

Modelling the Effects of Dilute Alkaline Pretreatment of Lignocellulosic Biomass on Biogas Production

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Abstract

This paper simulated an experimental data on biogas production initially aimed to determine the effect of different concentrations of NaOH on the pretreatment of lignocellulosic biomass for possible application in co-digestion with cow dung (CD) and food waste (FW). The data were divided in training and validation subgroups and simulation was run using the nonlinear regression models (modified Gompertz and Transference function models). The modified Gompertz model fitted well with the dataset obtained for 5 and 7% NaOH pretreated with R-squared of 0.999 for both concentrations and RMSE of 0.004 and 0.397 respectively. The Transference function model best fitted the data obtained for 6% NaOH pretreated biomass with an R-squared of 0.997 and RMSE of 0.03. Generally, both models have shown good prediction capacities with the data used in the study. Both experimental data and their simulations have shown that the concentrations of NaOH in solutions used for the pretreatment of biomass have affected the retention time, cumulative gas production, intermediary processes and the methanogenic activities.

Keywords: Model, dilute alkaline, pretreatment, lignocellulosic biomass, biogas.

Introduction

A model is an abstraction of reality. This abstraction represents a complex reality in the simplest way that is adequate for the modelling. The best model is always that which attains the greatest realism (measured objectively as agreement between model outputs and real-world observations, or less objectively as the process insight attained from the model) with the least parameter complexity and the least model complexity (Wainwright & Mulligan, 2002). Broadly, a model could be a scale model, a mathematical model, a sketch, a segment of computer code, an analogy, a working device, or many other things. A model can be used to describe or explain some aspect of the natural world, it can be used as part of the design of an artefact, it can be part of an attempt to convince someone of some argument or ideology, or to determine public or corporate policy (Bissell & Dillon, 2012). Modelling and simulation are tools that offer support for the planning, design, and appraisal of dynamic systems and the evaluation of strategies for system transformation and change. Its application continues to grow at a notable rate because its application is not limited by discipline borders (Birta & Arbez, 2013).

Lauwers *et al.* (2013) pointed out that there are two main approaches of model classification; dynamic or non-dynamic, and white-, grey- or black-box. Dynamic models

use several ordinary differential equations. These models are fundamentally based on considerations of mass-balance to generate predictions continuous in time. Non-dynamic models link substrate to products, by means of stoichiometry through calculations with C, H, N and O and the obtained gas yield and predict time-independent variables. White-box models are deductive and use prior information. Grey-box models are mechanistically inspired models including parameter estimation procedures. Black-box models are data-driven models that link input directly to the output.

The mathematical models for anaerobic digestion may be divided into mechanistically inspired models, reduced complexity models and data-driven models. Mechanistically inspired models express the kinetics of stages of biogas production according to Monod-type kinetics, Haldane kinetics or Andrew kinetics. Examples of the most popular models of this group are Anaerobic Digestion Model no. 1 (ADM1), and parts of Benchmark Simulation Model no. 2. The Reduced Complexity Models present equations expressing mass balance and process kinetics, and can be used for control strategies even for large-scale plants. Data-driven models, on the other hand, aim at predicting the behaviour of the system without any pre-knowledge of the occurring process (Kucharska *et al.* 2018). Linear and non-linear regression have been used previously in the simulation of cumulative biogas production (Li *et al.*, 2011). During the exponential phase, biogas production have earlier been estimated by the regression Equation 1.

$$B = B_o(1 - e^{-kt}) \quad \dots \dots \dots 1$$

Another classification put-forward by Lubken *et al.* (2010) showed that mathematical models of anaerobic digestion might be grouped into three: stoichiometry-based models, rate-limiting step models and multispecies models. Stoichiometry-based models assume that biochemical composition decides the anaerobic digestibility of an organic substrate (Buswell formula, Boyle equation). The rate-limiting step approach highlights the need for the description of the rate-limiting step during the anaerobic digestions. The models apply Haldane kinetics, Andrew kinetics, Contois model or Monod model. These are dynamic mathematical models and are like mechanistically inspired models discussed by Lauwers *et al.* (2013). Multispecies models account for the complex microbiological consortia responsible for the anaerobic processes. An example of such model is ADM1.

However, because of lack of universal classification of anaerobic digestion models, these authors (Kucharska *et al.* 2018, Lubken *et al.*, 2010 and Lauwers *et al.*, 2013) have classified anaerobic digestion models into ADM1-based models, substrate conversion-based models, kinetic-based models, and black-box models. Veluchamy & Kalamdhad (2020) argued that kinetic model analysis is an effective tool to control and optimize various anaerobic processes by providing suggestions related to reactor design and operation that may lead to a more efficient performance that diminishes dependence on skilled operators. They classified kinetic models into two major divisions as structural and non-structural models. A major limitation of structural models is their dependence on the metabolic pathways that are more complicated. This author recommended the application of non-structural models

(Modified Gompertz, Logistic function and Transference function models). Moreover, the use of only one model to simulate anaerobic process in anaerobic reactors has been argued to be insufficient owing to its complexity. To sort this challenge, careful appraisal of different model outputs may give reliable and precise kinetic parameters and this brings the need for model comparison (Aromolaran & Sartaj, 2021).

According to Adamu and Aluyor (2013), scientists researching on biogas production have struggled to use several models to fit empirical data. Gibson *et al.* (1987) developed the MGM to a function that defines cell density during bacterial growth periods in terms of exponential growth rates and lag phase duration. An assumption of methane production rate in a batch digester corresponding to the specific growth rate of methanogenic bacteria led to the development of Equation 2 (Kafle & Chen, 2019; Lay *et al.*, 1998). Because the MGM has been identified as a good empirical non-linear regression model and commonly used in the simulation of methane accumulation. Tsapekos *et al.* (2018) modelled the experimental data obtained from digestion of biofibres subjected to mechanical pretreatment methods using the Modified Gompertz equation and found that more intense operation (Extreme pretreatment condition) was not associated with higher methane yield and a fair R^2 of 0.61 was obtained.

Jijai and Siripatana (2017) studied the kinetic modelling of Thai rice noodle wastewater co-digested with chicken manure using the Gompertz model and its related extensions to represent the experimental data. Gompertz model described growth and product formation data and well fitted the batch data. It was found that nutrient balance, suitable initial pH, and suitable VFA-to-alkalinity ratio promoted the growth of microorganisms and increased the biogas production rate. These were indicated by the kinetic parameters such as the maximum methane production rate (ml/d) and the methane production potential (ml) but not for the shorter lag-phase period.

Noteworthy, Bala *et al.* (2019) pointed out that, the values of the parameters such as maximum methane produced (B_0), lag phase period (λ) and maximum biogas production rate (R_m) are derived from the experimental results. Panigrahi *et al.* (2020) and Veluchamy & Kalamdhad (2020) have used Logistic function (LF) and Transference function (TF) models alongside the MGM and found them fitted to the experimental data obtained during co-digestion of lignocellulosic biomass with FW and animal manure. Yoruklu *et al.* (2020) attempted to optimise biogas production from seaweed collected from Istanbul's shores to determine optimal seaweed to FW ratio with the ratio of substrate to inoculum for maximum biogas production, as well as estimations of the methane production potentials for a practical scale application. The study utilised four different models including TF (Equation 3) models and the TF model fitted the experimental data of all the models and has described the kinetics of methane production potential at practical applications. In this study, the experimental data will be simulated to identify which of the MG and TF models best fitted the data.

Methodology

This study is an experimental modelling and the data used was acquired from the results of experimental study published elsewhere (Gidado & Clarkson, 2022). The data have been split into two: part of the data was used as the training data and the other dataset was used to validate the model. The training data including the maximum production rate, lag phase and time while data that was used in the validation was the cumulative biogas output. The simulations were run in the SPSS statistical package using the modified Gompertz and Transference Function models represented in equations 2 and 3:

$$B = B_o \exp\{-\exp[\frac{R_m e}{B_o}(\lambda - t) + 1]\}$$

$$B = \frac{B_0}{1 + \exp\left\{\frac{4Rm_0(\lambda - t)}{B_0} + 2\right\}}. \quad (3)$$

Where: R_m = maximum biogas production rate (ml), λ = lag phase (day), t = incubation time (day), $e = \exp(1) = 2.7183$, B is the cumulative methane yield (ml), B_0 is the ultimate methane yield (ml).

Assumption: gas production in batch mode is a function of the specific growth rate of microorganisms in the biodigester.

Model validation

The root mean squared error (RMSE) was computed to estimate the residual errors with lower values indicating best fit. It will be cross validated with the R-squared obtained from the results of simulations. The RMSE was computed using equation 4 for all treatments.

$$RMSE = \sqrt{\frac{1}{m} \sum_{j=1}^m \left(\frac{d_j}{y_j} \right)^2} \quad (4)$$

Where m represents the number of data pairs, y_j is experimental biogas yield at j th value and d_j is deviation of experimental and predicted value.

Note: $d_j = d_{jex} - d_{jest}$, where d_{jex} is the observed methane produced at j th value, d_{jest} is the predicted methane production at j th value.

Results and Discussion

Effects of 5% NaOH-pretreated biomass incorporation into digester

The experimental data used in the simulation was to determine the effect of different dilutions of NaOH on structural composition (lignin, cellulose and hemicellulose) and biogas potential when the pretreated biomass was used as co-substrates in digestion involving CD and FW. The experimental results and estimates for digesters where 5% NaOH-pretreated SBS was incorporated have been plotted in Figure 1. It is shown that the curves for the estimated values for both MG and TF models behaved closely with the experimental curve. The kinetic estimates (Table1) such as the cumulative biogas output for this digester and its replicates suggested that the simulated values are within acceptable ranges.

Table 1. Experimental and estimated kinetic parameters for the modified Gompertz and Transference Function models

Parameter Estimates									
Treatments	P_E (ml)	R_E (ml/day)	$\hat{\Delta}_E$ (days)	P_{MG} (ml)	R_{MG} (ml/day)	$\hat{\Delta}_{MG}$ (days)	P_{TF} (ml)	R_{TF} (ml/day)	$\hat{\Delta}_{TF}$ (days)
5% NaOH	298.5	22.0	4	305.0	27.2	6.6	295.8	28.0	7.1
6% NaOH	345.5	13.3	2	418.9	19.2	6.4	366.9	21.5	7.6
7% NaOH	322.9	13.5	3	347.9	20.5	5.7	324.9	21.8	6.2

E= Experimental, MG= Modified Gompertz estimates, TF= Transference Function model estimates

The biogas production rate obtained with MG model was similar to the one obtained for TF but substantially higher than the experimental value. This may explain why the lag phase estimated for MG and TF models (6.6 and 7.1 days respectively) were higher than the experimental incubation period but the predicted outputs were either insignificantly higher or lower than the observed data.

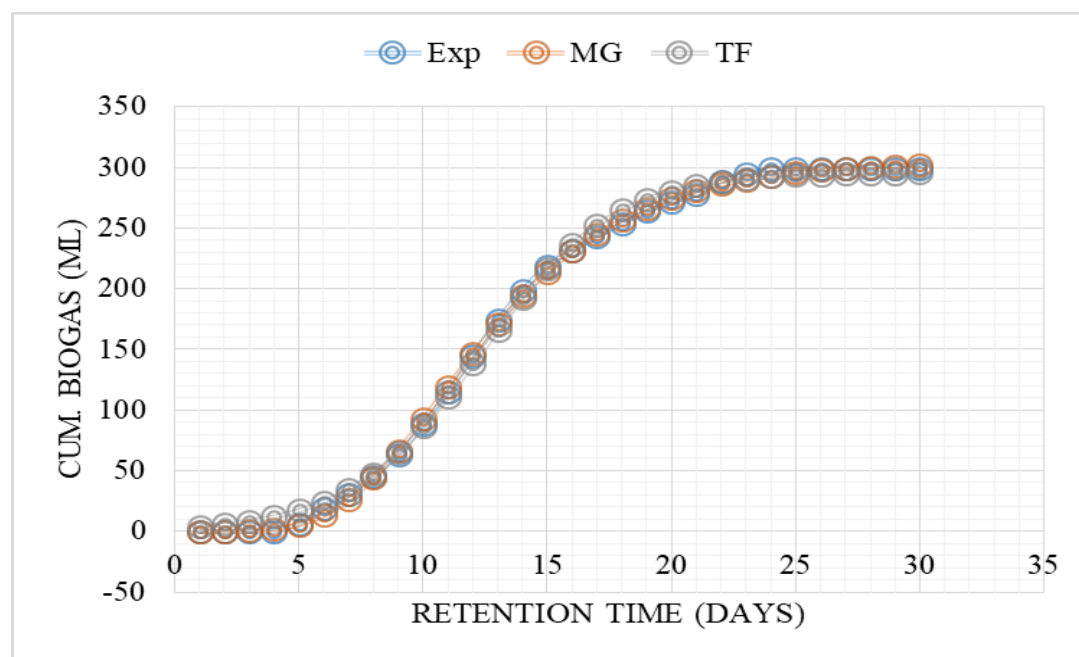


Figure 1. Experimental cumulative biogas production and their estimates using modified Gompertz (MG) and Transference Function for SBS pretreated with 5% NaOH solution (**Source:** simulations of experimental results acquired from Gidado and Clarkson, 2022).

The relative measure of fit R-squared determined for the digester containing 5% NaOH-pretreated biomass was 0.999 for MG as shown in Table 2 indicating that the MG model best fitted the experimental data compared to TF model with R-squared of 0.997. A root mean squared error (Table 2) was used to cross validate the estimates of both models corroborated the assertion hitherto pegged on the R-squared values. The actual measure

of model fit RMSE for MG and TF models were 0.004 and 0.089 respectively which suggested that both models fitted the experimental data but the MG demonstrated highest level of fit. The major effects of pretreatment that can be noticed from the curves were the short lag phase and early cessation of biogas production. This could mean that the pretreatment depolymerises the biomass, reduces its crystallinity, improves its surface area and thus making the biomass component susceptible to microbial action and consequently improved biogas production. Conversely, the presence of minute traces of residual NaOH in the biomass might have triggered early production of inhibitory substances often leading to raise in substrate pH and salt build-up, previously argued to be detrimental to methanogenesis (Clarkson, 2018).

Table 2. R-squared and RMSE for the modified Gompertz and Transference Function models.

Treatments	Parameter Estimates			
	R^2_{MG}	R^2_{TF}	$RMSE_{MG}$	$RMSE_{TF}$
5% NaOH	0.999	0.997	0.004	0.089
6% NaOH	0.995	0.997	0.110	0.030
7% NaOH	0.999	0.995	0.397	1.064

Effects of 6% NaOH-pretreated biomass incorporation in digester

The experimental and simulated data have been plotted and presented in Figure 2. Like the previous curves, the curves of the estimates with MG and TF presented here showed similarity and have followed the path assumed by the experimental curve. Although, the lag phase was substantially shorter than those for the estimates and that production continued much longer than in the digester with 5% NaOH, there was observed suppression of biogas production as illustrated in Figure 2 for experimental plot and both estimates.

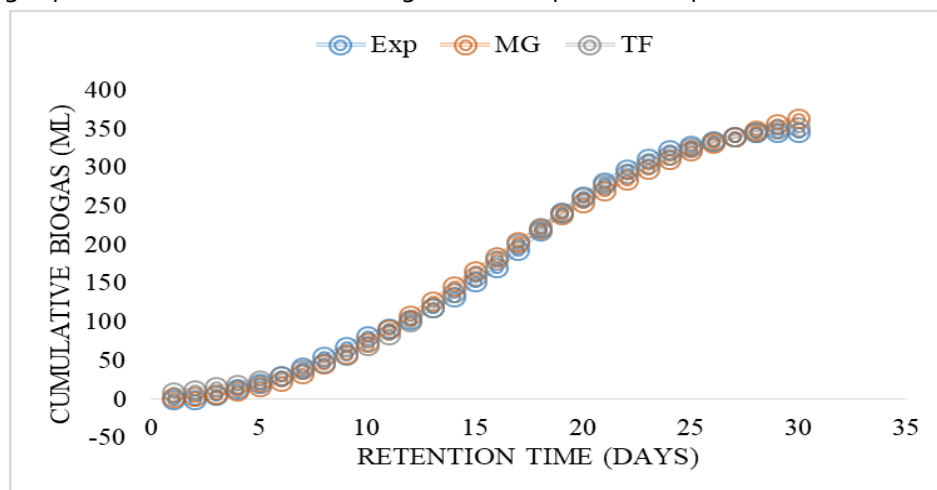


Figure 2. Experimental cumulative biogas production and their estimates using modified Gompertz (MG) and Transference Function for SBS pretreated with 6% NaOH solution (**Source:** simulations of experimental results acquired from Gidado and Clarkson, 2022).

For this digester, the R-squared were 0.995 and 0.997 for the MG and TF models respectively suggesting that both models fitted the experimental data. In this case, the performance of the TF model appeared better than that of the MG model. The RMSE of 0.11 and 0.03 buttressed the decision that the TF model best fitted the experimental data.

Effects of 7% NaOH-pretreated biomass incorporation into digester

The information in Figure 3 is the plot of the data for cumulative biogas production against substrates retention time for 7% NaOH-pretreated biomass incorporated onto CD and FW in co-digestion. Comparing experimental data and their estimates from MG and TF models presented in Figures 1 and 2 for 5 and 6% NaOH, it could be argued that reaction rates (13.3 and 13.5 ml/day for 6 and 7% NaOH) decreased with increasing concentrations of NaOH (Table 1). Moreover, there was increase in retention time which may be attributed to the increased dose of NaOH.

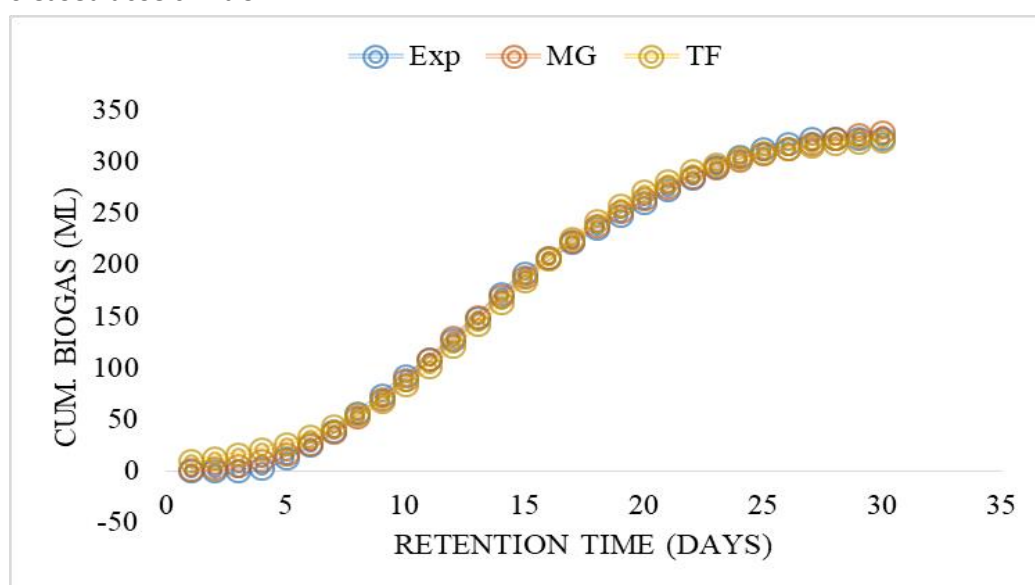


Figure 3. Experimental cumulative biogas production and their estimates using modified Gompertz (MG) and Transference Function for SBS pretreated with 7% NaOH solution (**Source:** simulations of experimental results acquired from Gidado and Clarkson, 2022).

The R-square values in Table 2 indicated that the experimental data fitted both models with values of 0.999 and 0.995 for MG and TF respectively, suggesting that the data fitted best with MG model. A cross validation with RMSE which indicated (also in Table 2) 0.397 and 1.064 for MG and TF models support the earlier decision that the model that with high simulation capability for the data use is MG model. These findings have been supported by the results reported by Deepanraj *et al.* (2015) where minimal fitting error were document.

Conclusion

The primary purpose of this work was to simulate cumulative biogas production using the modified Gompertz and Transference Function models from data obtained experimentally. The R-squared for both the MG and TF predictions ranged from 0.995-0.999 suggesting that models fitted the experimental data and this has been corroborated by the RMSE which ranged from 0.004 to 1.064. However, for data obtained from the 5% and 7% NaOH pretreated biomass incorporation into co-digestion, MG model has the best fit while 6% NaOH pretreated biomass driven data indicated that TF model is was a better estimator. It was also found that for both models as well as the experimental results, 5% NaOH pretreatment led to shorter retention time while 6 and 7% NaOH led to higher cumulative biogas output. The implication of the findings was that for batch reactors, pretreatment SBS with 6 or 7% NaOH may be appropriate but for continuous flow reactors, 5% NaOH pretreatment may yield more satisfactory out with economically more viable cost of production coupled with decreased use of chemicals.

Recommendations

Taking cognisance of the output of this simulation studies, the following recommendation has been proposed:

- In batch reactors, pretreatment of biomass with 5% NaOH will be more beneficial to the biogas production process as short retention time was its major effect.
- In continuous flow reactors, the cumulative difference in biogas production with relatively longer retention time and over a number of regular additions of substrates is valuable to continuous process and these are what made the researchers to conclude that the application of 6 or 7% NaOH in the pretreatment of biomass for possible use in co-digestion with CD and FW are appropriate.

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