

CHAPTER III

FUNDAMENTAL OF DISTILLATION

3.1 Theoretical Model for Multicomponent Multistage Distillation Column.

The theoretical model for this thesis has the assumptions as follows :

- This column is continuous distillation.
- It is operated at steady-state conditions.
- The liquid and vapor flows are countercurrent.
- No chemical reaction occurs.
- Phase equilibrium is achieved at each stage.
- The stages are numbered down from condenser to reboiler.
- Each stage has feed, vapor-liquid interstage streams, vapor-liquid sidestreams and heat transfer that are shown in figure 3.1.

Considering stage j in figure 3.1. The single or two phase feed enter stage j with flow rate F_j which contains overall composition in mole fractions $z_{i,j}$ of component i , temperature T_{Fj} , pressure P_{Fj} and overall enthalpy H_{Fj} .

The interstage liquid stream from stage above enters stage j with flow rate L_{j-1} contains the liquid composition in mole fractions $x_{i,j-1}$ of component i , temperature T_{Lj-1} , enthalpy H_{Lj-1} and pressure P_{Lj-1} which is equal to or less than the pressure of stage j .

Similarly, the interstage vapor liquid stream from stage $j+1$ below flows into stage j which has flow rate V_{j+1} , the vapor composition in mole fraction $y_{i,j+1}$,

temperature T_{j+1} , enthalpy $H_{V,j+1}$ and pressure P_{j+1} that is equal to or higher than P_j .

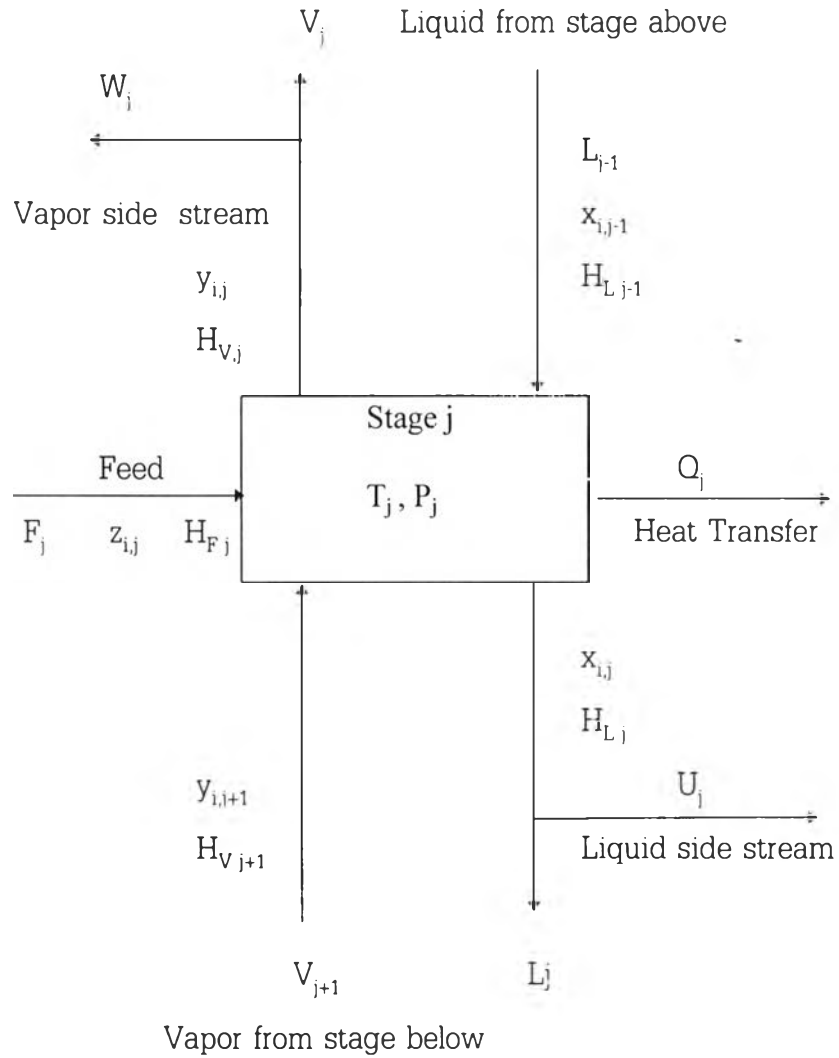


Figure 3.1 Equilibrium Stage

The vapor and liquid leaving stage j have the intensive properties P_j and T_j . The vapor can be divided into vapor sidestream of flow rate W_j and the interstage vapor of flow rate V_j , with the composition of component i $y_{i,j}$ and enthalpy $H_{V,j}$. The liquid stream is similar to vapor stream that has liquid

sidestream U_j , interstage liquid flow rate L_j , liquid composition $x_{i,j}$ and enthalpy $H_{L,j}$.

In this system, the C components mixture is separated by N stages distillation column. The distillation calculation can be described by the set of equations that are defined from four relations. (Henry, E. J., 1981)

1. Material balance equation for component i on stage j .

$$L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} + F_1 z_{i,j} - (L_j + U_j) x_{i,j} - (V_j + W_j) y_{i,j} = 0 \quad (3-1)$$

2. Phase equilibrium relation component i on stage j .

$$y_{i,j} - K_{i,j} x_{i,j} = 0 \quad (3-2)$$

where $K_{i,j}$ is the phase equilibrium constant of component i at stage j .

3. Mole fraction summation on stage j .

$$\sum_{i=1}^c y_{i,j} - 1.0 = 0 \quad (3-3)$$

or

$$\sum_{i=1}^c x_{i,j} - 1.0 = 0 \quad (3-4)$$

4. Energy balance on stage j .

$$L_{j-1} H_{L,j-1} + V_{j+1} H_{V,j+1} + F_1 H_{F_1} - (L_j + U_j) H_{L,j} - (V_j + W_j) H_{V,j} - Q_j = 0 \quad (3-5)$$

where kinetic and potential energy changes are assumed to be insignificant.

H_L , H_V , and H_F are mixture enthalpy of the corresponding stream.

A total material balance equation can be used in place of equation (3-3) or (3-4). It is derived by combining these two equations and $\sum_i z_i = 1.0$ with (3-1) summed over the C components and over stages 1 through j to yield

$$L_j = V_{j+1} + \sum_{m=1}^j (F_m - W_m - U_m) - V_1 \quad j = 1, 2, 3, \dots, N \quad (3-6)$$

In general, it is known that $K_{i,j} = K_{i,j} \{T_j, P_j, x_{i,j}, y_{i,j}\}$, $H_{Vj} = H_{Vj} \{T_j, P_j, y_{i,j}\}$, and $H_{Lj} = H_{Lj} \{T_j, P_j, x_{i,j}\}$. If these relations are not counted as equations and three properties are not counted as variables, this column has $2C+3$ equations for each equilibrium stage. If N and all F_j , $z_{i,j}$, T_{Fj} , P_{Fj} , P_j , U_j , W_j and Q_j are specified, the model is represented by $N(2C+3)$ simultaneous algebraic equations in $N(2C+3)$ unknown. (Shuzo Ohe, 2536) This model has a large of nonlinear equations that must be solved by iterative techniques.

3.2 Tridiagonal Matrix Algorithm.

There are many iterative solution procedures for solving nonlinear algebraic equations. For separators where the feeds contains only components of similar volatility (narrow-boiling case), the bubble-point (BP) method is recommended. The key to the success of BP method is the tridiagonal matrix that is resulted from a modified material balance equations (3-1) when T_j and V_j are selected as the tear variables. The material balance equations are modified in the unknown liquid mole fractions. This set of equations for each component is

solved by highly efficient and reliable algorithm due to Thomas as applied by Wang and Henke.

The $y_{i,j}$ in equation (3-1) are substituted by equation (3-2). The material balance equations are obtained by substituting equation (3-6) into equation (3-1) to eliminate L_j . The result for each component and each stage is shown as equation (3-7).

$$A_j x_{i,j-1} + B_j x_{i,j} + C_j x_{i,j+1} = D_{i,j} \quad (3-7)$$

where

$$A_j = V_j + \sum_{m=1}^{j-1} (F_m - W_m - U_m) - V_1 \quad j = 2, 3, 4, \dots, N \quad (3-8)$$

$$B_j = - [V_{j+1} + \sum_{m=1}^j (F_m - W_m - U_m) - V_1 + U_j + (V_j + W_j) K_{i,j}]$$

$$j = 1, 2, \dots, N$$

$$i = 1, 2, \dots, C \quad (3-9)$$

$$C_j = V_{j+1} K_{i,j+1} \quad j = 1, 2, 3, \dots, N-1 \quad (3-10)$$

$$i = 1, 2, 3, \dots, C$$

$$D_{i,j} = - F_1 z_{i,j} \quad j = 1, 2, 3, \dots, N \quad (3-11)$$

$$i = 1, 2, 3, \dots, C$$

with $x_{i,0} = 0$, $V_{N+1} = 0$, $W_1 = 0$, and $U_N = 0$.

If the modified equations are grouped by component, they can be represented by tridiagonal matrix equations (3-12).

$$\begin{bmatrix}
 B_1 & C_1 & 0 & 0 & \dots & 0 & 0 \\
 A_2 & B_2 & C_2 & 0 & \dots & 0 & 0 \\
 0 & A_3 & B_3 & C_3 & \dots & 0 & 0 \\
 0 & 0 & \dots & \dots & \dots & 0 & 0 \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
 0 & 0 & \dots & \dots & A_{N-1} & B_{N-1} & C_N \\
 0 & 0 & \dots & \dots & 0 & A_N & B_N
 \end{bmatrix}
 \begin{bmatrix}
 x_{i,1} \\
 x_{i,2} \\
 x_{i,3} \\
 \dots \\
 x_{i,N-1} \\
 x_{i,N}
 \end{bmatrix}
 =
 \begin{bmatrix}
 D_1 \\
 D_2 \\
 D_3 \\
 \dots \\
 D_{N-1} \\
 D_N
 \end{bmatrix}
 \quad (3-12)$$

The Thomas algorithm for solving the equation (3-12) is a Gaussian eliminating $x_{i,j}$. Firstly, the forward elimination starts from stage 1 and works toward stage N to find $x_{i,N}$. Then, the other $x_{i,j}$ are obtained starting with $x_{i,N-1}$ by backward substitution.

The equations used in the Thomas algorithm are as follows:

$$p_1 = C_1/B_1 \quad (3-13)$$

$$q_1 = D_1/B_1 \quad (3-14)$$

$$p_j = \frac{C_j}{(B_j - A_j p_{j-1})} \quad j = 2, 3, 4, \dots, N-1 \quad (3-15)$$

$$q_j = \frac{(D_j - A_j q_{j-1})}{(B_j - A_j p_{j-1})} \quad j = 2, 3, 4, \dots, N \quad (3-16)$$

The equation (3-7) is rearranged as

$$x_{i,j} = q_j - p_j x_{i,j+1} \quad (3-17)$$

The forward elimination starts from stage 1 to stage N. For stage N, (3-17) isolate $x_{i,N}$ as

$$x_{1,N} = q_N \quad (3-18)$$

Then, the backward substitution eliminates the other $x_{i,j}$ by equation (3-19).

$$x_{i,j} = q_j - p_j x_{i,j+1} \quad j = N-1, N-2, \dots, 1 \quad (3-19)$$

In general, computed values of $x_{i,j}$ are always positive.

3.3 The Bubble-Point (BP) Method for Distillation.

The effective solution procedure for this work is referred to the bubble-point (BP) method because a new set of stage temperatures is computed during each iteration from bubble-point equation.

Computational procedure:

Step 1. Specify feed and column configuration as follows:

- All of feeds and feed conditions (F_j , z_{ij} , T_{Fj} , P_{Fj} or H_{Fj}).
- Column configurations N , L (reflux rate), V_1 (vapor distillate rate), P_j , U_j , W_j , and Q_j except Q_1 (condenser duty) and Q_N (reboiler duty).

Step 2. Initialize tear variables T_j and V_j .

- To initiate a set of V_j values based on the assumption of constant interstage flows.
- To initiate a set of T_j values by assuming a linear variation of temperatures with stage location.

Step 3. Solve equation (3-12) for each set of $x_{i,j}$ values by the Thomas algorithm.

Step 4. Normalize the set of x_{ij} values for each stage by the relation

$$(x_{i,j})_{\text{normalized}} = \frac{x_{ij}}{\sum_{i=1}^c x_{ij}} \quad (3-20)$$

Step 5. Compute the new set of T_j from bubble point equation (3-21) and set of y_{ij} values from (3-2).

$$\sum_{i=1}^c K_{ij} x_{ij} - 1.0 = 0 \quad (3-21)$$

The equation (3-21) is nonlinear. It must be solved by iterative method.

Step 6. Compute condenser duty from (3-5) and reboiler duty from (3-22).

$$Q_N = \sum_{j=1}^N (F_j H_{Fj} - U_j H_{Lj} - W_j H_{Vj}) - \sum_{j=1}^{N-1} Q_j - V_1 H_{V1} - L_N H_{LN} \quad (3-22)$$

Step 7. Compute the new set of V_j from modified energy balance equation, which is obtained by combining equations (3-5) and (3-6) twice to eliminate L_{j-1} and L_j .

$$\alpha_j V_j + \beta_j V_{j+1} = \gamma_j \quad (3-23)$$

where

$$\alpha_j = H_{Lj-1} - H_{Vj} \quad (3-24)$$

$$\beta_j = H_{Vj+1} - H_{Lj} \quad (3-25)$$

$$\begin{aligned} \gamma_j = & \left[\sum_{m=1}^{j-1} (F_m - W_m - U_m) - V_1 \right] (H_{L_j} - H_{L_{j-1}}) + F_j (H_{L_j} - H_{F_j}) \\ & + W_j (H_{V_j} - H_{L_j}) + Q_j \end{aligned} \quad (3-26)$$

The modified energy balance is written in didiagonal matrix from.

It is applied over stages 2 to N-1 as follow:

$$\begin{bmatrix} \beta_2 & 0 & 0 & 0 & \dots & 0 & 0 \\ \alpha_3 & \beta_3 & 0 & 0 & \dots & 0 & 0 \\ 0 & \alpha_4 & \beta_4 & 0 & \dots & 0 & 0 \\ 0 & 0 & \dots & \dots & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \dots & \alpha_{N-2} & \beta_{N-2} & 0 \\ 0 & 0 & \dots & \dots & 0 & \alpha_{N-1} & \beta_{N-1} \end{bmatrix} \begin{bmatrix} V_3 \\ V_4 \\ V_5 \\ \dots \\ \dots \\ \dots \\ V_{N-1} \\ V_N \end{bmatrix} = \begin{bmatrix} \gamma_2 - \alpha_2 V_2 \\ \gamma_3 \\ \gamma_4 \\ \dots \\ \dots \\ \dots \\ \gamma_{N-2} \\ \gamma_{N-1} \end{bmatrix} \quad (3-27)$$

Using Gaussian elimination procedure to solve equation (3-27) from the top where V_2 is computed by equation (3-6).

$$V_j = \frac{\gamma_{j-1} - \alpha_{j-1} V_{j-1}}{\beta_{j-1}} \quad (3-28)$$

Then, compute the set of L_j from equation (3-6).

Step 8. Check the convergence of this procedure.

$$\sum_{j=1}^N \left[\frac{T_j^{(k)} - T_j^{(k-1)}}{T_j^{(k)}} \right]^2 + \sum_{j=1}^N \left[\frac{V_j^{(k)} - V_j^{(k-1)}}{V_j^{(k)}} \right]^2 \leq \epsilon \quad (3-29)$$

where k is the iteration index.

ϵ is prescribed tolerance.

However, Wong and Henke suggested that the following simpler criterion which is based on successive sets of T_j values only is adequate.

$$\tau = \sum_{j=1}^N [T_j^{(k)} - T_j^{(k-1)}]^2 \leq 0.01N \quad (3-30)$$

and

$$\tau = \sum_{j=1}^N [V_j^{(k)} - V_j^{(k-1)}]^2 \leq 0.01N \quad (3-31)$$

The new set of V_j and T_j values change 10% from last iterations.

Step 9. Use the new set of V_j and T_j as the initial guesses for calculating step 3 to 9 when the result of step 8 is false. Stop the calculation when which result become true.

The algorithm for the Wang-Henke BP method is shown in figure 3.2.

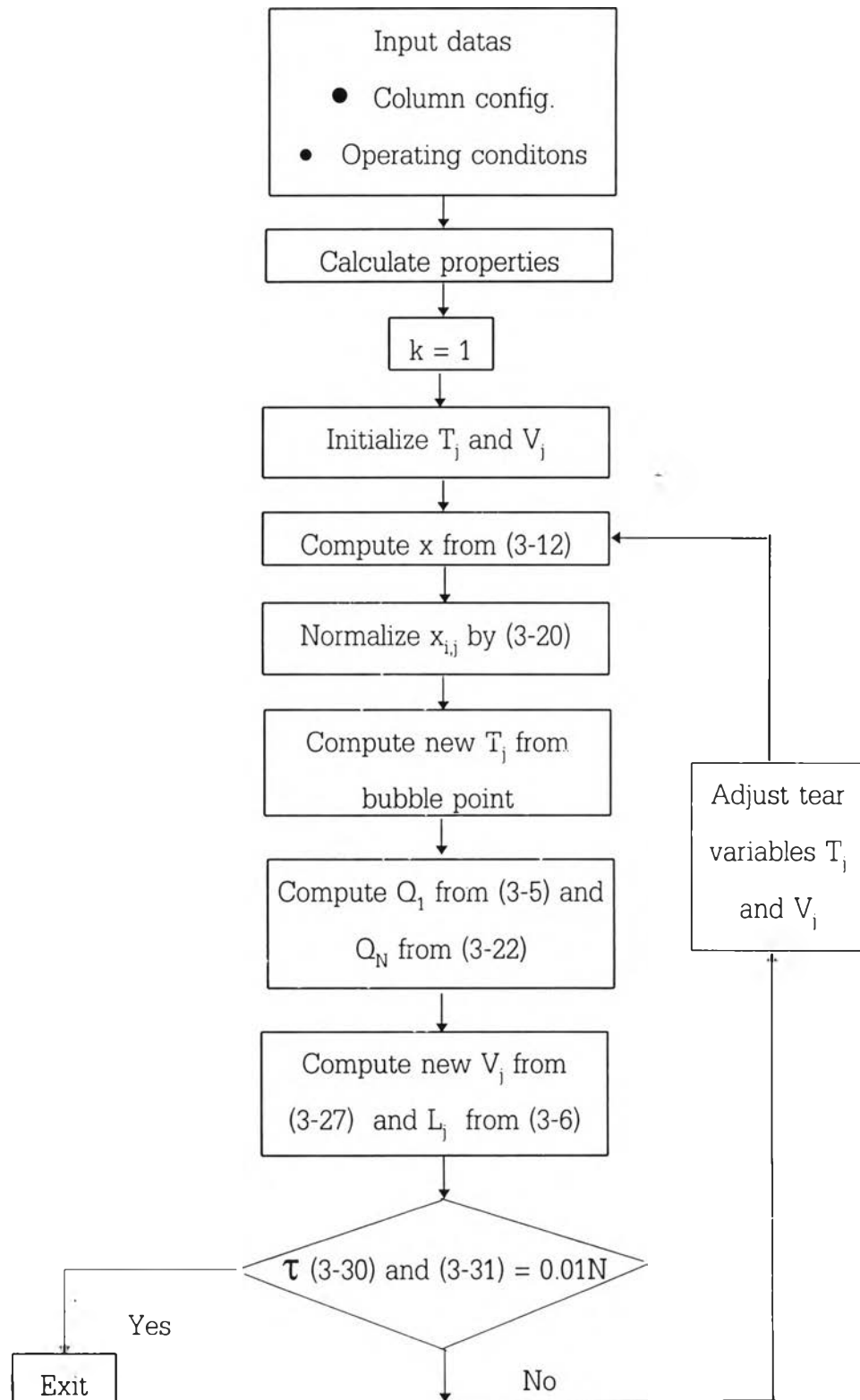


Figure 3.2 Algorithm for Wang-Henke BP method (Henry, E. J., 1981)

3.4 Vapor Liquid Equilibria (VLE)

The liquid mixture at temperature T and pressure P is in equilibria with vapor mixture at the same temperature and pressure. (Van Ness, H. C., 1982) The condition of thermodynamic equilibria for every component i in the mixture is given by

$$\bar{f}_i^V = \bar{f}_i^L \quad (3-31)$$

The Raoult's Law shown in equation (3-32) is applied for VLE of the ideal mixture that the liquid phase is an ideal solution, vapor phase is an ideal gas, and the liquid phase fugacities are independent of pressure.

$$y_i P = x_i P_i^* \quad (3-32)$$

Vapor liquid equilibria are often expressed in term of phase equilibria ratio.

$$K_{i,j} = \frac{y_{i,j}}{x_{i,j}} \quad (3-33)$$

K values for ideal mixture are defined as

$$K_{i,j} = \frac{P_{i,j}^*}{P} \quad (3-34)$$

For vapor liquid equilibria at high pressure are conveniently calculated by using an equation of state applicable to both phases. Equation (3-33) can be rewritten in terms of coefficients which defined by

$$\phi_i^v = \frac{f_i^v}{y_i P} \quad (3-35)$$

and

$$\phi_i^l = \frac{f_i^l}{x_i P} \quad (3-36)$$

Phase equilibrium ratio is derived by combining equation (3-35) and (3-36) into equation (3-31) to give

$$K_i = \frac{\phi_i^l}{\phi_i^v} \quad (3-37)$$

Assuming that the equation of state, can be expressed as

$$P = f(T, V, z_1, z_2, \dots) \quad (3-38)$$

And assuming further that this equation of state holds for all fluid densities (i. e., gases and liquids) and for all compositions z_1, z_2, \dots , we can calculate ϕ_i^l and ϕ_i^v from

$$RT \ln \phi_i^l = \int_{V^L}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - RT \ln Z^L \quad (3-39)$$

$$RT \ln \phi_i^v = \int_{V^V}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - RT \ln Z^V \quad (3-40)$$

where compressibility factor Z is given by

$$Z^L = \frac{PV^L}{RT} \quad (3-41)$$

$$Z^v = \frac{PV^v}{RT} \quad (3-42)$$

In the liquid phase, the total volume V_T^L is related to the molar volume V^L by

$$V^L = \frac{V_T^L}{n_T^L} \quad (3-43)$$

where n_T^L is the total number of moles in the liquid phase.

Similarly,

$$V^v = \frac{V_T^v}{n_T^v} \quad (3-44)$$

In principle, Equations (3-37) to (3-38) are sufficient for finding all K factors in a multicomponent system containing two fluid phases. However, if a realistic equation of state is used, the required computations are strongly nonlinear and often require extensive iterations.

3.5 Bubble Point Calculation

The bubble point calculation used for computing a new set of temperatures is very important step of BP method. It is particularly effective for mixtures having a narrow range of K values because temperature is not then sensitive to composition.

The bubble point criterion is

$$1 = \sum_{i=1}^c z_i K_i \quad (3-45)$$

with $x_i = z_i$ and $y_i = K_i x_i$

Equation (3-45) is used for calculating bubble point temperature at a given pressure. It is highly nonlinear in temperature. Therefore, iterative procedures are required to solve bubble point temperatures. Calculation procedure for ideal case is shown in figure 3.3. (Henry, E. J., 1981)

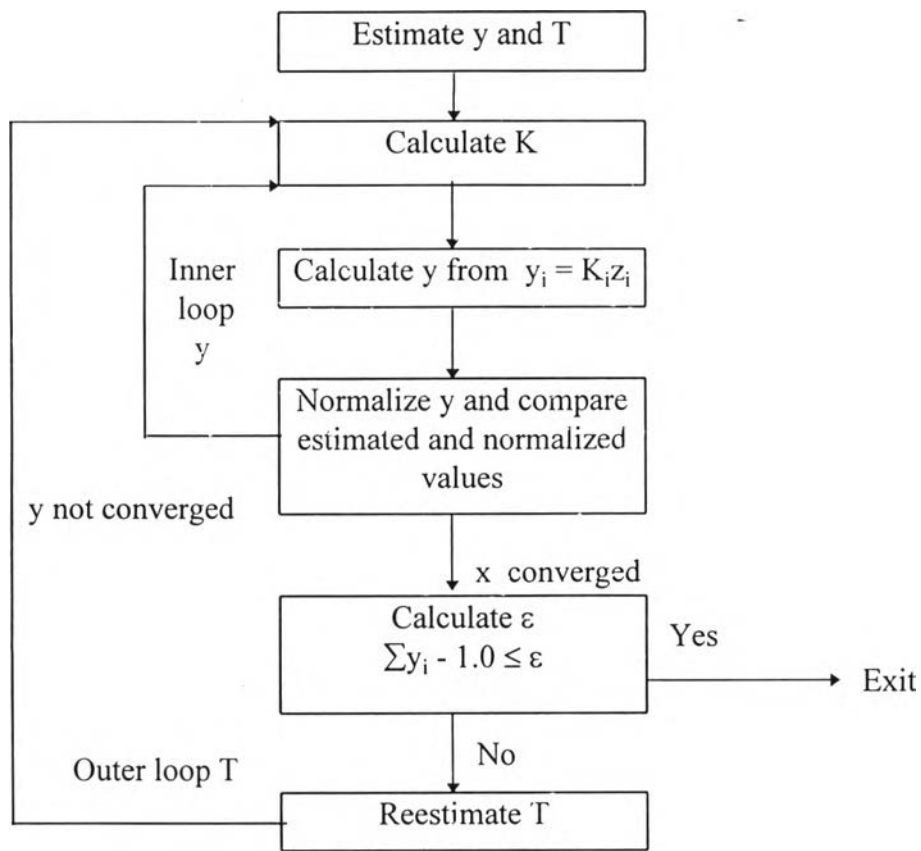


Figure 3.3 An algorithm for solving the bubble point temperature.

The bubble point calculation using equations of state is shown in figure 3.4.

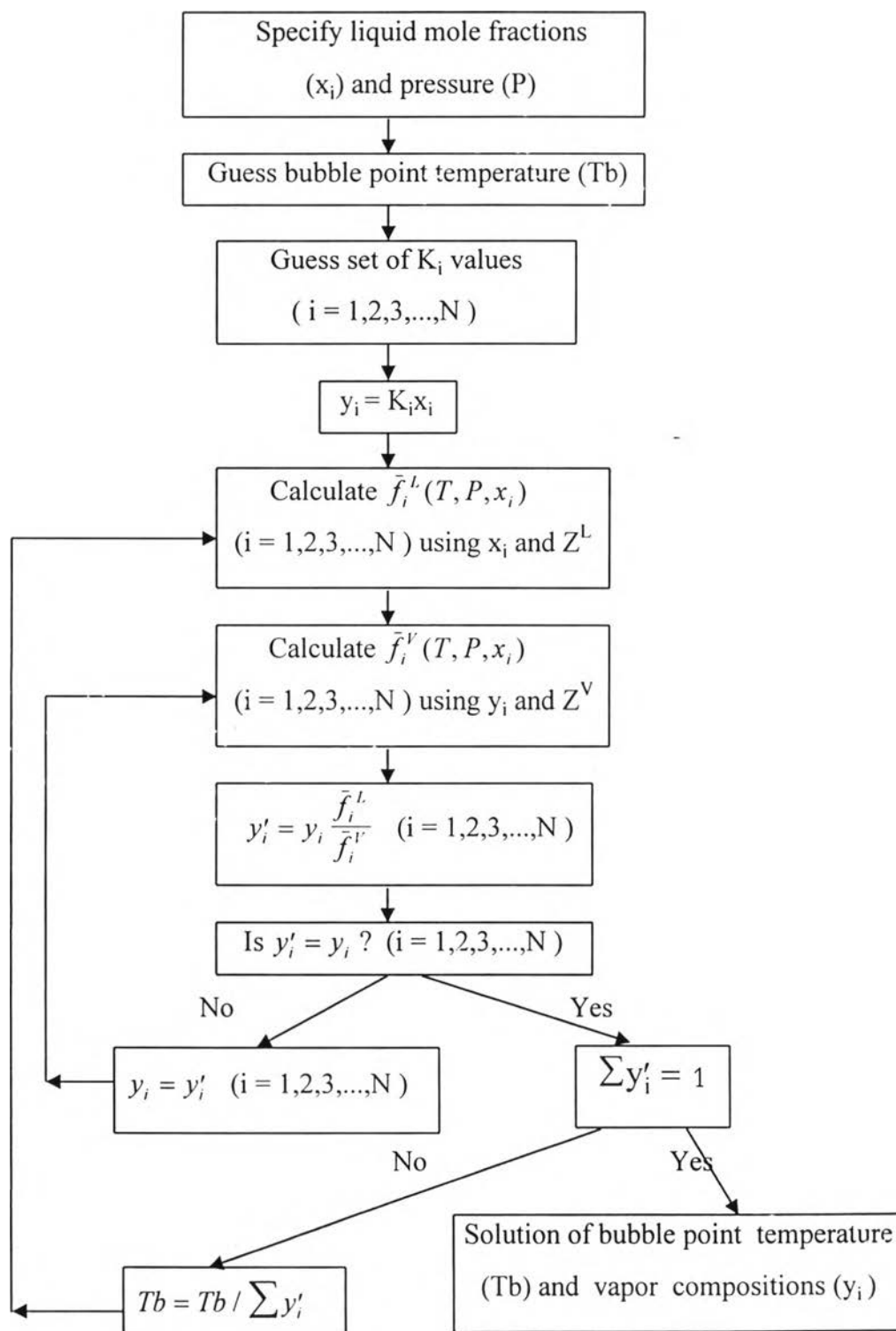


Figure 3.4 An algorithm for solving the bubble point temperature using equation of state. (Sandler, S. I., 1989)

3.6 The thermodynamices Properties

The thermodynamic properties presented in this chapter are widely used for distillation calculation

3.6.1 Vapor Pressure

The widely used vapor pressure correlation is the Antoine equation

$$\ln P_i^* = A_i - \frac{B_i}{T+C_i} \quad (3-46)$$

where P_i^* = Vapor Pressure

T = Temperature

A_i , B_i and C_i = constant parameters

The applicable temperature range is not large and corresponds to a pressure interval of about 0.01 to 2 bar. The Antoine equation should not be used outside the temperature limits stated. (Reid, R. C., 1988)

The other correlation predicting vapor pressure over wide range of temperature is the Wagner's equation.

$$\ln \left[\frac{P^*}{P_c} \right] = \frac{a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6}{Tr} \quad (3-47)$$

where $\tau = 1 - Tr$

$$Tr = \frac{T}{T_c}$$

3.6.2 Enthalpy

The enthalpy used in energy balance equation is very important for solving distillation problems.

The molal specific heat of gases is conventionally given as a polynomial in temperatures. The superscript ^o refers to the ideal condition.

$$c_{p_v}^o = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \quad (3-48)$$

The integral of equation (3-48) between a referent temperature, T_0 , to a desired temperature, T , provides ideal gas molar enthalpy at that temperature, as below:

$$H_v^o = \int_{T_0}^T c_{p_v}^o dT = \sum_{k=1}^5 \frac{a_k (T^k - T_0^k)}{k} \quad (3-49)$$

For real gas the estimated expression of enthalpy must be modified to yield

$$(H - H_v^o) = P_v - RT - \int_{\infty}^v [P - T \left(\frac{\partial P}{\partial T}\right)_v] dv \quad (3-50)$$

where V is the total volume equal to $v \sum n_i$.

For a mixture at given temperature T and pressure P , the vapor enthalpy

is

$$H_v = \left[\sum_{i=1}^c (y_i H_{i,v}^o) \right] + (H_v - H_v^o) \quad (3-51)$$

Equations (3-48) and (3-50) particularly suitable by using equations of state are explicit in pressure.

$$H_L = \left[\sum_{i=1}^c (y_i H_{i,v}^{\circ}) \right] + (H_L - H_v^{\circ}) \quad (3-52)$$

The equation of state mentioned above also does not apply with polar compound, large molecules (polymer) and electrolytes. (Thanit Sawasdisevi, 1996)