CHAPTER IV

MATHEMATICAL MODEL

In dynamic simulation of distillation column, the conventional empirical methods are replace by the rigorous calculation using mathematical models. In the present work two models, one for debutanizer column and one for thermodynamic models have been developed for process simulation.

4.1 Dynamic model development for multicomponent distillation column

Dynamic model of multicomponent distillation is similar to the steady state model but the dynamic model would consider accumulative term in each equation. The mathematical model for a multicomponent, nonideal column with NC component, nonequimolal overflow and inefficient trays will be developed with the following assumption:

1. Liquid on the tray is perfectly mixed and incompressible
2. Tray vapor holdups are negligible
3. Dynamic of the condenser and the reboiler will be neglected
4. Vapor and liquid are in thermal equilibrium (same temperature) but not in phase equilibrium. A Murphree vapor-phase efficiency will be used to describe the departure from equilibrium.

$$Enj = \frac{Ynj - Y^T n-1,j}{Y^* nj - Y^T n-1,j} \qquad 4\text{-}1)$$

Where Y^*nj = composition of vapor in phase equilibrium with liquid on n^{th} tray with composition Xnj

Ynj = actual composition of vapor leaving n^{th} tray

$Y^T n-1,j$ = actual composition of vapor entering n^{th} tray

Enj = Murphree vapor efficiency for j^{th} component on n^{th} tray

Multiple feeds, both liquid and vapor, and side stream draw off, both liquid and vapor are permitted. A general n^{th} tray is sketched in Fig 4-1. Nomenclature is summarized in Table 4-1. the equations describing this tray are:

Total continuity :

$$\frac{dMn}{dt} = L_{n+1} + F_n^L + F_{n-1}^V + V_{n-1} - V_n - L_n - S_n^L - S_n^V \qquad 4\text{-}2)$$

Component Continuity equation :

$$\frac{d(MnXnj)}{dt} = L_{n+1}X_{n+1,j} + F_n^L X_{nj}^F + F_{n-1}^V Y_{n-1,J}^F + V_{n-1}Y_{n-1,j} - V_nY_{nj} - L_nX_{nj} - S_n^L X_{nj} - S_n^V Y_{nj} \qquad 4\text{-}3)$$

Energy equation :

$$\frac{d(MnUn)}{dt} = L_{n+1}h_{n+1} + F_n^L h_n^F + F_{n-1}^V H_{n-1}^F + V_{n-1}H_{n-1} - V_nH_n - L_nH_n - S_n^L h_n - S_n^V H_n \qquad 4\text{-}4)$$

Where h = Liquid Enthalpies, BTU/mole

H = Vapor Enthalpies, BTU/mole

U = Internal energy, BTU/mole

The Francis weir formula :

$$F_L = 3.33\ \mathrm{lh}^{3/2} \qquad 4\text{-}5)$$

Where F_L = liquid rate, $ft^3/\sec$

l	=	length of weir, ft.
h	=	height of liquid over weir, ft.

Phase equilibrium :

$$Y^*nj = f(Xnj, Pn, Tn) \qquad 4\text{-}6)$$

Thermal properties :

$$hn = f(Xnj, Tn) \qquad 4\text{-}7)$$

$$Hn = f(Ynj, Tn, Pn) \qquad 4\text{-}8)$$

$$h_n^F = f(X_{nj}^F, T_n^F) \qquad 4\text{-}9)$$

$$H_n^F = f(Y_{nj}^F, T_n^F, P_n) \qquad 4\text{-}10)$$

4.2 Thermodynamics functions from cubic equation of state

4.2.1 Fugacity Coefficient

Fugacity coefficient was proposed as a more convenient function for use in making equilibrium calculations. Expressions for computing the fugacity coefficients from P-V-T data are obtained by starting with the equations relating free energy and fugacity with volume and pressure and integrating to pure real datum points, Fugacity coefficients can be evaluated from an equation of state that has been fitted to PVT data. For this purpose the equation of state must fit the PVT data of the pure components and the mixture as well. These data fits are accomplished by developing a set of constants for each component and then combining these constants to get constants for any mixture

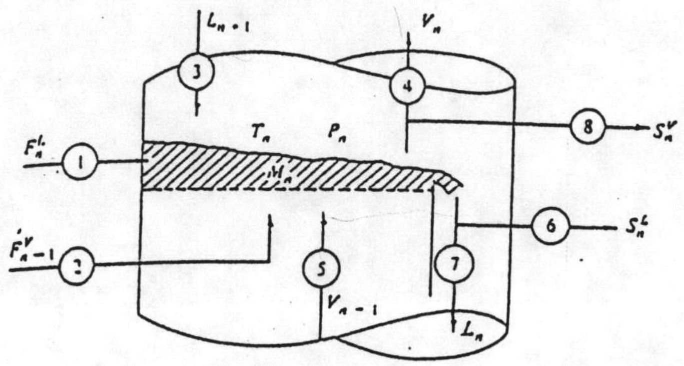

Figure 4-1 A general Nth tray

Number	Flow Rate	Composition	Temperature
1	Fn^{v}	$X^{F}nj$	Tn^{F}
2	$F^{v}n-1$	$Y^{F}n-1, j$	$T^{F}n-1$
3	Ln+1	Xn+1, j	Tn+1
4	Vn	Ynj	Tn
5	Vn-1	Yn-1, j	Tn-1
6	Sn^{L}	Xnj	Tn
7	Ln	Xnj	Tn
8	$S^{v}n$	Ynj	Tn

Table 4-1 Nomenclature of Nth tray

Source : William L. Luyben, Process Modeling, Siulation and Control for Chemical Engineers, pp 71, Mc Graw-Hill publishing company, Second Edition, 1990 of the components. The followings express the fugacity coefficient from GRK, SRK and PR equation of state.

$$\ln\phi_i \quad = \quad \frac{1}{RT}\int_{\alpha}^{V}\left[\frac{RT}{V}-\left(\frac{\partial P}{\partial ni}\right)_{T,V,nj}\right]dv-\ln Z \qquad 4\text{-}11)$$

<u>GRK equation of state</u> :

$$\ln\phi_i \quad = \quad (Z-1)\frac{Bi}{B}-\ln(Z-BP)-\frac{A^2}{B}\left(2\frac{Ai}{A}-\frac{Bi}{B}\right)\ln\left(1+\frac{BP}{Z}\right) \qquad 4\text{-}12)$$

$$ai \quad = \quad 0.0278\ R^2Tc^{2.5}/Pc$$

$$bi \quad = \quad 0.0867\ RTc/Pc$$

$$Ai \quad = \quad ai^{0.5}/RT^{1.25} \qquad 4\text{-}13)$$

$$Bi \quad = \quad b/RT \qquad 4\text{-}14)$$

$$A \quad = \quad \sum yiAi \qquad 4\text{-}15)$$

$$B \quad = \quad \sum yiBi \qquad 4\text{-}16)$$

<u>SRK equation of state</u> :

$$\ln\phi i \quad = \quad \frac{bi}{b}\left(\frac{PV}{RT}-1\right)-\ln\left(\frac{PV}{RT}-B\right)-\frac{A}{B}\left(2\frac{ai^{0.5}}{a^{0.5}}-\frac{bi}{b}\right)\ln\left(1+B\frac{RT}{PV}\right) \qquad 4\text{-}17)$$

$$bi \quad = \quad 0.08664\ \frac{RTci}{Pci}$$

$$b = \sum_{i=1}^{N} Xibi$$

$$b = 0.08664\ R\sum_{I=1}^{N} X_I T_{CI} / P_{CI} \qquad 4\text{-}18)$$

$$ai = 0.42748\ \frac{R^2 T_{ci}^2}{P_{ci}} \alpha$$

$$a = \sum_{i} \sum_{j} X_i X_j (a_i a_j)^{0.5} (1 - Kij)$$

$$a = 0.42748\ R^2 \sum_{i} \sum_{j} X_i X_j \frac{T_{ci} T_{cj}}{(P_{ci} P_{cj})^{0.5}} (1 - Kij) \alpha \qquad 4\text{-}19)$$

$$\alpha^{1/2} = 1 + (0.480 + 1.57\omega - 0.176\ \omega^2)(1 - Tr^{1/2}) \qquad 4\text{-}20)$$

$$A = \frac{aP}{R^2 T^2} \qquad 4\text{-}21)$$

$$B = \frac{bP}{RT} \qquad 4\text{-}22)$$

<u>PR equation of state</u> :

$$\ln \phi i = \frac{bi}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2B}} \left(\frac{2\sum_{k=1}^{N} x_x a_{ki}}{a} - \frac{b_i}{b} \right) \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \qquad 4\text{-}23)$$

$$bi = 0.07780\ \frac{RT_{ci}}{P_{ci}}$$

$$b = \sum_{i=1}^{N} x_i b_i$$

b = $0.07780\,R\sum \frac{X_i T_{ci}}{P_{ci}}$ 4-24)

ai = $0.45724\ \frac{R^2 T_{ci}^{\ 2}}{P_{ci}}\left[1+m(1-Tr^{1/2})\right]^2$

a = $0.45724\ ^2 \sum_i \sum_j x_i x_j \frac{T_{ci} T_{cj}}{P_{ci}^{\ 0.5} P_{cj}^{\ 0.5}}\left[1+m_i(1-T_{ri}^{\ 1/2})\right]$
$\left[1+m_j(1-T_{rj}^{\ 1/2})\right](1-k_{ij})$ 4-25)

m = $0.37464 + 1.54226\,\omega - 0.26992\omega^2$ 4-26)

A = $\frac{aP}{R^2T^2}$ 4-27)

B = $\frac{bP}{RT}$ 4-28)

Z = $\frac{PV}{RT}$ 4-29)

4.2.2 Enthalpy Departure

$$\frac{H-H^*}{RT} = Z-1+\frac{1}{RT}\int_{\alpha}^{v}\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]dv \qquad 4\text{-}30)$$

H* is an enthalpy of ideal gas,

$$H^* = \sum_i^N x_i H_i^*$$

$$H_i^* = \int_{T_0}^{T} C^{\circ}_{PV}\, dT = \int_{T_0}^{T} (\ a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4\ )dT$$

$$H_i^* = a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + \frac{a_5}{5}T^5 \qquad 4\text{-}31)$$

a_1 through a_5 are constant.

<u>GRK equation of state</u>:

$$\frac{H-H^*}{RT} = Z-1-1.5\frac{A^2}{B}*\ln\left(1+\frac{BP}{Z}\right) \qquad 4\text{-}32)$$

$$ai = 0.0278\ R^2Tc^{2.5}/Pc$$

$$bi = 0.0867\ RTc/Pc$$

$$Ai = ai^{0.5}/RT^{1.25}$$

$$Bi = b/RT$$

$$A = \sum yiAi$$

$$B = \sum yiBi$$

$$Z = \frac{PV}{RT}$$

<u>SRK equation of state</u> :

$$\frac{H-H^*}{RT} = Z-1-\frac{A}{B}\left[1-\frac{T}{a}\left(\frac{da}{dT}\right)\right]\ln\left(1+\frac{B}{Z}\right) \qquad 4\text{-}33)$$

$$T\left(\frac{da}{dT}\right) = \sum_i\sum_j x_i x_j m_j (a_i a_{cj} T_{rj})^{0.5}(1-K_{ij}) \qquad 4\text{-}34)$$

$$bi = 0.08664\ \frac{RTci}{Pci}$$

$$b = \sum_{i=1}^{N} XiBi$$

$$b = 0.08664\ R\sum_{I=1}^{N} X_I T_{CI} / P_{CI}$$

$$ai = 0.42748\ \frac{R^2 T_{ci}^2}{P_{ci}}\alpha$$

$$a = \sum_i \sum_j X_i X_j (a_i a_j)^{0.5}(1-Kij)$$

$$a = 0.42748\ R^2 \sum_i \sum_j X_i X_j \frac{T_{ci}T_{cj}}{(P_{ci}P_{cj})^{0.5}}(1-Kij)\alpha$$

$$\alpha^{1/2} = 1+(0.480+1.57\omega-0.176\omega^2)(1-Tr^{1/2})$$

$$A = \frac{aP}{R^2T^2}$$

$$B = \frac{bP}{RT}$$

<u>PR equation of state</u> :

$$\frac{H-H^*}{RT} = Z-1-\frac{A}{2.8284B}\left[1-\frac{T}{a}\frac{da}{dT}\right]*\ln\left[\frac{Z+2.4142*B}{Z-0.4142*B}\right] \quad 4\text{-}35)$$

$$T\left(\frac{da}{dT}\right) = \sum_i^N \sum_j^N x_i x_j m_j (a_{ci} a_{cj} T_{rj}^{\ 0.5}) * (1-K_{ij}) \quad 4\text{-}36)$$

$$bi = 0.07780\ \frac{RT_{ci}}{P_{ci}}$$

$$b = \sum_{i=1}^{N} x_i b_i$$

$$b = 0.07780\, R \sum \frac{X_i T_{ci}}{P_{ci}}$$

$$ai = 0.45724\, \frac{R^2 T_{ci}^{\,2}}{P_{ci}} \left[1 + m(1 - Tr^{1/2})\right]^2$$

$$a = 0.45724^{\,2} \sum_i \sum_j x_i x_j \frac{T_{ci} T_{cj}}{P_{ci}^{\,0.5} P_{cj}^{\,0.5}} \left[1 + m_i (1 - T_{ri}^{\,1/2})\right] \left[1 + m_j (1 - T_{rj}^{\,1/2})\right] (1 - k_{ij})$$

$$m = 0.37464 + 1.54226\, \omega - 0.26992\, \omega^2$$

$$A = \frac{aP}{R^2 T^2}$$

$$B = \frac{bP}{RT}$$

$$Z = \frac{PV}{RT}$$