Research article

Effects of Air Injection and Iron Oxide Pellet Addition on Hydrogen Sulfide Removal and Biogas Production

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Abstract Hydrogen sulfide (H_2S) in biogas resulting from anaerobic digestion process is unwanted trace compound, because it is toxic and can corrode biogas engine. This study aimed to compare the 2 desulfurization methods, air injection and iron oxide pellets addition, on H_2S removal and quantity and quality of biogas. The experiment was carried out with two floating drum digesters (1 m^3 each) constructed at Royal University of Agriculture, Phnom Penh, from January to August 2020. Three levels of air injection at 2%, 4%, and 6% of O_2 regarding the daily biogas production and iron oxide pellets application at 1 kg, 2 kg, and 4 kg per m^3 of biogas were applied to remove H_2S in biogas from different raw materials of pig manure and food waste. The amount of daily biogas production was quantified by gas flow meter, also gas quality was measured using a GEM5000 gas analyzer. The experimental results indicated that food waste had higher daily biogas production comparing to pig manure in both desulfurization methods. Biogas from food waste increased from 544 L d^{-1} without iron oxide pellets addition (0 kg) to 657 L d^{-1} with 4 kg iron oxide pellets addition; and to 566.5 L d^{-1} with 2% of injected O_2. To the contrary, desulfurization for pig manure with 2% of O_2 and 1 kg of iron oxide showed high daily biogas yield of 348 L d^{-1} and 340 L d^{-1}, respectively. For raw materials of pig manure, in both desulfurization methods, had higher CH_4 content than food waste. Air injection was more effective in H_2S removal than iron oxide for both substrates, but higher level of H_2S reduction was observed with pig manure. Accordingly, it was concluded that desulfurization methods with air injection and iron oxide pellets addition were effective in biogas production as well as H_2S removal, but a clear trend appeared in the raw material of food waste.

Keywords floating drum digester, anaerobic digestion, food waste, pig manure, H_2S removal

INTRODUCTION

Biogas is a product generated from the anaerobic digestion of organic substances by appropriate microorganisms through four metabolic stages; namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Dumont, 2015). It is considered one of the renewable energy sources that can provide both heat and electricity for use in households, in farms, or in industries. Gas compositions contained in biogas include methane (CH_4), carbon dioxide (CO_2), and other trace elements such as ammonia (NH_3), water vapor (H_2O), and hydrogen sulfide (H_2S). The majority of them are CH_4 (60-70%) and CO_2 (30-40%) (Okoro and Sun, 2019), but the only energy source is CH_4, which has both benefits and drawbacks. If released into the atmosphere unused, CH_4 is a greenhouse gas which has 28 times more powerful than CO_2, which actually accelerates global warming (National Geographic, 2019). When burned or used for internal combustion engine, its harmful effects are reduced and at the same time, its beneficial energy can be harnessed. Nevertheless, the presence of H_2S in biogas may causes problems in terms of health hazard and economic aspects (Pinate et al., 2017).

H_2S is an unwanted gas mixed in biogas because it is toxic to humans at low concentrations and corrosive to engines. High concentrations of H_2S can corrode engines or metal parts, and lead to faster degradation of engine lubricant oil. A maximum recommended level for generator operation ranges from 200 to 500 ppm (Rodrighez et al., 2014). If it is used without treatment, oil lubricants must be changed more often, or the lifespan of a generator is reduced, resulting in high investment and operating costs. Furthermore, H_2S limits for gas heating boilers, combined heat and power (CHP), fuel cells, and national gas upgrade are 1,000, 1,000, 1, and 4 ppm, respectively (Choudhury et al., 2019). However, different substrates used for biogas production produce different concentrations of H_2S. Substrates that contain high-level protein produce higher H_2S content than those contain carbohydrate and lipid due to the presence of more sulfurous elements in it. Biogas produced from organic waste may contain H_2S in the range of 10-20,000 ppm, but about 10-40 ppm is found in biogas produced from sewage and 50-300 ppm from landfill (Dumont, 2015). Moreover, Huertas et al. (2020) stated that H_2S produced from organic waste such as pig manure can be as high as 30,000 ppm.

To reduce its concentration to an acceptable level, desulfurization techniques can be applied physically, biologically, and chemically. Biologically removal is done by air injection into digester with regulated amounts of oxygen (O_2) between 0.3 and 3% of produced biogas; however, this reaction may result in sulfur build-ups in the digester space (Hines et al., 2019). Many kinds of chemical methods have been studied. Pinate et al. (2017) proposed a small batch test for H_2S removal by absorbent granules soaked in ferric chloride ($FeCl_3$) and in sodium hydroxide solution (NaOH), the removal efficiency was around 90%. Zulkeflia et al. (2016) stated that H_2S removal could be done by activated carbon soaked in NaOH, potassium hydroxide (KOH), and potassium carbonate (K_2CO_3), but added that the last chemical element was the most effective. Biological H_2S removal methods are also increasing popular and considered highly effective. Those biological methods include biofilters, biotrickling filters, bioscrubbers, and activated sludge (Barbusiński and Kalemba, 2016). However, H_2S removal techniques are limited, or have not been well documented in Cambodia, which makes it difficult for promotion of biogas use inside the country. Therefore, proposing an applicable desulfurizing technique is highly valuable for economic reasons.

Pig manure is a major waste from animal productions in Cambodia. According to MAFF (2020), the number of pigs was around 2.18 million heads in 2019 of which more than half raised in commercial farms. On the other hand, kitchen waste amounted from 63.30% to 80.46% of all solid wastes from households (Sour, 2017). Proper management of these two wastes by converting them to biogas will provide both environmental and economic benefits.

OBJECTIVE

The objectives of this study were (1) to compare the effects of air injection and iron oxide pellets on H_2S removal and quantity and quality of biogas produced from two different substrates, food waste and pig manure; and (2) to identify relations between biogas production with CH_4 content in the two substrates.

METHODOLOGY

This research was conducted at the pilot biodigesters belonging to the Biogas Technology and Information Center (BTIC), at the Royal University of Agriculture, Cambodia, starting from January to August 2020. Two floating drum biodigesters (1 m^3 each) were used for this experiment. Two different substrates, food waste and pig manure, were daily fed into the systems. At its full production, biogas was then treated by two desulfurizing methods: air injection and iron oxide pellets. Air injection was applied directly into the gas holders (the floating drum) on top of the digesters at O_2 levels of 2%, 4%, and 6% of daily produced biogas. Meanwhile, iron oxide pellets were placed in a gas treatment container through which raw biogas was passed through and treated before being quantified. The levels of iron oxide pellets were applied at 1, 2, and 4 kg m^{-3} of daily produced biogas. Effectiveness of the desulfurizing methods was also determined by comparing the results with raw untreated biogas.

Materials

Two floating drum biodigesters used in this experiment had concrete bases and walls constructed under the ground. The whole volume was 1 m^3, one third of which was for gas storage. The gas holders were high-grade polyethylene plastic water tanks that were cut in half and used as covers for the digesters. They can move up and down, depending on the biogas pressure produced inside.

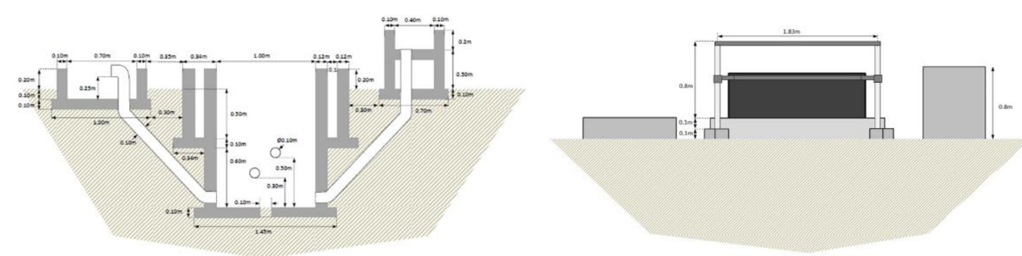

Fig. 1 Technical drawing of a floating drum biodigester used in this experiment

Substrates used in this experiment were food waste and pig manure. Their physical and chemical properties were analyzed in advance. Still, there might be some variations due to everyday fresh collection of the substrates. To reduce errors, substrate collection was done at the same place throughout the experimental period.

Food waste was daily collected from the university canteen. It contained 21.9% dry matter, 1.4%

ash, 5.6% protein, 3.2% lipid, and a C/N ratio of 12.6:1. For high efficiency, bones and other organic materials that were slowly biodegradable were removed. Before being fed into the digester, food waste was thoroughly mixed with water at a ratio of 1:1, or 5 kg each. Pig manure used in this experiment was collected from two small-scale pig farms nearby the university. It contained 25% dry matter, 8.1% ash, 10.4% protein, 0.5% lipid, and a C/N ratio of 6:1. It was freshly collected, mixed with water, and fed into the system on daily basis at a ratio of 1:1, or 5 kg each.

Sampling Methods

Feeding time was done in the morning and repeated regularly every day for 30 days, which was assumed as a minimum hydraulic retention time (HRT) for the digesters. Then, volume of untreated biogas was measured for 7 days to determine average daily biogas production, followed by air injection, which lasted 7 days for each O_2 level. In total, the whole process of air injection lasted one month. After this process was completed, the untreated biogas was measured another 7 days before application of iron oxide pellets in filter for H_2S removal. Experiments with each level of iron oxide lasted 7 days, which took 1 month in total. The iron oxide pellets used in the experiment were proprietary ones which had been imported from China.

To measure the quality of biogas produced from the two substrates, a GEM5000 gas analyser was utilized. It was a product supplied by Geotech, UK, and was capable of measuring biogas quality such as CH_4, CO_2, and O_2, all in percentage; and H_2S in ppm with the maximum concentration of 5,000 ppm. Biogas quality was measured three times a day for each treatment after it was treated with air injection a day before, or went through the desulfurizing container on the day of the measurement.

To quantify daily biogas production, a gas flow meter was used. When the biogas was used for boiling water, the flow meter started to record the consumption at the average outdoor temperature of 28-33 ℃.

Data Analysis

Analysis of Variance (ANOVA) were used for the data analysis, and when significant differences were observed, a post-hoc LSD-test was then used to show significant differences among the treatments at $\alpha = 5\%$. Besides that, the data for air injection and iron oxide pellets were presented separately because the experiments were done separately.

RESULTS AND DISCUSSION

Daily Biogas Production

Daily biogas production was compared among the two substrates, when treated with air injection at different levels of O_2 (Fig. 2a). Significant differences were detected among the treatments, and it was observed that biogas produced from food waste was higher than from pig manure. Daily biogas quantity was similar for both substrates, when measured without application of air injection. It was about 484 L d^{-1}. For food waste, daily biogas production increased slightly with 2% of injected O_2 to almost 500 L d^{-1}, but decreased continuously at O_2 levels of 4% and 6%. Similar results were obtained for pig manure. Daily biogas quantity decreased more and more, as levels of air injection increased. Daily biogas production from pig manure was 384, 260, 227 L d^{-1} at injected O_2 levels of 2%, 4%, and 6%, respectively. This finding indicates that putting more air into the digester may affect biogas production because its ideal condition is anaerobic. Hines et al. (2019) proposed a maximum air injection level of 3%.

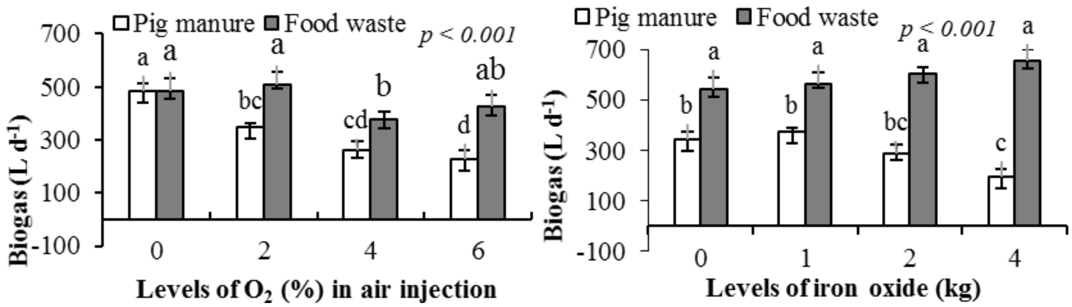

Fig. 2 Comparison of biogas production with air injection (a) and with iron oxide pellet (b)

Daily produced biogas quantity was compared among the two substrates when using iron oxide pellets (Fig. 2b). It was not affected by different levels of pellet, but by different substrates. Higher daily biogas production was observed with food waste at all levels of applied iron oxide pellets. Its average value was 585 L d^{-1}. In contrast, daily biogas production from pig manure was quite low, averaging 320 L d^{-1}. Moreover, it was surprising to see the lowest daily biogas production with 4 kg of iron oxide pellets. The reason why biogas quantity was higher for food waste used as a substrate because it contained more lipid. Lipid has more carbon atoms than protein, thus producing more biogas (Morales-Polo et al., 2018).

Methane Content

CH_4 content contained in biogas was compared among the two substrates with air injection at different levels (Fig. 3a). It was found that there were significant differences among the treatments and CH_4 content was higher for pig manure, when compared with food waste. CH_4 fluctuated for pig manure at different levels of inject O_2; however, the average value ranged from 57 to 61%. Meanwhile, CH_4 content for food waste increased, as the levels of O_2 increased. The highest value was only around 56%. Similar results were found for food waste when iron oxide pellets were applied at different levels (Fig. 3b). CH_4 increased, as the amounts of pellets increased for both food waste and pig manure. Still, the average value was 60% for pig waste and 56% for food waste.

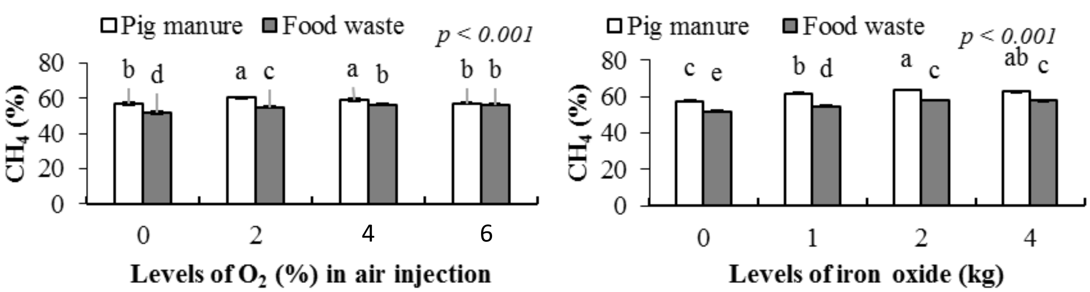

Fig. 3 Comparison of CH_4 content with air injection (a) and with iron oxide pellet (b)

Hydrogen Sulfide Content

H_2S cotent was compared between the two substrates under different levels of injected O_2 (Fig. 4a). Significant differences in H_2S was observed among the treatment, and the higher level of O_2 was injected, the more H_2S was reduced. Greater H_2S reduction was observed with the use of pig manure. Without air injection, the level of H_2S was 840 ppm and 1,000 ppm for pig manure and food waste, respectively. this level decreased sharply for pig manure, as levels of injected O_2 increased. H_2S

content was 522 ppm at O_2 level of 2%, and decreased to 351 ppm at 4% and then to 271 ppm at 6%. For food waste, H_2S content decreased from 923 ppm at O_2 level of 2% to 626 ppm at 4%, and then slighly increased to 674 ppm at 6%. Higher levels of injected O_2 reduced H_2S, but also affected overal biogas production (Fig. 2a). Thus, it should be applied at recommended levels only. Nevertheless, different levels of pellets did not affect H_2S content, but different substrates did (Fig. 4b). It was observed that H_2S content for pig manure was higher than for food waste, and varied greatly from about 800 to over 3,000 ppm, though treated with high levels of iron oxide pellets. Such unsual increase was due to using pig manure from a different, as the first one emptied the barns. However, a tendency for H_2S removal was observed at 4 kg of pellets, as H_2S decreased to above 2,500 ppm. For food waste, iron oxide did not affect H_2S content, and its average ranged from 1,000 to 1,100 ppm.

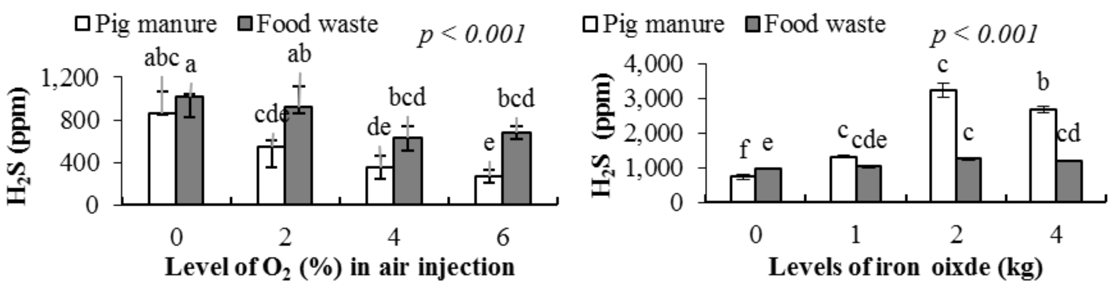

Fig. 4 Comparison of H_2S reduction by air injection (a) and by iron oxide pellets (b)

CONCLUSION

Pig manure and food waste were fed into two floating drum digesters for biogas production and inspection of biogas quality, along with H_2S removal techniques by air injection and ferrous oxide pellets. It was observed that food waste produced more biogas than pig manure, but less CH_4 content. H_2S contents were similar for both substrates, and the use of air injection tends to be more effective than ferrous oxide in this study.

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