CHAPTER IV
MATHEMATICAL SOLVING METHOD

In the previous work by Uttamaroop (2003), the breakthrough model for multi-layer adsorber was developed. It was an axial dispersion plug flow model, according to a mass balance of the column. In order to understand the dynamic adsorption in packed bed adsorber, it was necessary to study the equilibrium adsorption because it was needed in modeling of breakthrough curves. In order to fulfill the breakthrough model proposed by Uttamarop (2003), a deactivation model for the adsorption of water vapor from natural gas onto the activated alumina and molecular sieve zeolites in a packed bed adsorber was developed in this work.

4.1 Adsorption isotherm equation

The adsorption isotherm equation is a function of the equilibrium adsorbed phased concentration;

$$q = f(c) \tag{4.1}$$

Many adsorption isotherms in the literatures describe the adsorption behavior of water vapor onto a solid adsorbent. The general adsorption isotherm type of activated alumina is normally type II Brunauer, and the molecular sieve zeolite is of the type I Brunauer or Langmuir isotherm.

4.2 Mass Balance for Adsorber

The derivation of the basic differential equation governing the dynamic behavior on fixed bed adsorber is the followings.

From the c onservation of chemical species (Deen, 1998),

$$\frac{Dc_i}{Dt} = -\nabla \cdot N_i + R_{vi} \tag{4.2}$$

Where, c_i = concentration of species i

N_i = molar flux of species i relative to fixed coordinates and

R_{vi} = net rate of formation species i by chemical reactions

When there is fluid flow the preferred way to write the total flux is

$$N_i = C_i v + J_i \tag{4.3}$$

Where, J_i = molar flux of i relative to the mass-average velocity and at constant density, the flux equation for each component is

$$J_i = -D_i \nabla C_i \tag{4.4}$$

Based on the foregoing, when all components of gas mixture except one are present in small concentrations and the density and diffusivities are constant. The equation (4.2) can be written as;

$$\frac{Dc_i}{Dt} + v\nabla C_i = D_i \nabla C_i^2 + R_{vi} \tag{4.5}$$

Species conservation equation for a mixture in the cylindrical coordinate can be written as

$$\frac{\partial c_i}{\partial t} + v_r \frac{\partial c_i}{\partial r} + v_\Theta \frac{\partial c_i}{\partial \Theta} + v_z \frac{\partial c_i}{\partial z} = D_i \left[\frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial c_i}{\partial r}\right) + \frac{1}{r^2} \frac{\partial^2 c_i}{\partial \Theta^2} + \frac{\partial^2 c_i}{\partial z^2} \right] + R_{vi} \tag{4.6}$$

The concentration profile in r and θ directions are assumed to be negligible, so the equation (8.6) becomes,

$$\frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial z} = D_L \frac{\partial^2 c_i}{\partial z^2} - R_{vi} \tag{4.7}$$

Where, R_{vi} explain the rate of adsorption of a single adsorbate into an adsorbent particle in the packed bed adsorber

$$R_{vi} = -\frac{(1-\varepsilon)}{\varepsilon} \frac{\partial \overline{q}}{\partial t} \tag{4.8}$$

Where, ε = bed porosity

$\dfrac{\partial \overline{q}}{\partial t}$ = mass transfer of component term described as linear driving force model, which is defined as the difference between the equilibrium water

concentration and the actual uptake on the particle (Brosillon *et al.*, 2001). The linear driving force model can be written as,

$$\frac{\partial \overline{q}}{\partial t} = k\left(q^* - \overline{q}\right)$$

(4.9)

Where, q^* = equilibrium adsorbed phase concentration

$\overline{q}$ = average adsorbed phase concentration

k = adsorption equilibrium constant

From equation (4.7) mass balance on an adsorber, therefore, is

$$-D_L \frac{\partial^2 c_i}{\partial z^2} + \frac{v\partial c_i}{\partial z} + \frac{\partial c_i}{\partial t} + \frac{(1-\varepsilon)}{\varepsilon}\frac{\partial \overline{q}}{\partial t} = 0$$

(4.10)

Rearranging eq. (4.10) in order to determine the variation of gas phase concentration with time or breakthrough curve obtains

$$\frac{\partial c_i}{\partial t} = D_L \frac{\partial^2 c_i}{\partial z^2} - v\frac{\partial c_i}{\partial z} - \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial \overline{q}}{\partial t}$$

(4.11)

The dynamic response of the column is given by the solution $\left[c(z,t),\overline{q}(z,t)\right]$ to equation (4.9) and (4.11) subject to the initial and boundary conditions imposed on the column. The boundary and initial conditions for the adsorption in the column are

$$c(0,t) = c_o$$

(4.12)

$$c(z,0) = 0$$

(4.13)

$$\overline{q}(z,0) = 0 \text{ ; and}$$

(4.14)

$$\left(\frac{\partial \overline{q}}{\partial z}\right)_{z=L} = 0$$

(4.15)

The location of the front at any time may be found simply from an overall mass balance, but to determine the form of the concentration front equation (4.9) and (4.11) must be solved simultaneously.

4.3 Deactivation Modeling Approaches

The deactivation of the adsorbent along with the adsorption process was considered in order to correct and fulfill the mass balance equation in order to predict the real breakthrough time of the adsorber. In this work the adsorption isotherm of deactivated adsorbents were developed and combined with the previous mass balance equation (Uttamaroop, 2003). The breakthrough time of fresh and deactivated adsorbent were examined from experiment and mathematical solving program. Then, the relationship of the breakthrough time and several adsorbents was analyzed. There are 2 approaches, which can be used to develop the deactivation model.

- **Approach 1: Real times approach**

Firstly, the adsorption isotherm of fresh and deactivated adsorbents with various degree of deactivation was developed. The adsorption isotherm equation was constructed by using regression technique also the adsorption constant was obtained. Then, the breakthrough time of each condition of the adsorbents was generated by using the parameters from the experiments and calculation.

In a packed bed adsorber where the water vapor are removed from the gas phase by adsorption on the specific sites of the adsorbent, the adsorption capacity in the deactivation process can move through the packed bed as a wave front as shown in Figure 4.1. Therefore the corresponding deactivation profile for the deactivation can be plotted with the breakthrough time as shown in Figure 4.2. In this case the activity described as

$$a(t) = \frac{R_{vi}(t)}{R_{vi}(t = 0)} \qquad (4.12)$$

Where, a = adsorbent deactivation at time t, defined as the ratio of the rate of adsorption on the adsorbent that has been used for a time t to the rate of adsorption on a fresh adsorbent (Fogler, 2002).
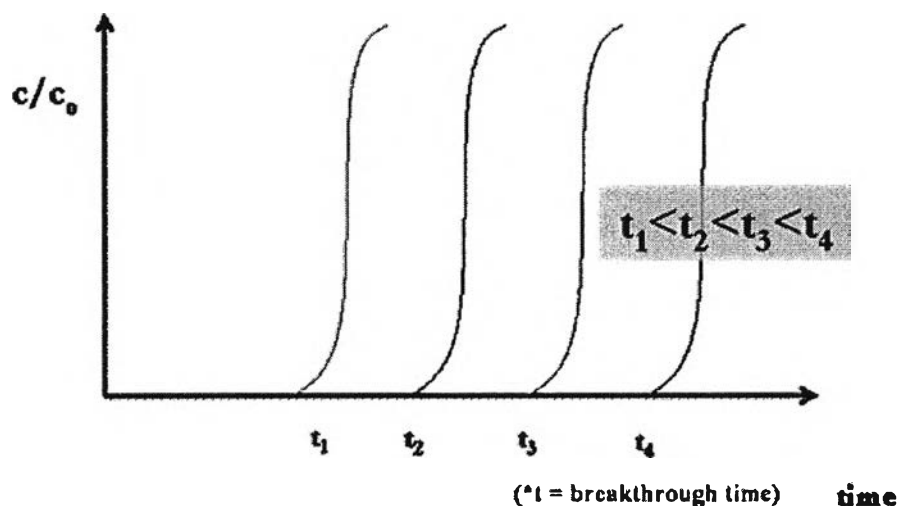
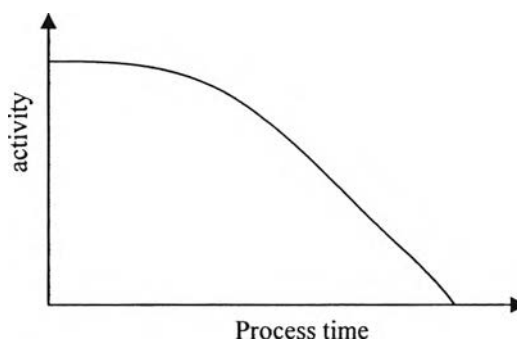**Figure 4.1** Change of the breakthrough time upon degree of deactivation in a packed bed adsorber.

Figure 4.2 Activity as a function of process time.

The activity in figure 4.2 is related with the percentages of deactivation of the adsorbent. Since the reaction rate law accounting for catalyst activity or rate of deactivation (R_d) can be written as

$$R_d = -\frac{da}{dt} = k_d a^q (t) C_i^n \qquad (4.13)$$

Therefore, the specific decay constant (k_d) can be determined by regression the plot of activities versus operating time. As seen in equation 4.13 that the decay can be any order which depended on the plot of activity as a function of time. If it is linear or zero decay reaction order, the equation is in the form

$$a_{(t)} = 1 - k_d t \qquad (4.14)$$

But if decay reaction orders are 1st (exponential) or 2nd (hyperbolic) order, the equation can be written as

$$a_{(t)} = e^{-k_d t}$$ (4.15)

$$a_{(t)} = \frac{1}{1 + k_d t}$$ (4.16)

After deactivation rate developed it will be include in the mass balance equation of the adsorber to get the complete model used for predict the breakthrough time in real operation with consider the deactivation along with the adsorption process. The mass balance can be written as

$$-D_L \frac{\partial^2 c_i}{\partial z^2} + \frac{v \partial c_i}{\partial z} + \frac{\partial c_i}{\partial t} + \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial \bar{q}}{\partial t} + R_d = 0$$ (4.17)

- **Approach 2: Breakthrough time approach**

The adsorption isotherm models of fresh and deactivated adsorbents are determined and implemented in the linear driving force model which is one part of the mass balance equation.

$$\frac{\partial \bar{q}}{\partial t} = k \left(q^* - \bar{q} \right)$$ (4.18)

And from the equilibrium adsorption isotherm equation,

$$q^* = q^*(c, T)$$ (4.19)

When adsorption was conducted at a constant temperature, the adsorption isotherm equation becomes a function of adsorbed concentration only,

$$q^* = q^*(c)$$ (4.20)

The adsorption behavior of the adsorbents can be changed due to the change of surface area and the structure of the deactivated adsorbents. So, the equilibrium adsorption isotherms of fresh adsorbents and deactivated adsorbents can be developed over the various extents of deactivation.

$$q^* = q^* \ (c)_{fresh} \tag{4.21}$$

$$q^* = q^* \ (c)_{deactivated} \tag{4.22}$$

Then, the equilibrium adsorption isotherms of fresh and deactivated adsorbents, Equations 4.21 and 4.22, can be substituted into the dynamics adsorption or breakthrough equation, equation 4.11. As the equilibrium adsorption isotherm is combined in the mathematical model, the theoretical breakthrough time from various isotherms can be predicted.

Therefore, the relationship between the breakthrough time and the deactivation in dimensionless term can be developed. Figure 4.3 represents the relationship of the breakthrough time and deactivation ratio of deactivated adsorbents.
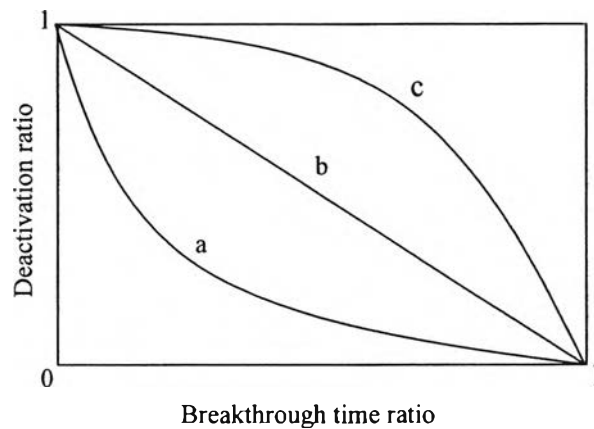

Figure 4.3 Relationship between the breakthrough time ratio and deactivation ratio
of the deactivated adsorbents in various expected manners.