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Review – Biogas Technology to Treat Bioethanol Vinasse

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Abstract – *Bioethanol industries generate by-product that is called vinasse. Vinasse is generated from button product of distillation unit. It has high COD, high TS, high temperature, very low pH and some variety compounds. Because of these contents, vinasse can be discharged directly into the water bodies such as the rivers. Vinasse causes negative impact to environment. Therefore, treatment of vinasse must be done. Vinasse treatment methods that had investigated by some authors are aerobic treatment and anaerobic treatment. Anaerobic treatment is more interesting than aerobic treatment, because it can treat wastewaters that contain high COD and it can produce biogas that can be used as alternative fuels.*

Keywords – *Bioethanol, Biogas, Technology, Treatment, Vinasse, Waste*

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1. Introduction

1.1 Bioethanol vinasse

Bioethanol is produced by using fermentation process with help of *Saccharomyces cerevisiae*, then it is distillated to separate bioethanol formed from fermentation broth. The raw materials that can be used to generate bioethanol are corn, cassava, sugar and wheat [1]. Besides that, molasses also can be processed into bioethanol [2]. Production of bioethanol from molasses has many advantages, there are (1) high bioethanol yield, (2) less fermentation time, (3) low cost operation [3].

Bioethanol is produced and utilized as alternative fuel because of the increasing of fossil fuel demand that is contradiction with available of these [4]. Bioethanol is used as liquid biofuel for motor vehicles, because it is more eco-friendly than fossil fuel [5-6]. Besides that, it is also used widely as solvent and for drinking [7]. Therefore, production of bioethanol is became main focus in many countries. Hence, bioethanol production in the world that is predicted will be increasing significantly until 2017 in the future [8].

In bioethanol industry, there are four main steps to produce bioethanol, which are feed preparation, fermentation, distillation and packaging [9]. In fermentation step, feed (raw materials of bioethanol) is inoculated with 10% by volume of *Saccharomyces cereviseae*. The process is operated under anaerobic condition, with range temperature of 25-32^oC, during 24-36 hours, efficiency of 95%. Some units of spray cooling water are on the walls of fermenter to maintain temperature constant in the range, because of its exothermic reaction. In this step, bioethanol is produce with concentration of 6-8 %. Furthermore, the sludge that contains yeast cell is separated by settling. The fermentation broth is delivered for next step, which is distillation.

In distillation step, the fermentation broth is preheated to 90^oC by heat exchanger. Distillation is consisted of two-stage process. The fermentation broth preheated is sent to first stage (using analyzer column). Bioethanol with concentration of 40-45% is generated in this stage. Then, it is followed second stage (using rectification column), concentration bioethanol is up to 96%. Bioethanol with concentration of 96% usually is used for manufacture of chemicals and beverages. Whereas, bioethanol that can be used for fuel-blending application must have concentration of >99.5%.

The buttom product of distillation unit in bioethanol production is known as vinasse waste [10-11]. It has dark color, acidic pH and high temperature [1,12]. The more bioethanol is produced, the more vinasse is generated. Every 1 liter of bioethanol is produced, 8-15 liter of vinasse will be generated.

1.2 Characteristics of bioethanol vinasse

Vinasse has dark color and acidic pH. Concentration of total solid and COD value are very high [10]. The pH condition of vinasse is 3.25-4.97 [1,10-11]. The total solid (TS) value in vinasse is 63,000-79,000 mg/L [13-14].

Meanwhile, Benitez *et al.* [15] stated that vinasse contain 100,000 mg/L of total solid. In the fact, vinasse can contain TS more than that [10]. The COD content of vinasse is more than 100,000 mg/L [12]. Whereas, Budiyono *et al.* [11] reported that vinasse contains COD content of 299,250 mg/L. Because of these contents, vinasse cannot be discharged directly in the water bodies, such as the rivers. High COD content in vinasse reduces the oxygen concentration in the water, so the water biota will be death.

Vinasse contains many kinds of organic compounds such as acetic acids, lactic acids, glycerol, phenols, polyphenols and melanoidins. Budiyono *et al.* [11] reported that organic substances such as acetic acid, lactic acid and glycerol are easy to be degraded using anaerobic technology. Hence, biogas from vinasse is generated easily. In other hand, phenolic compounds in vinasse are difficult to be destroyed through anaerobic technology. It has phytotoxic character so microbial growth in digester will be disturbed [1,10]

The characteristic of vinasse is depended on raw material which is used in bioethanol production. The characteristic of vinasse can be seen in Table 1.

Table 1. Characteristic of vinasse

Parameters	From molasses	From cane juice	From wheat straw
pH	3.25 - 4.97 [1,2,3]	3.75 [5]	3.6 [6]
COD_{total}(mg/L)	104,640 – 299,250 [1,2]	68,560 [5]	150,000 [6]
$COD_{soluble}$ (mg/L)	57,390 [2]	55,830 [5]	61,000 [6]
BOD_5 (mg/L)	36,400 [2]	29,700 [5]	N.A.
Total Organic Carbon (mg/L)	30,750 [2]	20,160 [5]	N.A.
Betaine (mg/L)	22,530 [2]	N.A.	N.A.
Glycerol (mg/L)	3,333 [2]	N.A.	N.A.
Protein (mg/L)	6,894 [1]	N.A.	7,700 [6]
Lipids (mg/L)	6,894 [1]	N.A.	990 [6]
Carbohydrates (mg/L)	9,117 [1]	N.A.	84,500 [6]
Total Nitrogen (mg/L)	153 - 4,004 [1,2,4]	102 [4]	1,400 [6]
Ammonia Nitrogen (mg/L)	187 [2]	N.A.	160 [6]
Total Phosphorus (mg/L)	1 – 102 [2,4]	71 [4]	N.A.
Total K	4,078 – 10,705 [4]	1,733 [4]	N.A.
Total Ca	143 – 2,039 [4]	408 [4]	N.A.
Total Mg	61 – 1,529 [4]	102 [4]	N.A.
Total Phenol (mg/L)	469 [3]	450 [5]	61 [6]
Total Solid (%)	27.865 [1]	N.A.	12 [6]
Soluble Solid (mg/L)	4,640 [2]	N.A.	N.A.
Mineral Solid (mg/L)	N.A.	31,000 [5]	N.A.
Volatile Solid (mg/L)	284, 659 [1]	46,390 [5]	N.A.
Mineral Suspended Solid (mg/L)	N.A.	5,300 [5]	N.A.
Volatile Suspended Solid (mg/L)	N.A.	15,860 [5]	69.1 [6]
Ash Content (mg/L)	19,879 – 50,972 [4]	15,292 [4]	1.8 [6]
Lignin (mg/L)	N.A.	N.A.	75,600 [6]
Xylose (mg/L)	N.A.	N.A.	6,900 [6]
Glucose (mg/L)	N.A.	N.A.	10,300 [6]

References: 1. Syaichurrozi *et al.*, 2013; 2. Lutoslawski *et al.*, 2011; 3. García- García *et al.*, 1997; 4. Cortez and Perez, 1997; 5. Siles *et al.* 2011; 6. Kaparaju *et al.*, 2010.
Remarks: N.A., Not Analyzed

1.3 Environmental impact of vinasse

Vinasse contains abundant organic materials and has strongly acidic. It's COD and BOD content are very high [12]. If vinasse is discharged directly in to the rivers without treatment, water biota will be death. Dissolved oxygen in the rivers is used by oxidation bacteria to degrade COD and BOD. Hence, the availability of dissolved oxygen is running out, so water biota cannot breath and finally death [18]. Strongly acidic of pH vinasse causes remobilization of heavy metal in soil [16]. The dark color in vinasse is not good for environment. Environment will be dirty and unsightly. Besides that, it also can hamper penetration of sun light in to the rivers, so water plant in the riverbed cannot do photosynthesis [19].

Soluble salts in vinasse can cause soil salinity and sodicity. Hence, soil structure become poor, not fertility. Vlyssides *et al.* [20] stated that high concentration of P and N nutrients cause eutrophication in water bodies. The temperature of fresh vinasse that is out from distillation unit is 65 – 105^{o}C [1,12]. If vinasse is disposed to bodies water, not cooled before, temperature of bodies water can increase. It can disturb the fish activity [21]

Furthermore, presence of phenolic compounds in vinasse interfere the degradation process of vinasse. Oxydation bacteria cannot degrade the phenolic compound, so if vinasse is disposed in the environment, it will be difficult to be degraded [10].

Thus, bioethanol industries look for the method to treat vinasse, not only effective for environment, but also for cost. Some researchers did study to find the best method to treat vinasse. Tang *et al.* [22] reported that vinasse-treatmet using aerobic method has some drawbacks, (1) requires extensive land, (2) requires high capital cost, (3) requires high operating cost, (4) produces poison during treating. On the other side, Budiyono *et al.* [23] stated that anaerobic method is better to treat vinasse than aerobic method. Anaerobic method uses digester that is operated under anaerobic condition. Using anaerobic treatment, COD that is contained in the wastewater will be converted in to biogas. Recently, Study of Syaichurrozi *et al.* [10] showed that phenolic content in vinasse bothers the methanogenic bacteria in the digester. The maximum COD removal is just 38.088±0.872 %. Therefore, pretreatment to remove phenol must be done to get maximum degradation of COD and maximum production of biogas.

2. Biogas Technology

2.1 Biogas from bioethanol vinasse

In the anaerobic technology, COD content in wastewater will be converted in to biogas with help of bacterial activity [10,23-24]. According to Speece [24], 1 gram of COD will be generated 0.35 liter of CH_4 at STP condition (0^{o}C, 1 atm). Whereas, at temperature of 35^{o}C and pressure of 1 atm, 1 gram of COD will be converted in to 0.395 liter of CH_4.

Phang *et al.* [25] stated that COD value can be used to obtain the value of C in wastewater, where C = COD value × (12/32). Wastewaters not only contain C, but also contain the others such as H, O and N. Richards *et al.* [26] purposed the stoichiometry to predict biogas composition of biogas produced. Substrates that contain element of C, H, O, N can be predicted the composition of biogas using stoichiometry below:

$$C_nH_aO_bN_c + (n-0.25a-0.5b+1.75c)\ H_2O \rightarrow (0.5n+0.125a-0.25b-0.375c)\ CH_4 + (0.5n-0.125a+0.25b-0.625c)\ CO_2 + c\ NH_4^+ + c\ HCO_3^- \quad (1)$$

Syaichurrozi *et al.* [10] reported that vinasse has elemental composition of C, H, O, N. The ratio of these is C:H:O:N = 76.9:192.2:45.2:1. The ratio of elemental composition in vinasse is depended on raw materials that are used to produce bioethanol. Thus, the composition of biogas produced from fermentation of vinasse can be identified as stoichiometry [10]:

$$C_{76.9}H_{192.2}O_{45.2}N + 8\ H_2O \rightarrow 50.8\ CH_4 + 25.1\ CO_2 + NH_4^+ + HCO_3^- \quad (2)$$

The value of CH_4, CO_2, NH_4^+ and HCO_3^- is depended on ratio of element in vinasse (C:H:O:N). If amount of urea is added in to substrates, the ratio of element will be changed, so that the value of CH_4, CO_2, NH_4^+ and HCO_3^- also will be changed in prediction.

Many authors have studied biogas production from vinasse. Espinoza-Escalante *et al.* [27] studied the effect of pH, temperature and HRT to production of hydrogen and methane from vinasse using semi-continuous bioreactor. The results showed that temperature of 55^{o}C is optimal temperature to generate hydrogen. Whereas, temperature of 35^{o}C is optimal temperature to produce methane. The longer of HRT, the more methane is produced. The optimal pH is 6.5.

Soeprijanto *et al.* [28] studied the effect of various COD content in the substrate vinasse. The UASB reactor was used in this study. The results showed that the more COD content in vinasse, the more total biogas and % COD removal obtained. In the contras, the most of methane concentration in biogas is produced from substrate with the least COD content. The best of yield methane is 0.11 m^3 CH_4/kg COD.

Buitron and Carvajal [29] studied the influence of substrateconcentration, temperature and HRT using batch reactor. The variation of substrate concentration is 0.5, 1, 2, 3 gram COD/L; the variation of temperature is 25 and 35^{o}C; the variation of HRT is 12 and 24 hours. The results showed that the more temperature condition is used, the more biogas volume and concentration hydrogen in biogas. The less HRT, the more biogas volume and concentration hydrogen in biogas. The best conditions are temperature of 35^{o}C, HRT of 12 hours, substrate concentration of 3 gram COD/L.

Siles *et al.* [1] conducted vinasse pretreatment before vinasse was treated using anaerobic technology. The obtained of this study was reduce the concentration of phenolic compounds in vinasse. The method of pretreatment obtained was ozonation process. The results showed that phenol removal of 39 % after pretreatment during 15 minutes and 65 % after pretreatment during 60 minutes. After vinasse pretreatment processing, vinasse was used as feed stock to produce biogas. The methane yield increased 13.6% and methane production rate increased 41.6%. The ozonation process is very expensive and it need to be combined with other pretreatment to reduce operating cost.

Budiyono *et al.* [23] studied the effect of pH and urea addition to biogas production from vinasse. Variation of initial pH is 6, 7, 8. The best of initial pH condition was 7 with total biogas of 3.81 mL/g COD. Biogas production with urea addition is 52.47% greater than without urea addition.

Sumardiono *et al.* [18] used batch digester to treat vinasse. This study investigated the effect of pH control during fermentation process. Digesters were operated at room temperature and initial pH of 7. The results showed that total biogas produced without pH control was 3.673 – 6.096 mL/gram COD. Whereas total biogas produced with pH control during fermentation was 17.875 – 21.229 mL/gram COD.

Syaichurrozi *et al.* [10] conducted investigation to get information of the effect of COD/N ratio to biogas production. Variation of COD/N was control variable (1436/7), 400/7, 500/7, 600/7, 700/7. Batch digesters were carried out at room temperature, during 60 days. Initial pH of all variables was 7. pH control was done to maintain pH substrate in digester at rage 7±0.2. After 60 days, substrate with COD/N ratio of 600/7 produced the most total biogas, which was 139.17 mL/gram COD. This variable also had the most COD removal value, which was 38.088±0.872%.

Budiyono *et al.* [11] investigated the effect of total solid content in vinasse to biogas production. The variation of total solid in vinasse is 4.655, 5.700, 7.015, 9.310, 14.005, 27.910 %. This study used batch digester that was carried out during 30 days and at room temperature. Initial pH is 7. The results showed that total solid content of 7.015 % was the optimal condition with total biogas of 37.409 mL/gram COD. Meanwhile, total solid content of 9.310 % had the most COD removal value (23.580±0.532%).

2.2 Operating parameters

a. pH

According to Espinoza-Escalante *et al.* [27], initial pH of 6.5 is better than pH of 4.5 and 5.5. Biogas produced is maximum at initial pH of 6.5. Furthermore, Budiyono *et al.* [23] focuses the study on initial pH at neutral range (6, 7, 8). After carrying out during 30 days, substrate at initial pH of 7 generated the more biogas than two others, which are pH of 6 and 8.

During vinassefermentation in the digester, pH is function of time [23]. A the beginning of vinasse fermentation (in the first four days), pH substrate decreases drastically from 6-8 to 3.7-4.5. Then, pH condition is decreasing until the end fermentation. The final of pH substrate is 3.3-3.4. However, initial pH of 7 gives the satisfy result than the others (pH of 6 and 8). Budiyono *et al.* [23] stated that pH of 7 is good condition for anaerobic bacteria to adapt in digester.

Elbeshbishy and Nakhla [30] explained that drop in pH is caused by accumulation of VFAs (Volatile Fatty Acid) in digester. Vinasse is by-product of bioethanol industry that contains variety of organic materials such as acetic acid, lactic acid and glycerol [31]. These are simple organic compound that are easy to be degraded by bacterial activity. This is caused VFAs generated in large amount, so pH is drop drastically. Besides that, vinasse also contains high carbohydrate [10]. Substrate contained high carbohydrate generates VFAs easily in anaerobic biotechnology, so the large amount of VFAs will be produced in vinasse fermentation anaerobic technology [32].

The low pH condition inhibits the bacterial activity, so bacterial in the digesters can thrive and finally death, especially methanogenic bacteria [24]. Furthermore, Sumardiono *et al.* [18] tried to maintain pH substrate in neutral pH range (7±0.2) using NaOH 2 M. This method is very effective to increase total biogas volume i.e. from 2.2781 mL/gram COD to 11.0754 mL/gram COD. When pH is maintained at neutral range, the perfect link between acidogenetic bacteria and methanogenic bacteria will be occurred in system.

b. Total Solid (TS)

Concentration of total solid in vinasse also leads to total biogas produced. Budiyono *et al.* [11] reported that the more total solid value of vinasse, the more organic matter contained in vinasse. The optimum range of total solid content in vinasse fermentation anaerobic is 7.015 – 9.310 %. Budiyono *et al.* [33] and Zennaki *et al.* [34] also reported the same result that solid concentration of 7-9.2 % in substrates will generated biogas optimally, although Budiyono *et al.* [33] and Zennaki *et al.* [34] used solid waste.

Vinasse contains high total solid [10-11,18]. Therefore, vinasse must be diluted using water to get optimum total solid, which is 7.015 – 9.310 %. If TS in vinasse more than the range, overload of organic materials is occurred in digester. While, TS below of the range, process decomposition is unstable. Water in substrate causes the movement and transport nutrient easily; mixing of substrate, nutrient and bacteria; support of bacterial growth.

c. COD/N ratio

The optimum ratio of COD/N is in range of 350/7 – 1000/7. If the ratio of COD/N in substrate is not in the range, bacterial growth in digester will be disrupted [24]. In vinasse fermentation anaerobic, the optimum range of COD/N was investigated by Syaichurrozi *et al.* [10] and Sumardiono *et al.* [18]. Vinasse contains high COD but low total nitrogen, so ratio COD/N of vinasse is too high, which is 1436/7 [10-11,18]

Nitrogen is used by bacteria to build the cell structure. The sources of nitrogen that can be used by bacteria are protein, amino acid and urea[35]. Syaichurrozi *et al.* [10] and Sumardiono *et al.* [18] utilized urea (N contained 46%) as nitrogen source. Ratio of COD/N in vinasse was varied 400/7, 500/7, 600/7, 700/7. After fermentation using batch anaerobic digesters, COD/N ratio of 500/7 – 600/7 is optimum COD/N for vinasse waste either in Syaichurrozi *et al.* [10] or Sumardiono *et al.* [18]. Syaichurrozi *et al.* [10] used vinasse with TS 7.015±0.007%, while Sumardiono *et al.* [18] used vinasse with TS 27.940±0.085%. Therefore, can be concluded that at different TS content in vinasse, the optimum ratio of COD/N is the same, which is 500/7-600/7.

Protein and urea will be decomposed in to ammonium (NH_4^+) by bacterial activity. Furthermore, ammonium is used as nitrogen source to build cell structure by bacteria [36]. To support bacterial growth, ammonium concentration must be maintained in excess of 40-70 mg/L

[24]. If in the system does not have ammonium concentration of 40-70 mg/L, bacteria will be death. Syaichurrozi *et al.* [10] predicted total ammonium production using mole equalization concept through stoichiometry of Richards *et al.* [26] above (Equation 1). The variables of 1436/7 (without urea addition), 400/7, 500/7, 600/7 and 700/7 generate total ammonium of 3,220; 12,142; 10,672; 9,289; 6,851 mg/L. According to Speece [24], bacterial need 40-70 mg/L of ammonium concentration per day. Syaichurrozi *et al.* [10] carried out fermentation in 60 days, so bacteria need ammonium concentration in 60 days is 60 × 70 = 4200 mg/L. Furthermore, ammonium remaining in digester can be calculated by formula = total ammonium production – ammonium needed by bacteria [10]. Thus, the ammonium remaining in digester for variable of 1436/7, 400/7, 500/7, 600/7, 700/7 is -980; 7,942; 6,472; 5,089; 2,651. According to Niu *et al.* [37-38], ammonium concentration of 5,000 mg/L in digester is good for bacterial growth. Among the variables, variable of 500/7 and 600/7 have ammonium remaining in digester that approach the 5,000 mg/L, but the best variable is 600/7 [10].

d. Temperature

Buitron and Carvajal [29] reported that biogas production from vinasse at temperature of 35°C is more than at temperature of 25°C. Fermentation process at 25°C produces more acetone and ethanol than that of 35°C. Whereas, fermentation carried out at 35°C produces VFAs (acetic, propionic, butyric, iso-butyric acids) in large amount. Espinoza-Escalante *et al.* [27] also gets same conclusion that optimum temperature condition to produce methane is 35°C (mesophilic temperature).

e. Hydraulic Retention Time (HRT)

HRT also becomes important parameter in vinasseanaerobic biotechnology. Buitron and Carvajal [29] did combination variables between temperature and HRT using a sequencing batch reactor. At 25°C and 12-h HRT, biogas is not produced. Furthermore, at 25°C and 24-h HRT, biogas is produced in little amount. Biogas production at 35°C and 12-h HRT is 2590 mL, while at 35°C and 24-h HRT is 3200 mL. Furthermore, Buitron and Carvajal [29] stated that using HRT 24-h at both temperature (25 and 35°C), methane is up to 35-44%.

f. Presence of Phenolic Compound

Vinasse contains phenolic compounds in large amount, which is 61-469 mg/L [2,16,14].Phenolic compounds have anti-microbial characteristic. Hence, it is very difficult to degrade through biological activity [39]. Presence of phenolic compounds in vinasse disrupts degradation process of organic materials in anaerobic digester [1,10,16]. Phenolic compounds can react with bacterial membrane cell, inactivate essential enzymes and materials genetic functions [40].

Degradation partially of lignin can form phenolic compounds. Furthermore, Taherzadeh and Karimi [41] and Syaichurrozi *et al.* [10] stated that formation phenol process is occurred in hydrolysis step in bioethanol industry. The more lignin content in raw material of bioethanol production, the more phenolic compounds may be formed in vinasse [10]

According to García-García *et al.* [16], aerobic biological pretreatment usingfungi is good optional method to remove phenol in vinasse. Fungi of *Aspergilusterreus* and *Geotrichumcondidum* are chosen in this method. These two fungi have the ability to degrade phenolic compounds. *Aspergilusterreus* can reduce 66 % of total phenols and 94% of o-diphenolic compounds. Whereas, *Geotrichumcondidum* can reduce 70 and 91% respectively.

Furthermore, Martin *et al.* [39] and Siles *et al.* [1] proposed new method to reduce phenolic content in vinasse. Ozonation system is used to remove phenolic compounds before vinasse is treated using anaerobic digestion. This method is effective but it needs high operational cost.

3. Kinetic Model of Biogas Production

3.1 Modified Gompertz Equation

Modified Gompertz equation is proposed by Zwietering *et al.* [42]. Gompertz equation describes a sigmoidal growth curve using mathematical parameters (a, b, c). It is used to predict bacterial growth. According to Zwietering*et al.* [42], these mathematical parameters are difficult to describe (have no biological meaning). Thus, Zwietering*et al.* [42] modified original Gompertz equation through substitution the mathematical parameter (a, b, c) with ym, μ, λ respectively.ym is maximum value of bacterial population, μ is maximum specific growth rate of bacteria, λ is adaptation time (lag time).

Currently, many authors predict biogas production rate using modified Gompertz equation with assume that biogas production rate has correspondence to anaerobic bacteria growth in digester [43-44]. The formula of modified Gompertz equation can be seen below:

$$y(t) = ym.\exp\{-\exp[\frac{\mu.e}{ym}(\lambda - t) + 1]\} \qquad (3)$$

Where, y(t) is cumulative of biogas production at t times; ym is maximum cumulative of biogas production; μ is maximum biogas production rate; λ is lag time; e is mathematical constant (2.718282).

In vinasse fermentation anaerobic technology, some authors [10-11,45] make prediction of biogas production through modified Gompertz equation. This equation has good correlation coefficient (R^2), which based on Budiyono *et al.* [11] is 0.993 – 0.999, Syaichurrozi *et al.* [10] is 0.958 - 0.967, Budiyono *et al.* [45] is 0.986-0.998. Syaichurrozi *et al.* [10] stated that the value of kinetic constant (ym, μ, λ) is difference between vinasse and the other materials. The difference of that can be seen in Tabel 2 below.

Kinetic constant of λ in vinasse (0.213 – 0.959 days) is less than the other substrates (1.2 – 8.749 days). That means, in vinasse fermentation, biogas is produced after 0.213 – 0.959 days. While the other substrate can produce biogas after 1.2 – 8.749 days. Yavuz [31] stated that vinasse contains many simple organic compounds, so that anaerobic bacteria degrades easily these compounds into biogas. Whereas, waste from livestock (such as cattle manure, municipal solid waste, water hyacinth, poultry litter) contains highlignocellulosic so that it is need more time to be degraded [10].

Kinetic constant of ym describes maximum biogas that can be produced. Vinasse fermentation only produces maximum biogas in little amount, which is 39.406 – 140.164 mL/g VS. Whereas, the other substrates can produce total biogas 418.260 – 449.400 mL/g VS.This is caused by presence of phenolic compounds in vinasse [39]. Phenolic compounds is toxic materials that can disrupt bacterial activity in digester. While, manure contains no phenolic compounds, so that biogas is generated continuously until all of organic materials are degraded completely [10].

Table 2. Comparison kinetic constant in various substrates

Substrate	Ym (mL/g VS)	μ (mL/g VS.day)	λ (days)	R^2	Reff
Vinasse	140.164	16.066	0.213	0.965	Syaichurrozi *et al.* (2013)
Vinasse	114.974	24.669	0.803	0.998	Budiyono *et al.* (2013b)
Vinasse	39.406	7.007	0.959	0.999	Budiyono *et al.* (2014a)
Poultry Litter	390.400	16.500	8.749	0.999	Adiga *et al.* (2012)
Water Hyacinth	449.400	27.900	6.625	0.981	Patil *et al.* (2012)
Municipal Solid Waste	522.000	97.000	1.2	0.983	Zhu *et al.* (2009)
Cattle Manure	418.260	9.490	4.460	-	Budiyono *et al.* (2010)

3.2 First Order Kinetic

Beside modified Gompertz equation, some authors [44,48] also use first order kinetic to model biogas production rate from manure. Furthermore, Budiyono *et al.* [45] uses this concept to model biogas production from vinasse. Budiyono *et al.* [45] proposes first order kinetic equation in modeling biogas production below.

$$\frac{1}{t}\ln\left(\frac{dy(t)}{dt}\right) = \frac{1}{t}(\ln ym + \ln k) - k \quad (4)$$

Where y(t) is cumulative of biogas production at t times; ym is maximum cumulative of biogas production; -k is rate constant associated with degradation of organic materials. Equation (4) represent straight line equation y = mx+c, where slope of equation (m) represent the value of $(\ln ym + \ln k)$ and intercept of equation (c) represent the value of (-k).

Yusuf *et al.* [44] stated that the more negative the value of (-k), the faster the rate of degradation organic materials. The value of (-k) identifies the rate of removal of biodegradable fractions as biogas yield increased with time.Budiyono *et al.* (2013b) reported that in vinasse fermentation the value of (-k) is (-0.1852) to (-0.6466)/days with R^2 value of 0.9867 – 0.9996.

The first order kinetic equation has correlation with the modified Gompertz equation, which the more negatif of (-k) obtained from first order kinetic, the more value of ym obtained from modified Gompertz equation [44-45].

Equation (4) is shown straight line y = mx+c, no sigmoidal curve like modified Gompertz equation. Furthermore, Budiyono *et al.* [49] proposed Equation (5) that is also made based on first order kinetic. This equation describe a sigmoidal curve, so some authors [49-51] usually compare this equation with modified Gompertz equation to find which one is best to predict biogas production kinetic.

$$y(t) = ym\,(1 - \exp(-k * t)) \quad (5)$$

Where y(t) is cumulative of biogas production at t times; ym is maximum cumulative of biogas production; k is the biogas rate constant.

Budiyono *et al.* [49] reported that k value in kinetic modeling of biogas production from vinasse is 0.087-0.210/day. This value is higher that study of Kafle *et al.* [50] which is 0.017-0.040/day. That is caused by content of substrates that are used as biogas feedstock. Vinasse contains many simple compounds, so that it is easily to degrade into biogas. The difference between the predicted and measured biogas from vinasse is 1.54-4.70% with first order kinetic equation and 0.76-3.14% with modified Gompertz equation [49]. Raposo *et al.* [51] stated that good fitting between measured and predicted biogas is equal or less than 10%. Based on that, biogas production from vinasse can be modeled using both modified Gompertz equation and first order kinetic, although modified Gompertz equation has less error fit (0.76-3.14%) than first order kinetic (1.54-4.70%).

According to Kafle *et al.* [50] and Budiyono *et al.* [49], first order kinetic equation is good to make modeling of biogas production that has short lag time. The shorter of lag time, the better of fitting between measured and predicted biogas. Many authors report that lag time to produce biogas from vinasse substrate is very shortwhich is 0.213-0.959 days [10,45,49]. In anaerobic technology, substrates that contain high carbohydrate can be degraded rapidly (just few days), while substrates that contain high fat and protein need several weeks to be degraded [52-53]. Table 1 shows that vinasse has high carbohydrate contents and low fat and protein, so that degradation of vinasse is easily to occur and need little lag time.

Kafle *et al.* [50] reported that substrate such as fish waste cannot be modeled using first order kinetic, because the substrate contains high protein and fat, so that the lag time needed is very long. The fitting error of biogas production from fish waste is 0.7-13.7 % with modified Gompertz equation and 13.6-37.1 % with first order kinetic equation. Modeling of biogas kinetic from fish waste is not allowed using first order kinetic because of the big fitting error, more than 10%. Whereas, biogas form vinasse substrate is still allowed using first order kinetic because it has fitting error of less than 10% (1.54-4.70%)

4. Conclusions

The review indicates that vinasse must be treated first before discharged in to the environment. Vinasse has negative impact to environment because of its contents such as COD, TS, nitrogen, color, etc. High temperature and very acidic of pH in vinasse is also not eco-friendly for environment. Biogas technology is the best choice to treat vinasse. COD content in vinasse will be converted into biogas. Some authors have studied the vinasse treatment through biogas technology. It is more effective to degrade organic materials than aerobic treatment. However, the value of COD removal is not maximum. That is caused by presence of phenolic compounds in vinasse.

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