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Anaerobic digestion of corn stover pretreated with sulfuric acid in different soaking durations

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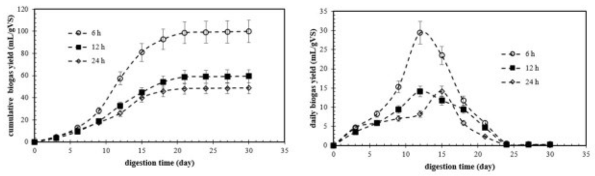
Graphical abstract



Abstract

The biogas production of pretreated corn stover has been determined in different soaking durations. Batch anaerobic digestion applies three different soaking durations in sulfuric acid pretreatment under room temperature. The study aimed to probe the effect of soaking durations during sulfuric acid pretreatment. The experiment was conducted in 600 mL digesters at room temperature. Biogas volume was measured using the water displacement method every three days. The observed cumulative biogas yields varied between 48.74 mL/g VS and 99.95 mL/g VS. The highest biogas yield was obtained when corn stover was soaked in sulfuric acid for 6 hours. The 24 h-pretreated corn stover got the lowest biogas yield. The statistical result proved a significant effect of soaking durations on biogas production ($p < 0.05$). The logistic model provided a better fit than the first-order model, with R^2 values ranging from 0.9923 to 0.9987 and divergence between experimental and predicted values varying between 0.12% and 1.48%.

Keywords: Acid pretreatment, biogas, first-order model, kinetic, logistic model

1. Introduction

Anaerobic digestion is a process that converts biodegradable organic material into biogas through biochemical stages, which are hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Hajji and Rhachi 2022). Its advantages are that it reduces the odour and the size of organic waste, diminishes greenhouse gas emissions, and produces a renewable fuel (Mirtsou-Xanthopoulou *et al.* 2019). Anaerobic digestion of corn stover has been a broad topic of discussion for renewable fuel production di the form of biogas. However, challenges are faced in treating corn stover as a biogas feedstock because of its characteristic as lignocellulosic biomass. Lignocellulose comprises cellulose bundles scattered with bundles of hemicellulose and lignin. This composition creates complex biodegradation leading to low biogas yield and longer retention times. A Pretreatment stage is needed to change the biomass structures. It also intends to split lignin from cellulose and hemicellulose, decrease cellulose crystallinity and enhance biomass porosity (You *et al.* 2018).

Pretreatment can be run by chemical, physical or biological pretreatment; nevertheless, chemical pretreatment becomes one of the most applied methods due to its high carbohydrate solubility efficiency (Alino *et al.* 2022). Taherdanak *et al.* (2016) reported that dilute sulfuric acid pretreatment enhanced biogas production and improved methane yield by 8.9% during the anaerobic digestion of wheat plants. Dahunsi *et al.* (2019) also stated that sulfuric acid pretreatment significantly reduced hemicellulose and partial cellulose solubilization. Furthermore, Domański *et al.* (2020) investigated that methane yield increased with increasing sulfuric acid concentrations during methane production of rye straw. Therefore, this study chose sulfuric acid pretreatment as chemical pretreatment for corn stover.

Based on past literature, the previous authors still need to study the biogas production from corn stover using sulfuric acid pretreatment. Olugbemide *et al.* (2020) produced biogas from corn stover without chemical pretreatment. Jie *et al.* (2020) compared mass ratio during anaerobic co-digestion of corn stover and cattle manure. Ajayi-Banji *et al.* (2020) investigated biogas production from corn stover with daily manure in different particle sizes of corn stover; thus, this study was original and novel. This study aims to investigate the effect of soaking durations in sulfuric acid pretreatment on the biogas production of corn stover. The kinetic model was also evaluated in predicting biogas production and determining the equivalent kinetic parameters.

2. Materials and methods

2.1. Substrate and inoculum preparation

Corn stover was collected from Yogyakarta, Indonesia. Corn stover was dried, milled into 2-3 mm mesh sieve lengths by a hammer mill, and then stored at room temperature. The bovine rumen fluid was used as inoculum.

2.2. Sulfuric acid pretreatment

Dried corn stover was pretreated with sulfuric acid (10% w/v) at 121°C at three different soaking times of 6, 12, and 24 h. Then, the pretreated corn stover was cooled and kept at room temperature until use.

2.3. Anaerobic digestion process

The pretreated corn stover was mixed with inoculum, and then the mixture was fed into a batch digester. The total working volume of each digester was 600 mL with the addition of water. The batch test was conducted at room temperature. The daily biogas volume was measured using the water displacement method every three days.

2.4. Kinetic model

2.4.1. First-order kinetic model

Anaerobic digestion assumes hydrolysis as a rate-limiting reaction, mainly when breaking down solid matter, and the degradation of the substrate may follow a first-order rate (Marañón *et al.* 2021). The production of biogas is written below:

$$B = B_0(1 - e^{-kt}) \quad (1)$$

Where, B is the cumulative biogas yield at time t (mL/gVS), B_0 is the biogas potential of the substrate (mL/gVS), k is the first-order biogas production rate constant (1/day), t is digestion time (days)

2.4.2. Logistic model

The logistic model represents a linear correlation between specific growth rate and biomass concentration. This model was used to express cell growth kinetics by way of the deviation of growth from the exponential ratio (Habchi *et al.* 2022).

$$B = \frac{B_0}{\left[1 + \exp\left\{\frac{4R_m(\lambda - t)}{B_0} + 2\right\}\right]} \quad (2)$$

R_m is the maximum biogas production rate (mL/gVS/d), λ is the lag phase time (days).

2.5. Statistical analysis

The significant deviation was determined using analysis of variance (ANOVA) with a p-value less than 0.05. Non-linear regression analysis was operated using solver Microsoft Excel to determine R_m, k, λ, and the predicted biogas potential. Microsoft Excel also implemented the coefficients of determination (R^2) and root means square error (RMSE).

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}\left(y_{\exp,i} - y_{\text{mod},i}\right)^2}{n}} \quad (3)$$

$Y_{exp,i}$ is the biogas yield obtained from the experimental results, $Y_{mod,i}$ is the biogas yield obtained from the model, and n is the number of observations

3. Results and discussion

3.1. Effect of pretreatment soaking on biogas production

The pretreated corn stover samples were subjected to batch anaerobic digestion, and the results of daily biogas production are illustrated in Figure 1. The initial biogas production from the 6 hours and 24 pretreated corn stover was the same in this period. (4.70 mL/g VS). The 12 h-pretreated corn stover gained the lowest initial biogas yield of 3.52 mL/g VS Biogas production increased gently from day 3 to day 12. During the 12 days of anaerobic digestion, 29.36 mL/g VS, 14.09 mL/g VS, and 8.22 mL/g VS of peak biogas yields were obtained from the 6 h, 12 h, and 24 h-pretreated corn stover samples, respectively. Afterwards, biogas production dropped gradually from day 15 to day 30. This phenomenon might occur due to fermentation and methanogenesis inhibition. The inhibition happened owing to the unsteadiness system caused by the accumulation of volatile fatty acids (VFA) in the early phases (Shyan *et al.* 2023). VFA accumulation depletes buffering capacity, decreases pH level, and inhibits methanogens' activities. The accumulated VFA repressed methanogenic activities, leading to lower methane production, unstable operational performance and poor biogas production (Park *et al.* 2018).

The cumulative biogas yield is presented in Figure 2. The highest biogas yield of 99.95 mL/g VS was obtained from the 6 hours-pretreated corn stover, which was 68% higher than the 12-hour-pretreated corn stover (59.43 mL/g VS). Meanwhile, the cumulative biogas yield of 12 hours of corn stover was 22% higher than the 24 hours of corn stover. Pretreatment for 6 hours led to the highest cumulative biogas yield, indicating that the decomposition of corn stover was easily degradable in soaking pretreatment of 6 hours.

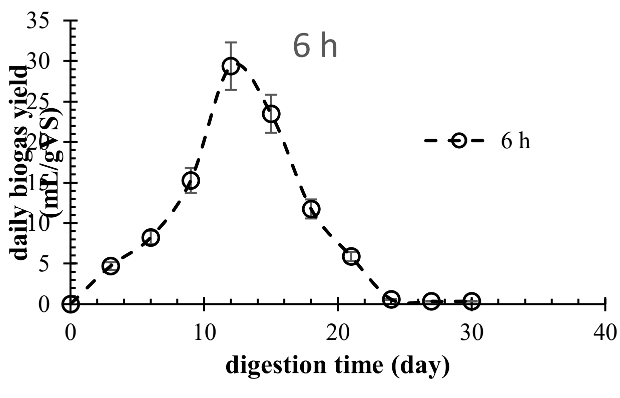


Figure 1. Daily biogas yield of pretreated corn stover at the soaking durations of 6 h, 12 h, and 24 h, respectively

As seen in Figure 2, biogas production decreased when the pretreatment time increased. This phenomenon might attribute to the loss of dry material during the pretreatment, which led to the reduction of feed for microbes, as a result, the biogas production declined when extending the pretreatment duration (Zheng *et al.* 2010).

The statistical result showed that soaking durations in sulfuric acid pretreatment affected biogas production significantly ($p < 0.05$).

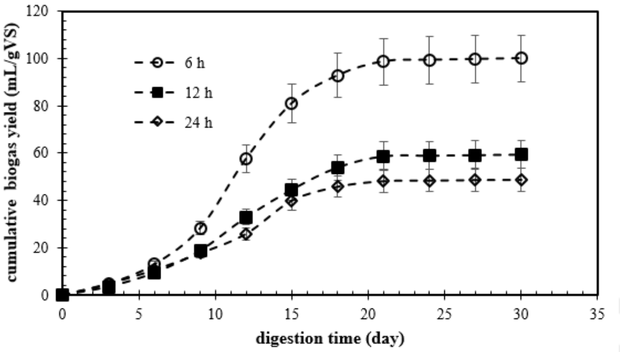


Figure 2. Cumulative biogas yield of pretreated corn stover at the soaking durations of 6 h, 12 h, and 24 h, respectively

3.2. Effect of pretreatment soaking on pH stability

The steadiness of the biodegradation process can be checked from the pH value. A pH value is one of the important parameters affecting the performance of biogas production. The pH value generated by pretreated corn stover is depicted in Figure 3.

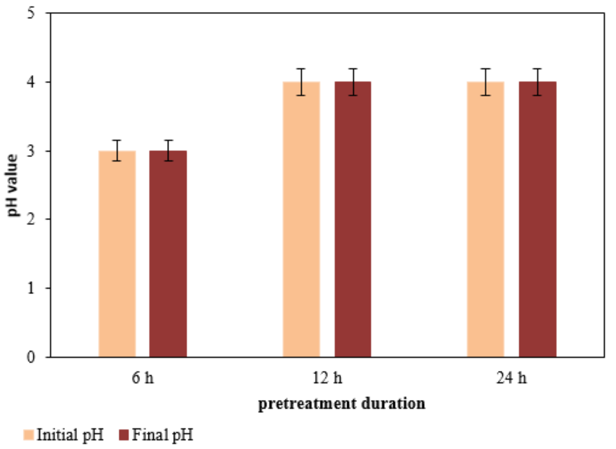


Figure 3. The initial and final pH of pretreated corn stover

The result showed that the longer pretreatment led to a lower pH. The initial pH of 6 h-pretreated corn stover was slightly lower than the 12 h and 24 h- pretreated corn stover. Pretreatment at lower pH generated greater yield signifying a higher degree of solubilization of complex organic material into particular monomers (Dasgupta and Chandel 2020). Therefore, pretreatment of 6 hours produced greater biogas yield than pretreatments of 12 hours and 24 hours (see Figure 2). The final pH of digestates remained constant with the initial pH for all different soaking durations. It indicates that the biogas performance was stable.

3.3. Effect of pretreatment soaking on kinetic parameters

The kinetic parameters obtained from the models are summarized in Table 1. The first-order kinetic and logistic models performed well with the determination coefficients (R^2) higher than 0.9. The logistic model got a higher R^2 (0.9923-0.9987) compared to the first-order kinetic model (0.9752-0.9884). The logistic model demonstrates less difference between the predicted and measured yield (0.12-1.48%).

Figures 4 and 5 the results of the non-linear fitting of the model for the soaking durations employing the first-order kinetic model and the logistic model, respectively. The logistic model fitted the experimental results more closely than the first-order model. The maximum biogas production rate (R_m) values varied between 3.93 and 28.94 mL/g VS/d. The highest R_m was obtained by the 6 h-pretreated corn stover, while the lowest R_m was obtained by the 12 h-pretreated corn stover. The first-order kinetic model's biogas rate constant (k) varied between 0.029 and 0.038 day^{-1}. The highest k was estimated for the 24-h pretreated corn stover. This result is contrary to the logistic model, which estimated the 6 h-pretreated corn stover obtained the highest Rm. The divergent results occurred due to the different assumptions or representations between logistic and first-order kinetic models. The logistic model considers the lag phase time, while the first-order kinetic model does not consider the lag phase time and maximum biogas production rate. Moreover, the first-order model reckons dry mass of waste, while the logistic model reckons specific rate of methane production and final digestion time as input parameters, hence, the limitations between both of the models provide different kinetic analysis.

The lag phase time (λ) of the three pretreated corn stovers ranged from 14.12-47.56 days. (Otobrise *et al.* 2022) discovered the values of λ within 5.3-9.6 days when applying the logistic model to the anaerobic digestion of goat dung and pawpaw seed. (Opurum 2021) reported lower λ(1.39-4.05 days) obtained from the batch anaerobic digestion of cabbage waste. Results may diverge due to the reliance on numerous factors and variables influencing anaerobic digestion, such as substrates, pH, inoculum, co-digestion, substrate/inoculum (S/I) ratio, and types of pretreatment (Casallas-Ojeda *et al.* 2021).

Table 1. Kinetic parameters model for First-order and Logistic for different soaking durations

Model	Soaking duration (hours)	B_0 (mL/g VS)	K (day^{-1})	λ (day)	R_m (mL/g VS/d)	R^2	RMSE	Difference
First-order	6	187.27	0.030	Not calc.	Not calc.	0.9844	11.19	10.36%
	12	112.42	0.029	Not calc.	Not calc.	0.9851	5.63	9.88%
	24	78.68	0.038	Not calc.	Not calc.	0.9752	4.38	9.27%
Logistic	6	300.43	Not calc.	14.12	28.94	0.9963	0.78	0.12%
	12	199.22	Not calc.	47.56	3.93	0.9923	1.95	1.16%
	24	148.85	Not calc.	14.54	11.47	0.9987	1.34	1.48%

The RMSE value ranged from 4.38 to 11.19 for the first-order kinetic model and 0.78 to 1.95 for the logistic model. Based on the statistical values, it can be evaluated that the logistic model gave a better fit to the experimental results with the higher R^2 and smaller RMSE values.

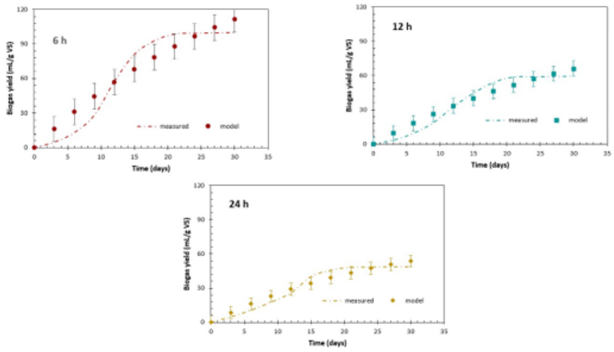


Figure 4. Biogas yield using the first-order kinetic model

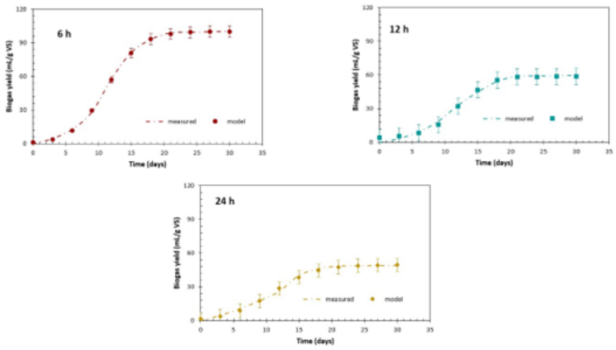


Figure 5. Biogas yield using the logistic model

4. Conclusion

The highest biogas yield was obtained for the 6-h pretreated corn stover (99.95 mL/g VS). Soaking duration in sulfuric acid pretreatment has a significant effect on biogas production from corn stover with a statistical value of $p < 0.05$. The substrate with the lowest biogas yield (48.74 mL/g VS) was pretreated corn stover with a soaking duration of 24 h. The logistic model fits the experimental results more accurately than the first-order kinetic model, with differences between measured and predicted yields varying between 0.12% and 1.48% and R2 values of 0.9923 to 0.9987.

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