

Improved Direct and Indirect Systems of Columns for Ternary Distillation

Rakesh Agrawal and Zbigniew T. Fidkowski
Air Products and Chemicals, Inc., Allentown, PA 18195

Separation of a ternary mixture into almost pure components is discussed. Systems of distillation columns, with higher thermodynamic efficiency, are developed from a direct sequence (or indirect sequence) of distillation columns by allowing for two interconnecting streams of the same composition and different enthalpy. This increases the reversibility of distillation in the second column, which results in replacing a portion of the high-temperature boiling duty with a lower-temperature heat in the direct split case. For the indirect split case, the improvement allows a portion of the low-temperature condensing duty to be replaced with a higher-temperature condensation.

Introduction

Agrawal and Herron (1997) have recently analyzed the impact of the thermodynamic state of the feed on the thermodynamic efficiency of a binary distillation column. They noted that the feed state, which maximizes distillation efficiency, may sometimes be naturally available from the unit operation providing the feed for distillation. Such opportunities exist in ternary distillation using direct sequence (DS) or indirect sequence (IS). Consider the separation of a ternary mixture *ABC* into almost pure components (where *A* is the most volatile component and *C* is the least volatile component). In the DS, component *A* is removed as a top product from the first column (split *A/BC*) and the remaining binary mixture *BC* is separated in the second column. There are many ways to transfer mixture *BC* from the first column to the second column. It can be transferred as a liquid stream, a vapor stream, a two-phase stream or as multiple feed streams, each in a different state. In the IS, component *C* is removed first as a bottom product from the first column (split *AB/C*) and then the mixture *AB* is separated in the second column. As for the DS, multiple options for transferring mixture *AB* from the first to the second column are available. These options can be implemented without adding new equipment, but can strongly affect the overall efficiency of the ternary distillation.

The complete set of alternative column configurations for ternary distillation is supposed to be known from exhaustive research over the last five decades (for example, Lockhart,

1947; Rod and Marek, 1959; Petlyuk et al., 1965; Heaven, 1969; Hendry and Hughes, 1972; Hendry et al., 1973; Sargent and Gaminibandara, 1976; Doukas and Luyben, 1978; Hlavacek, 1978; Tedder and Rudd, 1978; King, 1980; Westerberg, 1980; Nishida et al., 1981; Glinos, 1985; Westerberg, 1985; Westerberg and Wahnschaft, 1996). Surprisingly, these alternative column configurations do not include various possibilities of transferring the binary mixture from the first column to the second column of a DS or an IS. Recently, Wankat and Kesler (1993) have briefly mentioned the possible application of columns with two feeds (each feed of the same composition but different enthalpy) in distillation networks, however, all possible ternary configurations were neither drawn nor analyzed.

An important aspect of the synthesis and optimization of distillation systems is the criterion need to compare various alternatives. Some popular objective functions are based on economics (total cost of the plant) (Tedder and Rudd, 1978) or on thermodynamics (thermodynamic efficiency) (Petlyuk et al., 1965; Ho and Keller, 1987; Agrawal and Woodward, 1991). A limitation of cost optimization is that it may not provide general guidance or an understanding of the reasons for selecting one system over the other. This is because costs depend on several factors and some of these factors have nothing to do with distillation. Cost may vary with time, geographical location, or even a supplier. Furthermore, energy and material integration of the distillation process with some other processes or utilities may provide a step change in the cost. Therefore, a configuration with optimum cost selected

Correspondence concerning this article should be addressed to R. Agrawal.

at a certain time and location is not necessarily optimal for some other applications, built somewhere else or at some other time.

Synthesis and optimization strategies based on thermodynamic efficiencies also have limitations. For example, a process optimized for maximum efficiency will generally contain one or more units with zero thermodynamic driving forces and consequently with infinite capital cost. A real process, with the same equipment configuration and with nonzero driving forces, may be only slightly less efficient than the process with maximum thermodynamic efficiency. Accordingly, it has proved very useful to synthesize and optimize processes for maximum thermodynamic efficiency and then to perform energy-capital cost optimization on specific components of the overall process without changing its configuration.

A simple criterion that is somewhat related to economics and thermodynamics simultaneously is the total minimum vapor flow of the distillation system (Rod and Marek, 1959; Fidkowski and Krolikowski, 1987). This criterion has been selected as worthy of study, because it corresponds to reboiler duty (and consequently to heat utility cost and reboiler cost) and to column cross-sectional area (column cost). The limitation of this criterion is that it does not distinguish between the temperatures of utilities, which may lead to thermodynamically inefficient designs.

The objective of this article is to extend the thermodynamic efficiency analysis method of Agrawal and Herron (1997) to ternary distillation and to study the relative merits of new distillation systems derived from conventional direct and indirect sequences. The new systems include some of the options available for transferring a binary mixture from the first column to the second column in *DS* or *IS*, without adding any new reboilers or condensers. Separation of a ternary mixture *ABC* into almost pure components is discussed. We will assume constant relative volatility and constant molar overflow. Column sequences will be compared at minimum reflux conditions. Furthermore, for simplicity we will constrain our discussion to only cases where the feed to the first column is saturated liquid.

Direct and Indirect Sequence with Two Interconnecting Streams

In direct sequence, component *A* is removed as a top product from the first column and the remaining binary mixture *BC* is separated in the second column. In indirect sequence, component *C* is removed first as a bottom product from the first column and then mixture *AB* is separated in the second column. In the literature *DS* and *IS* are always shown with one interconnecting stream between the columns. The thermodynamic state of this stream is not specified, and it is usually assumed to be a liquid. We will denote these systems with a liquid interconnecting stream as *DS_L* and *IS_L*. However, there is no technical restriction on the thermodynamic state of the interconnecting stream. Moreover, we have a complete freedom to choose the thermodynamic state of this stream without adding any new equipment. The product from the first column of *DS* or *IS* can be withdrawn before or after the heat exchanger. Fidkowski and Krolikowski (1987) showed that minimum vapor flow in *DS_L* is lower than in

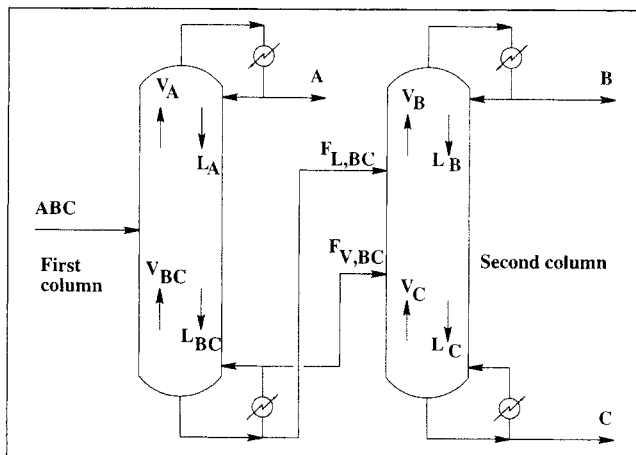


Figure 1. Direct sequence with liquid and vapor interconnecting streams (*DS_{LV}*).

DS_V, and minimum vapor flow in *IS_V* is lower than in *IS_L*. Before making any evaluations, one can postulate that it might be beneficial to have two interconnecting streams between the columns—one liquid and one vapor. For example, in *DS* the liquid feed will be the *BC* mixture withdrawn from the bottom of the first column before it enters the reboiler, and the vapor feed can be withdrawn as a side stream of the first column boilup (system *DS_{LV}* in Figure 1). The beneficial impact of having two feeds on thermodynamic efficiency of a binary distillation column is discussed in detail by Agrawal and Herron (1997). System *IS_{LV}* is shown in Figure 2. Systems *DS_L*, *DS_V* (*IS_L*, *IS_V*) are not shown on separate figures. They can be obtained from *DS_{LV}* (Figure 1) or *IS_{LV}* (Figure 2) by simply deleting either the vapor or the liquid interconnecting stream.

We will refer to particular reboilers and condensers according to the names of species that are boiled and condensed there, for example, we will call the condenser in the first column of *DS* condenser *A*, and we will call the reboiler in the second column of *IS* reboiler *B*. We will use a similar method to refer to the flow rates of the phases in the different sections of the distillation columns, such as if a given

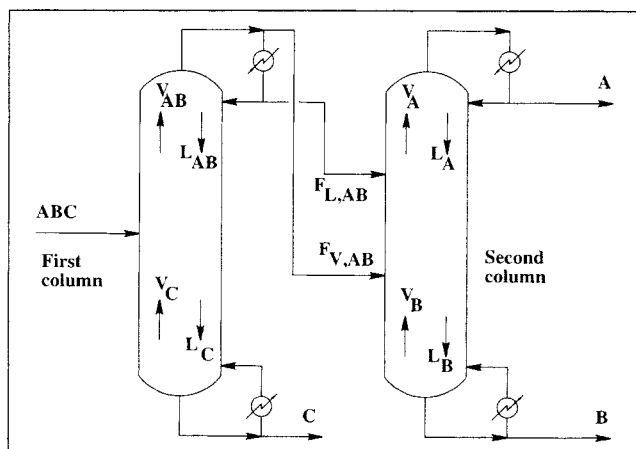


Figure 2. Indirect sequence with liquid and vapor interconnecting streams (*IS_{LV}*).

section is connected to reboiler BC, the vapor flow rate (kmol/s) inside this section will be called V_{BC} . (This notation is also shown in the figures.)

Minimum Vapor Flows in Direct Sequence with Two Interconnecting Streams

The systems are compared at minimum reflux conditions, that is, each column in *DS* (or *IS*) operates at its minimum reflux. Minimum vapor flow in the first column of direct sequence can be calculated by solving Underwood's equation (Underwood, 1948), for the ternary mixture ABC with saturated liquid feed

$$\frac{A\alpha_A}{\alpha_A - \phi} + \frac{B\alpha_B}{\alpha_B - \phi} + \frac{C\alpha_C}{\alpha_C - \phi} = 0 \quad (1)$$

Roots ϕ_1 and ϕ_2 satisfy the following inequality

$$\alpha_C < \phi_2 < \alpha_B < \phi_1 < \alpha_A \quad (2)$$

In all *DS* systems (DS_{LV} , DS_L , DS_V), the minimum vapor flow in the first column is the same, given by equation

$$V_A = V_{BC} = \frac{A\alpha_A}{\alpha_A - \phi_1} \quad (3)$$

Minimum vapor flows in the second column in DS_{LV} were calculated assuming pinch conditions at both (vapor and liquid) feed locations as shown on the McCabe-Thiele diagram in Figure 3

$$V_B = \frac{B\alpha_B + C\alpha_C}{\alpha_B - \alpha_C} \quad (4)$$

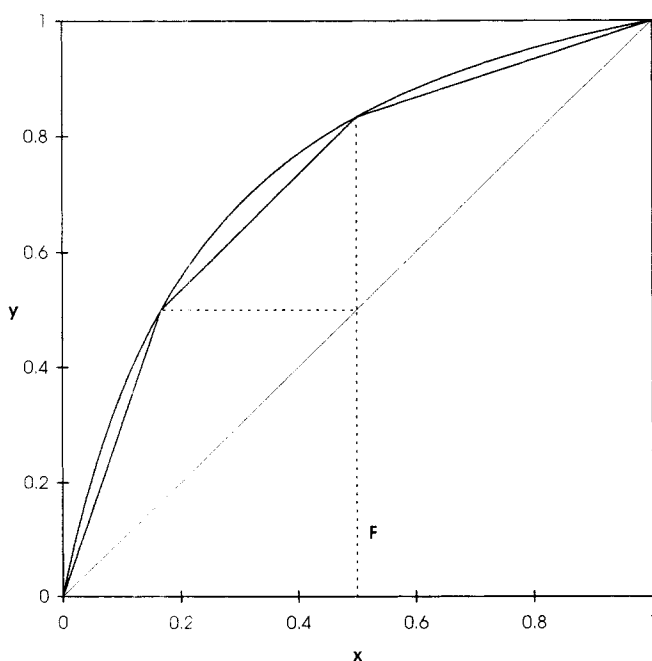


Figure 3. McCabe-Thiele diagram for the second column in DS_{LV} system at minimum reflux.

$$V_C = \frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} \quad (5)$$

From the equations above, we can calculate the flow rates of the vapor and liquid feed to the second column of DS_{LV} at minimum reflux

$$F_{V,BC} = V_B - V_C = B \quad (6)$$

$$F_{L,BC} = B + C - F_{V,BC} = C \quad (7)$$

Note that the column with liquid and vapor feed of the same composition, separating a binary mixture *BC* into pure components, has an interesting property at minimum reflux (with pinches at both feed locations). The flow rate of the vapor feed is equal to the flow rate of the more volatile component *B*, and the flow rate of the liquid feed is equal to the flow rate of the less volatile component *C*.

Condensing and boiling duties in *DS* systems, at minimum reflux conditions, are summarized in Table 1. By comparing these duties we can draw the following conclusions:

- Total boilup at minimum reflux is the same in DS_L and DS_{LV} ; however, DS_{LV} requires less high-temperature utility (at temperature T_C) and more lower-temperature utility (at temperature T_{BC}). The amount of duty shifted from reboiler *C* to reboiler *BC* (in terms of vapor flow) is equal to *B*. Therefore, a direct sequence with two interconnecting streams will be much more efficient than DS_L when the difference between T_C and T_{BC} is significant, or, when the feed contains a considerable amount of component *B*. In a given application, DS_{LV} could be attractive when the cost of heat at T_C is significantly greater than the cost of heat at T_{BC} .

- DS_V requires more total boilup than DS_{LV} and DS_L ; however, the heat duty in reboiler *C* in DS_V is lower than in DS_L (the difference is equal to *B*), but the heat duty in reboiler *BC* is higher (difference of *B* + *C*). It is probably recommended instead of DS_L when the high-temperature utility is expensive and amount of component *C* is small.

- Condensing duties in DS_{LV} and DS_L are the same and condensing duty in the second column of DS_V is higher (the difference is equal to *C*).

A similar discussion can be carried out for *IS* systems. Equations for minimum vapor flows in the remaining column sequences are given in Appendix A.

Thermodynamic Efficiency of Direct Sequence and Indirect Sequence

In order to compare various column configurations we use the thermodynamic efficiency method developed by Agrawal and Herron (1997). The authors used the Clausius-Clapeyron equation to express the effect of temperature difference between the top and bottom of the distillation column on the efficiency, which results in a simple equation containing only relative volatilities and compositions. Explicit knowledge of temperatures is not required. The authors verified the method by comparing its results with detailed calculations for various real, nearly ideal binary mixtures, achieving satisfactory agreement, despite all the simplifying assumptions. The other advantage of the method is that it provides the efficiency of the distillation process itself, without considering whether the

Table 1. Condensing and Boiling Duties (in Terms of Vapor Flows) in Direct Split Systems at Minimum Reflux Conditions

	DS_{LV}	DS_L	DS_V
Reboiler BC	$\frac{A\alpha_A}{\alpha_A - \phi_1} + B$	$\frac{A\alpha_A}{\alpha_A - \phi_1}$	$\frac{A\alpha_A}{\alpha_A - \phi_1} + B + C$
Reboiler C	$\frac{(B+C)\alpha_C}{\alpha_B - \alpha_C}$	$\frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B$	$\frac{(B+C)\alpha_C}{\alpha_B - \alpha_C}$
Total Boiling Duty	$\frac{A\alpha_A}{\alpha_A - \phi_1} + \frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B$	$\frac{A\alpha_A}{\alpha_A - \phi_1} + \frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B$	$\frac{A\alpha_A}{\alpha_A - \phi_1} + \frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B + C$
Condenser A	$\frac{A\alpha_A}{\alpha_A - \phi_1}$	$\frac{A\alpha_A}{\alpha_A - \phi_1}$	$\frac{A\alpha_A}{\alpha_A - \phi_1}$
Condenser B	$\frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B$	$\frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B$	$\frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B + C$
Total Cond. Duty	$\frac{A\alpha_A}{\alpha_A - \phi_1} + \frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B$	$\frac{A\alpha_A}{\alpha_A - \phi_1} + \frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B$	$\frac{A\alpha_A}{\alpha_A - \phi_1} + \frac{(B+C)\alpha_C}{\alpha_B - \alpha_C} + B + C$

heat rejected to the condensers is reused or not. This issue has often given rise to confusion in various definitions of distillation efficiency where minimum work of separation is compared to the heat supplied to the reboiler. Such a definition implicitly assumes that this heat, once it has entered the reboiler, is lost for all practical purposes and cannot be reused (for example, Ho and Keller, 1987). The thermodynamic efficiency of distillation calculated in such a way is small (usually in the range of 10–20%) and can never be equal to 100%, even for a fully reversible process. In another words the distillation process itself is being “blamed” for the fact that the degraded heat rejected in the condenser is not reused. For processes where this is not the case, for example, in highly integrated cryogenic processes, this definition (a ratio of minimum work of separation to reboiler heat duty) is not useful. Recognizing this fact, Agrawal and Herron (1997) used the following definition of distillation thermodynamic efficiency

$$\eta = \frac{\text{Minimum Work of Separation}}{\text{Minimum Work of Separation} + \text{Exergy Loss}} \quad (8)$$

Obviously, the value of this efficiency can reach 100% for a fully reversible process. Exergy loss is calculated by the exergy balance, taking into account all the streams entering and leaving a control volume containing the distillation column system, but excluding the heat exchangers. The way of calculating the exergy loss for DS_{LV} system is shown below

$$\Delta \epsilon_{\text{loss}} = \epsilon_{\text{in}} - \epsilon_{\text{out}} \quad (9)$$

where, assuming liquid feed and a unit feed flow rate ($F = 1$ kmol/s)

$$\epsilon_{\text{in}} = e_F + L_A e_A + L_B e_B + (V_{BC} + F_{V,BC}) E_{BC} + V_C E_C \quad (10)$$

$$\epsilon_{\text{out}} = V_A E_A + V_B E_B + (L_{BC} - F_{L,BC}) e_{BC} + L_C e_C \quad (11)$$

We eliminate all the liquid flows in Eqs. 10 and 11 using

$$L_A = V_A - A \quad (12)$$

$$L_B = V_B - B \quad (13)$$

$$L_C = V_C + C \quad (14)$$

$$L_{BC} = V_{BC} + B + C \quad (15)$$

From Eqs. 9–15 we have

$$\Delta \epsilon_{\text{loss}} = e_F - (Ae_A + Be_B + Ce_C) + V_A(e_A - E_A) + V_B(e_B - E_B) - V_C(e_C - E_C) - (V_{BC} + F_{V,BC})(e_{BC} - E_{BC}) \quad (16)$$

Feed exergy is the sum of exergy of mixing and the thermal component

$$e_F = RT_0 \sum_{i=A,B,C} z_i \ln z_i + e_F^T \quad (17)$$

Utilizing Eq. 17, the first two components of Eq. 16 can be rewritten as

$$e_F - (Ae_A + Be_B + Ce_C) = RT_0 \sum_{i=A,B,C} z_i \ln z_i + \delta + \mu \quad (18)$$

where

$$\delta = E_F^T - (AE_A + BE_B + CE_C) \quad (19)$$

$$\mu = (e_F - E_F) - A(e_A - E_A) - B(e_B - E_B) - C(e_C - E_C) \quad (20)$$

We may now assume that the thermal component of the exergy of the vapor mixture is approximately equal to the sum of thermal exergies of pure components in a saturated vapor state and so the term δ is negligibly small.

For each pure component i ($i = A, B, C$)

$$e_i - E_i = \Delta H \left(\frac{T_0}{T_i} - 1 \right) \quad (21)$$

where T_i is the constant temperature of phase change for component i and ΔH is the (positive) heat of vaporization. Because we have assumed constant molar overflow, the heat of vaporization ΔH (kJ/kmol) is the same for all components.

For a mixture

$$e_{\text{mix}} - E_{\text{mix}} = \Delta H \int_{q=0}^{q=1} \left(\frac{T_0}{T_{\text{mix}}} - 1 \right) dq \quad (22)$$

where T_{mix} is the variable temperature of the mixture, as it condenses from vapor state ($q=0$) to liquid state ($q=1$).

From Eqs. 20–22, we obtain

$$\mu = \Delta HT_0 \int_{q=0}^{q=1} \left[A \left(\frac{1}{T_F} - \frac{1}{T_A} \right) + B \left(\frac{1}{T_F} - \frac{1}{T_B} \right) + C \left(\frac{1}{T_F} - \frac{1}{T_C} \right) \right] dq \quad (23)$$

Using the Clausius-Clapeyron equation, Eq. 23 can be rewritten in terms of equilibrium coefficients of components (K_A , K_B , K_C) in ternary mixture ABC

$$\mu = RT_0 \int_{q=0}^{q=1} \left[A \ln \frac{1}{K_A} + B \ln \frac{1}{K_B} + C \ln \frac{1}{K_C} \right] dq \quad (24)$$

The above integrals can be numerically calculated. The relevant equations are summarized in Appendix B. After extensive calculations for various mixtures, we determined numerically that for a liquid feed

$$\mu \approx 0 \quad (25)$$

From Eqs. 16, 18 and 25, we obtain

$$\Delta \epsilon_{\text{loss}} = RT_0 \sum_{i=A,B,C} z_i \ln z_i + V_A(e_A - E_A) + V_B(e_B - E_B) - V_C(e_C - E_C) - (V_{BC} + F_{V,BC})(e_{BC} - E_{BC}) \quad (26)$$

Eliminating V_C using the following balance

$$V_C = V_A + V_B - (V_{BC} + F_{V,BC}) \quad (27)$$

and utilizing Eqs. 21 and 22, we express exergy loss as

$$\Delta \epsilon_{\text{loss}} = RT_0 \sum_{i=A,B,C} z_i \ln z_i + V_A \Delta HT_0 \left(\frac{1}{T_A} - \frac{1}{T_C} \right) + V_B \Delta HT_0 \left(\frac{1}{T_B} - \frac{1}{T_C} \right) - (V_{BC} + F_{V,BC}) \Delta HT_0 \int_{q=0}^{q=1} \left(\frac{1}{T_{BC}} - \frac{1}{T_C} \right) dq \quad (28)$$

Eliminating temperatures from Clausius-Clapeyron equation (see also Agrawal and Herron, 1997), we obtain the final expression for exergy loss

$$\Delta \epsilon_{\text{loss}} = RT_0 \left[\sum_{i=A,B,C} z_i \ln z_i + V_A \ln \alpha_A + V_B \ln \alpha_B - (V_{BC} + F_{V,BC}) \int_{q=0}^{q=1} \left(\ln \frac{1}{K_{C,BC}} \right) dq \right] \quad (29)$$

where α_A , α_B are volatilities of components A and B , relative to component C , and $K_{C,BC}$ is the equilibrium coefficient of component C in binary mixture BC . Equation 29 can be used to calculate the exergy loss in DS_{LV} at any value of reflux ratio. At minimum reflux conditions, all the flows are calculated from Eqs. 3–6. From Eqs. 6, 8 and 29, the final formula for thermodynamic efficiency of DS_{LV} is given by Eq. 30

$$\eta_{DS,LV} = \frac{- \sum_{i=A,B,C} z_i \ln z_i}{V_A \ln \alpha_A + V_B \ln \alpha_B - (V_{BC} + B) \int_{q=0}^1 \ln \frac{1}{K_{C,BC}} dq} \quad (30)$$

Equations for thermodynamic efficiency of the other discussed distillation systems at minimum reflux were obtained in a similar way. The final expressions are listed below

$$\eta_{DS,L} = \frac{- \sum_{i=A,B,C} z_i \ln z_i}{V_A \ln \alpha_A + V_B \ln \alpha_B - V_{BC} \int_{q=0}^1 \ln \frac{1}{K_{C,BC}} dq} \quad (31)$$

$$\eta_{DS,V} = \frac{- \sum_{i=A,B,C} z_i \ln z_i}{V_A \ln \alpha_A + V_B \ln \alpha_B - (V_{BC} + B + C) \int_{q=0}^1 \ln \frac{1}{K_{C,BC}} dq} \quad (32)$$

$\eta_{IS,LV}$

$$= \frac{- \sum_{i=A,B,C} z_i \ln z_i}{V_A \ln \alpha_A - V_B \ln \alpha_B + (V_{AB} - A) \left(\ln \alpha_B + \int_{q=0}^1 \ln \frac{1}{K_{B,AB}} dq \right)} \quad (33)$$

$$\eta_{IS,L} = \frac{- \sum_{i=A,B,C} z_i \ln z_i}{V_A \ln \alpha_A - V_B \ln \alpha_B + V_{AB} \left(\ln \alpha_B + \int_{q=0}^1 \ln \frac{1}{K_{B,AB}} dq \right)} \quad (34)$$

$$\eta_{IS,V} = \frac{-\sum_{i=A,B,C} z_i \ln z_i}{V_A \ln \alpha_A - V_B \ln \alpha_B + (V_{AB} - A - B) \left(\ln \alpha_B + \int_{q=0}^1 \ln \frac{1}{K_{B,AB}} dq \right)} \quad (35)$$

Minimum vapor flows are listed in Appendix A. Note that the minimum vapor flows in the different systems, although denoted by the same symbol (such as V_A, V_B, V_{AB}, V_{BC}), generally have different values.

We can use the equations above to compare thermodynamic efficiencies of discussed systems. For example, let us compare the thermodynamic efficiency of DS_{LV} with that of DS_L . Note that minimum vapor flows V_A, V_B and V_{BC} are the same in both systems. From Eqs. 30 and 31, we have

$$-\sum_{i=A,B,C} z_i \ln z_i \left(\frac{1}{\eta_{DS,L}} - \frac{1}{\eta_{DS,LV}} \right) = B \int_{q=0}^1 \ln \frac{1}{K_{C,BC}} dq > 0 \quad (36)$$

which gives

$$\eta_{DS,LV} > \eta_{DS,L} \quad (37)$$

Now let us compare DS_V with DS_{LV} . Note, that the minimum vapor flows V_B are different in both systems (Eqs. 4 and A2). From Eqs. 4, 30, 32 and A2 we have

$$\begin{aligned} -\sum_{i=A,B,C} z_i \ln z_i \left(\frac{1}{\eta_{DS,V}} - \frac{1}{\eta_{DS,LV}} \right) &= C \ln \alpha_B - C \int_{q=0}^1 \ln \frac{1}{K_{C,BC}} dq \\ &= C \frac{\Delta H}{R} \left[\left(\frac{1}{T_B} - \frac{1}{T_C} \right) - \int_{q=0}^1 \left(\frac{1}{T_{BC}} - \frac{1}{T_C} \right) dq \right] \\ &= C \frac{\Delta H}{R} \int_{q=0}^1 \left(\frac{1}{T_B} - \frac{1}{T_{BC}} \right) dq > 0 \quad (38) \end{aligned}$$

which gives

$$\eta_{DS,LV} > \eta_{DS,V} \quad (39)$$

Similar proof can be given for indirect splits. As expected, thermodynamic efficiency of DS_{LV} (IS_{LV}) is always higher than DS_L or DS_V (IS_L or IS_V).

An example of thermodynamic efficiencies for DS_L, DS_V and DS_{LV} is given in Figure 4. We chose an equimolar feed with $\alpha_A/\alpha_B = 4.0$ and α_B varied between 1.05 and 5.0. Efficiencies of separation are similar for $\alpha_B = 1.05$ (all equal to about 68%). As α_B increases, the difference between the thermodynamic efficiency for DS_{LV} and for the direct sequences with a single interconnecting stream increases up to about eight percentage points. Since the base level of effi-

ciency is about 60%, this corresponds to a potential savings in exergy for distillation of 12–15%. Note that in this example problem, feed to the second column is an equimolar mixture of B and C and, therefore, $\eta_{DS,L}$ is equal to $\eta_{DS,V}$. Generally, for other feed compositions, these two efficiencies will have different values.

Conclusions

The efficiencies of modified direct and indirect ternary distillation sequences with two interconnecting streams of the same composition and different thermodynamic state have not previously been analyzed. The new distillation systems are more thermodynamically efficient than the corresponding conventional direct and indirect splits with only one interconnecting stream. The improvement in case of a direct split results in a reduction of high-temperature heating utility at the expense of a lower-temperature heating utility. For an indirect split, a portion of the colder condensing utility can be replaced with a warmer one. If it is preferred to use the same heating (cooling) utility for both columns, the total heat-exchanger area can be reduced in the new systems. The drawback of the new systems is that a greater number of stages (in comparison with conventional direct or indirect systems) will be required in the second (binary separation) column.

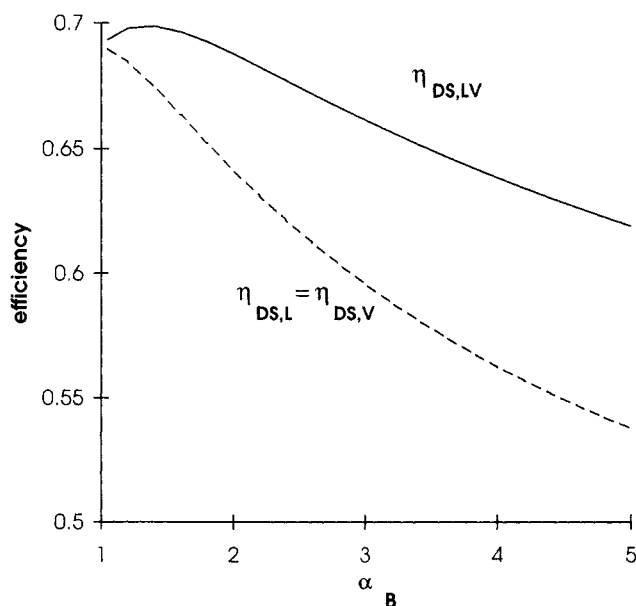


Figure 4. Example of thermodynamic efficiency for DS_{LV}, DS_L and DS_V for $\alpha_A/\alpha_B = 4.0$ and $z_A = z_B = z_C$.

Notation

A, B, C = flow rate of component A, B, C in the feed, kmol/s
 e = exergy of liquid phase, kJ/kmol
 E = exergy of vapor phase, kJ/kmol
 L = liquid flow rate, kmol/s
 q = fraction of liquid
 R = gas constant, 8.314 kJ/(kmol · K)
 x = mole fraction in liquid phase
 y = mole fraction in vapor phase
 z = mole fraction in feed
 ϵ = exergy, kJ/kmol

Subscripts and superscript

A, B, C = component A, B, C , or, when used with L or V , section of the column where A, B or C is produced
 AB = mixture of components AB , or, when used with L or V , section of the column where mixture AB is produced
 BC = mixture of components BC , or, when used with L or V , section of the column where mixture BC is produced
 T = thermal component of exergy
 0 = ambient conditions

Literature Cited

- Agrawal R., and D. M. Herron, "Optimal Thermodynamic Feed Conditions for Distillation of Ideal Binary Mixtures," *AIChE J.*, **43**, 2984 (1997).
 Agrawal, R., and D. W. Woodward, "Efficient Cryogenic Nitrogen Generators: An Exergy Analysis," *Gas Sep. Purif.*, **5**, 139 (1991).
 Doukas, N., and W. L. Luyben, "Economics of Alternative Distillation Configurations for Separation of Ternary Mixtures," *Ind. Eng. Chem. Process Des. Dev.*, **17**, 273 (1978).
 Fidkowski, Z., and L. Krolkowski, "Minimum Energy Requirements of Thermally Coupled Distillation Systems," *AIChE J.*, **33**, 643 (1987).
 Glinos, K., "A Global Approach to the Preliminary Design and Synthesis of Distillation Trains," PhD Thesis, Univ. of Massachusetts at Amherst (1985).
 Heaven, D. L., "Optimum Sequencing of Distillation Columns in Multicomponent Fractionation," MS Thesis, Univ. of California Berkeley (1969).
 Hendry, J. E. and R. R. Hughes, "Generating Separation Process Flowsheets," *Chem. Eng. Prog.*, **68**, 69 (1972).
 Hendry, J. E., D. F. Rudd, and J. D. Seader, "Synthesis in the Design of Chemical Processes," *AIChE J.*, **19**, 1 (1973).
 Hlavacek, V., "Synthesis in the Design of Chemical Processes," *Comp. Chem. Eng.*, **2**, 67 (1978).
 Ho, F. G., and G. E. Keller II, "Process Integration," *Recent Developments in Chemical Process and Plant Design*, Y. A. Liu, H. A. McGee, Jr., and W. R. Epperly, eds., Wiley, New York, p. 101 (1987).
 King, C. J., *Separation Processes*, McGraw-Hill, New York, p. 711 (1980).
 Lockhart, F. J., "Multi-Column Distillation of Natural Gasoline," *Petrol. Refiner*, **26**, 104 (1947).
 Nishida, N., G. Stephanopoulos, and A. W. Westerberg, "A Review of Process Synthesis," *AIChE J.*, **27**, 321 (1981).
 Petlyuk, F. B., V. M. Platonov, and D. M. Slavinskii, "Thermodynamically Optimal Method for Separating Multicomponent Mixtures," *Int. Chem. Eng.*, **5**, 555 (1965).
 Rod, V., and J. Marek, "Separation Sequences in Multicomponent Rectification," *Coll. Czech. Chem. Commun.*, **24**, 3240 (1959).
 Sargent, R. W. H., and K. Gaminibandara, "Optimum Design of Plate Distillation Columns," *Optimization in Action*, L. C. W. Dixon, ed., Academic Press, New York, p. 267 (1976).
 Tedder D. W., and D. F. Rudd, "Parametric Studies in Industrial Distillation," *AIChE J.*, **24**, 303 (1978).
 Underwood, A. J. V., "Fractional Distillation of Multicomponent Mixtures," *Chem. Eng. Prog.*, **44**, 603 (1948).
 Wankat, P. C., and D. P. Kessler, "Two-Feed Distillation: Same-Composition Feeds with Different Enthalpies," *Ind. Eng. Chem. Res.*, **32**, 3061 (1993).

- Westerberg, A. W., "A Review of Process Synthesis," *Computer Applications to Chemical Engineering Process Design and Simulation*, Amer. Chem. Soc. Symp. Ser., No. 124, 54 (1980).
 Westerberg, A. W., "The Synthesis of Distillation-Based Separation Systems," *Comp. Chem. Eng.*, **9**, 421 (1985).
 Westerberg, A. W., and O. Wahnschaft, "Synthesis of Distillation-Based Separation Systems," *Advances in Chemical Engineering*, J. L. Anderson, ed., Academic Press, New York, Vol. 23, 63 (1996).

Appendix A: Minimum Vapor Flows

Minimum vapor flows for the remaining systems are as follows

For DS_L

$$V_B = V_C = \frac{B\alpha_B + C\alpha_C}{\alpha_B - \alpha_C} \quad (A1)$$

For DS_V

$$V_B = \frac{(B + C)\alpha_B}{\alpha_B - \alpha_C} \quad (A2)$$

$$V_C = \frac{(B + C)\alpha_C}{\alpha_B - \alpha_C} \quad (A3)$$

For IS_{LV} , IS_L and IS_V (first column)

$$V_C = V_{AB} = \frac{A\alpha_A}{\alpha_A - \phi_2} + \frac{B\alpha_B}{\alpha_B - \phi_2} \quad (A4)$$

For IS_{LV}

$$V_A = \frac{A\alpha_A + B\alpha_B}{\alpha_A - \alpha_B} \quad (A5)$$

$$V_B = \frac{(A + B)\alpha_B}{\alpha_A - \alpha_B} \quad (A6)$$

$$F_{V,AB} = V_A - V_B = A \quad (A7)$$

$$F_{L,AB} = A + B - F_{V,AB} = B \quad (A8)$$

For IS_L

$$V_A = V_B = \frac{A\alpha_A + B\alpha_B}{\alpha_A - \alpha_B} \quad (A9)$$

For IS_V

$$V_A = \frac{(A + B)\alpha_A}{\alpha_A - \alpha_B} \quad (A10)$$

$$V_B = \frac{(A + B)\alpha_B}{\alpha_A - \alpha_B} \quad (A11)$$

Appendix B: Calculation of Integrals in Eq. 23

From the Clausius-Clapeyron relationships and the definition of relative volatility it follows

$$\Delta HT_0 \left(\frac{1}{T_F} - \frac{1}{T_A} \right) = RT_0 \ln \frac{1}{K_A}$$

$$= RT_0 \ln \left[\frac{\alpha_A x_A + \alpha_B x_B + x_C}{\alpha_A} \right] \quad (\text{B1})$$

$$\Delta HT_0 \left(\frac{1}{T_F} - \frac{1}{T_B} \right) = RT_0 \ln \frac{1}{K_B}$$

$$= RT_0 \ln \left[\frac{\alpha_A x_A + \alpha_B x_B + x_C}{\alpha_B} \right] \quad (\text{B2})$$

$$\Delta HT_0 \left(\frac{1}{T_F} - \frac{1}{T_C} \right) = RT_0 \ln \frac{1}{K_C}$$

$$= RT_0 \ln [\alpha_A x_A + \alpha_B x_B + x_C] \quad (\text{B3})$$

In order to solve the integrals, x_A , x_B and x_C need to be calculated as functions of q . This is achieved by writing component balance equations for a given q .

$$z_A = qx_A + (1-q) \frac{\alpha_A x_A}{\alpha_A x_A + \alpha_B x_B + x_C} \quad (\text{B4})$$

$$z_B = qx_B + (1-q) \frac{\alpha_B x_B}{\alpha_A x_A + \alpha_B x_B + x_C} \quad (\text{B5})$$

also

$$x_A + x_B + x_C = 1 \quad (\text{B6})$$

Equations B4–B6 can be manipulated to give

$$x_B = \frac{\alpha_A z_B x_A}{\alpha_B z_A + q(\alpha_A - \alpha_B)x_A} \quad (\text{B7})$$

$$q^2(\alpha_A - 1)(\alpha_A - \alpha_B)x_A^3 + \{q(\alpha_A - 1)\alpha_B z_A + q(\alpha_A - \alpha_B) \\ \times [q + (1-q)\alpha_A + z_A(1 - \alpha_A)]\}x_A^2 + \{\alpha_B z_A[q + (1-q)\alpha_A \\ + z_A(1 - \alpha_A)] + z_A(1 - \alpha_B)\alpha_A z_B - z_A q(\alpha_A - \alpha_B)\}x_A \\ - \alpha_B z_A^2 = 0 \quad (\text{B8})$$

Equation B8 is cubic in x_A and the desired root is readily calculated; x_B and x_C may then be calculated from Eqs. B7 and B6.

Manuscript received Aug. 18, 1997, and revision received Feb. 2, 1998.