CHAPTER IV
MATHEMATICAL SOLVING METHOD

A Theoretical breakthrough curve for adsorption of water vapor from natural gas onto a multi-layer adsorber was obtained by solving the set of mathematical equations. The calculation was based on an axial dispersion plug flow and Linear Driving Force (LDF) model. The method of lines (MOL) combined with the central finite difference was applied to express the partial differential equation (PDE) in terms of a series of ordinary differential equations (ODE). Then, the Runge-Kutta 4th order method was used to solve the finite difference equations using computer programming in FORTRAN language to obtain the breakthrough curve data and concentration profiles through the bed length.

4.1 Method of Lines (MOL)

The differential mass balance on the adsorption column is given by:

$$- D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z}(vc) + \frac{\partial c}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial \bar{q}}{\partial t} = 0 \qquad (4.1)$$

In order to determine the variation of gas phase concentration with time or breakthrough curve, Eq.(4.1) could be rearranged to be:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial \bar{q}}{\partial t} \qquad (4.2)$$

Then, the method of lines (MOL) was applied to convert a second order derivative and a first order derivative PDE presented in Eq.(4.1) into a set of ordinary differential equations by using the central finite difference method with the error of $O(\Delta z^2)$ as the following:

For a 2nd order derivative term, $\dfrac{\partial^2 c}{\partial z^2}$

$$\frac{d^2 c_{i,j}}{dz^2} = \frac{1}{\Delta z^2}\left(c_{i+1,j} - 2c_{i,j} + c_{i-1,j}\right) + O(\Delta z^2) \tag{4.3}$$

For a 1st order derivative term, $\dfrac{\partial c}{\partial z}$

$$\frac{dc_{i,j}}{dz} = \frac{1}{2\Delta z}\left(c_{i+1,j} - c_{i-1,j}\right) + O\left(\Delta z^2\right) \tag{4.4}$$

where

   i = step size number of axial direction, z ; and

   j = step size number of time, t.

In this model, the mass transfer can be described by Linear Driving Force (LDF) model. This model is based on the assumption that the uptake rate of water vapor by the adsorbent pellet is linearly proportional to a driving force. This driving force is defined as the difference between the equilibrium water concentration and the actual uptake on the particle (Brosillon *et al.*, 2001). The model expression can be written as

$$\frac{d\overline{q}}{dt}i,j = k\left(q^{*}_{i,j} - \overline{q_{i,j}}\right) \tag{4.5}$$

where $q^{*} = f(c_{i,j})$ represents the equilibrium adsorbed phase concentration, which is the adsorption isotherm equations. In modeling, these isotherm equations were obtained by fitting the experimental data as shown in CHAPTER 5.

The Eq.(4.2) can be re-written into the general formula as follows:

$$\left(\frac{dc}{dt}\right)_{i,j} = D_L\left[\frac{1}{\Delta z^2}\left(c_{i+1,j} - 2c_{i,j} + c_{i-1,j}\right)\right] - v\left[\frac{1}{2\Delta z}\left(c_{i+1,j} - c_{i-1,j}\right)\right]$$
$$-\left(\frac{1-\varepsilon}{\varepsilon}\right)k\left(q^{*}_{i,j} - \overline{q_{i,j}}\right) \tag{4.6}$$

4.2 Boundary and Initial Conditions

The boundary and initial conditions for the adsorption in the column are

$$c(0,t) = c_0 \tag{4.7}$$

$$c(z,0) = 0 \tag{4.8}$$

$$\overline{q}(z,0) = 0 \; ; \text{ and} \tag{4.9}$$

$$\left(\frac{\partial c}{\partial z} \right)_{z=L} = 0 \tag{4.10}$$

4.3 Numerical Solution for ODE

The Runge-Kutta 4th order method is the simplest technique used to solve ODE in Eq.(4.6) in order to predict the water concentration in the gas phase leaving from the adsorber with time. The explicit Runge-Kutta 4th formula for integrating the differential equations can be written as the following.

For concentration of adsorbed (water) in fluid phase;

$$c_{i,j+i} = c_{i,j} + \frac{\Delta t}{6} \left[KC1_{i,j} + 2 \times KC2_{i,j} + 2 \times KC3_{i,j} + KC4_{i,j} \right] \tag{4.11}$$

where

$$KC1_{i,j} = \frac{dc}{dt} \left[c_{i-1,j}, c_{i,j}, c_{i+1,j}, \overline{q}_{i,j}, \overset{\bullet}{q}_{i,j} \right]_{i,j} \tag{4.12}$$

$$KC2_{i,j} = \frac{dc}{dt} \begin{bmatrix} c_{i-1,j} + \dfrac{\Delta z}{2} KC1_{i-1,j}, c_{i,j} \dfrac{\Delta z}{2} KC1_{i,j}, c_{i+1,j} \dfrac{\Delta z}{2} KC1_{i+1,j}, \\ \overline{q}_{i,j} \dfrac{\Delta z}{2} Kq1_{i,j}, \overset{\bullet}{q}_{i,j} \end{bmatrix}_{i,j} \tag{4.13}$$

$$KC3_{i,j} = \frac{dc}{dt} \begin{bmatrix} c_{i-1,j} + \dfrac{\Delta z}{2} KC2_{i-1,j}, c_{i,j} \dfrac{\Delta z}{2} KC2_{i,j}, c_{i+1,j} \dfrac{\Delta z}{2} KC2_{i+1,j}, \\ \overline{q}_{i,j} \dfrac{\Delta z}{2} Kq2_{i,j}, \overset{\bullet}{q}_{i,j} \end{bmatrix}_{i,j} \tag{4.14}$$

$$KC4_{i,j} = \frac{dc}{dt}\left[\begin{array}{l} c_{i-1,j} + \Delta z KC3_{i-1,j}, c_{i,j}\Delta z KC3_{i,j}, c_{i+1,j}\Delta z KC3_{i+1,j}, \\ \bar{q}_{i,j}\Delta z Kq3_{i,j}, \overset{\bullet}{q}_{i,j} \end{array}\right]_{i,j} \qquad (4.15)$$

For concentration of adsorbed in solid phase;

$$\bar{q}_{i,j} = \bar{q}_{i,j-1} + \frac{\Delta t}{6}\left[Kq1_{i,j-1} + 2\times Kq2_{i,j-1} + 2\times Kq3_{i,j-1} + Kq4_{i,j-1}\right] \qquad (4.16)$$

where

$$Kq1_{i,j} = \frac{dq}{dt}\left[\bar{q}_{i,j}, \overset{\bullet}{q}_{i,j}\right]_{i,j} \qquad (4.17)$$

$$Kq2_{i,j} = \frac{dq}{dt}\left[\bar{q}_{i,j}\frac{\Delta z}{2}Kq1_{i,j}, \overset{\bullet}{q}_{i,j}\right]_{i,j} \qquad (4.18)$$

$$Kq3_{i,j} = \frac{dq}{dt}\left[\bar{q}_{i,j}\frac{\Delta z}{2}Kq3_{i,j}, \overset{\bullet}{q}_{i,j}\right]_{i,j} ; \text{ and} \qquad (4.19)$$

$$Kq4_{i,j} = \frac{dq}{dt}\left[\bar{q}_{i,j}\Delta z Kq4_{i,j}, \overset{\bullet}{q}_{i,j}\right]_{i,j} \qquad (4.20)$$

4.4 Other Correlations Relating to the Model

The axial dispersion coefficient (D_L) which was the lumped parameter accounted for the effects of all mechanisms with contribute to axial mixing was calculated by using the expression given by Edwards and Richardson correlation.

$$\frac{D_L}{2vR_P} = \gamma_1\frac{D_m}{2vR_P} + \frac{1}{Pe_\infty\left(1 + \beta\gamma_1\frac{D_m}{2vR_P}\right)} \qquad (4.21)$$

where $\gamma_1 = 0.73$, $\beta = 13.0$ and $Pe_\infty = 2.0$ are constant parameters.

The overall mass transfer coefficient (k) was estimated by using the correlation, which was defined by Seader and Henley in 1998 as the following:

$$\frac{1}{kK} = \frac{D_P}{6k_f} + \frac{D_P^2}{60D_e}, \qquad (4.22)$$

where k_f is the mass transfer resistant of the adsorbate from the bulk fluid to the surface of the particle, which is called mass transfer film coefficient. It was determined by Wakao-Funazkri correlation.

$$\frac{k_f D_P}{D_m} = 2 + 1.1 \left(\frac{D_P G}{\mu}\right)^{0.6} \left(\frac{\mu}{\rho D_m}\right)^{1/3} \tag{4.23}$$

The constant, D_e in Eq.(4.22) is effective diffusivity, which can be obtained from the following equation:

$$\frac{1}{D_e} = \frac{\tau}{\varepsilon_P} \left(\frac{1}{D_m} + \frac{1}{D_k}\right) \tag{4.24}$$

Here, τ is tortuosity factor. For straight, randomly oriented, and cylindrical pores, it may be approximated as $\tau = 3$ and 4 for 4A zeolite and Silica gel, respectively (Yang, 1987). The intrapellet void fraction or porosity of adsorbent pellet, ε_p was estimated from a typical range of numbers shown in Encyclopedia of Chemical Technology. The value of ε_p for silica gel was 0.55 while for 4A zeolite was 0.48.

The molecular diffusion coeffient or bulk diffusion coefficient, D_m was determined from Chapman-Enskog equation.

$$D_m = 1.86 \times 10^{-3} T^{3/2} \frac{\left[(M_{w,A} + M_{w,B})/M_{w,A} M_{w,B}\right]^{1/2}}{p \sigma_{AB}^2 \Omega_D} \tag{4.25}$$

Molecular diffusivity, also known as Maxwellian diffusion, is caused by collisions of molecules with other molecules.

The last diffusion coefficient related to mass transfer within a pore, is Knudsen diffusion coefficient which occurs when the molecule in the fluid collide with the pore wall.

$$D_K = 9.7 \times 10^3 r_P \left(\frac{T}{M}\right)^{1/2} \tag{4.26}$$

Finally, the lumped parameter, the overall mass transfer coefficient (k), which accounts for all mass transfer resistant, can be obtained by using backward substitutions.

FORTRAN language was programmed to solve the set of ODE equations. The programming detail, which show the consequence of running loops, were reported in Appendix G.