Agronomy Research Biosystem Engineering Special Issue 1, 167-174, 2012

Simulation of anaerobic digestion of cattle manure

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Abstract. IWA Anaerobic Digestion Model No.1 (ADM1) was used to simulate the anaerobic digestion process of cattle slurry. The model was applied to 200 l single stage completely stirred tank reactor. The simulation results of pH, biogas flow rate, acetate and methane concentration were under study. Ammonia inhibition constant was optimized during this study to improve modelling results compared to measurements of acetate concentration. Maximum methane yield during experiment was 291 l (kg VS_{added})$^{-1}$ at organic loading rate 2.0 kg VS (m^3 d)$^{-1}$.

Keywords: anaerobic digestion, cattle slurry, modelling.

Introduction

New technologies are available for manure management with new business opportunities, where energy and nutrients are extra income to farmers. Agricultural companies are interested to implement new technologies for better manure management, especially in large farms. In Estonia the total number of dairy and non-dairy cattle was 96,000 and 145,000 and share of large farms (more than 300 animals) was about 53 and 67% respectively in 2010 (Statistics of Estonia). There are no exact figures, but it is assumed that 50% of dairy cattle have slurry type manure management and this number is increasing every year. Annually about 0.5 million tons of cattle slurry and 1.2 million tons of cattle dung (non-dairy cattle and 50% of dairy cattle) in large farms are produced. Anaerobic digestion of manure is common technology in many countries, where biogas is produced and converted to electrical and thermal energy or upgraded to vehicle fuel. Several samples of cattle slurry from Estonia was analysed by Luna del Risco et al. (2011), biochemical methane potential (BMP) was 238 l (kg VS_{added})$^{-1}$. Annual methane potential of cattle slurry alone in large farms is around 7.3 million m^3, by rough calculation the renewable energy potential is 100 TJ of electricity and 130 TJ of thermal energy. However, today there is no biogas plant in Estonia treating cattly slurry, only one biogas plant processes pig slurry from eight farms in Saare County. In 2010 it produced 0.85 million m^3 of biogas and generated 5.2 TJ of electricity and 7.8 TJ of thermal energy (Overview of Estonian bioenergy market). For the whole country the theoretical annual electricity generation from animal manures could be 684 TJ and thermal energy 706 TJ (Kask et al., 2008). So, only 1% of this potential was utilized in 2010.

Anaerobic digestion is complex biochemical process where biogas is produced by degradation of organic matter in an oxygen-free environment. The process is natural

but in industrial plants it is difficult to manage because of limitations of monitoring and control applications and lack of knowledge (Steyer et al., 2006). Control systems with real time measurements and process models, such as Anaerobic Digestion Model No.1 (ADM1) should be used to achieve optimized biogas production (Ward et al., 2008). ADM1 was developed by the International Water Association (IWA) task group to support development of anaerobic technology, that is sustainable way for waste treatment and energy generation (Batstone et al., 2002b). ADM1 is implemented in several modelling packages, the most used are Aqusim 2.1 and Matlab (Batstone et al., 2006).

Modelling of agricultural biogas production processes with ADM1 is not numerous and according to our knowledge the cattle slurry as substrate has been used only by Lübken et al. (2007).

To utilize the renewable energy potential of cattle slurry in Estonia the development of modern anaerobic digestion control systems with modelling capabilities is necessary. The aim of the study was to define the usability of ADM1 in local conditions and specify the set of model parameters for simulation of anaerobic digestion of cattle slurry.

Materials and methods

Experimental set–up

Experiment was carried out during 42 days in biogas pilot's lab of Estonian University of Life Sciences. Cattle slurry from local farm was used as substrate. It was transported in 25 l canisters to laboratory and kept in pre-storage tank (600 l) at 10°C temperature to avoid active degradation processes before loading into anaerobic reactor.

Continuous stirred tank reactor (CSTR) (stainless steel, 200 l, 500 mm in diameter) was used, equipped with mechanical mixer, feeding pump and monitoring and control systems, including programmable logic controller (PLC) and SCADA system. Mixing was applied for 20 sec within every 2 minutes (30 rpm) to get stable biogas flow from the reactor. Temperature of the reactor was set to 38 °C. Loading of substrate was done once an hour. General experiment scheme is given on Fig. 1. Essential process parameters (gas flow, methane content in gas, digestate outflow, temperature, pH, etc) were measured online.

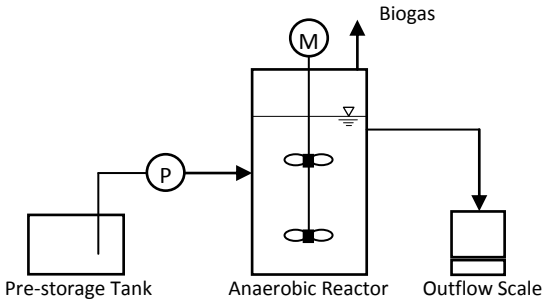

Fig. 1. Pilot reactor set-up. Main equipment: pre-storage tank, anaerobic reactor dosing pump (P), mixer (M), and outflow scale for digestate canister.

Biogas production was measured by drum-type gas meter RITTER TG5 (1–60 l h^{-1}, accuracy ± 0.5% of reading) and methane content by infrared sensor Bluesens BCT–50–100 (0–100 Vol. %, accuracy ± 3% of reading). pH in the reactor was measured online by Honeywell Durafet–III sensor. Temperature in reactor was measured by RTD sensors PT–100 at two different points, temperature control was applied by average of two measurements. Gas production was calculated for standard conditions 273.15 K, 101.325 kPa.

Chemical analyses

Substrate and digestate (at the end of experiment) were analysed for pH, total solids (TS), volatile solids (VS), total nitrogen (TN), neutral detergent fibre (NDF), acid detergent fibre (ADF), lignin, calcium (Ca), phosphorus (P), magnesium (Mg) and potassium (K), see Table 1.

Table 1. Chemical composition of substrate and digestate

Parameter	Unit	Cattle slurry	Digestate
TS	%	6.4	4.70
VS	%TS	80.60	69.9
pH		7.06	7.88
NH_4–N	mg l^{-1}	2,495.2	2,690.7
TKN	%	0.427	0.401
RL	%TS	3.29	1.14
NDF	%TS	41.93	36.87
ADF	%TS	28.98	32.06
ADL	%TS	15.04	19.67
Hemicellulose	%TS	12.94	ND
Cellulose	%TS	14.27	12.40
P	%	0.080	0.080
K	%	0.230	0.247
Ca	%	0.136	0.146
Mg	%	0.065	0.063
Acetic acid	mg l^{-1}	5,218	172
Propionic acid	mg l^{-1}	1,576	ND
Isobutyric acid	mg l^{-1}	169	ND
Butyric acid	mg l^{-1}	620	ND
Isovaleric acid	mg l^{-1}	208	ND
Valeric acid	mg l^{-1}	141	ND

ND – not detected

Total solids (TS) and volatile solids (VS) were analyzed according to method 1684 (U.S. Environmental Protection Agency). TS were determined after drying the sample at 105°C and VS after ignition at 550°C (total solids minus the ash content). pH of liquid samples was measured by a Sartorius pH–meter. TN was determined by copper catalyst Kjeldahl method using a Kjekltec Auto 1030. NDF and ADF were determined using a Foss Tecator Fibertec 1020. Cellulose, hemicellulose and lignin content in samples were calculated as proposed by Van Soest et al. (1991). Calcium

(o–Cresolphthaleincomplexone method; Connerty & Briggs, 1966), phosphorus (Stannous chloride method, ISO/FDIS 15681 method, ISO 3696), and magnesium (Titan Yellow method; Heaton, 1960) were determined using a Fiastar 5000.

Samples for VFA determination were collected daily and determined after centrifugation at 11,000 rpm for 20 min. Then filtered and acidified with 17% H_3PO_4 (150 µl to one ml of sample) and centrifuged again. Analyses were performed using GC 2014 ATF/SPL (Shimadzu), Zebron ZB–WAXplus capillary column (35 m, ID: 0.25 mm, film thickness: 0.25 µm) and flame ionization (FID) detector. Helium was used as carrier gas, with injection temperature 250°C, gas flow 1.69 ml min^{-1}, detector temperature 350°C. The temperature program used was 100°C for 3 min, to 200°C at rate of 7°C min^{-1}, to 260°C at 80°C min^{-1}.

Mathematical model

Matlab application of ADM1 adapted by Rosen & Jeppson (2006) was used. Calculations were made using Matlab and Simulink software. Most of the used parameters for ADM1 were default values (Batstone et al., 2002a), input parameters describing substrate are presented in Table 2.

Table 2. ADM1 model input parameters describing substrate

Parameter	Description	Unit	Value
S_{va}	total valerate (including isovalerate)	g l^{-1} COD	0.548[a]
S_{bu}	total butyrate (including isobutyrate)	g l^{-1} COD	1,148[a]
S_{pro}	total propionate	g l^{-1} COD	2,045[a]
S_{ac}	total acetate	g l^{-1} COD	5,566[a]
X_{xc}	dead bacteria	g l^{-1} COD	0.50[b]
X_{ch}	insoluble hydrocarbons	g l^{-1} COD	13.94[a]
X_{pr}	insoluble proteins	g l^{-1} COD	18.11[a]
X_{li}	insoluble lipids	g l^{-1} COD	7.49[a]
S_{in}	total ammonia nitrogen	mol l^{-1}	0.18[a]
X_{su}	bacteria consuming sugars	g l^{-1} COD	0.60[c]
X_{aa}	bacteria consuming aminoacids	g l^{-1} COD	0.60[c]
X_{fa}	bacteria consuming fatty acids	g l^{-1} COD	0.60[c]
X_{c4}	bacteria consuming valerate and butyrate	g l^{-1} COD	0.60[c]
X_{pro}	bacteria consuming propionate	g l^{-1} COD	0.60[c]
X_{ac}	bacteria consuming acetate	g l^{-1} COD	0.018[d]
X_{h2}	bacteria consuming hydrogen	g l^{-1} COD	0.018[d]
S_{cat}	inorganic cations (by charge)	mol l^{-1}	0.040[e]
S_{an}	inorganic anions (by charge)	mol l^{-1}	0.075[e]

[a] Calculated by substrate chemical composition measured.
[b] Calculated by assumptions of bacterial cell count in reactor by Lübken et al (2007).
[c] Calculated assuming that acidogenic bacteria found by Lübken et al (2007) are equally divided between 5 groups.
[d] Calculated assuming that methanogenic bacteria found by Lübken et al (2007) are equally divided between 2 groups.
[e] Determined back from the model.

In ADM1 the input substrate is described through 28 variables. These are concentrations of 12 dissolved and 12 particulate substances, concentration of cations and anions, liquid flow speed and temperature. Three additional parameters are needed to describe the state of the reactor. These are concentrations of H_2, CH_4 and CO_2 in headspace (Batstone et al., 2002a, 2002b).

Concentrations of VFA, insoluble proteins and lipids, and total ammonia nitrogen were taken directly from chemical composition of the substrate. Insoluble hydrocarbons were calculated by content of hemicellulose and cellulose. Hemicellulose was assumed to degrade completely but cellulose degradability was 36%, estimated by differences of cellulose concentration in substrate and digestate. Insoluble proteins were calculated by organic nitrogen (total nitrogen – inorganic ammonium nitrogen), ratio of insoluble proteins COD to nitrogen was 1/0.007 (Rosen & Jeppson, 2006).

Also several ADM1 model default parameters (Batstone et al., 2002a) were changed according to Lübken et al. (2007), as their study was performed with cattle slurry. Overview of default and changed values is presented in Table 3.

Table 3. ADM1 model parameter values changed according to Lübken et al. (2007).

Parameter	Description	Unit	ADM1 default	Changed value
$K_{hyd,ch}$	carbohydrate hydrolysis rate	1 d^{-1}	10.0	0.31
$K_{hyd,pr}$	protein hydrolysis rate	1 d^{-1}	10.0	0.31
$K_{hyd,li}$	lipid hydrolysis rate	1 d^{-1}	10.0	0.31
$pH_{UL,acid}$	upper pH limit for acidogens		5.5	8.0
$pH_{LL,acid}$	lower pH limit for acidogens		4.0	6.0
K_{m_c4}	maximum uptake rate of valerate and butyrate	1 d^{-1}	20.0	13.7
K_{S_c4}	half saturation concentration of valerate and butyrate uptake	g l^{-1} COD	0.2	0.357
K_{m_pro}	maximum uptake rate of propionate	1 d^{-1}	13.0	5.5
K_{S_pro}	half saturation concentration of propionate uptake	g l^{-1} COD	0.1	0.392
$K_{m\ ac}$	maximum uptake rate of acetate	1 d^{-1}	8.0	7.1
K_{S_h2}	half saturation concentration of hydrogen uptake	g l^{-1} COD	$7 \cdot 10^{-6}$	$3 \cdot 10^{-5}$

Results and discussion

Experiment was planned in two main steps: stable loading in first period for 30 days and the increase of loading for 12 days. But because of loading failure for 30 hours, the experiment was conducted finally in four steps as shown in Fig. 2.

The first stable period had average organic loading rate 1.3 kg VS $(m^3\ d)^{-1}$, and was then increased to 2.0 kg VS $(m^3\ d)^{-1}$. Average methane yield was 256 l $(kg\ VS_{added})^{-1}$ in first period and increased up to 291 l $(kg\ VS_{added})^{-1}$ (273.15 K, 101.325 kPa), being higher compared to BMP results (238 ± 42 l $(kg\ VS_{added})^{-1}$) published by Luna del Risco et al. (2011).

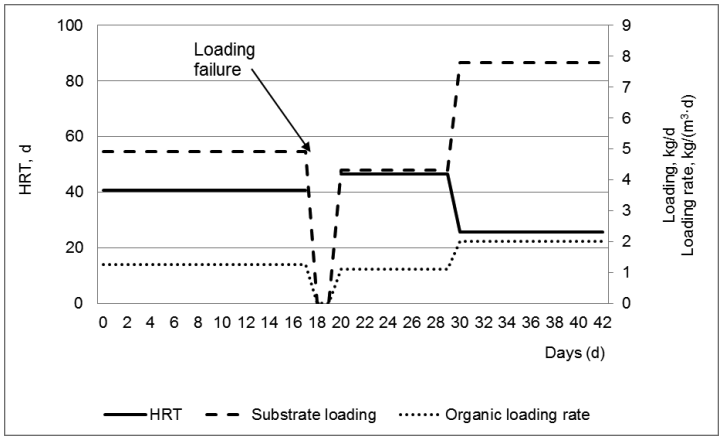

Fig. 2. Substrate and organic loading rate and hydraulic retention time (HRT) during the experiment.

Results of simulation are presented on Fig. 3 – biogas flow rate, methane content in biogas, reactor pH and acetate concentration. The simulation results of biogas production were close to measurements. There is one miscalculation of biogas flow after loading failure, probably caused by incorrect substrate loading measurements and therefore too low loading rate applied to the model.

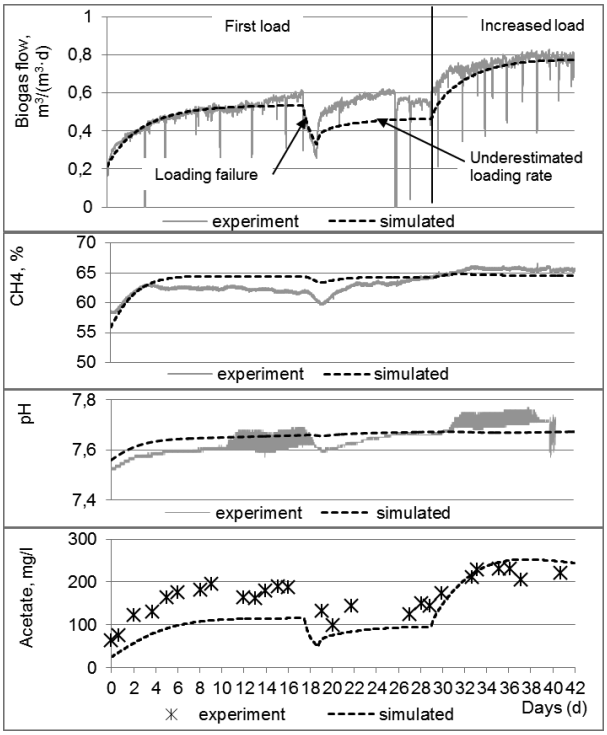

Fig. 3. Experimental and simulation results of chosen parameters.

Several default parameters of ADM1 were changed to simulate anaerobic digestion of cattle manure (Table 2 & 3). Additionally, the ammonia inhibition constant was optimized during this study to improve modelling results compared to measurements of acetate concentration. ADM1 default value was 0.0018 mol l^{-1} (Batstone et al., 2002a), but it overestimated inhibition effect and lead to acetate accumulation that was not observed in the experiment.

Chen et al. (2008) gave review of inhibitors of anaerobic digestion and concluded that bacteria are able to acclimate to higher concentrations of ammonia. It has been proposed that acetate accumulation in simulation could be solved with increased ammonia inhibition constant (Parker, 2005; Batstone et al., 2006).

We increased the value of ammonia inhibition constant (K_{inh3}) from 0.0018 to 0.006 mmol l^{-1}. After this we obtained good correlation between experimental and simulation results. Simulation results of pH and methane concentration were slightly higher than measurements in the beginning of experiment, but later this difference disappears. We assume that it is related to acclimatization of bacteria with high ammonia concentration in reactor (NH_4–N in reactor 2.7 g l^{-1}). Measurement of pH was fluctuating during some shorter periods, this problem was solved with sensor cleaning and recalibration.

Compared to other authors our ADM1calibration gave different results for free ammonia inhibition constant for acetate uptake. Agricultural wastes including pig slurry were studied by Gali et al. (2009), and they came to conclusion that the model gave correct simulation results for degradation of agro-wastes (NH_4–N concentration in reactor was 2.7 g l^{-1}). Cattle slurry anaerobic digestion with co–substrates was studied by Lübken et al. (2007), where a good agreement between simulation results and measurements was achieved and they did not report any changes of inhibition constant (NH_4–N in reactor 3.1 g l^{-1}). Koch et al. (2010) studied anaerobic digestion of grass silage. They found that higher ammonia inhibition constant gives better measurement reproducibility in simulation.

Conclusions

A pilot-scale continuous flow reactor for anaerobic digestion of cattle slurry was successfully put into operation. Cattle slurry from local farm had high methane yield, maximum value was 291 l (kg VS_{added})$^{-1}$ at organic loading rate 2.0 kg VS (m^3 d)$^{-1}$.

The ADM1 model was used to simulate the biogas flow rate, methane content in biogas, reactor pH and acetic acid concentration during the process. Several changes were made to model parameters to adjust it for cattle slurry fermentation. Good agreement between simulated and measured biogas flow was achieved. Simulation of pH and methane concentration had different tendency than measurements and slight underestimation of acetate concentration at the beginning of experiment was seen. We assume that it is related to bacteria acclimatisation with high ammonia concentration in reactor during the experiment. Additional research is needed to define inhibition levels related to culture adaptation to higher ammonia concentration.

ACNOWLEDGEMENTS. This research was co-financed by European Union, European Regional Development Fund in Estonian Energy Technology Research and Development project 3.02.0501.10–0020.

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