Biogas Purification by Uniform Bubbly Flow in Ethanolamine Solution

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Abstract

Purification of biogas could reduce corrosion in biogas equipment and increase the gas heating value. This research is to separate carbon dioxide from biogas by flowing through a column of ethanolamine solution. In the experiment, biogas of 60% CH_4 and 40% CO_2 with various flow rates of 2-4 liter/min was fed through a 10 liters column of 0.01-0.2 M ethanolamine solution. The biogas was fed through a porous nozzle of which the 1.5-2.5 mm gas bubbles could flow uniformly. By this technique, the solution could absorb the gas effectively. The CH_4 concentration could be up to 93-96 % and after that it tended to decrease with time since the solution was closing to the saturation point. The characteristic absorption time for CO_2 absorption could be set as $t = \frac{1}{k}\ln\left(\frac{C}{C_o - C}\right) + \tau$. The absorption constant (1/k) was found to be in a range of 7.94-21.36 which was lower than that from the literature which meant that the more effective absorption was obtained at the same operating period.

Key words: Carbon dioxide Separation, Biogas Purification, Uniform Bubbly Flow.

1. Introduction

Biogas from biogas pond consists mainly of methane (CH_4) which is about 60-70% of the biogas and about 30-40% is carbon dioxide (CO_2). Since the carbon dioxide in biogas is relatively high then the proportion of carbon dioxide in biogas gives some effects on the corrosion in biogas equipment and decreases the gas heating value. The heating value of each gas in biogas is shown in Table.1 [1].

Table. 1 The Heating Value of each gas in Biogas [1].

Type of Gas	Heating value (MJ/m^3)
CH_4	35.64
CO_2	-
H_2	10.80
H_2S	22.68
60%CH_4, 40%CO_2	21.60
65%CH_4, 34%CO_2, 1% and others	24.48

From Table.1, it could be seem that the heating value of 100% CH_4 is up to 35.64 MJ/m^3. Therefore, the study on carbon dioxide separation from biogas is another main topic that could increase the heating value and the total CO_2 emission could be reduced.

2. Theory

The separation of CO_2 from CH_4 is one of the important processes in many industrial areas such as natural gas processing, biogas purification, enhanced oil recovery and flue gas treatment [2].

Carbon dioxide (CO_2) absorption with ethanolamine solution is one method of carbon dioxide separation process. This technique is used in industries.

2.1 Amine Absorption Process [3]

Mono-ethanolamine (MEA, $(CH_2CH_2OH)N_2H$), Di-ethanolamine (DEA, $(CH_2CH_2OH)_2NH$) and Methyl Diglycolamine (DGA) are the chemicals usually used in carbon dioxide absorption process. The chemical reaction equations of carbon dioxide sorption and desorption with amine are shown as follows:

CO_2 sorption

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

CO_2 desorption

$RNH_3 + HCO_3^- + \text{Heat } (100^\circ C) \longrightarrow RNH_2 + H_2O + CO_2$ (2)

2.2 Absorption Characteristic [4,5]

Carbon dioxide could dissolve in alkaline or amine solution. The reaction depends strongly on pH, liquid solution and CO_2 concentration and other factors. The fraction of CO_2 in the biogas absorbed in a solution at time t was explained and shown by Fig. 1.

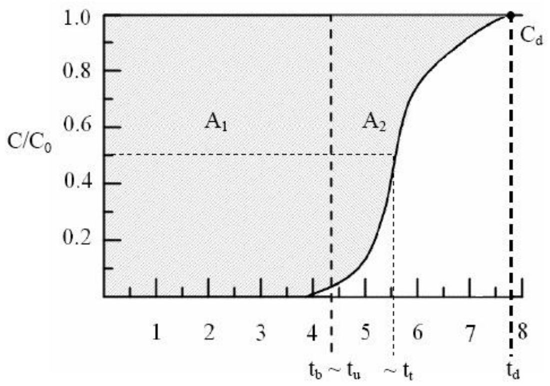

Fig. 1 Concentration curve of carbon dioxide absorption process [6].

The ratio of absorbed CO_2 with the CO_2 concentration at the inlet of the absorption column could be

$$A_{ab} = 1 - \frac{C}{C_0}, \quad (3)$$

where

C_0 and C are inlet and outlet CO_2 concentrations at time t.

The removal rate of declining CO_2 absorption was assumed to be proportional to the CO_2 fraction that was absorbed in the packed column, and the CO_2 fraction that passed through. It can then be expressed as

$$\frac{dA_{ab}}{dt} = -kA_{ab}(1 - A_{ab}). \quad (4)$$

Integration of equation, we get

$$\ln\left(\frac{A_{ab}(1 - A_{ab,o})}{A_{ab,o}(1 - A_{ab})}\right) = k(\tau - t). \quad (5)$$

The equation could be rearranged as

$$t = \frac{1}{k}\ln\left(\frac{C}{C_o - C}\right) + \tau, \quad (6)$$

where

k is an absorption constant and τ is the characteristic absorption time when 50% of CO_2 absorption occurs.

From the above equation, it could be seen that the solution should be saturated with carbon dioxide after time of 2τ.

3. Experiment

The experimental apparatus is shown in Fig. 2. The unit consists of 1) Gas Blower, 2) Gas flow meter (Range of 1-10 LPM), 3)Bubble Column (acrylic cylinder of 15 cm in diameter and 100 cm in height), 4)Dehumidifier (silica gel), 5) Gas flow distributor (porous media).

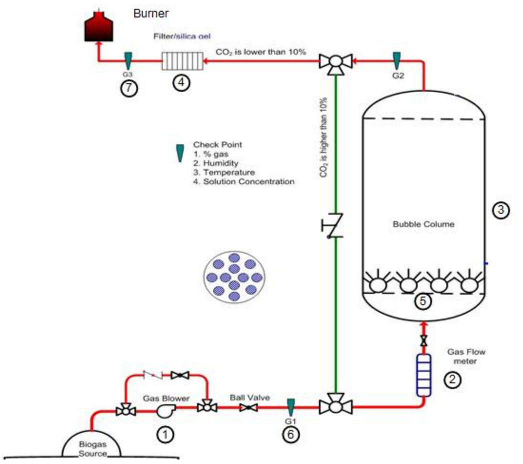

Fig.2 The absorption apparatus.

In our experiment, the biogas was obtained from a 16 m^3 biogas pond of a cattle farm at the Bio-Technology Center, Maejo University, Chiang Mai. The biogas was continuously sucked out and fed to the bottom of the tested column through a porous nozzle to create uniform gas bubbly flow. Since the fine bubbles were generated then the interaction area and the reaction rate could be performed effectively. The gas flow rate was controlled by a gas flow meter. Ethanolamine solution was used in this study.

In the experiment, biogas of 60% CH_4 and 40% CO_2 with various flow rates of 2, 3 and 4 liter/min was fed through a 10 liters column of 0.01, 0.1 and 0.2 M ethanolamine solution. The collected experimental data were CO_2 and CH_4 concentrations in the biogas entering and exiting the column which were continuously monitored (Biogas Check-Geotechnical Instrument Co., Ltd., Model: GA25). The pH of the liquid solvent was measured by a pH meter. The characteristic and size of bubble gas were determined by photographic method.

4. Results and Discussion

At present, biogas upgrading or enrichment of CH_4 in biogas has no standard specification on the composition of gases in the biogas. However, there is one standard settled by California Air Resources Board (CARB) which is the international standard of natural gas. The CARB suggested that the CH_4 in natural gas should be higher than 88 % [7].

To be close to the above Standard, the results were considered when the testing condition of which the yield having CH_4 over 80 %by volume.

4.1 Absorption Performance

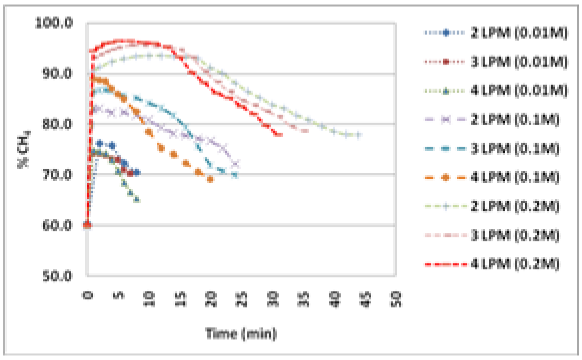

Fig. 3 Outlet CH_4 concentration with time; solution concentration of 0.01, 0.1 and 0.2 M, gas flow

rate of 2, 3 and 4 LPM, 40% inlet CO_2concentration.

Fig. 3 shows the percentage of CH_4 yielded from the column. During the starting period, it could be seen that high percentage of CH_4 was obtained. The maximum values were up to 75-77, 83-89 and 93-96%, respectively for 0.01, 0.1 and 0.2 M ethanolamine solution and the gas flow rate of 2-4 LPM. After that the solution was tending to its saturation then the percentage reduced with time. It could be noted that when the biogas flow rate increased, higher mixing of the gas with solution was obtained thus the maximum CH_4 concentration occurred faster and the solution entered to its saturation quicker.

The results were also supported by CO_2 absorption as shown in Fig. 4. High yield of CH_4 meant that high proportion of CO_2 was absorbed in the column.

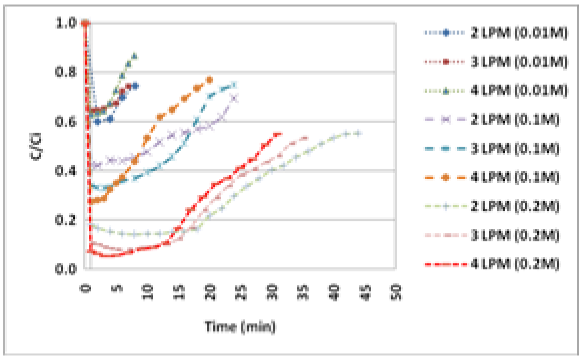

Fig. 4 The proportion of outlet/inlet CO_2 concentration with time; solution concentration of 0.01, 0.1 and 0.2 M, gas flow rate of 2, 3 and 4 LPM, 40% inlet CO_2 concentration.

4.2 Absorption Characteristics

The kinetics of CO_2 absorption with various conditions are shown in Fig.5.

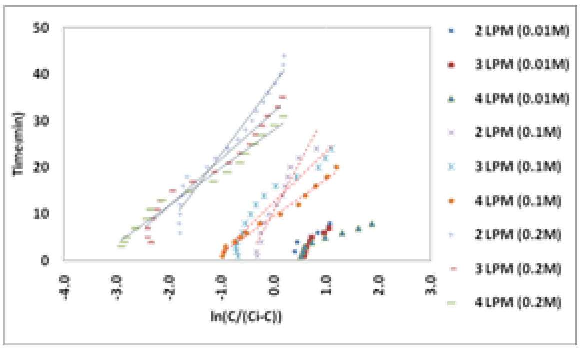

Fig. 5 Kinetics of CO_2 absorption with solution concentration of 0.01, 0.1 and 0.2 M, gas flow rate of 2, 3 and 4 LPM, 40% inlet CO_2concentration

Fig. 5 shows the relation between operating time (min) with natural logarithm of CO_2 fraction $\left\{\ln\left(\frac{C}{C_o - C}\right)\right\}$. The testing conditions were: solution concentration of 0.01, 0.1 and 0.2 M, gas flow rate of 2, 3 and 4 LPM and 40% inlet CO_2concentration.

From the equation of CO_2 absorption, $t = \frac{1}{k}\ln\left(\frac{C}{C_o - C}\right) + \tau$, the values 1/k and τ at the testing conditions could be evaluated and the results were shown in Table. 2.

Table. 2 Kinetic parameters for CO_2 absorption with different solution concentrations and gas flow rates.

Gas Flow Rate (LPM)	Solution Concentration (M)					
	0.1			0.2		
	1/k	τ	R^2	1/k	τ	R^2
2	21.36	10.38	0.93	14.89	37.67	0.96
4	7.94	9.55	0.98	8.12	27.93	0.98

From Table. 2, it was found that the absorption constant (1/k) was in a range of 7.94-21.36 which was low which meant that high absorption was obtained. The value was found to be lower than that reported in the literature from different method [4]. Tables. 3 and 4 showed the comparison.

Table.3 Comparison of kinetic parameters for CO_2 absorption reported in literature.

Case study	1/k	τ	R^2
This Study* (2 LPM of gas flow rate)	21.36	10.38	0.93
This Study* (3 LPM of gas flow rate)	11.03	14.49	0.91
This Study* (4 LPM of gas flow rate)	7.94	9.55	0.98
[4]**	26.71	36.00	0.84

* Condition test was about ethanolamine (EA) concentration of 0.1 M of 10 liters and 40% inlet CO_2 concentration

** Condition test is about mono-ethanolamine (MEA) concentration of 0.1 M, gas to solvent flow ratio of 1.0 and 40% inlet CO_2 concentration

Table. 4 Comparison of absorption performance reported in literature.

References	Gas composition	Aqueous solvents	Capacity (mol/mol)
[4]	47% CO_2 53% CH_4	0.10 M NaOH 0.10 M $Ca(OH)_2$ 0.10 M MEA	0.20 0.32 0.25
This study	40% CO_2 60% CH_4	0.1 M EA	0.41

It could be noted that the characteristic absorption time (τ) was longer when the ethanolamine solution concentration was higher and the value was shorter when the gas flow rate increased.

4.3 Photograph of the Bubbly Gas Flow

In this study the biogas was fed through a porous nozzle to create gas bubbles in the absorption column and the gas size was controlled to have diameter between 1.5-2.5 mm. The photograph of the bubbly gas flow was shown in Fig. 6. With this technique, the gas could be flowing uniformly and the surface area was high then the gas absorption could occur effectively. The bubble size in this study was smaller compared to that in the literature [8] of which the size was about 3-6 mm.

Fig. 6 Photograph of uniform gas bubbly flow.

5. Conclusion

Biogas could be purified by flowing the gas to a column of 10 liter ethanolamine solution having concentration between 0.01-0.2 M. In this study, the biogas of 2-4 LPM was fed through a porous nozzle and gas bubbles could be generated and flow uniformly. The gas size was controlled to be about 1.5 – 2.5 mm. The absorption phenomena and the absorption kinetics were considered. The results showed that the solution could absorb CO_2 effectively which resulted in high percentage of CH_4 in the outlet gas. The maximum CH_4 concentration could be up to 83-89 % by using 0.1 M ethanolamine and up to 93-96 % by using 0.2 M ethanolamine and after that the absorption performance tended to decrease with time since the solution was closing to the saturation point. The absorption constant (1/k) was found to be in a range of 7.94-21.36 which was rather low which meant that the uniform bubbly flow with small diameters gave high effective absorption of CO_2.

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7. References

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