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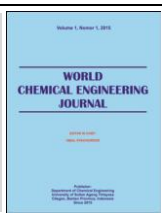

Triple Batch Digesters in Series Method to Analyze Biogas Potential from Bioethanol Vinasse

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ABSTRACT

The purpose of this study was to investigate biogas production from bioethanol vinasse using the simple method which was triple batch digester in series mode. Three digesters (A, B, C) were used in laboratory scale and carried out in 30 days respectively. The fresh rumen was added in substrates before that were put into each digester (A, B, C). Ratio of COD/N in substrat was adjusted in variation of 1436/7, 400/7, 500/7, 600/7, 700/7. The results showed that in digester A, biogas was produced in large amount a first time of fermentation. In digester B, biogas generated was less than that in digester A. Meanwhile, in digester C, biogas was not produced again. Ratio of 500/7 and 600/7 generated the most biogas volume which was 9,322 and 9,168 mL.

Keywords: *Bioethanol, Biogas, Series Method, Triple Batch, Vinasse,*

1. INTRODUCTION

Recently, many authors have studied waste-treatment using anaerobic technology. This technology is more popular than aerobic technology to solve waste-problems. That is caused by some reasons, which are: (1) it can treat wastes that contain high organic content, (2) it is simple to be operated, needs low operation cost and does not need large area, (3) it can generates biogas. Biogas that generated from this technology can be used to substitute the fossil fuel demand in the world. The main content of biogas is methane (CH_4) and by-products are CO_2, H_2S, etc.

Bioethanol vinasse is one kind of waste-waters, that is treated effectively using anaerobic technology. Bioethanol vinasse is waste that is generated through the bottom of distillation unit. Vinasse has characteristic of very low pH, high total solid (TS), high chemical oxygen demand (COD), and high temperature. Because of this characteristic, vinasse will pollute the environment, if it is discharged without treatment before.

Some authors have investigated biogas potential from vinasse using batch digester. Budiyono *et al.* (2013a) and Budiyono *et al.* (2014a) stated that pH optimum in batch digester is 7.0. Budiyono *et al.* (2014b) reported that total biogas will generated in large amount if substrate contains total solid (TS) of 7.015±0.007%. Budiyono *et al.* (2013b) and Syaichurrozi *et al.* (2013) showed that the optimum ratio to treat vinasse using biogas technology is 500/7 – 600/7. In this range, the COD removal value obtained is satisfied enough (36.573±1.689 – 38.088±0.872 %), although not all COD in vinasse is converted into biogas. The authors measured biogas in real time (biogas daily). The profile of biogas daily showed that biogas is generated in large amount at beginning fermentation, then the production is decreasing until 20th fermentation. The authors supposed the phenomenon is caused by pH drop in substrate. pH substrate is descending from neutral condition until pH ~ 3.0.

Furthermore, Sumardiono *et al.* (2013) tried to maintain pH substrate in neutral condition (7.0±0.2) using NaOH 2 M during fermentation. This method can increase total biogas from 3.673-6.096 mL/g COD until 17.875-21.229 mL/g COD. However, it cannot change profile biogas production daily. The longer fermentation time, the less biogas daily produced. Syaichurrozi *et al.* (2013) also reported same result. Biogas generated at 2nd day, then increased until 6th day, but after 6th day

which is 8th day to 60th day, biogas daily was decreased continuously.

Based on that, the biogas production from vinasse need to be investigated more. Author guessed that bacteria in the digesters was death, so author studied this research to prove it. Author tried to use triple batch digesters that were arranged in series system. This research using batch digesters laboratory scale that made from polyethylene bottle with volume 5 L. Substrate was varied into some ratio of COD/N. Variables that will be put into each digester, must be added rumen fluid as provider of fresh anaerobic bacteria in substrate. Also, pH substrate was adjusted on neutral condition (pH 7.0) using NaoH 2 M before substrate put into each digester. Biogas formed and pH substrate measured once in two days using water displacement method and pH meter, respectively.

2. METHODS

2.1 Wastewater and inoculum

Vinasse used in this study was obtained from bioethanol industry. The bioethanol industry produced bioethanol using molasses as raw material. It located in Solo, Central Java, Indonesia. The vinasse contained COD of 229,250±1,060 mg/L; TS of 300,942 mg/L; VS of 284,659 mg/L; pH of 3.25±0.212. The cow rumen fluid was used as inoculum. The rumen obtained from slaughterhouse in fresh condition to guarantee the anaerobic bacteria was still in good condition.

2.2 Preparation substrate

According to Budiyono *et al.* (2014b), vinasse substrate that contains TS of 7.015±0.007% can produce biogas maximally. Thus, Syaichurrozi *et al.* (2013) and Budiyono *et al.* (2014a) diluted vinasse using water with ratio of vinasse:water of 1:3 to get TS of 7.015±0.007%. In the recent research, author also used vinasse that had same characteristic with vinasse of Budiyono *et al.* (2014b). Therefore, substrate used was with vinasse:water ratio of 1:3 (TS 7.015±0.007%).

2.3 Experimental set up

Anaerobic batch digesters used were made from polyethylene bottles with volume of 5 L. The bottles were plugged using rubber plug and were equipped using valve for biogas measurement. The digesters were operated at room temperature. Biogas generated was measured by using water displacement method. In this method, digesters were connected to gas collector that usually was reserved gradual glass cylindrical. The connection between digesters and gas collector was done using tube. The gas collectors were immersed in through of water to ensure complete sealing and biogas generated was collected by the downward displacement of water.

2.4 Experimental design

Anaerobic digesters in laboratory scale were operated in batch system and at room temperature. The volume of digesters was 5 L and the volume of substrate was 1 L. The cow rumen fluid as bacteria provider was added into the digesters as much as 10% v/v substrate (100 mL). Vinasse used had COD/N ratio of 1436/7. According to Speece (1996), the optimum range of COD/N ratio was 350/7 – 1000/7. Thus, author varied COD/N ratio in substrate through urea addition. Urea that contained 46% N, was used as nitrogen source. The variation of COD/N ratio in this research was 1436/7 (~205.14), 400/7 (~57.14), 500/7 (~71.43), 600/7 (~85.71), 700/7 (~100).

2.5 Experimental procedures

This research used three digesters that arranged in series system, which were digester A, B and C. Before substrates (1000 mL) were put into digester A, pH of substrates must be adjusted on 7.0 using NaOH 10 N, then rumen fluid (100 mL) was added into substrate. Fermentation process in digester A was carried out in 30 days. Biogas generated was measured every once in two days and pH of substrates was measured using pH meter every once in two days.

After 30 days in digester A, substrates (effluent of digester A) were brought in the digester B. In digester B, pH of substrates was adjusted again on 7.0 using NaOH 10 N and rumen fluid (100 mL) was added into substrate to provide anaerobic bacteria especially methanogenic bacteria in fresh condition. Fermentation di digester B was conducted in 30 days. Biogas formed and pH substrates were measured every once in two days.

After 30 days in digester A, substrates (effluent of digester B) were sent to digester C. In digester C, pH of substrates was adjusted again on 7.0 using NaOH 10 N and rumen fluid (100 mL) was added into substrate to provide methanogenic bacteria in fresh condition. Same with digester A and B, digester C was operated in 30 days. Biogas formed and pH substrates were measured every once in two days.

3. RESULTS AND DISCUSSIONS

3.1 Biogas production in digester A

Biogas formed firstly at 2nd days of fermentation for all variables. The amount of biogas production daily was increasing at 3rd – 5th days of fermentation. Furthermore, biogas production daily was decreasing until end of fermentation (Fig. 1 (a)). Sumardiono *et al.* (2013) stated that vinasse contained simple organic compound. In the bioethanol production process, molasses was processed through some steps such as hydrolyze, fermentation and distillation. In the hydrolyze step, complex organic compound was convert into simple organic compound such as glucose. Then, in fermentation process, simple organic compound was converted into ethanol by help of *saccharomyces.* In the

distillation step, ethanol formed was separated from by-product. The bottom product of distillation was known as vinasse. Automatically, vinasse contained simple organic matter. Based on that, vinasse was easily to be degraded by bacterial activity and produced biogas just a little time of fermentation.

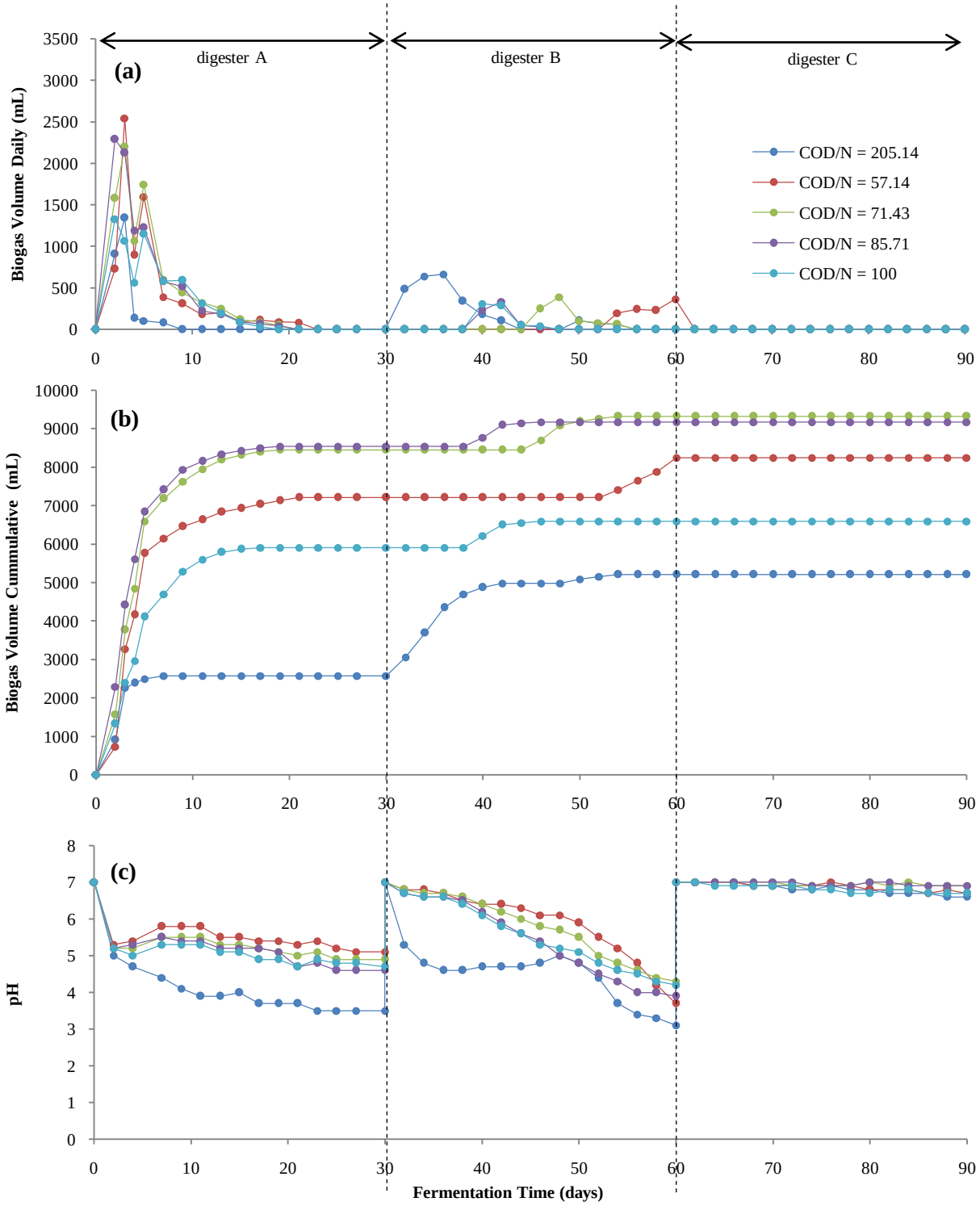

Fig. 1. (a) Biogas volume daily, (b) biogas volume cumulative, (c) pH profil in digester A, B and C, at variation of COD/N. The variation of COD/N ratio in this research was 1436/7 (~205.14), 400/7 (~57.14), 500/7 (~71.43), 600/7 (~85.71), 700/7 (~100)

In first step, which was in digester A, biogas formed from variable with COD/N of 1436/7, 400/7, 500/7, 600/7, 700/7 was 2,567; 7,212; 8,448; 8,532; 5,902 mL respectively (Fig. 1 (b)). Substrate with COD/N ratio of 500/7-600/7 produced the most total biogas volume. Syaichurrozi *et al.* (2013) predicted ammonium formed using stoichiometry concept in the digesters at variety of COD/N substrate. Substrate with COD/N of 1436/7, 500/7, 600/7, 700/7 generated total ammonium of 3,220; 12,142; 10,672; 9,289; 6,851; 4,751 mg/L (Syaichurrozi *et al.*, 2013). According to Speece (1996), anaerobic bacteria consumes amount of ammonium 40-

70 mg/L per day as nitrogen source. In digester A, all substrate was carried out in 30 days. Assume that, anaerobic digester need 70 mg/L per day, so amount of ammonium that was needed by bacteria in 30 days was 2,100 mg/L. With simple calculation, ammonium remaining in the digester was 1,120; 10,042; 8,572; 7,189; 4,751; 2,651 mg/L for variable of 1436/7, 400/7, 500/7, 600/7, 700/7 respectively.

According to Niu *et al.* (2013), ammonium concentration maximum in digester that was allowed to bacterial growth was 5,000 mg/L. If it was more than 5,000 mg/L, removal of protein and carbohydrate was decreasing. Among of all variable, COD/N of 700/7 was the best ratio if follow this concept, but biogas generated was less than COD/N of 500/7 and 600/7. Vinasse contained high carbohydrate, so that vinasse anaerobic technology will produce VFAs (Sumardiono *et al.*, 2013). The accumulation of VFAs in digester lead to pH substrate was drop. Elbeshbishy and Nakla (2012) stated that presence of ammonium in digester can maintain pH change (pH drop) in substrate. Author concluded that COD/N of 500/7 and 600/7 was the optimum ratio, although ammonium concentration formed was higher than that was allowed by Niu *et al.* (2013). Abundant of ammonium that was generated in substrate with COD/N of 500/7 and 600/7 can be used to counterbalance VFAs formed. Whereas, on COD/N of 1436/7 and 400/7, biogas formed was less than 500/7 and 600/7. That was caused by ammonium concentration formed was too excess. Too excess of ammonium was toxic for anaerobic bacterial growth. Author guessed that bacterial activity in variable with COD/N of 1436/7 and 400/7 was disrupted by (1) VFAs formed in large amount and (2) ammonium concentration was too excess.

3.2 Biogas production in digester B

Bottom products (slurry) from digester A, was used as substrates in digester B. All substrate were adjusted the pH condition of 7.0 using NaOH 10 N. After that, rumen fluid of 100 mL was added in to substrates as anaerobic bacteria provider. This concept was done to provide good condition and fresh bacteria in digester. Fermentation time of 30 days was done. Total biogas generated for COD/N of 1436/7, 400/7, 500/7, 600/7, 700/7 was 5,209; 8,242; 9,322; 9,168; 6,586 mL respectively.

Substrate with COD/N of 1436/7 began to produce biogas at first fermentation time (32nd day) in digester B. Then, the biogas production daily was increasing until 36th day, but after that it was decreasing until 52nd day. Whereas, the other variables needed long time to start in producing biogas. Biogas was generated firstly at 52nd day on COD/N of 400/7, at 46th day on COD/N of 500/7, at 40th day on COD/N of 600/7, at 40th on COD/N of 700/7.

Variable control (COD/N of 1436/7) was easy to produce because it still contained a large of organic materials. The Organic materials amount in variable of 1436/7 was largest than the others. It can be proved from biogas production in digester A, which variable 1436/7 generated the less biogas cumulative than the others. That means, just a little part of organic matter in vinasse was converted into biogas in digester A. From Fig. 2, effluent (slurry) of control variable from digester A had reddish black color, while variable of 600/7 had black color. It was evidence that control variable (1436/7) still contained many simple organic compound. The fresh vinasse had more reddish color than effluent of control variable (Fig. 1(a)). That means, the more simple organic matter in substrate, the more reddish color of substrate. However, after 36th day, biogas production was decreasing. This phenomenon was caused by VFAs formed. From Fig. 1(c), pH profile of control variable was decreasing until 3.1.

Meanwhile, biogas was formed firstly at 38th day in substrate with COD/N ratio of 600/7 and 700/7. The biogas was increasing until at 42nd day of fermentation. Furthermore, it was decreased and discharged completely at 46th day of fermentation. Total biogas volume generated in digester B for variable control was more than that for 600/7 and 700/7.

In substrate of 500/7, bacteria needed longer lag time than in substrate of 600/7 and 700/7. Biogas was formed firstly at 46th day of fermentation. While, bacteria in substrate of 400/7 needed the longest lag time than the others which was at 54th of fermentation. From this phenomenon, author concluded that the more ratio of COD/N in substrate, the faster biogas produced in digester B.

From Fig. 1(c), pH condition in substrate was decreasing during fermentation. That means, there was bacterial activity to form biogas in the digester. The decreasing pattern of profile pH was not drastically like profile pH in digester A. pH substrate was decreased from 7 until 5 in digester A just at second fermentation time, while pH substrate was decreased gradually in digester B, except variable control (COD/N of 1436/7). Variable control generated VFAs in large amount, so that pH substrate was drop. Variable control still contained simple organic matter was more than the other variable. The changing pH substrate proved that bacteria still can do activity in the digester B.

3.3 Biogas production in digester C

Digester C was operated in 30 days in room temperature. Rumen fluid was added into all substrate as fresh bacteria provider. From Fig. 1 (a) and 1 (b), biogas was not produced in all variables. Bacteria also cannot do activity in substrates during fermentation, it can be proved from Fig. 1 (c) that pH profile was not change. Substrates might be poison for bacteria because substrate contained much amount of VFAs and ammonium. The combination between VFAs and ammonium in system was very toxic for bacterial activity. From this method which was using three step (digester A, B and C), author concluded that vinasse was not treated effectively using anaerobic batch digester. Modified digester and pretreatment of vinasse must be done to increase biogas production.

(a) (b) (c)

Fig. 2. The color of (a) vinasse waste, (b) slurry of variable of 1436/7 from digester A, (c) slurry of variable of 600/7 from digester A

4. CONCLUSION

Triple Batch Digester in series method was done to investigate the potential biogas production from vinasse in batch mode. The study was carried out in 90 days, which was 30 days in digester A, 30 days in digester B and 30 days in digester C. The results showed that, in digester A, biogas production for control variable, 400/7, 500/7, 600/7, 700/7 was 2,567; 7,212; 8,448; 8,532; 5,902 mL respectively. Whereas, in digester B, total biogas for the variables became 5,209; 8,242; 9,322; 9,168; 6,586 mL respectively. Finally, in digester C, biogas was not produced in all of variables. Bacteria could not do activities in digester C, because the substrate was toxic.

5. REFERENCES

Budiyono, Syaichurrozi I., Sumardiono S. 2013a. Biogas Production from bioethanol waste: the effect of pH and urea addition to biogas production rate. Waste Technology, Vol. 1, No. 1, pp. 1-5.

Budiyono, Syaichurrozi I., Sumardiono S. 2013b. Biogas Production Kinetic from Vinasse Waste in Batch Mode Anaerobic Digestion. World Applied Sciences Journal, Vol. 26, No. 11, pp. 1464-1472.

Budiyono, Syaichurrozi I., Sumardiono S. 2014a. Kinetic Model of Biogas Yield Production from Vinasse at Various Initial pH: Comparison between Modified Gomperts Model and First Order Kinetic Model. Research Journal of Applied Sciences, Engineering and Technology, Vol. 7, No. 13, pp. 2798-2805.

Budiyono, Syaichurrozi I., Sumardiono S. 2014b. Effect of Total Solid Content to Biogas Production Rate from Vinasse. International Journal of Engineering, Vol. 27, No. 2, pp. 177-184.

Elbeshbishy E., Nakhla G. 2012. Batch anaerobic co-digestion of proteins and carbohydrates. Bioresource Technology Vol. 116, pp. 170–178.

Niu Q., Qiao W., Qiang H., Hojo T., Li Y.Y. 2013. Mesophilic methane fermentation of chicken manure at a wide range of ammonia concentration: stability, inhibition and recovery. Bioresource Technology, Vol. 137, pp. 358–367.

Speece R.E. 1996. Anaerobic Technology for Industrial Wastewaters. Archae Press, USA.

Sumardiono S., Syaichurrozi I., Budiyono, Sasongko S.B. 2013. The Effect of COD/N ratios and pH Control to Biogas Production from Vinasse. International Journal of Biochemistry Research & Review, Vol. 3, No. 4, pp. 401-413.

Syaichurrozi I., Budiyono, Sumardiono S. 2013. Predicting Kinetic Model of Biogas Production and Biodegradability Organic materials: Biogas Production from Vinasse at Variation of COD/N Ratio. Bioresource Technology Vol. 149, pp. 390-397.