Modelling the Biogas Production Kinetics of Anionic Surfactants Exposed Anaerobic Fermentation Process Using Sigmoidal Growth Functions

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Abstract. The kinetics of biogas production on anaerobic fermentation with anionic surfactants added was evaluated using the sigmoidal models (the modified Gompertz and Logistic). The mesophilic anaerobic co-fermentation experiments under different anionic surfactants concentrations were conducted with mixed cow dung and corn straw as feedstocks. The results showed that the anionic surfactants in appropriate concentrations on anaerobic fermentation increased the cumulative biogas yields while prolonged the lag phase time. The modified Logistic model performed better than modified Gompertz model in fitting the experimental results of anaerobic co-fermentation with anionic surfactants added. The results of this study were expected to provide theoretical guidance for studying the impact of anionic surfactants and modelling the kinetic process of anaerobic co-fermentation.

1. Introduction
Anaerobic fermentation is an effective way to utilize biomass energy, which can not only treat organic waste, but also recycle renewable energy [1]. In the practical application, the surfactants in sewage affected the gas production of anaerobic fermentation [2-4]. Previous studies about the impacts of surfactants on anaerobic fermentation were mainly focusing on direct analysis of experimental data [5-7], instead of modelling the biogas production kinetics. Although anionic surfactants (LAS) are common and highly toxic, the studies on the biogas production kinetics of anaerobic co-fermentation with LAS added are rare. In order to understand the impacts of LAS on anaerobic fermentation, it is necessary to study the dynamic process [8]. Therefore, it is important to study biogas production kinetics of anaerobic fermentation under different LAS concentrations by modelling.

Growth curves are a tool to describe a variable increase with time, until it approaches its saturation [9]. Bacterial growth curve is used to describe the change in the number of viable bacteria with time. When the growth curve is defined as the logarithm of number of organisms plotted against time, showing a sigmoidal curve [10]. The cumulative biogas yields curves in the early stage (the phase of slow gas production), the middle stage (the phase of rapid gas production) and the later stage (the phase in which the rate of gas production slows and eventually reaches zero) of anaerobic fermentation correspond to the lag, exponential and asymptotic or stationary phases, respectively [11].

Many sigmoidal models were established in literatures, such as the Gompertz model, the Logistic model and the Richards model [10,12-14]. Previous studies showed that the modified Gompertz equation was usually a common model for biogas production by simple organic substrate degradation [15-17]. For more complex substrate, the three-parameter Gompertz equation becomes less suitable. The Richards model introduces a fourth parameter v, which allows some flexibility in the shape of the curve. For v = 0 and 1 the Richards model is reduced to the Gompertz and Logistic model,
respectively [10,11]. However, the studies on the biogas production kinetics of anaerobic fermentation with LAS added using the modified Gompertz and Logistic model are lack.

In this study, the modified Gompertz model and Logistic model were used to study the kinetic process of anaerobic fermentation under different LAS concentrations. The correlation coefficients (R²) obtained from the two models were compared. Moreover, the maximum cumulative biogas yields (A), maximum biogas production rate (Rₘₐₓ) and the lag phase time (λ) were analyzed. The primary aim was to compare the similarities and differences of the two models, and determining whether they were sufficient to evaluate the biogas production kinetics of anaerobic fermentation process.

2. Data Collection and Models

2.1. Methane Yields of Anaerobic Co-fermentation Experiments

There were 5 groups of anaerobic co-fermentation experiments with cow dung (for 18 g dry weight) and corn straw (for 6 g dry weight) as feedstocks. No surfactant was added into the CK group. The concentrations of LAS were set as 1, 10, 50 and 100 mgLAS/L. Feedstocks were collected from Xuanhua District, Zhangjiakou City, Hebei Province, China in June 2018. The basic properties of fermentation feedstocks are shown in Table 1.

| Compositions            | Corn straw | Cow dung  |
|------------------------|------------|-----------|
| TS (%dry weight)       | 92.86 ± 0.21 | 29.70 ± 0.66 |
| VS (%TS)               | 90.56 ± 0.13 | 82.06 ± 0.58 |
| Total nitrogen (%TS)   | 0.34 ± 0.01  | 0.25 ± 0.20  |
| Organic carbon (%TS)   | 22.61 ± 0.13 | 10.53 ± 0.00 |
| Carbon-nitrogen ratio (C/N) | 66.47 ± 0.67 | 42.63 ± 0.43 |
| Cellulose (%TS)        | 68.62 ± 0.24 | 21.64 ± 0.48 |
| Hemicellulose (%TS)    | 15.46 ± 0.11 | 13.32 ± 0.88 |
| Lignin (%TS)           | 30.22 ± 0.46 | 16.22 ± 0.62 |

The TS value of the substrate in the reactor was adjusted to 8% by adding distilled water. Mesophilic (37.0±1.0 °C) fermentation experiments used a thermostatic water bath were conducted for 37 days in 500 mL fermentation tanks with a working volume of 300 mL. The volume of biogas produced on the day was measured according to the volume of saturated salt water discharged. Three parallel samples were set for each fermentation group. Before analysis, the data of the three parallel samples were averaged and used as the final biogas yields (standard conditions).

2.2. Model and Data Analysis

The plots of daily and cumulative biogas yields were drawn from the experimental data using Origin 9.0 software. A nonlinear regression analysis was performed to fit the equations (the modified Gompertz and Logistic) to the cumulative biogas yields curves with respect to fermentation time. Aiming at minimizing the sum of squares of the difference between the predicted value and the experimental value searches for values of A, Rₘₐₓ and λ. The minimum residual sum of squares and 95% confidence intervals were set to obtain the biogas cumulative yields curves and gave the R² values. R² reflected the degree of correlation between variables, and t test and F test were used to conduct statistical tests on the fitting results obtained from different models. From statistics part of the fitting report, p < 0.05 indicated the parameters were suitable for estimating the experimental results. According to the ANOVA part of the fitting statement, p < 0.05 indicated significant fitting effect.

The mathematical parameters in the original function are improved into biological parameters [10], and the modified Gompertz equation [14] is given by

\[ y = A \times \exp\left(- \exp\left[\frac{R_{\max} \times e^{-(\lambda \times t)}}{A} \times (t + 1)\right]\right) \]  

(1)
Where y represents the cumulative biogas yields (mL/g TS) with respect to time t (d), A is the maximum cumulative biogas yields (mL/g TS), \( R_{max} \) is the maximum biogas production rate (mL/g TS/d), \( \lambda \) is the lag phase time (d) and e is constant equal to 2.71.

The Logistic model \([9]\) is given by

\[
y = \frac{A}{1 + e^{4R_{max}x(\lambda-x)+2}}
\]

Where A, \( R_{max} \) and \( \lambda \) had the same meaning as above.

3. Results

3.1. Biogas Yields of Anaerobic Fermentation Under LAS

The maximum daily biogas yields of the LAS added groups were higher than that of the CK group, which were shown in Figure 1 (a). The highest maximum daily biogas yields were obtained in the 1 mgLAS/L added groups.

According to concentrations of LAS and the daily biogas yields, it was found that the maximum daily biogas yield in LAS added groups with low concentration were high.

As can be seen from Figure 1 (b), the variations of cumulative biogas yields presented “stable-rising-stable” trend, showing sigmoidal curves. The cumulative biogas yields of the 100 mgLAS/L added group were lower (other groups were higher) than that of the CK group, while the cumulative biogas yields of other groups were higher than that of the CK group. The cumulative biogas yields of the 1 mgLAS/L added group were highest. According to the daily and cumulative biogas yields, it was...
found that the anaerobic fermentation increased the cumulative biogas yields by increasing the maximum daily biogas yields and expanding the period with high yields.

3.2. Modelling Biogas Production Kinetics Using Modified Gompertz Model
The cumulative biogas yields were fitted using the modified Gompertz model (Figure 2). The $R^2$ values were all greater than 0.9 (Table 2), which showed that the good fitting results of the modified Gompertz model in expressing biogas cumulative process. The highest (or lowest) $R^2$ and A values were not obtained in the same group, therefore, there was no clear relationship between the $R^2$ and A.

### Table 2. The Gompertz model fitting results of cumulative biogas yields under LAS.

| Surfactants | Concentration (mg/L) | $A^a$ (mL/g TS) | $R_{\text{max}}^b$ (mL/g TS/d) | $\lambda^c$ (d) | $R^2d$ |
|-------------|----------------------|----------------|-------------------------------|----------------|--------|
|             | Fitting results | Experiment results | Fitting results | Experiment results |        |        |
| LAS$e$      | 0 | 66.39 | 65.40 | 4.54 | 5.46 | 12.36 | 0.9988 |
|             | 1 | 92.07 | 85.96 | 5.29 | 7.18 | 13.04 | 0.9985 |
|             | 10 | 85.04 | 76.63 | 4.63 | 6.69 | 13.15 | 0.9951 |
|             | 50 | 77.57 | 68.41 | 4.02 | 5.85 | 13.26 | 0.9887 |
|             | 100 | 43.06 | 42.70 | 3.80 | 5.51 | 14.31 | 0.9922 |

$a$ maximum cumulative biogas yield.

$b$ maximum biogas production rate.

$^c$ lag phase time.

$^d$ correlation coefficients.

$^e$ anionic surfactant.

The A values of fitting results were higher than that of experimental results in all groups (Table 2). The highest A values of both experimental and fitting results were obtained from the 1 mgLAS/L added groups. Therefore, the A values with high experimental results obtained high fitting results.

The $R_{\text{max}}$ values of experimental results were higher than that of fitting results in all groups (Table 2), confirming the results that LAS in appropriate concentrations increased the $R_{\text{max}}$. In addition, the highest $R_{\text{max}}$ value of both experimental and fitting results was obtained from the 1 mgLAS/L added group. The $R_{\text{max}}$ values with high experimental results generally obtained high fitting results.

The lag phase times ($\lambda$) of LAS added groups were longer than that of the CK group. The results showed that anaerobic fermentation with added LAS extended the start-up period. The $\lambda$ values of fitting results were more than 10 days. Biologically speaking, $\lambda$ is the time of slow biogas production stage[9]. In a mathematical sense, $\lambda$ represents the x-axis at which it intersects the x-axis[10]. Therefore, the fitting results were consistent with the experimental results.

3.3. Modelling Biogas Production Kinetics Using Modified Logistic Model
The cumulative biogas yields were fitted by the modified Logistic equation (Figure 3). $R^2$ values obtained from the modified Logistic model were higher than 0.99 indicating the good fitting of the modified Logistic model in expressing the biogas cumulative process.

For 1 mgLAS/L added groups, both fitting and experimental results of A values were highest (Table 3), which was consistent with the results of the modified Gompertz model. The A values with high experimental results obtained high fitting results, i.e., the fitting results of the A values were in line with the experimental results. The average A values obtained from the modified Logistic model were closer to the A values of the experiment compared to the modified Gompertz model.

As shown in Table 3, the $R_{\text{max}}$ values of the experimental results were higher than that of the fitting results in all groups, which was consistent with the results of the modified Gompertz model. The highest $R_{\text{max}}$ values of the fitting and experimental results were obtained from the 1 mgLAS/L added groups. Meanwhile, the $R_{\text{max}}$ results of the modified Logistic model were higher than the modified Gompertz model results. The fitting $R_{\text{max}}$ values were in line with the experimental $R_{\text{max}}$ values, except for CK group.
The average \( R^2 \) values of the LAS added groups obtained from the modified Logistic model were higher than that of the CK group (Table 3), which was consistent with the results of the modified Gompertz model. In addition, the \( \lambda \) values obtained from the modified Logistic model were higher than that obtained from the modified Gompertz model. The difference of results between the two models were interpreted that the different \( R_{\text{max}} \) values estimated by the program made the different \( \lambda \) values, which because the \( \lambda \) values were determined by the intersecting the line with the x-axis[10].

### 4. Discussion

As shown by the fitting results, the modified Logistic model obtained higher average \( R^2 \) than the modified Gompertz model in LAS added experiments. To verify the significance of these two models, t test and F test were conducted. Statistics part of the fitting report showed that the parameters in the modified Gompertz and Logistic models were suitable for estimating the experimental results. At the 0.05 level, the fitting function is significantly better than the function of experiment data.

Although the \( R^2 \) values were high, the fitting \( A \) and \( R_{\text{max}} \) values of the two models were different. Figure 4. shows the differences between fitting and experimental results of \( A \). When the experimental \( A \) values were high, the fitting \( A \) values were also high. In the LAS added experiments, the average \( A \) of the modified Logistic model (0.23% for LAS added experiments) was closer to the experimental results than the modified Gompertz model (7.38% for LAS added experiments). Therefore, the modified Logistic model was able to obtain more accurate \( A \) than the modified Gompertz model.

The discrepancies between the experimental and fitting values of \( R_{\text{max}} \) can be found in Figure 5. The results showed that the average \( R_{\text{max}} \) of the modified Logistic model were closer to experimental results than that of the modified Gompertz model. Therefore, for the \( R_{\text{max}} \), the modified Logistic model was able to represent experimental results better than the modified Gompertz model.

The modified Gompertz and Logistic models showed similar results for \( \lambda \), i.e., the \( \lambda \) values of LAS added groups were higher than that of the CK group. The low \( \lambda \) values were demonstrated simple nature and high biodegradability of the feedstocks[9]. The feedstocks between experimental and control groups were same. The high \( \lambda \) values obtained from the LAS added groups were understood that the addition of LAS affected the biodegradation process, and the start-up period was extended.

In general, the modified Logistic model performed better than the modified Gompertz model in fitting the experimental results of anaerobic co-fermentation under LAS. In addition to the modified Gompertz and Logistic models, there were other commonly sigmoidal models, such as the Richards model, the Stannard model and the Schnute model[10]. Among these models, the modified equation of the Stannard model was the same as that of the modified Richards equation. The replacement of \( a \) and \( b \) in the Schnute equation would result in the modified Richards model. Therefore, the modified Richards model was used to fit the experimental results in this study and compared with the modified Gompertz and Logistic models (data not shown). Although the average \( R^2 \) values obtained from the modified Richards model were higher than that obtained from the modified Gompertz and Logistic model in the LAS added experiments, the \( R_{\text{max}} \) values of part groups were not suitable for estimating the experimental results. In conclusion, the modified Gompertz and Logistic models performed better

### Table 3  The Logistic model fitting results of cumulative biogas yields under LAS.

| Surfactants | Concentrations (mg/L) | \( A^c \) (mL/g TS) | \( R_{\text{max}} \) (mL/g TS/d) | \( \lambda^c \) (d) | \( R^{2d} \) |
|------------|----------------------|-------------------|------------------|-----------------|---------|
|            | Fitting results | Experiment results | Fitting results | Experiment results |        |        |
|          |          |          |          |          |          |        |        |
| LAS        | 0        | 63.29   | 65.40   | 5.46   | 12.95   | 0.9973 |
|           | 1        | 85.56   | 85.96   | 5.58   | 13.77   | 0.9960 |
|           | 10       | 70.69   | 76.63   | 5.85   | 13.89   | 0.9976 |
|           | 50       | 41.98   | 42.70   | 5.51   | 14.49   | 0.9948 |
|           | 100      | 68.41   | 76.63   | 5.85   | 13.89   | 0.9976 |

\( a \): maximum cumulative biogas yield.
\( b \): maximum biogas production rate.
\( c \): lag phase time.
\( d \): correlation coefficients.
\( e \): anionic surfactants.

**The Logistic model fitting results of cumulative biogas yields under LAS.**

The \( \lambda \) values of the LAS added groups obtained from the modified Logistic model were higher than that of the CK group (Table 3), which was consistent with the results of the modified Gompertz model. In addition, the \( \lambda \) values obtained from the modified Logistic model were higher than that obtained from the modified Gompertz model. The difference of results between the two models were interpreted that the different \( R_{\text{max}} \) values estimated by the program made the different \( \lambda \) values, which because the \( \lambda \) values were determined by the intersecting the line with the x-axis[10].
than the modified Richards model in expressing the biogas cumulative process. From what has been discussed above, the modified Logistic model performed better than the modified Gompertez model in representing the experimental results in the anaerobic fermentation experiment with LAS added.

5. Conclusions
This study showed that the LAS in appropriate concentrations on anaerobic fermentation increased the cumulative biogas yields, while the start-up period was extended. According to the $R^2$ values and the discrepancies between the experimental and fitting values, it suggested that the better fitting results were obtained from the modified Logistic model compared with other models. The modified Logistic model could be used for modelling the biogas production kinetics with LAS added.

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