Accepted Manuscript

A Novel Process Simulation Model (PSM) for Anaerobic Digestion Using Aspen Plus

Karthik Rajendran, Harshavardhan R. Kankanala, Magnus Lundin, Mohammad J. Taherzadeh

PII: S0960-8524(14)00076-5

DOI: <http://dx.doi.org/10.1016/j.biortech.2014.01.051>

Reference: BITE 12903

To appear in: *Bioresource Technology*

Please cite this article as: Rajendran, K., Kankanala, H.R., Lundin, M., Taherzadeh, M.J., A Novel Process Simulation Model (PSM) for Anaerobic Digestion Using Aspen Plus, *Bioresource Technology* (2014), doi: <http://dx.doi.org/10.1016/j.biortech.2014.01.051>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A Novel Process Simulation Model (PSM) for Anaerobic Digestion Using Aspen Plus

Karthik Rajendran*, Harshavardhan R. Kankanala, Magnus Lundin &

Mohammad J. Taherzadeh

School of Engineering, University of Borås, 50190 Borås, Sweden

* Corresponding author

Phone: +46-33 435 4855

Fax: +46-33 435 4008

E-mail: Karthik.Rajendran@hb.se

Abstract

A novel process simulation model (PSM) was developed for biogas production in anaerobic digesters using AspenPlus®. The PSM is a library model of anaerobic digestion, which predicts the biogas production from any substrate at any given process condition. A total of 46 reactions were used in the model, which include inhibitions, rate-kinetics, pH, ammonia, volume, loading rate, and retention time. The hydrolysis reactions were based on the extent of the reaction, while the acidogenic, acetogenic, and methanogenic reactions were based on the kinetics. The PSM was validated against a variety of lab and industrial data on anaerobic digestion. The P-value after statistical analysis was found to be 0.701, which showed that there was no significant difference between discrete validations and processing conditions. The sensitivity analysis for a $\pm 10\%$ change in composition of substrate and extent of reaction results in 5.285% higher value than the experimental value. The model is available at <http://hdl.handle.net/2320/12358> (Rajendran et al., 2013b).

Keywords: *anaerobic digestion; process simulation model; aspen plus; model validation; sensitivity analysis*

1 Introduction

Biogas is mainly a combination of methane and carbon dioxide produced by the anaerobic digestion (AD) of organic materials. The methane, an energy-rich compound due to its high calorific value ($\sim 39.4 \text{ MJ m}^{-3}$) can be used for different purposes such as heating, cooking, and electricity production (British Standards Institution, 2005a; British Standards Institution, 2005b; Rajendran et al., 2012). If the biogas is upgraded, it can also be used as vehicle fuel (Deublein & Steinhauser, 2008; Rajendran et al., 2012). In AD, several groups of bacteria and archaea work in synergy to form methane and carbon dioxide. Biogas is obtained after four crucial steps including hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In the first step, the complex substrates such as carbohydrates, fats, and proteins are hydrolyzed into their respective monomers, such as glucose, fatty acids, and amino acids. Secondly, the hydrolyzed monomers are converted into different volatile fatty acids (VFA), such as capronic acid, valeric acid, iso-valeric acid, butyric acid, iso-butyric acid, propionic acid, and acetic acid. In the third step (acetogenesis), the VFA's are converted into acetic acid, hydrogen, and carbon dioxide. Finally, methanogens convert acetogenesis products into methane and carbon dioxide (Mata-Álvarez, 2003; Nijaguna, 2006; Rajendran et al., 2013a). Nonetheless, these intermediary reactions mechanism are hardly explained and understood in biogas production.

Biogas production is affected by several factors such as organic loading rate (OLR), hydraulic retention time (HRT), carbon-to-nitrogen ratio, pH, ammonia, temperature, and mixing.

Studying these factors, in addition to the bacterial metabolic reactions involved in anaerobic digestion or fermentation, is complicated in experimental studies. However, these factors and the intermediary metabolism in AD could be interpreted with the help of models. The first

model to explain AD was a mathematical model, which considered acetate as the rate limiting step (Andrews, 1968; Graef & Andrews, 1974). In this model, only substrate inhibitions were involved, while the later BIOTREAT model explained the intermediary reactions in AD based on electron donors and acceptors (Christensen & McCarty, 1975; Lawrence & McCarty, 1969).

The biogas production is affected by complex inhibitions such as ammonia, specific growth rate of microorganisms, pH, temperature, and other interactions. The important parameter such as pH and temperature determines the amount of ammonia released in the system, and the rate of ionization of ammonia affects the methanogenesis process. The complex models involving the inhibitions were developed by (Angelidaki et al., 2000; Angelidaki et al., 1993; Vavilin et al., 1994). Currently, Anaerobic Digestion Model No. 1 (ADM1) is getting more attention due to its complexity and kinetics of reactions mechanisms (Batstone et al., 2002). Recently, a computational model was proposed by Blesgen and Hass (2010), based on sub-models, including biological factors, physico-chemical factors, reactors, and plants. Most of the models developed were either theoretical or mathematical. Nevertheless, other process parameters, such as OLR, HRT, and thermodynamics of the reactions that affect the biogas production were not investigated in the aforementioned models.

Process simulations are well appreciated by industries and researchers, as these can forecast the real scenario accurately, and the costs to perform simulations are much cheaper.

Nevertheless, a process simulation model (PSM) has not been developed to predict and understand the mechanism of AD. Several process simulators are available of which Aspen Plus® has rigorous property methods and meticulous thermodynamic calculations. Hence, it is used as a tool to develop PSM for AD. In this work, a PSM was developed using Aspen Plus®

V 7.3.2. This PSM is a library model for AD, which includes intermediary reactions, inhibitions, and kinetics. The model was examined for biogas reactors operating at thermophilic conditions (55 °C). The PSM was also validated against experimental results obtained from earlier research studies and industrial plants. A sensitivity analysis of the model was performed in Aspen Plus® by changing the composition of the substrate and the extent of the reaction for the hydrolysis reactions by $\pm 5\%$, $\pm 10\%$, and $\pm 20\%$.

2 Methods and Model details

2.1 Model Description

The process simulation model divides the digestion or fermentation reactions into two groups of *reaction-sets*: (a) The reactions of hydrolysis operating based on the extent of reaction (Table 1), which is the fractional conversion of reactants into products on a scale of 0.0 – 1.0. Hydrolysis is one of the rate-limiting steps in AD, and henceforth a separate *reaction-set* was added. With a separate reactions set for hydrolysis, the effect of pretreatment, which improves the hydrolysis efficiency on different substrates, could be studied in PSM. The other *reaction-set* (b) constitutes reactions of other phases (acidogenic, acetogenic, and methanogenic reactions) in AD functioning on a kinetic basis (Table 2).

Figure 1 shows the block-flow diagram of the PSM. The model is accessible at the Swedish database <http://hdl.handle.net/2320/12358> (Rajendran et al., 2013b). The kinetic constants of the reactions were obtained from previous models, such as ADM 1 and comprehensive models (Angelidaki et al., 2000; Angelidaki et al., 1993; Batstone et al., 2002; Serrano, 2011). Reactions from ADM 1, which were not resolved for stoichiometry, were balanced in PSM.

The hydrolysis equations were included as carbohydrates, proteins, and fats in the *reaction-set (a)* (Table 1). Carbohydrates were incorporated as cellulose, starch, and hemicelluloses.

Proteins were added based on their solubility, such as soluble proteins and insoluble proteins.

Fats comprised of tripalmitate, triolein, palmito-olein, and palmito-linolein can be entered in PSM.

In the *reaction-set (b)*, different sub-set of reactions was added to calculate the kinetics of the reactions. Each sub-set had a FORTRAN program to determine the rate of reactions in acidogenic, acetogenic, and methanogenic phases. In total, ten different sub-sets or calculator blocks were used for glycerol, valeric acid, butyric acid, propionic acid, linoleic acid, amino acids, sugars, palmitic acid, oleic acid, methanogenesis, and hydrogen utilizing reactions (Figure 1).

The iterative solutions were obtained by passing the output of the *reaction-set (a)* to *reaction-set (b)* functioning on kinetic reactions. The results generated from PSM, are a stream table with mass and energy balance, where the amount of biogas production can be calculated. In each calculator block, the inhibitions in the form of pH, temperature, and ammonia were embedded as logic loops. For every input (fresh or recycled), the calculator blocks calculate the rate of each reaction, thus, rendering the simulation close to reality. Furthermore, process parameters such as OLR, the volume of the reactor, and HRT were entrenched in the model covering the important parameters in the biogas production.

2.2 Model development and operations

The process simulation model is developed mainly based on the four different stages of biogas production such as hydrolysis, acidogenesis, acetogenesis and methanogenesis. These four stages explain the intermediary metabolisms, how the complex substrates such as carbohydrates, proteins and fats are broke down to monomeric forms and finally to methane and carbon dioxide. For this purpose, the reactions involved in these four stages were collected from previous works (Andrews, 1968; Angelidaki et al., 2000; Angelidaki et al., 1993; Batstone et al., 2002; Lawrence & McCarty, 1969; Vavilin et al., 1994). The equations which were not solved for stoichiometry were solved using MATLAB® software (Anderson & Bjedov, 1996).

In this section, the step-by-step procedure for model development is explained. Firstly, all the compounds required for the simulation was obtained from the equations were added to Aspen Plus and its physical properties were simulated. Some of the complex compounds missing physical properties were obtained from Wooley & Putsche (1996). NRTL (Non-Random Two-Liquid model) was chosen as the property method as it correlates and calculates the mole fractions and activity coefficients of different compounds and also to facilitate the liquid and the gas phase in the biogas production. Once, the property check is over, the reactors were included for the simulation. From the reactor models available in Aspen Plus, stoichiometric reactor was used for the hydrolysis phase of the reactions, and the continuously stirred tank reactor (CSTR) was used for the other phases in digestion reactions.

All the processing conditions such as the total solids (TS), volatile solids (VS), flow rate, mass composition, temperature, and HRT of the substrates were given, the input parameters

were processed in the *reactions-set (a)* (Table 1). This will estimate the amount of monomers released to the second reactor, which contains *reactions-set (b)* (Table 2). Depending on the monomer, they pass through different calculator blocks. For instance, the amino acids released by the proteins in the *reaction-set (a)*, pass through the amino acid calculator block, where it is broken down to different VFA. Then, the VFA produced pass the butyric acid, valeric acid, and propionic acid calculator blocks before it reaches the final calculator block, methanogenesis. Thereafter, the amount of the methane, carbon dioxide and the left over TS are represented in the form of desired units.

Each calculator block in the *reaction-set (b)* has a FORTRAN program, which calculates the products released from each reactions. The calculator blocks is assigned with different variables such as the flow rate, VFA's, NH_4^+ , temperature, kinetic parameter and H_2 , which imports the amount of reactants and the reaction rate for each calculator block based on the inputs from the results of *reaction-set (a)*. The kinetic parameter was obtained from the previous literature studies (Andrews, 1968; Angelidaki et al., 2000; Angelidaki et al., 1993; Batstone et al., 2002). The power law was used to calculate the reaction rate, which includes the specific growth rate of microorganisms, and ammonia inhibitions. The pH was calculated based on the chemical equilibrium constants inside the calculator blocks for each VFA, based on Angelidaki et al. (2000) and Cheng (2010). The results obtained from the simulation are reported in the form of $\text{m}^3 \text{ day}^{-1}$, which can be recalculated, according to the desired units.

2.3 Model Validation

The PSM was validated against experimental data, which used different substrates with diverse process conditions, covering data from a small-scale laboratory research to large-scale industrial plants. Each case compared with PSM was further tested for statistical analysis

using Minitab® (V 15). The statistical analyses include probability plot to check the significance and normality of the experimental data. Table 3 shows the different cases with substrate and operational data used in PSM for calculating the differences between PSM and experimental data. Each case is described as follows:

Case (1): Cow manure was used as a substrate with a loading rate of 0.33 L day^{-1} at 15 days HRT. The volume of the reactor was 5 L and produced $353.5 \text{ L biogas kg}^{-1} \text{ vs day}^{-1}$ (Kaparaju et al., 2009). The composition of the cow manure were based on Budiyo (2011).

Case (2): In this validation, municipal solid waste (MSW) was used as a substrate in a reactor with 5 L volume at 21 days HRT. The biogas production obtained at $3 \text{ g vs L}^{-1} \text{ day}^{-1}$ was $0.54 \text{ m}^3 \text{ CH}_4 \text{ kg}^{-1} \text{ vs day}^{-1}$ (Forgács et al., 2012). The MSW consisted of 61.5% carbohydrates, 16% proteins, 10% fats, and the rest was ashes and inorganics (Borås Energy and Environment AB, 2012).

Case (3): A co-digestion study was used in this validation, using 70% MSW and 30% citrus wastes as a substrate. The composition and the wastes of MSW were obtained from Borås Energy and Environment AB (2012), and the citrus wastes from Forgács et al. (2012). The experimental biogas production for an OLR of $3.0 \text{ g vs L}^{-1} \text{ day}^{-1}$ at 21 days HRT was $0.555 \text{ m}^3 \text{ CH}_4 \text{ kg}^{-1} \text{ vs day}^{-1}$.

Case (4): In this case, a pilot study with a 600 L reactor volume digesting MSW was used.

The biogas production reported was $401 \text{ L kg}^{-1}_{\text{VS removed}}$ based on Eliyan et al. (2007) .

Case (5): An industrial AD located near Borås, Sweden was validated in PSM with a volume of 3000 m^3 , operating at a HRT of 21 days. The organic fractions of the MSW was used as a substrate in this plant with a loading rate of $150 \text{ m}^3 \text{ day}^{-1}$ and the biogas production was $9,600 \text{ m}^3 \text{ day}^{-1}$ (Borås Energy and Environment AB, 2012).

Case (6): Similar to Case 5, another industrial anaerobic fermentor plant in Norrköping (Sweden) operating on co-digestion of 75% slaughterhouse waste, 15% food waste, and 10% cow manure was used in the validation. The overall waste composition was carbohydrates 23.5%, proteins 12.18%, fats 60%, and the rest was ashes. The biogas production from the industrial plant was $10,959 \text{ m}^3 \text{ day}^{-1}$ with a HRT of 20 days (Budiyo, 2011; Palatsi et al., 2011).

Case (7): Pig manure was used as a feed in PSM in this validation. The volume of the reactor was 30 L, with a HRT of 8 days and a loading rate of $230.4 \text{ g}^{-1}_{\text{VS}} \text{ day}^{-1}$. The experimental biogas production was $0.269 \text{ m}^3 \text{ kg}^{-1}_{\text{VS}}$. The composition of the pig manure was 44.06% carbohydrates, 23% proteins, and 4.9% fats for a total VS of 72% (Fujita et al., 1980).

2.4 Sensitivity analysis

The two important factors in PSM, which affect the simulation results, are the extent of the reactions and the composition of the substrates. Therefore, a sensitivity analysis was performed by changing the extent of the reaction and the composition of the substrates by $\pm 5\%$, $\pm 10\%$, and $\pm 20\%$. A 2^3 experimental design was used for the sensitivity analysis considering factors such as carbohydrates, proteins, and fats. The differences between the PSM and experimental data were recalculated based on the sensitivity analysis. Based on the sensitivity analysis, a regression plot was drawn to evaluate the model fitting. The confidence interval (CI) was calculated to show how the change in the substrate or the extent of the reaction affects the simulation results.

3 Results and Discussion

The process simulation model (PSM) was developed to explain all the intermediary metabolisms of AD. The extension of stoichiometric *reaction-set (a)* in PSM could be used to predict the effect of different pretreatment methods used in the biogas production process. The kinetic *reaction-set (b)* reveals the intermediary metabolism in AD. The PSM was validated with several laboratory experimental and industrial data, and the differences between simulations and the reported data were calculated. Furthermore, the statistical validations and the sensitivity analysis calculate the interval range of the predicted value of biogas production.

Using the PSM provides an approximate prediction of the biogas produced in a wide variety of substrates. In biogas industries, the feed composition and biogas production varies a lot every day due to several parameters and problems. Although PSM prediction shows a

difference between experimental data, it could still result in better prediction for biogas production, for a change in substrates.

3.1 Validations in PSM

Table 3 shows the cases validated in PSM, and the differences between the experimental data and simulation data were calculated. The minimum and maximum difference obtained from the different validations used in PSM was 0.3% for Case 7 and -12.4% for Case 2, respectively. The biogas plant in Norrköping (case 6) works on co-digestion of substrates such as slaughterhouse waste, food waste, and cow manure and produced $10,959 \text{ m}^3 \text{ day}^{-1}$, while the PSM calculated $11,694.6 \text{ m}^3 \text{ day}^{-1}$ biogas production. The difference between simulation and reality for this case was 6.7%. In addition, the different cases considered had various scales of volume from lab until industrial plants. Furthermore, the different loading rate and HRT were different in all the cases, suggesting that the model can be applicable in a variety of scales.

The cases studied in PSM were further validated statistically to check for significant differences between the case studies, which used different process conditions. A probability plot with 95% CI was drawn to check the P-value, to determine if there were any significant differences between the cases. P-value is a tool in statistical analysis to check significant difference for different treatments. Figure 2 shows the probability plot for the cases validated against PSM. The P-value for the validations from PSM was 0.701, which is bigger than 0.05. This shows that there was no significant difference observed, between the different cases validated against PSM with different processing conditions such as OLR, HRT, TS, VS, substrate, etc.

3.2 Sensitivity analysis in PSM

The prediction from PSM is affected by two factors: extent of the reaction and composition of the substrates. Sensitivity analysis on these two factors reveals the robustness of the model.

The extent of the reactions and the composition of the substrates were changed by $\pm 5\%$, $\pm 10\%$, and $\pm 20\%$ to study the sensitivity of the PSM. However, the change in TS and VS concentration, affected some cases for the sensitivity analysis. For this reason, cases 1, 4, 5, and 7 were encompassed in the sensitivity analysis.

The sensitivity analysis based on the extent of the reaction and composition of the substrates individually by $\pm 5\%$, $\pm 10\%$, and $\pm 20\%$ revealed that the PSM could predict the changes rigorously. Figure 3 and Figure 4 shows the sensitivity analysis for the changes in the extent of the reaction and the composition of the substrates, respectively. The changes in the extent of the reaction followed linearity, where an average R^2 value was 0.9695 showing the robustness and accuracy of the model. Similarly, the R^2 value for the changes in the composition of the substrates was 0.9102 enlightening that the composition of the substrate is an important factor to predict the biogas production using PSM.

CI shows the range of the predicted biogas production from PSM. A 95% CI was calculated for both the extent of the reactions and the composition of the substrates. For a $\pm 5\%$ in the extent of the reaction and the composition of the substrate, CI was in the range of 3.208% - 7.536%. On average, 5.203% higher value can be expected from PSM for a $\pm 5\%$ and it increases by 5.285% and 5.35% for a change in $\pm 10\%$, and $\pm 20\%$ in the extent of the reaction

and the composition of the substrates. This suggests that even if the composition of the substrate and the extent of the reaction were varied until $\pm 20\%$, PSM could predict the biogas production accurately.

4 Conclusion

Process simulation model for anaerobic digestion was developed using Aspen Plus. PSM involves intermediary metabolisms of all four phases of anaerobic fermentation. Furthermore, the PSM was validated against industrial and research studies. The average difference in biogas production between simulation results and real scenario up to $\pm 20\%$ change in substrate composition and the extent of the reaction is 5.279%. Using computational and mathematical power, the PSM shows that decoding AD mechanisms is easier with the proposed model. PSM helps to save time, money, and energy to study new substrates or changes in the composition of substrates for industries and researchers.

Acknowledgments

This work was financially supported by Sparbank foundation in Sjuhärad (Sweden). The authors would like to acknowledge Borås Energy and Environment AB for their collaboration and providing the data for their process, and Thomas Södergren for the computer support.

Abbreviations

PSM – Process Simulation Model

AD – Anaerobic Digestion

ADM1 – Anaerobic Digestion Model No. 1

TS – Total Solids

VS – Volatile Solids

HRT – Hydraulic Retention Time

OLR – Organic Loading Rate

CSTR – Continuously Stirred Tank Reactor

MSW – Municipal Solid Waste

CI – Confidence Intervals

References

1. Anderson, P.K., Bjedov, G. 1996. Chemical stoichiometry using MATLAB. *Frontiers in Education Conference*. IEEE. pp. 612-615.
2. Andrews, J.F. 1968. A mathematical model for the continuous culture of microorganisms utilizing inhibitory substrates. *Biotechnol. Bioeng.*, **10**(6), 707-723.
3. Angelidaki, I., Ellegaard, L., Ahring, B.K. 2000. A comprehensive model of anaerobic bioconversion of complex substrates to biogas. *Biotechnol. Bioeng.*, **63**(3), 363-372.
4. Angelidaki, I., Ellegaard, L., Ahring, B.K. 1993. A mathematical model for dynamic simulation of anaerobic digestion of complex substrates: focusing on ammonia inhibition. *Biotechnol. Bioeng.*, **42**(2), 159-166.
5. 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. The IWA Anaerobic Digestion Model No 1 (ADM 1). *Water Sci. Technol.*, **45**(10), 65-73.
6. Blesgen, A., Hass, V.C. 2010. Efficient Biogas Production through Process Simulation. *Energ. Fuel.*, **24**(9), 4721-4727.
7. Borås Energy and Environment AB. 2012. Sobacken Composition data. *Borås, Sweden*.
8. British Standards Institution. 2005a. *Natural gas - Calculation of calorific values, density, relative density & Wobbe index from composition*. BS EN ISO 6976:2005.
9. British Standards Institution. 2005b. *Natural gas - standard reference conditions*. BS EN ISO 13443:2005.
10. Budiyo, I.N.W. 2011. Study on Slaughterhouse Wastes potency and Characteristic for Biogas Production. *Int. J. Water Resour.*, **1**, 4-7.
11. Cheng, J. 2010. *Biomass to renewable energy processes*. CRC Press LLC., Florida, USA.
12. Christensen, D.R., McCarty, P.L. 1975. Multi-process biological treatment model. *J. Water Pollut. Con. F.*, 2652-2664.
13. Deublein, D., Steinhauser, A. 2008. *Biogas from waste and renewable resources*. Wiley-VCH, Weinheim, Germany.
14. Eliyan, C., Adhikari, R., Juanga, J.P., Visvanathan, C. 2007. Anaerobic Digestion of Municipal Solid Waste in Thermophilic Continuous Operation. *International Conference on Sustainable Solid Waste Management*, Thailand.
15. Forgács, G., Pourbafrani, M., Niklasson, C., Taherzadeh, M.J., Hováth, I.S. 2012. Methane production from citrus wastes: process development and cost estimation. *J. Chem. Technol. Biotechnol.*, **87**(2), 250-255.

16. Fujita, M., Scharer, J.M., Moo-Young, M. 1980. Effect of corn stover addition on the anaerobic digestion of swine manure. *Agr. Wastes*, **2**(3), 177-184.
17. Graef, S.P., Andrews, J.F. 1974. Stability and control of anaerobic digestion. *J. Water Pollut. Con. F.*, 666-683.
18. Kaparaju, P., Ellegaard, L., Angelidaki, I. 2009. Optimisation of biogas production from manure through serial digestion: Lab-scale and pilot-scale studies. *Bioresour. Technol.*, **100**(2), 701-709.
19. Lawrence, A.W., McCarty, P.L. 1969. Kinetics of methane fermentation in anaerobic treatment. *J. Water Pollut. Con. F.*, 1-17.
20. Mata-Álvarez, J. 2003. Biomethanization of the organic fraction of municipal solid wastes, (Ed.) J. Mata-Álvarez, International Water Association, TJ International (Ltd), Padstow, Cornwall, UK, pp. 1-18.
21. Nijaguna, B.T. 2006. *Biogas technology*. New Age International, New Delhi, India.
22. Palatsi, J., Viñas, M., Guivernau, M., Fernandez, B., Flotats, X. 2011. Anaerobic digestion of slaughterhouse waste: Main process limitations and microbial community interactions. *Bioresour. Technol.*, **102**(3), 2219-2227.
23. Rajendran, K., Aslanzadeh, S., Johansson, F., Taherzadeh, M.J. 2013a. Experimental and economical evaluation of a novel biogas digester. *Energ. Convers. Manage.*, **74**, 183-191.
24. Rajendran, K., Aslanzadeh, S., Taherzadeh, M.J. 2012. Household Biogas Digesters—A Review. *Energies*, **5**(8), 2911-2942.
25. Rajendran, K., Kankanala, H.R., Lundin, M., Taherzadeh, M.J. 2013b. A Novel Process Simulation Model for Anaerobic Digestion Using AspenPlus. <http://hdl.handle.net/2320/12358> accessed on (link available when article published).
26. Serrano, R.P. 2011. Biogas Process Simulation Using Aspen Plus. in: *Chemical Engineering*, Syddansk Universitet. Denmark, pp. 86.
27. Vavilin, V.A., Vasiliev, V.B., Ponomarev, A.V., Rytow, S.V. 1994. Simulation model 'methane' as a tool for effective biogas production during anaerobic conversion of complex organic matter. *Bioresour. Technol.*, **48**(1), 1-8.
28. Wooley, R.J., Putsche, V. 1996. *Development of an ASPEN PLUS physical property database for biofuels components*. National Renewable Energy Laboratory Golden, CO, USA.

List of Figures

Figure 1 Block flow diagram of the process simulation model.

Figure 2 Probability plot for the cases validated in PSM.

Figure 3 Sensitivity analysis of PSM based on change in the extent of reaction in reaction-set (a) by $\pm 5\%$, $\pm 10\%$, and $\pm 20\%$.

Figure 4 Sensitivity analysis of PSM based on change in the composition of the substrate by $\pm 5\%$, $\pm 10\%$, and $\pm 20\%$.

Table 1 List of hydrolysis reactions (reaction-set (a)) included in PSM functioning on extent of reaction.

No.	Compound	Hydrolysis Reaction	Extent of reaction
1	Starch	$(C_6H_{12}O_6)_n + H_2O \rightarrow n C_6H_{12}O_6$	0.6±0.2
2	Cellulose	$(C_6H_{12}O_6)_n + H_2O \rightarrow n C_6H_{12}O_6$	0.4±0.1
3	Hemicellulose	$C_5H_8O_4 + H_2O \rightarrow 2.5 C_2H_4O_2$	0.5±0.2
4	Hemicellulose	$C_5H_8O_4 + H_2O \rightarrow C_5H_{10}O_5$	0.6±0.0
5	Xylose	$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3 H_2O$	0.6±0.0
6	Cellulose	$C_6H_{12}O_6 + H_2O \rightarrow 2 C_2H_6O + 2 CO_2$	0.4±0.1
7	Ethanol	$2 C_2H_6O + CO_2 \rightarrow 2 C_2H_4O_2 + CH_4$	0.6±0.1
8	Soluble protein	$C_{13}H_{25}O_7N_3S + 6 H_2O \rightarrow 6.5 CO_2 + 6.5 CH_4 + 3 H_3N + H_2S$	0.5±0.2
	Insoluble protein	$I.P + 0.3337 H_2O \rightarrow 0.045 C_6H_{14}N_4O_2 + 0.048 C_4H_7NO_4 + 0.047 C_4H_9NO_3 + 0.172 C_3H_7NO_3 + 0.074 C_5H_9NO_4 + 0.111 C_5H_9NO_2 + 0.25 C_2H_5NO_2 + 0.047 C_3H_7NO_2 + 0.067 C_3H_6NO_2S + 0.074 C_5H_{11}NO_2 + 0.07 C_6H_{13}NO_2 + 0.046 C_6H_{13}NO_2 + 0.036 C_9H_{11}NO_2$	
9	(I.P)		0.6±0.1
10	Triolein	$C_{57}H_{104}O_6 + 3 H_2O \rightarrow 3 C_3H_8O_3 + 3 C_{18}H_{34}O_2$	0.5±0.2
11	Tripalmitate	$C_{51}H_{98}O_6 + 8.436 H_2O \rightarrow 4 C_3H_8O_3 + 2.43 C_{16}H_{34}O$	0.5±0.3
12	Palmito-olein	$C_{37}H_{70}O_5 + 4.1 H_2O \rightarrow 2.1 C_3H_8O_3 + 0.9 C_{16}H_{34}O + 0.9 C_{18}H_{34}O_2$	0.6±0.2
13	Palmito-linolein	$C_{37}H_{68}O_5 + 4.3 H_2O \rightarrow 2.2 C_3H_8O_3 + 0.9 C_{16}H_{34}O + 0.9 C_{18}H_{32}O_2$	0.6±0.2

Table 2 List of amino acids, acidogenic, acetogenic, and methanogenic reactions with kinetic constants included in PSM (*reaction-set* (b)).

No.	Compound	Chemical Reactions	Kinetic constant
Amino acid Degradation Reactions			
1	Glycine	$\text{C}_2\text{H}_5\text{NO}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N}$	1.28×10^{-02}
2	Threonine	$\text{C}_4\text{H}_9\text{NO}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4\text{O}_2 + 0.5 \text{ C}_4\text{H}_8\text{O}_2 + \text{H}_3\text{N}$	1.28×10^{-02}
3	Histidine	$\text{C}_6\text{H}_8\text{N}_3\text{O}_2 + 4 \text{ H}_2\text{O} + 0.5 \text{ H}_2 \rightarrow \text{CH}_3\text{NO} + \text{C}_2\text{H}_4\text{O}_2 + 0.5 \text{ C}_4\text{H}_8\text{O}_2 + 2 \text{ H}_3\text{N} + \text{CO}_2$	1.28×10^{-02}
4	Arginine	$\text{C}_6\text{H}_{14}\text{N}_4\text{O} + 3 \text{ H}_2\text{O} + \text{H}_2 \rightarrow 0.5 \text{ C}_2\text{H}_4\text{O}_2 + 0.5 \text{ C}_3\text{H}_6\text{O}_2 + 0.5 \text{ C}_5\text{H}_{10}\text{O}_2 + 4 \text{ H}_3\text{N} + \text{CO}_2$	1.28×10^{-02}
5	Proline	$\text{C}_5\text{H}_9\text{NO}_2 + \text{H}_2\text{O} + \text{H}_2 \rightarrow 0.5 \text{ C}_2\text{H}_4\text{O}_2 + 0.5 \text{ C}_3\text{H}_6\text{O}_2 + 0.5 \text{ C}_5\text{H}_{10}\text{O}_2 + \text{H}_3\text{N}$	1.28×10^{-02}
6	Methionine	$\text{C}_5\text{H}_{11}\text{NO}_2\text{S} + 2 \text{ H}_2\text{O} \rightarrow \text{C}_3\text{H}_6\text{O}_2 + \text{CO}_2 + \text{H}_3\text{N} + \text{H}_2 + \text{CH}_4\text{S}$	1.28×10^{-02}
7	Serine	$\text{C}_3\text{H}_7\text{NO}_3 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + \text{H}_2$	1.28×10^{-02}
8	Threonine	$\text{C}_4\text{H}_9\text{NO}_3 + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_6\text{O}_2 + \text{H}_3\text{N} + \text{H}_2 + \text{CO}_2$	1.28×10^{-02}
9	Aspartic acid	$\text{C}_4\text{H}_7\text{NO}_4 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + 2 \text{ CO}_2 + 2 \text{ H}_2$	1.28×10^{-02}
10	Glutamic acid	$\text{C}_5\text{H}_9\text{NO}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + 0.5 \text{ C}_4\text{H}_8\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2$	1.28×10^{-02}
11	Glutamic acid	$\text{C}_5\text{H}_9\text{NO}_4 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + \text{H}_2$	1.28×10^{-02}
12	Histidine	$\text{C}_6\text{H}_8\text{N}_3\text{O}_2 + 5 \text{ H}_2\text{O} \rightarrow \text{CH}_3\text{NO} + 2 \text{ C}_2\text{H}_4\text{O}_2 + 2 \text{ H}_3\text{N} + \text{CO}_2 + 0.5 \text{ H}_2$	1.28×10^{-02}
13	Arginine	$\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2 + 6 \text{ H}_2\text{O} \rightarrow 2 \text{ C}_2\text{H}_4\text{O}_2 + 4 \text{ H}_3\text{N} + 2 \text{ CO}_2 + 3 \text{ H}_2$	1.28×10^{-02}
14	Lysine	$\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{C}_4\text{H}_8\text{O}_2 + 2 \text{ H}_3\text{N}$	1.28×10^{-02}
15	Leucine	$\text{C}_6\text{H}_{13}\text{NO}_2 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_5\text{H}_{10}\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + 2 \text{ H}_2$	1.28×10^{-02}
16	Isoleucine	$\text{C}_6\text{H}_{13}\text{NO}_2 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_5\text{H}_{10}\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + 2 \text{ H}_2$	1.28×10^{-02}
17	Valine	$\text{C}_5\text{H}_{11}\text{NO}_2 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_4\text{H}_8\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + 2 \text{ H}_2$	1.28×10^{-02}
18	Phenylalanine	$\text{C}_9\text{H}_{11}\text{NO}_2 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + \text{H}_2$	1.28×10^{-02}
19	Tyrosine	$\text{C}_9\text{H}_{11}\text{NO}_3 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_6\text{H}_6\text{O} + \text{C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + \text{H}_2$	1.28×10^{-02}
20	Tryptophan	$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_8\text{H}_7\text{N} + \text{C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + \text{H}_2$	1.28×10^{-02}
21	Glycine	$\text{C}_2\text{H}_5\text{NO}_2 + 0.5 \text{ H}_2\text{O} \rightarrow 0.75 \text{ C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + 0.5 \text{ CO}_2$	1.28×10^{-02}
22	Alanine	$\text{C}_3\text{H}_7\text{NO}_2 + 2 \text{ H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + 2 \text{ H}_2$	1.28×10^{-02}
23	Cysteine	$\text{C}_3\text{H}_6\text{NO}_2\text{S} + 2 \text{ H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{H}_3\text{N} + \text{CO}_2 + 0.5 \text{ H}_2 + \text{H}_2\text{S}$	1.28×10^{-02}

Table 2 - Contd.,

No.	Compound	Chemical Reactions	Kinetic constant
Acidogenic Reactions			
24	Dextrose	$C_6H_{12}O_6 + 0.1115 H_3N \rightarrow 0.1115 C_5H_7NO_2 + 0.744 C_2H_4O_2 + 0.5 C_3H_6O_2 + 0.4409 C_4H_8O_2 + 0.6909 CO_2 + 1.0254 H_2O$	9.54×10^{-03}
25	Glycerol	$C_3H_8O_3 + 0.4071 H_3N + 0.0291 CO_2 + 0.0005 H_2 \rightarrow 0.04071 C_5H_7NO_2 + 0.94185 C_3H_6O_2 + 1.09308 H_2O$	1.01×10^{-02}
Acetogenic Reactions			
26	Oleic acid	$C_{18}H_{34}O_2 + 15.2396 H_2O + 0.2501 CO_2 + 0.1701 H_3N \rightarrow 0.1701 C_5H_7NO_2 + 8.6998 C_2H_4O_2 + 14.4978 H_2$	3.64×10^{-12}
27	Propionic acid	$C_3H_6O_2 + 0.06198 H_3N + 0.314336 H_2O \rightarrow 0.06198 C_5H_7NO_2 + 0.9345 C_2H_4O_2 + 0.660412 CH_4 + 0.160688 CO_2 + 0.00055 H_2$	1.95×10^{-07}
28	Isobutyric acid	$C_4H_8O_2 + 0.0653 H_3N + 0.8038 H_2O + 0.0006 H_2 + 0.5543 CO_2 \rightarrow 0.0653 C_5H_7NO_2 + 1.8909 C_2H_4O_2 + 0.446 CH_4$	5.88×10^{-06}
29	Isovaleric acid	$C_5H_{10}O_2 + 0.0653 H_3N + 0.5543 CO_2 + 0.8044 H_2O \rightarrow 0.0653 C_5H_7NO_2 + 0.8912 C_2H_4O_2 + C_3H_6O_2 + 0.4454 CH_4 + 0.0006 H_2$	3.01×10^{-08}
30	Linoleic acid	$C_{18}H_{32}O_2 + 15.356 H_2O + 0.482 CO_2 + 0.1701 H_3N \rightarrow 0.1701 C_5H_7NO_2 + 9.02 C_2H_4O_2 + 10.0723 H_2$	3.64×10^{-12}
31	Palmitic acid	$C_{16}H_{34}O + 15.253 H_2O + 0.482 CO_2 + 0.1701 H_3N \rightarrow 0.1701 C_5H_7NO_2 + 8.4402 C_2H_4O_2 + 14.9748 H_2$	3.64×10^{-12}
Methanogenic Reactions			
32	Acetic Acid	$C_2H_4O_2 + 0.022 H_3N \rightarrow 0.022 C_5H_7NO_2 + 0.945 CH_4 + 0.066 H_2O + 0.945 CO_2$	2.39×10^{-03}
33	Hydrogen	$14.4976 H_2 + 3.8334 CO_2 + 0.0836 H_3N \rightarrow 0.0836 C_5H_7NO_2 + 3.4154 CH_4 + 7.4996 H_2O$	2.39×10^{-03}

Table 3 Different case studies used to validate PSM with their differences in simulation and experimental results.

	Volume of the reactor	HRT (days)	Loading rate	TS (%)	VS (%)	Substrate	Experimental results	Simulation results	Difference (%)
Case 1	5 L	15	0.33 L day ⁻¹	6	80	Cow manure	353.5 L kg ⁻¹ vs day ⁻¹	365.83 L kg ⁻¹ vs day ⁻¹	3.4
Case 2	5 L	21	3.0 g vs L ⁻¹ day ⁻¹	15	85	MSW	0.54 m ³ CH ₄ kg ⁻¹ vs day ⁻¹	0.473 m ³ CH ₄ kg ⁻¹ vs day ⁻¹	-12.4
Case 3	5 L	21	3.0 g vs L ⁻¹ day ⁻¹	13	87	70% MSW and 30% citrus waste	0.555 m ³ CH ₄ kg ⁻¹ vs day ⁻¹	0.537 m ³ CH ₄ kg ⁻¹ vs day ⁻¹	-3.2
Case 4	600 L	25	2.0 g vs L ⁻¹ day ⁻¹	10	90	MSW	401 L kg ⁻¹ vs removed	448.76 L kg ⁻¹ vs removed	11.9
Case 5	3000 m ³	21	150 m ³ day ⁻¹	15	85	MSW	9600 m ³ day ⁻¹	10176 m ³ day ⁻¹	6.0
Case 6	3700 m ³	20	150 m ³ day ⁻¹	12.5	95	75% slaughter house waste, 15% food waste and 10% cow manure	10959 m ³ day ⁻¹	11694.6 m ³ day ⁻¹	6.7
Case 7	30 L	8	230.4 g vs day ⁻¹	6.4	72	Pig manure	0.269 m ³ kg ⁻¹ vs	0.268 m ³ kg ⁻¹ vs	0.3

Figure 1

Figure 2

Figure 3

Figure 4

Highlights

- **Process simulation model (PSM) for anaerobic digestion was developed using AspenPlus**
- **The model was validated from industrial and previous research studies**
- **Any substrates' biogas potential can be predicted using the model**
- **PSM is statistically validated**

ACCEPTED MANUSCRIPT

Graphical Abstract