Effect of Nutrients on Biogas Production from Rice Straw

KHIN WIN AYE[1], NI NI WIN[2]
[1] *Department of Engineering Chemistry, Pyay Technological University*
[2] *Department of Engineering Chemistry, Technological University (Meiktila)*

Abstract- Nowadays, huge energy demand has become a critical problem in the world. Excessive utilization of fossil fuel as a primary source of energy brings about several crisis. Therefore, an alternative source of renewable energy, preferably biogas, production via anaerobic digestion technology has become the best solution for these energy issues. In this study, rice straw was used as the raw materials and mixed with 20% cow dung starter in batch type anaerobic digestion. Among the four different dilution ratios of straw and water (1:0.5, 1:1, 1:1.5 and 1:2 v/v), 1:1 ratio was the optimum for biogas production within 20 days period. The addition of nutrient, ammonium molybdate (0.01%, 0.02%, 0.03% and 0.04% w/v) to the anaerobic digester of optimum ratio of rice straw and water were studied and 0.02% w/v was observed to be the best for biogas production. The compositions of gases in biogas without nutrient were observed as 9.8% H_2S, 20.2% CO_2, 7.5% O_2 and 62.5% CH_4 and with (0.02% w/v) nutrient were observed as 0.1% H_2S, 28.3% CO_2, 1.8% O_2 and 69.8% CH_4. This nutrient addition method was improved the volume of biogas as well as the percentage of methane gas.

Indexed Terms- Biogas; rice straw; ammonium molybdate; methanegas

I. INTRODUCTION

Nowadays, huge energy demand due to the increase in population, global industrialization and urbanization has become a critical problem in the world. Excessive utilization of fossil fuel as a primary source of energy brings about environmental pollution, global climate change and health hazard. In most developing countries, animal dung, agricultural residues and firewood are used as fuel. The air pollutants in the smoke as a result of burning these fuels cause serious health problem.

The ultimate aim of the biogas program is to return cattle dung and agricultural residues to the soil for improving soil fertility and increasing crop production. In addition, biogas is important energy source for organized use in rural development. It is a gaseous mixture (H2S, O2, H2, CO2 and CH4) comprised mainly of methane and carbon dioxide liberated in the process of fermented biodegradation of organic waste by methanogenic bacteria under anaerobic condition, of which methane (60 to 70 percent) is the combustible component. In principle, production of methane by anaerobic is a two-step process:

i. photosynthetic fixation of carbon dioxide into biomass, and
ii. A partial microbial conversion of this biomass into CH4 + CO2.

The chemical composition of straw sample is shown in Table 1. To produce the maximum amount of biogas, straw must be mixed with large quantity of higher nitrogen source materials such as animal wastes.

Table 1. Chemical composition of straw sample

Chemical component	Content (%)
Carbohydrate	32.33- 35.69
Amylose	24.81- 30.26
Protein	5.87- 6.68
Albuminoids	3.70
Fats	1.42
Lignin	14-22
Ash	12.82
Carbon	42.96
Nitrogen	0.63
C/N ratio	68

This study was aimed to develop the best yield of biogas from the optimum dilution ratio of the typical raw material, rice straw; to observe the effect of a nutrient (ammonium molybdate) addition to anaerobic digester; and to measure the purity of biogas by using Orsat gas analyzer.

II. MATERIALS AND METHODS

A. Raw Materials for Biogas Production

Rice straw was used as the raw material for biogas production. It was collected from the farms near Mandalay Technological University (MTU), located in Patheingyi Township, upper Myanmar. It was piled up in a well ventilated room. The starter (cow dung) for the anaerobic digestion was also collected from the farms near MTU.

B. Chemicals and Solvents

Ammonium molybdate,$(NH_4)_6Mo_7O_{24}$. $4H_2O$, from (BELL COMPANY, U.S.A) was used to increase the biogas production rate. Pellets potassium hydroxide (JUNSEI CHEMICAL Co.Ltd., JAPAN) was used for the absorption of carbon dioxide in the analysis of biogas. Pyrogallol (BDH, ENGLAND) was used to determine the composition of oxygen in the biogas mixture. 95% methyl alcohol (BDH, ENGLAND) was utilized to absorb the methane gas in the Orset meter for the percentage of methane in the biogas. 95% reagent grade (sp.gr 1.84) concentrated sulphuric acid, H_2SO_4 (BDH, ENGLAND) and 98% copper (II) sulphate, $CuSO_4$ (BDH, ENGLAND) were used as hydrogen sulphide absorbent acidified solution in the Orset meter.

C. Equipment's for Analysis of Biogas

An Orset meter (Cabinet model No.39-289 Burell Corpo-ration, PGH.PA) with 100 mL glass materials was served as a platform for this experiment.

D. Equipment for Process Running

Lab scale digester (20 Liter, Plastic bottle), Gas holder (1 Liter, Glass), Circulation oven (230V, 30 Watt, 80 Hz, MRK Inc., JAPAN), Pipes (0.5 cm Φ and 0.4 cm Φ, Plastic), U-tube (0.5 cm, Glass), Thistle funnel (10 cm Φ, Glass) were used for process running.

E. Analysis of Raw Materials (Rice Straw)

1) Determination of Total solid and moisture content of rice straw

Total solid and moisture content of rice straws were tripli-cate determined by oven drying method. Accurately weighed rice straw sample (1g) was placed into a lid covered porcelain crucible which had previously been ignited to con-stant weight. And then it was heated in an oven (105ºC) for about two hours. During the heating, the crucible was kept slightly uncovered. After heating, the crucible was removed from the oven, and cooled in a desiccator. Heating, cooling and weighing were repeated at hourly intervals until the loss in weight between successive weighing didn't exceed 0.5 mg. The results are shown in Table 2.

Table 2. Total Solid and Moisture Contents of Rice Straw

No;	Total Solid Content (%)	Moisture Content (%)
1	83.04	16.96
2	84.00	16.00
3	84.22	15.78
Average	83.75	16.25

2) Experimental Set up for Lab-scale Digester

The prepared straw samples were placed in each 20L digester and capped tightly with rubber stopper which had two holes for adding lime and the biogas outlet. Then, the adapter was joined with the open end U tube by a plastic pipe. The open-end U tube was entered the inverted measuring cylinder which was on the bee-hive shelf in the water bowl. Another open-end U tube coming out from the measuring cylinder was joined to the Orset meter by using an adapter. All the junctions were sealed with grease to ensure that there was no leakage within the system.

3) Effect of Dilution Ratio of Rice Straw for Anaerobic Digestion

Firstly, raw materials rice straws were cut into small pieces (0.5 cm) long. This study was conducted by four digesters (20 Liter), with straw sample and water ratio of (1:0.5, 1:1, 1:1.5 and 1:2) by volume. And then the starter, fresh cow dung 20% by volume was added to each digester. The digesters were thoroughly shaken thrice a day. The gas production rate was measured hourly in a day time. The daily gas production rates for four different dilution ratios of slurry (1:0.5, 1:1, 1:1.5 and 1:2 v/v) are as shown in Table 4.

4) Effect of Ammonium Molybdate as a Nutrient for Anaerobic Digestion of Straw Sample

To study the effect of ammonium molybdate on microbial degradation of each digester, we used the 20L digesters along with the optimum dilution ratio of (1:1) already mixed with fresh cow dung 20% by volume. And then, 0.01% to 0.04% (w/v) of ammonium molybdates were added to four different digesters. Biogas production from each digester was measured hourly by simple water displacement methods. The percentage of CH4 content was observed by constant pressure volumetric analysis using an Orset apparatus. During the experiments the temperature was observed as the room temperature. The pH of the slurry was recorded by pH paper.

III. ANALYSIS OF BIOGAS COMPOSITION

A. Apparatus

Orset-type gas analysis apparatus consisting of the absorp-tion pipettes for H2S, CO2, O2, CH4, and water jacketed gas burette with leveling bottle was used for analysis of biogas composition.

B. Preparation of Absorbents

i. Concentrated sulphuric acid (2 cm3) was added to 100 cm3 of 10% copper (II) sulphate solution. This solution was used for H2S Absorption.
ii. 100 cm3of 33% Potassium hydroxide solution was prepared and this solution was used for CO2 Absorp-tion.
iii. Pyrogallol (20 g) was dissolved in 500 cm3 of po-tassium hydroxide solution and this solution was used for O2 Absorption.
iv. 95% methyl alcohol was used for CH4 Absorption.

C. Procedure for biogas Analysis

Four gas absorption pipettes were connected to the gas burette in series according to the priority order as shown in Table 3.

Table 3. The Priority Order of Absorption of the Gases

Constitu-ents	Absorbent	Priority Order
H_2S	Acidic copper (II) sulphate solution	1
CO_2	33% potassium hydroxide solution	2
O_2	Alkaline pyrogallol solution	3
CH_4	Methyl alcohol	4

D. Injection of the Biogas

After setting up the apparatus, 100 cm3 of the gas sample was injected with a gas syringe into the 100 cm3 calibrated gas burette (previously filled with water). The volume of the gas in the gas burette was recorded as V1.

E. Performing Gas Absorption to Determine the Composition of the Biogas

By opening the tap for the acidic copper (II) sulphate solution, while closing the other taps, the H2S in the gas sample was absorbed by raising and lowering three or four times of the pressure bottle: connected to the gas burette. After absorbing H2S completely, the volume of the gas in the burette was recorded as V2. CO2 from the gas sample was removed by passing it through CO2 – absorption pipette filled with the potassium hydroxide solution. The gas sample was passed by raising and lowering three or four times of the pressure bottle. When the absorption of CO2 was complete, the volume of the gas in the gas burette was recorded as V3. O2 from the gas sample was absorbed in alkaline solution of potassium pyrogallate by using the same procedure as above. After the complete absorption of O2, the volume of the gas in the gas burette was recorded as V4. Similarly, CH4 in the gas sample was absorbed in methyl alcohol. After the complete absorption of CH4, the volume of the gas in the gas burette was recorded as V5. The percentage by volume of each gas present in biogas was calculated as follows:

% H2S = (V_1-V_2)/V_1 ×100
% CO2 = (V_2-V_3)/V_1 ×100
% O2 = (V_3-V_4)/V_1 ×100
% CH4 = (V_4-V_5)/V_1 ×100

Biogas from the digestion of straw sample using four different dilution ratios and four different ammonium molybdate ratios were analyzed by employing the above procedure. The results from the calculation were shown in Table 5 and Table 6.

IV. RESULTS AND DISCUSSION

A. Effect of Water on Anaerobic Digestion

The amount of water is an important factor for anaerobic digestion. With too much water, the rate of gas production per unit volume in the pit will fall, preventing optimum use of pit. If the water content is too low, acetic acid will accumulate inhibition the fermentation process and hence a rather thick scum will form on the surface.

Table 4. Analysis Data for Four Different Dilution Ratios of Slurry

Dilution ratio (by vol;)	Avg. Gas production rate (cm^3/hr)	% Gas composition (by Vol;)			
		H_2S	CO_2	O_2	CH_4
1:0.5	98	12.3	29.6	10.5	47.6
1:1	143.6	9.8	20.2	7.5	62.5
1:1.5	107	4.3	25.7	14.9	55.1
1:2	118	10.5	31.3	7.5	50.7

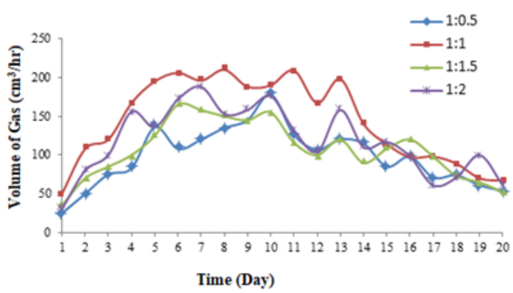

Figure 1. The Daily Gas Production Rates for Four Different Dilution Ratios of Slurry

Therefore the experiments were carried out to observe the optimum production of biogas from four different dilution ratios of straw and water (1:0.5, 1:1, 1:1.5 and 1:2 v/v) within 20 days periods. Each experiment is mixed with 20% cow dung starter and recorded gas production rate. In early stage, fewer biogas come out from the 20L digesters. When the enough aging time of straw pieces for anaerobic digestion was reached, the biogas evolved daily faster and faster. 1:1 dilution ratios of straw and water gave the best result as shown in Table 4.

The daily gas production rates for four different dilution ratios of slurry (1:0.5, 1:1, 1:1.5 and 1:2 v/v) are as shown in Figure 1. We observed that the optimum dilution ratio (1:1) gave the maximum average gas production rate (143.6 cm^3/hr). The pH range was 7-8 and the temperature range was 27-32℃ for that optimum dilution ratio.

B. Effect of Nutrient (Ammonium Molybdate) for Anaerobic Digestion

This research part is to produce the maximum biogas production from the observed optimum dilution ratio by adding the ammonium molybdate as a nutrient.

Table 5. Analysis Data for Four Different Amounts of Am-monium Molybdate in Slurry

Ammonium Molybdate (weight %)	Avg. Gas production rate (cm^3/hr)	% Gas composition (by Vol;)			
		H_2S	CO_2	O_2	CH_4
0.01%	126.1	5.3	31.7	1.3	61.7
0.02%	174.2	0.1	28.3	1.8	69.8
0.03%	146.8	2.6	24.6	5.2	67.6
0.04%	121.3	5.1	28.4	6.4	60.1
Nil	143.6	9.8	20.2	7.5	62.5

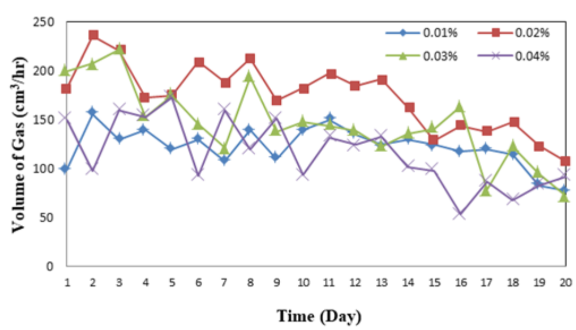

Figure 2. Daily Gas Volume Rate for Four Different Amounts of Ammonium Molybdate in the Anaerobic Diges-tion of Rice Straw

The cumulative gas production for different experiments was measured at various ratios of nutrient ammonium mo-lybdate (0.01%, 0.02%, 0.03% and 0.04%) as shown in Fig-ure 2. The nutrient amount (0.02% w/v) gave the average maximum gas production rate (174.2 cm3/hr) among the four different ratios . It showed that addition of nutrients enhance biogas production and lead to process stability . The pH range was 7 - 8 and the temperature range was 22 - 29℃ (mesophillic condition) for that optimum dilution ra-tio.

According to Figure 2, addition of ammonium molybdate to rice straw gave an increase in cumulative gas evolution for a retention time of 20days. It was observed that addition of ammonium molybdate had no adverse effect at very low concentration while the addition of 0.02% ammonium molybdate to the slurry at start up give a significant increase in the gas evolved. It also indicates that addition of ammonium molybdate highly activates the methanogenic process as well as reduce the retention time period. The ex-act mechanism for this biochemical reaction is still under investigation. In addition to an organic carbon energy source, anaerobic bacteria appear to have relatively simple nutrient requirements. Which include Nitrogen, Phosphorous, Magnesium, Sodium, Maganese, Calcium, order to permit growth in digestion of raw sample. Essential nutrient can become toxic to organisms if its concentration in the substrate becomes too great. Therefore it may be required to maintain an optimum level and to achieve good digester performance for the best biogas production without toxic effects. The imbalance between the high nitrogen content and the carbon source cause toxicity by generating ammonia.

High C/N ratio favors ammonia production but low C/N ratio retards the growth of microorganisms [10]. If the C/N ratio is wider, there will be also biodegradation and microbial growth, but retarded by nitrogen lack. If the C/N ratio is lower, the microbial development is undisturbed, but the losses of nitrogen as gaseous ammonia are relatively high, because the microorganisms cannot use it rapidly. Straw sample was carbon (42.96%) and nitrogen (0.63%). Accordingly, carbon to nitrogen ratio of straw sample was about 68[12]. This ratio is more than 30, which is the reported optimum ratio for biogas production. Therefore, it can be seen that the straw sample has low percentage of nitrogen con-tent. So nitrogen fortification is necessary to obtain the optimum ratio. For nitrogen fortification, addition of ammonium molybdate and animal wastes with high nitrogen con-tent into the digester were carried out in the present research work. When 0.02% (w/v) ammonium molybdate was added, the gas production was increased. Therefore to boost up biogas production the 0.02 %(w/v) of ammonium molybdate must be used as nutrient in the digestion of straw waste material.

C. Analysis of Biogas Composition

The compositions of gases in biogas without nutrient were observed as 9.8% H2S, 20.2% CO2, 7.5% O2 and 62.5% CH4 and with (0.02% w/v) nutrient were observed as 0.1% H2S, 28.3% CO2, 1.8% O2 and 69.8% CH4. The results show that the percentage of H2S is significantly decreased and CH4 gas is increased about 7%. It can be seen that ammonium molybdate acts as a microbial activator in the methanogenesis process and improves the volume of biogas as well as the percentage of methane gas which is the combustible component [12].

Table 6. Comparison of Biogas Composition between Experimental Results (Optimum Ammonium Molybdate 0.02% (w/v)) and Literature

Constituents	% by volume	
	Experimental results	Literature
H_2S	0.1%	0.1%
CO_2	28.3%	27-43%
O_2	1.8%	0.5-1%
CH_4	69.8%	54-70%

V. CONCLUSIONS

In this biogas production process, rice straw was used as the raw materials and mixed with 20% cow dung starter in batch type anaerobic digestion. Among the four different dilution ratios of straw and water, 1:1 (v/v) ratio was the optimum for biogas production rate (143.6 cm3/hr) within 20 days period. The addition of various concentration of nutrient, ammonium molybdate to optimum ratio of the anaerobic digester of straw and water were studied and 0.02% w/v was observed the best for biogas production and the gas rate was (174.2cm3/hr). The compositions of gases in biogas without nutrient were observed as 9.8% H2S, 20.2% CO2, 7.5% O2 and 62.5% CH4 and with (0.02% w/v) nutrient were observed as 0.1% H2S, 28.3% CO2, 1.8% O2 and 69.8% CH4. Although trace elements are essential for bacterial growth, an overdose of these nutrients may result in methane inhibition. It can be conclude that the addition of cowdung and (0.02% w/v) ammonium molybdate changed the C/N ratio of the slurry, which may have eventually increased the gas production rate, through support of a higher microbial population. This nutrient addition meth-od was improved the volume of biogas as well as the percentage of methane gas. This research work would be helpful in future studies on the continuous two-stage biomethanation or methanogenesis process.

REFERENCES

[1] D. Deublein, & A. Steinhauser, “Biogas from waste and re-newable resources: an introduction”, John Wiley & Sons, 2001.

[2] F. Cherubini, N.D. Bird, A. Cowie, G. Jungmeier, B. Schlamadinger, & S. Woess-Gallasch, “Energy and green-house gas-based LCA of biofuel and bioenergy system: Key issues, ranges and recommendations”.

[3] A. Demirbas, “Biomass resource facilities and biomass con-version processing for fuels and chemicals, “Energy conver-sion and management. Vol. 42, pp. 1357-1378, 2001.

a. http://dx.doi.org/10.1016/S0196-8904(00)00137-0

[4] M. Lebuhn, F. Liu, H. Heuwinkel, & A. Gronauer, “Biogas production from mono-digestion of maize silage-long-term process stability and requirements.

[5] L. Molnar, & I. Bartha, “Factors influencing solid-state anaer-obic digestion”, Biological wastes, Vol. 28, pp. 15-24, 1989.

a. http://dx.doi.org/10.1016/0269-7483(89)90045-1

[6] A. Wilkie, M. Goto, F.M Bordeaux, and P.H. Smith, “En-hancement of anaerobic methanogensis from napiergrass by addition of micronutrients”, Biomass, Vol. 11, pp 135-146, 1986.http://dx.doi.org/10.1016/0144-4565(86)90043-0

[7] I.A. Nges, A. Bjoim, & L. Bjornsson, “Stable operation dur-ing pilot scale anaerobic digestion of nutrient supplemented maize/sugar beet silage”,

[8] Zaw Lay Win, “Biogas Production from Distillery Waste”, M.E (THESIS), Dept; of Chemical Engineering, Yangon Technological University, Myanmar, pp 24, 2004.

[9] A. Wahab, Y.R Sumantri and L. Kartangara, “Energy Re-sources in National Development in Indonesia”,

[10] Phyu Phyu Win, “Production and Utilization of Biogas from Straw Waste Materials” M.Sc (THESIS), Dept; of Chemistry, Mawlamyine University, Myanmar, pp 42, 1992.

[11] V.B.D Skerman, “A Guide to the Identification of the Genera of Bacteria: with Methods and Digest of Generic Characteris-tics”, Williams & Wilkins Co., pp 18, 1967.

[12] Sudha Singh, SK Singh, “Renewable Energy”, 6(4), pp 441-443, 1995.