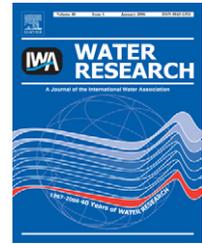


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Modelling the energy balance of an anaerobic digester fed with cattle manure and renewable energy crops

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ABSTRACT

Knowledge of the net energy production of anaerobic fermenters is important for reliable modelling of the efficiency of anaerobic digestion processes. By using the Anaerobic Digestion Model No. 1 (ADM1) the simulation of biogas production and composition is possible. This paper shows the application and modification of ADM1 to simulate energy production of the digestion of cattle manure and renewable energy crops. The paper additionally presents an energy balance model, which enables the dynamic calculation of the net energy production. The model was applied to a pilot-scale biogas reactor. It was found in a simulation study that a continuous feeding and splitting of the reactor feed into smaller heaps do not generally have a positive effect on the net energy yield. The simulation study showed that the ratio of co-substrate to liquid manure in the inflow determines the net energy production when the inflow load is split into smaller heaps. Mathematical equations are presented to calculate the increase of biogas and methane yield for the digestion of liquid manure and lipids for different feeding intervals. Calculations of different kinds of energy losses for the pilot-scale digester showed high dynamic variations, demonstrating the significance of using a dynamic energy balance model.

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1. Introduction

Over the last few years, mathematical modelling has become very popular as a supporting tool for the design, operation and control of activated sludge systems. Particularly, the publication of the Activated Sludge Model (ASM) series can be accounted for this development (Henze et al., 2000). As it is supposed that there will be an increased application of the anaerobic treatment technology in the future, the demand for a qualified model will increase in the same way. The development of anaerobic digestion models was affected,

similar to the development of the ASMs, by the progressive identification of the underlying biological conversion processes. To date, many existing anaerobic digestion models have been developed for specific applications or fermenters fed with a very specific substrate. Batstone (2000) used the information of the research work carried out before and developed a model for complex wastewaters and produced a broad set of parameters for different substrates. To extend the use of mathematical models in anaerobic digestion, it is necessary to have a model that is applicable for both different reactor types and various substrates.

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The International Water Association (IWA) task group for mathematical modelling of anaerobic digestion processes was formed in 1997 to develop a generally applicable model, the Anaerobic Digestion Model No. 1 (ADM1, [Batstone et al., 2002](#)). ADM1 is a structured model with disintegration and hydrolysis, acidogenesis, acetogenesis and methanogenesis steps. ADM1 is expected to stimulate model application for full-scale plant design, operation and optimization or generally to support an increased application of anaerobic technology in the future.

As anaerobic digestion (AD) is a complex process carried out by a consortium of highly different microorganisms ([Gujer and Zehnder, 1983](#)), a mathematical model able to describe the main single pathways and to predict biogas production will be inevitably complex. At a low degree of model complexity only the two main steps of AD, acidogenesis and methanogenesis, will be considered. Disintegration and hydrolysis steps, main process pathways of carbohydrates, proteins and lipids conversion and different forms of inhibition must be considered for a higher degree of model complexity. This is achieved by the IWA ADM1 model, though the model still has some simplifications.

Hydrogen produced by Volatile fatty acid (VFA) degradation can be transferred to sulphate reducing, homoacetogenic or methanogenic bacteria, depending on the availability of such bacteria and their respective electron acceptors ([Schink, 1997](#)). This example clarifies that the process pathways implemented in ADM1 are a simplification of reality. [Kleerebezem and van Loosdrecht \(2006\)](#) criticized that ADM1 contains no restrictions for thermodynamic boundaries encountered in methanogenic environments. [Hoh and Cord Ruwisch \(1996\)](#) e.g., proposed a model to describe hydrogen inhibition of acetogenesis by including thermodynamic limits. However, the results of [Batstone et al. \(2006\)](#) using ADM1 simulation at a microbial resolution, implemented in a multidimensional domain, suggest that thermodynamic inhibition compared with non-competitive inhibition only has an impact at smaller substrate field grid sizes.

AD produces products such as renewable energy, as well as a fertilizer rich in nutrients and organic soil conditioners. In Germany, about 4000 plants are currently operated for biogas generation out of agricultural substrates. New potentials for agricultural biogas technology can be expected due to the amendment of the statute for renewable energies 2004 (Erneuerbare Energien Gesetz; EEG). Usage of renewable energy sources like cultivated crops will certainly increase agricultural biogas plants in Germany. Liquid manure from livestock husbandry is used as a base substrate in most of the plants to produce a wet, pumpable mixture since dry fermentation concepts are still in testing. As the need for alternative sources of energy continues to rise, the role of AD in the treatment of organics from agricultural waste will be further increased. If a mathematical model is used to investigate an agricultural biogas reactor, the model has to be particularly able to predict the net energy yield of the plant, considering high variation of input material and its chemical, and physical characteristics as well as biodegradability.

ADM1 can be used to simulate the biogas production and thus the energy yield of fermenters digesting different kinds

of substrates. However, one part of the energy produced is consumed by the digester itself. The process energy is needed to heat the fed substrate and to compensate for the irradiation loss of the digester. Stirrers together with pumps are additional energy consumers. Therefore, a dynamic energy balance model was derived in this study to allow the dynamic calculation of the net energy production of anaerobic bioreactors.

The importance of knowing the actual energy within anaerobic systems has recently been described by [Lindorfer et al. \(2005\)](#). In some cases, the authors reported that using energy crops in monofermentation can lead to a self-heating of the digester. Several full-scale biogas plants were cooled down in order to avoid instabilities. The authors also showed that self-heating can be explained by the microbial activity of anaerobic microorganisms. We therefore used the derived energy balance model to evaluate the self-heating potential of anaerobic reactors.

2. Material and methods

2.1. Analytical methods

Analytical methods for total solids (TS), volatile solids (VS), chemical oxygen demand (COD) and ammonia nitrogen ($\text{NH}_4\text{-N}$) were based on German Standard Methods for the examination of water, wastewater and sludge. VFAs were measured using an AGILENT 6890N gas chromatograph. Column: HP FFAP, 25 m, 0.32 mm. The temperature programme was as follows: initial temperature 80 °C (holding time: 1 min), 120 °C in 20 °C min⁻¹ (holding time: 3 min), 220 °C in 6.13 °C min⁻¹ (holding time: 20.13 min).

Determination methods according to [van Soest and Wine \(1967\)](#) and [Weender](#) (described in [Naumann and Bassler, 1993](#)) were performed to characterize the substrate in terms of carbohydrates, proteins and fats. The methods applied resulted in a fractionation of the organic matter between crude protein, crude fat, crude fibre and N-free extract (Weender analysis). Carbohydrates were further divided into hemicellulose (neutral detergent fibre (NDF)–acid detergent fibre (ADF)), cellulose (ADF–acid detergent lignin (ADL)) and lignin (ADL), approximately analysed by the so-called van Soest-fractions NDF, ADF and ADL.

Total biogas production was measured by the RITTER drum chamber gas meter TG5/5. Values for biogas production were normalized. Methane and carbon dioxide were quantified by means of the infrared two-beam compensation method with pressure compensation (measuring error as specified: $\pm 2\%$). Oxygen and hydrogen were measured by electrochemical sensors (measuring error as specified: $\pm 3\%$).

Experimental data were available for a period of 180 days. Biogas production, distribution of the major biogas compounds (CH_4 , CO_2 and H_2), temperature and pH values were measured continuously over the whole period. TS, VS, COD and $\text{NH}_4\text{-N}$ were measured semi-continuously for both influent and effluent. Data for VFA production (acetate, propionate, butyrate and valerate) were available for the first 65 days of the entire period.

In situ hybridization was performed according to the method of Wagner et al. (1995). Samples were fixed with paraformaldehyde (PFA; 4%, w/v) for 2–3 h at 4 °C. For cell counting, 10–20 microscopic fields were randomly selected and 1000–2000 cells were counted for each probe as described by Glöckner et al. (1999). Cell counting was done using a Zeiss Axioplan2 microscope equipped with an appropriate filter set and a 100× Plan Apochromat oil objective lens (Carl Zeiss, Jena, Germany) and a HBO 100 W Hg vapour lamp. The abundance and distribution of *Archaea* populations were investigated by using specific oligonucleotide probes complementary to the SSU rRNAs of the two domains *Archaea* (Arch915) and *Bacteria* (EUB338 (I+II+III)).

2.2. Anaerobic reactors

The simulation study was carried out based on data of a pilot-scale bioreactor. Data of a lab reactor were additionally used to characterize the digestion of rape-oil as an energy-rich co-substrate. All simulation results shown in the following, however, refer to the pilot-scale reactor.

2.2.1. Pilot-scale biogas reactor

The pilot-scale biogas reactor used for the simulation study was a 3.5 m³ digester run at mesophilic conditions at 38 °C. Within the reactor, liquid manure was digested together with total mixed ration (TMR—fodder for cows). The liquid volume varied between 2.5 and 3.0 m³. The hydraulic retention time (HRT) was 20 d. The mixer stirred the contents every half hour for 10 min with an outer wing velocity of 0.34 m s⁻¹. The digester was fed 6 days a week with a 175 kg mix of liquid manure and TMR. Table 1 shows substrate characteristics of the input materials manure and TMR and the resulting effluent.

The average inflow VS load was 3.2 kg m⁻³ d⁻¹. During the period investigated, an average VS reduction of 28% could be achieved. Average biogas production was about 3.58 m³ d⁻¹,

and it varied from a minimum of 1.97 m³ d⁻¹ to a maximum of 5.72 m³ d⁻¹.

The data used in this study are typical for the performance of a pilot-scale digester operated with liquid manure as base substrate. The co-substrate TMR was composed of 43% corn silage, 18% gramineous silage, 12% crop groats, 9% water, 7% soy pellets, 7% cow grain and 4% hay. The mix ratio of manure and TMR referred to VS was 80:20.

2.2.2. Anaerobic flow-through lab reactor

The lab reactor consisted of a double-walled cylindrical vessel with an inner diameter of 250 mm and an inner height of 750 mm. This resulted in a maximum capacity of about 36 L. The temperature was kept constant by a water bath between the two walls. Rape-oil was digested within the reactor at 38 °C together with liquid manure (ratio rape-oil to liquid manure: 2% v/v). The rape-oil had a COD concentration of 2415 g kg⁻¹ with a lipid content of 98.6%.

Digestion of rape-oil led to a biogas yield of 1053 L kg VS⁻¹ with a methane content of 70.7% (values for liquid manure have been subtracted). The rape-oil used as co-substrate in lab experiments proved to be energy rich leading to both high biogas yield and high methane content.

3. Anaerobic Digestion Model No. 1 (ADM1) and energy model

Simulation was done with the SIMBA software in its version 4.0 (ifak, 2000) running under the MATLAB/SIMULINK simulation environment.

3.1. Setup of the kinetic model ADM1

Difficulties in using ADM1 for inhomogeneous substrates like liquid manure may be identified in the measurement of COD used in the model as a balance term and in the necessity for a detailed inflow characterization. For cattle manure and energy crops, we propose to replace the COD by measurement of VS and to use Weender analysis with the van Soest method to characterize the substrate.

COD is commonly used to characterize organic compounds in wastewater. As this parameter enables a closed mass balance in mathematical models, COD is the predominant parameter for most of the models describing wastewater treatment processes. For digestion of liquid manure, however, organic matter is predominantly described in terms of VS. The high organic content and inhomogeneous structure of liquid manure argue for the measurement of VS instead of COD. Therefore, a correlation between COD and VS has to be formulated by measurement.

During the start-up phase, the reactor was filled with water and nitrogen to avoid oxygen within the headspace. The reactor was then loaded with a mix of 150 kg cattle manure and TMR each day. This enabled us to obtain a dataset of COD and VS of steadily increasing values (Fig. 1).

Fig. 1 represents the development of TS, VS and COD during the start-up phase. VS and by it TS steadily increased over the first 50 days. The continuously increasing difference between both parameters is a consequence of the proceeding

Table 1 – Mean substrate characteristics for manure, total mixed ration (TMR) and effluent

Parameter	Manure	TMR	Effluent
TS (%)	6.7	47.7	5.9
VS (% TS)	79.9	93.3	77.6
COD (g kg ⁻¹)	74.5	574	66.8
VFA _{total} (mg L ⁻¹)	7182	1608	2030
pH (–)	7.4	4.8	7.8
NH ₄ -N (mg L ⁻¹)	3090	4574	3105
RP (raw protein) (% TS)	16.9	16.7	17.7
RF (raw fibre) (% TS)	17.5	18.6	18.3
RL (raw lipid) (% TS)	5.3	2.1	2.9
NfE (% TS)	40.2	55.9	38.7
NDF (% TS)	44.2	51	43.2
ADF (% TS)	33.1	24.5	34
ADL (% TS)	14.9	4.9	16.6

Explanations of abbreviations for tested parameters are given in Section 2.

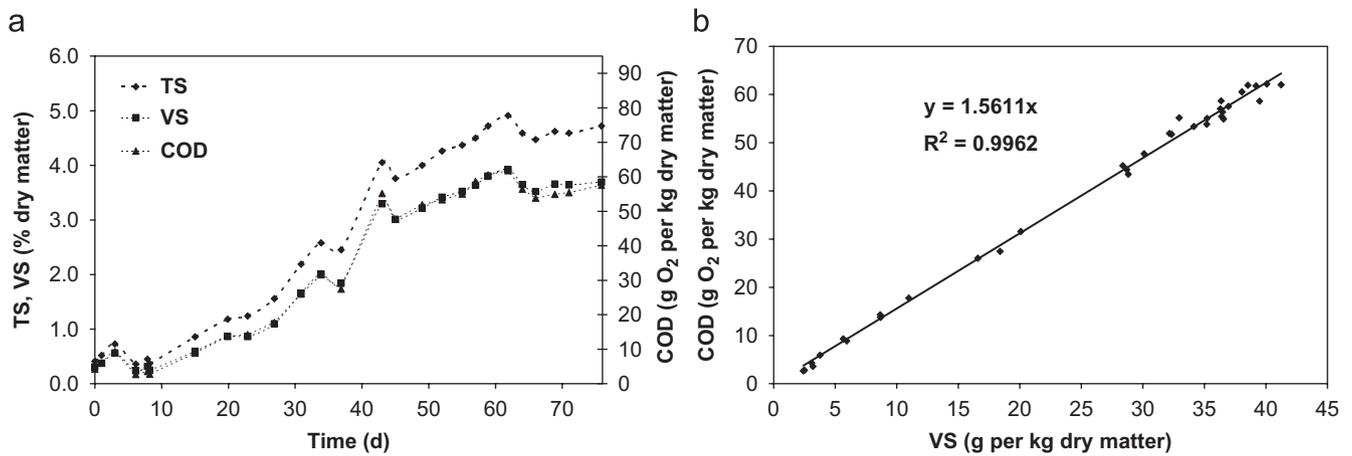


Fig. 1 – (a) Course of TS, VS and COD during start-up phase and (b) correlation between COD and VS.

Table 2 – Parameters used for describing initial state variables of ADM1

Parameter	Value	Source	
$i_{\text{COD/VS}}$	COD equivalent of VS	1.5611 gCOD gVS ⁻¹	This study (Fig. 1)
N_{cells}	Total number of cells per unit volume	1.47×10^{10} cells ml ⁻¹	This study (FISH analysis)
f_{bac}	Proportion of bacteria to total cells	85%	This study (FISH analysis)
$f_{\text{methanogens}}$	Proportion of methanogens to total cells	1%	This study (FISH analysis)
m_{cell}	Weight of one bacterial cell	14×10^{-11} mg cell ⁻¹	Von Münch and Pollard (1997)
$i_{\text{COD/Xbac}}$	COD equivalent of biomass	1.416 gCOD gbiomass ⁻¹	Von Münch and Pollard (1997)

mineralization process. In later progress, the difference was kept relatively constant due to the daily discharge before loading. As mentioned above, a qualitative congruent course of COD and VS was detected. Fig. 1 shows that a close correlation between both parameters exists. Therefore, only one parameter needs to be measured.

Compared with other AD models, ADM1 considered the disintegration process. Disintegration describes the degradation of composite particulate material with lumped characteristics, such as activated sludge. Within the model, composites are converted to inerts, particulate carbohydrates, proteins and lipids. The characterization of the substrate in terms of carbohydrates, proteins and lipids is essential as it determines the biogas composition. In this study, the ADM1 model component for composites was not used as an inflow fraction. Substrate composition in terms of carbohydrates, proteins and lipids was instead defined within the input stream. Inflow fractionation, which meets the complexity of the model, was done as follows (all parameters used are listed in Tables 1 and 2):

- Determination of ADM1 inflow content of proteins:

$$X_{\text{pr}} = Q_{\text{in}} \text{RP TS } i_{\text{COD/VS}} \quad (\text{kgCOD d}^{-1}), \quad (1)$$

where $i_{\text{COD/VS}}$ is the COD equivalent of VS according to Fig. 1. The unit for the inflow load Q_{in} is kg d^{-1} , for TS is %, for RP is %TS and for $i_{\text{COD/VS}}$ is kgCOD kgVS^{-1} . Based on Eq. (1) and the parameters listed in Table 1, the protein content of 1 kg of liquid manure used was calculated to 0.018 kgCOD. Eq. (1) implies that the COD equivalent of VS

is also valid for raw proteins. This is a necessary approximation due to the complex nature of the organic content of the substrate used. The following Eqs. (2), (3) and (4) are based on the same considerations.

- Determination of ADM1 inflow content of lipids:

$$X_{\text{li}} = Q_{\text{in}} \text{RL TS } i_{\text{COD/VS}} \quad (\text{kgCOD d}^{-1}). \quad (2)$$

- Determination of ADM1 inflow content of carbohydrates:

$$X_{\text{ch}} = Q_{\text{in}} [\text{RF} + \text{Nfe} - \text{ADL} - (\text{ADF} - \text{ADL})_{\text{not degradable}}] \\ \times \text{TS } i_{\text{COD/VS}} \quad (\text{kgCOD d}^{-1}), \quad (3)$$

where the sum of RF and Nfe represents the total carbohydrate content, ADL the lignin content, which was assumed as not degradable and the difference between ADF and ADL is the cellulose content. The part of the cellulose, which was not degradable in the digester presented, was calculated upon mass balances between input and output. During 20 days HRT, 28% of the input cellulose was degraded. Fuchigami et al. (1989) report for rumen simulation systems a cellulose degradation of 61% for days 1–4 and a further 50% for the rest of the experiment (up to 26 days) using a continuous reactor. Digestion near 100% could be assumed for the study carried out by Gijzen et al. (1988). The present degradation of 28% within this study is reasonable as cattle manure has already been subjected to a degradation process and therefore is likely to contain a greater proportion of slowly degradable material.

- Determination of ADM1 inflow content of particular inerts:

$$X_i = Q_{in}[ADL + (ADF - ADL)_{not\ degradable}] \times TS\ i_{COD/VS} \quad (\text{kgCOD d}^{-1}) \quad (4)$$

Particular inerts are mainly determined by the lignin content. Degradation of lignin was not observed in this study as it is an extremely slow process.

- Determination of ADM1 inflow content of biomass:

$$X_{bacteria} = Q_{in}N_{cells}f_{bac}m_{cell}\ i_{COD/Xbac} \cdot 10^{-3} \quad (\text{kgCOD d}^{-1}), \quad (5)$$

$$X_{methanogens} = Q_{in}N_{cells}f_{methanogens} m_{cell}i_{COD/Xbac} \cdot 10^{-3} \quad (\text{kgCOD d}^{-1}), \quad (6)$$

where $X_{bacteria}$ comprises the biomass used in ADM1 for uptake of sugars (X_{su}), amino acids (X_{aa}), fatty acids (X_{fa}), valerate and butyrate (X_{C4}) and propionate (X_{pro}). $X_{methanogens}$ comprises the biomass used in ADM1 for the uptake of acetate (X_{ac}) and hydrogen (X_{H_2}). All of the variables are defined in Table 2. According to Eq. (5), anaerobic bacteria in the fed liquid manure was calculated to 4.2% of TCOD.

Using Eq. (6), the content of methanogens was calculated to 0.05% of TCOD, which proved negligible for simulation results.

Von Münch et al. (1999) estimated for primary sludge an anaerobic biomass in the feed of 13% of TCOD and that the proportion of acidogens/acetogens and methanogens was equal to 90% and 10%, respectively. Values in this study for liquid manure and renewable energy crops, based on fluorescent in-situ hybridization analysis and Eqs. (5) and (6), are perspicuously lower.

For the undigested liquid manure, 85% of the total DAPI cell counts hybridized to the bacterial probe mixture EUB338 (I+II+III), and 1% hybridized to the archaeal probe Arch915 (Fig. 2).

During fermentation process, *Methanosarcina* cells appeared after 11 days and were the most abundant methanogenic population after 32 days. The *Methanosarcina* cells were identified as aggregates of up to a hundred cells, and the diameter ranged between 4 and 8 μm. In all, 12% of the total DAPI-cell-counts hybridized to the *Methanosarcina* probe

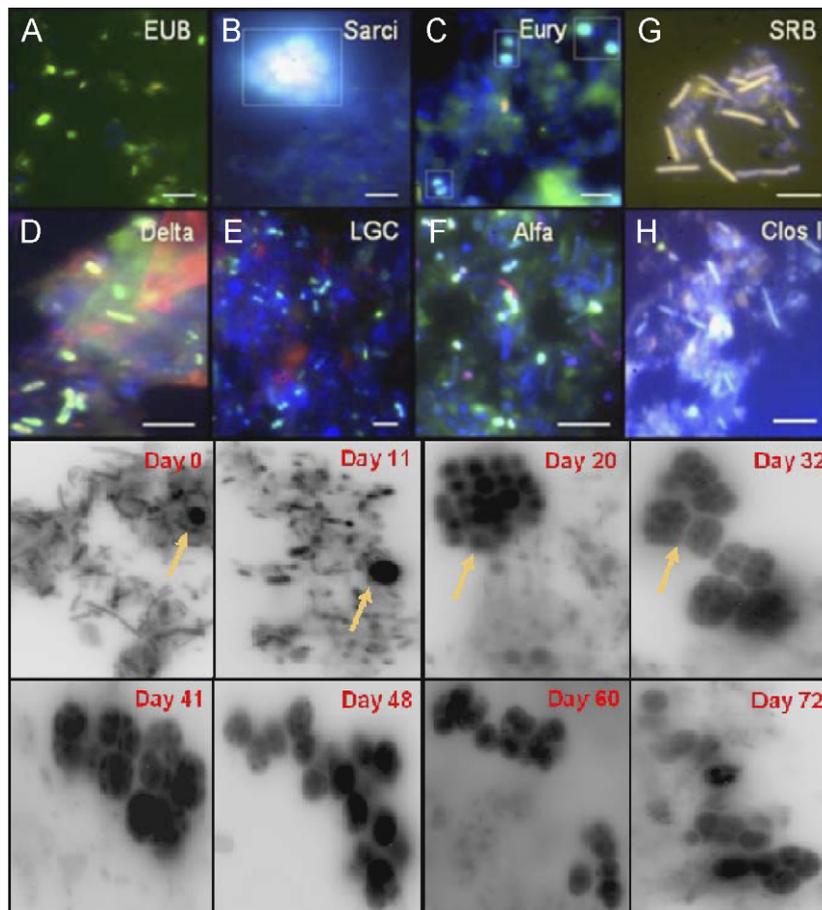


Fig. 2 – Upper part: epifluorescence microscopy view of dominant groups of microorganisms detected by specific fluorescence probes. Bars indicate 5 μm. Green for stained with Cy3-probes, red for stained with Cy5-probes and blue for counterstained with DAPI (for all microorganisms). Signals were for bacteria (A), methanosarcina (B), euryarchaea (C), delta-proteobacteria (D), LGC-bacteria (E), alfa-proteobacteria (F), sulphate-reducing bacteria (G) and Clostridium cluster I (H). Lower part: negative microscopic view of FISH analysis showing development of a *Methanosarcina* population during the fermentation process.

Sarci645. Other methanogenic populations such as *Methanosaeta* or *Methanobacterium* species, usually found in liquid manure digesting systems, were not detected during the complete fermentation process.

3.2. Setup of the energy model

For the pilot-scale digester a dynamic energy balance model was derived, which comprises the major forms of energy produced and consumed. Energy is mainly produced as biogas, and to a minor degree as microbial heat. Consumption of energy results mainly due to pumping, stirring, substrate heating and the compensation of radiation loss. The basic equation for the dynamic energy balance model is

$$\frac{dP_{\text{net}}}{dt} = (P_{\text{elect}}^{\text{prod}} - P_{\text{pump}}^{\text{loss}} - P_{\text{stir}}^{\text{loss}}) + (P_{\text{therm}}^{\text{prod}} - P_{\text{rad}}^{\text{loss}} - P_{\text{sub_heat}}^{\text{loss}} + P_{\text{mic_heat}}^{\text{prod}}) \quad (\text{kWh d}^{-1}), \quad (7)$$

where P_{net} is the net energy production of the digester (kWh d^{-1}), $P_{\text{elect}}^{\text{prod}}$ is the electrical energy production (kWh d^{-1}), $P_{\text{pump}}^{\text{loss}}$ is the mechanical power of the pump (kWh d^{-1}), $P_{\text{stir}}^{\text{loss}}$ is the mechanical power of the stirrer (kWh d^{-1}), $P_{\text{therm}}^{\text{prod}}$ is the thermal energy production (kWh d^{-1}), $P_{\text{rad}}^{\text{loss}}$ is the radiation loss (kWh d^{-1}), $P_{\text{sub_heat}}^{\text{loss}}$ is the heat requirement for substrate heating (kWh d^{-1}) and $P_{\text{mic_heat}}^{\text{prod}}$ is the microbial heat production (kWh d^{-1}). The single terms were calculated as follows:

$$P_{\text{elect}}^{\text{prod}} = Q_G P_{\text{CH}_4} H_C \eta_{\text{elect}} \quad (\text{kWhd}^{-1}), \quad (8)$$

$$P_{\text{therm}}^{\text{prod}} = Q_G P_{\text{CH}_4} H_C \eta_{\text{therm}} \quad (\text{kWhd}^{-1}), \quad (9)$$

where Q_G is the biogas production ($\text{m}^3 \text{d}^{-1}$), P_{CH_4} is the methane content (%), H_C is the calorific value of methane (kWh Nm^{-3}), η_{elect} is the electrical degree of efficiency (–) and η_{therm} is the thermal degree of efficiency (–). Biogas composition depends on substrate composition in terms of carbohydrates, proteins and fats. Methane can be further used to produce energy. By the combustion of biogas, energy is produced as both mechanical/electrical energy and thermal energy. Electrical energy is produced in a combined heat and power unit (CHP) with a mechanical/electrical degree of efficiency of approximately 35%. Thermal energy is produced with a thermal degree of efficiency of approximately 50%.

$$P_{\text{pump}}^{\text{loss}} = Q_{\text{in}} H \rho g t_p \frac{1}{\eta_{\text{ecc_worm}}} \quad (\text{kWh d}^{-1}), \quad (10)$$

where Q_{in} is the inflow rate (kg s^{-1}), H is the conveyor height (m), ρ is the density of the pumped media (kg m^{-3}), g is the acceleration of gravity (m s^{-2}), t_p is the time for pumping (h d^{-1}) and $\eta_{\text{ecc_worm}}$ is the degree of efficiency (–). Reactor loading was done within 15 min once a day. The degree of efficiency strongly depends on the type of pump used and can vary over a wide range. For the eccentric worm pump, used for the pilot-scale digester, η values between 0.3 and 0.7 can be applied.

$$P_{\text{stir}}^{\text{loss}} = V_{\text{liq}} S t_s \quad (\text{kWhd}^{-1}), \quad (11)$$

where V_{liq} is the liquid volume (m^3), S is the specific power of the stirrer (kW m^{-3}) and t_s is the time for stirring (h d^{-1}). A stirrer is needed to provide fresh substrate for the microorganisms. The required energy depends on reactor volume, reactor geometry and viscosity of the medium. Energy consumption

was referred to a specific power, which was 0.005 kW m^{-3} for the pilot-scale digester. Stirrers are generally not controlled, justifying a constant power input (Ifak, 2000). The stirrer of the investigated reactor was in use every half hour for 10 min.

$$P_{\text{rad}}^{\text{loss}} = K_{\text{heat_trans}} [(T_{\text{liq}} - T_{\text{ambient}}) V_{\text{liq}} + (T_{\text{gas}} - T_{\text{ambient}}) \times (V_{\text{tot}} - V_{\text{liq}})] \frac{2}{r} \frac{24}{1000} \quad (\text{kWhd}^{-1}), \quad (12)$$

where $K_{\text{heat_trans}}$ is the heat transfer coefficient ($\text{Wh m}^{-2} \text{h}^{-1} \text{K}^{-1}$), T_{liq} is the temperature of the substrate within the digester (K), T_{ambient} is the ambient temperature, V_{liq} is the liquid volume (m^3), T_{gas} is the gas temperature (K), V_{tot} is the total digester volume (m^3) and r is the radius of the digester (m). The term $2/r$ represents the surface to volume ratio of the cylindrical digester ($\text{m}^2 \text{m}^{-3}$). By multiplying the surface to volume ratio by the liquid volume (headspace), the corresponding surface was calculated. The investigation period used for simulation ranged from July 2004 to December 2004. The ambient temperature values were recorded as mean temperatures for each day, which varied between 25 and -10°C .

$$P_{\text{sub_heat}}^{\text{loss}} = Q_{\text{in}} c (T_{\text{digester}} - T_{\text{substrate}}) \frac{1}{3.6} \quad (\text{kWhd}^{-1}), \quad (13)$$

where Q_{in} is the reactor inflow ($\text{m}^3 \text{d}^{-1}$), c is the heat capacity of the substrate ($\text{kJ kg}^{-1} \text{K}^{-1}$), T_{digester} is the temperature of the digester (K) and $T_{\text{substrate}}$ is the temperature of the stored substrate (K). The substrate was stored outside. This resulted in a wide temperature range of the substrate during the whole simulation period. Generally, the substrate had approximately the same temperature as the air.

$$P_{\text{mic_heat}}^{\text{prod}} = \sum_{j=5-12} \Delta E_j f_j \rho_j V_{\text{liq}} \frac{1}{3.6} \quad (\text{kWhd}^{-1}), \quad (14)$$

where ΔE_j is the energy released to the environment due to microbial activity of process j (kJ mole^{-1}), f_j is the molar mass per gCOD of the educt of process j (mol gCOD^{-1}), ρ_j is the kinetic rate equation of process j of ADM1 ($\text{kgCOD m}^{-3} \text{d}^{-1}$) and V_{liq} is the liquid volume (m^3). ΔE values are listed in Table 3 and its derivation is described in the following.

Table 3 gives various thermodynamic parameters of selected anaerobic biochemical reactions. Glucose was chosen to be representative for monosaccharide and palmitate was chosen to be representative for long chain fatty acids. This is in agreement with ADM1. For simplification, in contrast to the biochemical reactions implemented in ADM1, the thermodynamics of amino acids in this study were calculated for glycine and alanine degradation in the Stickland reaction. Standard Gibbs free energies (ΔG^0) of the reactions were calculated from standard Gibbs free energies of formation (G_f^0) of reactants and products (Thauer et al., 1977). Considerable differences between ΔG^0 ($\text{pH} = 0$) and $\Delta G^{0'}$ ($\text{pH} = 7$) can be found in Table 3. Additionally, $\Delta G^{0'}$ was replaced by $\Delta G_T^{0'}$ that is corrected for 38°C , which was the operation temperature within the digester. Table 3 demonstrates that the available energy for microorganisms gained by fermentative degradation of organic material in anaerobic environments is very low. The synthesis of ATP as metabolic energy in living cells requires $+32 \text{ kJ mol}^{-1}$ at equilibrium under standard conditions; under the conditions assumed to prevail in an actively growing cell ($[\text{ATP}] = 10 \text{ mM}$, $[\text{ADP}] = 1 \text{ mM}$, $[\text{P}_i] = 10 \text{ mM}$), about $+50 \text{ kJ mol}^{-1}$ is required (Schink 1997). Therefore, the

Table 3 – Thermodynamics of biochemical reactions implemented in ADM1

Reaction	ΔH_f^0 (kJ M ⁻¹)	ΔG_f^0 (kJ M ⁻¹)	$\Delta G^{0'}$ (kJ M ⁻¹)	$\Delta G_T^{0'}$ (kJ M ⁻¹)	ATP (M ⁻¹)	ΔE (kJ M ⁻¹)
Glucose						
(i) C ₆ H ₁₂ O ₆ +2H ₂ O→2CH ₃ COO ⁻ +2H ⁺ +2CO ₂ +4H ₂	89.5	-136.0	-215.7	-225.53	4	-25.53
(ii) 3C ₆ H ₁₂ O ₆ →	-183.4	-231.5	-311.3	-313.35	4/3	-246.69
4CH ₃ CH ₂ COO ⁻ +2CH ₃ COO ⁻ +6H ⁺ +2CO ₂ +2H ₂ O						
(iii) C ₆ H ₁₂ O ₆ →CH ₃ CH ₂ CH ₂ COO ⁻ +H ⁺ +2CO ₂ +2H ₂	-47.5	-224.1	-264.0	-271.70	3	-121.70
Amino acids						
CH ₃ CH(NH ₃ ⁺)COO ⁻ +2CH ₂ (NH ₃ ⁺)COO ⁻ +2H ₂ O→	-4.0	-51.1	-51.1	-53.13	1/3	-36.46
3CH ₃ COO ⁻ +CO ₂ +3NH ₄ ⁺						
Palmitate						
CH ₃ (CH ₂) ₁₄ COO ⁻ +14H ₂ O→8CH ₃ COO ⁻ +7H ⁺ +14H ₂	966.2	670.2	391.1	378.22	14/6	494.88
Valerate						
CH ₃ CH ₂ CH ₂ CH ₂ COO ⁻ +2H ₂ O→	136.2	88.2	48.3	46.24	0.875	89.99
CH ₃ CH ₂ COO ⁻ +CH ₃ COO ⁻ +H ⁺ +2H ₂						
Butyrate						
CH ₃ CH ₂ CH ₂ COO ⁻ +2H ₂ O→2CH ₃ COO ⁻ +H ⁺ +2H ₂	137.0	88.2	48.3	46.17	0.75	83.67
Propionate						
CH ₃ CH ₂ COO ⁻ +2H ₂ O→CH ₃ COO ⁻ +CO ₂ +3H ₂	204.7	71.7	71.7	65.87	0.50	90.87
Acetate						
CH ₃ COO ⁻ +H ⁺ →CH ₄ +CO ₂	16.2	-75.7	-35.8	-39.84	0.25	-27.34
Hydrogen						
4H ₂ +CO ₂ →CH ₄ +2H ₂ O	-63.2	-32.7	-32.7	-31.36	1/4	-18.86

Values for the thermodynamic parameters refer to the molar mass of the educts chosen. The fraction of glucose that degrades via the first, second and third reaction is: (i) = 50%, (ii) = 35% and (iii) = 15%.

energy requirement for ATP formation was subtracted. The result is the energy ΔE in kJ released to the environment per mole of degraded educts. Different ΔE values transformed to a COD basis were implemented into the stoichiometric matrix of ADM1. The amount of educts degraded in the pilot-scale digester was calculated by ADM1 allowing additionally the dynamic calculation of ΔE .

4. Simulation results

4.1. Model calibration

The suggested biochemical parameter values given in Table 6.2 of the Scientific and Technical Report by [Batstone et al. \(2002\)](#) were set as initial values of the model used. To achieve the best agreement between measured and simulated values, kinetic parameters listed in [Table 4](#) had to be adjusted.

Hydrolysis rates for different particulate biodegradable COD fractions were adapted to predict the measured biogas production. Hydrolysis is generally considered the rate-limiting step during the AD of particulate organic matter ([Pavlostathis and Giraldo-Gomez, 1991](#)). In ADM1, hydrolysis is described with first-order kinetics. Different values for hydrolysis constants can be found due to changes in the particle size distribution of the substrate ([Sanders et al., 2000](#)). In other anaerobic hydrolysis models ([Vavilin et al., 1996](#)), it is assumed that the substrate particles are totally covered with bacteria. By this approach, the hydrolysis constant in the model is independent of the particle size of the substrate. In this study, after decreasing the absolute values to 0.31 d⁻¹, the

first-order kinetic was capable of describing the measured biogas production. Hydrolysis constants of the lipid, protein and carbohydrate fractions may differ. Carbohydrates, e.g., are assumed to be hydrolysed faster than proteins and lipids under anaerobic conditions. For the single carbohydrate fractions, different hydrolysis rates can be assumed for starch, hemicellulose or cellulose. The liquid manure treated in our study contained a significant amount of cellulose and a negligible amount of starch. The hydrolysis rate for cellulose can be assumed to be much lower than for starch. Furthermore, proteins can be differentiated into a fraction of animal origin and into a fraction of plant origin. Both fractions may have different hydrolysis rates. ADM1 only distinguishes between degradable particulate carbohydrates, proteins and lipids. Different hydrolysis constants for these single fractions did not lead to a better prediction of the measured biogas production. Hence, it was decided not to make any further adjustment.

4.2. Simulation of reactor performance

[Fig. 3](#) presents the comparison between simulation results and measurements for biogas production, biogas composition and the effluent concentrations of acetate and propionate.

A good agreement between simulation results and measurements was achieved. A good prediction of the measured biogas composition is an indicator for a realistic influent characterization. Both dynamic course and absolute values could be reproduced for the biogas compounds methane and carbon dioxide. The hydrogen curve revealed discrepancies between measurements and simulation results within the

Table 4 – Kinetic parameters changed for simulation

Parameter	Description	Unit	Initial value	Optimized value	Notes
k_{hyd_ch}	Hydrolysis rate for carbohydrates	(d^{-1})	10	0.31	1
k_{hyd_pr}	Hydrolysis rate for proteins	(d^{-1})	10	0.31	1
k_{hyd_li}	Hydrolysis rate for lipids	(d^{-1})	10	0.31	1
$pH_{UL,acid}$	Upper pH limit for acidogens	(–)	5.5	8	1
$pH_{LL,acid}$	Lower pH limit for acidogens	(–)	4	6	1
K_{m_c4}	Maximum uptake rate of valerate and butyrate	($kgCOD\ kgCOD^{-1}\ d^{-1}$)	20	13.7	2
K_{s_c4}	Half saturation coefficient of valerate and butyrate uptake	($kgCOD\ m^{-3}$)	0.2	0.357	2
K_{m_pro}	Maximum uptake rate of propionate	($kgCOD\ kgCOD^{-1}\ d^{-1}$)	13	5.5	2
K_{s_pro}	Half saturation coefficient of propionate uptake	($kgCOD\ m^{-3}$)	0.1	0.392	2
K_{m_ac}	Maximum uptake rate of acetate	($kgCOD\ kgCOD^{-1}\ d^{-1}$)	8	7.1	2
K_{s_h2}	Half saturation coefficient of hydrogen uptake	($kgCOD\ m^{-3}$)	7×10^{-6}	3×10^{-5}	1

Notes: (1) Values were determined by best fit between measurements and simulation results. (2) Values were taken from the literature: Angelidaki et al. (1999). Substrate: manure/oil. Determination: dynamic.

first 3 days. Additionally, a few measured hydrogen peaks could not be reproduced by the model. Weender analysis and the van Soest method were not carried out daily. These fractions are given as mean values over the whole period, multiplied with the daily loading. Single feeding events may vary from these mean values. Higher hydrogen values measured could be the result of higher amounts of fast degradable components.

As all processes of AD strongly depend on the pH value, a realistic prediction of the inhibition effect of this parameter by the model is essential. Batstone et al. (2002) proposed the following pH inhibition form when only low pH inhibition occurs:

$$I = \exp\left(-3\left(\frac{pH - pH_{UL}}{pH_{UL} - pH_{LL}}\right)^2\right) \quad \text{if } pH < pH_{UL}$$

$$\text{and } I = 1 \quad \text{if } pH > pH_{UL}, \quad (15)$$

where pH_{UL} is the point at which the organisms are not inhibited and pH_{LL} is the point at which inhibition is complete. The suggestion to set the inhibition term to 1, when the pH is beyond pH_{UL} is unsatisfactory. Eq. (15) will generate leaps when the pH is oscillating around pH_{UL} . We recommend avoiding these leaps and using the following modified inhibition term:

$$I = 1 - \frac{((pH_{UL} + pH_{LL})/2)^{pH_{UL}pH_{LL}}}{((pH_{UL} + pH_{LL})/2)^{pH_{UL}pH_{LL}} + pH^{pH_{UL}pH_{LL}}} \quad (16)$$

Both equations have the same dynamic course as can be seen in Fig. 4, but with the distinction that Eq. (16) allows a smooth change when the pH is around pH_{UL} .

4.3. Mathematical assessment of different operation modes

Liquid manure-digesting full-scale plants are often fed manually once or twice a day by mixing the components in a pit and pumping them into the digester. It is often stated

that automated feeding in a more continuous way is less stressful for the microbial population; hence the biogas yield should be higher. For quantifying the effect of the influence of feed intervals on gas yield by microbial inhibition, the following ADM1 simulation runs were performed (Table 5).

In the current situation, the reactor was fed 6 times a week (except Sundays). The first two lines of Table 5 contain the comparison between measurements and simulation results as described above. In the third line of Table 5, simulation results are listed in which the reactor is continuously fed 7 days a week without interruptions. Here, an increase in biogas production of about 1% was calculated, whereas the average CH_4 concentration in biogas is slightly lower. The effect of continuous feeding over the entire week on methane yield is negligible. Moreover, the calculation results of the energy balance model showed a slight decrease in the net energy production. In a second study the inflow is given twice a day, 7 days a week to the reactor. Finally, feeding is further split into 4, 8 and 24 times a day, each for 7 days. In all cases, the total input load is the same. According to the model and as seen in Table 5, a continuous feeding regime and splitting of the reactor input is disadvantageous in terms of net energy production.

Cattle manure has already been subjected to a degradation process (within cattle). However, biogas and especially methane production are affected by the amount of energy-rich inflow compounds. Therefore, we repeated the simulation runs by defining an additional amount of lipids in the model inflow. The model lipids were defined according to the characteristics of the rape-oil used in the 36L lab reactor. Results of simulated scenarios with varying feeding intervals using rape-oil as co-substrate are shown in Fig. 5.

Fig. 5 shows that in the case of rape-oil as co-substrate the operation mode clearly influences the production of biogas. Increase of feeding intervals can lead to both higher biogas and methane yields. This effect can be described by an exponential function. The exponent of the function is rising at higher proportions of rape-oil, meaning that the effect of

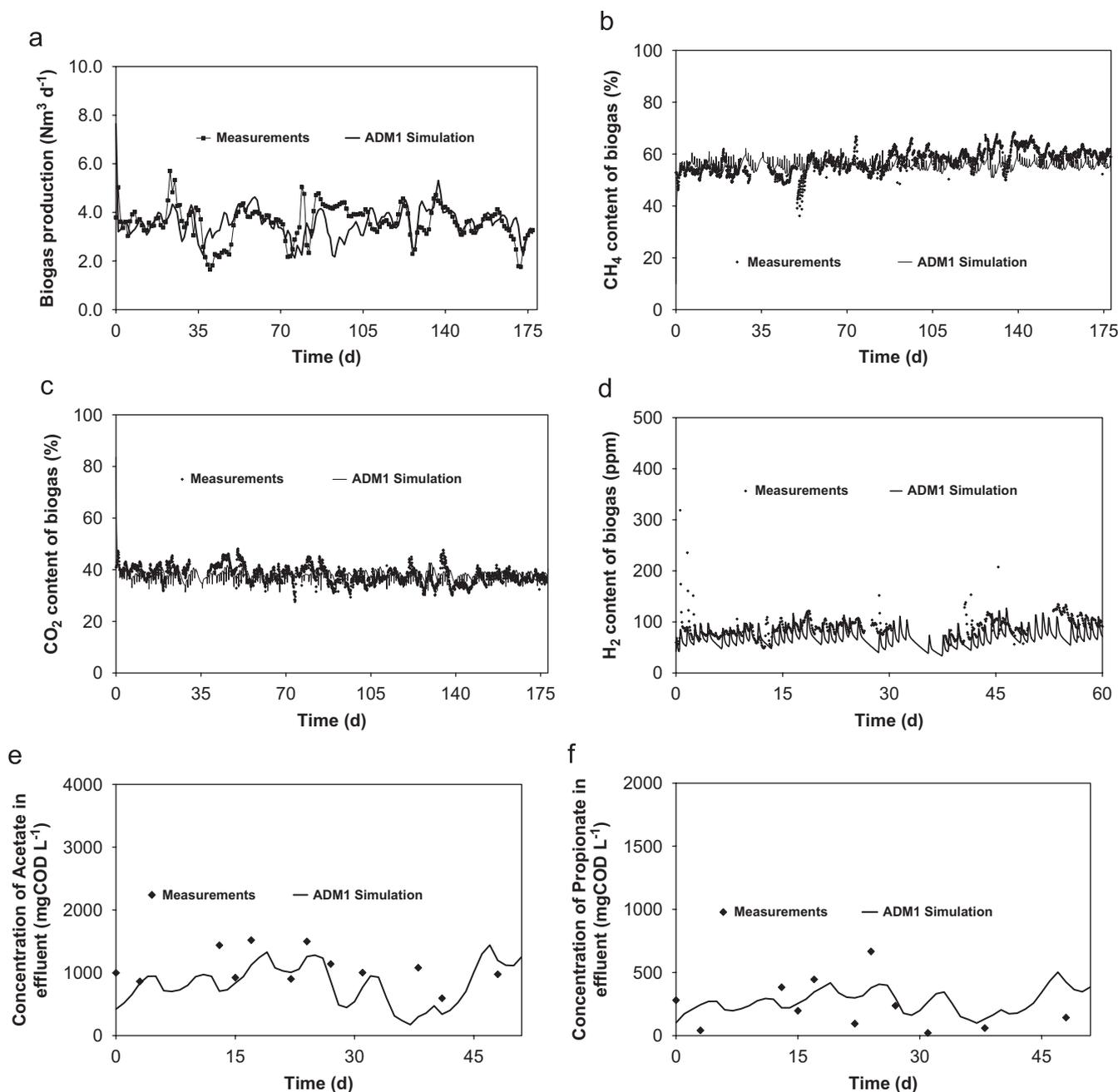


Fig. 3 – Simulation results: (a) biogas production, (b) methane content in biogas, (c) carbon dioxide content in biogas, (d) hydrogen content in biogas, (e) acetate effluent concentration, and (f) propionate effluent concentration.

higher feeding intervals is becoming higher. At a proportion of rape-oil of 3.0% v/v and 3.5% v/v, the exponent describing an increase in methane yield is larger than the exponent describing the increase in biogas yield. This signifies that methanogens are strongly benefiting from splitting the influent at high proportions of lipids in the feed. According to the model, splitting the inflow into 24 times a day has the same effect on biogas yield as increasing the proportion of rape-oil in the feed by 10%.

All of the simulation runs with rape-oil as co-substrate showed an accumulation of VFA and a drop in pH in the first hours after substrate feeding to demonstrate that the

microbial utilization of substrate is inhibited. The model indicated that smaller inflow heaps led to a more consistent utilization of substrate. The total time for the system to stabilize itself after loading is shorter in these cases.

4.4. Simulation of net energy production

Simulation results for the dynamic energy balance model are presented in Fig. 6.

Fig. 6 suggests that energy production was nearly constant for the entire period. Energy consumption, however, depended strongly on the season. The least energy consumption

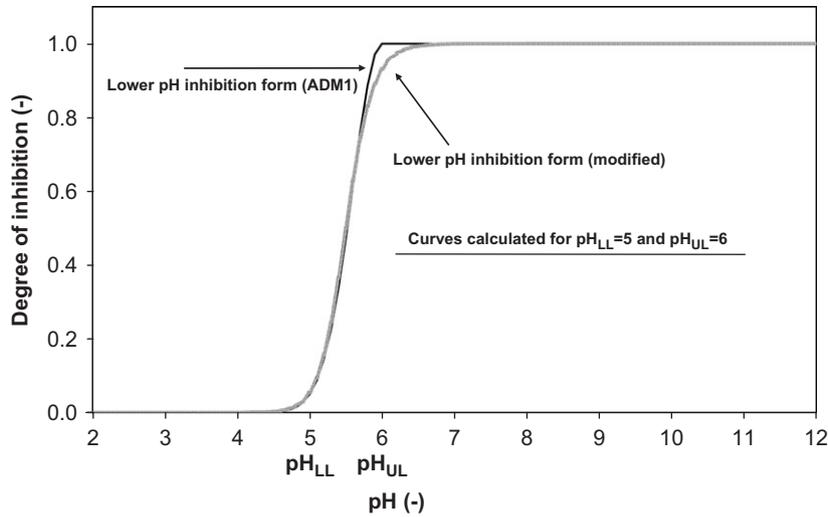


Fig. 4 – Dynamic course of pH inhibition forms.

Table 5 – Changed feeding intervals investigated by simulation while keeping total mass input constant

Feeding interval	Gas yield ($L_N d^{-1}$)	CH ₄ content (%)	CH ₄ yield ($L_N d^{-1}$)	Net energy production ($kWh d^{-1}$)
1/day, 6/week (measurements)	3583	57.24	2051	nm
1/day, 6/week (simulation)	3572	55.51	1983	11.49
1/day, 7/week (simulation)	3607	55.23	1992	11.30
2/day, 7/week (simulation)	3572	55.24	1973	11.13
4/day, 7/week (simulation)	3565	55.26	1970	11.09
8/day, 7/week (simulation)	3519	55.26	1945	11.02
24/day, 7/week (simulation)	3518	55.26	1944	10.83

Average values for the entire investigation period (180 days).

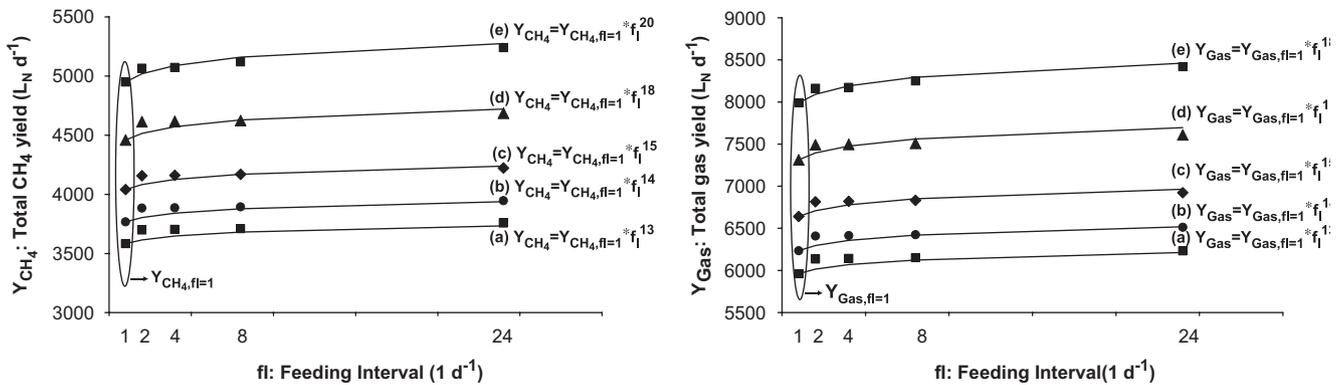


Fig. 5 – Results of simulated scenarios with varying feeding intervals investigated with ADM1 for the digestion of manure and rape-oil as co-substrate. Left: impact on total methane yield. Right: impact on total gas yield. The proportion of rape-oil was set to (a) 2% v/v, (b) 2.2% v/v, (c) 2.5% v/v, (d) 3.0% v/v and (e) 3.5% v/v.

was simulated for July 2004, and the maximum for December 2004. Referring to sewage sludge digesters, radiation losses are often described as the most energy consuming. For the

pilot-scale digester, heating of substrate needed the most energy, followed by radiation loss. Compared with these parameters, energy consumption by the eccentric worm

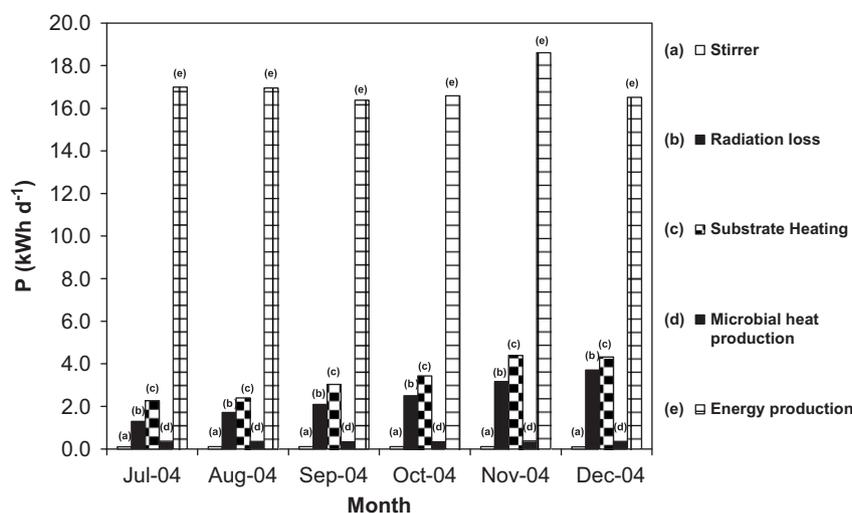


Fig. 6 – Comparison of the simulated energy production and the simulated energy consumption: (a) energy consumption of stirrer, (b) energy consumption due to radiation loss, (c) energy consumption due to substrate heating, (d) energy production due to microbial activity and (e) energy production of CHP.

pump (not depicted) and the stirrer was negligible. According to the simulation model, the heat released due to microbial degradation of organics could compensate for about 11% of the energy necessary for substrate heating.

To investigate the temperature change of the pilot-scale digester if no external heat is applied, we used the following equation:

$$\Delta T = \frac{(p_{mic_heat}^{prod} - p_{rad}^{loss} - p_{sub_heat}^{loss})3.6}{(4.180X_w + 1.547X_{ch} + 1.711X_{pr} + 1.928X_{li} + 0.908X_a)V_{Liquid}} \quad (K/d), \quad (17)$$

where ΔT is the temperature change of digester ($K d^{-1}$), X_w is the mass fraction of water (%), X_{ch} is the mass fraction of carbohydrates (%), X_{pr} is the mass fraction of proteins (%), X_{li} is the mass fraction of lipids (%), X_a is the mass fraction of ash (%) and V_{Liquid} is the liquid volume of the digester (m^3). The heat capacity of the substrate ($kJ kg^{-1} K^{-1}$) is calculated according to Choi and Okos (1986) taking into account the composition of the substrate and the solid content. The heat capacity of liquid manure was calculated to be $4.05 kJ kg^{-1} K^{-1}$, of TMR to be $3.24 kJ kg^{-1} K^{-1}$ and of the mixture of both to be $4.03 kJ kg^{-1} K^{-1}$. The heat capacity of the substrate used is similar to the value of water. However, a detailed calculation of this parameter for substrates with a higher solid content is important as it influences the temperature change within the digester according to Eq. (17).

Eq. (17) indicated an average daily temperature change of about $-1.82 K d^{-1}$. This temperature loss had to be compensated by the thermal energy produced (p_{therm}^{prod}).

5. Conclusions

A dynamic energy balance model was developed to calculate the net energy production of the digestion of liquid manure and renewable energy crops in a pilot-scale digester. The

Anaerobic Digestion Model No. 1 (ADM1) was used to simulate the biochemical conversion of the process and to calculate biogas production and composition. In order to facilitate model application, an approach for a detailed inflow characterization of the substrate used and modifications of ADM1 were suggested.

The model was used to assess different operation modes. A simulation study showed that there is no general advantage for applying a continuous feeding regime and splitting the inflow load into smaller heaps when only liquid manure and a small amount of co-substrate is used. The calculated increase of biogas production was negligible, while the net energy yield decreased. Simulation results for increasing amounts of lipids in the inflow showed higher biogas and methane yields when the feeding interval was increased. The effect was described by mathematical equations.

The energy balance model demonstrated for the pilot-scale digester that the course of energy consumption has a higher dynamic than the course of energy production. The main part of the energy produced is consumed by the digester itself, justifying a detailed calculation of the net energy production. Energy losses were strongly influenced by the season. A detailed knowledge of the system energy could be gained by using mathematical simulation.

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