CALORIFIC VALUE IMPROVEMENT OF BIOMETHANE PRODUCED FROM CO-DIGESTION OF COW DUNG AND VEGETABLE WASTES AT AMBIENT CONDITIONS

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Abstract - *Many technologies of scrubbing CO_2 from bio-methane are in operation including water scrubbing, chemical scrubbing with amine and even biological scrubbing with micro-organisms. Some of these technologies exhibit high operational costs and environmental impacts, hence planning of a bio-methane plant in order to decide the optimal technological configuration considering these constraints is pertinent. Production of bio-methane was done using cow dung and vegetable wastes as substrates and the raw bio-methane laboratory analysis showed 69.62% methane and 30.32% CO_2.The optimization of CO_2 scrubbing from bio-methane produced at ambient conditions was done with Optimal (Custom) Design of RSM and the outcome revealed that a quality bio-methane of up to 98.98% was produced using 1 mole of NaOH in a packed bed scrubber with desirability of 99%. The ambient conditions of temperature and pressure applied in scrubber has greatly reduced installation costs prevalent in other scrubbing methods and with application of 1 mole, the effluent discharged is less hazardous to the environment.*

Key words: bio-methane, scrubbing, optimization, ambient conditions, effluent, optimal (custom) design, less hazardous, environment

1. INTRODUCTION

The atmosphere is replete with various kinds of contaminants emanating from industrial activities, domestic wastes and poor environmental management of wastes. The organic waste fraction in these wastes as contained in many journals could be converted to bio-methane. Bio-methane from anaerobic digestion of organic materials is a renewable energy that contains mainly CH_4 and CO_2 and the trace components that are often present in bio-methane are water vapor, H_2S, siloxanes, hydrocarbons, ammonia, O_2, CO and N_2 in varying concentrations. [3].

Bio-methane is one of the most sustainable fuels available nowadays, which can be used as a transport fuel or incorporated into natural gas grids. Bio-methane is being used in some homes for cooking as a kind of alternative to fossil natural gas. CO_2 reduces the bio-methane specific calorific value, while the presence of H_2S triggers corrosion of pipelines, storage tanks and compressors [7] and in fact any metal parts it comes in long contact with. Hence there is need for improvement.

Some technologies (physical and chemical) exist for production and purification of bio-methane but some of them exhibit high operational costs and environmental impacts.

Production of bio-methane through anaerobic process can take place at different temperatures determined by the operating temperature ranges: psychrophilic (below 25^oC), mesophilic (25^oC – 45^oC), and thermophilic (45^oC – 70^oC) and these processes has varying hydraulic retention time (HRT) ranges of (70 – 80) days, (30 – 40)days and (15 – 20) days respectively [6].

Psychrophilic and thermophilic processes need application of heat but mesophilic process need no heat for the operation. The thermophilic process has some disadvantages which includes larger degree of imbalance, large energy demand due to high temperature and higher risk of ammonia inhibition. More so thermophilic bacteria are more sensitive to temperature fluctuations of ±1°C and require longer time to adapt to a new temperature [6].

Individual planning of a bio-methane plant in order to decide the optimal technological configuration and size is a prerequisite for both economical and environmental success [5].

The aim of this research work was the optimization of bio-methane upgrading using alkaline solution of sodium hydroxide at ambient conditions, considering the operational cost and environmental impacts. The major contaminant considered in this work was CO_2. The experiment was carried out at ambient temperature and pressure, thereby reducing capital and operational costs. The optimization done using Optimal (Custom) Design was to ascertain the best operational conditions among many that will give removal efficiency of up to 98% CO_2.

Mathematical modelling had been used to optimize bio-methane use that included the different parameters that will influence the final outcome and enables its analysis in a simplified way [5]. The author analysed the available technologies for CO_2 removal which included water scrubbing, organic solvent scrubbing, amine scrubbing and pressure swing adsorption methods. The main disadvantages of methane enrichment technologies were summarized by [5] as follows:

- Higher investment costs apply for the whole process
- It is currently suitable only for larger plants due to high costs.
- Energy is needed for the upgrading process.
- Methane that is lost in the upgrading process must be prevented from causing a methane slip to the atmosphere.

Upgrading at ambient conditions as seen from the experiment has the following advantages:

- Lower investment costs because raw bio-methane compressor and initial storage vessel will be removed. Raw bio-methane enters upgrading compartment direct from bio-digester though controlled by a valve.
- This ambient condition of upgrading is most suitable for smaller plants making it affordable for low income earners.
- Energy is not needed for the upgrading process except when bottling the finished product into pressure cylinder is desired.
- Methane slip is minimized as the produced raw bio methane is not stored. It enters the purification chambers immediately, so the environment is protected.

Analyzing bio-methane energy potential and its natural gas equivalent, it was discovered by [4] that methane (CH_4) is the main component for both gases being 91% in natural gas and 55 – 70% for raw bio-methane. In addition, CO_2 is much higher in bio-methane than in natural gas as contained in table 1.

Table -1: Physical Properties of Natural Gas and Bio-methane

Key numbers	unit	Natural gas	Bio-methane
CH_4 (methane)	Vol%	91.0	55 – 70
CO_2 (carbondioxide)	Vol%	0.61	30 – 45
N_2(nitrogen)	Vol%	0.32	0 -2
H_2S(hydrogen sulphide)	Ppm	1	100 – 50,000
Net calorific value	MJ/m3	39.2	23.3
Upper Wobbe index	MJ/m3	54.8	27.3
Lower Wobbe index	MJ/m3	49.6	25.1

Source: [4]

These contaminants affect the calorific value and other useful properties of the bio-methane. With the upgrading of bio-methane product quality of up to 98% methane obtained at ambient conditions, the result can compete favorably with natural gas quality.

2. METHODOLOGY

An experiment was performed by co-digesting cow dung and vegetable wastes anaerobically for 30 days hydraulic retention time (HRT) at mesophilic(ambient) temperature of 30°C. The raw bio-methane generated was analyzed at Springboard Laboratory, Awka Anambra State Nigeria, using Buck 930 type of Gas Chromatography. The same raw bio-methane quality was purified chemically in the second vessel by the addition of solution of Sodium hydroxide (NaOH) at varying concentrations – 0.05, 0.10 and 1mole respectively with a control sample in the absence of NaOH. The purified bio-methane was passed through de-moisturizer to eliminate the moisture content of the product.

The yield of bio-methane was optimized using the results got from chemical purification.

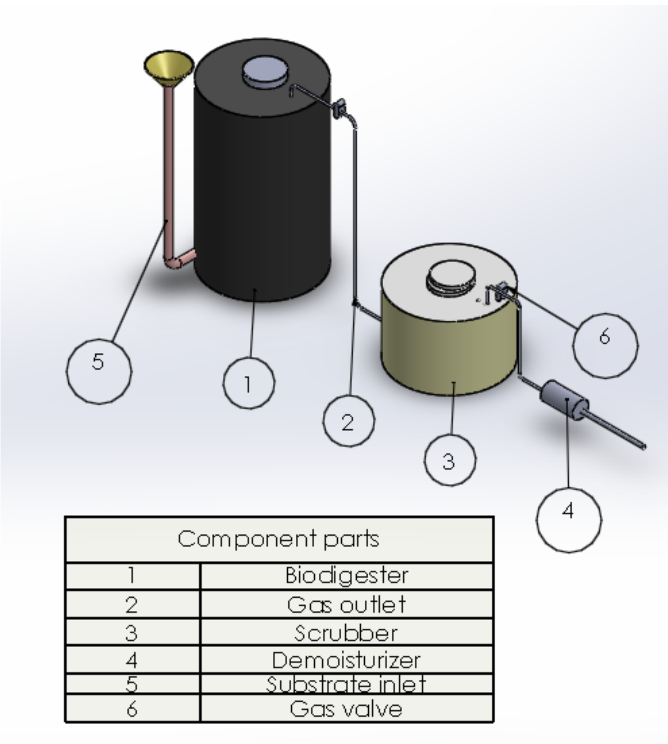

Figure 1: Bio-methane Production and CO_2 Scrubbing Set Up

2. RESULTS AND DISCUSSION

The bio-methane was produced at the prevailing temperature and pressure conditions [9]. The raw bio-methane generated in the digester showed the result of 69.67% raw bio-methane and 30.32% CO_2. It was scrubbed chemically and the top product was analyzed using Gas Chromatography as displayed in Table 2 and also represented in the bar chart below (figure 2). Different molarities of sodium hydroxide solution were applied.

Table -2: Summary of Gas Absorption GC Results at Different Molarities

Raw Bio-methane (Vol. %)	CO_2 In raw Bio-methane (vol. %)	Aqueous NaOH for Scrubbing (Moles)	Bio-methane Yield (vol. %)
69.67	30.32	Control sample	85.3
69.67	30.32	0.05	89.12
69.67	30.32	0.1	93.25
69.67	30.32	1	98.96

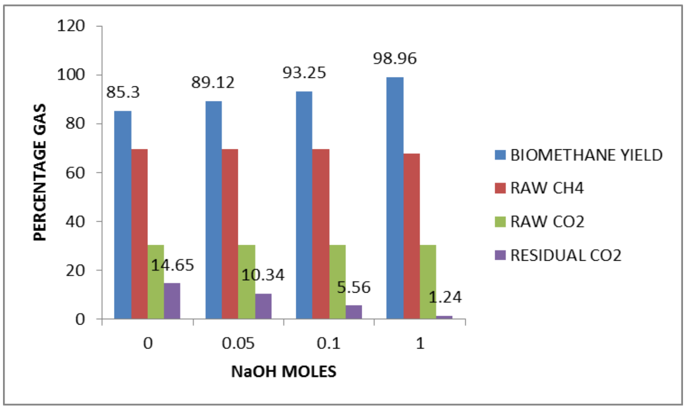

Figure 2: GC result of Scrubbing performance.

4. OPTIMIZATION USING OPTIMAL (CUSTOM) DESIGN

This design was selected because it is a flexible design structure to accommodate custom models, categoric factors and irregular (constrained) regions [8]. Runs are determined by selection criteria chosen during the build. It is flexible to accommodate 2 levels and 2 numeric factors to generate as much as 16 runs for one response, which other designs could not do. It gave no negative factor in the simulation process.

Table -3: Response of Interaction of Factor 1 (Raw Bio-methane) and Factor 2 (NaOH Moles) Respectively

Run	Factor 1 A:RAW BIO... %	Factor 2 B:MOLES OF... MOLES	Response 1 BIOMETHAN... %
1	30.3076	0.57	41.7666
2	0	1	0
3	69.6726	0.3	95.1136
4	47.029	0.35	64.6649
5	69.6726	1	98.955
6	32.7717	1	46.5452
7	0	0.5	0
8	48.4225	0	59.2835
9	0	0.5	0
10	22.992	0.195	31.1195
11	69.6726	0.3	95.1136
12	54.693	0.7	76.5395
13	0	0	0
14	48.4225	0	59.2835
15	30.3076	0.57	41.7666
16	30.3076	0.57	41.7666

The response column above (Table 3) was produced based on the results generated by the software for 16 runs. In the experimental results, at constant value of percentage raw bio-methane and carbon dioxide, the experimental response depicted proportional increase with increase in molarities of NaOH as scrubbing liquid. From that fact the Response was calculated for the generated RSM FACTOR1 (Raw Bio-methane) and FACTOR 2 (NaOH moles).

Table -4: Model Summary Statistics Table Suggesting Cubic Response:

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	2.09	0.9969	0.9964	0.9945	99.65	
2FI	1.68	0.9981	0.9977	0.9959	73.31	
Quadratic	1.26	0.9991	0.9987	0.9957	77.86	
Cubic	0.054	1.0000	1.0000	0.9991	16.86	Suggested
Quartic	0.000	1.0000	1.0000		+	Aliased

Table - 5: Analysis of Variance Table (Partial Sum of Squares)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	17986.10	9	1998.46	6.890E+005	< 0.0001	significant
A-RAW BIOC	796.43	1	796.43	2.746E+005	< 0.0001	
B-MOLES OI	6.700E-003	1	6.700E-003	2.31	0.1793	
AB	25.40	1	25.40	8757.85	< 0.0001	
A^2	0.31	1	0.31	105.80	< 0.0001	
B^2	13.25	1	13.25	4567.49	< 0.0001	
A^2B	0.096	1	0.096	32.96	0.0012	
AB^2	5.80	1	5.80	2000.73	< 0.0001	
A^3	0.021	1	0.021	7.26	0.0358	
B^3	3.69	1	3.69	1271.62	< 0.0001	
Residual	0.017	6	2.900E-003			

International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395 -0056
Volume: 03 Issue: 09 | Sep -2016 www.irjet.net p-ISSN: 2395-0072

5. CONTOUR PLOT AND 3-DIMENSIONAL PLOT

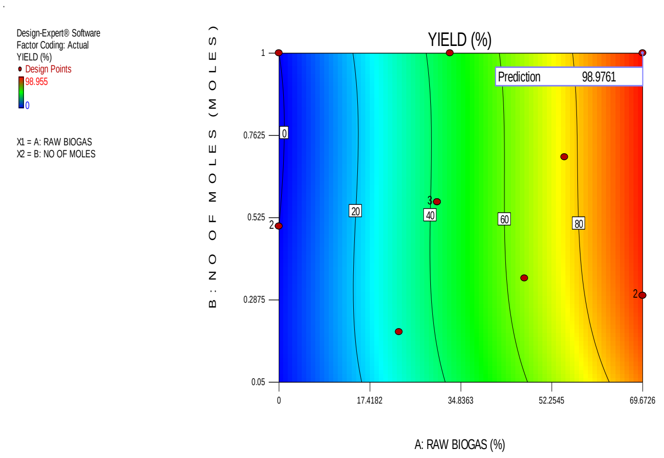

Figure 3a: contour plot

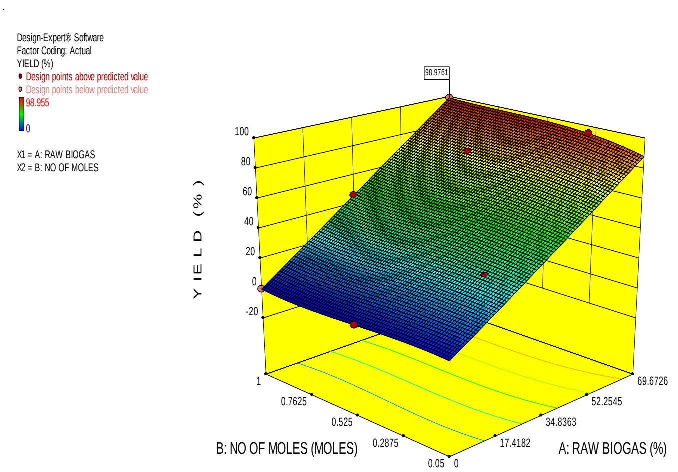

Figure 3b: 3D plot of cubic response

A contour plot is used to explore the potential relationship between three variables. Contour plots display the 3-dimensional relationship in two dimensions, with x- and y-factors (predictors) plotted on the x- and y-scales and response values represented by contours (figure 2a). The contour plot provided a 2-dimensional view of the surface where points that have the same response were connected to produce contour lines of constant responses. Contour plots are useful for establishing the response values and operating conditions that one wants.

The contour plot and 3D response plot in figures 3a and 3b respectively showed that there is a significant interaction between raw bio-methane and number of moles of aqueous Sodium Hydroxide for a complete scrubbing to take place. None of the factors worked in isolation. The increase in percentage raw bio-methane and number of moles of aqueous Sodium Hydroxide to an upper limit of 1mole lead to a corresponding increase in percentage bio-methane yield of up to 98.96%. The maximum production of purified bio-methane was predicted at a given ranges of raw bio-methane and aqueous sodium hydroxide moles. The response followed a parabolic shape of increasing response with increasing interactive predictors at varying values.

The optimized result showed the percentage raw bio-methane at 69.67% and 1 mole of aqueous NaOH with the percentage biomethane yield of 98.98%. It could be inferred that when the percentage raw bio-methane increases and with increased number of aqueous NaOH moles, the percentage yield would increase. From figure 2, scrubbing with ordinary water as control (0 moles of NaOH) produced 85.3% of bio-methane. It was discovered by [2] that addition of 2% concentration of NaOH with stirrer gave 70% improvement with 96% CO_2 removal efficiency compared with water scrubbing alone. However balance must be placed between environmental hazards to be created with increased use of aqueous sodium hydroxide and desired product purity.

6. CONCLUSION

The optimization of process parameters for CO_2 scrubbing from bio-methane at ambient conditions using co-digestion of cow dung and vegetable wastes gave a high performance as compared with the works done under controlled conditions. Historical and Tagushi design was applied in optimizing process parameters [1] and after upgrading, it was discovered that bio-methane has been increased from 44.15% to 91.89% and the calorific value increased from

18,983KJ/m^3 to 30,525KJ/m^3 [1] though optimization was not done at ambient conditions. This research work gave the optimization value of 98.98 vol% as seen from the contour and 3D plot (figure 3a and 3b) which implies that the calorific value has been improved. There is a good balance between upgrading costs and market value for the gas.

It is therefore concluded that production and scrubbing of bio-methane at ambient conditions should be encouraged especially at small scale levels instead of being scared of high installation costs of lager plants, to help reduce emission of Green House Gases (GHGs) for a safer environment and at the same time quality cooking gas is obtained plus rich organic fertilizer as by product. This gas could as well be used as vehicle fuel when compressed. This is because the production and scrubbing of bio-methane from cow dung and vegetable wastes at ambient conditions has been tested and proved.

7. RECOMMENDATIONS

Optimization of biodigester for bio-methane production at ambient conditions should be done. The dew point of scrubbed gas should also be tested as well. This will direct knowledge on compression into pressure cylinder.

It is also recommended that other constituents like H_2S, water vapor be analyzed too for more detailed project.

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