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Biogas Production from Sugarcane Vinasse: A Review

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ABSTRACT

Biogas is a renewable energy sources that could replace the role of fossil fuel. Biogas could be produced from biomass or agro-industrial wastewater. Sugarcane vinasse has potential of biogas production due to its high BOD concentration (10–65 g BOD/L). However, the biogas production from sugarcane vinasse has several drawbacks that hinders the maximum biogas yield, such as: acidic pH (pH 3.5 – 5.0), high temperature (80–90°C) and high concentration of sulfuric acid (> 150 mg/L). Theoretically, the methane potential per gram COD is 0.35 L/gr COD, containing of 60% methane. However, up to date, the maximum biogas production from vinasse was less then its theoretical value. To get the full potential of biogas production from vinasse wastewater as well as to reduce the capital cost for full scale application, combination of suitable pre-treatment, selected microorganisms and bioreactor design-configuration are the most important parameters to be considered. This paper aims to explore the potential of sugarcane vinasse to produce biogas, by elaborating the aforementioned key parameters. In this review the basic characteristic and the potency of sugarcane vinasse wastewater will be elaborated. Furthermore, the effect of key parameters such as pH, temperature, and organic load to biogas production will also be discussed. The biogas technology will also be explored. Lastly, conclusion will be determined.

1. INTRODUCTION

Indonesia is amongst the biggest ethanol producer in the world, alongside Brazil, India, and China (OECD/FAO, 2019). At recent days, the ethanol production demand increases due to the extreme need for disinfectant. In Indonesia, sugar cane and molasses are the major feedstocks in the ethanol agro-industry. There are big, as well as small-medium scale of agro-industries that produce ethanol from molasses. For instance, one big ethanol industry in Central Java-Indonesia, PT Indo Acidatama has maximum production capacity of 80 million liter ethanol per year (Harihastuti & Marlena, 2018). As for small scale industries, there are about 130 industries in Polokarto, Sukoharjo, Central Java that produce alcohol total amount of 13,000 L/per day (around 80-100 L alcohol/industry/day) (Harihastuti et al., 2020; Harihastuti & Marlena, 2018)

The environmental problem related to the developing ethanol agro-industry is vinasse wastewater, as a by-product of ethanol production. For every liter of ethanol production, approximately 10 – 15 liters vinasse is generated (Bernal et al., 2017; Naspolini et al., 2017). Figure 1 depicts a flowchart of ethanol production from sugarcanes and pollution prevention strategies. Figure 1 shows that vinasse is a wastewater that generated from stripping and distillation process. Vinasse wastewater has low pH, high COD, dark-colored, high concentration of

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sulfur and bad odor (Cristiano E Rodrigues Reis, Hu, & Hu, 2017). The easiest way to utilize vinasse wastewater is using it as fertilizer/fertirrigation. Technologies, such as anaerobic digestion (AD), advanced oxidation process (AOP), biological based treatment using algae and fungi are also commonly used as treatment strategy. The aforementioned technologies could treat vinasse wastewater so that the effluent can fulfil the water reuse standard. The effluent could be reused in the fermentative process. Bagasse, the solid waste that comes from juice extraction process, is used as feed to the boiler to produce steam and heat.

Anaerobic digestion (AD) is proven to be the most beneficial treatment for vinasse wastewater mitigation management. AD produces bioenergy (methane) that can be utilized as fuel replacing fossil fuel in the distillation process, as well as generate bio-fertilizer. Theoretically, the methane potential per gram COD is 0.35 L/gr COD, with 60% methane content. From 1 m^3 vinasse, about 115–312 m^3 of biogas can be produced, from which 169 kW of energy can be generated (Meyer, Rein, Turner, Administrative, & Mcgregor, 2011). The energy efficiency of the biogas produced from the vinasse in reciprocating combustion engines is 29%, while it is 32% in the gas turbines and microturbines (Parsaee, Kiani, Kiani, & Karimi, 2019). The total energy in vinasse is about 18% of the energy produced by bioethanol produced in the plant (Meyer et al., 2011). Unfortunately, methane production from vinasse cannot reach to its maximum potential due to many factors, such as: high level of inhibitors (Jesus, Bastos, & Altenhofen, 2019), low C/N ratio than the optimum C/N yield in biogas system (Janke, Leite, Nikolausz, Schmidt, & Liebetrau, 2015; Kayhanian & Rich, 1995), the needed HRT to achieve full organic degradation (Janke et al., 2015), low pH (Harihastuti et al., 2021; Cristiano E Rodrigues Reis et al., 2017), type of microorganisms (Oliveira et al., 2020), etc. Hence, for full scale application, addressing those factors is important thing to do.

Literatures about biogas potential from vinasse wastewater are still limited. This paper will generally review the potential of biogas production from vinasse wastewater. Specifically, the characteristic of vinasse along with its environmental effect and treatment technology will be elaborated. In addition, this paper also addresses the various aspects that have to be considered to enhance biogas generation of vinasse. Furthermore, its full-scale applications are also discussed. Lastly, the conclusion is determined.

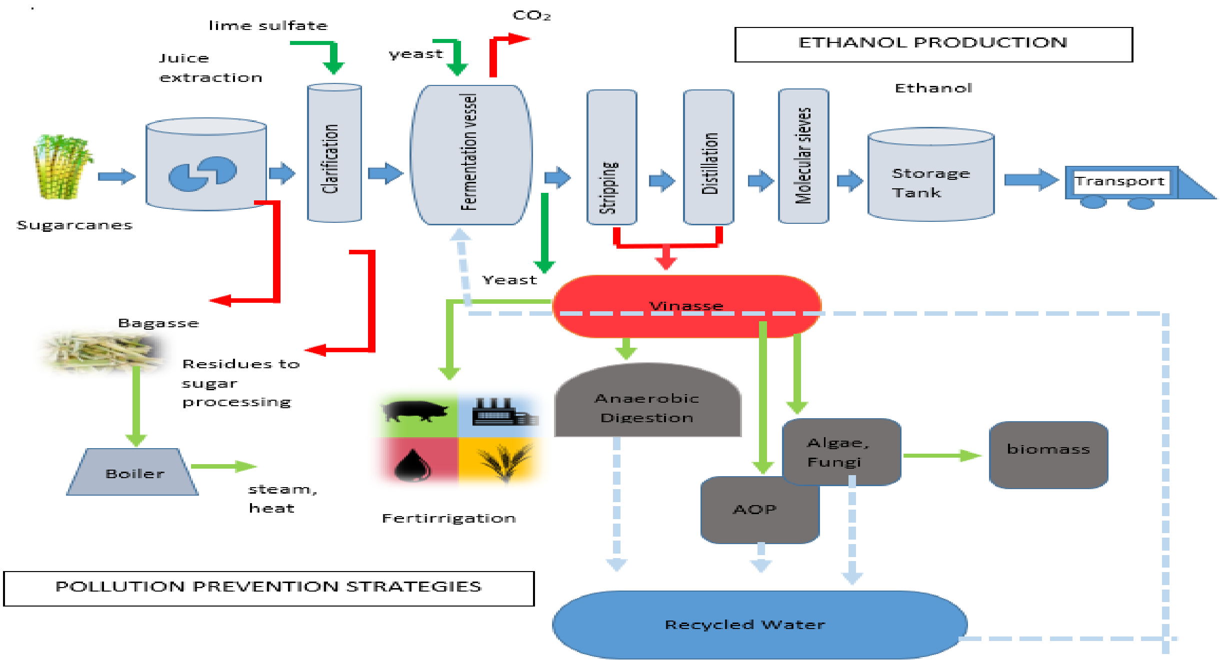

Figure 1. Flowchart of ethanol production and pollution prevention strategies

Table 1. Properties of sugarcanes vinasse wastewater

Parameter	Unit	Concentration range	Ref.
pH	-	3.0 – 5.0	(Harihastuti et al., 2021; Iqbal Syaichurrozi, 2016)
Temperature	°C	40 - 50	(Harihastuti & Marlena, 2018)
Biochemical Oxygen Demand (BOD)	mg/L	23,182 -109,038	(Harihastuti & Marlena, 2018; Soares et al., 2019; Iqbal Syaichurrozi, 2016)
Chemical Oxygen Demand (COD)	mg/L	32,400 – 353,797	(Harihastuti & Marlena, 2018; Janke et al., 2015)
Total Organic Carbon (TOC)	mg/L	30,750	(Iqbal Syaichurrozi, 2016)
C/N ratio	-	11-15/1	(Janke et al., 2016)
Total Suspended Solid (TSS)	mg/L	7,200	(Harihastuti & Marlena, 2018)
Total Solid (TS)	mg/L	27,000 -81,500	(Parsaee, Kiani, et al., 2019)
Volatile Suspended solid (VSS)	mg/L	1,620 –15,860	(Parsaee, Kiani, et al., 2019)
Total Nitrogen (TN)	mg/L	17,920	(Janke et al., 2016)
Total Phosphate (TP)	mg/L	1 – 102	(Iqbal Syaichurrozi, 2016)
Sulfide (H_2S)	mg/L	6.55 - 39.7	(Harihastuti et al., 2020, 2021)
Volatile Fatty Acid (VFA)	mg/L	1,310	(Lebrero & Zaiat, 2017)
Bicarbonate Alkalinity	mg $CaCO_3$/L	295	(Parsaee, Kiani, et al., 2019)
Phenols	mg/L	0.45–0.469	(Parsaee, Kiani, et al., 2019)
Iron (Fe)	mg/L	200 – 488	(Janke et al., 2015)
Manganese (Mn)	mg/L	55.4 - 194	(Janke et al., 2016, 2015)
Nickel (Ni)	mg/L	0.47 – 2.30	(Janke et al., 2016, 2015)
Copper (Cu)	mg/L	3.62 – 7.96	(Janke et al., 2016, 2015)
Zinc (Zn)	mg/L	29.4 – 36.8	(Janke et al., 2016, 2015)
Cobalt (Co)	mg/L	0.53 -0.62	(Janke et al., 2016, 2015)
Molybdenum (Mo)	mg/L	0.48 -0.84	(Janke et al., 2016, 2015)
Selenium (Se)	mg/L	0.08	(Janke et al., 2015)

2. CHARACTERISTICS OF SUGARCANES VINASSE WASTEWATER

The characteristics of vinasse wastewater depends on the raw materials (i.e. the variety of sugarcanes and the quality of molasses) and the process technology (i.e. the operating condition of the ethanol production, type of fermentation and distillation process , the quantity of the chemicals used, etc (Soares, Zaiat, Augusto, & Tadeu, 2019;

Wilkie, Riedesel, & Owens, 2000). Sugarcanes wastewater, that comes from ethanol distillation process, is considered as recalcitrant. It has temperature of 65–107 °C and a pH of 3–5 (Albuquerque, Ratusznei, & Rodrigues, 2019; Harihastuti & Marlena, 2018). Sugarcane vinasse contains of 93-97% water (Pazuch et al., 2017), 5% organic matter and 2% inorganic insoluble solid (Parsaee, Kiani, et al., 2019). It easily dissolves in water and has dark brown color. The dark brown pigment is derived from phenolic compounds (tannin and humic acids), melanoidins and caramels that makes vinasse is toxic to microorganisms. The characteristic of sugarcanes vinasse can be seen in Table 1.

3. ENVIRONMENTAL IMPACT

Sugarcane vinasse is considered very polluting because of high organic load that causes proliferation of microorganisms that reduces the dissolved oxygen (DO) in the water body that makes water unconsumable. Sugarcane vinasse also has low pH and corrosive. Its degree of pollution can be 100 times more dangerous than domestic waste (Marafon, Salomon, & Lucena, 2020). The lowest maintenance utilization of vinasse wastewater is using it as fertirrigation, as it requires low initial investment, low maintenance cost and simple technology (Marafon, Salomon, & Lucena, 2020). However, the bad effect of the excessive use of vinasse as fertirrigation are ground water contamination, soil salinization, metal leach and greenhouse gas emission (GHG) such as nitrous oxide, which is about 300 times more polluting than carbon dioxide (CO_2) (Marafon, Salomon, Amorim, & Peiter, 2020). Furthermore, over a long period of time, frequent discharges to the soil, rivers or lake could be harmful to the biota. However, vinasse wastewater fertirrigation could be very beneficial to improve soil fertility, with optimum dosage supplement that should not be exceed the soil's ion retention capacity (Tadeu, Loureiro, & Zaiat, 2018). Thus, the optimum dosage should be determined based on soil properties.

4. SUGARCANES VINASSE TREATMENT METHODS

Due to its high organic content, the treatment of vinasse wastewater should not be only rely on single method. The combination of several technology should be applied for the effluent in order to fulfill stream standard regulation. Biological treatment is till most common preference. The combination of biological anaerobic and aerobic treatment is the best solution to treat vinasse wastewater (Harihastuti et al., 2021). To improve the effluent's quality for re-use, another add-on advance technology such as ozonation catalytic might be used. Beside proven technologies, there are also several advance methods that also able to treat sugarcane vinasse wastewater effectively. Table 2 shows sugarcanes vinasse wastewater treatment technology.

5. ANAEROBIC DIGESTION OF SUGARCANE VINASSE

Sugarcane vinasse anaerobic digestion follows the already known mechanism of anaerobic process that involves anaerobic bacteria. Anaerobic process is consisting of four phases that works simultaneously, namely : hydrolysis, acidogenesis, acetogenesis and methanogenesis phase. Figure 2 shows anaerobic digestion phase of sugarcane vinasse wastewater. The process begins with the decomposition of complex organic compound into smaller molecules such as polysaccharide, lipid and protein. The second stage is called hydrolysis, where polysaccharide would be hydrolyzed into glucose, lipid was hydrolyzed into fatty acid, and protein into amino acid. Third phase, acidogenesis, is where glucose degrades into different types of VFA's (acetic, butyric, propionic, etc), ethanol and CO_2. The forth phase is called acetogenesis, where all VFA's change into acetic acid and CO_2. The last phase is methanogenic, where methane, CO_2 and water are the only products left. The type microorganism involved in the anaerobic process was also a mixture of different types of bacteria that follows syntrophic reaction. The dominant microbial community is shifting at each phase, as shown in figure 3 (Zimmerman, 2016).

Table 2 Reviews several methods that are able to treat sugarcanes vinasse wastewater. Better formatting of the table below

Treatment methods	COD in (g/L)	% COD removal (%)	Design Parameter	Type of Application	Ref.
Two stages anaerobic digestion (AD) with sodium hydroxide addition (ph adjustment) and effluent recirculation	- Acidogenesis stage : 84.2 kg-COD m^{-3} d^{-1} - methanogenesis stage= 25 kg-COD m^{-3} day^{-1}	- Acidogenesis stage: 21.2% - methanogenesis stage = 73.9%	HRT 232 days (harvested time)	- Acidogenesis stage : packed bed reactor lab scale - Methanogenesis stage: structured-bed reactors	(Tadeu, Messias, Júnior, Loureiro, & Zaiat, 2017)
Two-stage Anaerobic Membrane Bioreactor	16.706	97	HRT 3.1 – 5.3 days. With two separated acidogenic and methanogenic tank	Membrane bioreactor (MBR) Lab scale	(Santos, Ricci, Neta, & Amaral, 2017)
Single stage Thermophilic UASB	35.2 ± 2.6	71.7	HRT = 34 - 56 hrs	UASB reactor, Lab scale	(Ferraz, Koyama, Araújo, & Zaiat, 2016)
Two-stage Thermophilic UASB	24.0 ± 1.8	90.3	HRT = 32-39 hrs	UASB, Lab scale	(Ferraz et al., 2016)
Combination coagulation flocculation and fenton oxidation	6.836	69.2	1)pH adjustment with NaOH and H_2SO4 2)Coagulant $FeCl_3$, stirring 150 rpm for 3 mins 3)Flocculation = 15 mins, 4)Settling = 20 hrs 5)Fenton $FeCl_3$ + H_2O_2, HRT 3 hrs	Lab scale	(Guerreiro et al., 2016)
Two stage Up flow Anaerobic Filter, with pH adjustment and effluent recirculation	61 – 104	71	Addition of $CaCO_3$ to pH 6, 25% effluent recirculate, HRT 30 days	Two stages UAF, Full scale	(Harihastuti et al., 2021)
Anaerobic digestion using UASB, with Ozonation (AOP) post treatment	120	AD removes 95% to the level COD of 4.5 g/L (as bio recalcitrant color). AOP post treatment removes 80% of the color.	Sludge granules from settled UASB reactor, VFA/Alk = 0.4, pH 7.5 Optimum Ozone dosage of 90 mg/L/ min	UASB, Lab scale	(Otieno & Apollo, 2020)
Ozone, anaerobic, aerobic	39.4	95%	120 mins ozonation followed with aeration and peroxide removal with using a Na_2CO_3 dosage at 20 g L−1 following heating at 90 °C and magnetic stirring for 14 h. Aerobic treatment was using *M. circinelloides*	Lab scale	(Cristiano E R Reis, Bento, Alves, Carvalho, & Castro, 2019)

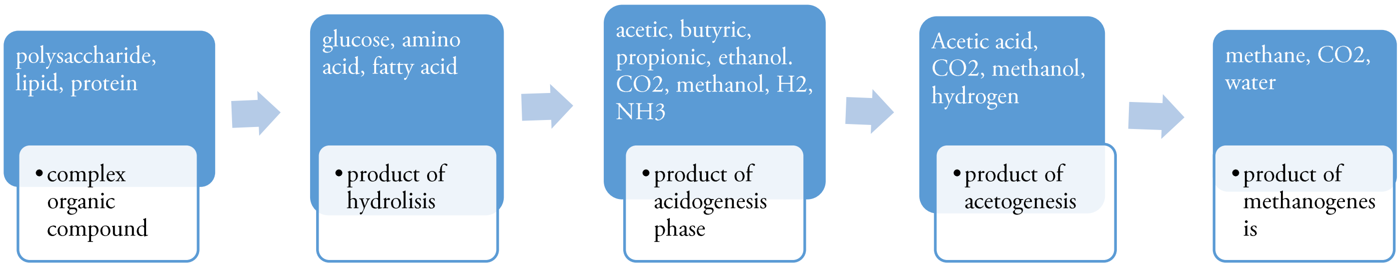

Figure 2. Anaerobic degradation phase of vinasse wastewater

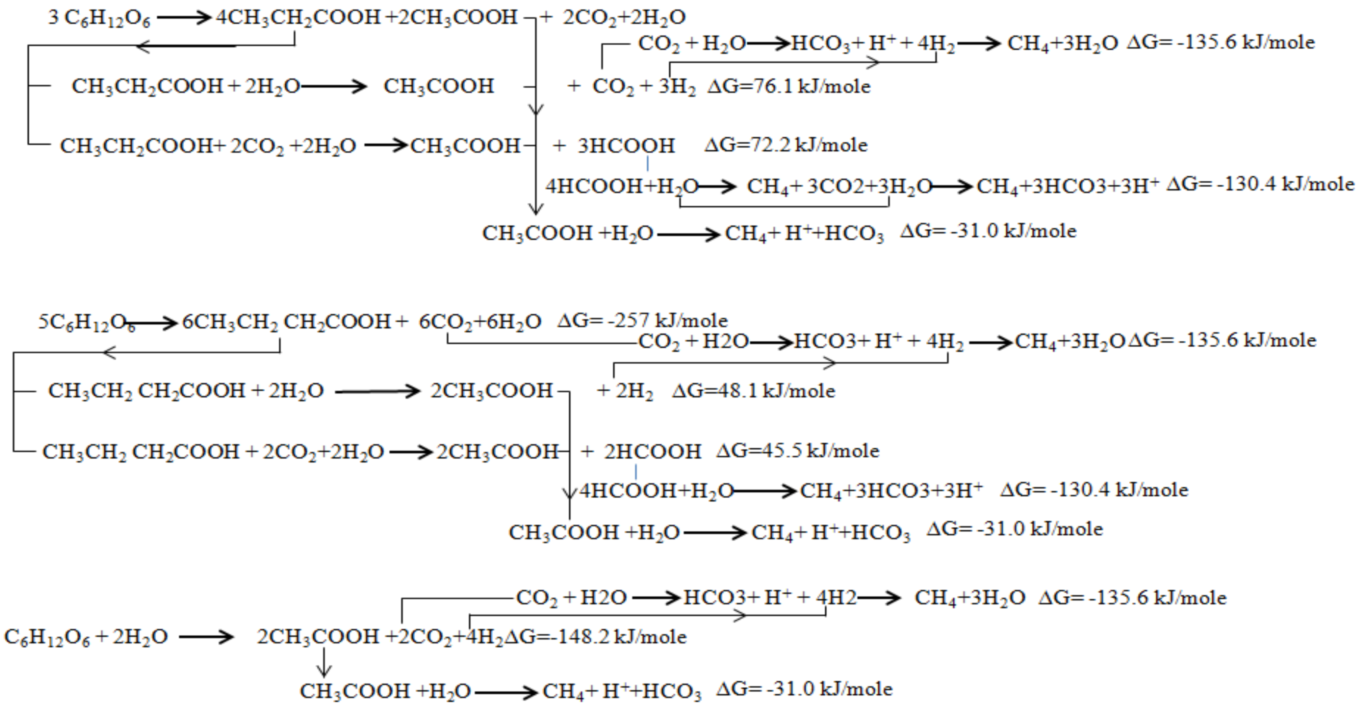

Figure 3. Biological reaction in anaerobic digestion, as referred from Al-mashhadani et.al (Zimmerman, 2016)

6. VINASSE BIOGAS GENERATION

A full-scale application for sugarcane vinasse treatment could be costly due to its high investment of infrastructure. To reduce the cost, utilization of biogas generated from sugarcane vinasse, as alternative energy, could be the better option. Sugarcane vinasse has high methane potential. Approximately, for every 1 m^3 vinasse, 10–26.4 m^3 of biogas could be produced, and equal to1.5–10 kW energy that could power engine-generator with a thermal power of 6.5 kWh/m^3 (Barrera, Spanjers, Dewulf, Romero, & Rosa, 2013; Pazuch et al., 2017). If sugarcane vinasse is converted into bioethanol, from 1m^3 bioethanol, about 115–312m^3 of biogas can be produced, from which 169 kW of energy can be generated (Meyer et al., 2011). The total energy in vinasse is about 18% of the energy produced by bioethanol produced in the plant (Parsaee, Kiani Deh Kiani, & Karimi, 2019). Sugarcane vinasse wastewater has high organic loading, so anaerobic system would be suited to lower down the concentration of organic, as well as utilized by-product biogas for alternative energy, prior treatment using aerobic system to fulfill stream standard. Thus, for full-scale application and to completely treated sugarcane vinasse wastewater with low cost technology, the combination of anaerobic-aerobic treatment technology could be the best option.

Anaerobic technology is still the main tools for vinasse wastewater treatment. However, there are expected conditions that should be met in order to generate maximum biogas production. Nutrients are important due to the low ratio of carbon-to-nitrogen (Moraes, Triolo, Lecona, Zaiat, & Sommer, 2015). The optimum range is reported as being between 25 and 35 for biogas production (Moraes et al., 2015). To modify carbon-to-nitrogen ratio, addition of materials with high carbon-to nitrogen ratio such as bagasse, straw or filter cake could be done(Moraes et al., 2015). Another preferable co-substrate could be domestic wastewater (Tena, Perez, & Solera, 2021a, 2021b), wastewater from biodegradable food beverage industries (Boncz, Formagini, Santos, Marques, & Paulo, 2012) or agriculture waste (Meng et al., 2020; Moraes et al., 2015; Oliveira et al., 2020).

Dilution as a pretreatment is proven to be necessary to lower down the levels of inhibitors, thus it should be maintained. It was shown that vinasse to water ratio of 1:3 produced biogas of 37.409 mL/g COD (Budiyono & Sumardiyono, 2013; I Syaichurrozi & Sumardiono, 2014). Harihastuti, et al (Harihastuti et al., 2021) also proved that theoretical methane yield of diluted vinasse sample (with ratio vinasse to water: 1:4) was higher than undiluted sample. Acidic pH in vinasse wastewater is not an optimum growth condition for methanogenic bacteria, hence the amount of certain level of alkalinity should be maintained to ensure the buffering capacity in wastewater. To enhance the alkalinity, addition of urea is one of the option. In the anaerobic digestion (AD), urea will be converted into OH^- + NH_4^+. However, the urea addition could not higher than C:N : 20-40:1 to prevent process failure caused by ammonia inhibition (Boncz et al., 2012). Beside Nitrogen, the addition of phosphate is also important for the stability of anaerobic digestion system, but the phosphate cannot be directly injected to the system. Therefore, urea, ($CO(NH_2)_2$) and sodium phosphate, (NaH_2PO_4), are added as soluble to optimize nitrogen phosphorus, respectively (Taylor, Siqueira, Damiano, & Silva, 2013). A study conducted by Boncz, et.al,(Boncz et al., 2012) showed that the optimum urea concentration was 0.215 g/g COD for maximum biogas production of 10 L/g COD. Review of key parameters for vinasse degradation process is shown in table 3.

Table 3. Review of key parameters to maximize vinasse degradation process

Key parameters	Range value	remarks	reference
Ratio C/N	20-40 : 1	Above the value can cause ammonia inhibition that lead to reactor failure	(Boncz et al., 2012)
Dilution factor	vinasse : water = 3 : 1	Could lower down the concentration of inhibitors, thus enhance methanogenic activity. Dilution could also lower down the concentration of Total Solid to improve the vinasse biodegradability	(Budiyono & Sumardiyono, 2013; I Syaichurrozi & Sumardiono, 2014)
Effluent recirculation	15% ratio	Effluent recirculation could stabilize pH. Recirculation could be applied after initial addition of alkaline at start up period.	(Fuess, de Araújo Júnior, Garcia, & Zaiat, 2017)
pH	Feed stock has to be pH 6 at minimum by adding alkaline with concentration not more than 4 g/g COD.	Alkaline such as urea ($CO(NH_2)_2$,) and sodium phosphate (NaH_2PO_4) could be used	(Janke et al., 2016)
HRT	10- 40 days	Sufficient HRT range to achieve at least 80% degradation	(Janke et al., 2015)
Co-digested substrate	Addition of bagasse, straw, filter cake, cow manure, sludge	Sludge has typical methanogenic activity of 0.25 – 0.30 mg CH4/g VS	(España-gamboa, Mijangos-cortés, Hernández-zárate, & Maldonado, 2012; Gomes, Barros, Maria, Alves, & Oliveira, 2016)

7. CONCLUSION

This paper reviews the characteristic, the environmental effect, treatment methods, and the key parameters for maximum biogas production from vinasse. Vinasse has high organic load, thus it is one of the main source of industrial pollution that potentially harmful to the environment. Anerobic digestion is still the most effective treatment method for mitigation, because it can produce biogas as renewable energy. To enhance biogas production, key parameters such as : C/N ratio, dilution factor, recirculation, pH, HRT and co-digested substrate should be maintained. To reduce cost and to fulfil the stream standard regulation, the combination of several technologies should be applied for wastewater management strategy.

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