



Mathematical Model for Quantitative Analysis of Acidogenic Performance under Microaeration Condition in Anaerobic Vinasse Treatment

Gregorius Prima Indra Budianto^{1*} and Wisnu Arfian Anditya Sudjarwo²

¹ Program Studi Teknik Kimia, Universitas Setia Budi, Jl. Letjend Sutoyo, Mojosongo, Surakarta 57127, Indonesia

² Program Studi Analisis Kimia, Universitas Setia Budi, Jl. Letjend Sutoyo, Mojosongo, Surakarta 57127, Indonesia

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ABSTRACT

Vinasse anaerobic treatment is a one alternative process to treating vinasse. Microaeration is a one of process modification in anaerobic vinasse digestion that can improve the acidogenic performance. In this paper presents the influence microaeration in anaerobic vinasse treatment in kinetics aspect. The kinetics aspect was develop to approach and quantifying the effect of microaeration in anaerobic vinasse treatment systematically. Extract of cow dung was used as inoculums and vinasse 100 ppm as a substrate. Laboratory experiments using 4L vertical reactor (UASB) was conducted in 28 days and performed in batch recirculation mode. During the experiment, dosing air in different concentrations was injected in the slurry phase into different anaerobic digesters once a day. The variation of air concentrations are 0 L air/L feed; 0.5 L air/L feed; and 100 L air/L feed. As the result, the addition of 0.5 L air/L feed could increase biodegradability ($k=5.7239$) and accelerate acidogenesis phase ($\mu_{mi}=2.03/\text{day}$) that can be proven by the percentage of VS removal reaching up to 77% and cuts the lag phase ($\lambda=1.028$ days) and HRT making it shorter.

1. INTRODUCTION

1.1. Fundamental aspect of anaerobic vinasse treatment

Vinasse is a wastewater of the ethanol industry. In the ethanol industry, 1 L of ethanol produced will emit 10-15 L of vinasse (Moraes, Zaiat, & Bonomi, 2015). In general vinasse contains COD (80,000 – 100,000 mg/L) and BOD (40,000 – 50,000 mg/L), trace minerals (Sodium in 9,600 – 17,475 mg/L, Phospor in 225 – 3,000 mg/L and Nitrogen in 1,600 – 4,200 mg/L, phenol (in melanoidin form) and sulphate in 450 mg/kg and 3,500 – 3,720 mg/L respectively (Budhijanto, Purnomo, & Siregar, 2012; Espana-Gamboa, E., Mijangos-Cortes, J., Barahona-Perez, L., Dominiguez-Maldonado, J., Hernandez-Zarate, G., Alzate-Gaviria, 2011).

Based on the characteristics, vinasse potentially can be treated by anaerobic digestion. Anaerobic digestion is a serial reaction which starts from a complex organic compound and degraded by acid-forming bacteria to form volatile fatty acids and immediately converted into biogas by biogas-forming bacteria (Moraes et al., 2015). Figure 1 shows the reaction of anaerobic digestion.

The mechanism of anaerobic digestion could be simplified by assuming that all of organic compounds are Volatile Solids (S); the intermediate product is Volatile Fatty Acids (A) and the product is biogas (Budhijanto et al., 2012). The mechanism is shown in Figure 2.

*Correspondence author. Tel. : xxxxxxxx

E-mail : gregoriusjoseph87@gmail.com

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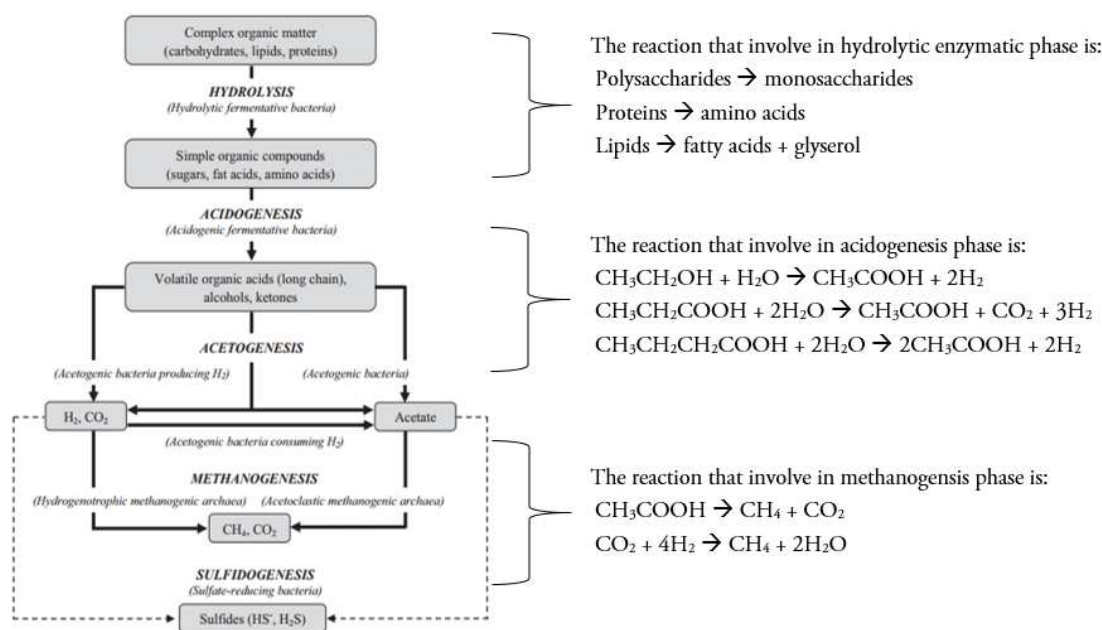


Figure 1. Anaerobic digestion

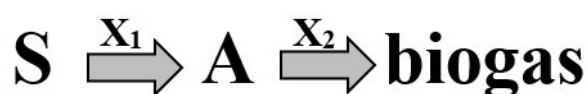


Figure 2. Simplify mechanism of anaerobic digestion

Adjustment of anaerobic vinasse treatment condition is needed because the anaerobic bacteria is slow in growth and high wash out possibility in continuous system (Moraes et al., 2015; Purnomo, Mellyanawaty, & Budhijanto, 2017). The other problem correlates with anaerobic vinasse treatment system is the long of hydrolic retention time (HRT). It affect in reactor volume which is bigger, so it is not economically qualified for industrial application (Moraes et al., 2015).

1.2. The importance of microaeration in vinasse anaerobic treatment

One effort that can be made in order to maintain the anaerobic process stability and cut the HRT is the addition of microaeration. Microaeration is defined as the dosing air in small amounts into a vinasse anaerobic digester. Systematically, the different between aeration and microaeration is shown in figure 3.

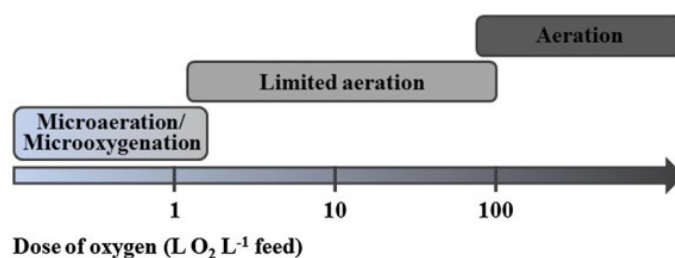


Figure 3. Dose of oxygen/aeration

An increase of anaerobic bacteria performance occurs in this condition (Jenicek, Celis, Koubova, & Pokorna, 2011; Krayzelova et al., 2015). The similar thing is said by Fu that corn straw treatment with microaeration addition in anaerobic digester obtained efficiency and yield of methane accumulation is 54.3% and 216.8 ml/g VS respectively (Fu, Wang, Shi, & Guo, 2016). Microaeration process in bioreactor could give the COD and phenolic content removal in the carcoal gasification wastewater up to 60% and 50% respectively (Wang, Zhang, Wang, Shen, & Pan, 2014). The main objective of this research is to quantifying the acidogenic performance under microaerobic in anaerobic vinasse treatment process by kinetic aspect.

1.3. Mathematical model to assess anaerobic vinasse treatment in microaerobic condition.

First Order Kinetics Model

Substrate (VS) biodegradability is assessed by first order kinetics model. Based on Yusuf, the correlation between biodegradability and formed biogas can be described (Yusuf, Debora, & Ogheneruona, 2011) :

$$\frac{1}{t} \ln \left(\frac{dyt}{dt} \right) = \frac{1}{t} (\ln ym + \ln k) - k \quad (1)$$

Where yt is volume of biogas formed at any time; ym is specific biogas production (mL/g VS); -k is rate of biodegradability (day⁻¹).

Bacterial Growth Kinetic Model

Substrate or VS (S) will be degraded by acid-forming bacteria consortium to grow and forming bacteria with the intermediate product being Volatile Fatty acids (A). The mathematics equation to represent this process is:

$$-\frac{dS}{dt} = \left[\frac{1}{Y_{X1/S}} \right] \frac{dX_1}{dt} + \left[\frac{1}{Y_{A/S}} \right] \frac{dA}{dt} \quad (2)$$

Where $-\frac{dS}{dt}$ is a rate of degradation of substrate; $\frac{dX_1}{dt}$ is a rate of acid-forming growth; $\frac{dA}{dt}$ is a rate of acid formation; $Y_{X1/S}$ is a yield of 1 g X_1 formed every 1 g S degraded; $Y_{A/S}$ is a yield of 1 g A formed every 1 g S degraded.

A is a product of acid-forming bacteria too, so the rate of A formation can be written:

$$\frac{dA}{dt} = \left[\frac{1}{Y_{X1/A}} \right] \frac{dX_1}{dt} \quad (3)$$

Where $Y_{X1/A}$ is a yield of 1 g X_1 formed every 1 g A formed. Then, equation (3) is substituted into equation (2), and rewritten:

$$-\frac{dS}{dt} = \left[\frac{1}{Y_{X1/S}} \right] \frac{dX_1}{dt} \quad (4)$$

In the next process, A is a product of acid-forming bacteria and will be used as a nutrition source for biogas-forming bacteria. The equation that can represent this process is:

$$\frac{dA}{dt} = \left[\frac{1}{Y_{X1/S}} \right] \frac{dX_1}{dt} - \left[\frac{1}{Y_{X2/A}} \right] \frac{dX_2}{dt} \quad (5)$$

Where $\frac{dX_2}{dt}$ is a rate of biogas-forming bacterial growth and $Y_{X2/A}$ is a yield of 1 g X_2 formed every 1 g A consumed. The growth rate of acid-forming and biogas-forming bacteria is approached by Contois Equation. The Equations respectively written in equation (6) and (7). The equation of acid-forming bacteria growth rate:

$$\frac{dX_1}{dt} = \frac{\mu_{m_1} S}{K_{S_{X1}} X_1 + S} X_1 \quad (6)$$

The equation of biogas-forming bacteria growth rate:

$$\frac{dX_2}{dt} = \frac{\mu_{m_2} A}{K_{S_{X2}} X_2 + A} X_2 \quad (7)$$

Where μ_{m_1} is specific growth rate of acid-forming bacteria (day⁻¹); $K_{S_{X1}}$ is a saturated constant of acid-forming bacteria; μ_{m_2} is specific growth rate of biogas-forming bacteria (day⁻¹); and $K_{S_{X2}}$ is saturated constant of biogas-forming bacteria.

Modified Gompertz Equation Model

Besides, kinetic of biogas production also can be approached by Modified Gompertz Equation. This equation is based on correlation between the rate of biogas-forming bacteria with its specific growth rate (Budiyono, Widiya, Johari, & Sunarso, 2010).

$$V_p = B \exp \left\{ -\exp \left[\frac{\mu e}{B} (\lambda - t) + 1 \right] \right\} \quad (8)$$

Where V_p is the biogas accumulation volume (L); B is the biogas production potential (L); μ is the maximum biogas production rate (L/d); λ is a lag phase (day).

Equation (1), (4), (5), (6), (7), and (8) is used to evaluate the experiment data. The following data are VS, VFA, accumulation biogas volume. Quantitatively, the influence of dosing air can be reflected in the value of -k; μ_{m_1} ; μ_{m_2} ; $Y_{X1/S}$; $Y_{X2/S}$; μ ; and λ .

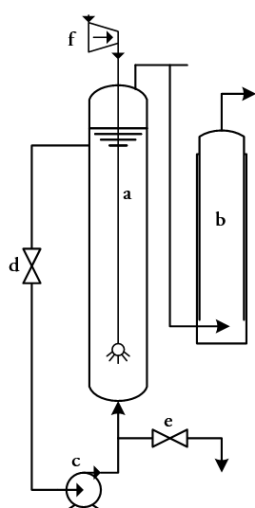


Figure 4. Experimental Setup (a. UASB reactor; b. Gasmeter; c. Centrifugal pump; d. Recycle valve; e. Sampling valve; f. Artificial air Injector)

2. METHODS

2.1. Materials

In this research, cow dung was used as a starter. Starter activation was conducted by mixing 2 kg of cow dung and vinasse 10 ppm at a 1 to 1 ratio. The mixture was filled in the sealed container until the gas is formed. After that, the mixture where the gas was formed, was screened from the solids and excessing extract as a ready starter. Vinasse taken from one of alcohol industry in Polokarto, Sukoharjo, Jawa Tengah was used as a substrate in this research. The vinasse was dissolved in tap water until the concentration 100 ppm. Additional materials for sample analysis was H_2SO_4 95-97% p.a., HCl 37-38% p.a., NaOH pellet p.a. (Merck), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ 99.5% (Merck), CH_3COOH 96% p.a. (Merck).

2.2. Experimental

The experimental setup illustrated in Figure 2. The main equipment is vertical UASB digester with 4 L of volume equipped with a gasmeter. Both of them were made from poly-methyl-methacrylate. The dimension of UASB is 50 cm in height and 9.4 cm in inside diameter and the dimension of gasmeter is 50 cm in height and 4.4 cm in

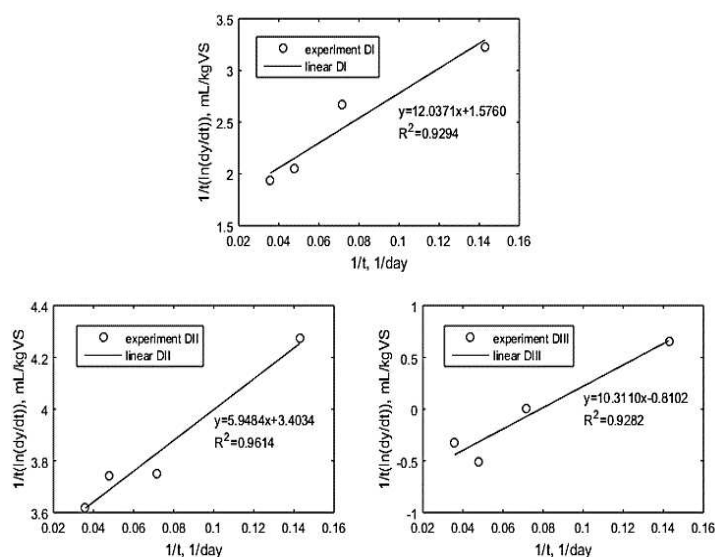


Figure 5. First order reaction

inside diameter. The performance of gasmeter in biogas volume calculation is followed by water displacement method. The other equipments are centrifugal pump with Sanyo Brand 175 Watt, recycle and sampling gate valves, and calibrated artificial air injector, it is a like a gas syringe to inject air in certain amount. The schematic of UASB reactor is shown in Figure 4.

The mixture of starter and vinasse 100 ppm as a substrate with the 1 to 1 ratio and known as VS and VFA contents were placed into the digester UASB. The digester was tightly closed and the process was conducted. Sludge recirculation was conducted by pumping the effluents in the top of reactor, then recirculate it through the bottom reactor. Once daily, 300 ml samples were taken for VS and VFA analysis through sampling valve. The VS and VFA analysis was done in 3 series per day per digester and followed by APHA (American Public Health Association - APHA, 2005). The formed biogas flow into gasmeter. Then, the biogas would push the water in gasmeter until it reached certain level. After that, the biogas volume in gasmeter can be calculated from its diameter and biogas level (Walker, Zhang, Heaven, & Banks, 2009). The process completed when the biogas has not been produced anymore.

Table 1. Composition of digester

Parameter	DI	DII	DIII
Dose of air ^{*)}	0 L air/L feed/d	0.5 L air/L feed/d	100 L air/L feed/d

^{*)} assuming the feeds is 0.1L of feed.

Every day, after sampling, a dose of air injected into each digester by artificial air injector from the top of digester. The variation of dosing air is used to analyse the performance of acidogen bacteria. The following are the variation of dosing air is (DI) without adding air, (DII) adding small amount of air, and (DIII) adding big amount of air. The scheme of dosing air injection in each digester is show in Table 1.

3. RESULT AND DISCUSSION

3.1. Vinasse Anaerobic Digestion

In this research, vertical pipe (UASB type) were used as a digester, that is conducted on recirculate batch mode. The consideration in reactor selecting is narrow area needed and higher product's rate if compared with conventional reactor (Wresta & Budhijanto, 2013). The UASB reactor is also equipped by recirculation to maintain homogenous of inner environmental condition of the reactor, as we know the weakness of vertical reactor is gradient of concentration in the inside of reactor start from the inlet until the outlet of digester. Besides, 80% effluent of digester was recycled into reactor could be increasing the biogas production until more than 30% (Budhijanto et al., 2012). Next, the focus of discussion is only on the influence of dosing air into kinetic parameters that could represent the performance of each digester.

3.2. Biodegradability

Figure 7 and Table 2 present the result of optimizing based on the first order kinetics. Analogous to equation (1), this is equal to linear line equation, in which $(\ln y_m + \ln k)$ is the slope and $-k$ is the intercept.

Yusuf said the parameter $(\ln y_m + \ln k)$ is availability of biodegradable substrate. This parameter can be used to know the potential of substrate (volatile solids)

Table 2. Rate of biodegradability constant

Parameter	DI	DII	DIII	Significant ^{*)}
$(\ln y_m + \ln k)$	12.0950	5.7632	3.9390	0.0000
$-k$	-3.8545	-5.7239	-2.3982	0.0000

^{*)} significant level 95%

to convert into biogas in the short retention time $(\frac{1}{t})$. Higher value from the parameter represents the potential of volatile solids to convert into a high quantity of biogas in the short retention time, while the lower value represents the potential of volatile solids to produce a low quantity of biogas under short retention time.

The other parameter is $-k$. According to Yusuf, $-k$ is the rate of substrate biodegradable. This is the primary parameter in the first order kinetic model. This parameter also represents the accumulation of effect which happens in the inner reactor environment (i.e. quality and quantity substrate, inhibition material, dosing air, etc). Thus, the more negative values of $-k$, it shows the faster rate of the substrate biodegradable, the same order in the reverse (Yusuf et al., 2011).

Based on Figure 5, the R-squared in each digester is closer to 1. It means that the equation is linear exactly. Moreover, the values of significant for each parameter is lower than 5%, it means that the parameter value in each data group is different significantly.

The availability of degradable substrate in DII is the lower than DI, it is due to the rate of biodegradability in this digester is the fastest, so the degradable substrate is faster to breaks into simple acids under microaerobic than anaerobic condition. This phenomenon is also appropriate with the statement of Xu that microaeration addition influences the activity of hydrolize bacteria (Xu, Selvam, & Wong, 2014). Increasing hydrolyze bacteria activity is linear with vinasse biodegradability. In contrast to the other digesters, the value of availability of degradable substrate and the rate of biodegradability in DIII is the lowest one. It is probably the potential substrate to form biogas is low as the one effect of big amount of air addition into the system so that is affected into the rate of

biodegradability become low too. The amount of availability degradable substrate in each

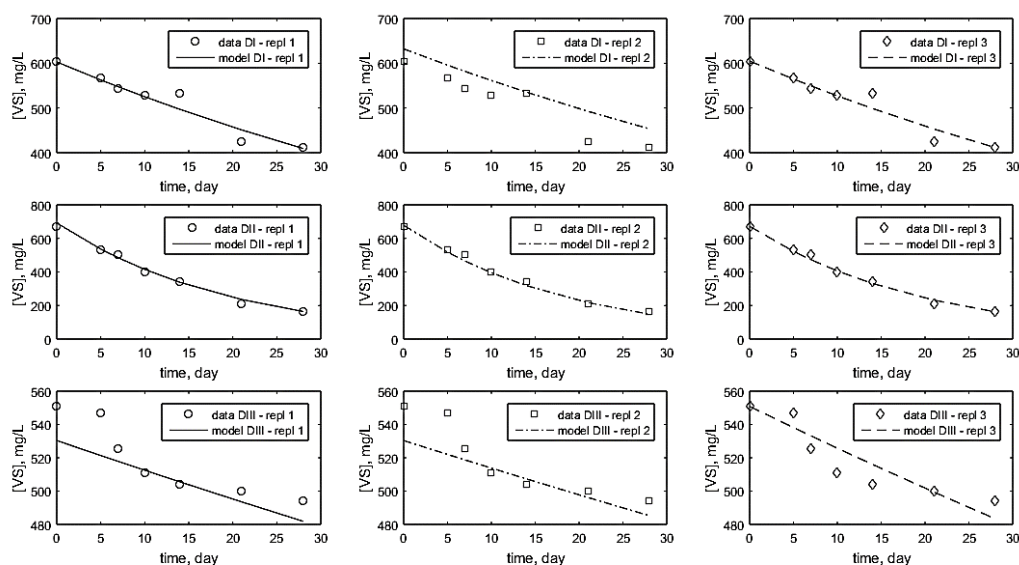


Figure 6. Profile of volatile solid

digester cannot show clearly in this model, but the profile of degradable substrate, simple acids and biogas formation and also the number of kinetic parameters to quantify the effect of dosing air in each digester will discuss in the next section.

3.3. Volatile Solids Removal

The dosing air in anaerobic system has to be considered, because the system contains anaerobic bacteria consortium consisting of facultative and strict anaerobic bacteria. VS is one parameter that can be used for approaching the effect of dosing air in the anaerobic digester. It represents all organic compounds that have potential for converting into biogas. In the beginning of the anaerobic process, acid-former bacteria is involved.

Figure 6 shows the profile of VS between experiment and simulation. The profile shows that VS decreases in each digester and could be simulated as well by a mathematical model. It means that during the anaerobic process, the reaction is only based on bacteria activity in VS being consumed as a nutrition source to grow and produce VFA so the trend of VS in each digester is decreasing over the time.

If we compare among the three digesters respect in Figure 6 and Table 3, the difference among them is about

VS degradation rate where VS degradation rate on DII is the fastest and DIII is the slowest one. This is significantly shown among them in the 5th day, where the highest VS degradation occurs in DII compared to another digester showing in Figure 6. It shows the bacteria especially acid-forming bacteria under microaerobic condition is more confident in the beginning of the process (lag phase). In addition, the digester under microaeration causes the vinasse treatment duration to become shorter. It is shown in Table 3 that treating vinasse 100 ppm with 77% VS efficiency only needs 28 days. Jenicek said that acid-forming bacteria is facultative-anaerobic bacteria group, so small amount of air addition into the anaerobic process will not effect its stability (Jenicek et al., 2011).

3.4. Volatile Fatty Acids and Biogas Formation

VFA is an intermediate product of the anaerobic process so the rate of VFA formation depends on the VS degradation's rate. Figure 7 shows VFA's profile in all digesters. The profile of VFA in DI and DII increases at the beginning process respectively but VFA's profile in DIII decreases overall.

Figure 7 shows the different value of VFA between DI and DII. VFA accumulation in DII is bigger than DI. This is respect to the degraded VS into VFA in DII is

faster than DI too. The same argue with Botheju that

VFA formation by the increased performance of acidogen

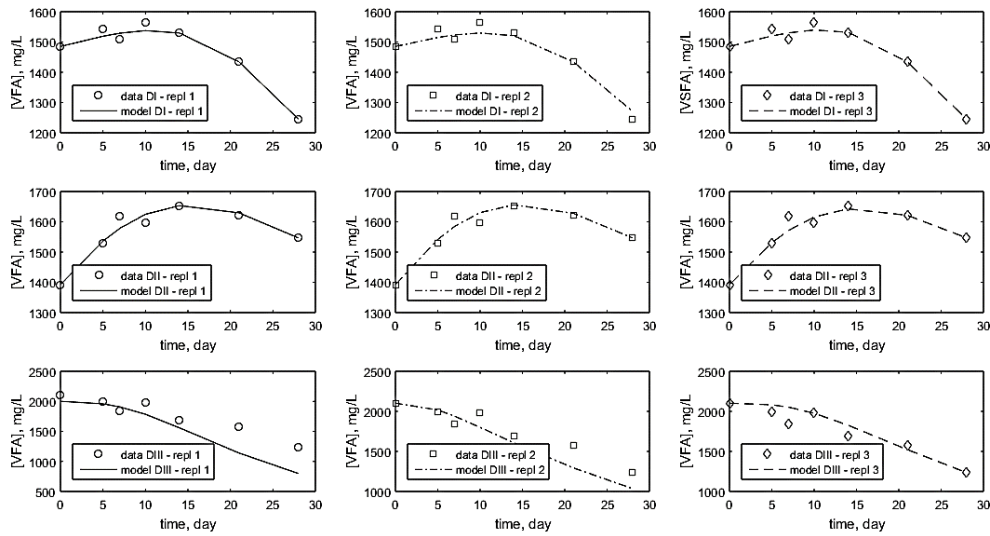


Figure 7. Profile of volatile fatty acids

bacteria occurs concurrently. The further argument, VFA accumulation is caused by microaeration condition (Botheju, 2011). On the flip side, VFA accumulation until certain level potential inhibition triggered on biogas-forming bacteria ($VFA > 4000$ mg acetate/L). However, VFA accumulation in DII ineffectual in biogas-forming bacteria performance (It shows in Figure 8). In a sense, microaerobic condition just increasing VFA accumulation and slightly influence but not inhibit the biogas-forming bacteria performance.

Based on Figure 7, the VFA's content in DIII decreases the fastest one if compared with others. The decreasing number of VFA is due to biological decomposition. Botheju said VFA oxidizing was found and happen under big amount of air condition (Botheju, 2011). Theoretically, the simple acids represented by VFA will be oxidized into CO_2 and H_2O . The similar thing is said by Hanajima about the decreasing of VFA that caused by addition of big amount of air. In addition, Hanajima is also took conclusion that decreasing VFA drastically is followed by increasing pH until 8.2 (Hanajima et al., 2011), so the anaerobic process could not run well surely because the acidogenesis phase is indicated inhibit. It is proven by the lowest efficiency number of VS in this

digester until HRT 28 days and decreasing VFA drastically over time.

Biogas is the final product of the anaerobic process. It is only formed by acetic acid oxydizing in anaerobic system. In Figure 8 it presents the profile of the accumulation volume of biogas after optimized by Modified Gompertz equation in each digester. Based on equation (8), the kinetic parameters of biogas production for each digester was calculated and presented in Table 4. The number of B , μ , λ are used to quantify the productivity of biogas.

Based on Figure 8 and Table 4, the existence of air in small amount is significant influence into biogas production rate. Digester with microaerobic condition (DII) can improve the maximum production of biogas reaches three times and also cut the lag phase until 36% in compare with digester anaerobic condition (DI). This occurs because the limited air can help the degradation process in acidogenesis phase, the faster organic degraded is indicated that lag phase of the bacteria in the reactor is faster so the bacteria can grow well and stable to forming biogas. Nevertheless, theoretically, all of organic compound will be degraded and produce VFA and CO_2 as a gas product in the acidogenesis phase (Moraes et al., 2015), so biogas which formed in the beginning of the

anaerobic process was most likely content higher CO₂ than CH₄. In contrast to the other digesters, DIII is the lowest one regarding the accumulated biogas volume aspect and is

caused by the existence of air in big amount inhibition start from in the beginning of the process.

Table 3. Percentage of volatile solids removal

Digester	Replication	VS _{HRT=0} (mg/L)	VS _{HRT=28} (mg/L)	%VS removal	Average of % VS removal
DI	1	602.8	409.4	32 %	33 %
	2	632.1	406.7	36 %	
	3	604.8	411.4	32 %	
DII	1	691.5	164.3	76 %	77 %
	2	677.8	148.4	78 %	
	3	672.4	162.3	76 %	
DIII	1	530.4	481.9	9 %	9 %
	2	528.6	490.3	7 %	
	3	550.9	494.0	10 %	

Table 4. Kinetic parameters of biogas production

Digester Code	B (L)	μ (L/d)	λ (d)
DI	4.0284	0.16073	1.6152
DII	9.4114	0.35885	1.0280
DIII	0.5080	0.01234	3.2242

3.5. Bacteria Growth Kinetic Parameters

Based on the calculation, parameters of microbial and biogas production kinetics in the anaerobic vinasse treatment are shown in Table 5. There are parameters of microbial kinetics related to bacterial growth in vinasse anaerobic treatment. These are used to quantify the effect of the amount of air injected into the anaerobic system.

Then, the parameter of each variation was tested by Analysis of Variance (ANOVA) to know whether each variation giving significant difference into kinetic parameters. This test was used 95% significant level. According to statistics calculation, the acid-forming's specific growth rate (μ_{max1}) in the digesters show the value with significant difference. The digester with microaeration got the highest one and shows that acid-forming bacteria could live and grow better in a

Table 5. Kinetic parameters of bacterial growth in vinasse anaerobic digestion

Parameters	DI	DII	DIII	Significant*)
μ_{max1}	1.2067	2.0300	0.3060	0.000
KS_{X1}	2106.7	829.30	1114.7	0.000
$Y_{X1/S}$	0.0497	0.0455	0.0075	0.014
μ_{max2}	0.2414	0.3445	0.0808	0.000
KS_{X2}	3.7653	15.507	13.970	0.000
$Y_{X2/A}$	1.5713	1.2367	0.5690	0.008

*) significant level 95%

microaerobic condition rather than in a strict anaerobic condition. But acid-forming bacteria couldn't grow well in excess air. It was proven by the value of specific growth rate of acid bacteria in each digester. The same of this phenomenon, the specific growth rate biogas-forming bacteria (μ_{max2}) got a significant value among the digesters. In the digester with microaeration it got a better value than that of the strict anaerobic digester. This means that microaeration slightly influences biogas-forming bacteria growth. But, in the digester with the addition of excess air, it shows that the specific growth rate of biogas-forming bacteria is the lowest one. In this case, it shows that the digester has been being inhibited start from the acidogenesis phase.

Moreover, Table 5 shows the difference of productivity among three digesters.

$Y_{X1/S}$ and $Y_{X2/A}$ are productivity parameters of acid-forming and biogas-forming bacteria respectively. The difference of productivity only occurs in acid forming bacteria, and is shown by $Y_{X1/S}$ value in each digester being significantly different, where the digester with microaeration got the highest value of all. Nevertheless, the biogas-forming bacteria productivity among the digesters is not significantly different. This phenomenon reinforces that the addition of microaeration is only influence in acid-forming bacteria performance, starting from the increase of specific acid-forming bacteria growth rate until the productivity of acid-forming bacteria is the best one.

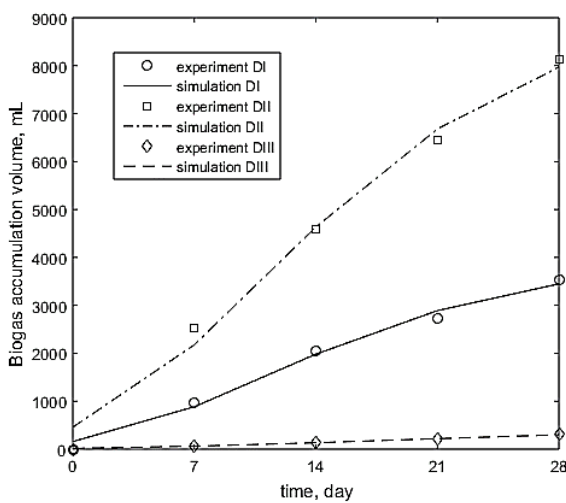


Figure 8. Accumulation volume of biogas

CONCLUSION

The addition of microaeration injected into the anaerobic process significantly enhances the performance of organic matter biodegradation and acid-forming bacteria in anaerobic vinasse treatment. It can be proven by the bacterial lag phase is short ($\lambda = 1.028$ days), the highest rate of biodegradability ($k = -5.7239$) and percentage of VS removal is reaching up to 77%, cuts the HRT making it shorter and the value of acid-forming specific growth rate is 2.03 /day.

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