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3	22 November 2022	Konfirmasi penerimaan article submission
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7	17 Juli 2023	Konfirmasi proof-sheet
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Dear Lukhi Mulia Shitophyta, ST., M.T.,

Thank you for your interest to publish your manuscript in Research in Agricultural Engineering. Your manuscript **Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid** written by Shitophyta Lukhi Mulia (mulia.lukhi@gmail.com) has been registered as 98/2022-RAE. You will be duly informed about the assessment procedure. The "corresponding author" (the one who has submitted the manuscript) can view the status of the manuscript at any time by checking the Author's account after logging to the editorial system.

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Detail History

Corresponding author Lukhi Mulia Shitophyta, ST., M.T.
Authors Lukhi Mulia Shitophyta, Armita Armita and Hilda Wulansari
Title Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid
ID 98/2022-RAE

Abstract Corn stover is one of the potential lignocellulosic biomasses as the raw material of biogas production. Pretreatment of lignocellulose substrates can enhance biodegradability and biogas yield. This study investigates the effect of oxalic acid pretreatment on biogas production during batch anaerobic digestion of corn stover. Kinetic parameters during biogas production from pretreated corn stover are predicted by the first-order, logistic, modified Gompertz and transference models. Results showed that oxalic acid pretreatment significantly affected biogas production ($p < 0.05$). The highest cumulative biogas yields of pretreated corn stover and untreated corn stover were 95.14 mL/gVS and 57.55 mL/gVS, respectively. Pretreated substrates improved biodegradability by 165%. Four kinetic models provided the determination coefficients R^2 higher than 0.9. The logistic model and modified Gompertz provided the best deviation of 1.57% and 3.75%, respectively. The logistic model proved the best fitting in predicting cumulative yields and simulating the kinetic model of anaerobic digestion of pretreated corn stover among the three models.

Keywords kinetic model; first-order model; logistic model; modified Gompertz; transference model

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Nov 22, 2022, 6:03 PM ☆ ↶ ⋮

Dear Lukhi Mulia Shtophyta, ST., M.T.,

Please, register to the editorial system all the co-authors of your manuscript 98/2022-RAE. Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid, submitted on 10. 11. 2022 into the Research in Agricultural Engineering.
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Dear author,

We would like to inform you, that the manuscript **Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid** written by Shtophyta Lukhi Mulia (mulia.lukhi@gmail.com), Arnita Arnita (arnita1900020054@webmail.uad.ac.id) and Wulansari Hilda (hilda1900020055@webmail.uad.ac.id) has been submitted to the Research in Agricultural Engineering on 10. 11. 2022. The manuscript is registered under ID 98/2022-RAE.

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Konfirmasi revisi artikel (18 Februari 2023)

[CAAS Agricultural Journals] 98/2022-RAE Article for correction Inbox x

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Sat, Feb 18, 12:16 AM

Dear Lukhi Mulia Shitophyta, ST., M.T.,
We would like to inform you that your manuscript **Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid** (submitted as 98/2022-RAE) should be corrected according to the reviewers' comments.

For correction use the MS Word Track Changes function. Please submit the corrected manuscript and also the Accompanying letter in anonymized form. See the Instructions to Authors.

Please see the file attached for the reviewers' comments.

We kindly ask you to resubmit the corrected manuscript under the same identification number. To do so, login to the system, click on the manuscript and fill in the "Corrected Text File and Attachments" input field. Please attach an Accompanying letter where you will respond to all suggestions of reviewers and where you will inform us whether you accepted their suggestions or not and what revisions you made in the original text of the paper according to these suggestions.

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Executive Editor
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Czech Academy of Agricultural Sciences
Slezská 7, Prague 2
Czech Republic

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- **Reviewers' comments**

Review I

Publish as Original Paper without change

Completeness: good

Scientific merit: good

Citations: good

International relevance: good

Importance to field: good

Language quality: good

Conciseness: good

Technical quality: good

Clarity of presentation: good

Originality: good

Comment for author: I think the study results will be helpful to the field, especially when people are struggling with the energy crisis nowadays. So, we encourage you to do more research in the future. Best regards."

Review II

Publish as Original Paper after minor revisions

Completeness: good

Scientific merit: good

Citations: excel

International relevance: good

Importance to field: excel

Language quality: good

Conciseness: good

Technical quality: good

Clarity of presentation: good

Originality: good

Comment for author: The research objectives are missing from the paper. Add a sentence that describes what the aim of the research is at the end of the Introduction chapter. In the Materials and methods chapter, the input material should be better described. Such as moisture content, bulk density,..

The weight of input material loading into the batch digester should also be listed. Perhaps it would be appropriate to add a picture of a laboratory biogas station as the research was carried out. But that's up to the authors.

Executive Editor's requirements:

- Please carefully check how to write the references- your reference **should not be like** this:
 - Phutela, G. U., & Sahni, N. (2012). Effect of Fusarium sp. On Paddy Straw Digestibility and Biogas Production. *Journal of Advanced Laboratory Research in Biology*, 3(1), 9–12. www.sospublication.co.in

But it should be:

- Phutela G.U., Sahni N. (2012): Effect of Fusarium sp. On paddy straw digestibility and biogas production. *Journal of Advanced Laboratory Research in Biology*, 3: 9–12.

Please adjust all the references accordingly.

Please let your manuscript check by a native english speaker. Or upload the certificate of English language proofreading (the better option).

- **Authors' response**



ACCOMPANYING LETTER

|
Accompanying letter

February 20, 2023

Ing. Petra Hovorková, Ph.D.
Executive Editor
Research in Agricultural Engineering
Czech Academy of Agricultural Sciences
Slezská 7, Prague 2
Czech Republic

Dear editors, Research in Agricultural Engineering,

We thank you for the letter dated 18/02/2023 and the opportunity to resubmit a revised copy of this manuscript. We also want to thank the reviewers for the positive feedback and helpful comments for correction or modification.

The manuscript has been revised to address the reviewer's comments and the executive editor's requirements, which are appended alongside our responses to this letter. Revisions in the manuscript are shown in red font.

We hope that the revisions in the manuscript and our accompanying responses will be sufficient to make our manuscript suitable for publication in the Research in Agricultural Engineering.

Sincerely yours,

Reviewers' Comments to the Authors:**Reviewer I**

Comment for author: I think the study results will be helpful to the field, especially when people are struggling with the energy crisis nowadays. So, we encourage you to do more research in the future. Best regards.

Author's Response: Thank you. We will do more research in the future per the reviewer's suggestion.

Reviewer II

Comment 1: The research objectives are missing from the paper. Add a sentence that describes what the aim of the research is at the end of the Introduction chapter.

Response 1: Thank you for pointing this out. We have added the research objective in the manuscript (paragraph three), where the change can be found in the revised manuscript.

Comment 2: In the Materials and methods chapter, the input material should be better described. Such as moisture content, and bulk density. The weight of input material loading into the batch digester should also be listed.

Response 2: Thank you for this suggestion. Although we agree that this is an important consideration, we can't describe the input material in detail ((including the weight of the input material) because providing confidential data regarding our research since we have been collecting data sources for patent filing. Concerning the moisture content and bulk density data, we cannot describe those data because we neither involve nor require those data in the research method. Thus, we do not measure those data.

Comment 3: Perhaps it would be appropriate to add a picture of a laboratory biogas station as the research was carried out. But that's up to the authors.

Response 3: We appreciate the reviewer's suggestion. We don't add a picture of a laboratory biogas station because, in the manuscript, we have described clearly the equipment for producing biogas, including the measurement method of biogas volume.

Executive Editor's requirements: asking for writing the references

Author's Response: We have corrected the writing of references in the manuscript, where the change can be found in the revised manuscript.

Konfirmasi corrected paper submission (21 Februari 2023)

[CAAS Agricultural Journals] Corrected paper submission Inbox x

rae@cazv.cz Feb 21, 2023, 2:25 PM

to me, arnita1900020054, hilda1900020055

Dear Lukhi Mulia Shitophyta, ST., M.T.,
Many thanks for the corrected manuscript submission.

Yours sincerely,

Ing. Gabriela Uhlířová
on behalf of

Ing. Petra Hovorková, Ph.D.
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rae@cazv.cz Sat, Feb 25, 12:25 AM

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Dear Madam/Sir,

We would like to inform you that on the basis of the peer review results, your manuscript **Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid** (submitted as 98/2022-RAE) has been accepted for publication in Research in Agricultural Engineering.

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Konfirmasi proof-sheet (17 Juli 2023)

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Thank you very much for your cooperation.

Yours sincerely,

Ing. Gabriela Uhlířová
on behalf of

Ing. Petra Hovorková, Ph.D.
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Author(s): [Lukhi Mulia Shitophyta, Amita Amita, Hilda Wulansari](#)

Signature of corresponding author: 

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Original Paper Research in Agricultural Engineering
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Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid

LUKHI MULIA SHITOPHYTA*, ARNITA, HILDA DYAH ANA WULANSARI

¹Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Ahmad Dahlan, Yogyakarta, Indonesia
 *Corresponding author: lukhi.mulia@che.uad.ac.id

Citation: Shitophyta L.M., Arnita Wulansari H.D.A. (2023): Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid. Res. Agr. Eng.

Abstract: Corn stover is one of the potential lignocellulosic biomasses as the raw material of biogas production. Pretreatment of lignocellulose substrates can enhance biodegradability and biogas yield. This study investigates the effect of oxalic acid pretreatment on biogas production during batch anaerobic digestion of corn stover. First-order, logistic, modified Gompertz and transference models predicted kinetic parameters during biogas production from pretreated corn stover. Results showed that oxalic acid pretreatment significantly affected biogas production ($P < 0.05$). The highest cumulative biogas yields of pretreated and untreated corn stover were $95.14 \text{ mL} \cdot \text{g}^{-1} \text{ VS}$ and $57.55 \text{ mL} \cdot \text{g}^{-1} \text{ VS}$, respectively. Pretreated substrates improved biodegradability by 165%. Four kinetic models provided the determination coefficients R^2 higher than 0.9. The logistic model and modified Gompertz provided the best deviation of 1.57 and 3.75%, respectively. The logistic model proved the best fitting in predicting cumulative yields and simulating the kinetic model of anaerobic digestion of pretreated corn stover among the three models.

Keywords: First-Order model; Logistic model; Kinetic model; modified Gompertz; Transference model

Anaerobic digestion (AD) is a biological process to produce biogas through organic material degradation by microbes without oxygen. Biogas composition consists of 50–70% CH_4 and 30–50% CO_2 with small components such as hydrogen sulphide, nitrogen, oxygen, siloxanes, volatile organic compounds (VOCs), carbon monoxide, and ammonia (Adnan et al. 2019). AD process can be divided into four stages, i.e., hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Xu et al. 2019). Corn stover belongs to lignocellulosic biomass since it is composed of cellulose ($46.16 \pm 0.46 \text{ wt\%}$), hemicellulose ($24.95 \pm 0.33 \text{ wt\%}$) and lignin ($5.90 \pm 0.21 \text{ wt\%}$) (Yang et al. 2022). Lignocellulose is a significant component of the plant cell wall composed of mainly cellulose, hemicellulose, and lignin (Pram et al. 2019). Anaerobic digestion can digest cellulose and hemicellulose, while lignin is a barrier against organic material degradation inhibiting AD processes (Abraham et al. 2020). Pretreatment is essential to enhance biodegradability, thus making the lignocellulosic biomass more accessible to microbes (Olughemide et al. 2021). Lignocellulosic biomass has applied many pretreatment methods. Chemical pretreatment, especially acid pretreatment, reduces hemicellulose (Antonopoulou et al. 2020). Acid pretreatment can also condense and deposit lignin fraction; hydrolytic enzymatic activity runs well in acidic conditions (Dasgupta and Chandel 2020). There are few studies on producing biogas from lignocellulosic biomass using chemical pretreatment. Amnuaycheewa et al. (2016) re-

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1

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1) The original notation was mL/gVS. According to the journal's instructions, the unit style was modified throughout the text. Please check

2) please explain the VS abbreviation

3) Shouldn't there be a gap between g-1 and VS?

US User Jul 18

it should be mL/gVS. Thanks for correcting it

▼ Page 2 2

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ported that pretreatment using 5.01% oxalic acid generates the highest biogas yield of 322.1 mL.g⁻¹ during the anaerobic digestion of rice straw. It is 740 times higher than untreated rice straw. Taherdanak et al. (2016) stated that pretreatment using dilute sulfuric acid for 120 min generates the maximum biogas yield of 513.9 mL.g⁻¹ VS during biogas production from wheat plants. The pretreated wheat plant obtains a 4% higher biogas yield than the untreated wheat plant. Jankovičová et al. (2022) revealed that pretreatment of 0.5% H₂SO₄ increased specific biogas production of rapeseed straw (by 71%) and wheat straw (by 32%). However, the kinetic model in producing biogas from corn stover using oxalic acid pretreatment has not been widely evaluated. Therefore, the study's objective was to evaluate kinetic models on batch anaerobic digestion of corn stover to obtain the best fitting biogas production curves and describe kinetic parameters using the First-Order, Logistic model, Modified Gompertz and Transference model. This study also investigated the effect of oxalic acid pretreatment on biogas production. A kinetic anaerobic digestion model can be used to expect stability factors, types of reactors and substrates, and dynamic simulation of anaerobic digestion (Bakraoui et al. 2020).

MATERIAL AND METHODS

Feedstock preparation. Corn stover was collected from the fields in Yogyakarta. Corn stover was dried in the sun and ground into 1–2 mm using a grinder. Dried and ground corn stover was stored at room temperature before use. The fresh fluid rumen of the cow was obtained from a Slaughterhouse in Yogyakarta and used as inoculum.

Oxalic acid pretreatment. Chemical pretreatment was conducted using 10% (w : w) C₂H₂O₄ (oxalic acid) solution at room temperature for 6 hours. The pretreated corn stover was washed with distilled water and dried in the sun. The pretreated substrates were stored at room temperature until use.

Biogas production. The untreated and pretreated corn stover were mixed with inoculum and water to adjust a feed-to-inoculum ratio 1:1. The substrates were loaded into a 1 L batch digester. Biogas production was carried out at room temperature for 30 days. Daily biogas volume was measured every three days using the water displacement method.

Kinetic analysis. The kinetic model predicts anaerobic digestion parameters such as the potential

biogas production, biogas maximum rate and the lag phase time obtained from the experimental results (Khadka et al. 2022).

First-Order kinetic model. This model assumes the hydrolysis step as a rate-limiting step in anaerobic digestion. The cumulative biogas yield is shown in Equation (1):

$$M = P_0 [1 - \exp(-kt)] \quad (1)$$

where: *M* – the cumulative biogas yield at time *t* (mL.g⁻¹ VS); *P*₀ – the methane potential of the substrate (mL.g⁻¹ VS); *k* – the first-order biogas production rate constant (1.day⁻¹); *t* – digestion time (days).

Logistic model. The logistic model assumes the biogas production rate is proportional to the amount of biogas produced. This model fits an initial exponential increase and final stability at the highest production level. The logistic model is written in Equation (2):

$$M = \frac{P_0}{1 + \exp\left(\frac{4R_m(\lambda - t)}{P_0} + 2\right)} \quad (2)$$

where: *R*_m – the maximum methane production rate (mL.g⁻¹ VS.d⁻¹); *λ* – the lag phase time (days).

Modified Gompertz model. This model illustrated the lag phase and the highest biogas production rate. The biogas production rate is supposed to parallel the specific growth of methanogens. The modified Gompertz model is given by Equation (3):

$$M = P_0 \times \exp\left[-\exp\left(\frac{R_m \times e}{P_0}(\lambda - t) + 1\right)\right] \quad (3)$$

where: *e* – ?

Transference model. The transference model described the correlation between biogas production and microbial activity. It also analysed the anaerobic digestion process as the system's input and output signal of the system. It predicted the maximum biogas production based only on cumulative biogas over time. The model is presented in Equation (4):

$$M = P_0 \times \left[1 - \exp\left(-\frac{R_m}{P_0}(t - \lambda)\right)\right] \quad (4)$$

Data analysis. The *P*-value was adjusted at 0.05, and the significance of the results was checked with

P-values < 0.05, while no significant results were with *P*-values > 0.05 during the ANOVA. The kinetic parameters were determined using non-linear regression by Solver in MS Excel (version?).

The best-fit model can be identified through the highest *R*² coefficients, and the smallest root mean square error (RMSE) value. The deviation between experimental and predicted results can also be used to determine the best-fit model. The low deviation values (< 10%) suggest the accurate prediction of the model (Zahan et al. 2018).

Biodegradability. Biodegradability was determined by dividing cumulative biogas yields by theoretical biogas yields. The theoretical yield obtained from this study was 99.18 mL.g⁻¹ VS. It was estimated using the Buswell equation. The Equation (5) to determine biodegradability is written below (Lahboubi et al. 2022).

$$\text{Biodegradability (\%)} = \frac{\text{cumulative BY (mL.g}^{-1}\text{VS)}}{\text{theoretical BY (mL.g}^{-1}\text{VS)}} \quad (5)$$

where: BY – biogas yield

RESULTS AND DISCUSSION

Effect of oxalic acid pretreatment on biogas production. The effect of oxalic acid (C₂H₂O₄) pretreatment on biogas production was investigated using C₂H₂O₄ of 10%. Figure 1 presents the daily biogas yield for 30 days.

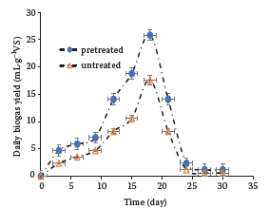


Figure 1. Daily biogas yield during anaerobic digestion of corn stover

Biogas production started on day 3 with biogas yields of 4.70 mL.g⁻¹VS and 2.35 mL.g⁻¹VS for pretreated and untreated substrates, respectively. Biogas yield then increased gradually until reaching peak yields of 25.89 mL.g⁻¹VS and 17.62 mL.g⁻¹VS on day 18 at the pretreated and untreated substrate, respectively. Biogas production then decreased regularly, with the lowest yields on day 30.

Results showed that adding C₂H₂O₄ positively affected biogas production, as shown in Figure 2.

The pretreated substrate generated a higher cumulative yield of 95.14 mL.g⁻¹ VS than the untreated substrate (57.55 mL.g⁻¹VS). Pretreatment using oxalic acid (C₂H₂O₄) could increase biogas yield by 65%. This result occurs because oxalic acid can hydrolyse hemicelluloses during lignocellulose pretreatment (Cheng et al. 2018). Deng et al. (2016) also stated that oxalic acid had high selectivity for hemicellulose degradation. The break of hemicellulose content can increase the degradability of substrate, as a result, biogas production also increases (Phutela and Sahni 2012). The previous result also reported that biogas production increased by 61.87% during the anaerobic digestion of water hyacinth using oxalic acid pretreatment (Tantayotai et al. 2019). Statistical analysis also verified that oxalic acid pretreatment had a significant effect on biogas production with a *P*-value of 0.0149 (*P* < 0.05).

Biogas production kinetic using a First-Order model. The First-Order model fitted the cumulative biogas yields of anaerobic digestion from pretreated

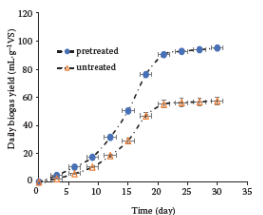


Figure 2. Cumulative biogas yield during anaerobic digestion of corn stover

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corn stover. The comparison between experimental results and the model is presented in Figure 3.

The kinetic constant (k) was found to be 0.1123 day^{-1} . The simulation results were 0.9302 , 0.9125 , 8.9793 , and 9.2371×10^{-14} for R^2 , adjusted R^2 , RMSE, and sum of square error (SSE) values, respectively. The methane potential of the substrate obtained from the first-order model was $6.103 \text{ mL.g}^{-1}\text{VS}$. The cumulative yields' deviation from experimental results and model was $\pm 13.71\%$. The result showed that the First-Order model gave a good fit in expressing cumulative biogas yield because the R^2 value obtained from the first-order model was higher than 0.9 . Previous results conducted by Pečar and Goršek (2020) and Nweke et al. (2022) also stated that the First-Order model was an excellent fit to predict the kinetic of anaerobic digestion with $R^2 > 0.9$.

Biogas production kinetic using the logistic model. Figure 4 compares cumulative yields obtained from the logistic model and experimental results. The simulation model obtained R^2 , adjusted R^2 , SSE, and RMS values of 0.9452 , 0.9384 , 3.1964 , and 2.3029 , respectively.

The cumulative yield difference between experimental results and the logistic model was $\pm 15.7\%$. The R^2 value obtained from the logistic model was higher than 0.9 , which indicated that the model could become a suitable model for predicting biogas kinetic from pretreated corn stover. Compared to the R^2 value obtained from the First-logistic model, the logistic model had a higher R^2 value. The logistic model had a better simulation than the First-Order model. The lag phase time (t_l)

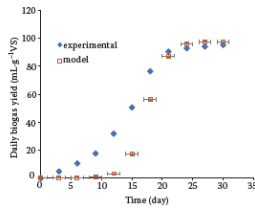


Figure 4. Biogas kinetic model using the logistic model during anaerobic digestion of pretreated corn stover VS - ?

of relevant results was 14.22 days. The maximum methane production rate ($R_{m, \text{max}}$) and the methane potential of the substrate (P_m) obtained from the logistic model were $14.9614 \text{ mL.g}^{-1}\text{VS.day}^{-1}$ and $97.419 \text{ mL.g}^{-1}\text{VS}$, respectively. A previous result also reported that the logistic model gave the R^2 value higher than 0.9 on kinetic modelling of biogas production from poultry slaughterhouse wastes (Ware and Power 2017). Gong et al. (2019) also found the R^2 coefficients > 0.9 during a kinetic analysis of the anaerobic digestion of sewage sludge using a logistic model.

Biogas production kinetic using a modified Gompertz model. The modified Gompertz equation was used to model cumulative biogas yield,

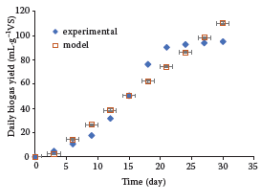


Figure 3. Biogas kinetic model using the First-Order model during anaerobic digestion of pretreated corn stover VS - ?

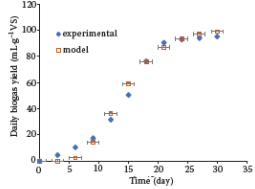


Figure 5. Biogas kinetic model using modified Gompertz model during anaerobic digestion of pretreated corn stover VS - ?

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as presented in Figure 5. The cumulative biogas yield obtained from the experimental results and the modified Gompertz model had a difference of $\pm 3.75\%$.

The simulation results gave the R^2 , adjusted R^2 , SSE, and RMSE values of 0.9416, 0.9344, 0.0013, and 4.4800, respectively. The R^2 value obtained from the modified Gompertz was higher than 0.9, signifying the excellent fit of the modified Gompertz in calculating the accumulation process of biogas yields. The prior study (Zahan et al. 2018) also found that the modified Gompertz gave the $R^2 > 0.9$ in kinetic modelling of the anaerobic digestion of agricultural wastes.

The R^2 value fitted by the modified Gompertz was higher than R^2 fitted by the First-Order model, indicating the modified Gompertz model predicted cumulative yields more fitted than the First-Order

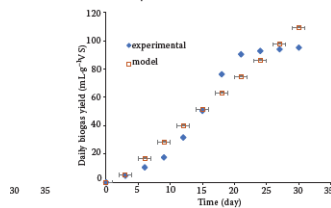


Figure 6. Biogas kinetic model using transference model during anaerobic digestion of pretreated corn stover

Table 1. Summary of kinetic parameters

Parameters	Units	Model			
		First-Order	logistic	modified Gompertz	transference
(P_0)	$\text{mL.g}^{-1}\text{VS}$	6.1080	97.419	37.1681	2.54×10^4
(R_m)	$\text{mL.g}^{-1}\text{VS.d}^{-1}$	–	14.9614	2.9245	3.8476
λ	day	–	14.23	12.13	1.68
k	day^{-1}	0.1123	–	–	–
R^2		0.9302	0.9452	0.9416	1
Adjusted R^2		0.9215	0.9384	0.9344	1
SSE		9.23×10^{-14}	3.9164	0.0013	6.4551
RMSE		8.9793	2.3029	4.4800	2.7369
Difference between measured and predicted biogas yield	%	13.71	1.57	3.75	12.69

– not calculated; P_0 – methane potential of the substrate; R_m – maximum methane production rate; λ – lag phase time; k – the rate constant; R^2 – coefficient of determination; SSE – sum of square error; RMSE – root mean square error

5

As seen in Table 1, all models proposed for the kinetic simulation were a good fit for predicting the cumulative yields due to the R^2 values > 0.9 . Though the transference model had the perfect R^2 of 1 and a relatively small RMSE value, the deviation of this model was higher than 10%; thus, the kinetic model simulation does not recommend the transference model as the best-fit model. The best-fit model suggested for kinetic modelling of anaerobic digestion of pretreated corn stover was the logistic model because it had the smallest RMSE and the lowest deviation among the other models. The R^2 value obtained from the logistic model also met the accuracy of the regression model due to the $R^2 > 0.9$.

Biodegradability. Figure 7 presents biodegradability on untreated and pretreated substrates.

Pretreated and untreated substrates provided the highest biodegradability of 95.93 and

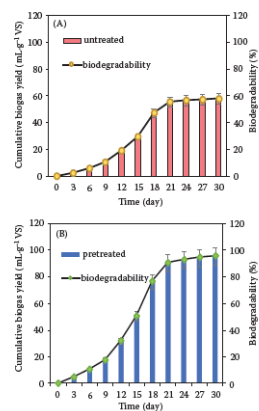


Figure 7. Cumulative biogas yield and biodegradability as the function of (A) untreated substrate, and (B) pretreated substrate

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model. However, R^2 obtained from the modified Gompertz was lower than R^2 fitted by the logistic model, denoting that the modified Gompertz was less accurate to be applied to the kinetic model of biogas production from pretreated corn stover. The kinetic parameters resulted in the lag phase time (λ) of 12.13 days, maximum methane production rate (R_m) of 2.9245 $\text{mL.g}^{-1}\text{VS.day}^{-1}$, and the methane potential of the substrate (P_0) of 37.1681 $\text{mL.g}^{-1}\text{VS}$.

Biogas production kinetic using the transference model. Figure 6 shows cumulative biogas yields between the experimental results and the transference model. The simulation of the transference model provided a high R^2 value of 1, followed by an adjusted R^2 of 1, an SSE value of 6.4551, and an RMSE value of 2.7369. The experimental and model cumulative biogas yields had a difference of $\pm 12.69\%$.

The transference model had the highest R^2 value among the three models (the First-Order, logistic, and modified Gompertz models). The kinetic parameters observed by the transference model were the λ value of 1.63 days, the R_m value of 3.8476 $\text{mL.g}^{-1}\text{VS.day}^{-1}$, and the P_0 value of 2.5547×10^4 $\text{mL.g}^{-1}\text{VS}$. The R^2 coefficient of 1 signifies that the regression model expresses all predicted variables, which means that the relationship between measured and predicted variables is perfect (Ilerula et al. 2021). The prior study reported by Ali et al. (2018) also found that the logistic model obtained R^2 values > 0.9 during the kinetic analysis of the anaerobic digestion of cow manure.

Table 1 summarises the kinetic parameters obtained from the first-order, logistic, modified Gompertz, and transference models.

58.03%, respectively. Pretreated substrate increased biodegradability by $\pm 165\%$. As seen in Figure 7, the higher cumulative yields generated higher biodegradability. Pretreated substrates had a higher biodegradability than untreated substrates. This result indicated that pretreatment could improve biogas production from corn stover.

CONCLUSION

Oxalic acid pretreatment significantly affected biogas yields with a p -value < 0.05 . Pretreated substrates had higher biodegradability (95.93%) than untreated substrates (58.03%). Cumulative yields obtained from pretreated corn stover increased by 65%. The result of the kinetic analysis showed that the determination coefficients R^2 obtained from all models were higher than 0.9. All four models could describe the kinetic of anaerobic digestion from pretreated corn stover. According to the RMSE values and the difference between the experimental and predicted values, it was suggested that the logistic model was more accurate and a better fit than the First-Order model, modified Gompertz model, and transference model in fitting experimental biogas yields.

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Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid

Original Paper

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Corn stover is one of the potential lignocellulosic biomasses as the raw material of biogas production. Pretreatment of lignocellulose substrates can enhance biodegradability and biogas yield. This study investigates the effect of oxalic acid pretreatment on biogas production during batch anaerobic digestion of corn stover. First-order, logistic, modified Gompertz and transference models predicted kinetic parameters during biogas production from pretreated corn stover. Results showed that oxalic acid pretreatment significantly affected biogas production ($P < 0.05$). The highest cumulative biogas yields of pretreated and untreated corn stover were 95.14 mL/gVS and 57.55 mL/gVS, respectively. Pretreated substrates improved biodegradability by 165%. Four kinetic models provided the determination coefficients R^2 higher than 0.9. The logistic model and modified Gompertz provided the best deviation of 1.57 and 3.75%, respectively. The logistic model proved the best fitting in predicting cumulative yields and simulating the kinetic model of anaerobic digestion of pretreated corn stover among the three models.

Keywords: First-Order model; Logistic model; Kinetic model; modified Gompertz; Transference model

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Evaluation and modelling of biogas production from batch anaerobic digestion of corn stover with oxalic acid

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Abstract: Corn stover is one of the potential lignocellulosic biomasses as the raw material of biogas production. Pretreatment of lignocellulose substrates can enhance biodegradability and biogas yield. This study investigates the effect of oxalic acid pretreatment on biogas production during batch anaerobic digestion of corn stover. First-order, logistic, modified Gompertz and transference models predicted kinetic parameters during biogas production from pretreated corn stover. Results showed that oxalic acid pretreatment significantly affected biogas production ($P < 0.05$). The highest cumulative biogas yields of pretreated and untreated corn stover were 95.14 mL/gVS and 57.55 mL/gVS, respectively. Pretreated substrates improved biodegradability by 165%. Four kinetic models provided the determination coefficients R^2 higher than 0.9. The logistic model and modified Gompertz provided the best deviation of 1.57 and 3.75%, respectively. The logistic model proved the best fitting in predicting cumulative yields and simulating the kinetic model of anaerobic digestion of pretreated corn stover among the three models.

Keywords: First-Order model; Logistic model; Kinetic model; modified Gompertz; Transference model

Anaerobic digestion (AD) is a biological process to produce biogas through organic material degradation by microbes without oxygen. Biogas composition consists of 50–70% CH_4 and 30–50% CO_2 with small components such as hydrogen sulphide, nitrogen, oxygen, siloxanes, volatile organic compounds (VOCs), carbon monoxide, and ammonia (Adnan et al. 2019). AD process can be divided into four stages, i.e., hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Xu et al. 2019).

Corn stover belongs to lignocellulosic biomass since it is composed of cellulose (46.16 ± 0.46 wt%), hemicellulose (24.95 ± 0.33 wt%) and lignin (5.90 ± 0.21 wt%) (Yang et al. 2022). Lignocellulose is a significant component of the plant cell wall composed of mainly cellulose, hemicellulose, and lignin

(Pram et al. 2019). Anaerobic digestion can digest cellulose and hemicellulose, while lignin is a barrier against organic material degradation inhibiting AD processes (Abraham et al. 2020). Pretreatment is essential to enhance biodegradability, thus making the lignocellulosic biomass more accessible to microbes (Olugbemide et al. 2021). Lignocellulosic biomass has applied many pretreatment methods.

Chemical pretreatment, especially acid pretreatment, reduces hemicellulose (Antonopoulou et al. 2020). Acid pretreatment can also condense and deposit lignin fraction; hydrolytic enzymatic activity runs well in acidic conditions (Dasgupta and Chandel 2020). There are few studies on producing biogas from lignocellulosic biomass using chemical pretreatment. Amnuaycheewa et al. (2016) reported that

pretreatment using 5.01% oxalic acid generates the highest biogas yield of 322.1 mL/g during the anaerobic digestion of rice straw. It is 7.40 times higher than untreated rice straw. Taherdanak et al. (2016) stated that pretreatment using dilute sulfuric acid for 120 min generates the maximum biogas yield of 513.9 mL/g volatile solid (VS) during biogas production from wheat plants. The pretreated wheat plant obtains a 4% higher biogas yield than the untreated wheat plant. Jankovičová et al. (2022) revealed that pretreatment of 0.5% H_2SO_4 increased specific biogas production of rapeseed straw (by 71%) and wheat straw (by 32%). However, the kinetic model in producing biogas from corn stover using oxalic acid pretreatment has not been widely evaluated. Therefore, the study's objective was to evaluate kinetic models on batch anaerobic digestion of corn stover to obtain the best fitting biogas production curves and describe kinetic parameters using the First-Order, Logistic model, Modified Gompertz and Transference model. This study also investigated the effect of oxalic acid pretreatment on biogas production. A kinetic anaerobic digestion model can be used to expect stability factors, types of reactors and substrates, and dynamic simulation of anaerobic digestion (Bakraoui et al. 2020).

MATERIAL AND METHODS

Feedstock preparation. Corn stover was collected from the fields in Yogyakarta. Corn stover was dried in the sun and ground into 1–2 mm using a grinder (Hammer mill, Henan, China) Dried and ground corn stover was stored at room temperature before use. The fresh fluid rumen of the cow was obtained from a Slaughterhouse in Yogyakarta and used as inoculum.

Oxalic acid pretreatment. Chemical pretreatment was conducted using 10% (w : w) $C_2H_2O_4$ (oxalic acid) solution at room temperature for 6 hours. The pretreated corn stover was washed with distilled water and dried in the sun. The pretreated substrates were stored at room temperature until use.

Biogas production. The untreated and pretreated corn stover were mixed with inoculum and water to adjust a feed-to-inoculum ratio 1. The substrates were loaded into a 1 L batch digester. Biogas production was carried out at room temperature for 30 days. Daily biogas volume was measured every three days using the water displacement method.

Kinetic analysis. The kinetic model predicts anaerobic digestion parameters such as the potential

biogas production, biogas maximum rate and the lag phase time obtained from the experimental results (Khadka et al. 2022).

First-Order kinetic model. This model assumes the hydrolysis step as a rate-limiting step in anaerobic digestion. The cumulative biogas yield is shown in Equation (1):

$$M = P_0 [1 - \exp(-kt)] \quad (1)$$

where: M – the cumulative biogas yield at time t (mL/gVS); P_0 – the methane potential of the substrate (mL/gVS); k – the first-order biogas production rate constant (1-day⁻¹); t – digestion time (days).

Logistic model. The logistic model assumes the biogas production rate is proportional to the amount of biogas produced. This model fits an initial exponential increase and final stability at the highest production level. The logistic model is written in Equation (2):

$$M = \frac{P_0}{1 + \exp\left\{\frac{4R_m(\lambda - t)}{P_0} + 2\right\}} \quad (2)$$

where: R_m – the maximum methane production rate (mL/gVS d⁻¹); λ – the lag phase time (days).

Modified Gompertz model. This model illustrated the lag phase and the highest biogas production rate. The biogas production rate is supposed to parallel the specific growth of methanogens. The modified Gompertz model is given by Equation (3):

$$M = P_0 \times \exp\left\{-\exp\left[\frac{R_m \times e}{P_0}(\lambda - t) + 1\right]\right\} \quad (3)$$

where: e – Euler's number.

Transference model. The transference model described the correlation between biogas production and microbial activity. It also analysed the anaerobic digestion process as the system's input and output signal of the system. It predicted the maximum biogas production based only on cumulative biogas over time. The model is presented in Equation (4):

$$M = P_0 \times \left\{1 - \exp\left[\frac{-R_m(t - \lambda)}{P_0}\right]\right\} \quad (4)$$

Data analysis. The P -value was adjusted at 0.05, and the significance of the results was checked with

P -values < 0.05 , while no significant results were with P -values > 0.05 during the ANOVA. The kinetic parameters were determined using non-linear regression by Solver in MS Excel (version 2019).

The best-fit model can be identified through the highest R^2 coefficients, and the smallest root mean square error (RMSE) value. The deviation between experimental and predicted results can also be used to determine the best-fit model. The low deviation values ($< 10\%$) suggest the accurate prediction of the model (Zahan et al. 2018).

Biodegradability. Biodegradability was determined by dividing cumulative biogas yields by theoretical biogas yields. The theoretical yield obtained from this study was 99.18 mL/gVS. It was estimated using the Buswell equation. The Equation (5) to determine biodegradability is written below (Lahboubi et al. 2022).

$$\text{Biodegradability (\%)} = \frac{\text{cumulative BY (mL / gVS)}}{\text{theoretical BY (mL / gVS)}} \quad (5)$$

where: BY – biogas yield

RESULTS AND DISCUSSION

Effect of oxalic acid pretreatment on biogas production. The effect of oxalic acid ($C_2H_2O_4$) pretreatment on biogas production was investigated using $C_2H_2O_4$ of 10%. Figure 1 presents the daily biogas yield for 30 days.

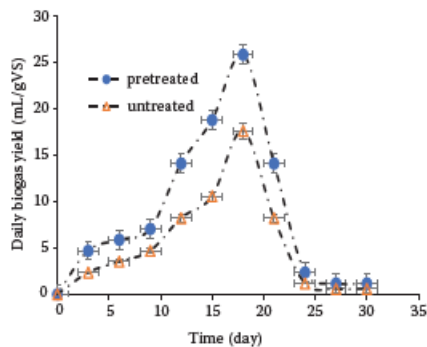


Figure 1. Daily biogas yield during anaerobic digestion of corn stover
VS – volatile solid

Biogas production started on day 3 with biogas yields of 4.70 mL/gVS and 2.35 mL/gVS for pretreated and untreated substrates, respectively. Biogas yield then increased gradually until reaching peak yields of 25.84 mL/gVS and 17.62 mL/gVS on day 18 at the pretreated and untreated substrate, respectively. Biogas production then decreased regularly, with the lowest yields on day 30.

Results showed that adding $C_2H_2O_4$ positively affected biogas production, as shown in Figure 2.

The pretreated substrate generated a higher cumulative yield of 95.14 mL/gVS than the untreated substrate (57.55 mL/gVS). Pretreatment using oxalic acid ($C_2H_2O_4$) could increase biogas yield by 65%. This result occurs because oxalic acid can hydrolyse hemicelluloses during lignocellulose pretreatment (Cheng et al. 2018). Deng et al. (2016) also stated that oxalic acid had high selectivity for hemicellulose degradation. The break of hemicellulose content can increase the degradability of substrate; as a result, biogas production also increases (Phutela and Sahni 2012). The previous result also reported that biogas production increased by 61.87% during the anaerobic digestion of water hyacinth using oxalic acid pretreatment (Tantayotai et al. 2019). Statistical analysis also verified that oxalic acid pretreatment had a significant effect on biogas production with a P -value of 0.0149 ($P < 0.05$).

Biogas production kinetic using a First-Order model. The First-Order model fitted the cumulative biogas yields of anaerobic digestion from pretreated

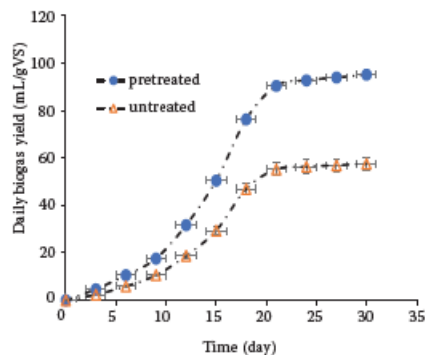


Figure 2. Cumulative biogas yield during anaerobic digestion of corn stover
VS – volatile solid

corn stover. The comparison between experimental results and the model is presented in Figure 3.

The kinetic constant (k) was found to be 0.1123 day^{-1} . The simulation results were 0.9302, 0.9125, 8.9793, and 9.2371×10^{-14} for R^2 , adjusted R^2 , RMSE, and sum of square error (SSE) values, respectively. The methane potential of the substrate obtained from the First-Order model was $6.103 \text{ mL}\cdot\text{g}^{-1}\text{VS}$. The cumulative yields' deviation from experimental results and model was $\pm 13.71\%$. The result showed that the First-Order model gave a good fit in expressing cumulative biogas yield because the R^2 value obtained from the first-order model was higher than 0.9. Previous results conducted by Pečar and Goršek (2020) and Nweke et al. (2022) also stated that the First-Order model was an excellent fit to predict the kinetic of anaerobic digestion with $R^2 > 0.9$.

Biogas production kinetic using the logistic model. Figure 4 compares cumulative yields obtained from the logistic model and experimental results. The simulation model obtained R^2 , adjusted R^2 , SSE, and RMS values of 0.9452, 0.9384, 3.1964, and 2.3029, respectively.

The cumulative yield difference between experimental results and the logistic model was $\pm 1.57\%$. The R^2 value obtained from the logistic model was higher than 0.9, which indicated that the model could become a suitable model for predicting biogas kinetic from pretreated corn stover. Compared to the R^2 value obtained from the First-Order model, the logistic model had a higher R^2 value. The logistic model had a better simulation than the First-Order model. The lag phase time (λ)

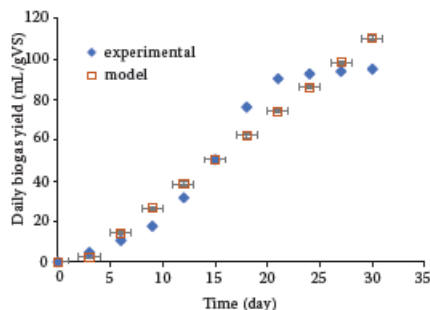


Figure 3. Biogas kinetic model using the First-Order model during anaerobic digestion of pretreated corn stover VS – volatile solid

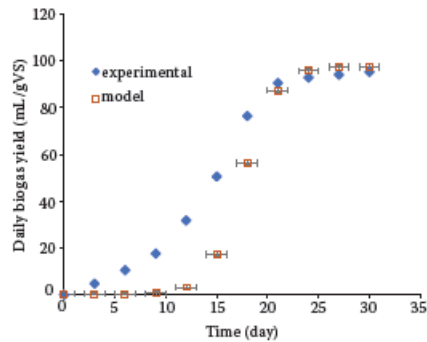


Figure 4. Biogas kinetic model using the logistic model during anaerobic digestion of pretreated corn stover VS – volatile solid

of relevant results was 14.22 days. The maximum methane production rate (R_m) and the methane potential of the substrate (P_0) obtained from the logistic model were $14.9614 \text{ mL/gVS}\cdot\text{day}^{-1}$ and 97.419 mL/gVS , respectively. A previous result also reported that the logistic model gave the R^2 value higher than 0.9 on kinetic modelling of biogas production from poultry slaughterhouse wastes (Ware and Power 2017). Gong et al. (2019) also found the R^2 coefficients > 0.9 during a kinetic analysis of the anaerobic digestion of sewage sludge using a logistic model.

Biogas production kinetic using a modified Gompertz model. The modified Gompertz equation was used to model cumulative biogas yield,

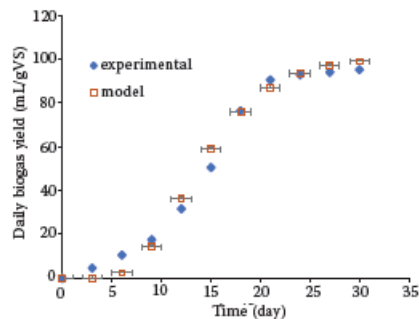


Figure 5. Biogas kinetic model using modified Gompertz model during anaerobic digestion of pretreated corn stover VS – volatile solid

as presented in Figure 5. The cumulative biogas yield obtained from the experimental results and the modified Gompertz model had a difference of $\pm 3.75\%$.

The simulation results gave the R^2 , adjusted R^2 , SSE, and RMSE values of 0.9416, 0.9344, 0.0013, and 4.4800, respectively. The R^2 value obtained from the modified Gompertz was higher than 0.9, signifying the excellent fit of the modified Gompertz in calculating the accumulation process of biogas yields. The prior study (Zahan et al. 2018) also found that the modified Gompertz gave the $R^2 > 0.9$ in kinetic modelling of the anaerobic digestion of agricultural wastes.

The R^2 value fitted by the modified Gompertz was higher than R^2 fitted by the First-Order model, indicating the modified Gompertz model predicted cumulative yields more fitted than the First-Order

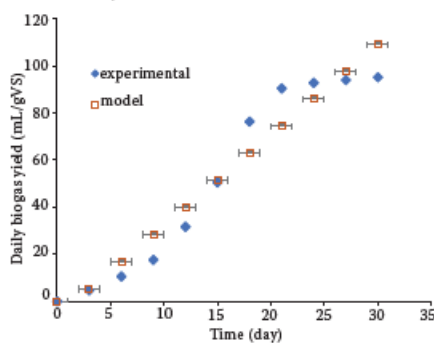


Figure 6. Biogas kinetic model using transference model during anaerobic digestion of pretreated corn stover VS – volatile solid

model. However, R^2 obtained from the modified Gompertz was lower than R^2 fitted by the logistic model, denoting that the modified Gompertz was less accurate to be applied to the kinetic model of biogas production from pretreated corn stover. The kinetic parameters resulted in the lag phase time (λ) of 12.13 days, maximum methane production rate (R_m) of 2.9245 mL/gVS-day⁻¹, and the methane potential of the substrate (P_0) of 37.1681 mL/gVS.

Biogas production kinetic using the transference model. Figure 6 shows cumulative biogas yields between the experimental results and the transference model. The simulation of the transference model provided a high R^2 value of 1, followed by an adjusted R^2 of 1, an SSE value of 6.4551, and an RMSE value of 2.7369. The experimental and model cumulative biogas yields had a difference of $\pm 12.69\%$.

The transference model had the highest R^2 value among the three models (the First-Order, logistic, and modified Gompertz models). The kinetic parameters observed by the transference model were the λ value of 1.63 days, the R_m value of 3.8476 mL/gVS-day⁻¹, and the P_0 value of 2.5547×10^8 mL/gVS. The R^2 coefficient of 1 signifies that the regression model expresses all predicted variables, which means that the relationship between measured and predicted variables is perfect (Jierula et al. 2021). The prior study reported by Ali et al. (2018) also found that the logistic model obtained R^2 values > 0.9 during the kinetic analysis of the anaerobic digestion of cow manure.

Table 1 summarises the kinetic parameters obtained from the First-Order, logistic, modified Gompertz, and transference models.

Table 1. Summary of kinetic parameters

Parameters	Units	Model			
		First-Order	logistic	modified Gompertz	transference
(P_0)	mL/gVS	6.1030	97.4190	37.1681	2.54×10^8
(R_m)	mL/gVS.d ⁻¹	–	14.9614	2.9245	3.8476
λ	day	–	14.2300	12.1300	1.6800
k	1/day	0.1123	–	–	–
R^2		0.9302	0.9452	0.9416	1.0000
Adjusted R^2		0.9215	0.9384	0.9344	1.0000
SSE		9.23×10^{-14}	3.9164	0.0013	6.4551
RMSE		8.9793	2.3029	4.4800	2.7369
Difference between measured and predicted biogas yield	%	13.7100	1.5700	3.7500	12.6900

– not calculated; P_0 – methane potential of the substrate; R_m – maximum methane production rate; λ – lag phase time; k – the rate constant; R^2 – coefficient of determination; SSE – sum of square error; RMSE – root mean square error

As seen in Table 1, all models proposed for the kinetic simulation were a good fit for predicting the cumulative yields due to the R^2 values > 0.9 . Though the transference model had the perfect R^2 of 1 and a relatively small RMSE value, the deviation of this model was higher than 10%; thus, the kinetic model simulation does not recommend the transference model as the best-fit model. The best-fit model suggested for kinetic modelling of anaerobic digestion of pretreated corn stover was the logistic model because it had the smallest RMSE and the lowest deviation among the other models. The R^2 value obtained from the logistic model also met the accuracy of the regression model due to the $R^2 > 0.9$.

Biodegradability. Figure 7 presents biodegradability on untreated and pretreated substrates.

Pretreated and untreated substrates provided the highest biodegradability of 95.93 and

58.03%, respectively. Pretreated substrate increased biodegradability by $\pm 165\%$. As seen in Figure 7, the higher cumulative yields generated higher biodegradability. Pretreated substrates had a higher biodegradability than untreated substrates. This result indicated that pretreatment could improve biogas production from corn stover.

CONCLUSION

Oxalic acid pretreatment significantly affected biogas yields with a P -value < 0.05 . Pretreated substrates had higher biodegradability (95.93%) than untreated substrates (58.03%). Cumulative yields obtained from pretreated corn stover increased by 65%. The result of the kinetic analysis showed that the determination coefficients R^2 obtained from all models were higher than 0.9. All four models could describe the kinetic of anaerobic digestion from pretreated corn stover. According to the RMSE values and the difference between the experimental and predicted values, it was suggested that the logistic model was more accurate and a better fit than the First-Order model, modified Gompertz model, and transference model in fitting experimental biogas yields.

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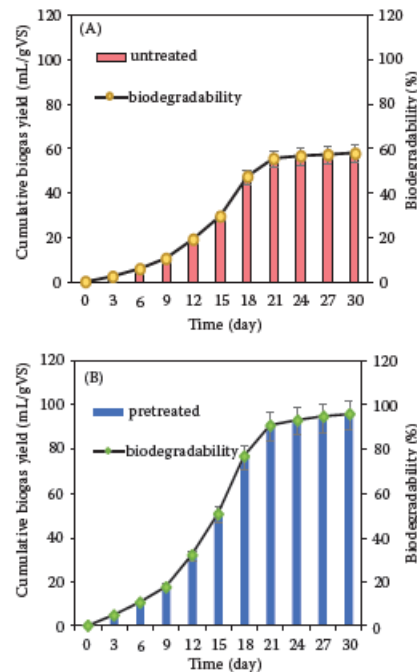


Figure 7. Cumulative biogas yield and biodegradability as the function of (A) untreated substrate, and (B) pretreated substrate

VS – volatile solid

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