# CHAPTER IV
RESULTS AND DISCUSSION

4.1 Characterization

Activated carbon (AC) and modified AC were characterized by thermogravimetry/different thermal analysis (TG/DTA), Brunauer-Emmett-Teller (BET) gas adsorption analysis, and Fourier transform infrared spectroscopy (FTIR). Surface area, pore volume, and pore diameter of the adsorbents are shown in Table 4.1. AC shows a specific surface area of 1,325 m^2/g, a pore volume of 0.4757 cm^3/g, and a pore diameter of 13.40 Å. The AC modified with 0.04, 0.16 and 0.22 wt% polyethyleneimine (PEI) loading has similar surface area, pore volume, and pore diameter compared to the AC. This result suggests that the amount of PEI on the AC does not significantly affect the AC surface properties. However, when the amount of PEI reaches 0.28 wt% PEI/AC and higher, a decrease in the surface area and the pore volume can be observed. The decrease brought about by stronger oxidation is generally explained by the restriction of the pore volume available for N_2 adsorption due to the formation of nitrogen-containing groups at the entrance and/or on the walls of micropores and by the possible destruction of the pore walls and its collapse when oxygenated terminal groups are created (Moreno-Castilla et al., 1997).

**Table 4.1** Surface area, pore volume, and pore diameter analysis of adsorbents

Adsorbents	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore Diameter (Å)
Activated carbon (AC)	1,325	0.4757	13.40
0.04 wt% PEI/AC	1,288	0.4620	13.20
0.16 wt% PEI/AC	1,248	0.4488	13.20
0.22 wt% PEI/AC	1,225	0.4406	13.18
0.28 wt% PEI/AC	1,177	0.4226	13.16
0.31 wt% PEI/AC	894	0.3814	12.40
0.35 wt% PEI/AC	855	0.3618	12.20

A nitrogen adsorption isotherm is a standard tool for the characterization of porous materials especially porous carbonaceous adsorbents. The adsorption isotherm can be made to yield valuable information about the surface area and pore structure of the adsorbent. The definition of pore size, originally proposed by Dubinin and now adopted by IUPAC as follows: micropores width less than 2 nm; mesopores width from 2 to 50 nm; the macropores width greater than 50 nm Micropores can be subdivided into ultramicropores (less than 0.7 nm), and supermicropores (from 0.7 to 2 nm) (Gregg and Sing, 1982). Nitrogen isotherms obtained for AC, 0.04 wt% PEI/AC, 0.16 wt% PEI/AC, 0.22 wt% PEI/AC, 0.28 wt% PEI/AC, 0.31 wt% PEI, and 0.35 wt% PEI/AC are shown in Figure 4.1. In almost all samples, 70% of the pore volume is filled below $p/p^0 = 0.1$, indicating that these samples are highly microporous. After the sharp movements up to p/p^0 of 0.1, the isotherms slowly bend showing smaller increments in adsorption. After a p/p^0 of 0.2, the adsorption becomes further smaller but still continuing the adsorption process almost up to the saturation vapor pressure (Gregg and Sing, 1982). The results show the presence of pores with almost all diameters despite of different extents in most samples. These pores vary from thin micropore to probably broader micropore that is wide open so that the evaporation takes place at the same p/p^0 as in the adsorption process (Pradhan and Sandle, 1998).
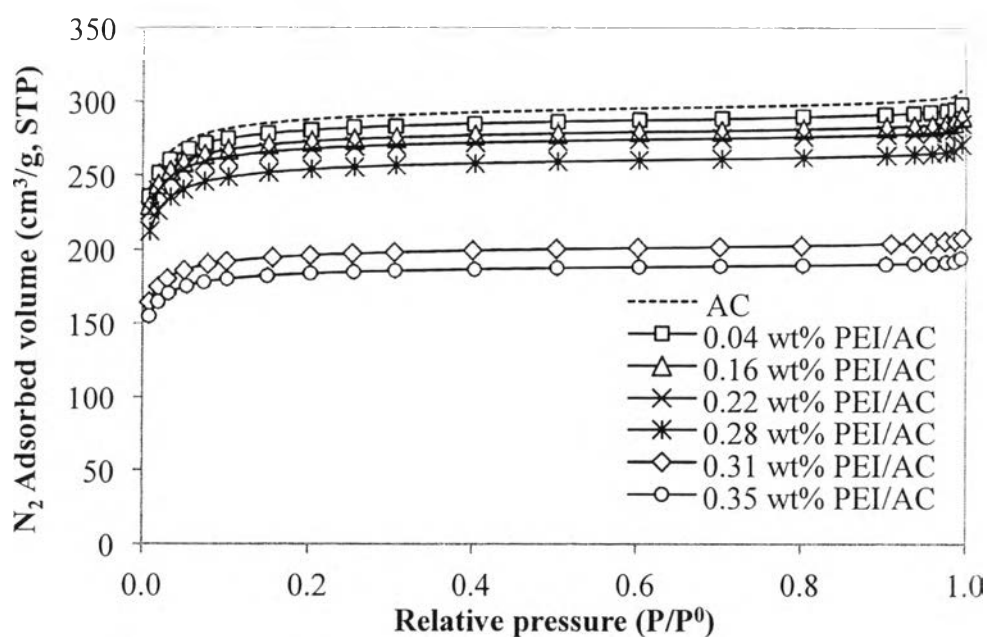
**Figure 4.1** Nitrogen adsorption isotherms of AC and modified AC at -196 °C.

The FTIR transmission spectra of AC, 0.04 wt% PEI/AC, and 0.16 wt% PEI/AC are shown in Figure 4.2. The band at 1,480 cm^{-1} represents the N–H bond, in which its slight increase in the absorbance for the PEI-impregnated samples compared to AC as PEI contains NH$_3$ group (Przepiorski *et al.*, 2004). The band at 2,360 cm^{-1} is usually ascribed to the single C–H bond, which decreases in the absorbance for the PEI-impregnated samples (Attia *et al.*, 2006). From this observation, it can be assumed that PEI-impregnation decreases the ratio of the C–H bonds. The reduction of the C–H bond indicates the relative reduction in the presence of these generally hydrophobic bonds, which enables the more hydrophilic N–H bonds to be attached on the AC. The broad band from 2,400 to 2,900 cm^{-1} is due to the presence of aliphatic groups of the adsorbed long chained-PEI (Tomaszewski *et al.*, 2003). The stretching vibrations from approximately 3,450 to 4,000 cm^{-1} are possibly due to the presence of surface hydroxylic groups and chemisorbed water (Swiatkowski *et al.*, 2004). These results confirm that PEI was successfully loaded on the AC.
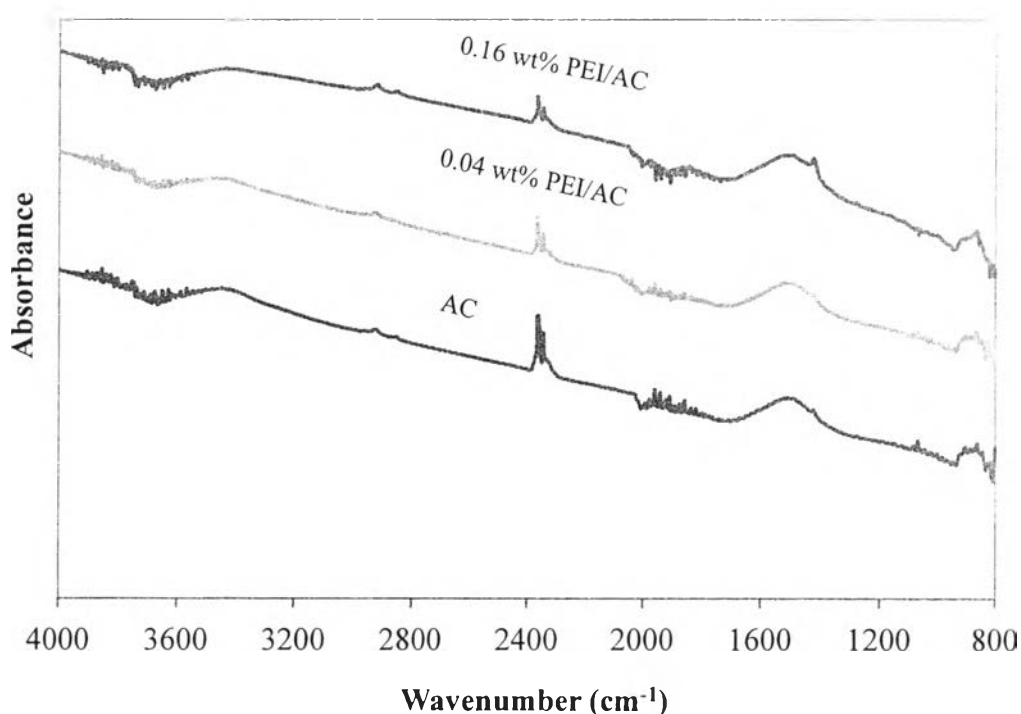

Figure 4.2 FTIR transmission spectra of AC and modified AC.

The effects of temperature on the AC were investigated using thermogravimetric analysis (TG/DTA). The TG/DTA profiles obtained under inert gas (N_2) condition are presented in Figures 4.3-4.6.

In Figure 4.3, the TGA profile of the AC is shown. There are two steps with distinct weight loss. The weight loss at 85.5 °C is probably caused by thermodesorption of physically adsorbed material such as water vapor, hydrocarbon, and in the case of raw material, residual volatile content (Mercedes *et al.*, 2004). The weight loss above 290.7 °C can be attributed to the starting decomposition of the AC (Plaza *et al.*, 2008). In addition, at a higher temperature, the AC presents a gradual and pronounced weight loss up to 800 °C.
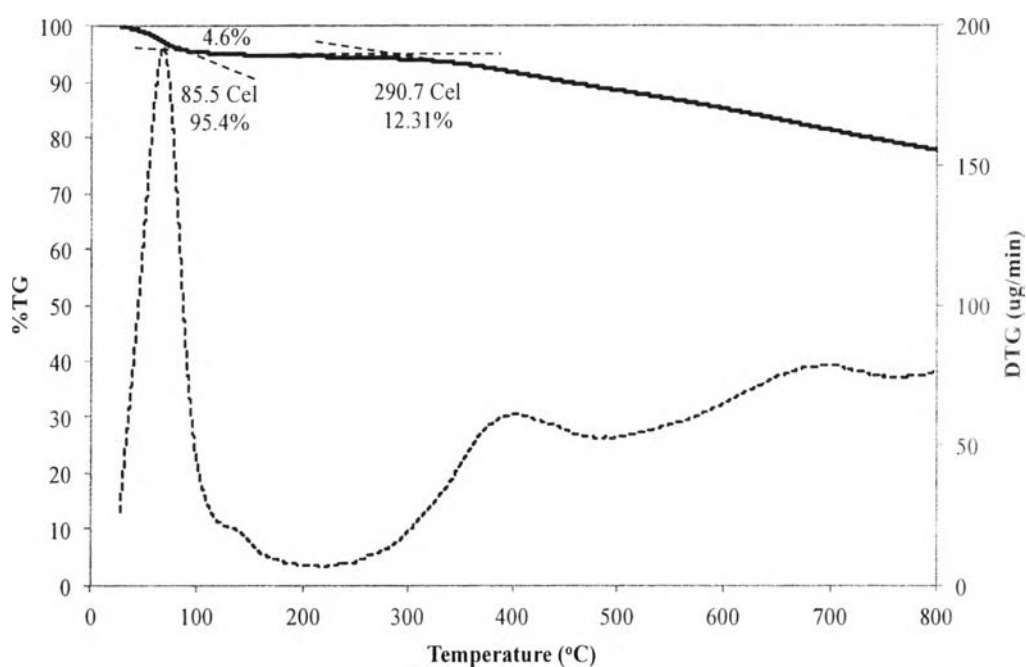
Figure 4.3 TGA profile of AC; dTG(---), TG(—).
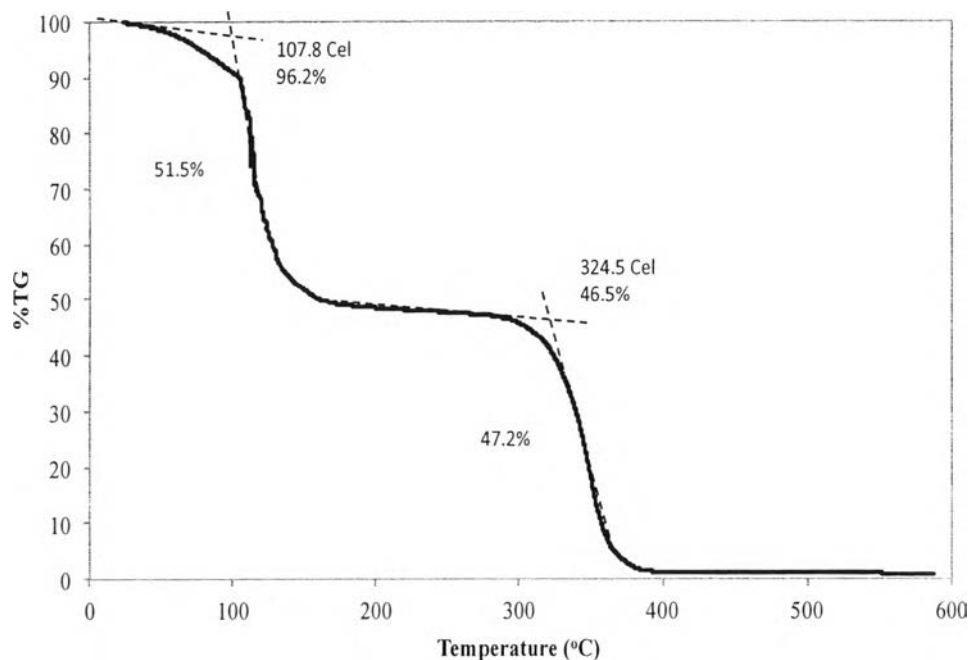
Figure 4.4 TGA profile of PEI (50 wt% in water).

The TGA profile of PEI (50 wt% in water) is shown in Figure 4.4. There are two steps with distinct weight loss at 107.8 and 324.5 °C. The temperature at 107.8 °C indicates the maximum desorption of water. And the temperature at 324.5 °C indicates the maximum decomposition of PEI.

Figures 4.5 – 4.6 show the TGA data for the AC modified with PEI (0.04 wt% PEI/AC and 0.16 wt% PEI/AC). As seen in the figures, there are two steps with distinct weight loss. The first weight loss around 85 °C is probably caused by thermodesorption of physically adsorbed material such as water vapor and volatile components (Mercedes *et al.,* 2004). At 270 °C, the small weight loss can be attributed to the continuous decomposition of PEI and some particles of AC. At high temperature up to 600 °C, it can be attributed to the decomposition of some particles of the AC.
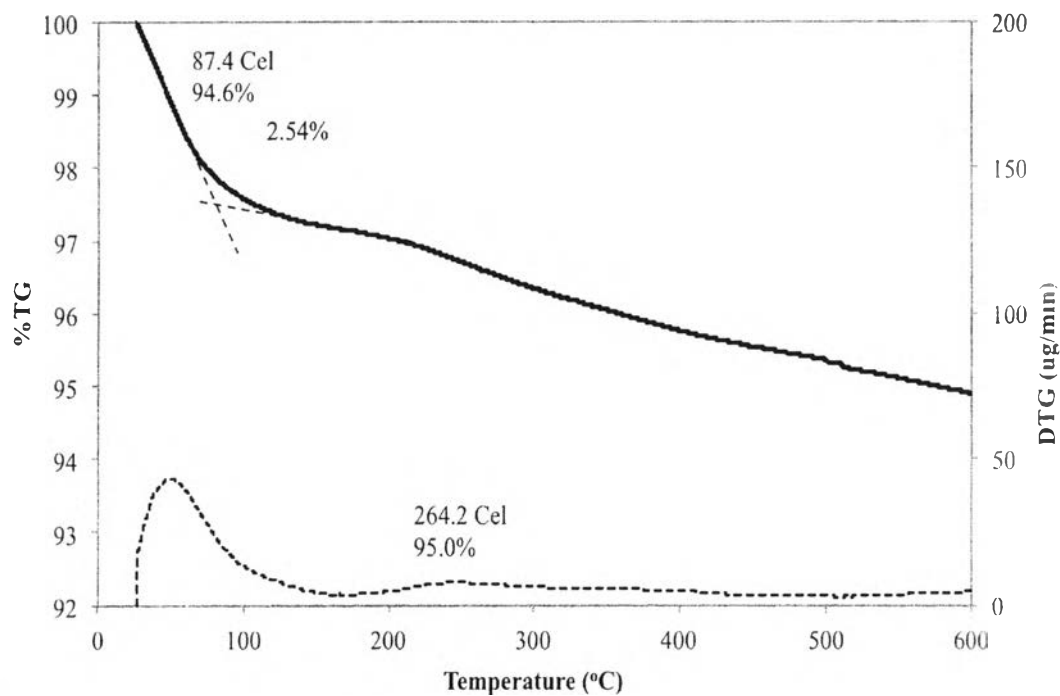
Figure 4.5 TGA profile of 0.04 wt% PEI/AC; dTG(---), TG(—).
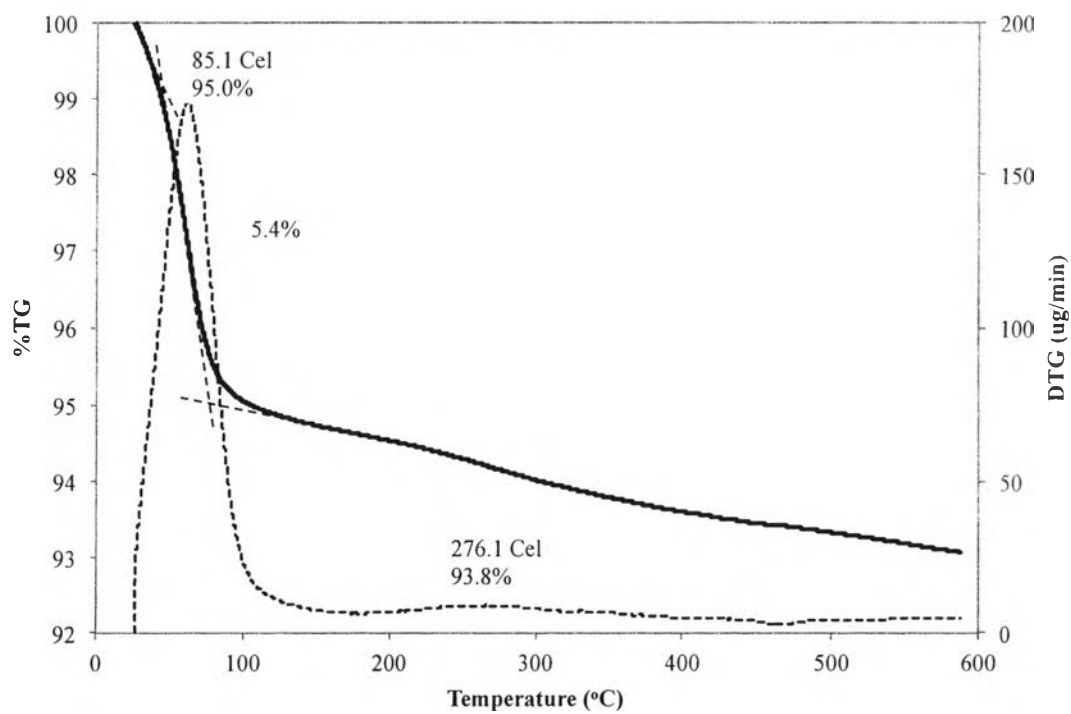

Figure 4.6 TGA profile of 0.16 wt% PEI/AC; dTG(---), TG(—).

The amounts of PEI impregnated on AC were analyzed by measuring their absorbance at 203 nm via the UV-visible spectrometer. Table 4.2 shows the amounts of PEI-impregnated on the AC related to the initial concentration of PEI solution. A calibration curve, which was plotted from 5 different concentrations of PEI solution, was used to calculate the amount of PEI adsorbed by using simple mass balance.

Table 4.2 Amount of PEI impregnated on the AC

| Initial concentration of PEI solution (g/L)	PEI impregnated on AC (wt% PEI)
0.1	0.04
0.5	0.16
1.5	0.22
2.0	0.28
2.25	0.31
2.5	0.35

4.2 Effects of PEI Loading on CO_2 Adsorption

The adsorption capacity of adsorbents strongly depends on the amount of micropores of a specific diameter present in AC as well as their volume (Ma et al. 2009). Figure 4.7 shows the isotherms of CO_2 on the AC and the modified AC samples at 30 °C and 0 to 1 atm pressure. It can be observed that the AC has higher CO_2 adsorption capacity than the AC modified with PEI. Table 4.1 shows that the pore volume decreases with the increase in the amounts of PEI loading. However, Figure 4.7 shows that the adsorption capacity increases with the increase in the amounts of PEI loading from 0.04 to 0.22 wt%. That may be because PEI reduces the physical adsorption of AC and increases the chemical adsorption. Nevertheless, when the amount of PEI loading reaches 0.25 wt%, the surface area, pore volume, and the adsorption capacity significantly decrease. This is because the excess amount of PEI blocks the micropores of the AC. The results imply that physical adsorption dominates the CO_2 adsorption on the AC at 30 °C.
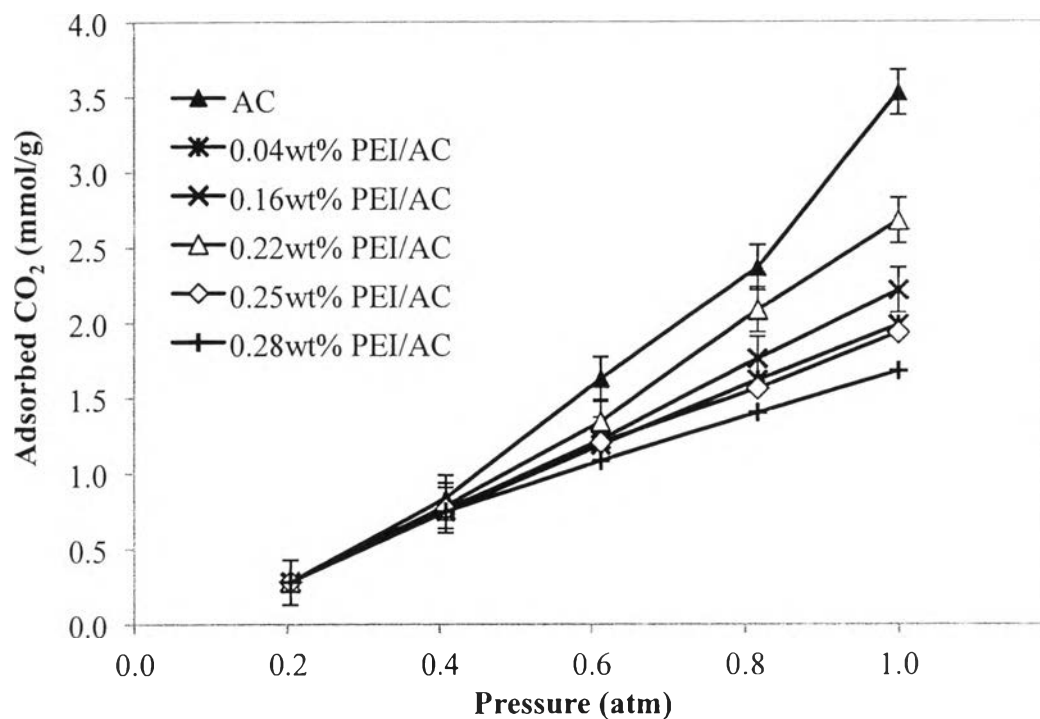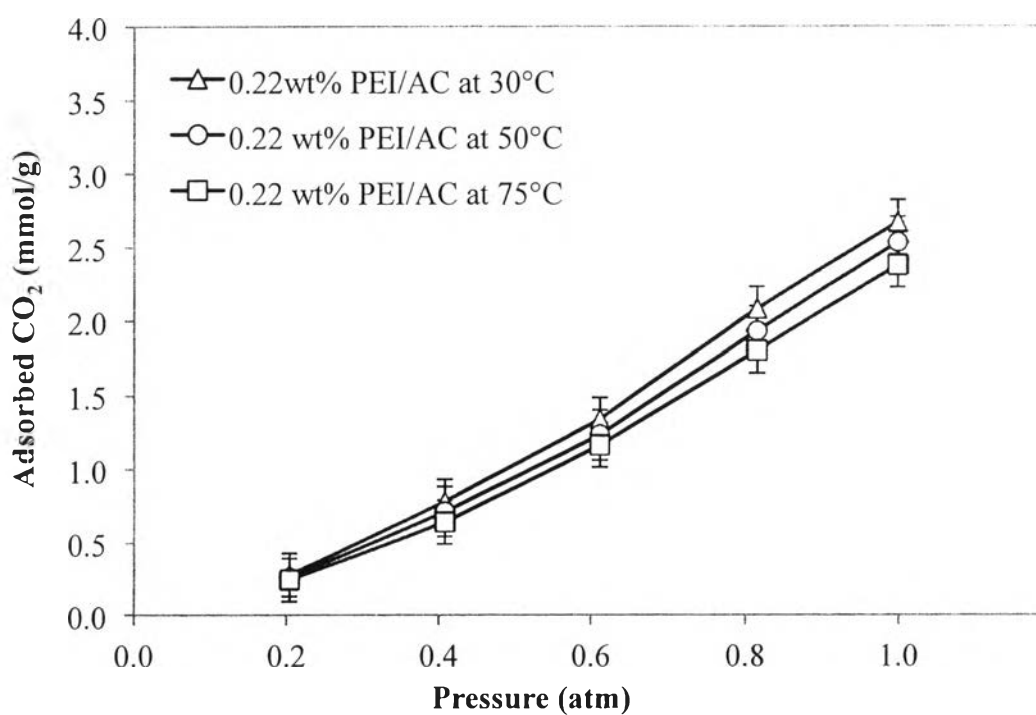
Figure 4.7 CO_2 adsorption isotherms of AC and AC modified with different PEI loadings at 30 °C.

Figure 4.8 shows the isotherms of CO_2 on the AC and the modified AC samples at 75 °C and 0 to 1 atm pressure. Compared to the results at 30 °C, a significant drop in the CO_2 adsorption on the AC can be clearly observed. That is simply due to the nature of physical adsorption on the sample. Surprisingly, the sample loaded with 0.22 wt% PEI seems to maintain the CO_2 adsorption capacity, which can be seen in Figure 4.9. In addition, further increase in the PEI loading results in the slight increase in the adsorption capacity until the optimum loading at 0.28 wt%. However, when the PEI loading reaches 0.31 wt%, a decrease in the adsorption capacity can be seen. That may be resulted from the pore filling effect that blocks the pores of the adsorbent preventing CO_2 to diffuse into the pores (Jadhav *et al.*, 2007, Xu *et al.*, 2005). The results imply that an amount of PEI on the AC should be high enough for the reaction with CO_2 but not too high to overshadow the physical properties of the AC.
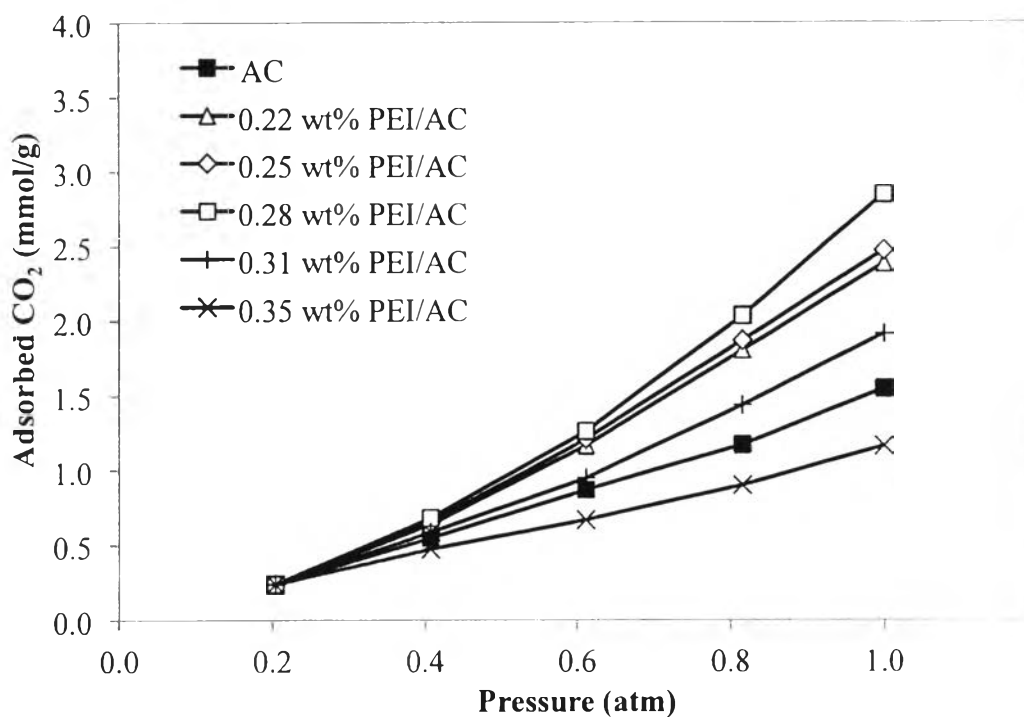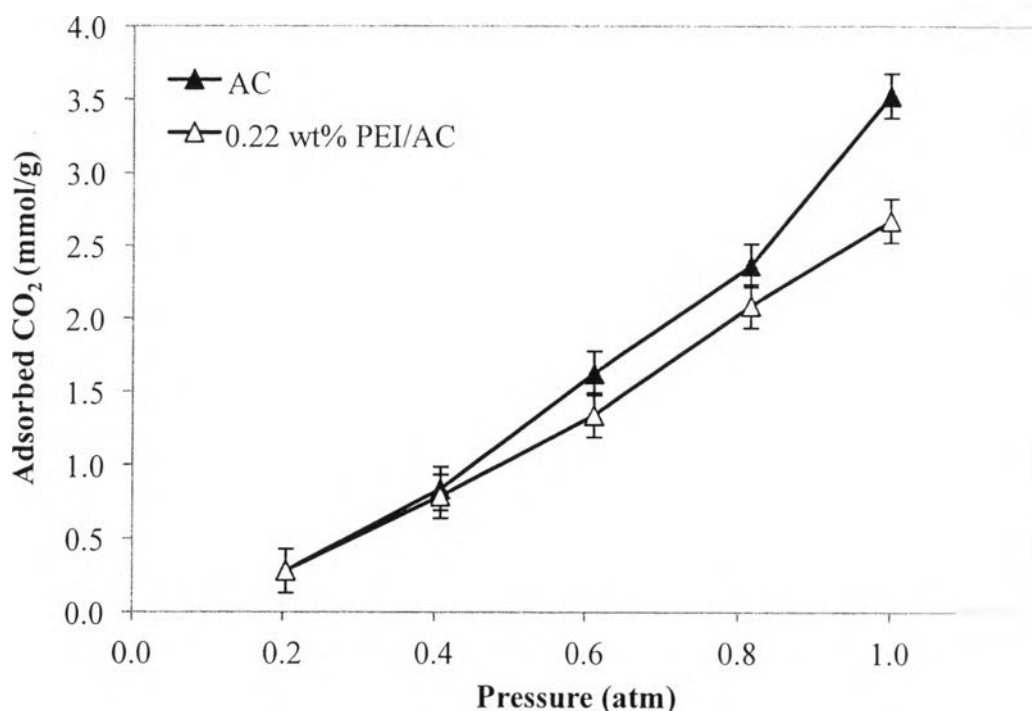
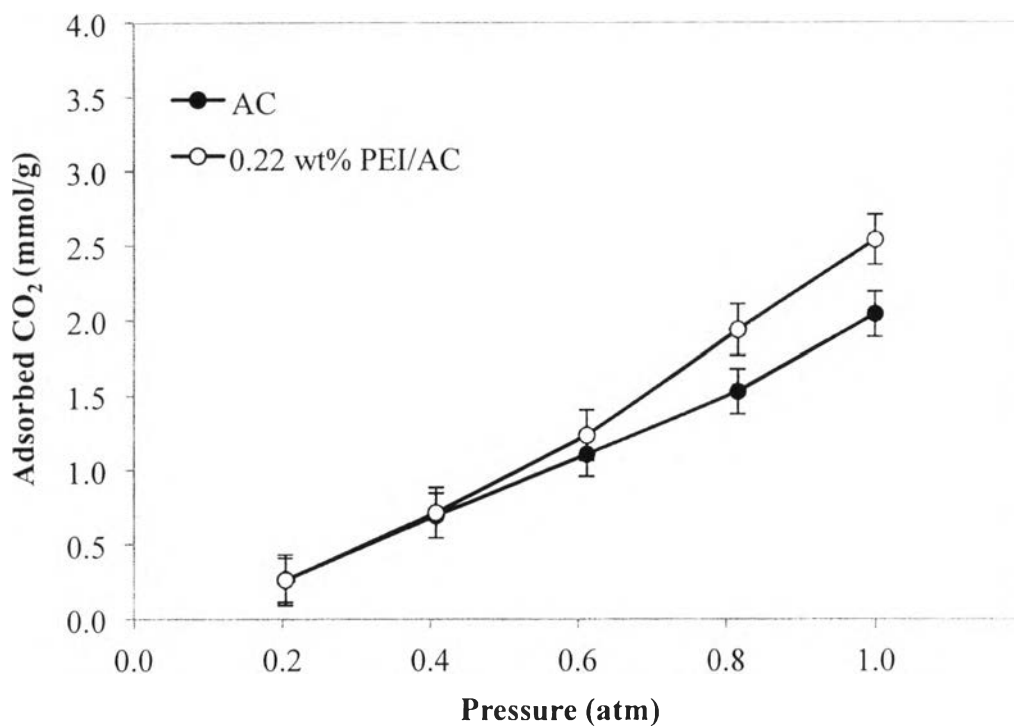**Figure 4.8** CO_2 adsorption isotherms of AC and AC modified with different PEI loadings at 75 °C.

Figure 4.9 CO_2 adsorption isotherms of AC modified with PEI at 30, 50, and 75 °C.

## 4.3 Effects of Temperature on CO_2 Adsorption

From Figure 4.10, it can be observed that the AC has higher CO_2 adsorption capacity than the AC modified with PEI at 30 °C, but at the elevated temperatures (50 and 75 °C), the AC modified with PEI shows higher adsorption capacities than the AC at the same temperature. In Figures 4.11–4.12, at the beginning, the adsorption capacities of all samples are very close. When the pressures are increased, the adsorption capacities of the AC modified with PEI are significantly higher though the surface area and pore volume are comparable to those of the AC. It implies that there may be chemical interaction between CO_2 and PEI. Such a phenomena is possible when the increase in the temperature facilitates the CO_2 molecule to form bond with PEI (Ma *et al.*, 2009).

Figure 4.10 CO_2 adsorption isotherms of AC and AC modified with 0.22 wt% PEI at 30 °C.
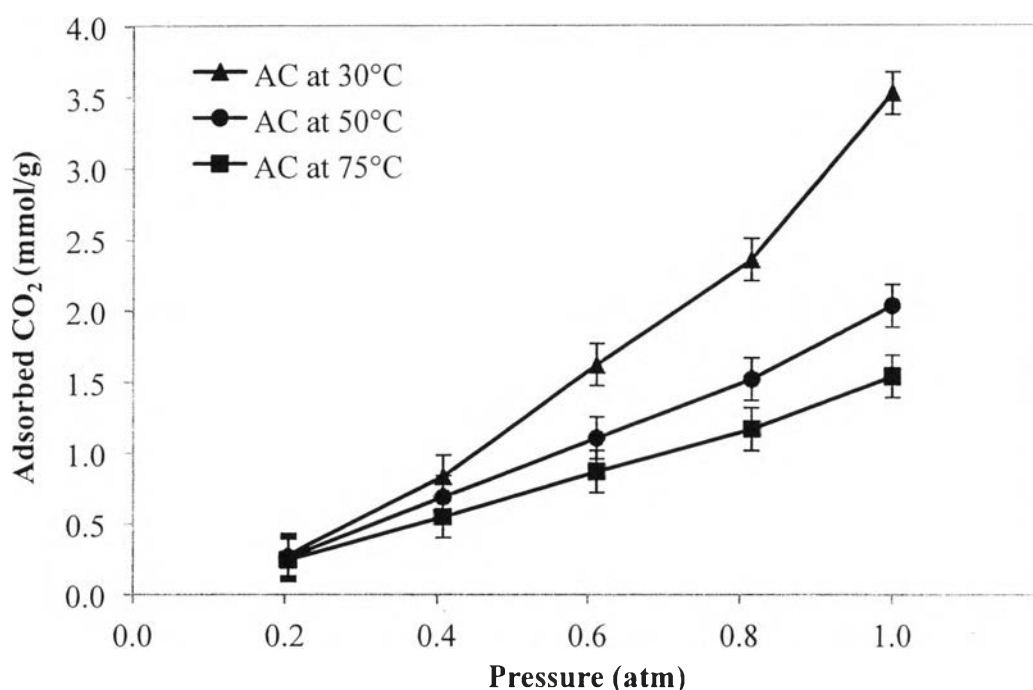
Figure 4.11 CO_2 adsorption isotherms of AC and AC modified with 0.22 wt% PEI at 50 °C.
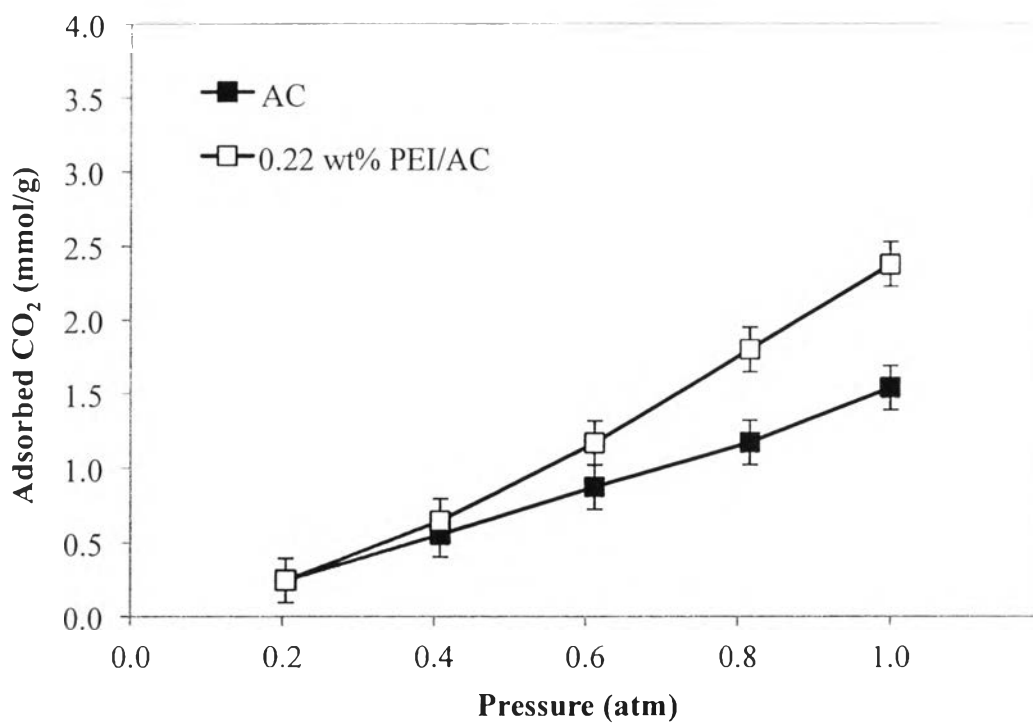
Figure 4.12 CO_2 adsorption isotherms of AC and AC modified with 0.22 wt% PEI at 75 °C.

The adsorption capacities of AC at 75 °C have the same trend and are close to the adsorption capacities at 50 °C. Figure 4.13 represents adsorption isotherms of the AC at different temperatures (30, 50 and 75 °C). This figure shows that the CO_2 adsorption of the AC at 30 °C gave the highest adsorption capacity. It indicates that the adsorption capacities of the AC decrease with the increase in the temperature, suggesting that the adsorption of CO_2 on the AC is physical adsorption.
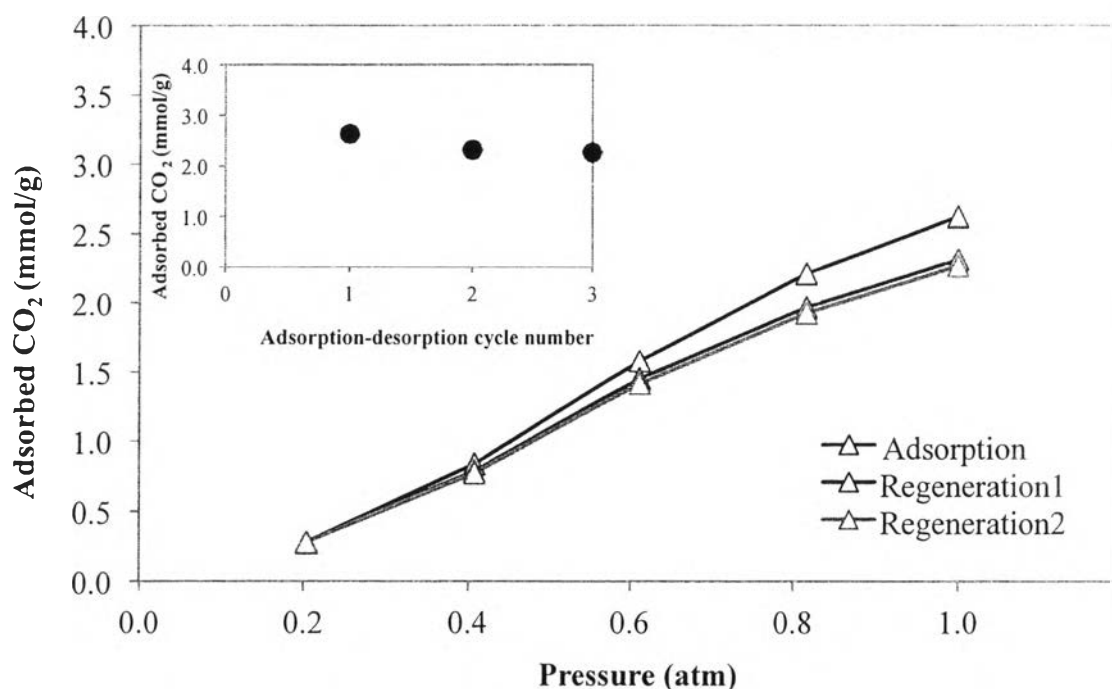

Figure 4.13 CO_2 adsorption isotherms of AC at 30, 50, and 75 °C.

4.4 CO_2 Adsorption after Regeneration

For practical applications, an adsorbent should not only have a high adsorption capacity and high selectivity, but also can be regenerated with an insignificant decrease in the adsorption capacity. Figure 4.14 shows the adsorption isotherms at 30 °C of the AC modified with 0.22 wt% PEI and that of the sample after regeneration. During the three cycles, the CO_2 adsorption capacity of the AC modified with 0.22 wt% PEI was not significantly changed, indicating that the desorption is complete, and the adsorbent is stable even subject to the regeneration. The surface area and pore volume of the AC modified with 0.22 wt% PEI and the

regenerated AC modified with 0.22 wt% PEI are shown in Figure 4.15. The surface area of the regenerated AC modified with 0.22 wt% PEI is not significantly decreased compared with that of the AC modified with 0.22 wt% PEI. A small decrease in the surface area of the regenerated AC modified with 0.22 wt% PEI may be attributed to the degradation of PEI. In addition, small particles of the AC could be decomposed after regeneration. The amounts of adsorbed CO_2 that cannot be desorbed do not affect the adsorption capacity at 30 °C because the physical adsorption dominates the CO_2 adsorption on the AC. The pore volume of the regenerated AC modified with 0.22 wt% PEI remains unchanged, which indicates that the heat at 120 °C in the regeneration process does not change the pore structure of the AC and PEI dispersed into the support pores does not degrade. These results ascribe that the heat at 120 °C in the regeneration process only affects the outer surface of the adsorbents (Xu *et al.*, 2005).
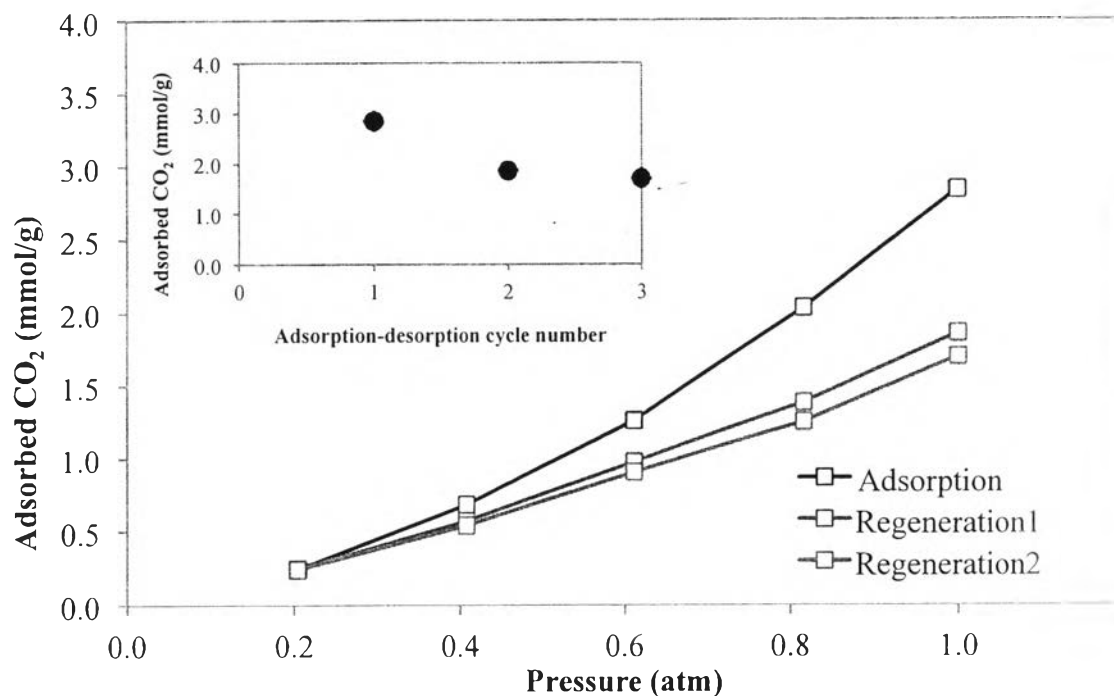

Figure 4.14 CO_2 adsorption isotherms at 30 °C of AC modified with 0.22 wt% PEI and the regenerated sample.
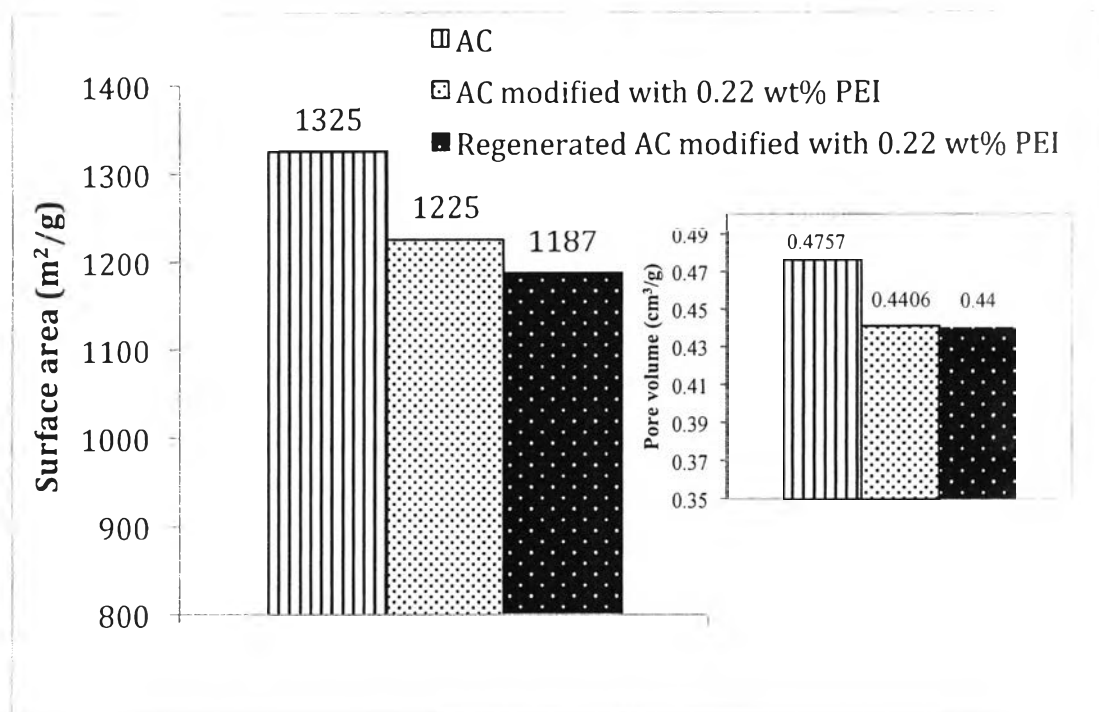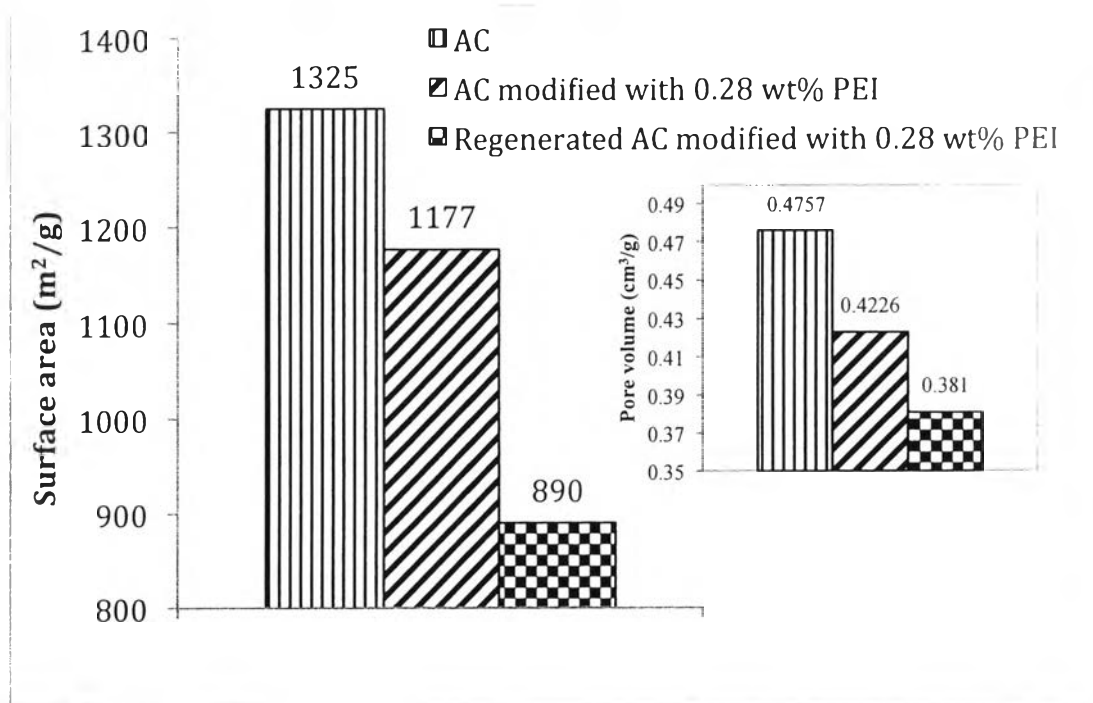
Figure 4.15 Comparison of the surface area and pore volume of AC, AC modified with 0.22 wt% PEI, and regenerated AC modified with 0.22 wt% PEI.

The decrease in the CO_2 adsorption capacity at 75 °C is more significant than that at 30 °C. Figure 4.16 shows a 50% decrease in the adsorption capacity after regeneration. This is not unexpected as the results correspond with the decrease in the nitrogen-containing group, which, in turn, decreases the CO_2 adsorption. That may be because some PEI could degrade. In addition, the chemical bond between CO_2 and PEI that dominates the CO_2 adsorption on the AC is too strong to be broken at the regenerated condition of 120 °C. Moreover, the surface area and pore volume of the regenerated AC modified with 0.28 wt% PEI significantly drop as seen in Figure 4.17. It implies that the adsorption temperature has effects on the surface area and pore volume of the AC modified with 0.28 wt% PEI (Gregg and Sing, 1982).

Figure 4.16 CO_2 adsorption isotherms at 75 °C of AC modified with 0.28 wt% PEI and the regenerated sample.

Figure 4.17 Comparison of the surface area and pore volume of AC, AC modified with 0.28 wt% PEI, and regenerated AC modified with 0.22 wt% PEI.

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

For comparison, Table 4.3 lists the maximum CO_2 adsorption capacities of some adsorbents reported by other investigators and available in the present work. It is evident that the 0.28 wt% PEI/AC exhibits higher adsorption capacity of CO_2 compared with the previous research that used PEI(50)/MCM-41 to modify the adsorbent, but lower than PEI(50)/SBA-15 at 75 °C though PEI(50)/SBA-15 has lower surface area (950 m²/g for SBA-15 and 80 m²/g for PEI(50)/SBA-15) than AC produced from coconut shell (1,325 m²/g for AC and 1,177 m²/g for 0.28 wt% PEI/AC). The table also shows that N_2/AC has higher the adsorption capacity of CO_2 than 0.22 wt% PEI/AC, suggesting that the use of N_2 to modify the AC surface by microwave irradiation in the N_2 atmosphere can increase the basicity of the AC.

Table 4.3 Comparison of maximum adsorption capacities of CO_2 with other adsorbents and AC and AC modified with PEI

Adsorbent	Adsorption capacity (mmol/g)	Pressure (atm)	Temperature (°C)	Reference
SBA-12/AP	1.04	1	25	Zelenak et al., 2008
PEI(50)/MCM-41	1.87	1	75	Xu et al., 2005
PEI(50)/SBA-15	3.18	1	75	Ma et al., 2009
ZIF-100	1.05	1	25	Wang et al., 2008
MOF-505	3.30	1	25	Chen, 2005
IRMOF-1	1.92	1	25	Millward and Yaghi, 2005
N_2/AC	3.75	1	25	Zhang et al., 2010
FS-PEI-50	1.71	1	25	Goeppert et al., 2011
AC	3.53	1	30	This work
0.22 wt% PEI/AC	2.75	1	30	This work
0.28 wt% PEI/AC	2.84	1	75	This work