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Various Types of Acids on Pretreatment of Corn Stover for Enhancing Biogas Yield

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Abstrak

Produksi biogas dari biomassa lignoselulosa telah mendapat perhatian dalam pengembangan bahan bakar terbarukan. Brangkasan jagung tergolong biomassa lignoselulosa. Pretreatment diperlukan untuk membantu pemecahan biomassa karena sifat rekalsitran dalam lignoselulosa. Penelitian ini bertujuan untuk membandingkan variasi jenis asam guna meningkatkan produksi biogas. Percobaan dilakukan dalam digester batch 1 L pada suhu kamar dengan asam yang berbeda yaitu HCl, H_2SO_4, and $C_2H_2O_4$ pada konsentrasi 0%, 5%, 10% dan 15%. Pretreatment asam dilakukan selama 24 jam. Hasil penelitian menunjukkan bahwa pretreatment $C_2H_2O_4$ memiliki dampak positif terhadap peningkatan hasil biogas. Hasil kumulatif biogas tertinggi sebesar 580,8 mL/gVS diperoleh pada $C_2H_2O_4$ 15%. Peningkatan konsentrasi asam menurunkan nilai pH awal. Nilai pH di bawah 6 menurunkan yield biogas.

Kata kunci: *biogas, biomassa lignoselulosa, brangkasan jagung, pretreatment asam*

Abstract

Biogas production from lignocellulosic biomass has gained attention in the development of renewable fuels. Corn stover belongs to lignocellulosic biomass. Pretreatment is needed to help the digestion of biomass due to its lignocellulosic recalcitrance. This study aims to compare the different types of acids for enhancing biogas production. The experiment was carried out in a 1 L batch digester at room temperature with different acids of HCl, H_2SO_4, and $C_2H_2O_4$ at concentrations of 0%, 5%, 10%, and 15%. The acids pretreatment was performed for 24 hr. Results show that pretreatment of $C_2H_2O_4$ has a positive impact on increasing biogas yield. The highest cumulative yield of 580.8 mL/gVS is obtained at 15% $C_2H_2O_4$. The increase in acid concentrations decreases the initial pH value. The pH value below 6 reduces biogas yield.

Keywords: acid pretreatment, biogas, corn stover, lignocellulosic biomass

I. INTRODUCTION

Consumption of fossil fuels has led to environmental pollution and an energy crisis. Renewable energy has been developed to reduce the depletion of fossil fuels [1]. Conversion of organic wastes into biogas becomes a suitable choice to produce renewable fuel. Biogas consists of biogenic matter with methane as a major component. Biogas is commonly utilized to generate power, heat, and electricity [2].

Biogas production via anaerobic digestion is a biological process, which comprises four stages, i.e. hydrolysis, acidogenesis, acetogenesis, and methanogenesis [3]. Producing biogas using lignocellulosic biomass contributes to effective waste management and becomes a major bioenergy resource [4]. Agricultural waste such as corn stover belongs to lignocellulosic materials. Lignocellulosic biomass has drawn widespread attention as biogas feedstock because of its abundance and renewability [5] However, lignocellulosic biomass has complex structures due to the presence of hemicellulose and lignin, which creates the main barrier to cellulose accessibility and impedes biogas production [6]. Therefore, pretreatments are used to

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break down organic materials and make degradation easily by microbes [7].

Pretreatment is an important technique in the cellulose transformation process to alter the composition of cellulose. Physical pretreatment is a crucial step in increasing biodegradability, particle compaction and composition, enzymatic accessibility, and total conversion of lignocellulosic material into biogas without the production of toxic substances [8].

One of the most popular pretreatments for lignocellulosic biomass is acid pretreatment. Acid leaves the glucosidic bonds which assist the solubilization of the hemicellulose fraction into oligomers and monomers by enzymatic hydrolysis, thus enhancing accessibility to microbes and improving biogas production [9]. Acid pretreatments for lignocellulosic biomass have been conducted in previous studies. Jankociva et al. [10] studied the effect of acid and alkaline pretreatment on maize waste, rapeseed straw, and wheat straw using NaOH and H_2SO_4. Amnuaycheewa et al. [11] expressed that organic acid (acetic acid, citric acid, and oxalic acid) pretreatment generated higher biogas than inorganic acid (hydrochloric acid) in biogas production from rice straw. Dasputa and Chandel [12] investigated the effect of hydrochloric acid and acetic acid on biogas production from the organic fraction of municipal solid waste. However, no studies have investigated the variation of acids in the pretreatment of corn stover. Hence, the study aims to compare different kinds of acids (sulfuric acid, hydrochloric acid, and oxalic acid) to improve biogas yield through acid pretreatment.

II. RESEARCH METHOD

A. Feedstock Preparation

Corn cobs were dried and cut into 1-2 cm by a chopper. The fluid rumen of the cow as inoculum was obtained from a Slaughterhouse in Yogyakarta.

B. Acid Pretreatment

Corn cobs were mixed with various chemical reagents of HCl, H_2SO_4, and $C_2H_2O_4$ with concentrations of 0% w/w, 5% w/w, 10% w/w, and 15% w/w, respectively. Acid pretreatment was carried out at room temperature by soaking corn cobs in each chemical reagent for 24 hours.

C. Biogas Production

The treated corn cobs were mixed with rumen liquid (1:1 ratio) and added water to adjust the total solid (TS) content of 22%, then the substrate was fed to a 1 L digester. The biogas production was carried out for 28 days using Solid-State Anaerobic Digestion (SS-AD). The biogas volume was measured every 3 days using the water displacement method.

III. RESULTS AND DISCUSSION

A. Effect of HCl on Biogas Production

The effect of HCl on biogas production was identified by varying HCl concentrations, i.e., 0%, 5%, 10%, and 15%. Figure 1 presents the daily biogas yield for 28 days.

Biogas yields began on day 4 and then increased continuously until reaching peak yields of 258.4 mL/gVS, 282 mL/gVS, 163 mL/gVS, and 141,4 mL/gVS on day 16 at HCl concentrations of 0%, 5%, 10%, and 15%, respectively. Biogas production then decreased gradually from day 19 to day 28.

The highest concentration of HCl had no significant impact to improve biogas yield. HCl of 15% produced the lowest biogas yield as seen in Figure 2.

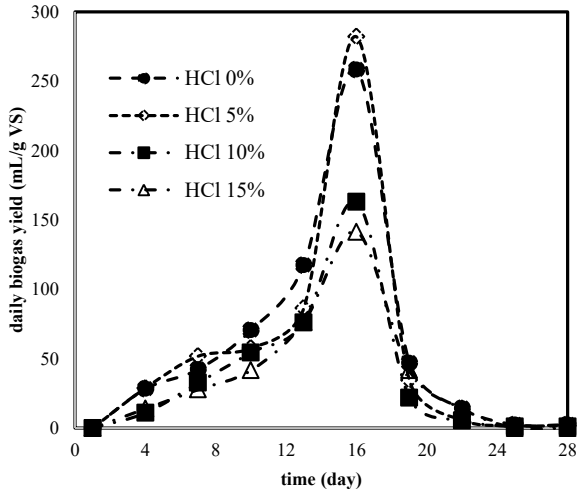


Figure 1. Daily biogas yield at the variation of HCl concentration

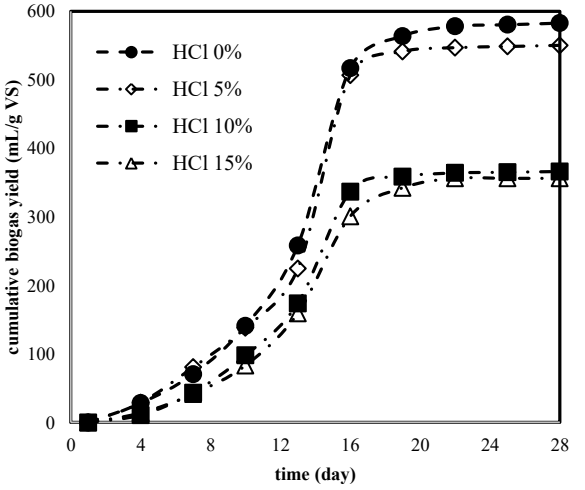


Figure 2. Cumulative biogas yield at the variation of HCl concentration

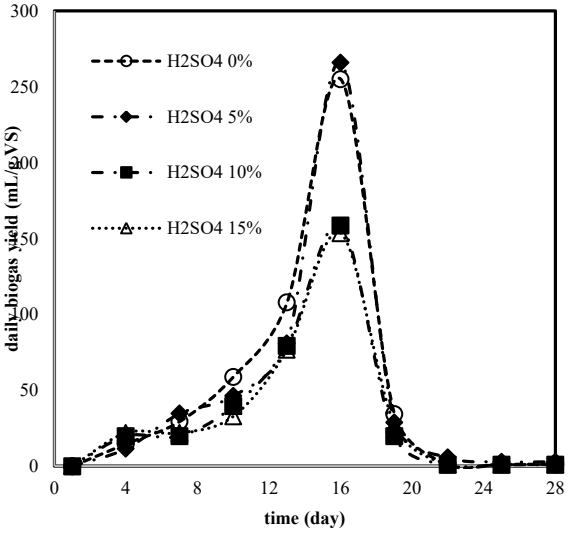


Figure 3. Daily biogas yield at the variation of H_2SO_4 concentration

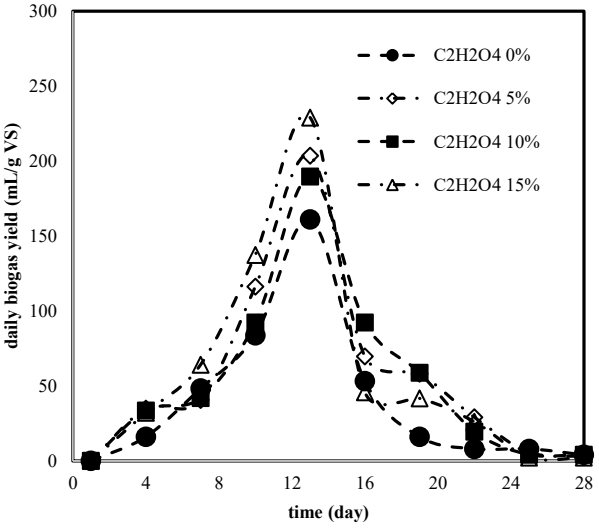


Figure 5. Daily biogas yield at the variation of $C_2H_2O_4$ concentration

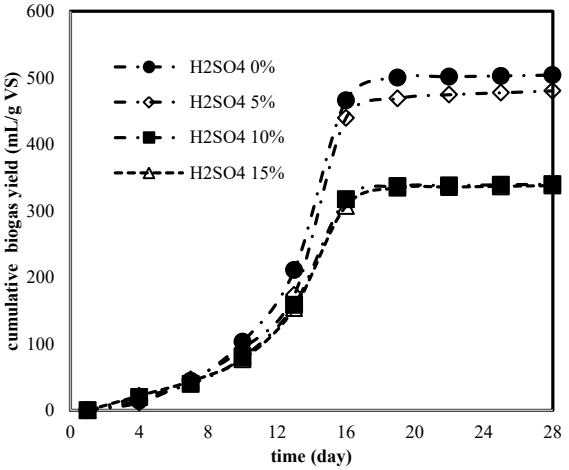


Figure 4. Cumulative biogas yield at the variation of H_2SO_4 concentration

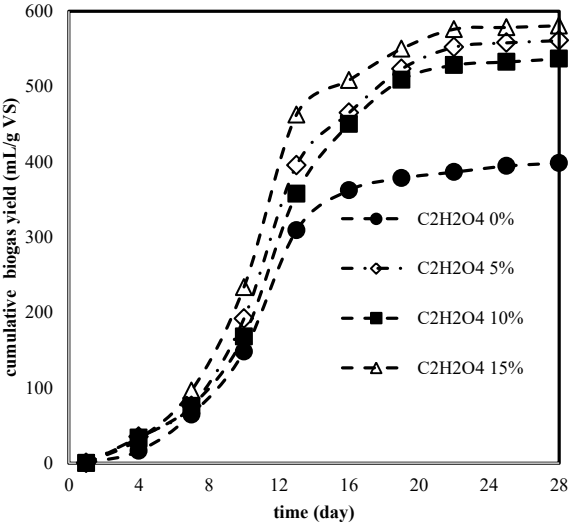


Figure 6. Cumulative biogas yield at the variation of $C_2H_2O_4$ concentration

HCl of 0% obtained the highest cumulative yield of 563,7 mL/gVS followed by cumulative yields of 540.9 mL/gVS, 358,5 mL/gVS, and 342.3 mL/gVS at HCl concentrations of 5%, 10%, and 15%, respectively. Results showed that increasing HCl concentrations could not enhance biogas yield. This phenomenon may occur because acid pretreatment produces inhibitory compounds that may impede anaerobic digestion [13]. Hydrochloric acid produces furfural and hydroxy methyl furfural (HMF) which leads to the inhibition of methanogen activity[14].

B. Effect of H_2SO_4 on Biogas Production

As presented in Figure 3, the daily biogas yield started on day 4. The highest peak yield of 255 mL/gVS was obtained at 0% H_2SO_4, followed by peak yields of 266.1 mL/gVS, 158.6 mL/gVS, and 153.5 mL/gVS at H_2SO_4 concentrations of 5%, 10%, 15%, respectively on day 16. After reaching peak values, biogas production decreased regularly with the lowest yields on day 28. Results showed that adding concentrations of H_2SO_4 had no positive impact on biogas production as proven in Figure 4.

The highest cumulative yield of 503.9 mL/gVS was obtained at H_2SO_4 of 0%. H_2SO_4 of 5% obtained a higher cumulative yield of 480.1 mL/gVS than 10% H_2SO_4 and 15% H_2SO_4 with cumulative yields of 339.9 mL/gVS and 337.8 mL/gVS, respectively. Acid pretreatment generates inhibitor products like phenolic acids, furfurals, aldehydes, and 5-hydroxymethylfurfural [8]. It can inhibit methanogen activity and decrease biogas production.

Table 1. Initial and final pH values

Acid concentration	Initial pH			Final pH		
	HCl	H_2SO_4	$C_2H_2O_4$	HCl	H_2SO_4	$C_2H_2O_4$
0%	6	6	6	7	6	9
5%	6	6	6	7	6	8
10%	4	4	6	5	5	8
15%	2	2	4	3	3	6

C. Effect of $C_2H_2O_4$ on Biogas Production

The effect of $C_2H_2O_4$ on biogas yield can be seen in Figure 5. Biogas yield began on day 4 for all concentrations of $C_2H_2O_4$ then biogas increased gently until attaining peak yield on day 13 with peak yields of 161 mL/gVS, 203,5 mL/gVS, 189,8 mL/gVS, and 229,03 mL/gVS for $C_2H_2O_4$ concentrations of 0%, 5%, 10%, 15%, respectively.

Increasing the concentration of $C_2H_2O_4$ from 10% to 15% increased cumulative yield from 536.9 mL/GV to 580.8 mL/gVS. Increasing $C_2H_2O_4$ from 0% to 5% also improved cumulative yield from 398, 5 mL/gVS to 561 mL/gVS. As shown in Figure 6 the highest cumulative yield was obtained at $C_2H_2O_4$ concentration of 15%.

Pretreatment of $C_2H_2O_4$ enhanced biogas yield more than pretreatment of HCl and H_2SO_4. $C_2H_2O_4$ may be produced by microbial fermentation and degraded easily compared to H_2SO_4. $C_2H_2O_4$ also generates fewer inhibitors and higher catalytic activity [15]. Therefore, pretreatment of $C_2H_2O_4$ had a positive impact on biogas production.

D. pH Function

The constancy of the process was evaluated via pH value. The pH was checked at initial and final conditions. pH is a crucial factor affecting anaerobic digestion performance. The ideal pH for anaerobic digestion is between 5.5 and 8.5 [16]. Table 1 presents the initial and final pH at various concentrations of acids.

During the experiment, the initial pH was 6 for acid concentrations of 0% and 5%. The anaerobic digestion of raw and pretreated substrates was in ideal pH conditions assuring the process stability, meanwhile, increasing acid concentrations from 10% to 15% generated lower pH values below 6, however, the initial pH of 10% $C_2H_2O_4$ was still in ideal pH conditions.

Increasing acid concentrations generated low pH values because the acid is getting more concentrated, so the pH value is getting smaller. The pH reduction may also happen due to the accumulation of acid leading to system inhibition [17]. Methanogens are sensitive to acid conditions, as a result, the methanogens' growth will be slow and inhibited [16].

The final pH was higher than the initial pH at all acid concentrations. Increasing pH values may occur due to ammonia accumulation [16]. The final high pH causes inhibition of methanogens leading to low conversion and small biogas yield [18].

IV. CONCLUSION

Corn stover is lignocellulosic biomass which not easily degraded by microbes. Acid pretreatment is utilized to enhance biogas yield. The best yield enhancement was achieved on pretreatment of $C_2H_2O_4$ with a $C_2H_2O_4$ concentration of 15%. The increase in HCl and H_2SO_4 concentrations could not enhance biogas yield, on the contrary, increasing concentrations of $C_2H_2O_4$ has a positive effect on the enhancement of biogas production. Increasing acid concentrations also affect pH conditions and biogas production. The low pH at initial and final conditions causes inhibition problems and decreases biogas production.

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REFERENCES

[1] L. M. Shitophyta, G. I. Budiarti, Y. E. Nugroho, and M. Hanafi, "The effect of effective microorganisms-4 (em-4) on biogas yield in solid-state anaerobic digestion of corn stover," in *IOP Conference Series: Materials Science and Engineering*, vol. 830, no. 2, May 2020.

[2] S. Abanades *et al.*, "A critical review of biogas production and usage with legislations framework across the globe," *International Journal of Environmental Science and Technology*, vol. 19, no. 4. Springer Science and Business Media Deutschland GmbH, pp. 3377–3400, Apr. 01, 2022.

[3] N. Xu *et al.*, "Biomethane production from lignocellulose: Biomass recalcitrance and its impacts on anaerobic digestion," *Front Bioeng Biotechnol*, vol. 7, no. AUG, 2019.

[4] K. O. Olatunji, N. A. Ahmed, and O. Ogunkunle, "Optimization of biogas yield from lignocellulosic materials with different pretreatment methods: a review," *Biotechnology for Biofuels*, vol. 14, no. 1. BioMed Central Ltd, Dec. 01, 2021.

[5] P. Yeganeh *et al.*, "Pretreatment of lignocelluloses for enhanced biogas production A review on influencing mechanisms and the importance of microbial diversity," *Renewable and Sustainable Energy Reviews*, vol. 135, p. 110173, 2021.

[6] B. J. Poddar *et al.*, "A comprehensive review on the pretreatment of lignocellulosic wastes for improved biogas production by anaerobic digestion," *International Journal of Environmental Science and Technology*, vol. 19, no. 4. Springer Science and Business Media Deutschland GmbH, pp. 3429–3456, Apr. 01, 2022.

[7] L. M. Shitophyta, A. Permadi, N. Rahmawati, and N. S. Sembiring, "Perbandingan Pretreatment Kimia dan Biologi pada Limbah Makanan untuk Produksi Biogas," *JTERA (Jurnal Teknologi Rekayasa)*, vol. 6, no. 2, p. 297, Dec. 2021.

[8] K. O. Olatunji, N. A. Ahmed, and O. Ogunkunle, "Optimization of biogas yield from lignocellulosic materials with different pretreatment methods: a review," *Biotechnology for Biofuels*, vol. 14, no. 1. BioMed Central Ltd, Dec. 01, 2021.

[9] B. J. Poddar *et al.*, "A comprehensive review on the pretreatment of lignocellulosic wastes for improved biogas production by anaerobic digestion," *International Journal of Environmental Science and Technology*, vol. 19, no. 4. Springer Science and Business Media Deutschland GmbH, pp. 3429–3456, Apr. 01, 2022.

[10] B. Jankovičová, M. Hutňan, M. N. Czölderová, K. Hencelová, and Z. Imreová, "Comparison of acid and alkaline pre-treatment of lignocellulosic materials for biogas production," *Plant Soil Environ*, vol. 68, no. 4, pp. 195–204, 2022.

[11] P. Amnuaycheewa, R. Hengaroonprasan, K. Rattanaporn, S. Kirdponpattara, K. Cheenkachorn, and M. Sriariyanun, "Enhancing enzymatic hydrolysis and biogas production from rice straw by pretreatment with organic acids," *Ind Crops Prod*, vol. 87, pp. 247–254, Sep. 2016.

[12] A. Dasgupta and M. K. Chandel, "Enhancement of biogas production from organic fraction of municipal solid waste using acid pretreatment," *SN Appl Sci*, vol. 2, no. 8, Aug. 2020.

[13] J. Kainthola, A. S. Kalamdhad, and V. v Goud, "A review on enhanced biogas production from anaerobic digestion of lignocellulosic biomass by different enhancement techniques," *Process Biochemistry*, vol. 84, pp. 81–90, 2019.

[14] A. G. Costa, G. C. Pinheiro, F. G. Pinheiro, A. B. D. Santos, S. T. Santaella, and R. C. Leitão, "The use of thermochemical pretreatments to improve the anaerobic biodegradability and biochemical methane potential of the sugarcane bagasse," *Chemical Engineering Journal*, vol. 248, pp. 363-372, 2014.

[15] T. Sar *et al.*, "Organosolv pretreatment of oat husk using oxalic acid as an alternative organic acid and its potential applications in biorefinery," *Biomass Convers Biorefin*, 2022.

[16] L. M. Shitophyta, Budiyono, and A. Fuadi, "Solid-state anaerobic digestion of rice straw for biogas production : a review," *CHEMICA: Jurnal Teknik Kimia*, vol. 3, no. 1, p. 17, 2016.

[17] N. Lahboubi, F. Karouach, M. Bakraoui, Y. el Gnaoui, A. Essamri, and H. el Bari, "Effect of Alkali-NaOH Pretreatment on Methane Production from Anaerobic Digestion of Date Palm Waste," *Ecological Engineering and Environmental Technology*, vol. 23, no. 2, pp. 78–89, 2022.

[18] L. Mulia Shitophyta, G. Indah Budiarti, Y. Eko Nugroho, and D. Fajariyanto, "Biogas Production from Corn Stover by Solid-State Anaerobic Co-digestion of Food Waste," *Jurnal Teknik Kimia dan Lingkungan*, vol. 2020, no. 1, pp. 44–52, 2019.