CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorbent Characterization

PEI with difference molecular weights, which were low molecular weight PEI (Low Mw PEI, Mw = 2,000), medium molecular weight PEI (Med Mw PEI, Mw = 25,000), and high molecular weight PEI (High Mw PEI, Mw = 600,000-1,000,000), were impregnated on activated carbons (ACs). The amounts of PEI impregnated on ACs were determined by UV-Vis spectroscopy. The concentrations of PEI solutions were measured using absorbance at 203 nm. According to Beer-Lambert law, a calibration curve was constructed by absorbance at different PEI concentrations. The absorbance of the PEI solutions, which was filtered after impregnation, was measured and calculated to the final concentration. Table 4.1 shows the amounts of PEI impregnated on ACs.

Table 4.1 Amounts of PEI impregnated on ACs

Initial concentration of PEI solution (g/L)		PEI impregnated on activated carbon (wt% PEI)
Low Mw PEI	1.0	1.68
	2.5	2.18
	5.0	2.84
Med Mw PEI	1.0	0.73
	2.5	1.16
	5.0	1.90
High Mw PEI	1.0	0.16
	2.5	0.45
	5.0	0.86

Interestingly, the higher concentration of the PEI solution increased the amount of impregnated PEI due to the increased driving force (concentration gradient) of diffusion in the impregnation step. It can also be seen that the Low Mw PEI can be impregnated on the ACs more than the other PEIs at the same initial PEI concentration because the Low Mw PEI has smaller molecular size than the others, which can easily diffuse and easily be impregnated on the ACs.

The thermal stability of the adsorbents was investigated by thermogravimetric and differential thermal analysis (TG-DTA). The thermograms of the adsorbents are shown in Figures 4.1 – 4.7. Figure 4.1 shows the thermogram of the AC with one step weight loss due to the removal of volatile and moisture. Furthermore, the AC continues to be degraded or carbonized till 1,000 °C but cannot be detected as a step of weight loss due to the slight change in the weight loss and heat flow. From Figures 4.2 – 4.7, the thermograms show the weight loss in two steps. The first step is below 100 °C, which is from the desorption of volatile and moisture. The second step is around 250 °C, which is from the PEI degradation.

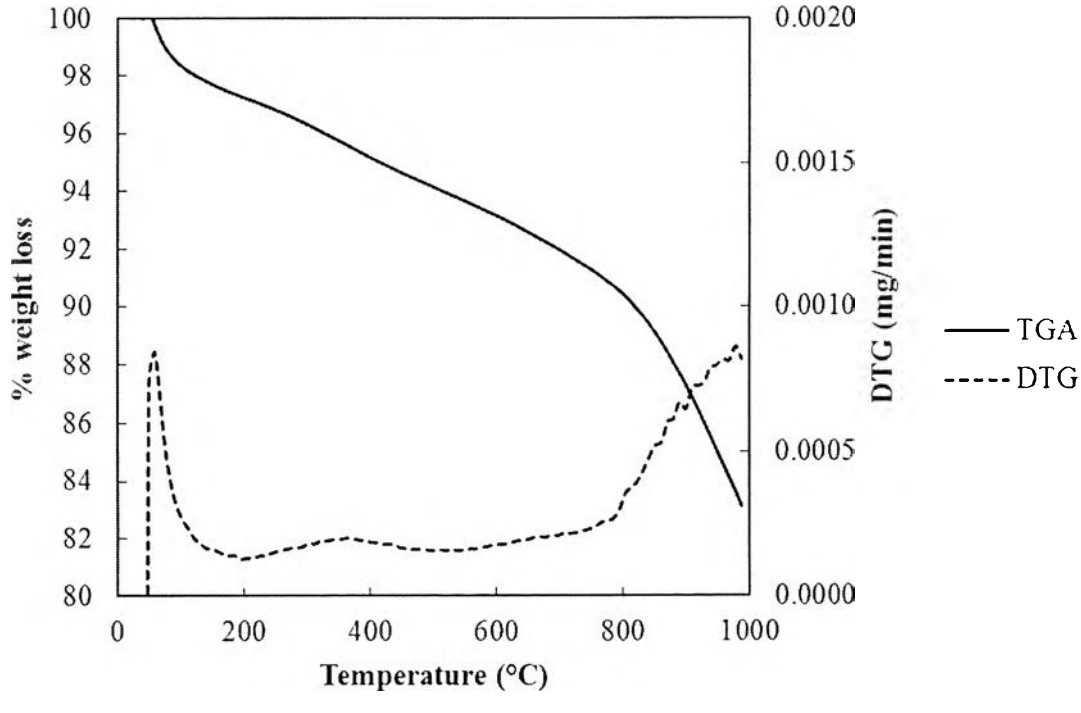

Figure 4.1 TGA and DTG thermogram of the AC.

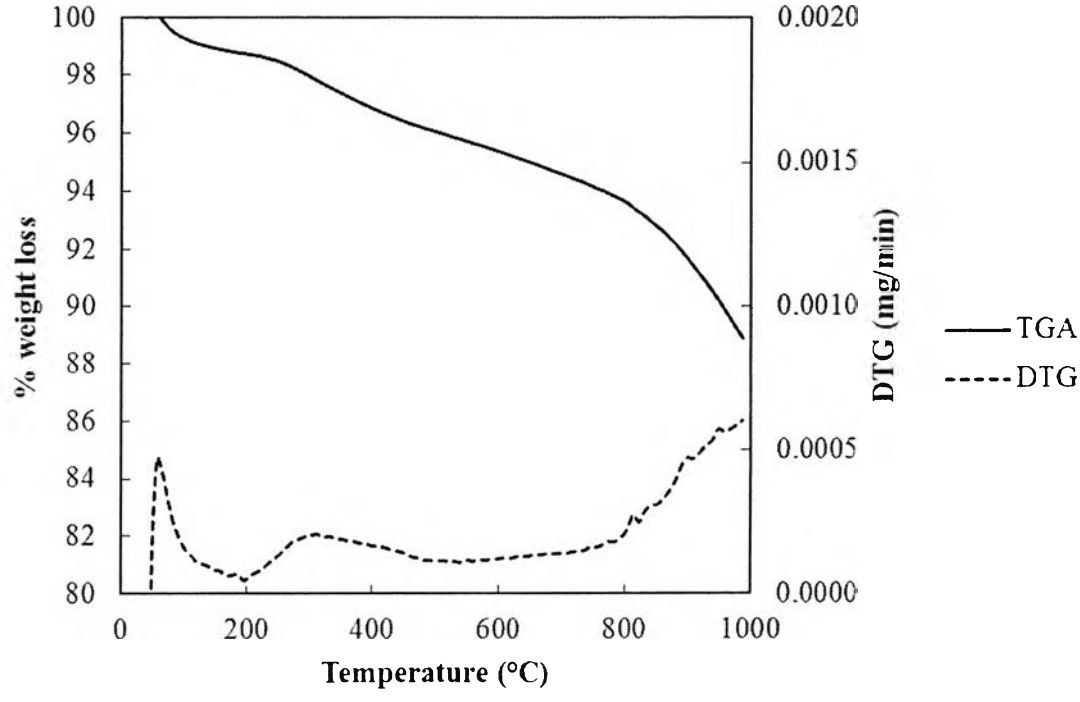

Figure 4.2 TGA and DTG thermogram of the 1.68 wt% Low Mw PEI/AC.

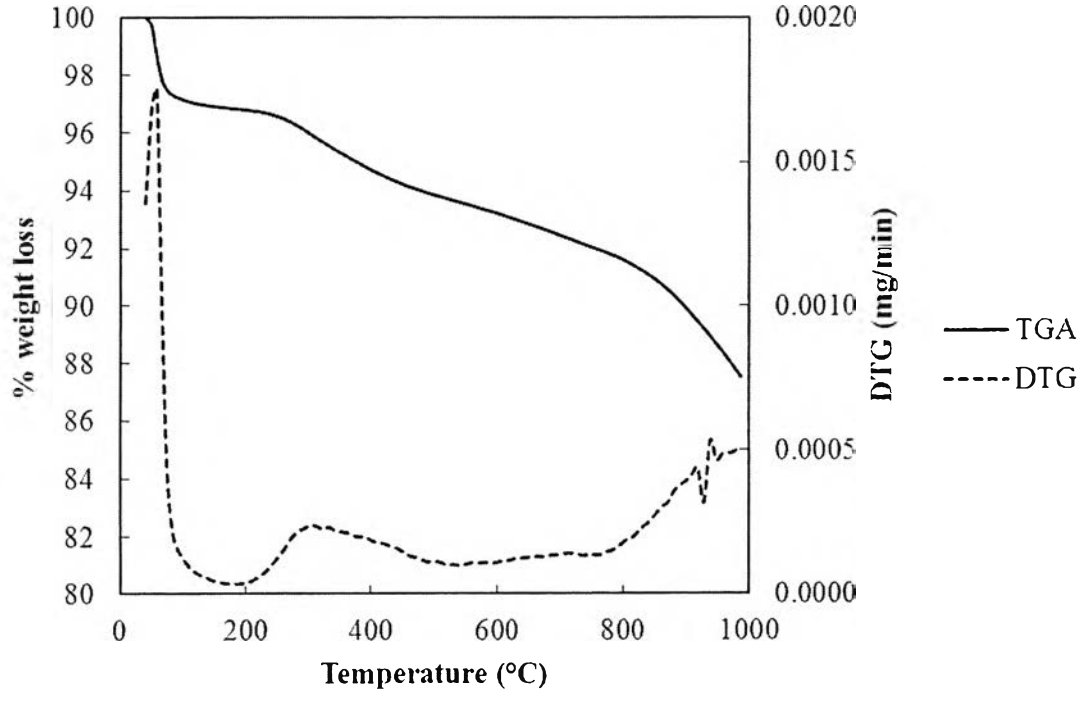

Figure 4.3 TGA and DTG thermogram of the 2.84 wt% Low Mw PEI/AC.

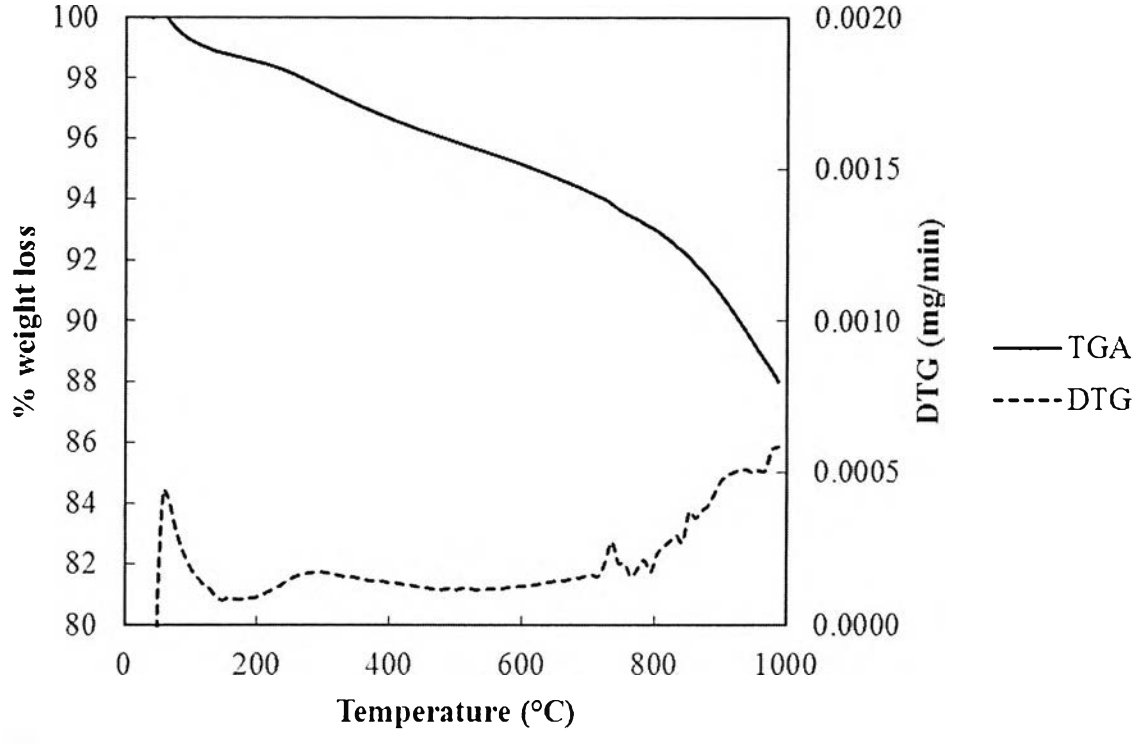

Figure 4.4 TGA and DTG thermogram of the 0.73 wt% Med Mw PEI/AC.

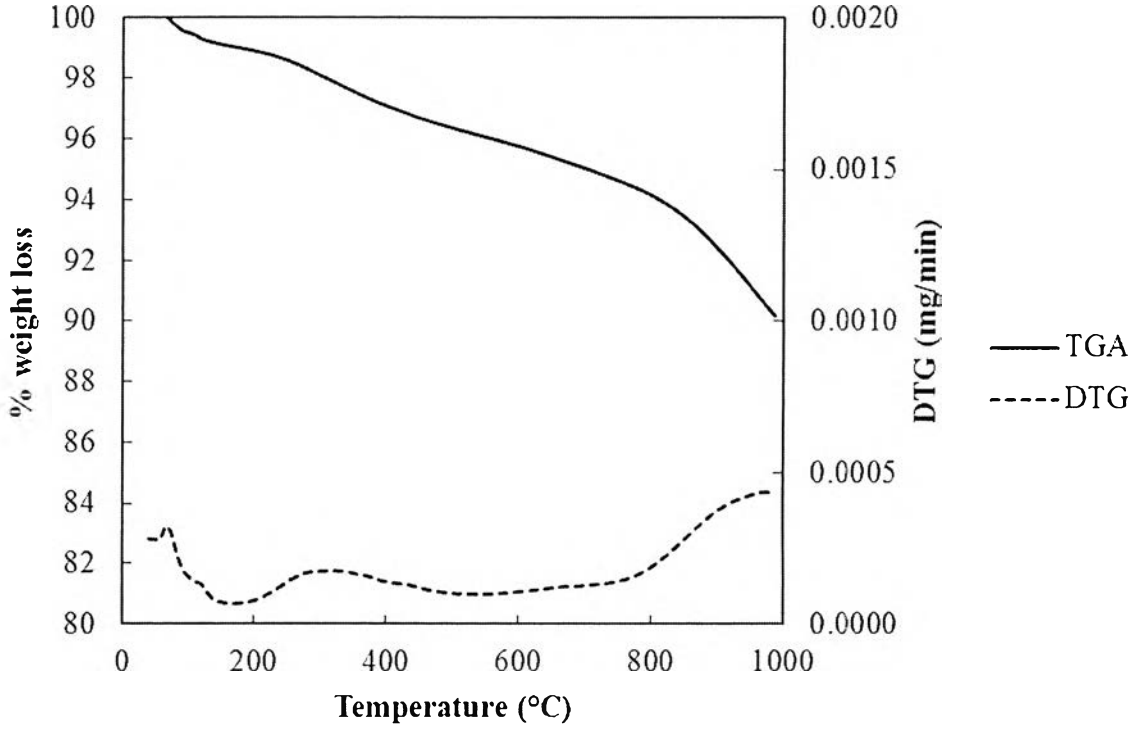

Figure 4.5 TGA and DTG thermogram of the 1.90 wt% Med Mw PEI/AC.

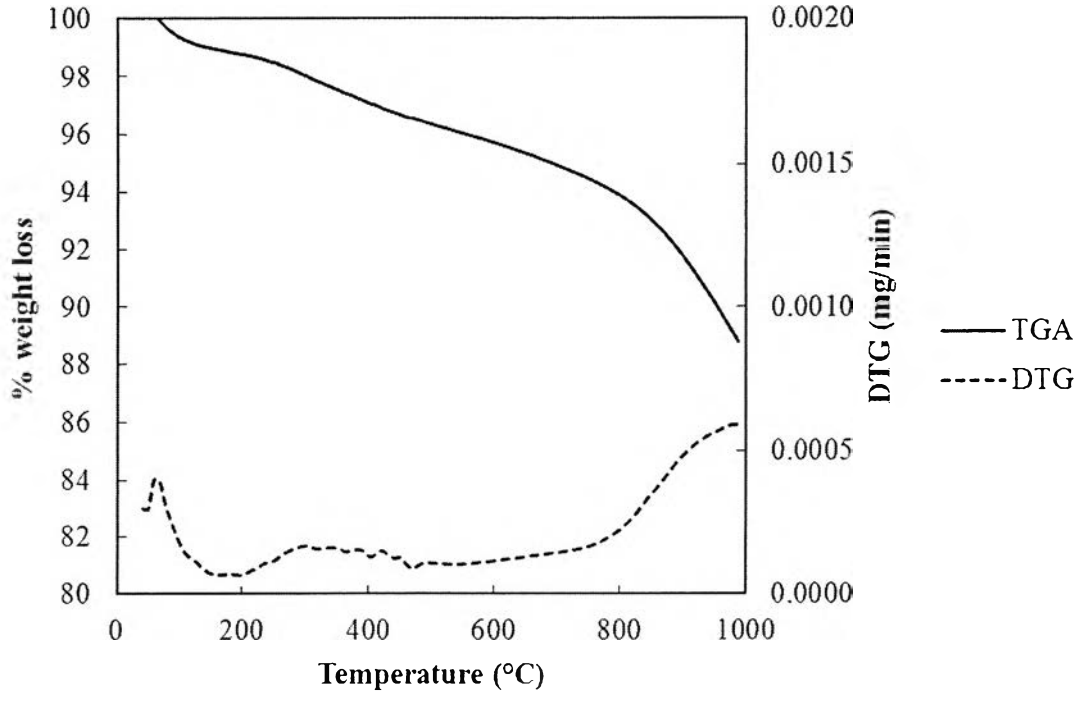

Figure 4.6 TGA and DTG thermogram of the 0.16 wt% High Mw PEI/AC.

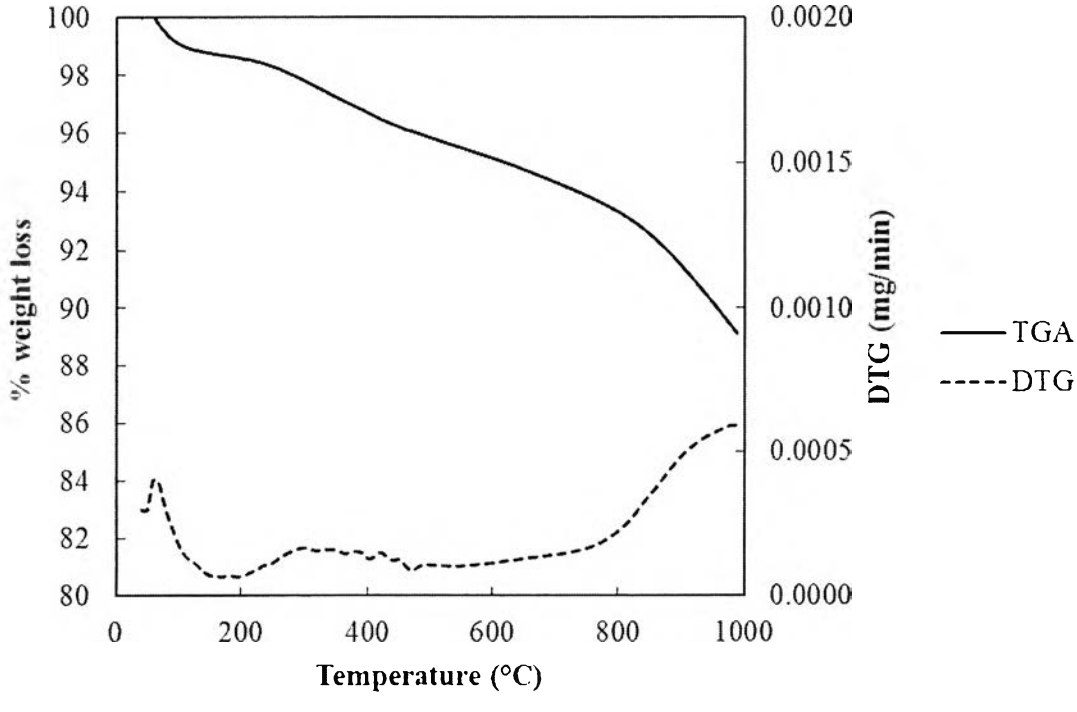

Figure 4.7 TGA and DTG thermogram of the 0.86 wt% High Mw PEI/AC.

Table 4.2 TGA results of the adsorbents

Adsorbent	Step of weight loss	% Weight loss	Weight loss temperature (°C)	
			Onset	Endset
Activated Carbon (AC)	1st	1.57	47.53	72.28
1.68 wt% Low Mw PEI/AC	1st	1.25	48.62	85.25
	2nd	1.77	266.48	372.70
2.84 wt% Low Mw PEI/AC	1st	3.24	45.93	70.23
	2nd	2.11	271.81	379.16
0.73 wt% Med Mw PEI/AC	1st	1.27	49.15	86.45
	2nd	1.48	244.69	364.81
1.90 wt% Med Mw PEI/AC	1st	1.03	53.00	90.96
	2nd	1.82	238.47	407.58
0.16 wt% High Mw PEI/AC	1st	1.33	47.63	90.54
	2nd	2.12	221.84	444.89
0.86 wt% High Mw PEI/AC	1st	1.50	48.26	89.18
	2nd	2.28	253.84	457.49

The summary data from the TGA results is presented in Table 4.2. It shows the temperatures of the weight loss of each sample are about the same. However, the TG-DTA is not a good technique to determine the amount of PEI impregnated on the AC because the PEI and AC are degraded in the same temperature range, and the results may not be accurate.

The functional groups in the adsorbents were detected by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of all adsorbents are shown in Figure 4.8. The wavelength at around 1,480 cm^{-1} shows the signal of N-H bond,

which could represent the N-H functional group in the PEI structure and also the AC structure. In addition, the band of C-N stretching can be absorbed at around 1,100 cm^{-1}. The presence of weak peaks between 2,800 – 2,950 cm^{-1} represents the C-H stretching of CH_2 in the PEI molecule. At 1550 cm^{-1}, the band represents the C=C bending of aromatics in the AC.

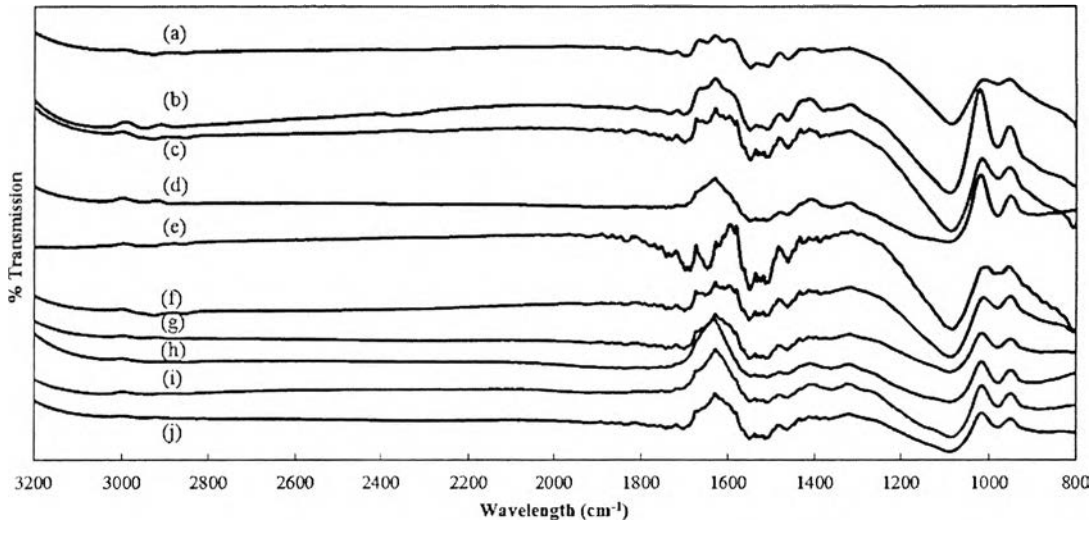

Figure 4.8 FTIR Spectra of the (a) AC, (b)-(d) 1.68, 2.18, and 2.84 wt% Low Mw PEI/AC, (e)-(g) 0.73, 1.16, and 1.90 wt% Med Mw PEI/AC, and (h)-(j) 0.16, 0.45, and 0.86 wt% High Mw PEI/AC.

The ACs and PEI impregnated ACs were characterized by surface area and pore size analysis. Surface area, pore volume, and pore diameter of the adsorbents are shown in Table 4.3. The results show that the impregnation of PEI on the ACs changes the surface properties and porosity. The surface area and pore volume decrease with the increase in the amount of PEI with all molecular weights. It can be explained that, as the High Mw PEI has larger molecular size than the other PEI samples, the PEI tends to entangle between itself much easier, which, in turn, results in the significant surface area reduction of the ACs impregnated with the PEI. However, it should be noted that the High Mw PEI results in the surface area reduction in a greater extent compared to the other two PEIs. Surprisingly, the pore diameter is hardly affected with the impregnation. It is likely that the molecular sizes

of the Low Mw, Med Mw, and High Mw PEI are larger than the micropore and could not diffuse through the AC micropore. Yin *et al.* (2008) described that PEI, which has molecular weight more than 600, cannot fill into the micropore that is smaller than 2 nm.

Table 4.3 Surface area, pore volume, and pore diameter of adsorbents

Adsorbent	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore Diameter (Å)
Activated Carbon (AC)	996	0.4985	8.52
1.68 wt% Low Mw PEI/AC	913	0.4564	8.52
2.18 wt% Low Mw PEI/AC	810	0.4090	8.52
2.84 wt% Low Mw PEI/AC	803	0.4030	8.52
0.73 wt% Med Mw PEI/AC	907	0.4538	8.52
1.16 wt% Med Mw PEI/AC	877	0.4383	8.52
1.90 wt% Med Mw PEI/AC	840	0.4214	8.52
0.16 wt% High Mw PEI/AC	902	0.4534	8.52
0.45 wt% High Mw PEI/AC	890	0.4479	8.52
0.86 wt% High Mw PEI/AC	869	0.4347	8.52

Nitrogen adsorption was a common technique to characterize porous materials. The adsorption isotherms could describe a type of material. Nitrogen isotherms of the adsorbents are shown in Figure 4.9. The result shows that 70% of pore volume is filled below $P/P^0 = 0.1$ in all adsorbents. This indicates that all the adsorbents are highly microporous materials. In addition, the adsorbents show the IUPAC type I or Langmuir isotherm.

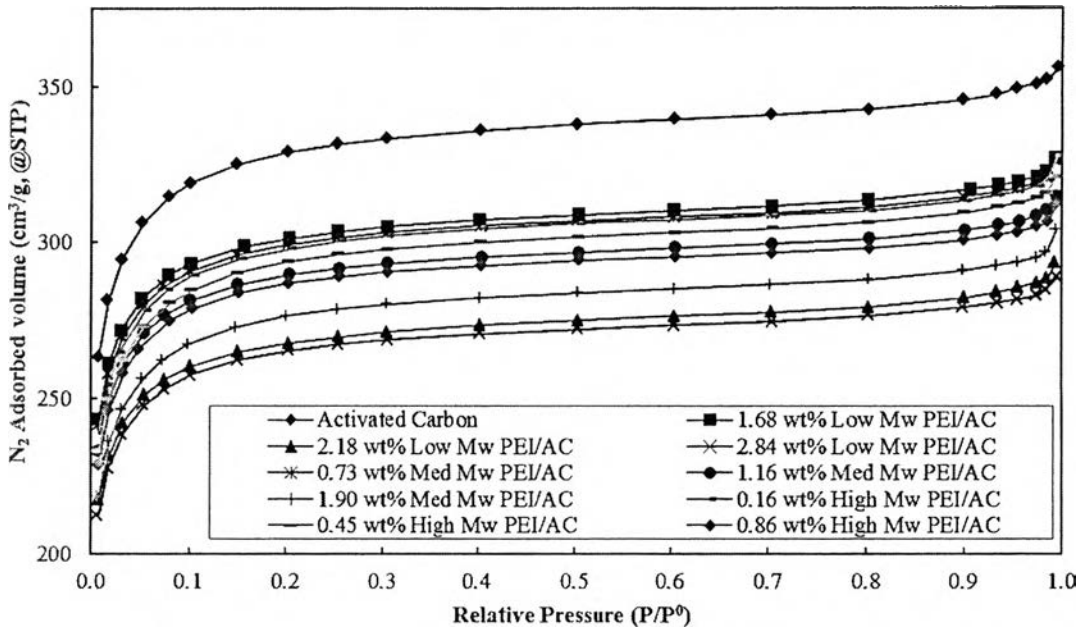

Figure 4.9 Nitrogen adsorption isotherms of adsorbents at -196 °C.

4.2 Effects of PEI Loading on CO_2 Adsorption

CO_2 adsorption isotherms were constructed at 30, 50 and 75 °C as shown in Figures 4.10 – 4.12, 4.13 – 4.15, and 4.16 – 4.18, respectively. At 30 °C (Figures 4.10 – 4.12), the AC has the CO_2 adsorption capacity of 2.75 mmol/g adsorbent at 1 atm. The addition of Low Mw PEI and Med Mw PEI significantly improves the CO_2 adsorption capacity. At the low temperature, chemical reactions between the amine group and CO_2 are not preferred but it could be proposed that the PEI provides the acid-base interaction between its amine group and CO_2 and synergizes with the physisorption to increase the CO_2 adsorption capacity. The impregnation of the High Mw PEI also shows the increase in the capacity but the 0.86 %wt High Mw PEI/AC shows lower capacity near 1 atm. It may be described that the High Mw PEI has lower CO_2 accessibility to the amine group. Too high a loading of PEI decreases the capacity because it decreases the surface area and physisorption. A balance between the chemisorption and physisorption is needed for the increase in the CO_2 adsorption capacity. At 30 °C, the 1.68 wt% Low Mw PEI and 0.73 wt% Med Mw PEI have the

highest CO_2 adsorption capacity, which are 3.02 and 3.08 mmol/g adsorbent, respectively.

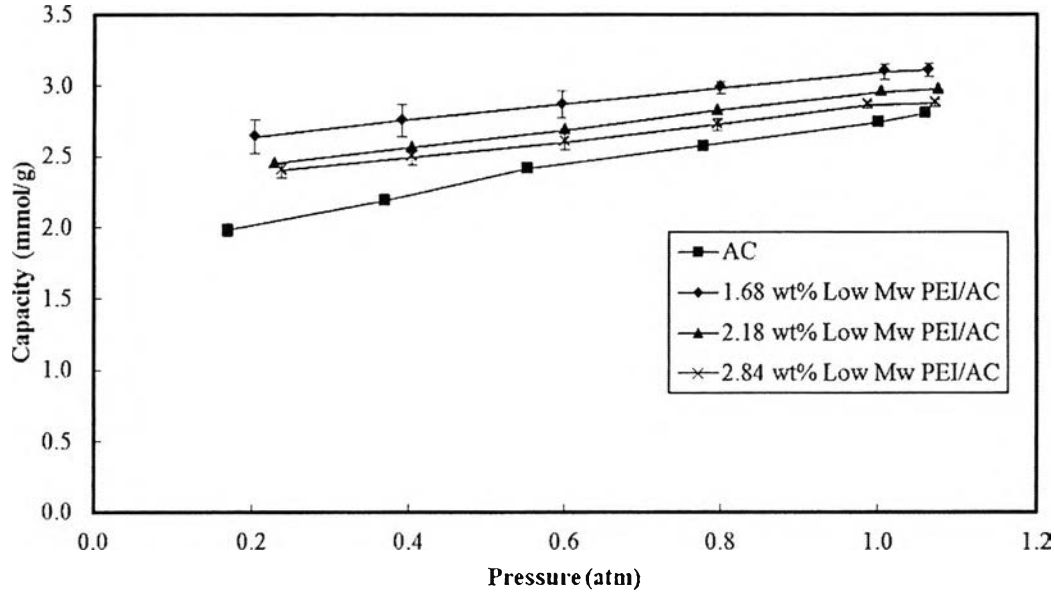

Figure 4.10 CO_2 adsorption isotherms of the AC and Low Mw PEI/ACs at 30 °C.

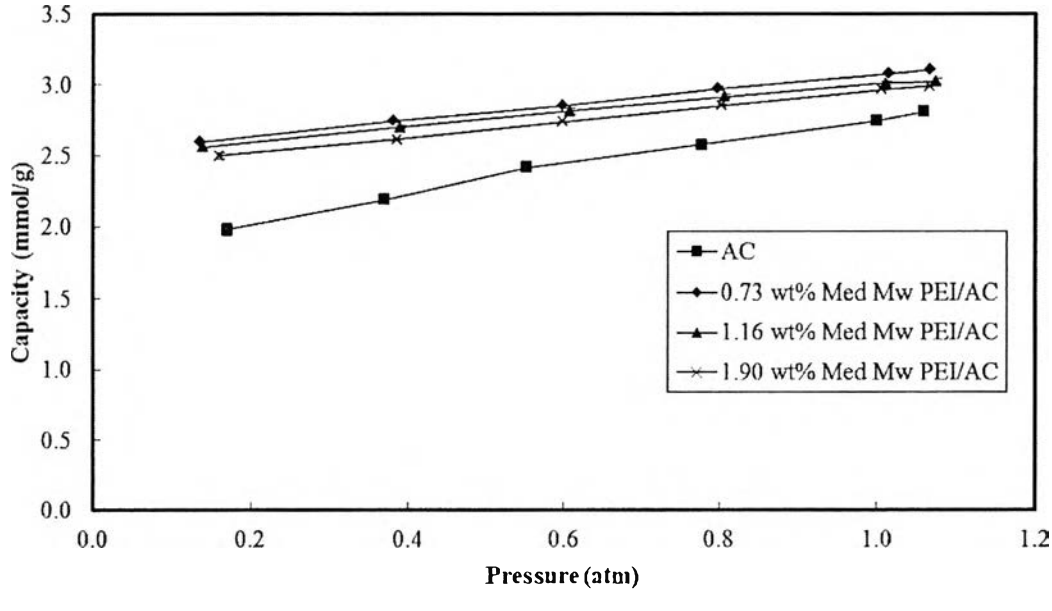

Figure 4.11 CO_2 adsorption isotherms of the AC and Med Mw PEI/ACs at 30 °C.

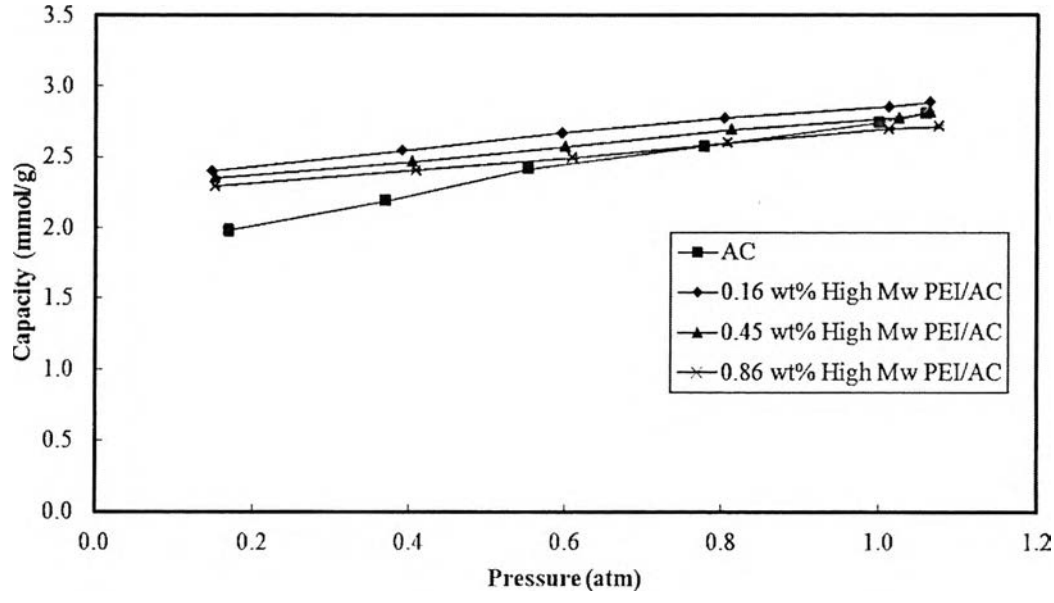

Figure 4.12 CO_2 adsorption isotherms of the AC and High Mw PEI/ACs at 30 °C.

At 50 °C (Figures 4.13 – 4.15), the AC has the CO_2 adsorption capacity of 2.00 mmol/g adsorbent at 1 atm. The addition of Low Mw, Med Mw, and High Mw PEI increases the capacity because the chemical reaction is more favorable at higher temperature. Too high a loading of PEI decreases the capacity because it decreases the surface area and physisorption. At 50 °C, the 1.68 wt% Low Mw PEI and 0.16 wt% High Mw PEI have the highest CO_2 adsorption capacity, which are the same at 2.13 mmol/g adsorbent.

At 75 °C (Figures 4.16 – 4.18), the AC has the CO_2 adsorption capacity of 1.29 mmol/g adsorbent at 1 atm. Even the chemisorption is favorable at the high temperature, the Low Mw PEI/ACs have lower CO_2 adsorption capacity than the unmodified AC. The decrease in the capacity may be due to the relaxation of PEI molecules at the high temperature leading to the decrease in the density of amine per area. Although the relaxation of PEI is the cause of the reduction in the density of amine per area, the Med Mw PEI/ACs and High Mw PEI/ACs have larger molecular size than the Low Mw PEI and tend to entangle between itself much easier. Therefore, the decrease in the amine density is not so significant. Hence, the Med Mw PEI/ACs and High Mw PEI/ACs show the increase in the capacity. Another reason for the increase in the capacity of the Med Mw PEI/ACs and High Mw

PEI/ACs is that the higher temperature also increases the polymer flexibility that provides higher CO_2 accessibility. At 75 °C, the capacity of all Med Mw PEI/ACs is about the same at 1.35 mmol/g adsorbent at 1 atm. That can be explained that the increase in the pressure can drive CO_2 to the PEI bulk easier and the balance of chemisorption and physisorption of the Med Mw PEI/ACs may not be different in a significant degree. The 0.45 %wt High Mw PEI/AC has the highest CO_2 adsorption capacity, which is 1.33 mmol/g adsorbent. That may be due to the appropriate amount of High Mw PEI and the suitable balance between CO_2 accessibility and density of amine group per area.

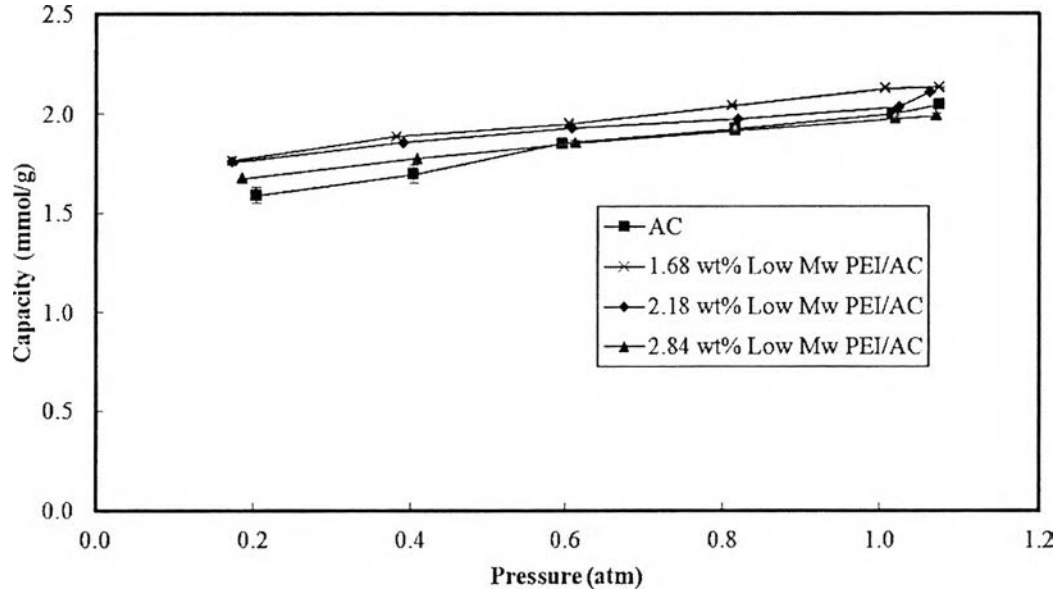

Figure 4.13 CO_2 adsorption isotherms of the AC and Low Mw PEI/ACs at 50 °C.

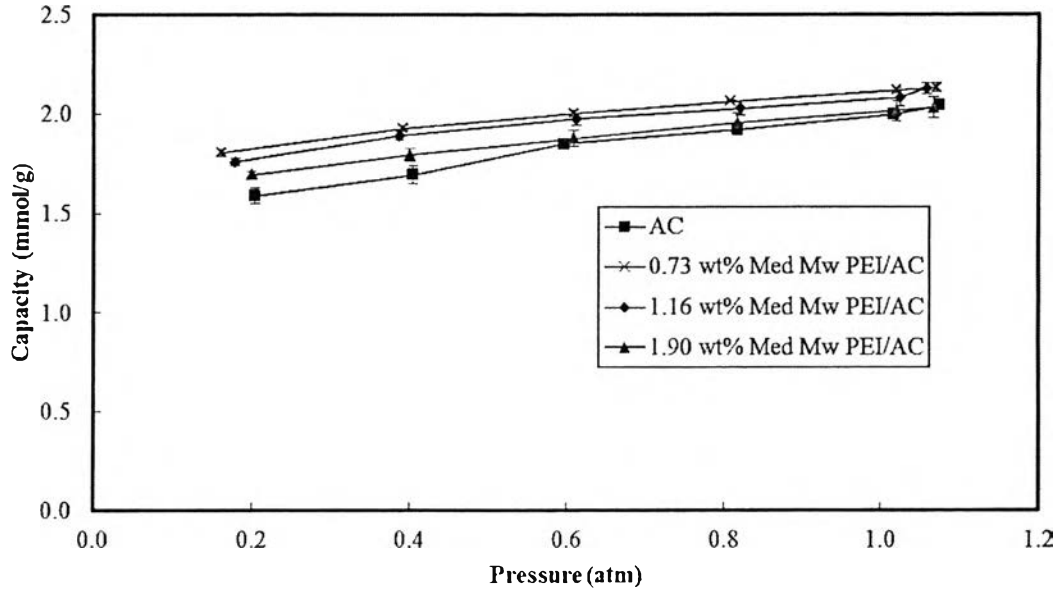

Figure 4.14 CO_2 adsorption isotherms of the AC and Med Mw PEI/ACs at 50 °C.

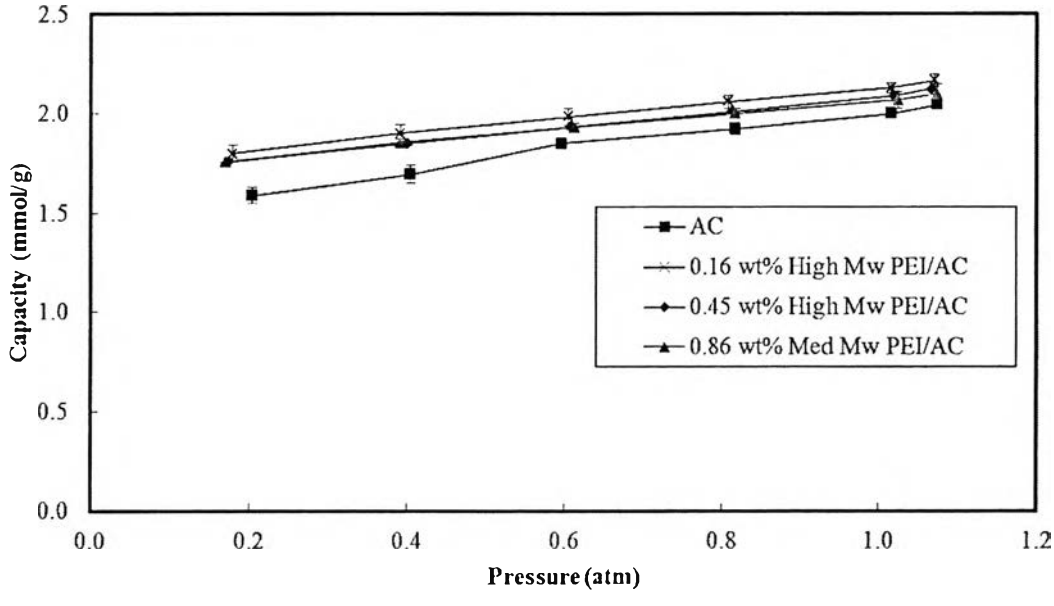

Figure 4.15 CO_2 adsorption isotherms of the AC and High Mw PEI/ACs at 50 °C.

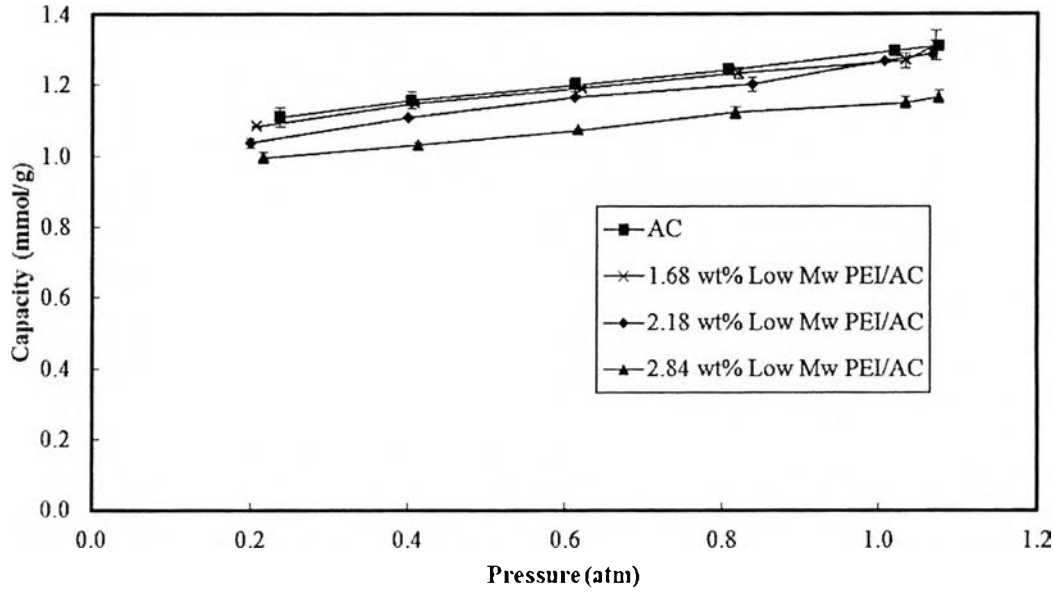

Figure 4.16 CO_2 adsorption isotherms of the AC and Low Mw PEI/ACs at 75 °C.

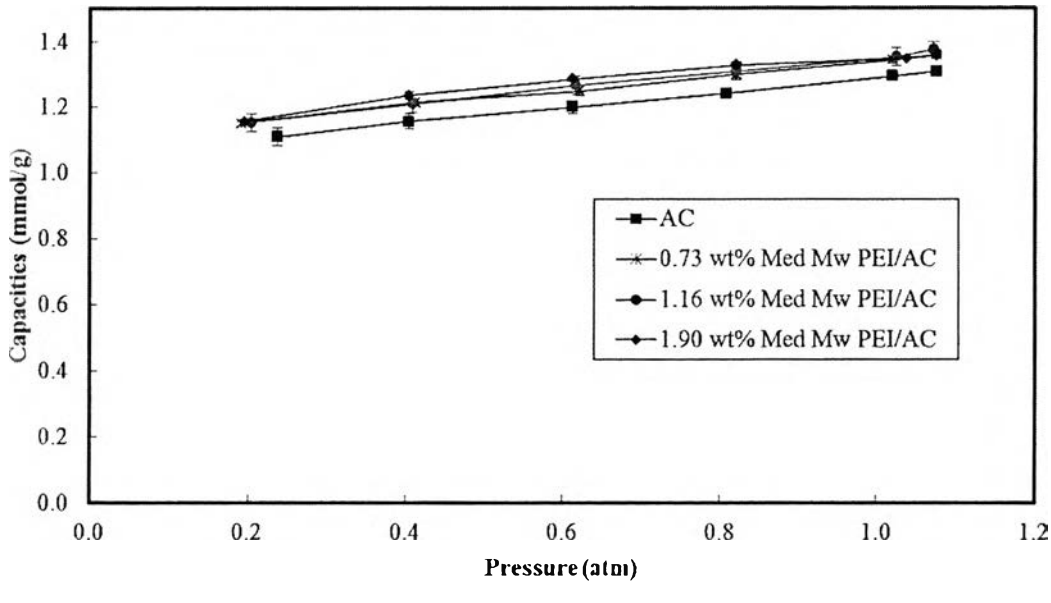

Figure 4.17 CO_2 adsorption isotherms of the AC and Med Mw PEI/ACs at 75 °C.

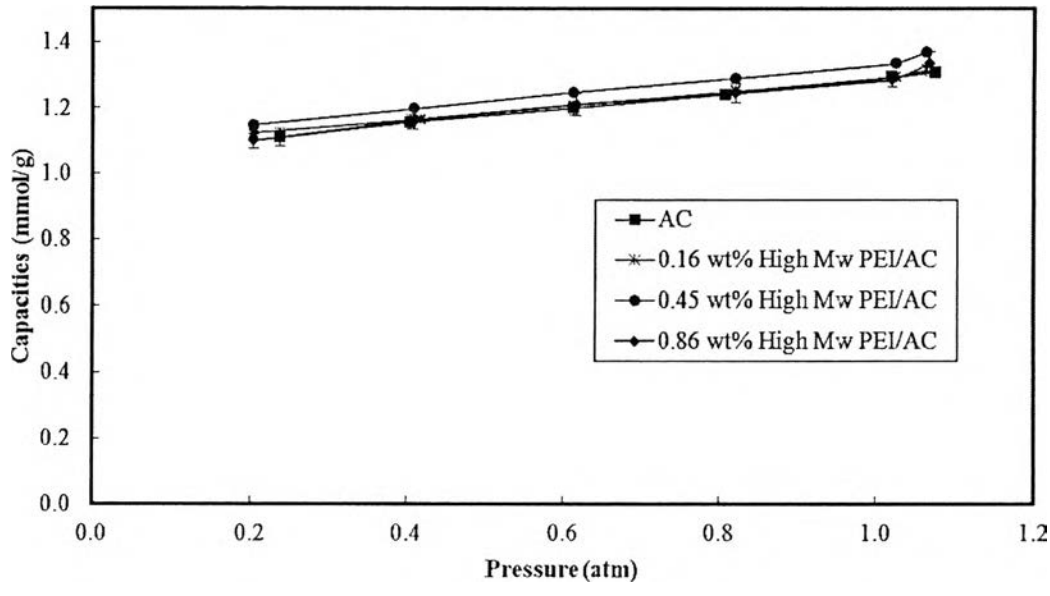

Figure 4.18 CO_2 adsorption isotherms of the AC and High Mw PEI/ACs at 75 °C.

4.3 Effects of Temperature on CO_2 Adsorption

CO_2 adsorption isotherms of the AC were constructed at 30, 50, and 75 °C as shown in Figure 4.19. The AC has the CO_2 adsorption capacity of 2.75, 2.20, and 1.29 mmol/g adsorbent at 30, 50, and 75 °C, respectively. For the unmodified AC, the increase in the adsorption temperature reduces the CO_2 adsorption capacity because the physisorption of the AC is exothermic phenomenon or not favorable at the high adsorption temperature.

For the Low Mw PEI/AC (Figures 4.10, 4.13, and 4.16), it can be observed that the capacity decreases because the physisorption is not favorable at the higher adsorption temperature. The trends of the Low Mw PEI/AC at 30 and 50 °C are similar because the addition of the PEI can enhance the CO_2 adsorption capacity by synergistic effect between the physisorption and chemisorption. Even the chemisorption is favorable at the high temperature, the Low Mw PEI/AC shows the decrease in the capacity at 75 °C. It can be described that the relaxation of the Low Mw PEI molecules at the higher temperature leads to the decrease in the density of amine per area. Figure 4.20 is a simplified model of the Low Mw PEI polymer chain behavior at the low and high adsorption temperatures. At the low temperature, the

polymer chain of Low Mw PEI is randomly coiled. In this state, the PEI bulk has low CO_2 accessibility and high amine density on the polymer chain stays packed. When the temperature is increased, the polymer chain is more flexible due to the increase in the energy. That results in the higher CO_2 accessibility to the PEI bulk and lower amine density per area.

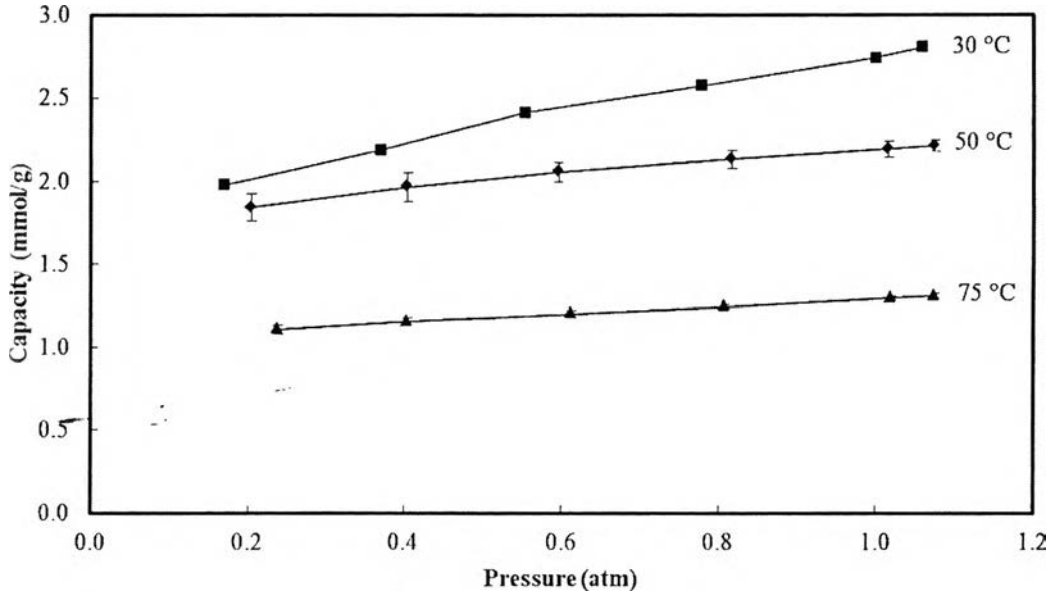

Figure 4.19 CO_2 adsorption isotherms of the AC at 30, 50, and 75 °C.

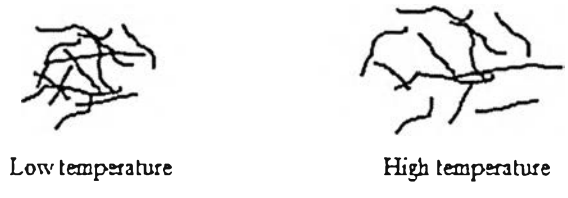

Figure 4.20 Proposed model of Low Mw PEI behavior at low and high temperatures.

For the Med Mw PEI/AC (Figures 4.11, 4.14, and 4.17), it can be observed that the capacity decreases because the physisorption is not favorable at the higher adsorption temperature. The CO_2 adsorption trends of the Med Mw PEI/AC at 30, 50, and 75 °C are similar because the addition of the PEI can enhance the CO_2 adsorption capacity by synergistic effect between the physisorption and chemisorption. The trend of the Med Mw PEI/AC is opposite from the trend of the

Low Mw PEI/AC at 75 °C. It can be explained by Figure 4.21. Similar to the Low Mw PEI, an increase in the temperature leads to the relaxation state of PEI but the Med Mw PEI has more entanglement between the polymer chains due to its large molecular size. The entanglement restricts the polymer chain motion resulting in the relatively constant amine density per area of Med Mw PEI.

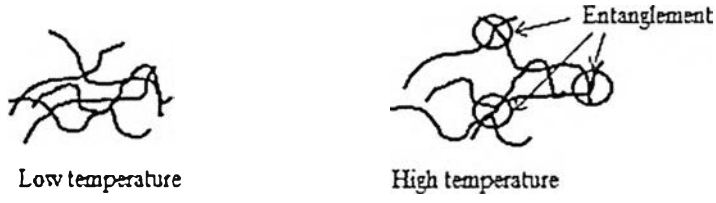

Figure 4.21 Proposed model of Med Mw PEI behavior at low and high temperatures.

For the High Mw PEI/AC (Figures 4.12, 4.15, and 4.18), it can be observed that the capacity decreases because the physisorption is not favorable at the higher adsorption temperature. At 30 °C, the addition of High Mw PEI increases the capacity. Too high a loading of PEI decreases the capacity because it decreases the surface area and physisorption. Furthermore, the High Mw PEI has low CO_2 accessibility leading to the lower capacity. At 50 °C, the High Mw PEI/AC still shows the increase in the capacity because the chemisorption is more favorable. In addition, the situation is similar to the Med Mw PEI case. At 75 °C, the increase in the loading should result in the enhancement of CO_2 adsorption due to the increase in the amine functional group and favorable chemisorption. However, too high a loading can decrease the capacity with the same reason. Another reason for the decrease in the capacity is explained by Figure 4.22. Again, the same reason mentioned above on the restriction of polymer motion due to the entanglement is applicable. In addition, the High Mw PEI has the largest molecular size among the PEIs leading to plenty of entanglements. However, many entanglements result in low CO_2 accessibility.

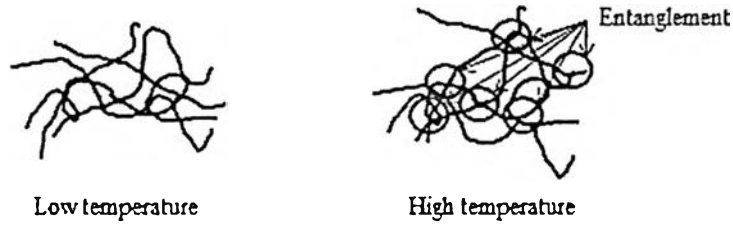

Figure 4.22 Proposed model of High Mw PEI behavior at low and high temperatures.

4.4 CO_2 Adsorption after Regeneration

The good adsorbents should not only have high capacity, selectivity, and fast kinetics. The regeneration with relatively constant adsorption performance also needs to be considered. After the adsorbent saturates with CO_2, the regeneration is needed to remove CO_2 from adsorbent. The TGA results (Figures 4.1 – 4.7 and Table 4.2) show that the desorption of volatile and adsorbed gas is achieved in the range of 100 - 200 °C without the degradation of the AC and PEI. Therefore, the regeneration temperature of 120 °C was chosen to ensure that the volatile and adsorbed gas are completely desorbed, and the structures of the AC and PEI are not destroyed. Figures 4.23 – 4.26 illustrate the adsorption capacity of the fresh and regenerated adsorbents. From Figures 4.23 and 4.25, the AC shows a slight change in the adsorption capacity after regeneration. This indicates the desorption of CO_2 can be achieved at 120 °C. Figures 4.24 and 4.26 show that the PEI/AC still possesses adsorption capacity with no significant change. Table 4.4 shows the surface area of the fresh and regenerated adsorbents. The surface area of regenerated adsorbent is relatively constant compared to the fresh adsorbent.

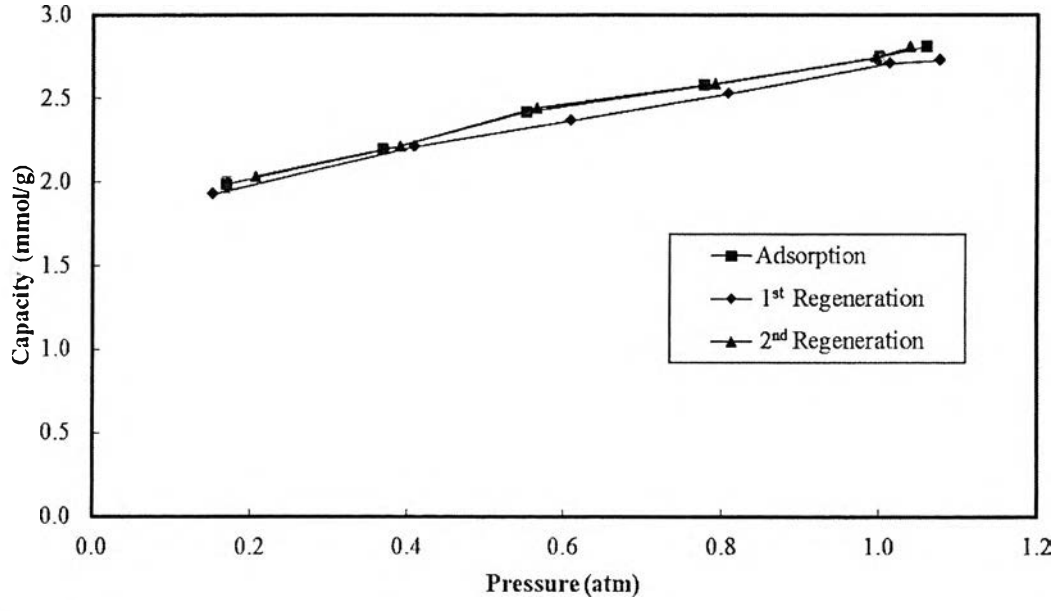

Figure 4.23 CO_2 adsorption isotherms at 30 °C of the AC and the regenerated AC.

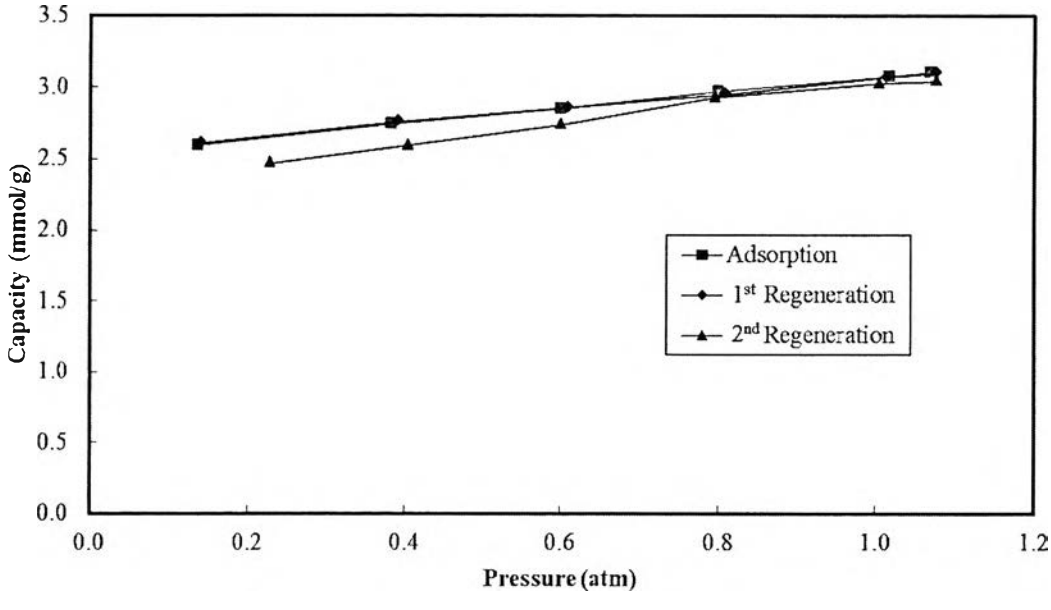

Figure 4.24 CO_2 adsorption isotherms at 30 °C of the 0.73 wt% Med Mw PEI and the regenerated sample.

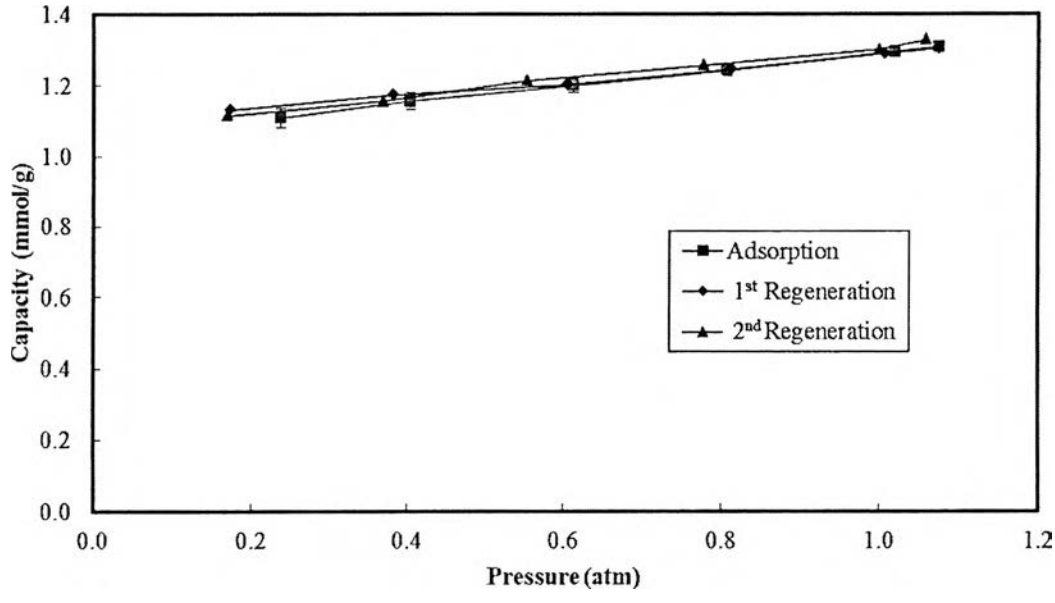

Figure 4.25 CO_2 adsorption isotherms at 75 °C of the AC and the regenerated AC.

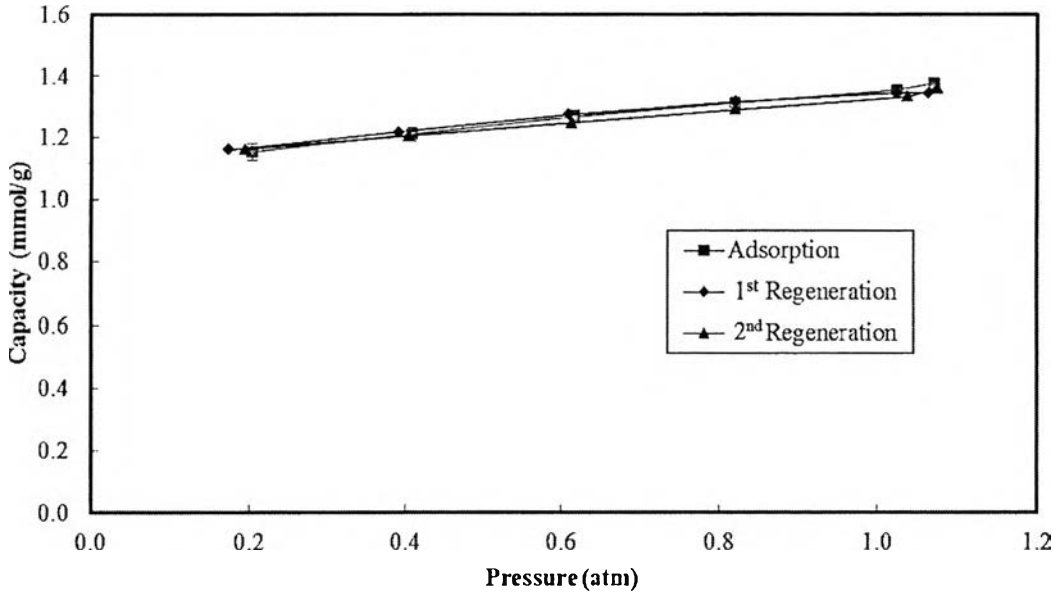

Figure 4.26 CO_2 adsorption isotherms at 75 °C of the 1.16 wt% Med Mw PEI and the regenerated sample.

Table 4.4 Surface area of fresh and regenerated adsorbent

Adsorption Temperature °C	Adsorbent	Surface area (m^2/g)
30	Activated Carbon (AC)	996
	1st regenerated AC	962
	2nd regenerated AC	988
30	0.73 wt% Med Mw PEI/AC	907
	1st regenerated 0.73 wt% Med Mw PEI/AC	904
	2nd regenerated 0.73 wt% Med Mw PEI/AC	891
75	Activated Carbon (AC)	996
	1st regenerated AC	994
	2nd regenerated AC	1,019
75	1.16 wt% Med Mw PEI/AC	877
	1st regenerated 1.16 wt% Med Mw PEI/AC	852
	2nd regenerated 1.16 wt% Med Mw PEI/AC	840

4.5 Comparison of CO_2 Adsorption of PEI/AC with Other Adsorbents

The CO_2 adsorption capacity of all adsorbents is shown in Tables 4.5 – 4.7. Table 4.8 reports the CO_2 adsorption capacity of adsorbent in this work comparing with other adsorbent. At 75 °C, the PEI/AC of previous work (Pipatsontipong (2011)'s work) shows higher adsorption capacity than this work. It may be explained that the 0.28 wt% PEI/AC (surface area = 1,177 m^2/g) has higher surface area than the High Mw PEI/AC. In addition, the original AC then may also be some differences resulting in the difference property. At 30 °C, most of this work's adsorbents show higher adsorption capacity than the previous work. It can be explained that the Low Mw and Med Mw PEI has higher CO_2 accessibility than the High Mw PEI. Furthermore, the surface area of previous work's AC is very high (1,325 m^2/g). The reduction in the surface area by PEI impregnation decreases the

physisorption, which is favorable at the low temperature. Xu *et al.* (2003) investigated the Si-MCM-41-PEI-50 and found that the addition of PEI (Mw= 600) increased the capacity due to the synergistic effect. KIT-6-PEI 50 was investigated and showed the effective increase in the CO_2 adsorption capacity (Son *et al.*, 2008). Even the decrease in the surface area of MCM-41 and KIT-6, the chemisorption from the PEI still helps to increase the capacity. Heydari-Gorji and Sayari (2011) investigated the impregnation of PEI on the pore-expanded MCM-41 (PME). The results showed the amount of PEI loading affected the capacity at the varied temperature. At the high temperature, the low loading of PEI showed the decrease in the capacity because of too fast kinetics of diffusion and less amount of PEI. At the high loading of PEI, they found that capacity increases with temperature. They described that, at higher temperature, the chemical adsorption of amine group is favorable and CO_2 accessibility or diffusion to PEI bulk is favorable. The higher amount of the amine group means the higher CO_2 adsorption capacity. However, when the temperature is too high, the diffusion is faster than the chemical adsorption, and the reaction is not favorable.

Table 4.5 CO_2 adsorption capacity of adsorbents at 30 °C and 1 atm

Adsorbent	CO_2 adsorption capacity (mmol/g adsorbent)
Activated Carbon (AC)	2.74
1.68 wt% Low Mw PEI/AC	3.02
2.18 wt% Low Mw PEI/AC	2.96
2.84 wt% Low Mw PEI/AC	2.86
0.73 wt% Med Mw PEI/AC	3.08
1.16 wt% Med Mw PEI/AC	3.01
1.90 wt% Med Mw PEI/AC	2.96
0.16 wt% High Mw PEI/AC	2.85
0.45 wt% High Mw PEI/AC	2.77
0.86 wt% High Mw PEI/AC	2.70

Table 4.6 CO_2 adsorption capacity of adsorbents at 50 °C and 1 atm

Adsorbent	CO_2 adsorption capacity (mmol/g adsorbent)
Activated Carbon (AC)	2.00
1.68 wt% Low Mw PEI/AC	2.13
2.18 wt% Low Mw PEI/AC	2.03
2.84 wt% Low Mw PEI/AC	1.97
0.73 wt% Med Mw PEI/AC	2.12
1.16 wt% Med Mw PEI/AC	2.08
1.90 wt% Med Mw PEI/AC	2.02
0.16 wt% High Mw PEI/AC	2.13
0.45 wt% High Mw PEI/AC	2.09
0.86 wt% High Mw PEI/AC	2.07

Table 4.7 CO_2 adsorption capacity of adsorbents at 75 °C and 1 atm

Adsorbent	CO_2 adsorption capacity (mmol/g adsorbent)
Activated Carbon (AC)	1.29
1.68 wt% Low Mw PEI/AC	1.27
2.18 wt% Low Mw PEI/AC	1.27
2.84 wt% Low Mw PEI/AC	1.15
0.73 wt% Med Mw PEI/AC	1.34
1.16 wt% Med Mw PEI/AC	1.35
1.90 wt% Med Mw PEI/AC	1.35
0.16 wt% High Mw PEI/AC	1.29
0.45 wt% High Mw PEI/AC	1.33
0.86 wt% High Mw PEI/AC	1.29

Table 4.8 Comparison of CO_2 adsorption capacity of adsorbents at 1 atm

Adsorbent	Adsorption Temperature (°C)	CO_2 adsorption capacity (mmol/g adsorbent)	Reference
AC	30	2.74	This work
0.73 wt% Med Mw PEI/AC	30	3.08	
AC	75	1.29	
1.16 wt% Med Mw PEI/AC	75	1.35	
AC	30	3.53	Pipatsantipong, 2011 (Previous work)
0.22 wt% PEI/AC	30	2.75	
AC	75	1.54	
0.28 wt% PEI/AC	75	2.84	
PEI	75	2.48	Xu *et al.*, 2003
Si-MCM-41	75	0.20	
Si-MCM-41-PEI-50	75	2.55	
KIT-6-PEI 50	75	2.95	Son *et al.*, 2008
SBA-15	75	0.11	Ma et al., 2009
PEI(50)/SBA-15	75	3.18	
PME-PEI(30)	25	2.64	Heydari-Gorji and Sayari, 2011
PME-PEI(30)	50	2.61	
PME-PEI(30)	75	2.34	
PME-PEI(55)	75	4.73	