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Are Thermally Coupled Distillation Columns Always Thermodynamically More Efficient for Ternary Distillations?

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The thermodynamic efficiency of five ternary distillation configurations to distill ideal saturated liquids into pure product streams are calculated and compared. A striking result of this study is that for the fully coupled column (Petlyuk) configuration, which is known to have the lowest heat demand for ternary distillation, the range of values of feed composition and relative volatilities for which it is the most thermodynamically efficient configuration is quite limited. Among the three thermally coupled column configurations, the side-rectifier and side-stripper configurations tend to provide the most efficient configuration more often than the fully coupled configuration. Generally, the modified direct and indirect split configurations together provide the most thermodynamically efficient configuration for more feed compositions and relative volatilities than do the three thermally coupled column configurations. The high thermodynamic efficiency of these two configurations is primarily due to their ability to either accept or reject heat at the intermediate temperatures of binary mixtures.

Introduction

The energy demand of thermally coupled distillation columns to distill ternary mixtures has been well-studied.[1−7] In thermally coupled configurations at least one end of a distillation column has both liquid and vapor exchange with another column. This eliminates either the reboiler or the condenser from this end of the distillation column. Three known thermally coupled column configurations for ternary separations are shown in Figure 1. In this and other figures, A is the most volatile component and C is the least volatile component in the feed mixture ABC. The thermally coupled column in these configurations can be characterized as the following: side rectifier (SR), side stripper (SS), and fully coupled (FC). The FC configuration is often referred to as the Petlyuk configuration. The conventional direct split (DS_L) and indirect split (IS_V) configurations are shown in Figure 2.

Several studies[4] have proven that for the separation of ideal ternary feed mixtures into pure product streams, the FC configuration has the lowest energy demand of the five configurations shown in Figures 1 and 2. It has been said that, on average, the FC configuration requires 30% less energy than the corresponding conventional arrangement.[6,8] FC has also been described as the most efficient arrangement for three-component mixtures.[8] It has been written[6] that, "For most separations, the fully thermally coupled distillation column is thermodynamically more efficient than the conventional arrangements, and as a consequence, has lower energy requirements." The lower energy requirements of the FC configuration leads to smaller column diameters and

lower overall heat exchanger area in the reboiler and condenser. The reduced number of reboilers and condensers also results in a lower capital investment. However, in spite of all these apparently attractive features, the FC configuration has not found a wide industrial use. Even for subambient temperature distillations, where energy consumption is of great importance, the FC configuration is yet to be used. This is rather surprising because the FC configuration has been known for nearly 50 years.[9]

The lack of widespread use of the FC configuration has been attributed to its difficult design and control. However, considerable advancement has been made recently in both the design and control aspects of the FC configuration.[7]

Even though the FC configuration has been claimed to have higher thermodynamic efficiency for most separations, no systemic study of its thermodynamic efficiency has been reported. A thermodynamic efficiency analysis should account not only for the heat duty (first law) but also for the temperature levels at which heat is required (second law). It has been stated that nature trades first law heat for second law ΔTs, and we clearly do not get something for nothing.[10] For any given ternary separation, the FC configuration needs the lowest first law heat, but this heat is required for reboiler C (the highest temperature) and is rejected at condenser A (the lowest temperature). This observation raises the question as to whether or not the FC configuration is indeed the thermodynamically most efficient configuration for ternary distillation.

It has been suggested[11] that one cannot be certain whether the side-column arrangements SR and SS will be significantly more thermodynamically efficient than the conventional DS_L and IS_V sequences, unless exergy analysis is employed. As an example problem, the

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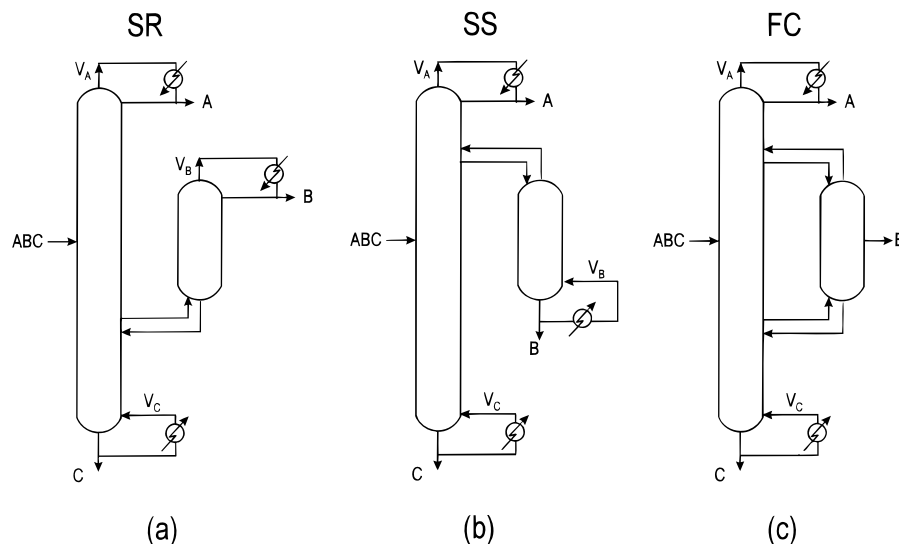
Figure 1. Thermally coupled distillation column configurations for ternary separation: (a) side-rectifier, (b) side-stripper, and (c) fully thermally coupled.
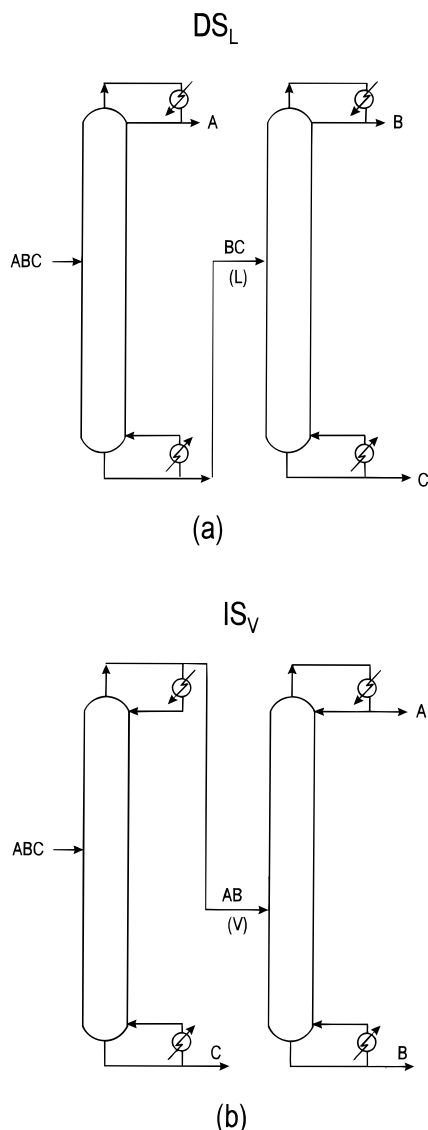

Figure 2. Conventional distillation column configurations for ternary separation: (a) direct split (DS_L) and (b) indirect split (IS_V).

author of ref 11 studied the separation of a feed mixture of 80% propane, 10% *i*-butane, and 10% *n*-butane using

SR and DS_L configurations. For this example problem, his calculations showed that reduction in the total heat duty for the SR configuration is significant but that the actual work requirement of SR is marginally higher than that of DS_L. However, no general conclusion regarding the thermodynamic efficiency of the SR configuration relative to DS_L was drawn; it was concluded that more investigation was needed to understand the thermodynamic efficiency of the SR and the SS configurations relative to the DS_L and the IS_V sequences. In a later publication[12] Finn concluded that thermodynamic efficiencies of configurations with thermally coupled side columns (SR and SS) are similar to those of the conventional DS_L and IS_V configurations. Clearly, there is a need to understand the thermodynamic efficiencies of the SR and SS configurations vis-a-vis the conventional configurations for a wide range of feed compositions and relative volatilities.

The primary aim of this paper is to study and compare the thermodynamic efficiencies of all five configurations for ternary separation. In order to achieve this, some simplifying assumptions are made and thermodynamic efficiency equations are developed for each configuration in which a ternary liquid feed is distilled into pure product streams. These equations are found to be functions of only the feed composition and the relative volatilities. The temperatures of the reboilers and condensers do not appear explicitly in these equations. This enables some general conclusions to be drawn regarding the relative efficiency of each configuration, as a function of the feed composition and the relative volatilities.

We have also mapped the total heat duty requirement of the FC configuration relative to the other configurations over the ternary composition space for certain values of relative volatilities. This corroborates the often-stated claim of 30% less total heat input for the FC configuration relative to other conventional arrangements.[13]

In ref 14, the ease of separation index (ESI) has been introduced and heuristics have been developed using ESI to discriminate between several ternary distillation configurations on the basis of their overall performance. The overall performance included the total heat demand as well as the capital costs. In this study we have

systematically examined whether the ESI can be used to differentiate between several ternary configurations solely based on thermodynamic efficiency.

Thermodynamic Efficiency Equations

Recently, a method was published[15] to calculate thermodynamic efficiency of ideal binary distillation columns. This method was then extended[16] to study the thermodynamic efficiency of the DS_L and IS_V configurations of Figure 2. The method will now be applied to develop thermodynamic efficiency equations for the thermally coupled column configurations SR, SS, and FC.

The simplifying assumptions used in the method are ideal vapor phase, ideal liquid solution, equal latent heats for all three components A, B, and C, no pressure drop losses, latent heat independent of temperature (within the operating temperature range of the distillation columns), and vapor pressures of the components given by the Clausius–Clapeyron equation. The following definition of distillation thermodynamic efficiency is used:

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

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 reboiler and condenser heat exchangers. Equations were derived for a saturated ternary liquid feed which is distilled into pure products A, B, and C:

$$\eta_{SR} = \frac{-RT_0 \sum\limits_{i=A,B,C} z_i \ln z_i}{\delta + \mu + V_A RT_0 \ln \alpha_A + V_B RT_0 \ln \alpha_B} \quad (2)$$

$$\eta_{SS} = \frac{-RT_0 \sum\limits_{i=A,B,C} z_i \ln z_i}{\delta + \mu + V_C RT_0 \ln \alpha_A + V_B RT_0 \ln(\alpha_A/\alpha_B)} \quad (3)$$

$$\eta_{FC} = \frac{-RT_0 \sum\limits_{i=A,B,C} z_i \ln z_i}{\delta + \mu + V_C RT_0 \ln \alpha_A} \quad (4)$$

where

$$\delta = E_F^T - (AE_A + BE_B + CE_C) \quad (5)$$

$$\mu = (e_F - E_F) - A(e_A - E_A) - B(e_B - E_B) - C(e_C - E_C) \quad (6)$$

We assume that the thermal component of the exergy of the vapor mixture (E_F^T) is approximately equal to the sum of thermal exergies of the pure components (E_A, E_B, E_C) in their saturated vapor states (reference pressure is equal to the pressure of the distillation column), which makes the value of δ negligibly small:

$$\delta \approx 0 \quad (7)$$

It was also determined numerically[16] that for a liquid feed the value of μ is negligibly small:

$$\mu \approx 0 \quad (8)$$

This reduces eqs 2–4 to simpler forms:

$$\eta_{SR} = \frac{-\sum\limits_{i=A,B,C} z_i \ln z_i}{V_A \ln \alpha_A + V_B \ln \alpha_B} \quad (9)$$

$$\eta_{SS} = \frac{-\sum\limits_{i=A,B,C} z_i \ln z_i}{V_C \ln \alpha_A + V_B \ln (\alpha_A/\alpha_B)} \quad (10)$$

$$\eta_{FC} = \frac{-\sum\limits_{i=A,B,C} z_i \ln z_i}{V_C \ln \alpha_A} \quad (11)$$

The temperatures of the reboilers and condensers do not appear explicitly in the above equations. This makes it easier to calculate thermodynamic efficiency over a wide range of values of relative volatilities and feed compositions. It should be emphasized that in spite of the simplifying assumptions described above, a very good agreement for distillation of several real binary mixtures between the thermodynamic efficiencies calculated from the model and the thermodynamic efficiencies calculated using detailed simulations without simplifying assumptions was found.[15]

Results and Discussion

A. Thermodynamic Efficiency. In this section we compare the thermodynamic efficiencies of the three thermally coupled configurations not only with each other but also with the modified direct and indirect split configurations shown in Figure 3. The direct and indirect configurations of Figure 2 have only one transfer stream from the first distillation column to the second distillation column. It has been shown, however, that it is more beneficial to have two interconnecting streams between the columns—one liquid and one vapor.[16] For example, in the direct split configuration, the liquid feed to the second column is the BC mixture withdrawn from the bottom of the first column, and the vapor feed is withdrawn as a portion of the first column boilup (configuration DS_{LV} in Figure 3a). A similarly modified indirect split configuration IS_{LV} is shown in Figure 3b.

Thermodynamic efficiencies were calculated for each of the five configurations at the pinched column conditions. The minimum vapor flow in each column was calculated using Underwood's method.[17] For the three thermally coupled configurations, equations to calculate minimum vapor flow were taken from the previous works.[4,18] Both the minimum vapor flow and the thermodynamic efficiency equations for the DS_{LV} and IS_{LV} systems were derived in the work.[16]

Calculations were done for a range of values of relative volatilities and feed compositions to observe trends in thermodynamic efficiencies as functions of these variables. Even though calculations were done for pinched columns, we expect the trends to be applicable to most real columns distilling ideal mixtures and operating in unpinched conditions. Some relevant observations are given below.

(i) For an *equimolar* feed, thermodynamics efficiency is generally highest for the DS_{LV} or IS_{LV}. Depending
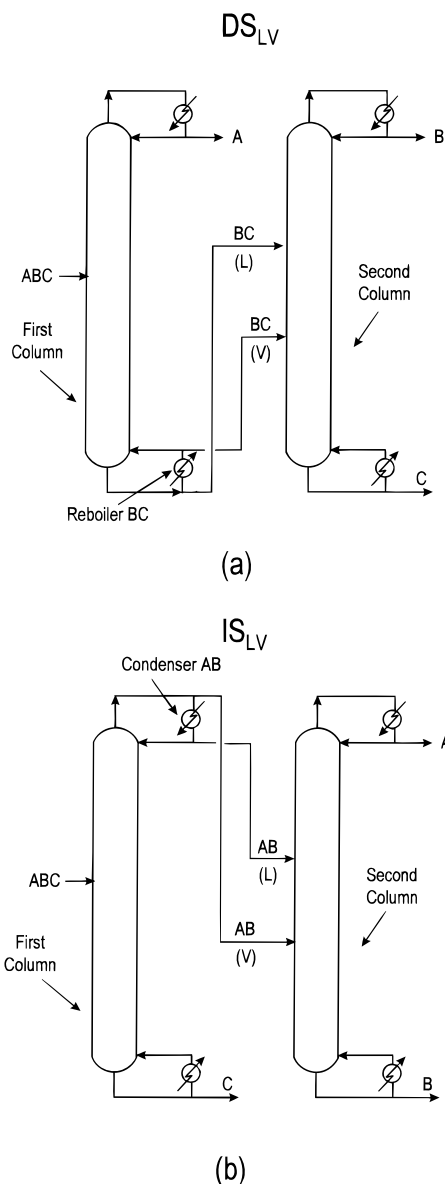
Figure 3. Modified direct and indirect split sequences with a liquid and a vapor transfer stream from the ternary feed column to the second column: (a) direct split (DS_{LV}) and (b) indirect split (IS_{LV}).

on the values of the relative volatilities, the thermodynamic efficiency of the FC configuration can be extremely low. Thermodynamic efficiencies of all the five configurations for several values of relative volatility of A with respect to B (α_{AB}) are plotted in Figure 4.

It is observed that when relative volatility between A and B is low ($\alpha_{AB} = 1.1$, Figure 4a), the most efficient configuration is generally (for $\alpha_B > 1.5$) IS_{LV} or SS. For these values of relative volatilities, the thermodynamic efficiency of both FC and SR can be extremely poor. This is caused by the fact that, at the low value of α_{AB}, a relatively large vapor flow is needed to separate A from B, while the temperature of condenser A (T_A) is much closer to the bubble-point temperature of B (T_B) than to the temperature of reboiler C (T_C). Thus, it is preferable to supply the large fraction of heat needed for the separation of A from B through a lower level heat source in reboiler B than to supply it at temperatures higher than T_B. In configurations FC, DS_{LV}, and SR it is not possible to supply heat at T_B. This leads to greater degradation of some of the heat which is rejected

in condenser A. Consequently, efficiencies of IS_{LV} and SS are higher than efficiencies of FC, DS_{LV}, and SR.

For moderate to high values of α_{AB} ($\alpha_{AB} \geq 2$, Figures 4b–d), the most efficient configuration is clearly DS_{LV}. The only time we see the efficiency of the FC configuration approaching that of DS_{LV} is in Figure 4b for $\alpha_{AB} = 2$. This raises the question as to whether there may be certain values of α_A and α_B where FC would be the most efficient. To answer this question, the most efficient configuration was determined for several values of α_A and α_B, and the results were plotted in Figure 5. It is observed that FC is the most efficient configuration in an extremely narrow band of values of α_A and α_B. This narrow band is bounded by regions where IS_{LV} and DS_{LV} are most efficient, where $\alpha_A < 5.5$ and $\alpha_B < 2.7$. From Figure 5 it can be safely concluded that, for the distillation of an *equimolar* feed mixture, the most efficient configuration is almost always either the DS_{LV} or the IS_{LV}.

A curious observation from Figure 5 is that one of the boundaries between the DS_{LV} and IS_{LV} regions is almost a straight line with a slope of 2. Therefore, for an *equimolar* mixture it can be deduced that, for all practical purposes, for the values of both α_A and α_B less than or equal to 11 (the applicable range of Figure 5), DS_{LV} is the most efficient configuration when $\alpha_A > 2\alpha_B - 1$ and IS_{LV} is the most efficient configuration when $\alpha_A < 2\alpha_B - 1$. For those values of α_A and α_B which are within a narrow band of $\alpha_A = 2\alpha_B - 1$, the difference in efficiency between the two configurations is small.

(ii) Calculations were also done for feeds *rich in one of the components*. For this purpose, the mole fraction of the major component was taken to be 90% and the mole fraction of each of the other two components was 5%. The results for A-rich, B-rich, and C-rich feeds are plotted in Figure 6 for $a_{AB} = 3$. The most efficient configurations for different values of α_A and α_B are shown in Figure 7.

For the A-rich feed, it is found that the overall thermodynamic efficiency is quite low (Figure 6a). This is due to the fact that the feed is saturated liquid and most of it must be vaporized at temperatures higher than the feed temperature. We suspect that a saturated vapor feed or a two-phase feed would give higher efficiency (i.e., it may be worthwhile to use a feed vaporizer for an A-rich feed).

Generally, it would be expected that for an A-rich feed, a direct split configuration would be attractive. This is supported by Figure 6a. However, from Figure 7a it is observed that for certain values of relative volatilities, the SS configuration has the highest efficiency. FC, SR, and IS_{LV} configurations do not show up in Figure 7a. Similar to Figure 5, the boundary between the two regions is nearly a straight line with a slope of 2. Therefore, for this A-rich feed, DS_{LV} is the most efficient configuration when $\alpha_A > 2\alpha_B - 1$, and SS is the most efficient configuration when $\alpha_A < 2\alpha_B - 1$. For values of α_A and α_B, that are within a narrow band of $\alpha_A = 2\alpha_B - 1$, the difference in efficiency between the DS_{LV} and SS configurations is small.

For the B-rich feed, DS_{LV} is almost always found to be the most efficient configuration (Figures 6b and 7b). This is not surprising because the given feed is saturated liquid and DS_{LV} is the only configuration, which allows a large fraction of the heat input at T_{BC} (in reboiler BC) and transfers some vapor to the second column which is then condensed at T_B. This reduces
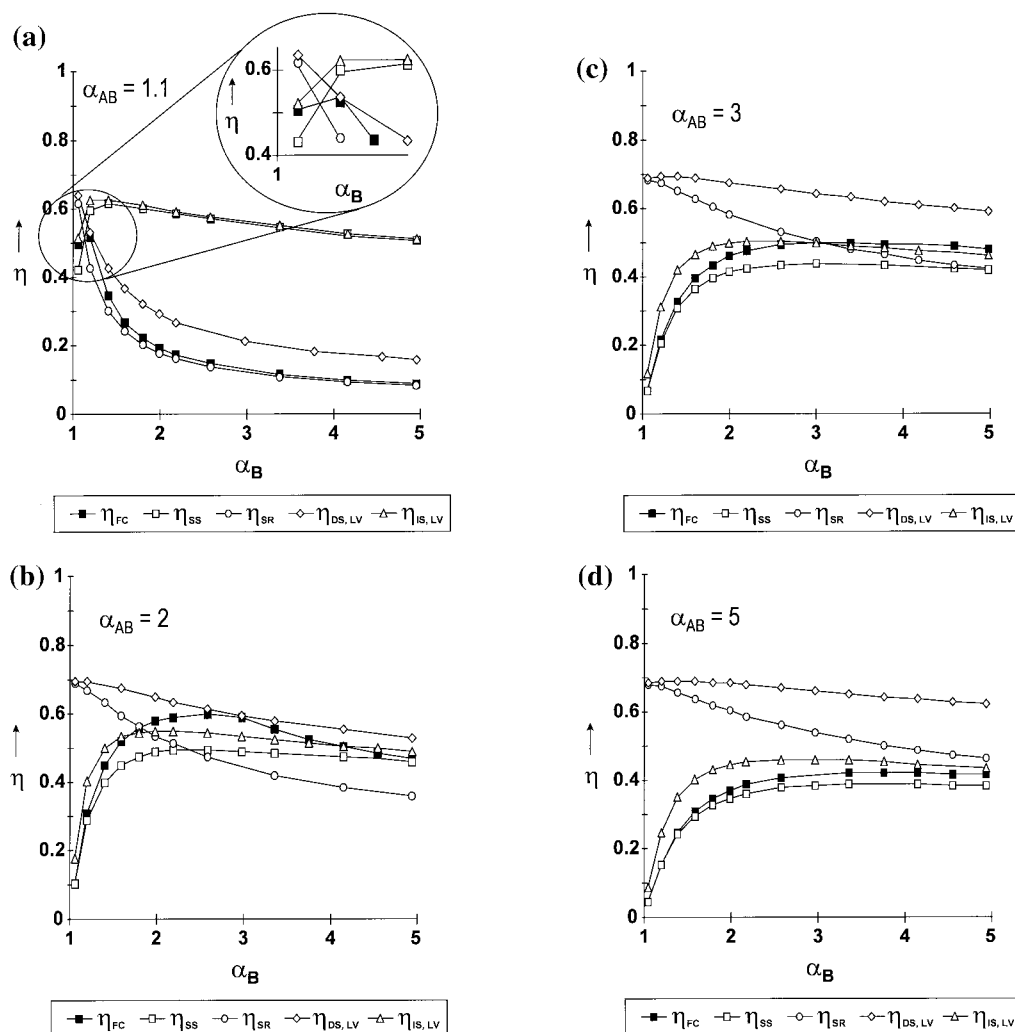
(a)

(c)

(b)

(d)

Figure 4. Thermodynamic efficiency for an equimolar feed mixture ($z_A = z_B = z_C$) as a function of α_B for several values of α_{AB}: (a) α_{AB} = 1.1, (b) α_{AB} = 2, (c) α_{AB} = 3, and (d) α_{AB} = 5.
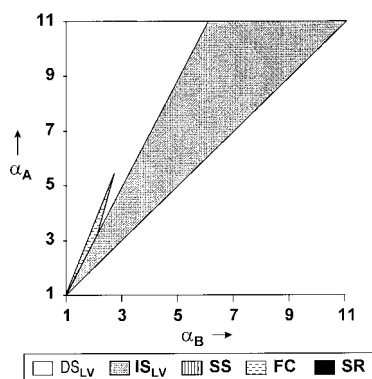

Figure 5. The most efficient configuration to distill an equimolar mixture ($z_A = z_B = z_C$) as a function of α_A and α_B.

the degradation of a sizable fraction of the heat needed for this distillation.

For the C-rich feed, the most efficient configuration is generally SR or IS_{LV}. In Figure 7c, only for some values of α_A and α_B, the FC configuration is found to be the most efficient. For such values of α_A and α_B, the difference in thermodynamics efficiencies of the FC and the IS_{LV} configurations is quite small. Therefore, it can be said that for $\alpha_A < 2.8\alpha_B - 1.8$, the IS_{LV} is generally the most efficient configuration for this C-rich feed. For greater values of α_A (i.e., $\alpha_A > 2.8\alpha_B - 1.8$), the SR is

the most efficient configuration. It is interesting to note that the thermodynamic efficiency of the SS configuration to distill a C-rich feed is the lowest (Figure 6c).

(iii) In Figures 4 and 6 it is observed that as α_B approaches unity, the efficiency of all configurations except the DS_{LV} and the SR drops rapidly. This results from the fact that as α_B approaches unity (and its value is significantly lower than α_{AB}), the separation between B and C becomes more demanding relative to the separation between A and B. The vapor traffic in sections separating B and C will be relatively large. In order to have reasonable values of efficiency, it is essential that some heat be rejected at the higher temperature T_B rather than at the significantly lower temperature T_A. Out of the five configurations, DS_{LV} and SR are the only ones which allow rejection of heat at T_B. These configurations are therefore preferred at lower values of α_B when α_B is significantly less than α_{AB}. Since a sizable fraction of heat can be added at temperature T_{BC}, which is lower than T_C, the DS_{LV} configuration has a slightly higher efficiency than the SR configuration for such cases.

(iv) For the compositions examined so far, the thermodynamic efficiency of the FC configuration has generally been found to be lower than that for one of the other configurations. A composition-space search was therefore made for some fixed values of relative
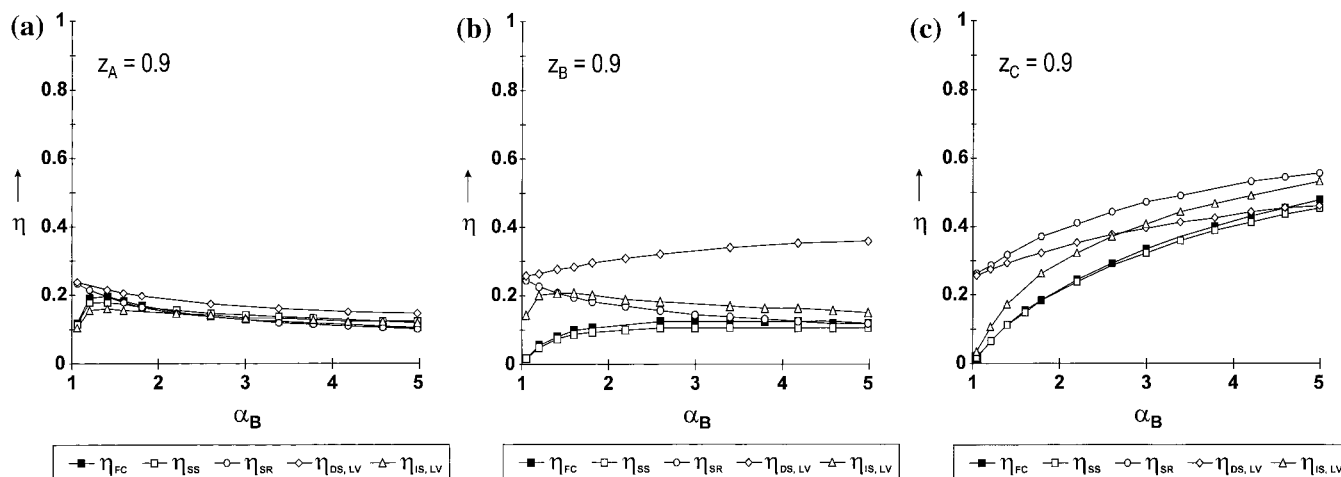
Figure 6. Thermodynamic efficiency for feeds rich in only one component as a function of α_B at a fixed value of $\alpha_{AB} = 3$: (a) A-rich feed ($z_A = 0.9$, $z_B = z_C = 0.05$), (b) B-rich feed ($z_B = 0.9$, $z_A = z_C = 0.05$), and (c) C-rich feed ($z_C = 0.9$, $z_A = z_B = 0.05$).

Figure 7. The most efficient configuration to distill a feed rich in only one component: (a) A-rich feed ($z_A = 0.9$, $z_B = z_C = 0.05$), (b) B-rich feed ($z_B = 0.9$, $z_A = z_C = 0.05$), and (c) C-rich feed ($z_C = 0.9$, $z_A = z_B = 0.05$).
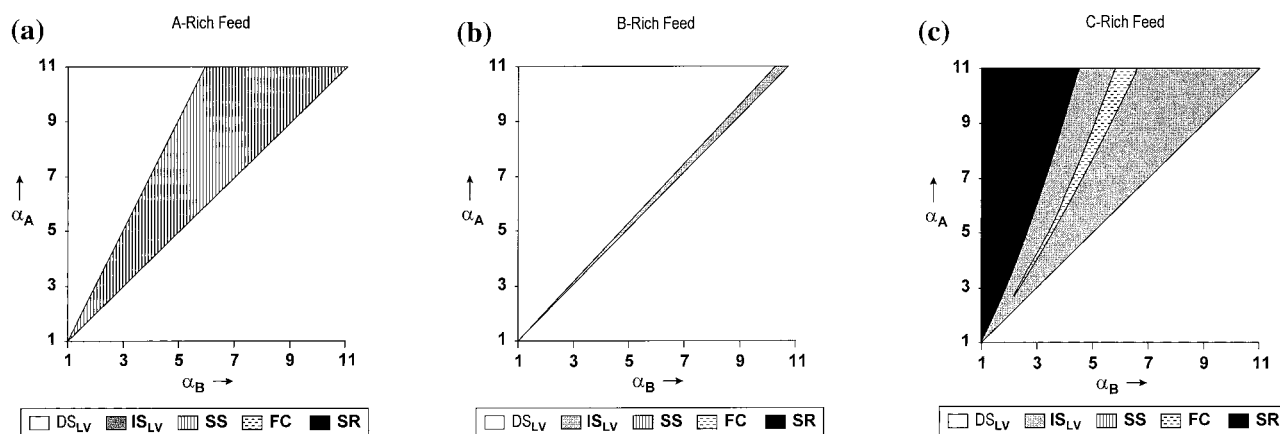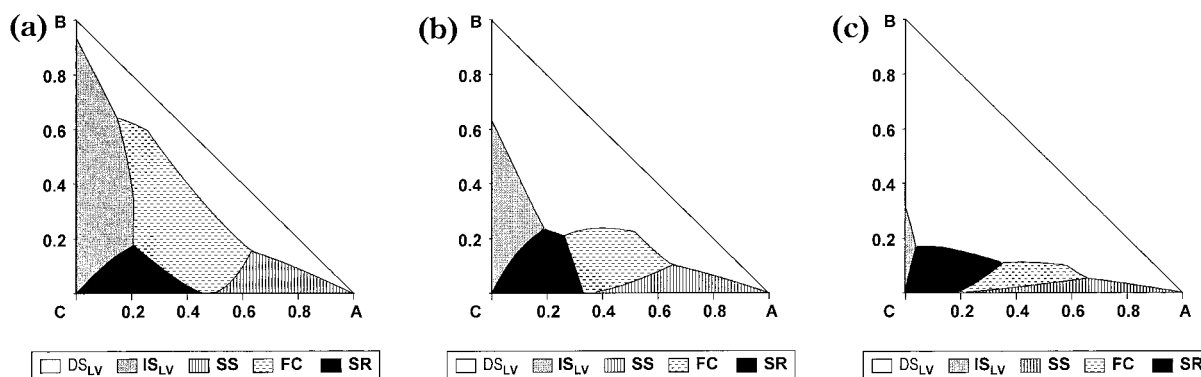

Figure 8. The most efficient configuration at each composition for fixed values of α_A and α_B ($ESI = 1$): (a) $\alpha_A = 1.21$, $\alpha_B = 1.10$; (b) $\alpha_A = 4$, $\alpha_B = 2$; (c) $\alpha_A = 25$, $\alpha_B = 5$.

volatilities to try to locate compositions for which the FC configuration would be the most efficient. Some of the results are shown in Figure 8, which displays most efficient configurations as a function of feed composition. *For all the runs in Figure 8, the relative volatility between A and B (α_{AB}) was kept equal to the relative volatility between B and C (α_B).*

In Figure 8a, where the separation is relatively difficult due to lower values of α_A and α_B, the thermally coupled configurations are found to dominate the composition space. The FC configuration is generally found to be the most efficient for compositions close to equimolar. While the SS and SR configurations are found to

be the most efficient when B is present in small concentrations (along the AC axis), DS_{LV} is found to be most efficient for low concentrations of C (along the AB axis) and IS_{LV} is most efficient for low concentrations of A (along the BC axis).

As the separation between the components becomes less difficult (i.e., as the values of α_A and α_B are increased), it is found from Figure 8b,c that the zone where thermally coupled columns are the most efficient shrinks. The DS_{LV} configuration's zone increases in size and the zones of the thermally coupled configurations are confined to areas with lower concentrations of B (along the AC axis). The FC configuration is the most

efficient only when both A and C are present in comparable concentrations, and with much smaller concentrations of B. This observation contrasts with the statement made in the literature[19] that the FC configuration is often attractive when there is a large amount of B, with significant amounts of both A and C.

It is interesting to observe that for the moderate-to-high values of relative volatilities in Figure 8b,c, the IS_{LV} configuration is the most efficient for a C-rich feed containing more B than A. This configuration has the highest efficiency in a narrow zone along the BC axis.

(v) It has been suggested in the literature[19] that the SS configuration would be most attractive when the amount of B is small and the amount of A is substantially less than the amount of C. However, from the thermodynamic efficiency point-of-view, a contrary observation is made from Figure 8a−c; the SS configuration is most efficient when the amount of B is small and the amount of A is substantially more than the amount of C. Similarly, the SR rather than the SS configuration is found to be the most efficient when B is present in small concentrations and the amount of C is more than the amount of A. These somewhat unexpected results can be explained as follows. When the amount of A is substantially more than the amount of both B and C, the majority of the vapor traffic goes through condenser A to produce A. Two possible methods to increase the efficiency are either to provide a significant fraction of heat at T_B (the SS configuration) or to reject heat at T_B (the SR configuration). It was shown[4] that total the vapor demand for both SR and SS is the same. However, when the amount of B is low, the concentration of B in the liquid feed to the side stripper is considerably lower than that in the vapor feed to the side rectifier. This is because the liquid feed to the side stripper is diluted with a large quantity of A, whereas the vapor feed to the side rectifier has comparable quantities of C. Therefore, in order to produce the same quantity of B, the vapor traffic through the side stripper must be considerably more than the vapor traffic through the side rectifier. This provides an opportunity to supply a much larger fraction of heat at the intermediate temperature T_B for the SS configuration as compared to the smaller quantity of heat rejected at T_B for the SR configuration. As a result, for the A-rich feed with small quantities of B and C, the SS is more efficient than the SR configuration. Similarly, for a C-rich feed with smaller quantities of A and B, the high efficiency of the SR configuration as compared to that of the *SS* configuration can be easily explained.

(vi) Figure 8 displays results obtained when the relative volatility of A with respect to B was the same as the relative volatility of B with respect to C (i.e., $\alpha_{AB} = \alpha_B$). It is also worthwhile to examine the effects of unequal values of α_{AB} and α_B. The ease of separation index (ESI), which was introduced in ref 14, is defined as follows:

$$ESI = \frac{\alpha_{AB}}{\alpha_B} = \frac{\alpha_A}{\alpha_B^2} \qquad (12)$$

When *ESI* is greater than 1, distillation between A and B is easier as compared to distillation between B and C and vice versa.

Figure 9 shows results for two different sets of α_A and α_B when ESI is sufficiently greater than 1. Figure 9a can be compared with Figure 8a to observe the effect of
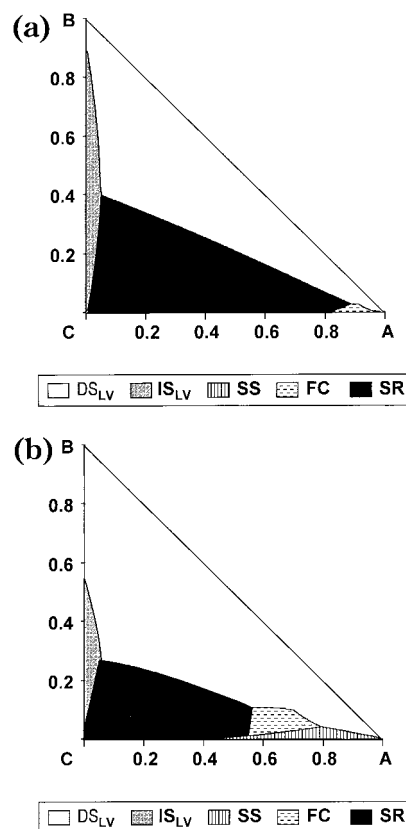

Figure 9. The most efficient configuration at each composition for fixed values of α_A and α_B (ESI > 1): (a) $\alpha_A = 1.65$, $\alpha_B = 1.10$, ESI = 1.36; (b) $\alpha_A = 6$, $\alpha_B = 2$, ESI = 1.5.

increasing ESI. While the value of α_B is the same in both these figures, the value of α_A is considerably higher in Figure 9a. Similarly, Figure 9b can be compared with Figure 8b. It is observed that as α_{AB} is increased beyond α_B (as ESI increases beyond unity), the zones where the DS_{LV} and the SR configurations are most efficient increase. This result is consistent with the situation previously described in observation (iii). For values of ESI generally greater than 1.5, the two configurations SR and DS_{LV} occupy almost the total space in the composition diagram. However, the value of ESI cannot be used alone to define the boundary between the zones where the DS_{LV} and SR configurations are most efficient. When ESI exceeds 1.5, the SR configuration is almost always the most efficient configuration for a C-rich feed; the SS configuration is rarely the most efficient configuration for any composition; for an A-rich feed, the most efficient configuration is usually DS_{LV} or SR, but the FC configuration is occasionally of relevance.

Figure 10 shows the results of two cases when ESI is less than 1 (i.e., the distillation between B and C is easier than the distillation between A and B). Figure 10a,b can be compared with Figure 8b. We find that the zone where the SR configuration is most efficient practically disappears as ESI is lowered to a value of 0.65. As expected, the most efficient configurations are the SS and the IS_{LV}. However, for moderate-to-high values of α_B, DS_{LV} can be the most efficient configuration along the AB axis. For A-rich feeds, the most efficient configuration is between DS_{LV} and SS with SS being most favored when C is present in reasonable amounts. For a C-rich feed, the efficient configuration is generally between IS_{LV} and SS with the FC config-
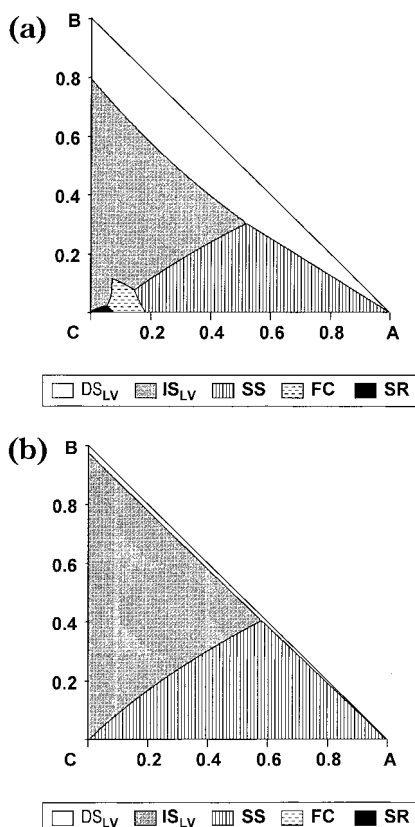
Figure 10. The most efficient configuration at each composition for a fixed value of α_A and α_B (*ESI* < 1): (a) $\alpha_A = 2.6$, $\alpha_B = 2$, ESI = 0.65; (b) $\alpha_A = 2.05$, $\alpha_B = 2.0$, ESI = 0.51.
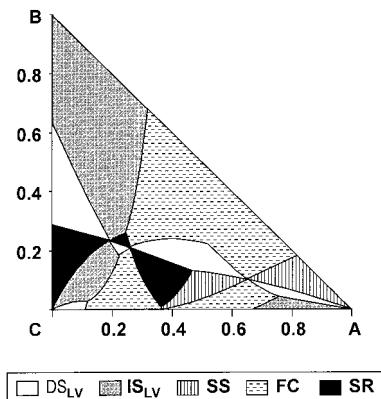

Figure 11. The second most efficient configuration at each composition: $\alpha_A = 4$, $\alpha_B = 2$, ESI = 1.

uration sometimes being of relevance. For a highly B-rich feed, ($z_B > 90\%$), DS$_{LV}$ is generally the most efficient configuration. The FC configuration is the most efficient when the amount of B is low and there is more C than A in the mixture (along the CA axis).

(vii) It is interesting to inspect the second most efficient configurations in composition space for comparison with the most efficient configurations. One such plot is shown in Figure 11, which may be compared with Figure 8b. As expected, the second most efficient configurations are those obtained by interchanging the most efficient configurations across the boundary in Figure 8b. Thus, near the boundary of the DS$_{LV}$ and the FC in Figure 8b, the second most efficient configurations are obtained by interchanging the DS$_{LV}$ and FC configurations. It can be concluded from inspection of Figures 8b and 11 that, for modest values of α_A and α_B

(with ESI not too different from one), when the two most efficient configurations are considered together, the FC configuration is found to fill a much larger composition space. However, this conclusion is not valid when ESI is much different from 1.

On the basis of these observations, the following conclusions can be drawn for the distillation of a saturated ternary liquid feed into pure product streams:

(1) The FC configuration does not always have the highest thermodynamic efficiency. As a matter of fact, the range of values of relative volatilities and the feed composition for which it is the most efficient is quite limited. Also, for certain values of relative volatilities and feed compositions, it can have considerably lower values of efficiency in comparison to the other configurations.

(2) Thermally coupled column configurations as a group (compared to FC alone) occupy much more composition space as the most efficient configurations.

(3) The modified direct split (DS$_{LV}$) and indirect split (IS$_{LV}$) configurations are found to have fairly high thermodynamic efficiencies. Together, they generally occupy more composition space as the most efficient configuration than does the thermally coupled column group. The high thermodynamic efficiency of the DS$_{LV}$ and the IS$_{LV}$ configurations is primarily due to their ability to supply heat at an intermediate temperature T_{BC} or to reject heat at an intermediate temperature T_{AB}.

(4) The relationship between the most efficient configuration and the feed composition cannot be correlated on the basis of ESI alone. For ESI = 1, it is found that for any given composition, the most efficient choice depends on the actual values of α_A and α_B. Similarly, the location of the boundary between the adjacent most efficient configurations shifts as actual values of α_A and α_B are changed, for any given value of ESI.

(5) However, some gross generalizations based on ESI can be made. The FC configuration is found to occupy considerable composition space as the most efficient configuration only when the value of ESI is in the neighborhood of 1. When ESI is significantly greater than 1 (say 1.5 or higher), the two configurations which are generally found to be the most efficient are DS$_{LV}$ and SR. Similarly, when ESI is considerably less than 1 (say 0.65 or lower), the two configurations which are generally found to be the most efficient are IS$_{LV}$ and SS; however, DS$_{LV}$ can be of interest along the AB axis.

(6) For a B-rich feed ($z_B \geq 80\%$), DS$_{LV}$ is almost always the most efficient configuration; the IS$_{LV}$ can be the most efficient when α_A is only marginally greater than α_B.

(7) Thermally coupled columns are found to be the most efficient choice along the AC axis. Specifically, when B is in small quantity ($z_B < 20\%$) and A and C are present in comparable amounts, the most efficient configuration is always one of the thermally coupled columns.

(8) For an A-rich feed ($z_A \geq 80\%$), the most efficient choice is not always the DS$_{LV}$ configuration, but it may also be the thermally coupled configurations SS (for ESI less than 1 or in the neighborhood of 1), or SR or FC (for ESI significantly greater than 1).

(9) Similarly for a C-rich feed, IS$_{LV}$ is not the universal choice for the most efficient configuration. Such a choice is found to be between the configurations IS$_{LV}$ and SR (when ESI is in the neighborhood of 1 or greater than 1) or SS and FC (when ESI is significantly less than 1).
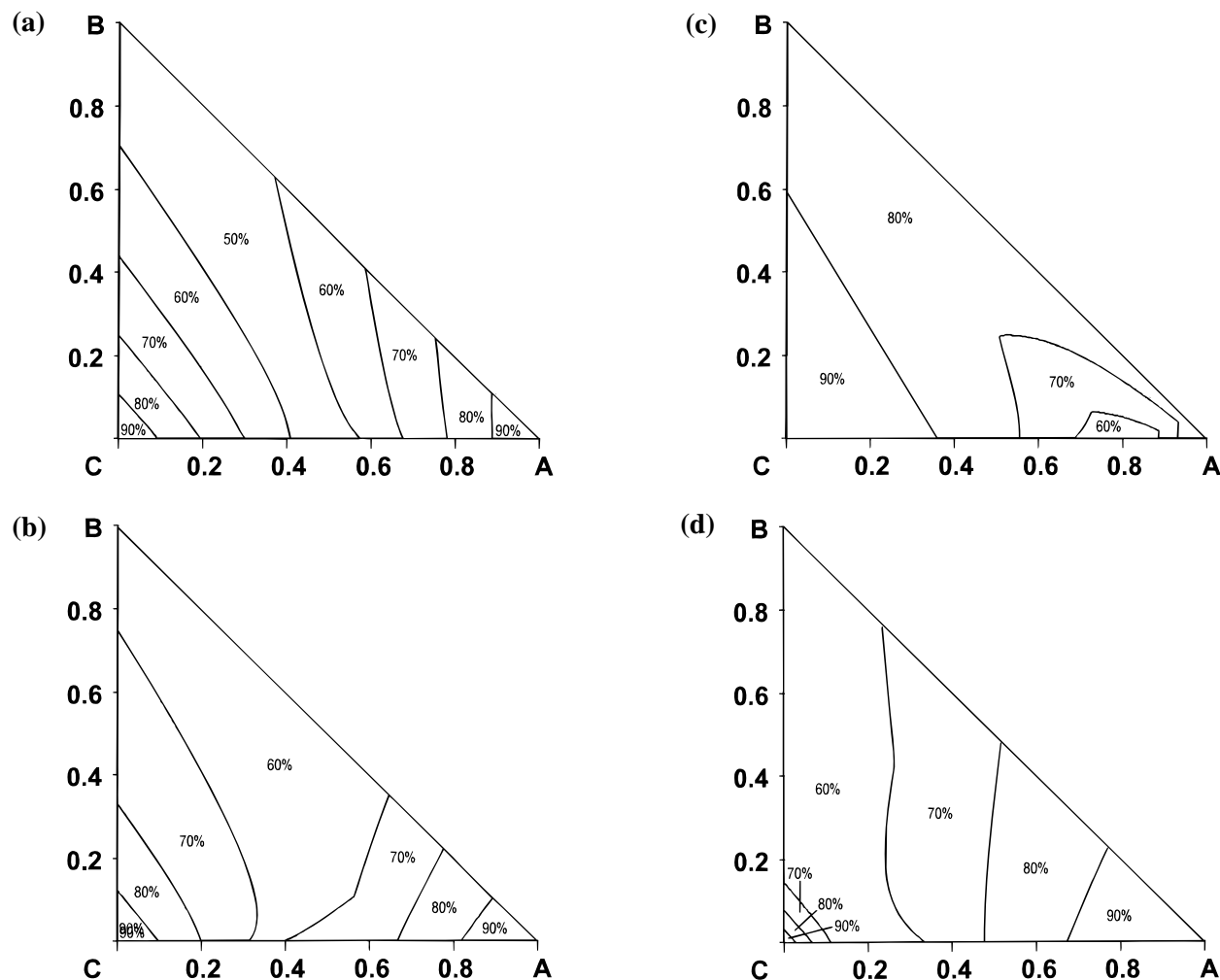
Figure 12. Total heat demand of the FC configuration compared to that of the DS_{LV} or IS_{LV} configuration. The $n\%$ denotes that the total heat demand for the FC configuration lies between $n\%$ and $(n+10)\%$ of the lower of the two heat demands of the DS_{LV} and the IS_{LV} configurations. (a) $\alpha_A = 1.21$, $\alpha_B = 1.10$, ESI = 1.0; (b) $\alpha_A = 4$, $\alpha_B = 2$, ESI = 1.0; (c) $\alpha_A = 1.65$, $\alpha_B = 1.10$, ESI = 1.36; (d) $\alpha_A = 2.6$, $\alpha_B = 2$, ESI = 0.65.

(10) When the value of α_B is lower than the relative volatility of A with respect to B (i.e., ESI > 1) and α_B approaches 1, the thermodynamic efficiencies of all configurations except DS_{LV} and SR fall precipitously; this is true for all feed compositions.

B. Total Heat Demand. In order to generate the thermodynamic efficiency–composition diagrams presented above, vapor flows in each distillation column under pinched conditions were calculated for all five configurations. It is useful to compare the vapor flow generated in the reboiler of the FC configuration with the lower of the two total vapor flow generated in the DS_{LV} and the IS_{LV} configurations; Figure 12 displays these comparisons. In these figures, the composition zones labeled $n\%$ denotes that the vapor generated in the reboiler of the FC configuration lies between $n\%$ and $(n+10)\%$ of the minimum of the total vapor flows generated in either of the DS_{LV} or the IS_{LV} configurations. It is worth noting that, for pinched conditions, the modified direct split configuration DS_{LV} requires the same total vapor flow as the conventional direct split configuration DS_L shown in Figure 2a.[16] The same is true for the IS_{LV} and the IS_V configurations. Thus, a number of 70% in Figure 12 means that the FC configuration requires somewhere between 70% and 80% of the total flow required by the direct or indirect split configurations. By inspection of Figure 12a–d it

is observed that the FC configuration is capable of substantial reduction in the total heat demand as compared to the DS_{LV} and the IS_{LV} configurations; however, the magnitude of the savings depends considerably on the feed composition and on the values of relative volatilities.

It is interesting to compare the contours in Figure 12 with the most efficient configuration maps shown in earlier figures. For this purpose, the figures to compare are 12a with 8a, 12b with 8b, 12c with 9a, and 12d with 10a. One sees, for example, that for a highly B-rich feed, the FC configuration can require 10–50% less total vapor flow than for the DS_{LV} or IS_{LV} configuration, and yet it is thermodynamically less efficient than one of these configurations. This clearly shows the importance of accounting for the temperature level at which heat is supplied or rejected in determining the thermodynamic efficiency of a distillation configuration.

C. An Industrial Example. The separation of air to produce argon is an important industrial application of cryogenic distillation. For this example, air is treated as a ternary mixture of N_2 (A), Ar (B), and O_2 (C). Generally, a high-pressure and a low-pressure distillation column with a side rectifier is used.[20,21] Air (78.12% N_2, 0.93% Ar, and 20.95% O_2) is first cooled to near its dew point and is distilled in a high-pressure column to produce a liquid nitrogen stream at the top of the

column and a crude liquid oxygen bottoms stream. The bottoms stream generally has about 65% nitrogen and 1.5% argon, and the rest is oxygen. The crude liquid oxygen stream then forms the feed to a lower pressure column. It is in this column that final distillation is performed to produce nitrogen at the top and oxygen from the bottom. A side rectifier is used with the low-pressure column to produce argon. This general configuration using a side rectifier to recover argon has been in use for over 65 years.[22]

Recently, a number of attempts have been made to replace the SR configuration with the FC configuration. However, for the same energy input, the recovery of argon is lower for the FC configuration than for the SR configuration. Attempts have also been made[23] to improve the performance of the FC configuration through additional thermal linking between the two columns of this configuration. The higher energy consumption (or the lower argon recovery) for the FC configuration can be easily understood using the methods described here. For this example, the crude liquid oxygen bottoms from the high-pressure column is taken to be the ternary liquid feed which needs to be separated into three pure product streams. Under the typical operating pressure of near atmospheric pressure, the relative volatility between nitrogen and oxygen (α_A) is about 3.8 and the relative volatility between argon and oxygen (α_B) is about 1.1. Calculations were done for $z_A = 0.65$ and $z_B = 0.015$. It is found that the minimum vapor flow needed per unit feed flow in the reboiler of the FC configuration is 3.57 and for the SR configuration is 3.58. The thermodynamic efficiency of the FC configuration is 14.9% and for the SR configuration it is 44.5%! For this application, the efficiency of the SR configuration may be further improved by using a portion of the feed (crude liquid oxygen bottom) to provide condensing duty for the side-rectifying column, and thereby providing two feeds (one liquid and one nearly vapor) to the main low-pressure column (Siedel, 1935; ref 21). Therefore, it is not a surprise that, in spite of many attempts, the FC configuration has not found application in cryogenic air separation.

D. Miscellaneous Comments. For a given separation of an ideal ternary mixture, rather than relying on heuristics, a quick calculation can be done for the vapor flows of pinched columns and the corresponding thermodynamic efficiencies to provide guidance in the selection of distillation system configuration. For real mixtures, relative volatilities are generally not constant along the length of the distillation columns, and therefore these calculations may need to be done for more than one set of values of relative volatilities to cover the range of relative volatilities of interest. A search for the optimum configuration requires that, along with other issues such as operability and capital cost, both first law heat demand and thermodynamic efficiency be part of the decision-making process. There is no simple correlation between thermodynamic efficiency and the final cost of a separation process; the capital and energy trade-off is project-specific and the relative importance of each is quite situation-specific. In situations where only one heat source and one heat sink are available, thermodynamic efficiency is of less consequence and the solution may involve a choice between configurations which have similar lower total vapor flow rates for pinched columns. On the other hand, when heat sources and heat sinks are available at multiple levels,

or when heat to and from the reboilers and condensers of the columns is to be integrated with other process equipment in the plant, the choice may be between configurations which have similar high thermodynamic efficiencies. These conditions arise, for example, for subambient temperature distillations where heat from the condenser needs to be pumped to the reboiler. This is the main reason why the FC configuration has yet to be used for cryogenic distillation. Also, the calculation of thermodynamic efficiencies helps to identify situations such as the one in Figure 6a when thermodynamic efficiency of all the ternary configurations is quite low. This encourages a process engineer to either search for innovative solutions that would boost the thermodynamic efficiency of a distillation configuration or look for alternative solutions to these distillation configurations.

Conclusions

The thermodynamic efficiency of three thermally coupled column configurations (side rectifier, side stripper, and fully coupled) to distill an ideal ternary saturated liquid into pure product streams has been calculated and compared with the modified direct and indirect split configurations. A striking result of this study is that, for the fully coupled column configuration, which is known to have the lowest heat demand for ternary distillation, the range of values of feed composition and relative volatilities for which it is the most efficient is quite limited. Also, for certain values of relative volatilities and feed compositions, this configuration can have considerably lower values of thermodynamic efficiency than the other configurations. When compared to the fully coupled configuration alone, the thermally coupled columns as a group are found to contain the most efficient configuration in a greater area of feed composition space. Thermally coupled columns are generally found to be the most efficient selection when B is present in the feed in a much smaller quantity.

The modified direct and indirect split configurations generally provide the most thermodynamically efficient configurations for more feed compositions than does the thermally coupled column group. Surprisingly, it is found that even for some of those situations when the modified direct and indirect split configurations have much higher total heat duty than do the thermally coupled column configurations, the former can still be thermodynamically more efficient. One such case is found for highly B-rich feeds. The high thermodynamic efficiency of these two configurations is primarily due to their ability to accept heat at an intermediate temperature T_{BC}, or to reject heat at an intermediate temperature T_{AB}.

Even though some generalized relationships between the thermodynamic efficiency of ternary distillation configurations and the feed composition and relative volatilities have been drawn in this work, it is suggested that such heuristics should not be used to make the selection between various configurations. Because thermodynamic efficiency and vapor flow calculations for pinched column configurations can be quickly performed for any application, a much better selection can be made based on such calculated numbers.

Acknowledgment

encouraging him to extend the exergy analysis method, developed originally for a binary distillation, to the distillation of ternary and multicomponent mixtures.

Notation

A, B, C: flow rate of component A, B, and C in the feed, kmol/s

DS_{LV}: direct split configuration in Figure 3a

e: exergy of saturated liquid phase, kJ/kmol

E: exergy of saturated vapor phase, kJ/kmol

ESI: ease of separation index, defined by eq 12

F: feed flow rate, kmol/s

FC: fully coupled configuration

IS_{LV}: indirect split configuration in Figure 3b

R: gas constant (8.314 kJ/(kmol·K))

SR: side-rectifier configuration

SS: side-stripper configuration

T: temperature, K

V: vapor flow rate, kmol/s

z: mole fraction in feed—also, occasionally mol %

α_A: relative volatility of A with respect to C

α_B: relative volatility of B with respect to C

α_{AB}: relative volatility of A with respect to B

δ: defined by eq 5

η: thermodynamic efficiency, defined by eq 1

μ: defined by eq 6

Subscripts

A, B, C: component A, B, and C, or when used with V, section of the column where A, B, or C is produced

AB: mixture of component A and B

BC: mixture of component B and C, or when used with V, section of column where mixture BC is produced

F: feed

i: component

0: ambient conditions

Superscripts

T: thermal component of exergy

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