.5$L, $HRT = 20$ d) were operated under mesophilic conditions ($T = 35$°C) in a constant temperature room over a seven month period. The digesters were initially inoculated with effluent from an anaerobic digester at the Potsdam Wastewater Treatment Plant to provide a sufficient microorganism population. Manure was collected once biweekly from a storage lagoon at North Harbor Dairy (NHD), a 550 milking cow dairy located in Sackets Harbor, NY. Manure was stored at 4°C until transported to an influent tank with a two day residence time in the constant temperature room. Manure was pumped into the digesters from the influent tank once daily using a peristaltic pump (Cole Parmer Masterflex High Performance Pump Drive and Head, Cole Parmer, Vernon Hills, Ill.). Biogas was re-circulated in each digester with an air cadet pump (Air Cadet, Cole Parmer, Vernon Hills, Ill.) through a ring diffuser to provide mixing. Intensity and duration of mixing varied between the digesters. Data obtained from the digester with a biogas recirculation rate of 4 L·min^{-1} twice daily for 30 s has been used for comparison to ADM1 in this study.

Biogas composition

Biogas was sampled using 1.6 L Tedlar™ Bags (Fisher Scientific, Waltham, MA) to measure gas flow and composition. Average biogas production rates were determined by measuring the volume of water displaced by the Tedlar™ Bags that had filled with biogas over a given time. Biogas composition was measured using a gas chromatograph (GC) equipped with a thermal conductivity detector (Series 550 Thermal Conductivity Detector, Model # 69-570, GOW-MAC, Bethlehem, PA) and a packed column (180 cm x 0.6 cm i.d. S.S. 80/100 Porapak Q, GOW-MAC, Bethlehem, PA). The operating temperatures for the GC were 50°C for the column and detector, and 30°C for the injection port. Detector output was recorded using a data acquisition system (Model # 191039C-02, National Instruments, Austin, TX), and peaks were integrated using a customized Matlab® routine. One millilitre of gas was sampled from the Tedlar™ Bags and injected into the GC. Standards of 99% (by volume) UHP methane (Merriam-Graves, Charlestown, NH) and 99% UHP carbon dioxide (Merriam-Graves, Charlestown, NH) were injected into the GC to develop a calibration curve for each biogas component.

Influent and effluent manure characterization

COD of influent and effluent manure was measured using Standard Method 5220 D (APHA 1998). Total inorganic nitrogen was measured by Titanium Trichloride Reduction using HACH Test 'N Tube™ Vials (HACH Method 10021).

Volatile fatty acid estimation was carried out using gas chromatography (Hewlett Packard Series II 5980, Palo Alto, California). A Nukol™ fused silica capillary column of 30 m × 0.25 mm i.d. × 0.25 μm film thickness was used with a flame ionization detector. The injector port and column were operated at temperatures of 230°C and 185°C, respectively. The detector temperature was maintained at 240°C. Helium was used as the carrier gas at 1.0 mL·min^{-1}. Two microlitres of sample were injected into the gas chromatograph for analysis. Volatile fatty acids were identified by

comparing their retention time with those of volatile acid standard mixture (Supelco, Bellefonte, PA). Standard curves were prepared separately for each acid, relating area under peak to concentration, with seven different concentrations (prepared by different dilutions of the stock) and were used to estimate the concentrations of the different acids in the samples. Values of R^2 for acetic, propionic, butyric, and valeric acid standard curves were 0.93, 0.97, 0.99, and 0.99, respectively.

Methanogen population was estimated by quantitation of Coenzyme M (Elias *et al.* 1999). High pressure liquid chromatography was used to measure CoM (Waters™ 474 Scanning Fluoresence Detector, 717 plus Autosamples, 600s Controller, and 616 Pump, Milford, MA). CoM detection was achieved at excitation of 338 nm and emission of 450 nm. The system included a C-18 column (25 cm × 4.5 mm i.d., Supelco, Bellefonte, PA) and was operated under isocratic conditions using a mobile phase of 50 mM sodium acetate buffer (pH 5.7) and acetonitrile (80:20) at 1.0 mL·min^{-1} and an injection volume of 20 μl. Standard curves were prepared using five dilutions of the stock relating area under peak to CoM. Values of R^2 ranged from 0.97 to 0.98. The constant used to relate CoM to methanogen concentration was 39fmol CoM·cell^{-1} (Elias *et al.* 1999).

To estimate the concentration of acetogens in the digesters, samples were incubated in heterotrophic acetogen medium (Wellsbury *et al.* 2002) for 4 hrs at 35°C. Cell concentration monitored after 4 hrs at 620 nm (Shimadzu spectrophotometer, Model # 206-82301-92, Kyoto, Japan) was related to absorbance values from acetogen growth curves, which were established independently. Using the standard growth curves, absorbance at 4 h was related to initial acetogen concentration in the medium. Absorbance measurements of acetogens during the batch growth incubations were correlated to cell concentrations using the LIVE/DEAD® *Bac*Light™ Bacterial Viability Kit (Catalog # L7007, Molecular Probes, Invitrogen Corporation, Carlsbad, CA) and counting cells under a microscope (Olympus BX-51, Center Valley, Pennsylvania) using MetaMorph 6 software (Meta Imaging Series®, Universal Imaging Corporation™, Downingtown, PA). A plot of total number of cells vs. absorbance over 12 h of incubation was used to estimate cell counts from absorbance readings.

Bench-scale digester modeled as a continuously stirred tank reactor

The bench-scale digester was modeled in Matlab–Simulink® using the implementation of the ADM1 from Lund University, copyright 2006. Initial digester concentration was assumed to be a 2:1 wastewater effluent to dairy manure mixture. Wastewater treatment effluent values were estimated using the steady state output obtained from the model when run with the default parameter set from Lund University.

Conversions from measured concentration units in mass per unit volume to COD per unit volume were made based on theoretical oxygen demand (ThOD) for the various parameters. Measurements of total cell counts were first converted to a mass basis after approximating cell mass as 0.52 μg, assuming a cylindrical cell of dimensions 1 μm in diameter and 3 μm in length (Rittmann & McCarty 2001) and a cell density equal to water.

Full-scale plug-flow digesters

AA Dairy and Gordondale Farms

AA dairy and Gordondale Farms are two medium sized dairy farms, each using plug-flow anaerobic digesters. AA dairy is an 890 ha dairy with a milking heard size of 550 cows, located in Candor, NY. Gordondale Farms is a 1,295 ha dairy with a milking herd size of 860 cows, located in Nelsonville, Wisconsin. AA Dairy has a conventional mesophilic plug-flow digester ($V = 1{,}120\ m^3$, $HRT = 34$ d) and Gordondale farms has a mesophilic modified plug-flow digester ($V = 2{,}006\ m^3$, $HRT = 29$ d) with vertical gas mixing. Data from these two digesters, presented in reports by U.S. EPA (2004, 2005) were used to evaluate the effectiveness of ADM1 to accurately predict the performance of both full-scale systems.

Plug-flow digesters modeled as tanks in series

The full-scale plug-flow anaerobic digesters for dairy manure were each modeled as four continuously stirred tank reactors (CSTRs) in series using the ADM1. The particulate and soluble components were assumed to be carried to the next reactor in series, while gas flows were

summed. The final partial pressure of each individual gas component was calculated as a flowrate-adjusted weighted average of all the reactors. Influent substrate concentrations to the first tank for each of the two full-scale plug-flow digesters were obtained from reported results (U.S. EPA 2004, 2005). When data for specific parameters were not given, they were estimated based on measured characteristics of manure from NHD and literature values, and adjusted to maintain accurate total and soluble COD. For example, total VFA concentration was reported but the concentrations of individual acids were not, so input concentrations were changed while maintaining the same individual acid ratios as measured in manure from NHD. A full set of parameter values and initial conditions used to model the two full-scale plug-flow digesters can be obtained from the corresponding author.

RESULTS AND DISCUSSION

Input parameter set

Input parameters used in the model for the treatment of dairy manure in the bench-scale digester are shown in Tables 1–5. Parameters not listed have been kept as found in the ADM1 implementation from Lund University. Total methanogen concentration was determined to be 1.7 ± 0.1 (kgCOD·m^{-3}), 63% higher than the summation of the default values for acetate and hydrogen degraders. Therefore, acetate and hydrogen degrader concentrations were increased to 1.2 and 0.5 (kgCOD·m^{-3}), respectively, maintaining a 63% increase in both concentrations (Table 3). Similarly, acetogens were estimated based on the measured total concentration of 1.6 ± 0.02 (kgCOD·m^{-3}), 66% lower than the summation of the default individual acetogen values (Table 3). Bench-scale digester data were used to adjust kinetic parameters for aciticlastic methanogenesis in order for model predictions to better fit measured results (Table 4). Increasing the yield and uptake rate and decreasing the half saturation constant of acetate allowed

Table 1 | Soluble components

Description	Symbol	Value	Unit	Reference
Monosacharides	S_su	5	kgCOD·m^{-3}	1
Total valerate	S_va	1.21	kgCOD·m^{-3}	3
Total butyrate	S_bu	0.77	kgCOD·m^{-3}	3
Total propionate	S_pro	1.3	kgCOD·m^{-3}	3
Total acetate	S_ac	2.16	kgCOD·m^{-3}	3

References: 1. Zaher & Chen (2006), 3. Experimental measurement.

Table 2 | Particulate components

Description	Symbol	Value	Unit	Reference
Carbohydrates	X_ch	18	kgCOD·m^{-3}	2
Proteins	X_pr	31	kgCOD·m^{-3}	1
Lipids	X_li	1.7	kgCOD·m^{-3}	1
Particulate inerts	X_I	35.3	kgCOD·m^{-3}	2

References: 1. Zaher & Chen (2006), and 2. Batstone et al. (2004).

Table 3 | Degraders

Description	Symbol	Value	Unit	Reference
Acetate degraders	X_ac	1.2	kgCOD·m^{-3}	4
Hydrogen degraders	X_h2	0.5	kgCOD·m^{-3}	4
Sugar degraders	X_su	0.27	kgCOD·m^{-3}	4
Amino acid degraders	X_aa	0.78	kgCOD·m^{-3}	4
LCFA degraders	X_fa	0.15	kgCOD·m^{-3}	4
Valerate and butyrate degraders	X_c4	0.28	kgCOD·m^{-3}	4
Propionate degraders	X_pro	0.09	kgCOD·m^{-3}	4

References: 4. Estimated from experimental results.

Table 4 | Kinetic parameters for aceticlastic methanogenesis

Description	Symbol	Value	Unit	Reference
Yield of acetate	Y_ac	0.07	kgCOD_X· kg COD_AC^{-1}	4
Uptake rate of acetate	k_m_ac	15	kgCOD_AC/ (kg COD_X·d)	4
Half saturation constant for acetate	K_S_ac	0.05	kgCOD_AC/ (kg COD_X·d)	4

References: 4. Estimated from experimental results.

Table 5 | First order decay rates

Description	Symbol	Value	Unit	Reference
Decay rates for acetogens	k_dec_Xi	0.04	d^{-1}	4

References: 4. Estimated from experimental results.

for higher predicted values of methanogen concentration and lower acetate concentrations, more closely matching experimental results. Other studies have also shown that lower K_s values are more appropriate (Siegrist *et al.* 2002; Parker 2005). The decay rates for all acetogens were increased to $0.04 d^{-1}$ (Table 5), in agreement with other research indicating decay rates higher than $0.02 d^{-1}$ (Batstone *et al.* 2004).

Comparison of ADM1 to bench-scale digester performance

The comparison of model predictions for biogas production and composition, COD reduction, inorganic nitrogen, biomass concentrations, and VFAs are summarized in Figures 1–3. Error bars represent 1 standard deviation of experimental data. The model overpredicted biogas production, but fit methane and carbon dioxide content when compared to bench-scale results (Figure 1). The lower measured gas production might be explained because the digester did not operate exactly as a CSTR, since it was not continually mixed and fed only once per day. Also, mixing intensity may not have been sufficient to provide maximum mass transfer of substrate to microorganisms. Model predictions for COD reduction and methanogen biomass fit experimental data, but measured concentrations of acetogens were lower than predicted (Figure 2).

Measured values of propionate, butyrate, and valerate were higher than predicted, while measured acetate was lower than predicted (Figure 3). However, total VFA concentration fit experimental results well (Figure 3).

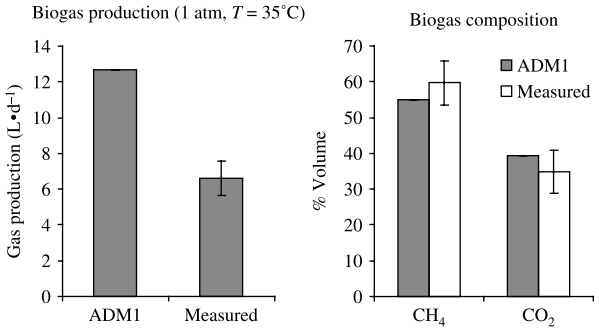

Figure 1 | Comparison of model predictions of biogas production and composition with experimental results.

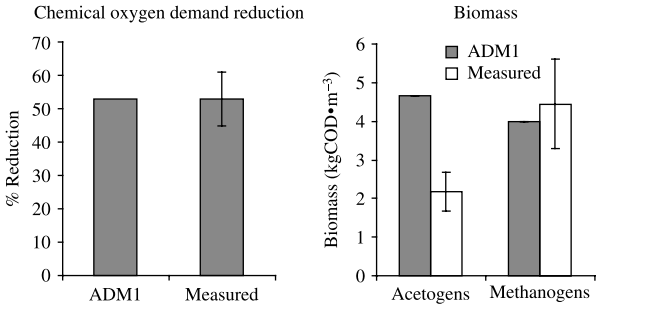

Figure 2 | Comparison of model predictions of COD reduction and biomass concentrations with experimental results.

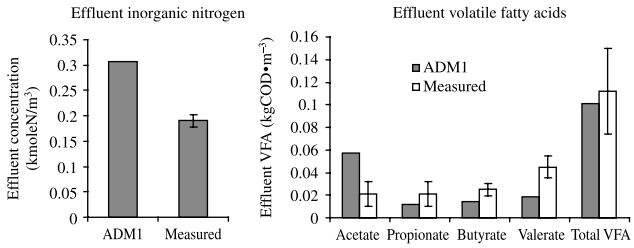

Figure 3 | Comparison of model predictions of inorganic nitrogen and VFAs with experimental results.

Lower measured acetate concentrations are consistent with measured lower than predicted acetogen concentrations, indicating that acetogenesis may be inhibited or slower in manure treatment compared to municipal waste. Reduced acetogenesis could also explain lower than predicted gas production, as less acetate would be available to methanogens for methane and carbon dioxide production. Predicted effluent inorganic nitrogen was much higher than experimental measurements due to simulated accumulation of soluble NH_4 (Figure 3).

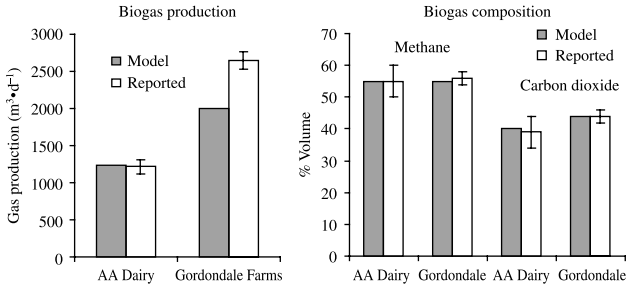

Figure 4 | Comparison of model predictions of biogas production and composition with plug-flow digesters.

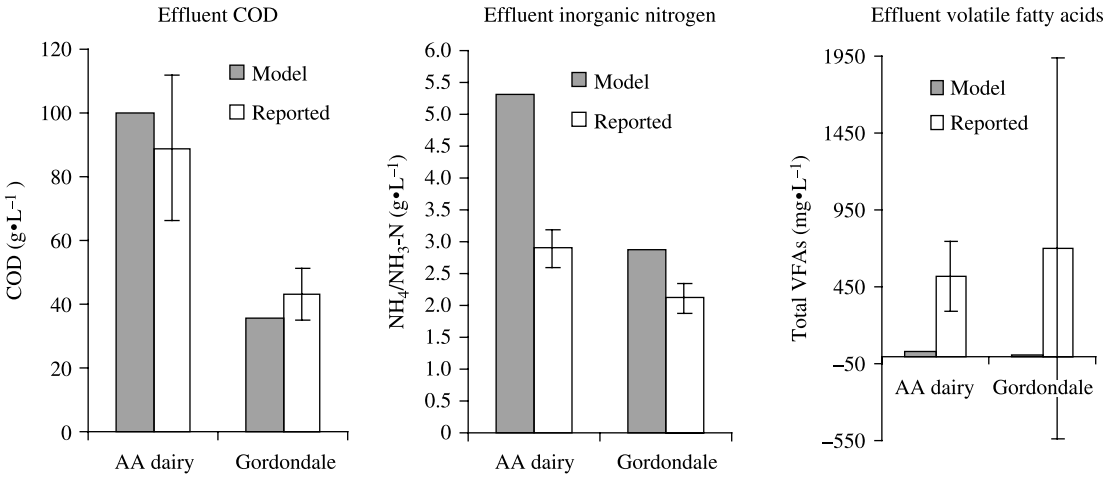

Figure 5 | Comparison of model predictions of COD, inorganic nitrogen, and total VFAs with plug-flow digesters.

Comparison of ADM1 in series to plug-flow digester performances

Model predictions for biogas production and composition, COD, inorganic nitrogen, and VFAs were compared to reported values (Figures 4 and 5). Biogas production fit reported measurements for AA Dairy, but not for Gordondale Farms (Figure 4). The plug-flow digester at Gordondale Farms used vertical gas mixing, which likely caused enhanced gas production. The mean rate of biogas production for the Gordondale Farms digester was $3.1\,m^3{\cdot}(cow\text{-}day)^{-1}$ compared to $2.2\,m^3{\cdot}(cow\text{-}day)^{-1}$ observed with the conventional plug-flow digester at AA Dairy (U.S. EPA 2005). Reported and modeled results of biogas composition (Figure 4) and COD (Figure 5) matched well. Modeling the plug-flow digesters as a series of CSTRs resulted in nearly complete degradation of VFAs (Figure 5). Reported results of total VFA concentration were higher for AA dairy than predicted (Figure 5). The standard deviation of the reported measurements of total VFAs for Gordondale Farms is large; however, the average is also higher than predicted (Figure 5). These results indicate that ADM1 may overpredict acetogenesis in dairy waste systems. Further study is needed to elucidate the specific mechanisms. As with experimental results from the bench-scale digester, effluent inorganic nitrogen predictions were higher than reported for both plug-flow digesters due to simulated accumulation of ammonium-nitrogen (Figure 5). Differences between predicted and reported results are also because model input values for carbohydrate, monosaccharide, protein, and lipid concentrations were estimated, since they were not reported.

CONCLUSIONS

In summary, the ADM1 applied to anaerobic digestion of dairy manure can provide reasonable predictions for many of the model effluent values given an input matrix of manure parameters. The calibrated model provided good predictions of biogas composition and COD concentration for a laboratory scale and two full-scale systems. The model may overpredict biogas production in bench-scale digesters, but in full-scale systems it seems to provide adequate results. It is unknown at this time why the model overpredicted acetate biodegradation. For a CSTR configuration, results suggest that the model can provide accurate predictions of total VFA concentration, but the concentration of individual acids may be incorrect and requires further study. However, for practical application of the model, total VFA concentration may be sufficient detail in order to make informed decisions for the operation of the digester. The model consistently predicted higher inorganic nitrogen than measured or reported results, suggesting that nitrogen transformations will have to be reviewed when the model is applied to high organic loadings such as farm waste.

ACKNOWLEDGEMENTS

This work was supported by funding from US Department of Agriculture (USDA), US Department of Energy (USDOE), New York Ag and Markets, and New York State Energy Research and Development Authority (NYSERDA). We gratefully acknowledge Benjamin Durfee for his assistance with operation of the bench-scale digesters and analytical tests.

REFERENCES

American Public Health Association 1998 *Standard Methods for the Examination of Water and Wastewater*, 20th edition. American Public Health Association, Washington, DC, USA.

Angelidaki, I., Brigitte, L. E. & Ahring, B. K. 1999 A comprehensive model of anaerobic bioconversion of complex substrates to biogas. *Biotechnol. Bioeng.* **63**(3), 363–372.

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 *Anaerobic Digestion Model No. 1*. IWA Publishing, London, UK.

Batstone, D. J., Keller, J. & Blackhall, L. L. 2004 The influence of substrate kinetics on the microbial community structure in granular anaerobic biomass. *Water Res.* **38**(6), 1390–1404.

Batstone, D. J., Keller, J. & Steyer, J. P. 2006 A review of ADM1 extensions, applications, and analysis 2002–2005. *Water Sci. Technol.* **54**(4), 1–10.

Blanchard, J. P. & Gill, T. A. 1987 Methane production by continuous digestion of farm wastes. In: Wise, D. L. (ed.) *Global Bioconversions Vol.1*. CRC Press, Boca Raton.

Elias, D. A., Krimholz, L. R., Tanner, R. C. & Suflita, J. M. 1999 Estimation of methanogen biomass by quantitation of Coenzyme M. *Appl. Environ. Microbiol.* **65**(12), 5541–5545.

Hill, D. T. 1982 A comprehensive dynamic model for animal waste methanogenesis. *Trans. ASAE* **25**(5), 1374–1379.

Keshtkar, A., Meyssami, B., Abolhamd, G., Ghaforian, H. & Khalagi Asadi, M. 2003 Mathematical modeling of non-ideal mixing continuous flow reactors for anaerobic digestion of cattle manure. *Bioresour. Technol.* **87**, 112–124.

Kifle, G. B. & Inglis S. 2006 Biogas production model for plug-flow anaerobic digesters. *Proc. of the 2006 ASAE Annual Meeting*, Portland, Oregon, USA, paper number 064172.

Parker, W. J. 2005 Application of the ADM1 model to advanced anaerobic digestion. *Bioresour. Technol.* **96**, 1832–1842.

Rittmann, B. E. & McCarty, P. L. 2001 *Environmental Biotechnology, Principals and Applications*. McGraw-Hill, Boston, MA.

Siegrist, H., Vogt, D., Garcia-Heras, J. L. & Gujer, W. 2002 Mathmatical model for meso- and thermophilic anaerobic sewage sludge digestion. *Environ. Sci. Technol.* **36**, 1113–1123.

U.S. EPA 2004 *A comparison of dairy manure management with and without anaerobic digestion and biogas utilization*, report prepared by J.H. Martin, Eastern Research Group, Inc., Boston.

U.S. EPA 2005 *An evaluation of a mesophilic, modified plug flow anaerobic digester for dairy cattle manure*, report prepared by J.H. Martin, Eastern Research Group, Inc., Boston.

Vavilin, V. A., Vasiliev, V. B., Ponomarev, A. V. & Rytow, S. V. 1994 Simulation model *methan*e as a tool for effective biogas production during anaerobic conversion of complex organic matter. *Bioresour. Technol.* **48**, 1–8.

Wellsbury, P., Mather, I. & Parkes, R. J. 2002 Geomicrobiology of deep, low organic carbon sediments in the Woodlark Basin, Pacific Ocean. *FEMS Microbiol. Ecol.* **42**, 59–70.

Wu, B., Bibeau, E. L. & Gebremedhin, K. G. 2006 Three-dimensional numerical simulation model of biogas production for anaerobic digesters. *Proc. of the 2006 ASAE Annual Meeting*, Portland, Oregon, USA, paper number 064060.

Zaher, U. & Chen, S. 2006 Interfacing the anaerobic digestion model no. 1 (ADM1) with manure and solid waste characteristics. *WEFTEC 79th Annual Technical Exhibition and Conference*, Dallas, TX, USA.