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Effect of Heat Transfer on the Transient Dynamics of Temperature Swing Adsorption Process

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Abstract–The effect of radial heat transfer on temperature swing adsorption (TSA) was studied by using an air-drying TSA experiment. The experimental dynamics of water adsorption and thermal regeneration in a fixed bed packed with zeolite 13X were used to evaluate the predicted results from the developed models. One- and two-dimensional models for energy balance with various equations describing internal velocity were compared in terms of the prediction of transient dynamics of TSA. Since the heat effect in adsorption step depended on the isosteric heat of adsorption, a dynamic simulation was performed under adiabatic, near-adiabatic, and constant wall temperature conditions. A comparison between one- and two-dimensional models was also made under near-adiabatic condition, which reflected on the experimental condition. There was little difference between adsorption breakthrough curves predicted by the one- and two-dimensional models because the radial distribution of temperature was negligible at the adsorption step. In the case of the regeneration step, a small difference between two models was expected just at the early period of time because the radial effect disappeared with time. One-dimensional model could provide an adequate prediction of the transient dynamics in this system when the wall energy balance was included.

Kew words: Radial Heat Transfer, Adsorption, Thermal Regeneration, TSA, Air-Drying

INTRODUCTION

The thermal swing adsorption (TSA) process is most commonly used to prevent contamination of air by organic solvents of low concentration and to dehumidify gases. Especially, the drying of air by a TSA is one of the major commercial gas separation processes among others because removal of low concentrations of water vapor from gases or air is important for the protection of compressors and electronic equipment. In this process cycle, the bed is primarily regenerated by heating, which is usually provided by preheating a purge gas.

Commercial applications of TSA processes are more common for the purification of gases and liquids than for the bulk separation of gases. Although pressure swing adsorption (PSA) operation has been adopted for many drying plants, especially when the air or gas pressure supply is available at a moderately high pressure, it is not preferable for adsorption and desorption of strong adsorbates. In addition, availability of low grade steam or waste heat at an adjacent plant location would be one factor favoring the choice of TSA [Thomas and Crittenden, 1997]. Furthermore, the choice of adsorbent for the beds depends on the particular drying application. In the engineering plastic industry and pharmaceutical industry, zeolite is extensively used to produce dry air not only because of a need for extremely low dew point gas but also because of the small scale of air-drying TSA process.

The adsorption dynamics at a fixed bed has been studied extensively because fixed-bed adsorption has been an important unit operation for purification or bulk separation of gaseous mixtures [Shim et al., 2004a]. And its dynamic characteristics play a key role in the design, control, and optimization of the process. In the analysis and estimation of the TSA process, equilibrium theory has been widely used to obtain exact solutions from coupled mass and energy balances [Carter and Husain, 1974; Basmadjian, 1975; Basmadjian et al., 1975; Davis and LeVan, 1987]. However, in the numerical method, the mass and energy balances are solved with the equations describing the mass- and heat-transfer rate [Kumar and Dissinger, 1986; Schork and Fair, 1988; Ahn and Lee, 2003]. Although this approach has a limitation resulting from computational difficulty, it has become a general method to solve the coupled differential equations [Yang, 1987; Ruthven et al., 1994; Tien, 1994; Shim et al., 2004b]. This is because in a practical adsorption process a one-dimensional model seems to be enough for design and operation of the system, where the radial temperature and concentration distributions are neglected. Some studies related to radial temperature gradient at a fixed bed have been published, but every such study has dealt with only adsorption or cold purge step as the implement of both experimental and numerical conducts. However, it is very important to estimate the thermal dynamics of the thermal regeneration step accurately in evaluating the economical efficiency of a TSA process because the thermal regeneration step in a TSA process requires a great deal of energy to heat the bed. Furthermore, the thermal properties of adsorbates and adsorbents, radial temperature gradient, and heat transfer through the column wall can affect the column dynamics due to high temperature of purge gas.

In this work, one- and two-dimensional models including mass and energy balances were developed to understand the effect of radial temperature distribution on the dynamics of water adsorption and thermal regeneration. The nonisothermal and nonadiabatic condition used for a fixed adsorption bed was similar to that in the previous study [Ahn and Lee, 2003]. In order to clarify the effect of radial heat transfer on the dynamics of the adsorption bed system-

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atically, the simulation results by one- and two-dimensional models were compared with the experimental results.

MATHEMATICAL MODEL

The system is a fixed bed packed with porous spherical adsorbent particles, in which adsorption of adsorbable component and desorption of adsorbed component are carried out. During adsorption step the feed gas is supplied to the bed at ambient temperature, and during regeneration step the hot purge gas flows in the opposite direction. The non-isothermal, non-adiabatic and non-equilibrium models are necessary to simulate this transient process. The assumptions are as follows:

1. The flow pattern of gas phase in the bed can be described by an axially dispersed plug flow model.
2. The gas phase behaves as an ideal gas mixture.
3. The frictional pressure drop is neglected.
4. Velocity distribution and second order concentration gradient in the radial direction are neglected. Because only axial dispersion is considered both in one- and in two-dimensional models, the same component and overall mass balance equations for the gas phase were used.
5. Since the adsorption capacity of water in zeolite 13X is incomparably greater than that of nitrogen, as carrier gas in the adsorption breakthrough and hot purge gas in the regeneration breakthrough, the contribution of nitrogen to the total adsorption dynamics can be negligible. Therefore, this binary component system (nitrogen and water) can be simplified to a single-component system for water vapor. On the other hand, the heat capacity of the adsorbed water was considered in thermal-energy balance because of the large heat capacity of water.
6. Thermal equilibrium is assumed between the gas and solid phases. The temperature gradients of the solid phase, intraparticle, are also assumed to be negligible because effective thermal conductivities of the commercial adsorbent particles are relatively high. Subject to this assumption, a homogeneous energy balance inside the column was constructed without the division of the temperature into the gas and solid phase. Applicability of this pseudo-homogeneous model to TSA process is described in previous work and elsewhere [Ahn et al., 2003; Lin et al., 1999; Yang, 1987]. Therefore, no attempt was made to assess the necessity for a heterogeneous model in this study.
7. Axial conduction in the column wall can be neglected, but heat loss through the column wall and heat accumulation in the wall cannot be neglected. Therefore, another energy balance in the column wall was introduced.

These assumptions were widely accepted by several studies in the adsorption process [Yang, 1987]. Subject to the above assumptions, the equations describing the mass balance are as follows:

Component mass balance:

$$-D_z\frac{\partial^2 c}{\partial z^2}+\frac{\partial(uc)}{\partial z}+\frac{\partial c}{\partial t}+\rho_p\left(\frac{1-\varepsilon_B}{\varepsilon_B}\right)\frac{\partial \bar{q}}{\partial t}=0 \tag{1}$$

In order to consider both the internal velocity change and the gas-phase concentration change caused by the temperature variation, it is necessary to include an overall mass balance equation.

Overall mass balance:

$$\frac{\partial(u/T)}{\partial z}-\frac{1}{T^2}\frac{\partial T}{\partial t}+\rho_p\frac{R}{P}\left(\frac{1-\varepsilon_B}{\varepsilon_B}\right)\frac{\partial \bar{q}}{\partial t}=0 \tag{2}$$

Another characteristic of the adsorption process is the temperature variation caused by the heat of adsorption. Temperature changes generally affect the adsorption equilibrium relation and, in some cases, adsorption rate. Moreover, the depth of the temperature variation in the TSA process has a great effect on the adsorption and desorption behaviors. In addition to the distinction between heterogeneous and homogeneous models, the models of heat transfer in packed beds may also be divided into one-dimension and two-dimension, depending on whether radial temperature gradients are taken into account or not.

1. Two-Dimensional Pseudo-homogeneous Model

The more realistic model for the description of heat transfer in a fixed adsorption bed is a two-dimensional model which considers radial temperature gradients. This model is necessary for a rigorous analysis of the thermal dynamic behavior of the fixed bed particularly when the radial temperature profiles cannot be neglected. The corresponding thermal-energy balance within the bed was constructed as follows:

Energy balance in the bed:

$$(\alpha\rho_g C_{pg}+\rho_B C_{ps}+\rho_B\bar{q}C_{pa}M_a)\frac{\partial T}{\partial t}+\frac{\partial}{\partial z}(\varepsilon_B u\rho_g C_{pg}T)$$
$$-\rho_B(-\Delta H_s)\frac{\partial \bar{q}}{\partial t}-K_z\frac{\partial^2 T}{\partial z^2}-K_r\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)\right]=0 \tag{3}$$

Liu and Ritter [1997] suggested a cubic temperature dependence for the prediction of the heat capacity of gas in simulating the PSA process for the solvent vapor recovery. The same cubic equation, which considers the effect of temperature variation on the thermodynamic property of fluid phase, was used to estimate the heat capacity of water and nitrogen. All the parameters in the cubic equation came from Reid et al. [1988].

In practical process, finite heat loss through the column wall and heat accumulation in the wall should be considered. Though the column used in the experiment is wrapped by glass wool, the temperature change of the column wall was monitored, particularly during the regeneration step. Therefore another energy balance in the column wall was used as follows:

Energy balance in the wall:

$$\rho_w C_{Pw}A_w\frac{\partial T_w}{\partial t}=2\pi R_{Bi}\alpha_w(T|_{r=R_{Bi}}-T_w)-2\pi R_{Bo}h_o(T_w-T_{atm}) \tag{4}$$

The boundary conditions and initial conditions for both adsorption and regeneration breakthrough are listed in Table 1. In the axial direction, the Danckwerts boundary conditions were used for the mass and energy balance equations. Heat transfer in the radial direction of the bed by exchange with the column wall was expressed by the radial boundary condition in the two-dimensional model. In addition, a "clean bed" condition and a "saturated bed" condition were used as the initial conditions for the adsorption breakthrough and the regeneration breakthrough, respectively.

Since the column dynamics of an adsorption-based operation greatly depend on the adsorption equilibria and kinetics, it is essential

Table 1. The boundary conditions and initial conditions of two-dimensional model

	Eq.	Direction	Boundary condition	Initial condition
Component mass balance	(1)	Axial	$-D_z\left.\frac{\partial c}{\partial z}\right\|_{z=0}=u_f(c_i\|_{z=0^-}-c_i\|_{z=0^+}),\ \left.\frac{\partial c}{\partial z}\right\|_{z=L}=0$	$c(0, x, r)=c_0$
Overall mass balance	(2)	Axial	$u\|_{z=0}=u_f$	$C_t(0, x, r)=C_{to}$
Energy balance in the bed	(3)	Axial	$-K_z\left.\frac{\partial T}{\partial z}\right\|_{z=0}=\varepsilon_B\rho_g C_{pg}u_f(T\|_{z=0^-}-T\|_{z=0^+}),\ \left.\frac{\partial T}{\partial z}\right\|_{z=L}=0$	$T(0, x, r)=T_0$
		Radial	$\left.\frac{\partial T}{\partial r}\right\|_{r=0}=0,\ -K_r\left.\frac{\partial T}{\partial r}\right\|_{r=R_{Bi}}=\alpha_W(T\|_{r=R_{Bi}}-T_W)$	
Energy balance in the wall	(4)			$T_W(0, x)=T_{W0}$

that the adsorption characteristics should be measured and correlated precisely. For H_2O/zeolite 13X system, Ryu et al. [2001] measured the characteristics using a gravimetric method. In their study, the isotherms of this system were type II according to Brunauers classification and the experimental results were fitted by various models. Though the excess surface work (ESW) model agreed well with the experimental data over the whole pressure region, the Langmuir-Freundlich (L-F) model could be successfully applied to the low water concentration range used in this study. The linear driving force (LDF) model and L-F isotherm model were used for adsorption rate and equilibrium, respectively, as suggested in the experimental results [Ryu et al., 2001].

$$\frac{\partial \bar{q}}{\partial t}=\omega(q^*-\bar{q}) \tag{5}$$

$$q^*=\frac{q_m BP^n}{1+BP^n} \tag{6}$$

In these models, a single lumped mass transfer parameter, ω, was assumed constant and was obtained from the mean value in the range of partial pressure of water vapor. And the dependence of equilibrium constants on temperature is described as follows:

$$q_m=k_1+k_2T,\ B=k_3e^{k_4/T},\ n=k_5+k_6/T \tag{7}$$

In Eq. (3), the isosteric heat of adsorption ($-\Delta H_s$) was evaluated from the following Clausius-Clapeyron equation by using a set of equilibrium data obtained at several temperatures [Suzuki, 1990].

$$\left[\frac{\partial \ln P}{\partial T}\right]_n=\frac{-\Delta H_s}{RT^2} \tag{8}$$

According to the ideal Langmuir model, the heats of adsorption are independent of the change of the coverage. In real adsorption systems, however, they are dependent on the coverage. This is owing to the heterogeneity of surface energy and the lateral interactions between adsorbates [Ross and Oliver, 1964]. In this study, the isosteric heat of adsorption of water vapor on zeolite 13X was calculated as a function of the moles adsorbed and then expressed by the following cubic equation analogous to that of heat capacity.

$$-\Delta H_s=\sum_{i=0}^{3}\gamma_i q^i \tag{9}$$

2. One-Dimensional Pseudo-homogeneous Model

When the radial temperature profiles can be negligible, overall heat transfer model (one dimensional pseudo-homogeneous model) can be applied for the description of heat transfer in the bed. In this model, the resistance of the bed (effective radial conduction) and the wall resistance (wall heat transfer coefficient) in the one-dimensional model are combined into a single overall heat transfer coefficient related to the bed radial average temperature. Then, the temperature in the bed, T, can be given as:

$$(\alpha\rho_g C_{pg}+\rho_B C_{ps}+\rho_B\bar{q}C_{pa}M_a)\frac{\partial T}{\partial t}+\frac{\partial}{\partial z}(\varepsilon_B u\rho_g C_{pg}T)$$
$$-\rho_B(-\Delta H_s)\frac{\partial \bar{q}}{\partial t}-K_z\frac{\partial^2 T}{\partial z^2}+\frac{2h_i}{R_{Bi}}(T-T_w)=0 \tag{10}$$

$$\rho_w C_{Pw}A_w\frac{\partial T_w}{\partial t}=2\pi R_{Bi}h_i(T-T_w)-2\pi R_{Bo}h_o(T_w-T_{atm}) \tag{11}$$

As shown in Table 1, analogous boundary conditions in the axial direction and initial conditions to the two-dimensional model were used.

As for the one-dimensional model, the component mass balance equation takes the same form as that of the two-dimensional model according to assumption 4. Within this equation, there is no difference between the two models except for the dimension of variables.

On the other hand, it is well known that the flow velocity in an adsorption bed can be significantly changed if the quantity of adsorbate in the feed is not dilute and the variations of both temperature and pressure in the bed are great. In this study, the following three velocity models were applied to the one-dimensional model.

2-1. Velocity Model I: Overall Mass Balance Equation

Since the variation of the temperature in the bed was significant in the thermal regeneration of the fixed bed, its effect on the fluid velocity could not be negligible. Therefore, the interstitial velocity in model I was calculated from the overall mass balance, Eq. (2).

2-2. Velocity Model II: Velocity Equation Considering the Node Temperature

In this model, the interstitial velocity was assumed to depend mainly on the bed temperature at each position because the pressure drop in the bed was negligible and there existed a trace amount of water in the feed. By using the ideal gas law, the following algebraic equation was substituted for the overall mass balance equation.

$$u=\frac{T}{T_0}u_0 \tag{12}$$

2-3. Velocity Model III: Constant Velocity Equation

Model III used the constant velocity calculated from the flow

rate of the feed or hot purge as follows:

$$u=u_0 \quad (13)$$

3. Numerical Implement

The numerical solution of the above model is very complex and difficult because the equations to determine the behavior of this system are called partial differential-algebraic equations (PDAEs). Furthermore, the exponential terms of nonlinear isotherms (Langmuir-Freundlich model) often make numerical simulation inexecutable. In this study, the gPROMS modeling tool developed by Process Systems Enterprise Ltd. was used to obtain the solution of dynamic simulation from the above model. The PDAEs are solved by using a method of line (MOL) methodology which discretizes the spatial dimension to reduce the PDAEs to differential-algebraic equations (DAEs). Typically, 15 to 30 distance steps were used for normal computation. A centered finite difference method (CFDM) of the second order was applied to the spatial partial derivatives. And thereafter, the DAEs for temporal domain were integrated by employing an integrator, called a DASOLV, included in the gPROMS. The results of numerical simulation were stable for the range of conditions used in this work.

In the case of adsorption breakthrough, the CPU time for solving the above PDAEs was less than 100 second on a computer (PC, pentium 1.0 GHz), whereas each experimental run was executed for 500 minutes.

EXPERIMENTAL

Water mixtures with nitrogen were used as a feed gas, and dry nitrogen was used as a carrier gas in the adsorption breakthrough and as a hot purge gas in the regeneration breakthrough. The zeolite 13X (Aldrich Co.) was used as an adsorbent. The physical properties of the adsorbent are presented in Table 2. Before each experiment, adsorbents were regenerated for more than 12 hours at 593 K.

Table 2. Physical properties of adsorbents

Adsorbent	Zeolite 13X
Form	Bead
Particle size	4-8 mesh
BET surface area	402 m^2/g
Particle void fraction	0.24
Particle density	1.10 g/cm^3

Table 3. Characteristics of adsorption bed

Bed length	30.0 cm
Inner bed diameter	3.0 cm
Flange length	4.0 cm
Flange diameter	6.3 cm
Column thickness	0.23 cm
Column density	7.83 g/cm^3
Heat capacity of column	0.12 cal/g·K
Bed void fraction	0.37
Total void fraction	0.52
Bed density	0.69 g/cm^3

The adsorption bed was made of a stainless steel pipe with a length of 30 cm, 3.0 cm ID, and 0.23 mm wall thickness. The characteristics of the adsorption bed are listed in Table 3. Three J type thermocouples were installed at a position of 5, 15, and 25 cm from the bottom of the bed in order to measure the temperature inside the bed. In the breakthrough experiments, the effluent gas was monitored by both a hygrometer (VAISALA, HMD40U) and a dew-point meter (Panametrics, MMS 35) located above the top of the bed. In the regeneration experiment, the effluent from the adsorber was condensed by a heat exchanger and the amount of the condensed liquid was measured in real time with a microbalance. All the experimental data such as time, temperature, pressure, feed flow rate, humidity and mass were stored on a computer. And more details of the equipment and operating procedures used are described in the previous work [Ahn and Lee, 2003].

To determine the heat transfer coefficients of the one- and two-dimensional models, hot nitrogen heating experiments were performed at various flow rate and temperature of purge gas. The adsorption breakthrough experiment was performed under a feed condition of 16,000 ppm water concentration, 9 LSTP/min feed flow rate, and 297 K ambient temperature. The corresponding regeneration breakthrough experiment was performed under the purge condition of 593 K regeneration temperature, 45 LSTP/min purge flow rate, and 297 K ambient temperature.

RESULTS AND DISCUSSION

1. Evaluation of One-Dimensional Models for Adsorption and Regeneration Dynamics

In order to verify that the two-dimensional model developed in this study is realistic and representative for the air-drying TSA process, a detailed analysis and estimation of simplified mathematical equations composing one-dimensional model is required. In this study, the experimental results of adsorption and regeneration breakthroughs

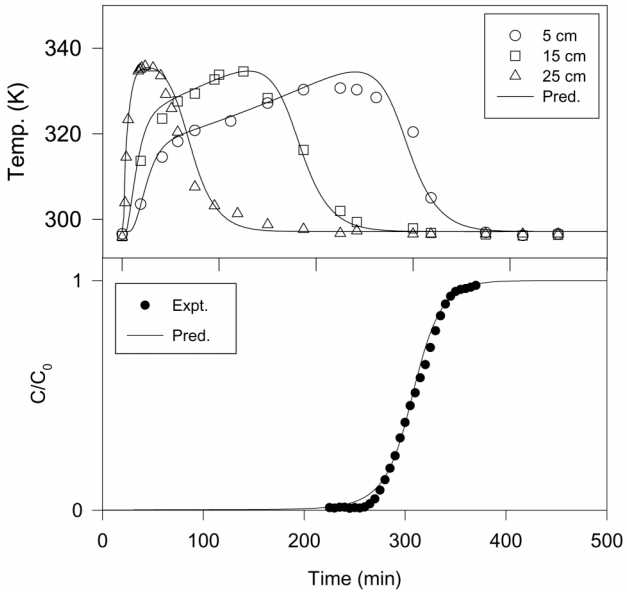

Fig. 1. Breakthrough curves and temperature history at adsorption step. Adsorption condition: 16,000 ppm, 9 LSTP/min feed flow rate, and 297 K ambient temperature.

were compared with simulated results.

Fig. 1 shows the experimental and simulated results of the adsorption breakthrough curve. To provide a clearer insight into the adsorption dynamics, the temperature history inside the beds is also presented. The adsorption breakthrough is intrinsically exothermic and the heat released during the adsorption leads to the non-isothermal breakthrough. As the concentration wave fronts propagated along the bed, the temperature inside the bed was steeply increased due to the high heat of adsorption. While the front part of the temperature profile propagated to the product end much faster than the concentration wave front, the rear part of the temperature profile kept pace with the concentration wave front. As a result, a broad temperature profile was formed at each position of the bed, as shown in Fig. 1. In an equilibrium model, which assumes negligible resistance to mass transfer, it is reported that high-concentration fronts propagate faster than low-concentration fronts for a favorable isotherm [Yang, 1987]. Thus, the concentration front becomes self-sharpening type, referred to as a compressive wave.

Fig. 2 shows the thermal regeneration breakthrough curves of the bed pre-saturated in the adsorption breakthrough experiment in Fig. 1. And the corresponding simulated results using various velocity models were also compared. The regeneration condition was 45 LSTP/min purge flow rate, 593 K purge temperature, and 297 K ambient temperature. Concentration breakthrough measured at the column exit could be considered as a time-average value since the amount of the desorbed water was measured in the form of the continual water drops through the heat exchanger. Therefore, the experimental errors at the early period occurred inevitably in the desorbed amount because some amount of water was vented with nitrogen.

As can be seen in Fig. 2, the experimental regeneration curves

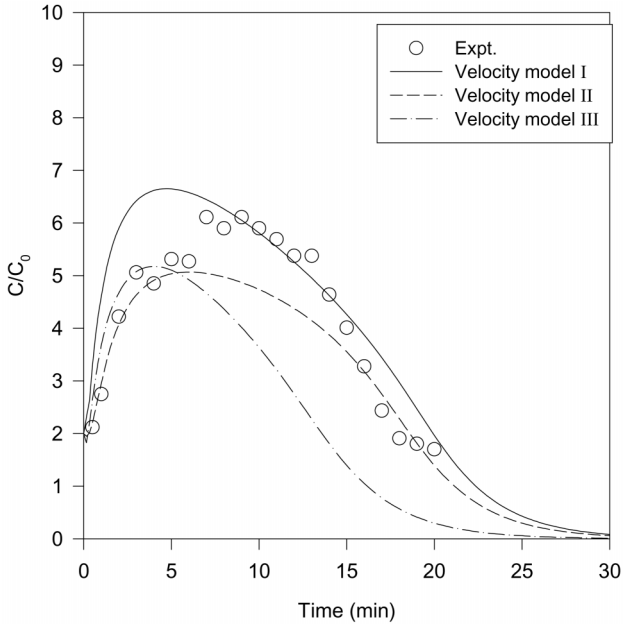

Fig. 2. Regeneration breakthrough curves. Adsorption condition: 16,000 ppm, 9 LSTP/min feed flow rate, and 297 K ambient temperature. Regeneration condition: 593 K purge temperature, 45 LSTP/min purge flow rate, and 297 K ambient temperature.

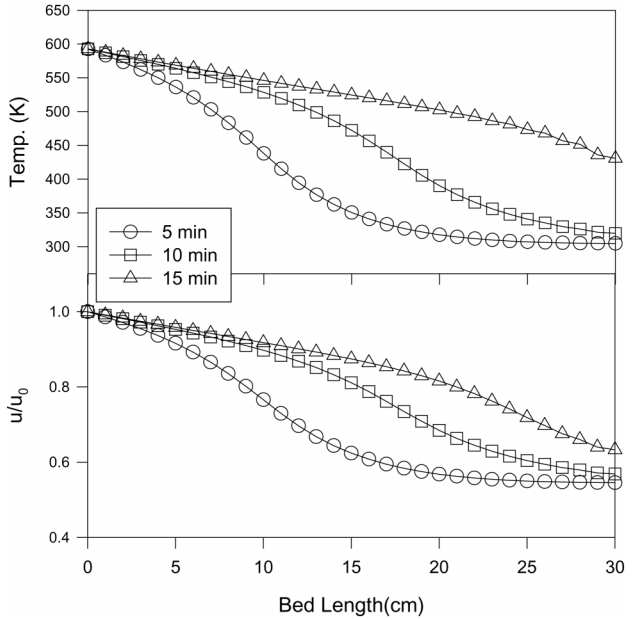

Fig. 3. Temperature and velocity profile in the bed at regeneration step.

were well predicted by the simulation using the velocity model I. For velocity model II and III, on the other hand, effluent concentration in the regeneration breakthrough was grossly underestimated. However, there was a little difference among simulated complete regeneration times using three different velocity models. As a result, the velocity model I was adopted in the two-dimensional model, though this additive partial differential equation made numerical implementation complex. It is noteworthy that there is no significant difference among the simulated results of these velocity models in the adsorption breakthrough. It implies that the flow velocity during adsorption step does not change significantly because the quantity of adsorbate in the feed is dilute and the variations of both temperature and pressure in the bed are not great.

The temperature and velocity profiles simulated by the model I at different times are shown in Fig. 3. It can be seen that the distribution of velocity in the axial direction exists especially at the early period of regeneration step due to the volumetric change of fluid by temperature variation.

2. Comparison between One- and Two-Dimensional Models

In each step of the TSA process, heat of adsorption, the thermal properties of adsorbates and adsorbents, and heat transfer through the column wall can affect the temperature profile inside the bed. In particular, the heat transfer through the wall should be taken into account unless adiabatic condition can be guaranteed. Especially, under conditions of finite heat loss at the wall, there is a significant radial temperature gradient that will, in general, affect the adsorption and desorption dynamics. Compared to the simulation of PSA process, it is expected that more rigorous models should be used to predict the accurate thermal dynamics in the simulation of the TSA process. In order to investigate the effects of the radial direction on temperature distribution, radial thermal conduction and wall heat transfer were taken into account in the two-dimensional model used in this study.

One of the simplest models for the description of thermal condi-

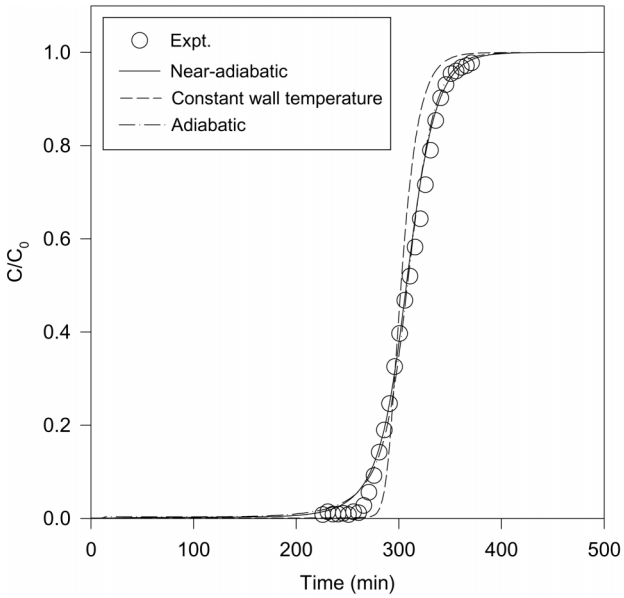

Fig. 4. Effect of thermal conditions on the adsorption breakthrough curves.

tions in a fixed bed is the adiabatic model with negligible heat transfer at the column wall. It is well known that the behavior of an industrial bed with a large diameter can be adequately simulated by using adiabatic models. However, in an adsorbent bed of relatively small diameter, heat exchange through the wall becomes appreciable when the insulation cannot be guaranteed. If heat losses increase, an ideal isothermal behavior is eventually approached. Another characteristic representation of thermal condition in a fixed bed is that the column wall is kept at a constant temperature. Heat transfer between packed bed and the column wall of constant temperature has been widely studied because of its relevance to the design and operation of wall-cooled catalytic reactors.

In Fig. 4, the breakthrough results simulated under non-adiabatic condition were compared with those of adiabatic and constant wall temperature conditions. Whereas the wall heat transfer coefficient, α_w, is zero in an adiabatic condition, the wall temperature, T_w, is constant in a constant wall temperature condition. Therefore, the energy balance equation in the wall, Eq. (4), is not necessary in both cases.

Though the column used in the experiment was wrapped by a heat shield material, glass wool, a little heat transfer between external surface of the wall and atmosphere is inevitable. The breakthrough time increased about 100 min in the constant wall temperature condition compared with that in adiabatic condition, while there was little difference between the adiabatic and the non-adiabatic condition, as shown in Fig. 4.

Representative two-dimensional temperature profiles in the bed at the early adsorption stage are shown in Fig. 5. For a constant wall temperature in Fig. 5(a), the radial distribution of temperature was

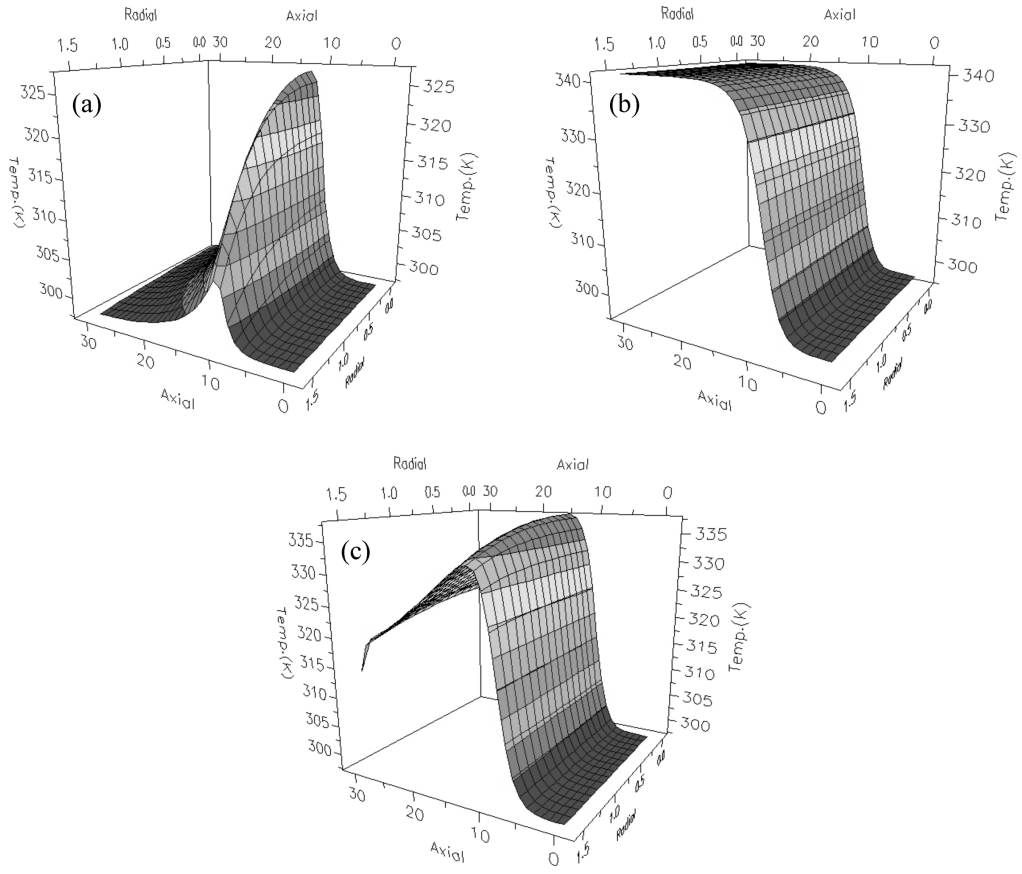

Fig. 5. Effect of thermal conditions on the temperature profiles in the bed at adsorption step (t=100 min).
(a) constant wall temperature, (b) adiabatic, and (c) near-adiabatic condition

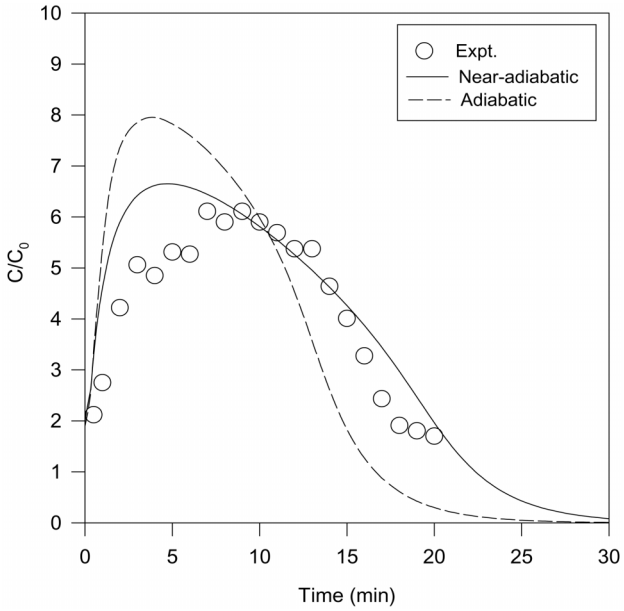

Fig. 6. Effect of thermal conditions on the regeneration breakthrough curves.

clearly shown at a certain time. However, it can be seen that the radial distribution of temperature at the other conditions is not prominent. Furthermore, the near-adiabatic condition in the experimental system just showed a negligible radial distribution at a certain axial position in Fig. 5(c).

Fig. 6 shows the comparison of adiabatic and near-adiabatic conditions in the regeneration step. Unlike the results in the adsorption step in Fig. 4, the difference between both conditions was prominent because the heat loss through the wall is not negligible at the near-adiabatic condition in the hot nitrogen regeneration. Therefore, it is shown clearly that the adiabatic condition overestimated the regeneration curve. However, even at the near-adiabatic condition in the regeneration step, the radial distribution of temperature was not prominent as shown in Fig. 7. In addition, as the regeneration time proceeded, the distribution of temperature approached to the adiabatic condition, showing small radial distribution at near wall.

Figs. 8 and 9 show the experimental adsorption and regeneration breakthrough curves with the corresponding simulated results by the one- and two-dimensional models. Available empirical correlations for estimating the parameter were mostly based on the model of constant wall temperature and developed under steady-state conditions. But they do not predict well the transient dynamics in an adsorption bed. In this study, the heat transfer coefficients of a one-dimensional model were estimated from the hot nitrogen heating experiments at a near-adiabatic bed packed with thermally regenerated zeolite 13X. It is clear from a prior estimation of coefficients

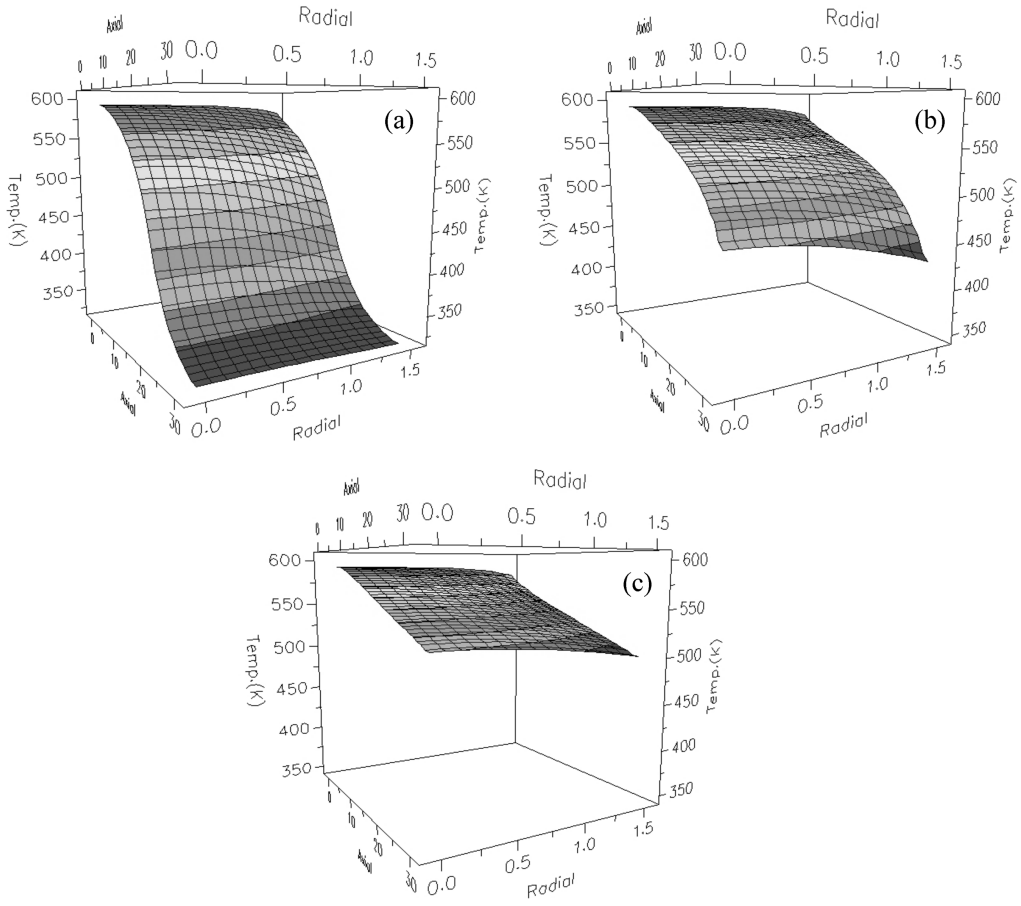

Fig. 7. Simulated temperature profiles in the bed at regeneration step under near-adiabatic condition at (a) t=10 min, (b) 20 min, and (c) 30 min.

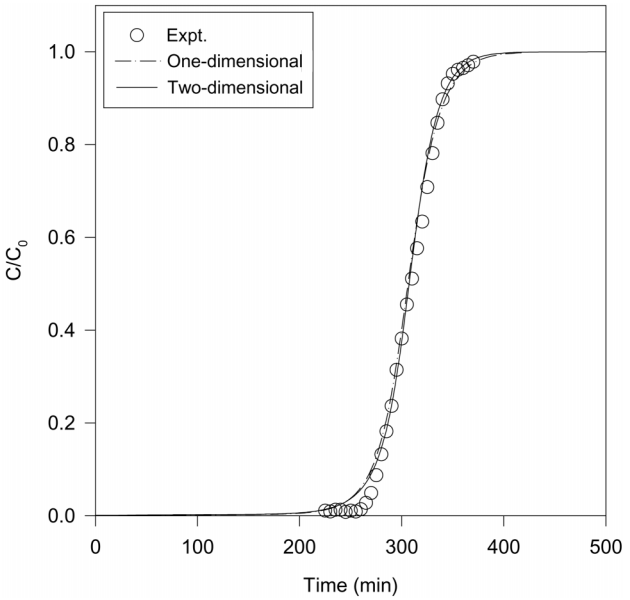

Fig. 8. Comparison of one- and two-dimensional models in the adsorption breakthrough curves.

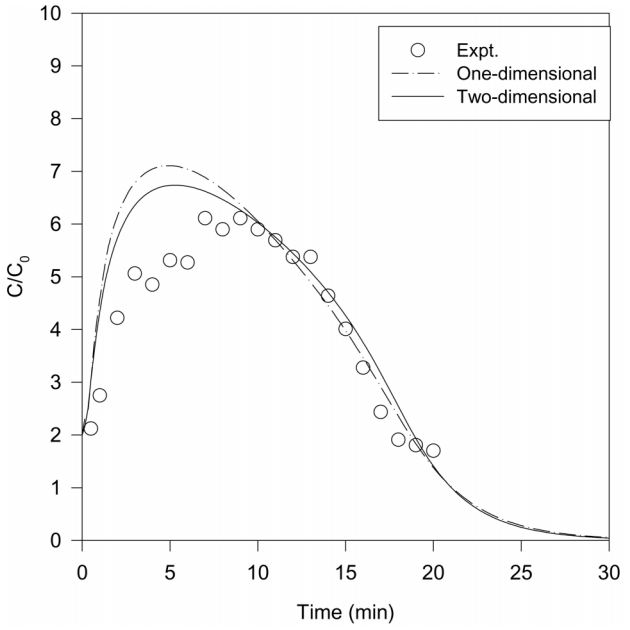

Fig. 9. Comparison of one- and two-dimensional models in the regeneration breakthrough curves.

that the most crucial parameter for the success of one-dimensional analysis is the heat transfer coefficient at the inner wall, h_i, which is normally obtained by fitting the experimentally measured temperature at various locations of the column with the model solution. It is noteworthy that the value of h_o was assumed to be constant because it was not related to the flow condition and limited variation of temperature.

As expected in Fig. 5, there is little difference between adsorption breakthrough curves predicted by the one- and two-dimensional models because the radial distribution of temperature was negligible at the adsorption step. In the case of the regeneration step in Fig. 9, there is a small difference between two models at the early period of time. It is because the radial effect disappears with time as mentioned in Fig. 7. As a result, it is clear from this study that the one-dimensional model could provide an adequate representation of the column dynamics in a TSA process if the distribution of temperature profiles is not severe and heat transfer to the column wall is properly reflected in the overall effective heat transfer coefficient.

CONCLUSIONS

This work was conducted to study the heat transfer effect on the transient dynamics of the TSA process. The adsorption breakthrough experiment and the corresponding regeneration breakthrough experiment for an air-drying TSA process were performed under near-adiabatic condition in a fixed bed packed with zeolite 13X. The experimental results were predicted by using one- and two-dimensional pseudo-homogeneous models developed to evaluate the effect of the thermal dynamics on the radial direction.

The distribution of velocity in the axial direction exists especially at the early regeneration step due to the volumetric change of fluid by temperature variation. Consequently, better predicted results were obtained when the velocity distribution was calculated from the overall mass balance equation. And it is expected that only marginal improvements would be obtained from using complex models with temperature difference between fluid and particle, conduction in the wall, pressure drop in the axial direction.

In adiabatic TSA systems with strong heat of adsorption, heat transfer plays an important role in the dynamic behavior of the separation process. Since the values of h_i and α_w had a strong influence on thermal dynamics among others and showed a dependency on flow condition, it was important to estimate these values accurately.

As a result, the simulated results of concentration breakthrough by two-dimensional model resemble those by one-dimensional model with a column-wall energy balance. In addition, the one-dimensional pseudo-homogeneous model has sufficient accuracy when temperature rise is mild and heat transfer to the column wall is reasonably represented by the overall effective heat transfer coefficient.

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NOMENCLATURE

A_W : cross sectional area of the wall [cm^2]
B : equilibrium parameter for Langmuir-Freundlich model [1/atm]
C : concentration in bulk phase [mol/cm^3]
C_{pg}, C_{ps}, C_{pw} : gas, pellet, and wall heat capacity, respectively [cal/g K]
D_z : axial dispersion coefficient [cm^2/sec]
h_i : heat transfer coefficient at the inner wall [$cal/cm^2 \cdot K \cdot sec$]
h_o : heat transfer coefficient at the outer wall [$cal/cm^2 \cdot K \cdot sec$]
$-\Delta H_s$: average heat of adsorption [cal/mole]

K_r : radial thermal conductivity [cal/cm sec K]
K_z : axial thermal conductivity [cal/cm sec K]
L : bed length [cm]
P : total pressure [atm]
q, q^*, $\bar{q}$: amount adsorbed, equilibrium amount adsorbed, and average amount adsorbed, respectively [mol/g]
q_m : equilibrium parameter for Langmuir-Freundlich model [mol/g]
R_{Bi}, R_{Bo}: inside and outside radius of the bed, respectively [cm]
r : radial distance in bed [cm]
t : time [sec]
T_{atm} : temperature of atmosphere [K]
T, T_w : bed temperature and wall temperature, respectively [K]
u : interstitial velocity [cm/sec]
z : axial distance in bed from the inlet [cm]

Greek Letters

α_w : heat transfer coefficient between the bed and the column wall [cal/cm^2·K·sec]
ε_B, α : voidage of adsorbent bed and total void fraction, respectively [-]
ρ_g, ρ_p, ρ_B, ρ_w : gas density, pellet density, bulk density, and bed wall density, respectively [g/cm^3]
ω : LDF coefficient [1/sec]

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