CHAPTER IV
MATHEMATICAL MODEL AND SOLVING METHOD

In order to obtain the theoretical breakthrough curves for adsorption of moisture from natural gas in a multi-layer adsorber, the mass balance equation was set and solved by using the numerical methods. The mathematical model was based on an axial dispersion plug flow and Linear Driving Force (LDF) model. The method of lines (MOLs) with central finite difference approximation and fourth-order Runge-Kutta method were employed to solve the partial differential equations. After that, FORTRAN language was utilized in numerically solving.

4.1 Mass Balance in Packed Bed

The differential mass balance of the adsorption column was given by:

$$-D_{L,i}\frac{\partial^2 c}{\partial z^2}+\frac{\partial}{\partial z}(cv_i)+\frac{\partial c}{\partial t}+\left(\frac{1-\varepsilon_i}{\varepsilon_i}\right)\frac{\partial \overline{q_i}}{\partial t}=0 \qquad (4.1)$$

where i represents the index for the parameters of each adsorbent, which depends on step size number of axial direction.

In order to determine the variation of water concentration in gas phase with time, Equation (4.1) could be rearranged as:

$$\frac{\partial c}{\partial t}=D_{L,i}\frac{\partial^2 c}{\partial z^2}-c\frac{\partial v_i}{\partial z}-v_i\frac{\partial c}{\partial z}+\left(\frac{1-\varepsilon_i}{\varepsilon_i}\right)\frac{\partial \overline{q_i}}{\partial t} \qquad (4.2)$$

The parameters and the equilibrium adsorption isotherm constructed for each adsorbent were utilized in Equation (4.2). In contrast to the previous work (Chaikasetpaiboon *et al.*, 2002), the parameters and the equilibrium adsorption isotherm used in the model were treated as the effective values for the entire bed.

The parameters used in this model comparing with the previous work are shown in Table 4.1.

Table 4.1 Parameters applied in mathematical model

Parameter	This work			Previous work (Chaikasetpaiboon *et al.*, 2002)
	Silica gel	4A MolSiv 1/8"	4A MolSiv 1/16"	Effective value
Bed void fraction, ε	0.37‡	0.35‡	0.34‡	0.52058
Axial dispersion coefficient, D_L	0.02824†	0.02773†	0.02717†	0.13002
Bulk density of adsorbent	0.74323*	0.65673*	0.65673*	0.74523
Packing range (cm)	0-0.4	0.4-5.9	5.9-8.8	-
Step size number, i	1-5	6-60	61-88	-

‡Appendix A

†Appendix B

* UOP's adsorbent information

In this model, the mass transfer rate could be described by linear driving force model. This model is based on the assumption that the uptake rate of moisture 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. The model expression could be written as:

$$\frac{d\bar{q}}{dt} i,j = k\left(q^{*}_{i,j} - \overline{q_{i,j}}\right) \qquad (4.3)$$

where

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

j = step size number of time, t.

k is the overall mass transfer coefficient and q^* represents the equilibrium adsorbed phase concentration. The term $\partial\bar{q}/\partial t$ represents the overall rate of mass transfer for adsorbed component average over a particle. A general equilibrium relation can be expressed as:

$$q^* = f(c) \tag{4.4}$$

The dynamic response of the column is given by the solution $[c(z,t), \bar{q}(z,t)]$ to Equations (4.2) and (4.3) subject to the initial and boundary conditions imposed on the column. The response to a perturbation in the feed composition involves a mass transfer zone or concentration front which propagates through the column with a characteristic velocity determined by the equilibrium isotherm. The location of the front at any time may be found simply from an overall mass balance, but in order to determine the form of the concentration front, Equations (4.2) and (4.3) must be solved simultaneously.

In addition, the following assumptions were applied to the mathematical model to obtain the theoretical breakthrough curves:

- negligence of competitive adsorption by other components,
- negligence of concentration profile in r and θ directions,
- axial dispersion plug flow,
- no pressure drop along the bed,
- not constant fluid velocity, and
- isothermal system.

For the assumption of inconstant fluid velocity, the overall mass balance for the bulk gas must be involved:

$$-D_{L,i}\frac{\partial^2 C}{\partial z^2} + v\frac{\partial C}{\partial z} + C\frac{\partial v}{\partial z} + \frac{\partial C}{\partial t} + \left(\frac{1-\varepsilon_i}{\varepsilon_i}\right)\frac{\partial \bar{q}_i}{\partial t} = 0 \tag{4.5}$$

where the total concentration, C = ZP/RT, with Z being the compressibility factor of the gas mixture.

If the pressure drop is assumed to change along the bed, Ergun's law is applied in the mathematical model to locally estimate the bed pressure drop:

$$-\frac{\partial P}{\partial z} = 150.0\frac{(1-\varepsilon_i)^2}{\varepsilon_i^3}\frac{\mu}{d_p^2}v + 1.75\frac{(1-\varepsilon_i)}{\varepsilon_i^3}\frac{\rho}{d_p}v^2 \qquad (4.6)$$

where μ is the gas mixture viscosity, ρ is the gas density, and d_p is the paricle diameter.

For the assumption of no pressure drop along the bed, the total concentration in fluid phase (C) remains constant. Thus, Equation (4.5) can be rewritten as:

$$\varepsilon C\frac{\partial v}{\partial z} + (1-\varepsilon)\frac{\partial q^*}{\partial t} = 0 \qquad (4.7)$$

or

$$\frac{\partial v}{\partial z} = -\left(\frac{1-\varepsilon}{\varepsilon C}\right)\frac{\partial q^*}{\partial t} \qquad (4.8)$$

where, total concentration, C = ZP/RT.

4.2 Numerical Method

The method of lines (MOL) was applied to convert a second order derivative and a first order derivative PDE presented in Equation (4.2) into a set of ordinary differential equations by using the central finite difference method. Then, the 4th order Runge-Kutta method was applied to solve ODE in order to predict the water concentration in the gas phase leaving from the adsorber with time. FORTRAN language was programmed to solve the set of ODE equations.

4.2.1 Method of Lines

For 1st order derivative, $\frac{\partial c}{\partial z}$ in terms of central finite differences with error of order h^2 can be expressed in terms of their respective definitions:

$$\frac{dc_{i,j}}{dz} = \frac{1}{2\Delta z}\left(c_{i+1,j} - c_{i-1,j}\right) + O\left(\Delta z^2\right) \tag{4.9}$$

For 2nd order derivative term, $\frac{\partial^2 c}{\partial z^2}$ in terms of central finite differences with the error of order h^2 can be expressed in terms of their respective definitions:

$$\frac{d^2 c_{i,j}}{dz^2} = \frac{1}{\Delta z^2}\left(c_{i+1,j} - 2c_{i,j} + c_{i-1,j}\right) + O(\Delta z^2) \tag{4.10}$$

where

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

j = step size number of time, t.

4.2.2 Fourth-order Runge-Kutta Method

The most widely used methods of integration for ordinary differential equations are the series of methods called Runge-Kutta second, third, and fourth order, plus a number of other techniques that are variations on the Runge-Kutta theme. This method is the technique used to solve ODE in order to predict the breakthrough time. The explicit 4th order Runge-Kutta formula for integrating the differential equations can be written as the following:

$$c_{i,j+1} = c_{i,j} + \frac{\Delta t}{6}\left[K1_{i,j} + 2\times K2_{i,j} + 2\times K3_{i,j} + K4_{i,j}\right] \tag{4.11}$$

where each of the trajectories K_i are evaluated by:

$$K1_{i,j} = \frac{dc}{dt}\left[c_{i-1,j}, c_{i,j}, c_{i+1,j}\right]_{i,j} \tag{4.12}$$

$$K2_{i,j} = \frac{dc}{dt}\left[c_{i-1,j} + \frac{\Delta z}{2}K1_{i-1,j}, c_{i,j} + \frac{\Delta z}{2}K1_{i,j}, c_{i+1,j} + \frac{\Delta z}{2}K1_{i+1,j}\right]_{i,j} \tag{4.13}$$

$$K3_{i,j} = \frac{dc}{dt}\left[c_{i-1,j} + \frac{\Delta z}{2}K2_{i-1,j}, c_{i,j} + \frac{\Delta z}{2}K2_{i,j}, c_{i+1,j} + \frac{\Delta z}{2}K2_{i+1,j}\right]_{i,j} \tag{4.14}$$

$$K4_{i,j} = \frac{dc}{dt}\left[c_{i-1,j} + \Delta zK3_{i-1,j}, c_{i,j} + \Delta zK3_{i,j}, c_{i+1,j} + \Delta zK3_{i+1,j}\right]_{i,j} \tag{4.15}$$

Finally, FORTRAN language was programmed to solve the set of ODE equations. The programming details were reported in Appendix D.