CHAPTER 2
DYNAMIC MODEL OF A DISTILLATION COLUMN

2.1 Theory

To study a dynamic model, a sufficiently rigorous tray-by-tray model with nonideal vapor-liquid and stage equilibrium will be developed. Such dynamic model of a disitllation column will include continuity equations of mass and energy. Several methods of thermodynamic physical property data used for calculation are also studied, and the proper one will be selected. The following topics are focused in this chapter:

1. Dynamic models of distillation,
2. Thermodynamic property data base.

The development of a dynamic distillation model can be simple if the designer wisely use the process knowledge and engineering judgement. It can also be difficult if he /she try to model details that are not needed to solve the problem at hand. One may find it interesting that to simulate the distillation column at dynamics state may be easier than at steady state. For steady-state model all the algebraic equations for mass and energy simulation must be solved. While the dynamic simulation model the change in mass and energy will be computed. A dynamic simulation is more intuitive with the way in which is about distillation operation than a steady-state simulation.

2.2 Dynamic Model of Distillation

This section will discuss about the method to develop the dynamic distillation model. To develop a distillation model it is begun by writing dynamic continuity equations of mass and energy for each unit operation in which mass or energy can accumulate. For the distillation column the continuity equations for the stages, condenser, reflux accumulator, bottom sump, and reboiler will be developed. The dynamic continuity equations state that the rate of accumulation of mass and energy in

a system is equal to the amount of material entering and generated, less the amount leaving and consumed within the system:

[rate of accumulation of mass (energy)] = [mass (energy) flow into the system]

- [mass (energy) flow out of the system]

+ [mass (energy) generated within the system]

- [mass (energy) consumed within the system]

The accumulation term is a first order time derivative of the total mass or energy. The flow terms are algebraic. This result in a first order ordinary differential equation that is usually nonlinear. Material balance for each component (or the total flow combined with all but one component flow) and one energy balance. The component balances are modelled as

$$\frac{d(xM)}{dt} = (zF)^{in} - (xF)^{out} + M_i^{gen} - M_i^{con} \qquad (2.1)$$

where z = feed composition (mole fraction)

x = composition of material in system

M = material in system (lbmol)

F = flow rate (lbmol/hr)

M_i^{gen} = rate of generation of component i in system (lbmol/hr)

M_i^{con} = rate of consumption of component i in system (lbmol/hr)

This will not consider reactive distillation systems in the model, so there are no chemical components generated consumed in any part of the distillation column. The material generation or consumption terms are zero.

A general energy balance is represented as

$$\frac{d(E^{out}M_n)}{dt} = (EF)^{in} - (EF)^{out} + Q - W \qquad (2.2)$$

$$E = U + PE + KE \qquad (2.3)$$

$$U = H - PV \tag{2.4}$$

where
M = material in system (lbmole)

F = material flow in/out of the system (lbmol/hr)

E = specific total energy (Btu/lbmol)

Q = heat added to system (Btu/hr)

W = work produced by the system (Btu/hr)

U = specific internal energy (Btu/lbmol)

PE = specific potential energy (Btu/lbmol)

KE = specific kinetic energy (Btu/lbmol)

H = specific enthalpy (Btu/lbmol)

PV = pressure-volume work (Btu/lbmol)

The PE, KE and PV terms of total energy are negligible in distillation columns. Vapor recompression systems will not be considered, so there is no work produced by the system.

Heat can be added or removed from many unit operations in distillation, such as reboilers, condensers, or interstage heat exchangers. This means that the energy term considered in this distillation model are equal to enthalpy. The overall energy balance can be written as

$$\frac{d(H^{out}M)}{dt} = (HF)^{in} - (HF)^{out} + Q \tag{2.5}$$

The system of differential equations will be solved, for all units in the process, by integrating forward in time. First a set of initial conditions for the state variables at the starting time is specified. Next all differentials are calculated from the material and energy flows at the current time. Each equation is integrated to the next time step. The current time is increased by the time step, and the integration process continues. Figure 2.1 contains a representation of steps in this process.
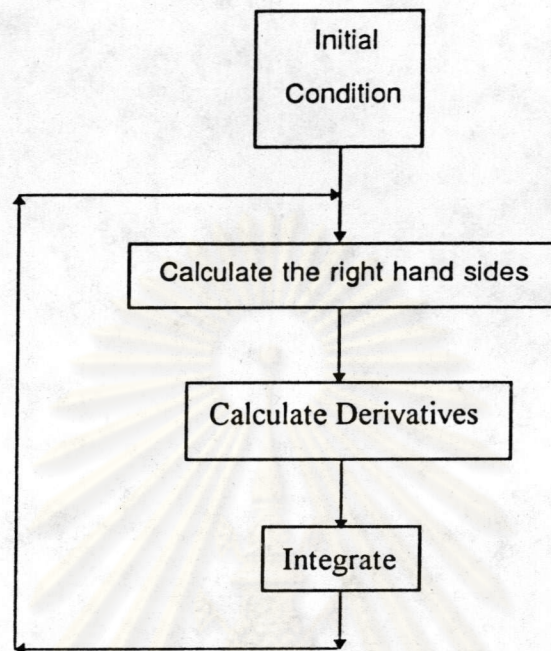
Fig.2.1 Integration block diagram.

The integration procedure must be started with a set of initial conditions for each state variable. Initial conditions may or may not correspond to a steady-state solution. If a steady-state solution is not available for the first run, a set of consistent values may be chosen. The solution will usually converge, dynamically, to a bonafide steady state as the integration proceeds. This method of initialization is useful to get a dynamic simulation running quickly. In fact, often it is numerically more stable to converge to the steady state dynamically than to solve for the steady state algebraically.

The liquid on the tray are perfectly mixed and incompresssible. Vapor and liquid are in thermal equilibrium but not in phase equilibrium (nonideal). The dynamic of the condenser and the reboiler will be neglected.

Distillation column dynamic for this thesis has the additional assumptions as following:

1. Negligible Vapor Holdup.

2. Negligible Specific Enthalpy Change.

3. Constant Pressure Drop or Constant Tray Pressure Drop.

The general dynamic distillation model includes of many continuity equations for the distillation stage model, the condenser and reflux accumulator model, and the reboiler and colun base model.
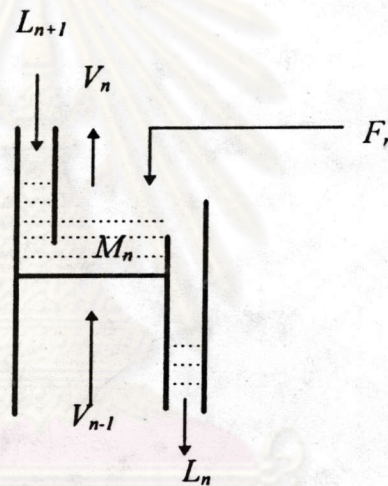
2.2.1 Distilation tray model

Fig.2.2 Distillation tray model

From figure 2.2, a general dynamic model for a stage is developed. There is counter-current flow of liquid and vapor. Liquid flows over the outlet weir into the downcomer and the stage beow. Vapor enters the tray from the stage below. The stage will contain a feed stream. A dynamic model for the stage will contain N_c differntial matrial balances, where N_c is the number of components in the system, and one overall energy balance. In this thesis the system will be modelled as N_c-1 differntial matrial balances and one overall material balance.

If the column pressure is high (greater than 150 psi), the vapor can represent a significant fraction of the total stage mass. the liquid mass should be increased to

account for the vapor if it is up to 30% of the total material. If the vapor mass is more than 30 or 40% of the total stage material and variable, the vapor phase must be modelled independently.

The change in specific liquid enthalpy is usually very small compared to the total stage enthalpy. Therefore, the enthalpy balance may often be reduced to an algebraic relation that can be used to calculate the vapor rate leaving the stage. The following procedure can be used to solve the stage model. The procedure is started from the bottom and proceeds up through the column.

1. Calculate the equilibrium composition and temperature from pressure and liquid composition by a bubble point calculation.

2. Calculate the actual vapor composition from the Murphree vapor phase stage efficiency.

3. Calculate the vapor and liquid enthalpy from their composition and stage temperature.

4. Calculate the clear liquid density from composition and temperature.

5. Calculate the liquid froth density at the stage vapor rate.

6. Calculate the liquid rate leaving the stage from the Francis weir formula.

7. Calculate the vapor flow leaving the stage from the energy balance.

8. Calculate the component and total mass derivatives.

The stage model is the keystone of the dynamic distillation column model. For each stage in the column, it will be repeated in a loop. The stage model that wil be presented here can be modified easily to meet the specific modelling needs. For example, if precise froth density is not important for your needs, the correlation can be replaced easily with a constant frothing factor.

The dynamic behavior is determined by the accumulative rate of material and energy. Each stage has three sets of differential equations which must be developed to describe the dynamic responses of distillation:

Total material balance:

$$\frac{d(M_n)}{dt} = L_{n+1} + V_{n-1} - L_n - V_n + F_n \quad [\text{ if feed stage }] \tag{2.6}$$

where M_n = liquid hold up on stage n

    L_n = Liquid flow rate from stage n

    V_n = vapor flow rate from stage n

    F_n = feed rate to stage n

The component material balance:

$$\frac{d(x_{i,n} M_n)}{dt} = x_{i,n+1} L_{n+1} + y_{i,n-1} V_{i,n-1} - x_{i,n} L_n - y_{i,n} V_n + z_{i,n} F \tag{2.7}$$

where $x_{i,n}$ = mole fraction of component i in liquid on stage n.

    $y_{i,n}$ = mole fraction of component i in vapor on stage n.

    $z_{i,n}$ = mole fraction of component i in feed on stage n.

The energy balance:

$$\frac{d(h_n^L M_n)}{dt} = h_{n+1}^L L_{n+1} + h_{n-1}^V V_{n-1} - h_n^L L_n - h_n^V V_n + h_n^F F \tag{2.8}$$

where h_n^L = molar enthalpy of liquid on stage n

    h_n^V = molar enthalpy of vapor on stage n

    h_n^F = molar enthalpy of feed on stage n
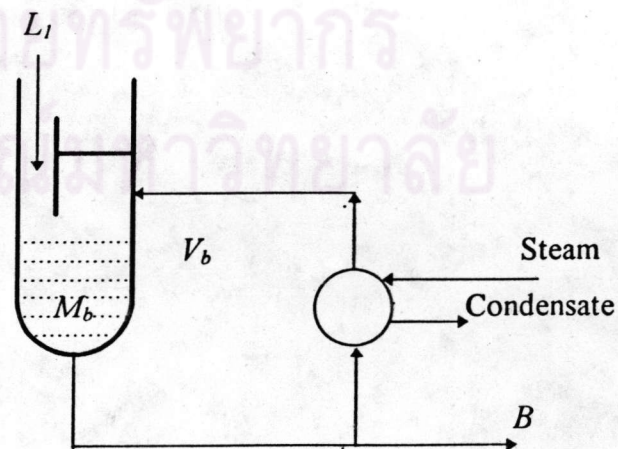
2.2.2 Reboiler and column base Model

Fig.2.3 Column base model

The model of the reboiler and column base is similar to that of the column stage. This part of the disitllation column is modelled as an equilibrium stage. There is heat input from the reboiler. Material holdup is large and variable. Changes in specific enthalpy will not be neglected. The time derivative of the specific enthalpy can be approximated numerically by backward difference. The specific enthalpy is saved at each time step. The current value is subtracted from the previous valusand the result is divided by the time step. It is necessary to compute the specific enthalpy derivative so that the vapor rate leaving the sump can be calculated from the energy balance. The dynamic model is presented as below.

Total mass balance:

$$\frac{d(M_b)}{dt} = L_1 - V_b - B \tag{2.9}$$

Where M_b = liquid holdup on the column base

L_1 = liquid flow rate from stage 1 to column base

V_b = vapor flow rate from the reboiler to stage 1

B = bottom product flow rate

Component material balance:

$$\frac{d(x_{i,b}M_b)}{dt} = x_{i,1} L_1 - y_{i,b} V_b - x_{i,b} B \tag{2.10}$$

where $x_{i,b}$ = mole fraction of component i in liquid on column base.

$x_{i,1}$ = mole fraction of component i in liquid on tray 1.

$y_{i,b}$ = mole fraction of component i on the column base.

Energy balance:

$$\frac{d(h_b^L M_b)}{dt} = h_1^L L_1 - h_b^V V_b - h_b^L B + Q_r \tag{2.11}$$

where h_b^L = molar enthalpy of liquid on column

h_1^L = molar enthalpy of liquid on stage 1

h_b^V = molar enthalpy of vapor on the column base

Q_r = molar enthalpy of reboiler

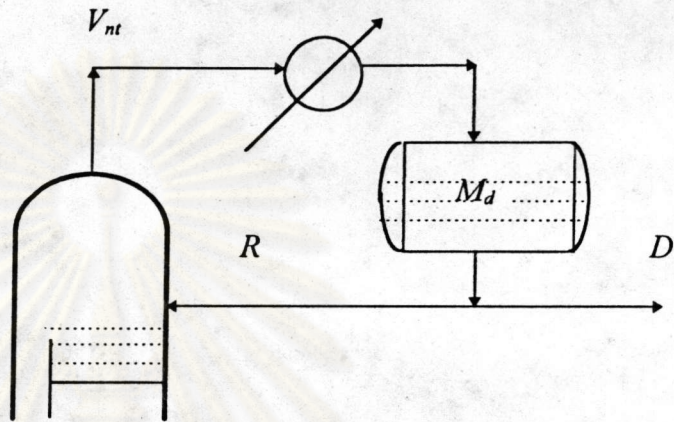### 2.2.3 Condenser and Reflux accumulator Model

V_{nt}

M_d

R

D

Fig.2.4 Condenser and reflux accumulator model

From figure 2.4, there is vapor flow rate (V_{nt}) from stage nt to reflux accumulator through the condenser. The vapor is condensed to liquid at the condenser. The distillate rate (D) is the product. The reflux rate enters backward to the stage nt.

The dynamic of condenser is small relative to the reflux accumulator dynamics. It will be specified the condensate temperature of the liquid leaving the condenser to allow equilibrium (the same as the reflux accumulator). The reflux accumulator contains a significant and variable quantity of material. There is no heat into or leaving the accumulator and there is no vapor leaving from the accumulator.

Total mass balance:

$$\frac{d(M_d)}{dt} = V_{nt} - R - D \tag{2.12}$$

Compenent material balance:

$$\frac{d(x_{i,b}M_b)}{dt} = y_{i,d}V_{nt} - x_{i,d}(R-D)$$ (2.13)

2.2.4 Liquid hydraulics

Liquid flow rate from any tray can be calculated by Francis weir equation:

$$L_n = C\rho_n^L W_{len} H_{ow}^{1.5}$$ (2.14)

where L_n = liquid flow rate from stage n

   C = conversion constant

   ρ_n^L = liquid density of liquid on stage n

   W_{len} = weir length

   H_{ow} = liquid hight overweir

2.3 Thermodynamics Properties

When all of the conservation equations are written, the thermodynamics principles and other relationships will be studied in order to calculate the remaining variables.

2.3.1. Vapor-Liquid Equilibrium

It is essential to have an accurate model or correlation for the vapor-liquid equilibrium (VLE) and physical properties of the components in the distillation column. The phase equilibrium of some systems is essentially ideal. Raoult's law,

$$y_i P = x_i P_i^*$$ (2.15)

represents ideal systems. Other may have constant relative volatility:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{(\frac{y_i}{x_i})}{(\frac{y_j}{x_j})}$$ (2.16)

Some can be correlated simply as a polynomial in temperature:

$$K_i = \frac{y_i}{x_i} = A_i + B_i T + C_i T^2 + \ldots \qquad (2.17)$$

where A_i, B_i, C_i = correlation constants for component i

x_i = mole fraction of component i in liquid

y_i = mole fraction of component i in vapor

P = total pressure

P_i^* = vapor pressure of component i

α_{ij} = relative volatility

K_i = vapor-liquid composition ratio of component i

Many chemical systems have significant nonidealities in the liquid phase, and somtimes also the vapor phase. A more rigirous VLE model is required. The fugacities of the vapor and liquid phases are equal at equilibrium:

$$f_i^V = f_i^L \qquad (2.18)$$

Expressions can be written for the fugacity of each phase:

$$\phi_i^V y_i P = \phi_i^L x_i \qquad (2.19)$$

$$\phi_i^V y_i P = \gamma_i x_i P_i^* \, exp[\frac{\gamma_i(P - P_i^*)}{RT}] \qquad (2.20)$$

where f_i^V, f_i^L = vapor, liquid fugacity

ϕ_i^V, ϕ_i^L = vapor, liquid fugacity coefficient

γ_i = activity coefficient of component i

If an equation of state is available that acculately represents both the vapor and liquid phases, use equation (2.19). If the liquid phase can not be modelled by an equation of state, which is usually the case, use equation (2.20), which models the idealities of the liquid phase by a correlation of the liquid phase activity coefficient. The exponential term corrects the liquid fugacity for high pressure (greater than 150

psia). Most of the nonideal effects for low pressure (less than 150 psia) chemical systems can be represented by a simplified form of equation (2.20), given as

$$y_i P = \gamma_i x_i P_i^*$$ (2.21)

Where y_i, x_i = mole fraction of component i in vapor and liquid, respectively.

P = total pressure

P_i^* = vapor pressure of component i

The liquid activity coefficient can be modelled for binary mixtures by a correlating equation such as the Van Laar equation.

$$T \ln \gamma_1 = \frac{B}{1 + A(\frac{x_1}{x_2})}$$ (2.22)

$$T \ln \gamma_2 = \frac{AB}{A + (\frac{x_2}{x_1})}$$ (2.23)

where $A = \frac{T_{C1} P_{C2}}{T_{C2} P_{C1}}$

$$B = 3.375 T_{C1} [1 - \frac{P_{C2}}{P_{C1}}]$$

At best these approximations could be applicable only to binary mixtures showing no chemical interaction effects.

2.3.2 Vapor Pressure

A widely used vapor pressure correlation is the Antoine equation:

$$\ln(P_i^*) = A_i - \frac{B_i}{T + C_i}$$ (2.24)

where P_i^* is the vapor pressure and T is temperature. The constant parameters A_i, B_i, and C_i must be obtained by regressing experimental data, however, these parameters bave been tabulated for many substances. The applicable temperature range is not

large and in most cases corresponds to a pressure interval of 0.19 to 29.4 psi (0.0133 to 2 bar). This equation should not be used outside the stated temperature limits.

To extend the correlation interval, a more complicated expression such as the Riedel equation. The vapor pressure of pure component can defined by the Reidel's equation:

$$ln\,(P^{*}_{ri}) \;=\; A_i \,-\, \frac{B_i}{T_r} \,+\, C_i\,ln\,(T_r) \,+\, D_i\,T_r^6 \tag{2.25}$$

where $\quad A_i\,,\,B_i\,,\,C_i\;=$ Reidel's constants for component i

$\qquad\qquad P^{*}_{ri}\quad=$ reduce vapor pressure of component i

$\qquad\qquad T_r\quad\;=$ reduce tempeature

When the constant parameters are determined by regressing experimental data, the range of this equation extends to the critical point. A better fit of the data is often obtained when the exponent 6 is allowed to vary to other integer values.

If the critical pressure P and the critical temperature T are known along with one other vapor-pressure point (such as the normal boiling point), then a reduced form of the Reidel equation may be used:

$$A_i \;=\; -35Q \tag{2.26}$$

$$B_i \;=\; -36Q \tag{2.27}$$

$$C_i \;=\; 42Q + \alpha_c \tag{2.28}$$

$$D_i \;=\; -Q \tag{2.29}$$

where $\quad Q \;=\; 0.0838\,(3.758 - \alpha_c) \tag{2.30}$

$$\alpha_c \;=\; \frac{0.315\,\psi - ln\,P^{*}_{ri}}{0.0838\,\psi - ln\,T_r} \tag{2.31}$$

$$\psi \;=\; -35 + \frac{36}{T_r} + 42\,ln\,T_r - T_r^6 \tag{2.32}$$

2.3.3 Murphree Vapor Phase Stage Efficiency

Stage vapor composition can be calculated from the relationships developed in the previous section. Mass transfer limitations prevent the vapor leaving a stage from being in precise equilibrium with the liquid on the stage. This limitation can be modelled as a deviation from equilibrium. Three types of stage efficiencies are commonly used:

1. Overall efficiency

2. Murphree efficiency

3. Local efficiency

Overall efficiency pertains to the entire column, relating the total number of actual to ideal stage. Murphree efficiency pertains to the efficiency at a specific stage whereas local efficiency pertains to a specific location on a single stage. For this thesis ,Murphree efficiency will be used. Stage efficiency is the fractional method to an equilibrium stage which is attained by a real stage. This thesis uses Murphree Efficiency to correct the vapor composition. The Murphree efficiency is the ratio between the real difference in vapor composition between two stage and the difference that happens if the vapor was in equilibrium with the liquid leaving the stage.
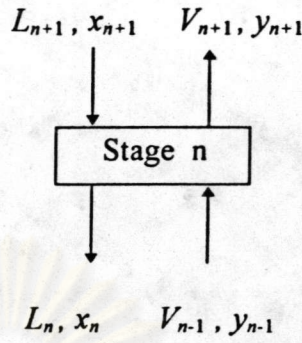
The Murphree efficiency of the stage is :

$$E_n = \frac{y_{i,n} - y_{i,n-1}}{y_{i,n}^* - y_{i,n-1}}$$
(2.33)

where E_n = Murphree efficiency of the stage n

$y_{i,n}$, $y_{i,n-1}$ = mole fraction of component i in vapor on stage n and stage n-1,

respectively.

$y_{i,n}^*$ = mole fraction of component i in vapor on stage n. (at equilibrium)

$$L_{n+1} , x_{n+1} \qquad V_{n+1} , y_{n+1}$$

$$\boxed{\text{Stage } \; n}$$

$$L_n , x_n \qquad V_{n-1} , y_{n-1}$$

Assume the liquid and vapor are in thermal equilibrium, but not in phase equilibrium
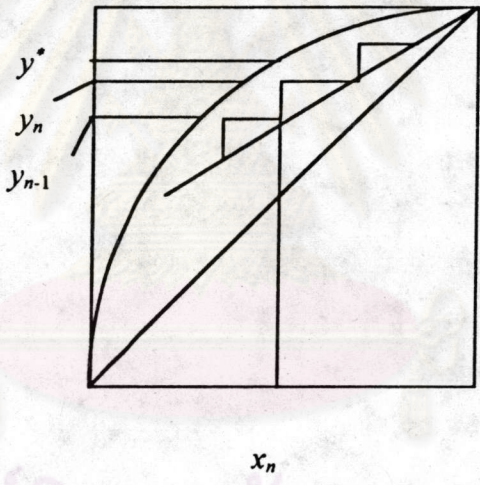

Fig.2.5 Murphree vapor phase stage efficiency

2.3.4 Enthalpy

The energy can be expressed in term of enthalpy in the distillation model. The enthalpy of liquid and vapor must be calculated. The general enthalpy equation is the function of temperature, pressure, and compositions.

$$h = f(T, P, x) \tag{2.34}$$

Liquid enthalpy is not the function of pressure because liquids are incompressible. Pressure effects on vapor enthalpy are negligible for low to moderate pressure systems. Selecting 0 °F as the reference temperature results in the correlations.

$$h_i^L = a_i^L T + b_i^L T^2 \tag{2.35}$$

$$h_i^V = a_i^V T + b_i^V T^2 + c_i^V T^3 \tag{2.36}$$

where h_i^L, h_i^V = Liquid and vapor enthalpy of pure component i

a_i^L, b_i^L = specific heat capacity coefficient of component i in liquid phase

a_i^V, b_i^V, c_i^V = specific heat capacity coefficient of component i in vapor phase

The correlation constants for equations (2.35) and (2.36) can be obtained from heat capacity data. Mixing rules are used to find multicomponent properties. The vapor phase enthalpy is mixed ideally as the molar average of the pure component enthalpies. The liquid rate can contain significant nonidealities (heat of mixing) unless the liquid activity coefficient is unity. Heat of mixing can be modelled with

$$h_{mix}^L = -R T^2 \sum x_i \left(\frac{\partial \ln y_i}{\partial T}\right) \tag{2.37}$$

The liquid activity coefficient in equation (2.22) and (2.23) is modelled with the same correlation that is used for vapor- liquid equilibrium in equation (2.20) and (2.21). Good results can be obtained often, even with significant liquid nonidealities, neglecting the heat of mixing or substituting a constant value.

Vapor and liquid enthalpy for mixtures can be represented as

$$h^L = \sum x_i h_i^L + h_{mix}^L \tag{2.38}$$

$$h^V = \sum y_i h_i^V \tag{2.39}$$

where h^L, h^V = Liquid and vapor enthalpy for mixtures, respectively.

2.3.5 Liquid Density

The liquid density for a mixture can be calculated from the pure component liquid density and their mole fractions.

$$\rho^L = \Sigma\, x_i\, \rho_i^L \tag{2.40}$$

where ρ^L = mixture liquid density

ρ_i^L = pure component i liquid density

x_i = mole fraction of component i in the mixture

Vapor passing through a distillation column tray aerates the liquid, creating a froth. The clear liquid density, is corrected for frothing by correlations, usually obtained from the tray design guides or generalized correlations. Computing the froth density as a function vapor rate is necessary if you want to study flow hydraulics. There is no need to compute the froth density continuously if you are not interested in froth dynamics. Omitting this calculation at time step will improve the speed of the simulation.