

Continuous absorption of CO₂ in packed column using MDEA solution for biomethane preparation

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Abstract. Nowadays, the energy consumption in Indonesia is increasing. Raising of energy consumption force Indonesia to find other energy resources. Biogas is one of the renewable energy, which was developed in anticipation to the fossil energy reduction. Reducing the content of impurities in biogas may reduce the corrosion impact and increase the combustion efficiency. The biomethane can be utilised as fuel for generator in small and medium scale industries (IKM). Continuous CO₂ absorption in packed column using MDEA solution as absorbent is studied for biomethane preparation. CO₂ absorption experiments was performed continuously in the packed absorption column with a diameter of 6 cm and 75 cm length. Gas is sparged from the bottom of the column while the liquid is pumped through the top of the column. The concentration of CO₂ at exit gas is analysed by GC and recorded as a function of time. The flowrate of the inlet gas was varied at 1 LPM; 1.5 LPM; and 1.8 LPM. Variation of MDEA solution concentration used was 20% and 35.31%. Mathematical model for unsteady state CO₂ absorption in packed column was developed. The reaction rate constant (k) and mass transfer coefficient K_{Ga} were determined by fitting the outlet CO₂ concentration data as a function of time to the model solution with smallest Sum of Square of Errors (SSE). The experimental data shows that absorption of 1 LPM gas flow rate with 0,15 LPM MDEA solution flow rate may reduce 40 % CO₂ to be 17 % CO₂ in outlet gas. The steady state process reaches at 10 minutes. Increasing gas flow rates shows the higher overall mass transfer coefficient. The reaction rate constant is not affected by gas flow rate variation.

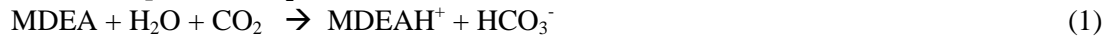
1. Introduction

Energy scarcity is a latent risk from our dependence in nonrenewable energy source. In order to anticipate energy scarcity, renewable energy source development is a must. Biogas promises a sustainable energy source, is produced from biomass anaerobic bacterial digestion. Biogas consists of methane, carbon dioxide, hydrogen sulfide and some trace element. Biogas quality is determined by methane content. Generally CO₂ is the biggest impurity of biogas, hence biogas purification is best achieved by CO₂ removal. The chosen absorbent must be economic, nontoxic, having high CO₂ absorption ability, and easy to regenerate. Abharchaei, 2010 studied the absorption of CO₂ by 2(Methyl)-Aminoethanol (MEA) solution, but the solution is corrosive[1]. Normal methyldiethanolamine (MDEA) is a widely used in industry due to high absorption capacity, especially for acid gases including CO₂. In addition to the large absorption capacity, MDEA also has degradation proof property due to exposure to heat and direct contact with chemicals [4]. Another reason that encourages the use of MDEA extensively on industrial scale is a low corrosivity and low vapor pressure of MDEA [2]. The advantage of chemical absorption is the bond formed between CO₂ with MDEA is stronger compared to physical absorption. But the chemical absorption has shortcomings such as high energy requirements for regeneration of solvent [5]. CO₂ absorption with MDEA is an exothermic reaction with heat of reaction -72 kJ / mol. During absorption process CO₂

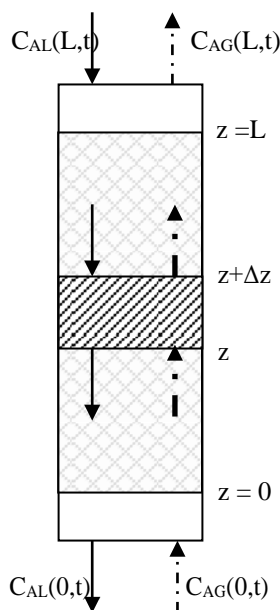


rich gas is contacted directly with absorbent. During this process, CO_2 is transferred from gas bulk into liquid body [6]. This condition continues until liquid reaches a saturated point where absorption can no longer take place since absorbent has already lost its absorption capability. In this paper effect of gas flow rate dan MDEA concentration on absorption process of CO_2 in MDEA solution is studied.

The chemical absorption of CO_2 in MDEA solution follows this reaction (Gao et al, 2013).



Mathematical model of unsteady state continuous absorption in packed column is developed by applying mass balance.



Mass balance of CO_2 in gas phase:

$$\frac{\partial C_{AG}}{\partial t} = -\frac{Q_G}{S \cdot \epsilon} \cdot \frac{\partial C_{AG}}{\partial z} - K_G a \cdot (C_{AG} \cdot R \cdot T - H \cdot C_{AL}) \quad (2)$$

Mass balance of CO_2 in liquid phase :

$$\frac{\partial C_{AL}}{\partial t} = \frac{Q_L}{S \cdot \epsilon} \cdot \frac{\partial C_{AL}}{\partial z} + K_G a \cdot (C_{AG} \cdot R \cdot T - H \cdot C_{AL}) - k \cdot C_{AL} \cdot C_{BL} \quad (3)$$

$$\frac{\partial C_{BL}}{\partial t} = \frac{Q_L}{S \cdot \epsilon} \cdot \frac{\partial C_{BL}}{\partial z} - k \cdot C_{AL} \cdot C_{BL} \quad (4)$$

IC : $t = 0, z = z, C_{AL} = 0, C_{AG} = 0$

BC : $t = t, z = 0, C_{AL} = C_{AL}(0,t), C_{AG} = C_{AG}(0,t)$

$z = L, C_{AL} = C_{AL}(L,t), C_{AG} = C_{AG}(L,t)$

Differential Equations (2), (3) and (4) with boundary conditions was solved using MATLAB.

Figure 1. Continuous absorption of CO_2 by MDEA solution in packed bed column

The solution are C_{AG} and C_{AL} as function of time, for a certain value of k and $K_G a$. The values of k , $K_G a$ and H will be applied to absorber design.

2. Methodology

2.1. Material

1. MDEA is provided by PT.Pupuk Kujang
2. Gas CO_2 (99%) is supplied by CV Gas Sumber Agung Sukses, Yogyakarta
3. Mixed gas (CO_2 and N_2 40 %, 74 % v/v) are supplied by PT Samator Gas, Jln Ringroad utara, Yogyakarta.

2.2. Method

Continuous absorption experiments was conducted in the absorption column as shown in Figure 2. MDEA solution with a certain concentration was flowed from the top of the packed column ($D = 6$ cm, $L = 75$ cm), then the mixed gas was sparged from the bottom of the column. At a certain time the gas and liquid samples were taken. Gas samples were analyzed using GC while the liquid sample was analyzed by conductivitymeter. The same experiments were conducted for variation of MDEA concentration, gas flow rate.

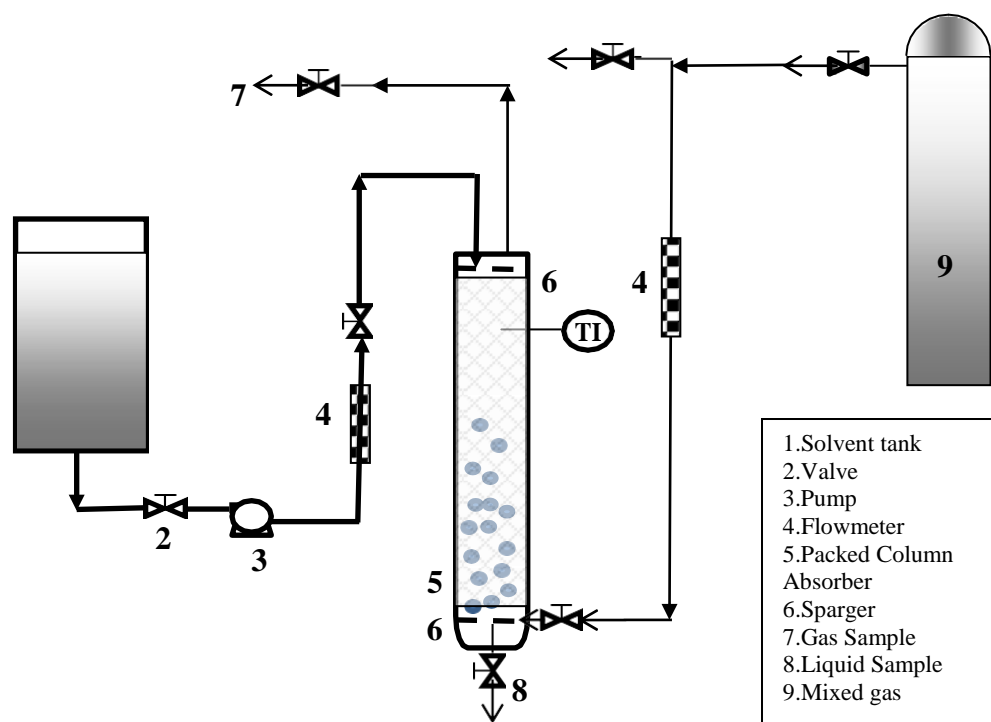


Figure 2. Experimental rig

The unsteady state absorption of CO₂ mathematical model was developed. Together with Initial and boundary condition, the differential equations were solved. The solution were outlet CO₂ concentration as a function of time. Equilibrium parameter (H) was taken from previous experiment which are 37.64 atm.L/mol. Reaction rate constant (k) and mass transfer coefficient KGa were determined by fitting the outlet CO₂ concentration data as a function of time to the model solution with smallest Sum of Square of Errors (SSE).

3. Result and Discussion

Figure 3 and Figure 4 show the experimental data for CO₂ absorption for initial gas content 40% at various gas flow rate which are 1 LPM, 1.5 LPM and 1.8 LPM with 0.15 LPM MDEA solution flow rate at different MDEA solution concentrations which are 20 % and 35.3 %. The outlet CO₂ concentrations for different MDEA concentration have only 1 % difference, it is not significant. The absorption experimental data for various gas flow rate is shown in Figure 5 for 40 % inlet CO₂ concentration and Figure 6 for 74 % inlet CO₂ concentration. At 0.15 LPM MDEA flowrate with inlet gas flow rate 1 LPM, the outlet CO₂ concentration drop from 40 % to 17 %. It meets the requirement to be the fuel of electric generator which is less than 20 % CO₂. By increasing the flow rate of MDEA solution and conduct the absorption at several columns, it is possible to get the composition of biomethane more than 90%, and fulfill the requirement as generator fuel.

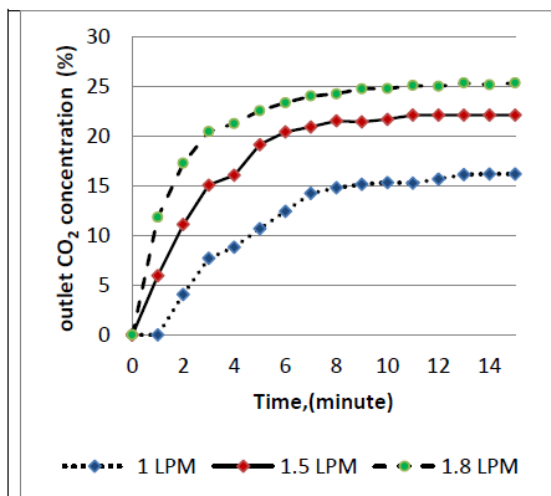
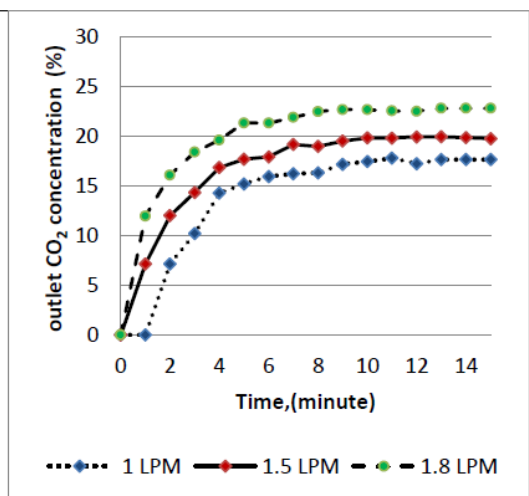
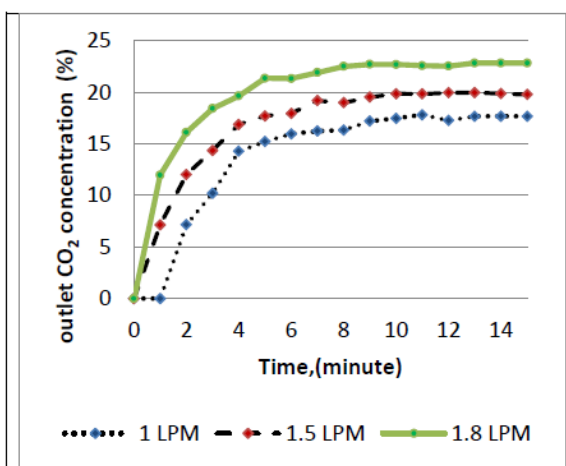
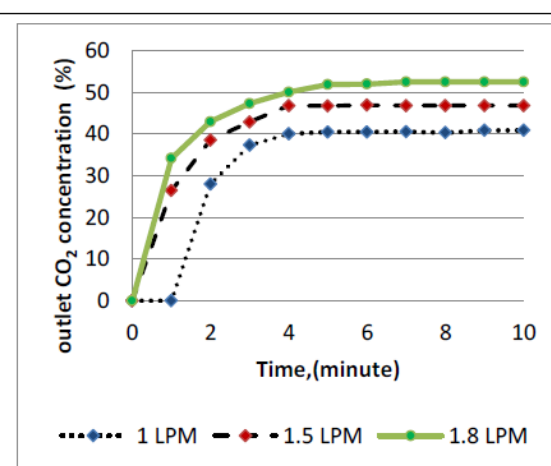
Figure 3. Outlet CO₂ concentration for MDEA 20 %Figure 4. Outlet CO₂ concentration for MDEA 35,3 %Figure 5. Outlet CO₂ concentration for MDEA 20 %, inlet CO₂=40%Figure 6. Outlet CO₂ concentration for MDEA 20 %, inlet CO₂=74%

Table 1 and table 2 show the parameters determined from the data obtained, the parameters are reaction rate constant and overall mass transfer coefficient at various gas flow rate. Henry constant (H) was taken from previous experiment, $H = 37,64$ (atm.L/mol).

Table 1. Gas mass transfer coefficient of CO₂ at various gas flowrates for MDEA concentration of 20% dan 35,31 %, inlet CO₂ concentration 40 %

MDEA 20 %			MDEA 35,31 %		
Q _G (L/menit)	k (L/mol.min)	K _{Ga} (mol/atm.min.L)	Q _G (L/menit)	k L/(mol.min)	K _{Ga} (mol/atm.min.L)
1	0,302	0,0367	1	0,301	0,0402
1,5	0,291	0,0412	1,5	0,307	0,0510
1,8	0,281	0,0415	1,8	0,292	0,0535

Table 2. Gas mass transfer coefficient of CO₂ at various gas flowrates for MDEA concentration of 20% dan 35,31 %, inlet CO₂ concentration 70 %

MDEA 20 %			MDEA 35,31 %		
Q _G (LPM)	k (L/mol.min)	K _{Ga} (mol/atm.min.L)	Q _G (LPM)	k L/(mol.min)	K _{Ga} (mol/atm.min.L)
1	0,199	0,0167	1	0,282	0,032
1,5	0,152	0,0201	1,5	0,285	0,047
1,8	0,197	0,022	1,8	0,294	0,0455

The experiments were conducted at isothermal condition, the values of reaction rate constant is almost constant. The overall mass transfer coefficient are affected by gas flow rate. The higher the flow rate, the higher the mass transfer coefficient.

4. Conclusion

Continuous absorption of CO₂ using MDEA solution at ambient temperature in packed column is possible to reduce the 40 % CO₂ concentration to 17 % CO₂. By applying some stages of this absorption method, it is possible to get biomethane from biogas, and to be utilised as fuel for electrical generator in the small and medium scale industries. 20 % MDEA solution is not significantly different from 35.3 % MDEA solution in absorbing CO₂, therefore based on economical point of view, 20 % MDEA is more feasible.

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Nomenclature

Q _G , Q _L	Gas flow rate, Liquid flow rate, L/min (LPM)
k	reaction rate constant (L/mol.min)
K _{Ga}	volumetric mass transfer coefficient (mol. atm/min/L)
C _{AG}	Concentration of CO ₂ in gas phase, (mol/L)
C _{AL}	Concentration of CO ₂ in solution, (mol/L)
C _{BL}	Concentration of MDEA in solution, (mol/L)
H	Henry constant, (atm.L/mol)

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