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A novel process simulation model (PSM) for anaerobic digestion using Aspen Plus

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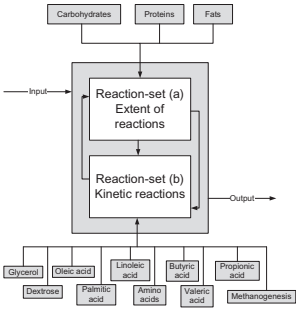
HIGHLIGHTS

- Process simulation model (PSM) for biogas production was developed using Aspen Plus.
- The model was validated from industrial and previous research studies.
- Any substrates' biogas potential can be predicted using the model.
- PSM is statistically validated.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel process simulation model (PSM) was developed for biogas production in anaerobic digesters using Aspen Plus®. 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 ±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).

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 (~39.4 MJ m^{-3}) can be used for different purposes such as heating, cooking, and electricity production (British Standards Institution, 2005a,b; Rajendran et al., 2012). If the biogas is upgraded, it can also be used as vehicle fuel (Deublein and 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

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.

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acids, and amino acids. Secondly, the hydrolyzed monomers are converted into different volatile fatty acids (VFA), such as caproic 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 and 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 and McCarty, 1975; Lawrence and 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, 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 ±5%, ±10%, and ±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.

Fig. 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, 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 tripalmate, 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, acetogeneic, and methanogenic phases. In total, ten different subsets 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 (Fig. 1).

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
9	Insoluble protein (I.P)	$I.P + 0.3337\ H_2O \rightarrow 0.045\ C_6H_{14}N_4O_2 + 0.048\ C_4H_7NO_4 + 0.047\ C_4H_9NO_3 + 0.172\ C_3H_7NO_3 + 0.074\ C_5H_9NO_4 + 0.111\ C_5H_9NO_2 + 0.25\ C_2H_5NO_2 + 0.047\ C_3H_7NO_2 + 0.067\ C_3H_6NO_2S + 0.074\ C_5H_{11}NO_2 + 0.07\ C_6H_{13}NO_2 + 0.046\ C_6H_{13}NO_2 + 0.036\ C_9H_{11}NO_2$	0.6 ± 0.1
10	Triolein	$C_{57}H_{104}O_6 + 3\ H_2O \rightarrow C_3H_8O_3 + 3\ C_{18}H_{34}O_2$	0.5 ± 0.2
11	Tripalmate	$C_{51}H_{98}O_6 + 8.436\ H_2O \rightarrow 4\ C_3H_8O_3 + 2.43\ C_{16}H_{34}O$	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