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# Biogas Yielding Potential of Maize Chaff Inoculated with Cow Rumen and Its Characterization

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***Authors' contributions***

*This work was carried out in collaboration between both authors. Author SCI designed the study, performed the analysis and wrote other chapters apart from the introduction of the manuscript. Author KCO wrote the protocol, the introduction, and helped with the general guidance on the analysis to be performed as a surpervisor. Both authors read and approved the final manuscript.*

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## ABSTRACT

Human Life on earth is driven by energy and with the global challenge on best ways to manage waste, there is need to convert organic waste to bioenergy which will help reduce the rate of environmental pollution and over dependence on conventional source of energy. In this investigation maize chaff were inoculated with cow rumen using different concentration ratios (S/I) of 1:1, 1: 1.55, 1:3.5 for 25, 31 and 37 days Retention Time (RT) as design by Central Composite Face Centered Design to optimize the process and predict the best response. The result obtained shows that the mixture ratio of 0.65 (1:1.55) for 31 days gave the optimum yield while 0.65 mixing ratio for 37 days gave the maximum yield at 0.42L under mesophilic (20°C to 45°C) condition. The Flash point of the cummulative maximum yield was -164°C which is really flammable. The model F-value is 95.03, p-values is $< 0.0001$ which is less than 0.05 and both values indicate model terms are significant. Lack of Fit F-value of 0.43 implies the fitting effect is good. Its $R^2$ value of 0.9855 is very close to 1 which is good. In addition, the biogas products were characterized by FTIR spectroscopy and Gas chromatography–mass spectrometry (GC-MS). The FTIR analyzes showed

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the presence of Alcohol and was further proven by 69% methane gotten as indicated by the GC-MS. Thus, the result shows high methane yield, flammability and suitability for maize chaff inoculated with cow rumen for energy production.

*Keywords: Cow rumen; anaerobic digestion; maize chaff; biogas production; optimization; inoculation; bioenergy; characterization.*

## ACRONYMS

*GC : Gas Chromatography*
*MS : Mass Spectrometry*
*AD : Anaerobic Digester*
*FTIR : Fourier Transform Infrared Spectroscopy*
*TS : Total Solids*
*VS : Volatile Solids*
*RSM : Response Surface Methodology*
*CCD : Central Composite Design*
*ABUAD : Afe Babalola U niversity, Ado-Ekiti*

## 1. INTRODUCTION

Energy is one of the most significant drivers for global growth and societal development. Over the years the world has largely depended on non-renewable energy as primary energy source which produces excessive emission leading to global warming, environmental degradation, and human health problems and whose fossil input is in decline [1,2]. In Nigeria, the cost of energy for domestic, commercial and industrial use has risen astronomically in the past few years [2,3]. Hence, the global call for alternative source of energy that is non-polluting, cheap and sustainable to reduce the over dependence on fossil fuel. The use of non-convectional energy is essential to alleviate global warming and to achieve the global call for greener energy [4,5,6].

Biogas production from biodegradable waste could be an alternative to reduce landfill and emissions into the air, water, and soil [7]. Bioenergy is the energy derived from decomposition or fermentation of organic materials from plant and animal waste in an anaerobic digester [8,2]. Tropical regions which include Nigeria have very high biomass productivity compared to other regions [1,9]. Large amount of biomass waste is generating every year from agricultural, forestry, food, and other industries [10,3]. As a result, there is an opportunity to improve the sustainability of energy production in tropical regions by converting this locally abundant biomass waste into biofuel products using anaerobic digestion [11,12,13]. Presently, due to increasing demand and shortage of fossil fuels, the interest of people all over the world has shifted to renewable energy like bioenergy [14].

In the entire world, the use of biogas creates a greener city which is good for everyone and it boost the heath and quality of life of residents, encourage business success and draw more investors especially in rural areas like Nigeria, Tanzania etc. Currently, 80% of Tanzanians live in rural areas, and 90% of the energy requirements of these people are met by firewood and charcoal. About 23% of the people in the country use electricity for lighting this cannot facilitate improved student performance. Specifically, the sources of energy being used by the majority of Tanzanians are either very ineffective and/or inefficient for realizing the socioeconomic development [15]. It would also reduce environmental pollution such as air pollution caused by burning of fossil fuels and improve public health, reduce premature mortality due to pollution and save associated health costs that amount to several 100 billion dollars annually only in the United States [16].

In rural areas, farmers predominantly cultivate maize, plantain, yam, among others, choosing a source of waste that can be converted to bioenergy becomes essential. Recently, Nigerian government work towards diversifying the economy through providing incentives for farmers, there is great need to tackle the challenges associated with waste management by researching on feasibility and accelerating ways of converting these biodegradable waste materials to bioenergy and manure to enhance the environment, energy and food securities [5,6,10]. This can be achieved by employing science and technology in developing new ways of utilizing, accelerating and extending the biogas shelf-life using alternative means. Depending upon the type of organic materials used in anaerobic digestion, biogas contains typically 60-70% of methane [17,18,7]. An anaerobic digestion (AD) is an important method to decrease the quantity of organic wastes by utilizing them for bioenergy and heat production. The main product in biogas is methane, a colorless, flammable gas that can be used for heating, cooking, electricity and possibly for transportation while the by-product is the digestate which can be used as inoculums or fertilizer in farms. Thus, biogas generated from anaerobic digestion process is clean and environmentally friendly.

Ruminants can eat different types of feed that are digested by microbial biomass resulting in better metabolism [19]. The rumen bacteria are 99.5% obligatory anaerobic. In rumen, 200 species with many subspecies of bacteria are present and this aids fermentation process [20]. Cow rumen has been considered as an attractive animal waste for anaerobic digestion (AD). It is a potential substrate for biogas production due to high buffering capacity and having nutrients where it is necessary for bacterial growth [21,22]. Thus, cow rumen can be used in combination with other biodegradable wastes to yield higher methane production [23,22]. Maize (*Zea mays*), is one of the world's most consumed cereal grains [24]. It's the seed of a plant in the grass family, native to Central America but grown in countless varieties worldwide. Maize products are widely consumed, frequently as ingredients in processed food, but their wastes from processed food (Palp) like the chaff are breeding ground for mosquitoes and environmental pollution due to poor waste management especially in rural areas worldwide which in turn causes ill health on humans within the area.

Previous findings have established the possibility of generating biogas and fermented organic liquid fertilizer (digestate) from cow dung and other animal excretory products in an anaerobic digester (AD) [25,26,27]. However, the costs of cow dung digesters are not favorable due to their relatively low biogas yield in comparison with several other types of organic wastes [24,10]. Also, in other reports, cow rumen has been used to co-digest corn straw but it yielded 60% methane which can be improved on by trying other maize waste like the chaff [28]. Thus, this work evaluates the feasibility of using maize chaff inoculated with cow rumen in mesophilic conditions (20–45°C). The information on the complete biogas chemical composition is indispensable for determining the quality and quantities of combustible and hazardous components before using it as a fuel. Hence, this study focused on the characterization and optimization of the production yield of biogas from the hybridized maize chaff and cow rumen with the best inoculums in mesophilic conditions.

## 2. MATERIALS AND METHODS

### 2.1 Data Collection

Fresh maize chaff is from *Zea mays* (maize) and it was obtained from palp producers. Cow rumen was gotten from slaughter-house. Twenty-six (256 mL each one) bottles was used as the digester for this experiment, buckets, funnel for measurement, a digital weight scale in grams to measure the mixing ratio, a digital pressure gauge to access the daily pressure inside the bottles, crucibles for storing each material for Total Solids (TS) and Volatile Solids (VS) in the furnace, desiccators, furnace for TS and VS, Respond Surface Methodology was used to optimized the biogas produced in liters, others includes Cleavage Close Cup: For detecting the flash point and ignition temperatures of each concentration for a period of 37 days.


**Fig. 1. Nature of the samples after 105°C Total Solid (TS) from the furnace**

## 2.2 Data Analysis/Design/Model Development

### 2.2.1 Procedure for TS and VS

All the feed stocks selected for the digestion was analyzed for TS and VS using standard methods [29]. To find out the TS in the substrates, samples were kept in an oven at 105°C for 24 hrs and the weight was taken before and after the period. The samples withdrawn from the oven was kept in a desiccator to prevent errors in weighing of crucibles by providing a 0% humidity atmosphere while the crucibles cool to room temperature.

To find out the VS in the samples, the oven dried crucibles was kept in a muffle Furnace at 550°C for 2 hrs. The crucibles were removed from furnace and cooled in air until most of the heat had dissipated. It was subsequently transferred to desiccators to cool to room temperature. The sample was then weighed. Once the sample attains a constant weight, it was noted down and used for calculation of VS.

### 2.2.2 Preliminary experimental analysis

Calculations:

For Cow Rumen:

➢ Total Solids (TS) = $\frac{(R-P)}{(Q-P)}$×1000 (1)

❖ Crucible name;

- 5c Total Solids (TS) = $\frac{(41.2953-36.5863)}{(68.4363-36.5863)}$×1000 = $\frac{4709}{31.85}$ = 147.85
- 3A Total Solids (TS) = $\frac{(40.8908-36.2379)}{(71.2787-36.2379)}$×1000 = $\frac{4652.9}{35.0408}$ = 132.79
- 2B Total Solids (TS) = $\frac{(38.5203-33.3191)}{(67.6670-33.3191)}$×1000 = $\frac{5201.2}{34.3479}$ = 151.43

- Let $A_v$ be the average for Total Solid of Cow dung digestate Inoculums,

$A_v$ = $\frac{(151.43+132.79+147.85)}{3}$ = 144.02 (2)

➢ Ash weight = $\frac{(S-P)}{(Q-P)}$ ×1000 (3)

- 5C Ash weight = $\frac{(S-P)}{(Q-P)}$ ×1000 = $\frac{958.8}{31.85}$ = 30.10
- 3A Ash weight= $\frac{(S-P)}{(Q-P)}$ ×1000 = $\frac{366.5}{35.0408}$ = 10.46
- 2B Ash weight = $\frac{(S-P)}{(Q-P)}$ ×1000 = $\frac{1140.6}{34.3479}$ = 33.21

Ash Weight average total $A_v$ = $\frac{(30.10+10.46+33.21)}{3}$ = **24.59**

➢ Volatile Solids (VS) = Total Solid (TS) - Ash Weight (4)

- 5C Volatile Solids = 5C TS - 5C Ash Weight = 147.85 - 30.10 = 117.75
- 3A Volatile Solids = 3ATS- 3A Ash Weight = 132.79 – 10.46 = 122.33
- 2B Volatile Solids = 2B TS – 2B Ash Weight = 151.43 – 33.21 = 118.22

Volatile Solids average total $A_v$ = $\frac{(117.75+122.33+118.22)}{3}$ = **119.43**

$Z_v$ are average total`s for Maize chaff. The above formulars/procedures apply also to Maize chaff calculations for TS, Ash weight and VS to confirm the values in Table 1.

All the feedstocks were analyzed for TS content to find the amount of moisture required and for VS to know the amount of organic materials present.

### 2.2.3 Experiment Set-up

The experiment was carried out in an air tight glass reactors of volume 256 ml with butyl rubbers stoppers. All the experiments were performed simultaneously within 25°C – 33°C and the outcome was taken for conversion from Pressure (mbar) to volume (litres).

In order to maintain anaerobic conditions, the bottles were closed with air tight butyl rubber stoppers. The bottles were kept static throughout, except manual mixing during gas measurements. The volume of biogas generated in the batch reactor was measured at regular intervals using gas pressure build-up detector device in mbar.

Calculated amount of the substrate (S) and inoculums (I) that will be added into the bottles separately for the feedstock composition are as follows:

Cow Rumen Inoculum and maize chaff

Cow Rumen:

VS ----- if 100g = 11.94gVS (5)
3g = x

$X = \frac{3\times 11.94}{100} = 0.357\text{gVS}$ (6)

Maize chaff:

VS------- if 100g = 31.44gVS (7)
3g = y

$Y = \frac{3\times 31.44}{100} = 0.943\text{gVS}$ (8)

1:1 ratio:

If 0.943gVS maize chaff requires 1× $0.943gVS$ for 0.357gVS (9)

Then 3g

$= \frac{3\times 0.943}{0.357} = 7.92\text{g rumen}$ (10)

1:1.55 ratio:

If 0.943gVS maize chaff requires 1.55× $0.943gVS$ (11)

$= \frac{3\times 1.55\times 0.943}{0.357} = 12.29\text{g rumen}$ (12)

1:3.5 ratio:

If 0.943gVS maize chaff requires 3.5× $0.943gVS$, (13)

Then 3g

$= \frac{3\times 3.5\times 0.943}{0.357} = 30.52\text{g rumen}$ (14)

Calculated amount of the substrate and inoculums that were added into the bottles separately for each feedstock composition is tabulated in Table 2. Substrate = maize chaff. Inoculum = cow rumen.

S/I ratio (mixing ratio) is the ratio of the substrate to the inoculum used to jump-start the fermentation process.

**Table 1. Calculations for Volatile solids (VS) and Total solids (TS) for the experiment**

| Crucible name | Crucible (g) (P) | C+S (wet) (g) (Q) | C+S (dried) 105°C (R) | C + Ash (g) (550°C) (S) | TS g/kg wet (T) | Ash g/kg wet (U) | VS g/kg Wet (T - U) |
|---|---|---|---|---|---|---|---|
| 1 | | | **Cow Rumen Inoculum** | | | | |
| 5C | 36.5863 | 68.4363 | 41.2953 | 37.5451 | 147.85 | 30.10 | 117.75 |
| 3A | 36.2379 | 71.2787 | 40.8908 | 36.6044 | 132.79 | 10.46 | 122.33 |
| 2B | 33.3191 | 67.6670 | 38.5203 | 34.4597 | 151.43 | 33.21 | 118.22 |
| **$D_v$** | | | | | **144.02** | **24.59** | **119.43** |
| 2 | | | **Maize chaff (Native one in Nigeria)** | | | | |
| 15 | 79.3406 | 129.3656 | 95.2369 | 79.7934 | 317.77 | 9.05 | 308.72 |
| 11 | 89.1688 | 141.9350 | 106.3921 | 89.5663 | 326.41 | 7.53 | 318.87 |
| 3 | 92.0314 | 146.1857 | 109.8607 | 92.7760 | 329.46 | 13.75 | 315.46 |
| **$Z_v$** | | | | | **324.46** | **10.11** | **314.35** |

**Table 2. Reaction loading mass**

| Substrate/Inoculum (S/I) | 1:1 | 1:1.55 | 1: 3.5 |
|---|---|---|---|
| Rumen | 7.92 g | 12.29 g | 30.52 g |
| Maize chaff | 3 g | 3 g | 3 g |

*Note: Substrate/Inoculum(S/I) 1:1.55 = 0.65, 1:3.5 = 0.3, 1:1 = 1*

The values in the table above was used in sizing/loading the laboratory experiment bottles of 256 mL, the addition of the different mixtures respectively gives total volume of the substrate in each reactor while the remaining space left is for biogas collection at the top of the bottles known as the Gas Holder Chamber.

## 2.3 Characterization and Flash Point Test

The flash point was tested using Digital Cleavage Closed Cup to detect the flash point.

The Digital Cleavage Closed Cup has a node for detecting and a chamber for inserting the sample plus temperature scale and time on it.

At Flash point (5s) the temperature of the 69.01% methane was observed to be -164°C.

### 2.3.1 Materials and method for Gas Chromatography-Mass Spectrometry (GC-MS) analysis

#### *2.3.1.1 Introduction*

Chromatography is an important analytical tool that allows for the separation of components in a gas mixture. GC is a common type of chromatography used to separate and analyze compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance or separating the different components and relative amounts of different components of a mixture. GC can also be used to prepare pure compounds from a mixture [30]. GC-MS uses two techniques that are combined into a single method for analyzing mixtures of chemicals. Gas chromatography separates the components of a mixture, and mass spectroscopy characterizes each of the components individually. Combining the two techniques helps to analyze the samples both qualitatively and quantitatively. As the sample is injected into the chromatograph, the sample mixture gets separated into individual components due to different flow rates. This results in quantitative analysis of the components, along with a mass spectrum of each component. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. Strengths of GC-MS analysis are (a) identification of organic components from complex mixtures, (b) quantitative analysis, and (c) determination of traces of organic contamination.

The samples were analyzed for biogas composition with an Varian 3800/4000 gas chromatograph/mass spectrometer (Agilent Technologies, USA), with Nitrogen as the gas carrier at a constant pressure of 100 kpa and a flow rate of 20 mL/min, equiped with an Agilent column, HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm ID) and a thermal conductivity detector (TCD). The temperature of the injector, column oven and detector were 120°C, 120°C and 160°C respectively at the rate of 10°C/min increase, injection port temperature at 250°C. Calibration was done using standard methane concentrations of 100, 300 and 10 000 ppm respectively and 500 ppm carbon dioxide gas. Samples which dissolved in chloroform were run fully at a range of 60-550 amu and the results were compared by using NIST $10^7$ Spectral library search programme.

After the instrument is warm up for 30 minutes the sample button is pressed to determine the composition of methane.

Before the gas is charged to the GC-MS, water is removed in a cold trap because the presence of the water disturbs the measurement.

#### *2.3.1.2 Procedure*

The procedure for the set up is as follows:

- Turn ON PA-2400 using red switch provided on front panel of the equipment.
- PA-2400 will show following message for 10 seconds
- “ENTER ABUAD CPE”

- Then after this it will display model no for 10 second “MODEL VARIAN-4800”
- Finally VARIAN-4800 will display “ READY “ “PRESS FN\SAMPLE”
- If Fn key is pressed it will enter into function mode.
- If SAMPLE key is pressed it will enter into sampling mode. In this mode sample is collected along with data-logging.
- “SAMPLING PL…”
- ….WAIT”
- “DATA LOGGING PL…”
- ….WAIT”
- NOW all parameter can be displayed one by one
- After one scan it will go to Ready Mode as
- $O_2$: 20.9 %V/V

CO: 000.0 PPM
CO2: 00.0%
NOx: 0000 PPM
HC: 000 PPM
Temp.: 030°c
Eff.: 80.0

- In this mode the data gets stored.
- For ready mode press” sample”

The relative percentage amount of each component was calculated by comparing its average peak area to the total areas. Software adopted to handle mass spectra and chromatograms was MS Work station 8. The NIST Version 2.0 library database of National Institute Standard and Technology (NIST) having more than 62,000 patterns was used for identifying the chemical components.

## 3. RESULTS AND DISCUSSION

### 3.1 Optimization Studies with Central Composite Design (CCD)

In this experimental design v12, CCD was used for the optimization of biogas production. The two factors used in this study were mixing ratio (S/I) and retention time (RT). By using CCD, a total of 13 runs were generated with different set up condition. The response was biogas yield (L) in term of Response 1 (R1). The result data shown in Tables 3, 4 and 5 was obtained from the laboratory experimental run. With CCD, the goodness of fit was determined by coefficient variation, R-squared while the statistical significance of the regression model was checked by the Fisher statistical test (F-test) in analysis of variance (ANOVA). Effects with p-value less than 0.05 and $R^2$ close to 1 were preferable to represent the reliability of a result.

#### 3.1.1 Experimental result for optimization of maize inoculated with cow rumen

**Table 3. Maize chaff with rumen inoculum**

| Std | Run | Factor 1 A: Mixing ratio | Factor 2 B: RT (days) | Response 1 cumulative biogas yield (L) |
|---|---|---|---|---|
| 10 | 1 | 0.65 | 31 | 0.3632 |
| 12 | 2 | 0.65 | 31 | 0.3678 |
| 5 | 3 | 0.3 | 31 | 0.3657 |
| 13 | 4 | 0.65 | 31 | 0.3746 |
| 4 | 5 | 1 | 37 | 0.3946 |
| 11 | 6 | 0.65 | 31 | 0.3713 |
| 2 | 7 | 1 | 25 | 0.3451 |
| 3 | 8 | 0.3 | 37 | 0.4187 |
| 7 | 9 | 0.65 | 25 | 0.3547 |

| Std | Run | Factor 1 A: Mixing ratio | Factor 2 B: RT (days) | Response 1 cumulative biogas yield (L) |
|---|---|---|---|---|
| 9 | 10 | 0.65 | 31 | 0.3654 |
| 1 | 11 | 0.3 | 25 | 0.3421 |
| 8 | 12 | 0.65 | 37 | 0.4223 |
| 6 | 13 | 1 | 31 | 0.3553 |

The result of Table 3 shows that mixing ratio of 0.65 (1:1.55) for 37 days gave the highest volume 0.4223 Liters (L). Below is its characterization to determine the best experimental run for biogas base on its methane percentage contained which is the primary constituent needed for combustion.

## 3.2 FTIR and GC-MS Analysis

### 3.2.1 FTIR Chart for bottle 147

Fig. 2a shows the FTIR chart analysis for bottle 147.

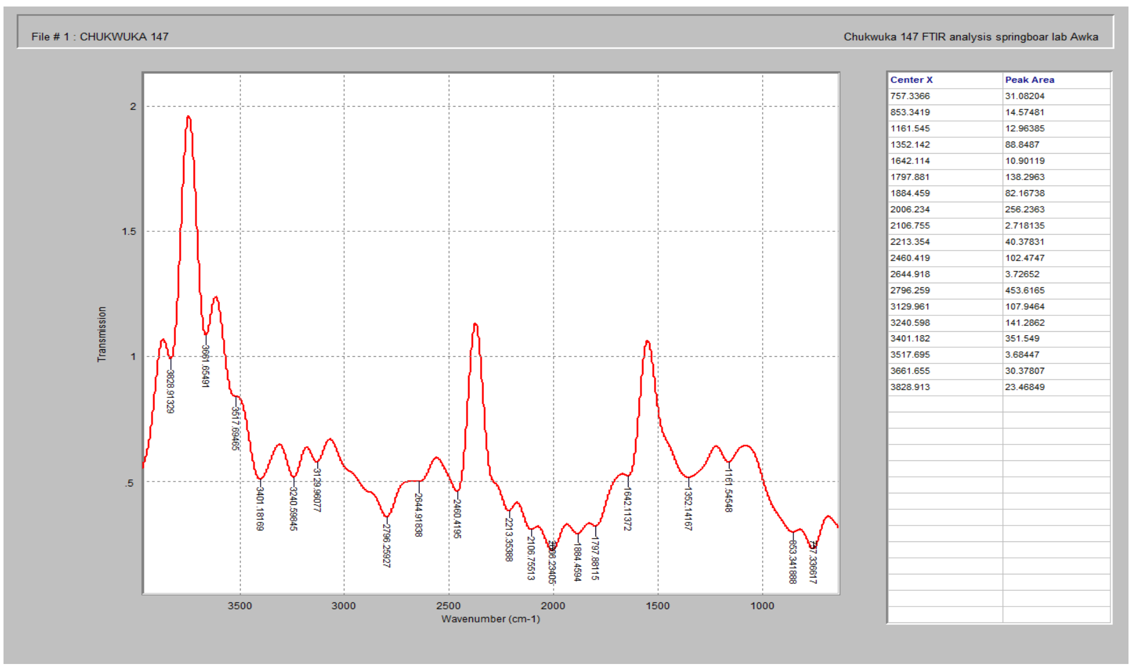


**Fig. 2a. Biogas from bottle 147**

**Table 4a. Functional group composition of bottle number 147**

| Functional group | Wavelength ($cm^{-1}$) Range | Wavelength ($cm^{-1}$) Actual | Molecular motion |
|---|---|---|---|
| 3° Alcohol | 4000 – 3850 | 3828.913 | O-H Stretch |
| 2° Alcohol | 3700 – 3400 | 3661.655 | O-H Stretch |
| Hydroxy | 3550 – 3450 | 3517.695 | O-H Stretch |
| Aromatic amines | 3510 – 3460 | 3401.182 | N-H Stretch |
| Alcohol and Hydroxy | 3400 – 3200 | 3240.598 | O-H Stretch |
| Aromatic ring | 3130 - 3070 | 3129.961 | C-H Stretch |
| Methyl | 2845 – 2650 | 2796.259 | C-H Stretch |
| Methylene | 2845 – 2610 | 2644.918 | C-H Stretch |
| Nitriles | 2500 – 2400 | 2460.419 | R-C≡N Stretch |
| Alkyne | 2260 – 2100 | 2213.354 | C≡C Stretch |

| **Functional group** | **Wavelength ($cm^{-1}$)** | | **Molecular motion** |
|---|---|---|---|
| | **Range** | **Actual** | |
| Isothiocyanate | 2150 – 1990 | 2106.755<br>2006.234 | -NCS Stretch |
| Carbonyl | 2100 – 1800 | 1884.459 | C=O Stretch |
| Acid anhydride | 1800 – 1750 | 1797.881 | C=O Stretch |
| Alkenyl | 1680 – 1620 | 1642.114 | C=C Stretch |
| Phenol | 1410 – 1310 | 1352.142 | O-H bend |
| Secondary amine | 1190 – 1130 | 1161.545 | C-N Stretch |
| Ether and Oxy (Peroxides) | 890 – 820 | 853.3419 | C-O-O Stretch |
| Alkyl halides | 785 – 540 | 757.3366 | C-Cl Stretch |
| Alkyl halides | 785 – 540 | 696.1469 | C-Cl Stretch |

### 3.2.2 FTIR Chart for bottle 179

Fig. 2b shows the FTIR chart analysis for bottle 179.

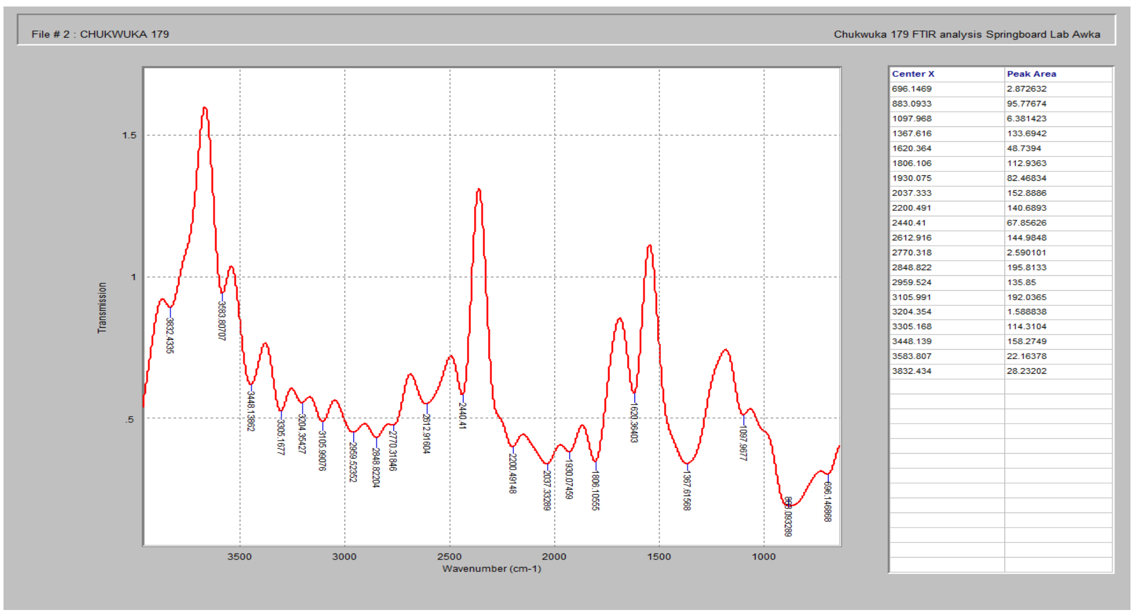


**Fig. 2b. Biogas from bottle 179**

Functional group compositions present in bio-fuel have been identified at a wavelength range between 4000 – 785 $cm^{-1}$ in FT-IR spectrum analysis as shown in Fig. 2a and 2b. Potential functional group compositions and potential compounds are shown in Table 4a and 4b.

The existence of a broad absorption band between 4000 – 3200 $cm^{-1}$ is due to the O-H stretching of the hydroxyl group from alcohols, phenols and the carboxylic group bonding to aromatic rings. The 3204.354 $cm^{-1}$ band was allocated to the N-H stretching of 2° amine compounds. The peak value between 3130 $cm^{-1}$ and 2850 $cm^{-1}$ region is assigned as the extension of C-H saturated bonds indicating the presence of aliphatic alkenes and methylene. The absorbance peak at 2460.419 and 2440.41 $cm^{-1}$ in Fig. 1 indicates the presence of C≡N stretching compounds as nitriles. The observed peaks at 2106.755 $cm^{-1}$ and 2037.333 $cm^{-1}$ indicate the presence of C=O isocyanate-and isothiocyanate-stretching vibrations, while the band-absorption at 2213.354 $cm^{-1}$ and 2200.491 $cm^{-1}$ may be caused by alkyne C≡C stretching vibrations. The band in the region from 2100 – 1800 $cm^{-1}$ shows the possible existence of carbonyl in the C=O stretching group. The observed peak at 1620.364 $cm^{-1}$ shows the presence of C=N stretching vibrations in the form of organic nitrates, while the deformation vibration at 1642.114 $cm^{-1}$ suggests the existence of C=C stretching aliphatic alkyl. The value at 853.3419 $cm^{-1}$ 883.0933 $cm^{-1}$ (as in Fig. 1) refers to the ether and oxy C-O-O stretching. 752.4573 $cm^{-1}$ as C-Cl bonds indicates the presence of alkyl halides when considering the band between 785 – 540 $cm^{-1}$ of the C-Cl stretch group. The majority of functional groups were identified by researchers working with other biomass classes. [3,31,5,6] and their classifications are similar to those reported in this study. These results indicate the presence of hydrocarbons, alcohols, ethers and phenolic compounds which suggest that the feedstocks can be used as biogas and fertilizers industries.

To analyze the methane percentage using the GC-MS, all bottle was left for 37 days for all during the experiment since Run 12 in Table 3 gave the highest volume at a temperature within 25°C – 33°C. And also determine the methane percentage at maximum retention time irrespective of the mixing ratio (S/I) as indicated in Table 5. From the biogas characterization using gas chromatograph, indicates that bottle number 179 has the highest methane composition (69.01%) while the average value of the percentage composition of the biogas for all the bottles is 61.70692, which is also within the required range (60% – 70%) as indicated in the literature of this work.

**Table 4b. Functional group composition of bottle number 179**

| Functional group | Wavelength ($cm^{-1}$) | | Molecular motion |
|---|---|---|---|
| | Range | Actual | |
| 3° Alcohol | 4000 – 3850 | 3832.434 | O-H Stretch |
| Phenols | 3640 – 3530 | 3583.807 | O-H Stretch |
| Aromatic amine | 3510 – 3415 | 3448.139 | N-H Stretch |
| Alcohol and Hydroxy | 3400 – 3200 | 3305.168 | O-H Stretch |
| 2° Amine | 3300 – 3200 | 3204.354 | N-H Stretch |
| Aromatic ring | 3130 - 3070 | 3105.991 | C-H Stretch |
| Aliphatic alkene/alkyl | 2970 – 2950 | 2959.524 | C-H Stretch |
| Methyl | 2880 – 2860 | 2848.822 | C-H Stretch |
| Methylene | 2850 – 2500 | 2770.316 | C-H Stretch |
| Methylene | 2850 – 2500 | 2612.916 | C-H Stretch |
| Nitriles | 2500 – 2400 | 2440.41 | R-C≡N Stretch |
| Alkyne | 2260 – 2100 | 2200.491 | C≡C Stretch |
| Isothiocyanate | 2150 – 1990 | 2037.333 | -NCS Stretch |
| Thiocyanate | 1980 – 1900 | 1930.075 | R-S-C≡N Stretch |
| Acid anhydride | 1850 – 1800 | 1806.106 | C=O Stretch |
| Organic nitrates | 1640 – 1620 | 1620.364 | C=N Stretch |
| Methyl | 1370 – 1365 | 1367.616 | C-H bend |
| Aliphatic Fluoro | 1150 – 1000 | 1097.968 | C-F Stretch |
| Ether and Oxy (Peroxides) | 890 – 820 | 883.0933 | C-O-O Stretch |
| Alkyl halides | 785 – 540 | 696.1469 | C-Cl Stretch |

**Table 5. Gas chromatograph biogas characterization**

| S/I ratio | Days | Bottle no- | Methane $CH_4$% | Carbon dioxide $CO_2$ % | Nitrogen $N_2$ % | Hydrogen Sulphide $H_2S$ % |
|---|---|---|---|---|---|---|
| 0.65 | 37 | 87 | 61.63 | 30.44 | 1.19 | 0.74 |
| 0.65 | 37 | 179 | 69.10 | 21.77 | 1.37 | 0.91 |
| 0.65 | 37 | 132 | 63.14 | 30.00 | 1.31 | 0.97 |
| 0.65 | 37 | 66 | 53.46 | 40.18 | 1.17 | 0.71 |
| 0.65 | 37 | 111 | 63.94 | 30.27 | 1.16 | 0.89 |
| 0.65 | 37 | 126 | 65.32 | 27.13 | 1.28 | 0.95 |
| 1 | 37 | 77 | 61.35 | 32.21 | 1.17 | 0.70 |
| 1 | 37 | 114 | 61.40 | 31.11 | 1.25 | 0.92 |
| 0.3 | 37 | 155 | 62.41 | 29.26 | 1.33 | 0.96 |
| 1 | 37 | 147 | 67.04 | 26.05 | 1.30 | 0.97 |
| 0.3 | 37 | 36 | 48.75 | 39.08 | 2.12 | 0.35 |
| 0.65 | 37 | 171 | 66.70 | 24.80 | 1.34 | 0.71 |
| 0.3 | 37 | 58 | 57.95 | 36.33 | 1.16 | 0.36 |

**Table 6. ANOVA Result (ANOVA Quadratic Model)**

| Source | Sum of square | Df | Mean square | F-value | p-value |
|---|---|---|---|---|---|
| Model | 0.0075 | 5 | 0.0015 | 95.03 | <0.0001 Significant |
| A-Mixing ratio | 0.0002 | 1 | 0.0002 | 10.49 | 0.0143 |
| B- HRT | 0.0063 | 1 | 0.0063 | 396.63 | <0.0001 |
| AB | 0.0002 | 1 | 0.0002 | 11.65 | 0.0112 |
| $A^2$ | 0.0003 | 1 | 0.0003 | 19.59 | 0.0031 |
| $B^2$ | 0.0008 | 1 | 0.0008 | 53.20 | 0.0002 |
| Residual | 0.0001 | 7 | 0.0000 | | |
| Lack of Fit | 0.0000 | 3 | 9.044E-06 | 0.4346 | 0.7402 not significant |
| Pure Error | 0.0001 | 4 | 0.0000 | | |
| Cor Total | 0.0076 | 12 | | | |

From the Table 6, the p-values is less than 0.05 which indicates the model terms are significant. In this case A, B, AB $A^2$, $B^2$ are significant model terms. Values greater than 0.1 indicate the model terms are not significant.

Lack of Fit F-value of 0.43 implies the lack of Fit is not significant relative to the pure error. There is 74.02% chance that a lack of fit p-value this large could occur due to noise. Non-significant lack of fit is good, because we want the model to fit.

**Table 7. Fit statistics**

| | |
|---|---|
| Std. Dev. | 0.0040 |
| Mean | 0.3724 |
| C.V% | 1.07 |
| $R^2$ | 0.9855 |
| Adjusted $R^2$ | 0.9751 |
| Predicted $R^2$ | 0.9566 |
| Adeq Precision | 28.9586 |

From the above the $R^2$ of 0.9855 is very close to 1 which is good.

The Predicted $R^2$ of 0.9566 is in reasonable agreement with the Adjusted $R^2$ of 0.9751; i.e the difference is less than 0.2.

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. My Adeq Precision of 28.9586 indicates an adequate signal. Thus, this model can be used to navigate the design space.

The percentage of coefficient of variation (C.V. %) is a measure of residual variation of the data relative to the size of the mean. Usually, the higher the value of CV, the lower is the reliability of experiment. Here a lower value of C.V. (1.07%) indicates a greater reliability of the experiment.

From the Table 8, the focus will be on the model maximizing the Adjusted $R^2$ and the Predicted $R^2$. Also, the Predicted Residual Sum of Squares (PRESS) is a measure of how well the model fitted each point in the design. The smaller the PRESS statistics, the better the model fitting the data points. Here the value of PRESS found as 0.0003.

### 3.2.3 Optimization of biogas production

The objective of this study was to investigate the effects of mixing ratio and retention time on biogas production from this study. The maximum levels for the independent variables and the effect of their interaction on biogas production were further explored using the central composite design of RSM. By applying multiple regression analysis on the experimental data, the second-order polynomial Equation (15) was derived to explain the biogas production.

**Table 8. Model summary statistics**

| Source | Std. Dev. | $R^2$ | Adjusted $R^2$ | Predicted $R^2$ | PRESS |
|---|---|---|---|---|---|
| Linear | 0.0109 | 0.8444 | 0.8133 | 0.7080 | 0.0022 |
| 2FI | 0.0105 | 0.8686 | 0.8248 | 0.7526 | 0.0019 |
| **Quadratic** | **0.0040** | **0.9855** | **0.9751** | **0.9566** | **0.0003 Suggested** |
| Cubic | 0.0045 | 0.9864 | 0.9673 | 0.6749 | 0.0025 Aliased |

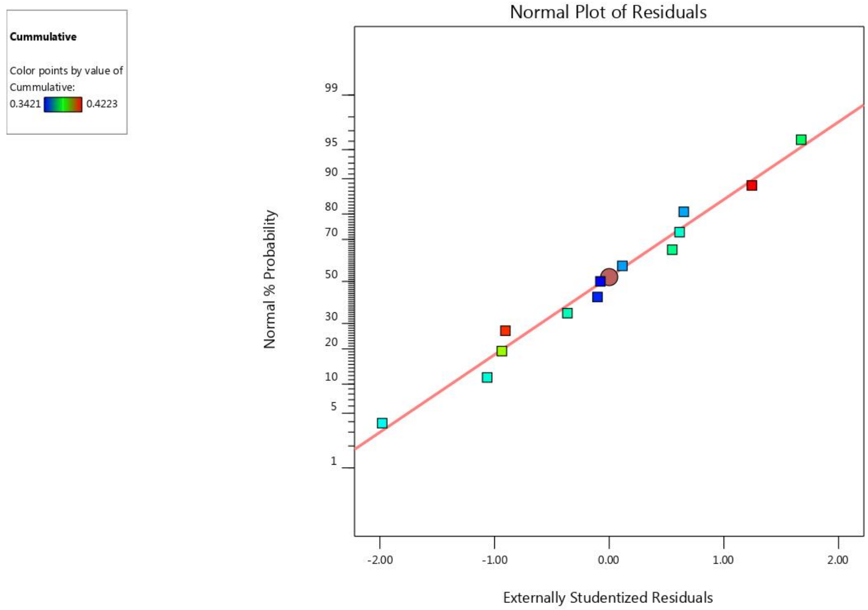


**Fig. 3. Normal probability plot of residuals for biogas yield data**

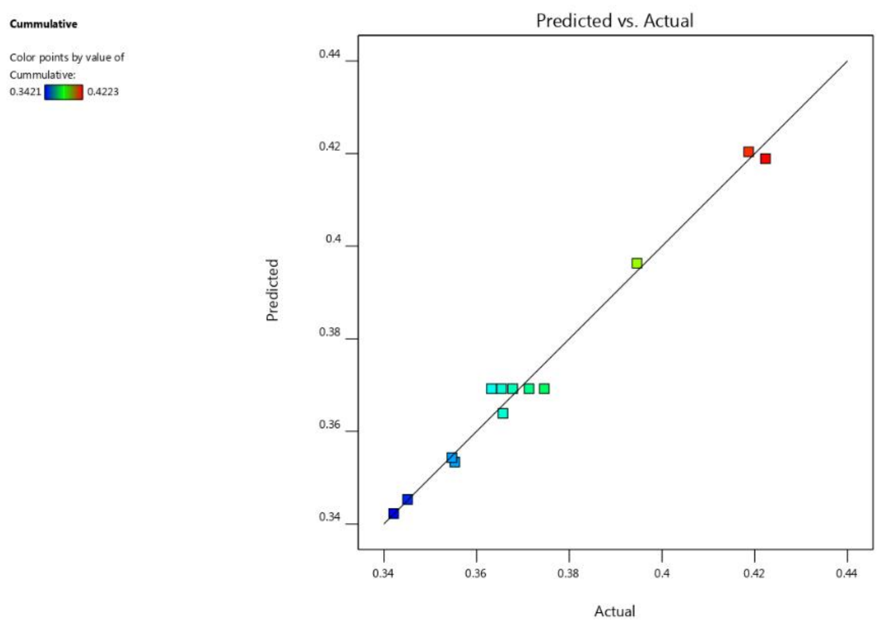


**Fig. 4. Predicted vs. Actual values of cumulative biogas yield**

**ANOVA Equations:**

**Actual**

$$\text{Cummulative} = +0.575856+0.197227\times\text{Mixing ratio} -0.022534\times\text{RT} - 0.003226\times\text{Mixing ratio} \times \text{RT} - 0.086319\times\text{Mixing ratio}^2+ 0.000484\times\text{RT}^2 \quad (15)$$

Let Cumulative biogas yield in Liters = $Y_{L,}$ Mixing ratio = $X_{1,}$ RT = $X_2$

Therefore,

$$Y_L = 0.575856+0.197227\ X_1 - 0.022534\ X_2 - 0.003226\ X_1\ X_2 - 0.086319\ X_1^2 +0.000484\ X_2^2 \quad (16)$$

This equation will be used to make predictions about the response for given levels of each factors.

**Coded**

$$\text{Cummulative} = +0.3692 -0.0053A +0.0323B -0.0068AB -0.0106A^2 +0.0174B^2 \quad (17)$$

This equation in terms of coded factors can be used to make predictions about the response for given level of each factors. By default, the high levels of the factors are coded as +1 and low levels of the factors are also coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factors coefficients.

From the Predicted vs the Actual plot in Fig. 4, shows that its cummulative biogas yield is in close alliance with the actual biogas yield because of the close to the slanting line.

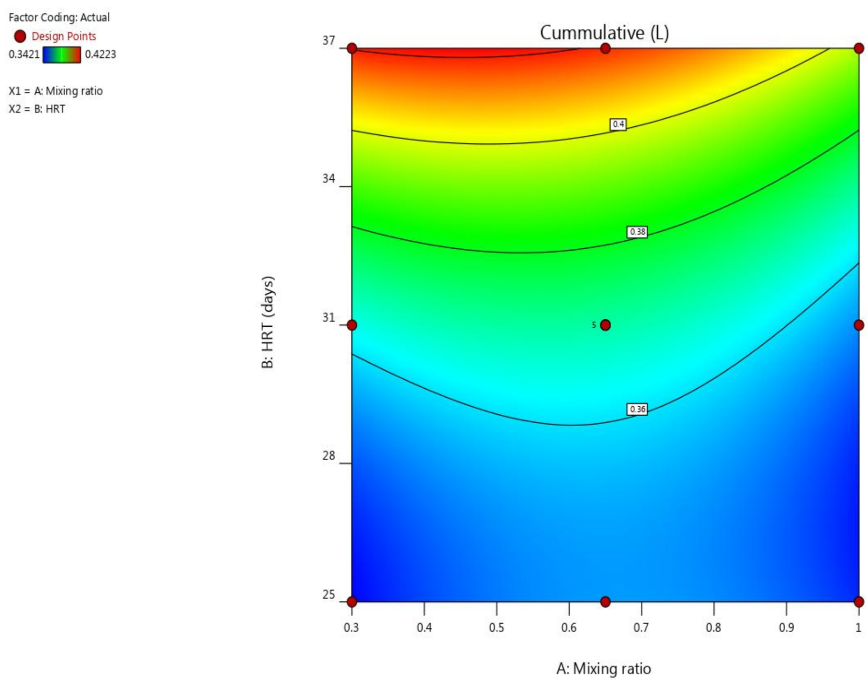


**Fig. 5. Contour plot graph of optimization**

This result in maximum conditions was at mixing ratio of 0.65 and retention time of 37 days. The final equation was defined a repeat of equation (15):

Let Cumulative biogas yield in Liters = $Y_{L,}$ Mixing ratio = $X_1$, HRT = $X_2$

Therefore,

$$Y_L = 0.575856 + 0.197227\ X_1 – 0.022534\ X_2 – 0.003226\ X_1\ X_2 – 0.086319\ X_1^2 + 0.000484\ X_2^2 \quad (18)$$

Actual Equation will be used to calculate the maximum yield at 1:1.55 and 37 days.

$$Y_L = 0.575856 + 0.197227\ X_1 - 0.022534\ X_2 - 0.003226\ X_1\ X_2 - 0.086319\ X_1^2 + 0.000484\ X_2^2$$

Y = 0.41884(L) = 0.42L which is in close alignment with the experimental value of run 12 in Table 3.

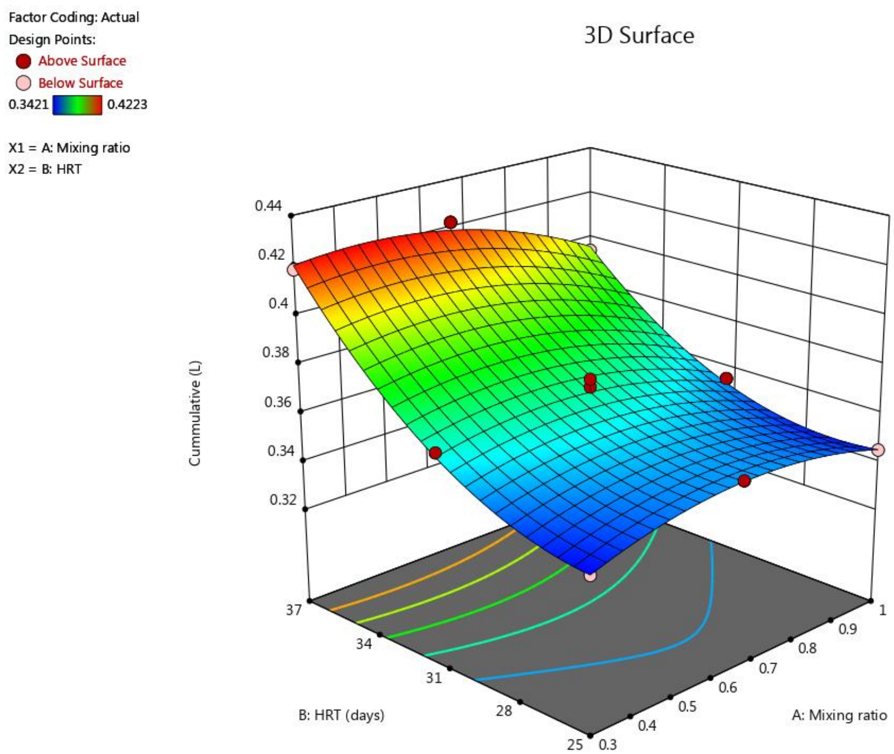


**Fig. 6. Model graph of optimization**

## 3.3 Comparison with Previous Studies

According to [28] corn straw and livestock digestion yielded 60% methane within 32days period, but the study validated that rumen microbes can be used and they promote biogas yield. Other reports are stated.

**Table 9. $CH_4$ percentage (%) of some organic wastes**

| Gas composition | $CH_4$ (%) | $Co_2$ (%) |
|---|---|---|
| 1 | 62.5 | 33.8 |
| 2 | 58.1 | 37.5 |
| 3 | 60.3 | 36.2 |
| 4 | 64.8 | 31.0 |

*[32]*

As shown in Table 9, is the methane characterization of biogas obtained for 40 days from a mixture ratio of 1:3 and the maximum volume of 15day for (1) Water Melon Peel + Sugar cane bagasse; (2) Water Melon Peel + Sugar cane bagasse + Cow Dung; (3) Water Melon Peel + Sugar cane bagasse + Pig Dung; (4) Water Melon Peel + Sugar cane bagasse + Poultry droppings.

The flash point of methane according to engineering toolbox is -135°C from non-renewable source.

Thus, after this experiment the flash point of 69.01% methane was -164°C. Also, mixing ratio of 1:1.55 is the best as against 1:2, 1:3, 1:4 etc. as reported in literatures.

## 4. CONCLUSION

CCD was used to determine the maximum condition for the production of biogas from maize chaff inoculated with cow rumen. The experiment showed that the effect of mixing ratio and retention time for biogas yield was significant. And suggested that a better mixing ratio of S/I should be 1:1.55 as against 1:2, 1:3, 1:4 etc.

earlier reported in literatures. The maximum yield parameters were 1:1.55 mixing ratio and 37 days of retention time as indicated in the 3D model graph. The $R^2$ value of 0.9855 which is close to 1 demonstrated that the model can efficiently be used for predicting methane production from the inoculation of cow rumen and maize chaff. Thus, the FTIR and GC-MS analysis performed, further validate the content of combustibility present in the biogas produced. And the analysis showed the presence of Alcohol and different methane percentage to the tone of 69%. As a result, we can say that this feedstock is highly recommended for biogas production as its methane content is higher than many others as stated in literatures, since its 69% close to 70%. And its average of all the bottles (61.7%) is within the acceptable range of 60% - 70%.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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