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Equilibrium Isotherms of the Adsorption of Pyrolysis Gases from Polymer Products

Ming-Hong Lai,[†] Yi-Ling Shih,[‡] Yi-Hua Chen,[‡] Shih-Hong Shu,[‡] and Tsair-Wang Chung*,[‡]

Department of Disaster Management, Taiwan Police College, Taipei 11696, Taiwan, Republic of China, and Department of Chemical Engineering/R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli, Taoyuan 32023, Taiwan, Republic of China

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There are many polymer products used in homes, and there is great concern about the toxic compounds which may be produced from these in the case of fire. Typical polymer-based products used in homes—poly(ethylene terephthalate), Nylon6, Nylon66, polystyrene, polypropene, and polyethylene products—have been selected to identify pyrolysis gases for adsorption equilibrium study. Pyrolysis gases from heating the samples of polymer-based products were analyzed by thermogravimetric analysis/automatic thermal desorption/gas chromatography/mass spectrometry. On the basis of the adsorption equilibrium data, activated carbon was more efficient than silica gel and zeolite 13X in the adsorption of the pyrolysis gases. Adsorption uptakes of the pyrolysis gases of aromatic, alkane, alkene, alcohol, ketone, epoxide, and acid gases on activated carbon were observed to be in the range of (10 to 50) ppm, and the adsorption uptake of acid gases was the highest. The regression model for the equilibrium isotherm data using the Freundlich equation was also developed in this study.

Introduction

In our daily life, there are many products made of polymers. Many of these products may produce toxic gases in the case of fire. Polyethylene (PE) and polypropylene (PP) start to release volatiles at about (718 and 683) K, respectively, in pyrolysis heating.[1] Poly(ethylene terephthalate) (PET) release volatiles at about 573 K.[2] Polystyrene (PS) produce aromatics when heat-decomposed.[3] Nylons produce various volatile gases and also carbon monoxide and carbon dioxide.[4,5] In this study, combined thermogravimetric analysis/automatic thermal desorption/gas chromatography/mass spectrometry (TGA-ATD-GC/MS) was used to analyze the pyrolysis gases from selected polymer products. Coupling TGA with GC/MS and ATD make it possible to identify the different volatile species emitted during pyrolysis; for example, this technique has been used to study polyolefins distinguished by different levels of tertiary hydrogen.[6,7] The purpose was to obtain adsorption equilibrium data for potentially toxic components in pyrolysis gases from polymers. In industry, activated carbon, silica gel, and zeolite are the typical adsorbents employed to adsorb volatile organic compound (VOC) emissions.[8] Compared with other zeolites, zeolite 13X is well-known to have better properties to remove VOCs.[9] To achieve a better understanding of the adsorption behavior of oxygenated hydrocarbons in the pyrolysis gases, we compared activated carbon, silica gel, and zeolite 13X as sorbents for the equilibrium adsorption analysis. The Freundlich isotherm model was then used to develop the equilibrium isotherm model.[10]

To design an adsorption apparatus, equilibrium isotherm data are required. Isotherm data are usually obtained from equilibrium sorption experiments.[11,12] For example, the required amount of sorbent for an adsorption unit is determined by the equilibrium uptake data, and the selection of an effective sorbent is also dependent on the equilibrium isotherm data. In this study, equilibrium isotherm data were obtained by a gravimetric method in which the uptake of pyrolysis gas was measured with a microbalance.

From our analysis of the pyrolysis gases from selected polymer-based products by TGA-ATD-GC/MS, together with perusal of available literature data for pyrolysis products from pure polymers, a short list (see Table 2) of pyrolysis gases which potentially may seriously affect the health of fire safety personnel were selected as the adsorbates in a subsequent equilibrium adsorption study. The experimental adsorption equilibrium data and the regression model for the isotherm curves of these selected pyrolysis gases are presented in this work. The adsorption equilibrium data reported here may be useful as reference data to authenticate witness reports at a fire scene and as a fire safety database for firemen, especially since technical reports in the published literature are lacking.

Experimental System

Sorbents. Commercial activated carbon (China Activated Carbon Industries Co.), silica gel (Kanto Chemical Co.), and zeolite 13X (Lancaster Synthesis Co.) were selected as sorbents in this study. The surface properties were measured using a Brunauer−Emmett−Teller (BET) sorptometer (Micromeritics ASAP 2000). The sorbent was degassed at (373 ± 1) K under vacuum for 24 h before the adsorption measurements were carried out at (77 ± 1) K. The calculations of specific surface area and average pore diameter were based on the BET model by assuming the pore shape to be a cylinder.

Sorbates. Pentane (Tedia, 95 + %), methyl alcohol (Seedchem, 95 + %), acetic acid (Scharlau, 99.8 %), formic acid (Acros, 99 %), acetone (Leda, 99.5 %), 2-pentanone (Tedia, 99.47 %), benzene (Acros, 99 %), 1,2-epoxybutane (Tokyo, 98 %), isobutylene oxide (Tokyo, 97 %), and 4-methyl-1-pentene (Tokyo, 99 %) were selected as the sorbates in this study.

Apparatus and Procedure. The Perkin-Elmer TGA-7, with the operating temperature adjusted to increase from room

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* Corresponding author. E-mail: twchung@cycu.edu.tw. Fax: +886-3-2654125.

[†] Taiwan Police College.

[‡] Chung Yuan Christian University.

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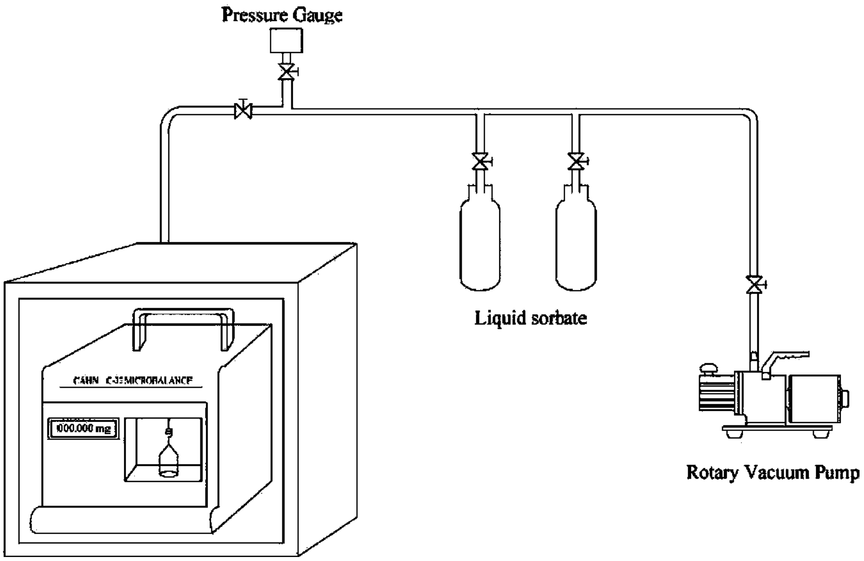

Figure 1. Static adsorption apparatus, gravimetric method.

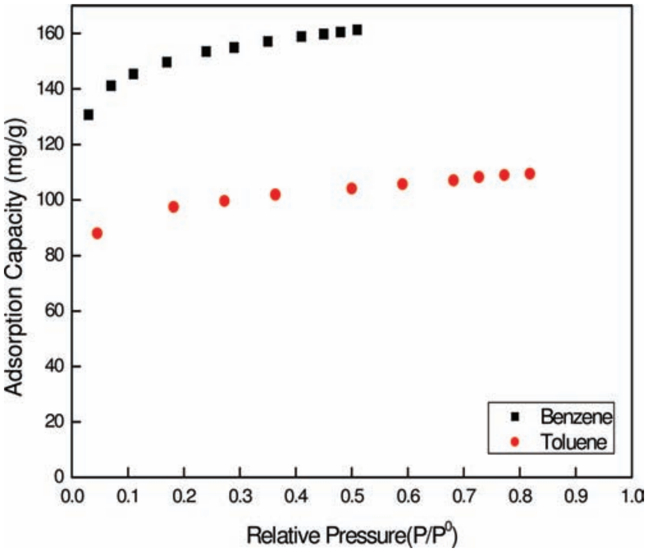

Figure 2. Adsorption capacities for aromatic compounds on activated carbon.

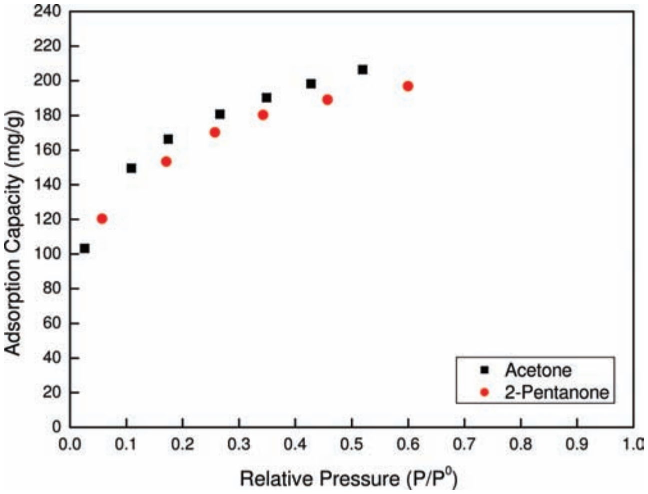

Figure 3. Adsorption capacities for alkanone on activated carbon.

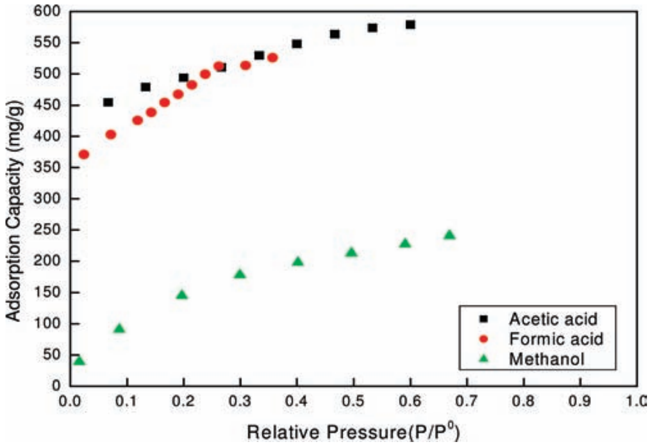

Figure 4. Adsorption capacities for alkanol and acid on activated carbon.

temperature to 900 °C at the rate of 10 °C·min^{-1}, was connected to an ATD to accumulate the emitted pyrolysis gases from the selected heat-decomposed samples. The desorption in ATD was carried out by using N_2 gas at 50 °C for 2 min (desorption flow cycle at 30 mL·min^{-1}, line temperature of 250 °C, trap at 250 °C) and then flashed at 250 °C for 1 min (N_2 at the pressure of 10.5 psi, outlet split 100 mL·min^{-1}). The desorption gas from ATD was then injected to a GC/MS. An Elite 5 ms column (30 m × 0.25 mm × 0.25 μm) was used for GC, and the oven temperature was set to heat at 50 °C for 2 min, increased at the rate of 10 °C·min^{-1} to 250 °C, and held at 250 °C for a further 10 min. The rate of carrier gas He was controlled at 1 mL·min^{-1}. In MS the electron impact ionization was set at 70 eV for quadrupole mass separation (scanning *m*/*z* (35 to 300) per 0.2 s).

Figure 1 shows the adsorption equilibrium apparatus used in this study.[13,14] The mass change during adsorption was measured by an electronic microbalance (Cahn C-33). The uncertainty of the microbalance was 0.1 μg. The pressure of this system was controlled from (1 to 300) mmHg and measured with a pressure gauge (Cole Parmer U-68700, uncertainty of ± 0.001 mmHg). The temperature of the microbalance compartment was maintained at 298 K, and the adsorption isotherms were plotted as the adsorption capacity (mg sorbate per g sorbent) versus relative pressure, P/P^0, where P is the operating pressure (mmHg) and P^0 is the saturated vapor pressure of the liquid solvent (mmHg). After regeneration in a vacuum dryer (at 373 K for 24 h), about 50 mg of granular sorbent was placed on the pan of the

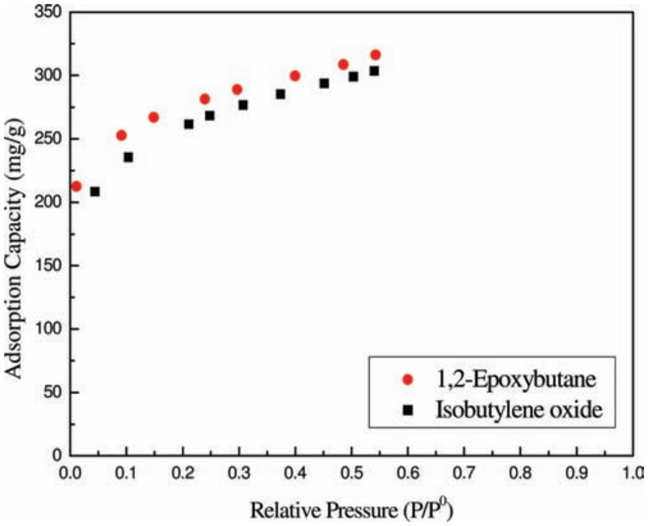

Figure 5. Adsorption capacities for epoxide and acid on activated carbon.

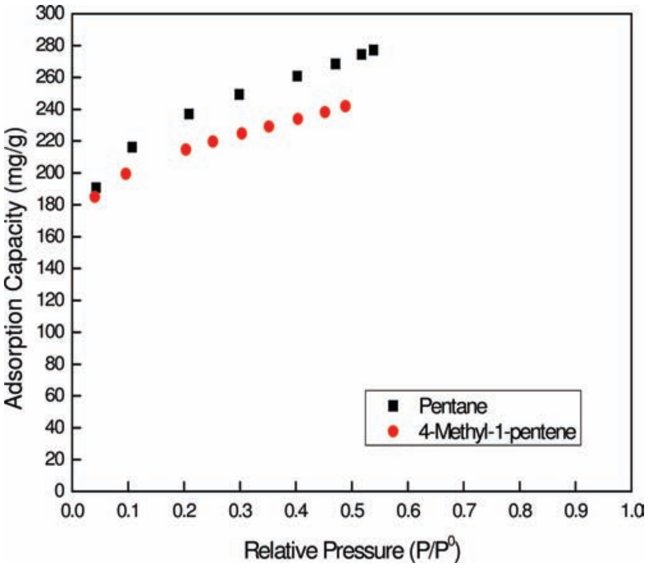

Figure 6. Adsorption capacities for alkane and alkene on activated carbon.

Table 1. Surface Properties of the Sorbents

sorbent	BET surface area m^2·g^{-1}	pore size Å
activated carbon	885	20
silica gel	490	41
zeolite 13X	392	8.4

microbalance. The liquid sorbate was then put into the glass bottles in a constant temperature water bath (see Figure 1). Degassing (thawing then freezing) was repeated at least three times. To get the desired amount of volatile vapor into the adsorption chamber, the temperature of the water bath was varied. At equilibrium, the amount of sorbent and sorbate was recorded together with the equilibrium pressure of the adsorption system. The amount of sorbate vapor for adsorption was increased, and the system was allowed to come to equilibrium again for another reading.

Results and Discussion

Experimental Adsorption Isotherms. It should be noted that most studies in the literature on heat-decomposed samples are for pure polymers. There may be some difference in the observed mix of pyrolysis gases when the samples are polymer-based products used in homes. For example, dye and fire retardant treatment of polymer-based household products would give pyrolysis gases with different compositions. The principal interest in this present work was to obtain sorption data for potentially toxic compounds which may be emitted from pyrolysis gases in the case of fire. The gases identified from the pyrolysis of selected polymers were compared with the literature for pyrolysis of various pure polymer samples to select the sorbate gases listed in Table 2 for use in this study.

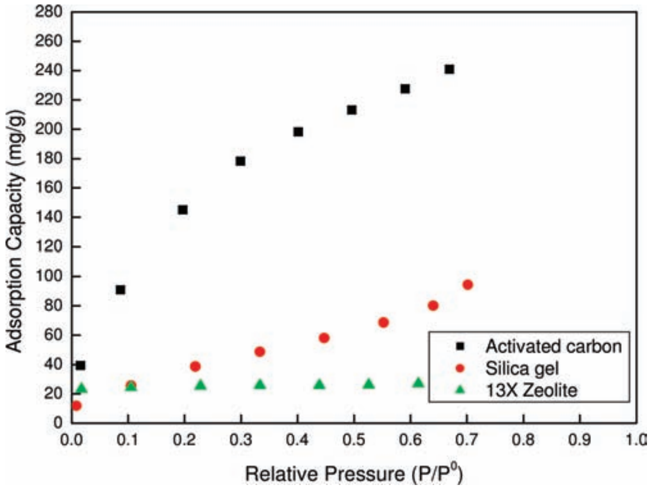

Figure 7. Adsorption capacities for methyl alcohol on selected adsorbents.

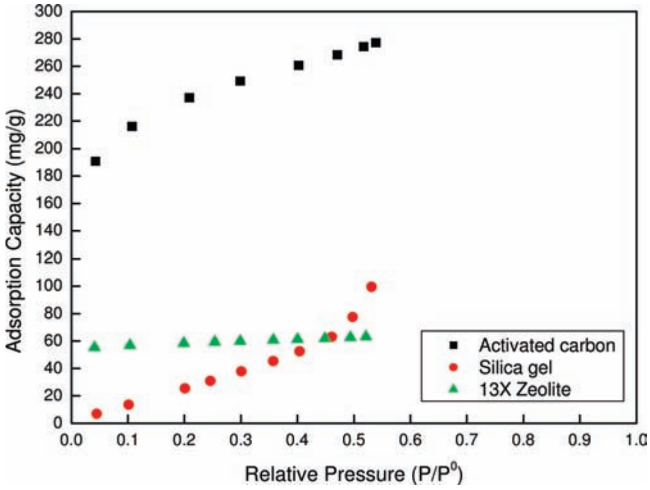

Figure 8. Adsorption capacities for pentane on selected adsorbents.

Activated carbon has been widely used for removing organic compounds because of its high surface area. Moreover, activated carbon for removal of organic vapor is nonpolar. Silica gel and zeolite 13X are polar sorbents which are also employed in industry to adsorb various gas emissions. In this study, silica gel and zeolite 13X were selected to compare with the adsorption of pyrolysis gases onto activated carbon.

Equilibrium uptakes of aromatics on activated carbon at 298 K increase with system pressure. From Figure 2, the adsorption capacity of toluene is much lower than benzene. Benzene has a simple aromatic ring structure. The geometric barrier due to toluene's methyl side group caused its adsorption capacity to be lower than benzene.

The adsorption behavior of alkanones on activated carbon is shown in Figure 3. It is observed that the adsorption capacity

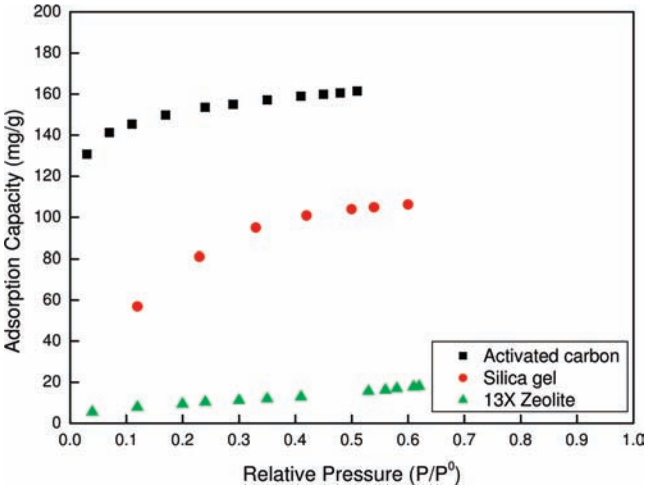

Figure 9. Adsorption capacities for benzene on selected adsorbents.

of activated carbon for acetone is more than that of 2-pentanone. The carbon chain of 2-pentanone is longer than that of acetone. In other words, the molecular mass of 2-pentanone is larger than acetone. However, acetone (2.9 D) is slightly more polar than 2-pentanone (2.5 D). The observed results indicated that, mainly due to its smaller molecular size, the adsorption capacity of acetone was greater than 2-pentanone.

As shown in Figure 4, the adsorption of acids is greater than that of methanol. Since the numbers of electrons in a molecule increase with its molecular weight, the polarity-induced force is proportional to its molecular weight. It may result that the order of the uptake of methanol, acetic acid, and formic acid is found to be acetic acid > formic acid > methanol.

The epoxide 1,2-epoxybutane has one methyl group less than isobutylene oxide (Figure 5). Therefore the order of the adsorption capacity was found to be 1,2-epoxybutane > isobutylene oxide. This result again states that adsorption capacity would be decreased by a geometric hindrance effect.

Because of the nonpolar nature of its internal surface, activated carbon for organic vapor removal would have a strong affinity for pentane. In Figure 6, the uptake of 4-methyl-1-pentene was lower than pentane due to the geometric barrier effect of the methyl group in 4-methyl-1-pentene.

Comparison of Different Adsorbents. Table 1 shows that activated carbon has a much larger surface area compared to silica gel and zeolite 13X. As shown in Figures 7, 8, and 9, the adsorption uptakes of pyrolysis gases (methanol, pentane, and benzene, respectively) on activated carbon are significantly greater than with silica gel and zeolite 13X. The activated carbon selected for organic vapor removal for this study was nonpolar and would strongly favor sorption of the nonpolar pentane and benzene. On the other hand, the negatively charged framework of silica gel and zeolite 13X would be expected to repel the hydroxyl group of methanol. In addition, from the shape of the isotherm curves in Figures 7 to 9, it is observed that the isotherm curves of these pyrolysis gases on activated carbon are “favorable”; however, the isotherm curves for silica gel are “unfavorable” according to the classification of the typical isotherm curves.[15] The isotherm curves for zeolite 13X are flat or approximately a horizontal line. It means that regeneration of zeolite 13X for this type of adsorption will be difficult.

Table 2. Regression Values of *A* and *n* in the Freundlich Equation at 298 K

			Freundlich isotherm		
	adsorbate		regression parameters		
adsorbent	pyrolysis gas	health effects	*A*	*n*	R^2
activated carbon	pentane	headache, nausea, insentience, skin inflammation, and excitement[a]	119.727	0.147	0.995
	methyl alcohol	cough, headache, loss of unconsciousness, asthenia, drowsiness, nausea, blurry vision to blindness, insentience, panting, stupor, skin inflammation, and erythema[a]	32.726	0.452	0.993
	acetic acid	bronchitis, pleural effusion, burns, hematemesis, kidney trouble, conjunctivitis, and enamel erosion[a]	441.845	0.119	0.961
	formic acid	respiratory tract irritation, ulcer, nausea, and gastralgia[a]	348.989	0.147	0.927
	acetone	headache, asthenia, drowsiness, nausea, collapse, stupor, and skin inflammation	71.685	0.223	0.994
	2-pentanone	cough, panting, headache, nausea, loss of consciousness, and skin inflammation[a]	150.753	0.209	0.991
	benzene	headache, drowsiness, loss of consciousness, narcotism, respiratory failure, skin inflammation, bronchopneumonia, nausea, sphygmus quickening, and pulmonary edema, and leukemia[a]	122.034	0.071	0.995
	toluene	eye, skin, and respiratory tract irritation, narcosis, headache, fatigue, loss of consciousness, nausea, central nervous system suppression, and insensibility[a]	87.64	0.07	0.997
	1, 2-epoxybutane	pulmonary edema, pneumonia, headache, nausea, skin irritation, eye irritation, sore throat, cramp, and diarrhea[a]	189.272	0.110	0.964
	isobutylene oxide	skin, eye, and respiratory system irritation[b]	142.805	0.150	0.999
	4-methyl-1-pentene	mucous membrane, eye, and skin inflammation, central nervous system suppression, nausea, dyspnea, loss of consciousness, insentience, and death[a]	140.712	0.107	0.984

[a] Globally harmonized system (http://ghs.cla.gov.tw/). [b] ChemExper chemical directory (http://www.chemexper.com/).

Therefore, on the basis of the results presented above, the removal of the aromatic, alkane, alkene, alcohol, ketone, epoxide, and acid gases listed in Table 2 (which may be produced from the pyrolysis of polymer products) could be suitably accomplished using activated carbon. It is noted that the adsorption uptake of the acid gases on activated carbon is highest among the gas species evaluated in this work.

Development of the Isotherm Model. Since the pressure of the pyrolysis gases was kept at low to intermediate pressure level in the adsorption apparatus, the Freundlich equation was selected to be the isotherm model for the equilibrium data obtained in this study. The Freundlich equation can be expressed as

$$q = Ap^n$$

where q is the adsorption capacity (mg sorbate per g sorbent), A is the Freundlich constant, p is the pressure of the pyrolysis gas (mmHg), and n is an exponent. The regressions to determine the Freundlich constant A and exponent n for all of the gases on activated carbon at 298 K are shown in Table 2. The values of R^2 for the predicted adsorption isotherms on activated carbon are from (0.927 to 0.999). The regression parameters are important in the design of adsorption equipment. These equilibrium isotherm curves would also be useful as reference data to authenticate witness reports at the fire scene and to provide a fire safety database for firemen.

Conclusions

The equilibrium isotherms of gases from the pyrolysis of polymer products on activated carbon, silica gel, and zeolite 13X are investigated in this study. Activated carbon preferentially adsorbs nonpolar gases. The adsorption capacity of toluene is lower than benzene, and the uptake of pentane is greater than 4-methyl-1-pentene onto activated carbon. On the basis of the adsorption performance of the pyrolysis gases onto different adsorbents, it was found that activated carbon is the best one. In addition, it is observed that the equilibrium uptake of acid gases is higher than those of alkane, alkene, epoxide, aromatic, and alkanone gases. The Freundlich equation gives a good fit of the equilibrium isotherms, and the average value of R^2 is 0.98.

Literature Cited

(1) Masuda, T.; Miwa, Y.; Tamagawa, A.; Mukai, S. R.; Hashimoto, K.; Ikeda, Y. Degradation of Waste Poly(Ethylene Terephthalate) in a Steam Atmosphere to Recover Terephthalic Acid and to Minimize Carbonaceous Residue. *Polym. Degrad. Stab.* **1997**, *58*, 315–320.

(2) Martın-Gullon, I. M. Kinetic Model for the Pyrolysis and Combustion of Poly(Ethylene Terephthalate) (PET). *J. Anal. Appl. Pyrolysis* **2001**, *58−59*, 635–650.

(3) Masuda, T.; Kushino, T.; Matsuda, T.; Mukai, S. R.; Hashimoto, K.; Yoshida, S. Chemical Recycling of Mixture of Waste Plastics Using a New Reactor System with Stirred Heat Medium Particles in Steam Atmosphere. *Chem. Eng. J.* **2001**, *82*, 173–181.

(4) Levin, B. C. A Summary of the NBS Literature Reviews on the Chemical Nature and Toxicity of the Pyrolysis and Combustion Products from Seven Plastics: Acrylonitrile - Butadiene - Styrenes (ABS), Nylons, Polyesters, Polyethylenes, Polystyrenes, Poly(Vinyl-Chlorides) and Rigid Polyurethane Foams. *Fire Mater.* **1987**, *11*, 143–157.

(5) Nagasawa, Y.; Hotta, M.; Ozawa, K. Fast Thermolysis/ FT-IR Studies of Fire-Retardant Melamine - Cyanurate and Melamine - Cyanurate Containing Polymer. *J. Anal. Appl. Pyrolysis* **1995**, *33*, 253–267.

(6) Commereuqn, S.; Vaillant, D.; Philippart, J. L.; Lacoste, J.; Lemaire, J.; Carlsson, D. J. Photo and Thermal Decomposition of IPP Hydroperoxides. *Polym. Degrad. Stab.* **1997**, *57*, 175–182.

(7) Willoughby, B. G.; Golby, A.; Davies, J.; Cain, R. Volatile Component Analysis as a Routine Characterisation Tool: an Approach to Fingerprinting Polyolefin Type and Process History Using ATD-GC/MS. *Polym. Test.* **2003**, *22*, 553–570.

(8) Zhu, W.; Groen, J. C.; Kapteijn, F.; Moulijn, J. A. Adsorption of Butane Isomers and SF_6 on Kureha Activated Carbon: 1. Equilibrium. *Langmuir* **2004**, *20*, 5277–5284.

(9) Wu, C. Y.; Chung, T. W.; Yang, T. C. K.; Chen, M. T. Dynamic Determination of the Concentration of Volatile Alcohols in a Fixed Bed of Zeolite 13X by FT-IR. *J. Hazard. Mater.* **2006**, *B137*, 893–898.

(10) Vasanth Kumar, K.; Sivanesan, S. Prediction of Optimum Sorption Isotherm: Comparison of Linear and Non-linear Method. *J. Hazard. Mater.* **2005**, *B126*, 198–201.

(11) Lin, S. H.; Chen, Y. W. Gas-Phase Adsorption Isotherms and Mass Transfer Characteristics of 1,1-Dichloro-1-Fluoroethane (HCFC-141b) by Various Adsorbents. *J. Hazard. Mater.* **1998**, *57*, 193–207.

(12) Yang, R. T. *Gas Separation by Adsorption Processes*; Butterworth: London, 1987.

(13) Wang, C. M.; Chang, K. S.; Chung, T. W.; Wu, H. Adsorption Equilibrium of Aromatic Compounds on Activated Carbon, Silica Gel, and 13X Zeolite. *J. Chem. Eng. Data* **2004**, *49*, 527–531.

(14) Wang, C. M.; Chung, T. W.; Huang, C. M.; Wu, H. Adsorption Equilibrium of Oxygenated Hydrocarbons on Activated Carbon, Silica Gel, and 13X Zeolite. *J. Chem. Eng. Data* **2005**, *50*, 811–816.

(15) Hines, A. L.; Maddox, R. N. *Mass Transfer Fundamentals and Applications*; Prentice Hall: Upper Saddle River, NJ, 1985.

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