Optimal Thermodynamic Feed Conditions for Distillation of Ideal Binary Mixtures

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Optimal thermodynamic feed conditions for distillation of ideal binary mixtures are identified through thermodynamic efficiency analysis of distillation columns. Due to simplifying assumptions, temperatures do not appear explicitly in the final thermodynamic efficiency equations. These equations are found to be functions of only feed composition, the thermodynamic state of the feed, and the relative volatility of the more volatile component A with respect to component B! When a single one-phase feed, AB, is used, the preferred state of the feed is all liquid when the amount of heavy component B is greater than 50% and is all vapor when the amount of volatile component A is greater than 50%. For a single two-phase feed, a simple heuristic is presented to adjust the liquid fraction of a given feed to maximize the thermodynamic efficiency of the distillation column. For most binary mixtures, two feeds with the same composition, but one saturated vapor and the other saturated liquid, can improve a distillation column's efficiency substantially. The maximum benefit is obtained for a 50−50 mixture. This two-feed case is less efficient than the single two-phase feed case when the relative volatilities exceed certain calculable values.

Introduction

Distillation processes take heat from a heat source and generally reject most of this heat to a heat sink while performing the task of separation. A key question of interest is to find how efficient a distillation column is at converting thermal exergy to work of separation. For this reason, several studies have applied exergy analysis to distillation columns (Itoh et al., 1980; Kaiser and Gourlia, 1985; Taprap and Ishida, 1996). Analysis of exergy loss in a distillation column can often provide useful understanding and insights, which can lead to a better design of a distillation system (Fitzmorris and Mah, 1980). This is particularly true for cryogenic distillations, as they operate well below ambient temperatures and use work rather than heat to perform a given separation. Therefore, exergy analysis of distillation columns is widely used for gas separation (Atkinson, 1987; Atkinson and Rathbone, 1990; Agrawal and Woodward, 1991). Exergy analysis is also useful when the heat supplied to a distillation column or the heat rejected from a distillation column is to be integrated with another unit operation within the plant.

Exergy analysis has been applied to distillation columns in different forms. Taprap and Ishida (1996) break overall exergy loss in a distillation column into individual components and present results on energy-utilization diagrams. These diagrams identify the amount of energy transformation and exergy loss of individual process steps. Atkinson (1987) developed a method that produces a graphical representation of losses throughout a distillation column—the magnitude of losses and useful work performed can be seen at a glance from these diagrams. Several definitions of efficiency based on minimum work and exergy losses have also been proposed to analyze distillation columns (Linhoff and Smith, 1979; Malykh, 1989; Agrawal and Woodward, 1991). A proper definition of exergy efficiency, together with an evaluation of exergy losses, can be very beneficial in the analysis of distillation columns to identify inefficiencies and to suggest potential improvements. Furthermore, the proper use of thermodynamic efficiency allows a meaningful comparison of distillation with other competing separation technologies. This can often provide an insight for the synergies that may exist for hybrid separation processes using distillation.

In spite of the abundance of literature on exergy losses in distillation columns, it is surprising that very little information is available on the impact of feed condition on the thermodynamic efficiency of a simple binary distillation column.

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Quite often, the feed to a binary distillation column originates from another distillation column or another unit operation in a process that presents the real potential of obtaining this feed either as a saturated liquid, a saturated vapor, or a two-phase stream. If the impact of the feed condition on the efficiency of binary distillation column were known *a priori*, the opportunity could then be exploited by collecting the feed at its optimum thermodynamic condition from the unit operation that produced the feed. In this article, ideal binary distillation columns are analyzed using an efficiency based on exergy losses. The key question answered is: How does the efficiency of an ideal binary distillation column depend on the feed composition, the feed's thermodynamic state, and the relative volatility of its components?

Another question addressed in this article is whether or not it is worthwhile to have more than one feed, each having the same composition but with different thermodynamic states. The advantages of having two feeds with the same composition but different enthalpies have been known in ternary air distillation for some time, and several air-separation plants that exploit this concept are currently in operation (Fidkowski and Agrawal, 1995). Recently, Wankat and Kessler (1993) have suggested the use of two feeds with the same composition but different enthalpies to improve the performance of a binary distillation column. Such two-feed cases generally allow the effective use of waste heat effectively and should be useful in heat-integrated plants. In this article, we have quantified the improvement in efficiency for binary distillation when two feeds, each of the same composition but different enthalpies, are fed to a distillation column. This is done for several feed compositions and relative volatilities.

Efficiency of a Binary Distillation Column

In the literature, distillation efficiencies based on comparing minimum work of separation with the heat supplied to the reboiler are suggested; however, such efficiencies have limitations that are discussed in the Appendix. The following definition of thermodynamic efficiency is used in this article (Agrawal and Woodward, 1991):

$$\eta = \frac{\text{minimum work of separation}}{\text{total exergy loss} + \text{minimum work of separation}}. \quad (1)$$

The denominator in this equation is the actual total work used to achieve the desired separation. In order to calculate the efficiency of the distillation column alone, only the exergies of the streams entering and leaving the distillation columns will be considered. Exergy losses in reboilers, condensers, and any other heat exchangers are excluded from the control volume under consideration.

Consider a distillation column, separating a binary mixture AB into pure products, as shown in Figure 1. Two feeds, each of the same overall composition but different enthalpies, are fed to this distillation column. This approach is adopted first to derive a more generalized expression of efficiency that will be used later to analyze specific cases of only one feed to the distillation column. Total exergy loss around the distillation column is given by

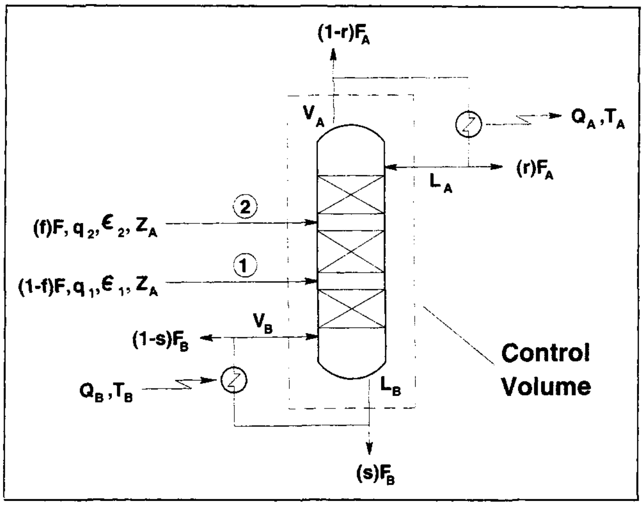

Figure 1. Binary distillation column.

The control volume used to calculate thermodynamic efficiency is indicated ($q_1 < q_2$).

$$\Delta\epsilon_{\text{loss}} = \epsilon_1 + \epsilon_2 - (V_A E_A - L_A e_A) - (L_B e_B - V_B E_B), \quad (2)$$

where ϵ_1 and ϵ_2 are the exergies of feed streams 1 and 2; E is the molar exergy of a saturated vapor; e is the molar exergy of a saturated liquid; and subscripts A and B refer to components A and B, respectively. In order to calculate various exergy terms, some additional simplifying assumptions are made: no pressure drop losses, ideal vapor phase, ideal liquid solution, latent heats are equal for both components and independent of temperature (over the operating temperature range of the distillation column), and the vapor pressure of a component is given by the Clausius–Clapeyron equation. These assumptions also imply that the mixture to be separated is an ideal binary mixture of constant relative volatility. The derivation is based on the total feed flow of one mole ($F = 1$ and f is the fraction of the total feed in stream 2) and complete separation of the feed into pure A and pure B. A mass balance in and around the distillation column gives:

$$V_A = L_A + F_A \quad (3)$$

$$V_B = L_B - F_B \quad (4)$$

$$L_B = L_A + fq_2 + (1-f)q_1 \quad (5)$$

where q_1 and q_2 are the qualities (liquid fraction) of feeds 1 and 2.

In order to calculate the exergy of the feed, exergy is divided into physical and chemical components. For the case under consideration, which does not entail chemical reaction, the chemical component is simply the exergy due to mixing at reference temperature and pressure. Let pure A and pure B in vapor state at reference temperature T_o and reference pressure P be the reference state. Since it has been assumed that there are no pressure drops, for simplicity, reference pressure is chosen to be the pressure of the distillation column. Reference temperature T_o can be the ambient temperature. The exergy of the feed streams is given by (Kotas, 1985; Agrawal and Woodward, 1991):

$$\epsilon_1 = (1-f)\left[RT_o(Z_A \ln Z_A + Z_B \ln Z_B) + E_F^T + \Delta H \int_0^{q_1}\left(\frac{T_o}{T}-1\right)dq\right] \quad (6)$$

$$\epsilon_2 = f\left[RT_o(Z_A \ln Z_A + Z_B \ln Z_B) + E_F^T + \Delta H \int_0^{q_2}\left(\frac{T_o}{T}-1\right)dq\right], \quad (7)$$

where Z_A and Z_B are overall mole fractions of components A and B in the feed; ΔH is molar latent heat; and E_F^T is thermal exergy component of the feed at the dewpoint temperature. In Eqs. 6 and 7, the first term on the righthand side is the exergy due to mixing of vapor streams at T_o and P, the second term is the exergy of bringing this mixed vapor stream from T_o and P to the dewpoint temperature at P, and the last term is the exergy due to the partial condensation of this feed. When pure A or B is condensed, the change in exergy can be calculated from:

$$e_A - E_A = \Delta H\left[\frac{T_o}{T_A}-1\right] \quad (8)$$

$$e_B - E_B = \Delta H\left[\frac{T_o}{T_B}-1\right]. \quad (9)$$

The minimum work of separation, $W_{\min}$, is given by

$$W_{\min} = -RT_o(Z_A \ln Z_A + Z_B \ln Z_B). \quad (10)$$

Substitution of Eqs. 3 through 9 in Eq. 2, and after some algebraic manipulation, substituting the resulting equation along with Eq. 10 in Eq. 1 provides:

$$\eta = \frac{-RT_o(Z_A \ln Z_A + Z_B \ln Z_B)}{\delta + \Delta H T_o \int_0^{q_1}\left[\frac{1}{T}-\frac{1}{T_A}\right]dq + f\Delta H T_o \int_{q_1}^{q_2}\left[\frac{1}{T}-\frac{1}{T_A}\right]dq + L_B \Delta H T_o\left[\frac{1}{T_A}-\frac{1}{T_B}\right]}, \quad (11)$$

where

$$\delta = E_F^T - F_A E_A - F_B E_B. \quad (12)$$

The term δ is the difference between the thermal exergies of saturated vapor feed and those of saturated vapors A and B with flow rates F_A and F_B. Generally this difference is small.

It is clear from the sketch of the control volume in Figure 1 that the thermodynamic efficiency as defined by Eq. 11 depends on the thermodynamic state of the feed, but does not depend on the thermodynamic state of the distillate nor bottoms products. However, it is possible to assign physical meanings to the terms in the denominator of Eq. 11 provided we invoke the product states as shown in Figure 1 and impose the constraint that reboiler heat is equal to condenser heat. Let r be the fraction of product A produced as saturated liquid and s be the fraction of product B produced as saturated liquid, then

$$L_B - sF_B = L_A + rF_A$$

$$rF_A + sF_B = q_2 f + q_1(1-f).$$

Use of these equations along with rearrangement of terms in Eq. 11 gives:

$$\eta = \frac{-RT_o(Z_A \ln Z_A + Z_B \ln Z_B)}{\delta + \mu + (L_B - sF_B)\Delta H T_o\left[\frac{1}{T_A}-\frac{1}{T_B}\right]}, \quad (13)$$

where

$$\mu = \Delta H T_o \int_0^{rF_A}\left(\frac{1}{T}-\frac{1}{T_A}\right)dq + \Delta H \cdot T_o \int_{rF_A}^{q_1}\left(\frac{1}{T}-\frac{1}{T_B}\right)dq + f\Delta H \cdot T_o \int_{q_1}^{q_2}\left(\frac{1}{T}-\frac{1}{T_B}\right)dq. \quad (14)$$

It is interesting to examine the terms in the denominator of Eq. 13. The first integral of the middle term, μ, is the exergy change due to transfer of heat from the feed to the product A. It is as if the saturated vapor feed were partially condensed to form liquid of the amount rF_A and the resulting heat were transferred to totally vaporize liquid product rF_A (Figure 2). In this case, the value of this integral is negative, indicating that exergy is generated in this process. The middle integral of μ is the work needed when the feed is further condensed to make an additional amount of liquid ($q_1 - rF_A$), and this heat is reversibly pumped to bottom liquid product B. At this point, the feed is divided in two parts and one part (stream 1) is fed to the distillation column. The last term in μ is the work needed to reversibly transfer heat from the second portion of the feed that is further condensed to form $f(q_2 - q_1)$ amount of liquid to the bottom liquid product. The total heat transferred to the bottom product is such that the liquid fraction sF_B could be totally vaporized. Thus μ is the total exergy needed to transfer heat from a saturated vapor feed, as it is condensed to the desired thermodynamic state, to the liquid product streams, as they are completely vaporized to saturated vapor conditions. The last term in the denominator of Eq. 13 is the work needed to reversibly pump condenser heat from temperature T_A to the reboiler at temperature T_B. It is interesting that all the nonzero terms (with $\delta = 0$) in the denominator of efficiency Eq. 13 are work terms to reversibly transfer heat from one temperature to another.

All the temperature terms in the denominator of the effi-

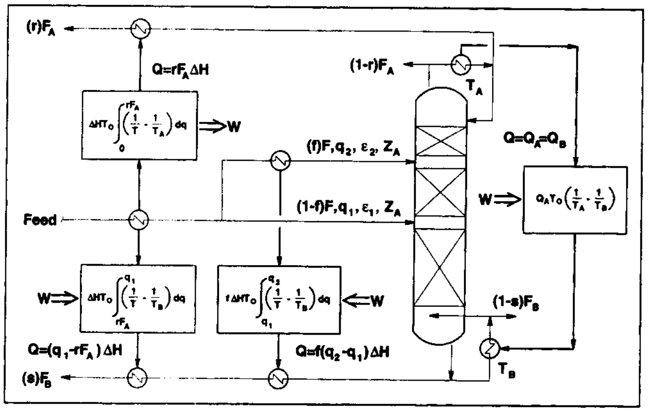

Figure 2. Various work terms appearing in the denominator of the thermodynamic efficiency equation (Eq. 13).

Unit operations enclosed in the boxes correspond to reversible Carnot heat pumps.

ciency equation (Eq. 11) are calculated using the Clausius–Clapeyron equation with the additional assumption that latent heat, ΔH, does not vary with temperature over the temperature range T_A to T_B. The relation between the vapor pressure of A ($P_{VP,A}$) at any temperature, T, and the pressure (P) of the distillation column is given by

$$\ln \frac{P}{P_{VP,A}} = \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_A}\right), \tag{15}$$

where the pressure of the distillation column is also the vapor pressure of A at temperature T_A. Similarly, for component B:

$$\ln \frac{P}{P_{VP,B}} = \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right) \tag{16}$$

where T is any temperature in the distillation column. Equations 15 and 16 can be combined to yield

$$\ln \alpha = \ln \frac{P_{VP,A}}{P_{VP,B}} = \frac{\Delta H}{R}\left[\frac{1}{T_A} - \frac{1}{T_B}\right], \tag{17}$$

where α is the relative volatility of A with respect to B ($\alpha = (y_A/x_A)/(y_B/x_B)$). From Eq. 15, when T is the temperature of the feed as it is being condensed from the vapor phase, and treating both vapor and liquid phases as ideal:

$$\frac{P}{P_{VP,A}} = \frac{x_A}{y_A} = \frac{x_A(\alpha - 1) + 1}{\alpha}.$$

Equation 15 becomes

$$RT_o \ln\left[\frac{x_A(\alpha - 1) + 1}{\alpha}\right] = \Delta H T_o\left(\frac{1}{T} - \frac{1}{T_A}\right), \tag{18}$$

where x and y are mole fractions in the liquid and vapor phase as feed is being condensed. Similarly, Eq. 16 can be expressed as

$$RT_o \ln[x_A(\alpha - 1) + 1] = \Delta H T_o\left(\frac{1}{T} - \frac{1}{T_B}\right). \tag{19}$$

To calculate x_A as a function of q, that is, to calculate the mole fraction of A in the liquid phase as feed is condensed from the vapor phase, use is made of a component A material balance between the two phases of the feed:

$$Z_A = q x_A + (1 - q)\frac{\alpha x_A}{1 + x_A(\alpha - 1)}. \tag{20}$$

This quadratic equation in x_A can be solved for any value of q.

Substitution of Eqs. 17 and 18 in Eq. 11 along with Eq. 20 reveals that within the assumptions of the derivation, efficiency (η) is a function of only feed composition (Z_A), quality of feeds (q_1 and q_2), and relative volatility (α)! The fact that temperature does not explicitly appear in the final expression allows one to make a more generalized interpretation from the calculated results.

The following four cases are discussed in detail in this article.

Case 1. One Saturated Liquid Feed. For this case, $f = 1$, $q_2 = 1$, and

$$\eta_l = \frac{-RT_o(Z_A \ln Z_A + Z_B \ln Z_B)}{\delta + RT_o \int_0^1 \ln\left[\frac{x_A(\alpha - 1) + 1}{\alpha}\right] dq + L_B \cdot RT_o \ln \alpha}. \tag{21}$$

Case 2. One Saturated Vapor Feed. For this case, $f = 0$, $q_1 = 0$, and

$$\eta_v = \frac{-RT_o(Z_A \ln Z_A + Z_B \ln Z_B)}{\delta + L_B RT_o \ln \alpha}. \tag{22}$$

Case 3. One Two-Phase Feed. For this case $f = 0$, $q_1 = q$, and $0 < q < 1$:

$$\eta_{2\phi} = \frac{-RT_o(Z_A \ln Z_A + Z_B \ln Z_B)}{\delta + RT_o \int_0^q \ln\left[\frac{x_A(\alpha - 1) + 1}{\alpha}\right] dq + L_B RT_o \ln \alpha}. \tag{23}$$

Case 4. One Saturated Vapor Plus One Saturated Liquid Feed. For this case, $q_1 = 0$ and $q_2 = 1$. For illustration only a subcase is considered where the amount of liquid feed is equal to the bottom product, that is, $fF = F_B$. This subcase is chosen because it gives minimum reboiler duty:

$$\eta_{vl} = \frac{-RT_o(Z_A \ln Z_A + Z_B \ln Z_B)}{\delta + F_B RT_o \int_0^1 \ln\left[\frac{x_A(\alpha - 1) + 1}{\alpha}\right] dq + L_B RT_o \ln \alpha}. \tag{24}$$

Clearly there are many more cases. For example, it is possible to have one of the feeds as two phase and the other as saturated liquid or saturated vapor; or both feeds two phase with different values of q. Also, one can have three feeds, one saturated vapor, another two phase, and a third saturated liquid. However, such cases are not analyzed in this study.

Discussion

We now discuss binary distillation efficiencies for each of the four cases in detail. For this purpose, the distillation column is always taken to be pinched, that is, for given feed conditions the vapor flow is at its minimum and an infinite number of separation stages are used in the distillation column. Furthermore, the value of δ in Eq. 11 is taken to be zero for every case under consideration. The generalized statements made in this section should be taken within the context of the simplifying assumptions made for the analysis.

Case 1: One Saturated Liquid Feed. It can be shown that for a pinched column the vapor traffic is given by

$$V_B = \frac{(1-Z_A)+\alpha Z_A}{\alpha - 1}. \tag{25}$$

Using the relation $V_B = L_B - F_B$ and substitution in Eq. 21 gives

$$\eta_l = \frac{-(Z_A \ln Z_A + Z_B \ln Z_B)}{\int_0^1 \ln\left[\frac{x_A(\alpha-1)+1}{\alpha}\right] dq + F_B \ln \alpha + \frac{[(1-Z_A+\alpha Z_A)]\ln \alpha}{\alpha - 1}}. \tag{26}$$

Furthermore, for all the values of α and Z_A considered in these calculations, the numerically calculated sum of the first two terms in the denominator has been found to be zero. Even though an analytical proof is unavailable, based on numerical calculations, the sum of the first two terms in the denominator will now be set equal to zero. Thus, the preceding equation simplifies to give

$$\eta_l = \frac{-Z_A \ln Z_A - (1-Z_A)\ln(1-Z_A)}{\frac{[(1-Z_A)+\alpha Z_A]\ln \alpha}{\alpha - 1}}. \tag{27}$$

Values of η_l were calculated for several values of α and feed composition, and some results are plotted in Figures 3 and 4. Several observations can be made from these figures.

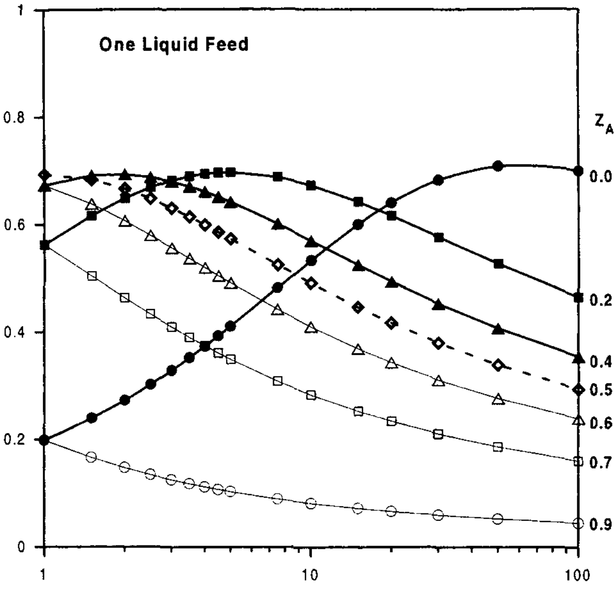

Figure 3. One liquid feed: thermodynamic efficiency as a function of relative volatility (α) for different feed compositions, Z_A.

1. For relative volatilities less than 10 and feed compositions between 25 and 75%, the values of efficiency, η_l, are generally in the range of 30 to 70%. These values are substantially greater than the usually cited efficiencies of less than 10%. This implies that the majority of the inefficiency of a distillation process resides in the reboiler and condenser; it depends on what kind of temperature differences are used in these heat exchangers and what is done with the heat rejected in the condenser. It is worth noting that even for an unpinched column where the boilup would be 10–20% higher than the one given by Eq. 25, the denominator value in Eq. 27 would go up by only 10–20%, and the column efficiencies would still be substantially greater than 10%. This indicates that the efficiency of a distillation *process* (as distinct from the distillation column) can be greatly improved by paying attention to reboilers and condensers.

2. As relative volatility approaches 1, even though the boilup goes up rapidly (Eq. 25), the efficiency approaches a limiting value dependent on feed composition. From Eq. 27

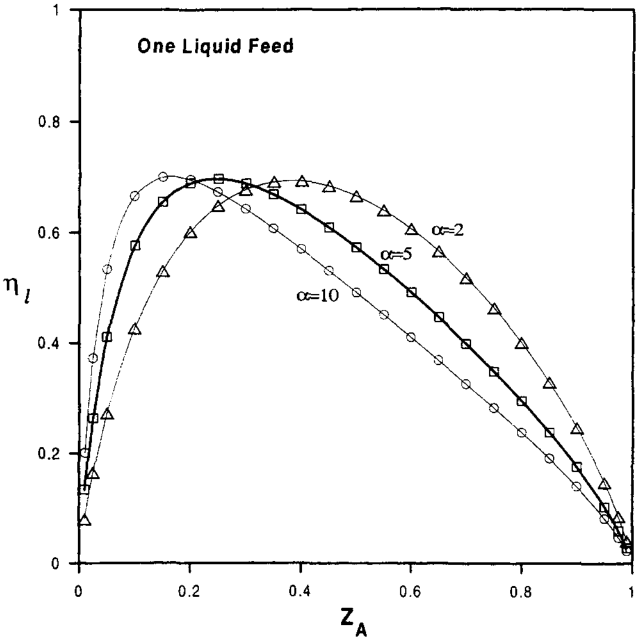

Figure 4. One liquid feed: thermodynamic efficiency as a function of feed composition (Z_A) for several values of relative volatility (α).

it is observed that as $\alpha \to 1$, the denominator also approaches one. The limiting value is given by the numerator of Eq. 27. Basically, as the value of relative volatility decreases, the temperature difference between the top and bottom of the distillation column decreases and the work needed to pump a unit amount of heat from T_A to T_B decreases. This leads to acceptable values of efficiency at low values of relative volatility even though the total boilup demand increases sharply. In such circumstances it is critical that reboiler and condenser temperature approaches be minimized.

3. For a 50–50 feed mixture, the efficiency declines monotonically with increasing relative volatility. Whereas, for feeds with a lower percentage of A, the efficiency goes through a maximum with relative volatility. As concentration of the more volatile component decreases, the location of maxima moves to higher values of relative volatility. However, for lower concentrations of A, the maxima are quite flat. For example, at 25% A, the maximum occurs at $\alpha = 5$; however, there is only a slight variation in the value of η_l between $\alpha = 3$ and $\alpha = 10$. Interestingly, for feeds with concentration of A greater than 50%, the efficiency always declines with increasing relative volatility. Information such as this can be quite useful in applications where heat rejected in the condenser is not wasted but is usefully integrated with heat supply to some other equipment within the process flowsheet.

One method of changing relative volatility is by changing the pressure of the distillation column. Information in Figure 3 clearly shows that while thermodynamically it is more efficient to run the distillation columns for heavy-rich feeds ($Z_A < 50\%$) at lower pressures, the light-rich feeds should preferably be distilled at higher pressures. Furthermore, for a feed with $Z_A = 25\%$, decreasing the pressure of distillation to increase relative volatility beyond 3.5 (up to 10) has only a modest impact on the efficiency of the distillation column; and any incentive to decrease pressure has to come from some other factor.

4. For feed mixtures with concentration of the more volatile component A greater than 50%, the drop in efficiency with increasing value of relative volatility is due to the fact that vapor-flow rate is unnecessarily high for these cases and the increase in the temperature span between the two ends of the distillation column leads to an increase in the reboiler–condenser heat-pump work. Clearly, partial boilup of the feed or use of an intermediate reboiler, which uses a lower level of heat source, will lead to significant improvement in efficiency for such cases.

To check the validity of assumptions invoked in the derivation of Eq. 27, detailed distillation column simulations were performed using a design software package with actual vapor–liquid equilibrium data for nitrogen and oxygen mixtures. Distillation efficiencies were computed from the simulation results for nitrogen–oxygen feed mixtures containing 25% and 75% nitrogen (component A). Efficiency values using Eq. 27 with value of α at the feed location were also calculated and are plotted as continuous curves in Figure 5. Values of relative volatility were changed by varying the pressure of distillation. The molar latent heat of oxygen is about 20 to 30% higher than nitrogen, and their latent heats do decrease with increasing pressure. The agreement between the two sets of calculations is quite reasonable and gives confidence in the results presented in Figures 3 and 4.

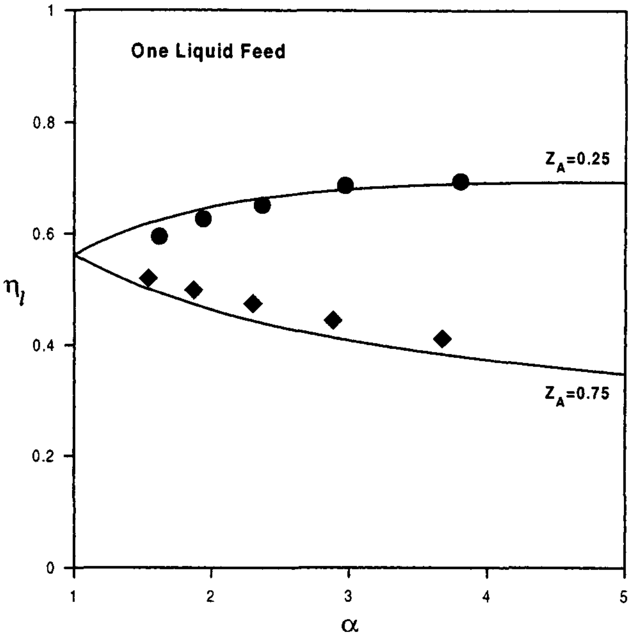

Figure 5. Thermodynamic efficiency of one liquid feed: calculation by computer simulations (solid points) vs. prediction of Eq. 27 (solid lines).

Comparison was made using a mixture of nitrogen and oxygen at the feed compositions indicated.

Case 2: One Saturated Vapor Feed. For a pinched column, liquid traffic is given by

$$L_B = \frac{\alpha(1 - Z_A) + Z_A}{\alpha - 1} \tag{28}$$

therefore, from Eq. 22,

$$\eta_v = \frac{-Z_A \ln Z_A - (1 - Z_A)\ln(1 - Z_A)}{\dfrac{[\alpha(1 - Z_A) + Z_A]\ln \alpha}{\alpha - 1}} \tag{29}$$

It is interesting to note that the preceding equation reduces to the one for a single liquid feed (Eq. 27) if Z_A is replaced by $(1 - Z_A)$. Therefore, an efficiency curve in Figure 3 for a liquid-feed composition Z_A is identical to one for this case when the feed composition is $(1 - Z_A)$. These results are replotted for this vapor feed in Figure 6. Due to this symmetry, observations made for the liquid case 1 can be easily extended to this case and will not be discussed in detail.

It may be worth emphasizing, however, that most gas separations are done by distillation at temperatures below ambient and heat is indeed pumped from the condenser to the reboiler using compression work. Therefore, the variation of distillation efficiency with pressure is of great interest. Generally, there is an incentive to run cryogenic distillation columns at higher pressures to minimize exergy loss due to pressure drop. From Figure 6 it is observed that the desire to increase pressure is in harmony with an increase in thermodynamic efficiency only for feeds containing more heavy component B ($Z_A \leq 0.5$). In such situations, potential exists to

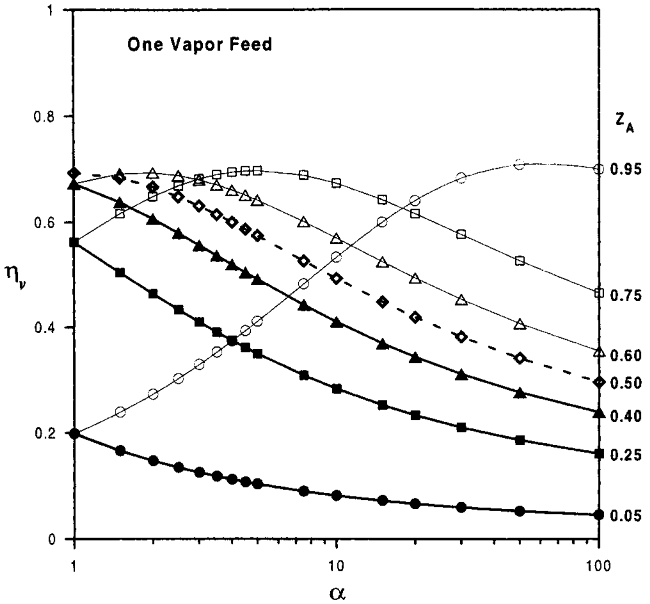

Figure 6. One vapor feed: thermodynamic efficiency as a function of relative volatility (α) for different feed compositions, Z_A.

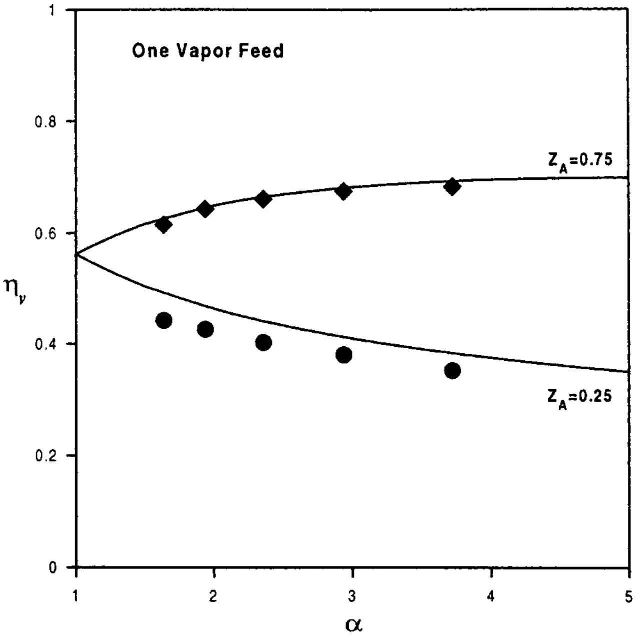

Figure 7. Thermodynamic efficiency of one vapor feed: calculation by computer simulations (solid points) vs. prediction of Eq. 29 (solid lines).

Comparison was made using a mixture of nitrogen and oxygen at the feed compositions indicated.

save both compression energy as well as capital cost due to reduced equipment size. On the other hand, for feeds containing more light component A ($Z_A > 0.6$), there can be a trade-off between an increase in energy consumption and reduction in capital cost as the pressure of distillation is increased. For example, for a feed composition of 75% A, an increase in pressure such that α falls significantly below 3 will lead to an increase in compression work required for distillation. Of course, all this analysis assumes that when a distillation is performed at a high pressure, the pressure exergy contained in both the products can be effectively utilized.

Similar to Figure 5, a comparison of the actual thermodynamic efficiencies calculated through detailed computer simulation of N_2-O_2 binary mixtures with those calculated from Eq. 29 is shown in Figure 7. Again, the agreement is quite encouraging.

Case 3: One Two-Phase Feed. The liquid traffic in a pinched column is given by

$$L_B = y_A\left[\frac{1-x_A}{y_A-x_A}-(1-q)\right], \tag{30}$$

where q is the feed quality and x_A and y_A are mole fractions of A in the liquid and vapor phases of the feed, respectively. For any given values of Z_A, q, and α, thermodynamic efficiency $\eta_{2\phi}$ can be calculated from Eq. 23.

In Figure 8, calculation results are presented for the specific case where the amount of liquid in the feed is equal to the bottom product B, that is, $q = 1 - Z_A = F_B$. With the assumptions made, the problem is symmetric around 50 % feed composition—the efficiency curve for feed composition Z_A is identical to the one for feed composition $1 - Z_A$. Comparison of the efficiency curves in Figure 8 with those in Figures 3 and 6 reveal:

1. In the range of relative volatility studied, the efficiency for the two-phase feed case is found to always increase with an increase in relative volatility.
2. For a given value of α, the two-phase thermodynamic efficiency is highest for a 50-50 feed mixture and declines symmetrically as the composition deviates on either side (Figure 9).

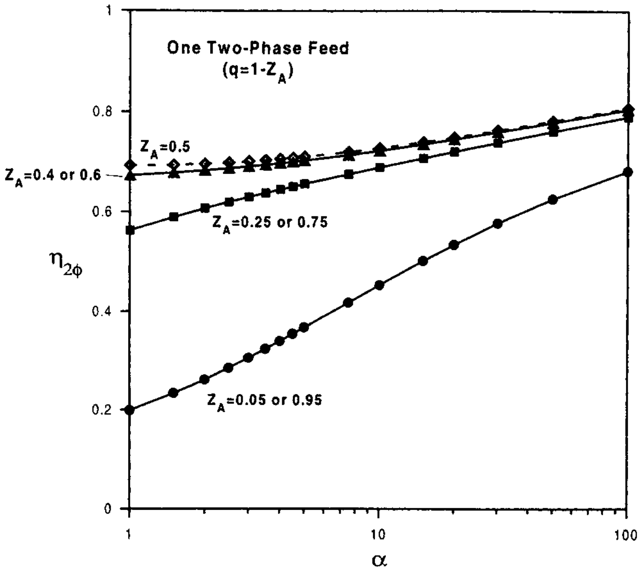

Figure 8. One two-phase feed: thermodynamic efficiency as a function of relative volatility (α) for different feed compositions, Z_A and $q = 1 - Z_A$.

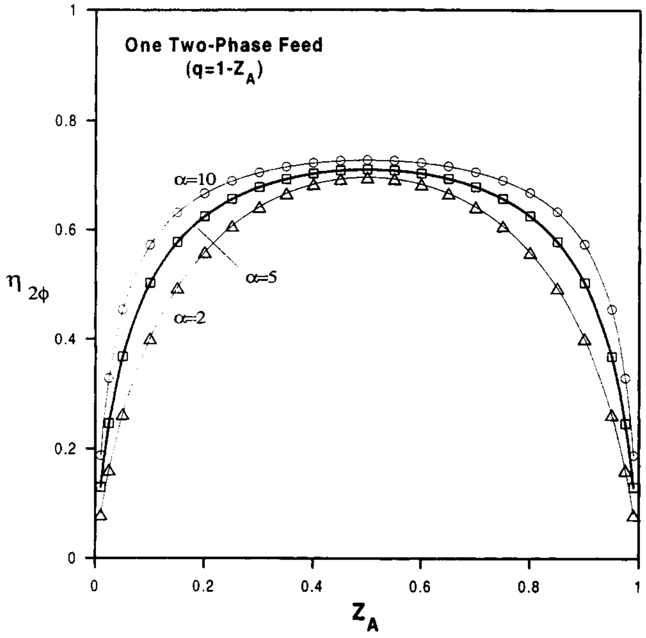

Figure 9. One two-phase feed: thermodynamic efficiency as a function of feed composition (Z_A) for several values of relative volatility (α).

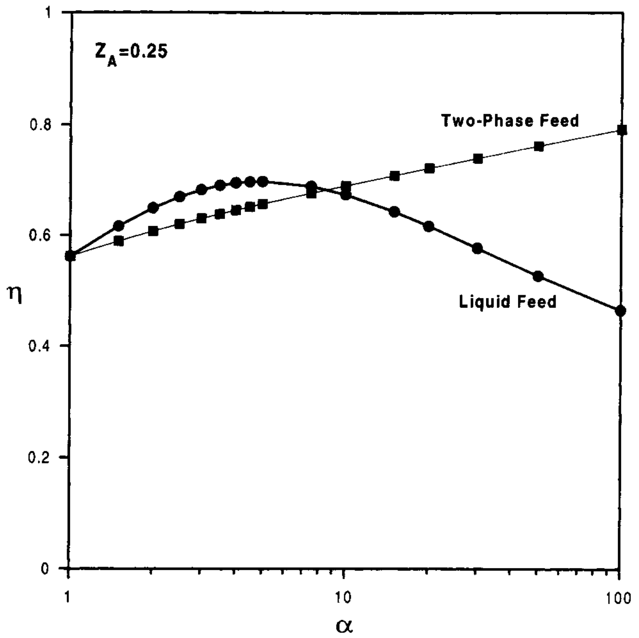

Figure 10. Thermodynamic efficiency: one liquid feed (case-1) vs. one two-phase feed (case-3) as a function of relative volatility (α) at a single feed composition ($Z_A = 0.25$).

3. Compared to the earlier two cases, the two-phase thermodynamic efficiency curves for different feed compositions (in the range of 20 to 80% A) are much closer. Furthermore, for any given feed composition, changes in the value of relative volatility seem to have a smaller impact on the two-phase thermodynamic efficiency as compared to thermodynamic efficiencies of the earlier two cases.

4. As $\alpha \to 1$, the thermodynamic efficiency for this case approaches the same value as observed in the earlier two cases.

5. For a feed with 50% A, the thermodynamic efficiency with the two-phase feed is always higher than the thermodynamic efficiency when the feed is either all liquid or all vapor.

6. However, for any other feed composition, up to a certain value of α, the two-phase thermodynamic efficiencies of Figure 8 are lower than the thermodynamic efficiencies calculated for the preferred case 1 or case 2. For example, when $Z_A = 0.25$, the two-phase thermodynamic efficiency is lower than the all-liquid feed case 1 up to $\alpha \approx 10$ (Figure 10).

Calculations were made to check the effectiveness of Eqs. 23 and 30 in predicting thermodynamic efficiencies of real systems. Accurate thermodynamic efficiencies were calculated through detailed computer simulations for two nitrogen–oxygen binary mixtures at several pressures. Results are plotted in Figure 11 as a function of α calculated at the feed condition. Once again the agreement is quite good.

In addition to the nitrogen–oxygen binary, detailed computer simulations were made for 50–50 mixtures of other binary systems to provide thermodynamic efficiencies at several values of relative volatility. The results are shown for all three cases in Figure 12. The additional binary mixtures are indicated in the key to Figure 12 and include selected cryogens, alcohols, and a benzene–toluene mixture. The agreement between accurately calculated values and the ones calculated through equations with simplifying assumptions is good. This provides confidence in the generalized conclusions drawn through simplifying assumptions. However, it should be

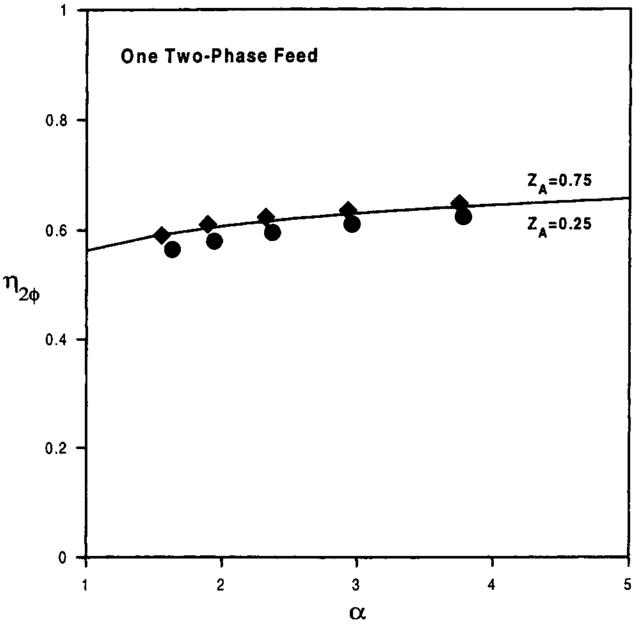

Figure 11. Thermodynamic efficiency of one two-phase feed: calculation by computer simulations (solid points) vs. prediction of Eq. 23 (solid lines).

Comparison was made using a mixture of nitrogen and oxygen at the feed compositions indicated.

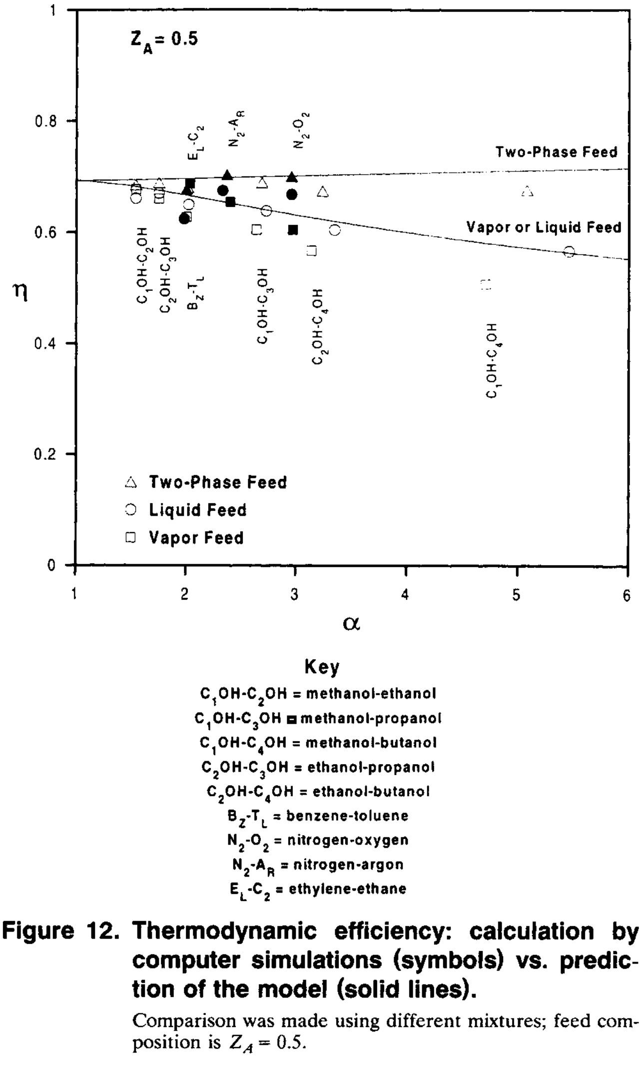

Figure 12. Thermodynamic efficiency: calculation by computer simulations (symbols) vs. prediction of the model (solid lines).

Comparison was made using different mixtures; feed composition is $Z_A = 0.5$.

pointed out that for systems where the variation in relative volatility from the top condenser to the bottom reboiler is quite large (example: CH_4–C_2H_6 mixture) or there is a tangent or near-tangent pinch in either section of the distillation column (example: Ar–O_2), the simplifying assumptions made in the derivation of Eqs. 21–23 are not valid. In such cases, the quantitative agreement between the actual thermodynamic efficiencies and the ones calculated through simplifying assumptions will not be good and only qualitative agreements are expected at best. Care should be taken in extending the current observations to such systems.

Return now to observation 6 illustrated in Figure 10, where for a feed other than a 50–50 mixture, the greater of the two thermodynamic efficiencies from cases 1 or 2 can be greater than the two-phase thermodynamic efficiency. This suggests that $q = 1 - Z_A$ does not always provide the maximum value of $\eta_{2\phi}$. Calculations were done to find optimum values of q. For a given α, as the mole fraction of the more volatile component A is decreased below 50%, the optimum value of q is found to be greater than $1 - Z_A$ and at some value of Z_A it becomes equal to 1. This is shown in Figure 13. In our calculations we have found that the composition for the onset of all liquid feed is less than x_A^* but close to x_A^*. Similarly, when the amount of A is increased in the feed above 50%, the

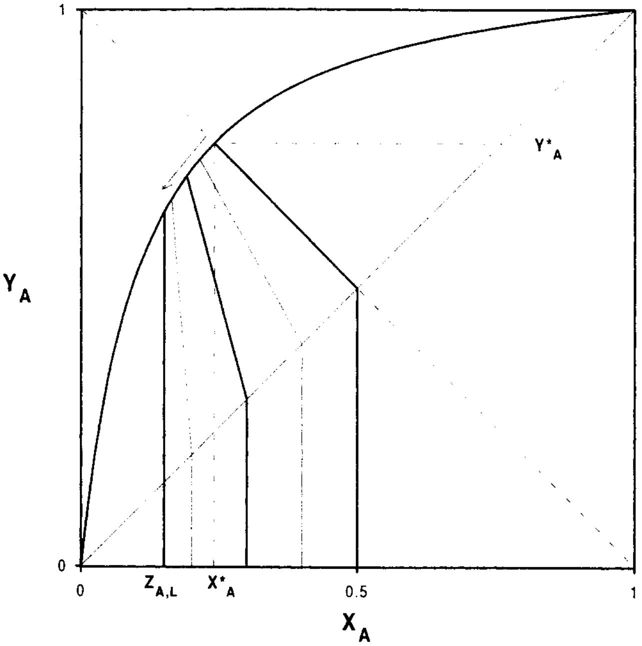

Figure 13. Effect of decreasing concentration of the light component (A) below 0.5 on the optimum value of liquid fraction of the feed (q).

value of q is less than $1 - Z_A$ and for some $Z_A > y_A^*$ it becomes equal to zero, that is, the optimal feed condition is all vapor. The values of x_A^* and y_A^* in Figure 13 are given by

$$x_A^* = \frac{1}{\sqrt{\alpha} + 1} \tag{31}$$

$$y_A^* = 1 - x_A^*. \tag{32}$$

These values are easy to locate on a McCabe–Thiele diagram, as they are the coordinates of the point of intersection of the equilibrium curve and inverse diagonal. The maximum value of thermodynamic efficiency for a given feed composition and the optimal feed condition is shown in Figure 14 for $\alpha = 5$. As observed from this figure, the optimum feed state is a function of feed composition: for $Z_A < 0.22$ it is all liquid; for $0.22 < Z_A < 0.78$ it is two-phase, and for $Z_A > 0.78$ it is all vapor. The corresponding value of x_A^* is 0.31 and y_A^* is 0.69. Note that for feed compositions of x_A^* and y_A^* there is little difference between the efficiency of the optimum two-phase feed and either the single-phase feed or two-phase feed (with $q = 1 - Z_A$). This observation, along with results from calculations for other values of α, leads to an approximate but useful conclusion that for single-feed case, the thermodynamic efficiency of distillation can be maximized by having all liquid feed for $Z_A < x_A^*$, all vapor feed for $Z_A > y_A^*$, and a two-phase feed with $q = 1 - Z_A$ for $x_A^* \le Z_A \le y_A^*$. Since x_A^* and y_A^* can be easily located on a McCabe–Thiele diagram, this provides a quick method of locating the optimum liquid fraction to maximize thermodynamic efficiency of a distillation. As a corollary, this observation provides guidance regarding when it is not beneficial to further boil or condense a feed before the distillation column. When the feed to a distillation column is a by-product of another unit operation, this

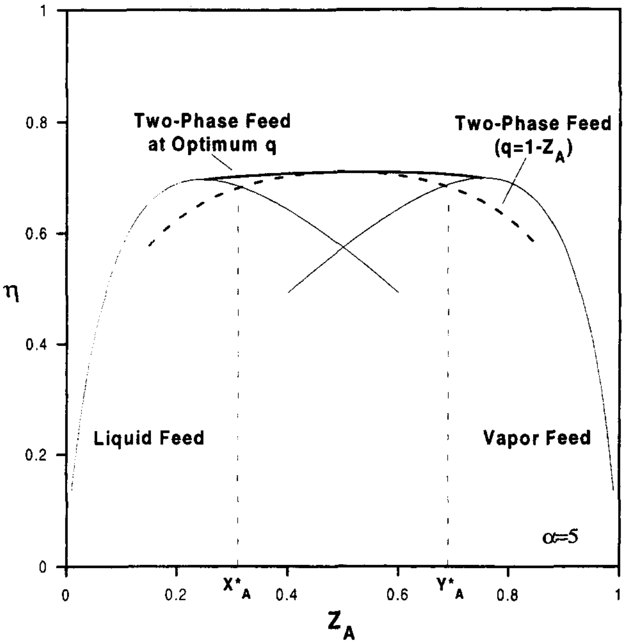

Figure 14. Single feed: optimum thermodynamic state at several feed compositions (Z_A).

The relative volatility (α) is 5.

observation provides some clue as to the preferred state in which feed should be recovered from that unit operation.

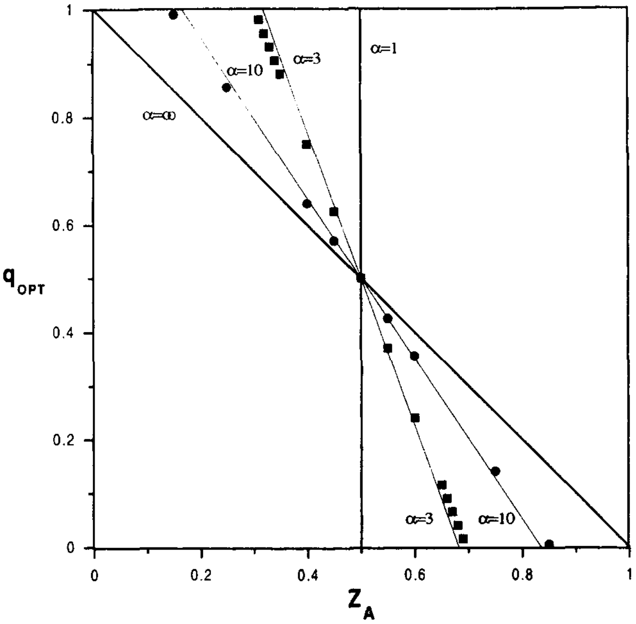

Figure 15. Single feed: liquid fraction of the feed (q_{OPT}) which results in the maximum thermodynamic efficiency as a function of feed composition (Z_A) for different relative volatilities (α).

Detailed model calculations are shown as symbols; simplified prediction based on Eqs. 33–38 is represented by lines.

When a more accurate value of optimum q is needed, the curves in Figure 15 may be used. Calculated values of optimum feed quality for a single-feed case that produce maximum thermodynamic efficiencies are plotted as a function of feed composition for several values of α. For a given α, let Z_l^* be the maximum value of Z_A for which the optimum feed state is all liquid ($q_{\text{opt}} = 1$), and Z_v^* the minimum value of Z_A for which the optimum feed state is all vapor ($q_{\text{opt}} = 0$). It is observed that for any given value of α and $Z_l^* \leq Z_A \leq Z_v^*$, the calculated values of q_{opt} fall on a straight line as a function Z_A. This observation allows one to calculate the value of q_{opt} for any given feed composition provided values of Z_l^* and Z_v^* as function of α are available:

$$q_{\text{opt}} = 1 \qquad \text{for} \quad Z_A \leq Z_l^* \tag{33}$$

$$q_{\text{opt}} = \frac{Z_A - Z_v^*}{Z_l^* - Z_v^*} \qquad \text{for} \quad Z_l^* \leq Z_A \leq Z_v^* \tag{34}$$

$$q_{\text{opt}} = 0 \qquad \text{for} \quad Z_v^* \leq Z_A. \tag{35}$$

Since Z_l^* and Z_v^* are symmetric about $Z_A = 0.5$, it is sufficient to know only one of the values. The other can be easily calculated from

$$Z_v^* = 1 - Z_l^*. \tag{36}$$

The value of Z_l^* can be approximated through an observation from Figure 14 that as the value of Z_A is increased from zero, the transition from all liquid feed to a two-phase feed (at q_{opt}) takes place in the neighborhood of Z_A where the maximum in thermodynamic efficiency for the all liquid-feed cases occurs. For a given α, an expression for the value of feed composition, $Z_{l,\max}$, can be derived from Eq. 27 to be

$$Z_{l,\max} = 1 - Z_{l,\max}^{1/\alpha}. \tag{37}$$

A similar transition occurs from two-phase feed (at q_{opt}) to all vapor feed and, if needed, an expression for $Z_{v,\max}$ may be derived from Eq. 29. It is found that Z_l^* is very slightly less than $Z_{l,\max}$ and for all practical purposes they can be considered equal. The difference between the calculated value of the maximum thermodynamic efficiency with the correct value of q_{opt} at the feed composition of $Z_{l,\max}$ and the thermodynamic efficiency calculated assuming all liquid feed at this composition is insignificant. Therefore, it is justified to make the following approximation:

$$Z_l^* \approx Z_{l,\max}. \tag{38}$$

For any given feed composition and α, the value of Z_l^* is calculated from Eqs. 37 and 38, and then Eqs. 33–36 are used to find the optimum feed quality (q_{opt}) for the maximum thermodynamic efficiency. For comparison purposes, the values of q_{opt} calculated from Eqs. 33–38 are plotted as straight lines in Figure 15. The agreement between the correctly calculated values of q_{opt} and the approximate straight lines is fairly good.

Case 4. One Vapor and One Liquid Feed. Once the maximum thermodynamic efficiency and the associated thermodynamic state for a given feed are known, it is of interest to check the potential of the two-feed case (one vapor and one liquid feed) in providing even higher efficiencies. For a pinched column where liquid-feed flow is equal to the bottom product rate, efficiency is given by Eq. 24, with L_B calculated from:

$$L_B = \frac{1}{\alpha - 1} + (1 - Z_A). \tag{39}$$

Some results for this case are plotted in Figures 16 and 17. Once again, as in Figures 5, 7 and 11, the agreement between the results shown in Figure 16 and the accurate thermodynamic efficiencies calculated through detailed computer simulations for N_2–O_2 binary at different pressures was excellent and therefore a figure comparing the results is not shown. Some quick observations from Figures 16 and 17 are:

1. As observed with the single two-phase feed case, the efficiency curve for a feed with composition Z_A is the same as for a feed with composition $1 - Z_A$.
2. In Figure 16, the efficiency curves are much closer than those for cases 1 and 2 (see Figures 3 and 6) except near extremes of feed composition.
3. Up to a certain value of α, the efficiency increases with increasing relative volatility for all feed compositions. Generally for a given composition, there is a maximum in thermodynamic efficiency as α is increased, and this value of α seems to be higher than the ones for cases 1 and 2.
4. For relative volatilities < 10, the efficiency for a 50–50 mixture is greatest and it declines as the concentration of either component is increased in the feed (Figure 17).
5. The benefit of having two feeds virtually disappears for very high mole fractions of A or B. In Figure 17, at $\alpha = 5$ and $Z_A < 0.1$ or $Z_A > 0.9$ the benefit of having two feeds as compared to a single feed is little.

In our calculations for a single two-phase feed, the value of thermodynamic efficiency is found to increase monotonically with relative volatility, while the other three cases show a maximum in thermodynamic efficiency. This leads to the interesting observation that for mixtures with relatively high values of α, a single two-phase feed can provide higher efficiencies than a two-feed case with one saturated vapor and the other saturated liquid feed. This can be seen in Figure 17 for $\alpha = 50$ and is further illustrated in Figure 18. To some extent these results are intuitively expected and suggest that for two feeds at relatively high values of α, it may be beneficial to have at least one two-phase feed.

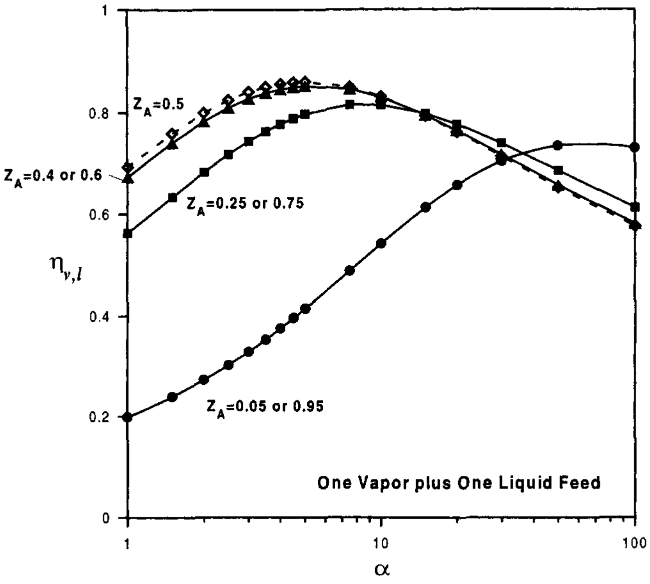

Figure 16. One vapor feed plus one liquid feed: thermodynamic efficiency as a function of relative volatility (α) for two separate feeds (a liquid and a vapor) at several compositions, Z_A.

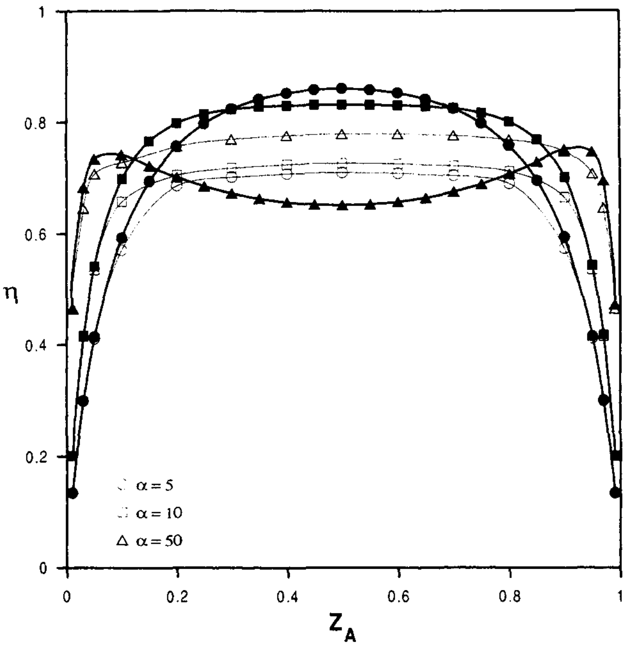

Figure 17. Thermodynamic efficiency: one vapor plus one liquid (case 4, solid symbols) vs. single feed at optimum feed liquid fraction, q_{OPT}, (open symbols), as a function of feed compositions, Z_A.

Curves correspond to different relative volatilities (α) as indicated.

Conclusions

Simplified assumptions were made to study thermodynamic efficiency of ideal binary distillation columns producing pure products for several feed conditions at various relative volatilities. It was found that within the validity of the assumptions used, temperatures of pure products A and B at the top and bottom of the distillation column do not explicitly appear in the final thermodynamic efficiency equations; rather these equations are found to be functions only of feed composition, thermodynamic state of the feed, and relative volatility of the more volatile component A with respect to component B. This enabled generalization of observations made through calculations for several feed conditions. Good quantitative agreement between such calculated thermodynamic efficiencies and accurate thermodynamic efficiency values calculated through detailed computer simulations for various real binary mixtures at different composi-

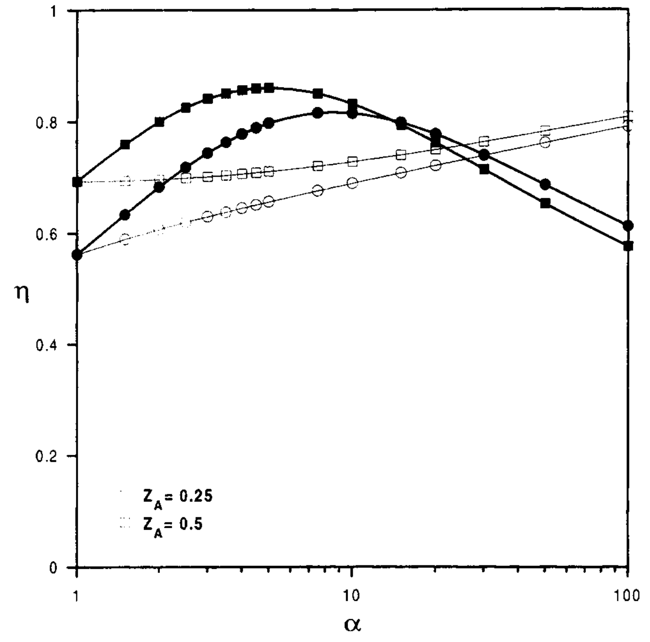

Figure 18. Thermodynamic efficiency: single two-phase feed (open symbols) vs. two feeds (closed symbols) as a function of relative volatility (α) at the feed compositions, Z_A.

tions and pressures, gives confidence in the value of the generalized observations.

Low values of efficiencies (below 10%) in the literature for distillation processes are not supported by the results presented and are most likely due to inefficiencies outside the distillation column, such as in reboilers and condensers. The efficiency of the distillation column alone is generally very high if the feed is properly conditioned; for optimum thermodynamic feed conditions (for $0.15 < Z_A < 0.85$) it is normally in the range of 30 to 80%. This efficiency is generally either comparable to or greater than alternative separation processes such as membranes and adsorption. This emphasizes the need to improve the performance of reboiler and condenser heat exchangers and, when the opportunity arises, to find the optimum use of heat rejected in a condenser.

When a single one-phase feed, AB, is used, the preferred thermodynamic state of the feed, based on thermodynamic efficiency, is all liquid when the amount of heavy component B is greater than 50%, and is all vapor when the amount of volatile component A is greater than 50%. For these preferred-state cases, a maximum in thermodynamic efficiency is observed as a function of relative volatility, α. Therefore, if the pressure of distillation is decreased to increase α, the efficiency increases down to a certain value of pressure and then begins to decrease. The greater the deviation from a 50–50 mixture, the greater the value of α at which the maximum in efficiency occurs. For the nonpreferred feed state, that is, saturated liquid when component A is greater than 50% or vapor when B is greater than 50%, an increase in relative volatility has a negative effect on efficiency. For such cases, the efficiency of the distillation column actually increases with increasing pressure.

Unlike the all-liquid or all-vapor feed cases, for a single two-phase feed, distillation column efficiency is found to monotonically increase with an increase in value of the relative volatility. Furthermore, for a 50–50 mixture and for other feed compositions bounded by x_A^* and y_A^*, the thermodynamic efficiency is higher than either all-liquid or all-vapor feed cases (x_A^* and y_A^* are the coordinates of the point of intersection of an equilibrium curve and the inverse diagonal and can be easily located on a McCabe–Thiele diagram or calculated for any given value of α from Eqs. 31 and 32). For some Z_A slightly less than x_A^*, the preferred feed state is all liquid; and similarly for some Z_A slightly greater than y_A^*, the preferred feed state is all vapor. For quick estimates, it is suggested that for $x_A^* < Z_A < y_A^*$, the value of q may be taken equal to $1 - Z_A$.

For most binary mixtures of commercial interest, the two-feed case with both feeds of the same composition but one saturated vapor and the other saturated liquid can lead to a substantial improvement in a distillation column's thermodynamic efficiency. As compared to the single-feed case with optimum feed condition, the maximum improvement is obtained for a 50–50 mixture and the benefit declines as the concentration of either A or B is increased in the mixture. For a feed mixture highly enriched in A or B, the difference between the optimum single feed case and this two-feed case is vanishingly small. For example, when a feed mixture with relative volatility of 5 contains greater than 90% A or less than 10% A, there is no incentive to have both a saturated vapor and a saturated liquid feed.

At high values of relative volatilities, the benefit of having one saturated vapor feed and another saturated liquid feed (both of the same composition) as compared to the optimum single feed starts to decrease. For relative volatilities above a certain value, a two-phase single-feed case is found to be more efficient than this two-feed case. Generally, this happens for reasonably high values of relative volatilities.

It is observed that for cases where the feed condition is at its optimum, the thermodynamic efficiency is highest for a 50–50 mixture and declines with increasing amounts of A or B in the feed mixture. Generally, this efficiency declines rapidly as either the concentration of A or B is increased beyond 85 to 90%. This indicates that it may be beneficial to investigate alternative separation methods or a means to improve the efficiency of distillation columns for such enriched mixtures.

Finally it must be stated that in this article all the observations about the preferred feed states are made solely on the basis of thermodynamic efficiency of the distillation column. Inefficiencies and capital costs associated with converting a feed to the optimum state have not been considered. Needless to say, these and other factors such as any resulting operating complexity due to additional processing steps will have a strong impact on the process conditions at which a distillation column would be eventually run. However, this exercise does provide guidance on the preferred state of a feed in the event that it might be collected in such a state from another unit operation within a plant. It also provides insight on when it is disadvantageous to change a feed state to those conditions that have a negative impact on the distillation column's thermodynamic efficiency. Furthermore, these observations are quite useful for distillations, such as subambient distillations, where work energy rather than heat energy is used.

Acknowledgment

Discussions with Dr. Keith Wilson are acknowledged with gratitude.

Notation

E_A, E_B = molar exergy of saturated vapor for A and B
f = fraction of total feed fed as feed 2
F_A, F_B = flow rate of products A and B
L = molar liquid flow rate
R = universal gas constant
T_A = condensation temperature of A at distillation column pressure
T_B = condensation temperature of B at distillation column pressure
V = molar vapor flow rate

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Appendix

A definition of efficiency based on heat supplied to the reboiler is given by Ho and Keller (1987):

$$\eta_H = \frac{W_{\min}}{Q_B}. \tag{A1}$$

Consider a reversible separation process run by a heat engine operating between a heat source at T_{so} and a heat sink at T_{si}. An amount of heat $Q_{\min}$ from the heat source T_{so} is taken and same amount of heat is rejected to the heat sink T_{si}. The value of $Q_{\min}$ is chosen such that the reversible heat engine due to this heat transfer will generate work $W_{\min}$:

$$W_{\min} = Q_{\min} T_o \left[\frac{1}{T_{si}} - \frac{1}{T_{so}} \right]. \tag{A2}$$

$W_{\min}$ is the minimum amount of work that would be needed to separate mixture AB by a totally reversible process. Clearly, the thermodynamic efficiency of this process is 100% and cannot be improved further. This would be true even when the reversible separation process was a reversible distillation column and the heat source a reversible reboiler and the heat sink a reversible condenser. A schematic of a reversible distillation column operating with $W_{\min}$ and without an external heat source for reboiler and an external heat sink for condenser, but using multiple expanders and a compressor, is given by Haselden (1989). $W_{\min}$ to such a distillation process can conceptually be supplied by the reversible heat engine. The use of Eqs. A1 and A2 (with $Q_B = Q_{\min}$) to calculate efficiency of such a distillation column will generally lead to a value much less than 100%, and yet this proces is totally reversible. For a thermodynamic efficiency to be useful to a process engineer, it is essential that it provides a true picture of reversibility. We suggest that a better definition based on heat supplied to the reboiler is

$$\eta_Q = \frac{Q_{\min}}{Q_B}, \tag{A3}$$

where $Q_{\min}$ is given by Eq. A2. However, it is evident that Eq. A3 also has limitations and the correct practice would be to use a proper definition based on exergy.

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