Journal of Science Research and Reviews
PRINT ISSN: 1595-9074
E-ISSN: 1595-8329
DOI: https://doi.org/10.70882/josrar.2024.v1i1.1
Homepage: https://josrar.esrgngr.org
Original Research Article

Comparative Measurement of Biogas Generation of Ziziphusspina - Christi (L.) Wild Leaves and Cow Dung

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KEYWORDS
Biodigester,
Biogas,
Proximate,
Ziziphusspina.

CITATION
Okoh, E. V. C., & Adiya, I. S. G. Z. (2024). Comparative Measurement of Biogas Generation of Ziziphusspina - Christi (L.) Wild Leaves and Cow Dung. *Journal of Science Research and Reviews*, *1*(1), 1-5. https://josrar.esrgngr.org/index.php/josrar/article/view/3

ABSTRACT
To increase the production of biogas from an appropriate substrate, anaerobic co-digestion techniques are required. Methane generation and process stability can be enhanced by co-digesting animal dung and suitable biomass with a low carbon content. The objective of the study is to determine the proximate parameters and compare the biogas generation from a sample of plants sown with cow manure and leaves of Ziziphusspina. Over the course of 42 days, the experiment was conducted using a homemade anaerobic digester in the lab. Even yet, the amount of biogas produced by the plant sample was not as high as that produced by the plant sample that was fertilized with cow manure.For additional advantageous uses, such as the creation of biofertilizers, the physico-chemistry of fresh samples and spent slurries in the biodigesters might be investigated. This work has potential applications in underdeveloped nations, particularly in rural areas with abundant biological waste and limited access to energy.

INTRODUCTION

The continuous global depletion of petroleum and coal has lead researchers to explore ways to diversify man's energy need (Bagudo,*et al* 2008).An combustible gas known as biogas is created during the anaerobic fermentation of organic molecules. Other names for the gas include sewage gas, gobar gas, dung gas, marsh gas, and swamp gas (Dangoggo *et al*., 1986). The temperature, pH, loading rate, toxicity, stirring, nutrients, slurry concentration, digester construction and size, carbon to nitrogen ratio, retention time, alkalinity, initial feeding, total volatile acids, chemical oxygen demand (COD), biological oxygen demand (BOD), total solids (TS), volatile liquids, and other factors all affect the rate at which biogas is produced (Abubakar, 2017).In contrast to other renewable energy sources such as solar, wind, thermal, and hydro sources, biogas is unique due to its easy process control, which simultaneously produces fertilizer and water for agricultural irrigation(Ziana and Rajesh, 2015).

Ziziphusspina - Christi is a tiny tree or spiky shrub that can withstand extreme heat and drought rather well. Ziziphus is a genus of plants with a number of therapeutic uses, including liver protection, hypoglycemia, hypotension, anti-inflammatory, antibacterial, antioxidant, and immune system stimulant (Said *et al.,* 2006). Although it is an evergreen tree, during the dry season it does lose some of its leaves (Von-Maydell, 1986).

With three prominent veins that go up to the apex and petioles that are between 0.5 and 1 cm long, the plant's leaves are simple, alternating, narrowly ovate, and lanceolate, ranging in length from 1 to 9 cm and width from 1 to 3.5 cm. The leaves are glabrous above and minutely and densely pubescent below (Von-Maydell, 1986; Arbonnier, 2004). Deeply fissured, the bark is yellowish brown or pale grey. However, the fruit is a reddish-brown globose drupe of about 1–1.5 cm in diameter, with a hard stone surrounded by a sweet edible pulp. The flowers are typically small, greenish-yellow, 2 mm long sub-sessile sepals, with five 1.5 mm long petals. The flowers are found in dense clusters in the axils of the leaves (El Amin, 1990). As part of our ongoing search for environmentally friendly energy alternatives, our study looked at the plant's leaves' potential for both nutritional value and the production of biogas under anaerobic conditions, comparing them to cow manure.

MATERIALS AND METHODS

Sample Collection and Identification

In June of 2019, fresh Z. spina leaves and cow dung were purchased from the Kasuwan Daji abattoir and the central market in Gusau. Fresh plant samples were delivered right away to the Sokoto Energy Research Centre's core laboratory at Usmanu Danfodiyo University in Sokoto, Sokoto State, Nigeria. Mallam Abdulaziz Sani of the Botany Unit, Department of Biological Sciences, Usmanu Danfodiyo University Sokoto, where a herbarium specimen was deposited for future use, identified and verified them.

Sample Preparation

After rinsing the samples under running water to get rid of any dust or earthy impurities, they were shade dried for two weeks to ensure full drying and then ground with a clean mortar and pestle. Before being used, the ground sample was stored in an airtight glass container.

Making Digesters

Plastic basins served as the water trough, while cylindrical cans served as the digesters. To make sure the digester was airtight, a hole was bored into the lid of each can, and a polyvinyl chloride tube was placed within the hole and secured with Araldite® adhesive. This functioned as the biogas produced's outflow. The rubber tube's free end was then placed into an inverted measuring cylinder that had also been filled with water, acting as the biogas collection system, through water that was held in a partially full water trough. Water was displaced downhill to capture the biogas. The tins have clear labels on them to make identification simple.

Slurry Preparation

100 g of the plant sample plus 1000 cm^3 of water (Setup A) and 100 g of the plant sample plus 400 g of cow dung plus 1000 cm^3 of water (Setup B) were used to create the slurry of the dried sample of each substrate. Before entering the digester, the mixes were well combined for greater homogeneity. Six digesters were fed with each of the slurry concentrations listed in triplicate for the purpose of determining each substrate. The setup was checked at least twice a day, but throughout the 42-day (6-week) retention period, readings were taken at noon every day for 24 hours.

Proximate analysis of substrates and spent slurry

Using the procedures used by (Garba, 1999), the moisture and ash contents of the substrates and spent slurry were ascertained. The analysis of the nitrogen concentration followed (Dangoggo *et al*., 2004) instructions . The percentages of moisture and ash content were subtracted from 100% to find the volatile solid (VS) (Garba 1999), and the formula %C = 0.58 X % VS was used to estimate the carbon content of the substrates (Allen, 1994). By dividing the amount of organic carbon content by the amount of nitrogen content, the carbon to nitrogen ratio was determined using the following formula:

$$\frac{C}{N} = \frac{\%\,Organic\ carcon\ in\ the\ sample}{\%\,Nitrogen\ in\ the\ sample}$$

Determination of pH before and after digestion

Each slurry's pH was measured using a calibrated pH meter both before and on the final day of the retention period in order to determine the pH.

Statistical Analysis

The data were evaluated using one-way analysis of variance (ANOVA) and expressed as mean ± standard deviation (S.D). P less than 0.05 was regarded as statistically significant.

RESULTS AND DISCUSSION

Tables 1 through 3 show the outcomes of the proximate analysis, pH determination, and biogas production by the various substrates.

Table 1: Proximate composition and pH of the raw substrates

Parameters	Substrate	
	Setup A	Setup B
Moisture (%)	3.30 ± 3.11	11.75 ± 1.14
Ash (%)	11.00 ± 0.46	15.50 ± 1.10
Organic matter (%)	21.12 ± 0.33	67.82 ± 0.11
VS (%)	85.70 ± 0.62	72.75 ± 0.53
Carbon (%)	49.71 ± 2.67	42.20 ± .2.44
Nitrogen (%)	5.86 ± 2.14	9.68 ± 3.54
pH	6.90	6.50
C: N ratio	8.48	11.47

Key: C:N = Ration of organic Carbon to Nitrogen; VS = Volatile solid; Values are mean ± standard deviation of three replicates.

Table 2: Proximate composition and pH of the spent slurries

Parameters	Substrate	
	Setup A	**Setup B**
Moisture (%)	11.00 ± 1.74	17.90 ± 1.32
Ash (%)	17.10 ± 1.11	21.30 ± 1.02
Organic matter (%)	19.12 ± 0.95	24.90 ± 0.65
VS (%)	72.00 ± 2.43	60.80 ± 0.55
Carbon (%)	41.76 ± 3.23	35.26 ± 2.22
Nitrogen (%)	6.33 ± 0.44	14.40 ± 2.11
pH	6.40	6.20
C: N ratio	6.60	2.45

Key: C:N = Ration of organic Carbon to Nitrogen; VS = Volatile solid; Values are mean ± standard deviation of three replicates.

Table 3: Biogas production (cm^3) by substrates

Week / Total Volume of Biogas Produced	Substrate	
	Setup A	**Setup B**
1	100 ± 21.22	291 ± 8.88
2	280 ± 11.35	425 ± 24.22
3	460 ± 9.34	775 ± 17.34
4	656 ± 5.22	925 ± 15.23
5	392 ± 17.44	575 ± 11.45
6	180 ± 11.05	358 ± 10.34
Total	2068	3349

The values are the mean ± standard deviation of three replicates; substantially different values ($p < 0.05$) are indicated by distinct superscripts.

The moisture, ash, organic matter, volatile solid, percentage of carbon, percentage of nitrogen, pH values, and C/N ratios of the fresh and spent slurries were provided in Tables 1 and 2. With the exception of organic matter, VS, C, pH, and the C/N ratio, which generally decreased from the fresh to the spent slurry, the overall trend of the two tables indicated that all the metrics had increased. Water lessens the restriction on the mass transfer of non-homogenous or particle substrate and allows bacteria to move and develop, which facilitates the dissolution and transport of nutrients (Yadav, 2014). In the process of producing biogas,the process of producing biogas involves hydrolysis, the degree of which is influenced by the moisture content (Von-Maydell 1986) (Arbonnier, 2004). The portion of the substrates that remain after the moisture is expelled is shown by the total solids content. It is made up of the ash content of the substrates as well as the volatile solids. Total solid content and the amount of biogas produced are directly correlated, according to research (Bagudo *et al.,* 2008). Thus, the generation of organic acids, H_2, and CO_2 by facultative bacteria was most likely the only anaerobic process that reduced carbon (Hobson,1999). These carbon molecules are what give rise to CO_2, CH_4, and other gases. Along with phosphorus and potassium, nitrogen is a crucial macronutrient needed for plant growth.Maintaining a stable operation and improving process stability are also crucial for the anaerobic digestion of municipal solid waste (Kayhanian, 1995). The potential of spent slurries to be manufactured as biofertilizer is indicated by the rise in the % nitrogen content of the spent slurries when compared to fresh samples (Tambuwal and Ogbiko, 2018).. The observed trend for these proximal metrics may be explained by the volatile organic matter in the fresh slurries being converted into diluent components (Bagudo *et al.,* 2008). It was discovered that the wasted slurries had a little lower pH than the new ones.

The production of sulphide (S^{2-}) in the spent slurries as a result of the breakdown of biodegradable sulphur containing organic and inorganic compounds as well as the formation of fatty acids by acetogenic methanogens during the digestion process may be the cause of the spent slurries' lower pH than the fresh ones. The pH of the water used to create the slurry may also be to blame for the observed decline (Ahmad, 2000; Bagudo *et al.,* 2008). Nonetheless, the pH values were within ranges where substrate bioconversion may occur, in accordance with the findings of Lusk's study (Lusks, 1998)

There are several reasons for the weekly fluctuations in gas production, including the digester's acidic condition, the gradual depletion of raw materials for microbial digestion, incomplete material digestion, and lower digester temperature (Ezekoye *et al*., 2014; Yerima *et al*., 2019) The fluctuation in gas production peaked at week 4 before declining at weeks 5 and 6 at the maximum organic load rate, finer particle size might cause acidification, which can ultimately cause process failure. For every day of the retention period, the amount of biogas produced by cow dung exceeded that of the substrate. This could be explained by the increased moisture content, which always promotes hydrolysis and increases gas production. The sample's lignin content may also act as a barrier to the production of biogas because a larger lignin content will make the trash less biodegradable, which will reduce the amount of biogas produced (Richard, 1996; Wilkie, 2005).

CONCLUSION

Although the amount of biogas produced by the plant sample was not statistically significant when compared to that of the cow dung control, the results are nonetheless encouraging, particularly in developing nations where fuel wood has historically been the primary source of domestic energy without an alternative, contributing to deforestation, climate change, desertification, and decreased soil fertility.

ACKNOWLEDGMENTS

We would like to express our gratitude to the Sokoto Energy Research Center's central laboratory team for their technical assistance during the study.

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