Green House Gases Emission Reduction Potential through Wastewater Utilization in Bioethanol Industry

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Abstract. Bioethanol industry was developed to support renewable energy development. In other side, bioethanol industry has also potential to emit green house gases from their wastewater. Wastewater treatment in bioethanol industry used a conventional biological anaerobic process in an open lagoon that emitted methane to the atmosphere. Methane capturing and utilization as a renewable energy reduced green house gases emission. The objective of this study was to calculate the green house gasses emission reduction from wastewater treatment in bioethanol industries using cassava and molasses as raw materials. Complete Mixed Stirrer Tank Reactors with 50-litre working volume were used to evaluate the COD removal and biogas production potential from vinasse (wastewater from molasses based bioethanol) and thinslop (wastewater from cassava-based bioethanol). The averages of COD removal were 84,55% and 74,11%, respectively for vinasse and thinslop. Biogas production potentials from vinasse and thinslop were 542,12 m^3/kL ethanol and 105,86 m^3/kL ethanol, respectively. Methane concentration in the biogas was practically same for both wastewaters, namely 57,34% for vinasse and 57,0% for thinslop. The biogas from vinasse and thinslop treatment potentially reduces green house gases emission about 4,19 ton CO_2e/kL etanol and 0,82 ton CO_2e/kL etanol, respectively. Biogas utilization to replace coal in ethanol industry reduced GHG emission into 0,213 ton CO_2e/kL ethanol and minus 0,81 ton CO_2e/kL ethanol for cassava-based and molasses-based, respectively.

Keywords: *bioethanol wastewater, biogas,emission, methane, and green house gases*.

1 Introduction

According to UNFCCC (United Nations Framework Convention on Climate Change), there are six greenhouse gases (GHGs) important to be considered including carbon dioxide (CO_2), dinitro oxide (N_2O), methane (CH_4), sulphurhexafloride (SF6), perflourocarbons (PFCs), and hydroflourocarbons (HFCs) [1]. Main source of GHG emission is fossil fuels combustion. Recently, emission of these gases is of interest due to their relation to global warming effect. Accumulation of these gases in the atmosphere acts as a green house that is allowing short waves from solar radiation but becomes a barrier for long waves reflected from earth surfaces. As a consequence, temperature of the earth is increasing globally (just like interior temperature of a car parked in open yard at a sunny day). Therefore, emission of GHGs should be reduced.

As told by the Second National Communication [2], total GHG emission from Indonesia was 1,38 Gton CO_2e and 11% from it was released from waste. Indonesia has targeted to reduce the emission by 41% with increasing CO_2 absorption capacity by reforestation program, deforestation reduction, peat land management, mix energy program, and waste management. The last was performed with 3R (reuse, reduce, and recycle) principle. Waste becomes important source of GHG emission because it produces CH_4 during its anaerobic decomposition. Global Warming Potential (GWP) or global warming index of CH_4 is 21 meaning that every unit of CH_4 will affect 21 times as much effect of CO_2. Methane has contributed to GHG effect of around 15-20%. On the other side, CH_4 has a great economic value due to its energy value that can be used as a renewable fuel. One of important methane sources is wastewater from many agriculture-based industries, including bioethanol industry.

Bioethanol industry was developed to support renewable energy development. To produce ethanol, the industry used either cassava or molasses feedstock. Bioethanol industry has potential to emit GHG from their wastewater. Every liter of ethanol being produced, 17-25 liter of wastewater is released. Wastewater treatment using a conventional biological anaerobic process in open lagoons emits methane to the atmosphere. This becomes environment problem if wastewater is improperly treated [3]. Generally speaking, agro-based industries use a lot of water for production process and therefore they also release a lot of wastewater [4]

Wastewater from bioethanol industry has a great potential to lower environment quality and to hassle biological ecosystem. This is caused by high COD value of the wastewater. Thinslop, that is wastewater generated by cassava-based bioethanol industry, has a chemical oxygen demand (COD) of around 35.000-50.000 ppm [5]. Using molasses as raw material, bioethanol industry produces wastewater, called vinasse, having Biochemical Oxygen Demand (BOD) of around 35.000-50.000 mg/L and COD of around 100.000-150.000 mg/L [6]. High COD value of vinasse and thinslop implicate high content of organic matter in the wastewater which is good source of carbon. In the anaerobic pond, organic compound will be decomposed into CH_4 and CO_2 that can be recognized with the decrease in COD value of wastewater.

This research was point out to evaluate the GHG emission reduction potential of wastewater treatment while producing biogas in bioethanol industry. The research was also intended to investigate the possibility of using biogas digester as a mean to mitigate GHG emission in bioethanol industry.

2 Materials and Methods

Thinslop and vinasse were received from PT. Medco Ethanol Lampung, an ethanol producer operated at North Lampung. The wastewaters were characterized by their pH and COD (chemical oxygen demand) values. The COD measurement was based on the SNI number 06-6989.2-2004. A stainless steel vessel of 50 L capacity equipped with a stirrer was used as anaerobic reactor to study COD removal and biogas production using different substrates: thinslop and vinasse.

Sludge of wastewater as much of 14,5 L was introduced into the vessel. Adaptation stage was performed by removing 1 L of wastewater in the vessel and replacing it with a new one. This was performed daily till the pH has already stable at 6,5-7,5. Methane forming is initiated by organic acids production. The acids tend to increase acidity of the substrate (lower the pH value). Methanogenic bacteria are highly sensitive to the pH changes and the optimum pH for the growth of methanogenic bacteria is aroud 6-8 [7]. For experiment using vinasse substrate, COD load was 2,0 g/L per day. However, to avoid shocks, the addition of wastewater was started from COD load of 0,5 g/L per day for a week and increased by 0,5 increment each week till COD load was 2,0 g/L per day. From this time forward, new substrate was added at an equal quantity to the substrate removing from the reactor. Similar experiment was performed using thinslop substrate.

Temperature of anaerobic process was measured daily. The same was done for pH measurement of spent sludge. COD measurement of spent substrate was done every another day. Gas analysis was performed every week. Methane fraction in the biogas analyzed using gas chromatograph (GC Shimadzu 2014) with TCD detector and Shincarbon column (ST 50-80 D-1794). Biogas production was estimated from methane fraction [CH_4] using the following equation:

$$\text{Biogas} = \frac{0{,}35 \times \text{COD}_r}{[\text{CH}_4]} \quad (1)$$

where biogas production was presented in m^3, COD_r is COD removal; 0,35 is a conversion factor of CH_4 yield (m^3) per kg of COD removal [8].

Green house gas reduction potential (REP) of CH_4 was calculated as the following:

$$REP = BP - PE \qquad (2)$$

where BP is baseline emission, that is emission value without utilization, and PE is project emission, that is emission value with utilization. Baseline emission (in CO_2e) is equivalent to emission potential of CH_4. The value of PE was calculated assuming that emission during anaerobic digester project is 10% [1].

3 Results and Discussion

Table 1 showed wastewater characteristic using in our experiment. Even though there was no significant difference of pH value, a big different of COD value of the substrates was observed. Vinasse had a COD value of 105.000 mg/L, much higher as compared to 28.233 mg/L for thinslop. This implicated a high content of organic matter in the vinasse.

Table 1 Wastewater characteristic based on feedstock type used in bioethanol industry.

Feedstock (Wastewater)	pH	COD (mg/L)
Cassava (Thinslop)	4,30-4,80	28.233
Molasses (Vinasse)	4,99-5,00	105.000

During experiment it was observed that outlet temperature was 28,5 ^oC and outlet pH was 7,53 using thinslop substrate. Using vinasse substrate, outlet temperature was 27 ^oC and outlet pH was 7,60. This condition was favorable for methanogenic bacteria which grow up best in the range of 25-40 ^oC and pH of 7-8.

Figure 1 showed the COD value of inlet and outlet of wastewater, both for thinslop and vinasse. Whilst, Figure 2 revealed COD load and COD removal during experiment, both using thinslop and vinasse. Chemical oxygen demand is defined as a quantity of oxygen required in order organic matter in the wastewater is oxidized chemically. The main products of fermentation process (acetate, hydrogen, and carbon dioxide) are precursor for methane formation. Vinasse was thicker with COD value of much higher than thinslop and therefore is more difficult to decompose. The COD outlet vinasse substrate was relatively high, 36.883 mg/L. At COD load of 2 g/L.day, average COD removal for vinasse was 1,48 g/L.day or 74,11%. High content of organic matter decreased the effectiveness of microorganism to degrade organic compound in the wastewater. On the contrary, COD value for thinslop outlet was 4.362 mg/L.

Average COD removal for thinslop substrate was 0,596 g/L.day or 84,55% at COD load of 0,706 g/L.day. The different of COD removal was also influenced by COD load. High COD value combined with high COD load of vinasse has resulted in a slightly lower COD removal as compared to those of thinslop. In both cases, optimum condition for anaerobic fermentation was achieved.

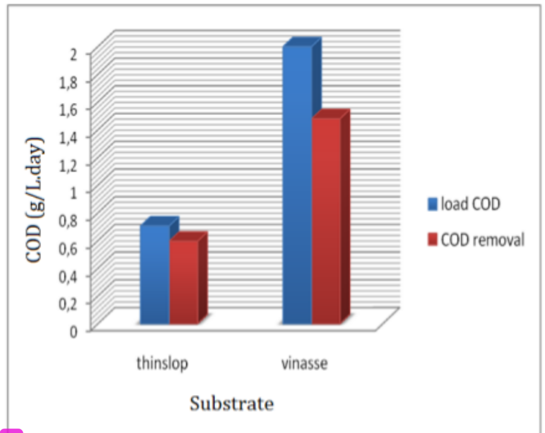

Figure 1 COD load and COD removal (g/L.day) for thinslop (0,706 and 0,596) and vinasse (2,00 and 1,48).

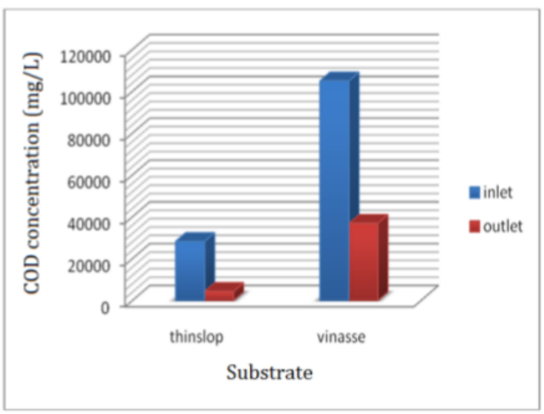

Figure 2 Average COD value (mg/L) of thinslop and vinasse at the inlet and outlet of wastewater treatment.

3.1 Emission Reduction Potential

Emission reduction potential was calculated based on bioethanol industry working at a capacity of 180 KLPD (kilo liter per day) of ethanol. This industry may use cassava tuber at a rate of 1.200 ton/day or molasses, by product from sugar industry, at a rate of 700 ton/day [5]. It was observed that producing 1 kL ethanol required 6,48 ton of cassava tuber with 7,22 m^3 thinslop, or 3,89 ton of molasses with 11,40 m^3 vinasse. Table 2 demonstrated emission potential at bioethanol industry based on feedstock used. The first choice will generate 1.300 m^3 thinslop daily with COD load of 36.703 kg/day. Using COD removal of 84,4% and a factor of 0,35 m^3 CH_4 per kg COD removal, this thinslop is possible to produce CH_4 at a rate of 10.861 m^3/day or 60,34 m^3/kL of ethanol. The second option generates 2.053 m^3 vinasse with COD load of 215.565 kg/day having potential to produce CH_4 at a rate of 55.914 m^3/day or 105,86 m^3/kL of ethanol.

Table 2 Calculation for emission potential from thinslop and vinasse treatment at a bioethanol industry with capacity of 180 KLPD.

Description	Unit	Type of wastewater	
		Thinslop	Vinasse
Raw material (feedstock)		Cassava	Molasses
Flow rate	m^3/day	1.300	2.053
COD input	g/L	28,23	105,00
COD load	kg/day	36.703	215.565
COD removal (COD_r)	%	84,55	74,11
	kg/day	31.032	159.755
Conversion factor of COD_r to CH_4 [d)]	m^3 CH_4/kg COD_r	0,35	0,35
CH_4 potential	m^3/day	10.861	55.914
	m^3/kL ethanol	60,34	310,63
CH_4 consentration	%	57,00	57,34
Biogas potential	Nm^3/day	19.055	97.582
	Nm^3/kL ethanol	105,86	542,12
CH_4 mass rate	ton/day	7,76	39,94
GWP CH_4 [c)]		21,00	21,00
Emission potential of CH_4 (BE)	ton CO_2e/day	162,96	838,74
	ton CO_2e/kL ethanol	0,91	4,66
Emission project (PE)	%	10	10
Reduction emission potential (REP)	ton CO_2e/day	146,63	759,95
	ton CO_2e/kL ethanol	0,82	4,19

It was observed that methane concentration was almost same for both substrates, specifically 57% using thinslop and 57,34% using vinasse. This meant that equivalent biogas potentially produced from thinslop and vinasse was respectively 19.055 and 97.582 m^3/day. Our calculation resulted that

GHG emission potential from thinslop and vinasse was 0,91 ton CO_2e/kL ethanol and 4,66 ton CO_2e/kL ethanol, respectively. It was surmised that producing bioethanol from molasses potentially emit GHG 5,14 times as much of those from cassava (Figure 3).

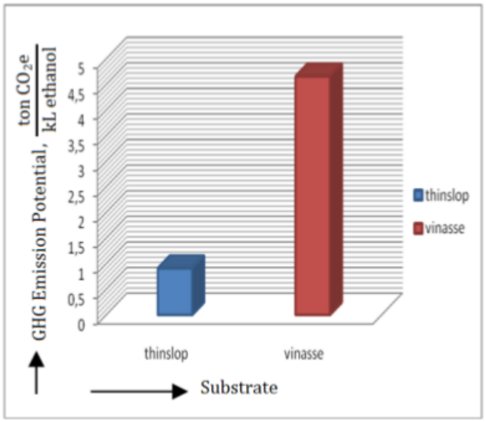

Figure 3 GHG potential emission (ton CO_2e/kL ethanol) from thinslop and vinasse treatment.

Project emission for anaerobic digester was assumed to be 10% [1]. Based on this assumption, proper thinslop treatment is capable to reduce GHG emission by 146,63 ton CO_2e/day or 0,82 ton CO_2e/kL ethanol in the cassava-based bioethanol industry with a capacity of 180 KLPD. Similarly, vinasse management is potentially reduce GHG emission by 759,95 ton CO_2e/day or 4,19 ton CO_2e/kL ethanol for molasses-based bioethanol industry. It is concluded that wastewater management is significant to reduce GHG emission.

3.2 GHG Emission Reduction in Bioethanol Industry

Generally, bioethanol industry uses coal to generate electricity required in production process. Our observation noted that cassava-based bioethanol industry with 180 KLPD capacity required 3,1 MW electricity power. According to West and Marland [9], emission factor for coal-bsed power plant was 0,282 kg C/kWh or 1,034 kg CO_2e/kWh. Thus, GHG from cassava-based ethanol industry was 76,93 ton CO_2e/day or 0,427 ton CO_2e/kL etanol. One way to reduce GHG emission is treating wastewater to produce biogas and subsequently utilize the biogas as fuel to generate electricity. Based on calculation presented in Table 2, biogas from thinslop treatment was expected to replace coal of about 50% at a conversion efficiency of 35%. This meant GHG emission can be reduced to 38,46 ton CO_2e/day or 0,213 ton CO_2e/kL ethanol.

Producing ethanol from molasses required little lower energy, that was 2,1 MW for the same capacity. Similar calculation was performed for molasses-based ethanol industry. The results revealed that GHG emission was 52,10 ton CO_2e/day or 0,289 ton CO_2e/kL ethanol. The biogas potential from vinase, however, was higher and able to excess power of 5,87 MW. Hence, the utilization of biogas in the industry can entirely replace coal. The excess power potentially reduce GHG emission into minus 145,70 ton CO_2e/day or minus 0,81 ton CO_2e/kL ethanol (Figure 4).

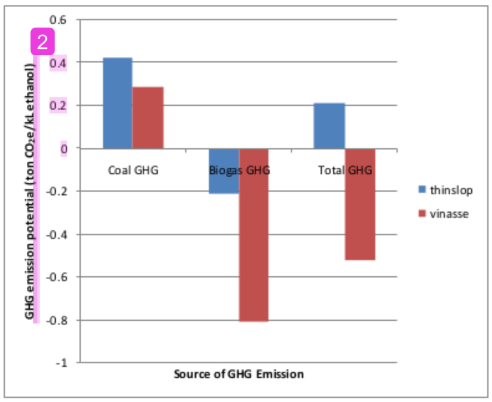

Figure 4 GHG emission comparison between cassava- and molasses-based ethanol industry.

Molasses-based ethanol industry required less power for production process than that of cassava-based one. Furthermore, utilization of vinasse to produce biogas had a great potential as renewable fuel and for reducing GHG emission. From this point of view, molasses-based ethanol industry was more attractive than cassava-based one.

4 Conclusion

1. GHG emission potential from wastewater treatment in bioethanol industry was 4,19 ton CO_2e/kL ethanol with molasses feedstock and 0,82 ton CO_2e/kL ethanol with cassava feedstock.

2. Wastewater utilization to produce biogas as renewable fuel to replace coal in ethanol industry reduced GHG emission into 0,213 ton CO_2e/kL ethanol and minus 0,81 ton CO_2e/kL ethanol for cassava-based and molasses-based, respectively.

5 Acknowledgements

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