

# Effects of Different Polyethyleneimine Molecular Weights on CO<sub>2</sub> Adsorption on Activated Carbon

Promporn Ritmongkolpun<sup>a</sup>, Pramoch Rangsunvigit<sup>\*a</sup>, Santi Kulprathipanja<sup>b</sup>

<sup>a</sup>The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

<sup>b</sup>UOP, A Honeywell Company, Des Plaines, Illinois, USA

Pramoch.r@chula.ac.th

Effects of different polyethyleneimine (PEI) molecular weights on CO<sub>2</sub> adsorption on activated carbon (AC) were investigated. The PEI loading was varied using different PEI initial concentrations from 1 to 5 g/L. CO<sub>2</sub> adsorption isotherms were investigated at 30 and 75 °C. Adsorbents were characterized by TG-DTA, FTIR, and surface area and pore size analysis. The results showed that PEI impregnated on activated carbon improved the CO<sub>2</sub> adsorption capacity due to the synergistic effects between physical and chemical adsorption. AC impregnated with low molecular weight PEI showed improvement in the CO<sub>2</sub> adsorption capacity at a low temperature. Higher PEI molecular weights showed higher adsorption capacity at a high temperature. An optimum amount of PEI loading and appropriate PEI molecular weight are needed to increase the CO<sub>2</sub> adsorption capacity.

## 1. Introduction

The amine-functionalized adsorbents were investigated as adsorbents which can overcome a limitation of classic adsorbents in the CO<sub>2</sub> adsorption field by synergistic effects of physical and chemical adsorption (Chang et al., 2009). Polyethyleneimine (PEI) is a very attractive polymer for the CO<sub>2</sub> adsorption due to its high affinity with CO<sub>2</sub>. Because of different amines and large amount of amines, PEI can adsorb CO<sub>2</sub> via different mechanisms and enhance CO<sub>2</sub> adsorption performance (Heydari-Gorji and Sayari, 2011). Dejburi et al. (2012) loaded PEI into the high internal phase emulsion polymer (polyHIPE) to enhance the CO<sub>2</sub>. In addition, PEI impregnated materials were investigated and shown to improve the CO<sub>2</sub> adsorption capacity (Xu et al., 2003). From previous work, Pipatsantipong (2011) showed that the use of PEI-impregnated activated carbons enhanced the CO<sub>2</sub> adsorption. However, there is only one type of PEI investigated despite of the wide variety of PEI available. This work prepared PEI impregnated on activated carbon with different loadings and molecular weights. The CO<sub>2</sub> adsorption capacity was performed using static adsorption technique.

## 2. Experimental

Coconut-shell based ACs were ground and sieved to obtain a particle size of 20-40 mesh. Then, ACs were dried at 120 °C for 24 h. ACs were added to PEI solution or liquid PEI (with various Mw) with methanol of desired PEI initial concentration (1.0 – 5.0 g/L). The solid to liquid ratio was 1 g of ACs to 20 mL of PEI solution in a closed system. The ACs together with the PEI solution were agitated in an orbital shaker at 180 rpm at 25 °C for 3 days. The adsorbents were dried at 120 °C for 24 h to remove volatile solvent and moisture. The adsorbents were characterized by various techniques described as follows. The amounts of PEI impregnated on ACs were determined by Shimadzu/UV-1800 UV-Vis Spectrophotometer (at  $\lambda_{\max}$  = 203 nm). Thermal stability of adsorbents was investigated by TG-DTA (Perkin-Elmer/Pyris Diamond). Thermo Nicolet/Nexus 670 FTIR instrument was used to confirm and detect functional group. Surface area and porosity of adsorbents were measured by surface area and pore size analyzer (Quantachrom/Autosorb1-MP). The experiment set-up was modified from Pipatsantipong (2011) by

installing a gas storage vessel, as shown in Figure 1. A pressure transmitter was installed to measure pressure of the system. One gram of an adsorbent was loaded into the adsorption chamber. Helium gas

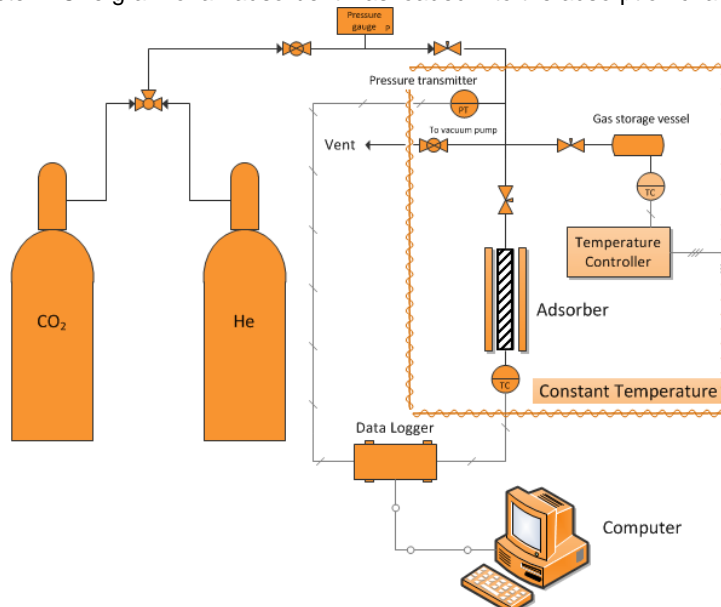


Figure 1: schematic of experimental setup.

(99.999%) was used to measure the system volume by expansion principal. The adsorption processes were carried out using high purity CO<sub>2</sub> gas (99.99 %). Effect of adsorption temperature was investigated by varying the temperature from 30 to 75 °C within a pressure range of 0 – 1 atm.

### 3. Results and discussion

PEI with different molecular weights - Mw, 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). Table 1 shows the amounts of PEI impregnated on ACs. 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. Figure 2(a) shows thermogram of the AC with one step weight loss due to the removal of volatile and moisture. From Figures 2(b) - 1(d), the thermograms show 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. The FTIR spectra of all adsorbents are shown in Figure 3. The wavelength at 1,480 cm<sup>-1</sup> shows the signal of N-H bond, which could represent the N-H functional group in the PEI structure and also the AC structure.

Surface area, pore volume, and pore diameter of the adsorbents are shown in Table 2. 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 hence, 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 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

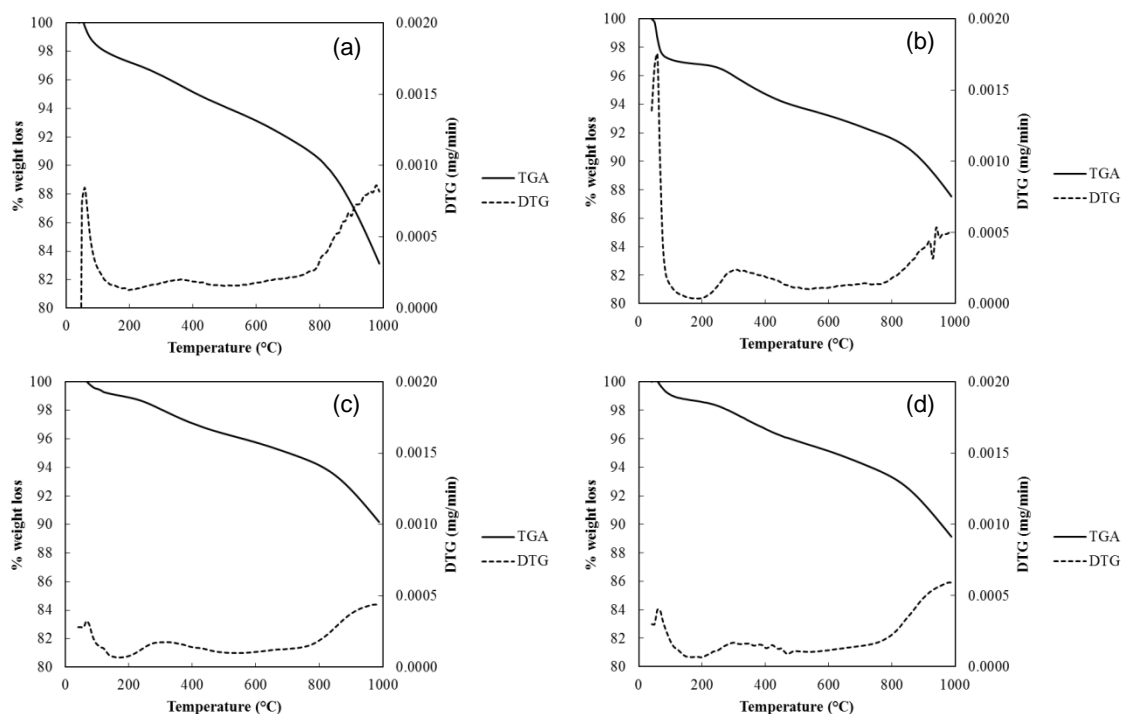


Figure 2: TGA and DTG thermograms of (a) AC, (b) 2.84 wt% Low Mw PEI/AC, (c) 1.90 wt% Med Mw PEI/AC, and (d) 0.86 wt% High Mw PEI/AC

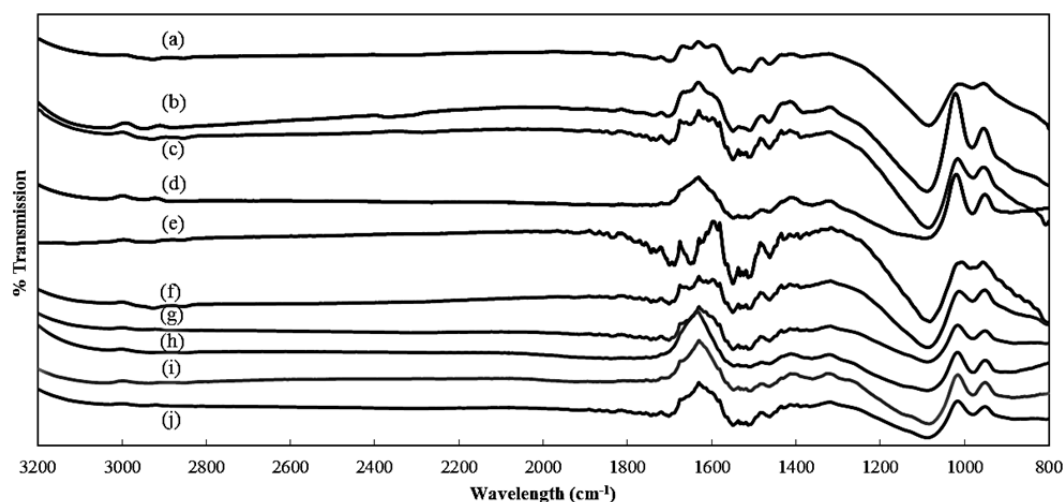


Figure 3: FTIR Spectra of (a) AC, (b)-(d) 1.68, 2.18, and 2.84 wt% Low Mw PEI/AC, (e)-(g) 0.73, 1.16, and 1.90 wt% Med Mw PEI/AC, and (h)-(j) 0.16, 0.45, and 0.86 wt% High Mw PEI/AC

Table 2: Surface area, pore volume, and pore diameter of adsorbents

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

CO<sub>2</sub> adsorption isotherms were constructed at 30 and 75 °C as shown in Figure 4. AC has the CO<sub>2</sub> adsorption capacity of 2.75 and 1.29 mmol/g adsorbent at 30 and 75 °C. For the unmodified AC, the increase in the adsorption temperature reduces the CO<sub>2</sub> adsorption capacity because physisorption of AC is not favourable at the high adsorption temperature. At 30 °C (Figures 4(a) - 3(c)), the addition of Low Mw PEI and Med Mw PEI significantly improves the CO<sub>2</sub> adsorption capacity. At the low temperature, chemical reactions between the amine group and CO<sub>2</sub> are not preferred but it could be proposed that the PEI provides the acid-base interaction between their amine group and CO<sub>2</sub> and synergizes with the physisorption to increase the CO<sub>2</sub> adsorption capacity. 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<sub>2</sub> accessibility to the amine groups. 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<sub>2</sub> adsorption capacity. At 30 °C, the 1.68 wt% Low Mw PEI and 0.73 wt% Med Mw PEI have the highest CO<sub>2</sub> adsorption capacity, which are 3.02 and 3.08 mmol/g adsorbent, respectively. At 75 °C (Figures 4(d) - 3(f)), the Low Mw PEI/ACs have lower CO<sub>2</sub> adsorption capacity than the unmodified AC because the decrease in the capacity may be due to the relaxation of PEI molecules at the higher 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 it 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<sub>2</sub> accessibility. At 75 °C, the capacity of all

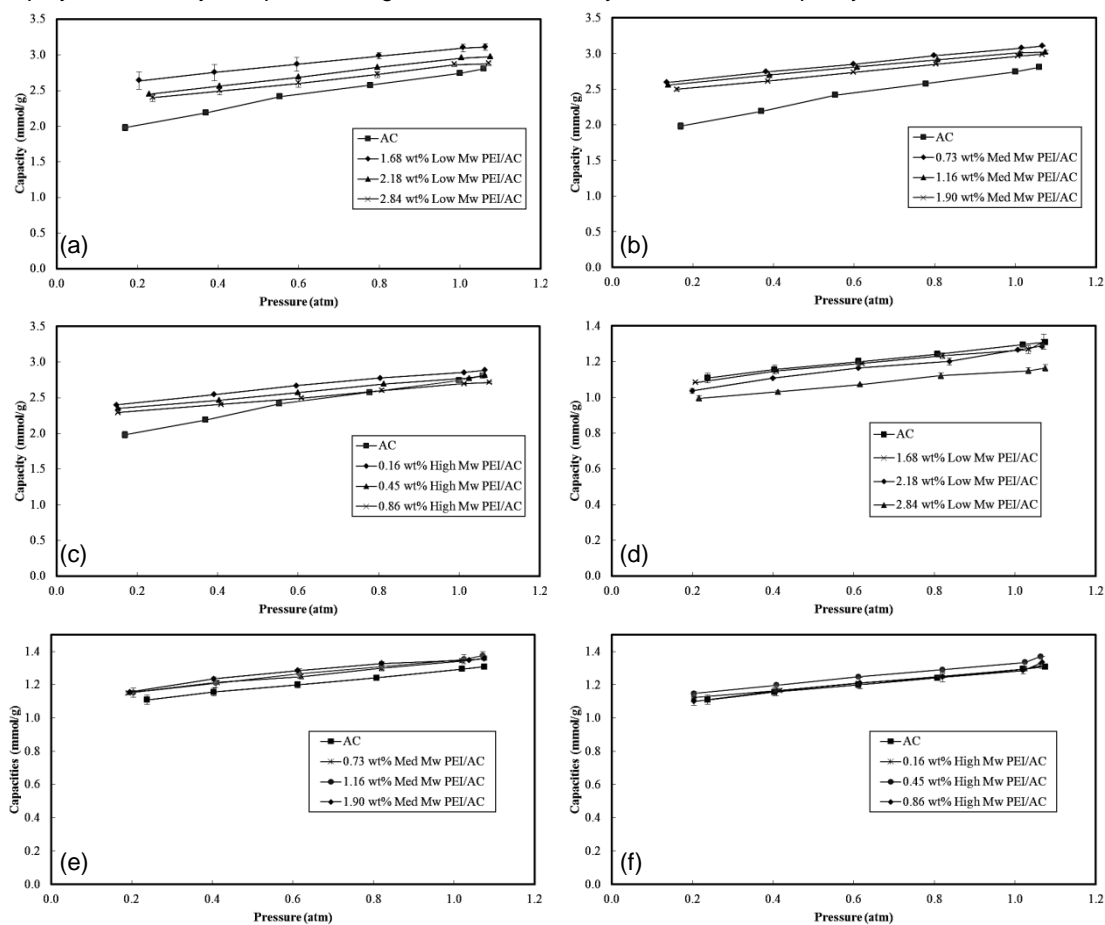


Figure 4: CO<sub>2</sub> adsorption isotherms of AC and PEI/ACs at (a)-(c) 30 °C and (d)-(f) 75 °C

Med Mw PEI/ACs is about the same at 1.35 mmol/g adsorbent at nearly 1 atm. That can be explained that the increase in the pressure can drive CO<sub>2</sub> to the PEI bulk easier and a 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<sub>2</sub> 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<sub>2</sub> accessibility and density of amine group per area.

#### 4. Conclusions

The impregnation of PEI can improve the CO<sub>2</sub> adsorption capacity due to the synergistic effects between physical and chemical adsorption. However, the results showed that different molecular weights of the polymer affected the CO<sub>2</sub> adsorption. The Low Mw PEI/AC showed the enhancement in the CO<sub>2</sub> adsorption capacity at 30 °C with a significant extent. The Med Mw PEI/AC and High Mw PEI/AC showed higher adsorption capacity at 75 °C. That is partly due to the amount and molecular size of the polymer impregnated on the activated carbon. On a whole, an optimum amount of PEI loading and appropriate PEI molecular weight are needed to increase the CO<sub>2</sub> adsorption capacity.

#### Acknowledgements

The authors would like to sincerely thank the Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University(RES560530021-CC); Center of Excellence on Petrochemicals, and Materials Technology; The Petroleum and Petrochemical College, Chulalongkorn University, Thailand; and UOP, A Honeywell Company, USA.

**References**

- Chang F.Y., Chao K.J., Cheng H.H., Tan C.S., 2009, Adsorption of CO<sub>2</sub> onto amine-grafted mesoporous silicas, *Separation and Purification Technology*, 70, 87-95.
- Dejburum P., Saiwan C., Tontiwachwuthikul P., 2012, Polyethyleneimine loading into high internal phase emulsion polymer for CO<sub>2</sub> adsorption: Synthesis and Characterization of the PolyHIPE, *Chemical Engineering Transactions*, 29, 193-198. DOI: 10.3303/CET1229033.
- Heydari-Gorji A., Sayari A., 2011, CO<sub>2</sub> capture on polyethyleneimine-impregnated hydrophobic mesoporous silica: Experimental and kinetic modeling, *Chemical Engineering Journal*, 173, 72-79.
- Pipatsantipong S., 2011, Enhanced CO<sub>2</sub> adsorption by activated carbon impregnated with PEI, MS Dissertation, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
- Yin C.Y., Aroua M.K., Daud W.M.A.W., 2008, Polyethyleneimine impregnation on activated carbon: Effects of impregnation amount and molecular number on textural characteristics and metal adsorption capacities, *Materials Chemistry and Physics*, 112, 417-422.
- Xu X., Song C., Andrésen J.M., Miller B.G., Scaroni A.W., 2003, Preparation and characterization of novel CO<sub>2</sub> "molecular basket" adsorbents based on polymer-modified mesoporous molecular sieve MCM-41, *Microporous and Mesoporous Materials*, 62, 29-45.