

## The Influence of Mass Transfer Effect to Design of Ideal Distillation System

En Ko Lee<sup>ab</sup> (李恩各)

a Department of Chemical Engineering  
Ta Hwa Institute of Technology  
Chiunglin, Hsinchu, Taiwan 307, R. O. C.  
celek@thit.edu.tw

David S. H. Wong<sup>b\*</sup> (汪上曉)

b Department of Chemical Engineering  
National Tsing Hua University  
Hsinchu, Taiwan 300, R. O. C.  
dshwong@che.nthu.edu.tw

### Abstract

*A mass transfer limited model is proposed to evaluate the influence of mass transfer effect to minimum reflux ratio calculations of ideal distillation system. The used ideal ternary system is composed of n-hexane(C<sub>6</sub>), n-heptane(C<sub>7</sub>), and n-nonane(C<sub>9</sub>), which is tested to determine the design of distillation column by the mass transfer resistance of column stage. However unreasonable of trace component specifications of products will lead to erroneous minimum reflux ratio values. This work demonstrated the distinctions between equilibrium and mass transfer limited model generate different conclusion on the feasibility of column separation. The mass transfer effects give the different calculation results to minimum reflux ratio which is affected by the type of column pinch points.*

### 1. Introduction

Distillation is the most frequently used separation technique in chemical and petroleum industries. It is an intensive energy-consumption process. In the past, design of distillation columns relied on the classical Fenske-Underwood shortcut design procedure followed by rigorous stage-to-stage simulation. The Fenske-Underwood procedure calculates the minimum reflux ratio and minimum number of theoretical stage based on assumptions constant molar over-flow and constant relative volatility. It is applicable only to systems that are relative ideal in terms of vapor-liquid phase equilibrium behavior. Hence they are not applicable to complex distillation columns such as azeotropic distillation, reactive distillation etc. Over the last decade, design of complex distillation columns have been substantially advanced by geometric modeling using residual curve maps and distillation curves [1-21]. Both Fenske-Underwood procedure and geometric modeling method are equilibrium theory which

assumes that the vapor is in equilibrium with the liquid along the entire column length. Sundaresan et al. [22] analyzed that the extensively applied "equilibrium theory" between interphase mass transfer process is deficient because the ratios of mass transfer coefficients are lost during the model formulation. They found that the mass transfer rate influence the composition of the pinch in a countercurrent adsorption column, and suggested that it is necessary to reexamine whether minimum reflux ratio is affected by mass transfer. Agarwal and Taylor [23] used a non-equilibrium model to determine the minimum reflux ratio and found the identical results whether an equilibrium model or non-equilibrium model is applied. However, the effect of non-key component specifications was not considered. Castillo and Towler [24] implied the non-equilibrium stages relationship at total reflux to calculate the Murphree tray efficiency of real column showed that mass transfer effect can cause significant changes in the shape of the residual curve maps and distillation lines for homogeneous azeotropic distillation systems. However, the

calculations of true minimum reflux ratio under mass transfer effect have not been illustrated in the literature.

## 2. Distillation Curve with Mass Transfer

Using the assumption of constant molar over-flow, the rectifying operating line of a stage-wise system is written as:

$$\bar{y}_{n+1} = \frac{R}{R+1} \bar{x}_n + \frac{1}{R} \bar{x}_D \quad (1)$$

Rewriting the above equation in terms of the difference between two stages, we have

$$(\bar{y}_{n+1} - \bar{y}_n) = \frac{R}{R+1} (\bar{x}_n - \bar{x}_{n-1}) \quad (2)$$

In case when there is mass transfer, the relation between liquid phase composition and vapor phase composition of stage n is given by:

$$\bar{y}_{out} - \bar{y}_{in} = \bar{E}^{oy} \bullet (\bar{y}^*(\langle \bar{x} \rangle) - \bar{y}_{in}) \quad (3)$$

$\bar{E}^{oy}$  is known as the overall vapor point efficiency matrix for the n<sup>th</sup> stage of the column. Combining equations (1), (2), and (3), we get:

$$\bar{x}_n - \bar{x}_{n-1} = -\bar{E}^{oy} \bullet \left( \bar{x}_{n-1} - \frac{R+1}{R} \bar{y}^*(\langle \bar{x} \rangle_n) + \frac{1}{R} \bar{x}_D \right) \quad (4)$$

The difference between two stages can be interpreted as the difference between two points in a continuous column. If we replace the difference term with a differential, we can obtain a rectification curve with mass transfer effect taken into account:

$$\frac{d\bar{x}}{d\xi} = -\bar{E}^{oy} \bullet \left( \bar{x} - \frac{R+1}{R} \bar{y}^*(\bar{x}) + \frac{1}{R} \bar{x}_D \right) \quad (5)$$

$\xi$  is a dimensionless column length. Similarly a stripping curve with mass transfer effect is given by:

$$\frac{d\bar{x}}{d\xi} = -\bar{E}^{oy} \bullet \left( \frac{S}{S+I} \bar{y}^*(\bar{x}) + \frac{I}{S+I} \bar{x}_B - \bar{x} \right) \quad (6)$$

The reflux and stripping ratios are related by:

$$S = (R+1) \left( \frac{x_{B,i} - z_i}{z_i - x_{D,i}} \right) \quad (7)$$

A residual curve with mass transfer effect for the

system can be obtained if we let the reflux and stripping ratio approaches infinity:

$$\frac{d\bar{x}}{d\xi} = -\bar{E}^{oy} \bullet (\bar{x} - \bar{y}^*(\bar{x})) \quad (8)$$

The overall vapor point efficiency matrix is related to the overall vapor phase mass transfer coefficients

$$\begin{aligned} \bar{E}^{oy} &= \bar{I} - \exp\left(-\bar{\Lambda}^{-1} \bar{\Gamma} N_{ref}^{oy}\right) \\ &= \bar{I} - \exp\left(-\bar{\Lambda}^{-1} \bar{\Gamma} \frac{k_{in}^{oy} ah}{G}\right) \end{aligned} \quad (9)$$

The matrix  $\bar{\Lambda}$  is the multi-component mass transfer factor relative to the overall vapor phase mass transfer coefficient of a reference component pair i and n,  $k_{in}^{oy}$ :

$$\Lambda_{ij} = \begin{cases} x_i + \sum_{\substack{k=1 \\ k \neq i}}^n x_k \frac{k_{in}^{oy}}{k_{ik}^{oy}} & j = i \\ -x_i \left( \frac{k_{in}^{oy}}{k_{ij}^{oy}} - 1 \right) & j \neq i \end{cases} \quad (10)$$

In this work, we assume that the ratio of components mass transfer coefficients of two different binary pairs can be estimated by the ratio of liquid phase diffusion coefficients:

$$\frac{k_{in}^{oy}}{k_{ij}^{oy}} = \frac{D_{in}}{D_{ij}} \quad (11)$$

The Wilke-Chang method [25] is used to estimate the binary molecular diffusion coefficients:

$$D_{ij} = 7.4 \times 10^{-8} \frac{(\phi_j M_j)^{1/2} T}{\mu_j V_i^{0.6}} \quad (12)$$

The thermodynamic factor matrix  $\bar{\Gamma}$  is given by

$$\Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \quad (13)$$

with  $\delta_{ij}$  being the Kroneckta delta and  $\gamma_i$  being the activity coefficient of component.  $a$  is the mass transfer area per unit volume of the column, and  $h$  is the height of the actual column section per unit dimensionless length (i.e. per unit actual stage).

$N_{ref}^{oy}$  is a "reference" number of mass transfer stages per unit actual stage. As the value of  $N_{ref}^{oy}$  increases, the column profiles and residual curve become identical with the common equilibrium model as the efficiency matrix approaches an

identity matrix.

### 3. Effects of Mass Transfer on Different Pinch Scenarios

A pinch is a point at which the distillation curve becomes stationary. Rectification and stripping pinches are therefore given by:

$$-\bar{E}^{oy} \bullet \left( \bar{x}^{RP} - \frac{R+I}{R} \bar{y}^* (\bar{x}^{RP}) + \frac{I}{R} \bar{x}_D \right) = 0 \quad (14)$$

$$-\bar{E}^{oy} \bullet \left( \frac{S}{S+I} \bar{y}^* (\bar{x}^{SP}) + \frac{I}{S+I} \bar{x}_B - \bar{x}^{SP} \right) = 0 \quad (15)$$

We can easily infer, using the above equations that the end-pinches of a system are not affected by mass transfer. The rectification and stripping curves of an ideal system of n-hexane(C<sub>6</sub>), n-heptane(C<sub>7</sub>), and n-nonane(C<sub>9</sub>) (see Agarwal and Taylor [23]), with R=6.1, x<sub>D</sub>=(0.99, 0.009, 0.001) and x<sub>B</sub>=(0.001,0.421,0.578) at various  $N_{ref}^{oy}$  are shown in Figure 1. The rectification end pinches (REP) and stripping end pinches (SEP) are invariant with respect to  $N_{ref}^{oy}$ .

#### 3.1 Stripping Pinch

Given that the feed (F) is a saturated liquid and a particular set of specifications for the splits of all the components, and a stripping pinch condition is found when the stripping end pinch (SEP) lies on the rectification curve (Figure 2). This scenario occur when the distillate contain only a small amount of the heavy key component and insignificant amount of all components heavier than the heavy key. While this reflux is the minimum given the particular set of split specifications, the minimum reflux obtained is very sensitive to the specification of the non-key splits. The true minimum reflux is achieved only when the non-key component splits to the top approaches zero, i.e. a sharp direct split. For an ideal system with no mass transfer effect, this happens when the rectification saddle (RSP), feed (F) and the stripping end pinch (SEP) are collinear.

If mass transfer effect is included, the position of SEP would not be affected. In fact the stripping curves are relatively unaffected by mass transfer.

However, the rectification curve at the same reflux move away from SEP so that the minimum reflux ratio obtained without mass transfer is no longer a feasible reflux (Figure 3). The minimum reflux increased to 8.4 as effect of mass transfer effect becomes more significant ( $N_{ref}^{oy}=10$ ). The stripping pinch condition, i.e. the stripping end pinch (SEP) lies on the rectification curve, still hold at minimum reflux when there is mass transfer, but the co-linearity condition between RSP, SEP, and F is no longer valid (Figure 4).

#### 3.2 Rectification Pinch

Similarly, if the specifications of all the components are given, and that the feed (F) is a saturated liquid, a rectification pinch condition is found when the rectification end pinch (REP) lies on the stripping curve (Figure 5). This usually occurs for a sharp indirect split system, i.e. the bottom contain only a small amount of the light key component and insignificant amount of all components lighter than the light key. Again the true minimum reflux is achieved only when the non-key component splits to the bottom approaches zero. For an ideal system with no mass transfer, this happens when the stripping saddle (SSP), feed (F) and the rectification end pinch (REP) are co-linear.

If mass transfer effect is included, the position of the rectification end pinch (REP) would not be affected. However, the stripping curve at the same stripping ratio move away from REP in a direction that makes the crossing of the rectification and stripping curves easier, so that the minimum reflux ratio obtained without mass transfer is no longer a minimum reflux (Figure 6). The true minimum reflux actually decreases to 0.25 as the mass transfer effect becomes more important ( $N_{ref}^{oy} = I$ ). As in the case of sharp direct split, the rectification pinch condition, i.e. the rectification end pinch (REP) lies on the stripping curve still hold at minimum reflux when there is mass transfer, but the co-linearity condition between SSP, REP and F is no longer valid (Figure 7).

#### 3.3 Feed Pinch

When the split is non-sharp, an intermediate component is distributed in both the distillate and

the bottom. In this case, minimum reflux occurs if the rectification end pinch and the stripping end pinch intersect at the feed (for a saturated liquid feed). A feed pinch occurs. Since mass transfer has no effect on the locations of the rectification and stripping end pinches, the value of minimum reflux will not be affected (Figure 8).

#### 4. Conclusion

The true minimum reflux ratio can be calculated only at right specifications of non-key components are estimated for ideal distillation systems. A “geometric modeling and multi-component mass transfer theory” is proposed to evaluate the influences of mass transfer to minimum reflux. The inefficient trays or other correlation of hardware design cause effect of mass transfer not negligible which will change the curvatures of RCM lead to increase the minimum reflux ratio to stripping end pinch, but reduce to rectification end pinch for an ideal system. Due to the identical end points of rectification and stripping profile, the minimum reflux ratio is not affected by mass-transfer-effect to feed pinch case.

#### Nomenclature

$a$	mass transfer area per unit volume of the column
$D_{ij}$	diffusion coefficient of solute $i$ in solvent $j$
$\bar{E}^{oy}$	efficiency matrix of stage
$G$	superficial molar mass velocity of vapor
$h$	height of the actual column section
$I$	identity matrix
$\bar{k}^{oy}$	multi-component overall vapor phase mass transfer coefficient matrix
$M_j$	molecular weight of solvent $j$
$\bar{N}^{oy}$	number of mass transfer stages
$R$	reflux ratio
$S$	boil-up ratio
$V_j$	molar volume of solute $j$
$x$	liquid mole fraction
$y$	vapor mole fraction
$z$	mole fraction of feed
$\delta_{ij}$	Kronecker delta, 1 if $i = k$ , 0 if $i \neq k$

$\phi$	association factor of solvent $j$ , 1.0
$\gamma$	activity coefficient
$\Lambda$	mass transfer factor
$\Gamma$	thermodynamics factor matrix
$\mu_j$	viscosity of solvent $j$
$\xi$	dimensionless column length

#### Superscripts

\* vapor and liquid equilibrium state

#### Subscripts

$B$	bottoms
$D$	distillate
$n$	the $n$ stage

#### References

- [1] Schreinemakers, F.A.H. “Dampfdrucke ternärer Gemische.” *Z. Phys. Chem.*, **36**, 257 (1901).
- [2] Stichlmair, J.G., Offers, H. and Potthoff, R.W. “Minimum Reflux and Minimum Reboil in Ternary Distillation.” *Ind. Eng. Chem. Research*, **32**, 2438 (1993).
- [3] Wahnschafft, O.M., Koehler, J., Blass, E. and Westerberg, A.W. “The Product Composition Regions of Single-Feed Azeotropic Distillation Columns.” *Ind. Eng. Chem. Research*, **31**, 2345 (1992).
- [4] Pollmann, P., Glanz, S. and Blass, E. “Calculating Minimum Reflux of Nonideal Component Distillation Using Eigenvalue Theory.” *Comput. Chem. Eng.*, **18**(suppl.), s49 (1994).
- [5] Van Dogen, D.B. and Doherty, M.F. “Design and Synthesis of Homogeneous Azeotropic Distillations. 1. Problem Formulation for a Single Column.” *Ind. Eng. Fundamental*, **24**, 454 (1985).
- [6] Koehler, J., Aguirre, P. and Blass, E. “Minimum Reflux Calculations for Nonideal Mixtures Using the Reversible Distillation Model.” *Chem. Eng. Sci.*, **46**, 3007 (1991).
- [7] Koehler, J., Poellmann, P. and Blass, E. “A Review on Minimum Energy Calculations for Ideal and Nonideal Distillations.” *Ind. Eng. Chem. Research*, **34**, 1003 (1995).
- [8] Fidkowski, Z.T., Malone, M.F. and Doherty, M.F. “Feasibility of Separations for Distillation of Nonideal Ternary Mixtures.” *A.I.Ch.E. J.*, **39**, 8, 1303 (1993).
- [9] Castillo, F.J.L., Thong, D.Y.C. and Towler, G.P. “Homogeneous Azeotropic Distillation. 1. Design Procedure for Single-Feed Columns at Nontotal Reflux.” *Ind. Eng. Chem. Research*,

- 37, 987 (1998).
- [10] Castillo, F.J.L., Thong, D.Y.C. and Towler, G.P. "Homogeneous Azeotropic Distillation. 2. Design Procedure for Sequences of Columns." *Ind. Eng. Chem. Research*, **37**, 998 (1998).
- [11] Bausa, J., Watzdorf, R.V. and Marquardt, W. "Shortcut Methods for Nonideal Multicomponent Distillation : 1. Simple Columns." *A.I.Ch.E. J.*, **44**, 2181 (1998).
- [12] Doherty, M.F. and Malone, M.F. *Conceptual design of distillation systems*, McGraw-Hill, New York (2001)
- [13] Doherty, M.F. and Perkins, J.D. "On the Dynamics of Distillation Processes-III : the Topological Structure of Ternary Residue Curve Maps." *Chem. Eng. Sci.*, **34**, 1401 (1979).
- [14] Doherty, M.F. and Calderola, G.A. "Design and Synthesis of Homogeneous Azeotropic Distillations. 3. The Sequencing of Columns for Azeotropic and Extractive Distillations." *Ind. Eng. Chem. Fundamental*, **24**, 474 (1985).
- [15] Levy, S.G., Van Dogen, D.B. and Doherty, M.F. "Design and Synthesis of Homogeneous Azeotropic Distillations. 2. Minimum Reflux Calculation for Nonideal and Azeotropic Columns." *Ind. Eng. Chem. Fundamental*, **24**, 463 (1985).
- [16] Levy, S.G. and Doherty, M.F. "Design and Synthesis of Homogeneous Azeotropic Distillations. 4. Minimum Reflux Calculations for Multiple-Feed Columns." *Ind. Eng. Chem. Fundamental*, **25**, 269 (1986).
- [17] Knight, J.R. and Doherty, M.F. "Design and Synthesis of Homogeneous Azeotropic Distillations. 5. Columns with Nonnegligible Heat Effects." *Ind. Eng. Chem. Fundamental*, **25**, 279 (1986).
- [18] Barbosa, D. and Doherty, M.F. "The Influence of Equilibrium Chemical Reactions on Vapor-Liquid Phase Diagrams." *Chem. Eng. Sci.*, **43**, 529 (1988a).
- [19] Barbosa, D. and Doherty, M.F. "The Simple Distillation of Homogeneous Reactive Mixtures." *Chem. Eng. Sci.*, **43**, 541 (1988b).
- [20] Barbosa, D. and Doherty, M.F. "Design and Minimum Reflux Calculations for Single-Feed Multicomponent Reactive Distillation Columns." *Chem. Eng. Sci.*, **43**, 1523 (1988c).
- [21] Julka, V. and Doherty, M.F. "Geometric Behavior and Minimum Flows for Nonideal Multicomponent Distillation." *Chem. Eng. Sci.*, **45**, 1801 (1990).
- [22] Sundaresan, S., Wong, J. K. and Jackson, R. "Limitations of the Equilibrium Theory of Countercurrent Devices." *A.I.Ch.E. J.*, **33**, 1466 (1987).
- [23] Agarwal, S. and Taylor, R. "Distillation Column Design Calculations Using a Non-equilibrium Model." *Ind. Eng. Chem. Research*, **33**, 2631 (1994).
- [24] Castillo, F.J.L., Thong, D.Y.C. and Towler, G.P. "Influence of Multicomponent Mass Transfer on Homogeneous Azeotropic Distillation." *Chem. Eng. Sci.*, **53**, 963 (1998).
- [25] Reid, R.C., Prausnitz, J.M. and Poling, B.E. *The Properties of GASES & LIQUIDS*, McGraw-Hill, New York (1988)

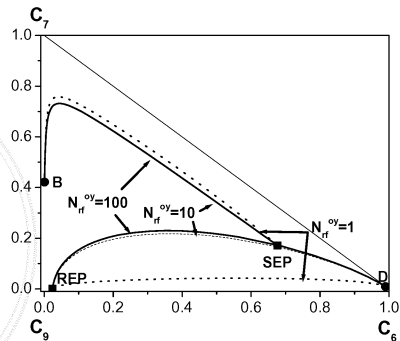


Figure 1: Effect of mass transfer on pinch point locations ( $x_F=[0.3, 0.3, 0.4]$ ,  $R=6.1$ ,  $x_D=[0.99, 0.009, 0.001]$  and  $x_B=[0.001, 0.421, 0.578]$ )

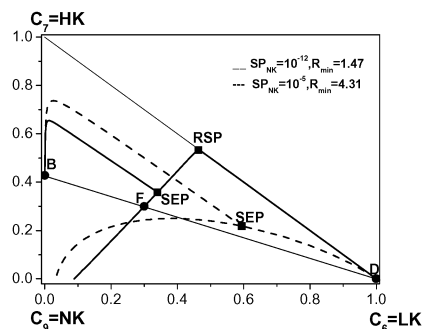


Figure 2: Stripping Pinch for a Sharp Direct Split System ( $x_F=[0.3, 0.3, 0.4]$ ,  $SP_{LK}=999$ ,  $SP_{HK}=0.001$ )

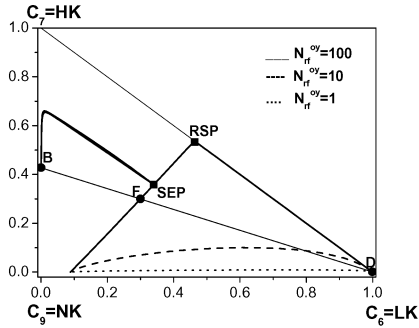


Figure 3: Effect of Mass Transfer on Stripping Pinch for a Sharp Direct Split System ( $x_F=[0.3, 0.3, 0.4]$ ,  $SP_{LK}=999$ ,  $SP_{HK}=0.001$ ,  $R=1.47$ )

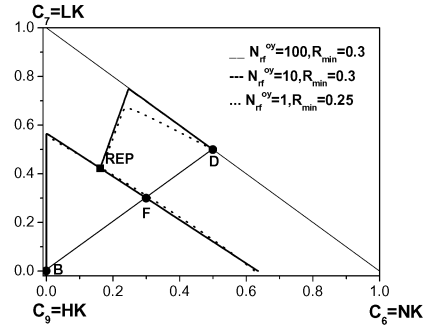


Figure 6: Effect of Mass Transfer on Rectification and Stripping Curves for a Sharp Indirect Split System ( $x_F=[0.3, 0.3, 0.4]$ ,  $SP_{LK}=999$ ,  $SP_{HK}=0.001$ )

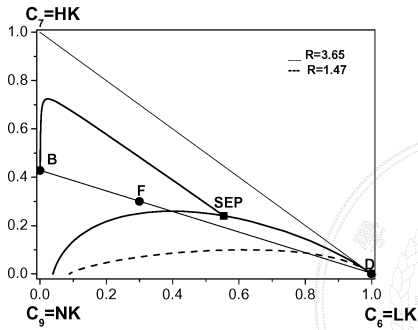


Figure 4: Effect of Mass Transfer on Minimum Reflux for a Sharp Direct Split System ( $x_F=[0.3, 0.3, 0.4]$ ,  $N_{rf}^{oy}=10$ ,  $SP_{LK}=999$ ,  $SP_{HK}=0.001$ ,  $SP_{NK}=10^{-12}$ )

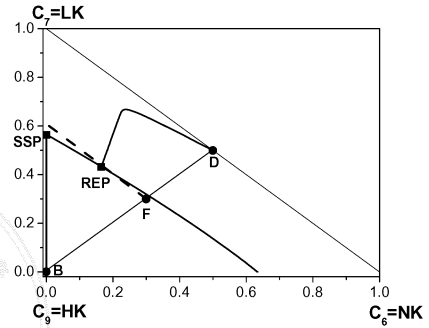


Figure 7: Effect of Mass Transfer on Minimum Reflux for a Sharp Indirect Split System ( $x_F=[0.3, 0.3, 0.4]$ ,  $N_{rf}^{oy}=10$ ,  $SP_{LK}=99$ )

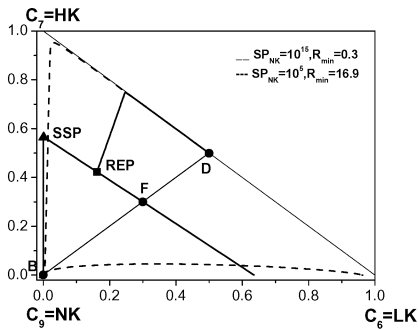


Figure 5: Rectification Pinch Condition for a Sharp Indirect Split System ( $x_F=[0.3, 0.3, 0.4]$ ,  $SP_{LK}=999$ ,  $SP_{HK}=0.001$ )