Codigestion of Press Mud and Distillery Waste Water with Sugarcane Bagasse for Enhanced Biogas Production

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Keywords: biogas, methane, anaerobic digestion, distillery wastewater, codigestion

Abstract**.** Anaerobic co-digestion was carried out at mesophilic condition (37°C) in 1-L media bottles with a working volume of 800 mL consisting of different dilution ratio of distillery wastewater (DWW), press mud, bagasse, and inoculum. Distillery waste water was diluted with tap water at two different ratios (2:3 and 3:2) and in two sample bottles, micronutrients were added. Batch test results showed that press mud mixed with diluted distillery wastewater with and without additional micronutrients gave the highest methane yield of 61.3% and 78.23% (v/v), respectively. Methane yield is affected by the sensitivity of microorganisms to pH variations. In this study, optimum pH was found out to be 5.0 to maximize methane yield. COD/BOD ratio was also evaluated and the optimum initial COD to BOD ratio of the sample that yields higher methane yield ranged from 1.8 to 2.6 which indicate that it is amenable to biological treatment. Meanwhile, the optimum C/N ratio is found to be in the range of 72:1 and 78:1. For the effect of dilution, higher methane yield occurred at higher dilution ratio. Moreover, anaerobic co-digestion of organic sugar waste was more favorable in biogas production compared to mono-digestion of a single biomass. Lastly, effect of micronutrients to the digestion and heterotrophic plate count were evaluated in this study.

1 INTRODUCTION

Biogas, the gas produced when organic matter of animal or plant ferments in an oxygen-free environment, occurs naturally in swamps and spontaneously in landfills containing organic waste. It can also be induced artificially in digestion tanks to treat sludge, industrial organic waste, and farm waste (Igoni and Jha Zhao, 2008). Biogas primarily consists of methane (CH_4) and carbon dioxide (CO_2), with varying amounts of water, hydrogen sulfide (H_2S), oxygen gas, and other compounds. Millions of cubic meters of methane in the form of swamp gas or biogas are produced every year by the decomposition of organic matter, from both animals and plants. A growing concern nowadays is the increasing amount of sludge produced from wastewater treatment (Yan and Wolf, 2015). At this time, the costs connected with sludge treatment and disposal may account for up to 60% of total operation cost of wastewater treatment. Treating various organic wastes, anaerobic digestion is used to transform organic substrates and wastes into energy (biogas) and a stabilized fertilizer (digestate). For anaerobic digestion (AD) to be economically viable, a continuous supply of homogeneous feedstock is required, which is not always possible in some regions due to increased demand for waste and varying waste composition. Consequently, there is a need for feedstock co-digestion, in order to avoid fluctuations in feedstock composition balance and availability (Lindorfer, Ahring and Verstraete, 2003). The anaerobic co-treatment of organic wastes, known as co-digestion, is not normally found in sugar plants, although it is a common practice with agro-industrial wastes (Mata-Alvarez and Rajoka, 2014).

Several research studies have been conducted to study the efficiency of the anaerobic digestion of sugar waste mixture. In one experiment (Agrawal and Barrington, 2016), the sample filter mud from the sugar mill which had a dry matter content of 315

C. Almendrala, M., Carlo T. Evidente, R., Marjorie C. Legarde, J. and Ray S. Pamintuan, K.
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DOI: 10.5220/0008692000460051
In *Proceedings of the International Conference on Future Environment Pollution and Prevention (ICFEPP 2019)*, pages 46-51
ISBN: 978-989-758-394-0

g per kg produced a methane content of 51.7% from 162.5 L of biogas sample. In the study conducted by (Budde *et al.*, 2014), the highest increase in methane yield (up to 63%) compared to the untreated press mud was found at a pre-treatment of 20 minutes in liquid hot water. In the study about reaction kinetics, about 160 mL of SMMW loadings with a substrate concentration of 48.3 g COD/L were carried out in a 1-L anaerobic digester wherein the specific rate constant was observed to be decreasing from 1.76 day-1 to 0.05 day-1 when the loading is increased from 40 to 140 mL, indicating an inhibition phenomenon (López González, Pereda Reyes and Romero Romero, 2017). Hence, co-digestion process is kinetically much faster than sole press mud or distillery waste water digestion.

Different research studies have shown that mixtures of agricultural, municipal and industrial wastes can be digested successfully and efficiently together. This is due to the directive of minimization of landfill and calling for reuse and recycle of various wastes by the new waste management policies, and the eagerness for extraction energy from waste including sewage wastewater to ease up the dependence on energy from fossil fuels (Chynoweth and Kim, 2009). However, no study in the writings was found on co-digestion of press mud with molasses-based distillery wastewater with bagasse. No articles have studied the dilution of distillery wastewater as co-substrate in anaerobic digestion of pre-treated press-mud. Effect of micronutrients and immobilization on methane yield were not also discussed in several literatures.

The main objective of this study is to determine the effects of co-digestion of hot alkali pre-treated sugarcane press-mud and distillery wastewater solution with bagasse on methane yield. The specific objectives are: (1) to compare the methane yield of diluted distillery wastewater co-digested with press-mud to that of pure distillery wastewater, (2) to determine the physico-chemical characteristics of the final digestate (pH, TSS, COD, BOD, and its microbial characteristics), and (3) to determine the effect of added nutrients to anaerobic digestion. It is hoped that the findings will contribute to the understanding of the factors that affect the full exploitation to produce high yield of biogas. It is also intended that the findings will be used to enhance large scale biogas production from co-digestion of press mud, distillery waste water and bagasse which in turn can be used to generate energy for combined heat and power.

2 METHODOLOGY

2.1 Materials

Molasses-based distillery wastewater (DWW), press mud, bagasse, and yeast were collected from Central Azucarera de Tarlac, in San Miguel, Tarlac City, Philippines. All reagents, which mostly served as the micronutrients for the substrate, were obtained from the Chemistry Laboratory Office of Mapua University. Distilled water was used to dissolve glucose, yeast, and micronutrients. Fresh cow manure which was gathered from a farm in YGGACC HAI Farms in San Pedro, Laguna, Philippines served as the inoculum and was stored in plastic bags. Cow manure was incubated in anaerobic condition for one week before use.

2.2 Pre-treatment

The press mud was pre-treated by two-step hydrolysis before mixing with the distillery wastewater solution. For the experiment, approximately 1108.8 g of press mud was soaked in 1.0 L of low concentration of alkali solution, 62.0 mEq of $Ca(OH)_2$/L, for 15 hours. The alkali hydrolysate was then heated up to the boiling point for about 20 minutes, followed by the addition of distillery wastewater solution (pre-heated to ~100□) and about 100 cm^3 of chopped sugarcane bagasse. The mixture was allowed to cool below 50□ before adding the micronutrients solution containing glucose (30 g/L), dry yeast (5 g/L), NH_4Cl (2g/L), KH_2PO_4 (0.5 g/L), $MgSO_4 \cdot 7H_2O$ (0.3 g/L), $MnSO_4 \cdot 7H_2O$ (0.02 g/L), $FeSO_4 \cdot 7H_2O$ (0.02 g/L), NaCl (0.02 g/L), $CuSO_4 \cdot 5H_2O$ (0.02 g/L), $CoCl_2 \cdot 6H_2O$ (0.02 g/L), and $ZnSO_4 \cdot 7H_2O$ (0.02 g/L).

2.3 Experimental Design

Anaerobic digestion batch experiments were conducted in 1-L media bottles. All batches were prepared using 300 mL of pre-treated press mud mixed with 200 mL of distillery wastewater solution and 100 cm^3 of bagasse. The control batch (A) was prepared using pure distillery wastewater. Distillery wastewater was diluted with tap water in 3:2 and 2:3 volume ratio for the batch experiments with and without micronutrients. Macronutrients were added in batches B and C: 30 g/L glucose and 5 g/L dry yeast. In each batch, 200 cm^3 of cow manure was added in the prepared media. Details of each batch composition is shown in Table 2. To ensure anaerobic condition, the system was purged with nitrogen gas (Figure 1) for 15 minutes. For the gas collection, a 2-L urine bag was connected to each media bottle (Figure 1). All experiments were carried out at room temperature for a digestion period of 30 days.

2.4 Measurement of Physico-chemical Properties of Digestate and Biogas

Table 1: Composition of experimental batches used

Batch	Distillery wastewater (mL)	H_2O (mL)	Nutrients added	Pre-treated press mud (mL)
A	200	0	Yes	300
B	120	80	Yes	300
C	80	120	Yes	300
D	120	80	No	300
E	80	120	No	300

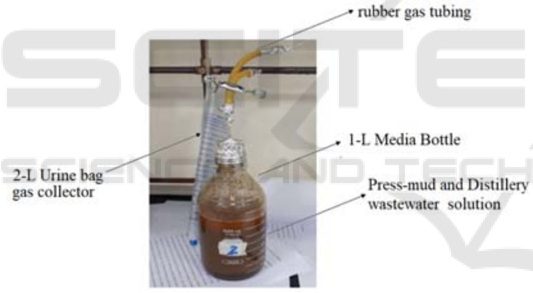

Figure 1: Anaerobic digestion set-up

Table 2: Physico-chemical properties measured and methods used

Parameter	Method	Units
Biochemical Oxygen Demand	5210 B. Azide Modification Dil. Technique	mg/L
Chemical Oxygen Demand	5220 B. Open Reflux Method	mg/L
Total nitrogen	4550-N C. Kjeldahl Method / 4500-NO3 D. Ion Selective	mg/L
Total organic carbon	5310 C. UV-Persulfate	mg/L
pH	4500-H B. Electrometric	-
Heterotrophic plate count	9215 B. Plate Method	CFU/mL

The initial and final values of physico-chemical characteristics of each batch such as COD, BOD, and pH values were determined. The methods used for determination are shown in Table 2. The methane richness of the biogas will be determined according to the American Standard Test method ASTM D2504-88(1998) using a gas chromatograph thermal conductivity detector (GC-TCD). This was conducted in an analytical laboratory of the Department of Energy, Taguig City, Philippines.

3 RESULTS AND DISCUSSION

3.1 Biogas Analysis

Batch test results showed that press-mud mixed with diluted distillery wastewater with and without additional micronutrients gave the highest methane yield of 61.3% and 78.23% (v/v), respectively (Table 3).

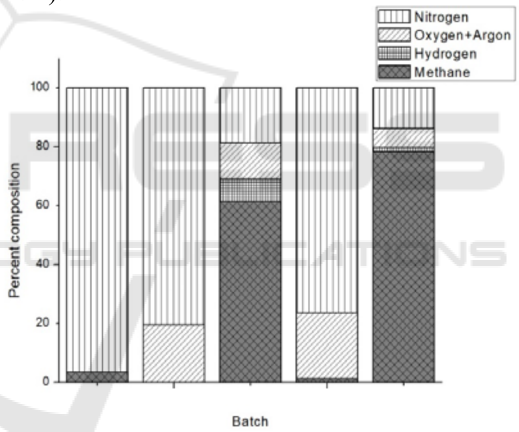

Figure 2: Determined composition of produced biogas

The methane content determines the quality of the biogas. Higher methane content in the biogas allows the substrates to be used more efficiently, thus more energy can be produced. Higher methane content also implies that smaller digesters are required, which ultimately results in reduced investment costs. The methane content of the biogas ranges between 52 and 82% according to past studies(Radjaram and Saravanane, 2017). In this study, the methane content of the biogas produced was significantly lower, except for the two batches with dilution ratio of 2:3 (distillery wastewater diluted with tap water), as seen in Table 4. The measured methane content ranged between 0.016%

(Batch B) and 78.23% (Batch E). A visualized comparison is presented in Figure 2.

Table 3: Methane content of biogas obtained from batch digesters

Batch	Composition	Methane content (wt%)
A	Pure Distillery Waste Water (DWW)	3.45
B	Diluted DWW (3:2, DWW:H_2O) with nutrients	0.0160
C	Diluted DWW (2:3, DWW:H_2O) with nutrients	61.3
D	Diluted DWW (3:2, DWW:H_2O)	1.36
E	Diluted DWW (2:3, DWW:H_2O)	78.23

From Figure 2, it can be noticed that hydrogen was detected in Batch C and Batch E with low yields of 7.70 and 1.46 %v/v, respectively. Hydrogen production was relatively low at mesophilic range (30-40°C) but higher at thermophilic range (50-55°C). The thermophilic condition reduces the solubility of hydrogen and thereby alleviates inhibition from hydrogen partial pressure (Radjaram and Saravanane, 2017). Batches A, B and D have higher composition in N_2, indicating that lower biodegradation occurred due to toxicity.

The AD of distillery wastewater alone is quite challenging since it is considered as a sulfur-rich substrate, and using these substrates results to undesirable effects: (a) sulfate reducing bacteria (SRB) outcompete methanogens for hydrogen and acetate due to thermodynamic advantages, resulting in sulfides and less methane production; (b) high sulfide concentrations has a direct toxic effect on certain anaerobic microorganisms; and (c) sulfide production and metal-sulfide precipitation is known as one of the most important processes limiting the availability of trace metals for microbial uptake, thus negatively affecting the efficiency and stability of the AD process (Radjaram and Saravanane, 2017).

3.2 Substrate Analysis

3.2.1 Change in pH

The percent decrease in pH for all batches is shown on Table 4. The pH of all samples decreased after the AD process because the digestion produces acetic and fatty acids which tend to lower the substrate pH. Most microorganisms grow best under neutral pH conditions, since other pH values may adversely affect metabolism by altering the chemical equilibrium of enzymatic reactions, or by actually destroying the enzymes. The methanogenic group of organisms is the most pH sensitive. Low pH or extreme pH changes can cause the chain of biological reactions in digestion to cease (Fisgativa, Tremier and Dabert, 2016). Thus, the minimal pH swing observed on batch E supported the discussion and produced the highest methane content.

3.2.2 Change in BOD and COD

The values of initial and final BOD and COD are shown on Table 5. Chemical oxygen demand (COD) is considered the most important parameter for the anaerobic digestion process. A possible reason for the observed higher COD values of the digestate is the performed alkaline pre-treatment which causes hemicelluloses and parts of lignin to solubilize and subsequently signify higher organic degradation (Fisgativa, Tremier and Dabert, 2016). The results showed that pre-treatment was more efficient with respect to promoting hydrolysis and increasing COD concentration. The highest COD solubilizations were achieved in batch E, followed by batch C. These two samples have produced higher methane yields compared to the other samples. This points out that solubilization is important as increasing the soluble organic matter content of samples will theoretically increase the easily biodegradable content of the waste and thus will lead to an improved performance of the anaerobic digestion (AD) process. Overall, however, there is no clear relationship between BOD, COD, percent change, and even BOD/COD ratio to the methane content of biogas produced and further studies are recommended.

Table 4: Effect of pH change on CH4 richness

Batch	Initial pH	Final pH	% decrease in pH	CH4 content
A	5.13	3.79	26.12%	3.45%
B	4.50	3.78	16.00%	0.0160%
C	4.97	3.78	23.94%	61.3%
D	4.80	3.85	19.79%	1.36%
E	5.11	4.55	10.96%	78.2%

According to past studies, the optimum initial BOD to COD ratio of the sugar waste products ranges from 0.38 to 0.56 which indicate that it is amenable to biological treatment. From the results, batches A, C, and E fit in the range and thus were able to produce methane. The wastewater containing high BOD, above 10,000 mg/L is generally considered suitable for anaerobic treatment. The chemical composition of the sugar waste products mainly contains carbohydrates and some protein and therefore it is suitable for anaerobic decomposition. Based on the results of this study, the BOD value decreases while COD increases during digestion.

To determine the effect of AD to the biodegradability of the samples, evaluation of BOD/COD ratio is necessary. All samples showed decreased BOD/COD ratios after digestion. Batch E has the lowest BOD/COD ratio, which in effect has the highest methane yield, meaning it already reached its peak state where biodegradation no longer occurs.

Table 5. Effect of changes in COD and BOD on CH_4 richness

Batch	Initial BOD	Final BOD	Initial COD	Final COD	Initial BOD/COD	Final BOD/COD	CH_4 content
A	33779	11012	143416	112684	0.2355	0.09772	3.45%
B	34004	9612	28683	133172	1.1855	0.07217	0.0160%
C	33859	10992	63513	143416	0.5331	0.07664	61.3%
D	34004	11012	28683	133172	1.1855	0.08269	1.36%
E	33859	10992	63513	245856	0.5331	0.04470	78.2%

3.2.3. Change in Carbon-to-nitrogen (C/N) Ratio

Nitrogen present in the feedstock has two benefits: (a) it provides an essential element for synthesis of amino acids, proteins and nucleic acids; and (b) it is converted to ammonia which, as a weak base, neutralizes the volatile acids produced by fermentative bacteria, and thus helps maintain neutral pH conditions essential for cell growth (Radjaram and Saravanane, 2017). An overabundance of nitrogen in the substrate (low C/N ratio) can lead to excessive ammonia formation, resulting in toxic effects. Thus, it is important that the proper amount of nitrogen be in the feedstock, to avoid either nutrient limitation (too little nitrogen) or ammonia toxicity (too much nitrogen). The composition of the organic matter added to a digestion system has an important role on the growth rate of the anaerobic bacteria and the production of biogas. The obtained C/N ratios are shown in Table 6. It should be noted, however, that there is no clear relationship between C/N ratios and methane content of biogas.

Table 6: Effect of C/N ratios on methane content of biogas

Batch	C/N ratio	CH_4 content
A	12.1362	3.45%
B	66.0087	0.016%
C	77.8372	61.3%
D	153.072	1.36%
E	72.3635	78.2%

For all the samples, bagasse and press mud were used as co-substrates, while batches B and C have added micronutrients. Batches C and E have a C/N ratio of 78:1 and 72:1, respectively. Their methane yields are 61.3% and 78.2%, respectively. Hence, in this study, the optimum C/N ratio is found to be in the range of 72:1 and 78:1. This shows that anaerobes utilize carbon 72 or 78 times faster than the nitrogen for optimum methane generation.

3.2.4 Changes in Microbial Community

All batches showed a final HPC of 57000 CFU/mL. This shows that the concentration of microorganisms does not directly correlate to methane generation. The compounding of several factors aside from HPC are the ones affecting the concentration of methane in the biogas.

3.2.5. Effect of Micronutrient Addition

Micronutrients are trace elements that are necessary to microbial nutrition. Deficiency of these elements reduces the methane yield but becomes toxic when used excessively. It is found that the addition of Mg, Fe, Co and Zn is favorable in methane production. Magnesium is recognized as a stimulator for single cell production responsible in limiting the aceticlastic activity loss of the process. Iron and zinc are essential cofactors that act as regulators in the methanogenesis phase of the digestion. Cobalt also plays a significant role in the formation of methane from acetate. Based on a previous study, adding micronutrients will increase the yield of methane production (Menon, Wang and Giannis, 2017).

In this study, twice the recommended amount of micronutrients was used to test for its impact on yield. Some might be adsorbed by the solid components of press mud or may be entrapped in the suspended particle of distillery wastewater. It is found that doubling the concentration of these micronutrients made the mixture toxic. Samples without micronutrients (Batches A, C and E) appeared to have higher methane yield compared to samples that have excessive amounts of micronutrients.

4 CONCLUSIONS

Overall, the main goal of this study which was to determine the effects of co-digestion of press mud and distillery waste water with the addition of bagasse for enhanced biogas production was achieved. Some important parameters were evaluated such as pH, BOD, COD, total carbon, and total nitrogen. Methane yield is affected by the sensitivity of microorganisms to pH variations. Optimum pH to have a higher methane yield has been found out to be 5.0. Also, COD/BOD ratio was evaluated and it was found out that the optimum initial COD to BOD ratio of the sample that yields higher methane yield ranged from 1.8 to 2.6 which indicate that it is amenable to biological treatment. Meanwhile, the optimum C/N ratio is found to be in the range of 72:1 and 78:1 which indicates that anaerobes utilize carbon 72 or 78 times faster than the nitrogen. Lastly, although micronutrients are necessary to microbial nutrition, this study shows that toxicity will occur if the concentration goes beyond the necessary.

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