CHAPTER 4

Adsorption and Desorption of Biomethane on Activated Carbon

4.1 Introduction

Upgraded biogas with high methane concentration is called biomethane. At present, the biomethane still has no standard of properties. However, compositions, properties and application features of biomethane are similar to natural gas. Therefore, the standard of natural gas, such as The Society of Automotive Engineering J1616 (SAE J1616), California Air Resources Board (CARB), New Zealand Standard (NZS) and California Public Utilities Commission (CPUC) could be used as standard references. The CARB has identified that the natural gas must contain over 88% of methane. [Laoonual *et al.* 2007]. In Thailand, the biomethane standard refer to the announcement of the Department of Energy Business, Ministry of Energy on properties of natural gas for vehicle of which the methane must be higher than 82% [Ministry of Energy 2014].

For the current application, biomethane is compressed into a tank for use in vehicles. The pressure of natural gas compression is around 200 bar and gas tank must also withstand the high pressures. As a result, the tank must be very thick, thus the unit is very expensive.

For natural gas, the Adsorbed Natural Gas (ANG) is one technique that the natural gas is adsorbed on the porous medium. This technique can store the gas amount higher than the compression method. [Matranga *et al.* 1992, Chiew *et al.* 2011, Rahman *et al.* 2010]. It was shown the methane adsorption capacity for an adsorbent filled tank (ANG) compared with a pressurized tank was higher as shown in Figure 4.1.

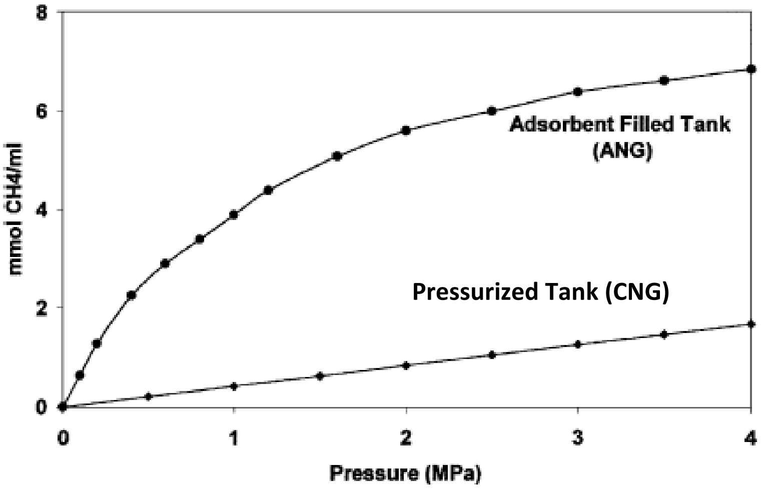


Figure 4.1 The methane adsorption capacity comparison of an adsorbent filled tank (ANG) and an empty tank pressurized [Rahman *et al.* 2010].

Several researchers studied on gas adsorption on activated carbon. Esteves *et al*. 2008 studied on natural gas and biogas adsorption 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. The pore size was less than 20 Å or around 0.78 cm^3/g. Temperature and pressure were controlled in ranges of 0-52 ^{o}C and 0-9 MPa, respectively. Before and after of each experiment, the values of temperature, pressure, and absorbent weight were measured by High-Pressure Balance. From the study, it was found that the activated carbon could properly adsorb all gases at any temperature and pressure. When the temperature was decreased, the gases adsorption increased. Guan *et al*. 2008 studied methane adsorption in granular activated carbon from by-products of sucrose sugar pyrolysis in ammonium-form zeolite Y at 1,100 ^{o}C. The porous size of the granular carbon was in micropore range of 11 Å (the suitable pore size of 8-10 Å was for methane adsorption) 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 in a ranges of -10 to 27^{o}C and 0-42 bar, respectively. It was found that, the granular activated carbon powder adsorbed CO_2 about 8 mmol/g of carbon at temperature of 27 ^{o}C and pressure of 35 bar while 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. On 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 CH_4, CO_2 and H_2 adsorption. The monolith activated carbon was made of coconut shell under pyrolysis. In the study, methane was fed at temperature of 25°C and pressure in range of 0-45 bar similar to other gases, such as H_2, and CO_2 for gas adsorptions. From the experiment, it was found that the monolith activated carbon with porosity of 5-10 Å could adsorb methane around 1.0-4.0 mmol/g of carbon. Furthermore, Zheng *et al*. 2015 studied on storage by adsorption of domestically used natural gas on activated carbon. The gas adsorption and desorption were considered. It was seen that the desorbed gas increased in the temperature of the heating water from 30-70 °C, but the total discharged amounts nearly remained the same. The desorbed gas was in a range of 69-75% at a gas discharge of 15 liter/min.

In this study, the biomethane adsorption on activated carbon was carried out. The adsorbed gas was desorbed by heating at low temperature. The parameters of the biomethane absorption and desorption on activated carbon were investigated.

4.2 Methodology

Gas adsorption on porous media is an exothermic process. The process depends strongly on pressure, temperature, gas concentration, and type of adsorbate and adsorbent. Normally, the temperature was kept constant, then for a given adsorbent-adsorbate system *x/m* depends on the equilibrium pressure [Bansal and Goyal 2005]. The relation of adsorption isotherm could be shown in Figure 4.2, and represented as:

$$\frac{x}{m} = f(P) \ [T\text{=constant}] \tag{4.1}$$

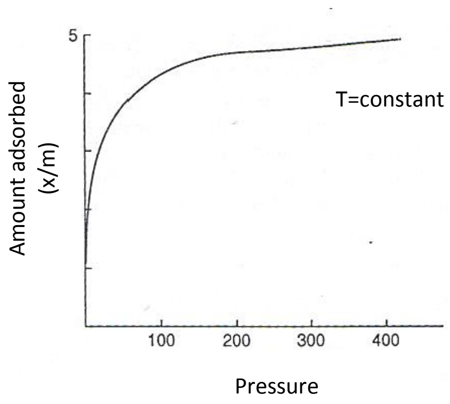


Figure 4.2 The adsorption isotherm [Bansal and Goyal 2005].

Adsorption isotherm depends on the use of adsorbent and it interaction behavior of adsorbate and adsorbent.

4.2.1 Langmuir's equation [Bansal and Goyal 2005]

The Langmuir equation is based on the assumption of a structurally homogeneous adsorbent, and described as

$$q = q_{\max}\left[\frac{K_L P}{1+K_L P}\right] \tag{4.2}$$

where q is the adsorbed biomethane on activated carbon at equilibrium temperature and pressure (g/g$_{(AC)}$), q_{max} is the limiting uptake of biomethane on the adsorbent (g/g$_{(A/C)}$), K_L is the Langmuir's constant, P is the equilibrium pressure (MPa).

From the equation (4.2), the relation between the adsorbed biomethane (q) on activated carbon at equilibrium temperature and pressure could be rearranged as

$$\frac{1}{q} = \left(\frac{1}{q_{\max} K_L}\right)\frac{1}{P} + \frac{1}{q_{\max}} \quad . \tag{4.3}$$

From the above equation, q_{max} and K_L could be evaluated by correlating $1/q$ and $1/P$ from the experimental data.

4.2.2 Dubinin's equation

Dubinin theory explains adsorption of vapor in microspores. A fundamental difference between the Dubinin and Langmuir theories is the postulated mechanism of pore filling. Dubinin-Radushkevich (D-R) developed the equation as

$$W = W_{max}\, exp\left[-\left(\frac{A}{E}\right)^2\right]. \tag{4.4}$$

Dubinin and Astakhov (D-A) [Tiansuwan *et al.* 1995, Loh *et al.* 2010] modified the D-R equation which could fit the data accurately and proposed the following model for adsorption of vapors and gases on nonhomogeneous carbonaceous solids with a wide pore size distribution. This D-A model allows for the surface heterogeneity and extends to high pressure and it could be expressed as

$$W = W_{max}\, exp\left[-\left(\frac{A}{E}\right)^n\right] \tag{4.5}$$

where A is the adsorption potential, W is the amount of uptake in ($cm^3/g_{(AC)}$), W_{max} is the limiting uptake of biomethane on the adsorbent ($cm^3/g_{(AC)}$), E is the characteristic energy of the adsorption system (J/mol) and n is the structural heterogeneity parameter.

A is the specific work done in the isothermal compression of a unit mass of vapor from P to the saturation vapor pressure P_s and given by

$$A = \bar{R}T\, ln\left(\frac{P_s}{P}\right) \tag{4.6}$$

From equations 4.5 and 4.6 the equations could be rewritten as

$$\frac{W}{W_{max}} = exp\left[-\left\{\frac{\bar{R}T}{E}\, ln\left(\frac{P_s}{P}\right)\right\}^n\right] \tag{4.7}$$

It could be written in term of adsorbed biomethane in $g/g_{(AC)}$ or $mmol/g_{(AC)}$ [Hao *et al.* 2014, Rahman *et al.* 2010] as

$$\frac{q}{q_{max}} = exp\left[-\left\{ \frac{\overline{R}T}{E} ln\left(\frac{P_s}{P} \right) \right\}^n \right]. \tag{4.8}$$

Note: The equation is obtained under the assumption that the vapor density in the porous medium was nearly constant.

The saturation vapor pressure (P_s), of a given isotherm temperature could be calculated by Dubinin's method. This was also used for methane in earlier studies [Loh *et al.* 2010] as

$$P_s = \left(\frac{T}{T_C} \right)^2 P_C \qquad ; \quad T > T_c \tag{4.9}$$

where P_c and T_c are the critical pressure and the critical temperature of gas.

In this study, Langmuir's equation and D-A equation were used for biomethane adsorption on activated carbon. The properties of biomethane, such as critical temperature, pressure and density could be found by REFPROP Program [REFPROP 2013], and the molecular weight of biomethane could be expressed as

$$Mw_{mix} = \sum y_i Mw_i \tag{4.10}$$

where Mw_{mix} is the molecular weight of biomethane (g/mol), y_i is the mol fraction of gas in biomethane and M_i is the molecular weight of gas in biomethane (g/mol).

4.2.3 Heat of adsorption [Ning *et al.* 2012]

The isosteric heat of adsorption is a critical parameter for adsorptive separation processes. The heat release during the adsorption process which is the heat of adsorption from the adsorption uptake data by assuming from ideal gas phase behavior of the adsorbate molecules in their gaseous phase could be calculated from the Clapeyron's equation with the assumption of an isotherm as

$$H_{ad} = -\overline{R}T^{2}\left(\frac{\partial \ln P}{\partial T}\right)_{q} . \tag{4.11}$$

From D-A isotherm model in equation (4.8), the heat of adsorption could be obtained, which is function of adsorbate surface loading (g), adsorption parameters (g_{max}, E, n) of the D-A isotherm model, saturation vapor pressure (P_s), and temperature (T). It could be rearranged as

$$H_{ad} = -\left(E\left[\ln \frac{q_{max}}{q} \right]^{1/n} \right) \tag{4.12}$$

where H_{ad} is the isosteric heat of adsorption at specific loading (J/mol), $\overline{R}$ is the universal gas constant (8.1345 J/mol-K), T is the temperature (K), P is the pressure at specific surface loading (MPa) and q is the adsorbate surface loading (mmol/g$_{(AC)}$).

4.2.4 Biomethane desorption on activated carbon

Gas discharge could be desorbed on activated carbon by several techniques. The high and low heating activation is one method to discharge the adsorbed gas [Zheng *et al.* 2015]. In this study, the biomethane desorption was considered by heating. The weight of desorbed biomethane was measured and calculated the percent of biomethane desorption as

$$\%desorbed\ biomethane = \frac{amount\ of\ biomethane\ desorption \times 100}{amount\ of\ biomethane\ adsorption} . \tag{4.13}$$

In this study, Langmuir and Dubinin-Astakhov models were considered on biomethane adsorption on activated carbon. In addition, the isosteric heat of adsorption was calculated by Clapeyron equation.

4.3 Experiment

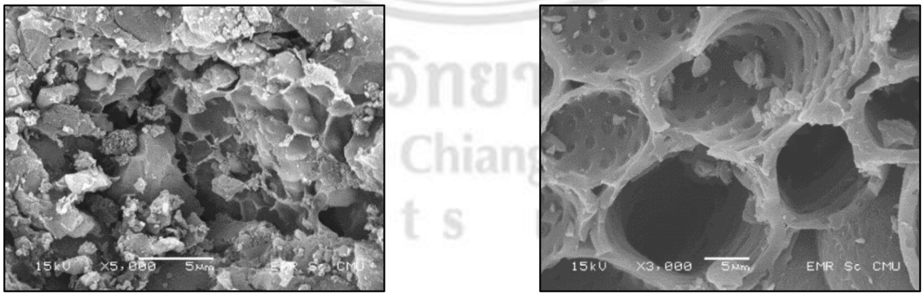
In this study, two activated carbons made from coal and coconut shell were used to study on biomethane adsorption. The coal and coconut shell activated carbon was produced by Calgon Carbon Corporation, Belgium and C. Gigantic Carbon Co., Ltd, Thailand, respectively. The activated carbons properties were analyzed by technique of BET surgace analysis and scanning electron microscope (SEM). The data could be shown in Table 4.1 and Figure 4.3.

Table 4.1 The surface analysis and porous analysis 8x16.

Sample	Surface Analysis	Porous Analysis		Bulk density (g/cm^3)
	BET Theory (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Diameter (Å)	
Coal	1,418.18	0.916	12.92	0.5024
Coconut shell	1,301.14	0.585	8.98	0.7229

Note: 1 Å = 0.1 nm

It could be note that the activated carbon from coal had more pore volume and higher pore diameter. Therefore, biomethane could be more easily adsorbed the adsorbent surface.

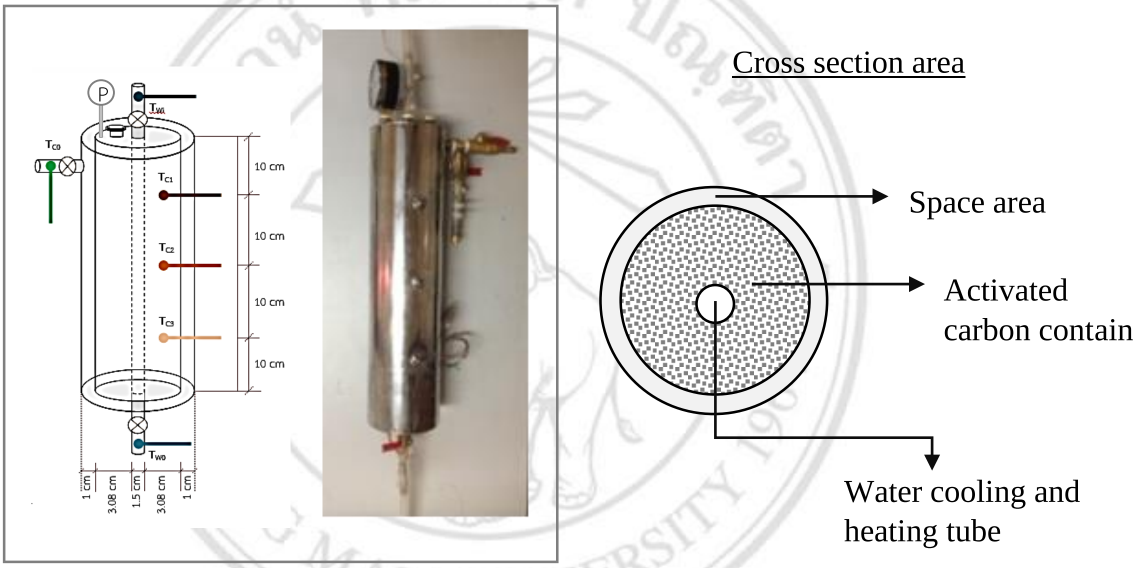


(a) Coal activated carbon (b) Coconut shell activated carbon

Figure 4.3 SEM photograph of the coal activated carbon (5,000 magnification) and coconut shell activated carbon (3,000 magnification).

4.3.1 Biomethane adsorption on Activated carbon

The activated carbon was contained in a cylindrical container. It made from stainless steel (SS 304). An internal volume of container was 1,773.4 cm^3 that could support activated carbon of 891 and 1,282 g from coal and coconut shell, respectively. A water cooling/heating was fed at the center of the container for temperature controlling. A schematic sketch of the biomethane adsorption container and the biomethane adsorption process experimental setup could be shown in Figures 4.4 and 4.5, respectively.



(a) The biomethane adsorption container (b) Cross section area

Figure 4.4 A schematic of the biomethane adsorption container.

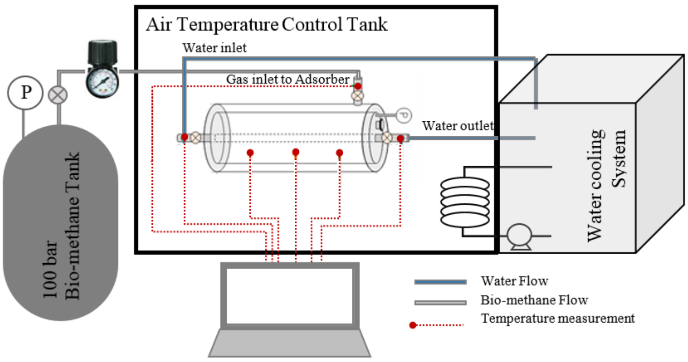


Figure 4.5 A schematic of the biomethane adsorption process experimental setup.

The biomethane was compressed into a tank at pressure of 100 bar and supported by Energy Research and Development Institute, Nakhonping, Chiang Mai University. The biomethane consists of CH_4:CO_2 of 80:20 % and 90:10 % by volume.

The activated carbon was heated at temperature of 100 ^{o}C and vacuumed at least 12 hours in degassing process. After that the biomethane was fed to the treated activated carbon in the container which controlled the temperature and pressure at range of 10-25^{o}C, 2-8 bar, respectively. In the experiment, the container was weighted before and after adsorption. The adsorbed biomethane on activated carbon could be calculated as

$$n_{ad} = n_{total} - n_{sp} \tag{4.13}$$

where n_{ad} is the adsorbed biomethane on activated carbon at equilibrium pressure and temperature (mol), n_{total} is the biomethane in container at equilibrium pressure and temperature (mol) and n_{sp} is the biomethane at space area at equilibrium pressure and temperature (mol).

The biomethane in the space volumn could be calculated at equilibrium pressure and temperature as

$$m_{sp} = \frac{PV_{sp}Mw_{mix}}{\bar{R}T} \tag{4.14}$$

where m_{sp} is absorbed biomethane (g), P is equilibrium pressure (Pa), V_{sp} is space volume in adsorption storage (m^3) , $\bar{R}$ is universal gas constant (8.314 m^3 Pa mol^{-1} K^{-1}) , T is biomethane adsorption temperature (K) and Mw_{mix} is molecular weight of biomethane (g/mol).

4.3.2 Biomethane desorption on Activated carbon

The 80% biomethane adsorbed and compressed on activated carbons at 8 bar. In the desorption procedure, the discharged testing were conducted immediately after the adsorption process has completed. In the experiment, the adsorbent was heated at 25-55°C. The desorbed biomethane was measured by volumetric method.

The biomethane desorption process experimental setup could be shown as Figure 4.6.

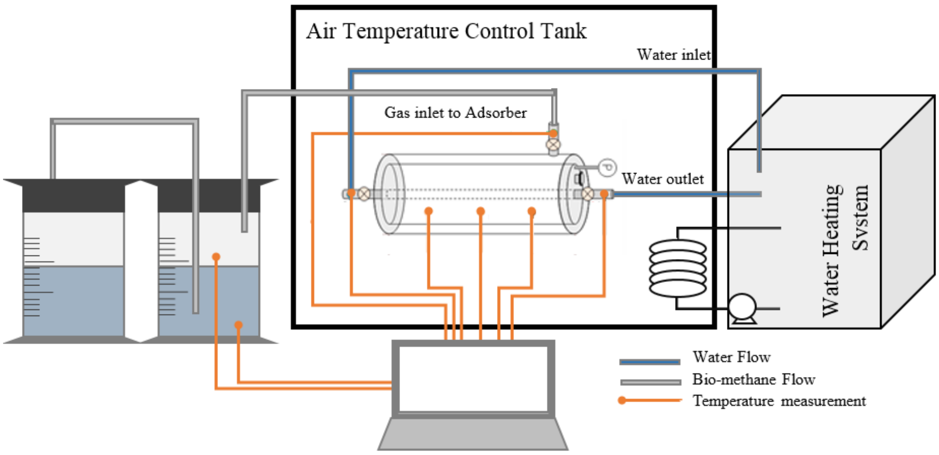


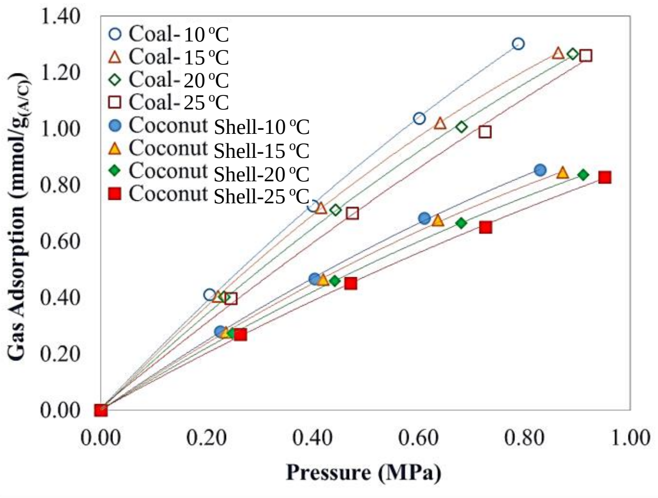
Figure 4.6 A schematic sketch of the biomethane desorption process experimental setup.

4.4 Results and Discussions

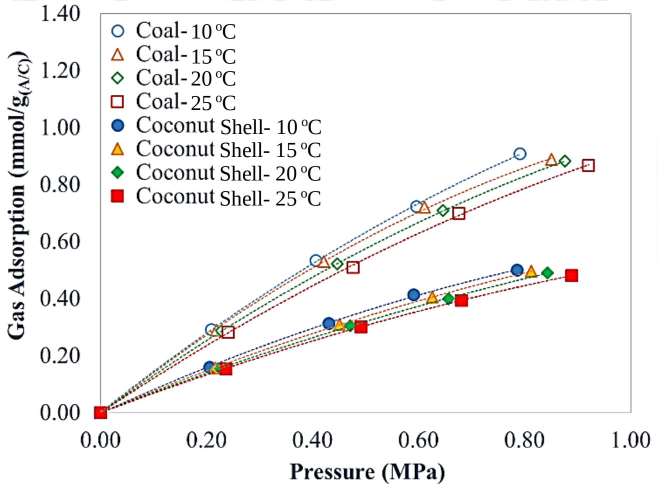
The bio methane adsorption and desorption on activated carbon could be presented as

4.4.1 Biomethane adsorption on activated carbon

The 80 and 90% biomethane adsorption on activated carbon from coal and coconut shell at adsorption temperature and pressure of 10-25 °C, 2-8 bar could be shown in Figure 4.7.



(a)



(b)

Figure 4.7 Langmuir Isotherm of biomethane on activated carbons;
(a) 80:20 % by volume; biomethane : CO_2
(b) 90:10 % by volume; biomethane : CO_2.

From the results, it could be seen that the adsorbed biomethane on activated carbon increased when the pressure increased and temperature decreased. Since the gas-solid adsorption was exothermic process, the adsorption could be highly effective at low temperature that lead to increase the adsorbed biomethane abilities. It was found that the adsorbed biomethane abilities on coal was higher than coconut shell. Due to the surface area of coal was higher than that of coconut shell then adsorbed biomethane abilities on coal was also higher. The biomethane adsorption on activated carbons at pressure of 8 bar and temperature of 10 and 25^{o}C were shown in Table 4.2.

Table 4.2 The biomethane adsorption on coal and coconut shell activated carbons at 8 bar, 10 and 25^{o}C.

Biomethane	Type of Activated carbon	Adsorbed temperature (^{o}C)	Adsorbed biomethane (mmol/$g_{(AC)}$)	Adsorbed biomethane (g/$g_{(AC)}$)
80:20 % by volume; biomethane: CO_2	Coal	25	1.0885	0.0236
		10	1.2886	0.0279
	Coconut shell	25	0.8141	0.0154
		10	0.9570	0.0184
90:10 % by volume; biomethane: CO_2	Coal	25	0.6839	0.0147
		10	0.7975	0.0178
	Coconut shell	25	0.4481	0.0085
		10	0.5180	0.0098

Considering the behavior of gas adsorption on activated carbon, it could be found that the 80% biomethane could be more adsorbed than 90% biomethane on activated carbon. Due to the activated carbons have a higher affinity for CO_2 than that for CH_4 [Garnier *et al.* 2011], and the molecular weight of CO_2 was higher than that of CH_4 then the amount of the adsorbate adsorbed by the activated carbon for high percent biomethane was lower than that of the low percentage biomethane gas.

The quantity of adsorbed biomethane from experiment was lower than those reported in literatures [Grande *et al.* 2013, Jeong *et al.* 2007, Zheng *et al.* 2015] which was about 2.5-3.79 mmol/$g_{(AC)}$ due to the lower surface area of activated carbons. The comparisons were shown in Table 4.3.

However, when considering on similar surface area, it could be found that the adsorbed biomethane was still lower than that reported in Jeong *et al.* 2007. Due to the amount of activated carbons which used in this study (891 and

1,282g) was higher than other researches. Also it meant that the gas adsorption process might be incomplete adsorption. Furthermore, it could be observed that when the amount of activated carbons increased, the adsorbed biomethane affinity on activated carbon would decrease as reported from the literature.

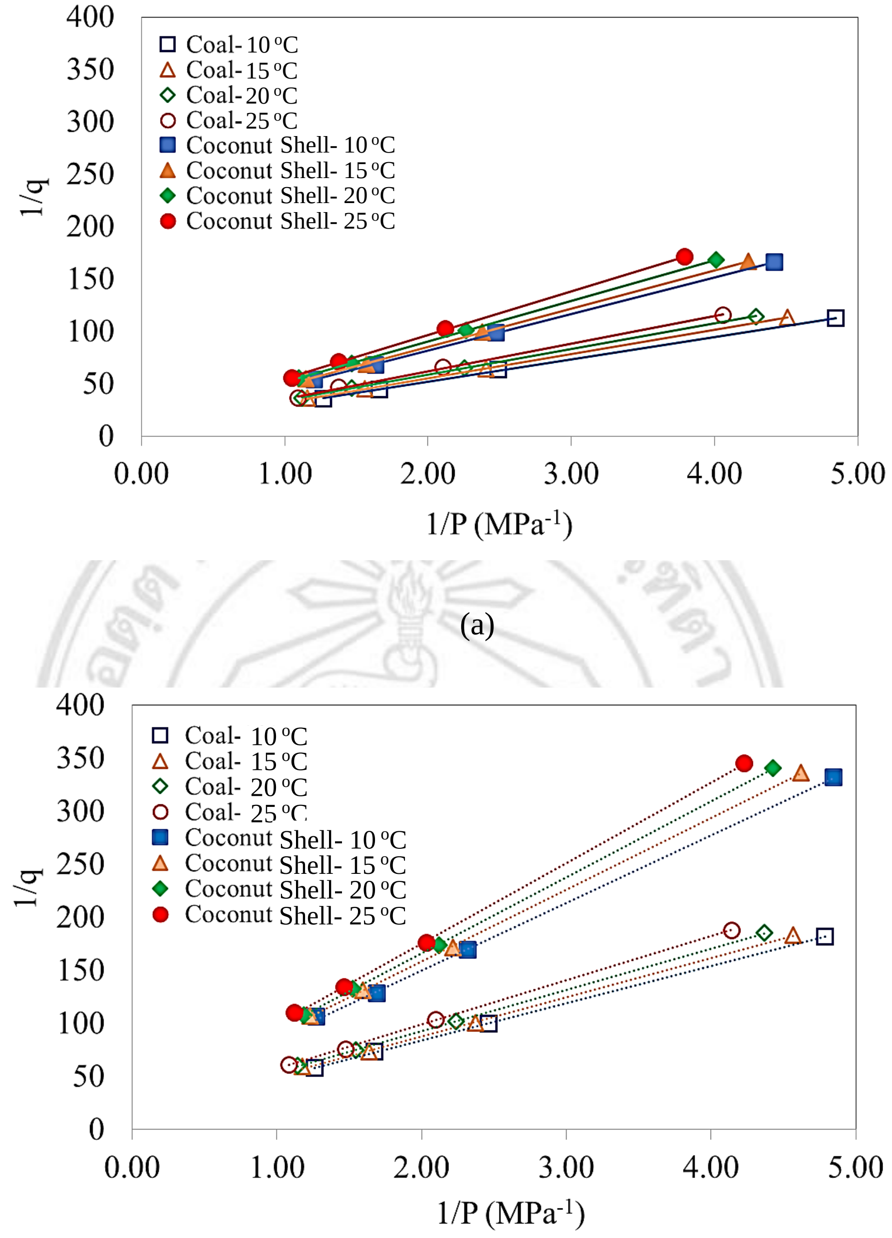
The biomethane adsorption on activated carbons at pressure of 8 bar and temperature of 10 and 25°C was shown in table 4.3.

From Langmuir model, the relation between the adsorbed biomethane on activated carbon at equilibrium temperature and pressure (q) with the equilibrium pressure (P) could be rearranged as $\frac{1}{q} = \left(\frac{1}{q_{max}K_L}\right)\frac{1}{P} + \frac{1}{q_{max}}$.

The relation of these parameters from experiments could be shown in Figure 4.8.

Table 4.3 The gas adsorption on activated carbon at 8 bar, 25^oC.

Adsorbed gas	**Type of A/C**	**Surface area $(m^2/g_{(AC)})$**	**Adsorbed biomethane $(mmol/g_{(AC)})$**	**Reference**
80:20 % by volume; biomethane: CO_2	Coal (891g)	1,418.18	1.0885	This study
	Coconut Shell (1282g)	1,301.14	0.8141	This study
90:10 % by volume; biomethane: CO_2	Coal (891g)	1,418.18	0.6839	This study
	Coconut Shell (1282g)	1,301.14	0.4481	This study
CH_4:CO_2 80:20% by volume	N/A (27g)	2,200	3.79	[Grande *et al.* 2013]
CH_4:CO_2 90:10% by volume	N/A (27g)	2,200	3.33	[Grande *et al.* 2013]
CH_4 99.9 % by volume	Coconut Shell (389g)	1,150–1,250	3.20	[Jeong *et al.* 2007]
Pure CH_4	N/A (700g)	2074	2.50	[Zheng *et al.* 2015]



(a)

(b)

Figure 4.8 The relation between *1/q* and *1/P* of biomethane on coal and coconut shell activated carbon at 10, 15, 20 and 25 °C; (a) 80 % by volume; biomethane: CO_2 (b) 90 % by volume; biomethane: CO_2.

From Figure 4.8, the biomethane adsorption isotherm on activated carbon at 10-25 °C were performed. The limiting uptake of biomethane on the adsorbent (q_{max}) and the Langmuir's constant (K_L) could be taken and the results were shown in Table 4.4.

Table 4.4 The limiting uptake (q_{max}) and the Langmuir's constant (K_L) of biomethane adsorption on the activated carbon.

Biomethane	Type of A/C	Adsorbed temperature (°C)	q_{max} (g/g(AC))	q_{max} (mmol/g(AC))	K_L
80:20 % by volume; biomethane: CO_2	Coal	25	0.1038	4.7989	0.3667
		20	0.1053	4.8651	0.3876
		15	0.1074	4.9636	0.4037
		10	0.1094	5.0557	0.4276
	Coconut Shell	25	0.0783	4.1512	0.3049
		20	0.0793	4.2036	0.3244
		15	0.0829	4.3942	0.3296
		10	0.0853	4.5186	0.3359
90:10 % by volume; biomethane: CO_2	Coal	25	0.0645	2.9829	0.3719
		20	0.0661	3.0538	0.3892
		15	0.0694	3.2066	0.3911
		10	0.0699	3.2290	0.4100
	Coconut Shell	25	0.0427	2.2618	0.3088
		20	0.0431	2.2860	0.3238
		15	0.0436	2.3106	0.3389
		10	0.0441	2.3390	0.3556

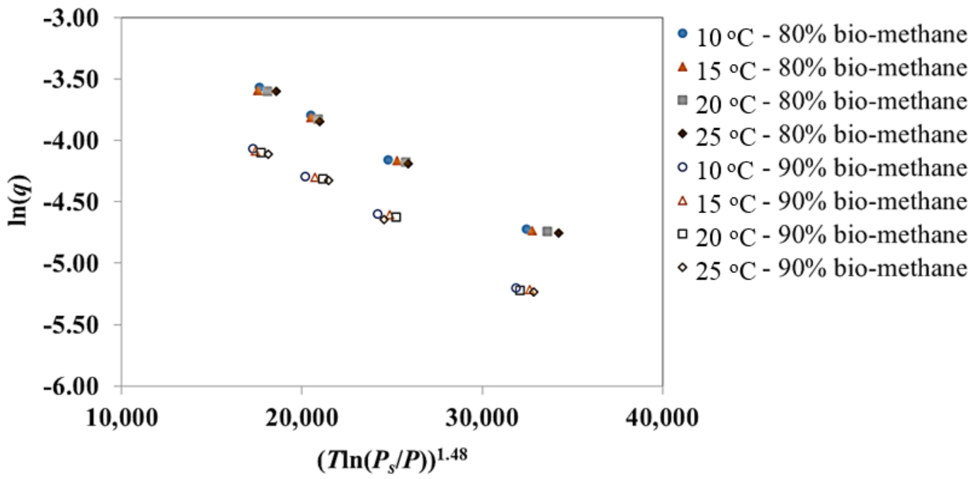
From Table 4.4, it could be seen that biomethane adsorption on the activated carbon from coal was better which resulted in higher the limiting biomethane adsorption. The limiting biomethane adsorption and Langmuir's constant increased when the temperature decreased.

4.4.2 Dubinin and Astakhov (D-A) Result

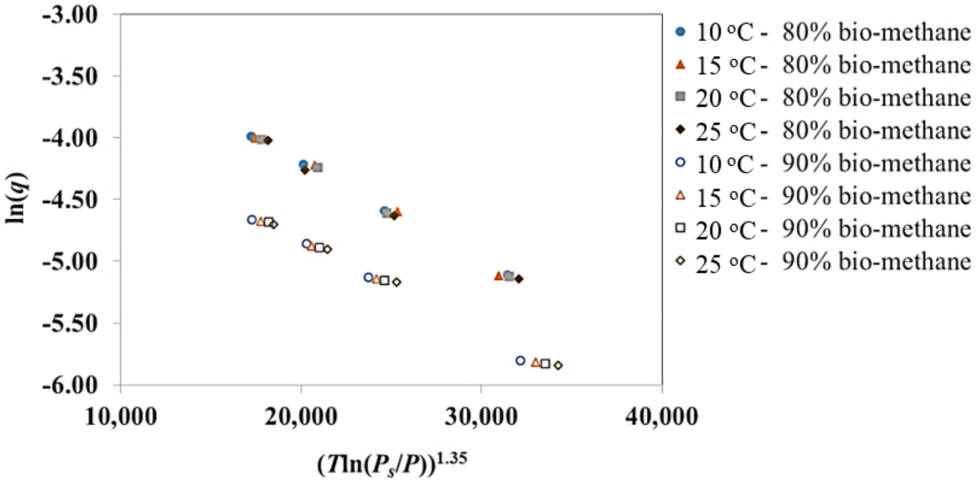
The biomethane adsorption temperature and pressure were considered in D-A model (equation 4.6) and it could be reduced and rearranged in a form as

$$ln(q) = ln(q_{max}) - \left(\frac{\bar{R}T}{E} ln\left(\frac{Ps}{P} \right) \right)^n . \tag{4.13}$$

The D-A equations for biomethane adsorption with various conditions were considered and the relation between adsorbate surface loading (ln(q)) and (Tln(Ps/P))^n evaluated and was performed. The characteristic energy of adsorption (E), the structural heterogeneity parameter (n), and the limiting uptake of biomethane on the adsorbent (q_{max}) could be shown in Figure 4.9 and Table 4.5.



(a) For coal; n = 1.48



(b) For coconut shell; n = 1.35

Figure 4.9 The relation between ln(q) and (Tln(Ps/P))^n for biomethane adsorption by activated carbons.

Table 4.5 The structural heterogeneity parameter (*n*), the characteristic energy of adsorption (*E*), and limiting uptake of biomethane on the adsorbent (q_{max}) for D-A model.

Biomethane	**Type of AC**	**BET Surface (m^2/g)**	**D-A model**			**Langmuir model**	**Reference**
			n	***E* (kJ/mol)**	**q_{max} ($mmol/g_{(AC)}$)**	**$q_{max,avg}$ ($mmol/g_{(AC)}$)**	
80:20 % by volume; biomethane: CO_2	Coal	1418.18	1.48	5.3358	4.6302	4.9208	This study
	Coconut Shell	1301.14	1.35	4.5689	3.8795	4.3169	This study
90:10 % by volume; biomethane: CO_2	Coal	1418.18	1.48	4.8755	3.3888	3.1181	This study
	Coconut Shell	1301.14	1.35	4.5689	2.0907	2.2994	This study
99.9995 % by volume CH_4	MaxsorbIII	3,140	1.33	5.2575	18.1620	N/A	[Loh *et al.* 2010]
99.9995 % by volume CH_4	ACF (A-20)	2,206	1.37	5.6405	10.5630	N/A	[Loh *et al.* 2010]
Pure CH_4	Calgon AC	N/A	2.41	8.96	0.88	N/A	[Rahman *et al.* 2013]
Pure CH_4	AAC-1	801	2.57	9.80	1.3	N/A	[Luo *et al.* 2014]

From Figure 4.9 and Table 4.5, it could be found that the limiting uptake of biomethane on the adsorbent (q_{max}) on coal activated carbon was higher than that on coconut shell. The average limiting uptake of biomethane on the adsorbent (q_{max}) at temperature of 10-25 ^{o}C from Langmuir model and q_{max} from D-A model were quite similar.

It could also be found that as the structural heterogeneity parameter (n) increased, the surface was more heterogeneity and the characteristic energy of adsorption (E) was higher. The n values for coal and coconut shell ACs were 1.48 and 1.35, respectively.

From the results in Table 4.5. The adsorbed biomethane in mmol/g$_{(AC)}$ could be formulated with the equilibrium pressure(MPa) and temperature(K) as

Coal activated carbon

80:20 % by volume; biomethane: CO_2

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

90:10 % by volume; biomethane: CO_2

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

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

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

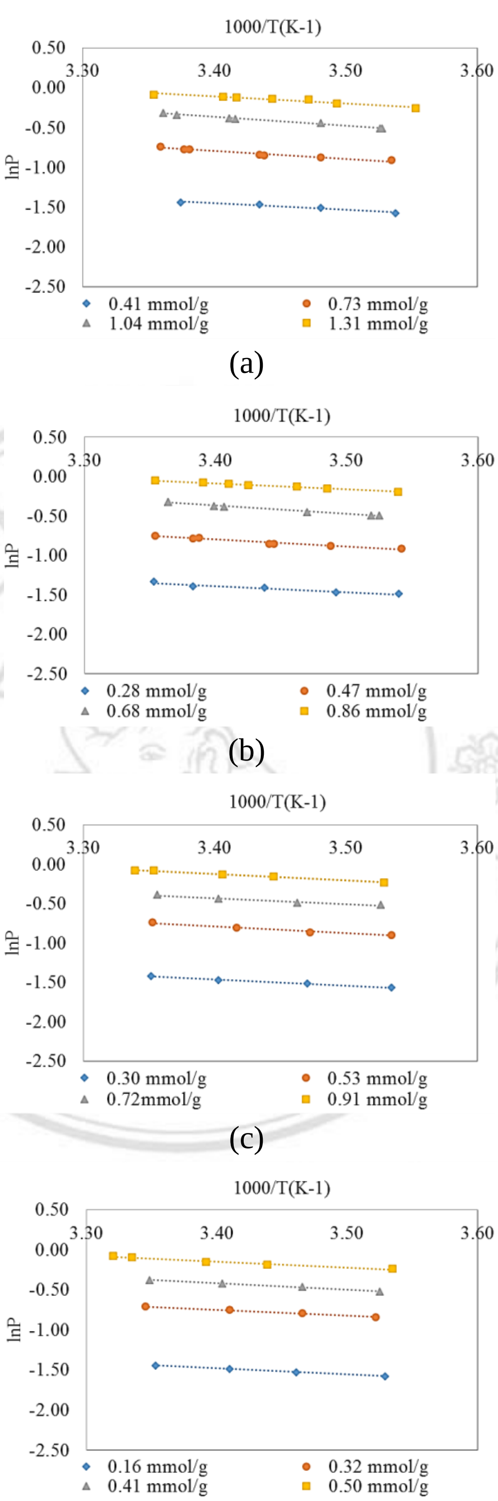
Note: 10°C ≤ T ≤ 25°C, 0 ≤ P ≤ 8 bar.

4.4.3 Isosteric heat of adsorption Result

The isosteric heat of adsorption could be calculated from the Clapeyron equation as

$$H_{ad} = -\bar{R}T^{2}\left(\frac{\partial \ln P}{\partial T}\right)_{q} . \tag{4.14}$$

From the experimental data, the isosteric heat of adsorption of 80% and 90% biomethane on coal and coconut shell activated carbon were in a range of 5.56-9.76 kJ/mol. The isosteric heat of adsorption on the coal was found to be higher than that on the coconut shell thus more biomethane could be adsorbed on the coal than that on the coconut shell. The isosteric heat of adsorptions for the biomethane were shown in Figure 4.10 and 4.11.



(d)

Figure 4.10 The isosteric heat of adsorption for biomethane at 10-25^{o}C, 0-8 bar; (a) 80% Biomethane on coal, (b) 80% Biomethane on coconut shell (c) 90% Biomethane on coal and (d) 90% Biomethane on coconut shell.

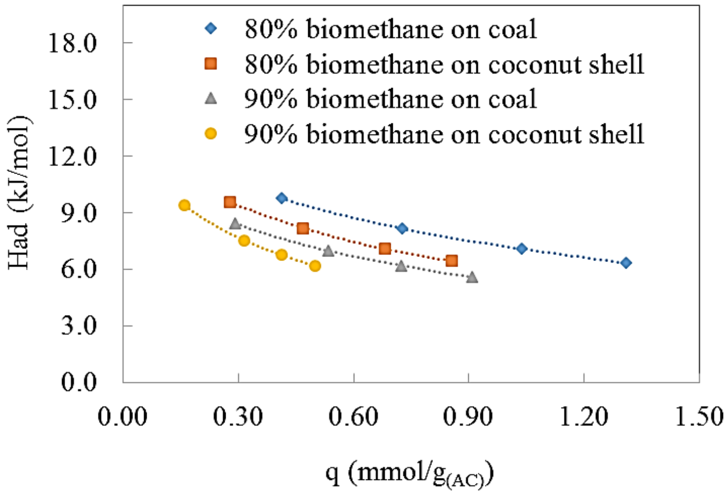


Figure 4.11 The isosteric heat of adsorption for biomethane.

The isosteric heat of adsorption for biomethane decreased, when amount of gas adsorption increased. It could be noted that, the isosteric heat of adsorption is a measure of the interaction between adsorbate molecules and adsorbent molecules. At the beginning, the adsorption occurred easily on the lively activity surface, highest adsorption heat was obtained. As the adsorbed amount increased, the adsorption at the surface was low active, the isosteric heat of adsorption also become low [Ning *et al.* 2012].

4.4.3 Biomethane desorption

In this research, desorption of biomethane from activated carbon after adsorption was considered. The process started up by adsorption of 80% biomethane on coal and coconut shell activated carbon under 8 bar, 25 °C till the equilibrium was obtained. After that the desorption was carried out by feeding water at a temperature in a range of 25-55 °C into the inner tube of the adsorber to generate heat for biomethane desorption. After complete desorption, the adsorber was cooled down to the room temperature and the next adsorption started.

The adsorption/desorption cycles were investigated. From the results, it could be shown that biomethane discharge increased, when the adsorbent temperature increased. The percentages of desorbed biomethane were in a range of 65-78% and 61-74% at temperature of 25-55°C for coal and coconut shell, respectively. The desorbed biomethane on activated carbon by 25-55°C heating could be shown in Figure 4.12.

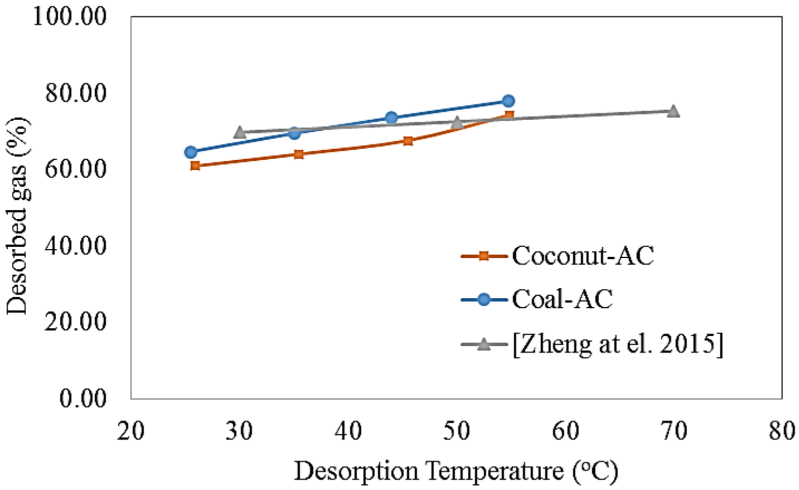


Figure 4.12 The percentage of gas desorption at 25-55 °C.

From the results, it could be seen that the percentage of the gas discharge increased when the adsorbent temperature increased. Since the gas-solid adsorption was exothermic process, when the gas on adsorbent was activated by heating, it would expand and detected from the porous medium. From Figure 4.12, the percentage of biomethane desorption was similar to that reported in the literature [Zheng *et al.* 2015]. The residual biomethane in adsorbent was around 22% and 26% at 55°C for coal and coconut shell, respectively. Due to the low desorption temperature, the amount of residual biomethane was quite high.

The amount of desorbed gas could be increased by heating at high temperature. However, a thermal conductivity of porous medium was low around 0.36-0.4 W/m-K [Zhequan *et al.* 2013] then the adsorbent temperature was slowly increasing.

The amounts and percentage of biomethane on adsorption/desorption cycles at 55°C were shown in Figures. 4.13 and 4.14, respectively.

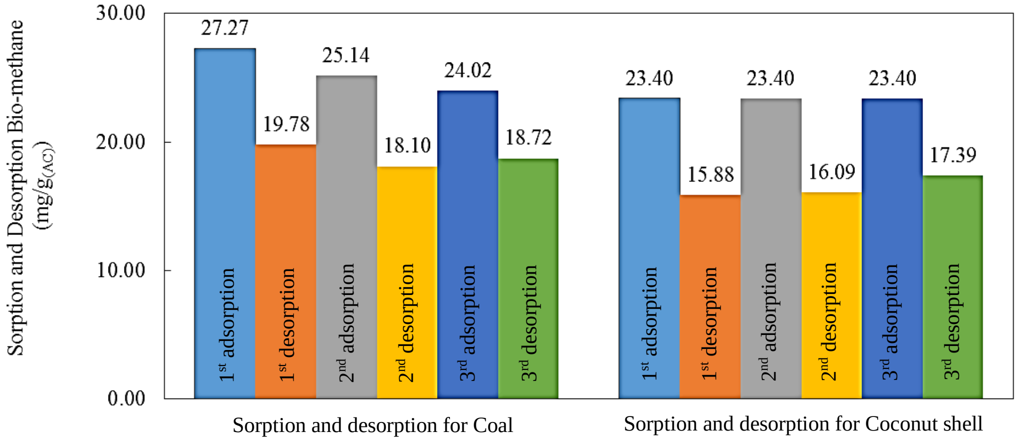


Figure 4.13 The biomethane adsorption/desorption cycles at 55°C for coal and coconut shell activated carbons.

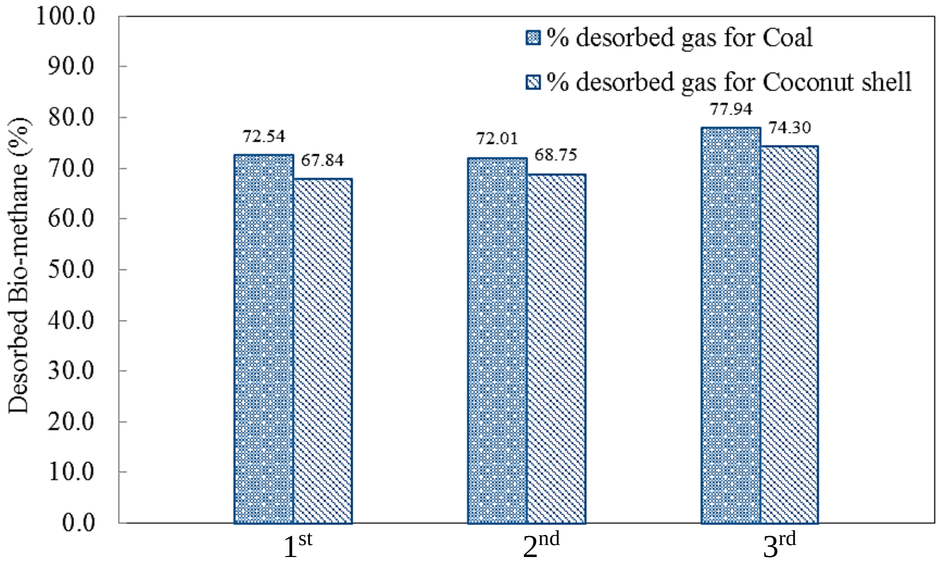


Figure 4.14 The percentages of biomethane desorption cycles at 55°C for coal and coconut shell activated carbons.

From Figures 4.13 and 4.14, it could be seen that the capabilities of adsorption of the recycled adsorbers tended to reduce due to the amount of adsorbate remained in the adsorbent. The amount of biomethane during desorption in each cycle seemed to be steady. The percentage of desorbed biomethane for coal activated carbon was slightly higher than that for coconut shell activated carbon.