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Effect of sulfuric acid pretreatment on biogas production from *Salvinia molesta*

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ABSTRACT

The effect of sulfuric acid pretreatment on biogas yield from *Salvinia molesta* (SM) was studied. The sulfuric acid concentration was varied to be 2, 4, 6% v/v. Pretreatment was carried out under batch system at room temperature and pressure of 1 atm for two days. Then, the digestion was carried out for 30 days under batch system at room temperature and pressure of 1 atm. The pretreatment decreased the lignin content and increased the nitrogen free extract content (non-fiber carbohydrate). The more the sulfuric acid concentration, the more the change of these contents. Furthermore, cumulative biogas yield from pretreated SM using sulfuric acid 2–6% (22.72–24.14 mL/g VS) was higher than that from raw SM (13.28 mL/g VS). For digestion during 30 days, the best pretreatment was 4% because it produced the highest total biogas yield (24.14 mL/g VS) and had very short lag time (0 day). The measured data was simulated using the modified Gompertz and first order kinetic model. The calculation showed that the modified Gompertz model (error 6.141–12.431%) was better than the first order kinetic model (error 7.336–47.606%).

1. Introduction

Indonesia, which is an agricultural country, has abundant lignocellulosic biomass. Because of the hot issue which is energy in the country, the lignocellulosic biomass is utilized as energy feedstock. The target of Indonesian government is to decrease fossil fuels need from 92% (at year of 2013) to 67% (at year 2050) and increase renewable energy need from 8% (at year 2013) to 33% (at year 2050) [1].

One of lignocellulosic biomasses, which thrive in Indonesia, is *Salvinia molesta* (SM). Like water hyacinth, SM is a free-floating aquatic weed growing well under Indonesian weather [2]. It grows quickly with doubling time just 3–10 days [3,4]. Besides that, it has high resistance to environmental changes. Therefore, the SM growth is difficult to be controlled. Presence of SM in water body is very detrimental because it will block the river surface, reduce the dissolved oxygen, reduce the water volume through evapotranspiration, decrease the aquatic organism movement, disturb the ship track and reduce the irrigation system efficiency [2,5,6]. SM is very potential to be used as a biogas feedstock because it contains high cellulose that can be converted to be biogas.

In Indonesia, biogas technology was introduced around 1970. Then, it have disseminated since 1980 by the Ministry of Agriculture. For last 30 years, the private and public institutions have participated in the biogas technology development [7]. However, biogas technology development is still low so the number of biogas digester is limited mainly in rural area [8]. That is caused by educational level of rural people. They still use firewood causing unhealthy cooking environment. SM is very abundant in rural area because it thrives in rice fields, rivers and lakes [9]. Thus, biogas from SM can be a good option for the rural people to replace the firewood need. In 2050 perspective, the total national energy in 2050 is approximately 595.1 million tonnes oil equivalent (TOE) [1]. Furthermore, 33% of the total national energy will be supplied by renewable energy which is 196.38 million TOE. Hence, biogas from SM is expected to fulfill part of the total renewable energy need.

In biogas technology, there are some catalyst techniques to enhance biogas production. Dubrovskis et al. [10] used metaferm as biocatalysts in digestion of vegetable processing wastes. Bogudo et al. [11] and Syaichurrozi et al. [12] used yeast as biocatalysts in digestion of wastes. Furthermore, Sarto et al. [6] successfully increased biogas from water hyacinth via chemical pretreatment. The ion H^+ or OH^- acted as acid or base catalyst increasing hydrolysis reaction rate, so that complex compounds were converted to be simple compounds. Chemical pretreatment is more interesting than biocatalyst addition (metaferm and yeast) because it is cheap and easy in preparation. In addition, chemical pretreatment is more interesting than physical and biological pretreatments. It is effective and inexpensive for improving the lignocellulosic substrate degradation [6].

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As lignocellulosic biomass, SM contains not only cellulose and hemicellulose but also lignin. The lignin in SM provides the mechanical-strong layer and has a complex linkage to cellulose and hemicellulose [6]. Therefore, the presence of lignin will decrease the conversion process of SM to biogas [13]. Based on the best study, the chemical pretreatment to increase biogas from SM has not been studied by other authors yet. Mathew et al. [4] just compared between biogas production from raw SM and raw water hyacinth. Furthermore, O'Sullivan et al. [14] also compared biogas production from raw SM, raw water hyacinth and raw cabomba. Abbasi and Nipaney [3] successfully produced biogas from raw SM with water addition of SM:water of 1:7 (w/w). Syaichurrozi [2] and Syaichurrozi et al. [9] studied co-digestion of raw SM and raw rice straw. Therefore, this study was new and original.

According to Song et al. [13] on chemical pretreatment, the best concentration of H_2SO_4, HCl, CH_3COOH, NaOH for biogas from corn straw was 2%, 2%, 4%, 8% respectively. Pretreatment using H_2SO_4 could produce higher biogas yield (175.6 mL/g VS) than that using NaOH (163.5 mL/g VS). Furthermore, chemical pretreatment using H_2SO_4 resulted higher biogas yield than HCl (163.4 mL/g VS) and CH_3COOH (145.1 mL/g VS). Moreover, cost of pretreatment using H_2SO_4 was lower than other chemicals (HCl, CH_3COOH, NaOH). Thus, the H_2SO_4 was the best chemical to be used in pretreatment because it was low price and produced high biogas yield. Furthermore, Sarto et al. [6] successfully increased biogas production from water hyacinth by using sulfuric acid pretreatment. Therefore, this study also used sulfuric acid (H_2SO_4) in chemical pretreatment for SM.

The purpose of this study was to investigate the effect of chemical pretreatment using sulfuric acid on chemical composition of SM, so biogas yield could be produced maximally. Recently, this study is urgent because the SM growth has not been controlled yet and the renewable energy production is still low. In this work, the sulfuric acid concentration was varied to be 2, 4, 6%v/v because Song et al. [13] suggested that concentration range in chemical pretreatment of lignocellulosic biomass was 1–10%. Pretreated SM was used as biogas feedstock in laboratory scale anaerobic digesters under room temperature (30 °C). The fermentation was carried out for 30 days. Biogas volume was measured through water displacement method.

Furthermore, the measured data was applied to build kinetic model using modified Gompertz and first order kinetic model. Then, the kinetic constants obtained from these models could be used to explain the effect of chemical pretreatment on biogas production. The two models are very popular in biogas production. Many authors found that the accuracy between the two models depends on substrates used. The modified Gompertz model is suitable to be used in biogas from mixture of vinasse and tofu-processing wastewater [15], tofu wastewater [12], brewery grain waste [16], bread waste [16], pacific saury fish waste [16], mackerel fish waste [16], vinasse [17], mixture of pig manure and dewatered sewage sludge [18], mixture of SM and rice straw [2]. On the other hand, the first order kinetic model is suitable to be used in biogas from mixture of waste activated sludge and *Egeria dense* [19], dairy manure [20], rabbit manure [20]. Therefore, comparison applying between the two models in biogas from pretreated SM is important to be studied.

2. Methods

2.1. SM and inoculums

SM was collected from water bodies located in Pandeglang Regency, Banten Province, Indonesia. Furthermore, fresh rumen fluid was applied as inoculums. It was collected from cow slaughterhouse in Cilegon City, Banten Province, Indonesia.

2.2. Pretreatment process

2.2.1. Preparation of materials

The raw SM, which was collected from the water bodies, was washed using clean water and then dried under the sun. Furthermore, the particle size of SM was reduced by using a blender and the fraction less or equal of 18 mesh was collected by using screener for experiments.

2.2.2. Experimental procedures

The SM as much as 25 g (total solid of 22.09 g) was soaked in 500 mL H_2SO_4 solution with concentration 2, 4, 6%v/v. The H_2SO_4 solution in specific concentration was only used once that means the solution was washed away after pretreatment. Pretreatment was carried out in batch condition during two days at room temperature (30 °C). After pretreatment, the SM was separated from the solvent using filter paper. Then, the pretreated SM (pSM) was washed using clean water. Furthermore, it was dried before it was analyzed through proximate and van soest. The proximate and van soest analyses was conducted by the analysis services of Fakultas Peternakan dan Pertanian - Universitas Diponegoro, Semarang city, Indonesia. There is no replication in this experiment.

2.3. Anaerobic digestion

2.3.1. Preparation of substrate

The pretreated SM (pSM) as much as 10 g resulted from pretreatment section was used as biogas feedstock. The water was added with pSM/water ratio of 1/13 (w/v). The acidic level of substrate was adjusted to be 7 ± 0.1 using NaOH 1 M. Then, the inoculum was added as much as 25 mL to make inoculum/substrate of 2.5 v/w based on previous study [2,9].

2.3.2. Experimental procedures

Lab-scale anaerobic digesters were built from polyethylene bottles having volume of 600 mL. The bottles were plugged by using rubbers. The bottle was connected to reversed cylindrical glass (as gas collector) by using plastic tubes. The reversed cylindrical glass was immersed in water. The valve was applied to close-open the plastic tubes for measuring biogas volume. When the valve was opened, the biogas flew through the tubes and it was storred and replaced the amount of water in the gas collector. This measuring method was called as water displacement method [2].

Digestion process was conducted for 30 days at room temperature (30 °C) and at pressure of 1 atm. The daily biogas volume was recorded at two days interval through water displacement method. Then, the daily biogas volume data was presented to be cumulative biogas volume. The daily and cumulative biogas yield (mL/g VS) were obtained by dividing the daily and cumulative biogas volume (mL) by initial volatile solid (g VS). Each digester was mixed by shaking it manually for 1 min after measurement. There is no replication in this experiment.

2.4. Analysis

The substrate pH level was monitored by using a digital pH meter with specification of Hanna-Digital-PHEP-98107-1 model. First, the rubber was taken from the digesters. Then, substrates as much as 10 mL were taken from the digesters for measuring the substrate pH level [21]. Furthermore, the substrates were stored at 4 °C before they were analyzed their ammonium ion concentration. The ammonium ion concentration (NH_4^+-N) was analyzed through the Standard Methods APHA 22nd edition 2012 [22]. Furthermore, the concentration of ammonia (NH_3-N) and volatile fatty acids (VFAs) was determined through equation (2) [23] and (3) [24] respectively. At the end of fermentation, the final total solid (TS) was also measured through the Standard Methods [22,25]. The percentage of TS removal was determined through equation (1) [26]. The methane percentage in biogas was

measured by using GC-TCD (Gas Chromatography-Thermal Conductivity Detector) 8 A Inject 130 column 100 × 100, column active carbon, Shimadzu. Biogas was stored in gas chamber for 30 days. Then, the biogas was injected to the GC-TCD for analyzing the methane content.

$$TS\ Removal\ (\%) = \frac{initial\ TS - final\ TS}{initial\ TS} \times 100\% \quad (1)$$

$$(NH_3 - N) = (NH_4^+ - N) \times \left[1 + \frac{10^{-pH}}{10^{-\left(0.1075 + \frac{2725}{T}\right)}}\right]^{-1} T$$

$$= absolute\ temperature,\ K \quad (2)$$

$$pH = 9.43 - 2.02\frac{VFAs}{[(NH_3 - N) + (NH_4^+ - N)]} \quad (3)$$

2.5. Kinetics on anaerobic digestion

The measured biogas yield was modeled using two proposed kinetic models, i.e. modified Gompertz model [21] and first order kinetic model [2]. The equations of modified Gompertz model and first order kinetic model were presented in Eqs. (4) and (5) respectively. The biogas production rate under batch condition was assumed that it had correspondence to bacterial growth rate in the digesters. By using non-linear regression, the Eqs. (4) and (5) could be solved and the kinetic constant value of ym, λ, μ, k could be obtained. The polymath software 5.0 Educational Version was used as tool to conduct the non-linear regression [6].

$$y(t) = ym.\ \exp\left\{-\exp\left[\frac{\mu.\ e}{ym}(\lambda - t) + 1\right]\right\},\ t \geq 0 \quad (4)$$

$$y(t) = ym\ (1 - exp(-k.\ t)),\ t \geq 0 \quad (5)$$

Where:

y(t) = the cumulative biogas yield at digestion time t days (mL/g VS)

ym = the maximum biogas yield potential (mL/g VS)

μ = the maximum biogas yield rate (mL/g VS.day)

λ = lag phase period or minimum time to produce biogas (days)

t = cumulative time for biogas production (days)

e = mathematical constant (2.718282)

k = the biogas production rate constant (/day)

Furthermore, the Mean Absolute Percent Error (MAPE) was calculated to show the mean absolute error between measured and predicted data obtained using the proposed models. The less the MAPE value, the better the model was used. The MAPE was determined through Eqs. (6).

$$MAPE = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{|Measured\ biogas - Predicted\ biogas|}{|Measured\ biogas|}\right) \times 100\% \quad (6)$$

3. Results and discussions

3.1. Effect of pretreatment on chemical composition of SM

Sulfuric acid pretreatment decreased the total solid (TS) of SM. Besides that, it also changed the chemical compositions of SM. The results of chemical composition analysis after pretreatment were shown in Table 1. Because of the decrease in total TS, the unit of %TS had to be converted to unit of g. Hence, the degradation of each component mass could be determined.

Based on Table 1, all of component mass decreased except the nitrogen free extract (NFE). The ash mass decreased from 10.04 (raw SM) to 3.53 g with increasing sulfuric acid concentration from 0 (unpretreatment) to 6%. Pattiya et al. [27] also reported the same results with this study. The soaking organic compound in acid solution would remove the ash content. The more the acid concentration, the more the ash mass was removed. The VS mass was total mass of crude lipid, crude protein and crude carbohydrate. Pretreatment decreased the mass of these components. The crude lipid was degraded to be fatty acids and glycerol. The protein was degraded to be amino acids. Meanwhile, the crude carbohydrate consisted of crude fiber and nitrogen free extract (NFE). The crude fiber dominantly consisted of cellulose and lignin. The NFE dominantly consisted of hemicelluloses, organic acids and sugars [28,29]. Cellulose and hemicellulose were converted to be sugars [30]. The rate of cellulose and hemicellulose degradation depends on the sulfuric acid concentration, where the higher the sulfuric acid concentration, the higher the cellulose and hemicellulose degradation rate [6]. Hence, the cellulose and hemicellulose content in SM decreased with increasing the sulfuric acid concentration. Different from cellulose and hemicellulose, the NFE increased because the sugars generated from degradation of cellulose and hemicellulose added the total sugars in SM. Meanwhile, the lignin in SM decreased because it was converted to be phenylic compound (phenolic compounds, benzoic acid, cinnamic acid) [30]. Decrease in cellulose, lignin, hemicellulose and NDF caused decrease in acid detergent fiber (ADF) (ADF = cellulose + lignin) and neutral detergent fiber (NDF) (NDF = ADF + hemicellulose) [28].

3.2. Biogas production

Cellulose, hemicellulose and lignin are converted to biogas under anaerobic digestion (AD). Commonly, there are four mayor phases for biogas production i.e. hydrolysis, acidogenesis, acetogenesis, methanogenesis [31,32]. Biogas from cellulose and hemicellulose follows the four mayor phases. In hydrolysis phase, they are hydrolyzed to monosaccharides or simple sugars [33]. Then they are converted to volatile fatty acids (VFAs) in acidogenesis phase. Furthermore, the VFAs are converted to acetic acid in acetogenesis phase, subsequently it is fermented to biogas in methanogenesis phase. However, biogas from lignin consists of six (6) phases, i.e. (1) depolymerization and solubilization: lignin is converted to monomers and lignin-derived monoaromatic compounds, (2) peripheral pathways and funneling to central monoaromatic intermediates: the monomers and lignin-derived monoaromatic compounds are converted to central monoaromatic intermediates, (3) dearomatization and ring cleavage: central monoaromatic intermediates are converted to aliphatic acids, (4) acidogenesis: aliphatic acids are converted to VFAs, (5) acetogenesis: VFAs are converted to acetic acid, (6) methanogenesis: acetic acid is converted to biogas [34]. However, lignin is a poorly degradable fraction of lignocellulosic biomass under anaerobic digestion [34]. The biogas production profile depends on composition of crude fiber carbohydrate (lignin and cellulose) and crude non-fiber carbohydrate (hemicelluloses, organic acids and sugars) in substrates [9].

The daily and cumulative biogas yield (mL/g VS) during digestion from all variables are shown in Fig. 1(A–B). In unpretreatment case, daily biogas yield in period of day 0–12 was just in little amount. Raw SM still contained high crude fiber, so that bacteria adapted in substrate condition in period of day 0–12. After that, biogas yield increased after day 12 until day 18. In that period, the NFE (Nitrogen Free Extract, non-fiber carbohydrate) was converted to biogas. Finally, biogas yield decreased after day 18 until the end of fermentation time because bacteria could not convert the organic materials again.

By using pSM 2% and 4% as biogas feedstock, biogas yield increased drastically in day 2. After day 2, it decreased until day 18. However, it increased again until day 26. Finally, it decreased until the end of fermentation time. By chemical pretreatment, the lignin in SM was degraded to be soluble compounds. Like lignin, cellulose in SM was also degraded to be disaccharide and monosaccharide. From Table 1, the lignin and cellulose content decreased with increasing the sulfuric acid from 0 (unpretreatment) to 6%. However, the NFE increased with

Table 1
Effect of pretreatment on chemical composition of SM.

Components	Sulfuric acid pretreatment										
	unpretreatment		2%			4%			6%		
	Composition (% TS)	Mass (g)	Composition (% TS)	Mass (g)	Changing based on mass (%)	Composition (% TS)	Mass (g)	Changing based on mass (%)	Composition (% TS)	Mass (g)	Changing based on mass (%)
Total solid (TS)	–	22.09	–	13.57	−38.54	–	11.73	−46.88	–	10.58	−52.08
Ash	45.44	10.04	38.22	5.19	−48.31	36.27	4.26	−57.60	33.37	3.53	−64.81
Volatile solid (VS)	54.56	12.05	61.78	8.39	−30.41	63.73	7.48	−37.95	66.63	7.05	−41.48
Crude lipid	1.49	0.33	1.48	0.20	−38.95	1.30	0.15	−53.65	1.22	0.13	−60.77
Crude protein	9.19	2.03	9.77	1.33	−34.66	10.29	1.21	−40.52	10.44	1.10	−45.57
Crude carbohydrate	43.88	9.69	50.53	6.86	−29.23	52.14	6.12	−36.87	54.97	5.82	−39.97
Crude fiber	34.76	7.68	32.71	4.44	−42.17	31.22	3.66	−52.29	28.36	3.00	−60.91
Nitrogen Free Extract (NFE)	9.12	2.01	17.82	2.42	+20.09	20.92	2.45	+21.86	26.61	2.82	+39.81
Neutral Detergent Fiber (NDF)	53.57	11.83	51.16	6.94	−41.31	47.55	5.58	−52.84	45.35	4.80	−59.44
Acid Detergent Fiber (ADF)	43.67	9.65	40.81	5.54	−42.57	36.49	4.28	−55.61	32.95	3.49	−63.85
Lignin	13.96	3.08	11.64	1.58	−48.76	11.49	1.35	−56.27	10.74	1.14	−63.14
Cellulose	29.71	6.56	29.17	3.96	−39.66	25.00	2.93	−55.30	22.21	2.35	−64.18
Hemicellulose	9.90	2.19	10.35	1.40	−35.75	11.06	1.30	−40.65	12.40	1.31	−39.98
Total nitrogen (TN)	1.47	0.32	1.56	0.21	−34.66	1.65	0.19	−40.52	1.67	0.18	−45.57
Total organic carbon (TOC)	30.31	6.69	34.32	4.66	−30.41	35.41	4.15	−37.95	37.02	3.92	−41.48
*C/N = TOC/TN	20.61		21.96			21.50			22.16		

Note:
*there was no unit for C/N ratio.
the sign (-) or (+) in "changing based on mass" presented "decreasing of mass" or "increasing of mass".
changing based on mass = (final component mass - initial component mass) / initial component mass × 100%.

increasing the sulfuric acid from 0 (unpretreatment) to 6%. The produced sugars (disaccharide and monosaccharide) increased the total NFE in SM. Therefore, biogas yield in day 2 was very high. However, in period of day 2–18, biogas yield decreased because the substrate pH dropped (Fig. 1(C)). The low substrate pH was due to accumulation of VFAs that was produced by NFE degradation during fermentation. Increase in biogas yield again after day 22 until day 26 was caused by bacterial activity where the bacteria were still tolerant in low acidic level. However, it was just in short period and biogas yield decreased again until the end of fermentation.

By using pSM 6% as biogas feedstock, biogas yield in period of day 0–8 was a little. It increased in period day 12-16. Then, it decreased until day 18 and it increased again until day 26. Finally, it decreased until end of fermentation. The little amount of biogas yield in first period (day 0–8) was caused by too high soluble organic amount in substrate. Inoculum volume used in all variables was 25 mL. In this case (sulfuric acid 6%), ratio of soluble organic compounds and inoculums was not appropriate, so that bacteria need a more time than case of 2 and 4% to adapt in substrates. After day 18, the bacteria produced biogas in large amount. At the time, the bacteria were tolerant in the substrate.

Profile of cumulative biogas yield during digestion was shown in Fig. 1(B). The total biogas yield after 30 days for variable control (unpretreatment), 2%, 4%, 6% was 13.28, 22.72, 24.14, 22.75 mL/g VS (Table 2). Biogas yield in pretreatment case was more than that in unpretreatment case. Interesting phenomena occurred when the sulfuric acid concentration increased from 2 to 4%, cumulative biogas yield was increased from 22.72 to 24.14 mL/g VS. However, at sulfuric acid more than 4%, the cumulative biogas yield decreased from 24.14 to 22.75 mL/g VS. From Table 1, the more the sulfuric acid, the more the lignin could be removed and the more the NFE was in SM. Theoretically, the less the lignin and the more the NFE in SM, the easier the substrates was degraded and then biogas was produced in larger amount. Factually, the case of 6% produced less total biogas than 4%. The ratio between inoculums and soluble compound was not appropriate in case of 6%. In this study, all variables used inoculums of 25 mL. Song et al. [13] also found that chemical pretreatment at high concentration would decrease biogas yield because the ratio of high soluble and inoculum volume was not appropriate. Furthermore, after fermentation, the TS removal for AD of pSM4% (TS removal 52.21%) was higher than others (TS removal 44.58–51.25%). It showed that the more the TS was removed, the more the total biogas yield was produced.

Substrate pH profile during digestion was presented in Fig. 1(C). The pH level decreased in day 2. After that, the pH level was stable until the end of digestion. The drop in pH in the first digestion was caused by accumulation of VFAs. The pH range after day 2 in AD process using feedstock of raw SM, pSM 2%, pSM 4%, pSM 6% was 6.0–6.5, 5.5–5.7, 6.0–6.4, 6.0–6.3 respectively. Hence, the pH range was same of all variables except the case of 2%. The pH level in case of 2% was the lowest. At day 2, the pH was in level of 5.7. It decreased gradually until 5.5 at the end of fermentation. That phenomenon was correlated with VFAs and total ammonia nitrogen (TAN) concentration. It would be discussed in section of 3.3.

The methane content in biogas for all variables was very good which was in range 72.09–83.63% (Table 2). In the unpretreatment case, methane content (83.63%) was higher than that in the pretreatment case (72.09–78.37%). The raw SM contained C/N of 20.61. This value was lower than that in pretreated SM (C/N of 21.50–21.96). According to Syaichurrozi [2], the decreasing C/N from 57.39 to 20.61 will increase the methane content from 29.09 to 74.34%. Hence, the methane content in biogas generated from raw SM was higher than that from pSM. The result of this study were in line with study of Syaichurrozi [2]. However, the percentage of methane content in biogas either from raw SM or from pretreated SM was very good (more than 70%).

Comprehensively, the best feedstock was pSM 4% producing the highest biogas yield 24.14 mL/g VS (methane yield = 72.09% × 24.14 mL/g VS = 17.40 mL/g VS). This result was better than biogas from paper sludge (methane yield 14.7 mL/g VS [35]) and vinasse waste (biogas yield 3.74 mL/g VS [17]). Like SM, the paper sludge was lignocellulosic biomass so it contained high lignin [36]. Lignin content in pretreated SM might be lower than that in paper

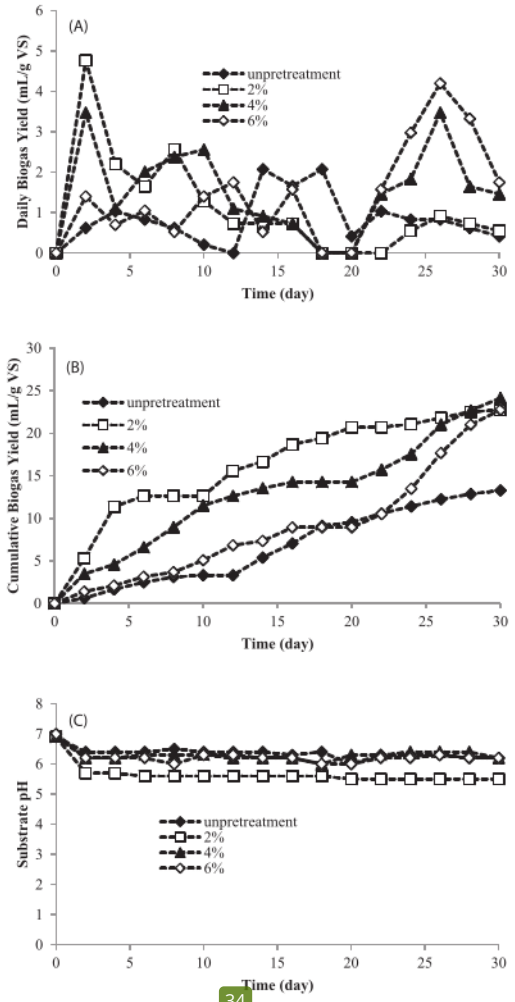

Fig. 1. Effect of pretreatment on (A) daily biogas yield, (B) cumulative biogas yield, (C) pH profile.

sludge. Furthermore, molasse vinasse contained high simple organic compound (acetic acid, lactic acid, glycerol), but it resulted low biogas yield compared with pretreated SM. The low biogas yield in digestion of vinasse was not caused by lignin content but it was caused by high phenolic compound [21]. Phenolic compound had toxic characteristic for anaerobic bacteria. On the other hand, this result was lower than biogas from *Chlorella* sp. (methane yield 44 mL/g VS [37]) and cow dung (biogas yield 104.3 mL/g VS [38]. *Chlorella* sp. contained high VS with low lignin content. Hence, biogas yield from *Chlorella* sp. was high enough. Cow dung was also lignocellulosic biomass which was alike SM. However, the cow dung contained higher biodegradable material because it was product of organic material digestion in cow's stomach. Besides that, it had contained a lot of anaerobic bacteria. Hence, the biogas yield from the cow dung was better than biogas yield in this study.

3.3. *Volatile fatty acids, ammonium, ammonia production*

Carbohydrate and protein in SM was degraded to be volatile fatty acids (VFAs) and ammonium ion (NH_4^+) or ammonia (NH_3) respectively during digestion [17]. The acidogenic bacteria converted the carbohydrate to be VFAs. The VFAs was intermediate products in which methanogenic bacteria converted it to be biogas. However, accumulation of VFAs in large amount decreased the substrate pH level. The low pH level disturbed the methanogenic bacteria [2,39]. In this study, substrate pH decreased in the first fermentation (day 2) and then it was stable enough until end of fermentation (Fig. 1(C)). The case of pretreatment 2%, the substrate pH was the lowest which was in range of 5.5–5.7 after day 2. This value was lower than that in variable of control, 4% and 6% (6.0–6.5, 6.0–6.4, 6.0–6.3 respectively). Based on Fig. 2(A), VFAs production in case of 2% was high enough. However, it was lower than that of control variable. Hence, the pH level not only depended on VFAs concentration but also total ammonium nitrogen (TAN). The ratio between VFAs and TAN was correlated with substrate pH. Fig. 2(F) showed that the higher the VFAs/TAN ratio, the lower the substrate pH with correlation of $y = -2.02x + 9.43$ ($R^2 = 1$) where y was substrate pH and x was VFAs/TAN ratio. Hence, the case of pretreatment 2% produced higher ratio VFAs/TAN than the others during digestion (Fig. 2(E)).

During digestion, ammonium ion or ammonia was useful for methanogenic bacteria to build their cell structure. The ammonium ion / ammonia ratio depended on substrate pH level. The ammonium ion / ammonia ratio at substrate pH of 7.0 was 99/1 [40]. Furthermore, ammonium ion is fully dominant at substrate pH lower than 7.0 [2]. Hence, the lower the substrate pH level, the higher the ammonium ion presented in the substrate. During digestion, pH substrate was lower than 7.0 in this study (Fig. 1(C)). The ammonium ion and ammonia concentration during digestion was presented in Fig. 2(B) and Fig. 2(C) respectively. The ammonium ion concentration (10.00–145.66 mg/L) was more than the ammonia concentration (0.0025-0.2580 mg/L) in all variables. Therefore, the ammonium ion was fully dominant with ammonium ion / ammonia ratio in range of 99.22/0.78–99.97/0.03.

Total of ammonium ion + ammonia was called as total ammonia nitrogen (TAN). TAN concentration in various ranges has various effects for bacterial growth i.e range of 50–200 mg/L was beneficial for bacterial growth [39], range of 200–1000 mg/L was not antagonistic effect [39], range of 1500-10,000 mg/L was start inhibition [41] and it more than 30,000 mg/L was toxic [41]. From Fig. 2(D), TAN concentration was in range of 10.00–145.92 mg/L (below 200 mg/L). Therefore, TAN produced during digestion was not negative effect for bacterial growth in all variables.

Table 2
The Results of Anaerobic Digestion.

Pretreatment	C/N	Initial pH	Final pH	Total Biogas yield (mL/g VS)	Biogas Composition			
					CH_4 (%)	CO_2 (%)	CO (%)	H_2 (%)
Unpretreatment	20.61	7.0 ± 0.1	6.2	13.28	83.63	16.23	0.06	0.08
2%	21.96	7.0 ± 0.1	5.5	22.72	73.08	25.73	0.24	0.94
4%	21.50	7.0 ± 0.1	6.2	24.14	72.09	26.99	0.32	0.61
6%	22.16	7.0 ± 0.1	6.2	22.75	78.37	20.68	0.24	0.71

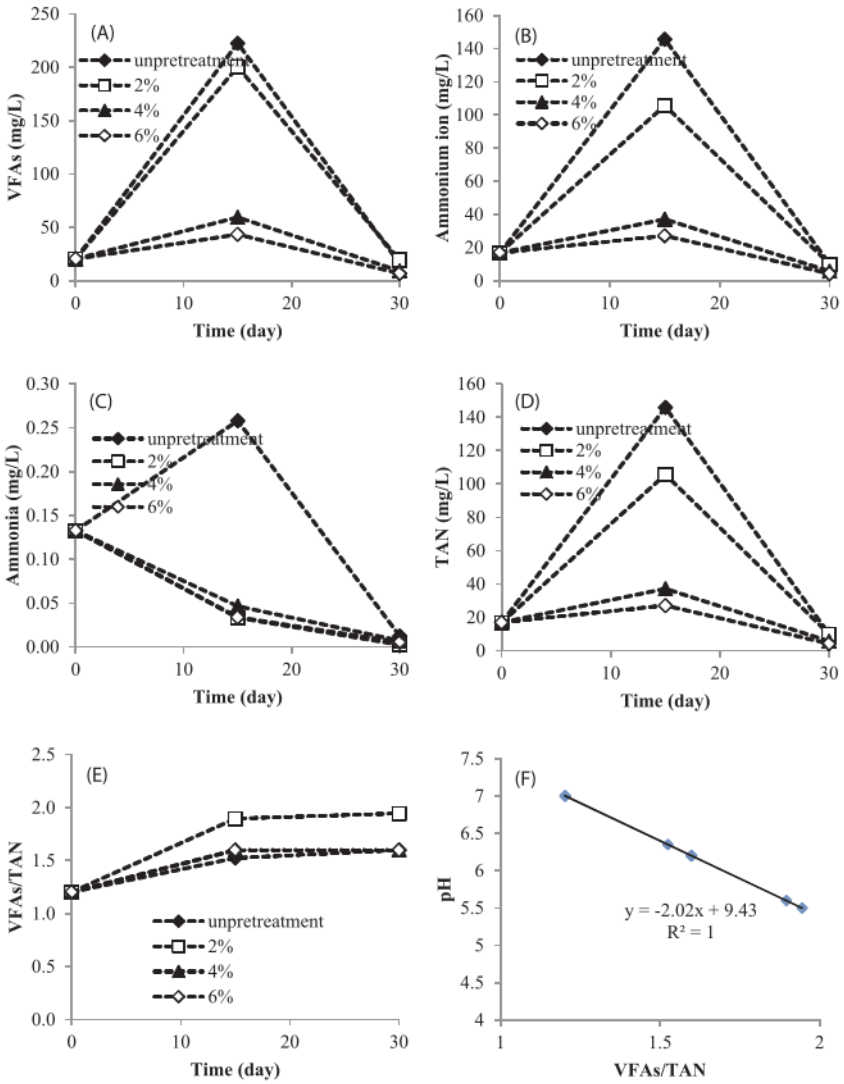

Fig. 2. Production of (A) volatile fatty acids (VFAs), (B) ammonium ion, (C) ammonia, (D) total ammonia nitrogen (TAN), (E) VFAs/TAN, and (F) correlation pH vs VFAs/TAN during fermentation for 30 days.

3.4. Kinetic model

3.4.1. Using modified Gompertz model

The kinetic constants (ym, μ and λ) in modified Gompertz model were shown in Table 3. Furthermore, Fig. 3 presented the plot of measured and predicted data as function of digestion time. Pretreatment increased the ym value. The more the sulfuric acid concentration, the more the ym value was obtained. The ym presented the potential biogas yield that could be reached until biogas was not produced again. Based on Table 1, pretreatment decreased the lignin and crude fiber content but it increased the NFE. Hence, the substrate was more degradable than that in unpretreatment case. The higher the sulfuric acid concentration was applied in pretreatment, the easier the substrate was degraded. Therefore, the ym increased with increasing the sulfuric acid concentration from 2% to 6%. However, digestion for 30 days, the pretreatment of 4% produced more cumulative biogas yield than 6% (Table 2). It was correlated to lag time where bacteria in case of 6%

Table 3
Results from using modified Gompertz and first order kinetic.

	unpretreatment	2%	4%	6%
Modified Gompertz				
λ (/d)	4.083	−2.725	−2.169	11.979
μ (mL/g VS.d)	0.593	1.189	0.763	1.090
ym (mL/g VS)	17.395	22.670	30.493	78.388
R^2	0.986	0.944	0.943	0.949
MAPE (%)	10.527	6.141	9.973	12.431
First order kinetic				
k (/d)	0.069	0.107	0.039	0.007
ym (mL/g VS)	12.464	22.960	29.857	90.871
R^2	0.827	0.960	0.940	0.881
MAPE (%)	47.606	7.336	11.092	18.941

Remarks: ym, the biogas yield potential; μ, the maximum biogas yield rate; λ, lag phase period or minimum time to produce biogas; k, biogas production rate constant; R^2, correlation coefficient; MAPE, mean absolute percentage error.

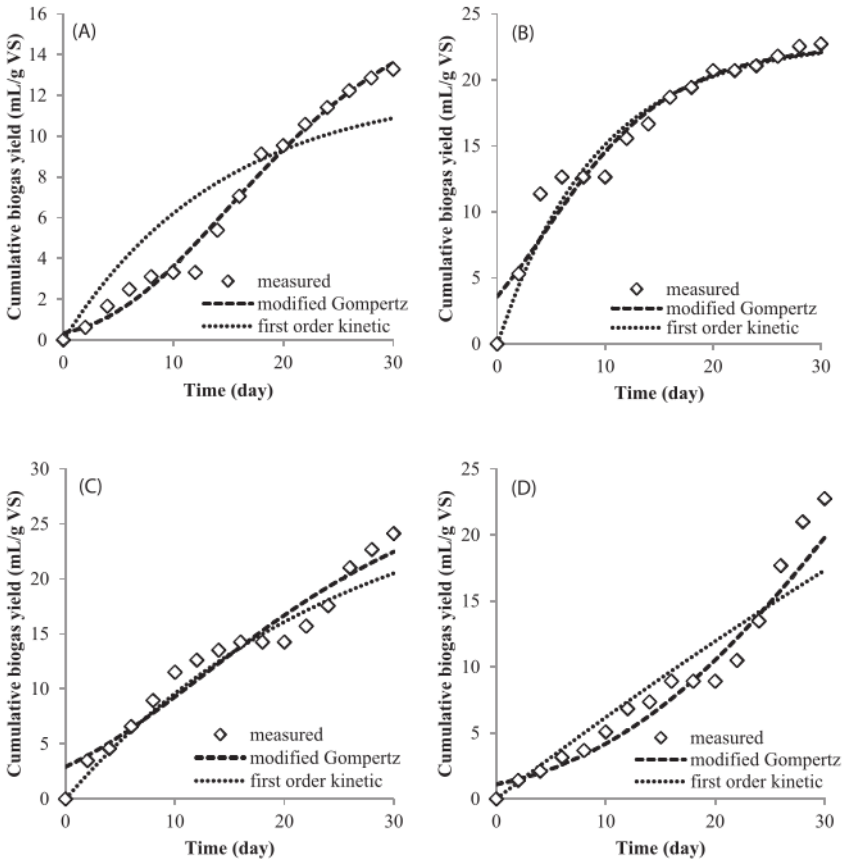

Fig. 3. Plot of measured data and predicted data at (A) unpretreatment, (B) pretreatment 2%, (C) pretreatment 4%, (D) pretreatment 6%.

need longer time than that in case of 4%.

Kinetic constant of λ presented the lag time needed by bacteria to adapt in the substrates [12,15]. The λ value in unpretreatment case (4.083 days) was higher than that in pretreatment case of 2–4% ((-2.725)-(-2.169) days). The λ value of ≤ 0 days indicated that bacteria did not need a time to adapt so that the lag time was 0 day. Pretreatment converted the complex compound to be simple compound while the lignin content decreased. Thus, the bacteria more easily degraded the pretreated substrate than the raw substrate. However, in pretreatment case of 6%, the lag time was very high (11.979 days). Case of 6% might contain very high simple compound. The inoculums volume for all variables was same. The bad ratio between the simple compound and inoculums caused the bacteria need long lag time. Thus, the total biogas yield for 30 days in case of 4% was higher than that in case of 6% but the ym value in case of 4% was lower than that in case of 6%.

Kinetic constant of μ presented the biogas production rate. The pretreatment also increased the biogas production rate. The pretreated SM was more degradable than raw SM so that the biogas production rate from pretreated SM (0.763–1.189 mL/g VS.d) was higher than from raw SM (0.593 mL/g VS.d).

3.4.2. Using first order kinetic model

The kinetic constants in first order kinetic model (ym and k) were shown in Table 3. The plotting between measured and predicted data was presented in Fig. 3. Like in modified Gompertz model, the ym value in first order kinetic increased with increasing sulfuric acid concentration from 0 (unpretreatment) to 6%. The definition of ym in first order kinetic was same with that in modified Gompertz. Furthermore the kinetic constant of k in case of 6% was the least of all variables. According to Kafle et al. [16], the more the k value in first order kinetic, the faster the rate of biogas production occurred. Syaichurrozi [2] reported that the value of k in first order kinetic had good correlation with λ in modified Gompertz, where the lower the k value, the higher the λ value. That was in line with this study. The case of 6% had the lowest k value (0.007 /day) and the highest λ value (11.979 days).

3.4.3. Comparison the modified Gompertz and first order kinetic model

The mean absolute percentage error (MAPE) of prediction in biogas production for 30 days observed in modified Gompertz model was 6.141–12.431% and in first order kinetic model was 7.336–47.606 % (Table 3). Clearly, the modified Gompertz model was better than first order kinetic model. The correlation coefficient (R^2) in modified Gompertz (0.943-0.986) was also better than the first order kinetic (0.827-0.960) (Table 3). According to Syaichurrozi [2], the first order kinetic could be used to predict biogas production if the lag time was very short. In thi study, for pretreatment case of 2 and 4%, the lag time was very short which was 0 days, so that the MAPE in first order kinetic was low (7.336–11.092%). However, for unpretreatment and pretreatment 6%, the lag time was very long which was 4.083–11.979 days, so the MAPE in first order kinetic was high (18.941–47.606%). Hence, the modified Gompertz model was suitable to be used in term of biogas production from either raw SM or pretreated SM. Correlation between measured and predicted data obtained using modified Gompertz and first order kinetic is shown in Fig. 4 and Fig. 5 respectively. From these figures, the modified Gompertz was better in predicting biogas production than first order kinetic.

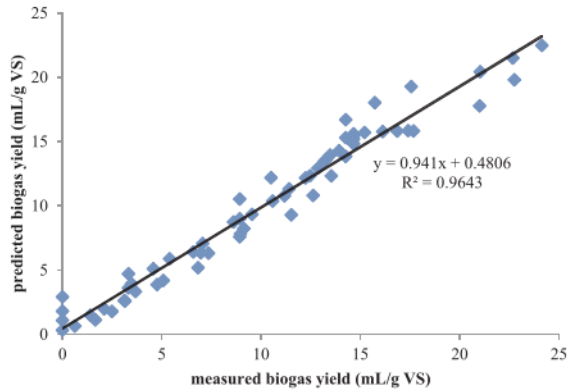

Fig. 4. Correlation of measured data and predicted data using modified Gompertz.

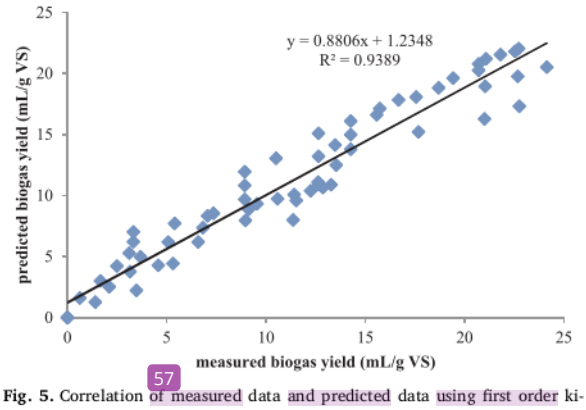

Fig. 5. Correlation of measured data and predicted data using first order kinetic.

3.5. Potential for scaling up and real implementation

Energy resulted from the combustion of biogas can be predicted using equation (7)–(9) [42].

$$V_b = y_{t-30d} \times M_s \quad (7)$$

$$V_{CH_4} = V_b \times C_{CH_4} \quad (8)$$

$$E_E = V_{CH_4} \times Ra_{CH_4} \times \eta_E \quad (9)$$

Where, y_{t-30d} = measured biogas yield after 30 days (mL/g VS), M_s = mass of substrate (g VS), V_{CH_4} = measured methane volume (mL), V_b = biogas volume (mL), C_{CH_4} = methane content (%), E_E = produced energy amount (MWh), Ra_{CH_4} = methane energy potential ratio (9.17×10^{-9} MWh/mL), η_E = electrical efficiency of the cogeneration unit (44%). In this section, we chose the variable of pSM4%. After calculation, the E_E value for biogas from pSM4% was 7×10^{-8} MWh / 1 g VS SM. That means every 1 g VS SM can produce biogas with energy value of 7×10^{-8} MWh.

Susan [43] stated that every 100 m^2 water surface can be grown by 36 ton SM. Pandeglang regency is one of areas in Banten Province. Main occupation of rural community in Pandeglang is a farmer. Total area of rice fields in Pandeglang is 32,049 Ha or 320,490,000 m^2 [44]. By assuming that SM grows on 30% of the total area of rice fiels, the total SM was 34,612,920 ton. Soerjani et al. [45] reported that growing time of SM was very short (3 weeks). Hence, SM as much as 34,612,920 ton is produced every 3 weeks. For 1 year (48 weeks), the total SM from Pandeglang Regency is 553,806,720 ton or $553,806.720 \times 10^9$ g. Based on Table 1, after the SM is pretreated using sulfuric acid 4%, the total SM is to be $294,182.130 \times 10^9$ g (VS $187,482.271 \times 10^9$ g). If it is fermented to biogas, the biogas will produce energy as much as 13,123,758.986 MWh per year. By assuming that 1 TOE is equal with 11.63 MW h, the energy value is as much as 1,128,440.154 TOE (1.13 million TOE).

This idea can be scaled up and implemented in Indonesia, especially in Pandeglang Regency. Based on calculation above, SM in pandeglang regency is very potential to be used as biogas feedstock. According to Kebijakan Energi Nasional (KEN), the total national energy need in year of 2050 is predicted around 595.1 million TOE. Furthermore, 33% of the total national energy will be supplied by renewable energy which is 196.38 million TOE. Hence, biogas produced by digestion of SM obtained from rice fields in Pandeglang Regency will cover 0.7% of the total renewable energy need in 2050. If the SM is obtained from other water bodies, the biogas is produced in larger amount. Consequently, the cultivation of SM must be applied to maintain sustainable availability of SM.

4. Conclusion

Chemical pretreatment using sulfuric acid (with concentration of 2, 4, 6%) successfully increased biogas production from SM. The pretreatment changed the chemical composition in SM. The pretreatment removed the lignin content. In addition, the cellulose content was also degraded to be simple organic compound. Hence, the crude fiber decreased and the NFE increased with increasing the sulfuric concentration used. Total biogas yield from pretreated SM (22.72–24.14 mL/g VS) was higher than that from raw SM (13.28 mL/g VS). Furthermore, the modified Gompertz model was more suitable to be used in this case than the first order kinetic. The MAPE for modified Gompertz and first order kinetic was 6.141–12.431% and 7.336–47.606 % respectively.

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