Absorption of CO_2 in Biogas with Amine Solution for Biomethane Enrichment

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Abstract. Biogas upgrading with carbon dioxide absorption in a column of monoethanolamine (MEA) solution was carried out. The effects of controlled parameters on the CO_2 absorption such as gas flow rate, solution concentration, height to diameter ratio of the column were considered. High CH_4 concentration could be achieved at low gas flow rate and high MEA concentration. The CH_4 concentration could be up from 70-75% to 92-95% by volume for 0.2 M MEA. A set of breakthrough curves was obtained to determine the absorption characteristics, such as the absorption constant (k), the absorption time when the CO_2 concentration at the outlet was 50% of the concentration at the inlet (τ), and the absorption period (t^*) when the CH_4 concentration was over 90%. An empirical equation of the methane enrichment with the related parameters was developed.

Keywords: *amine solution; biogas; biomethane enrichment; CO_2 absorption; monoethanolamine (MEA).*

1 Introduction

Biogas mainly consists of 40-70% methane (CH_4) and 30-60% carbon dioxide (CO_2) by volume [1]. Since the proportion of CO_2 is relatively high it causes corrosive effects on some parts of the biogas equipment and decreases the gas heating value [1,2]. Several techniques can be used for CO_2 separation from biogas such as physical absorption, chemical absorption, pressure swing absorption, membrane technologies and cryogenic separation. The advantages and disadvantages of each process are shown in Table 1.

Several researchers have studied CO_2 absorption with amine solutions. Tippayawong and Thanompongchart [3] experimentally investigated chemical absorption of CO_2 and H_2S from biogas by aqueous solutions, calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH) and monoethanolamine (MEA) in a packed column. The results showed that the aqueous solutions were effective in removing CO_2 from the biogas (> 90% removal efficiency), creating enriched CH_4 fuel. H_2S was also removed and the value was below the detection limit. Lin, *et al*. [4] studied the absorption of carbon dioxide by amine solutions,

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monoethanolamine and tertiary N-methyldiethanolamine in a packed column. The CO_2 absorption characteristics of these two amines were experimentally examined under various operating conditions. The results showed that an increase in the absorption rate was due to an increase of the inlet CO_2 concentration or gas flow rate, which shortened the absorption period. An increase in the amine concentration enhanced the amount of CO_2 absorption.

Table 1 Advantages and disadvantages of CO_2 separation with different methods [2].

Item	PSA	Water Scrubbing	MEA	Membrane
Separation Method	Adsorption	Physical process	Chemical process	Membrane separation
Cleaning	Necessary	Unnecessary	Necessary	Necessary
Pressure (bar)	7-4	7-4	Atmosphere	16-40
Methane loss	10-3%	1-2%	< 0.1%	-
Methane concentration	> 96%	> 97%	> 99%	90-94%
Operating temperature (k)	Normal	Normal	373	Normal
Regeneration ability	Yes	Yes	Yes	-
Energy consumption in regeneration process	Moderate	Moderate	High	-

Bonenfant, *et al.* [5] studied carbon dioxide absorption with various amine solutions. The absorption solutions were a series of aqueous 5 %wt ammonia, monoethanolamine, triethanolamine, triethylamine, pyridine, pyrrolidine, 2-(2-aminoethylamino) ethanol, and N-(2-aminoethyl)-1,3-propanediamine solutions. The results showed that the CO_2 absorption efficiencies of the 5 %wt monoethanolamine and pyrrolidine solutions were lower than those of the aqueous 2-(2-aminoethylamino) ethanol, N-(2-aminoethyl)-1,3-propanediamine and triethanolamine solutions, but the use of monoethanolamine may present a certain advantage due to its acceptable regeneration capacity.

In addition, Conway, *et al.* [6] and Kim, *et al.* [7] studied CO_2 absorption and the absorption mechanism using aqueous amine blended solutions. Blended solutions of monoethanolamine with 2-amino-2-methyl-1-propanol and N, N-dimethylethanolamine with N, N-diethyl ethanolamine were used and their absorption behavior was compared to that of a standalone monoethanolamine solution. The results showed that absorption capacities of the blended solutions were similar to that of the standalone MEA solution [6]. The blended solutions of monoethanolamine with piperazine, monoethanolamine with 2-amino-aminoethylethanolamine and mono ethanolamine with diethylenetetramine improved the CO_2 capturing capability of the monoethanolamine compared to the standalone monoethanolamine solution, while 2-methyl-1-propanol and diethanolamine decreased the performance of the monoethanolamine [7].

A monoethanolamine (MEA) solution can also be used to capture CO_2 for biogas purification. When the solution is saturated, a regeneration process is needed, after which the regenerated MEA can be reused in the next cycle for biomethane enrichment [8].

In this study, CO_2 separation from biogas to get biomethane by MEA solution was carried out. The parameters that affect carbon dioxide absorption from the MEA solution, i.e. biogas flow rate, monoethanolamine and carbon dioxide concentrations and reactor size, were considered.

2 Methodology

2.1 Carbon dioxide Absorption

Separation of CO_2 from CH_4 is an important process in many areas, such as natural gas processing, biogas purification, enhanced oil recovery and flue gas treatment [9].

CO_2 absorption using an MEA solution is a popular method of CO_2 separation used by industries. In this study, CO_2 absorption from biogas with MEA in a bubbly flow column was carried out. The effects of biogas flow rate, MEA concentration, and height to diameter ratio of the flow column on CO_2 absorption were investigated. The characteristic absorption time (τ) and the absorption constant (k) were analyzed using the CO_2 absorption breakthrough curves.

2.2 Carbon dioxide Characteristics [3,4,10,11]

Amine solutions are the chemicals usually used for CO_2 absorption [10]. The chemical reaction equations of CO_2 sorption and desorption with amine are as follows:

CO_2 sorption:

$$RNH_2 + H_2O + CO_2 \longrightarrow RNH_3^+ + HCO_3^- \quad (1)$$

CO_2 desorption:

$$RNH_3^+ + HCO_3^- + \text{Heat (373 K)} \longrightarrow RNH_2 + H_2O + CO_2 \quad (2)$$

CO_2 can be dissolved in an alkaline or an amine solution. The reaction depends strongly on pH, liquid solution and CO_2 concentration, and other factors [3]. The process of CO_2 absorption from biogas with MEA in a bubbly flow column is depicted in Figure 1.

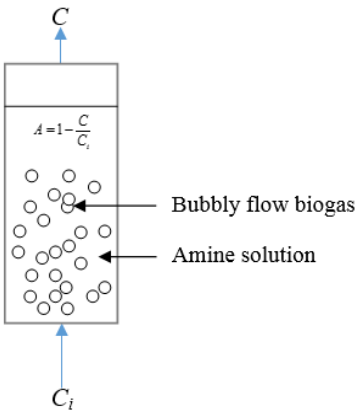

Figure 1 The overall mass balances at the reactor.

In this study, the reaction took place in the liquid phase with controlled input conditions, i.e. gas flow rate, solution concentration and height to diameter ratio (H/D). With the bubbly gas flow in the column, the fluid in the column can be treated as lumped, which means that heat, mass and momentum transfer in each section of the column are almost negligible.

The breakthrough curve of the mole fraction of CO_2 at the outlet and the inlet over time is shown in Figure 2.

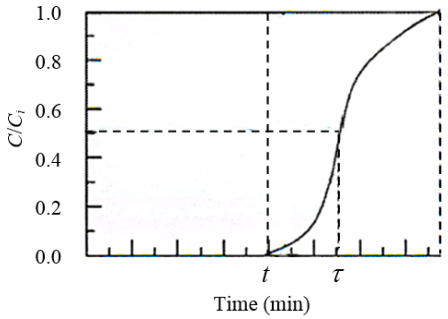

Figure 2 Breakthrough curve of CO_2 absorption process [11].

The mole of absorbed CO_2 with mole of CO_2 at the column inlet can be denoted as:

$$A = 1 - \frac{C}{C_i} \tag{3}$$

The removal rate of CO_2 by absorption can be expressed as [3]:

$$\frac{dA}{dt} = +kA(1-A)\,. \tag{4}$$

After integration, we get:

$$\ln\left(\frac{A(1-A_o)}{A_o(1-A)}\right) = k(\tau - t)\cdot \tag{5}$$

The equation can be rearranged as:

$$t = \frac{1}{k}\ln\left(\frac{C}{C_i - C}\right) + \tau \tag{6}$$

From the above equation, it can be seen that the solution should be saturated with CO_2 after a period of 2τ.

3 Experiment

The experimental apparatus is shown in Figure 3. The unit consisted of 1) gas distributor; 2) gas flow meter (in the range of 1-10 liter/min (LPM)); 3) bubble column (acrylic cylinder with height to diameter ratios of 1.4, 3.3 and 6.5 (the height to diameter ratios were 28.0:20.0, 49.5:15.0 and 78.0:12.0, respectively – all units in cm); 4) dehumidifier (silica gel); 5) gas flow distributor set (porous medium packing, regularly arranged at the bottom of the tested MEA solution column).

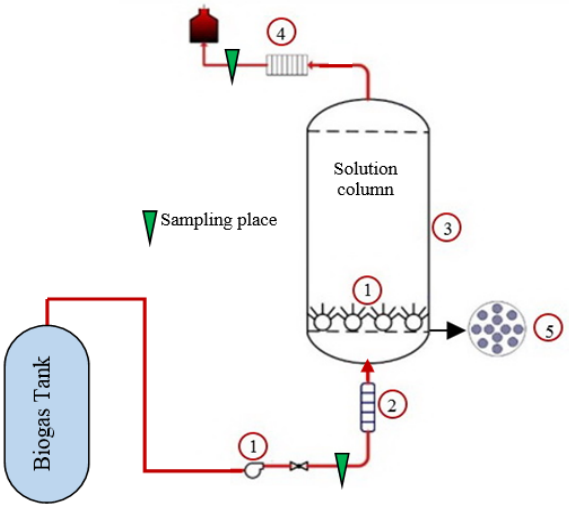

Figure 3 Schematic sketch of the CO_2 absorption experimental setup.

The biogas used in this experiment was obtained from a 300-m^3 biogas pond (120 m^3/day) of a swine farm at Mae Hia Agricultural Research, Demonstrative and Training Center, Chiang Mai University, Chiang Mai and kept in a high pressure storage. In the experiment, the biogas from the storage was fed continuously at the bottom of the tested MEA solution column. The gas flowed through a porous nozzle to create a uniform bubbly gas flow (the bubble diameter was in the range of 1.5-3 mm). Fine bubbles generate a high interaction area, so CO_2 absorption can be performed effectively. The gas flow rate was controlled by a gas flow meter.

In the experiment, biogas consisting of 70-75% CH_4 and around 30-25% CO_2 (other components such as N_2 and H_2S were less than 0.5% and were neglected) with various flow rates (1, 3 and 5 liter/min) were fed through an 8 liter column of 0.05, 0.1 and 0.2 M (molar) MEA solution. The inlet biogas flow rate and the inlet CO_2 and CH_4 concentrations in the biogas were kept constant during every experimental test. The collected experimental data of CO_2 and CH_4 concentrations in the biogas entering and exiting the column were continuously monitored (Biogas Check Analyzer from Geotechnical Instruments, Ltd., United Kingdom). The absorption characteristics, i.e. the absorption constant and the characteristic absorption time, were considered.

4 Results and Discussion

From the experiment it could be seen that the MEA solution could absorb CO_2 from the biogas effectively, which resulted in a high percentage of CH_4 in the outlet gas. The outlet CH_4 concentration over time with a solution concentration of 0.2 M; biogas flow rate at 1, 3 and 5 liter/min; height to diameter ratio of the column at 1.4, 3.3 and 6.5; and inlet CO_2 concentration at 25-30 % are shown in Figure 4.

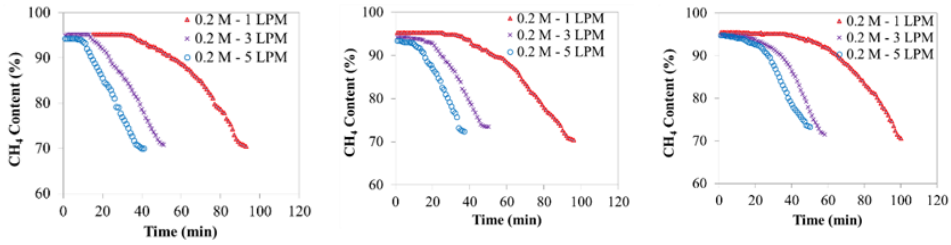

Figure 4 The outlet methane concentration over time. MEA concentration of 0.2 M, inlet biogas flow rates of 1, 3 and 5 liter/min (LPM), and column height to diameter ratios of 1.4, 3.3 and 6.5 – (a) H/D = 1.4 (b) H/D = 3.3 (c) H/D = 6.5.

From Figure 4, for all column sizes, a low biogas flow rate and a high MEA concentration, the MEA could absorb CO_2 effectively and a high biomethane concentration at the outlet was obtained. The maximum CH_4 concentration was up to 92-95 % with a 0.2 M concentration and up to more than 95% with a high height to diameter ratio and a low biogas flow rate. The absorption performance tended to decrease with time since the solution was close to the saturation point. It can be noted that low concentration solutions, such as 0.05 M of MEA, could not absorb CO_2 effectively since the maximum CH_4 concentration was less than 90% by volume.

The percentage of CH_4 at the outlet depended on the result of CO_2 absorption in the solution. The proportion of outlet/inlet CO_2 concentration over time is shown in Figure 5.

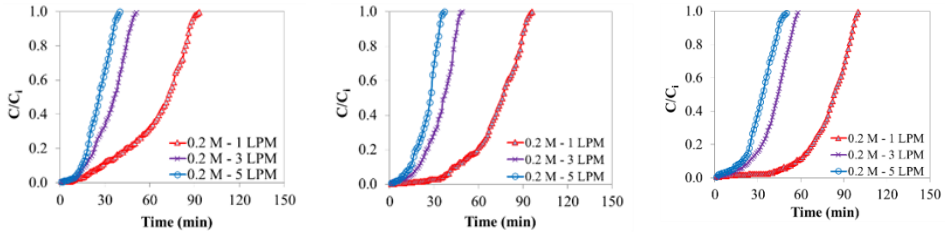

Figure 5 Proportion of outlet/inlet CO_2 concentration over time. MEA concentration of 0.2 M, inlet gas flow rates of 1, 3 and 5 liter/min (LPM) and height to diameter ratios of 1.4, 3.3 and 6.5 – (a) H/D = 1.4 (b) H/D = 3.3 (c) H/D = 6.5.

A high biogas flow rate will shorten the absorption period. When considering the height to diameter ratio (H/D) of the CO_2 absorption column, it was found that the absorbed CO_2 ability increased with H/D since the contact time for CO_2 absorption was longer.

The kinetics of CO_2 absorption with various conditions were considered with the relation between operating time (min) with the value of $\ln\left(\frac{C}{C_i - C}\right)$ for CO_2 absorption as $t = \frac{1}{k}\ln\left(\frac{C}{C_i - C}\right) + \tau$. The absorption constant (k) and the characteristic absorption time when the CO_2 concentration at the outlet was 50% of the concentration at the inlet (τ) are shown in Table 2.

Table 2 Kinetics of CO_2 absorption with MEA solution.

Item	Sol^{n} Conc. (M)	H/D 1.4 Gas Flow Rate (liter/min)			H/D 3.3 Gas Flow Rate (liter/min)			H/D 6.5 Gas Flow Rate (liter/min)		
		1	**3**	**5**	**1**	**3**	**5**	**1**	**3**	**5**
1/k (min)	0.05	5.30	5.12	5.07	3.68	2.66	2.55	3.57	2.52	2.36
	0.10	8.05	6.84	5.43	6.55	6.22	4.27	5.99	3.77	3.37
	0.20	16.03	8.33	6.35	12.83	8.08	6.24	11.43	8.08	6.08
k (min^{-1})	0.05	0.19	0.20	0.20	0.27	0.38	0.39	0.28	0.40	0.42
	0.10	0.12	0.15	0.18	0.15	0.16	0.23	0.17	0.27	0.30
	0.20	0.06	0.12	0.16	0.08	0.12	0.16	0.09	0.12	0.16
τ (min)	0.05	15.76	9.12	5.52	19.85	10.63	8.61	26.14	13.36	9.71
	0.10	38.81	19.74	13.71	41.43	19.96	14.42	49.94	33.73	17.62
	0.20	69.73	35.23	25.77	74.84	36.74	27.18	81.82	42.90	32.95

From the kinetics result, it was found that the CO_2 absorption capability by our technique was rather high. The absorption constant (k) in this study at a solution concentration of 0.1 M, H/D ratio of 6.5 and a gas flow rate of 1 liter/min was 0.17 min^{-1}, which is higher than that reported in the literature (0.04 min^{-1}) [3].

From Table 2, the characteristic absorption time when the CO_2 concentration at the outlet was 50% of the concentration at the inlet (τ, min) was related with solution concentration (SC), gas flow rate (GFR), height to diameter ratio (H/D) and biogas concentration (BC). The τ value can be formulated as

$$\tau = 0.60725 \frac{SC^{0.95977}\left(\frac{H}{D}\right)^{0.19723} BC^{1.4457}}{GFR^{0.62927}} \quad (7)$$

where $0.05 \le SC \le 0.2$ M, $1.4 \le \frac{H}{D} \le 6.5$, $70 \le BC \le 75$ % by volume and $1 \le GFR \le 5$ liter/min.

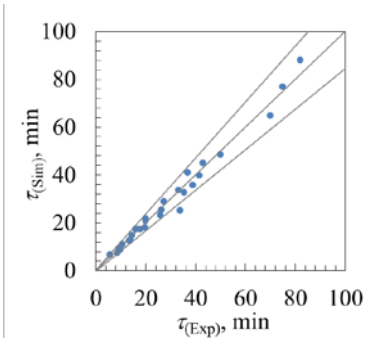

Figure 6 Characteristic absorption time when the CO_2 concentration at the outlet was 50% of the concentration at the inlet comparing the correlation and the experimental results.

A comparison of the characteristic absorption time when the CO_2 concentration at the outlet was 50% of the concentration at the inlet (τ, min) from the experimental data with those from Equation (7) are shown in Figure 6. The result showed that 96.3% of the experimental data was consistent with the simulation data within ±.%15

In addition, the absorption period (t^*, min) during which the CH_4 concentration was more than 90% can be formulated as:

$$t^* = 0.6286 \frac{SC^{1.0832}\left(\frac{H}{D}\right)^{0.33225} BC^{1.3899}}{GFR^{0.78285}} \tag{8}$$

where $0.1 \leq SC \leq 0.2$ M, $1.4 \leq \frac{H}{D} \leq 6.5$, $70 \leq BC \leq 75$ % by volume and $1 \leq GFR \leq 5$ liter/min.

A comparison of the absorption period (t^*, min) from the experimental data with that from Equation (8) is shown Figure 7. The result shows that 94.4% of the experimental data was consistent with the simulation data within ±.%15

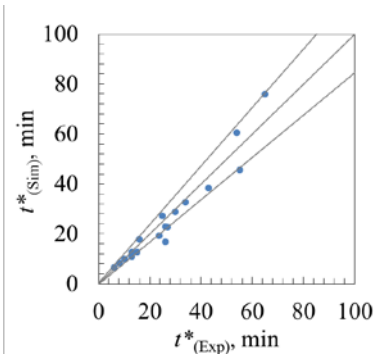

Figure 7 Comparison of the simulated absorption period (t^*) with the experimental data where the CH_4 concentration was over 90%.

5 Conclusion

For biogas upgrading, biogas of 70-75% CH_4 and 30-25% CO_2 was fed continuously through a column containing MEA solution. The effects of controlled parameters on the absorbed CO_2, i.e. gas flow rate, solution concentration, height to diameter ratio of the column, were measured. The CH_4 concentration was up to 92-95% by volume. With a high height to diameter ratio and a low biogas flow rate, a high absorption rate could be achieved. For low concentration solutions such as 0.05 M of MEA, the solution could not

absorb CO_2 effectively since the maximum CH_4 concentration was less than 90% by volume. The characteristic absorption time when the CO_2 concentration at the outlet was 50% of the concentration at the inlet (τ) with the related parameters was formulated in the form of

$$\tau = 0.60725 \frac{SC^{0.95977}\left(\frac{H}{D}\right)^{0.19723} BC^{1.4457}}{GFR^{0.62927}}.$$ The absorption period (t^*) during which the CH_4 concentration was over 90% can be formulated as

$$t^* = 0.6286 \frac{SC^{1.0832}\left(\frac{H}{D}\right)^{0.33225} BC^{1.3899}}{GFR^{0.78285}}.$$

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Nomenclature

A Mole of absorbed CO_2 with mole of CO_2 at the column inlet
C Mole fraction of outlet CO_2 compared to that of inlet biogas
C_i Mole fraction of inlet CO_2 compared to that of biogas at the initial time
k The absorption constant
t^* The absorption period where the CH_4 concentration is over 90%
τ The characteristic absorption time when CO_2 concentration at the outlet is 50% of the concentration at the inlet

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