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Monofermentation of grass silage under mesophilic conditions: Measurements and mathematical modeling with ADM 1

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ABSTRACT

In this paper experimental data from grass fermentation and simulation results with the Anaerobic Digestion Model (ADM) No. 1 are described. Two laboratory reactors were operated under mesophilic conditions with volumetric loading rates in between 0.3 and 2.5 $kg_{VS}/(m^3 \times d)$. Two different kinds of grass silage were used as substrates, resulting in an average specific biogas production of 600 L/kg_{VS}. The ADM 1 was calibrated both manually and with the help of a Genetic Algorithm in Matlab/Simulink. Results from calibration indicate that the NH_3 inhibition constant used to model the inhibition of acetate uptake is three to five times higher compared with digested activated sludge. The hydrogen inhibition constants applied for propionate and valerate/butyrate uptake are around two orders of magnitude lower than for sludge digestion.

1. Introduction

Anaerobic processes have been widely used for the treatment of municipal and industrial wastewater, sludge and agricultural wastes. Compared to aerobic methods, they are frequently more cost-efficient, they have a lower surplus sludge production, and reactors can be run with higher volumetric loads and thus smaller volumes.

Meanwhile, the ADM 1 (Batstone et al., 2002) has been used for the mathematical simulation of the fermentation of different substrates (Batstone et al., 2006). Amongst others, investigations were done on the digestion of activated sludge (Straub et al., 2006; Tomei et al., 2008) and primary sludge (Yasui et al., 2008).

Some experiences are available for the mathematical simulation of special substrates like starch (Sanders et al., 2000), blackwater (Feng et al., 2006) or olive pulp (Kalfas et al., 2006). Boubaker and Cheikh Ridha (2008) investigated on the mesophilic anaerobic co-digestion of olive mill wastewater with olive mill solid waste.

Up to now only little research has been done on the modeling of agricultural biogas plants. Analyses on the treatment and modeling of manure and co-substrates have been published by Angelidaki et al. (1993, 1999) for cattle manure, Amon et al. (2007a,b) for cattle manure and maize, Lübken et al. (2007) for cattle manure and co-substrates and Myint et al. (2007) for cattle manure.

Up to now publications on the anaerobic mono-fermentation of energy crops can be found but rarely. Research results not considering mathematical modeling are published for the co-digestion with cattle or piggery manure. Nordberg and Edström (2005) investigated the co-digestion of grass/clover with pasteurized municipal waste and Lindorfer et al. (2007) looked at the substrates pig manure, maize, wheat and agricultural residues from sugar and vegetable processing. Amon et al. (2007a,b) did research on methane production through anaerobic digestion of different energy crops. Gerin et al. (2008) investigated on energy yields through fermentation of maize and grass, Lehtomäki et al. (2008) on the anaerobic digestion of grass in one- and two-stage systems. Further publications on pure energy crops like maize, grass and sugar beet silage are available amongst others from Demirel and Scherer (2008), Preissler et al. (2007), Speckmaier et al. (2005) and Weiland et al. (2007).

In order to contribute knowledge on mono-fermentation of energy crops and especially on mathematical modeling of these substrates we present experimental data for grass fermentation and results from the application of the Anaerobic Digestion Model No. 1. Two reactors were operated under mesophilic conditions. Measurements were executed to determine COD (chemical oxygen demand), TS (total solids) and VS (volatile solids), gas flow, gas composition regarding CH_4, CO_2 and H_2. A detailed model

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calibration has been done based on additional data for propionate, acetate, valerate and butyrate. Besides executing a sensitivity analysis based on the SVM slope technique to identify highly sensitive model parameters, a genetic algorithm was applied to further improve model results.

2. Methods

2.1. Laboratory fermenter

Analyses of the grass ensilage and the reactor biomass were done by the Institute of Agricultural Engineering and Animal Husbandry, Bavarian State Research Center for Agriculture. The 36 l fermenters were discontinuously fed daily with untreated and pre-treated (heterofermentative) grass ensilage. Two reactors were run in parallel at 38 °C under mesophilic conditions. Feeding was once a day. The volumetric loading rates of the single reactors varied in between 0.3 and 2.5 $g_{VS}/(m^3 \times d)$ with an average COD load of 40 g_{COD}/d. Maximum gas production was 35 L/d, with a methane content in between 50% and 60% of the dry biogas. Average specific gas production was 600 L/kg_{VS}; pH was measured as 8.0.

2.2. Analytical methods

The concentrations of COD and nitrogen were determined spectro-photometrically with the Dr. Lange-Device ISIS 6000. TS and VS were determined according to the German standards (DEV, 1981). Analyzes were done to measure organic matter in detail, so that crude protein, crude fat, crude fiber and N-free extract (Weender analysis, described in Naumann and Bassler, 1993) could be determined. Carbohydrates were further divided into hemicellulose (NDF–ADF), cellulose (ADF–ADL) and lignin (ADL); approximately analyzed by the so-called van Soest-Fractions (van Soest and Wine, 1967): NDF (neutral detergent fiber), ADF (acid detergent fiber) and ADL (acid detergent lignin). VFAs were measured using an AGILENT 6890N gas chromatograph. Column: HP FFAP, 25 m, 0.32 mm. The temperature program was as follows: initial temperature 80 °C (holding time: 1 min), 120 °C in 20 °C/min (holding time: 3 min), 220 °C in 6.13 °C/min (holding time: 20.13 min). Total biogas production was measured by the RITTER drum chamber gas meter. Methane and carbon dioxide were quantified by means of the infrared two-beam compensation method with pressure compensation (measuring error as specified: ±2%). Oxygen and hydrogen were measured by electrochemical sensors (measuring error as specified: ±3%). Table 1 shows the characteristics of the influent substrate.

Table 1
Average influent characteristics of the ensilaged grass

Parameter	Unit	Grass silage	
		Untreated	Heterofermentatively treated
TS	[%]	25.9	23.2
COD	[kg/m^3]	441	345
VFA_{total}	[g/m^3]	11563	15671
pH	[–]	4.6	4.9
NH4–N[a]	[g/m^3]	11191	8857
Raw protein RP[a]	[% TS]	15.1	15.1
Raw fiber RF[a]	[% TS]	31.9	31.9
Raw lipid RL[a]	[% TS]	1.5	1.5
NfE[a]	[% TS]	41.8	41.8
NDF[a]	[% TS]	62.9	62.9
ADF[a]	[% TS]	38.0	38.0
ADL[a]	[% TS]	34.2	34.2

[a] Speckmaier et al. (2005), NfE = Nitrogen free extracts, NDF = Neutral detergent fiber, ADF = Acid detergent fiber, ADL = Acid detergent lignin.

2.3. Mathematical model

In 1997 the IWA Task Group on Mathematical Modeling of Anaerobic Digestion Processes was formed the work of which led to the Anaerobic Digestion Model No. 1 (Batstone et al., 2002). ADM 1 is a highly complex model, characterized by 19 biochemical conversion processes and 24 dynamic state variables. For this paper calculations were executed with the software SIMBA 4.2 (2002) that is based on Matlab/Simulink (Version 7.0).

2.4. Genetic algorithm

The Genetic Algorithm (GA) is a highly efficient method which uses concepts of biological evolution processes, like heredity, selection and mutation. For the work presented a Genetic Algorithm from the Direct Search Toolbox 1.0.1 (GA Toolbox) from Matlab 7.0 was used. 5 kinetic parameters from ADM 1 were determined by the GA. Each possible individual answer from the GA, resulted in values for the 5 parameters, which were used then to run the simulation. Finally 1000 simulation runs (100 individuals multiplied with 10 generations) have been executed during the application of the Genetic Algorithm (scaling function: rank, crossover rate: 0.6, elite count: 3, mutation function: uniform, probability of mutation: 0.05, crossover point: scattered).

Simulation results are evaluated by the following fitness function:

$$\text{Fitness function} = \text{Minimize}\left(\sum_{j=1}^{N}(\log(X_{ij,\text{exp}}) - \log(Y_{ij,\text{sim}}))^2\right) \quad [-] \tag{1}$$

where N is the number of measured data points for each parameter, X experimental data and Y simulation result.

The fitness values from all individuals of an entire population are used to select and apply the evolutionary process – elitism, crossover and mutation – to create a new generation. As measured data of anaerobic processes are of different magnitude of order (e.g. gas content of methane in percent, hydrogen in ppm), the logarithm of the measured data and the simulation result was used to optimize the performance of the GA algorithm.

2.5. Sensitivity analysis

Besides calibration and validation of the ADM 1 a sensitivity analysis was carried out. Following the publication of Kim et al. (2006), who did investigations on activated sludge models, the single step variation method (SVM) was used to identify sensitive parameters for the fermentation of grass. In the work presented dynamic calibration results were compared with the outcome of the variation of single parameters. The calibrated ADM 1 was used as reference parameter set.

The sensitivity index ΔEQ [–] results from a procedure, where each model parameter was changed stepwise by 10% (Ref: referring to reference simulation, Var: varied parameter).

$$\begin{aligned}\Delta EQ \cdot t = {} & \beta_{\text{orgA}}\frac{|\text{orgA}_{\text{Ref},e} - \text{orgA}_{\text{Var},e}|}{\text{orgA}_{\text{Ref},e}} + \beta_{\text{TS}}\frac{|\text{TS}_{\text{Ref},e} - \text{TS}_{\text{Var},e}|}{\text{TS}_{\text{Ref},e}} \\ & + \beta_{\text{CH}_4}\frac{|\text{CH}_4\%_{\text{Ref}} - \text{CH}_4\%_{\text{Var}}|}{CH_4\%_{\text{Ref}}} + \beta_{\text{CO}_2}\frac{|\text{CO}_2\%_{\text{Ref}} - \text{CO}_2\%_{\text{Var}}|}{\text{CO}_2\%_{\text{Ref}}} \\ & + \beta_{\text{H}_2}\frac{|\text{H}_{2\text{Ref}} - \text{H}_{2\text{Var}}|}{\text{H}_{2\text{Ref}}} + \beta_{\text{gasflow}}\frac{|q_{\text{gasflow,Ref}} - q_{\text{gasflow,Var}}|}{q_{\text{gasflow,Ref}}} \quad [-]\end{aligned} \tag{2}$$

where t is the number of simulation days, orgA_e are the organic acids acetate, propionate, butyrate and valerate [g_{COD}/m^3], TS are total solids [g_{TS}/m^3], CH_4% the percentage of methane in the dry

gas, CO_2% the percentage of carbon dioxide in the dry gas, H_2 the concentration of hydrogen [ppm] in the dry gas and $q_{gasflow}$ the dry gas flow in m^3/d. β are weighting factors ($\beta_{orgA} = 1$, $\beta_{TS} = 1$, $\beta_{CH4} = 2$, $\beta_{CO2} = 2$, $\beta_{H2} = 2$, $\beta_{gasflow} = 2$). This means, the impact of the parameters gas flow and gas composition on the sensitivity index is twice as much as for organic acids and TS. Because of their relevance to energy production the gas composition and gas flow were rated higher than other output values.

3. Results and discussion

3.1. Characterization of the influent

COD data for agricultural substrates is not measured as frequently as VS or fresh matter. Therefore, regression analyzes have been done to transfer measured data of VS to COD (see Fig. 1).

Additionally, the organic matter VS in the reactor was measured as 74% of total TS. The inflow fractioning of the total COD is of highest importance for the calibration of the ADM 1 and is strongly affecting the gas composition. For this, detailed measurements have been conducted to analyze the substrate. The following equations are implemented to define particular model fractions.

$$X_{Pr} = (FM \cdot TS \cdot i_{COD/TS}) \cdot RP \quad [kg_{COD}/d] \tag{3}$$

$$X_{Li} = (FM \cdot TS \cdot i_{COD/TS}) \cdot RL \quad [kg_{COD}/d] \tag{4}$$

Both parameters proteins X_{Pr} (kg_{COD}/d) and lipids X_{Li} (kg_{COD}/d) are dependent on fresh matter FM (kg_{FM}/d), total solids TS (%) as well as raw protein RP (% TS) and raw lignin RL (% TS) respectively. The COD content of grass was measured as $i_{COD/TS} = 1.21\ g_{COD}/g_{TS}$.

The calculation of carbohydrates X_{CH} (kg_{COD}/d) and inert material X_I (kg_{COD}/d) is more complicated and is based on additional information from the Van-Soest-Analysis (Van Soest and Wine, 1967).

$$X_I = (FM \cdot TS \cdot i_{COD/TS}) \cdot (ADL + (ADF - ADL)_{non\_deg}) \quad [kg_{COD}/d] \tag{5}$$

In order to quantify the inert material the load of lignin ADL (acid detergent lignin in% TS) is needed. ADF (acid detergent fiber in% TS) comprises lignin and cellulose.

$$X_{CH} = (FM \cdot TS \cdot i_{COD/TS}) \cdot [(RF + Nfe) - (ADL + (ADF - ADL)_{non\_deg})] \quad [kg_{COD}/d] \tag{6}$$

Raw fiber RF (% TS) and nitrogen-free extract Nfe (% TS) represent the total content of carbohydrates, whereas the latter part of the equation is describing the inert part consisting of lignin and non degradable cellulose. Detailed information on the substrate characterization can be found in Table 2.

Eqs. (3)–(6) are applied to divide the COD as shown above. All particular material was split during the disintegration process in the aforementioned fractions.

Table 2
Influent COD fractioning after the disintegration step calculated with the Eqs. (3)–(6): *f* gives the fraction of total COD

Parameter	Description	Unit	Grass silage	
			Untreated	Heterofermentatively treated
f_{Si}	Inert soluble COD	% COD_{tot}	2.4	2.4
f_{Sac}	Total acetate	% COD_{tot}	2.6	3.9
f_{Sfa}	Long chain fatty acids	% COD_{tot}	0.0	0.0
f_{Ssu}	Monosaccharides	% COD_{tot}	0.0	0.0
f_{Saa}	Amino acids	% COD_{tot}	0.0	0.0
f_{Spro}	Total propionate	% COD_{tot}	0.0	1.0
f_{Xi}	Inert particulate COD	% COD_{tot}	30.9	30.1
f_{Xpr}	Proteins	% COD_{tot}	14.7	14.3
f_{Xli}	Lipids	% COD_{tot}	1.5	1.4
f_{Xch}	Carbohydrates	% COD_{tot}	47.9	46.8

3.2. Manual calibration of biochemical parameters

In the following calibration results of the application of the ADM 1 to the mono-fermentation of grass silage are presented. Table 3 summarizes the adapted kinetic parameters. The manual calibration was done amongst others by changing the inhibition constants of hydrogen during the degradation of propionate and butyrate/valerate as well as the inhibition constant of NH_3 during the uptake of acetate. Literature values for biokinetic parameters for the mono-fermentation of grass silage still can be rarely found. Lübken et al. (2007) also decreased the half saturation coefficient for hydrogen in the same range to describe the co-fermentation of manure and agricultural co-substrates.

Furthermore, the disintegration constant k_{Dis} to 1 d^{-1} was increased, leading to a faster splitting up of the composite material X_C. To fulfill the nitrogen mass balance after the disintegration step, the nitrogen content of the composite material was fitted to $N_{XC} = 0.0011\ Mol_N/g_{COD}$. In the manual calibration only slight differences to the ADM 1 parameter set were determined concerning the propionate uptake rate $k_{m,pro}$ that is smaller if grass silage ($k_{m,pro} = 11.5\ d^{-1}$) is applied. Angelidaki et al. (1999) used a propionate uptake rate of $k_{m,pro} = 5.5\ d^{-1}$ describing the fermentation of manure and oil.

Most significantly are changes of the NH_3 inhibition constant during acetate uptake and the hydrogen inhibition constants during propionate and butyrate/valerate uptake. These results will be discussed in detail in chapter 3.5 after application of the GA.

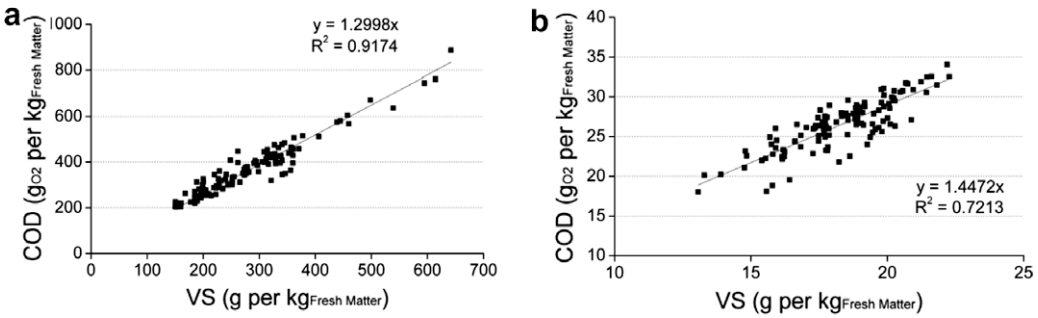

Fig. 1. Correlation between COD and VS for the inflow substrate (a) and the biomass in the reactor (b).

Table 3
Calibrated ADM1-parameters under mesophilic conditions for untreated grass silage

Parameter	Description	Unit	ADM 1 value	Manually calibrated	GA calibrated
k_{Dis}	Disintegration constant	d^{-1}	0.5	1.0	0.26
$k_{m,\ pro}$	Propionate uptake rate	$g\ g^{-1}\ d^{-1}$	13	11.5	13
$K_{S,\ H2}$	Half saturated coefficient for hydrogen uptake	$kg\ m^{-3}$	7×10^{-6}	7×10^{-5}	4.2×10^{-5}
$K_{I,\ H2,\ C4}$	H_2-Inhibition constant for butyrate/ valerate uptake	$kg\ m^{-3}$	1×10^{-5}	9×10^{-8}	5.4×10^{-8}
$K_{I,\ H2,\ pro}$	H_2-Inhibition constant for propionate uptake	$kg\ m^{-3}$	3.5×10^{-6}	9×10^{-8}	4.8×10^{-8}
$K_{I,\ NH3}$	NH_3–N-Inhibition constant for acetate uptake	$kmol\ m^{-3}$	0.0018	0.008	0.0084
N_{XC}[a,b]	Nitrogen content of composite material	$mol_N g_{COD}^{-1}$	0.002	0.0011	0.0011
$pH_{UL,\ acid}$[a]	Upper pH limit for acidogens	–	5.5	8.5	8.5
$pH_{LL,\ acid}$[a]	Lower pH limit for acidogens	–	4	6	6

[a] Calibrated, not part of the Genetic Algorithm.
[b] Calculated through nitrogen mass balance for the disintegration process (acc. to results from Weender and Van Soest Analysis).

3.3. Modeling of reactor performance

Fig. 2 presents measured data and simulation results for the gas flow, the gas composition, TS, pH and organic acids for the mesophilic fermentation of treated grass silage. Results of the untreated grass silage are shown in Fig. 3, compared with results from the Genetic Algorithm.

Although generally a good fit was achieved, dynamic hydrogen concentrations were not simulated. Hydrogen was measured only once a day as average sample for 24 h. Average concentrations could be modeled after decreasing the half saturation coefficient for hydrogen uptake. During anaerobic processes, hydrogen increases shortly after substrate addition. That means, hydrogen concentrations in the gas are very much depending on the specific point in time after reactor feeding. Unfortunately measurement data in greater detail was not available.

Furthermore Fig. 2 depicts the parameters TS, organic acids and pH for treated substrate. The simulation of pH and solids in the reactor effluent was very accurate. The comparison of measured data and simulation results for the organic acids is satisfying for butyrate. For propionate a good fit was achieved for the complete period, acetate concentrations are simulated well until simulation day 120. In order to improve modeling results, the Genetic Algorithm was applied.

Both, propionate and acetate degradation are sensible processes in modeling of anaerobic digestion. Alternatively to the Monod-type equations in ADM 1, degradation of acetate as well as degradation of propionate can be described by Haldane-Kinetics (Andrews, 1969). In addition to hydrogen inhibition, propionate degradation can be inhibited by its product acetate (Kus and Wiesmann, 1995).

If reactor performance of the untreated and pre-treated grass silage is compared, it can be seen that the pre-treatment does not have as much impact as expected. The average gas flow of the reactor fed with the heterofermentatively treated silage is approximately 2.5% higher, leading to a gas flow of 607 L/kg_{VS} (untreated silage 593 L/kg_{VS}). Also maximum gas production for the untreated and treated substrate does not differ substantially with 34.7 L/d and 35.1 L/d, respectively. Degradation of COD and VS is nearly the same with 84.8% of COD and 88.7% of VS for the untreated silage as well as 83.1% of COD and 87.4% of VS for the treated silage. The inflow COD fractioning of the two silages only differs marginally. Measurements showed that the treated silage has 1.3% higher concentration of acetate and 1% higher concentration of propionate. As the measured data did not reveal many differences in between the two types of silages, consequently also calibration results for the two substrates did not vary. Both substrates could be modeled with adequate results with a first order disintegration rate of $k_{Dis} = 1\ d^{-1}$ (GA application $k_{Dis} = 0.26$).

3.4. Application of the genetic algorithm

To evaluate the quality of the simulation results a fitness function (see Eq. (1)) was applied. After the use of the GA in 3000 simulation runs, the factor calculated with the fitness function improved from 34.94 (manual calibration) to 28.30 (GA). The factor is characterized by the square error sums, based on logarithm of measured data and simulation result. A low fitness factor therefore means less discrepancy in between measured data and simulation results. The improvement of model results is mainly caused by smaller deviations of the parameters gas flow, hydrogen, acetate, propionate and butyrate (see Table 4).

Only one parameter shows slightly higher discrepancies after the application of the GA than before. This is the parameter TS. Analyzing simulation results after and before the GA application for TS (see Fig. 3), it can be found that modeling results still are very good. TS effluent concentrations as well as the gas flow are both inversely dependent upon the disintegration constant k_{Dis}. The disintegration constant was decreased by the GA to get better modeling of gas flow, resulting in slightly worse TS effluent concentrations.

When comparing the results of the manually calibrated model with the outcomes of the GA, especially the parameters gas flow, hydrogen, acetate and propionate have been improved considerably.

Hydrogen concentrations were measured only once a day as average sample for 24 h. Therefore discrepancies in the dynamic behavior are still significantly after the GA application. Nevertheless average H_2 concentrations could be improved and modeled well.

Checking the kinetic parameters of the GA against the manually achieved ones, values of calibrated parameters could be further improved. Main discrepancies compared with the ADM 1 parameter set for sludge digestion can be found regarding the simulation of acetate and hydrogen uptake. The low hydrogen concentrations furthermore led to different values of the hydrogen inhibition constants during propionate and butyrate/valerate uptake. Both processes, the acetate uptake and the effect of hydrogen, will be discussed in more detail.

The simulation of acetate degradation is seriously influenced by the acetate uptake rate, the acetate half saturation coefficient and the NH_3 inhibition constant during acetate uptake. From the data available all three parameters cannot be individually determined as the three parameters are highly interdependent. To model acetate effluent concentration (see Table 3) the nitrogen inhibition constant K_{I,NH_3} was fitted to 0.0084 $kMol/m^3$, while the acetate uptake rate $k_{m,ac} = 8\ d^{-1}$ and the half saturation constant for acetate uptake $k_{S,ac} = 0.15\ g/m^3$ were kept constant according to Batstone et al. (2002). Supposed the same fitness factor for acetate is

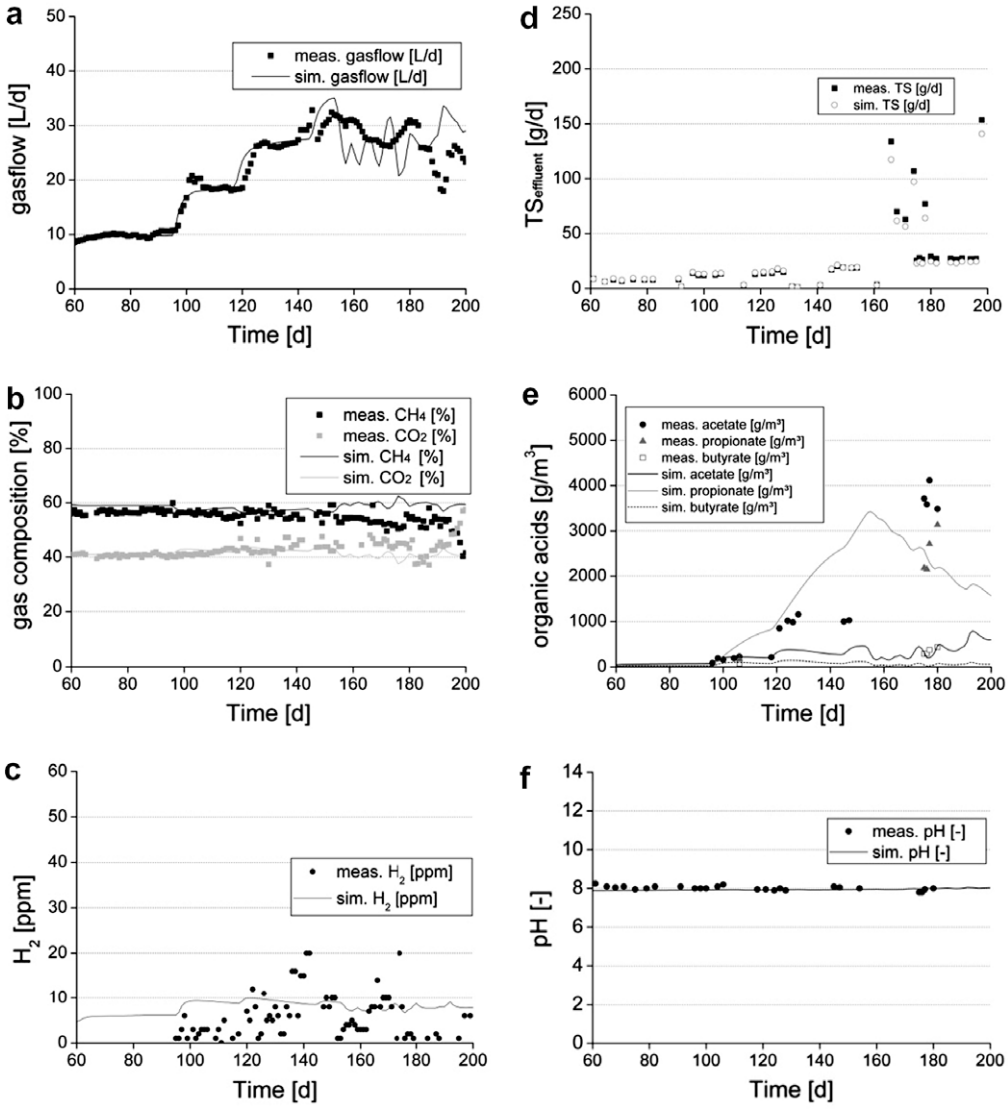

Fig. 2. Manually calibrated simulation and measurement results for mesophilic fermentation of treated grass silage: (a) dry gas flow [L/d], (b) CH_4 and CO_2 dry gas composition [%], (c) Hydrogen dry gas concentration [ppm], (d) TS in the effluent [g/d], (e) organic acids concentration (acetate, propionate, butyrate) in the effluent [g/m^3] and (f) pH [–].

needed, additionally $k_{m,ac}$ and $K_{S,ac}$ could be adapted. This leads to smaller values of K_{I,NH_3}. If it is assumed, that the acetate uptake rate for mono-digestion of grass is $k_{m,ac} = 12\ d^{-1}$ and $K_{S,ac} = 0.10\ kg_{COD}/m^3$, the nitrogen inhibition constant K_{I,NH_3} still needs to be 0.005 kMol/m^3 to fit measured acetate concentrations with the same quality. From the data available it can be concluded, that the range of K_{I,NH_3} must be in between 0.005 and 0.0084 kMol/m^3, still three to five times higher compared with digestion of activated sludge. The adaptation of biomass to higher ammonia concentrations is described in literature for different substrates. Angelidaki et al. (1993) documented the fermentation of cattle manure. The authors focused on free ammonia inhibition, reasoning that for average NH_3 concentrations of 1 g/L the inhibition constant K_{I,NH_3} is 0.23 g_{NH_3}/L. In our reactor free ammonia concentration of 0.4–1.7 g_{NH_3}/L are found, resulting in $K_{I,NH_3} = 0.143\ g_{NH_3}$/L. For blackwater and kitchen refuse Feng et al. (2006) indicate that the free ammonia inhibition constant for acetate uptake is up to 0.3 g_{NH_3}/L.

Hydrogen concentrations can be fitted via the calibration of the hydrogen uptake rate and the half saturation coefficient for hydrogen uptake. For the fermentation of pure grass silage kinetic parameters still cannot be found in literature. According to the publication of Lübken et al. (2007) about anaerobic digestion of cattle manure with agricultural co-substrates with $K_{S,H_2} = 3 \times 10^{-5}\ kg_{COD}/m^3$, here calibration was done only with the half saturation coefficient for hydrogen ($K_{S,H_2} = 4.2 \times 10^{-5}\ kg_{COD}/m^3$). Additional simulations revealed that it is impossible with reasonable values to calibrate hydrogen concentrations only by fitting the maximum hydrogen uptake rate. If k_{m,H_2} is considered to be at most 45 d^{-1}, the half saturation coefficient still needs to be $K_{S,H_2} = 6 \times 10^{-5}\ kg_{COD}/m^3$ to achieve same modeling quality. The range of K_{S,H_2} could therefore be determined to be in between 4.2×10^{-5} and $7.0 \times 10^{-5}\ kg_{COD}/m^3$.

The hydrogen inhibition constants for propionate and butyrate/valerate uptake are two orders of magnitude smaller than values used for the modeling of sludge digestion. Both inhibition constants were determined with the help of measured propionate and butyrate concentrations. Both are affected also by related maximum uptake rates and the half saturation coefficients. According to the above described method also ranges for the hydrogen inhi-

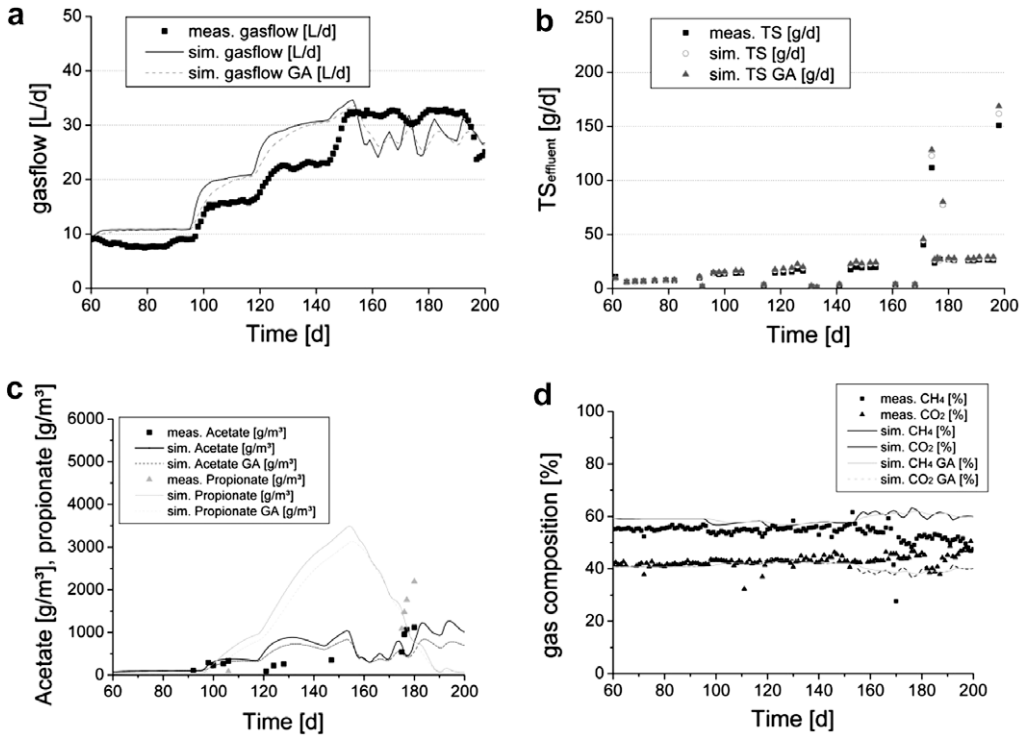

Fig. 3. Measured results and simulation results (manual calibration) compared with GA simulation results: (a) gasflow [L/d] (b) TS in the effluent [g/d], (c) acetate [g/m^3] and propionate [g/m^3], (d) gas composition CH_4 and CO_2 [%].

Table 4
Final square error sum [–], based on the logarithm of measured data and logarithm of simulation result

Parameter	Description	Manual calibration	GA
Q_{gas}	Gas flow	1.59	1.21
CH_4	Methane	0.47	0.47
CO_2	Carbon hydroxide	0.27	0.25
S_{ac}	Acetate	1.86	1.35
S_{pro}	Propionate	0.96	0.72
TS	Total solids	0.15	0.22
HCO_3^-	Hydro carbonate	0.17	0.16
S_{bu}	Butyrate	0.03	0.01
H_2	Hydrogen	29.62	23.91
Sum		**34.94**	**28.30**

bition constants could be calculated. If $k_{m,pro} = 6.5\ d^{-1}$ and $K_{S,pro} = 0.3\ kg_{COD}/m^3$ are considered as reasonable values, the upper limit of $K_{I,H_2,pro}$ can be calculated. The range of $K_{I,H_2,pro}$ is 4.8×10^{-8} to $1.1 \times 10^{-7}\ kg_{COD}/m^3$. The values for $k_{m,C_4} = 10\ d^{-1}$ and $K_{S,C_4} = 0.4\ kg_{COD}/m^3$ are resulting in a range for $K_{I,H_2,C_4} = 5.4 \times 10^{-8}$–$3 \times 10^{-7}\ kg_{COD}/m^3$. Information about hydrogen inhibition constants can rarely be found in literature. Results are mainly available for sludge digestion (e.g. Siegrist et al., 2002). The inhibition through hydrogen for propionate and butyrate uptake of granulars under thermophilic conditions is also content of a paper from Schmidt and Ahring (1993). Lehtomäki et al. (2008) are investigating the degradation of pure grass silage in a leach bed process. Although detailed information is given on pH no data regarding the inhibition of hydrogen can be found. Klocke et al. (2008) investigated the composition of microbial community and maximum loading rates for reactors operated with pure energy crops. Resch et al. (2007) did research about the effect of grass and clover addition on methane production during anaerobic digestion. Nevertheless, to date there is no data available about inhibitory effects of hydrogen during mono-fermentation of pure energy crops. Further research would be necessary.

3.5. Sensitivity analysis

Below results of the sensitivity analysis for ADM 1 are depicted (Fig. 4). With 225 single simulation runs the sensitivity of 15 kinetic parameters has been analyzed.

Sensitivities of the uptake rates for monosaccharides k_{m_su}, amino acids k_{m_aa}, long chain fatty acids (LCFA), the half saturation coefficient for ammonia $k_{S\_NH_4}$ and the inhibition constant for hydrogen during fatty acid uptake k_{I,H_2_fa} are not shown as they were very low.

The highest impact on modeling results of grass fermentation can be found for the uptake rates of propionate k_{m_pro} and hydrogen $k_{m\_H_2}$ as well as for the half saturation coefficient for hydrogen $k_{S\_H_2}$ and the hydrogen inhibition constant for propionate uptake. Higher hydrogen concentrations are quite important as they may inhibit LCFA and organic acids degradation. The analysis furthermore showed the sensitivity of decay rates of the seven modeled biomass groups in ADM 1. Similar results concerning the sensitivity of biomass decay rates have been found also for other agricul-

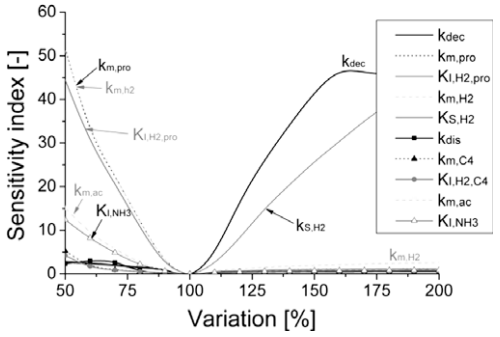

Fig. 4. Results from the sensitivity analysis for ADM 1: Highly and average sensitive parameters for reactor operation with grass silage.

tural substrates like co-substrates and manure (Wett et al., 2007; Wichern et al., 2008).

4. Conclusions

In this paper measured data and simulation results for the mono-fermentation of grass silage were presented. Two mesophilic reactors were operated with two kinds of grass silage with different volumetric loading rates in between 0.3 and 2.5 $kg_{VS}/(m^3 \times d)$. The average specific gas production was 600 L/kg_{VS} with a methane content of the dry biogas of 50–60%. The Anaerobic Digestion Model No. 1 (Batstone et al., 2002) was used for the dynamic simulation of the biochemical processes. The model was applied to describe the fermentation of grass silage as mono-substrate, which has not been realized up to now. After the COD influent fractionation based on detailed measurement data from the Weender- and Van-Soest-Analysis, the model was calibrated both manually and with the help of a Genetic Algorithm in Matlab/Simulink.

Results indicate (a) that the effect of the heterofermentatively treated grass silage compared to untreated grass silage was low regarding input concentrations of acetate and propionate, gas yield and VS degradation, (b) results from ADM-1-calibration indicate that the NH_3 inhibition constant used to model the acetate uptake is three to five times higher for grass silage compared to digested activated sludge, (c) the hydrogen inhibition constants applied for propionate and valerate/butyrate uptake are around two orders of magnitude lower than for sludge digestion, (d) the Genetic Algorithm is an appropriate method to further improve fitting of kinetic parameters and to identify ranges of biokinetic parameters, (e) ADM 1 is capable to describe degradation of mono-fermentation of grass silage.

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