Biogas from grass silage – Measurements and modeling with ADM1

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ABSTRACT

Mono fermentation of grass silage without the addition of manure was performed over a period of 345 days under mesophilic conditions (38 °C). A simulation study based on the IWA Anaerobic Digestion Model No. 1 (ADM1) was done in order to show its applicability to lignocellulosic biomass. Therefore, the influent was fractioned by established fodder analysis (Weender analysis and van Soest method). ADM1 was modified with a separate compound of inert decay products similar to the approach of Activated Sludge Model No. 1 (ASM1). Furthermore, a function, which described the influence of solids on the process of hydrolysis, has been integrated to reproduce reliable ammonium concentrations. The model was calibrated by using the modified Nash–Sutcliffe coefficient to evaluate simulation quality. It was possible to fit observed data by changing only hydrogen inhibition constants and the maximum acetate uptake rate. The extended ADM1 model showed good agreement with measurements and was suitable for modeling anaerobic digestion of grass silage.

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1. Introduction

Since ratification of the Renewable Energy Sources Act (EEG) in 2000, biogas production from agricultural material is subsidized in Germany. Especially high-capacity plants using energy crops as single substrate enforce the need of detailed research into the drawbacks and opportunities of monofermentation. Until now, monofermentation of grass silage has been successfully implemented only in a few instances (Yu et al., 2002; Lehtomäki et al., 2008; Koch et al., 2009) and therefore, further research is needed to fully understand degradation pathways. Especially protein-rich substrates like grass (approximately 17% protein of total solids) often indicate low process performance during monofermentation, which is generally a result of high ammonia concentrations within the fermenter (Angelidaki et al., 1993; Hansen et al., 1998; Sung and Liu, 2003). In the fermenter, inorganic nitrogen is present as ammonium (NH_4^+) and as ammonia (NH_3). Only the non-dissociated part is toxic because it is membrane permeable. The free ammonia nitrogen (FAN) concentration is a function of the total ammonia concentration, pH value, and temperature of the solution as follows (Anthonisen et al., 1976):

$$FAN = \frac{TAN}{1 + 10^{(pK_a - pH)}} \qquad (1)$$

and

$$pK_a = 0.09018 + \frac{2729.92}{T + 273.15} \qquad (2)$$

FAN = free ammonia nitrogen [g/l]; TAN = total ammonia nitrogen [g/l]; pK_a = dissociation constant Ammonium ion [–]; pH = pH value [–]; T = temperature [°C].

Gallert and Winter (1997) revealed a 50% inhibition of methanogenesis with a FAN concentration of 0.22 g/l at 37 °C. In a literature study, Poggi-Varaldo et al. (1997) have shown that the spread of toxic FAN concentrations is enormous. Beside temperature, FAN concentrations are further a function of other influences, e.g. substrate. Under mesophilic conditions, critical FAN concentrations vary between 2.8 g/l and 8.0 g/l. In general, experimental conditions implied adaptation of the reactor's microbial consortia to the increasing inhibitor concentration. The reason for inhibition is not understood so far, but several mechanisms for ammonium inhibition have been proposed including: the change of intracellular pH value, the increase of maintenance energy requirement, or the inhibition of specific enzymatic reactions (Wittmann et al., 1995; Chen et al., 2008).

Anaerobic digestion is a complex biological process requiring the involvement of a variety of microorganisms. Therefore, mathematical models can be useful for understanding the numerous processes or microorganisms involved. After successful calibration, a mathematical model is able to predict reactor behavior under varying conditions (e.g. inflow composition). The IWA Anaerobic Diges-

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Nomenclature

ADF	acid detergent fiber [% TS]
ADL	acid detergent lignin [% TS]
ADM1	Anaerobic Digestion Model No. 1
ASM1/3	Activated Sludge Model No. 1/3
D_{VS}	degradation level [%]
FAN	free ammonia nitrogen [g/l]
FM	fresh matter
K_{hyd}	hydrolysis influence coefficient [kg_{TS}/kg_{FM}]
n_{hyd}	hydrolysis influence degree index [–]
k_{m_Ac}	maximum uptake rate for acetate [$kg_{COD}/(kg_{COD}·d)$]
k_{m_Pro}	maximum uptake rate for propionate [$kg_{COD}/(kg_{COD}·d)$]
$K_{I\_H_2C_4}$	hydrogen inhibitions constant for valerate and butyrate uptake [kg_{COD}/m^3]
$K_{I\_NH_3}$	free ammonia inhibitions constant for acetate uptake [$kmol_N/m^3$]
$K_{I\_H_2\_Pro}$	hydrogen inhibitions constant for propionate uptake [kg_{COD}/m^3]
K_{S_Ac}	half saturation coefficient of acetate [kg_{COD}/m^3]
$K_{S\_H_2}$	half saturation coefficient of hydrogen [kg_{COD}/m^3]

K_{S_Pro}	half saturation coefficient of propionate [kg_{COD}/m^3]
NDF	neutral detergent fiber [% TS]
NfE	nitrogen free extracts [% TS]
NH_4-N	ammonium nitrogen concentration [g/kg]
pKa	dissociation constant Ammonium ion [–]
RF	raw fiber [% TS]
RL	raw lipid [% TS]
RP	raw protein [% TS]
TAN	total ammonia nitrogen [g/l]
TKN	total nitrogen concentration [g/kg]
TS	total solids [%]
TVFA/alkalinity	stability criterion [–]
VS	volatile solids [% TS]
ThOD	theoretical oxygen demand [kg_{COD}/kg_{TS}]
X_{Ch}	concentration of particular carbohydrates [kg_{COD}/m^3]
X_I	concentration of particular inerts [kg_{COD}/m^3]
X_{Li}	concentration of particular lipids [kg_{COD}/m^3]
X_{Pr}	concentration of particular proteins [kg_{COD}/m^3]

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tion Model No. 1 (Batstone et al., 2002) has mainly been used for simulation of the fermentation of different substrates, e.g. activated and primary sludge. Nevertheless, there is an increasing trend of simulations being used for agricultural substrates (Lübken et al., 2010). Examples include cattle manure (Myint et al., 2007; Schoen et al., 2009), cattle manure and maize (Amon et al., 2007), cattle manure and co-substrates (Lübken et al., 2007), grass silage (Wichern et al., 2009) and even aquatic plants (Zhao et al., 2009).

The quality of model results depends strongly on calibration of kinetic parameters, whose estimation is usually done manually by visual comparison of experimental results (Boubaker and Ridha, 2008; Qu et al., 2009; Ramirez et al., 2009; Schoen et al., 2009). This procedure however is quite subjective and requires experience. It is quite possible that two people, given the same experimental data set, would estimate parameters differently. Wichern et al. (2009) applied a genetic algorithm and defined a fitness function as an assessment tool by minimizing the sum of differences between the logarithm of measurements and simulation results (least squares method). In the field of hydrology, the so called Nash–Sutcliffe model efficiency coefficient (Nash and Sutcliffe, 1970) is widely used in order to assess the quality of simulations compared to observed data.

By running two reactors in parallel under mesophilic conditions fed with grass silage, experimental data from nearly one year of operation with stepwise increasing organic loading rates were collected. Koch et al. (2009) provided knowledge on the monofermentation of grass silage itself. The focus of this paper deals mainly with the calibration and application of the ADM1 to grass silage. A new approach to transfer measurements to COD via theoretical oxygen demand (ThOD) and another possibility to distinguish between degradable and non-degradable part of cellulose and hemicellulose via a factor d are presented. Furthermore, the ADM1 has been extended to describe the influence of high solids concentrations on hydrolysis. The modified Nash–Sutcliffe model efficiency coefficient was applied as an alternative methodology for model calibration. Besides the comparison of modeled parameters with observed data of biogas production and composition (methane, carbon dioxide and hydrogen) as well as the simulation of volatile fatty acids, the emphasis of the paper presented is the nitrogen cycle. This is of high interest as both ammonium and ammonia play an important part in anaerobic digestion of grass silage.

2. Methods

2.1. Reactor set-up and operation

Two loop reactors were run as duplicates, indicated in the following as reactor L and reactor R. Both reactors, each with an operating volume of 50 l, were fed daily with grass silage, mixed permanently at 60 rpm, and run as mesophilic fermenters at 38 °C. Depending on the organic loading rate (OLR) of 1.0–3.5 $kg_{VS}/(m^3$ d) and the amount of water added, substrate retention time in the fully mixed reactor was 50–440 days. A detailed description of the reactors, origin of material and its composition, as well as findings concerning the digestion process can be found in Koch et al. (2009).

2.2. Mathematical model

The Anaerobic Digestion Model No. 1 (ADM1) was published in 2002 (Batstone et al., 2002). This highly complex model is characterized by 19 biochemical conversion processes and 24 dynamic state variables. Simulations were executed with SIMBA 4.2 based on Matlab/Simulink (Version 7.0.4).

2.3. Nash–Sutcliffe coefficient

By qualifying the sum of differences to the average of measurements, it is not only possible to find parameter sets with best fit, but also quantitatively describe the accuracy of model outputs. The applied methodology to adapt ADM1 to grass silage followed a two-step procedure. First, all kinetic parameters were set to default ADM1 values. Second, simulations were run by varying sensitive parameters (e.g. maximum uptake rate k_m, half saturation coefficient K_S and inhibition constant K_I). The agreement of the simulation results compared to measurements has been evaluated on the basis of the modified Nash–Sutcliffe coefficient (Nash and Sutcliffe, 1970) by:

$$E = 1 - \frac{\sum_{i=1}^{n} |X_{measured} - X_{measured}|}{\sum_{i=1}^{n} |X_{measured} - \overline{X}_{measured}|} \tag{3}$$

where $X_{measured}$ and $X_{simulated}$ are measured and simulated values respectively, and $\overline{X}_{measured}$ is the average of all measurements. In

its modified version, the term of the squared differences is replaced by their absolute values to avoid sensitivity to outliers. This modification guarantees that a difference is as dominant as two differences with half the value each. An efficiency of 1 corresponds to a perfect match of modeled parameters to observed data, where an efficiency of 0 indicates that the model prediction is as accurate as the mean of the observed data. Values below 0 evaluate the simulation worse than the simple average of measurements.
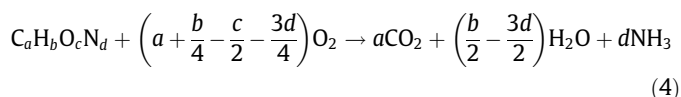
3. Results and discussion

3.1. Characterization of influent

As ADM1 is COD-based and its measurement is still unusual in biogas plants, COD needs to be calculated from available data. In fodder analysis, silages are typically characterized in terms of total solids (TS), volatile solids (VS) and nutrient content. Previous research correlated VS and COD to transfer measured data of VS to COD (Lübken et al., 2007; Wichern et al., 2009). In most cases this approach is sufficient. Nevertheless, as the composition of silage is known, a calculation of theoretical oxygen demand (ThOD) can be done easily. Therefore, grass silage that is fed is fractioned on the basis of the extended Weender analysis (Van Soest and Wine, 1967; Naumann and Bassler, 1993) according to Fig. 1 into raw protein (RP), raw fat (RL), raw fiber (RF) and nitrogen free extracts (NfE) as well as into neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL). On the basis of this analysis, carbohydrates (RF + NfE) can be further divided into starch (RF + NfE − NDF), hemicellulose (NDF − ADF), cellulose (ADF − ADL) and lignin (ADL). Table 1 shows average influent characteristics.

Oxidation of organic compounds can be described by the following reaction. By means of a relation between calculated and measured COD it became clear that nitrogen is not nitrified, but rather converted to ammonia (Gerike, 1984):

$$C_aH_bO_cN_d + \left(a + \frac{b}{4} - \frac{c}{2} - \frac{3d}{4}\right)O_2 \rightarrow aCO_2 + \left(\frac{b}{2} - \frac{3d}{2}\right)H_2O + dNH_3 \quad (4)$$

The basic molecule of starch, cellulose, and hemicelluloses is glucose. For the calculation of theoretical oxygen demand (ThOD), all three compounds were initially summarized into one fraction, independent of their digestibility. Lignin is an amorphous polymer, comprised of aromatic basic modules, that has no defined structure or elemental composition. Nadji et al. (2009) specified Dioxane Lignin isolated from Alfa grass as $C_{10.92}H_{14.24}O_{5.76}$. As lignin is not degradable under anaerobic conditions, it is completely allocated to the inert fraction. Elemental compositions of protein and lipid are taken from Angelidaki and Sanders (2004). The ThOD of different fractions with known elemental compositions can be calculated by the following equation:

$$ThOD = \frac{16(2a + 0.5(b - 3d) - c)}{12a + b + 16c + 14d} \left[\frac{g_{O_2}}{g_{C_aH_bO_cN_d}}\right] \quad (5)$$

With respect to the composition, the theoretical oxygen demand of any substrate ranges between 1.19 and 2.90 g_{O_2}/g_{TS} (see Table 2). As the lipid part is usually quite moderate in grass silage, the range is limited from 1.2 to 1.6 g_{O_2}/g_{TS}. The values received by the aforementioned regression analysis between COD and VS (Lübken et al., 2007; Wichern et al., 2009) are in a similar range (see Table 2). However, in contrast to the approach presented in this work, it is not universally applicable.

Since grass silage was fed as dried material and subsequently mixed with water, the influent is only divided into particular model fractions. For calculation of grass silage representing composite material X_c, the fractions of proteins (RP), lipids (RL), carbohydrates (RF + NfE − ADL), and inerts (ADL) are summed up after multiplication with their individual theoretical oxygen demand:
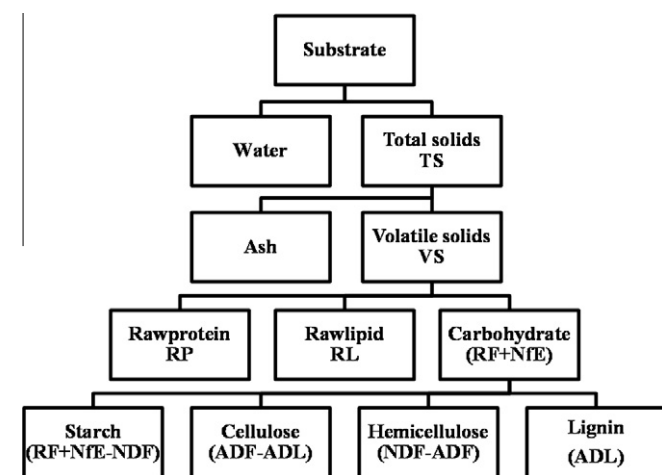
$$X_c = \rho_{Substract} \cdot TS \cdot ((RP \cdot ThOD_{Pr}) + (RL \cdot ThOD_{Li}) + (ADL \cdot ThOD_1)$$
$$+ (RF + NfE - ADL) \cdot ThOD_{Ch}) \quad [kg_{COD}/m^3] \quad (6)$$

where $\rho_{Substrate}$ is the density of grass silage in the reactor [kg/m³], TS is the total solids content [%] and $ThOD_x$ is the theoretical oxygen demand of the corresponding fraction [kg_{COD}/kg_x]. Independent of the degradation rate, cellulose, hemicellulose and starch are first summarized in one fraction. Afterwards, the fractionation into degradable carbohydrates and inert materials is done by f-factors (see below). As ADM1 is based on volumetric flow, mass is transferred via density of substrate. In the reactor, this density is equal to that of water (1.000 kg/m³). The sum of all four fractions is the composite material X_c, representing the grass silage in the influent. Water (1 − TS) and ash (TS-VS) are not considered as they by definition do not contain COD.

Fig. 1. Determination of substrate composition by extended Weender analysis.

Table 1
Main components of grass silage.

Parameter	Unit	Grass silage
Volatile solids VS	% TS	91.2
Raw protein RP	% TS	17.1
Raw fiber RF	% TS	26.4
Raw lipid RL	% TS	3.0
NfE[*]	% TS	44.7
NDF	% TS	54.0
ADF	% TS	32.3
ADL	% TS	5.3

[*] Calculated value.

Table 2
Theoretical oxygen demand (ThOD) of different fraction.

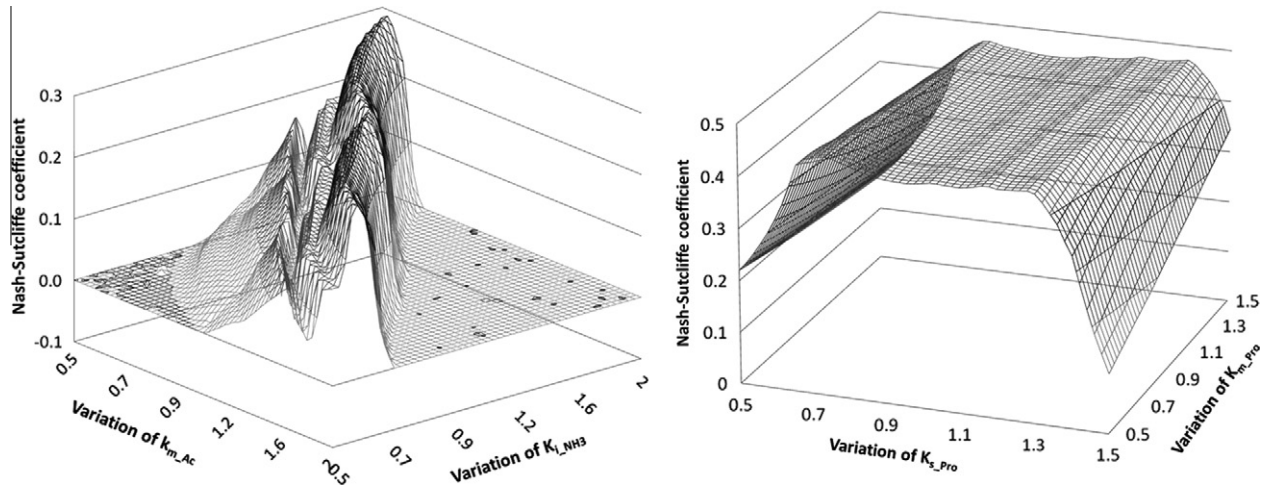| Fraction	Elemental formula	Molar mass [g/mol]	ThOD [kg_{O_2}/ kg_{TS}]
Protein (Pr)	$C_5H_7O_2N$	113	1.42
Lipid (Li)	$C_{57}H_{104}O_6$	884	2.90
Starch, cellulose, hemicelluloses (Ch)	$(C_6H_{10}O_5)_n$	$162n$	1.19
Lignin (I)	$C_{10.92}H_{14.24}O_{5.76}$	237.44	1.56
Lübken et al. (2007)	Agricultural substrate		1.56
Wichern et al. (2009)	Grass silage		1.30
	Reactor biomass		1.45

Fig. 2. Impact of the variation of kinetic parameters on the goodness of fit (measured as Nash-Sutcliffe coefficient).

The composite material X_c is first separated into the different fractions of proteins (X_{Pr}), lipids (X_{Li}), carbohydrates (X_{Ch}), and inerts (X_I) by fixed stoichiometric expressions (f-factors). It has been shown that the subsequent hydrolysis of starch, cellulose and hemicellulose and conversion to biogas runs at several rates (Myint et al., 2007). Hence, the mixed fraction of carbohydrates (RF + NfE − ADL) needs to be divided. One possibility is to introduce a slowly and a readily degradable carbohydrate fraction as has been proposed by Myint et al. (2007). Another possibility (see Eqs. (7)–(10)) is to divide the mixed fraction into a carbohydrate fraction of starch (RF + NfE − NDF) and a degradable part of cellulose and hemicellulose ((NDF − ADL)·d), while the rest is added to the inert fraction consisting of lignin (ADL) and the non-degradable part of cellulose and hemicellulose ((NDF − ADL)·(1 − d)). The factor d regulates the proportion. Dividing all f-factors by the VS content guarantees that the sum is 100% and composite material is completely split into single fraction (Table 3).

$$f_{Pr\_Xc} = \frac{RP}{VS} \quad [kg_{COD}/kg_{COD}] \tag{7}$$

$$f_{Li\_Xc} = \frac{RL}{VS} \quad [kg_{COD}/kg_{COD}] \tag{8}$$

$$f_{Ch\_Xc} = \frac{(RF + NfE - NDF) + (NDF - ADL) \cdot d}{VS} \quad [kg_{COD}/kg_{COD}] \tag{9}$$

$$f_{Xi\_Xc} = \frac{ADL + (NDF - ADL) \cdot (1 - d)}{VS} \quad [kg_{COD}/kg_{COD}] \tag{10}$$

where d is the percentage of the degradable part of cellulose and hemicellulose that is mainly influenced by the specific substrate, the biocenosis, and the retention time. Percentage d is generally calibrated with the gas curve, but as the degradation level (D_{VS}) is known, it can also be calculated. Assuming a total degradation of lipids (RL), proteins (RP), starch (RF + NfE − NDF) and degradable part of cellulose and hemicellulose ((NDF − ADL)·d), the degradation level can be calculated as follows:

$$D_{VS} = \frac{RL + RP + (RF + NfE - NDF) + (NDF - ADL) \cdot d}{RL + RP + (RF + NfE - NDF) + (NDF - ADL) + ADL} \quad [\%] \tag{11}$$

By solving d and introducing VS as the sum of RP, RL, RF and NfE, the equation for calculation of the degradable part of cellulose and hemicellulose d at a known level of degradation D_{VS} is obtained:

Table 3
Influent COD fractioning after disintegration according to f-factors.

Parameter	Unit	Description	Grass silage
f_{Pr_Xc}	–	Proteins from X_c	0.187
f_{Li_Xc}	–	Lipids from X_c	0.033
f_{Ch_Xc}	–	Carbohydrates from X_c	0.401
f_{Xi_Xc}	–	Inerts from X_c	0.379
d	–	Degradable part of cellulose and hemicellulose	0.36

$$d = \frac{NDF - VS(1 - D_{VS})}{NDF - ADL} \quad [\%] \tag{12}$$

With the values of VS, NDF and ADL from Table 1 as well as the total level of degradation based on VS (D_{VS}) from Koch et al. (2009) specified as 60%, d is determined as:

$$d = \frac{0.54 - 0.912 \cdot (1 - 0.6)}{0.54 - 0.053} = 0.36 \tag{13}$$

where d was estimated to be 0.4 through calibration with the gas curve (see Fig. 3). Based on Eqs (5)–(8), f-factors for disintegration of composite material X_c are obtained and presented in Table 3.

After fractionation the organic material is hydrolyzed and consequently available for the microorganisms. As factor d regulates the portion of the degradable part of cellulose and hemicellulose and as lipids are only present in small amounts, hydrolysis constants k_{hyd_Ch} and k_{hyd_Li} remain at the default ADM1 value of $10 \, d^{-1}$. Only the hydrolysis rate of proteins k_{hyd_Pr} has been changed from the default value of $10 \, d^{-1}$ to $0.8 \, d^{-1}$ for grass silage. This value corresponds with hydrolysis constants of proteinaceous substrates reported in literature (Pavlostathis and Giraldo-Gomez, 1991). Since hydrolysis is affected by solids concentration, an influence function on the hydrolysis of proteins, carbohydrates and lipids has been integrated (cf. chapter 3.3).

3.2. Nitrogen incorporation and release

High ammonia concentrations might be the driving force for instabilities in monofermentation of grass silage. A detailed description of nitrogen incorporation into and the release out of biomass seemed to be a basis for realistic modeling results. As the original ADM1 recycles decayed biomass to composite material
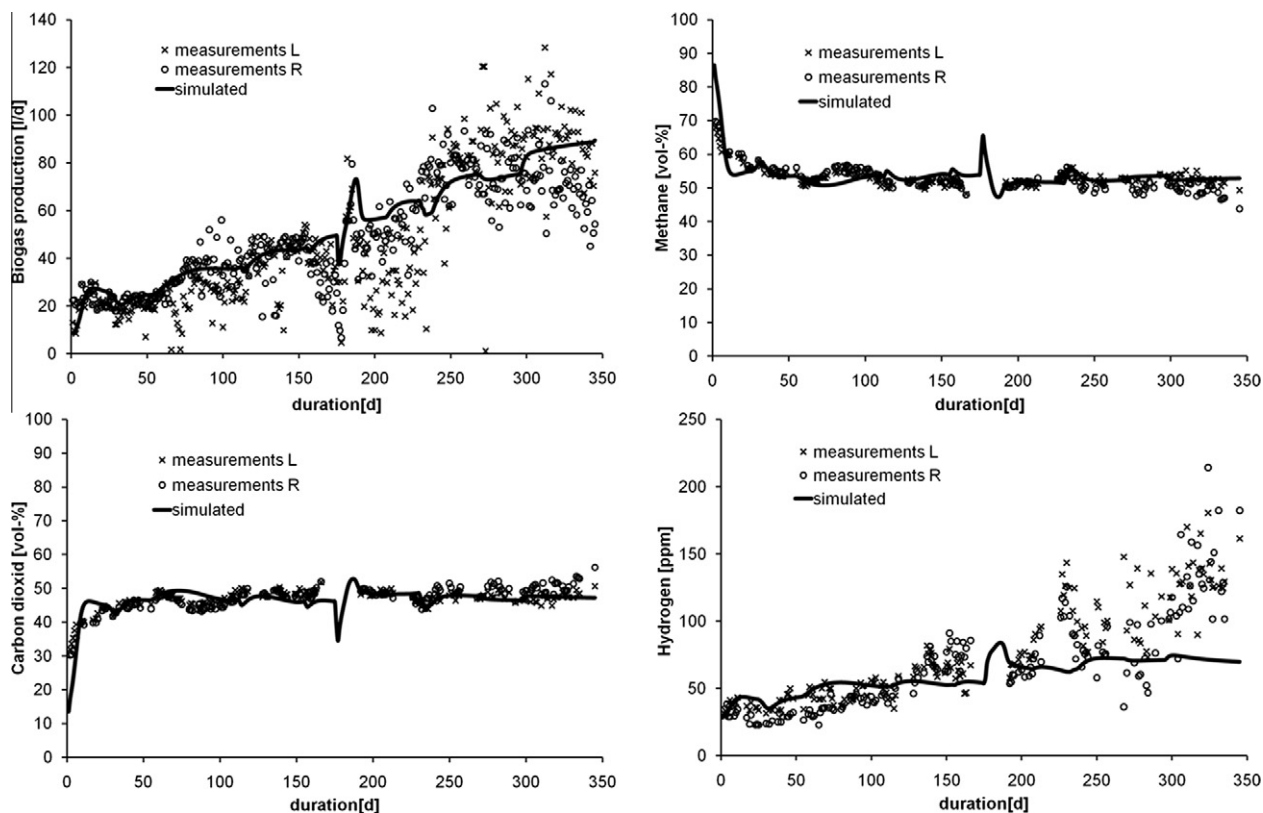
Fig. 3. Simulation results and measured data for biogas flow and composition.

X_c, substances with different characteristics (e.g. nitrogen content) are linked. Therefore, a separate compound of inert decay products similar to ASM1 as proposed by Wett et al. (2006) has been integrated in ADM1 for a more detailed description. A fraction of the decayed biomass (f_p) is converted to the biomass decay products X_p (implemented as a new model variable). Thus, nutrient mineralization is included in the model. It was possible to close the nitrogen mass balance by using the values of ASM1 (Henze et al., 1987) and from Wett et al. (2006) as presented in Table 4, which led to a good agreement concerning total nitrogen concentration. Without the fraction of the decayed biomass it would not be possible to simulate the accumulation of nitrogen.

3.3. Solids influence on hydrolysis

The above described modifications of ADM1 enabled the simulation of the total nitrogen concentration properly (see Fig. 4). Nevertheless, it was not possible to simulate the ammonia nitrogen release precisely. It was assumed that a constant hydrolysis rate in the model did not adequately describe the process. Lack of water or rather high solids content in the reactor negatively influences

the anaerobic digestions process (see Koch et al. (2009)). Pommier et al. (2007) focused on the influence of water on the solid waste methanization and observed a strong dependence of kinetic rates and maximum methane production with the moisture level. Qu et al. (2009) showed that the process of hydrolysis at low moisture is most likely inhibited. In order to cope with this claim, solids influence on hydrolysis has been integrated in ADM1 with the following equation. It has been added to the kinetic rate equations for hydrolysis of proteins, carbohydrates and lipids. Vavilin et al. (2004) used a similar approach to describe the inhibition of hydrolysis and methanogenesis by volatile fatty acids:

$$\rho_j = k_{hyd} X \frac{1}{1 + \left(\frac{TS}{K_{hyd}}\right)^{n_{hyd}}} \tag{14}$$

where k_{hyd} is the hydrolysis rate [d^{-1}], X is the concentration of the concerning fraction [kg$_{COD}$/m^3], TS is the concentration of solids [kg$_{TS}$/kg$_{FM}$], K_{hyd} is the hydrolysis influence coefficient [kg$_{TS}$/ kg$_{FM}$] and n_{hyd} is the corresponding degree index. Using the function allows for the description of sharp or smooth influence of solids on hydrolysis and for fitting the ammonia nitrogen curves.

3.4. Calibration of kinetic parameters

Once the influent is characterized and ammonia can be simulated due to the aforementioned modifications, default kinetic parameters need to be adapted to the substrate. In principle, all affecting parameters can be varied and a Nash–Sutcliffe coefficient is obtained for every combination. For a better visualization, a variation of only two parameters is advisable in order to draw the agreement on the z-axis. Two examples of changing agreement at varying factors (multiplied with ADM1 default parameter) are illustrated in Fig. 2. Compared to the left graph, where the maxi-

Table 4
Nitrogen content of involved fractions.

Parameter	Unit	Description	Value
N_{aa}	kmol$_N$/kg$_{COD}$	N content amino acids	0.007[a]
N_{Xc}	kmol$_N$/kg$_{COD}$	N content composite material	0.0013[b]
f_p	–	Stoichiometric factor	0.08[c]
N_{XB}	kmol$_N$/kg$_{COD}$	N content biomass	0.00625[a]
N_{Xp}	kmol$_N$/kg$_{COD}$	N content biomass decay product	0.0043[d]

[a] Default ADM1 value.
[b] Calculated value (N_{aa}·f_{Pr_Xc}).
[c] Absorbed from ASM1.
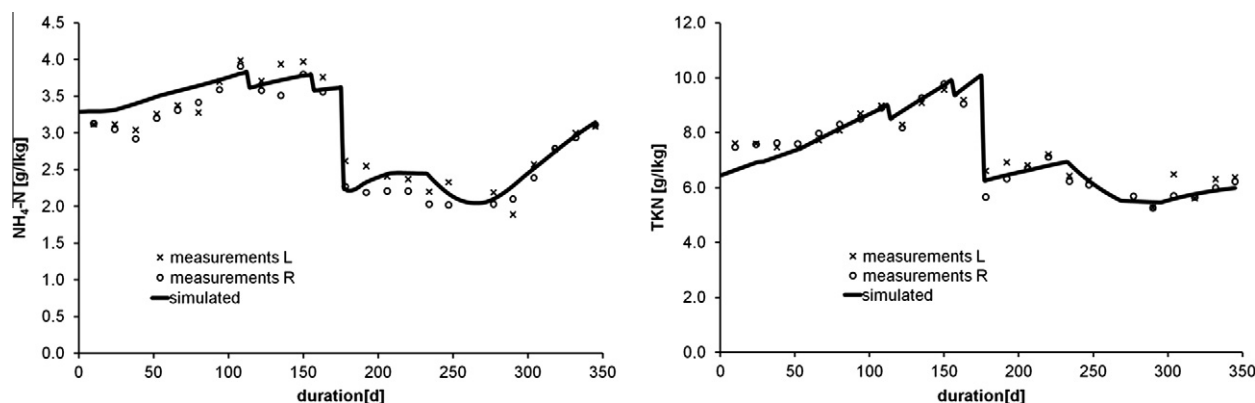[d] From Wett et al. (2006).

Fig. 4. Simulation results and measured data for ammonium and total nitrogen concentration.

mum of the Nash–Sutcliffe coefficients for k_{m_AC} and K_{I_NH3} are local ones, the maximum on the right graph is a global one and K_{S_Pro} and k_{m_Pro} may change over a large range without influencing the fit. Furthermore, it becomes clear that the Nash–Sutcliffe coefficient for the modeled and measured concentration of acetate (at constant K_{S_Ac}) is influenced by changing k_{m_Ac} as well as by changing K_{I_NH3}. The Nash–Sutcliffe coefficient tended to increase with a raised K_{I_NH3} and lowered k_{m_Ac} and vice versa. The fit of propionate at constant $K_{I\_H2\_Pro}$ is influenced more by changing K_{S_Pro} than k_{m_Pro}, but as the default ADM1 values (multiplication with 1.0) of both parameters are in the global maximum, adaption is not required.

By indicating a parameter set with the best fit, possible equifinality of models has to be kept in mind. Equifinality means that there is not simply one optimal parameter set that represents a system, but rather several combinations of parameter values for a chosen model structure may fit the data equally well. On this account, Ge et al. (2010) and Batstone and Keller (2001) for instance specified the parameter not by single values, but by confidence regions. Thus, not the parameter value itself is important, but rather the combination. The result of several combinations (as exemplary presented in Fig. 2) leads to a kind of map, consisting of global and local highs and lows. Specification of parameters is consequently problematic; however for running a simulation one tupel of parameter values needs to be chosen.

Based on knowledge of equifinality, the number of modified parameters was reduced to only a few sensitive ones. As can be seen in Table 5, it was possible to fit the data by changing only hydrogen inhibition constants and the maximum uptake rate for acetate. The range of calibrated parameters are quite similar to that of Wichern et al. (2009), who already stated that the hydrogen inhibition constant applied for propionate and valerate/butyrate uptake for grass silage is around two orders of magnitude lower than for activated sludge digestion. Furthermore, the maximum uptake rate for acetate has been decreased from 8.0 to 4.4. Both the hydrolysis influence coefficient K_{hyd} and corresponding degree

index n_{hyd} are calibrated with the curves of ammonium and total solids.

By inserting K_{hyd} and n_{hyd} in Eq. (14), the influence on hydrolysis is obtained. The influence term of total solids (TS) ranges between 0.05 for 9% TS and 0.014 for 16% TS. Hence, the hydrolysis constants k_{hyd_Ch} and k_{hyd_Li} are decreased from $10 \, \mathrm{d}^{-1}$ to $0.14 \, \mathrm{d}^{-1}$ by high solids concentration and to $0.5 \, \mathrm{d}^{-1}$ by low solids concentration. This rate is equal to that value received by Koch et al. (2009), who amounted the rate limiting step in anaerobic digestion of grass silage to $0.6 \, \mathrm{d}^{-1}$ under optimal conditions.

3.5. Modeling of reactor performance

Fig. 3 presents measured data of both reactor L and reactor R (run in duplicate) in comparison to simulation results for the gas flow and the main biogas compounds methane, carbon dioxide and hydrogen. A good agreement between simulation results and measurements was achieved, where a satisfying prediction of biogas flow and composition is an indicator for realistic influent characterization. Throughout the reactor operation, grass silage was added at the original water content of about 50% (dried and chopped grass silage and water one half each). This caused an increase of the TS content in the reactor up to 16% (cf. Fig. 5). The increase of reactor total solids content with higher organic loading rates subsequently worsened the substrate rheology as well as the hydrolysis and therefore, biogas production dropped in both reactors (day 145). In order to reduce the TS, a part of the reactor content was withdrawn and substituted by water on day 176. As a consequence, the rheology improved and the biogas production increased noticeably after several days of adaption. Despite the fact that the grass silage to water ratio was fixed afterward to 1:2, the concentration of solids still rose. It was set to 1:4 from day 234 on.

Up to the water addition at day 176, the hydrogen concentration was predicted quite well. Afterwards, the concentration is underestimated by the model. In order to find a better agreement to measurements, the concentration of hydrogen was calibrated

Table 5
Default ADM1 parameters and calibrated values under mesophilic condition for grass silage.

| Parameter	Unit	Description	ADM1 value	Wichern et al. (2009)	This study
K_{S_H2}	kg_{COD}/m^3	Half saturation coefficient of hydrogen	7×10^{-6}	4.2×10^{-5}	5.6×10^{-5}
$K_{I\_H2\_Pro}$	kg_{COD}/m^3	Hydrogen inhibition constant for propionate uptake	3.5×10^{-6}	4.8×10^{-8}	4.6×10^{-8}
$K_{I\_H2\_C4}$	kg_{COD}/m^3	Hydrogen inhibition constant for valerate and butyrate uptake	1×10^{-5}	5.4×10^{-8}	5×10^{-8}
k_{m_Ac}	d^{-1}	Maximum uptake rate acetate	8.0	8.0	4.4
K_{hyd}	kg_{TS}/kg_{FM}	Hydrolysis influence constant	–	–	2.5
n_{hyd}	–	Hydrolysis influence degree index	–	–	2.3
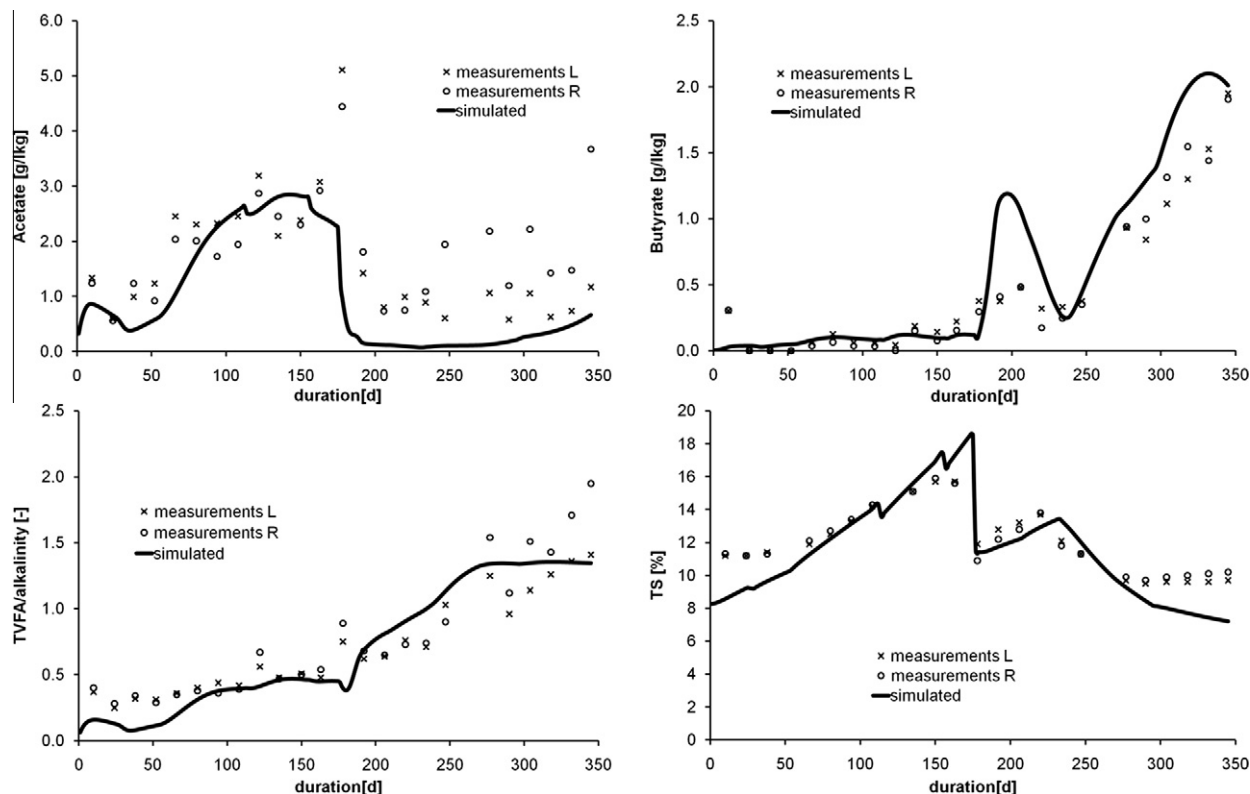
Fig. 5. Simulation results and measured data for acetate and butyrate concentration, stability criterion TVFA/alkalinity and total solids concentration.

with the maximum uptake rate and the half saturation coefficient of hydrogen. Nevertheless, the graph depicted in Fig. 5 was the one with the best fit. In contrast to that, the share of methane and carbon dioxide can be easily modeled.

As presented in Fig. 4, both total nitrogen (TKN) and ammonium content (NH_4-N) can be reproduced very well by the model even under changing conditions (e.g. after water addition at day 176). The maximum ammonium concentration (NH_4-N) of 4.0 g/l is equal to a free ammonia nitrogen (FAN) concentration of 0.5 g/l under mesophilic conditions and at a nearly constant pH value of 8.0. The 50% inhibition threshold value of 0.22 g/l published by Gallert and Winter (1997) is clearly exceeded. Hence, an inhibition of the digestion process by ammonia is supposable.

Increasing ammonium concentrations lowered the activity of methanogenic archaea, which led to an accumulation of intermediate products such as acetate. After the ammonium concentration was lowered by adding water, acetate was degraded. At the end, the process was overloaded as indicated by the accumulation of fatty acids (e.g. butyrate). In contrast to the less dynamic pH value (not shown), the ratio TVFA/alkalinity (so called FOS/TAC) is able to predict instabilities. Its calculation in the model has been implemented according to Schoen et al. (2009). As it has been pointed out by Koch et al. (2009), the concentration of total solids in the reactor is limited to a threshold value. According to the aforementioned calculation of theoretical oxygen demand (ThOD), COD-based output of the model can be related back to the solid concentration (Fig. 5).

Finally, the visual impression of the simulation results compared to observed data can be quantified by the Nash–Sutcliffe coefficient (Table 6). While biogas flow, total nitrogen, ammonium and butyrate concentrations as well as the stability criterion TVFA/alkalinity all show high agreement with a maximum of 75% of coverage, the methane and carbon dioxide contents prediction is slightly worse than the simple average. This is caused by the less dynamic progression of the graphs. Despite similar operation of both reactors, the value for acetate is highly different. Nevertheless, the Nash–Sutcliffe coefficient is a useful tool to assess the degree of fit of modeled to measured data. The simulations presented have mostly shown a high degree of agreement.

4. Conclusions

A detailed description of nitrogen incorporation and release and implementation of the hydrolysis influence function by solids allows for an adequate prediction of the ammonia nitrogen curve. Kinetic parameters from ADM1 were calibrated by evaluating simulation quality according to the modified Nash–Sutcliffe coefficient. Variable influence of the parameters on the degree of fit has been shown. It became clear that only a few needed to be modified. Only changes of hydrogen inhibition constants and maximum uptake of acetate compared to the ADM1 default values were necessary in order to fit the measurements. The adapted ADM1 showed good agreement with measurement data.

Table 6
Nash–Sutcliffe coefficient of simulation results compared to measurements.

Parameter	Description	Reactor L	Reactor R
Q_{Gas}	Biogas flow	0.52	0.51
CH_4	Methane	−0.11	−0.06
CO_2	Carbon dioxide	−0.11	−0.06
H_2	Hydrogen	0.23	0.20
TKN	Total nitrogen	0.68	0.75
NH_4-N	Ammonium	0.67	0.71
S_{Ac}	Acetate	0.08	−0.71
S_{Bu}	Butyrate	0.46	0.57
TVFA/alkalinity		0.63	0.59
TS	Total solids	0.27	0.19

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