International Conference on Sustainable Materials Processing and Manufacturing, SMPM 2017, 23-25 January 2017, Kruger National Park

Chemical Absorption of Carbon Dioxide in Biogas Purification

O.I. Maile [a]*, E. Muzenda [a, b], H. Tesfagiorgis [c]

[a]*Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Doornfontein Campus, John Orr Building, 3160 Beit Street, Johannesburg, South Africa*

[b]*Department of Chemical, Materials and Metallurgical Engineering, College of Engineering and Technology, Botswana International University of Science and Technology, Private Mail Bag16, Palapye, Botswana*

[c]*Agricultural Research Council – Institute for Industrial Crops, Private Bag X82075, Rustenburg 0300, South Africa*

Abstract

Biogas is produced from anaerobic digestion of organic biodegradable materials. However, its application is limited as it contains impurities such as carbon dioxide (CO_2), hydrogen sulphide (H_2S), and other trace gases. Chemical absorption is capable of producing gas of high methane content above 95% and has no methane losses hence it’s widely used on large scale applications. Sodium hydroxide was used for cleaning the biogas in this study at a concentration of 1M, 2M, and 3M. The effect of concentration on absorption and CO_2 removal efficiency was studied. It was observed that an increase in concentration lead to an increase in the absorption rate and the removal efficiency respectively. The highest removal efficiency was recorded to be 66%.

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Peer-review under responsibility of the organizing committee of SMPM 2017.

Keywords: absorption; concentration; purification; removal efficiency

1. Introduction

Energy production from renewable sources is a focus of the world at large. With different technologies being explored and applied such as solar energy, wind energy, hydropower, geothermal, biofuel and biomass [1]. Biomass is a significant source of energy supply for biogas production [2]. Other types of sources that are available can be organic waste from households, restaurants, parks, municipal waste collection and other industrial wastes which can be put to good use [3-5]. Biogas is produced from anaerobic digestion of organic biodegradable waste. The digestions can either be dry or wet with both having advantages and disadvantages. However, wet digestion is often preferred for processing organic waste except for cases where the substrate has high total solids content [6, 7].

The use of biogas is limited as it contains impurities that hinder its application. As a result, purification techniques are often applied to clean and upgrade it to biomethane which can be used in place of natural gas [8]. These techniques include membrane separation, cryogenic separation, adsorption and absorption. Various factors are considered prior to selecting the technique to use which include; efficiency, methane losses and energy consumption, costs [9, 10].

Chemical absorption is capable of producing gas of high methane content above 95% and has no methane losses hence it’s widely used, the advantages and disadvantages of some of the chemicals used are depicted in Table 1 [9]. The chemical used can either be alkaline solutions, amines solutions, ionic liquids and ammonia [10]. This study focus on the use of alkaline solution for the absorption of carbon dioxide. The main focus being on NaOH which is

* Corresponding author. Tel.: +27720789798
E-mail address: ireenmaile@yahoo.com

normally applied because it has low purchasing price and has the ability to even absorb the traces of H_2S contained in the biogas.

Table 1: Advantages and disadvantages of the different chemicals

Chemical	**Advantages**	**Disadvantages**
Ammonia	High CO_2 loading capacity	High volatility
	Requires low heat and electricity	Low CO_2 absorption rate
	No solvent degradation	Solvent slippage
NaOH	Low electricity requirement	Expensive operation and investment
	Low CH_4 losses	Requires high heat for regeneration
Amines	High efficiency	Expensive investment and corrosion possibility
	Cheap operation and Regenerative	Heat required for regeneration
	Absorbs more CO_2/volume	Precipitation of salts and possibility of foaming

2. Materials and methods

Sodium hydroxide is one of the alkaline solutions used in upgrading biogas. A semi-continuous system was used as shown in Fig. 1 where 1L digester was used for biogas production which was bubbled through an absorbent in 500mL gas washing bottle. The digester was kept in a water bath to maintain a constant operating temperature throughout the experiment. Nitrogen gas was used to purge and create anaerobic conditions in the system. A valve is used to let the N_2 gas into the digester and closed after purging is done. Two sampling points in a form of T's closed with septa between the processes, for the raw biogas and the purified gas. The gas exiting the absorption unit goes to 1L measuring cylinder for volume capturing using downward displacement.

Sodium hydroxide was used as an absorbent supplied by Sigma-Aldrich (South Africa). 1-3 M solution was used for the purification in a 500mL vessel which was kept at constant temperature. The gas exiting the absorption column was analyzed using Gas Chromatography (SRI 8610C GC) equipped with FID and TCD detectors, packed with 6' Hayesep-D/ 6' Molecular Sieve-13 X. 1 mL SGE gas tight syringe was used to draw the gas for sampling from the septum.

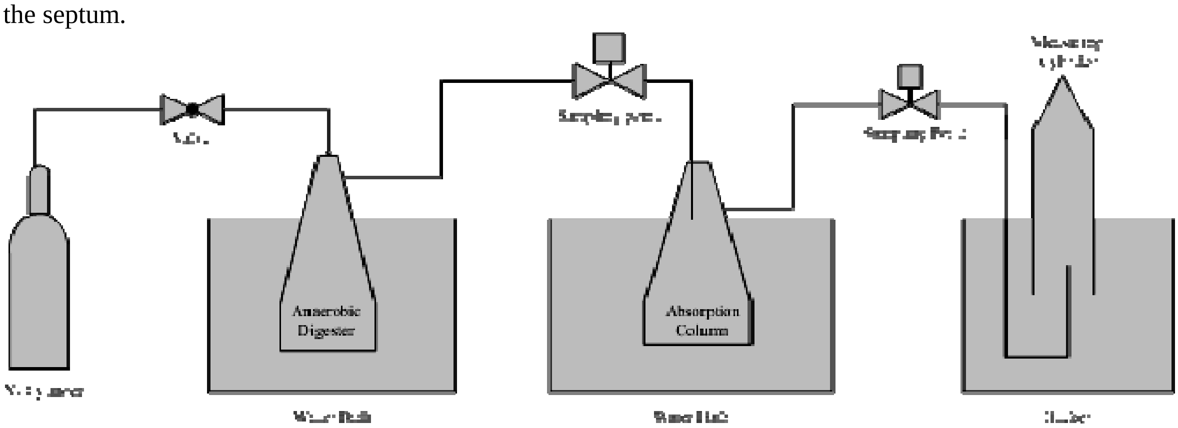

Fig. 1: Schematic diagram of lab set up for absorption of carbon dioxide using sodium hydroxide

3. Results and discussions

A stock solution was prepared using granules of sodium hydroxide dissolved into deionized water to different concentrations of 1-3 molL^{-1}. Table 2 shows the downstream and upstream composition of the biogas.

Table 2: Summary of the purification results for NaOH

Gas	**Composition**	**Raw Biogas**	**1M**	**2M**	**3M**
CH_4	%	52	62	74	80
CO_2	%	46	35	25	16

Removal Efficiency	%	-	23	46	66

3.1. Effect of using NaOH for purification on the overall gas yield

In biogas purification it is important to determine the biomethane potential to help determine project feasibility if it can be used in place of fossil fuel derived energy. The amount of gas produced per kg substrate helps in decision making of whether to pursue anaerobic digestion and the scale at which it can be done. Biogas and biomethane generation calculations were performed to determine how much yield can be obtained over a period of time.

The biomethane potential was determined for the substrate and it was found to be 0.275 m^3 CH_4/ kg VS. This is highly dependent and is affected by the type of substrate and amount used. The volume of biomethane that could be obtained per annum was found to be 13546 m^3 CH_4 which was used to determine the energy equivalence.

The daily methane production was recorded and is depicted in Fig. 2 where the effect of time and concentration are actually taken into consideration. From the analysis it was observed that both time and concentration had a significant impact on the methane daily production. The daily production for 1M is consistent throughout with day 6 having the highest yield; 2M had fluctuations with 2 hikes experienced on day 4 and 14; and 3M with the highest yields on day 4 and 11. As a result, it can be concluded that 3M is the optimal concentration for purification with NaOH.

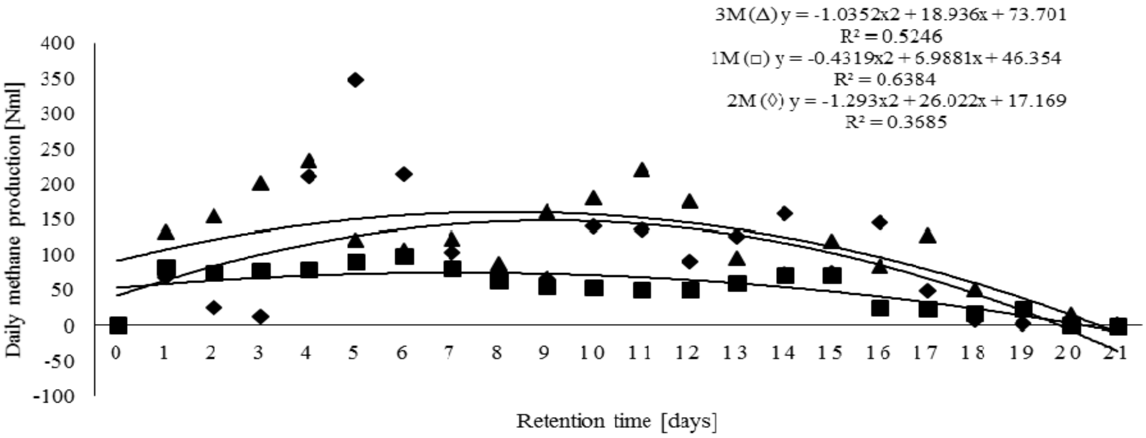

Fig. 2: Methane daily rate of production

3.2. Effect of concentration on the absorption rate

Sodium hydroxide reacts with carbon dioxide according to the following chemical reaction:

$$2\,NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \quad (1)$$

Which can be ionically represented as:

$$2OH^{-}_{(aq)} + CO_{2(g)} \rightarrow CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \quad (2)$$

The effect concentration has on absorption is depicted in Fig. 3 which shows the methane produced from each concentration. It had a significant impact on the methane production as observed on the graph. The higher concentration had high absorption capacity. Irrespective of the time the yield is affected by the concentration.

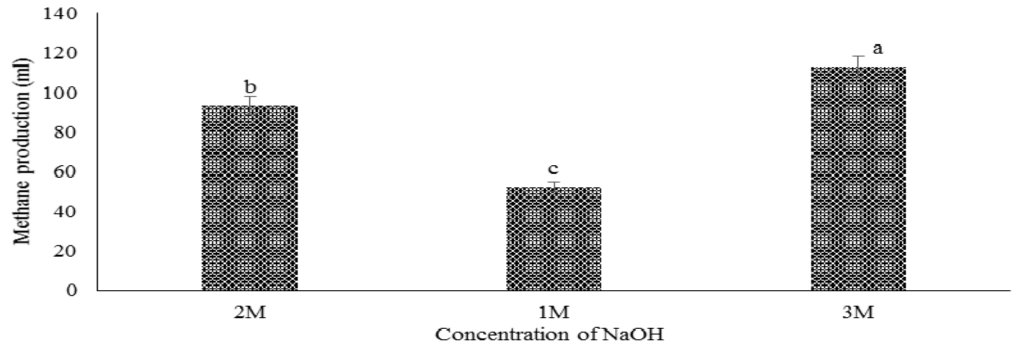

Fig. 3: M

The effect of sodium hydroxide concentration on the absorption of carbon dioxide was studied and the results obtained are represented graphically in Figs. 4 to 6. The observation was that the rate of absorption increased with increased concentration. Which also means that the quality of the gas increased as more carbon dioxide is removed from the biogas. Based on the reaction between carbon dioxide and sodium hydroxide it can be observed that increased solvent concentration means more OH^- ions are present in the solution and thus resulting to an increased carbon dioxide absorption. And as more carbon dioxide is absorbed the concentration of CO_3^{2-} ions increases as shown in equation 2. Thus, the factor that plays a key role is the solvent flowrate as compared to the gas flowrate. It was also observed that the reactions of carbon dioxide with hydroxide occurred at a very fast rate which is similar to the findings by Zeman et al. [11].

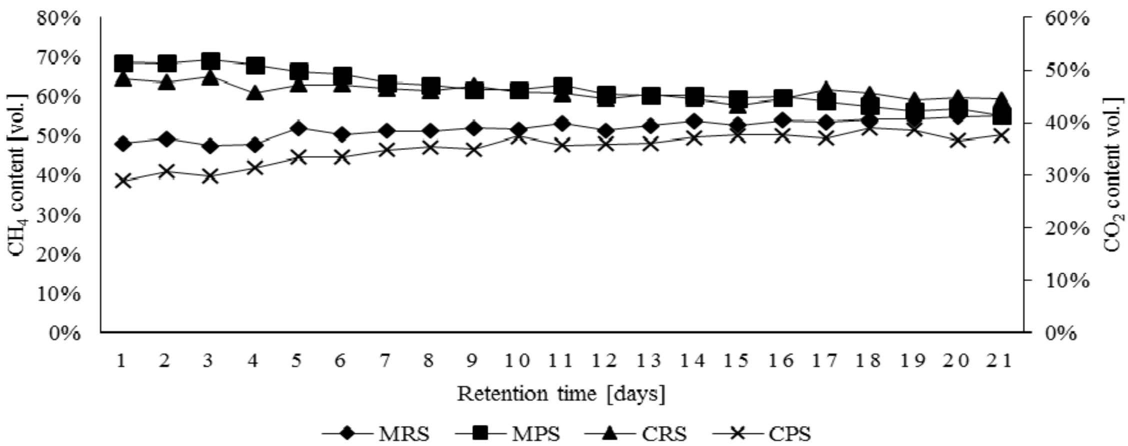

Fig. 4: Composition of biogas in absorption of CO_2 with NaOH at 1M concentration

Note: MRS= CH_4 content of the raw sample, MPS= CH_4 content of the purified sample, CRS= CO_2 content of the raw sample and CPS= CO_2 of the purified sample

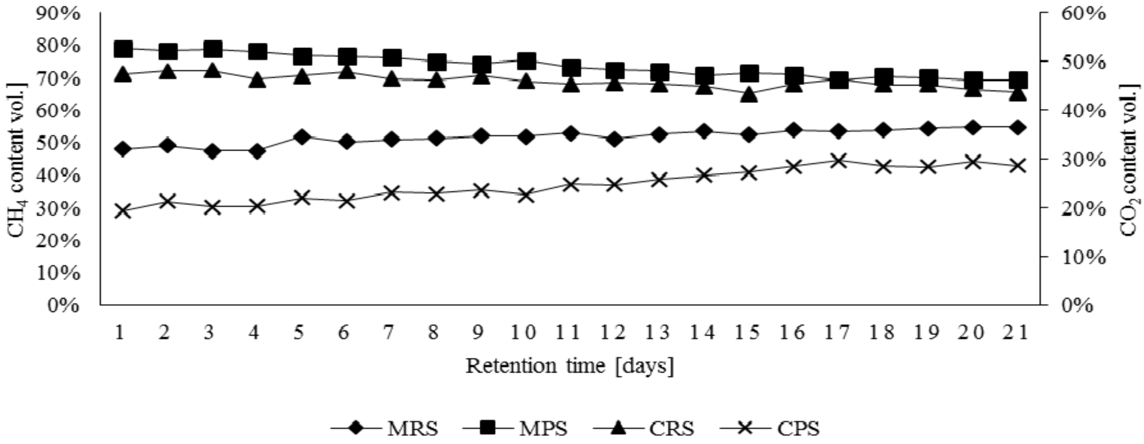

Fig. 5: Composition of biogas in absorption of CO_2 with NaOH at 2M concentration

Note: MRS= CH_4 content of the raw sample, MPS= CH_4 content of the purified sample, CRS= CO_2 content of the raw sample and CPS= CO_2 of the purified sample

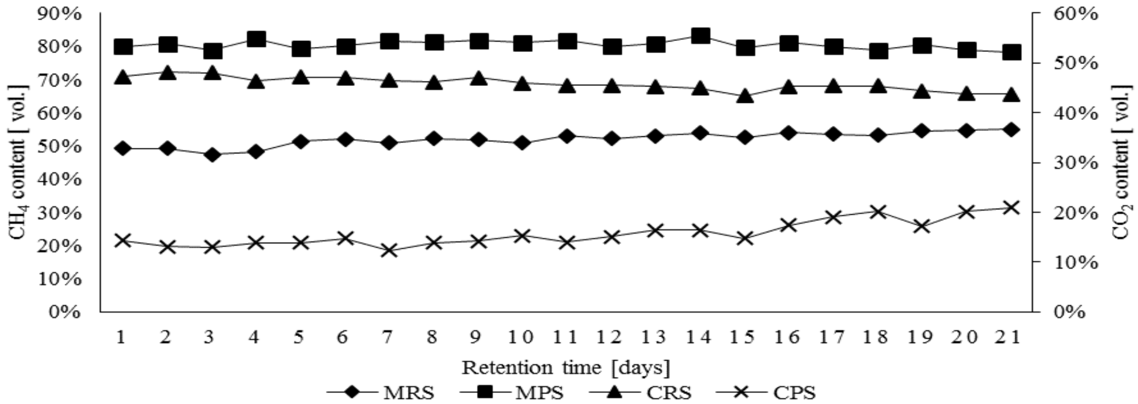

Fig. 6: composition of biogas in absorption of CO_2 with NaOH at 3M concentration

Note: MRS= CH_4 content of the raw sample, MPS= CH_4 content of the purified sample, CRS= CO_2 content of the raw sample and CPS= CO_2 of the purified sample

The absorption of carbon dioxide by sodium hydroxide was effective as the composition of the biogas moved from 52% volume to 80% volume overall. The absorption seems to be occurring at a faster rate at the beginning of the process as shown in Figs. 4 to 6. For the 1M concentration the absorption is observed to be decreasing gradually as the solution is becoming saturated with the carbon dioxide. The results obtained are not in agreement with the results obtained by [12], as in their study at the same concentration of 1M obtained a better methane concentration of 71.87 % volume against 62% volume for this work. This might be as the result of the initial concentration which was low (52%) in our case as compared to 63.20% in their findings. Furthermore, it could be due to the pressure effect as it was one of the studied variables in their work.

The absorption improved for the 2M solution as shown in Fig. 5. It was observed that the absorption also occurred steadily with gradual reduction of the absorption rate over time. An average of 74% volume methane was obtained which is higher than the 1M solution and this is an indication that absorption rate increases with increased solvent concentration.

The effect of concentration on absorption is observed and appreciated as the 3M solution yielded better results. However, the absorption seemed not to be occurring steadily as fluctuations are observed in the process. This might be due the fact that there are more OH^- ions present in the solution and thus a vigorous/ rapid absorption take place. At a later stage the sodium carbonate formed in the early stages of the absorption reacts with the carbon dioxide to form sodium bicarbonate and it is potent though it occurs at a slow rate.

3.3. Effect of concentration on CO_2 removal efficiency

The carbon dioxide removal efficiency was calculated according to the following equation:

$$\eta_{CO_2} = \left(1 - \frac{CO_{2\,pur}}{CO_{2\,raw}}\right) \times 100\% \tag{3}$$

It was observed that the carbon dioxide conversion is high at the beginning of the absorption process and diminishes towards the end of the process. This is mainly because the solution becomes saturated as more carbon dioxide is absorbed by the solvent. The highest removal efficiency obtained in this study was 66% on average which contrary to what was obtained by [13]. Upon operating a packed column absorber using NaOH as an absorbent, a removal efficiency of over 90% was obtained. However, the difference in the results can be attributed to the operating parameters and process conditions. In another study by reference [14] the removal efficiency obtained

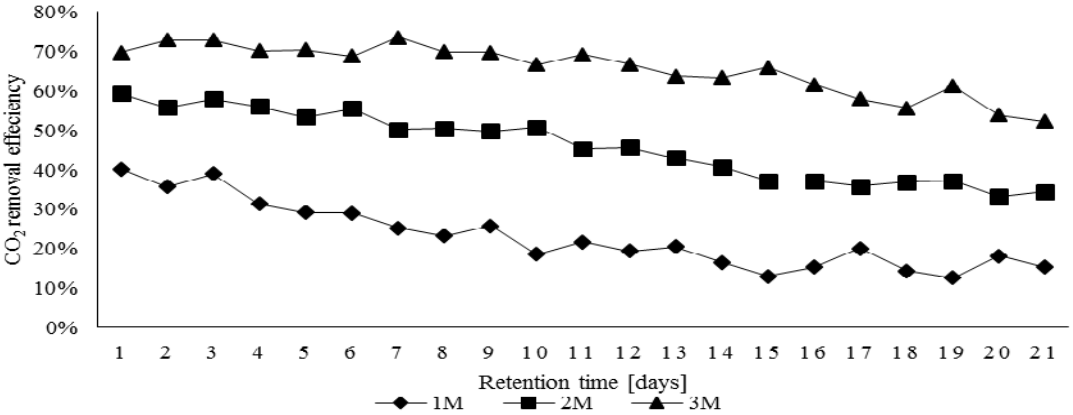

Fig. 7: Efficiency of CO_2 removal from the gas as a function of time using NaOH

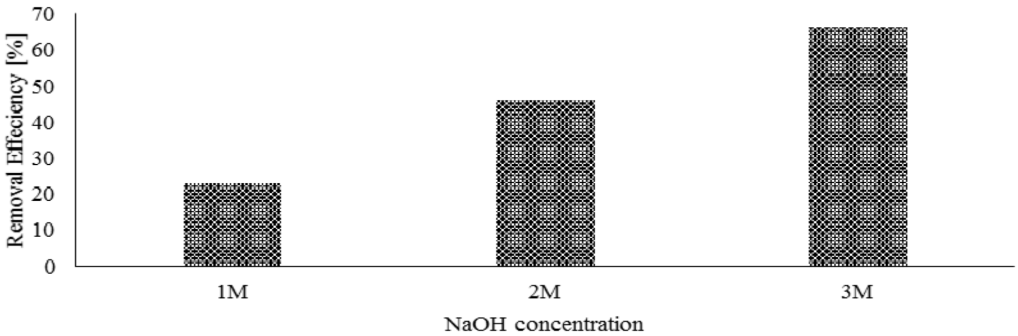

Fig. 8: CO_2 capture efficiency for absorption with NaOH

Conclusions

Biogas purification using sodium hydroxide was studied. The study revealed that sodium hydroxide is capable of absorbing the carbon dioxide from the biogas. The rate at which this happens was affected by the concentration and temperature of the process. High removal efficiency was observed at 3M concentration followed by 2M and 1M respectively. An increase in concentration resulted in an increase in absorption rate and thus the methane production. The highest removal efficiency was recorded to be 66%.

Acknowledgements

The authors acknowledge the South African National Energy Development Institute (SANEDI), University of Johannesburg's Global Excellence Scholarship (GES), City of Johannesburg (CoJ), University of Johannesburg's Process Energy and Environmental Technology Station (PEETS), Botswana International University of Science and Technology and the UJ Bioenergy research team for supporting this research.

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