ADM1 simulation of the thermophilic mono-fermentation of maize silage – Use of an uncertainty analysis for substrate characterization

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Abstract
The Anaerobic Digestion Model No. 1 (ADM1) was applied for the mathematical simulation of the thermophilic mono-fermentation of maize silage. Data from a period of 140 days of pilot plant operation were used for model calibration. The substrate characterization in terms of carbohydrates, proteins, lipids and inert matter was based on data derived from fodder analysis. The model was capable of adequately simulating the total biogas production, biogas composition, pH values and the concentrations of total nitrogen, ammonia nitrogen and volatile fatty acids. An uncertainty analysis was conducted considering variations in substrate composition in terms of carbohydrates, proteins and lipids. An uncertainty range of ± 20% for the measured feedstock composition in terms of proteins, lipids and lignin was used to calculate the main ADM1 inflow fractions. Within this uncertainty range the simulation results for the total biogas production and biogas composition showed only low variations. The simulated concentrations of propionic, butyric and valeric acids varied to a medium degree. Significant higher variations in model output were calculated for the parameters ammonium nitrogen and acetic acids, which in turn implies that model calibration is strongly correlated to the characterisation of the substrate.

Keywords
ADM1; thermophilic fermentation; maize silage; uncertainty analysis; substrate characterization

INTRODUCTION

The efficient utilization of anaerobic technologies depends on a comprehensive understanding of the complex processes involved in the conversion of organic matter to biogas. Mathematical models like ADM1 (Batstone et al. 2002) can be a very helpful tool for both process comprehension and optimization. Since its publications the ADM1 model was applied for a broad variety of organic substrates and reactor configurations. The model structure is complex and many kinetic and stoichiometric parameters influence to a certain degree the simulation results. The properly definition of model parameters is fundamental and several studies are available dealing with this topic (Donoso-Bravo et al. 2011). Simulation results are in general compared to measuring data, and the model is regarded as calibrated when the simulated values are not beyond the typical errors of measurement of the single process parameters. However, the uncertainty of feedstock characterisation in terms of single model state variables is hardly considered in such studies. Even more for a complex model like ADM1, which distinguishes between different nutrient matter like carbohydrates, proteins and lipids, the realistic description of the input substrate is fundamental (Kleerebezem & van Loosdrecht 2006; Girault et al. 2012).

When organic biomass with a distinct lignocellulosic content are used for anaerobic digestion, the inflow characterization for ADM1 has mainly been performed on measuring data derived from fodder analytics (Lübken et al. 2007; Wichern et al. 2009; Koch et al. 2010; Thamsiriroj & Murphy 2011). In that way the contents of proteins, lipids, fibers, cellulose, hemicellulose and lignin can be used to determine the single ADM1 fractions in terms of chemical oxygen demand (COD). However, such measurements are usually realized for control samples, and in the time period between sampling the substrate composition is probably not constant. The composition and

degradability kinetics of the agricultural lignocellulosic biomass, which is available as silages for digesters, can also vary depending on the storage conditions (Herrmann & Rath 2012). This study covers the uncertainty of substrate characterisation and assesses its impact on the simulation results.

MATERIAL AND METHODS

Analytical methods

Analytical methods were based on German Standard Methods for the examination of water, wastewater and sludge (DEV, 1981). Volatile fatty acids (acetic acid, propionic acid, i-butyric acid, n-butyric acid, i-valeric acid and hexanioc acid) were quantified by means of a GC/FID (CE Instruments, HRGC 5300). 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 (PR), crude fat (LI), crude fiber and N-free extract (Weender analysis). Carbohydrates were further divided into hemicellulose, cellulose and lignin (LG) (van Soest Analysis).

Experimental fermenter

The pilot plant consisted of a stirred cylindrical reactor and was operated for 140 days at a temperature of 55°C. The total volume of the reactor was 700 L, with 500 L working volume and 250 L headspace. The reactor was operated with maize silage in mono-fermentation without addition of manure. Maize silage was taken from a farm in the north of Munich, Germany. The mean total solids (TS) content of the substrate was 36.8%, and the volatile solids (VS) content was in average 97.5% of TS. The organic loading rates (OLR) applied were from days 0 to 35: 0.51 $kg_{VS}/(m^3 \cdot d)$; from days 36 to 61: 1.02 $kg_{VS}/(m^3 \cdot d)$; from days 62-131: 1.53 $kg_{VS}/(m^3 \cdot d)$; from days 132 to 140: no feeding.

RESULTS AND DISCUSSION

ADM1 was used for the simulation of the bio-chemical processes. For a better allocation of single substrate fractions, the composite material variable (Xc) and the disintegration process were omitted. The substrate composition was fractioned into carbohydrates (Xch), proteins (Xpr), lipids and inert material (XI) within the inflow stream. The calculation of the inflow fractions was done according to data from fodder analysis (Lübken et al. 2007). The content of each component was first calculated in terms of total solids (TS) and then converted to normalized COD fractions.

During the operation of the pilot plant high specific biogas production rates were achieved, varying between 992 to 1062 $LN/(kg_{VS} \cdot d)$. This corresponds to an almost complete degradation of the organic fraction of the maize silage. In a first step ADM1 was calibrated to predict main measured process variables (Figure 1). Calibrated kinetic parameters were not considered for the uncertainty analysis ($k_{hyd\_CH} = 1.05$ 1/d; $k_{hyd\_PR} = 0.60$ 1/d; $k_{hyd\_LI} = 2.00$ 1/d; $k_{dec} = 0.2$ 1/d; $k_{m,c4+} = 18$ 1/d; $K_{I,H2,c4+} = 5.55 \cdot 10^{-6}$; $k_{m,pro} = 12$ 1/d; $k_{m,ac} = 18.5$ 1/d; $K_{S\_h2} = 1.16 \cdot 10^{-4}$). The measured parameters used for model calibration include the total biogas production and composition (methane, carbon dioxide and hydrogen contents), the pH value, the volatile fatty acids concentrations, the total nitrogen and ammonia-nitrogen concentrations. In a second step the inflow fractions of the substrate in terms of carbohydrates ($f_{xc,ch}$), proteins ($f_{xc,pr}$), lipids ($f_{xc,li}$) and inert material ($f_{xc,xi}$) were considered for a Monte Carlo uncertainty analysis. The measured contents of proteins (PR), lipids (LI) and lignin (LG) from the Weender and van Soest analysis were considered with an uncertainty of $\pm$ 20%. The fraction of carbohydrates was determined to close the COD balance. For each simulation a set of the three fractions were randomly generated in the pre-defined ranges. The new values of PR, LI and LG were used to recalculate the COD fractions $f_{xc,ch}$, $f_{xc,pr}$, $f_{xc,li}$, $f_{xc,xi}$ and a simulation run was started; this process was sequentially repeated. The total COD in

the inflow stream was maintained constant for all simulation runs. The variation ranges of each parameter are given in Table 1. Figure 1 shows results of 300 simulation runs, considering the uncertainties of the substrate composition.

Table 1. ADM1 parameters for the uncertainty analysis of the substrate composition

Parameter		Unit	Basis	Min.	Max.
Carbohydrate inflow fraction	$f_{ch,xc}$	[g_{COD}/g_{COD}]	0.8200	0.7908	0.8469
Protein inflow fraction	$f_{pr,xc}$	[g_{COD}/g_{COD}]	0.0899	0.8469	0.1087
Lipid inflow fraction	$f_{li,xc}$	[g_{COD}/g_{COD}]	0.0597	0.0486	0.0720
Inert inflow fraction	$f_{xi,xc}$	[g_{COD}/g_{COD}]	0.0304	0.0244	0.0366
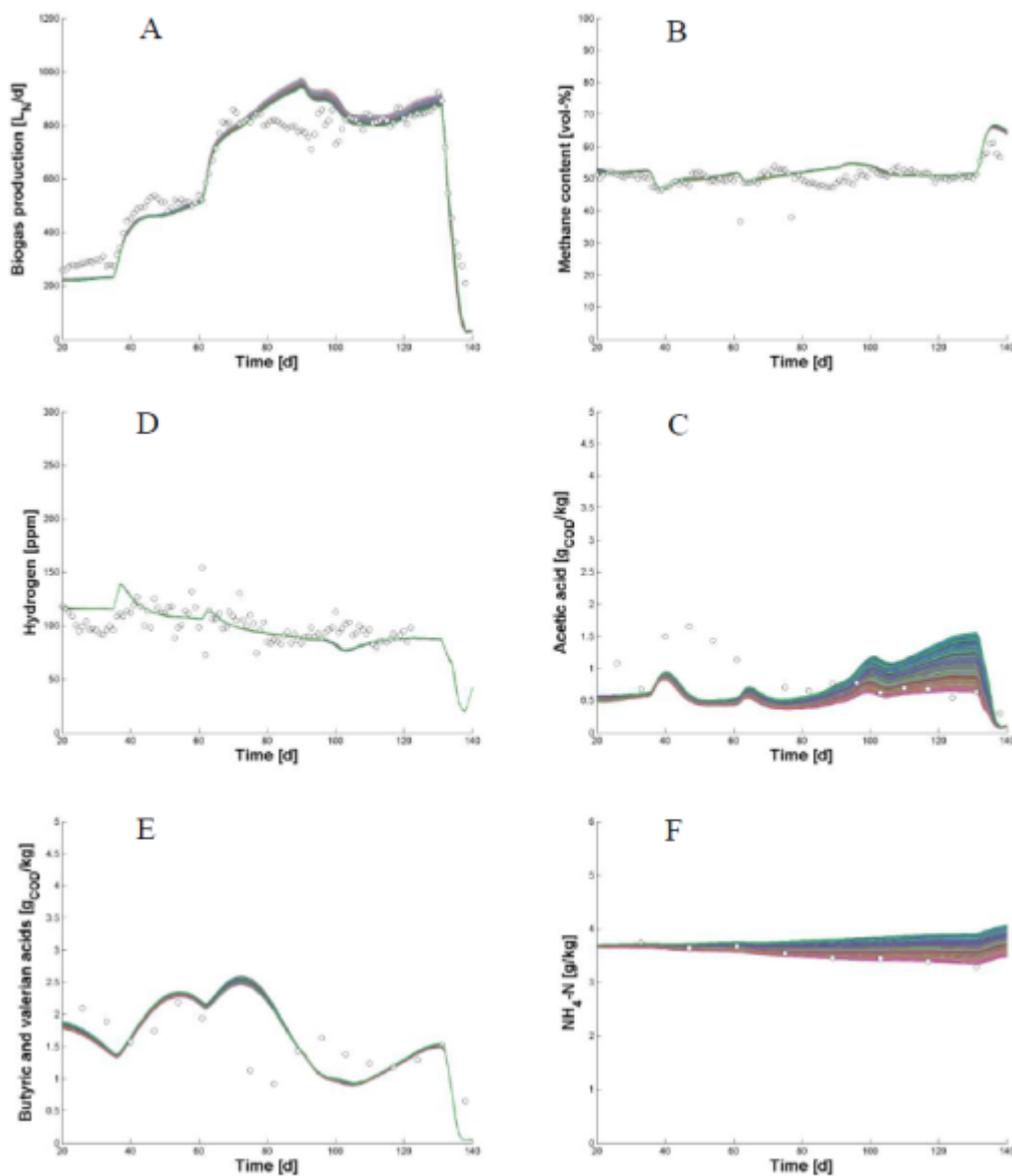
Figure 1. Measured data (doted) and simulations results (lines) for the uncertainty analysis of the substrate composition. (A) Normalized biogas production; (B) Methane content; (C) Hydrogen content; (D) acetic acid concentration; (E) Butyric and valerian acids concentrations; (F) ammonium nitrogen concentration

The results demonstrate that the sensitiveness of the total biogas production (Figure 1A) is small for lower organic loading rates. After the OLR is increased to 1.53 $kg_{VS}/(m^3 \cdot d)$ on day 62 the variation range of the simulated biogas productions increased. Biogas composition (Figures 1B and 1C) is insensitive to the applied range of parameters variation. The concentrations of the propionic (data not show), butyric and valeric acids (Figure 1E) revealed also low variations between the different simulation runs. The highest deviations during the sensitivity analysis were found for the acetic acid concentrations (Figure 1D) and for the ammonia nitrogen content. The deviation of acetic acid reached a maximum of 110% and ammonia nitrogen curve spread to a maximum of 15%. For all simulation runs the pH value showed almost no variation.

CONCLUSION

The fractionation of lignocellulosic biomass based on common fodder analysis data can be easily implemented in ADM1. Good simulation results could be obtained for thermophilic fermentation of maize silage after calibration of the model. Within an uncertainty range of ± 20% for the measured feedstock data the simulation results presented low variation ranges for the process parameters biogas production, biogas composition and selected volatile fatty acids. Significant variations in model results were calculated for the process parameters acetic acids and ammonia nitrogen. Hence, another set of kinetic parameters describing aceticlastic methanogenesis (and ammonia inhibition) could be found if the model calibration is done on the basis of different inflow characterisation. Therefore the uncertainty analysis performed in this study for feedstock analysis could be expanded to the kinetic ADM1 parameters.

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