CHAPTER 5

Conclusions

The studies was divided into two parts. First, biogas upgrading with carbon dioxide absorption by monoethanolamine solution was performed and the used solution was regenerated by heat in combination with ultrasonic wave. Second, biomethane from biogas upgrading adsorbed on two activated carbons, coal and coconut shell, at low pressure and temperature was investigated. The simplified equation from D-A model was developed for predicting biomethane adsorption. The conclusions of the results are as follows:

5.1 Carbon Dioxide Absorption with Monoethanolamine Solution

For biogas upgrading, biogas of 70-75% CH_4 and 30-25% CO_2 was fed continuously through a tested column of MEA solution. The effect of controlled parameters on the absorbed CO_2 such as gas flow rate, MEA concentration, height to diameter ratio of the column were carried out. The results on the CO_2 absorption were

5.1.1 For all of column height to diameter ratio, low biogas flow rate and high MEA concentration could absorb CO_2 effectively. The maximum CH_4 concentration could be up to 90-95 % by 0.1-0.2 M MEA. High height to diameter ratio and low biogas flow rate, high concentration could be achieved.

5.1.2 For low concentration solution such as 0.05 M of MEA, solution could not absorb CO_2 effectively and the maximum CH_4 concentration was less than 90% by volume.

5.1.3 The absorption constant (k) was in a range of 0.06-0.42 min^{-1}. The characteristic absorption time of 50% absorbed CO_2 (τ, min) with the related parameters was formulated in a form of

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

The absorption time (t, min) to get more than 90 % methane could be formulated as

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

For MEA regeneration, the used solution was regenerated by heat at temperature of 70-98 ^oC, in combination with ultrasonic wave frequency of 20 kHz. The pH was the indication of regeneration performance. The results were

5.1.4 The pH of used solution could be increased from 7.6 to 8.7-10.3 after regeneration. Regeneration at high temperature could recover pH of solution close to the new one. The regeneration by 80 and 90^oC heating with ultrasonic wave could increase the solution pH close to that by 98^oC heating only but it could operate at lower temperature and low energy consumptions of around 40.6 and 33.6% for 80 and 90^oC heating with ultrasonic wave, respectively.

5.1.5 The CO_2 absorption efficiencies were around 43.43, 40.29 and 36.87 % when regenerated in the 2nd time with 98^oC Heating, 90^oC heating with ultrasonic wave, and 80^oC heating with ultrasonic wave, respectively.

5.2 Biomethane Adsorption on Activated Carbon

Biomethane adsorption and desorption on activated carbon were considered. Coal and coconut shell activated carbons were used to study for adsorption of biomethane at 80 and 90% concentration at low pressure and low temperature. Langmuir model and D-A

model were used to investigated the biomethane adsorption. The isosteric heat of adsorption was considered. The conclusions were

5.2.1 The adsorbed biomethane on activated carbon increased when the pressure increased and the temperature decreased. The 80% biomethane adsorption on coal and coconut shell activated carbons at pressure of 8 bar, temperature of 10-25 ^{o}C were in a range of 1.0885-1.2886 and 0.8141-0.9570 mmol/$g_{(AC)}$, respectively, and the 90% biomethane adsorption were in a range of 0.6839-0.7975 and 0.4481-0.5180mmol/$g_{(AC)}$. The 80% biomethane was better adsorbed since the activated carbons had a higher affinity for CO_2 than for CH_4 and the molecular weight of CO_2 was higher than that of CH_4.

5.2.2 The 80 and the 90% biomethane adsorption isotherms on the two activated carbons at 10-25 ^{o}C could be presented by the Langmuir model. The limiting uptake (q_{max}) of the 80% biomethane adsorption on the coal and coconut shell activated carbons at temperature of 10-25 ^{o}C were in the ranges of 4.7989-5.0557 and 4.1512 - 4.5186 mmol/$g_{(AC)}$, respectively. For the 90% biomethane adsorption, they were in the ranges of 2.9829-3.2290 and 2.2618-2.3390 mmol/$g_{(AC)}$, respectively. The amount of biomethane adsorption and Langmuir's constant increased when the temperature decreased.

5.2.3 The D-A equation for biomethane adsorption with various conditions was used to consider the structural heterogeneity parameter (n) and the characteristic energy of adsorption (E). The structural heterogeneity parameter (n) for coal was 1.48 and it tended to be a heterogeneity surface more than the coconut shell of which the value was a 1.35. As the structural heterogeneity parameter (n) decreased, the characteristic energy of adsorption decreased as well. The limiting uptakes of biomethane on the adsorbent (q_{max}) between Langmuir models and D-A model were quite similar.

5.2.4 The simplify equation from D-A model for predicting biomethane adsorption was developed at 10-25 ^{o}C, 8 bar as

Coal activated carbon

80% Biomethane

$$\ln(q) = -2.2763 - 0.0001\left(T \ln \frac{6.1351\left(\frac{T}{213.6}\right)^2}{P}\right)^{1.48}$$

90% Biomethane

$$\ln(q) = -2.7249 - 0.0001\left(T \ln \frac{5.2615\left(\frac{T}{201.46}\right)^2}{P}\right)^{1.48}$$

Coconut shell activated carbon

80% Biomethane

$$\ln(q) = -2.4023 - 0.0002\left(T \ln \frac{6.1351\left(\frac{T}{213.6}\right)^2}{P}\right)^{1.35}$$

90% Biomethane

$$\ln(q) = -3.1602 - 0.0002\left(T \ln \frac{5.2615\left(\frac{T}{201.46}\right)^2}{P}\right)^{1.35}.$$

5.2.5 The isosteric heat of adsorption for 80 and 90% biomethane on two activated carbons were in a range of 5.56-9.76 kJ/mol. The isosteric heat of adsorption for coal was higher than that for coconut shell. The heat of adsorption decreases when the adsorbed mount of biomethane increased. Reduction of

heat of adsorption indicated that the activated carbon surface was close to substantially heterogeneous.

For biomethane desorption, 80% biomethane adsorption at a pressure of 8 bar on activated carbon was desorbed by low temperature heating at 25-55ºC. The adsorption/desorption cycle was considered. The results could be concluded as

5.2.6 The percentages of desorbed biomethane were in the ranges of 65-78% and 61-74% at 25-55ºC for coal and coconut shell, respectively. The percentage of the biomethane discharge increased when the adsorbent temperature increased. The biomethane residual in the adsorbent were around 22 and 26 % at 55ºC for coal and coconut shell, respectively.

5.2.7 For the adsorption/desorption cycles, it could be found that the amount of biomethane adsorption and desorption in the 2nd and the 3rd cycles were quite close to the initial values. The amount of biomethane desorption was in a range of 18.10-19.78 and 15.88-17.39 $mg/g_{(AC)}$ or 73-78% and 68-74% for coal and coconut shell, respectively.

5.3 Recommendations for Further Study

5.3.1 The carbon dioxide absorption with monoethanolamine solution.

This research demonstrated that the MEA solution could absorbed and purified effectively on the biogas. However, there is a problem due to porous nozzle corrosion occurring which effects on the solution cleaning and bubble sizing. The efficiency of the CO_2 absorption would be reduced under a long run operation. Therefore, a good designed distributor should be found out. In addition, a bigger scale should be demonstrated to be implemented for commercial scale.

5.3.2 The biomethane adsorption/desorption on activated carbons.

Improvement of biomethane adsorption on activated carbon should be performed by increasing thermal conductivity of the adsorbent, for example,

coating with nano-particles. In addition, to desorb the biomethane, a simplified method should be found out in real practice.