Modelling of dark fermentation from household organic waste based on modified ADM1

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Abstract
In this study, the IWA anaerobic digestion model N°1 (ADM1) was used to simulate and predict the dark fermentation process of a complex organic substrate: household waste. Since ADM1 does not account for metabolic products such as lactic acid, ethanol and some volatiles fatty acids like caproate, that appear during the dark fermentation process, the structure of ADM1 was modified to include them among the produced metabolites. Due to the complex structure of the substrate, a Contois model was included for the disintegration and hydrolysis steps instead of first-order kinetics. A global sensivity analysis using the variance decomposition based method was also performed to identify the most sensitive model parameters. The modified ADM1 simulated satisfactorily a batch experiment.
Keywords
Dark fermentation; ADM1; modelling; lactate; ethanol, caproic acid, sensivity analysis

INTRODUCTION

The dark fermentation phase of the anaerobic digestion process generates several substrates that may be of great interest in a framework where energy resources are increasingly restricted. In this process, methanogens are severely inhibited. Due to this inhibition, several interesting phenomena occur : accumulation of hydrogen and volatile fatty acids (VFAs), production of ethanol and high-carbon VFAs such as caproate and accumulation of lactate (*Han et al.(2012) Ding et al.(2010)).* Up to now, many batch and continuous experimental studies have investigated the dark fermentation process under varying substrate and operational regimes, achieving significant progress on the understanding of the metabolic pathways and on the optimal design of the reactors. However, even with these numerous studies, the kinetic models developed or used to describe the fermentation process are still limited (*Gadhamshetty et al.(2010))*. The aim of the present work is to explore and extend the applicability of the IWA Anaerobic Digestion Model N°1 (ADM1) *Batstone,et al.(2002)* to the fermentative process from a complex solid substrate: household organic waste. The structure of ADM1 was thus modified to include lactate, caproate and ethanol among the metabolites produced by the degradation of the household organic waste. A Contois model was included for better consideration of the disintegration and hydrolysis steps instead of first-order kinetics.

REACTOR DESIGN

Experiments were carried out in a batch stirred tank reactor of 2 L with a working volume of 1.5 L. The gas flow rate was measured with an electronic gas volumeter. Temperature was controlled using a platinum probe Pt100 and was maintained at 35°C ± 0.5°C with a heating electric resistance. Two sensors measured the redox potential and pH. Reactor pH was controlled by adding NaOH (2 M), when the pH dropped below 5.5. An anaerobic sludge from a granular reactor treating wine distillery wastewater was used as inoculum, after heat-treatment (90°C, 20 min.) to select hydrogen producing bacteria. Inoculum was added to obtain a final concentration of 5g $TSS.L^{-1}$. Organic fraction of household waste was used as feeding substrate. The initial substrate concentration was approximately 20g $VSS.L^{-1}$.

SUGGESTED MODIFICATIONS TO THE ADM1 MODEL AND THEORY ASSUMPTIONS

Recently, batch and continuous dark fermentation experiments modeling was carried out using ADM1 framework model (*Penumathsa et al. (2008) Antonopoulou et al. (2011) Peiris et al. (2005))*. Even though these modified ADM1 models were developed to describe dark fermentation of liquid substrates, only one model from *Arudchelvam et al. (2010)* reported successful modeling of dark fermentation of complex particulate substrates. Basically, ADM1 uses some simplifications in reactions for particulate organic compounds. In particular, the first-order kinetic may be inaccurate to describe the disintegration and hydrolysis steps as explained by *Ramirez et al.(2009)*. Thus, in the present work it was necessary to integrate a Contois disintegration and hydrolysis rates to take into account the limitations by biomass and substrate concentrations (*Vavilin et al. (2008))*.

Inclusion of lactate and ethanol required for accurate computation of pH, has already been successfully used for modelling dark fermentation (*Antonopoulou et al. (2011))*. Lactate and ethanol were assumed to be produced from the same group of acidogenic microorganisms (Xsu) that degrades sugars in the standard ADM1 model. Lactic acid was assumed to be an intermediate product which can be degraded mainly to acetate and/or propionate. However, ethanol was not assumed to be a final metabolic product of carbohydrate fermentation, as suggested in the modified ADM1 proposed by *Antonopoulou et al. (2011)*. Experimental data obtained in the present work showed that ethanol concentration decreased during the fermentation, implying that ethanol was an intermediate product. Ethanol can be fermented mainly to acetate and hydrogen (*PIPYN et al. (1981))*.

The addition of lactate and ethanol in the model was achieved by the addition of four extra state variables: soluble lactate (S_{lact}), soluble ethanol (S_{eth}), lactate degrading organisms (X_{lact}) and ethanol degrading organisms (X_{eth}). Lactate and ethanol uptake rates were modeled according to a Monod-type kinetic. Two inhibition terms were included to account for the lack of nitrogen in the reactor and the variations of pH. Furthermore, an equilibrium equation was included in ADM1 to model acid-base equilibrium due to lactate production. In addition, two dynamic equations for the decay of lactate and ethanol degrading microorganisms (first-order rate equation) were added.

Caproate always appears during dark fermentation, but the exact pathway for its formation has not been yet fully explained, several pathways being proposed in the literature (*Ding et al.(2010))*. In the modified ADM1 model, caproate was assumed to be a final product of butyrate, hydrogen and carbon dioxide consumption. Caproate production rate was modelled according to a two substrate Monod-type kinetic (*Bader (1978))*. The addition of caproate production in ADM1 model was achieved by the addition of another extra state variable (X_{C6}). An acid-base equilibrium due to caproate production (pKa=4.88) and the dynamic equation for the decay of caproate producing microorganisms (first-order rate equation) were also added.

In this work, the kinetic constants and yields used in the simulations corresponded to the recommended values for biogas reactors from the ADM1 model and were not adjusted for the specific case studied. The kinetic parameters regarding lactate and ethanol production and consumption were chosen according to *Antonopoulou et al. (2011)*. The two substrate Monod-type parameters were set equal to the kinetics parameters for butyrate and hydrogen degradation proposed by *Batstone et al.(2002)*.

Global and local sensivity analysis

To assess the influence of different model parameters on simulation results, a total and first order sensivity analysis was carried out on the proposed model to identify factors that mostly contribute to the output variability and those who are insignificant. This method is based on decomposing the variance of the output using the Extended Fourier Amplitude Sensitivity Test (EFAST) *Donoso-Bravo et al. (2011)*. The sensivity test was performed on: (1) the kinetic parameters for the Contois disintegration and hydrolysis functions, (2) the acidogenesis of sugars, lipids and long chain fatty acids, (3) the degradation of lactate and ethanol, and (4) the production of caproate. The Probability Density Functions of these parameters were defined as uniform with their means set to the default values found in the literature (*Antonopoulou et al. (2011))* and boundaries set as +/-50% of the mean. The evaluation criteria corresponded to the variability of total VFA production.

RESULTS & DISCUSSIONS

The main results of the experiment as well as simulations of both standard and modified ADM1 models are shown in figure 1. Mainly acetate, butyrate and caproate were produced. Valeric and propionic acids concentrations represented less than 5 % of total VFAs (results not shown). At the beginning of the experiment, lactate concentration was reduced and its consumption led to the production of propionate and acetate. A small amount of ethanol was also produced before its total transformation into acetate and hydrogen. At the same time, during the first 48 hours, biogas composition increased in H_2 to reach 30 %. After the fourth day, the major metabolic pathways were, concomitantly : (i) the consumption of hydrogen and carbon dioxide, (ii) the degradation of butyrate and ethanol and (iii) the production of acetate and caproate.

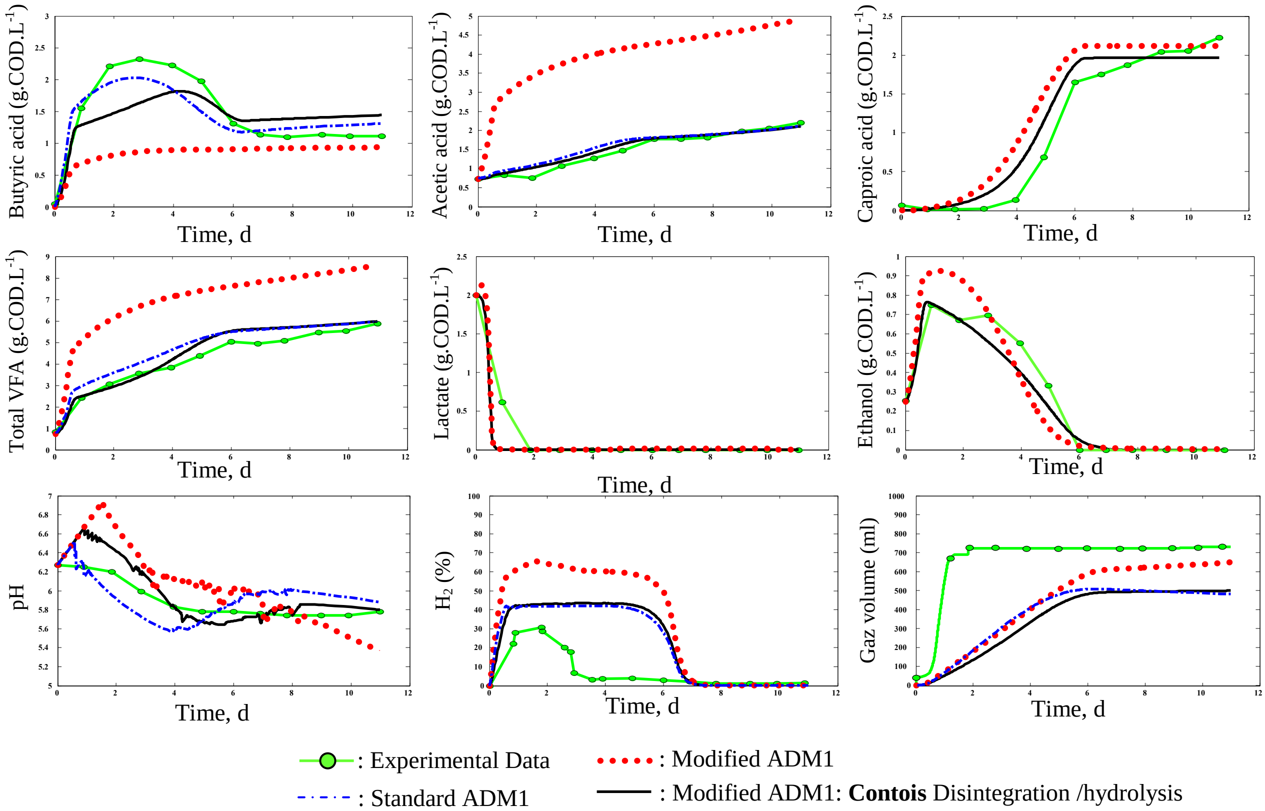

Figure1. Measurements and simulation of standard and modified ADM1 models for the dark fermentation of household organic waste.

Standard ADM1 was used to predict dark fermentation of household waste using the parameter values proposed in *Batstone,et al.(2002).* It is obvious that standard ADM1 model, without the modifications proposed in this study, does not simulate the experimental data satisfactorily. VFA predictions are far from real data. Predictions of hydrogen profile are particularly poor. Nevertheless, based on the above observations, standard ADM1 was found to be an excellent starting point to model the experimental results. By including the proposed modifications, modified ADM1 model achieved a better simulation of the experimental data. Thus, predictions using Contois rates for the disintegration and hydrolysis agreed well with the experimental data, even though some differences between simulated and experimental results remain. To reduce the differences, we first performed a global sensivity analysis on the modified ADM1 model to identify the most sensitive parameters that impact total VFA generation. Results are shown in figure 2. It is clear that most of the output variability according to the first and total order sensivity index was due to sugars, lactate and carbohydrates degradation. Parameter estimation of the identified sensitive parameters in continuous experiments should probably lead to a better fitting of experimental data to model simulation results. This approach is given priority in our next efforts as it, presumably, will yield more insight and a more robust model.

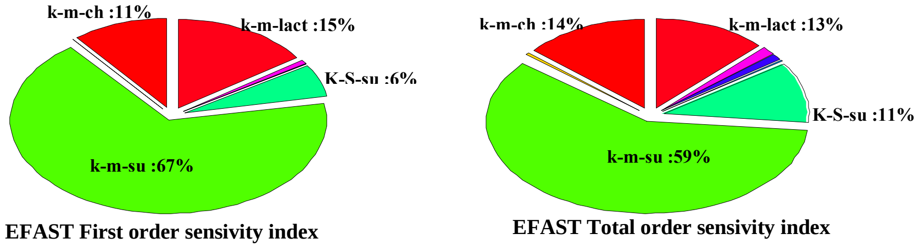

Figure2. Results from sensivity analysis of the modified ADM1 from variance based method EFAST

CONCLUSION

The aim of the present study was to assess the applicability of the ADM1 modelling framework to dark fermentation using organic fraction of household waste. The structure of the model was modified to include lactate, ethanol and caproate among the metabolites produced by the substrate degradation, leading to improved metabolites and volatiles fatty acids predictions. Finally, in order to be able to make a good prediction of the output profiles of the model, it was deemed necessary to perform a sensitivity analysis to identify factors that mostly contribute to the output variability. To go further an identification procedure should be done on the stoichiometric and kinetic parameters to improve the predictions for the fermentative process.

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