CHAPTER 1

Introduction

This chapter serves as introduction to this thesis. The first part of the chapter presented rationale of the current problem about biogas upgrading for biomethane. The second part presented a literature review of carbon dioxide absorption with monoethanolamine and regeneration, and the third part gave reviews on adsorption and desorption the biomethane on porous material. The objectives, the scope, and the benefits of the study were also presented in the last part of this chapter.

1.1 Rationale

Biogas is produced by organic matter digestion without oxygen by anaerobic bacteria. 95% of biogas consists of methane, carbon dioxide, hydrogen sulfide and traces of water vapor [Kapdi *et al.* 2006]. The general biogas compositions are shown in Table 1.1 [Hosseini and Wahid 2013].

Table 1.1 The biogas general composition [Hosseini and Wahid2013].

Biogas composition	**Typical analysis (% by Volume)**
Methane (CH_4)	55-65
Carbon Dioxide (CO_2)	35-45
Hydrogen sulfide (H_2S)	0-1
Nitrogen (N_2)	0-3
Hydrogen(H_2)	0-1
Oxygen (O_2)	0-2
Ammonia (NH_3)	0-1

From Table 1.1, the amount of methane in the biogas composition is highest. The biogas properties are also shown in Table 1.2.

Table 1.2 Some thermal and physical properties of gas components in biogas [ERDI 2010].

Property	**Gas Species**					
	CH_4	**CO_2**	**H_2**	**H_2S**	**gas***	**gas****
Heating Value (MJ)	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 (°C)	650-750	-	585	-	650-750	650-750
Density (kg/m^3)	0.72	1.98	0.09	1.54	1.2	1.15
Heat Capacity (kJ/m^3-°C)	1.6	1.6	1.3	1.4	1.6	1.6

Note: * Multi component gas of 60%CH_4, 40%CO_2

** Multi component gas of 65% CH_4, 34% CO_2, 1% other

From Table 1.2, it could be seen that the heating value of 100% methane is about 35.64 MJ/m^3 and if there is blending of carbon dioxide as that in biogas, the heating value will decrease. Thus for biogas, removal of the carbon dioxide, more energy intensity could be obtained. There was a report [ERDI 2010] showed that in 1 m^3 biogas there was a proportion of methane to carbon dioxide of 65% : 35% and the heating value of biogas could be equivalent to the following fuel as

Liquefied Petroleum Gas (LPG)	0.46	kilograms
Gasohol	0.67	liters
Diesel	0.60	liters
Wood	1.50	kilograms
Electricity	1.20	kWh.

In addition, the biogas could also be equivalent to other fuels as shown in Table 1.3.

Table 1.3 The properties of biogas [ERDI 2010].

Fuel	**Density**	**Heating Value (kJ/kg)**	**Ignition Temperature (°C)**	**Air/Fuel Ratio (kg/kg)**	**Research Octane Number**
Methane	0.72 kg/m^3	50,000	650	17.2	100
LPG	0.54 kg/l	46,000	400	15.5	30
Propane	2.02 kg/m^3	46,300	470	15.6	35
Butane	2.70 kg/m^3	45,600	365	15.6	10
Petrol	0.75 kg/l	43,000	220	14.8	-
Diesel	0.85 kg/l	42,500	220	14.5	-
Natural Gas	0.83 kg/m^3	57,500	600	17.0	80
Biogas (60% CH_4)	1.20 kg/m^3	18,000	650	10.2	130

From the data in Table 1.3, it could be seen that the biogas has a high potential to be used as other fuels. Moreover, use of upgraded biogas could reduce emission of polluting gases to the environment. Comparison of emissions from exhaust gas between diesel and biogas running in some buses is given in Table 1.4 [Kapdi *et al.* 2005].

Table 1.4 Comparison of emissions from exhaust gases between diesel and biogas driven busses in Vaxjo city [Kapdi *et al.* 2005].

No.	**Emission (kg/ annual)**	**Fuel used for driven buses**	
		Diesel/RME	**Biogas**
1	NO_x	16,200	800
2	SO_x	380	30
3	CO	430	930
4	CO_2	840,000	23,000
5	N_2O	700	0
6	CH_4	400	16,500
7	Particle	250	50

From Table 1.1, the biogas produced from biogas ponds consists of high content of carbon dioxide. In practice, for biogas applications, carbon dioxide would also be a cause of corrosion within the pipeline and it resulted in lower heating value in the biogas. In addition, uncontrolled gas quality would result in methane unstable concentration that gave unsteady combustion flame. A power outage or an explosion might happen in the combustion chamber.

Therefore, the carbon dioxide separation from biogas is one of the interested issues to increase the heating value of biogas and get higher efficiency combustion. Moreover, in this research study, adsorption and desorption of biomethane after carbon dioxide separation on porous material were also carried out. This was an another method to take the gas away from the biogas pond for utilization outside.

1.2 Literature Review

The main objectives of the study were to enrich methane in biogas to be biomethane. Adsorption/desorption of the biomethane on porous material was also considered. The details were as follows:

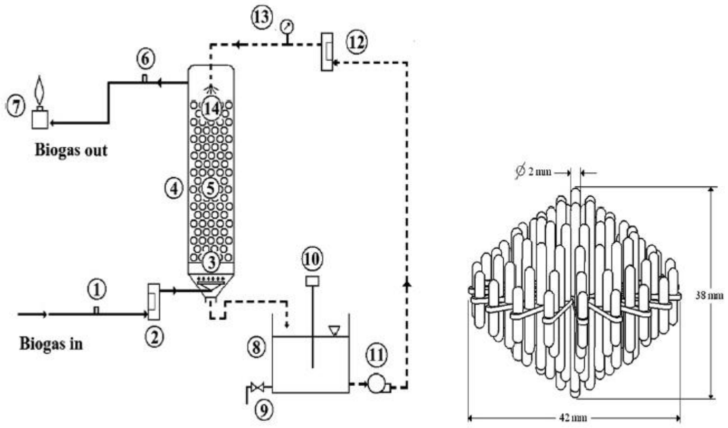
1.2.1 Carbon Dioxide Absorption with Ethanolamine and Regeneration.

Carbon dioxide separation method from biogas could be classified as: physical absorption process, chemical absorption process, pressure swing absorption, membrane technology, cryogenic process, and biological process.

The chemical absorption process could purify the methane up to 99% with a low cost operation with small leakage of methane loss. The used solution could be regenerated but at high temperature [Ryckebosch *et al.* 2011]. Lin *et al*. 1999 studied on absorption of carbon dioxide by amine solutions, monoethanolamine and tertiary N-methyldiethanolamine, in a packed column. The CO_2 absorption characteristics were experimentally examined by these two amines under various operating conditions which were the solution concentrations of 10, 30, 50 % by weight, the gas flow rates of 1.0, 1.5, 2.0 liter/min, and the inlet carbon dioxide concentrations of 5.26, 8.11 and 14.29 % by mole. A theoretical model was developed for describing the

CO_2 absorption behavior. The results from the model agreed very well with those of the observed CO_2 absorption. An increase in the absorption was due to an increase of 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. The solution could be regenerated by heating at 110°C for 24 hr. After regeneration, the amine solution was adjusted to 30 %wt concentration and used for a new CO_2 absorption. The results indicated that the tertiary amine was easily regenerated but the carbon dioxide absorption capability was slightly lower than that of the new solution. From the first to the fourth cycles, the decrease in the total CO_2 absorption capability was within 11%.

Tippayawong and Thanompongchart 2010 experimentally investigated chemical absorption of CO_2 and H_2S in biogas by aqueous solutions, calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH) and monoethanolamine (MEA), in a packed column. The liquid solvents were circulated through the column and contacted the biogas in countercurrent flow. The semi-batch experimental apparatus was shown in Figure 1.1 (a). The absorption column was randomly packed by a set of packing spherical balls (common trade name "plastic bio-ball") as shown in Figure 1.1 (b). Its surface area to volume ratio was 1,895 m^2/m^3. The results showed that the aqueous solutions were effective in removing CO_2 in the biogas (over 90% removal efficiency), creating enriched CH_4 fuel. H_2S was also removed and the value was below the detection limit.



(a) (b)

Figure 1.1 Experimental apparatus: (a) The countercurrent flow of carbon dioxide absorption column, and (b) Plastic Bio-ball [Tippayawong and Thanompongchart 2010].

Bonenfant *et al.* 2003 studied carbon dioxide absorption/ regeneration 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. At first, CO_2 absorption was performed at 1 atm of CO_2 with CO_2 flows of 1.337 and 3.067 L/min at 23°C with an interval from 0 to 120 s in a 150 mL aqueous absorbent solution. The CO_2 desorption was taken by heating the amine solutions at its boiling temperature for 210 s. The results showed that the structural properties of 2-(2-aminoethylamino) ethanol, N-(2-aminoethyl)-1,3-propanediamine and triethanolamine favored highest CO_2 loading compared to those of monoethanolamine, pyrrolidine, pyridine and ammonia. However, the efficiency of CO_2 absorption of 5 %wt monoethanolamine and pyrrolidine solutions was lower than those of aqueous 2-(2-aminoethylamino) ethanol, N-(2-aminoethyl)-1,3-propanediamine and triethanolamine solutions but a use of monoethanolamine might present certain advantage since its acceptable regeneration capacity.

1.2.2 Adsorption and desorption of biomethane on porous material

After biogas purification, the gas product became biomethane gas. In this study, biomethane adsorption on porous material was carried out. Literatures about biomethane adsorption on porous material could be given as follows:

Esteves *et al.* 2008 studied adsorption of natural gas and biogas on absorbent. The natural gas consisted of methane, ethane, propane butane, carbon dioxide, nitrogen, including smelly gases such as Tert-Butyl Mercaptan (TBM) and Tetrahydrothiphene (THT). These gases were absorbed on activated carbon of which the size was 2 mm. The activated carbon was made of coal and its total porous volume was 0.85 cm^3/g. Temperature and pressure were controlled in ranges of 0-52 ºC and 0-9 MPa, respectively. Before and after each experiment, the temperature, the pressure, and the absorbent weight were measured. The experiment setup was shown in Figure 1.2.

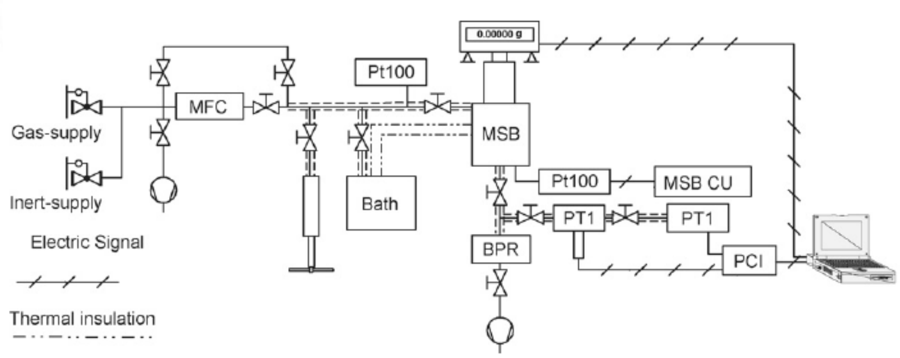


Figure 1.2 Absorption gas system for natural gas and biogas [Esteves *et al.* 2008].

From the study, it could be found that the activated carbon could properly adsorb all gases at any temperature and pressure. When the temperature was decreased, the gas adsorption increased.

Guan *et al.* 2008 studied methane adsorption in granular activated carbon from byproducts of sucrose sugar pyrolysis in ammonium-form zeolite Y at 1,100 ºC. The porous size of the granular carbon was in micropore range of 11 Å and about 40 % was in mesopore ranges of 26 and 38 Å. In the study, the granular activated carbon and carbon powder were compressed and used as gas adsorbents in gas adsorption analysis. Temperature and pressure were controlled at -10-27 ^{o}C and 0-42 bar, respectively. It was found that, the granular activated carbon powder adsorbed carbon dioxide about 8 mmol/g of carbon at temperature of 27 ^{o}C and pressure of 35 bar. The compressed carbon powder could adsorb CO_2 about 4.5 mmol/g of carbon. When the pressure was increased, the gas adsorption also increased. In the other hand, if the temperature was increased, the gas adsorption decreased.

Blanco *et al.* 2010 studied porous size distribution in monolith activated carbon that related to capability of methane carbon dioxide and hydrogen adsorption. The monolith activated carbon was made of coconut shell under pyrolysis. It was enameled by zinc chloride that could increase adsorption. In the study, methane was fed at temperature of 25^{o}C and pressure of 0-45 bar similar to other gases such as hydrogen, and carbon dioxide for gas adsorptions. From the experiment, it was found that monolith activated carbon of which the porosity of activated carbon at most was about 5-10 Å could adsorb methane around 1.0-4.0 mmol/g of carbon. Furthermore, Perrin *et al.* 2004 activated anthracite coal by sodium hydroxide to assist methane adsorption as well. The effect of activated temperature on porous size of coal concerned with methane adsorption was studied. The coal was activated in nitrogen atmosphere at temperature of 600-830 ^{o}C with a ratio of hydroxide to anthracite at 3:1. The carbon dioxide, nitrogen, ethane, and carbon tetrachloride were considered for measuring the porous size. From the study, It was found that as the activated temperature was increased, the porous size in micropore range decreased. The activated carbon at the temperature range of 600-750 ^{o}C could adsorb methane about 0.2-0.22 g/cm^3.

Alcaniz-Monge *et al.* 1997 studied methane adsorption on carbon fiber from petroleum derivatives and activated by CO_2 and water vapor. The activated carbon was in a range of micropore that appropriate to absorb methane. The methane adsorption was tested at temperature of 25^{o}C and pressure of 0-4 MPa. It was found that the activation could get the porous size of carbon fiber to be slightly less than 0.7 nm. Most of them were in a range of 0.7-2.0 nm.

The activation of carbon fiber by water vapor could get less porosity size than that by CO_2. Therefore, the activated carbon fiber with water vapor activation could adsorb less methane. Furthermore, simulation and experiment of methane adsorption on carbon fiber were 163 and 143 V/V (methane adsorbed in non-micro porous voids), respectively. It was indicated that the simulated results agreed quite well with the experimental data.

From the reviews, it could be seen that the biogas could be upgraded to be biomethane by absorption of carbon dioxide with amine solution. After that, the biomethane could be adsorbed by activated carbon. In this study, biogas upgrading by carbon dioxide separation with monoethanolamine solution was carried out. The considered parameters were the biogas flow rate, the monoethanolamine concentration, the carbon dioxide concentrations and the reactor size. Moreover, the techniques for regeneration of monoethanolamine were also investigated. In addition, a study on the biomethane adsorption and desorption by activated carbon adsorbent was performed by considering the operating parameters which were adsorption/desorption temperature and pressure including activated carbon type. In the study, two types of activated carbon made of coal and coconut shell were considered.

1.3 Objectives of the Present Study

1.3.1 To study the parameters which affected carbon dioxide absorption/ regeneration in monoethanolamine solution such as biogas flow rate, monoethanolamine and carbon dioxide concentrations, regeneration temperature, and reactor size etc.

1.3.2 To study the parameters which affected biomethane adsorption /desorption for activated carbon adsorbent such as activated carbon type, operating temperature and pressure.

1.3.3 To develop a simplified model to predict the ability of biomethane adsorption on porous medium.

1.4 Scope of the Study

Carbon dioxide absorption unit and biomethane adsorption unit are designed and set up in laboratory scale.

1.4.1 Biogas Upgrading Process

1) The carbon dioxide absorption with monoethanolamine solution is studied in upgrading process. The operating condition of this study was shown, as follows:

    1.1) The monoethanolamine solutions were 0.05, 0.1 and 0.2 M (mol/liter).

    1.2) The biogas flow rate were 1, 3 and 5 LPM (liter/min).

    1.3) The absorption unit consisted of a 8 liter bubble column, and a set of gas flow distributors at the bottom of bubble column. The height to diameter ratios of bubble column were 1.4, 3.3 and 6.5.

2) The used monoethanolamine solution regeneration was carried out by electrical heating and ultrasonic technique.

1.4.2 Biomethane adsorption on activated carbon from coal and coconut shell

1) The operating condition of this study were

    1.1) The adsorption tank was 1.77 liter.

    1.2) The adsorption temperatures were at 10, 15, 20 and 25^{o}C.

    1.3) The adsorption pressure was considered at 0-8 bar.

2) The operating conditions on biomethane desorption were as
The desorption could be performed by warm water at 25, 35, 45 and 55 ^{o}C was a heat source for biomethane desorption.

1.5 Benefit of the Study

1.5.1 The heating value of biomethane could be increased in biogas upgrading process. This result could be used to guide for upscale the carbon dioxide absorption with monoethanolamine solution and the solution regeneration process.

1.5.2 The result could be used to guide for designing biomethane storage in commercial scale. The simplified model to predict biomethane adsorption on activated carbon porous medium was developed.