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Rate Equation for Scrubbing Time of Bio-Methane Produced from Co-Digestion of Wastes for Household Application

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Abstract **Original Research Article**

Organic wastes constitute the major percentage of solid wastes generated globally especially in urban homes. When these organic wastes are left to decompose on their own, they release a blend of gases, primarily methane and carbon dioxide (CO_2) which are greenhouse gases. The greenhouse gases have contributed to climatic changes. However, the controlled conversion of these gases into purified bio-methane achieves bioremediation and source of alternative cooking fuel for households. Many technologies of scrubbing CO_2 have high operational costs, making them unsuitable for household applications. In this work, bio-methane was produced from a mixture of cow dung and vegetable wastes at prevalent temperature of 30°C and pressure of 1 bar. The raw gas was scrubbed with aqueous sodium hydroxide (NaOH) to achieve purity of 98.96% which is up to natural gas standard. The suitable order of reaction tested for the scrubbing of bio-methane was pseudo second order rate of reaction with rate constant of k = 0.0057$mol^{-1}s^{-1}$. The rate equation derived predicts the service life of the solvent to inform when to recharge the scrubber. Hence the sustainability of this work is highly advocated for, because it is affordable and technologically easy and safe to operate.
Keywords: sustainability, bioremediation, pollution, rate equation, greenhouse gases.

Introduction

One of the increasing needs of every household is accessibility to clean and affordable fuel for cooking. The fossil fuels which have been in use over the years come with various economic and environmental costs. Recently, biogas produced from farmyard and other organic wastes is being promoted as a suitable alternative to fossil fuels. This has not only provided solution for cooking fuel but has also become a strategy to contain the menace caused by numerous dumpsites in the environment.

The composition of every dumpsite is made up of organic wastes, paper, plastics, glass, metal and others (Figure 1). Organic waste makes up the highest proportion (46%) among all types of waste followed by paper (17%), plastic (10%), glass (5%), metal (4%), and others (18%) (Figure2) [1].These organic wastes comprise but not limited to animal wastes, food scraps, leaves, grass, and wood.

When these organic matter, such as vegetable wastes, food scraps and animal wastes break down in an anaerobic environment (an environment absent of oxygen), they release a blend of gases, primarily methane, hydrogen sulphide and carbon dioxide with their characteristic pungent smells. Methane gas has approximately 20 to 30 times the heat-trapping capabilities of carbon dioxide [2]. They explained that when a rotting loaf of bread converts into biogas, the loaf's environmental impact will be about 10 times less potent than if it was left to rot in a landfill. That implies that conversion of organic waste to bio-methane at household levels will reduce the negative environmental impact by about 46%.

Climate change is a severe threat to socio-economic development and has the potential of affecting a nation's Gross Domestic Product (GDP) [3]. This is because the climatic change affects every sphere of life including water, forest, sanitation, food security, industrial development, housing, energy, health and the very air we breathe. They therefore opined that development of biogas technology is a suitable alternative energy source that would be affordable and environmentally friendly and would help preserve the green forest thus achieving the 7th mandate of the Millennium Development Goal on environmental sustainability.

Fig-1: A typical dumpsite at Nnewi urban, Anambra state Nigeria

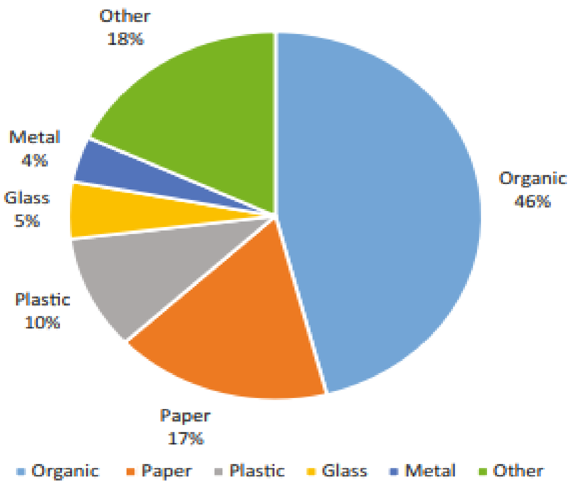

Fig-2: Global solid waste composition.
Source: Adapted from "What A Waste" (2012)

Several mixtures of organic wastes of animal manure, sewage, fruits and left over foods (co-digestion) have been used by several researchers to produce biogas. The potential for the use of co-digestion of organic wastes was demonstrated to generate bio-methane [4, 5]. Co-digestion of animal wastes or other organic wastes is more advantageous in terms of methane yield than processing the feedstock separately [6]. In analysing the effectiveness of co-digestion, it was noted that there was synergistic effect which was attributed to more balanced nutrients, increased buffering capacity, decreased effect of toxic compounds and the structural microbial growth for efficient digestion [7].

Bio-methane itself must be scrubbed of carbondioxide (CO_2), to increase the heating value and reduce corrosion of metal parts. The use of aqueous sodium hydroxide (NaOH) has been found to be economical and easily affordable for household level production and use. However, for effective use of the aqueous NaOH, the scrubbing time must be monitored to predict the service life of the scrubbing solvent for consistent biogas of standard quality. This will inform the user when to recharge the scrubber with a fresh solvent. It is therefore pertinent to derive a rate equation for predicting the residual concentration of the NaOH solvent.

METHODOLOGY

The methodology for this work followed two (2) processes: production and purification of the bio-methane and secondly derivation of the rate equation for the scrubbing time.

Production and purification of bio-methane

His bio-digestion to generate bio-methane for this work was carried out in a digester at prevalent atmospheric temperature of 30^{o}C and pressure of 1bar to favour methane forming bacteria (the mesophiles). The chemical method used for scrubbing raw bio-methane was done with alkaline solution i.e aqueous sodium hydroxide (NaOH) using concentration of 1mole/lit. This took place in a batch process using agricultural waste of palm kernel shells as packings in the scrubber. Local palm kernel shells can be used as packing materials for the scrubbing process to enhance mass and heat transfer contact between the gas and liquid phases [8] that is between the aqueous NaOH and inlet gas which entered through the bottom of the scrubber and facilitate exchange of volatiles between the solution and the gas phase. This scrubbing a prevalent temperature and pressure was to make it more adaptable for household application.

Derivation of rate equation for raw bio-methane scrubbing time at prevalent atmospheric conditions. In deriving the rate equation for scrubbing of raw biogas, the reaction kinetics of aqueous NaOH and CO_2 during scrubbing process was first monitored. The scrubbing of CO_2 from bio-methane at prevalent atmospheric conditions using aqueous NaOH followed an unsteady state manner whereby concentration of NaOH solution varied with time. The order of reaction and the rate constant were determined from which rate equation was developed. With the rate equation developed, the time of depletion of the solvent (aqueous NaOH) could be predicted. Raw bio-methane of 0.9kg was scrubbed with 1mole/lit of sodium hydroxide solution and the residual NaOH concentrations in the liquid analysed at varying times of 0, 30, 60, 90 and 150 seconds. The residual NaOH concentrations in the liquid at time *t* were determined by titrating with 0.5N hydrochloric acid (HCl).

RESULTS

Raw and purified bio-methane was collected and analysed using Buck 930 gas chromatography equipment. The raw bio-methane constituted methane (CH_4) concentration of 69.67% and carbondioxide (CO_2) of 30.32%. Scrubbing with 1 mole/lit gave the purity of 98.89% which is up to natural gas standard of 97% [9].

In deriving the rate equation the kinetics of reaction was determined. This is to predict the residual concentration of sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) forms when aqueous NaOH reacts with carbondioxide (CO_2) [10]. The residual concentrations of the NaOH solution in the scrubber was analysed at various scrubbing times and the result given in table 1.

Table-1: Bio-methane scrubbing time and residual NaOH concentration

Time (secs)	Concentration (mole/lit)	$-\ln \frac{CA}{CA0}$	$\frac{1}{CA}$
0	$1=CA_0$	0	1
30	0.86	0.15	1.15
60	0.71	0.34	1.32
90	0.64	0.45	1.56
150	0.57	0.56	1.75

The order of reaction was tested for pseudo first and pseudo second order reactions. The expressions depended on the stoichiometry as well as the kinetics.

$A + 2B \rightarrow$ products (1)

From the stoichiometry of reaction Na_2CO_3 was formed as the product [10].

$CO_2 + 2NaOH \rightarrow Na_2CO_3$ (2)

The pseudo first order reaction follows equations 3 and 4

$-\ln \frac{CA}{CAO} = kt$ [11] & [12] (3)

$\rightarrow \ln C_A = \ln C_{A0} - kt$

With rate equation $-r_A = \frac{dCA}{dt} = k\, C_A C_B$

$-r_A = kC_A (\, C_B = \text{constant})$ (4)

The pseudo second order of reaction follows the equations 5 and 6:

$\frac{1}{CA} = kt + \frac{1}{CA0}$ (5)

Rate equation $-r_A = \frac{dCA}{dt} = KC^2_A$ (6)

Plotting $-\ln\left(\frac{CA}{CA0}\right)$ vs t, for first order, and $\frac{1}{CA}$ vs t for second order, the plots are shown in the figure 2 and 3 respectively.

Note: carbondioxide (CO_2) has constant concentration; hence analysis was done considering only NaOH.

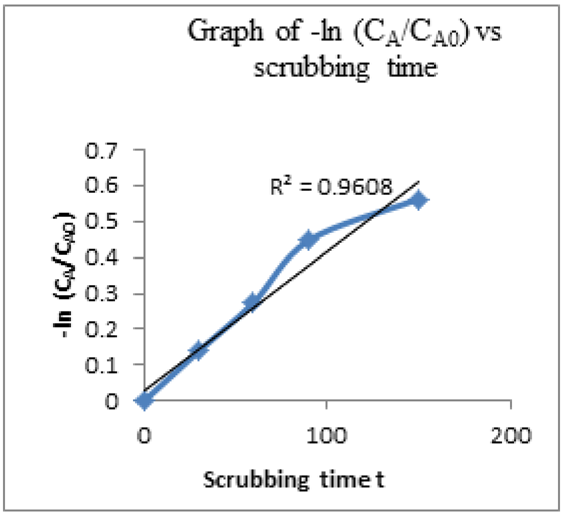

Fig-3: Test for pseudo first order reaction

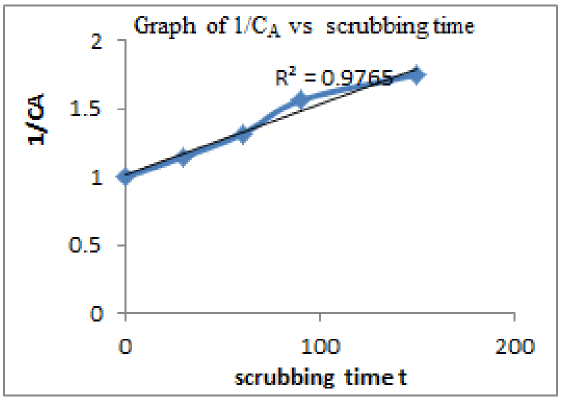

Fig-4: Test for pseudo second order reaction

Considering figures 3 and 4, it could be seen that pseudo second order reaction best suits the reaction. This was evidenced from their R^2 of 0.96 and 0.98 respectively with best line of fit on the figure 4 that was the pseudo second order reaction. Hence the scrubbing of bio-methane with 1 mole/lit of NaOH solution followed pseudo second order reaction for absorption of CO_2 in alkaline solutions that produced second order reaction rate constant k [13].

Determination of rate constant K and rate (equation) law

Since the CO_2 scrubbing reaction followed second order, the rate constant K was calculated from equation 5

$\frac{1}{CA} = kt + \frac{1}{CA0}$ [11] & [12]

And from figure 4, the slope of the straight line graph gives the reaction rate constant k.

Slope = $\frac{\Delta 1/CA}{\Delta t}$

$\therefore$ k = 0.0057mol^{-1}s^{-1} = reaction rate constant

Hence the rate law $\quad -r_A = KC^2A$

$-r_A = 0.0057C^2_A$ (7)

Substituting rate constant k and scrubbing time t, into equation 5, the concentration at time t = $[CA]_t$ could be calculated.

$$\frac{1}{CA} = kt + \frac{1}{CA0}$$

$$\frac{1}{CAt} = 0.0057t + \frac{1}{CA0} \quad (8)$$

Equation 8 becomes the rate equation derived for predicting at any time t, the concentration of aqueous sodium hydroxide (NaOH) with initial concentration (C_{A0}) of 1 mole/lit and vice versa. At 1579 seconds (roughly 27minutes), the residual concentration of the NaOH in the scrubber would be around 0.1 moles/lit and further scrubbing will produce lesser quality than natural gas standard, though there are other influencing factors. This rate equation would guide the user on the expected service life of the 1 mole/lit concentration of scrubbing liquid, as to ascertain when to recharge the scrubber with a fresh solvent liquid.

CONCLUSION

The production of high heating value of generated bio-methane at prevalent temperature and pressure has been achieved to upgrade from 67.69% to 98.86% bio-methane which is up to natural gas standard with rate equation derived also. This simple technology has been enhanced with the use of palm kernel shells which is an agricultural waste product for packings in the scrubber. The produced bio-methane is very suitable for household use like cooking, generator fuel and so on.

Recommendations

- Further research should be conducted on the scrubbing of raw biogas considering influencing variables like biogas flow rate in conjunction with time in order to develop mathematical model equation or if possible a chart to guide an ordinary user.
- The scrubbed bio-methane should further be de-moisturized to ensure complete corrosion-freesystem.

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