CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorbents Characterization

Table 4.1 Physical properties of adsorbents

Adsorbents	S_{BET} m^2/g	V_{DR} cc/g	Total pore volume cc/g	DA pore diameter Å
Basolite C300	2434	1.27	1.33	9.6
Basolite Z1200	1449	0.78	0.88	16.8
Calgon	877.8	0.48	0.53	13.4
Coconut Shell Granular Activated Carbon	865.4	0.47	0.49	13.6
Eucalyptus Powder Activated Carbon	861	0.47	0.61	14.8
Coconut Shell Powder Activated Carbon	713.5	0.39	0.42	11.2

The physical properties of the adsorbents were characterized by using BET surface area analyzer (Autosorb 1-MP). Table 4.1 presents the physical properties of adsorbents which include BET surface area (S_{BET}), micropore volume (V_{DR}), total pore volume, and pore diameter (using DUBININ-ASTAKHOV or DA method). The result shows that Basolite C300 has the highest BET surface area, micropore volume and total pore volume. Although Calgon, Coconut Shell Granular Activated Carbon, and Eucalyptus Powder Activated Carbon have similar BET surface area and micropore volume, but obviously different total pore volume. The Metal Organic

Frameworks (MOFs), Basolite C300 and Basolite Z1200, have higher BET surface area, micropore volume and total pore volume than Calgon, Coconut Shell Granular Activated Carbon, Eucalyptus Powder Activated Carbon, and Coconut Shell Powder Activated Carbon. Basolite Z1200 has the highest DA pore size diameter followed by Eucalyptus Powder Activated Carbon, Coconut Shell Granular Activated Carbon, Calgon, Coconut Shell Activated Carbon Powder, and Basolite C300 respectively.

4.2 Methane Adsorption Isotherm

Methane adsorption isotherm were measured at 3 different temperatures (303, 308, and 313 K) and with the pressure ranging from 0 to 900 psia. The equilibrium of methane adsorption was reached in 10 minutes after applying the methane pressure. Figure 4.1-4.3 show the amount of methane adsorption at 303 K and 900 psia as a function of each physical property of adsorbents; BET surface area, micropore volume, and total pore volume respectively.

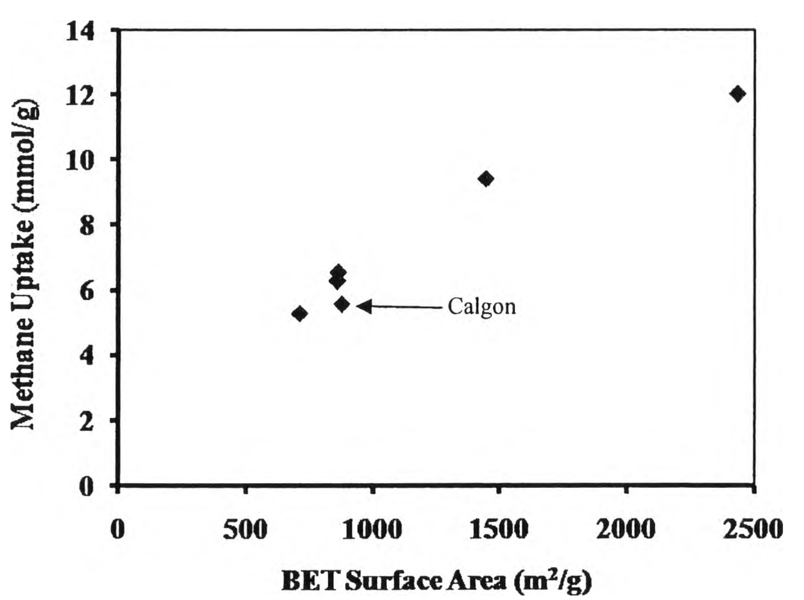

Figure 4.1 Adsorbed amount of methane at 900 psia and 303 K as a function of the BET surface area.

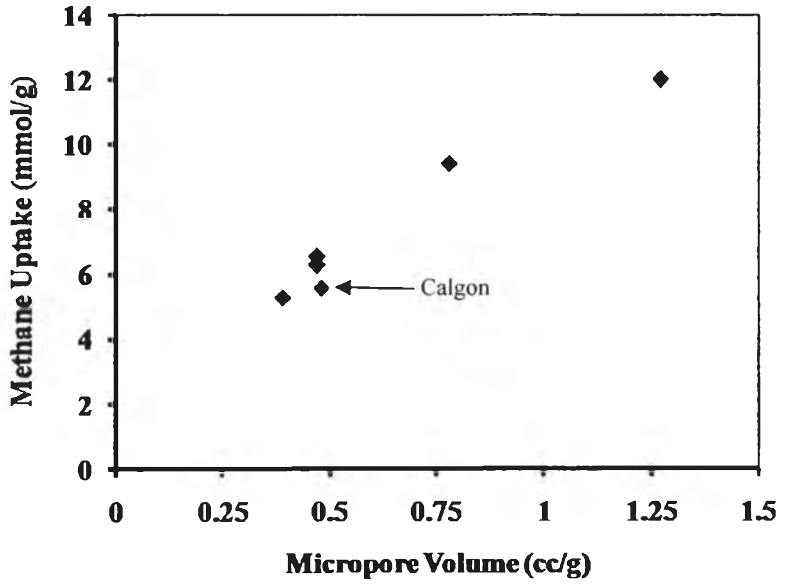

Figure 4.2 Adsorbed amount of methane at 900 psia and 303 K as a function of the micropore volume.

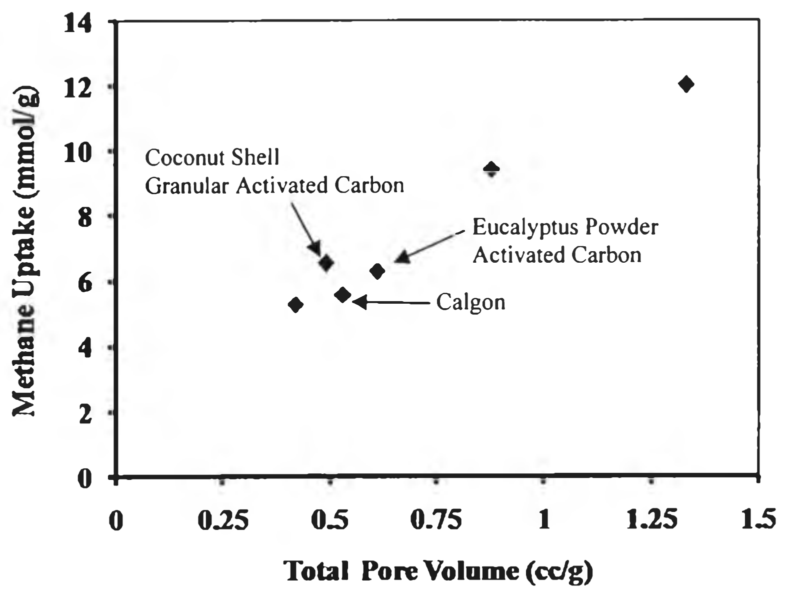

Figure 4.3 Adsorbed amount of methane at 900 psia and 303 K as a function of the total pore volume.

Figure 4.1 to 4.3 show that the trend of the amount of methane adsorption increases with BET surface area, micropore volume, and total pore volume. The above results are consistent with the studies by Bastos-Neto *et al.* (2007), Lozano-Castelló *et al.* (2002), Alcañiz-Monge *et al.* (2009), and Wang *et al.* (2011).

Figure 4.3 shows that although Eucalyptus Powder Activated Carbon has higher total pore volume than that of Coconut Shell Granular Activated Carbon, however, both of them have similar amounts of methane adsorption. This is due to the fact that they have similar micropore volumes.

Table 4.2 The adsorption capacity of methane on adsorbents at 303 K and 900 psia

Adsorbents	Gravimetric Adsorption of Methane at 303 K and 900 psia (mmol/g)	Volumetric Adsorption of Methane at 303 K and 900 psia (v/v)	Apparent Density (g/ml)
Basolite C300	12.01	66.44	0.23
Basolite Z1200	9.41	65.63	0.29
Calgon	5.56	59.71	0.45
Coconut Shell Granular Activated Carbon	6.52	81.13	0.52
Eucalyptus Powder Activated Carbon	6.28	87.60	0.58
Coconut Shell Powder Activated Carbon	5.27	65.91	0.52

Table 4.2 shows the gravimetric methane adsorption, volumetric methane adsorption and apparent density of adsorbents. Basolite C300 has the the highest gravimetric amount of methane adsorption, followed by Basolite Z1200, Coconut

Shell Granular Activated Carbon, Eucalyptus Powder Activated Carbon, Calgon and Coconut Shell Powder Activated Carbon respectively. It can be concluded that MOFs have higher gravimetric amounts of methane adsorption than those of activated carbons since MOFs have higher BET surface area and micropore volume. Eucalyptus Powder Activated Carbon has the highest volumetric amount of methane adsorption, followed by Coconut Shell Granular Activated Carbon, Basolite C300, Coconut Shell Powder Activated Carbon, Basolite Z1200, and Calgon respectively. Perrin *et al.* (2004) indicated that the volumetric amount of gas stored was not proportional to the gravimetric amount of gas stored, which is consistent with this study. The volumetric amount of methane adsorption was calculated from equation A. The unit of the volumetric amount of methane adsorption is expressed in STP volumes of methane storage per volume of storage vessel unit (v/v).

$$Q_v = Q_m * M_w * D * A \qquad \text{equation A}$$

where : Q_v = Volumetric amount of methane adsorption (v/v)

Q_m = Gravimetric amount of methane adsorption (mmol/g)

M_w = Molecular weight of methane

= 16.034 g/mol

D = Apparent density of adsorbent packing (g/cm^3)

A = Volume occupied by 1 g. of methane at STP condition

= 1.5 dm^3/g

From equation A, the volumetric amount of methane adsorption depends on the gravimetric amount of methane adsorption and the apparent density. It is found from this study that the apparent densities of MOFs are much lower than those of activated carbons. Thus, Basolite C300 and Basolite Z1200 have low volumetric amounts of methane adsorption while both of them have high gravimetric amounts of methane adsorption. In summary, it can be concluded that the physical properties; including BET surface area, micropore volume, total pore volume, and packing density; strongly affect the amount of methane adsorbed.

Table 4.3 The adsorption capacity of methane on adsorbents at 303 K and 900 psia in storage vessel 70 L

Adsorbents	Methane Uptake at 303 K and 900 psia (kg)	Percentage (%)
Empty	2.78	-
Basolite C300	3.10	+ 11.32
Basolite Z1200	3.06	+ 9.98
Calgon	2.81	+ 0.83
Coconut Shell Granular Activated Carbon	3.78	+ 36.64
Eucalyptus Powder Activated Carbon	4.08	+ 46.79
Coconut Shell Powder Activated Carbon	3.08	+ 10.44

Table 4.3 shows the comparison of the methane adsorption amount (kg) in a storage vessel of 70 L among various adsorbents at 303 K and 900 psia. The calculation of the amount of methane adsorption in the empty vessel was derived from the following equation of state.

$$PV = znRT$$

where : P = Pressure (atm)

V = Volume (L)

z = Compressibility factor of methane

n = Mole of methane (mol)

R = Gas constant

= 0.082 atm·L/mol·K

T = Temperature (K)

Table 4.3 indicates that without the adsorbents, the 70 L storage vessel at the condition of 303 K and 900 psia can accomodate only 2.78 kg of methane. However, with the adsorbents; including Basolite C300, Basolite Z1200, Calgon (granular activated carbon), Coconut Shell Powder Activated Carbon, Coconut Shell Granular Activated Carbon, and Eucalyptus Powder Activated Carbon; the amounts of methane adsorption were increased at the same condition. The best adsorbent in this study is Eucalyptus Powder Activated Carbon while the worst adsorbent is Calgon.

Figures 4.4 to 4.9 show methane adsorption isotherm of Coconut Shell Powder Activated Carbon, Coconut Shell Granular Activated Carbon, Calgon, Eucalyptus Powder Activated Carbon, Basolite C300, and Basolite Z1200 respectively. The adsorption isotherm were plotted between the mole of methane adsorption per gram of adsorbents and equilibrium pressure (psia). The amount of methane adsorption increases gradually at low pressure and stabilizes at high pressure. Delavar *et. al.* (2010) explained that at high pressure, the methane adsorption reached the saturation of the adsorbent bed. In addition, Balathanigaimani *et al.* (2006) also found that the methane adsorption decreased with increasing temperature.

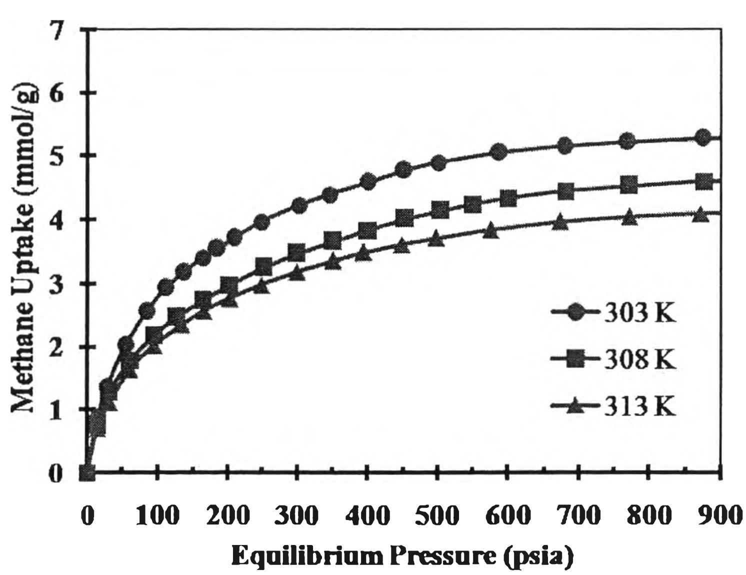

Figure 4.4 The experimental of methane adsorption isotherm from Coconut Shell Powder Activated Carbon.

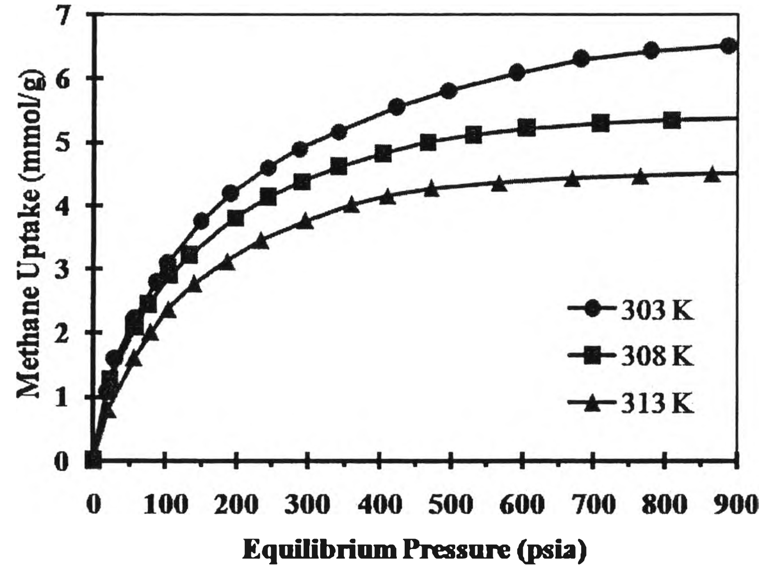

Figure 4.5 The experimental of methane adsorption isotherm from Coconut Shells Granular Activated Carbon (20-40 meshes).

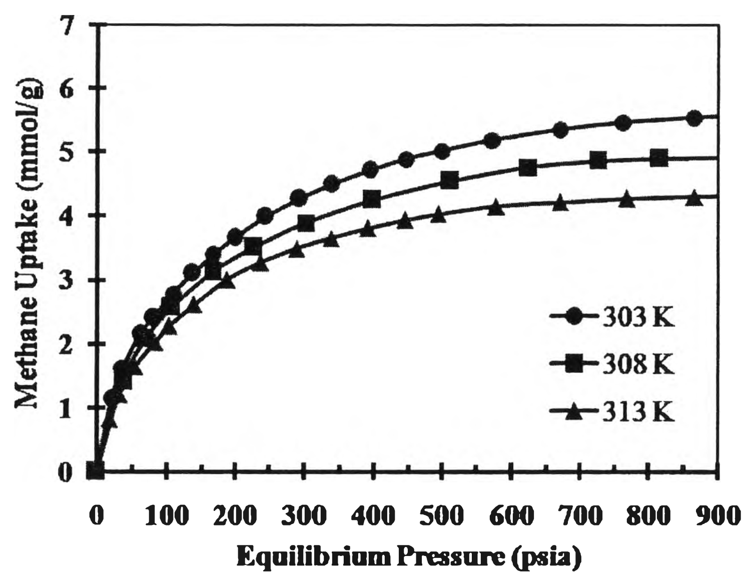

Figure 4.6 The experimental of methane adsorption isotherm from Calgon (20-40 meshes).

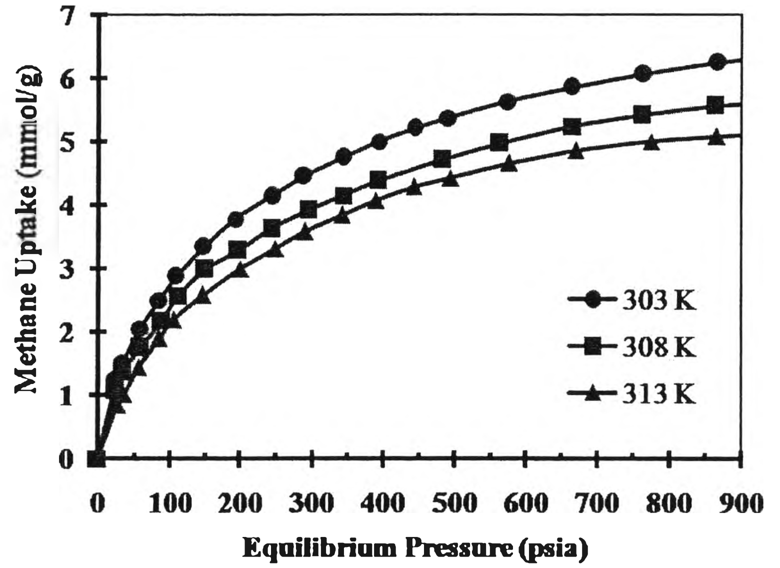

Figure 4.7 The experimental of methane adsorption isotherm from Eucayptus Powder Activated Carbon.

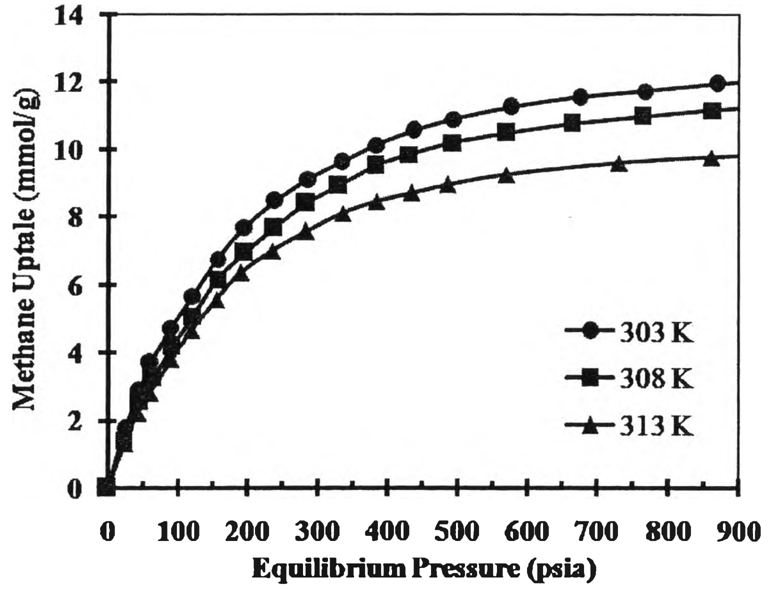

Figure 4.8 The experimental of methane adsorption isotherm from Basolite C300.

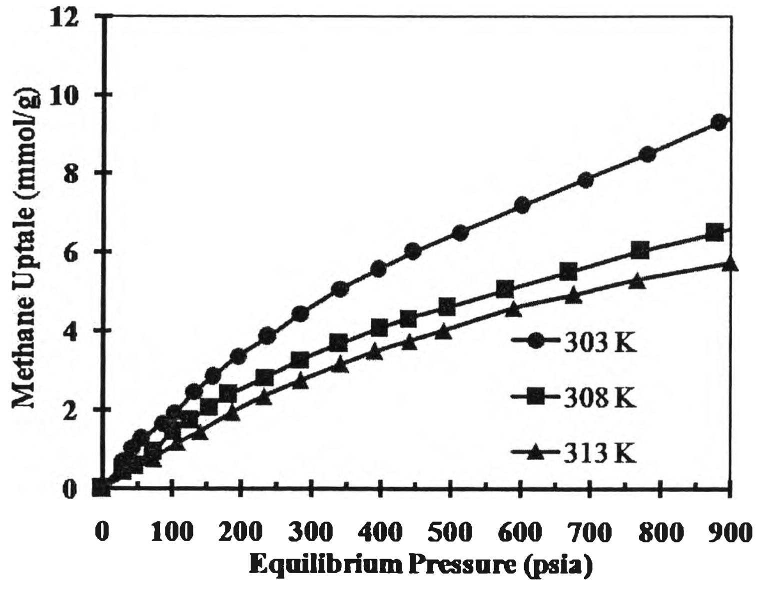

Figure 4.9 The experimental of methane adsorption isotherm from Basolite Z1200

4.3 Methane Adsorption Isotherm Models

The adsorption isotherm model is important to estimate how much methane is adsorbed at various temperatures and to understand adsorption behavior of different adsorbents of interest. In this experiment, 5 adsorption isotherm models; including Langmuir, Freundlich, Sips, Toth, and Unilan isotherm models; were studied.

Tables 4.4 - 4.8 show the isotherm parameters of Langmuir, Freundlich, Sips, Toth and Unilan respectively on the adsorbents used in this study. The isotherm parameters were obtained through nonlinear fitting of experimental data to the model equations.

Table 4.4 Langmuir isotherm parameters for methane adsorption on adsorbents

Langmuir isotherm model				
Adsorbents	Temperature (K)	q_m	b	R^2
Basolite C300	303	14.78	0.00543	0.997
	308	13.64	0.00539	0.997
	313	12.50	0.00535	0.997
Basolite Z1200	303	18.19	0.00109	0.990
	308	14.71	0.00108	0.990
	313	11.22	0.00107	0.990
Calgon	303	6.25	0.00798	0.998
	308	5.65	0.00792	0.998
	313	5.04	0.00785	0.998
Eucalyptus Powder Activated Carbon	303	7.39	0.00554	0.994
	308	6.70	0.00550	0.994
	313	6.01	0.00545	0.994
Coconut Shell Powder Activated Carbon	303	5.96	0.00822	0.994
	308	5.25	0.00816	0.994
	313	4.55	0.00809	0.994
Coconut Shell Granular Activated Carbon	303	7.30	0.00786	0.996
	308	6.32	0.00779	0.996
	313	5.34	0.00773	0.996

Table 4.5 Freundlich isotherm parameters for methane adsorption on adsorbents

Freundlich isotherm model					
Adsorbents	Temperature (K)	q_m	b	n	R^2
Basolite C300	303	284.3	5.02E-07	0.400	0.952
	308	262.5	4.98E-07	0.400	0.952
	313	240.8	4.94E-07	0.400	0.952
Basolite Z1200	303	1.02	0.02769	0.686	0.988
	308	0.82	0.02746	0.686	0.988
	313	0.63	0.02724	0.686	0.988
Calgon	303	1.16	0.14285	0.332	0.982
	308	1.05	0.14169	0.332	0.982
	313	0.94	0.14055	0.332	0.982
Eucalyptus Powder Activated Carbon	303	1.24	0.07291	0.399	0.985
	308	1.13	0.07231	0.399	0.985
	313	1.01	0.07173	0.399	0.985
Coconut Shell Powder Activated Carbon	303	1.13	0.13967	0.333	0.976
	308	0.99	0.13854	0.333	0.976
	313	0.86	0.13743	0.333	0.976
Coconut Shell Granular Activated Carbon	303	1.37	0.13022	0.335	0.966
	308	1.19	0.12915	0.335	0.966
	313	1.01	0.12812	0.335	0.966

Table 4.6 Sips isotherm parameters for methane adsorption on adsorbents

Sips isotherm model					
Adsorbents	Temperature (K)	q_m	b	n	R^2
Basolite C300	303	13.86	6.24E-03	1.130	0.998
	308	12.79	6.19E-03	1.130	0.998
	313	11.73	6.14E-03	1.130	0.998
Basolite Z1200	303	38.98	2.49E-04	0.796	0.990
	308	31.56	2.47E-04	0.796	0.990
	313	24.14	2.45E-04	0.796	0.990
Calgon	303	6.78	6.56E-03	0.852	0.999
	308	6.12	6.50E-03	0.852	0.999
	313	5.47	6.45E-03	0.852	0.999
Eucalyptus Powder Activated Carbon	303	12.14	1.36E-03	0.631	0.996
	308	10.98	1.35E-03	0.631	0.996
	313	9.83	1.34E-03	0.631	0.996
Coconut Shell Powder Activated Carbon	303	6.75	6.02E-03	0.792	0.997
	308	5.96	5.97E-03	0.792	0.997
	313	5.16	5.92E-03	0.792	0.997
Coconut Shell Granular Activated Carbon	303	7.62	7.12E-03	0.914	0.997
	308	6.60	7.06E-03	0.914	0.997
	313	5.58	7.00E-03	0.914	0.997

Table 4.7 Toth isotherm parameters for methane adsorption on adsorbents

Toth isotherm model				
Adsorbents	Temperature (K)	q_m	b	t
Basolite C300	303	12.88	0.00499	1.2829
	308	12.19	0.00495	1.2829
	313	11.53	0.00491	1.2829
Basolite Z1200	303	1322.65	6.34E-05	0.2083
	308	1065.99	6.28E-05	0.2083
	313	817.53	6.23E-05	0.2083
Calgon	303	7.75	0.011603	0.6397
	308	6.93	0.011508	0.6397
	313	6.15	0.011416	0.6397
Eucalyptus Powder Activated Carbon	303	8.94	0.007387	0.6510
	308	8.39	0.007327	0.6510
	313	7.85	0.007268	0.6510
Coconut Shell Powder Activated Carbon	303	17.49	0.088273	0.2491
	308	15.43	0.087554	0.2491
	313	13.43	0.086852	0.2491
Coconut Shell Granular Activated Carbon	303	21.47	0.083547	0.2488
	308	18.62	0.082866	0.2488
	313	15.86	0.082201	0.2488

Table 4.8 Unilan isotherm parameters for methane adsorption on adsorbents

Unilan isotherm model				
Adsorbents	Temperature (K)	q_m	s	b
Basolite C300	303	14.80	0.00543	-4.78E-14
	308	13.62	0.00539	-4.78E-14
	313	12.48	0.00535	-4.78E-14
Basolite Z1200	303	34.14	0.00026	-2.4781
	308	27.48	0.00026	-2.4781
	313	21.04	0.00026	-2.4781
Calgon	303	6.67	0.00686	1.4196
	308	6.01	0.00681	1.4196
	313	5.38	0.00675	1.4196
Eucalyptus Powder Activated Carbon	303	9.42	0.00294	2.2433
	308	8.52	0.00292	2.2433
	313	7.65	0.00289	2.2433
Coconut Shell Powder Activated Carbon	303	6.68	0.00627	1.8588
	308	5.87	0.00622	1.8588
	313	5.10	0.00617	1.8588
Coconut Shell Granular Activated Carbon	303	32.77	2.38E-06	-10.178
	308	28.89	2.37E-06	-10.178
	313	25.14	2.35E-06	-10.178

From the Figure 4.10 - 4.15 and Figure B1 - B24 from Appendix B, It can be concluded that Sips isotherm model is the best model to explain the adsorption behavior of methane on adsorbents. Sips isotherm model is applicable for heterogeneous adsorption systems. Balathanigaimani *et al.* (2003) reported that the activated carbon has heterogeneous surface. Foo *et al.* (2010) indicated that Sips isotherm model can well describe the behavior of many hydrocarbons adsorbed on activated carbon.

Figures 4.10 - 4.15 show the methane adsorption on different adsorbents from the experiment and Sips isotherm model. The symbols represent the experimental data while the lines represent Sips isotherm model which can fit all experimental data very well. The experimental data show the nonlinearity, which is the characteristic of both activated carbons (Balathanigaimani *et al.*, 2003) and MOFs.

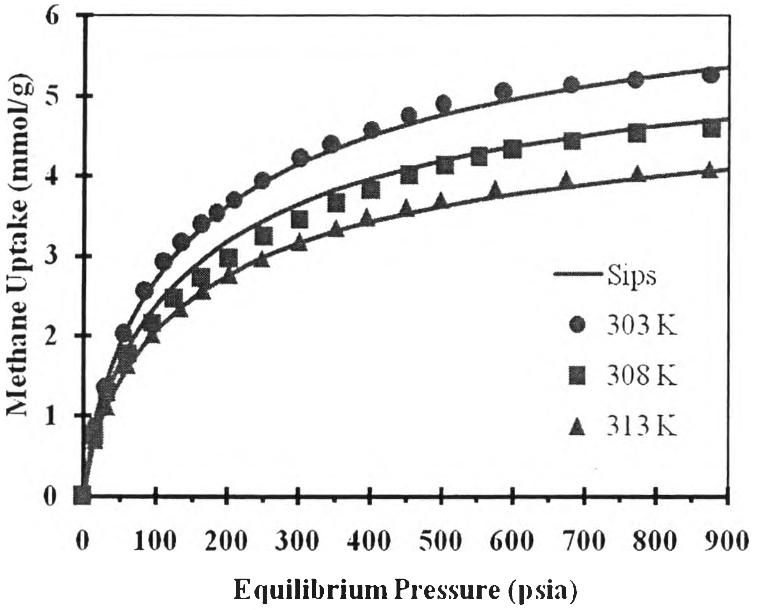

Figure 4.10 Methane adsorption on Coconut Shell Powder Activated Carbon. Symbols represent the experimental data while lines represent Sips isotherm model data.

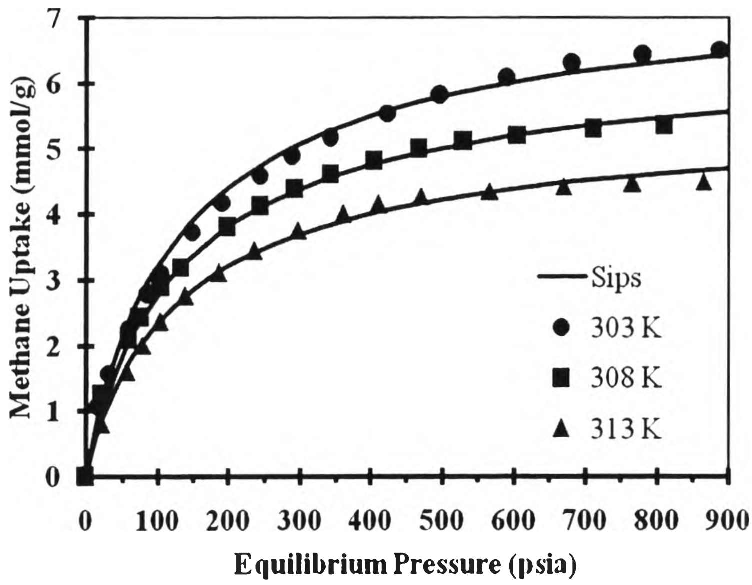

Figure 4.11 Methane adsorption on Coconut Shell Granular Activated Carbon. Symbols represent the experimental data while lines represent Sips isotherm model data.

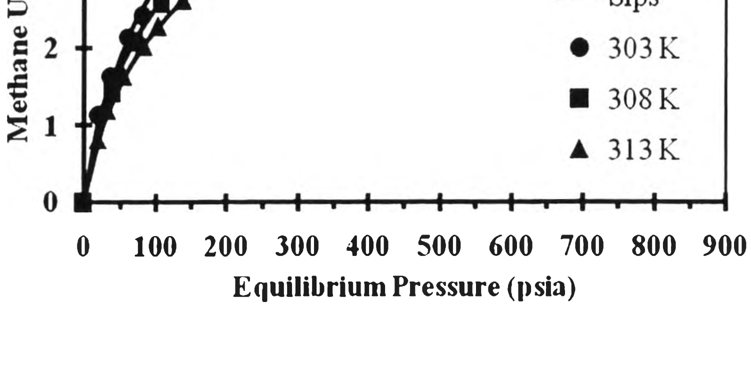

Figure 4.12 Methane adsorption on Calgon (20-40 meshes). Symbols represent the experimental data while lines represent Sips isotherm model data.

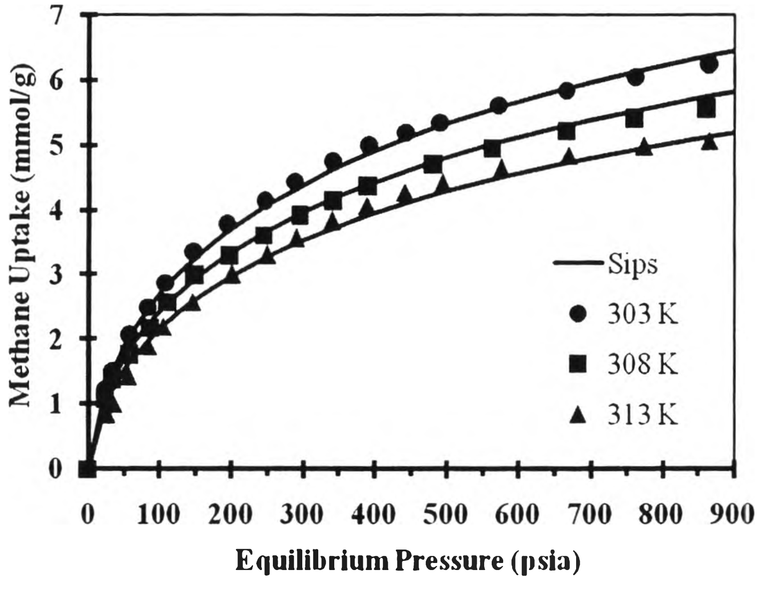

Figure 4.13 Methane adsorption on Eucalyptus Powder Activated Carbon. Symbols represent the experimental data while lines represent Sips isotherm model data.

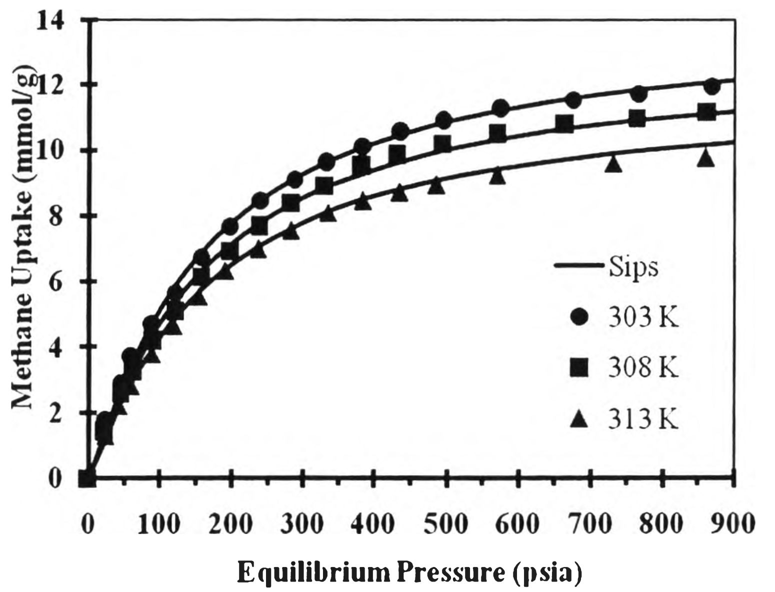

Figure 4.14 Methane adsorption on Basolite C300. Symbols represent the experimental data while lines represent Sips isotherm model data.

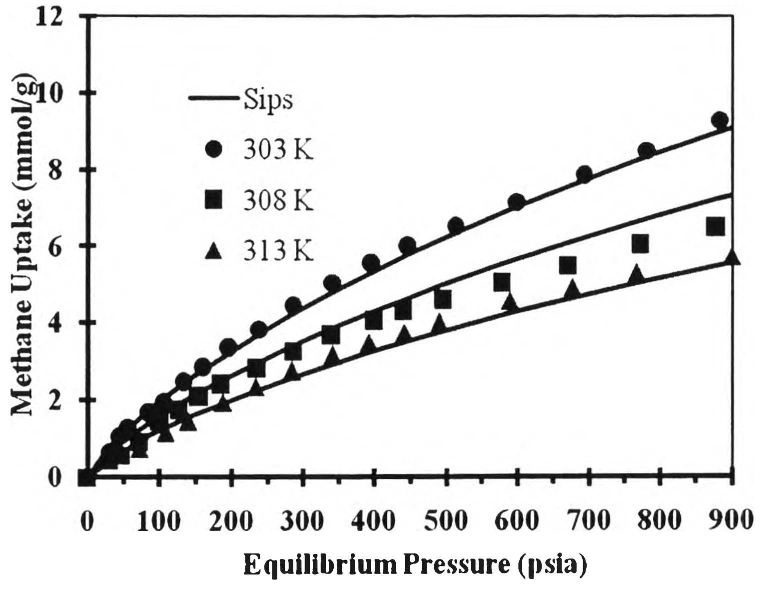

Figure 4.15 Methane adsorption on Basolite Z1200. Symbols represent the experimental data while lines represent Sips isotherm model data.