Implementation of sulphate reduction and sulphide inhibition in ADM1 for modelling of a pilot plant treating bioethanol wastewater

L. Hinken*, M. Patón Gassó**, D. Weichgrebe* and K.-H. Rosenwinkel*

* Institute for Sanitary Engineering and Waste Management (ISAH), Leibniz Universitaet Hannover, Welfengarten 1, 30167 Hannover, Germany
E-mail:
(E-mail: *hinken@isah.uni-hannover.de; weichgrebe@isah.uni-hannover.de; rosenwinkel@isah.uni-hannover.de)*
** Polytechnic University of Valencia, Departamento de Ingeniería Hidráulica y Medio Ambiente, Valencia, Spain (E-mail: *maupagas@epsg.upv.es*)

Abstract
In the current paper, the model and the simulation results of an anaerobic digestion process in a pilot plant treating bioethanol wastewater is presented. The pilot plant consists of an anaerobic contact reactor and was operated for about six months. At the end of the pilot plant operation, the reactor acidified as the loading rate increased, as well as the sulphate and volatile fatty acid concentration in the influent. As the Anaerobic Digestion Model No. 1 (ADM1) is only valid for influents with SO_4-concentration lower than 0.002 mol SO_4/L, an extension was necessary to get a good correlation between simulation results and experimental data. Therefore, a simplified model for sulphate reduction and sulphide inhibition was implemented and calibrated. The calibrated model could then be used to analyse the reactor failure. It was found that the high sulphate concentration in relation with increasing loading rates yield to the reactor acidification. If one of these two factors was reduced, the reactor failure could have been prevented.

Keywords
Bioethanol wastewater, Anaerobic treatment, ADM1, Sulphate reduction

INTRODUCTION

In the bioethanol production process, it is common practice to dry the whole mash (process by-product) to DDGS (dried distillers grains and solubles) and to use it as animal protein feed. The energy demand required for the drying process is very high and may exceed 50% of the total energy demand of bioethanol production. The Wilkening-process (patent no. DE 103 27 954) provides an alternative through the decanting of the stillage. The resulting liquid phase (thin stillage) is treated in the following anaerobic stage and used to produce biogas, and the remaining solid fraction is dried and used for animal feed. Thus, the energy balance is improved two-fold: by reducing the energy need for the drying of the stillage, and also by the production of biogas.

As part of a BMBF-funded research project (see Finke et al., 2010) the Wilkening-process was tested in a pilot plant for bioethanol production with downstream thin stillage treatment for half a year. Towards the end of the investigations, a decrease of the biomass' performance in the anaerobic stage led to a complete acidification of the methane reactor. By adding the sulphate reduction process to the ADM1, this load case could be adequately simulated, and thus studied in detail.

MATERIALS & METHODS

Pilot Plant Characteristics

The anaerobic stage of the pilot plant for thin stillage treatment consists of a storage tank (1 m^3), a completely mixed reactor (2 m^3) and a settling tank (0.8 m^2, ca. 0.25 m^3). A degassing tank is installed between the anaerobic reactor overflow and the settler in order to ensure better settling of

solids in the secondary clarifier. The temperature of the anaerobic reactor was adjusted to an average of 37 °C, and the pH was kept at 7 throughout operation. The anaerobic reactor was operated at an organic loading rate of 1.8 kg COD/(m^3·d) and at a sludge loading rate of ca. 0,25 kg COD/(kg oTR·d). The mean hydraulic retention time during the pilot plant operation was 17 d. During the stable operation of the pilot plant, a removal efficiency of > 95% of the filtered COD could be achieved. Due to solids in the effluent, the elimination was slightly lower for total COD, at 75-95%.

The gas produced averaged 55 L biogas/h at STP (Maximum: 100 L biogas/h). At an average influent load of ca. 125 g COD/h and a 96% COD removal efficiency, the biogas and the methane yield are 0.46 L biogas/g COD and 0.32 L CH_4/g COD (methane content: 70%) respectively. At the end of the investigations the COD removal and thus the biogas yield decreased almost completely, which was also indicated by a change in the gas composition (an increase in CO_2 concentration to 50% in the biogas).

Substrate Characteristics

The filtered COD of the raw wastewater was 20,000 - 100,000 COD_{fil}/L, and the total COD was about 20 - 30% higher. The nitrogen concentration was 850 - 5,000 mg Kjeldahl nitrogen/L, the concentration of filterable substances was 2,000 - 12,000 mg/L and the sulphate concentration was 700 - 6,000 mg SO_4/L. During the pilot plant operation, the wastewater was diluted to a 1:1 ratio.

The inflow-fractionation was based on available measurements and literature values for the composition of wheat stillage. The analysis shows that the ethanol concentration in the thin stillage is very low (<1%), so this fraction must not be considered separately. Fractionation of particulate COD was based on data on the composition of dried wheat stillage (Gruber et al., 2005). It is assumed that this composition is largely that of the particulate COD in the thin stillage (portion COD_{part}: f_{Xc} = 0,3, f_{Xch} = 0,15, f_{Xpr} = 0,3, f_{Xli} = 0,15, f_{Xi} = 0,1). Analogously, the dissolved COD fraction was essentially divided between the two fractions S_{su} (Monosaccharide, 30% of COD_{diss}) and $S_{aa,}$ (amino acids, 40% of COD_{diss}). The proportion of dissolved inert fraction (S_i) was determined using available data of the COD in the effluent of a downstream aerobic stage (1.8% of COD_{hom}). The concentrations of organic acids in the influent were also considered during fractionation. Furthermore, the fractions S_{nh4} and S_{so4} were determined from the measured ammonium and sulphate concentration respectively. The alkalinity in the inflow was on average 20 mmol/L and reached 10 mmol/L at the end of the investigations. This concentration is assigned to the parameter S_{cat} (cations) in the model.

Mathematical Model

The modeling basis was the ADM1 (Batstone et al., 2002) including the X_p fraction (ADM1_xp, extension from Wett et al., 2006). Initially, the Haldane kinetics was added to ADM1xp in the processes of acetogenesis and acetoclastic methanogenesis (see Bernard, 2001), as the performance decrease of the reactor could not be simulated adequately by using the standard ADM1. Due to the high sulphate concentration in the influent, the competition between sulphate reducing and methanogenic microorganism for substrates as well as the H_2S inhibition becomes rather relevant. Therefore, a further extension was implemented to consider the processes of sulphate reduction according to Batstone (2006). This approach is valid to S:COD ratios lower than 0.1 g S/g COD and only includes sulphate reduction by oxidation of available hydrogen (Batstone, 2006). In addition, an inhibition function for the parameter H_2S was introduced. In contrast to Federovich et al. (2003), who used a very strong linear inhibitory function, a non-competitive inhibition analog to the inhibition functions of ammonia and hydrogen was implemented. The inhibitory function has been considered in the processes of acidogenesis, acetogenesis and methanogenesis as well as in the process of sulphate reduction. In the following, the extended model is called ADM1xp_ SO_4. The simulations have been performed in SIMBA (based on Matlab®/Simulink™).

RESULTS & DISCUSSION

Model Calibration

The ADM1xp_SO_4 was calibrated with the available experimental data. The modified ADM1 parameters are summarized in Table 1 in comparison to the standard values. Furthermore, the Haldane-constants of valerate, butyrate and propionate uptake were determined to 0.4 kg COD/m³, and of acetate uptake to 1.0 kg COD/m³. Parameters for sulphate reduction were used according to Batstone (2006), but with an increased yield of sulphate reducing bacteria (0.15 instead of 0.08 kg COD/kg COD) and a lower half saturation constant of hydrogen for the sulphate reducing bacteria $K_{S,Sh2}$ ($1 \cdot 10^{-6}$ instead of $4 \cdot 10^{-6}$ kg COD/m³). As part of the calibration the inhibition constant $K_{I,h2s}$ is determined to 0.15 kg COD/m³.

Table 1. Modified parameter values for ADM1xp_SO_4

Parameter	Parameter value	
	Original ADM1*	Modified
$pH_{UL,a}$ [-]	5.5	6
$pH_{LL,a}$ [-]	4	5
$k_{m,c4}$ [kg COD/(kg COD·d)]	20	12
$k_{m,pro}$ [kg COD/(kg COD·d)]	13	10
$pH_{LL,ac}$ [-]	6	5
$k_{m,ac}$ [kg COD/(kg COD·d)]	8	10
$K_{S,ac}$ [kg COD/m³]	0.15	0.10

* Standard parameter for mesophilic high-rate reactors

Simulation Results

In **Figure 1a**, the modeling results of ADM1xp_SO_4 for pH are compared to the experimental data and to the results of the calculations with the ADM1xp. Since the pH measurement was installed at the beginning of the simulation period, the differences between measured and simulated values during this period can be attributed to incorrect calibration of the electrode. In the simulations using the standard ADM1xp, a synthetic addition of anions in the reactor is necessary in order to simulate the decrease in pH. When using the extended ADM1xp_SO_4 model, this decrease is simulated without a feed change. **Figure 1 (b, d)** also shows the high correlation between the experimental data and the simulation results of the extended ADM1xp_SO_4 model regarding methane production (at STP) and VFA in the effluent of the reactor. Despite very high fluctuations of sulphate concentrations, the simulation of H_2S-production can also lead to reasonable results (**Figure 1c**). Further effluent concentrations (COD_{total}, $COD_{dissolved}$, acetate, butyrate, propionate, and valerate, sulphate and NH_4-N and organic nitrogen) could also be simulated accurately by the model.

The reactor failure at the end of the pilot plant operation period was investigated in detail by simulations of different load cases. The results show that this failure is caused by an interaction of two factors: the increasing sulphate concentration during the period from 85 d to 115 d (from 180 to >600 mg SO_4/L) leads to an increase in the H_2S concentration in the reactor, and thus to an increased inhibition due to H_2S and to an decreasing concentration of microorganisms (especially of acetoclastic methanogenesis and acetogenesis) in the reactor. Due to the simultaneous increase of the sludge loading rate, the methanogenic and the acetogenic microorganisms are not able to convert completely the influent COD load, which causes an accumulation of organic acids in the system. Because of the low alkalinity in the wastewater, the pH decreases significantly and further increases the inhibition.

In general, the extended ADM1xp_SO4 is suitable for simulation of the anaerobic conversion processes in the pilot plant under dynamic inflow conditions. Both the simulations results for the

production of CO_2, CH_4 and H_2S and for the pH in the reactor, as well as the results in regard to the effluent concentration of various parameters correlate very well with the experimental data. In addition, the model can serve to analyze the performance impacts, and to identify key factors. In further simulations, model validation has to be carried out using the data of different industrial wastewater treatment plants.

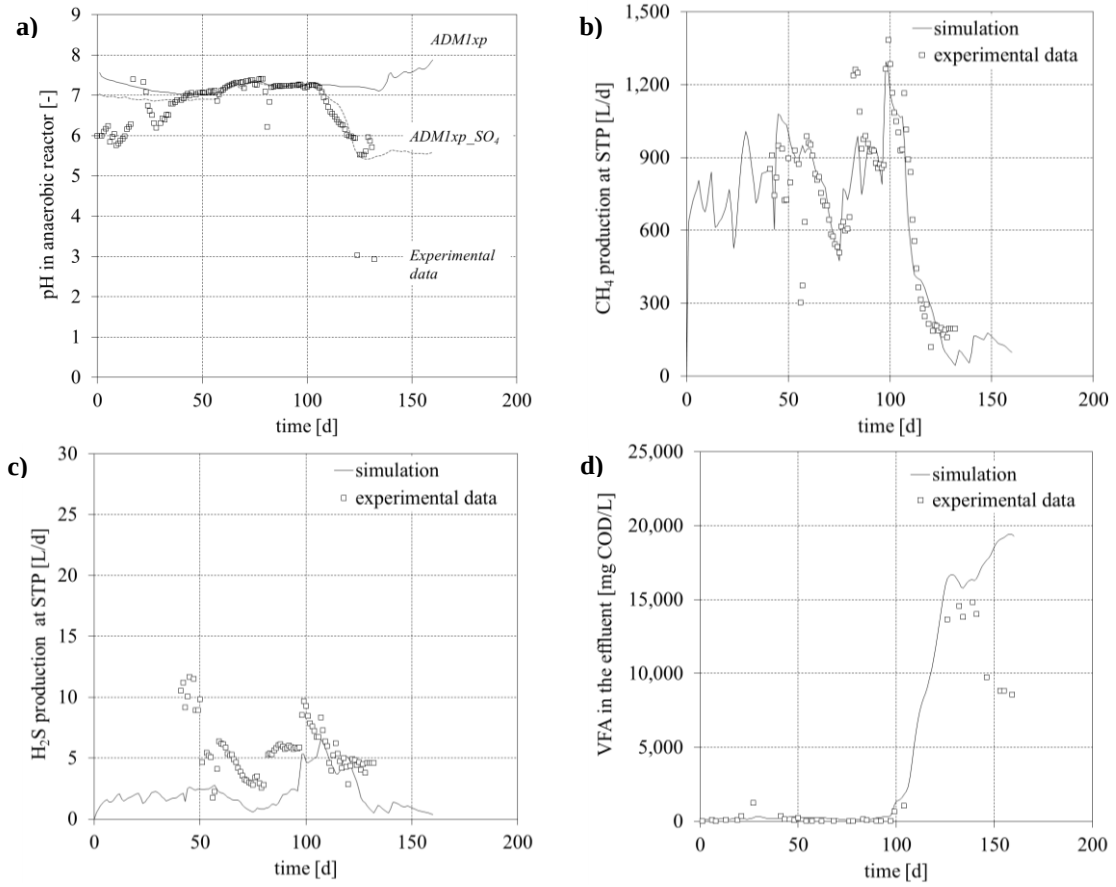

Figure 1. Comparison of experimental data with results of the calculation with the ADM1xp_SO4

REFERENCES

Batstone, D. J. 2006 Mathematical modelling of anaerobic reactors treating domestic wastewater: Rational criteria for model use. *Environmental Science and Bio/Technology* **5**, 57–71

Batstone, D. J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V., Pavlostathis, S. G., Rozzi, A., Sanders, W. T. M., Siegrist, H., Vavilin, V. A. 2002 Anaerobic Digestion Modell No. 1 (ADM1), Scientific and Technical Report No. 13. *IWA Publishing*, London, UK

Bernand, O., Hadj-Sadok, Z., Dochain, D., Genovesi, A., Steyer, J.-P. 2001 Dynamical Model Development and Parameter Identification for an Anaerobic Wastewater Treatment Process. *Biotechnology and Bioengineering* **75**(4), 424–438

Fedorovich, V., Lens, P., Kalyuzhnyi, S. 2003 Extension of Anaerobic Digestion Model No. 1 with processes of sulfate reduction. *Applied Biochemistry and Biotechnology* **109**(33), 33–45

Finke, R., Wilkening, C. L., Wilkening, L., Hinken, L., Beier, M., Rosenwinkel, K.-H. 2010 Entwicklung eines integrierten Verfahrens zur Bioethanol-/Biogasherstellung (Development of an integrated process for bioethanol/biogas production). *Abschlussbericht*, KMU-innovativ – Verbundvorhaben Klimaschutz, GZ Klima-25-018

Gruber, L., Stögmüller, G., Haberl, K., Maierhofer, G., Steiner, B., Steinwidder, A., Schauer, A., Knaus, W. 2005 Protein- und Kohlenhydrat-Fraktionen nach dem Cornell net carbohydrate and protein system sowie ruminaler Nähstoffabbau in situ von energie- und proteinreichen Kraftfuttermitteln (Proteine and carbohydrate fractions according to the Cornell net carbohydrate and protein system and ruminal nutrient degradation in situ of concentrated feedingstuff rich in energy and protein). *Übers. Tierernährung* **33**, 1–15

Wett, B., Eladawy, A., Ogurek, M. 2006 Description of nitrogen incorporation and release in ADM1. *Water Science and Technology* **54**(4), 67–76