

The Impact of Alkali Pretreatment and Organic Solvent Pretreatment on Biogas Production from Anaerobic Digestion of Food Waste

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ABSTRACT

Anaerobic digestion of food waste is an encouraging technology for biogas production. Pretreatment of the substrate is needed to increase biodegradation. This study aimed to investigate the effect of alkali pretreatment and organic solvent pretreatment on biogas production. Physical pretreatment was also applied in this study. NaOH (0%, 2%, 4% and 6%) was used as alkali pretreatment. Ethanol (0, 2, 4 and 6%) was used as organic solvent pretreatment. The experiment was conducted in a 1 L batch digester under room temperature. Results showed that 0% NaOH generated the highest cumulative biogas yield of 46.1 mL/gVS. The best biodegradability of 37.5% was achieved in NaOH of 0%. The lower concentration of ethanol generated a higher biogas yield. The greatest cumulative yield of 41.5 mL/gVS was obtained at an ethanol concentration of 0% with a biodegradability of 33.84%. Statistical analysis proved that alkali pretreatment and organic solvent pretreatment had no significant effect on biogas production ($p > 0.05$). Physical pretreatment had a significant effect ($p < 0.05$) with the highest cumulative yield of 58.2 mL/gVS. The kinetic model proved that the modified Gompertz was a suitable model for predicting and simulating the kinetics of anaerobic digestion from food waste ($R^2 > 0.9$).

Keywords: alkali pretreatment; biodegradability; biogas; food waste; organic solvent pretreatment.

INTRODUCTION

Biogas is one of the renewable fuels to reduce the consumption and dependence on fossil fuels (Shitophyta et al., 2022). Biogas production is carried out through anaerobic digestion. It degrades organic matter by microbes into biogas. Anaerobic digestion has certain advantages, such as a higher output/input ratio, reducing the cause of global warming, and being more efficient than other thermochemical or biological processes (Khan et al., 2022). Biogas can be applied in technology fields such as fuel cells, gas/steam turbines, Genset and other agricultural applications, for example, bio-fertilizers (Shitophyta, et al., 2021).

Raw materials of biogas come from various organic materials. Food waste is recommended as biogas raw material, because it can produce high methane. The content of macromolecules

and organic elements in food waste is sufficient for the growth of anaerobic microorganisms (Shitophyta, 2020). The generation of food waste is predicted to increase by 44% by 2025 and the methane production from food waste will increase from 3 Gkg to 48 Gkg in 2025 (Ar-iunbaatar, 2014.).

Pretreatment of organic matter aims to increase the value of soluble chemical oxygen demand (SCOD) which plays a role as the energy source for microorganisms during the digestion process (Junoh et al., 2016). SCOD denotes the available energy for the microorganisms to grow and expose the condition of the microorganism during the anaerobic digestion process (Saragih et al., 2019). Pretreatment can increase the biodegradability of food waste and increase the methane content. Pretreatment can also accelerate hydrolysis and reduce retention time in the

anaerobic digestion process (Shitophyta et al., 2021b). Previous studies on the pretreatment of food waste to produce biogas have been investigated. A study conducted by (Radmard et al., 2018) demonstrated that thermo-chemical (autoclave and microwave irradiation-assisted NaOH 5N) pretreatment enhances methane production by 68.37 L. Another study conducted by Gao et al. reported that daily biogas yield increases by 520 and 550 mL by adding 2% of activated yeast in biogas production from food waste (Gao et al., 2020). Another study showed that pretreated food waste results in a higher methane yield of 382.82 mL STP CH₄/g VS than untreated food waste during thermal pretreatment of food waste (Gnaoui et al., 2020). However, there is no study in the literature on utilizing alkali and organic solvent pretreatment in the anaerobic digestion of food waste. Therefore, the objective of the study was to determine the effect of alkali pretreatment and organic solvent pretreatment on biogas yield. The impact of physical pretreatment (grinding) on biogas production was also investigated. A kinetic study was also carried out for biogas production from food waste.

MATERIAL AND METHODS

Feedstock and inoculum preparation

Food wastes (rice, fruits and vegetables) were obtained from Traditional Market, Yogyakarta, Indonesia. The food wastes were ground into 1–2 cm by a crusher food processor. The cow rumen fluid used as inoculum was obtained from a slaughterhouse in Giwangan, Yogyakarta.

Alkali and organic solvents pretreatment

NaOH was used as an alkali reagent. C₂H₅OH was used as the organic solvent. Ground food waste was mixed with the chemical reagent of NaOH and C₂H₅OH with the concentration of 0% w/w, 2% w/w, 4% w/w, and 6% w/w, respectively. Pretreatment was carried out at room temperature by soaking food waste in chemical reagents for 24 hours.

Biogas production

The pretreated substrate was fed into a 1 L digester with a ratio of 1:1 (food waste: water). The

total volume of the substrate was 600 mL. The biogas production was carried out for 30 days. The biogas volume was measured every two days using the water displacement method.

Kinetic modelling

The kinetic model can be used to determine the anaerobic digestion parameters and constant kinetic values (Bakraoui et al., 2020). In this study, the kinetic model was evaluated using modified Gompertz and transference. The modified Gompertz model assumes that biogas production is proportional to the microbial growth rate (Moharir et al., 2020). The modified Gompertz model is written in Eq. (1) (Khadka et al., 2022).

$$M(t) = P \cdot \exp \left\{ -\exp \left[\frac{R_{max} e}{P} \right] (\lambda - t) + 1 \right\} \quad (1)$$

where: $M(t)$ – represents cumulative biogas yield at digestion time of $t(d)$ (mL/gVS),
 P – biogas production potential (mL/gVS),
 R_{max} – maximum biogas production rate (mL/gVS/d),
 λ – a lag phase (day),
 t – time (day),
 e – a constant value.

RESULTS AND DISCUSSION

Effect of physical pretreatment on biogas production

The influence of physical pretreatment on biogas yield is presented as daily and cumulative biogas yields in Figure 1 and Figure 2, respectively.

Both untreated and pretreated substrates biogas production started on day 2 with biogas yields of 1.4 mL/gVS and 5.7 mL/gVS, respectively. Furthermore, biogas production achieved peak yields of 8.6 mL/gVS and 14.3 mL/gV on day 8 at untreated and pretreated substrates, respectively. Biogas production slowly decreased and reached a constant value.

As shown in Figure 2, pretreated food waste produced a higher biogas yield (58.2 mL/gVS) than untreated food waste (33.9 mL/gVS). The result of the statistical analysis showed that physical pretreatment had a significant effect on biogas production ($p < 0.05$). A similar result was reported by Wadchasit et al., 2020 who found that physical pretreatment (size reduction) increased methane

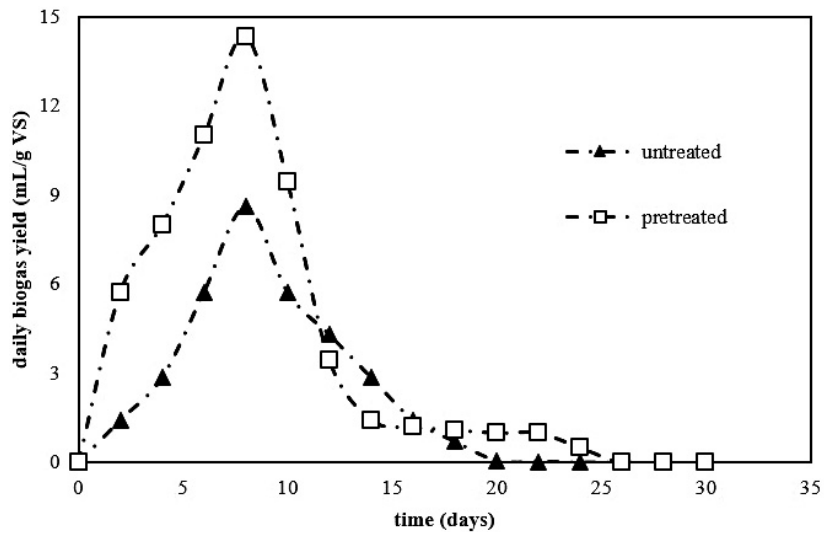


Figure 1. Daily biogas yield during 30 days

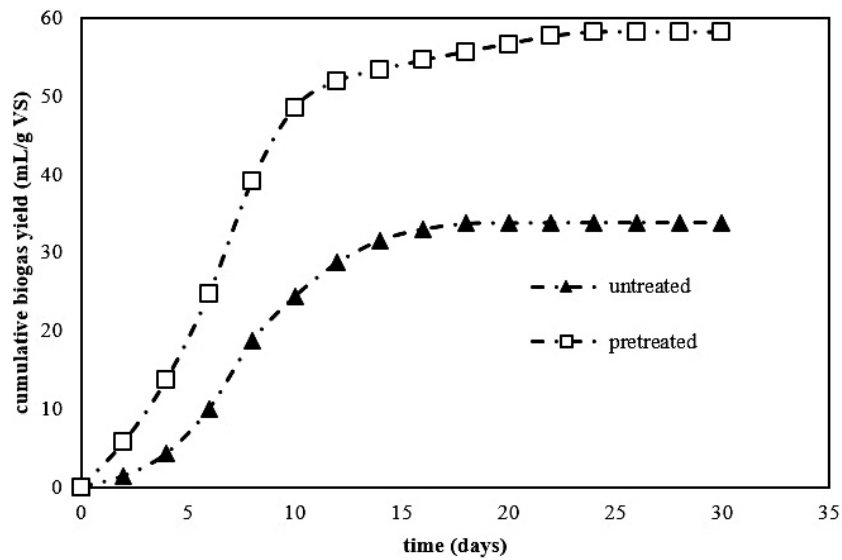


Figure 2. Cumulative biogas yield during 30 days

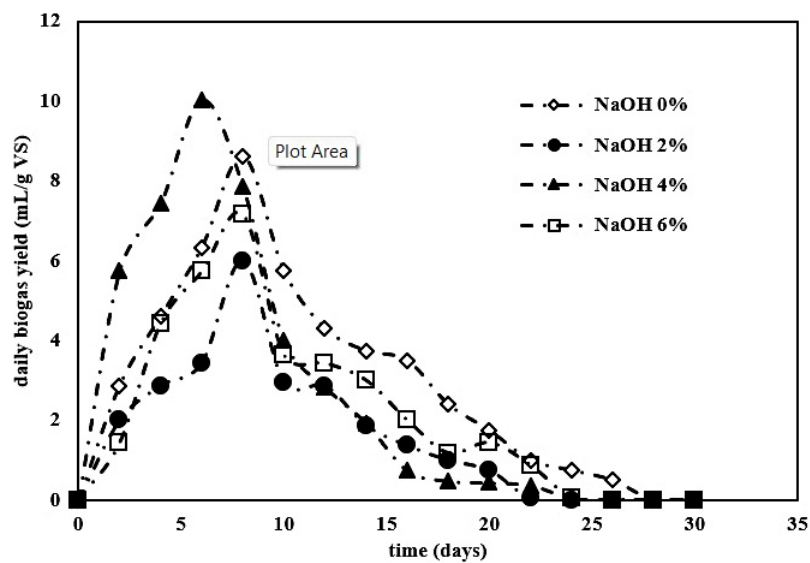


Figure 3. Daily biogas yield on alkali pretreatment during 30 days

yield beyond 90%. Bernat et al., 2020 also stated that mechanical pretreatment increased the rate of biogas production and the kinetic coefficient of biogas production.

Grinding pretreatment can increase pore size and accessible surface area. The reduction of particle size resists the acidification of the system (Poddar et al., 2022). A larger available surface area facilitates the degradation process and improves biogas production. The size reduction of food waste has the main benefit of equalizing the required retention time (Mirmohamadsadeghi et al., 2019).

Effect of alkali pretreatment on biogas production

Figure 3 shows that biogas production began on day 2 with daily biogas yields of 2.9 mL/gVS, 2 mL/gVS, 5.7 mL/gVS and 1.4 mL/gVS for NaOH concentrations of 0%, 2%, 4% and 6%, respectively. Biogas production then increased slowly until reaching peak values of 8.6 mL/gVS, 7.9 mL/gVS, and 7.2 mL/gVS on day 8 at NaOH concentrations of 0%, 2%, and 6%, respectively. However, NaOH of 4% reached a peak yield of 10 mL/gVS on day 6. Biogas production then dropped drastically with the constant yields obtained from day 24 to day 30.

As presented in Figure 4, the highest cumulative biogas yield of 46.1 mL/gVS was obtained at a NaOH concentration of 0% followed by cumulative yields of 41.9 mL/gVS, 34.4 mL/gVS, and 25.2 mL/gVS at NaOH concentrations of

4%, 6%, and 2% respectively. NaOH of 4% had a positive impact on biogas production. However, the highest concentration of NaOH (6%) could not improve the biogas yield. A previous study conducted by (Lahboubi et al., 2020) also reported that the high concentration of NaOH (30%) generated lower biogas than NaOH at a concentration of 18%.

The results showed that alkaline pretreatment was not effective on food waste. This phenomenon may occur due to the inhibition of sodium ions which causes bacteria toxicity and impedes biogas production (Ariunbaatar, 2014). Statistical analysis also proved that NaOH pretreatment had no significant effect on biogas production ($p > 0.05$). A similar result revealed that alkali pretreatment had no significant effect on yields during the anaerobic digestion of needle leaves (Salehian & Karimi, 2013).

Effect of organic solvent pretreatment on biogas production

The effect of organic solvent pretreatment on biogas production was investigated using C_2H_5OH (ethanol) concentrations of 0%, 2%, 4% and 6%. Figure 5 presents daily biogas yields for 30 days.

Biogas production started on day 2 with daily biogas yields of 2.9 mL/gVS, 1.7 mL/gVS; 2.2 mL/gVS, and 2.1 mL/gVS for ethanol concentrations of 0%, 2%, 4% and 6%, respectively. Biogas production increased continuously from day 4 until reaching peak yields on day 8 with peak biogas

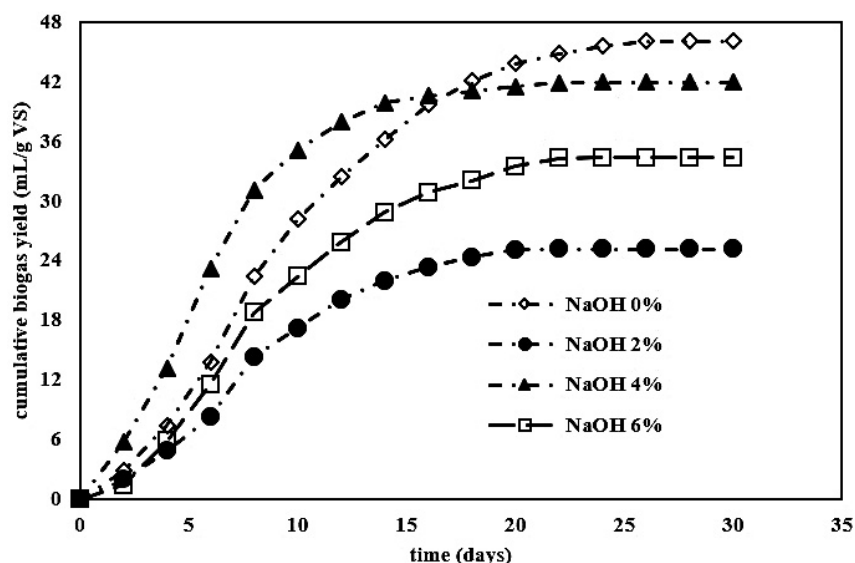


Figure 4. Cumulative biogas yield on alkali pretreatment during 30 days

yields of 8.6 mL/gVS (0% ethanol), 7.2 mL/gVS (2%), 4 mL/gVS (4% ethanol) and 5.4 mL/gVS (6% ethanol). Then, biogas production decreased gradually with the lowest biogas yield obtained on day 30.

Cumulative biogas yields were illustrated in Figure 6. The greatest cumulative yield of 41.5 mL/gVS was obtained at an ethanol concentration of 0% followed by cumulative yields of 39.1 mL/gVS, 21 mL/gVS, and 17 mL/gVS for ethanol concentrations of 2%, 4% and 6%, respectively. However, ethanol concentration of 2% generated a higher biogas yield than ethanol concentrations of 4 and 6%. Increasing ethanol concentration has no impact to increase biogas production.

The results showed that the pretreatment of organic solvents had no significant effect on biogas yield. Statistical analysis also shows that organic solvent pretreatment (ethanol) does not have a significant effect on biogas production ($p > 0.05$). A prior study reported by (Mirmohamadsadeghi et al., 2014) also found that pretreated rice straw generated a smaller biogas yield than untreated rice straw during ethanol pretreatment at 180 °C for 0.5 hours.

Biodegradability

Biodegradability was calculated by dividing cumulative biogas yield by theoretical biogas yield. The theoretical value was calculated using Buswell

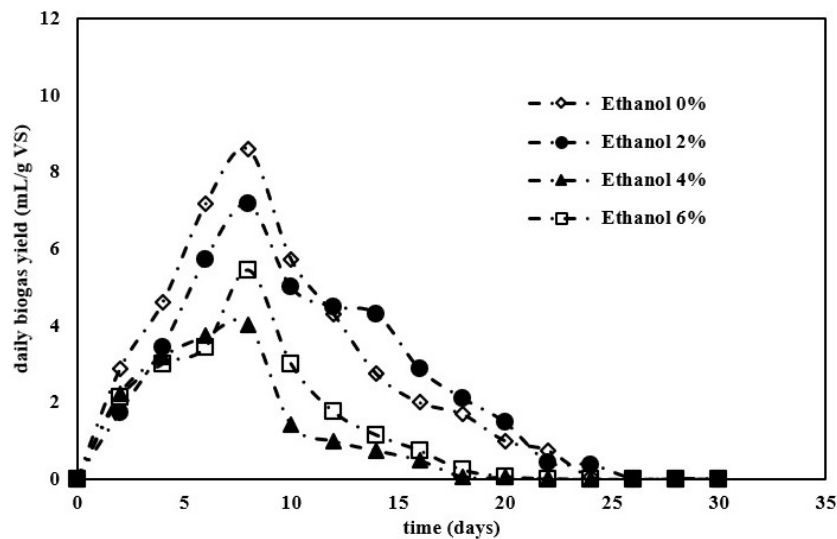


Figure 5. Daily biogas yield on organic solvent pretreatment during 30 days

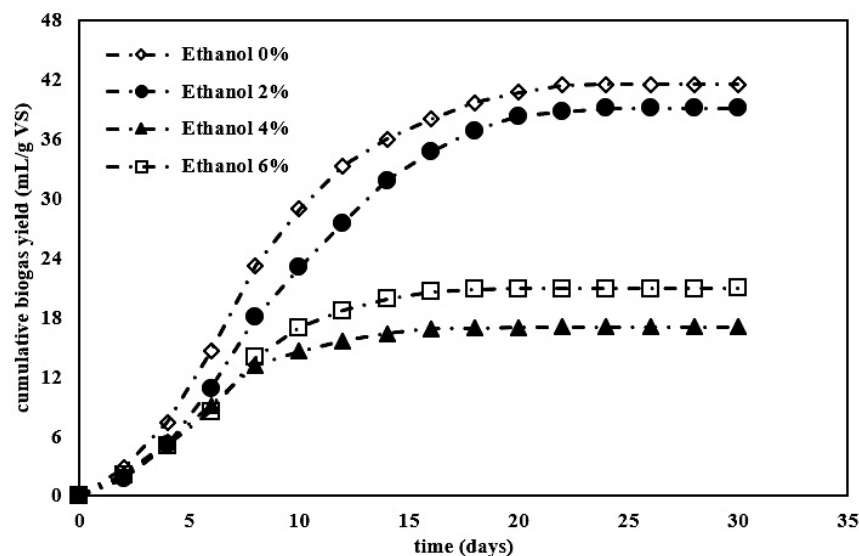


Figure 6. Cumulative biogas yield on organic solvent pretreatment during 30 days

Equation. The equation to calculate biodegradability is written below (Lahboubi et al., 2022).

$$Bd(\%) = \frac{\text{cumulative biogas yield (mL/gVS)}}{\text{theoretical biogas yield (mL/gVS)}} \quad (2)$$

The results of biodegradability on alkali pretreatment are presented in Figure 7. The highest biodegradability of 37.5% was obtained at 0% NaOH, while, 4% NaOH has higher biodegradability (34.1%) than 2% NaOH and 6% NaOH (20.5% and 28%, respectively). These results show that the higher the cumulative biogas yield,

the greater the biodegradability obtained. The pretreatment with the highest NaOH concentration (6%) obtained low biodegradability. This phenomenon might happen due to the high NaOH concentration leading to system inhibition (Lahboubi et al., 2022). Inhibition causes low biogas conversion and a high pH value, thus stopping biogas production (Shitophyta et al., 2020).

As shown in Figure 8, untreated substrate (0% ethanol) obtained the highest biodegradability of 33.84%. Unlike in alkali pretreatment, the lowest ethanol concentration (2% ethanol) generated

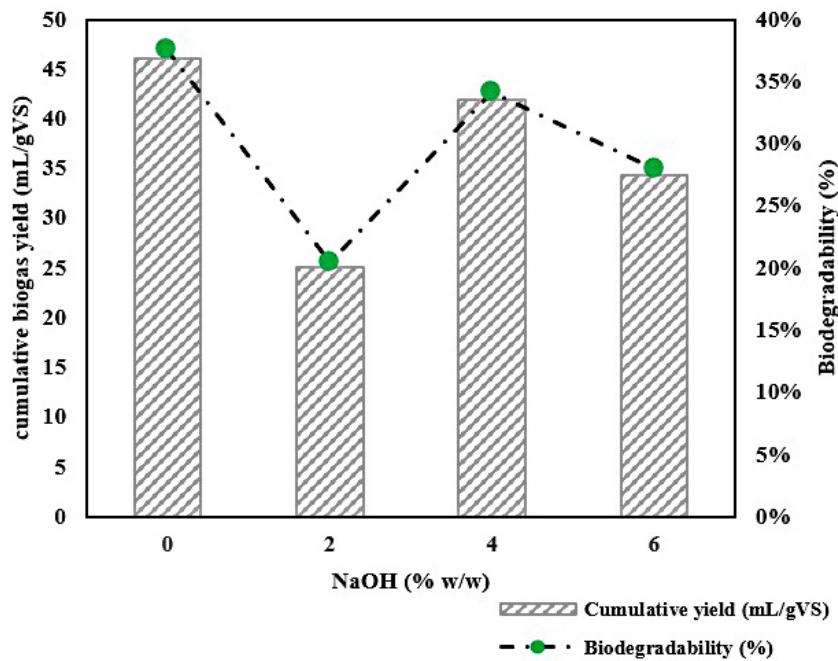


Figure 7. Cumulative biogas yield and biodegradability as a function of pretreated NaOH (%w/w)

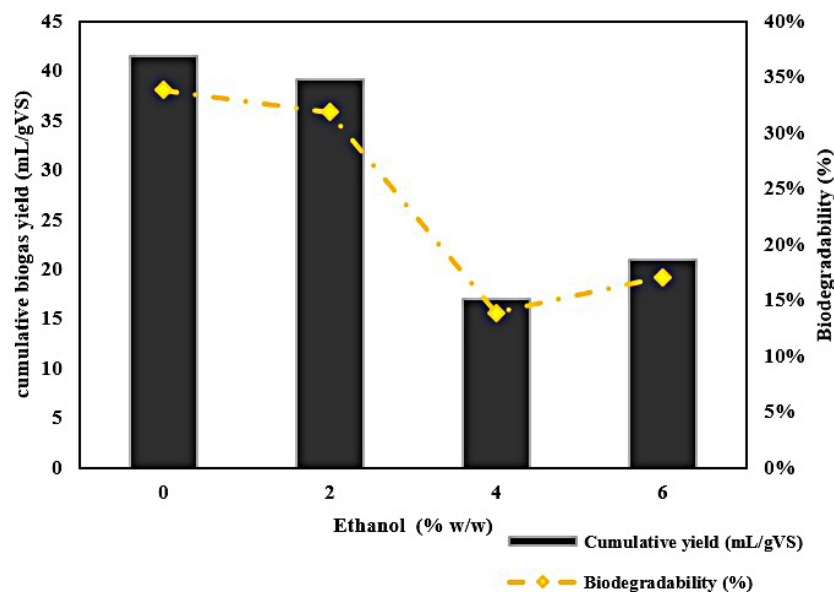


Figure 8. Cumulative biogas yield and biodegradability as a function of pretreated ethanol (%w/w)

a higher biodegradability of 31.88% than 4% and 6% ethanol concentration (13.89% and 17.08%, respectively). Thus, low ethanol concentration improves biodegradability.

Kinetic results

The cumulative biogas yields obtained from the experiment were fitted using Modified

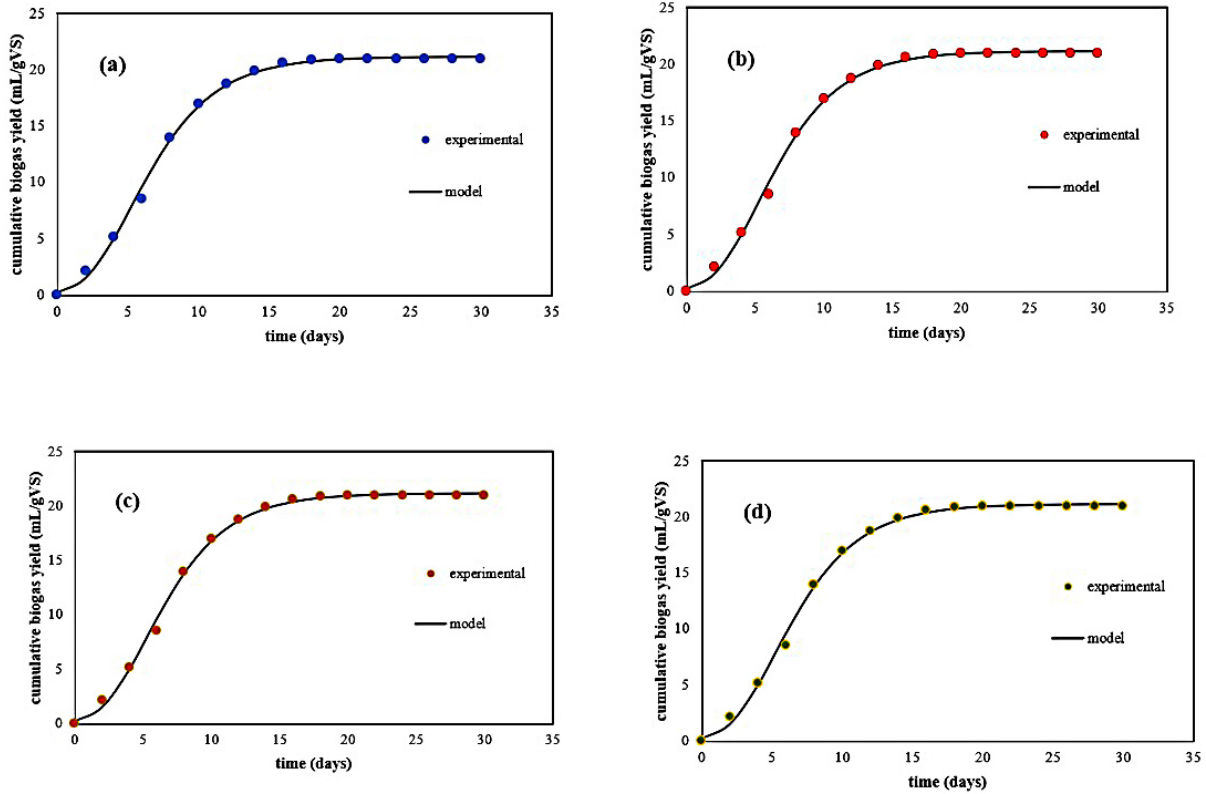


Figure 9. Experimental and model cumulative yields using Modified Gompertz for (a) untreated 0% NaOH, (b) pretreated 2% NaOH, (c) pretreated 4% NaOH and (d) pretreated 6% NaOH

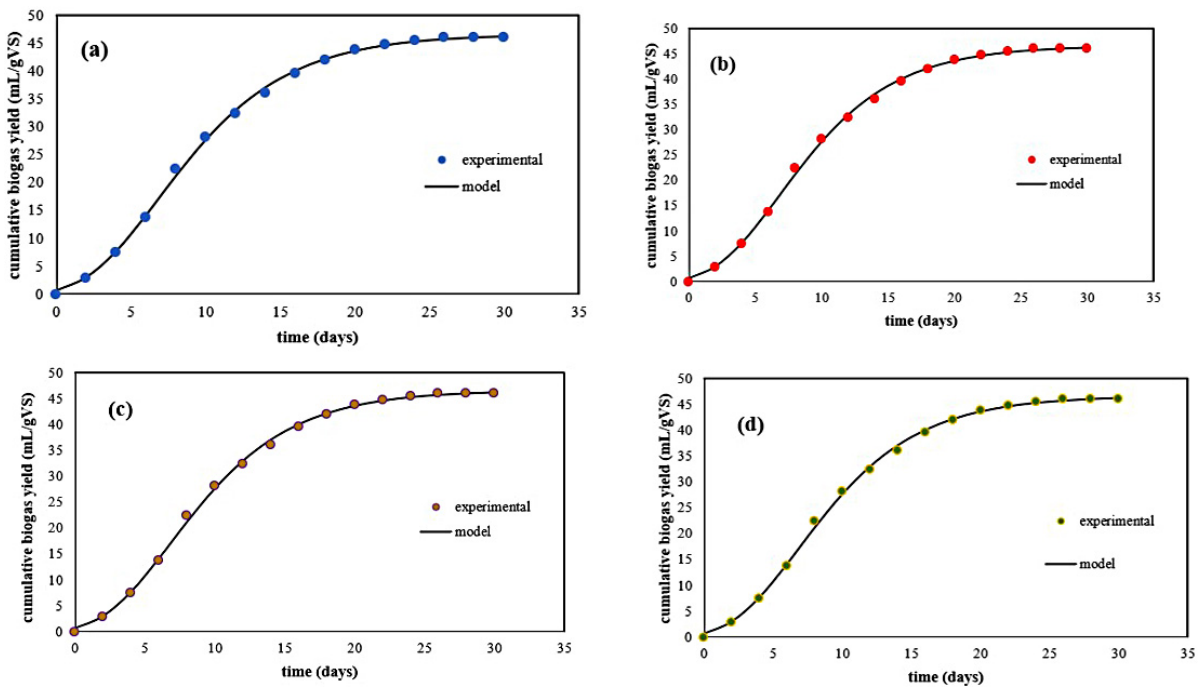


Figure 10. Experimental and model cumulative yields using Modified Gompertz for (a) untreated 0% C₂H₅OH, (b) pretreated 2% C₂H₅OH, (c) pretreated 4% C₂H₅OH and (d) pretreated 6% C₂H₅OH

Table 1. Kinetic parameters estimated from the fitting of the Modified Gompertz model

Parameters	P (mL/gVS)	R_{max} (mL/gVS/d)	l (d)	R^2
0% w/w NaOH	46.67	3.53	1.99	0.9987
2% w/w NaOH	25.46	2.32	2,09	0.9963
4% w/w NaOH	41.84	4.85	1.18	0.9981
6% w/w NaOH	34.63	2.98	2.11	0.9973
0% w/w C ₂ H ₅ OH	41.78	3.88	2.12	0.9998
2% w/w C ₂ H ₅ OH	39.89	3.26	2.67	0.9999
4% w/w C ₂ H ₅ OH	17.10	2.09	1.36	0.9998
6% w/w C ₂ H ₅ OH	21.17	2.37	1.97	0.9999

Gompertz. The comparison between fitting results from experiment results and the modified Gompertz model is presented in Figures 9 and 10.

Figures 9 and 10 show the curves of experimental cumulative biogas production and kinetic model curves. The curves of cumulative biogas production for pretreated NaOH and pretreated C₂H₅OH have the S-shape (sigmoidal) and stepped curves. It represents a slow degradation of complex substrates (Dolci et al., 2021). Modified Gompertz model on pretreated NaOH on biogas production from food waste determined R^2 lag phase, biogas production potential and maximum biogas production rate. The kinetic parameters obtained from the modified Gompertz model were summarized in Table 1.

As seen in Table 1, the R^2 values were greater than 0.9 for all substrates, which showed that the modified Gompertz model is good fitting in expressing the kinetic model of biogas production from food waste. The highest R^2 values were obtained in 2% w/w C₂H₅OH and 6% w/w C₂H₅OH. The highest lag phase time was obtained in 2% w/w C₂H₅OH. The highest lag phase time represents that the substrate has a longer biodegradation time. Similar studies conducted by Parra-Orobio et al., 2017; Pramanik et al., 2019; Marañón et al., 2021 also considered a modified Gompertz model as an appropriate model to estimate the kinetics of anaerobic digestion of food waste with $R^2 > 0.9$.

CONCLUSIONS

In this study, it was found that NaOH of 4% generated a higher biogas yield than NaOH of 2% and NaOH of 6%; however, NaOH of 0% generated the highest cumulative biogas yield of 46.1 mL/gVS. The highest biodegradability of 37.5% was obtained at NaOH of 0%. Statistical analysis showed that alkali pretreatment had no significant

effect on biogas production ($p > 0.05$). In organic solvent pretreatment, ethanol concentration of 2% produced higher cumulative biogas than ethanol concentration of 4% and 6%, but the highest cumulative yield was obtained at ethanol concentration of 0%, thus, organic solvent pretreatment had no significant effect on biogas production ($p > 0.05$). Physical pretreatment had a significant effect ($p < 0.05$) with the highest cumulative yield of 58.2 mL/gVS. The result of kinetic showed that the modified Gompertz model is a suitable fitting model for biogas production from food waste by coefficients of determination (R^2) > 0.9 .

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REFERENCES

1. Ariunbaatar, J. 2014. Methods to enhance anaerobic digestion of food waste. Agricultural Sciences. Universete Paris-Est. <https://tel.archives-ouvertes.fr/tel-01206170>
2. Bakraoui, M., Karouach, F., Ouhammou, B., Lahboubi, N., Gnaoui, Y. el, Kerrou, O., Aggour, M., el Bari, H. 2020. Kinetics study of methane production from anaerobic digestion of sludge and wastewater recycled pulp and paper. IOP Conference Series: Materials Science and Engineering, 946(1). <https://doi.org/10.1088/1757-899X/946/1/012009>
3. Bernat, K., Zaborowska, M., & Goryszewska, K. 2020. The impact of mechanical pretreatment on biogas production from waste materials of the chemical and brewing industries. Technical Transactions, 1–12. <https://doi.org/10.37705/techtrans/e2020037>
4. Dolci, G., Catenacci, A., Malpei, F., Grosso, M. 2021. Effect of Paper vs. Bioplastic Bags on Food

- Waste Collection and Processing. Waste and Biomass Valorization, 12(11), 6293–6307. <https://doi.org/10.1007/s12649-021-01448-4>
5. Gao, M., Zhang, S., Ma, X., Guan, W., Song, N., Wang, Q., Wu, C. 2020. Effect of yeast addition on the biogas production performance of a food waste anaerobic digestion system. Royal Society Open Science, 7(8), 200443. <https://doi.org/10.1098/rsos.200443>
 6. Gnaoui, Y. el, Karouach, F., Bakraoui, M., Barz, M., Bari, H. el. 2020. Mesophilic anaerobic digestion of food waste: Effect of thermal pretreatment on the improvement of the anaerobic digestion process. Energy Reports, 6, 417–422. <https://doi.org/10.1016/j.egy.2019.11.096>
 7. Junoh, H., Yip, C. H., Kumaran, P. 2016. Effect on Ca(OH)₂ pretreatment to enhance biogas production of organic food waste. IOP Conference Series: Earth and Environmental Science, 32(1). <https://doi.org/10.1088/1755-1315/32/1/012013>
 8. Khadka, A., Parajuli, A., Dangol, S., Thapa, B., Sapkota, L., Carmona-Martínez, A.A., Ghimire, A. 2022. Effect of the substrate to inoculum ratios on the kinetics of biogas production during the mesophilic anaerobic digestion of food waste. Energies, 15(3). <https://doi.org/10.3390/en15030834>
 9. Khan, M.U., Usman, M., Ashraf, M.A., Dutta, N., Luo, G., Zhang, S. 2022. A review of recent advancements in pretreatment techniques of lignocellulosic materials for biogas production: Opportunities and Limitations. Chemical Engineering Journal Advances, 10. <https://doi.org/10.1016/j.ceja.2022.100263>
 10. Lahboubi, N., Karouach, F., Bakraoui, M., el Gnaoui, Y., Essamri, A., el Bari, H. 2022. Effect of alkali-NaOH pretreatment on methane production from anaerobic digestion of date palm waste. Ecological Engineering and Environmental Technology, 23(2), 78–89. <https://doi.org/10.12912/27197050/144846>
 11. Lahboubi, N., Kerrou, O., Karouach, F., Bakraoui, M., Schüch, A., Schmedemann, K., Stinner, W., el Bari, H., Essamri, A. 2020. Methane production from mesophilic fed-batch anaerobic digestion of empty fruit bunch of palm tree. Biomass Conversion and Biorefinery. <https://doi.org/10.1007/s13399-020-00864-1>
 12. Marañón, E., Negral, L., Suárez-Peña, B., Fernández-Nava, Y., Ormaechea, P., Díaz-Caneja, P., Castrión, L. 2021. Evaluation of the Methane Potential and Kinetics of Supermarket Food Waste. Waste and Biomass Valorization, 12(4), 1829–1843. <https://doi.org/10.1007/s12649-020-01131-0>
 13. Mirmohamadsadeghi, S., Karimi, K., Tabatabaei, M., Aghbashlo, M. 2019. Biogas production from food wastes: A review on recent developments and future perspectives. Bioresource Technology Reports, 7(March), 100202. <https://doi.org/10.1016/j.biteb.2019.100202>
 14. Mirmohamadsadeghi, S., Karimi, K., Zamani, A., Amiri, H., Horváth, I.S. 2014. Enhanced solid-state biogas production from lignocellulosic biomass by organosolv pretreatment. BioMed Research International, 2014. <https://doi.org/10.1155/2014/350414>
 15. Moharir, S., Bondre, A., Vaidya, S., Patankar, P., Kanaskar, Y., Karne, H. 2020. Comparative Analysis of the Amount of Biogas Produced by Different Cultures using the Modified Gompertz Model and Logistic Model. European Journal of Sustainable Development Research, 4(4), em0141. <https://doi.org/10.29333/ejosdr/8550>
 16. Parra-Orobio, B.A., Donoso-Bravo, A., Torres-Lozada, P. 2017. Anaerobic digestion of food waste. Predicting of methane production by comparing kinetic models. Environmental and Sanitary – Engineering Ingeniería y Competitividad, 19(1).
 17. Poddar, B.J., Nakhate, S.P., Gupta, R.K., Chavan, A.R., Singh, A.K., Khardenavis, A.A., Purohit, H.J. 2022. A comprehensive review on the pretreatment of lignocellulosic wastes for improved biogas production by anaerobic digestion. International Journal of Environmental Science and Technology, 19(4), 3429–3456. <https://doi.org/10.1007/s13762-021-03248-8>
 18. Pramanik, S.K., Suja, F.B., Porhemmat, M., Pramanik, B.K. 2019. Performance and kinetic model of a single-stage anaerobic digestion system operated at different successive operating stages for the treatment of food waste. Processes, 7(9). <https://doi.org/10.3390/pr7090600>
 19. Radmard, S.A., Alizadeh, H.H.A., Seifi, R. 2018. Enhancement anaerobic digestion and methane production from kitchen waste by thermal and thermo-chemical pretreatments in batch leach bed reactor with down flow. Research in Agricultural Engineering, 64(3), 128–135. <https://doi.org/10.17221/16/2017-RAE>
 20. Salehian, P., Karimi, K. 2013. Alkali pretreatment for improvement of biogas and ethanol production from different waste parts of pine tree. Industrial and Engineering Chemistry Research, 52(2), 972–978. <https://doi.org/10.1021/ie302805c>
 21. Saragih, F.N.A., Priadi, C.R., Adityosulindro, S., Abdillah, A., Islami, B.B. 2019. The effectiveness of anaerobic digestion process by thermal pretreatment on food waste as a substrate. IOP Conference Series: Earth and Environmental Science, 251(1). <https://doi.org/10.1088/1755-1315/251/1/012014>
 22. Shitophyta, L. M. 2020. Model Kinetika Produksi Biogas dari Limbah Makanan. Jurnal Rekayasa Bahan Alam Dan Energi Berkelanjutan, 4(1), 15–18.
 23. Shitophyta, L.M., Budiarti, G.I., Nugroho, Y.E., Fajarriyanto, D. 2020. Biogas Production from Corn Stover by Solid-State Anaerobic Co-digestion of Food Waste.

- Jurnal Teknik Kimia Dan Lingkungan, 4(1), 44–52.
24. Shitophyta, L.M., Salsabila, A., Anggraini, F., Jami-latun, S. 2021. Development of kinetic models for biogas production from tofu liquid waste. *ELKAWNIE Journal of Islamic Science and Technology*, 7(1), 1–2.
25. Shitophyta, L.M., Salsabila, A., Putri, F.A., Jami-latun, S. 2022. Enhancement of biogas production through solid-state anaerobic co-digestion of food waste and corn cobs. *Makara Journal of Technology*, 26(1), 8–12. <https://doi.org/10.7454/mst.v26i1.1478>
26. Wadchasit, P., Siripattana, C., Nuithitikul, K. 2020. The effect of pretreatment methods for improved biogas production from oil-palm empty fruit bunches (EFB): Experimental and model. *IOP Conference Series: Earth and Environmental Science*, 463(1). <https://doi.org/10.1088/1755-1315/463/1/012126>