

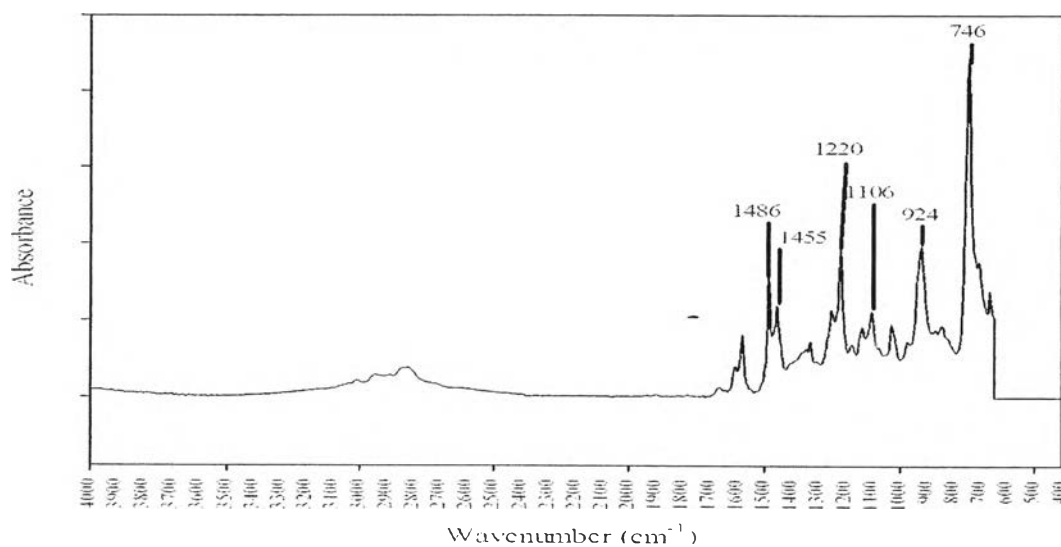
## CHAPTER IV

### RESULT AND DISCUSSION

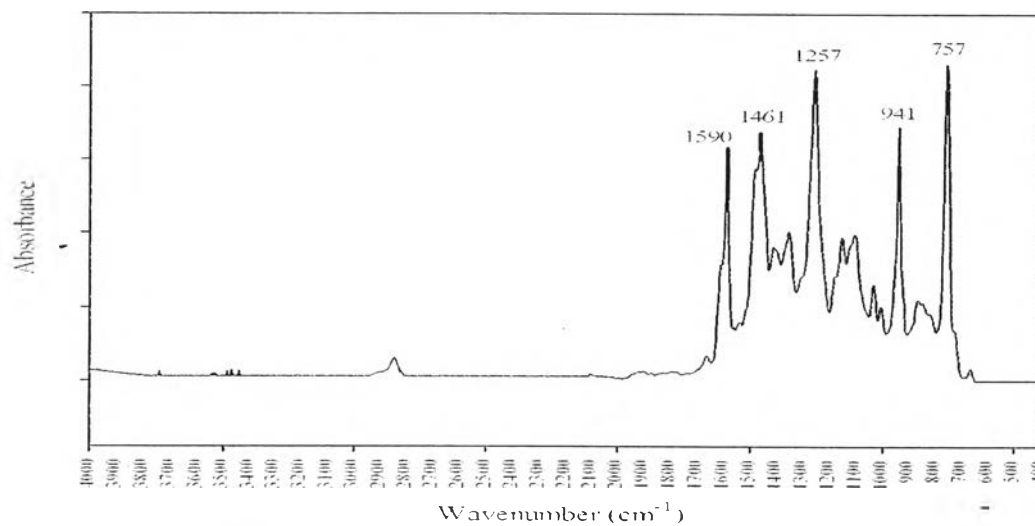
#### 4.1 Characterization of the Materials

##### 4.1.1 Benzoxazine Monomers Characterization

The FT-IR spectroscopy was employed to identify the functional groups of the benzoxazine monomers synthesized from using diethylenetriamine (DETA) as the amine reactant shown in Figure 4.1 and using pentaethylenhexamine (PEHA) as the amine reactant shown in Figure 4.2. The FT-IR spectra illustrated the absorption characteristic at  $924\text{ cm}^{-1}$  from Figure 4.1 and  $941\text{ cm}^{-1}$  from Figure 4.2 of the benzene ring to which oxazine ring is attached. The band at  $1486\text{ cm}^{-1}$  and  $1455\text{ cm}^{-1}$  from Figure 4.1 and  $1461\text{ cm}^{-1}$  from Figure 4.2 corresponded to the in-plane carbon-carbon stretching of tri-substituted benzene ring. Whereas the band between  $1220\text{ cm}^{-1}$  and  $1106\text{ cm}^{-1}$  in Figure 4.1 and  $1257\text{ cm}^{-1}$  in Figure 4.2 were related to the C-O-C asymmetric stretching modes which confirm the presence of the aromatic ether stretching. All of the absorption bands indicated to both benzoxazine monomers were agreed with the previous works (Agag *et al.*, 2009, Baqar *et al.*, 2012, and Huang *et al.*, 2013) and the band at  $746\text{ cm}^{-1}$  in Figure 4.1 and  $757\text{ cm}^{-1}$  in Figure 4.2 may be assigned to chloroform. Comparing between the two benzoxazine monomers, PEHA-derived benzoxazine reveals more bands between  $3500\text{ cm}^{-1}$  and  $3100\text{ cm}^{-1}$  due to the higher number of nitrogen in the structure of PEHA than that in the DETA.



**Figure 4.1** FT-IR spectrum of the benzoxazine monomer by DETA as reactant.



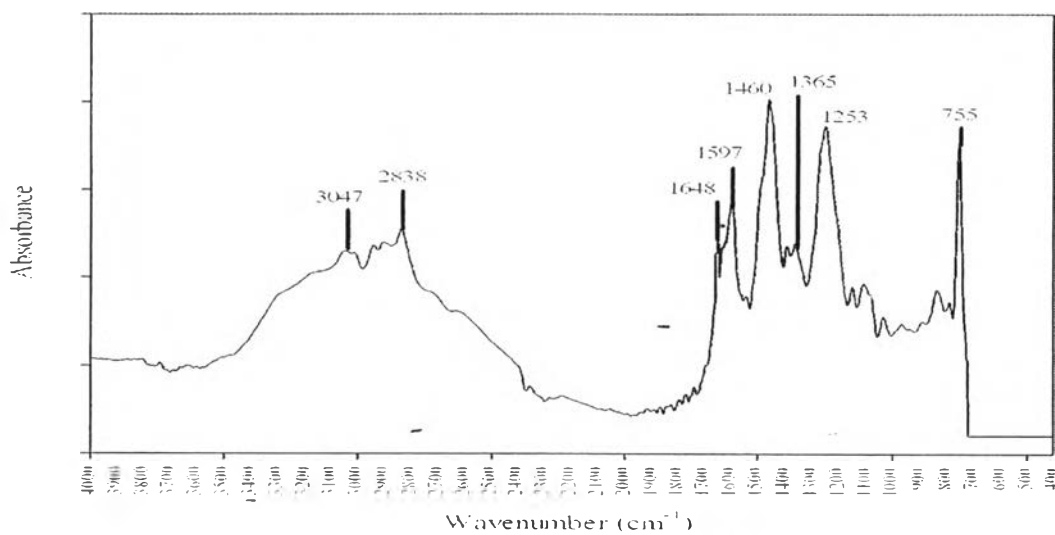
**Figure 4.2** FT-IR spectrum of the benzoxazine monomer by PEHA as reactant.

#### 4.1.2 Polvbenzoxazines Characterization

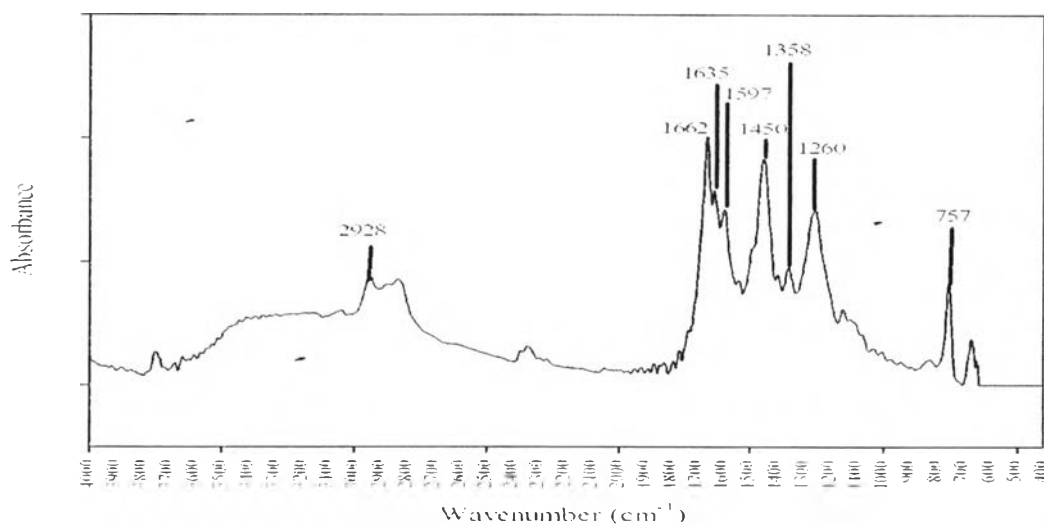
After curing both benzoxazine monomers at 180 °C for 90 min, the FT-IR spectroscopy was employed to determine the formation of polybenzoxazine. Figure 4.3 and Figure 4.4 show the FT-IR spectrum of DETA-derived polybenzoxazine and PEHA-derived polybenzoxazine, respectively. The absorption band charac-

teristics between  $1500\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$  in Figures 4.3 and 4.4 appeared higher than both benzoxazine monomers, showing the complete polymerization from the ring-opening mechanism. A tetra-substituted benzene ring and hydrogen-bonded hydroxyl group were generated as confirmed by the work from Huang *et al.* (2013). The absorption band between  $3500\text{ cm}^{-1}$  and  $2500\text{ cm}^{-1}$  were due to the OH stretching mode. The ring opening polymerization was also confirmed by the disappearance of the absorption band at  $924\text{ cm}^{-1}$  from Figure 4.1 and  $941\text{ cm}^{-1}$  from Figure 4.2 after the curing step.

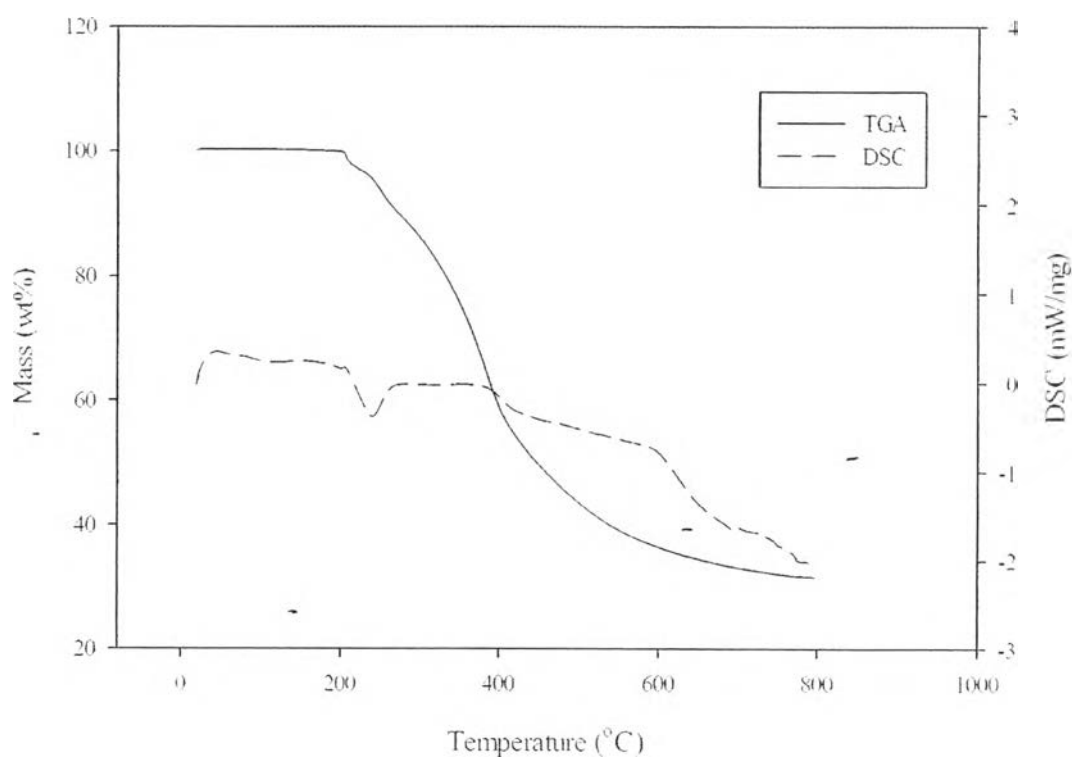
The decompositions of both polybenzoxazines were shown in Figure 4.5 and Figure 4.6. The results showed that DETA-derived polybenzoxazine started decomposed at  $200\text{ }^{\circ}\text{C}$  and PEHA-derived polybenzoxazine started decomposed at  $250\text{ }^{\circ}\text{C}$ . Thermal stability of PEHA-derived polybenzoxazine was higher than DETA-derived polybenzoxazine that caused by more hydrogen bonding effects from aliphatic chains in PEHA-derived polybenzoxazine. They had the different char yield at the last temperature ( $800\text{ }^{\circ}\text{C}$ ) of the experiment. The residue mass of DETA-derived polybenzoxazines and PEHA-derived polybenzoxazine were around 30wt% and 15wt%, respectively. The PEHA-derived polybenzoxazine yielded less char yield because this polymer contains longer aliphatic chains from the PEHA and at higher temperature these longer aliphatic chains were more difficult to form aromatic rings which finally resulted in bond breakage and less chars were formed.



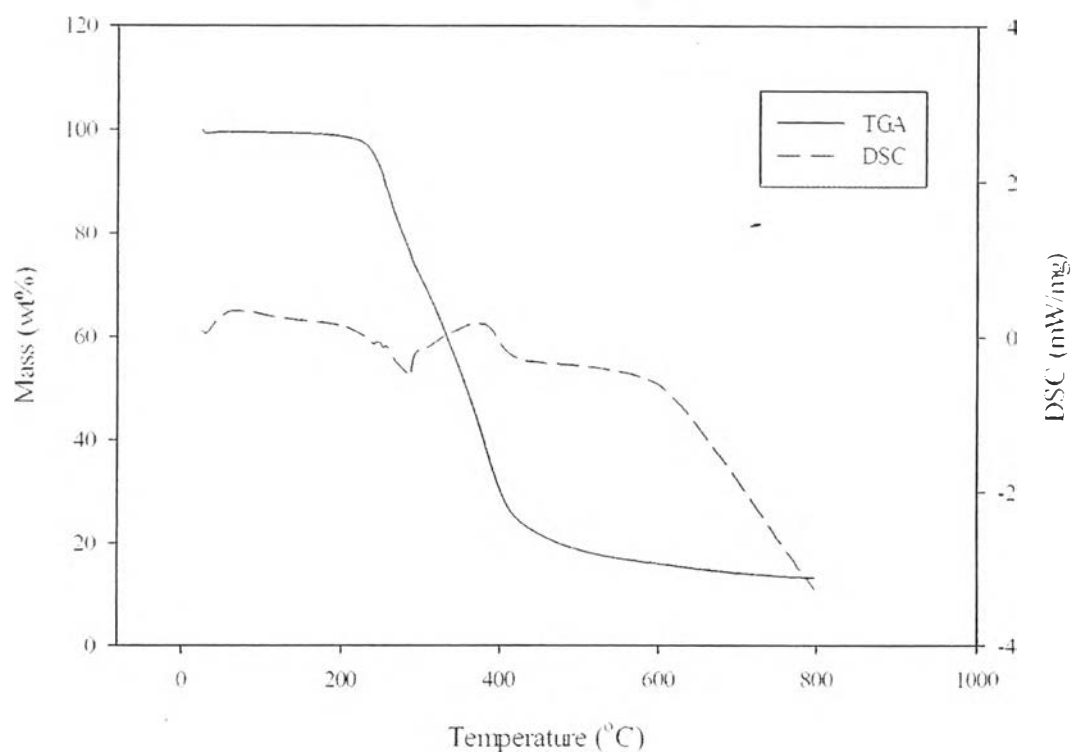
**Figure 4.3** FT-IR spectrum of the polybenzoxazine by DETA as reactant.



**Figure 4.4** FT-IR spectrum of the polybenzoxazine by PEHA as reactant.



**Figure 4.5** Decomposition of polybenzoxazine with DETA as reactant.



**Figure 4.6** Decomposition of polybenzoxazine with PEHA as reactant.

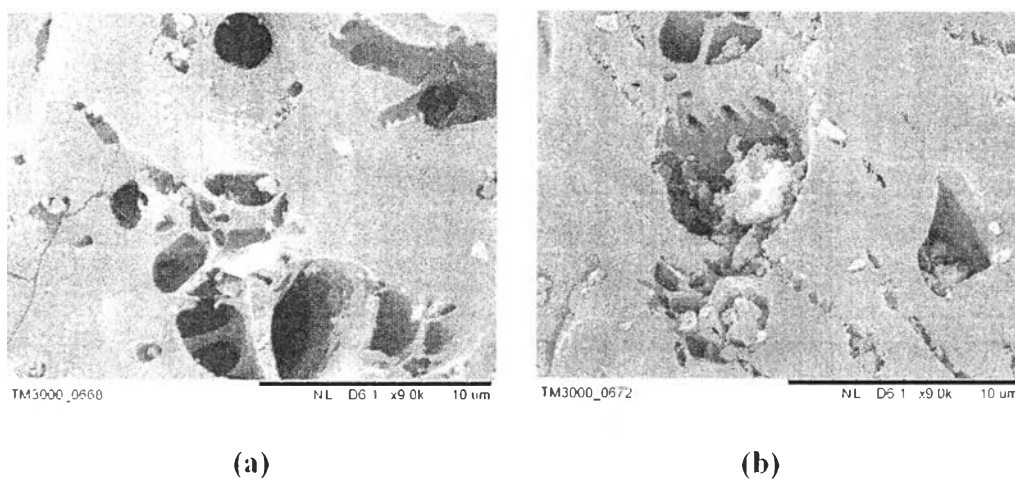
#### 4.1.3 Adsorbents Characterization

From the BET surface area analysis by using surface area analyzer (Sorptomatic), Table 4.1 showed the changes of BET surface area of untreated activated carbon and a series of both impregnating adsorbents, pore volume, and pore size distribution. The BET surface area and pore volume of untreated activated carbon are 1090.06 m<sup>2</sup>/g and 0.64 cm<sup>3</sup>/g, respectively. There was a decrease in the surface area and pore volume with higher concentration of impregnated loading. The decrease in the surface area could imply that there was some amount of polybenzoxazine blocking in the micropore which resulted in the decrease in pore volume that followed from the work of Xu *et al.*, (2003).

**Table 4.1** The BET surface area analysis of pure activated carbon and a series of impregnated adsorbents

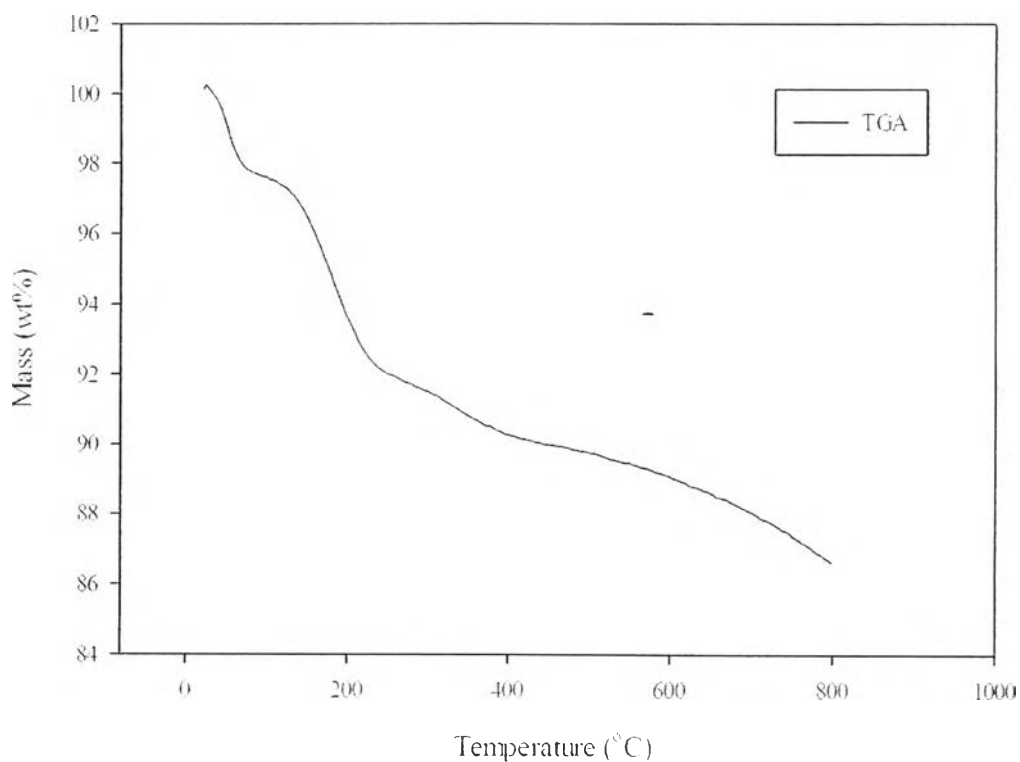
Adsorbents	BET surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
AC	1090	0.64	0.74
AC+ 1wt%PBZ(DETA)	877	0.51	0.76
AC+ 5wt%PBZ(DETA)	810	0.48	0.78
AC+ 10wt%PBZ(DETA)	764	0.47	0.79
AC+ 10wt%PBZ(PEHA)	812	0.45	0.79
PBZ-derived AC(DETA) (Carbonized at 200 °C)	134	0.28	0.66
PBZ-derived AC(DETA) (Carbonized at 300 °C)	267	0.30	0.78
PBZ-derived AC(DETA) (Carbonized at 400 °C)	102	0.29	0.83
PBZ-derived AC(PEHA) (Carbonized at 300 °C)	0	0.20	-

Figure 4.7 showed the surface morphology of the untreated activated carbon (Figure 4.7a) and activated carbon with 10wt% impregnated polybenzoxazine (Figure 4.7b) at a magnification of 9,000 times by using Scanning Electron Microscope (SEM). The result showed the surface and pores of activated carbon with 10wt% impregnated polybenzoxazine were blocked by some amount of polybenzoxazine that seen the some materials were in the pore from the comparison of Figure 4.7a and Figure 4.7b. These results were confirmed by BET surface area analyzer as shown in Table 4.1. The decrease in the surface area and in pore volume could indicate that there was some amount of polybenzoxazine blocking; however, these results may not confirm the polybenzoxazine blocking absolutely since the magnification range is too low and micropore could not be observed.



**Figure 4.7** SEM images of (a) untreated activated carbon and (b) activated carbon with 10wt% impregnated polybenzoxazine.

From Figure 4.8, the results showed the decomposition of 10wt% of PEHA-derived polybenzoxazine impregnating on activated carbon. First, the adsorbent decomposed around 50 °C because of moisture on the adsorbent. The adsorbent contains more moisture that may cause by preparation before characterized not good enough then weight change was stable until 160 °C, the polybenzoxazine that impregnating on the surface of activated carbon decomposed till 220 °C.



**Figure 4.8** Decomposition of 10wt% of PEHA-derived polybenzoxazine impregnating on activated carbon.

#### 4.1.4 Ultimate Analysis

Table 4.2 showed the ultimate analysis of untreated activated carbon and a series of activated carbon impregnated by benzoxazine derived from diethylenetriamine (DETA). Various impregnation methods were employed including vigorous stir using magnetic stirrer, shake using incubating shaker and agitation using sonic bath. After impregnation, the adsorbents were subjected to cure at 120 °C for 90 min and following by 180 °C for 90 min.



**Table 4.2** Ultimate analysis of all adsorbents in each preparation methods

Impregnation Method	Material	%C	%H	%N
	Untreated activated carbon	84.28	0.65	0.04
Stirred	Activated carbon+ 5wt%PBZ	79.94	0.51	0.25
	Activated carbon+ 10wt%PBZ	79.89	0.61	0.85
	Activated carbon+ 20wt%PBZ	73.26	0.81	1.55
	Activated carbon+ 30wt%PBZ	75.52	0.91	2.32
	Activated carbon+ 40wt%PBZ	78.61	1.72	3.25
		Activated carbon+ 5wt%PBZ	79.22	0.45
Shake	Activated carbon+ 10wt%PBZ	74.53	0.59	0.18
	Activated carbon+ 20wt%PBZ	74.40	0.89	0.70
	Activated carbon+ 30wt%PBZ	78.88	0.95	0.98
	Activated carbon+ 40wt%PBZ	75.63	1.19	1.26
		Activated carbon+ 5wt%PBZ	70.09	0.54
Sonic bath	Activated carbon+ 10wt%PBZ	70.98	0.64	0.08
	Activated carbon+ 20wt%PBZ	69.45	0.81	0.29
	Activated carbon+ 30wt%PBZ	69.42	0.93	0.67

The results showed the increasing amount of nitrogen content with increasing concentration of polybenzoxazine impregnated on the activated carbon. The same trend was observed for all impregnation method used, showing the successful of impregnation. The maximum amount of nitrogen component is 3.25% from activated carbon with 40wt%PBZ by stirring method. Then the stirring method was used for mechanical mixing in the impregnation method in this work.

Table 4.3 showed the ultimate analysis of untreated activated carbon, both benzoxazine monomers from different amine reactant (DETA and PEHA), both polybenzoxazines from different amine reactant (DETA and PEHA), and a series of activated carbon impregnated by both benzoxazine monomers. The impregnation method was stirring and varying benzoxazine loading (1wt%, 5wt%, and 10wt%).

**Table 4.3** Ultimate analysis of all materials

Material	%C	%H	%N	%S	%O
Untreated AC	84.28	0.65	0.04	0.03	15.00
BZ (DETA)	59.69	6.23	9.17	0.00	24.91
BZ (PEHA)	43.72	6.46	13.81	0.00	36.01
PBZ (DETA)	68.24	6.37	9.06	0.00	16.33
PBZ (PEHA)	67.37	7.28	14.78	0.00	10.57
PBZ-derived AC(DETA) (Carbonized at 200 °C)	77.21	0.56	4.44	0.00	17.79
PBZ-derived AC(DETA) (Carbonized at 300 °C)	80.00	0.28	4.31	0.00	15.41
PBZ-derived AC(DETA) (Carbonized at 400 °C)	83.65	0.22	3.61	0.00	12.52
PBZ-derived AC(PEHA) (Carbonized at 300 °C)	79.95	0.16	6.60	0.00	13.29
AC+1wt%PBZ (DETA)	79.64	0.25	0.11	0.03	19.97
AC+5wt%PBZ (DETA)	79.94	0.51	0.25	0.03	19.27
AC+10wt%PBZ (DETA)	79.89	0.61	0.85	0.02	18.63
AC+1wt%PBZ (PEHA)	81.25	0.21	0.17	0.02	18.35
AC+5wt%PBZ (PEHA)	80.27	0.25	0.72	0.02	18.74
AC+10wt%PBZ (PEHA)	81.19	0.78	1.25	0.02	16.76

\*AC = Activated carbon, BZ = Benzoxazine monomer, PBZ = Polybenzoxazine

The results showed that the increasing amount of nitrogen content with increasing concentration of polybenzoxazine impregnated on the activated carbon. The amount of nitrogen content of impregnated adsorbents by PEHA were higher than the impregnated adsorbents by DETA all of concentrations because pure PEHA-derived benzoxazines has more amount of nitrogen element content than DETA-derived benzoxazines (13.81 and 9.17%, respectively). In benzoxazine loading, the ultimate analysis showed that they were successful. In the example of activated

carbon with 1wt% polybenzoxazine (PEHA), nitrogen content of pure activated carbon (0.04%) and 1wt% polybenzoxazine (0.14%) as equivalent as compared with nitrogen content of activated carbon with 1wt% polybenzoxazine (PEHA) (0.17%).

#### 4.1.5 Surface Analysis by XPS

From the XPS analysis, the wide scans confirmed that the surface was composed mainly of carbon, oxygen, and nitrogen then the narrow scans confirmed the functional groups. Table 4.4 – 4.7 showed the percentages of deconvoluted peaks specified by types of possible bondings as assigned in Table 4.8 in this work.

**Table 4.4** Deconvolution results of untreated activated carbon and polybenzoxazine

Region	AC		PBZ(DETA)		PBZ(PEHA)	
	Binding		Binding		Binding	
	Energy (eV)	%	Energy (eV)	%	Energy (eV)	%
C 1s	284.619	67.80%	284.407	47.90%	284.565	65.90%
	-	-	285.514	16.60%	285.593	23.00%
	286.340	8.70%	286.579	12.80%	286.199	6.50%
	287.302	4.40%	287.450	9.40%	287.297	2.10%
	288.797	9.50%	288.921	13.30%	288.707	2.50%
	292.578	9.50%	-	-	-	-
O 1s	531.499	68.10%	531.648	50.70%	531.771	82.20%
	533.398	31.90%	533.202	49.30%	533.307	17.80%
N 1s	-	-	400.300	100.00%	400.274	100.00%

**Table 4.5** Deconvolution results of DETA-derived PBZ impregnating on AC

Region	AC+1wt%PBZ(DETA)		AC+5wt%PBZ(DETA)		AC+10wt%PBZ(DETA)	
	Binding		Binding		Binding	
	Energy (eV)	%	Energy (eV)	%	Energy (eV)	%
C 1s	284.600	60.90%	284.563	59.40%	284.577	57.20%
	285.621	10.90%	285.600	11.90%	285.612	13.40%
	286.407	7.70%	286.481	7.20%	286.482	7.40%
	287.407	6.50%	287.382	3.00%	287.378	4.00%
	288.943	8.00%	288.920	11.90%	288.984	11.00%
	292.370	6.10%	292.646	6.60%	292.959	7.10%
O 1s	531.500	68.70%	531.590	70.50%	531.608	71.80%
	533.298	31.30%	533.298	29.50%	533.224	28.20%
N 1s	400.112	100.00%	400.009	100.00%	399.968	100.00%

**Table 4.6** Deconvolution results of PEHA-derived PBZ impregnating on AC

Region	AC+1wt%PBZ(PEHA)		AC+5wt%PBZ(PEHA)		AC+10wt%PBZ(PEHA)	
	Binding		Binding		Binding	
	Energy (eV)	%	Energy (eV)	%	Energy (eV)	%
C 1s	284.623	60.40%	284.604	56.80%	284.574	56.60%
	285.625	9.90%	285.594	13.00%	285.632	12.60%
	286.489	7.90%	286.422	7.90%	286.450	10.50%
	287.431	3.90%	287.407	4.60%	287.409	4.30%
	288.897	10.00%	288.896	13.30%	288.959	12.40%
	291.944	7.90%	293.083	4.50%	292.305	3.70%
O 1s	531.576	72.00%	531.583	63.80%	531.574	69.90%
	533.285	28.00%	533.278	36.20%	533.278	30.10%
N 1s	400.279	100.00%	400.183	100.00%	400.250	100.00%

**Table 4.7** Deconvolution results of activated carbon from polybenzoxazine

Region	PBZ-derived AC (DETA) (200°C)		PBZ-derived AC (DETA) (300°C)		PBZ-derived AC (DETA) (400°C)	
	Binding		Binding		Binding	
	Energy (eV)	%	Energy (eV)	%	Energy (eV)	%
C 1s	284.579	51.20%	284.450	57.60%	284.636	68.70%
	285.557	18.20%	285.621	16.30%	285.700	9.80%
	286.579	13.00%	286.536	10.40%	286.550	8.20%
	287.429	6.20%	287.429	7.40%	287.357	4.80%
	288.947	7.20%	288.985	4.90%	288.935	6.10%
	291.077	4.20%	291.163	3.40%	291.648	2.40%
O 1s	531.686	50.90%	531.384	73.10%	531.465	81.10%
	533.218	49.10%	533.281	26.90%	533.286	18.90%
N 1s	399.946	100.00%	400.111	100.00%	400.188	100.00%

**Table 4.8** Assignments of deconvoluted peaks as analyzed by XPS

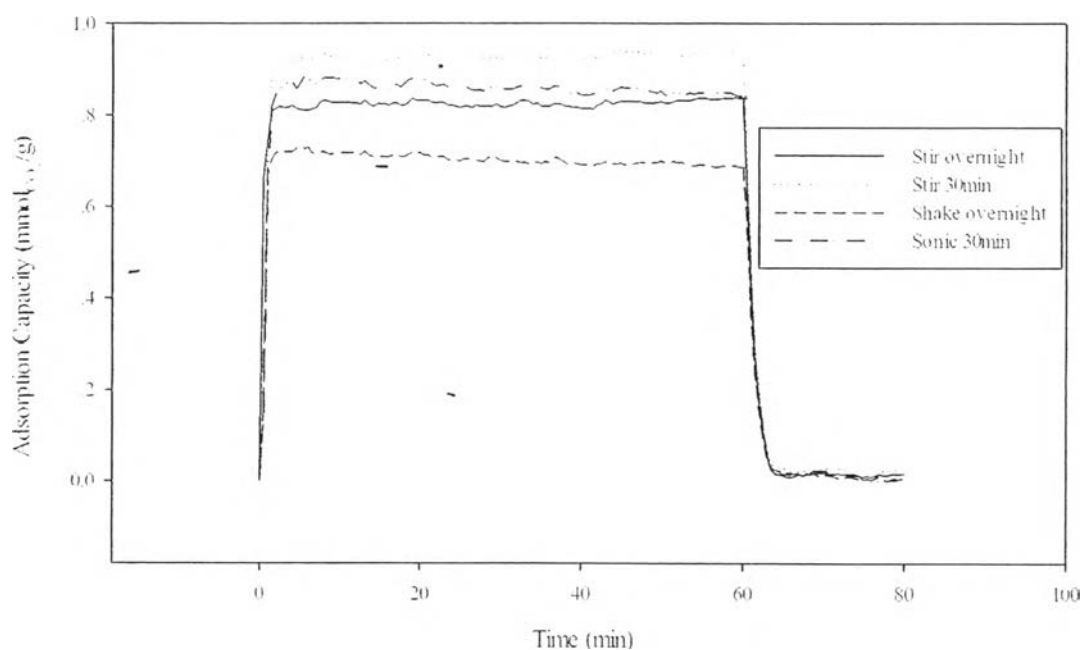
Region	Binding Energy (eV)	Assignment
C 1s	284.550±0.1	Carbon
	285.600±0.1	C with N
	286.390±0.2	C with N or Hydroxyl or Ether
	287.390±0.1	Carbonyl
	288.800±0.2	Carboxyl or Ester
O 1s	531.520±0.25	Hydroxide or Amide
	533.250±0.2	Ether or Alcohol or Carbonyl
N 1s	400.100±0.2	Amide or Lactame or Pyridone

From the results, all of adsorbents had similar surface functionalities. C1s was deconvoluted into five components commonly assigned in the analysis of carbon materials: (a) Carbon, (b) C with N, (c) C with N/Hydroxyl/Ether, (d) Carbonyl and (e) Carboxyl/Ester. The analysis of carbon materials are followed by XPS reference and Plaza *et al.* (2013). The O1s spectra is less complicated, with only two components, namely Hydroxide/Amide and Ether/Alcohol/Carbonyl that followed by XPS reference and Figueiredo *et al.* (1999). And the N1s spectra assigned to only one component namely Amide/ Lactame/Pyridone as suggested by Burg *et al.* (2012) and Pels *et al.* (1995). After benzoxazine impregnation on the untreated activated carbon, the C with N peaks approximately at 285.6 and 286.4 eV in the C1s region of impregnating adsorbents had more than the untreated activated carbon and this evidence confirms the impregnation on the surface of untreated activated carbon was successful. Moreover, the amounts of those two peaks increased when the DETA-derived benzoxazine loading or PEHA-derived benzoxazine loading were increased. The XPS analysis results from Table 4.7 showed that the amount of nitrogen functionalities at binding energy of 285.6 eV of the polybenzoxazine-derived activated carbon with carbonization temperature at 200 °C was comparable to the polybenzoxazine-derived activated carbon carbonized at 300 °C. In the polybenzoxazine-derived activated carbon with carbonization temperature at 400 °C, the amount of nitrogen functionalities was the lowest compared with others.

#### **4.2 Effect of Preparation Method on CO<sub>2</sub> Adsorption Performance**

Three methods of mechanical mixing, i.e. stirred, shake and sonic bath, between activated carbon and benzoxazine at various benzoxazine concentrations loading were employed for the preparation of polybenzoxazine impregnated adsorbents. From Table 4.1, the results showed that the stirring method obtained the highest amount of nitrogen component in all benzoxazine loading concentrations. The gravimetric technique was employed by using STA analyzer to measure CO<sub>2</sub> adsorption capacity. The CO<sub>2</sub> adsorption performance of activated carbon with 10wt%PBZ at 40 °C measured for all impregnation methods i.e. stirred for overnight, stirred for 30 min, shake for overnight and sonic for 30 min. The highest CO<sub>2</sub> adsorption capacity

is obtained at  $0.95 \text{ mmol}_{\text{CO}_2}/\text{g}_{\text{adsorbent}}$  from the sample with stirring for 30 min as shown in Figure 4.9. Hence, among all the impregnation method tested in this work, 30 min stirring method was selected for mechanical mixing in the impregnation method.



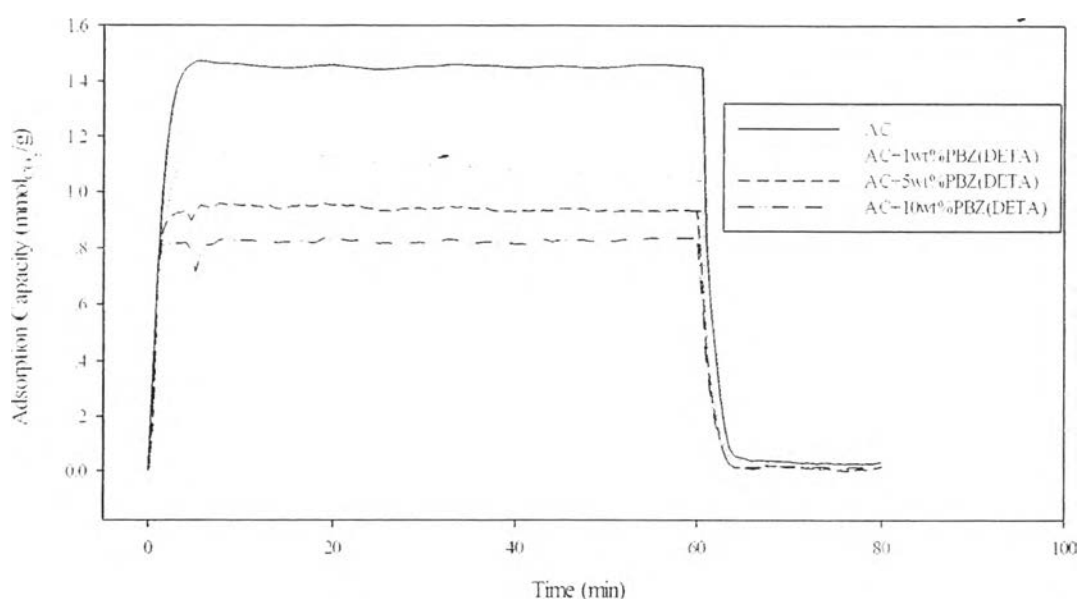
**Figure 4.9** Isothermal adsorption/desorption profiles at 40 °C of activated carbon impregnated with 10wt%PBZ using various impregnation methods.

### 4.3 Effect of Benzoxazine Loading on CO<sub>2</sub> Adsorption Performance

From the results by gravimetric method in Figure 4.10, Figure 4.12 and Figure 4.14, the CO<sub>2</sub> adsorption performance of untreated activated carbon and the series of DETA-derived polybenzoxazines impregnated adsorbents at 40 °C, 75 °C, and 140 °C. When increasing benzoxazine loading concentration to impregnate on the activated carbon surface (1wt%, 5wt%, and 10wt%), the CO<sub>2</sub> adsorption performance of all polybenzoxazine impregnated adsorbents was decreased in the same trend at all temperature conditions (at 40 °C ca. 1.09, 0.93, and 0.81  $\text{mmol}_{\text{CO}_2}/\text{g}_{\text{adsorbent}}$ , at 75 °C ca. 0.76, 0.64, and 0.53  $\text{mmol}_{\text{CO}_2}/\text{g}_{\text{adsorbent}}$  and at 140 °C ca. 0.30, 0.23, and 0.19  $\text{mmol}_{\text{CO}_2}/\text{g}_{\text{adsorbent}}$  at 1wt%, 5wt%, and 10wt% loading, respectively).

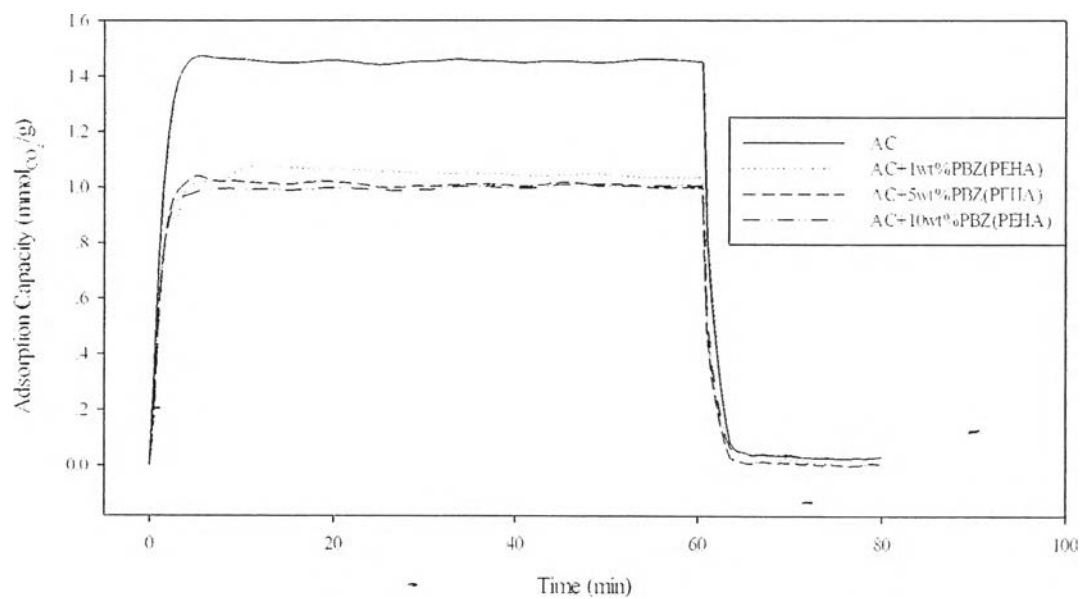
From Figure 4.11, Figure 4.13 and Figure 4.15, the results showed the CO<sub>2</sub> adsorption performance of same untreated activated carbon and the series of PEHA-derived polybenzoxazines impregnated on surface of adsorbents at 40 °C, 75 °C, and 140 °C. When increasing benzoxazine loading concentration to impregnate on the activated carbon surface (1wt%, 5wt%, and 10wt%), the CO<sub>2</sub> adsorption performance of all polybenzoxazine impregnated adsorbents was decreased in the same trend like the results from all polybenzoxazine with DETA as amine reactant impregnated adsorbents at all temperature conditions (at 40 °C ca. 1.07, 1.01, and 0.99 mmol<sub>CO<sub>2</sub></sub>/g<sub>adsorbent</sub>, at 75 °C ca. 0.77, 0.62, and 0.59 mmol<sub>CO<sub>2</sub></sub>/g<sub>adsorbent</sub> and at 140 °C ca. 0.31, 0.25, and 0.23 mmol<sub>CO<sub>2</sub></sub>/g<sub>adsorbent</sub> at 1wt%, 5wt%, and 10wt% loading, respectively).

The maximum CO<sub>2</sub> adsorption capacity is from the untreated activated carbon (AC) at 40 °C (1.45 mmol<sub>CO<sub>2</sub></sub>/g<sub>adsorbent</sub>). The decreasing in CO<sub>2</sub> adsorption with increasing benzoxazine loading may be caused by pore blocking effects during the curing process of polybenzoxazine after impregnation as evidence by the drastic reduction of BET surface area from Table 4.1. The benefits of chemisorption from impregnated polybenzoxazine were not clear from this work.

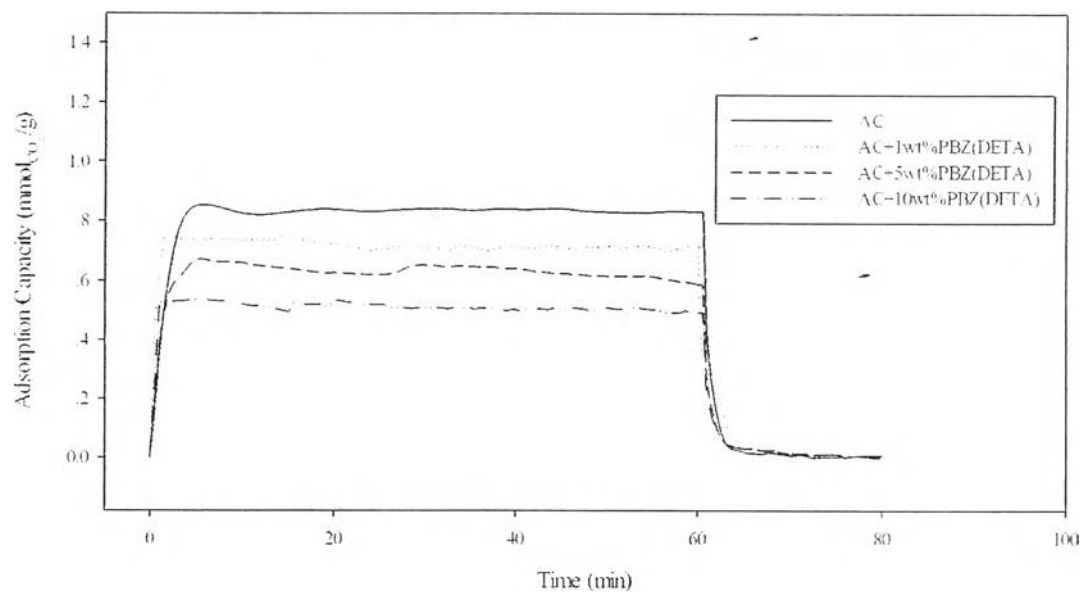


**Figure 4.10** Isothermal adsorption/desorption profiles at 40 °C of activated carbon impregnated with various PBZ (DETA) loading.

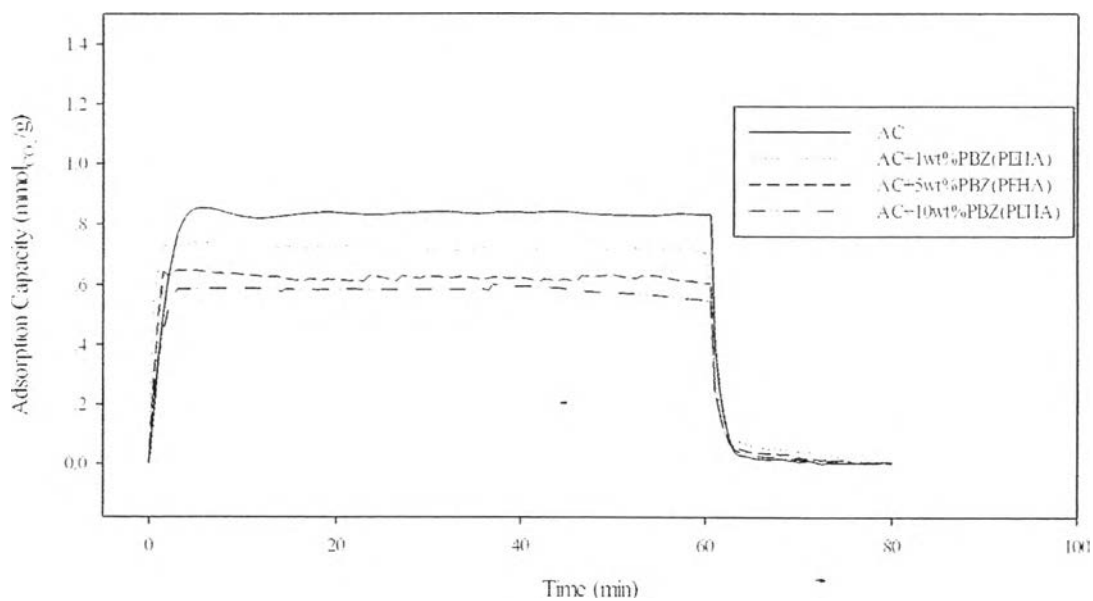




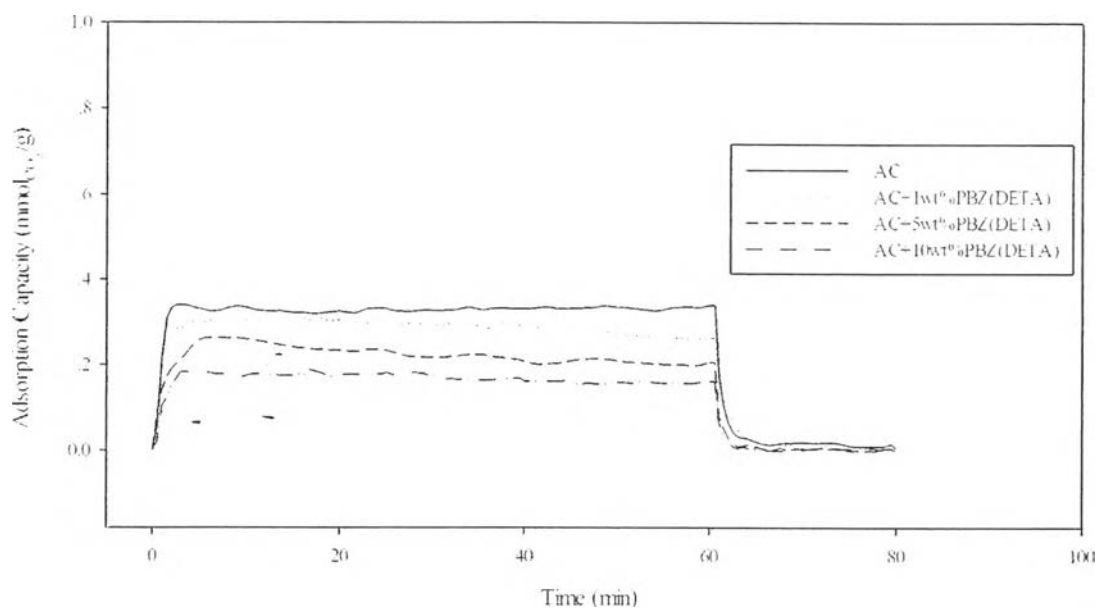
**Figure 4.11** Isothermal adsorption/desorption profiles at 40 °C of activated carbon impregnated with various PBZ (PEHA) loading.



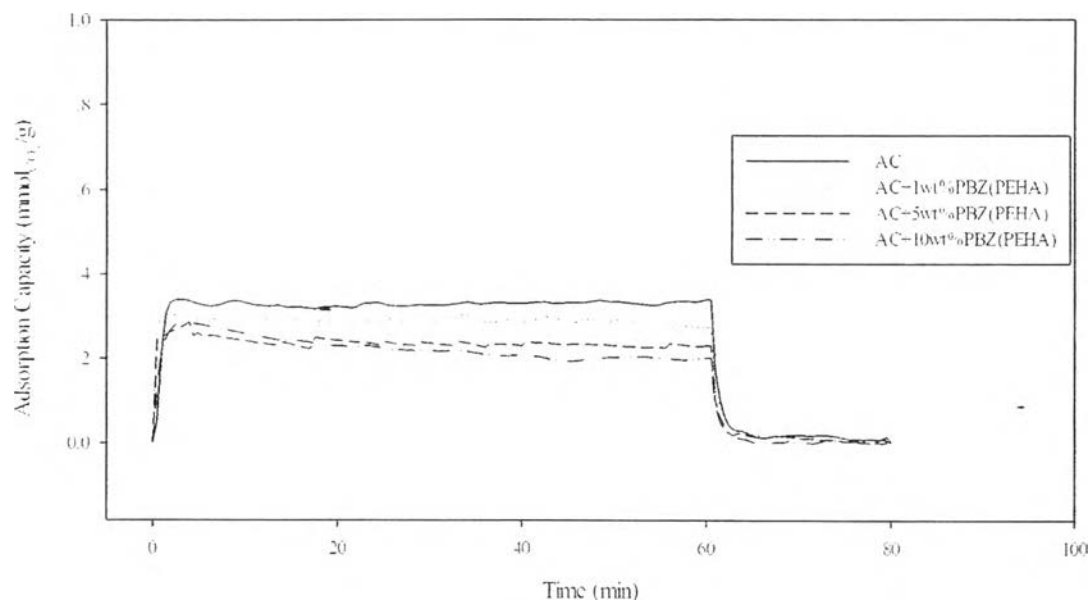
**Figure 4.12** Isothermal adsorption/desorption profiles at 75 °C of activated carbon impregnated with various PBZ (DETA) loading.



**Figure 4.13** Isothermal adsorption/desorption profiles at 75 °C of activated carbon impregnated with various PBZ (PEHA) loading.



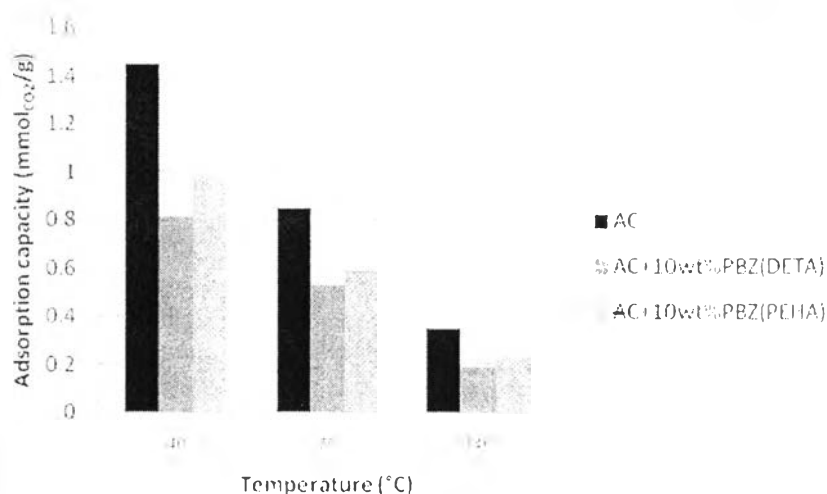
**Figure 4.14** Isothermal adsorption/desorption profiles at 140 °C of activated carbon impregnated with various PBZ (DETA) loading.



**Figure 4.15** Isothermal adsorption/desorption profiles at 140 °C of activated carbon impregnated with various PBZ (PEHA) loading.

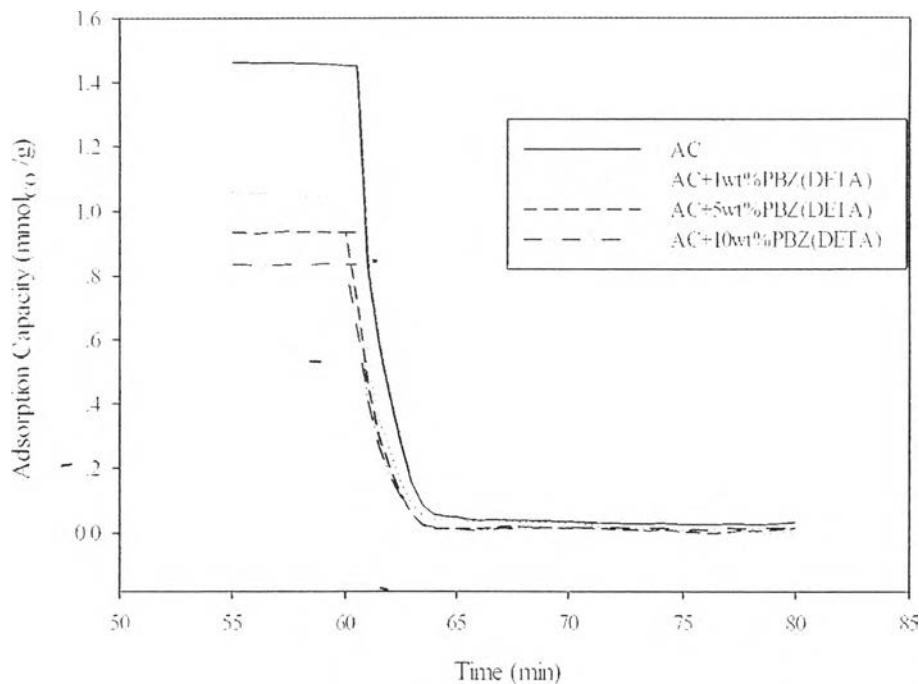
#### 4.4 Effect of Structure of Amine for the Benzoxazine Synthesis on CO<sub>2</sub> Adsorption Performance

From the results from gravimetric method by using STA analyzer to measure CO<sub>2</sub> adsorption capacity in Figure 4.16, the results showed the CO<sub>2</sub> adsorption capacity of 10wt% loading of polybenzoxazine derived from DETA and PEHA as impregnating materials at 40 °C, 75 °C, and 140 °C. The impregnated adsorbents with PEHA-derived benzoxazine perform a higher CO<sub>2</sub> adsorption capacity than those impregnated adsorbents with DETA-derived benzoxazine at all temperatures. This is directly because the BET surface area from Table 4.1 and the amount of nitrogen content of the PEHA-derived benzoxazine are higher than the benzoxazine derived from DETA as evidenced from the nitrogen content by the CHN analysis (13.81% and 9.17%, respectively).

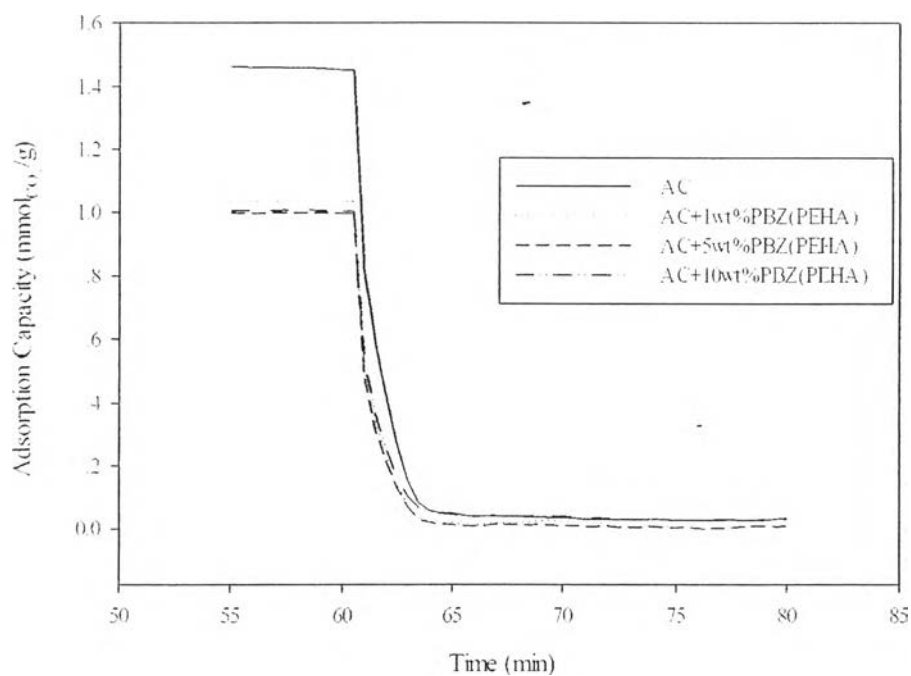


**Figure 4.16** CO<sub>2</sub> adsorption performance of modified adsorbents with varying amine as reactant at all temperatures.

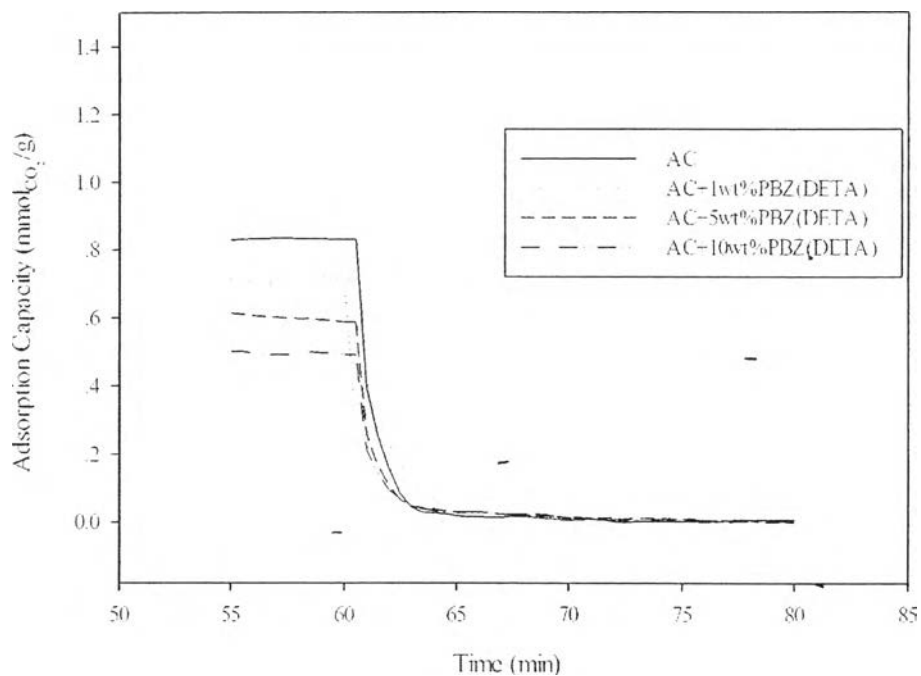
From Figure 4.17, Figure 4.18, Figure 4.19, Figure 4.20, Figure 4.21, Figure 4.22, and Table 4.9, the results showed that the adsorbents can be regenerated but not completely at low temperature (40 °C), however, when increasing temperature of adsorption/desorption, the regeneration was complete because the CO<sub>2</sub> on the surface could easily be regenerated at higher temperature. And when the benzoxazine loading concentrations increased, the adsorbents are more difficult to be regenerated due to the chemisorption by the nitrogen in polybenzoxazine and CO<sub>2</sub>.



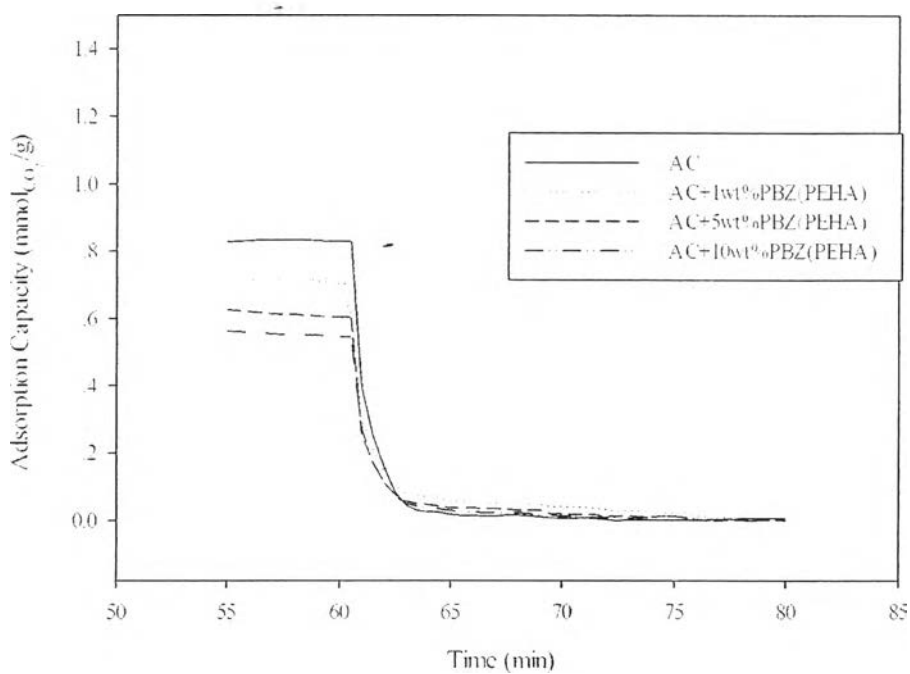
**Figure 4.17** Isothermal regeneration profiles at 40 °C of activated carbon impregnated with various PBZ (DETA) loading.



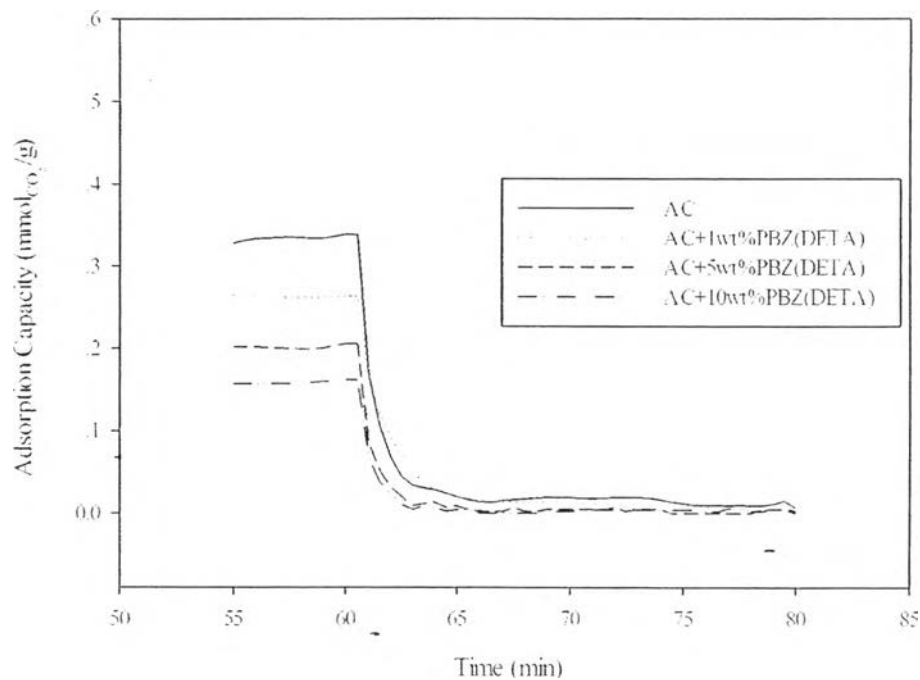
**Figure 4.18** Isothermal regeneration profiles at 40 °C of activated carbon impregnated with various PBZ (PEHA) loading.



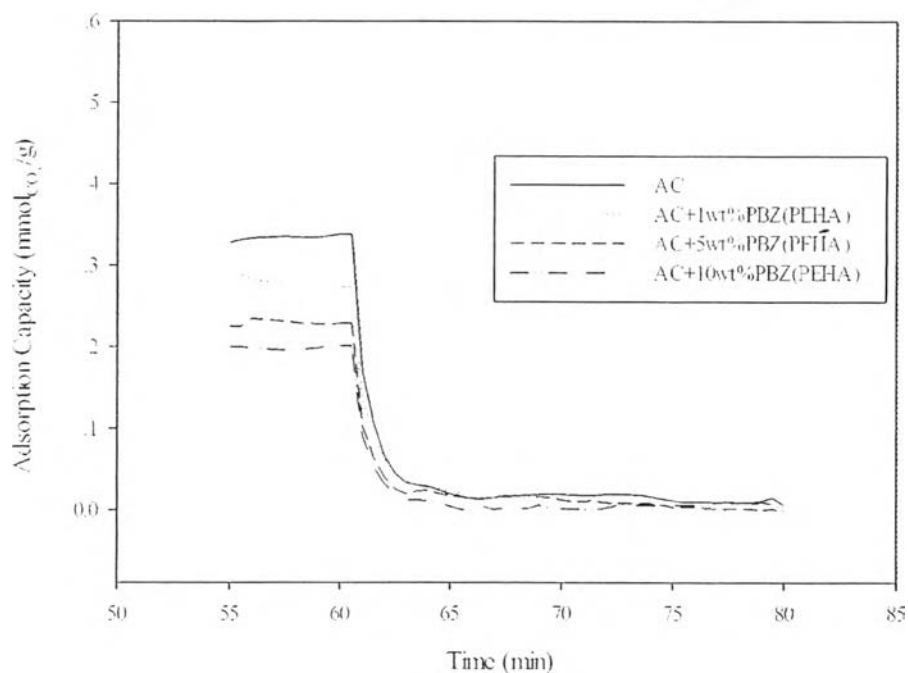
**Figure 4.19** Isothermal regeneration profiles at 75 °C of activated carbon impregnated with various PBZ (DETA) loading.



**Figure 4.20** Isothermal regeneration profiles at 75 °C of activated carbon impregnated with various PBZ (PEHA) loading.



**Figure 4.21** Isothermal regeneration profiles at 140 °C of activated carbon impregnated with various PBZ (DETA) loading.



**Figure 4.22** Isothermal regeneration profiles at 140 °C of activated carbon impregnated with various PBZ (PEHA) loading.

**Table 4.9** The comparison between benzoxazine loading and % of regeneration

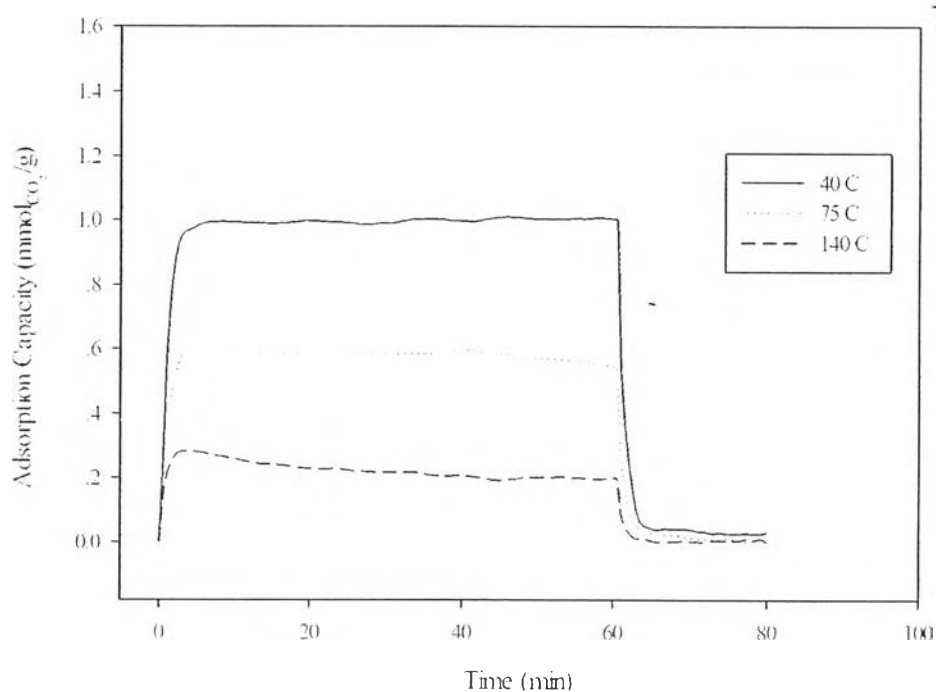
Temperature	Adsorbents	%Regeneration
40°C	AC + 1wt%PBZ (DETA)	100.00
	AC + 5wt%PBZ (DETA)	99.98
	AC + 10wt%PBZ (DETA)	99.98
	AC + 1wt%PBZ (PEHA)	99.99
	AC + 5wt%PBZ (PEHA)	99.99
	AC + 10wt%PBZ (PEHA)	99.97
75°C	AC + 1wt%PBZ (DETA)	100.00
	AC + 5wt%PBZ (DETA)	100.00
	AC + 10wt%PBZ (DETA)	100.00
	AC + 1wt%PBZ (PEHA)	100.00
	AC + 5wt%PBZ (PEHA)	100.00
	AC + 10wt%PBZ (PEHA)	100.00
140°C	AC + 1wt%PBZ (DETA)	100.00
	AC + 5wt%PBZ (DETA)	100.00
	AC + 10wt%PBZ (DETA)	100.00
	AC + 1wt%PBZ (PEHA)	100.00
	AC + 5wt%PBZ (PEHA)	100.00
	AC + 10wt%PBZ (PEHA)	100.00
40°C	PBZ-derived AC (DETA) (Carbonized at 200 °C)	99.96
	PBZ-derived AC (DETA) (Carbonized at 300 °C)	99.98
	PBZ-derived AC (DETA) (Carbonized at 400 °C)	99.97

\*AC = Activated carbon, PBZ = Polybenzoxazine



#### 4.5 Effect of Temperature on CO<sub>2</sub> Adsorption Performance

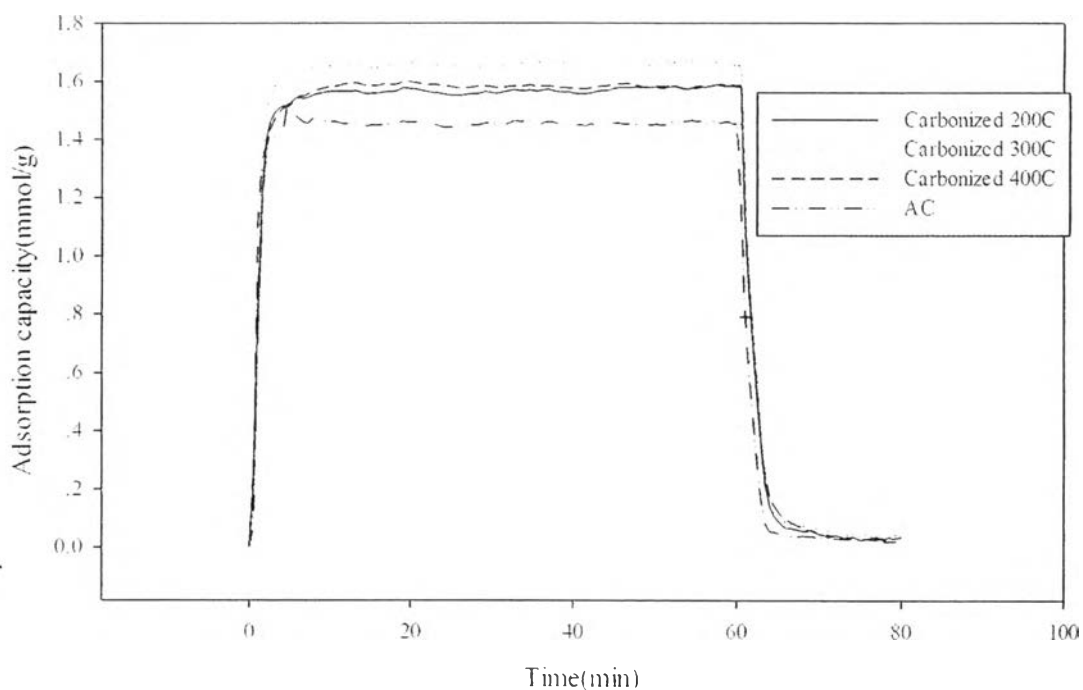
After varying temperature of adsorption for determining CO<sub>2</sub> adsorption performance. Figure 4.23 showed the adsorption/desorption profiles of the series of activated carbon with 10wt% loading of polybenzoxazine derived from PEHA at 40 °C, 75 °C, and 140 °C. With increasing temperature, the CO<sub>2</sub> adsorption capacity is decreased due to the physisorption but the chemisorption was not clearly observed.



**Figure 4.23** Isothermal adsorption/desorption profiles at various temperature of activated carbon impregnated with 10wt%PBZ (PEHA).

#### 4.6 Effect of Polybenzoxazine Carbonization and Activation on CO<sub>2</sub> Adsorption Performance

After carbonization by varying three carbonization temperature (200 °C, 300 °C, and 400 °C) under N<sub>2</sub> atmosphere and activation at 800 °C by CO<sub>2</sub>, Figure 4.24 shows the CO<sub>2</sub> adsorption performance of polybenzoxazine-derived activated carbon from gravimetric method.

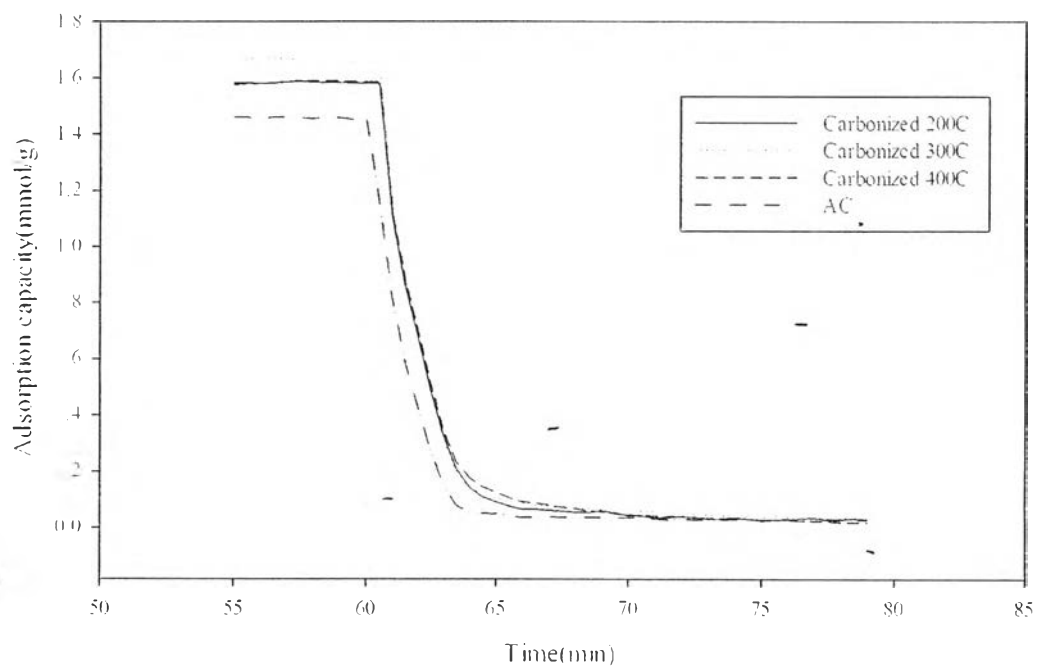


**Figure 4.24** CO<sub>2</sub> adsorption performances at 40 °C of untreated activated carbon and activated carbon from polybenzoxazine with varying carbonization temperatures.

The result showed that the CO<sub>2</sub> adsorption capacity of polybenzoxazine-derived activated carbon with carbonization temperature at 300 °C showed the highest CO<sub>2</sub> adsorption capacity at 1.65 mmol<sub>CO<sub>2</sub></sub>/g<sub>adsorbent</sub>. The polybenzoxazine-derived activated carbon from three carbonized temperature had higher CO<sub>2</sub> adsorption performance than the untreated activated carbon because the amount of nitrogen functionalities from all polybenzoxazine-derived activated carbon were higher than from the untreated activated carbon as evidenced from the XPS analysis in Table 4.4 and Table 4.7. At the binding energy of 285.6 eV of C 1s region referred to the bonding between carbon and nitrogen, the untreated activated carbon did not contain this peak. Although the BET surface area of the untreated activated carbon (1090 m<sup>2</sup>/g) was higher than all polybenzoxazine-derived activated carbon (134 m<sup>2</sup>/g, 267 m<sup>2</sup>/g, and 102 m<sup>2</sup>/g at carbonizing temperature of 200 °C, 300 °C and 400 °C, respectively, as shown in Table 4.1), all polybenzoxazine-derived activated carbon samples yield a higher CO<sub>2</sub> adsorption performance. This is clearly revealed that the chemisorption from bonding between CO<sub>2</sub> and nitrogen has more influence than the physisorption.

The comparison between the three different carbonization temperatures of polybenzoxazine-derived activated carbon, the CO<sub>2</sub> adsorption capacity of polybenzoxazine-derived activated carbon with carbonization temperature of 300 °C showed the highest performance. The XPS analysis results from Table 4.7 showed that the amount of nitrogen functionalities at binding energy of 285.6 eV of the polybenzoxazine-derived activated carbon with carbonization temperature at 200 °C was comparable to the polybenzoxazine-derived activated carbon carbonized at 300 °C but the BET surface area of polybenzoxazine-derived activated carbon with carbonization temperature at 300 °C was higher than at 200 °C (267 m<sup>2</sup>/g vs 134 m<sup>2</sup>/g). In the polybenzoxazine-derived activated carbon with carbonization temperature at 400 °C, the amount of nitrogen functionalities was the lowest compared with other polybenzoxazine-derived activated carbon and the BET surface area was similar to the polybenzoxazine-derived activated carbon with carbonization temperature at 200 °C (102 m<sup>2</sup>/g vs 134 m<sup>2</sup>/g). This lower in the nitrogen functionalities in the sample carbonized at 400 °C was directly due to the loss of nitrogen from the higher carbonizing temperature. The three different carbonization temperatures of polybenzoxazine-derived activated carbon had the different pore size (0.66 nm, 0.78 nm, and 0.83 nm at carbonizing temperature of 200 °C, 300 °C and 400 °C, respectively, as shown in Table 4.1) however, they were all in microporous ranges. In conclusion, the XPS results have revealed that the nitrogen functionalities were maintained at all carbonizing temperature of the polybenzoxazine-derived activated carbon. Carbonizing at 300 °C was the suitable temperature that optimized the BET surface area and the amount of nitrogen functionalities and, hence, gave the highest CO<sub>2</sub> adsorption capacity.

The regeneration capacity of the polybenzoxazine-derived activated carbon at 40 °C was shown in Figure 4.25 and Table 4.9. The results showed the polybenzoxazine-derived activated carbon adsorbents cannot be regenerated completely for all polybenzoxazine-derived activated carbon because of the chemical mechanism by the nitrogen in polybenzoxazine and CO<sub>2</sub>.



**Figure 4.25** Isothermal regeneration profiles at 40 °C of untreated activated carbon and activated carbon from polybenzoxazines.