PERFORMANCE EVALUATION OF CARBON ADSORBENTS FOR AUTOMOBILE CANISTERS

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Abstract – To assess the performance of carbon adsorbents for automobile canisters, we have studied the adsorption and desorption of n-butane and gasoline vapor experimentally in a column charged with pelletized carbons, Car-115 and DP-1. Norit Car-115, which is a well-known carbon adsorbent for canisters, was chosen as a standard adsorbent to compare with a domestic pelletized carbon (DP-1). The use of n-butane as a reference compound for the assessment of adsorbents was proven to be very reliable when compared with the adsorption of real gasoline vapors. According to the results obtained, the carbon adsorbent for automobile canisters requires at least two basic characteristics such as the development of well-defined mesopores and high specific area, which are essential for rapid uptake rate and high working capacity.

Key words : Automobile Canister, Carbon Adsorbents, Adsorption of n-Butane and Gasoline Vapor, Column Operation

INTRODUCTION

Hydrocarbon emissions from the distribution of gasoline and its use in cars represent 40 % of the about 10 million tons of man-made hydrocarbons emitted to the air in Western Europe annually [Fris, 1993]. Exhaust gases from uncontrolled gasoline cars contribute as much as 25 % to this total, and evaporative losses as much as 10 %. Consequently, motor vehicles are a major source of hydrocarbon pollution, which can produce ozone smog in sunlight through complex photochemical reactions. The direct exposure also threatens the public health. Therefore, the control of exhaust and evaporative losses of hydrocarbons, namely gasoline vapors, becomes a very important problem to prevent air pollution in addition to reducing the loss of fuel [McDowall et al., 1992; Reimerink et al., 1992]. In developed countries such as the U.S.A. and Japan, all motor vehicles have been required to be equipped with an evaporative loss control device (ELCD) to reduce hydrocarbon vapors from cars as early as at the end of 1960's [U.S.A. Federal Register, 1997; EPA, 1995]. In Europe, legislation has required each car to fulfill stringent emission requirements from 1993. Even in Korea, canisters for controlling the evaporative loss of gasoline have been used, particularly to match strict regulations of countries to which cars are exported. However, all carbon adsorbents are imported from Japan and the Netherlands even though the canister itself can be manufactured in Korea.

The ELCD is in general based on a controlled adsorption-desorption cycling in a carbon adsorbent system, to trap those hydrocarbon vapors which would normally be lost to the atmosphere, and later to feed them into the engine to be burnt [Clark et al., 1968; GM, 1986]. Therefore, the adsorbent for this purpose must have several basic properties: sufficient working capacity, high attrition resistance, low dust level, and low pressure drop.

In this study, n-butane was used as a reference compound to assess the performance of activated carbons for automobile canisters. This has been known as a reliable method because n-butane is one of the major hydrocarbons in the gasoline vapor. The adsorption of vaporized fuel gas was also measured to show the dynamic behavior of the fuel gas in the activated carbon column. The physical properties of carbons, namely pore size distribution and specific surface area, were measured by N_2 adsorption in a BET system. They are very important properties, which are related with the working capacity. Moreover, a dynamic model based on the homogeneous diffusion mechanism was chosen to simulate the adsorption and desorption dynamic behavior of n-butane in carbon columns.

THEORETICAL APPROACH

1. A Dynamic Model

A homogeneous diffusion model with external mass transfer resistance was selected for describing adsorption and desorption of n-butane and gasoline vapors from air onto activated carbons. In the model, we assume an isothermal adsorption column, packed with porous spherical particles. The flow pattern is described by an axially dispersed plug-flow model. Another assumption involved in the model is the fast intrinsic adsorption kinetics, resulting in instant equilibrium at the external surface of the carbon particles [Park et al., 1995].

According to the homogeneous diffusion, the mass balance inside a spherical sorbent particle can be described by the following equation:

$$\frac{\partial q_i}{\partial t} = D_{eff,i} \left(\frac{\partial^2 q_i}{\partial r^2} + \frac{2}{r} \frac{\partial q_i}{\partial r} \right) \tag{1}$$

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with the initial and boundary conditions:

$$q_i(r, t = 0) = 0 \tag{2}$$

$$\left. \frac{\partial q_i}{\partial r} \right|_{r=0} = 0 \tag{3}$$

$$\left. D_{eff,i} \, \rho_p \, \frac{\partial q_i}{\partial r} \right|_{r=R} = k_f(C_i - C_{si}) \tag{4}$$

The mass balance equation and the corresponding initial and boundary conditions for the bulk phase in the column are :

$$-D_L \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial v C_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{1 - \varepsilon_b}{\varepsilon_b} \frac{\partial q_i}{\partial t} = 0 \tag{5}$$

$$C_i(z, t = 0) = 0 \tag{6}$$

$$\left. D_L \frac{\partial C_i}{\partial z} \right|_{z=0} = -v(C_i|_{z=0^-} - C_i|_{z=0^+}) \tag{7}$$

$$\left. \frac{\partial C_i}{\partial z} \right|_{z=L} = 0 \tag{8}$$

These coupled parabolic second-order partial differential equations, Eqs. (1) and (5), cannot be solved analytically. Therefore numerical methods have been generally employed. In this work, two partial differential equations were first discretized by an orthogonal collocation method to form a set of first-order ordinary differential equations [Villadesen and Michelsen, 1978; Suwondo et al., 1991]. The resulting set of ordinary differential equations was integrated by a subroutine, LSODE, of the International Mathematical and Statistical Library (IMSL).

2. Adsorption Equilibrium

Single-species adsorption data of n-butane on activated carbons were simply correlated with two well-known isotherms such as the Freundlich and Langmuir equations :

$$q = KC^{1/n} \tag{9}$$

$$q = \frac{q_m \, bC}{1 + bC} \tag{10}$$

EXPERIMENTAL

Adsorbents used in this study are the pelletized activated carbons, Car-115 manufactured by Norit (Netherlands) and DP-1 by a domestic (Korean) company. The arithmetic average particle diameter was determined by sieving a sample of particles with a set of standard sieve trays. Various densities of the carbons were measured by weighing the sample and by displacing the void fraction with carbon tetra-chloride in a picnometer. Other properties, such as pore size distribution, pore volume, and specific surface area, were measured by N_2 adsorption in a BET system. The physical properties of these sorbents are summarized in Table 1.

Prior to use, the carbon particles were leached with boiling water for 48 hrs to remove impurities from internal pores of

the particles. The particles were then dried in an oven at 105 °C. The adsorption amounts of butane and gasoline vapor were measured by a quartz spring balance which was placed in a closed glass system. A given amount of carbon particles were placed on the dish which was attached to the end of quartz spring and the system was vacuumed for 4 hours at 10^{-5} torr and 300 °C to remove volatile impurities from carbon particles. The pressure of the system was measured by a pressure sensor and the variation of weight was measured by a digital voltmeter, which is connected with the spring sensor. Equilibrium experiments were carried out up to 1 atm at four different temperatures, 15, 25, 35, and 45 °C.

The working capacities of the carbons for butane and gasoline vapor were determined by column experiments. All column experiments were conducted in a 1/2 inch stainless-steel column. Prior to experimentation, the carbon particles charged in the column were dried by passing N_2 gas at 300 °C for 24 hours. The gasoline vapor was generated by passing N_2 through liquid gasoline in the saturator, which was packed with glass beads. Special care was needed in generating the gasoline vapor since the composition in the saturator was changing with time. Therefore, the liquid gasoline in the saturator was replaced with fresh one when about 10 % of the original amount was evaporated.

Adsorption and desorption breakthrough curves were measured in the column packed with 2 g of carbon particles. The column was lined with a jacket to maintain the column temperature. The flow rates were regulated by precision mass flow controllers. The gaseous mixture was introduced downward into the column. To prevent channeling and to enhance the distribution across the column, two layers of small glass beads were placed in the top and bottom regions of the column. Samples were withdrawn from the effluent line and analyzed by a gas chromatography (Shimadzu, model GC-14B) with a frame ionization detector.

RESULTS AND DISCUSSION

1. Adsorbent Characterization

The specific surface area of activated carbons is not the only factor affecting adsorption in many cases. Obviously their pore size distribution must be known. The surface area and pore volume of carbons measured by the BET analysis are listed in Table 1. The surface area of Car-115 was determined to be surprisingly about 1,500 m²/g, which is much larger than that

Table 1. Physical properties of activated carbons

Property	Car-115	DP-1	Unit
Particle size*	2.0	4.0	mm
Moisture content*	8.96	10.3	%
Packing density*	348.5	505.1	kg/m²
Particle density*	803	1083	kg/m²
Surface area**	1507	772.2	m²/g
Micro pore volume**	0.9139	0.4412	ml/g
Mean pore diameter**	24.26	22.86	Å

*from experiment result
**from B.E.T. experiments with N_2

of DP-1, 770 m²/g. The average pore diameter of Car-115 is 2.42 nm while that of DP-1 is 2.28 nm, respectively. However, according to the pore volume, DP-1 has a very broad distribution compared with that for Car-115. Such a difference will critically affect the adsorption characteristics.

2. Characteristics of Gasoline Vapors

Gasoline vapors contain various hydrocarbons, C_1-C_{10}. Table 2 shows the vapor composition of a domestic gasoline at different temperatures. Here, as a matter of convenience, all fractions were simply calculated from peak areas of the chromatogram of the gasoline without any adjustment. At 10-30 °C, the fraction of C_1-C_4 becomes about 70 % of the vapor. However, the fraction of heavy hydrocarbons increases with temperature. In this table, the fraction means a mixture or a pseudocomponent, which consists of several hydrocarbons, having similar physical and chemical properties. Considering that the normal operating temperature of automobile canisters is in the range of − 10-50 °C, the composition of gasoline vapors may vary according to a specific season or place. On the other hand, Table 2 shows that the major fraction of gasoline vapors is C_4. That is why n-butane can be used as a reference hydrocarbon to assess the performance of automobile canisters.

In order to assess an adsorbent for automobile canisters, two different methods can be applied. One is to use the gasoline vapor directly to get the adsorption capacity, the sorption rate, and the breakthrough behavior. The other is to use a reference hydrocarbon such as n-butane as an alternative method. The latter method is very efficient and simple, but its drawback is that it does not represent the adsorption characteristics of gasoline vapor perfectly. In this work, we compared two methods to find a simple approach for assessment of adsorbents.

3. Adsorption Equilibria

Adsorption isotherms provide important information for analyzing and modeling of a given adsorption system [Moon and Tien, 1988]. In this study, n-butane was used as a reference compound to assess the performance of selected activated carbons. Adsorption equilibrium data of n-butane measured are shown in Figs. 1 and 2. The domestic carbon, DP-1, has about half of the adsorption capacity of Car-115 at the same condition. This result seems to be closely related with the properties of two carbons listed in Table 1.

Adsorption equilibrium data of n-butane were fitted with two well-known equations : Langmuir and Freundlich isotherms. All parameters of individual isotherms were determined by minimizing the object function, namely the average percent deviation between experimental and predicted results and list-

ed in Tables 3 and 4.

As shown in Tables 3 and 4, the Freundlich equation fits equilibrium data of n-butane satisfactorily while the Langmuir equation does not give good results, particularly for the n-
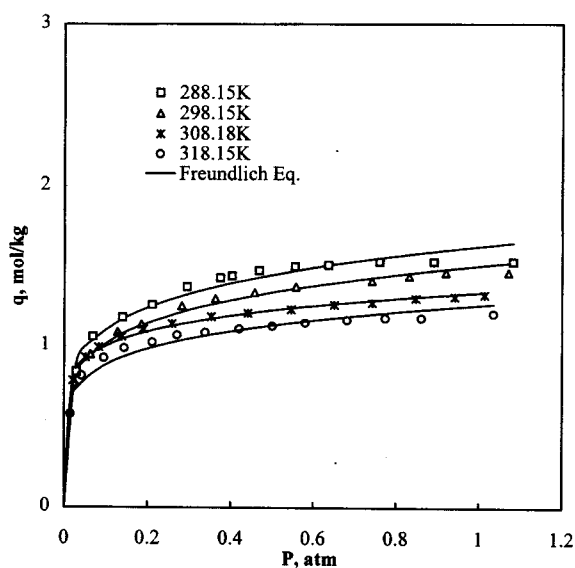

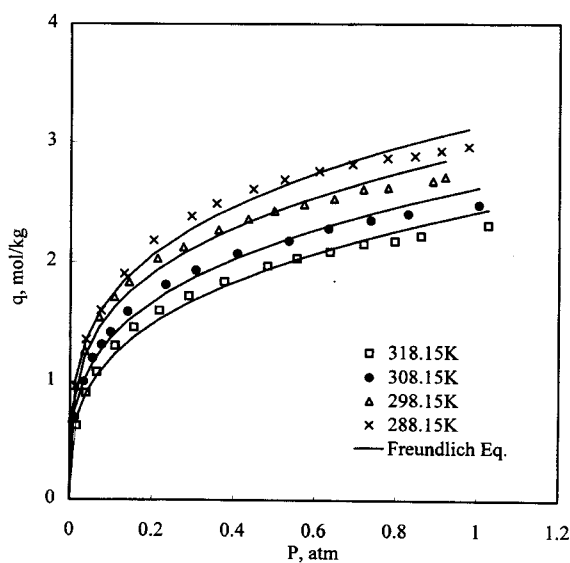**Fig. 1. Adsorption isotherms of n-butane on DP-1.**

Fig. 2. Adsorption isotherms of n-butane on Car-115.

Table 2. Fractions of gasoline vapor at different temperatures

Component	Gasoline (liquid)	Temperature, °C			
		10	20	30	40
C_1-C_3	0.16	0.28	0.26	0.28	0.12
C_4	0.12	0.38	0.42	0.38	0.27
C_5	0.12	0.13	0.15	0.14	0.17
C_6	0.13	0.06	0.07	0.08	0.14
BTX	0.23	0.04	0.04	0.06	0.14
others	0.24	0.11	0.06	0.06	0.16

Table 3. Adsorption equilibrium constants of n-butane on Car-115

Isotherm	Parameters	Temperature, °C			
		15	25	35	45
Langmuir	q_m	2.6619	2.2998	2.0742	2.0341
	b	37.919	64.94	36.437	24.609
	E (%)*	9.6340	11.9666	11.4091	9.1805
Freundlich	k	3.1303	2.9086	2.6243	2.4221
	n	3.8453	3.8051	3.5442	3.2814
	E (%)	3.0556	3.8347	3.3255	3.5457

* Average percent error

Table 4. Adsorption equilibrium constants of n-butane on DP-1

Isotherm	Parameters	Temperature °C			
		15	25	35	45
Langmuir	q_m	1.5192	1.3968	1.2472	1.1480
	b	39.844	43.561	73.594	67.371
	E (%)	3.6877	5.0264	4.4792	3.4237
Freundlich	k	1.6296	1.5074	1.3384	1.2595
	n	5.9268	5.8676	7.9230	6.4944
	E (%)	3.0278	2.0799	1.3165	3.8889

butane/Car-115 system. This result implies that activated carbons used here have energetically heterogeneous surfaces for n-butane adsorption [Ruthven, 1984].

4. Estimation of Kinetic Parameters

Analyzing or designing an adsorption process requires accurate kinetic information. There are essentially three consecutive mass transport steps associated with the adsorption of adsorbates by porous adsorbents. The mass transport through the external film of adsorbent particles is relatively fast. Therefore, the rate of adsorption in porous adsorbents is generally controlled by the intraparticle transport within the particle [Moon and Lee, 1983]. For spherical particles, the external film mass transfer coefficient, k_f, can be estimated from some correlations reported in literature. Among those correlations, the equation proposed by Wakao and Funazkuri has been widely used for column adsorptions [Ruthven, 1984].

$$k_f = \frac{D_m}{2R_p}(2.0 + 1.1\,Re^{0.6}Sc^{0.33}) \tag{11}$$

where Sc and Re are the Schmidt and Reynolds numbers, respectively and D_m is the molecular diffusion coefficient. The molecular diffusion coefficient of n-butane in air was estimated by the method of Fuller, Schettler, and Giddings [Yang, 1987]. Under the experimental conditions used here, the estimated k_f for n-butane was in the range of $0.89\text{-}1.513 \times 10^{-2}$ m/s. The axial dispersion coefficient included in the model was calculated from the following equation [Yang, 1987]:

$$\frac{\varepsilon_b D_L}{D_m} = 20 + 0.5Sc\,Re \tag{12}$$

It is generally known that intraparticle diffusion of adsorbates within adsorbent particles is the rate-controlling step in most adsorption processes that employ highly porous adsorbents such as activated carbons and zeolites. There are several methods for estimating or measuring the intraparticle diffusion coefficient experimentally. The most general method is to compare the experimental breakthrough curve with the predicted one using a specified diffusion model at the same operating conditions. In this study, it was assumed that the intraparticle diffusion obeys the homogeneous diffusion mechanism since the isotherm of n-butane is very favorable. However, the effective diffusion coefficient obtained by this method reflects all kinds of mass transfer resistance within the particle [Park et al., 1995; Moon and Lee, 1983]. The effective diffusion coefficients obtained are in the range of $0.92\text{-}1.62 \times 10^{-9}$ m²/s for n-butane. All kinetic parameters obtained are listed in Table 5.

Table 5. Experimental and kinetic parameters estimated at 25 °C

Adsorption system	$v \times 10^{-3}$ [m/s]	L [m]	$D_L \times 10^4$ [m²/s]	$k_f \times 10^2$ [m/s]	$D_{eff} \times 10^9$ [m²/s]
n-butane/Car-115	5.331	0.056	4.753	1.513	0.93
	2.031	0.056	4.676	1.285	0.92
n-butane/DP-1	5.331	0.039	4.560	0.890	1.62
	2.031	0.039	4.415	0.718	1.60

5. Column Adsorption of n-Butane

The performance of an adsorption-based process greatly depends upon the effectiveness of design and operating conditions. Therefore, rigorous approaches to the design and operation of the adsorption system must be used to ensure efficient applications. To do this, one has to understand the mechanism and dynamics of adsorption and desorption, as well as major variables that affect process performance.

Fig. 3 shows the breakthrough curves of n-butane from the column charged with Car-115 at two temperatures, 25 and 45 °C. As one might expect from adsorption isotherms, the breakthrough appears earlier with temperature since the adsorption capacity of carbons decreases with temperature. The solid lines represent the predicted breakthrough curves by the model. In these predictions, kinetic parameters obtained in the previous section were used without further adjustment. On the other hand, Fig. 4 shows the effect of inlet concentration on the breakthrough at 25 °C. The breakthrough appears earlier with the inlet concentration, but the shape of breakthrough curves is almost similar, showing a constant pattern. This result implies that adsorption behavior is controlled by its equilibrium relation rather than kinetics. Because the adsorption isotherms of n-butane are very favorable, the mass transfer zone (MTZ) in the breakthrough curve seems to be very short.

A comparison of two activated carbons is shown in Fig. 5. Two breakthrough curves were measured under the same
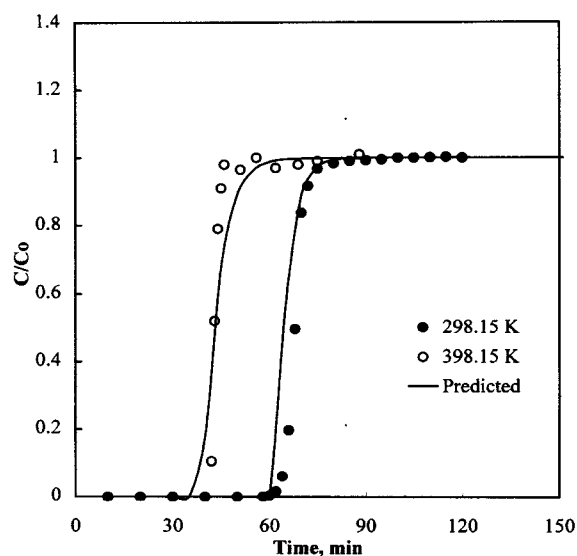

Fig. 3. Effect of temperature on breakthrough curves of n-butane on Car-115 (C_o=4.73 mol/m³).

operating conditions. As expected from equilibrium data, there is a considerable difference in their breakthrough times even though their breakthrough curves are similar. However, it is not proper to assess the performance of activated carbon by its breakthrough behavior. The most important factor would be the working capacity, namely the reversible adsorption capacity, because the automobile canister should be operated in a cyclic mode, which has two basic steps such as adsorption and desorption once it is installed in a car. These reversible capacities greatly depend on the adsorption and desorption rates as well as the number of reversible adsorption sites. That is why kinetic parameters should be known to assess the performance of activated carbon for automobile canisters.

6. Adsorption of Gasoline Vapors

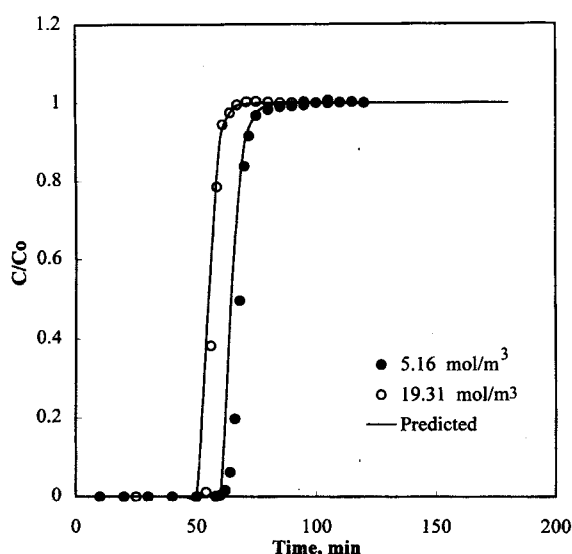The ultimate target of this work is to find a reasonable way

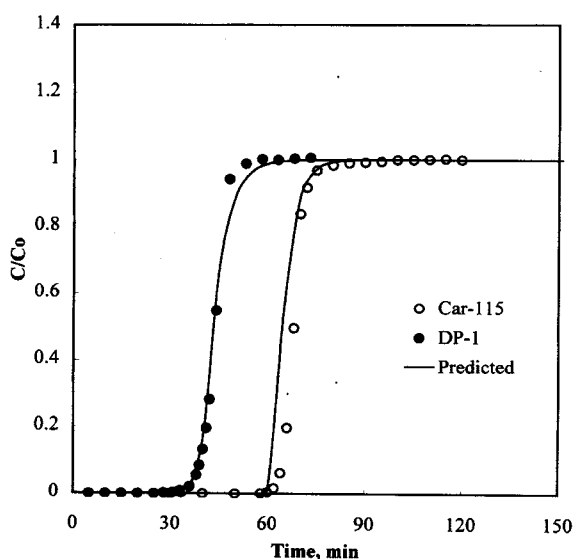Fig. 4. Effect of concentration on breakthrough curves of n-butane on Car-115 at 298.15 K.

to assess the performance of adsorbents for automobile canisters by simple adsorption and desorption experiments. Therefore, it would be essential to conduct several experiments using gasoline vapors directly and compare them with those for n-butane. Such an approach will provide a correlative way to use an alternative assessment using a reference hydrocarbon, n-butane, instead of the gasoline vapor itself.

Fig. 6 shows the breakthrough curves of gasoline vapor from the columns charged with Car-115 and DP-1, respectively. Data points represent total concentrations which were calculated from the total area of gas chromatograms using the concept of pseudospecies [Moon et al., 1991]. Since the gasoline vapor contains various hydrocarbons, we expected a complex breakthrough curve which has multiple plateaus because of competitive adsorption between components [Moon and Lee, 1986; Moon and Tien, 1988]. However, they are quite similar to single-species breakthrough curves, except the final portion. This result may come from the fact that the major portion of the gasoline vapor is composed of light hydrocarbons such as C_1-C_4.

In this work, we also placed our focus on the correlation between two results obtained from n-butane and the gasoline vapor. To quantify the adsorption equilibrium of the gasoline vapor, a simple correlation was applied. When the Freundlich equation was used, it was assumed that the Freundlich constant of the gasoline vapor, K_{gas}, could be correlated with that of n-butane, K_{but}, as follows:

$$K_{gas} = aK_{but} \qquad (13)$$

where a is an empirical parameter which can be calculated by comparing the middle points (C/C_0=0.5) of their breakthrough curves. From several breakthrough curves of the gasoline vapor, the mean value of a was determined to be approximately 2.6. The solid lines in Fig. 6 represent the curves predicted using the isotherm of n-butane with this value. In this prediction, the exponent of the Freundlich equation for
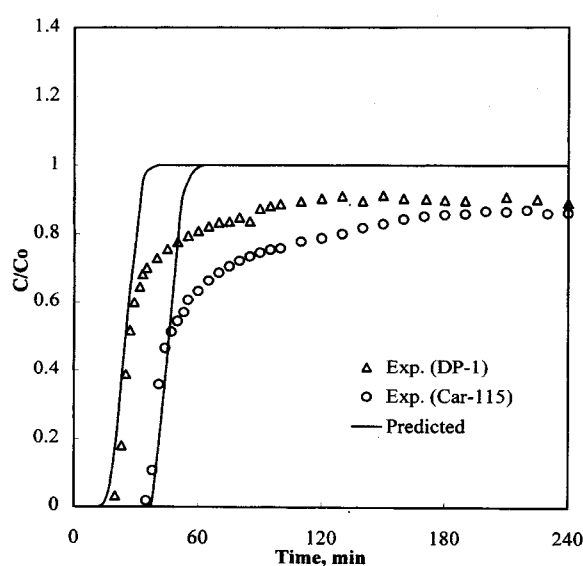

Fig. 5. Experimental results and predicted breakthrough curves of n-butane on activated carbons at 298.15 K (C_o= 4.73 mol/m³).

Fig. 6. Experimental results and predicted breakthrough curves of gasoline vapor on activated carbons at 298.15 K (C_o=6.03 mol/m³).
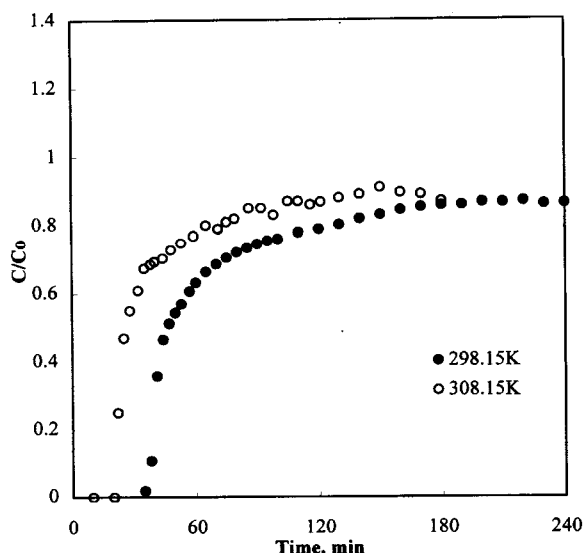
Fig. 7. Effect of temperature on breakthrough curves of gasoline vapor on Car-115 (C_o=6.03 mol/m³).

Fig. 8. Adsorption and desorption breakthrough curves of gasoline vapor on DP-1 at 298.15 K (C_o=6.03 mol/m³).

n-butane was used directly. Except the tailing area, the predicted results are reasonable compared with experimental data. This result shows that with the alternative method using n-butane, it is practically possible to assess the performance of activated carbons for the ELCD application. Concerning this simple approach, one can argue that real values for the gasoline vapor should be used. However, it should be noted that the direct use of gasoline vapor is not easy since the composition is varying with time. Fig. 7 shows the effect of temperature on the breakthrough curve of the gasoline vapor. The breakthrough time decreases with temperature because of the decrease in adsorption capacity.

7. Comparisons of Two Activated Carbons

As mentioned in the previous section, it is very critical to check the characteristics of desorption in assessing the performance of adsorbents. This is closely related with the surface character and pore size distribution of adsorbents. If the surface of activated carbon has energetically strong adsorption sites, the portion of irreversible adsorption will increase and eventually reduce the working capacity. On the other hand, the small micropores of adsorbent particles can reduce the rates of adsorption and desorption considerably. Even if it is proven that an adsorbent has very high adsorption capacity from equilibrium experiments, one cannot say that it is proper for the ELCD application unless its kinetic properties are checked properly.

In order to check the kinetic effect on the performance of the column charged with activated carbons, we carried out adsorption and desorption of the gasoline vapors. Figs. 8 and 9 show the adsorption and desorption breakthrough curves of the gasoline vapor on Car-115 and DP-1, respectively. After desorbing by nitrogen purging for 2 hours, the column was heated up to 300 °C to desorb strongly attached adsorbates on irreversible sites. Therefore, the sharp peak on the desorption breakthrough curve represents the amount of irreversible adsorption. In the case of Car-115, the amount of reversible desorption is very large, while the amount of irre-
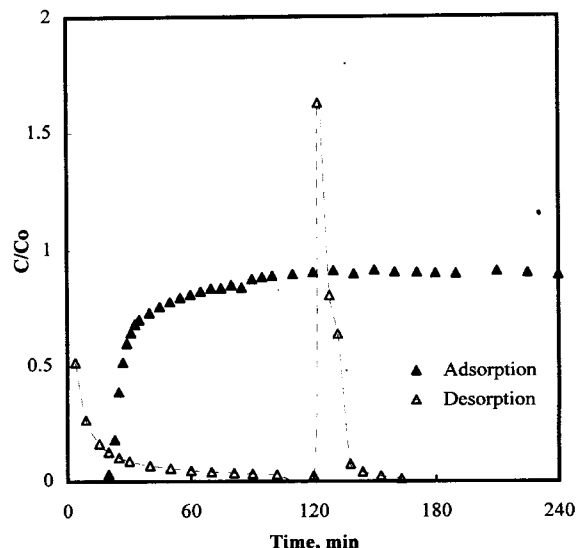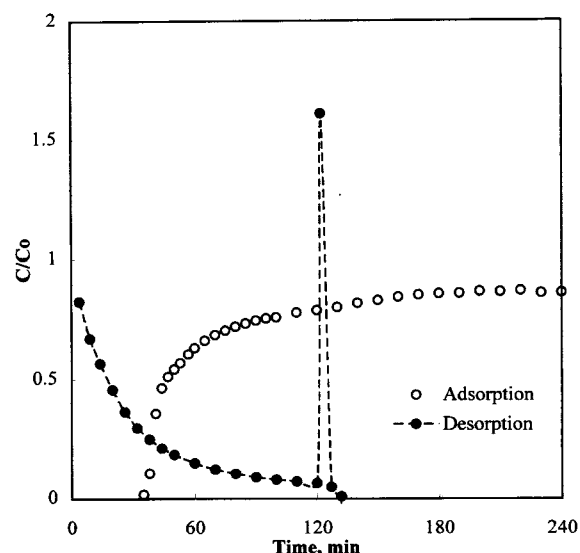
Fig. 9. Adsorption and desorption breakthrough curves of gasoline vapor on Car-115 at 298.15 K (C_o=6.03 mol/m³).

versible adsorption is relatively small, compared with that of DP-1. This result reflects the effect of specific surface area and pore size distribution of the carbon as mentioned previously. From Fig. 9, it is known that DP-1 has a larger portion of irreversible adsorption than 50 % of the total capacity. Considering the adsorption capacity and the kinetic characters, it is quite clear that Car-115 is much better than DP-1 for this purpose.

CONCLUDING REMARKS

From experimental work on the adsorption and desorption of n-butane and gasoline vapor, several conclusions can be drawn. First, it was proven that the alternative method using n-butane as a reference hydrocarbon is very reasonable for as-

sessing the performance of activated carbons for the ELCD application. A simple empirical correlation of the isotherm parameters was made in order to predict the breakthrough curve of the gasoline vapor using the isotherm of the reference component, n-butane. Since the composition of gasoline vapor is very complex and continuously changing with time, it is not easy to get a reliable result from direct use of gasoline vapors themselves.

Compared with the performance of Norit Car-115, a domestic carbon, DP-1, has about 50 % adsorption capacity and a considerable irreversible amount of more than 50 % of the total capacity. This means that DP-1 is not proper as an adsorbent for automobile canisters. As discussed earlier, the carbon adsorbent for this purpose should have at least two characters, a rapid uptake rate and a high working capacity. To obtain such properties, the control of the pore size distribution is very important. According to experimental results of Car-115, it can be concluded that the development of well-defined mesopores is critical, considering that the working capacity depends on the adsorption rate. On the other hand, special care should be taken not to make too strong adsorption sites during the activation process of carbon.

ACKNOWLEDGEMENT

NOMENCLATURE

b   : Langmuir constant [m^3/mol]
C   : concentration in the fluid phase [mol/m^3]
C_0 : inlet concentration [mol/m^3]
D_L : axial dispersion coefficient [m^2/s]
D_m : molecular diffusion coefficient [m^2/s]
D_{eff} : effective homogeneous diffusion coefficient [m^2/s]
E(%): average percent error [%]
K   : Freundlich constant
k_f : film mass transfer coefficient [m/s]
L   : bed length [m]
n   : Freundlich exponent
N   : number of data point
Pe   : Peclet number defined in Eq. (11)
q   : concentration in particle phase [mol/kg]
q_m : amount adsorbed for monolayer formation [mol/kg]
r   : radial distance [m]
Re   : Reynolds number
R   : particle radius [m]
Sc   : Schmidt number
t   : time [s or hr]

T   : temperature [°C]
z   : axial distance [m]

Greek Letters

ε_b : bed porosity
ρ_p : particle density [kg/m^3]

REFERENCES

Clarke, P. J., Gerald, J. E., Skarstrom, C. W., Vardi, J. and Wade, D. T., SAE Trans., 76, 824 (1968).

EPA, "95/96 Evaporative Emission Standards", 1995.

Fris, S. A., "Norit Activated Carbon for Gasoline Evaporative Emission Control", Norit Report, Amersfoort, 1-16, 1993.

G. M., "Evaporative Emission Control Products-Producer Function", Rochester product-G.M., 1986.

McDowall, J. D., McCrae, P. D. and Reimerink, M., "The Development of an Effective Activated Carbon for Evaporative Emission Control", 25th ISATA Meeting, Florence, 1992.

Moon, H., Park, H. C. and Tien, C., "Adsorption of Unknown Substances from Aqueous Solutions", Chem. Eng. Sci., 46, 23 (1990).

Moon, H. and Lee, W. K., "A Lumped Model for Multicomponent Adsorption in Fixed Beds", Chem. Eng. Sci., 41, 1995 (1986).

Moon, H. and Lee, W. K., "Intraparticle Diffusion in Liquid-phase Adsorption of Phenols with Activated Carbon in Finite Batch Adsorber", J. Colloid Interface Sci., 96, 162 (1983).

Moon, H. and Tien, C., "Incorporation of the Potential Theory into Liquid-phase Multicomponent Adsorption Calculations", Chem. Eng. Sci., 43, 1269 (1988).

Park, S. W., Park, H. S., Lee, W. K. and Moon, H., "Effect of Water Vapor on Adsorption of Methyl Iodide to Triethylenediamine-impregnated Activated Carbon", Sep. Technol., 5, 35 (1995).

Reimerink, M., McDowall, J. D., McCrae, P. D. and Fris, S. A., "The Development of an Activated Carbon for an Evaporative Loss Control Device (ELCD)", Norit N. V. Carbon Conference, Essen, 1992.

Ruthven, D. M., "Principles of Adsorption and Adsorption Process", John Wiley & Sons, New York, 1984.

U.S.A. Original Federal Register Vol. 42 No. 124, 1977 and Amended Federal register Vol. 59 No. 66, 1994.

Villadesen, J. V. and Michelsen, M. L., "Solution of Differential Equation Models by Polynomial Approximation", Prentice-Hall, Englewood Cliffs, New Jersey, 1978.

Villadesen, J. V. and W. E. Stewart, "Solution of Boundary-Value Problems by Orthogonal Collocation", Chem. Eng. Sci., 22, 1483 (1967).

Yang, R. T., "Gas Separation by Adsorption Processes", Butterworths, London, 1987.