Application of modified ADM1 to long-term experiments for methane/hydrogen production from model organic waste

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Abstract

The modified ADM1 including lactate and ethanol was verified using experimental data for methane/hydrogen production processes from model organic waste. Monosaccharides were presumably degraded into acetate, lactate, butyrate, and ethanol; lactate is further degraded into propionate and acetate; ethanol is degraded into acetate. The methane production experiment was carried out using an 8-L reactor operated at 55°C, pH 6.8, and sludge retention time (SRT) of 7-20 days for 370 days. Concentrations of carbohydrates, monosaccharides, butyrate, propionate, valerate, acetate, and the methane production rate were simulated well by the modified ADM1. The ratio of degradation pathways from monosaccharides to acetate, lactate, butyrate, and ethanol were inferred, respectively, to be 0.4, 0.6, 0.0, and 0.0. The hydrogen production experiment was carried out using a 2-L (1.5L) reactor operated at 35°C, pH 6.0-6.5, and SRT of 0.5-2.0 days for 370 days. The simulation results suggested that all bacterial populations except the sugar-degrading bacteria were washed out from the reactor because of the short SRT. The respective ratios of degradation pathways from monosaccharides to acetate, lactate, propionate, and ethanol were inferred to be 0.55, 0.0, 0.4, and 0.05 at pH 6.5 and 0.7, 0.2, 0.05 and 0.05 at pH 6.0.

Keywords: ADM1; ethanol; hydrogen production; lactate; metabolic pathway

INTRODUCTION

Various mathematical models for anaerobic digestion have been developed to elucidate microbial and chemical dynamics for different operational conditions. The IWA Task Group published the Anaerobic Digestion Model No. 1 (ADM1) with the aim of establishing a common platform for modeling the anaerobic digestion process for additional model development and validation studies (IWA Task Group, 2002). The ADM1 has been tested for various process configurations (Blumensaat and Keller, 2005; Parker, 2005; Derbal et al., 2009; Galí et al., 2009; Lee et al., 2009). However, it is difficult to measure and verify the various processes, components, and parameters in the ADM1 in long-term operation.

In addition, hydrogen is recently receiving much attention as a renewable and clean energy derived from organic wastes. Hydrogen is produced during anaerobic digestion processes of organic compounds with specific controlled parameters, such as pH, microbial species, and hydraulic retention time (HRT) (Fang and Liu, 2002; Van Ginkel and Logan, 2005). However, some limitations of ADM1 have been identified related to its applicability to non-methanogenic systems. Potentially relevant processes with hydrogen production are not included in the ADM1 to avoid unnecessary complexity in the simulation of conventional biogas production processes. For example, two intermediates, lactate and ethanol, are excluded from the original ADM1 because of their small impact on methanogenic and low loading systems. Only a few studies have applied mathematical models to bio-hydrogen production. Peiris et al. (2006) modified ADM1 by incorporating lactate and ethanol for simulating hydrogen production. This modified model was verified by comparing the final states of only pH and hydrogen yield of batch experimental results. However, dynamics of the intermediates and the hydrogen production were not fully verified.
Penumathsa et al. (2008) also incorporated lactate into the ADM1 for bio-hydrogen production. This modified model was verified by comparing the results of 20-day experiments, but the lactate concentrations were not measured in the experiment.

In this study, the modified ADM1 including lactate and ethanol was verified using long-term experimental data for methane/hydrogen production processes. The ratios of degradation pathways from monosaccharides to acetate, lactate, propionate, and ethanol were fitted to the experimental data. Difficulties of the modified model and recommendations for additional modifications for bio-hydrogen production will be presented.

**MATERIALS AND METHODS**

**Model description**

The ADM1 modified by Peiris et al. (2006) was used for this study. Figure 1 presents the COD flow in the model. The model includes lactate and ethanol as important intermediates in the hydrogen production process. In the modified ADM1, monosaccharides are degraded into acetate, lactate, butyrate, and ethanol. Different from the original ADM1, propionate is not produced directly from monosaccharide degradation. Lactate-degrading bacteria and ethanol-degrading bacteria were also included in the model. Subsequently, lactate is further degraded into propionate and acetate; ethanol is degraded into acetate. Outlines of the modified reactions are shown in Table 1. Kinetic parameters in the model were fitted to experimental data using a software package (Berkeley Madonna; Robert I. Macey and George F. Oster).

![Figure 1](https://iwaponline.com/wpt/article-pdf/6/1/wpt2011009/382809/9.pdf)
Methane production experiment

Data generated from a lab scale experiment to produce methane using a model organic waste were used for this study. Fully detailed descriptions of the experiments can be found in Kawano (2005). The experimental system consists of a completely mixed reactor with an 8.0 L working volume. The model organic waste was made using dog food, which was crushed and suspended in tap water to adjust the total solid (TS) concentration to 8–10%.

Data were collected during the reactor operation over 370 days in continuous mode at 55°C. The influent concentrations for carbohydrates, proteins, monosaccharides, amino acids, lactate, propionate, butyrate, valerate, ethanol, acetate, TS, and ammonia-nitrogen (NH$_4$-N) are depicted in Fig. 2. The HRT was reduced gradually from 20 to 5 days, allowing for some pump troubles, as presented in Fig. 3. In the completely mixed reactor, the HRT equals the sludge retention time (SRT). The actual variations of HRT and the substrate concentrations in influent were used for verification of the modified ADM1. The pH was not regulated but instead remained nearly constant at 6.8±0.2 in the reactor through the experimental period.

Hydrogen production experiment

Data generated from a lab experiment to produce hydrogen using the model organic waste were used for this study. Fully detailed descriptions of the experiments can be found in Kawano et al. (2005a; 2005b). The experimental system consists of a completely mixed reactor with a 2.0 L working volume on days 0–85. Because of operability, the working volume was set to 1.5 L on days 85–370.

Table 1 | Degradation pathways of monosaccharides, lactate, and ethanol

<table>
<thead>
<tr>
<th>Substrate → products</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar → acetate</td>
<td>C$<em>6$H$</em>{12}$O$_6$ + 2H$_2$O → 2CH$_3$COOH + 2CO$_2$ + 4H$_2$</td>
</tr>
<tr>
<td>Sugar → lactate</td>
<td>C$<em>6$H$</em>{12}$O$_6$ → 2CH$_3$CHOHCOOH</td>
</tr>
<tr>
<td>Sugar → butyrate</td>
<td>C$<em>6$H$</em>{12}$O$_6$ → 2CH$_3$CH$_2$CH$_2$COOH + 2CO$_2$ + 2H$_2$</td>
</tr>
<tr>
<td>Sugar → ethanol</td>
<td>C$<em>6$H$</em>{12}$O$_6$ → 2CH$_3$CH$_2$OH + 2CO$_2$</td>
</tr>
<tr>
<td>Lactate → propionate</td>
<td>CH$_3$CHOHCOOH + H$_2$ → CH$_3$CH$_2$COOH + H$_2$O</td>
</tr>
<tr>
<td>Lactate → propionate + acetate</td>
<td>3CH$_3$CHOHCOOH → 2CH$_3$CH$_2$COOH + CH$_3$COOH + H$_2$O + CO$_2$</td>
</tr>
<tr>
<td>Lactate → acetate</td>
<td>CH$_3$CHOHCOOH + H$_2$O → CH$_3$COOH + CO$_2$ + 2H$_2$</td>
</tr>
<tr>
<td>Ethanol → acetate</td>
<td>CH$_3$CH$_2$OH → CH$_3$COOH + 2H$_2$</td>
</tr>
</tbody>
</table>

Figure 2 | Substrate concentrations in influent for the methane production reactor. (A) X$_s$, carbohydrates; (B) X$_p$, proteins; (C) S$_m$, monosaccharides; (D) S$_a$, amino acids; (E) S$_l$, lactate; (F) S$_p$, propionate; (G) S$_b$, butyrate; (H) S$_v$, valerate; (I) S$_e$, ethanol; (J) S$_a$, acetate; (K) TS, and (L) NH$_4$-N. Experimental data and input value lines for simulation are shown, respectively.
Data were collected during reactor operation at 35°C in continuous mode. The HRT was gradually reduced from 2 to 0.5 days, as portrayed in Fig. 4. The experimental influent concentrations are presented in Fig. 5. The actual variations of HRT and the substrate concentrations in influent were used for verification of the model. The pH in the reactor was regulated at 6.5 on days 0–180 and 6.0 on day 180–370 using a pH controller.

RESULTS AND DISCUSSION

Model verification for methane production

The experimental and simulation results of effluent concentrations of the methane production reactor are depicted in Fig. 6. The model well simulated high degradation at 75–90% of carbohydrates. The concentrations of intermediates were also well simulated using the model. The model calibration suggests that the respective conversion ratios from monosaccharides to acetate, lactate, butyrate, and ethanol were 0.4, 0.6, 0.0, and 0.0. The lactate concentrations were low (< 5 g-COD/L), but a high conversion ratio of monosaccharides to acetate (0.6) was estimated. On the other hand, both the ethanol concentrations (< 0.1 g-COD/L) and the conversion ratio of monosaccharides to ethanol were low (0.0). Differences between the measured and simulated concentrations of proteins, amino acids, and NH₄-N are expected to result from the complicated compositions of the peptides in the influent.

The biogas production rates and microbial populations in the reactor are portrayed in Fig. 7. The trends of the experimental data of high methane production rates (of ca. 5 L/L/day) and low hydrogen production rates (< 0.5 L/L/day) were well simulated, although the model underestimated the methane production rate on days 250–330. The methane production rate increased with the organic loading rate. The rapid decrease in the methane production rate on days 341–349 might be attributable to the rapid increase in HRT (Fig. 3). According to the model, the average methane production ratio from acetate to that from H₂+CO₂ was about 2.3:1.0. Simulation results show that all microbial groups except ethanol-degraders (Xₑt) defined in this model survived in the reactor through the experimental period. Among those microbial groups, microorganisms that degrade sugars (Xₘa), acetate (Xₘc), long chain fatty acids (Xₘa), and hydrogen (Xₘh₂) were dominant in the reactor. The large population of methane producers (Xₘa and Xₘh₂) was consistent with high methane production and low hydrogen production in the reactor.
Figure 5 | Substrate concentrations in influent for the hydrogen production reactor. (A) $X_{ch}$, carbohydrates; (B) $X_{ac}$, proteins; (C) $S_{su}$, monosaccharides; (D) $S_{aa}$, amino acids; (E) $S_{lac}$, lactate; (F) $S_{pr}$, propionate; (G) $S_{va}$, butyrate; (H) $S_{va}$, valerate; (I) $S_{et}$, ethanol; (J) $S_{ac}$, acetate; (K) TS, and (L) NH$_4$-N. Experimental data plots and simulation lines are shown, respectively.

Figure 6 | Substrate concentrations in effluent in the methane production reactor. (A) $X_{ch}$, carbohydrates; (B) $X_{ac}$, proteins; (C) $S_{su}$, monosaccharides; (D) $S_{aa}$, amino acids; (E) $S_{lac}$, lactate; (F) $S_{pr}$, propionate; (G) $S_{va}$, butyrate; (H) $S_{va}$, valerate; (I) $S_{et}$, ethanol; (J) $S_{ac}$, acetate; (K) TS, and (L) NH$_4$-N. Experimental data plots and simulation lines are shown.

Figure 7 | Biogas production and microorganisms from the methane production reactor. (A) methane, (B) hydrogen, and (C) microorganisms. Experimental data plots and simulation lines are shown. Microorganisms capable of degradation of sugar ($X_{ch}$), amino acids ($X_{ac}$), acetate ($X_{ac}$), long chain fatty acids ($X_{la}$), lactate ($X_{lac}$), propionate ($X_{pr}$), valerate and butyrate ($X_{va}$), and hydrogen ($X_{ho}$).
Model verification for hydrogen production

The experimental and simulation results of effluent concentrations of the hydrogen production reactor are presented in Fig. 8. The modified ADM1 revealed that lactate and ethanol, as well as butyrate and acetate, were the major constituent products in the reactor. Proteins and lipids were degraded only slightly in the short-HRT conditions, compared to carbohydrates. Low degradation of proteins caused low concentrations of NH4-N.

![Figure 8](https://iwaponline.com/wpt/article-pdf/6/1/wpt2011009/382809/9.pdf)

**Figure 8** Substrate concentrations in effluent in the methane production reactor. (A) Xch, carbohydrates; (B) Xpr, proteins; (C) Ssu, monosaccharides; (D) Saa, amino acids; (E) Slac, lactate; (F) Spro, propionate; (G) Sbu, butyrate; (H) Sva, valerate; (I) Set, ethanol; (J) Sac, acetate; (K) TS, and (L) NH4-N. Experimental data plots and simulation lines are shown.

The biogas production rates and microbial populations in the hydrogen production reactor are shown in Fig. 9. The hydrogen production rate (< 0.2 L/L/day) was much higher than the methane production rate (ca. 2 L/L/day). The short SRTs allowed for the sugar degraders alone to be maintained in the reactor while other slow-growing microorganisms, such as methane producers (Xac and Xh2), were washed out. This result suggests that the concentrations of lactate, ethanol, acetate, propionate, butyrate and the production rate of methane and hydrogen were governed by the population dynamics and metabolic pathways of the sugar-degrading bacteria.

![Figure 9](https://iwaponline.com/wpt/article-pdf/6/1/wpt2011009/382809/9.pdf)

**Figure 9** Biogas production and microorganisms in the hydrogen production reactor. (A) methane, (B) hydrogen, and (C) microorganisms. Experimental data plots and simulation lines are shown. Microorganisms capable of degradation of sugar (Xsu), amino acids (Xaa), valerate and butyrate (Xc4), and hydrogen (Xh2).

The pH value in the reactor was regulated at 6.5 on days 0–180 and 6.0 on days 180–370. We expected an increase in the hydrogen production rate at pH 6.0 because the reported optimal pH values for hydrogen production from glucose are 5.0–6.0 (Fang and Liu, 2002). However, the
hydrogen production rate decreased after day 180. After day 180, the butyrate concentration decreased but the acetate, lactate, and propionate concentrations increased. The hydrolysis rates and the microbial activities are highly influenced by pH. Therefore, different ratios of degradation pathways from monosaccharides were set after day 180. The regulating mechanism to handle this parameterization is not included in the ADM1. The model calibration suggested that the conversion ratios from monosaccharides to acetate, lactate, butyrate, and ethanol were, respectively, 0.55, 0.0, 0.4, and 0.05 before day 180, and 0.7, 0.2, 0.05 and 0.05 after day 180. In this model, the hydrogen production rate increases with the ratio of pathways from monosaccharides directly to butyrate and acetate. On the other hand, the hydrogen production rate decreases with the ratio of the pathways to lactate and ethanol. Furthermore, the direct conversion from lactate to propionate consumes hydrogen. Actually, the hydrogen production rate was negatively correlated to lactate production. These results underscore the importance of addition of the intermediates, especially lactate, into the ADM1 in the hydrogen production reactor.

CONCLUSIONS

The modified ADM1 including lactate and ethanol was verified using long-term experimental data for methane/hydrogen production processes from model organic waste. In the methane production experiment, the lactate concentrations were low, but the modified model shows that the main product of degradation of monosaccharides is lactate. On the other hand, ethanol was a negligible intermediate in the methane production process. In the hydrogen production experiment, the simulation results suggest that all bacterial populations except the sugar-degrading bacteria were washed out from the reactor because of the short SRT. The concentrations of lactate, ethanol, acetate, propionate, butyrate, and the production rate of hydrogen were governed by the population dynamics and the metabolic pathways of the sugar-degrading bacteria. It can be concluded that the modified model including lactate and ethanol is a valuable tool for use in the design and operation of hydrogen production reactors. Mechanisms to predict the degradation pathway of monosaccharides to the fermentation products should be elucidated for effective hydrogen production from organic wastes.

REFERENCES


Parker, W. J. 2005 Application of the ADM1 model to advanced anaerobic digestion. *Bioresource Technology* **96** (16), 1832-1842.