

## Investigations and mathematical simulation on decentralized anaerobic treatment of agricultural substrate from livestock farming

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### ABSTRACT

Anaerobic processes are widely used for treatment of both municipal and industrial wastewater as well as agricultural substrates. In contrast to the aerobic methods, they are frequently more cost-efficient, they have a lower surplus sludge production, and the reactors can be run with higher volumetric loads and thus smaller volumes. In the paper presented both experimental data and the application of the Anaerobic Digestion Model No. 1 for agricultural substrate from livestock farming will be described. A 3,500 L reactor with mesophilic operation and loaded with cattle manure was examined with respect to its COD degradation, gas production, and gas composition. Results revealed a reduction of 30–35% COD and a biogas production of  $287 \text{ L}_{\text{Biogas}}/\text{kg}_{\text{VS}} \text{ when operated with a specific loading rate of } 3.6 \text{ kg}_{\text{VS}}/(\text{m}^3 \cdot \text{d})$ .

After calibration of the ADM 1, which was based predominantly on the acetate uptake rate ( $k_{\text{ac.m}} = 3.6 \text{ g}/(\text{g} \cdot \text{d})$ ), the disintegration constant ( $k_{\text{Dis}} = 0.05 \text{ d}^{-1}$ ) and the exact determination of the influent COD fractions contained in the agricultural substrate, it was possible to simulate the measured data of the plant in excellent quality. For future application of the ADM 1 as part of control strategies a sensitivity analysis was carried out. The analysis based on the SVM slope technique has been done to identify highly sensitive biochemical parameters. These are, amongst others, the acetate uptake rate, the disintegration constant, the biomass decay rates and the half saturation constant for ammonia inhibition. Sensitivity analysis of the inflow COD fractions (proteins, carbohydrates, lipids and inert) showed the necessity of detailed measurements for the prediction of the gas flow and composition as well as for prognosis of inhibitions in the anaerobic process. For cattle manure especially the fractions of inert material and carbohydrates should be observed carefully. Due to the high content of  $\text{NH}_4\text{-N}$  in manure the protein fraction is not as sensitive as the two mentioned above.

**Key words** | ADM 1, agricultural wastes, anaerobic treatment, mathematical simulation

### INTRODUCTION

Anaerobic processes are widely used for treatment of both wastewater and agricultural substrates. In contrast to the aerobic methods, they are frequently more cost-efficient, they have a lower surplus sludge production, and the reactors can be run with higher volumetric loads and thus smaller volumes. Energy crops like maize, rye and grass ensilage as well as manure from cattle, swine or chicken are treated to

win biogas and to close nutrient loops. Anyway the hygienic quality of the treated manure has to be assured (e.g. Lebuhn *et al.* 2005). Manure as one major source of environmental pollution from livestock farming should effectively be treated to avoid its hazardous impact on soil and groundwater.

Up to now only little research has been done on the modelling of agricultural biogas plants under both

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mesophilic and thermophilic conditions. Exceptions are the results from Angelidaki *et al.* (1993), who describe the inhibition of the anaerobic processes by ammonia, and Angelidaki *et al.* (1999) concerning the co-fermentation of agricultural substrate and fats. Both papers highlight the importance of a detailed fractioning of the input substrate as proteins, carbohydrates and lipids have different degradation paths in the anaerobic process. Myint *et al.* (2007) focused on the hydrolysis and acidogenesis of dry digestion of cattle manure with process TS concentrations higher than 20%. Anyway only few data can be found on wet fermentation of cattle manure.

To calibrate mathematical models sensitivity analysis is an adequate way to improve model results and has been done amongst others for wastewater (Kim *et al.* 2006). The sensitivity of ADM 1 parameters (Batstone *et al.* 2002) has been rarely publicized and no information can be found up to now for cattle manure. However, mathematical modeling of manure could help to improve reactor operation, increase methane yield and to decrease impact on the environment.

## MATERIAL AND METHODS

### Analytical methods

The analyses of the agricultural substrates were done by the Institute of Agricultural Engineering and Animal Husbandry, Bavarian State Research Center for Agriculture. The 3,500 L fermenter was discontinuously fed with liquid manure from cattle farming and TMR (Total Mixed Ratio) for cows, and run at 38°C under mesophilic conditions. The contact time of the substrate in the fully mixed reactor amounted to 21 days. The reactor was fed daily six times a week. Reactor content was stirred for 10 minutes every half hour. Measurements are based on German Standard Methods (DEV 1981). A method according to Van Soest & Wine 1967 and Weender (described in Naumann & Bassler 1993) was performed to characterize the substrate in terms of carbohydrates, proteins and fats. The method applied resulted in a fractionation of the organic matter between crude protein, crude fat, crude fiber and N-free extract (NFE) (Weender analysis). Carbohydrates were further divided into

hemi cellulose (NDF–ADF), cellulose (ADF–ADL) and lignin (ADL); analyzed by the so-called van Soest-Fractions NDF (Neutral Detergent Fibre), ADF (Acid Detergent Fiber) and ADL (Acid Detergent Lignin). 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:  $\pm 3\%$ ).

### Investigated anaerobic reactor

The investigated anaerobic reactor of 3,500 L, that was also investigated by Lübken *et al.* (2007) regarding energy balances, was operated with a substrate mixture from liquid manure of cattle and TMR (total mixed ratio, fodder for cows). 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 mean influent volume flow amounted to 175 litres per day. This resulted in a volumetric loading rate of  $3.6 \text{ kg}_{\text{VS}}/(\text{m}^3 \cdot \text{d})$  and a COD load of  $15.3 \text{ kg}_{\text{COD}}/\text{d}$ . COD in the effluent was reduced by 30–35% compared to the influent COD. The COD to TS ratio of the inflow substrate was  $i_{\text{COD}/\text{TS}} = 1.2 \text{ kg}_{\text{COD}}/\text{kg}_{\text{TS}}$ . The dry gas production was measured as  $3.65 \text{ m}^3_{\text{Gas}}/\text{d}$  ( $287 \text{ L}_{\text{Biogas}}/\text{kg}_{\text{VS}}$ ) at operation temperature. The pH in the reactor was relatively constant with 7.6. Table 1 presents the characteristics of the inflow substrate in detail.

### Mathematical model and sensitivity functions

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; Kleerebezem & van Loosdrecht 2006). ADM 1 is a highly complex model, characterized by 19 biochemical conversion processes and 24 substances. For the calculations the software AQUASIM (Reichert 1998) was used. Besides the calibration and validation of the ADM 1 to this up to now rarely investigated agricultural substrate a sensitivity analysis was done. Both sensitive ADM 1 parameters and the substrate inflow fractioning of proteins, carbohydrates and fatty acids

**Table 1** | Characteristics of the influent substrate

Parameter	Unit	Manure	TMR
TS	[%]	6.1	50.3
VS	[%TS]	81.4	93.7
COD	[kg/m <sup>3</sup> ]	76	609
$i_{\text{COD}/\text{VS}}$	[kgO <sub>2</sub> /kgVS]	1.53	1.29
VFA <sub>total</sub>	[g/m <sup>3</sup> ]	6,657	3,765
Alkalinity	[mmol/L]	241.9	48.2
pH	[-]	7.4	4.9
NH <sub>4</sub> -N	[g/m <sup>3</sup> ]	2,289	1,345
Raw protein	[% TS]	12.2	19.2
Raw fibre	[% TS]	17.8	17.2
Raw lipid	[% TS]	4.3	2.6
NFE	[% TS]	47.1	54.7
NDF	[% TS]	47.1	50.0
ADF	[% TS]	33.9	23.4
ADL	[% TS]	20.1	19.6

were studied. Following the publication of Kim *et al.* (2006), who did investigations on activated sludge models, the SVM-Slope technique was used here to identify sensitive parameters for the ADM 1. The calibrated ADM 1 model (see Table 2) was used as reference parameter set. An effluent base quality EQ was defined according to Equation (1).

$$\text{EQ} = \beta_{\text{COD}} \text{COD}_e + \beta_{\text{CH}_4} \text{CH}_4\% + \beta_{\text{CO}_2} \text{CO}_2\% + \beta_{\text{gasflow}} q_{\text{gasflow}}, \quad [-] \quad (1)$$

where COD<sub>e</sub> is chemical oxygen demand in the effluent [g/m<sup>3</sup>], CH<sub>4</sub>% the percentage of methane in the gas, CO<sub>2</sub>%

the percentage of carbon dioxide in the gas,  $q_{\text{gasflow}}$  the dry gas flow in m<sup>3</sup>/d and  $p$  are weighting factors (10, 20, 20, 20). The sensitivity index  $\Delta\text{EQ}$  is resulting from a procedure, where each model parameter was changed stepwise by 10% (Ref: referring to reference simulation, Var: varied parameter).

$$\begin{aligned} \Delta\text{EQ} = & \beta_{\text{COD}} |\text{COD}_{\text{Ref},e} - \text{COD}_{\text{Var},e}| + \beta_{\text{CH}_4} |\text{CH}_4\%_{\text{Ref}} \\ & - \text{CH}_4\%_{\text{Var}}| + \beta_{\text{CO}_2} |\text{CO}_2\%_{\text{Ref}} - \text{CO}_2\%_{\text{Var}}| \quad (2) \\ & + \beta_{\text{gasflow}} |q_{\text{gasflow, Ref}} - q_{\text{gasflow, Var}}| \quad [-] \end{aligned}$$

## RESULTS AND DISCUSSION

### Calibration of the ADM 1

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 (see Table 1). The following equations are implemented to define particular model fractions.

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

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

Both parameters proteins  $X_{\text{Pr}}$  and lipids  $X_{\text{Li}}$  are defined by the fresh mass FM (kg<sub>FM</sub>/d), the TS (%), the COD content of manure  $i_{\text{COD}/\text{TS}}$  as well as raw protein RP (%TS) and raw lignin RL (%TS) respectively. The calculation of

**Table 2** | Calibrated biochemical ADM1-parameters for the treatment of cattle manure

Parameter	Description	Unit	ADM 1 value	Calibrated	Notes
$k_{\text{Dis}}$	Disintegration constant	d <sup>-1</sup>	0.5	0.05	1
$k_{\text{m,ac}}$	Acetate uptake rate	gg <sup>-1</sup> d <sup>-1</sup>	8	4.2	1
pH <sub>UL,acid</sub>	Upper pH limit for acidogens	-	5.5	8	1
pH <sub>LL,acid</sub>	Lower pH limit for acidogens	-	4	6	1
$k_{\text{m,pro}}$	Propionate uptake rate	gg <sup>-1</sup> d <sup>-1</sup>	13	4.5	2
$K_{\text{S,pro}}$	Half saturation coefficient for propionate uptake	kg m <sup>-3</sup>	0.1	0.34	2
$K_{\text{S,H}_2}$	Half saturation coefficient for hydrogen uptake	kg m <sup>-3</sup>	$7 \times 10^{-6}$	$1.65 \times 10^{-5}$	1
$N_{\text{XC,I}}$	Nitrogen content of composite and inert material	mol <sub>N</sub> m <sup>-3</sup>	0.002	0.0014	1

(1) Values determined by best fit between dynamic simulation and measurement; (2) Values in accordance with Angelidaki *et al.* (1999).

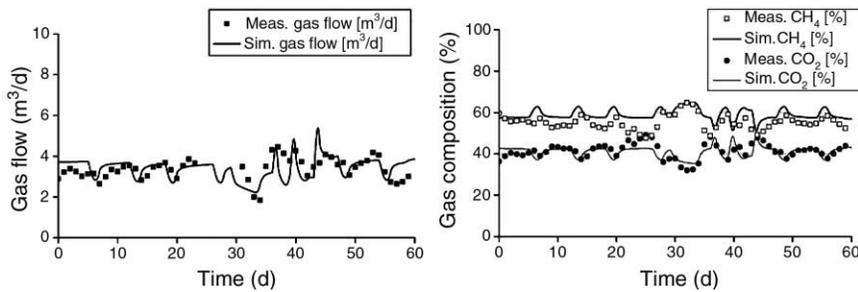


Figure 1 | Gas flow in m<sup>3</sup>/d (left) and dry gas composition in % (right).

carbohydrates  $X_{CH}$  and inert material is more complicated and is based on additional information from the Van-Soest-Analysis (Van Soest & Wine 1967).

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

To quantify the inert material the load of lignin ADL (%TS) is needed. ADF (%TS) comprises lignin and cellulose. Measurements showed that cellulose is degraded by 28%, what is reasonable according to Fuchigami *et al.* (1989). The low degradation of COD is implying that manure was degraded in the animal intestine before.

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

Raw fiber RF (%TS) and nitrogen-free extract NFE (%) 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.

If the Equations (3)–(6) are applied the particular COD that is 80% of total COD, can be divided as follows: raw protein  $X_{pr} = 13.6\%$  of  $COD_{part}$ , raw fat  $X_{li} = 4.0\%$  of  $COD_{part}$ , carbohydrates  $X_{ch} = 54\%$  of  $COD_{part}$  and inert material  $X_I = 28.4\%$  of  $COD_{part}$ . All particular material was split during the disintegration process in the aforementioned fractions. To fulfill the nitrogen mass balance after the disintegration step (Blumensaat & Keller 2004), the nitrogen content of the composite and inert material was fitted to  $N_{XC,I} = 0.0014 \text{ Mol}_N/\text{g}_{COD}$ . Acetate, propionate, butyrate and valerate were measured as 5.2, 3.5, 2.0 and 0.6% of  $COD_{tot}$ , respectively. Calibration was mainly done with the disintegration constant changed to  $k_{Dis} = 0.05 \text{ d}^{-1}$  and the acetate uptake rate to  $k_{m,ac} = 4.2 \text{ g}/(\text{g} \cdot \text{d})$ . The complete list of calibrated biochemical parameters can be found below in Table 2.

### Modeling reactor performance

Figure 1 presents measured data and simulation results for the gas flow (left) and the gas composition (right). As can be

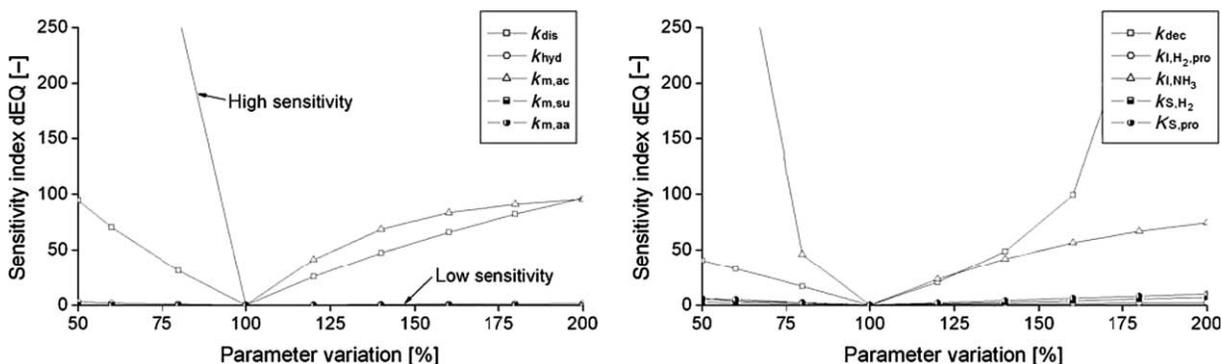


Figure 2 | Sensitivity index  $\Delta EQ$  for exemplary parameters of ADM 1 (left) and for the COD fractioning of agricultural waste (right).

seen results are very good. For acetate and propionate only average effluent concentrations of  $1,000 \text{ gCOD/m}^3$  and  $250 \text{ gCOD/m}^3$  were available but were met by model results (not shown).

### Sensitivity analysis for the biochemical parameters and the inflow fractioning

Results from the sensitivity analysis of both kinetic parameters and COD fractions are presented in Figures 2 and 3. For this 98 simulation runs were executed and analyzed. In Figure 2, amongst others, the four most sensitive kinetic parameters are described. It can be seen that for the agricultural substrate the hydrolysis rate  $k_{\text{Hyd}}$ , the uptake rates for amino acids  $k_{\text{m,aa}}$  and sugars  $k_{\text{m,su}}$ , the hydrogen inhibition constant  $K_{\text{I,H}_2,\text{pro}}$  and the half saturation coefficients for propionate  $k_{\text{s,pro}}$  and hydrogen  $k_{\text{s,H}_2}$  are less sensitive than the disintegration rate  $k_{\text{Dis}}$ , the acetate uptake rate  $k_{\text{m,ac}}$ , the ammonia inhibition constant  $K_{\text{I,NH}_3}$  and the biomass decay rates  $k_{\text{dec}}$ . Furthermore, for these four very sensitive parameters results are highly depending on weighting factors  $\beta$ . For the presented sensitivity index  $\Delta\text{EQ}$  the gas volume and gas composition ( $\text{CH}_4$  and  $\text{CO}_2$ ) were assessed higher than COD effluent values. If the acetate uptake rate  $k_{\text{m,ac}}$  and the inhibition constant for ammonia  $K_{\text{I,NH}_3}$  are further reduced compared with the calibrated parameter set, this would result in a complete process inhibition.

Figure 3 presents the results of the sensitivity analysis for the inflow fractioning of COD after the disintegration step. This means the total sum of composite material stayed the same, only the parts of proteins, carbohydrates, lipids

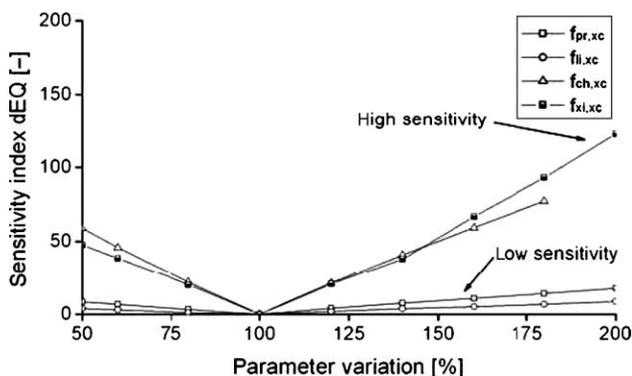


Figure 3 | Sensitivity index  $\Delta\text{EQ}$  for the COD inflow fractioning of cattle manure.

and inert material were changed. By this the effect of different measurement results from a Weender and Van Soest analysis can be shown. The diagram outlines the importance of the inert and the carbohydrates fraction regarding the gas flow and composition. Proteins are less sensitive as the quantity of ammonia nitrogen in cattle manure is much higher than the incorporated nitrogen in the COD fractions.

### CONCLUSIONS

Anaerobic treatment of agricultural waste is a seminal technology both from the environmental and the economic point of view. Manure as one mayor source of environmental pollution from livestock farming can effectively be treated anaerobically to avoid its hazardous impact on soil and groundwater. Reactor operation and biogas production were investigated to optimize the fermentation of cattle manure in a pilot-scale reactor of 3,500 L. The reactor was operated with a loading rate of  $3.6 \text{ kgVS}/(\text{m}^3\cdot\text{d})$ , resulting in a specific biogas production of  $287 \text{ L}_{\text{Biogas}}/\text{kgVS}$ . COD reduction in the reactor was around 30–35%. To optimize reactor operation and increase understanding of the microbial conversion processes the Anaerobic Digestion Model was calibrated to this agricultural substrate. Detailed investigations were done to describe the input substrate as exact as possible. For this Weender analyses were executed resulting in concentrations of raw fiber, raw protein and raw lipid of 12.2, 17.8 and 4.3% TS, respectively. Measurement according to Van Soest showed lignin concentrations of 20.1% TS and a degradation of cellulose by 28%. These data together with concentrations of organic acids was used to calibrate the ADM 1 and to model amongst others the gas flow and the gas composition in good quality. The main calibrated kinetic parameters were the acetate uptake rate of  $k_{\text{m,ac}} = 3.6 \text{ g}/(\text{g}\cdot\text{d})$  and the disintegration constant of  $k_{\text{dis}} = 0.05 \text{ d}^{-1}$ .

A sensitivity analysis according to the SVM slope technique revealed the most sensitive kinetic parameters: the acetate uptake rate, the inhibition constant for ammonia, the disintegration constant and the biomass decay rates. Furthermore, the analysis showed the necessity of measuring the single inflow COD fractions to exactly

reproduce the gas composition and organic acids concentration in the reactor. For the investigated agricultural substrate the fractions of carbohydrates and inert material were most sensitive.

## PARAMETERS

Parameter	Unit	Description
$\beta$	–	Weighting factors for sensitivity analysis
$\Delta EQ$	%	Sensitivity index
%CH <sub>4</sub>	%	Proportion of methane in the biogas
%CO <sub>2</sub>	%	Proportion of CO <sub>2</sub> in the biogas
ADF	% TS	Lignin and cellulose
ADL	% TS	Lignin
EQ	–	Quality index
$f_{Pr,xc}$	–	Proportion of proteins that are produced via the disintegration process
$f_{Ch,xc}$	–	Proportion of carbohydrates that are produced via the disintegration process
$f_{Li,xc}$	–	Proportion of lipids that are produced via the disintegration process
$f_{Xi,xc}$	–	Proportion of inert material that is produced via the disintegration process
S <sub>I</sub>	kg <sub>COD</sub> /d	Concentration of inert soluble COD
S <sub>ac</sub>	kg <sub>COD</sub> /d	Concentration of acetate
S <sub>aa</sub>	kg <sub>COD</sub> /d	Concentration of amino acids
S <sub>su</sub>	kg <sub>COD</sub> /d	Concentration of sugars
S <sub>fa</sub>	kg <sub>COD</sub> /d	Concentration of short chain fatty acids
X <sub>I</sub>	kg <sub>COD</sub> /d	Concentration of inert particular COD
X <sub>CH</sub>	kg <sub>COD</sub> /d	Concentration of carbohydrates
X <sub>LI</sub>	kg <sub>COD</sub> /d	Concentration of long chain fatty acids
X <sub>PR</sub>	kg <sub>COD</sub> /d	Concentration of proteins

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