CHAPTER 3

Absorption and Regeneration of Carbon Dioxide in Biogas in Monoethanolamine Solution

3.1 Introduction

Biogas from biogas pond mainly consists of 60-70% methane (CH_4) and 30-40% carbon dioxide (CO_2) by volume. Since the proportion of CO_2 is relatively high then it gives some corrosive effects on some parts of biogas equipment and also decreases the gas heating value. The heating value of each gas in biogas is shown in Table 3.1.

Table 3.1 Properties of gases in biogas [Thanompongchart 2009].

Gas Type and Properties	**CH_4**	**CO_2**	**H_2**	**H_2S**	**60%CH_4 40%CO_2**	**65% CH_4, 34% CO_2, 1% others**
Heating Value (MJ/m^3)	35.64	-	10.8	22.68	21.6	24.48
Air/Fuel Ratio (%)	5-15	-	4-80	4-45	6-12	7.7-23
Ignition Temperature (^oC)	650-750	-	585	-	650-750	650-750

From Table 3.1, it could be seen that the heating value of biogas is up to 35.64 MJ/m^3 for 100% CH_4 which means that reduction of CO_2 in biogas resulting in increase of the heating value in the product. In addition, the corrosion due to CO_2 could be reduced.

Several processes are used for CO_2 separation from biogas such as physical absorption process, chemical absorption process, pressure swing absorption, membrane technology, cryogenic process, and biological process. The advantage and disadvantage in each process could be shown in Table 3.2.

Table 3.2 The advantages and disadvantages of CO_2 separation with different methods [ERDI 2010].

Item	PSA	Water Scrubbing	MEA	Membrane
Characteristic Separation	Adsorption	Physical Process	Chemical Process	Membrane Separation
Cleaning	Necessary	Unnecessary	Necessary	Necessary
Pressure(bar)	4-7	4-7	Atmosphere	16-40
Methane loss	3-10%	1-2%	<0.1%	-
Methane Concentration	>96%	>97%	>99%	90-94%
Operating Temperature(°C)	normal	normal	100	normal
Regeneration	Yes	Yes	Yes	-
Energy consumption in Regeneration Process	Moderate	Moderate	High	-

CO_2 separation with amine absorption process is one popular method performed by many researchers in biogas upgrading due to its low operating pressure and lowest loss of methane. In addition, the used solution could be regenerated. The upgraded biogas is called biomethane.

2 mol of monoethanolamine (MEA) reacts with 1 mol of CO_2 during biogas purification. When the solution is saturated, a regeneration process is needed. The used MEA could be regenerated with 80-100 °C heating to desorb the CO_2 and the regenerated MEA could be reused in the next cycle. However, the solution regeneration cost is rather high around 70 % of CO_2 absorption with amine solution.

Several researchers studied on regeneration and reuse of used amine solution. Singh and Versteeg 2008 studied relationship of structure and activity of various amine-based CO_2 solvents. The used solution was regenerated at 80 °C at atmospheric pressure and it was found that 75% of CO_2 was desorbed. Moreover, Tanaka *et al.* 2014 found that ultrasound technique gave a high possibility to reduce the energy consumption from heating in regeneration process.

In this study, the CO_2 separation from biogas with MEA solution was carried out. The used MEA solution was also regenerated by heating and combination of heating and ultrasonic wave technique. The parameters of the CO_2 absorption and desorption in MEA solution were investigated.

3.2 Methodology

3.2.1 Carbon Dioxide Absorption

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 [Atchariyawut *et al.* 2007].

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

1) Amine Absorption Process [Filburn *et al.* 2005]

Several Monoethanolamine (MEA), Diethanolamine (DEA) and Methyl Diglycolamine (DGA) are the chemicals usually used in CO_2 absorption process [Filburn *et al.* 2005]. The chemical reaction equations of CO_2 sorption and desorption with amine are shown as follows:

CO_2 sorption

$$RNH_2 + H_2O + CO_2 \longrightarrow RNH_3^+ + HCO_3^- \quad (3.1)$$

CO_2 desorption

$$RNH_3^+ + HCO_3^- + \text{Heat } (100^oC) \longrightarrow RNH_2 + H_2O + CO_2 \quad (3.2)$$

2) Absorption Characteristic [Lin and Shyu 1999, Wankat 2007 and Tippayawong and Thanompongchart 2010]

The CO_2 could be dissolved 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 Figure 3.1.

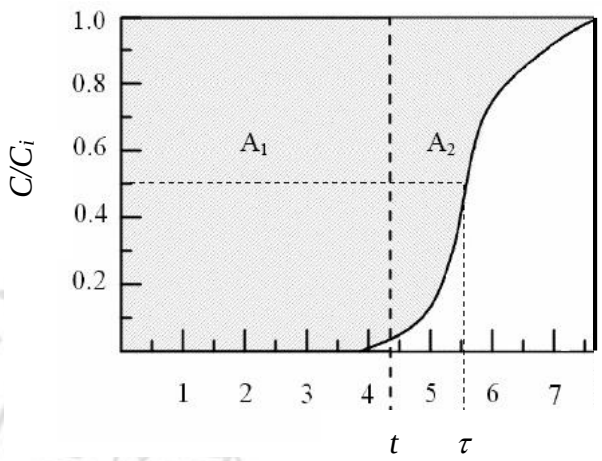


Figure 3.1 Concentration curve of CO_2 absorption process [Wankat 2007].

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

$$A_{ab} = 1 - \frac{C}{C_i} \tag{3.3}$$

where C_i is inlet CO_2 concentration at the initial time (% by volume) and C is outlet CO_2 concentration at time t (% by volume).

The removal rate of CO_2 by absorption could be expressed as

$$\frac{dA}{dt} = +kA(1-A) . \tag{3.4}$$

After integration, we get

$$\ln\left(\frac{A(1-A_o)}{A_o(1-A)}\right) = k(\tau - t) . \tag{3.5}$$

The equation could be rearranged as

$$t = \frac{1}{k}\ln\left(\frac{C}{C_i - C}\right) + \tau \quad (3.6)$$

where k is the absorption constant (min^{-1}) and τ is the characteristic absorption time when 50% of absorbed CO_2 is achieved (min).

From the above equation, it could be seen that the solution should be saturated with CO_2 after time of 2τ.

The amine solution should be completely saturated after 2τ. Tanaka *et al.* 2014 offered that the breakthrough curve of CO_2 is symmetry with respect to $\ln[C/(C_i\text{-}C)]$ at the 50% absorption point. Also the amount of absorbed CO_2 by the amine solution is equal to 0.5 of the total amount of CO_2 entering the absorption column within the 2τ period. The equation could be written as

$$W = \frac{1}{2}C_i F_i 2\tau = C_i F_i \tau \quad (3.7)$$

where W is the amount of absorbed CO_2 (liter), C_i is inlet CO_2 concentration (% by volume), F_i is inlet gas flow rate (liter/min) and τ is the characteristic absorption time when 50% of absorbed CO_2 is achieved (min).

However, in practice, the CO_2 fraction at the outlet (C) is not zero then the amount of absorbed CO_2 during time τ by the amine solution could be written as

$$W = \int_{t=0}^{t=\tau} (C_i F_i - CF)\,dt \quad (3.8)$$

where C is outlet CO_2 concentration (% by volume), F is outlet gas flow rate (lite/min) (it could be calculated by the stoichiometric of reaction).

Furthermore, The CO_2 absorption capacity in solution was calculated as

$$CO_2\ Capacity = \frac{Absorbed\ CO_2\ amount\ (g)}{MEA\ amount\ (g)} \times 100 \cdot \qquad (3.9)$$

3.2.2 Regeneration of Used Monoethanolamine

Some research indicated that CO_2 could be desorbed from MEA solutions by many techniques such as heating, nucleation, agitation, ultrasonic wave and etc. [Tanaka *et al.* 2014, Zhang *et al.* 2012]. The pH of solution could be taken as an indicator to show the concentration of CO_2 in the solution in absorption and regeneration processes. During regeneration, the pH of regenerated solution would be increased [Tanaka *et al.* 2014]. The regenerated solution could also be used in absorption cycle.

3.3 Experiment

3.3.1 Carbon Dioxide Absorption

The experimental apparatus is shown in Figures. 3.2 and 3.3. The unit consisted of 1) Gas Blower, 2) Gas flow meter (Range of 1-10 LPM), 3) Bubble Column (acrylic cylinder with height to diameter of 1.4, 3.3 and 6.5 (height to diameter 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).

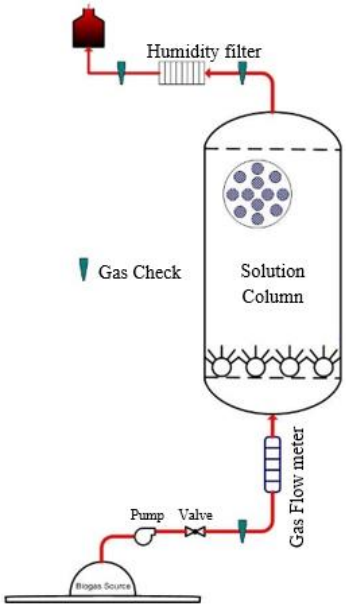


Figure 3.2 A schematic sketch of the CO_2 absorption process experimental setup.

Figure 3.3 The photographs of experimental setup for CO_2 absorption in this study.

In this experiment, the biogas 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. In the experiment, the biogas was fed continuously at the bottom of the tested column of which MEA solution was used in this study. The gas flowed through a porous nozzle to create uniform gas bubbly flow. Since the fine bubbles generated high interaction area then the CO_2 absorption rate could be performed effectively. The gas flow rate was controlled by a gas flow meter.

In the experiment, 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). The absorption characteristic, the absorption constant and the characteristic absorption time

were considered. The pH of the liquid solvent was measured by a pH meter. The testing conditions could be shown as Table 3.3.

Table 3.3 The testing conditions of the CO_2 absorption process.

Item	Values	Unit
Biogas; CH_4 : CO_2	70-75 : 25-30	%v/v
Gas Flow rates	1, 3 and 5	LPM
MEA solution	0.05, 0.1 and 0.2	M
Height to Diameter ratio	1.4, 3.3 and 6.5 (Volume control at 8 liter)	

3.3.2 Regeneration of Used Monoethanolamine

After CO_2 absorption in MEA solution, the pH of the solution dropped down from 11 to be about 7.6 which was the value when the solution was saturated with CO_2. After that a regeneration process was carried out to recover the solution. The used MEA solution was regenerated with 2 techniques which were heating process and combination of heating and ultrasonic wave technique.

Figures. 3.4 and 3.5 show the experimental setup for the regeneration of used MEA solution. For heating only, 8 liter of used MEA solution (pH 7.6) was heated at 70-98 ^oC for 75 min by a 2,000 watts heater. In the process, CO_2 and part of water vaporized and left the tank through a condenser. The water vapor was condensed and returned back into the solution tank to control the MEA concentration. For regeneration by the combination of heating and ultrasonic wave technique, the heated solution was fed through a 20 kHz ultrasonic generator unit to desorb the CO_2 and then the solution returned back to the solution tank. In the regeneration process, the pH of solution was monitored during the test.

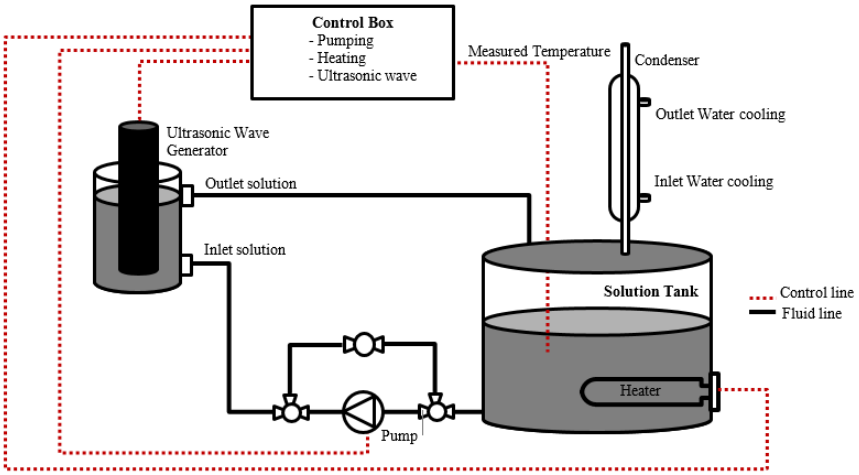


Figure 3.4 A schematic sketch of the used solution regeneration unit setup.

Figure 3.5 The photograph of the regeneration experimental setup in this study.

3.4 Result and Discussion

The CO_2 absorption and used solution regeneration in biogas upgrading process with MEA solution could be presented as

3.4.1 Carbon Dioxide Absorption

From the experiment, it could be seen that the MEA solution could absorb CO_2 in the biogas effectively which resulted in high percentage of CH_4 in the outlet gas. The outlet CH_4 concentration with time by the solution concentrations of 0.05, 0.1 and 0.2 M at biogas flow rates of 1, 3 and 5

liter/min; height to diameter ratios of 1.4, 3.3 and 6.5 and inlet CO_2 concentration of 25-30 % could be shown in Figure 3.6.

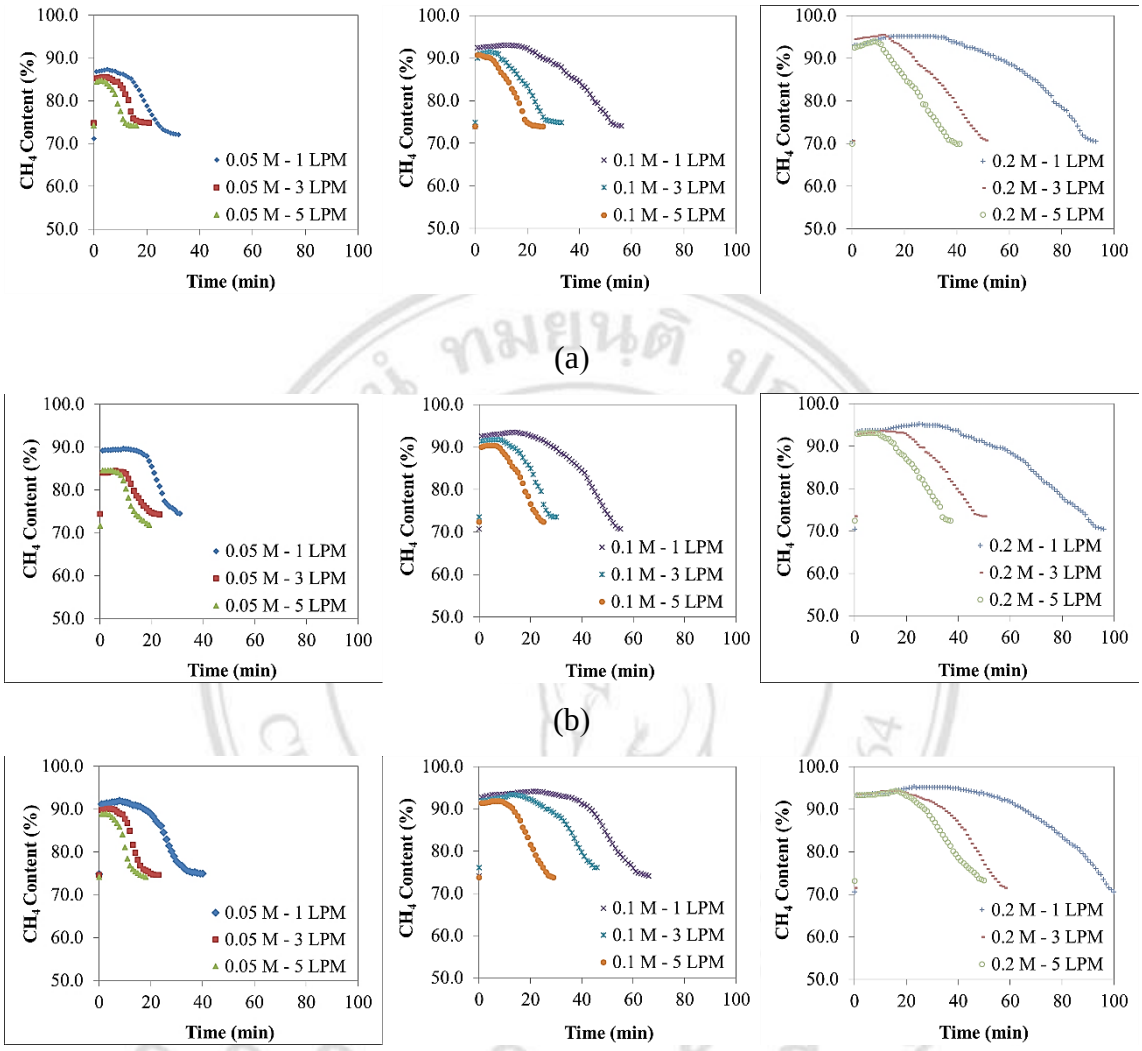


Figure 3.6 The outlet CH_4 concentration with time; MEA concentrations of 0.05, 0.1 and 0.2 M, inlet biogas flow rates of 1, 3 and 5 liter/min and height to diameter ratios of 1.4, 3.3 and 6.5 (a) H/D = 1.4 (b) H/D = 3.3 (c) H/D = 6.5

From Figure 3.6, for all column sizes, low biogas flow rate and high MEA concentration could absorb CO_2 effectively and high CH_4 concentration at the outlet could be obtained. The maximum CH_4 concentration could be up to 90-95 % by 0.1-0.2 M and up to more than 95% with high height to diameter ratio and low biogas flow rate. The absorption performance tended to decrease with time since the solution was closing to the saturation point.

However, the low concentration solution such as 0.05 M of MEA could not absorb CO_2 effectively and the maximum CH_4 concentration was less than 90% by volume which meant that the MEA concentration equal or less than 0.05 M was not suitable to be implemented in biogas upgrading process.

The percentage of CH_4 in the outlet gas depended on the result of CO_2 absorption in the solution. The proportion of outlet CO_2 concentration to inlet CO_2 concentration with time could be shown in Figure 3.7.

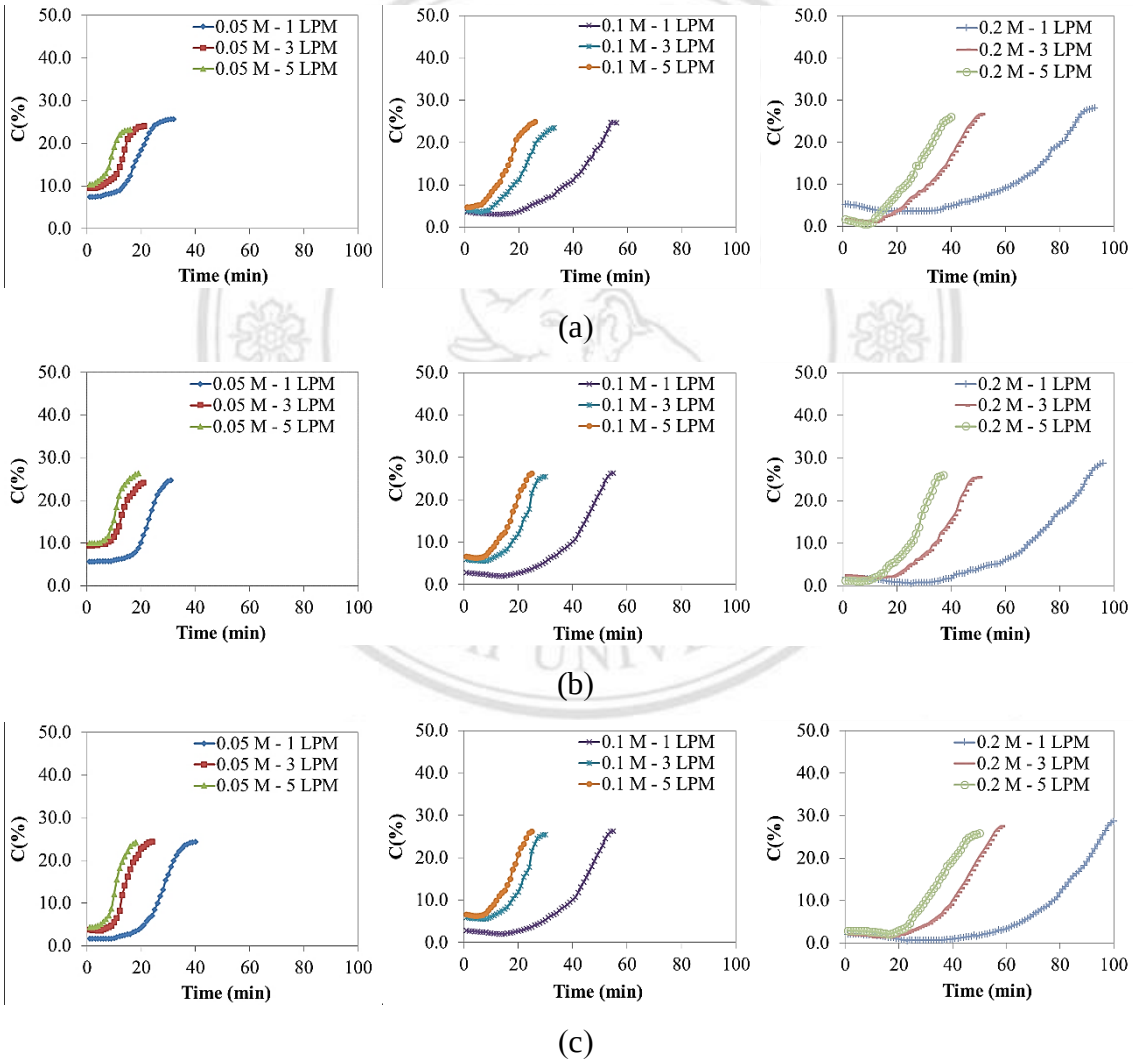


Figure 3.7 The proportions of outlet/inlet CO_2 concentration with time; MEA concentrations of 0.05, 0.1 and 0.2 M, inlet gas flow rates of 1, 3 and 5 liter/min and height to diameter ratios of 1.4, 3.3 and 6.5 (a) H/D = 1.4 (b) H/D = 3.3 (c) H/D = 6.5.

From Figure 3.7, it could be seen that when the biogas flow rate increased and the MEA concentration decreased, the proportion of outlet/inlet CO_2 concentration at time was high. When considerating of the height to diameter of CO_2 absorption column, it could be found that the absorbed CO_2 abilities increased with H/D since the contact time for CO_2 absorption was longer. As the biogas flow rate increased, the absorbed CO_2 abilities would decreased. Due to the high gas flow rate was limited with cross-sectional area of column. It resulted in the gas moving which was faster than the low gas flow rate. The absorbed CO_2 abilities decreased.

The kinetics of CO_2 absorption with various conditions were considered with the relation between operating time (min) with 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 of 50% absorbed CO_2 (τ) could be shown in Table 3.4.

Table 3.4 The kinetics of CO_2 absorption with MEA solution.

Item	Sol^{n}-Conc. (M)	H/D 1.4			H/D 3.3			H/D 6.5		
		Gas Flow Rate(LPM)			Gas Flow Rate(LPM)			Gas Flow Rate(LPM)		
		1	3	5	1	3	5	1	3	5
1/k	0.05	5.30	5.12	5.07	3.68	2.66	2.55	3.57	2.52	2.36
	0.1	8.05	6.84	5.43	6.55	6.22	4.27	5.99	3.77	3.37
	0.2	16.03	8.33	6.35	12.83	8.08	6.24	11.43	8.08	6.08
k	0.05	0.19	0.20	0.20	0.27	0.38	0.39	0.28	0.40	0.42
	0.1	0.12	0.15	0.18	0.15	0.16	0.23	0.17	0.27	0.30
	0.2	0.06	0.12	0.16	0.08	0.12	0.16	0.09	0.12	0.16
τ	0.05	15.76	9.12	5.52	19.85	10.63	8.61	26.14	13.36	9.71
	0.1	38.81	19.74	13.71	41.43	19.96	14.42	49.94	33.73	17.62
	0.2	69.73	35.23	25.77	74.84	36.74	27.18	81.82	42.90	32.95
R^2	0.05	0.9642	0.8617	0.8548	0.9116	0.9912	0.9799	0.9588	0.9903	0.9900
	0.1	0.9152	0.9845	0.9867	0.9433	0.9639	0.9443	0.9758	0.9950	0.9859
	0.2	0.9610	0.9927	0.9741	0.9541	0.9554	0.9848	0.9756	0.9812	0.9940

Table 3.5 Comparison of kinetics parameters for CO_2 absorption reported in literature.

Case	k (min^{-1})	R^2
[Tippayawong and Thanompongchart 2010]*	0.05	0.93
[Lin and Shyu 1999]**	0.13	N/A
This Study***	0.16	0.98

Note * MEA concentration of 0.1 M, gas to solvent flow ratio of 1.0 and 40% inlet CO_2 concentration (Packed column)

** MEA concentration of 30% by weight (Packed column)

*** MEA concentration of 0.1 M, biogas flow rate of 3 liter/min and 25.1% inlet CO_2 concentration (Bubble column)

From Table 3.4, it could be found that the absorption constant (k) increased when the biogas flow rate and H/D increased and solution concentration decreased. It was consistent to mass transfer coefficient and gas hold up which reported in the literature [Chisti and Moo-Young 1988, Gomez-Dıaz 2006, Shimizu *et al.* 2000].

From the kinetics result, the CO_2 absorption capability by our technique was rather high. The absorption constant (k) in this study was in a range of 0.06-0.42 min^{-1}. In the condition of MEA concentration of 0.1 M, biogas flow rate of 3 liter/min and 25.1% inlet CO_2 concentration in bubble column, The k value was found to be higher than that reported in the literature from different method [Tippayawong and Thanompongchart 2010, Lin and Shyu 1999] as shown in Table 3.5 which meant that high absorption was obtained by the present method.

From Table 3.4, the characteristic absorption time of 50% absorbed CO_2 (τ, min) could be related with solution concentration (SC, M), gas flow rate (GFR, liter/min), height to diameter ratio (H/D) and biogas concentration (BC, % by volume). The τ could be formulated as

$$\tau = 0.60725 \frac{SC^{0.95977}\left(\frac{H}{D}\right)^{0.19723} BC^{1.4457}}{GFR^{0.62927}} \qquad (3.10)$$

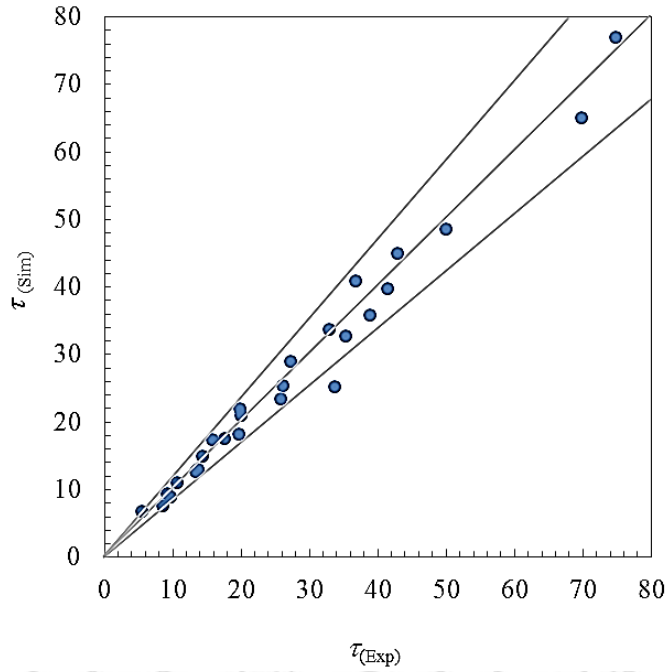


Figure 3.8 The characteristic absorption time at 50% absorbed CO_2 comparing the correlation and the experimental results.

The comparison of the characteristic absorption time when 50% of CO_2 is absorbed (τ, min) from experiment with the equation (3.10) could be shown as Figure 3.8. The result showed that 96.3% of the experimental data were consistent with the simulation data within ±15%.

In addition, the absorption period (t, min) where the CH_4 concentration over 90% is obtained, it could be formulated as

$$t = 3.6638 \times 10^{-6} \frac{SC^{1.2449}\left(\frac{H}{D}\right)^{0.30027} BC^{4.2988}}{GFR^{0.79462}} \qquad (3.11)$$

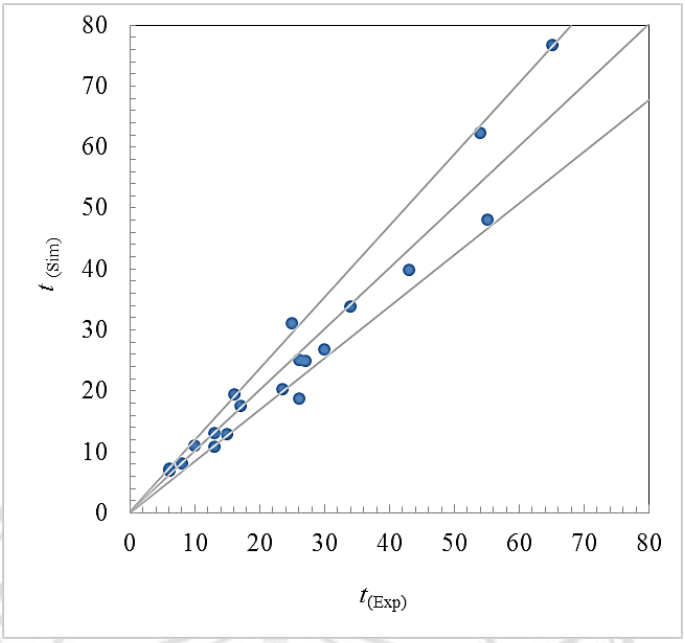


Figure 3.9 The absorption time at more than 90 % CH_4 (t) comparing the correlation and the experimental results.

The comparison of the absorption period (t, min) where the CH_4 concentration over 90% is obtained from equation 3.11 with that of the experiments could be shown as Figure 3.9. The result showed that 85 % of the experimental data were consistent with the simulation data within ±15%.

3.4.2 Monoethanolamine Regeneration

In the CO_2 absorption process, the pH of fresh MEA solution was found to be 11 and it would be decreased to 7.6 after CO_2 absorption. The used MEA solution was regenerated at 75 min by 2 techniques, the first was an electrical heating to a temperature of 70-98 ^oC and the second was the combination of heating at 70-90 ^oC with 20 kHz of ultrasonic wave. The results could be shown in Figure 3.10.

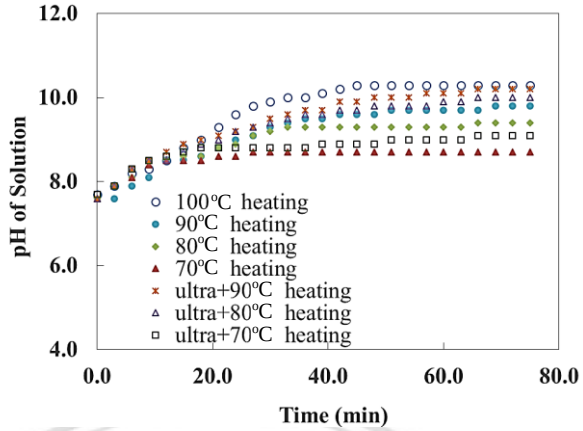


Figure 3.10 The pH values of the regenerated solution with time by heating and ultrasonic wave.

By electrical heating only, the pH increased from around 7.6 to be 8.6-9.8 at temperature between 70-90 °C and the value was up to 10.2 at 98 °C. With ultrasonic wave assisted, at 90 °C, the pH could also be up to around 10.

Figure 3.11 shows comparison of energy consumption for MEA regeneration. It could be noted that with ultrasonic wave assisted, at the same operating temperature, the recovered pH was higher with small increase in energy consumption. At 80-90°C, with ultrasonic, the recovered pH in the MEA solution was over 10 similar to that by only electrical heater operating at 98°C but the energy consumption was lower signification.

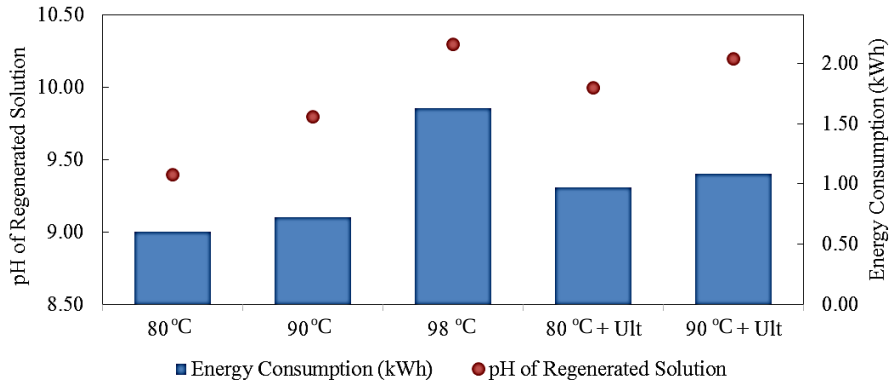
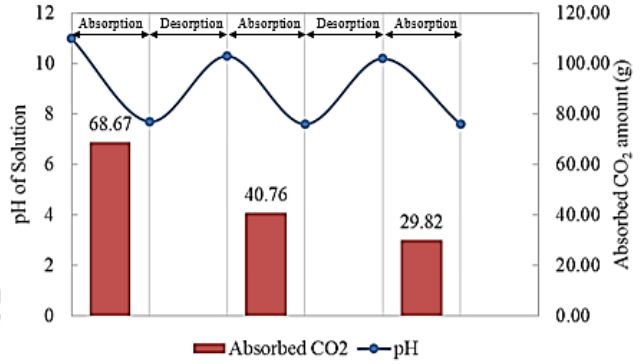
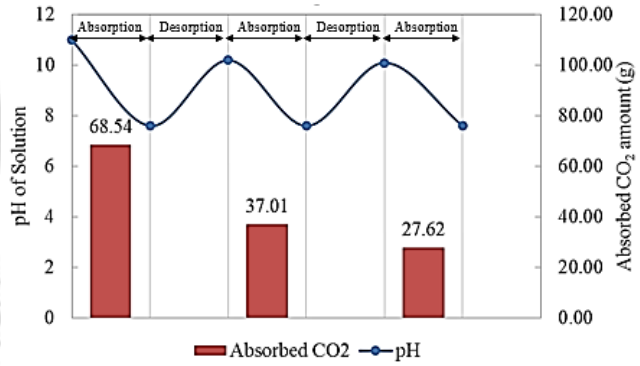


Figure 3.11 The pH of regenerated solution and energy consumption (kWh) in each regeneration technique.

The regenerated solution could be used to absorb CO_2 in biogas in the next cycle. Figure 3.12 and Table 3.6 show the results of the CO_2 absorption/desorption from the recycled MEA solution.



(a)



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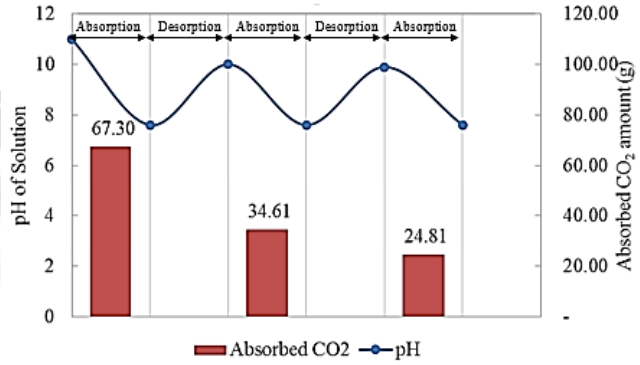

(c)

Figure 3.12 The pH of solution and absorbed CO_2 amount in absorption /regeneration Cycle (a) 98^{o}C heating regeneration (b) 90^{o}C heating + Ultrasonic wave regeneration and (c) 80^{o}C heating+Ultrasonic wave regeneration.

Table 3.6 The absorbed CO_2 abilities with different regeneration temperature.

Technique	**The absorbed CO_2 abilities (kg $_{absorbed\ CO_2}$/ kg $_{MEA}$)**		
	Fresh sol^{n}	**1st regenerated sol^{n}**	**2nd regenerated sol^{n}**
98^{o}C heating	0.70	0.42	0.31
90^{o}C heating + ultrasonic wave	0.70	0.38	0.28
80^{o}C heating + ultrasonic wave	0.69	0.35	0.25

The CO_2 absorption efficiency with regenerated solution was calculated by

$$\eta = \frac{CO_2\ capacity(kg/kgMEA)_{(with\ n^{th}\ regeneration)}}{CO_2\ capacity(kg/kgMEA)_{(with\ fresh\ solution)}} \times 100 . \qquad (3.12)$$

It could be found that the CO_2 absorption efficiencies were around 43.43, 40.29 and 36.87 % when regenerated in the 2nd time with 98^{o}C Heating, 90^{o}C heating + ultrasonic wave and 80^{o}C heating + ultrasonic wave, respectively. The values were higher than that reported in the literature which was around 32.5% by Tanaka *et al.* 2014.