Anaerobic digestion of distillery wastewater and napier grass: characterization and process performance parameters

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Abstract. The BOD/COD ratio of napier grass (NG) + distillery wastewater (DWW) was found to be 0.4982, which reflected that the biodegradability of organic material is high and can be degraded and treated efficiently via biological processes. Moreover, further reductions in total solids (TS) and volatile solids (VS) were observed after thermal pretreatment at temperatures of 60°C and 100°C. VS/TS ratio also increased from 0.8767 to 0.9508 indicating a more significant proportion of organic matter are favorable for biogas production. This was evidenced by the resulting removal efficiencies ranging from 15% to 32% and 23% to 42%, for TS and VS, respectively. Overall, the study reported relevant effects of the application of thermochemical pretreatment in the process performance parameters in anaerobic digestion.

1 Introduction

Alcohol manufacturing companies produce vast amounts of wastewater that can be treated accordingly to recover valuable materials for biogas production. In 2015, only 10% of wastewater was treated in the Philippines, while 58% of the groundwater was contaminated; as the primary issue is the lack of sludge treatment and disposal facilities, untreated effluent is dumped into bodies of water [1]. Molasses-based ethanol distillery wastewater (DWW) is a byproduct of alcoholic fermentation and is essential for cost-effective biogas production. Around 10-15 L of DWW are believed to be created for every 1 liter of ethanol produced. When DWW is discharged into water streams, economic burden on businesses and environmental consequences are posed [2]. Effluent from sugar and alcohol industries today commonly undergoes anaerobic digestion (AD) not only for energy generation but also for solids removal and treatment.

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The insufficiency of studies addressing the potential of the utilization of the by-products from sugarcane processing industries and for biofuel production implies the urgency for its research and development especially due to the increasing sugar demand. This study aims to determine substrate characteristics such as pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS) and volatile solids (VS) of the substrates and final digestate and evaluate the solids removal efficiency that could address the current problems with solids and wastewater management in ethanol distilleries in the Philippines. Moreover, this work also endeavors to determine AD process performance parameters such as TS reduction, VS reduction, and pH change, all of which are relevant in the future of anaerobic treatment systems. Ultimately, valuable information may be provided throughout the study regarding an improved waste-to-energy technique for DWW that will aid in recommending better pollution control strategies.

2 Methodology

2.1 Raw materials and inoculum

Fresh samples of napier grass (Pennisetum purpureum), also known as Elephant grass, were harvested from South Cotabato, while the DWW used in this study was collected from Absolut Distillers Inc. in Lian, Batangas. To prevent unwanted fermentation, the DWW sample was stored in a plastic container at a temperature of 4°C before the experiment. The nutrients required were sourced from the chemistry laboratory of Mapúa University in Intramuros, Manila. Before use, the fresh NG was blended. The substrates and micronutrients were diluted with Type III water, while the inoculum was prepared by combining cow manure and DWW in a 50:50 ratio, followed by seven days of inoculation before use.

2.2 Experimental setup and pretreatment

The batch AD setup followed the liquid displacement method during biogas collection [3] while all runs were subjected to chemical pretreatment using $Ca(OH)_2$, from which reactors R1 and R2 were focused on mono-digestion, R3 on co-digestion, and R4 and R5 on thermal pretreatments at temperatures of 60ºC and 100ºC, respectively.

2.3 Analytical methods

A 50:50 ratio by volume mixture of DWW and NG was mixed homogenously, wherein an 800 mL sample was sealed in a 1L HDPE bottle. Each sample were tested for biochemical oxygen demand (BOD) and chemical oxygen demand (COD) characterization (see Table 1).

Table 1. Test method used by NASAT Labs for feedstock characterization

Parameter	Test Method
BOD	5210-B: 5-Day BOD Test
COD	Closed reflux, Colorimetric Method

2.3.1 TS and VS

To measure TS and VS levels, the EPA Method 1684 was used. Samples placed on crucibles were then labeled, weighed, and heated at 105°C for 24 hours. Afterward, they were cooled in a desiccator before being weighed again. The sample is heated once more for an hour, cooled again, and weighed until the weight change is less than 4%.

$$TS = \frac{W_{final} - W_{dish}}{W_{initial} - W_{dish}} \tag{1}$$

To analyze volatile solids, it is necessary to ignite the dried residues in a furnace for a duration of two hours at a temperature of 550°C. After cooling in a desiccator, the residues must be weighed. This cycle of igniting, cooling, and weighing must be repeated until the weight difference is below 4%.

$$VS = \frac{(W_{final} - W_{ash}) - W_{dish}}{W_{final} - W_{dish}} \tag{2}$$

The mentioned procedures were carried out on the samples both before and after the onset of AD.

2.3.2 pH

Modifying the initial pH of samples before AD is critical to maintain digestion process stability, optimize microbial activity, and prevent inhibition. All pH values were adjusted within the range of 6.25 to 7.9 using 1M NaOH, creating an environment conducive to the effective functioning of methanogenic bacteria, as it significantly enhances biogas production and yield [4]. The sludge's pH levels were determined using a pH meter before and after digestion.

2.4 Removal efficiency

The advantage of the pre-treatment techniques was also measured by determining their removal efficiencies of TS and VS using Equation 3.

$$\text{Removal efficiency (\%)} = \frac{C_i - C_f}{\mathrm{C_i}} \times 100 \tag{3}$$

where C_i is the initial concentration of the variable and C_f is its final concentration. This measure is an important indicator of organic matter decay which implies biogas production [5].

3 Results and Discussion

3.1 Feedstock characterization

The results of the feedstock characterization are shown in Table 2. The BOD:COD ratio is a metric used to assess the biodegradability of a substrate. A threshold value of 0.4 is indicative of easy biodegradability, while a value greater than 0.5 is considered most effective [6]. The BOD/COD ratio of NG + DWW was found to be 0.4982, the biodegradability of organic material is considered high. In order to achieve greater efficacy, a value exceeding 0.5 is regarded as more favorable. As a result, NG underwent thermochemical pretreatment (TCP) in an effort to increase its suitability for the AD process and enhance its ability to biodegrade. The values of TS and VS evaluated in the substrate were within the acceptable range outlined in the existing literature as indicated in Table 2. A reduction in the values of TS and VS was detected after the TCP stage. The decrease in biomass size has been attributed to chemical reactions and alterations in the biomass structure induced by the breakdown of lignin in NG with Ca(OH)2. Increased cellulose and hemicellulose accessibility for subsequent microbial digestion was a factor in the reduction of solid composition as a whole [7,8]. Previous research has also reported comparable decreases in TS and VS [9,10].

Moreover, further reductions in TS and VS were observed after TP at temperatures of 60°C and 100°C, which is consistent with the results reported by Pumpoung et al. [11], who observed an increase in the removal of TS and VS as the temperature raised. In contrast, empirical evidence also suggests that TP does not always result in a statistically significant reduction in TS. This is because a significant proportion of lignocellulosic components continue to exist in a volatile state despite undergoing an increased dissolution process [12]. A notable disparity, conversely, was noted in the reduction of VS, which signifies that TP effectively degraded complex compounds into simpler molecules that were more readily digestible, resulting in lower VS levels than previously observed [13].

Nevertheless, after TCP, the VS/TS ratio increased from 0.8767 to 0.9508. As they are more susceptible to complete digestion, substrates with a higher VS/TS ratio—which indicates a more significant proportion of organic matter—are more favorable for biogas production [7,13]. In addition, the AD must maintain an optimal pH around neutral; the initial pH was adjusted as outlined in Table 4 (Appendix D). The pH value of NG alone was 7.93, while those of NG + DWW after pretreatment ranged from 6.67 to 7.04.

Table 2. Feedstock characterization.

Parameter	**NG**	**DWW**	**NG***	**DWW***	**NG + DWW**	**NG (TCP)**
TS (g/g_{sample})	0.1056	0.0769	0.3220^{a}, 0.3110^{b}, 0.8600^{c}, 0.1630^{d}	0.0903^{e}, 0.0799^{f}, 0.1520^{g}	0.0871	0.0903^{+} 0.10259^{++} 0.09254^{+++}
VS (g/g_{sample})	0.0926	0.0649	0.8500^{a}, 0.2888^{b}, 0.8600^{c}, 0.1432^{d}	0.0855^{e}, 0.0762^{f}, 0.8168^{g}	0.0762	0.08586^{+} 0.09056^{++} 0.07998^{+++}
VS/TS	0.8767	0.8449	-	-	0.8753	0.9508^{+} 0.8827^{++} 0.8643^{+++}
pH	7.93	6.78	7.5^{h}	6.52^{f}	6.7	7.04^{+}, 7.23^{++}, 6.67^{+++}
BOD (mg/L)	-	-	-	-	31,000	-
COD (mg/L)	-	-	-	-	62,228.78	-
BOD/COD	-	-	-	-	0.4982	-

* From literature
[14]^{a}, [15]^{b}, [16]^{c}, [17]^{d}, [18]^{e}, [19]^{f}, [20]^{g}, [11]^{h}, $^{+}$60°C, $^{++}$80°C, $^{+++}$100°C

3.2 C/N Ratio

The production of biogas is significantly impacted by the carbon-to-nitrogen (C/N) ratio, given that carbon provides energy for microorganisms and nitrogen induces the formation of ammonia gas. An overly high C/N ratio can promote acidogenic bacteria over methanogenic bacteria, impeding biogas formation [21]. On the other hand, a very low C/N ratio encourages microbial development by causing rapid nitrogen consumption. For the production of biogas, a C/N ratio between 20 and 30:1 is ideal [22]. Previous research on the C/N ratios for DWW and NG is shown in Table 3.

Table 3. C/N Ratio of DWW and NG based on existing literatures.

	C/N Ratio	Reference
DWW	2.11	[23]
	3.75	[24]
	10.4	[25]
Napier Grass	39.35	[17]
	35	[26]
	30.62	[27]

NG has a high cellulose and xylan content that can be hydrolyzed to produce monomeric sugars applicable to microorganisms. Due to its high C/N ratio, it can be used as a proper compensatory element for substrates with lower C/N ratios and helps control the presence of inhibitory substances. C/N ratios of 8.22 for chicken manure and 39.35 for NG were recorded by Weerayutsil et al. [17], suggesting that mono-digestion based purely on manure did not produce the maximum amount of methane because an excessive amount of nitrogen inhibited the growth of methane-forming bacteria. On the other hand, methane generation was enhanced during co-digestion with materials with different C/N ratios while preserving system stability. Adjama et al. [28] investigated co-digestion using human waste and lignocellulosic feedstock (rice straw), and they found that a mixture of 50% rice straw and 50% human waste produced the most methane. Dube's research on pretreated napier grass and butcher shop waste showed that the best biogas yield was obtained with a 50:50 co-digestion ratio (70.3 Nml/g•VSadded) [29]. In light of these findings, the 50:50 DWW: NG ratio employed in this investigation is consistent with achieving a balanced C/N ratio in the substrate composition. The averaged values from existing literatures point to biogas production's ideal C/N ratio (20-30:1). This explains why the biogas output from DWW was the lowest (753.0 mL), the biogas output from NG alone was more significant (1253.0 mL), and the biogas output from DWW + NG were the highest (< R3 < R4 < R5).

3.3 Removal efficiency

The application of pretreatment procedures yielded noticeable reduction in TS and VS concentrations, as seen in Figure 1. The corresponding removal efficiencies observed ranged from 15% to 32% and 23% to 42%, respectively. Studies report that lignin and hemicellulose begin to solubilize at a temperature range of 150-180oC, paving way from easier degradation [30]. Nevertheless, the occurrence of inhibitors in such elevated temperatures could lead to decreased biogas yield and supplementary expenses. [31]. Hence, exploring the optimal exposure time for the low-temperature pretreatment (LTPT) of NG is recommended.

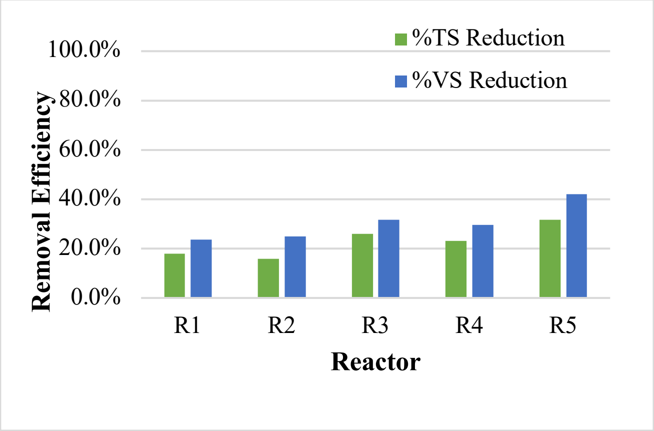

Fig. 1. Removal efficiency.

3.4 pH change

The digesters' initial and final pH values, as illustrated in Table 4 (Appendix D), are all situated between 6.25 and 7.9, thereby establishing an environment favorable for the efficient operation of methanogenic bacteria [4]. It is worth mentioning that the pH of R1 peaked at 7.93, whereas R5 displayed its lowest point at 6.67. Jayaraj et al. conducted a study wherein they observed that the degradation efficiency and biogas yield were significantly greater at pH 7, while the lowest values were documented at pH 5 [32]. The reduced biogas production can be attributed to the possible development of inhibitors, including furfural and soluble phenolic compounds, which are recognized to hinder biogas synthesis [33]. The influence of pH was more significant than the increase in organic acid yield. This is due to the inhibition of hydrolytic bacteria, which are accountable for the initial hydrolysis reaction during biogas production. As a result, the degradation of complex polymers into simpler monomers, which is necessary for the subsequent reaction in methanogenesis, was impeded [34]. One preventive measure suggested by prior research is to regulate the pH level between 4 and 7 to prevent the formation of inhibitory compounds [35]. The increased probability of producing inhibitory compounds, including volatile fatty acids (VFA) and ammonia, this finding is consistent with previous studies that have established a link between elevated pH levels, heightened ammonia toxicity, and the buildup of volatile fats [36].

The data in Figure 2 indicates that the final pH values for the NG treated with DWW fell within the acidic range, precisely at 5.86, 6.25, and 5.08. In contrast, the control (R1) maintained a pH of 7.44, considered normal. This result is consistent with prior investigations, in which NG-containing substrates tended to acidic final pH values, whereas the control group maintained a normal pH range [27]. The decrease in biogas generation observed in samples R2, R3, R4, and R5 can be ascribed to the pH dropping to toxic levels, specifically below pH 6.5. Such a low pH level impairs the sensitivity of microbial communities involved in AD. On the contrary, R1 maintains biogas production beyond the 28-day digestion period due to its pH remaining in close proximity to neutrality [37].

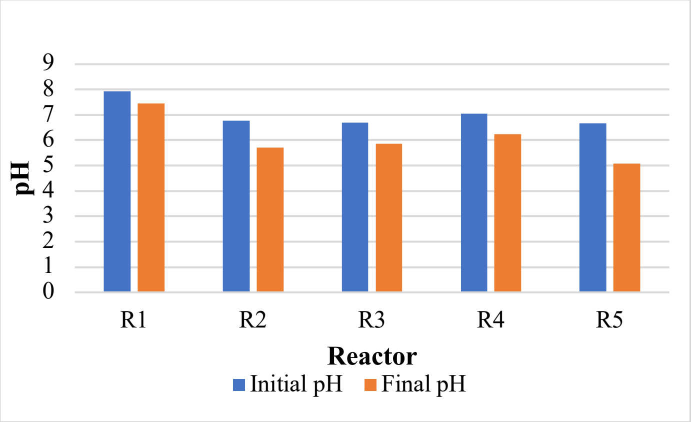

Fig. 2. pH values of digesters before and after AD.

4 Conclusion

This study examined the valorization of DWW and NG via AD for future energy generation and solid/wastewater management and treatment. Because of its higher C/N ratio, NG is an effective stabilizer for substrates like DWW with lower C/N ratios. The findings revealed that R4 and R5 experienced the most substantial decrease in VS. Moreover, the feedstock characterization indicated that NG + DWW had an easy biodegradability ratio, to further increase its effectiveness, there is a need for TCP to improve its suitability for AD. Furthermore, it was discovered that the utilization of TCP resulted in a more significant decrease in the percentage of VS, indicating its importance in facilitating subsequent microbial digestion. The digesters maintained consistent initial and final pH values between 6.25 and 7.9, which created a conducive environment for the effective growth and development of methanogenic microbes. Therefore, it was recommended that future research adopt continuous monitoring of pH levels and biogas production to evaluate the stability and sustainability of the AD process.

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