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The potency of monoethanolamine in biogas purification and upgrading

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ABSTRACT

Biogas has been exploited as one of the alternative sources of renewable energy having the potential to replace fossil fuels. It contains impurities when raw, as it consists of 50–70% methane (CH₄), 30–50% carbon dioxide (CO₂) and trace gases such as hydrogen sulfide (H₂S). Chemical absorption is often a preferred purification technique in industrial applications because it has high efficiencies, removes H₂S completely, operates at low pressures, and has higher reaction rates. The focus of this study is on amines as they are widely used worldwide to purify biogas. A continuous system was used where 1 L digester was used for biogas production which was bubbled through an absorbent in 500 mL gas washing bottle. The gas exiting the absorption column was analyzed using Gas Chromatography. The methane yield obtained in this study was higher because MEA is a good absorbent. The biomethane potential was found to be 0.40 m³ CH₄/kg VS (volatile solids). An increase in concentration resulted in increased CO₂ absorption capacity and rate, an average of 76%, 78%, and 84% vol from an initial concentration of 52% vol were achieved for the respective concentrations. The CH₄ content of the purified biogas improved with increasing temperature. The removal efficiency of carbon dioxide increased from 66% at room temperature to 77% at 40 °C. Temperature of the solvent increased the absorption capacity and carbon dioxide removal efficiency of the process.

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1. Introduction

Due to increasing fuel prices, greenhouse gas emissions and high energy demands from the ever-increasing developing world, with high technology and new process developments a sustainable and renewable source of energy is needed (Fan et al., 2016; Kainiemi et al., 2015; Mao et al., 2014). South Africa is also facing electricity challenges seen through the load

shedding implemented in the year 2008 and 2015 to ease the burden of the electricity demand on the national grid. This is proof positive that other forms of renewable energy sources to supplement the currently available energy are required.

Biogas has been exploited as one of the alternative sources of renewable energy having the potential to supplement the current energy requirements. Its advantage is that it has physical and chemical properties similar to those of natural

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gas. Putting it on the map to be able to replace natural gas in all applications such as the production of heat, electricity, and use as vehicle fuel or NGV (natural gas vehicle) (Rongwong et al., 2012; Hagmann et al., 2001; Deublein and Steinhauser, 2008). Biogas is economical and environmentally advantageous because it helps minimize land, water, and air pollution by utilizing waste to produce energy.

Biogas contains impurities when raw, as it consists of 50–70% CH₄, 30–50% CO₂ and trace gases such as H₂S (Maile et al., 2015). This is the limitation to its applications as gases like H₂S can corrode the interior of engines and compressors (Hagmann et al., 2001; Cantrell et al., 2007; Ryckeboosch et al., 2011). The CO₂ is incombustible and causes the gas to be denser, and poses compression challenges as it freezes at pressures above 250 bar, which result in storage into cylinders difficult (Freund et al., 2005). Hence purification and upgrading are necessary.

There are four main techniques to remove impurities from biogas, namely; absorption, adsorption, cryogenic separation and membrane separation. Pressure swing adsorption (PSA) is a sensitive process which requires H₂S removal before the adsorption which may harm the adsorbing material. It also incurs some high cost of operation (Zhao et al., 2010; Hullu et al., 2008). Cryogenic separation is not often used as it requires a number of process equipment such as heat exchangers, turbines, and compressors irrespective of the fact that it produces upgraded gas of high purity (Zhao et al., 2010). It also has the highest cost of purification as compared to the other techniques (Hullu et al., 2008). Membrane separation is widely used because it yields high methane quality gas (Harasimowicz et al., 2007). Although it yields gas of high purity which is often achieved by increasing the number of modules which in turn leads to methane losses (Zhao et al., 2010). Chemical absorption is often preferred in industrial applications because it has high efficiencies, removes H₂S completely, operates at low pressures, and has higher reaction rates (Zhao et al., 2010; Palmeri et al., 2008).

Different chemical absorbents are used in absorption which has advantages and disadvantages. They include but not limited to; alkalis, alkanolamines, ionic liquids and some blends of readily available chemicals. The focus of this study is on amines as they are widely used worldwide to purify biogas. They are mainly preferred for their higher reliability, greater suitability, and lower investment and running costs

(Molina and Bouallou, 2015). The main focus being the primary amine Monoethanolamine (MEA) as it has high carbon dioxide absorptivity (Mao et al., 2014). The topic on purification of biogas using MEA has been studied, but not much has been done in the effect of temperature.

2. Materials and methods

A continuous system was used as shown in Fig. 1 1 L digester was used for biogas production which was bubbled through an absorbent in 500 mL gas washing bottle. The digester was kept in a water bath to maintain a constant operating temperature throughout the experiment. To study the effect of temperature on absorption, the absorption column was also kept in a water bath and the temperature varied accordingly. Nitrogen gas was used to purge and create anaerobic conditions in the system. A valve is used to let the N₂ gas into the digester and closed after purging is done. Two sampling points in a form of T's closed with a septum between the processes, for the raw biogas and the purified gas. The gas exiting the absorption unit goes to 1 L measuring cylinder for volume capturing using downward displacement.

Monoethanolamine was used as an absorbent supplied by Sigma-Aldrich (South Africa). 10–30 %wt solution was used for the purification in a 500 mL 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 septa.

3. Results and discussions

Alkanolamines are widely used in chemical absorption, especially MEA. MEA is a primary amine and it's good in the absorption of carbon dioxide with the potential of also absorbing the hydrogen sulfide. MEA in concentrations of 10%, 20%, and 30% were investigated in this study and the obtained results are summarized in Table 1. The use of MEA in the absorption of acidic gases has been under investigation mainly because of its effectiveness. The methane yield obtained in this study was higher because MEA is a good absorbent. The biomethane potential was found to be 0.40 m³ CH₄/kg VS.

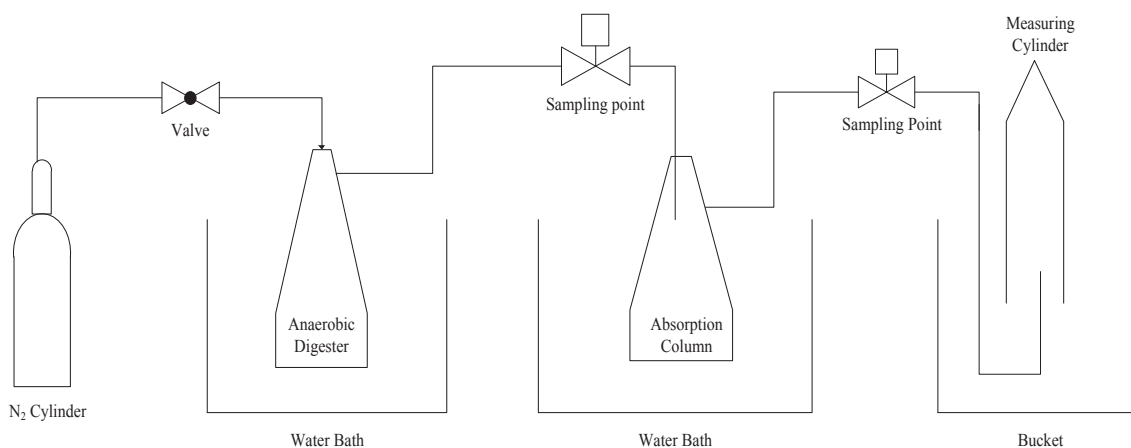


Fig. 1 – Schematic diagram of lab set up for absorption with monoethanolamine.

Table 1 – MEA effectiveness.

Gas	Composition	Raw biogas	10% MEA	20% MEA	30% MEA
CH ₄	%	52	76	78	85
CO ₂	%	46	22	20	15
X	%	—	51	56	67

3.1. The effect of solvent concentration on the absorption rate

The results obtained from the experiments as shown in Fig. 2–Fig. 4 represent the findings on CO₂ absorption using MEA, with Table 2 displaying the notation for the acronyms in the graphs. The effect of solvent concentration was studied and it was observed from the graphs that an increase in absorbent concentration results in an increase in CO₂ absorption. This led to an improved CH₄ content in the gas, an average of 76%, 78%, and 84% vol from an initial concentration of 52% vol was achieved for the respective concentrations of 10%, 20%, and 30%. These observations are comparable to the results obtained by (Ye et al., 2013). They observed that 30% MEA concentration achieved higher CO₂ absorption and had a higher absorption rate.

Fig. 2 represent absorption behavior of MEA at 10% concentration at ambient temperature. Methane enrichment and carbon dioxide removal were plotted on the same set of axis. An improvement in methane content was observed from the

methane content of the raw (MRS) of the biogas and the methane content of the purified sample (MPS) which from the plot which shows the highest methane content of 80% on day 20. The carbon dioxide of the purified sample (CPS) reached the lowest content of 19%.

The absorption behavior of the absorbent at 20% concentration was presented in Fig. 3. The increase in concentration didn't yield significant improvement to the absorption capacity of the solvent as the highest methane attained was 81% on day 3 as presented by the MPS plot. While the lowest carbon dioxide observed at 18% from the CPS plot which is still high for biomethane purposes.

Fig. 4 represents the absorption behavior of the solvent at 30% concentration. An improvement was observed as methane content reached its peak at 87% for the MPS plot. This however still needs improvement which can be aided by increasing the gas flow and the temperature of the absorbent. The carbon dioxide content reduced to a low 12% as seen in CPS plot at this concentration which is improved from the low concentration of 10%.

The system like that of ammonia absorption was not that stable and this may be the result of the inconsistent gas flow rate into the absorption unit. The contact time between the gas-liquid plays a huge role in the absorption process, it can either hinder or enhance it. However, an increase in the MEA concentration may lead to an increase in the solution viscosity which in turn may affect the absorption rate. Consequently, the concentration of CO₂ also affects the absorption rate in that it is directly proportional (Ye et al., 2013).

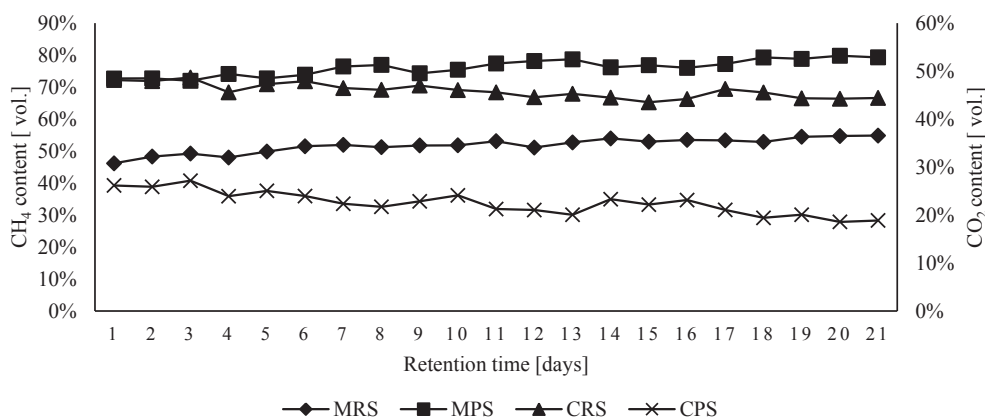


Fig. 2 – Composition of biogas in the absorption of CO₂ with MEA at 10% concentration.

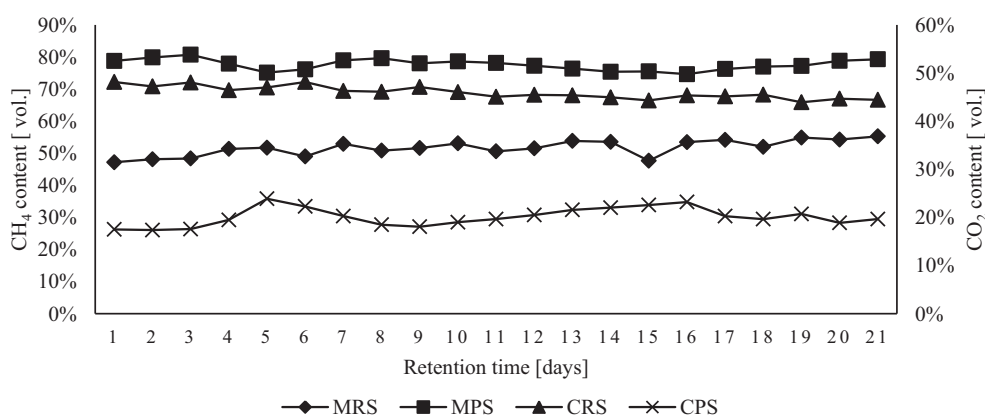


Fig. 3 – Composition of biogas in the absorption of CO₂ with MEA at 20% concentration.

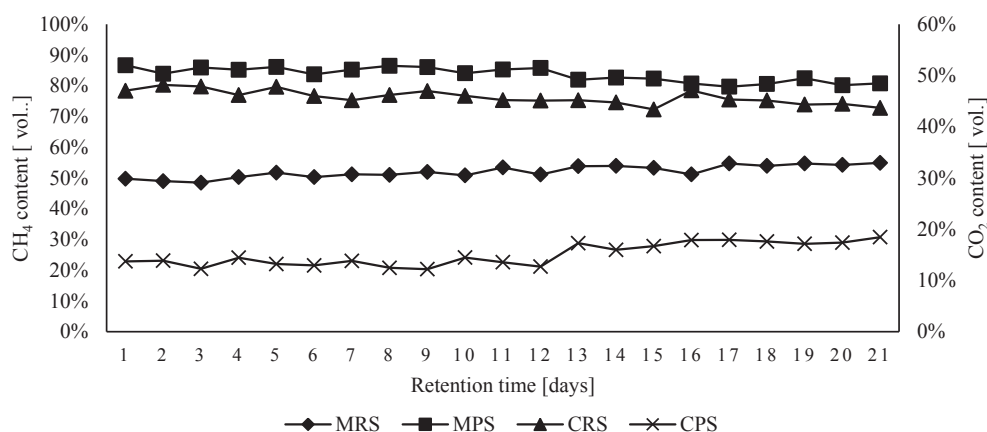


Fig. 4 – Composition of biogas in the absorption of CO₂ with MEA at 30% concentration.

Table 2 – Notation table for Figs. 2–4.

Acronym	Meaning
MRS	Methane (CH ₄) content of the raw sample
MPS	Methane (CH ₄) content of the purified sample
CRS	Carbon dioxide (CO ₂) content of the raw sample
CPS	Carbon dioxide (CO ₂) of the purified sample

3.2. The effect of solvent concentration on CO₂ removal efficiency

$$\eta_{\text{CO}_2} = \left(1 - \frac{\text{CO}_{2\text{pur}}}{\text{CO}_{2\text{raw}}}\right) \times 100\% \quad (1)$$

Where:

η_{CO_2} - carbon dioxide removal efficiency.

$\text{CO}_{2\text{pur}}$ -carbon dioxide content of the purified sample.

$\text{CO}_{2\text{raw}}$ -carbon dioxide of the raw sample.

The removal efficiency of MEA on CO₂ was calculated using Eq. (1). The daily and average CO₂ removal efficiency obtained as depicted in Figs. 5 and 6 are 51, 56, 67% for the 10, 20, and 30% respectively. The results obtained are not in agreement with the results obtained by reference Ye et al. (2012). They achieved a removal efficiency of over 80%. However, they also observed that at ambient pressure the removal efficiency is lower as compared to the high efficiency at 3 MPa. Thus, justifying the low removal efficiency obtained in this study.

3.3. The effect of temperature on chemical absorption

Temperature affects any process and it was studied to determine the effect it on the absorption of carbon dioxide by MEA. Increasing the concentration in MEA has a slightly negative impact as it increases the viscosity of the absorbing solution which may, in turn, affect the absorption capacity. However, an increase in temperature leads to a decrease in viscosity of the solution and thus improves the absorption of the solvent. Table 3 show the overall averages of the compositions and carbon dioxide removal efficiency at the different temperatures.

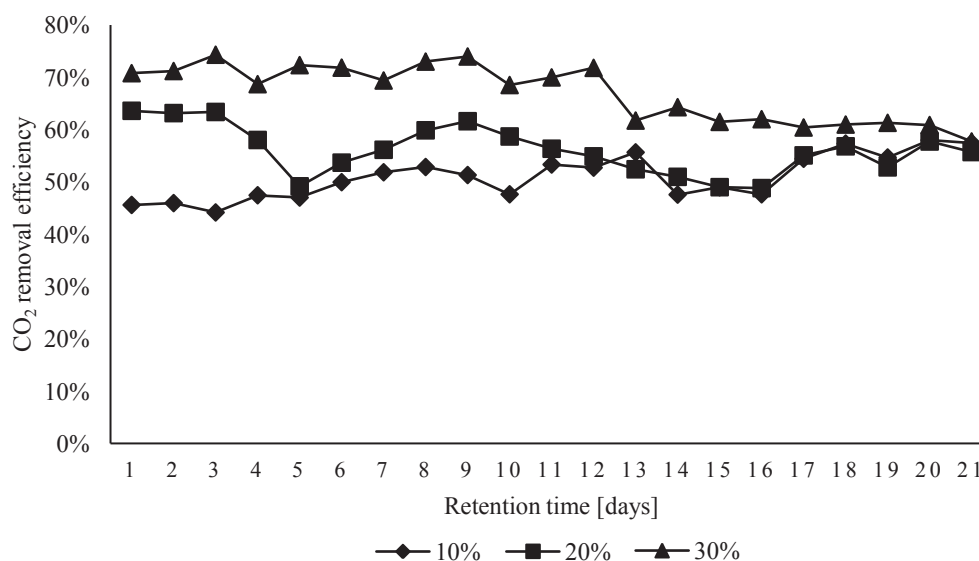


Fig. 5 – Efficiency of CO₂ removal from the gas as a function of time using MEA.

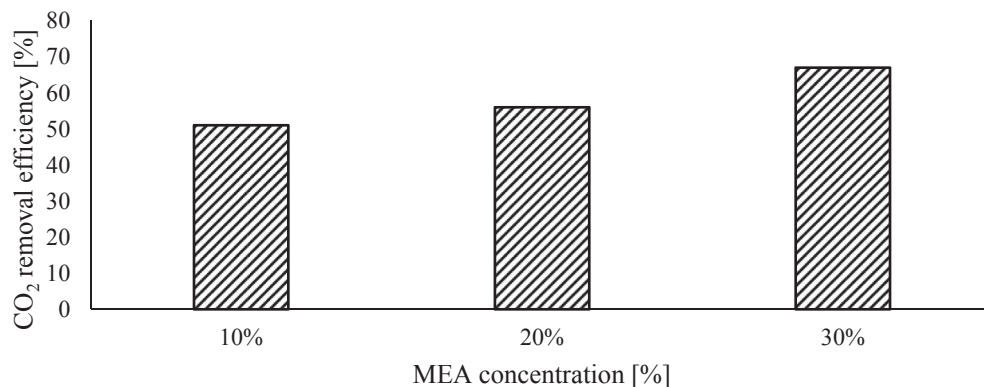


Fig. 6 – CO₂ capture efficiency for absorption with MEA.

Table 3 – Summary of results on temperature variation.

Parameter	RMT	30 °C	40 °C
CH ₄	83	84	88
CO ₂	16	15	11
η	66	68	77

Where: RMT- ambient temperature.

The CH₄ content of the purified biogas improved with increasing temperature, as depicted in Fig. 7. There was not a significant improvement at 30 °C as it increased from 83 to 84%, however, a significant rise is observed when the temperature is 40 °C. An increase in temperature results in the breaking of the hydrogen bonds in MEA which makes it more reactive, enhancing the absorption of CO₂ (Balabaev et al., 2015). As a result, 88% CH₄ vol was obtained at 40 °C, as represented in Fig. 8.

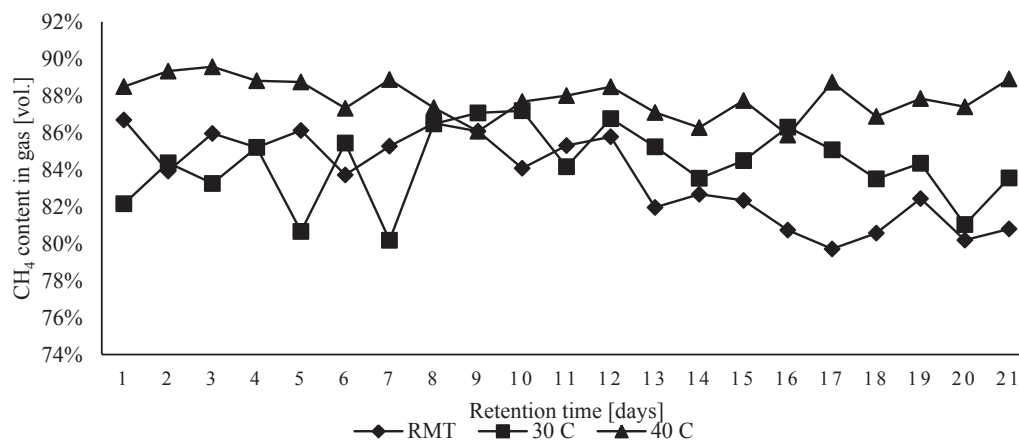


Fig. 7 – Methane content from different temperatures.

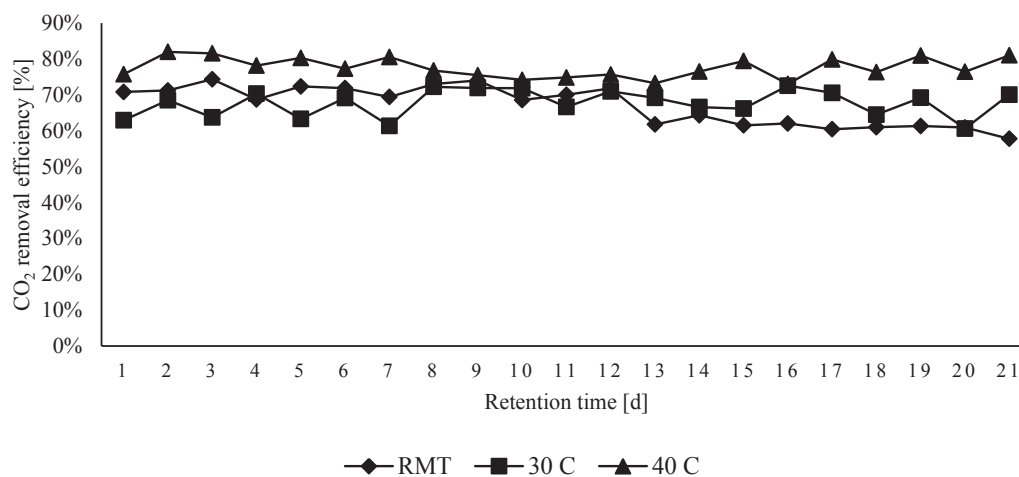


Fig. 8 – Removal efficiency.

3.4. Effect of solvent temperature on removal efficiency

The removal efficiency is dependent on the rate of absorption of the process. It is also affected by the factors that affect absorption, the general expectation is a direct proportion between the rate of absorption and removal efficiency. Increasing temperature of the solvent promotes the absorption and therefore leads to a formation of bicarbonate instead of the carbamate which is undesired. The removal efficiency increased from 66% at room temperature to 77% at 40 °C. There are several factors that can be optimized to increase the removal efficiency such as the absorbent distribution in the absorption unit.

4. Conclusions

MEA is effective in absorbing impurities in biogas. It can remove CO₂ in biogas resulting in biomethane that is over 85% CH₄. The temperature of the solvent affects the absorption process. Higher MEA concentration results in high absorption as 30% MEA solution had the cleanest gas. The temperature of the solvent also affected the absorption process because the rate of reaction is dependent on temperature. The removal efficiency increased with increasing temperature and was recorded to be 77% at 40 °C.

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