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Parameter estimation and long-term process simulation of a biogas reactor operated under trace elements limitation

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HIGHLIGHTS

- Estimation of ADM1 parameter uncertainty by nonlinear, correlated parameter analysis.
- Unbounded confidence regions were obtained for single hydrolysis rate constants.
- ADM1 carbohydrates were divided into a slowly and readily degradable part.
- Bioavailability of trace metals explained discrepancies between modeled and measured data.

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ABSTRACT

The Anaerobic Digestion Model No. 1 (ADM1) was modified to describe the long-term process stability of a two-stage agricultural biogas system operated for 494 days with a mono-substrate. The ADM1 model fraction for carbohydrates was divided into a slowly and readily degradable part. Significant different hydrolysis rate constants were found for proteins and single fractions of carbohydrates in batch experiments. Degradation of starch, xylan (hemicellulose), cellulose and zein (protein) were modeled with first order hydrolysis rate coefficients of 1.20 d^{-1}, 0.70 d^{-1}, 0.18 d^{-1} and 0.30 d^{-1}, respectively. While the hydrolysis rate coefficients found in batch experiments could be used for predicting continuous process data, the statistically calculated confidence regions (nonlinear parameter estimation) showed that the upper limits were unbounded. Single discrepancies between measured and modeled process data of the two-stage pilot system could be explained by the lack of bioavailability of trace elements. Addition of iron, as $Fe(III)Cl_3$, allowed stable process conditions for an organic loading rate (OLR) up to 2.5 g_{VS} L^{-1} d^{-1}. Additional supplement of trace elements was necessary for process operation at OLRs above 2.5 g_{VS} L^{-1} d^{-1}.

1. Introduction

The ability to produce bioenergy from a broad range of organic substances has stimulated innovations in biogas technology during the last years. The fast progress in both technology development and substrate usage for anaerobic digestion leads to a demand of a general mathematical model, which can be used by scientists and practitioners to understand and optimize system's behavior under dynamic conditions. When the methanization of new substrates is evaluated, such as microalgae [1,2] or lignocellulosic biomass [3,4], biomechanical methane potential (BMP) tests in batch mode or continuously operated lab-scale studies are commonly performed; and this often without complemental mathematical process simulation. While the basic objective of BMP test is to estimate biodegradability of selected substrates, this method is beyond that increasingly used to determine the apparent first order hydrolysis rate constant [5,6]. However, the validation of parameters obtained in batch assays on continuous systems is often neglected [7].

The Anaerobic Digestion Model No 1 (ADM1) [8] has been established in recent years as a common platform for modeling anaerobic digestion systems. The model has been used, besides generally to predict digester performance, to assess reactor failure under external stress conditions [9–11]. One of the strengths of structured mathematical models is seen in their ability to assist in controlling the complex and often unstable anaerobic digestion process [12–14]. This, however, depends on the availability of reliable kinetic model parameters, at least for the key processes. Intensive studies on kinetic parameters estimation with respect

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to agricultural feedstock have been done so far [15–18]. However, as Donoso-Bravo et al. [19] have pointed out the determination of parameter variability and uncertainty is often neglected in model calibration studies. Within this context, the study in [20] has demonstrated that estimation of parameter uncertainty should not be done by linear, uncorrelated analysis. Confidence intervals of parameter estimates will only provide approximations of the model's uncertainty. In general, joint confidence areas for two parameters, such as the Monod half saturation constants (K_S) and the maximum specific substrate uptake rate constants (k_m), allow an estimate about the true parameter value (expressed, e.g., with a probability of 95%). Only few ADM1 simulation studies in which confidence regions for optimized parameters have been determined can be found [20–22,7].

Besides parameter uncertainty, there is a lack of experience in model applications for mono-substrates (without manure) fermentation. Mono-substrate fermentation is generally considered as less stable in long-term operation. Sufficient supply of trace elements is regarded as a limitation factor in steadily achieving high biogas production rates [23,24]. Especially at high organic loading rates the addition of trace elements can avoid process instabilities due to, e.g., ammonia inhibition [25]. Model calibration upon a system which is operated with an unrecognized deficit of micronutrients could possibly lead to a wrong estimation of kinetic parameters. On the other hand, a calibrated model could contribute knowledge to the demand of micronutrients, when discrepancies between model output and system behavior can clearly be explained by the lack of bioavailability of trace elements.

Within this study, the ADM1 was modified to describe mono-fermentation of maize silage, the most commonly used energy crop for biogas production. Process data were obtained for a two stage pilot reactor consisting of a horizontal digester as the main process step and a second vertical tank reactor, which represents a typical layout for energy crops digester. Hydrolysis rate constants were estimated on both batch and continuous process data. A two-parameter analysis method was applied to ADM1 key kinetic parameters, and the values and uncertainties were assessed by non-linear, correlated parameter estimation. An extended simulation period of 494 days was performed to enable insights into the model's capability of simulating long-term process performance.

2. Methods

2.1. Chemical analyses

Analytical methods were based on German Standard Methods for the examination of water, wastewater and sludge [26]. Volatile fatty acids (acetic acid, propionic acid, i-butyric acid, n-butyric acid, i-valeric acid, n-valeric acid and hexanioc acid) were quantified by means of a GC/FID (CE Instruments, HRGC 5300). Analysis of the single organic fractions of the lignocellulosic biomass was similar as described in [27]. At this, an extended Weender analysis [28] is performed to measure organic matter more detailed in terms of raw lipid (RL), raw protein (RP), raw fiber (RF) and N-free extract (NfE) as well as in terms of neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL). All those parameters are expressed as percentage of TS (% TS). Raw proteins can be further distinguished into amides, like for instance free amino acids, acid amides, or peptides. The residue is consequently pure protein. The term "N-free extracts" refers to the soluble carbohydrate of the feed and is the only component, which is not determined analytically, but calculated by difference. Carbohydrates are further

Table 1
Mean substrate characteristics for the maize silage used in this study.

Parameter	Unit	Maize silage
TS	(%)	36.8
VS	(% TS)	97.5
COD	(g kg^{-1})	461
Lactic acid	(mg kg^{-1})	30,000
Propionic acid	(mg kg^{-1})	400
Acetic acid	(mg kg^{-1})	4,900
pH	(–)	3.9
TKN	(g kg^{-1})	4.8
NH_4–N	(g kg^{-1})	0.78
RP (raw protein)	(% TS)	8.0
RF (raw fiber)	(% TS)	17.7
RL (raw lipid)	(% TS)	2.6
Hemicellulose	(% TS)	22.1
Cellulose	(% TS)	18.7
Lignin	(% TS)	3.2
N-free extract (NfE)	(% TS)	69.2
C, H, O, N, S	(% VS)	44.1, 6.0, 44.1, 1.3, 0.06

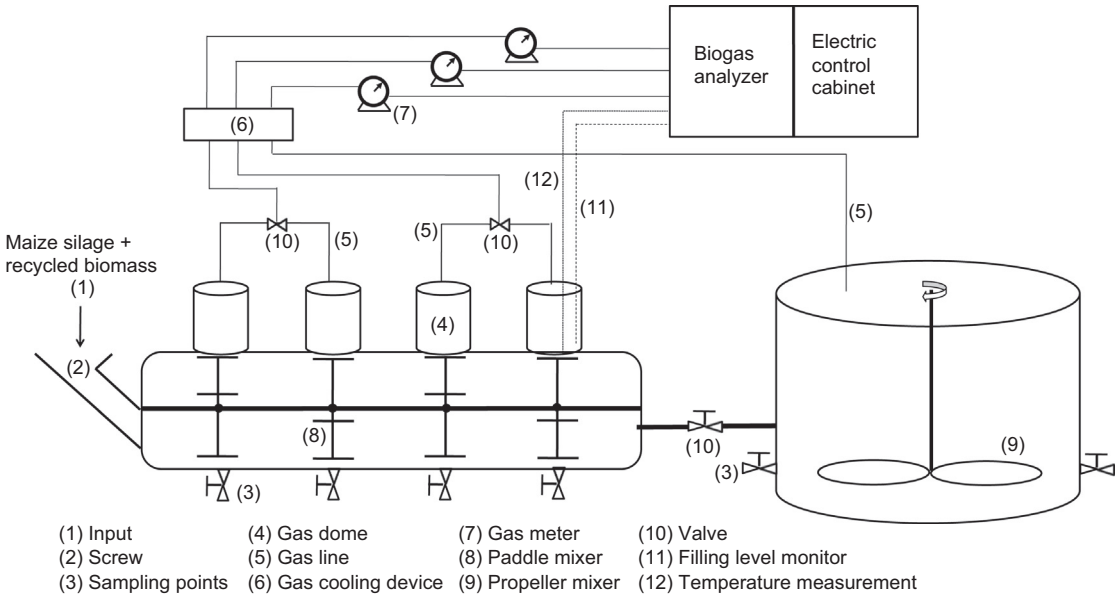

Fig. 1. Schematic drawing of pilot plant and technical equipment. The horizontal digester was equipped with four sample points at the bottom and four samples points at the upper part. Bulk level reached shortly into the gas domes to avoid gas mixing between the four compartments.