〈研究発表〉

Control Scheme for Efficient Recovery of Volatile Fatty Acids during Anaerobic Digestion of Food Waste

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Abstract

By refining the existing ADM1 to incorporate a pH inhibition equation on methanogen's decay, the critical pH for acid failure was determined during anaerobic fermentation of food waste. The optimal operating conditions for efficient VFA recovery were established by simulating experimental data from other researchers. A range of pH parameters affecting methanogens was identified. For conservative operations, employing low pH inhibition parameters （$pH_{UL}=6.41$, $pH_{LL}=5.47$ and $n=0.23$） allows for stable methane fermentation against acid failure. On the other hand, optimistic curves （$pH_{UL}=5.55$, $pH_{LL}=5.11$ and $n=0.24$） can be utilized to decrease the specific decay rate of methanogens by 0.4 d^{-1}, thereby promoting adequate acidification and maximizing VFA yield. Experimental results indicate that the optimal pH range for activity of acid-producing bacteria is between pH 5.5–6.2, which also benefits VFA recovery by significantly reducing VFA consumption due to acid inhibition.

キーワード：anaerobic processes, food wastes, methanogens, pH inhibition, VFA recovery
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1. Introduction

VFAs are intermediate products of anaerobic digestion with diverse industrial applications. Precise control of acidogenesis and methanogenesis kinetics is crucial for efficient VFA recovery from anaerobic processes. pH plays a significant role in obtaining the maximum VFA production and the desired VFA product. Controlling pH could enhance hydrolysis/acidogenesis activity while inhibiting VFA consumption by methanogens. Alkaline pH conditions promote optimal VFA production by facilitating organic matter disintegration, providing biodegradable substrates, and inhibiting methanogenic archaea. However, maintaining high alkaline pH requires significant consumption of chemical reagents, which is not economically viable.

Acidogens responsible for VFA production tolerate low pH concentrations better than methanogens. Acidic pH fermentation may also improve VFA production compared to alkaline pH. Fermentation is classified into ethanol type, mixed acid-type, and butyric acid-type based on the produced organic acids, occurring within pH ranges of 4.0–4.5, 4.5–5.5, and 5.5–6.5, respectively. Thus, future studies should focus on optimizing operational parameters and selecting a feasible recovery pH range.

2. Methods and Materials

2.1 Modified low-pH inhibition function on methanogens

The relationship between pH and the experimentally determined values of methanogen specific decay rate （b_{pH}） was expressed using **Equation (1)**. The proposed equation increases the specific decay rate at low pH conditions. According to the proposed expression, at a pH value equal to the lower limit pH （pH_{LL}）, the value of pH inhibition factor I_{pH} becomes 0.05 （$I_{pH}=\exp(-3)$） leading to 20 times increase in the methanogen decay rates. The high level of pH （pH_{UL}） is the threshold pH at which the acceleration of biomass decay is initiated. The power coefficient （n） is to adjust the shape of the curve between the plots. As the switching function （I_{pH}） ranges between zero to one, the specific decay rate changes between b and infinity.

$$\begin{cases} b_{\mathrm{pH}} = \dfrac{b}{I_{\mathrm{pH}}} \\ I_{\mathrm{pH}} = \exp\left(-3\left(\dfrac{\mathrm{pH_{UL}} - \mathrm{pH}}{\mathrm{pH_{UL}} - \mathrm{pH_{LL}}}\right)^{n}\right) \\ I_{\mathrm{pH}} = 1 \text{ if } \mathrm{pH} \geq \mathrm{pH_{UL}} \end{cases} \tag{1}$$

Where, b_{pH}=specific decay rate of methanogens (d^{-1}), b=inherent decay rate of methanogens without inhibition (d^{-1}), I_{pH}=empirical lower-only inhibition switching function (−), n=coefficient, (−), pH=pH in the system (−), $\mathrm{pH_{UL}}$=upper level pH where low-pH inhibition is initiated (−), $\mathrm{pH_{LL}}$=lower level pH.

2.2 Benchmarks from literatures

The accuracy and applicability of the optimized model were validated by utilizing various experimental data from references. Two categories of data selection process were employed: short-term batch experiments to analyze VFA concentration changes under different pH conditions, and long-term experimental scenarios where the anaerobic VFA recovery system was operated with pH fluctuations.

For the above programming and process calculations, a commercial process simulator, GPS-X ver. 8.0 (Hatch Co., Ltd., Mississauga, Canada) was used. The kinetic and stoichiometric parameters were adapted from IWA Anaerobic Digestion Model No. 1 (ADM1)[1]. Subsequently, the simulation results and parameter ranges for each benchmark data were compared, enabling further improvements and adjustments to the pH inhibition model.

3. Results and Discussion

To calculate the potential risks of acidic failure and obtain preferable operating conditions for VFA recovery reactors, a safety-margin parameters was provided. From this, a methanogen-wide specific decay rate against pH was obtained as shown in the thin-line of **Fig. 1**, where the values of n, $\mathrm{pH_{UL}}$ and $\mathrm{pH_{LL}}$ were 0.25, 6.25 and 5.74, respectively. For application of the biocidal model to practical use, two artificial curves (dashed-lines) were plotted on the graph (upper artificial curve: $\mathrm{pH_{UL}}$=6.41, $\mathrm{pH_{LL}}$=5.47 and n=0.23; lower artificial curve: $\mathrm{pH_{UL}}$=5.55, $\mathrm{pH_{LL}}$=5.11 and n=0.24). The upper curve was intended to allow a conservative calculation for the low pH inhibition (the specific decay rate plus about 0.4 d^{-1}). This parameter set may be used for plant operation and/or process design, which has a safety margin to avoid the unwanted risks from the acidic failure. For the lower curve covering the lower limit of CI_{95} below pH 5.5, this would yield an optimistic calculation result for the acidic failure (b_{pH} minus about 0.4 d^{-1}). Using this parameter set, it is possible to ensure the acidifying process for VFA recovery.

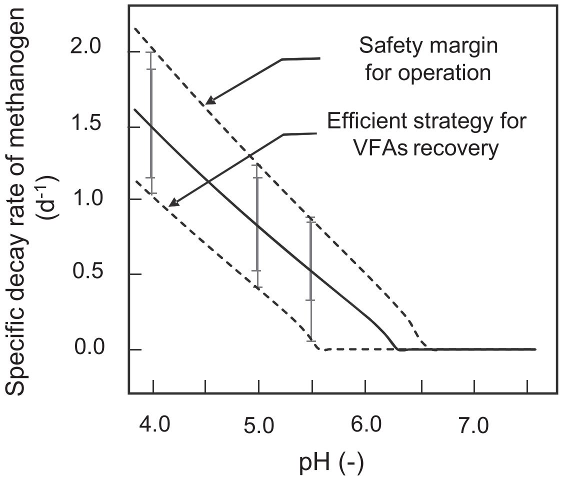

Fig. 1 Specific decay rates of methanogens along with pH[2]. (error bar: the range between the upper CI95 and the lower CI95, dashed line: regression curves to cover the error bars).

Since acidogens and acetogens are faster than methanogens, the higher biodegradability of bio-pulp led to a rapid increase in total VFA and subsequent decrease in pH at day 110 in **Fig. 2**. By day 8, the total VFA concentration had reached 9 g/L, resulting in process failure. On day 121, the feedstock in the digester was switched to manure with a 2 % VS content. This resulted in an immediate conversion of accumulated VFAs to biogas. The benchmarks were fitted by adjusting the pH inhibition parameters, resulting in a set of inhibition parameters of $\mathrm{pH_{UL}}$=6.21, $\mathrm{pH_{LL}}$=5.57 and n=0.25. The model was able to match the observed trends and provide insight into the mechanisms behind the inhibition of the system at different pH levels.

Previous studies revealed that maintaining a neutral to slightly acidic pH (7 and 6) improved the solubilisation of particulate organic matter in food waste, resulting in higher levels of COD leaching. As shown in **Fig. 3**, fermentation conducted at a pH of 6.5 appears to be a promising approach for achieving high VFAs production efficiencies.

The acidic conditions (pH 4 and 5) not only inhibited hydrolysis but also reduce VFA production from

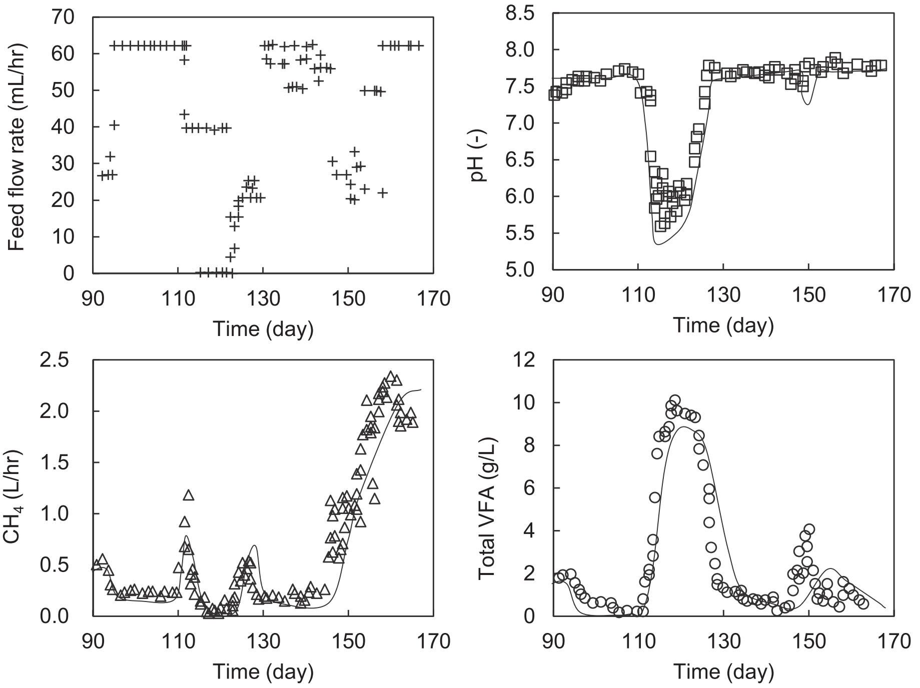

Fig. 2 Reactor performance by manipulated Feed flow rate[3]. [day 94-110]: organic underload by stopping the addition of glucose and returning to 2 % VS; [day 110-121]: changing the feed to bio-pulp containing 6 % VS; [day 121-145]: back to manure with 2 % VS; [day 145-170]: changing the feed to bio-pulp containing 6 % VS.

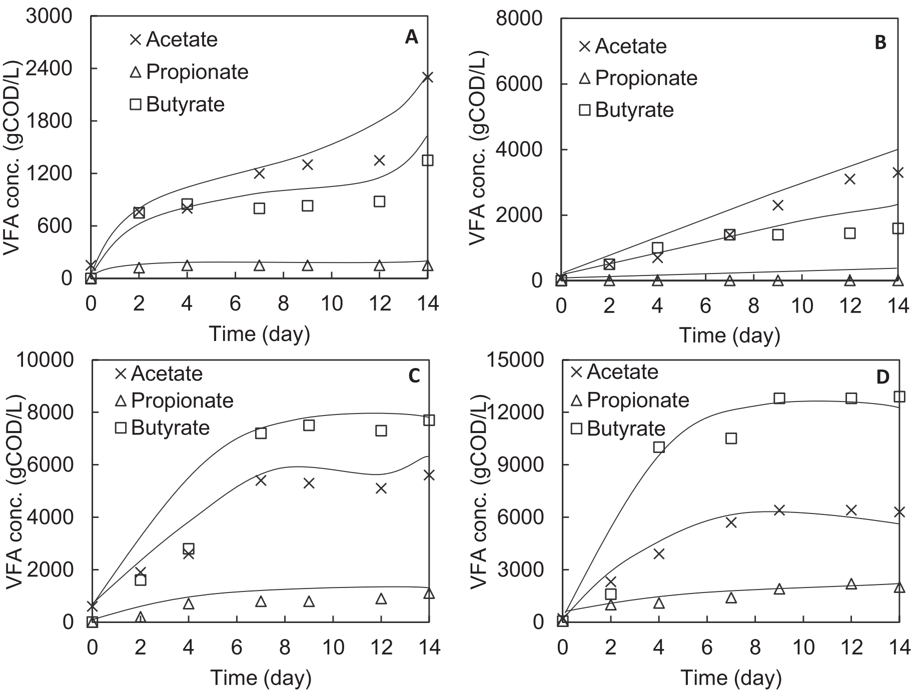

Fig. 3 Concentration of main VFAs in different pH conditions[4]. (A: pH 4.0, B: pH 5.0, C: pH 6.0, D: pH 7.0).

solubilised substrates, resulting in low VFA concentrations and yields. Although hydrolysis performance was better at pH 5 than 4, this did not translate into higher VFA production due to a metabolic shift towards lactate production at pH 5. The experimental data was fitted at $\mathrm{pH}_{UL}=6.33$, $\mathrm{pH}_{LL}=5.56$, and $n=0.25$ respectively.

4. Conclusions

The empirical formula for low-pH inhibition on methanogens was derived from the experimental data, providing a set of parameters for the design and operation of anaerobic reactors.

The highest possible VFA yield from food waste can be achieved by maintaining the pH level within the range of 5.5–6.2 in the anaerobic digester. This particular pH range stimulates the acidogens' activity while inhibiting methanogens, leading to an optimal VFA recovery rate.

While the parameters in the pH inhibition model may vary slightly for different substrates, they can still provide accurate predictions of reactor performance at acidic pH conditions. To obtain specific target VFA products, the reaction process must carefully and accurately control the pH.

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