

density and bond polarization factors are affecting one or more of the mechanisms of reactions leading to hot products such as acetylene.

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Minimization of Entropy Production in Distillation

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The distillation process is analyzed on the basis of its entropy production. Methods of reducing that entropy production are evaluated. An analytical treatment is given for a simple model of binary distillation for total and partial separation. The model is shown to be compatible with descriptions of real systems. The method finds the optimal location of intermediate heat exchangers which are known to reduce entropy production. Performance goals must be defined precisely in order to assess the impact of optimal process modification. Reversible distillation is shown to result for a special case from an infinite number of optimally placed heat exchangers. A comparison is made of the effectiveness of intermediate heat exchangers and multiple columns for reducing entropy production in a binary separation.

Introduction

The first and one of the most important applications of thermodynamics is the provision of limits on the performance of any system. Maximum efficiencies can be found by considering processes which operate at the limit of reversibility. However, it is often important to understand the limiting performance of processes with irreversibilities inherent in either their fundamental description or their execution in practice. Methods are evolving to augment reversible thermodynamics with generalized descriptions accounting for irreversibilities and finite-time behavior for various classes of processes.¹ These descriptions lead naturally to the use of optimization to achieve the various performance goals.¹

In this presentation we extend our analyses of chemical processes^{2,3} by examining one of the simplest cases in which the work performed is chemical, namely, separation by distillation. We carry out an analytic solution of the optimization for various methods of reducing the entropy production for a given separation or, equivalently, of increasing the effectiveness of the distillation. The standard thermodynamic efficiency is not a suitable criterion of merit for several idealized processes of separation such as distillation because heat is not consumed but only degraded. For distillation as we describe it, minimizing the entropy production is equivalent to minimizing the net work consumption. This equivalence relates the concepts of effectiveness and efficiency. It will also be seen, from a comparative analysis of different distillation processes, that minimizations of the absolute and the fractional entropy production yield markedly different results.

Distillation

A brief review is given here of the pertinent essentials of the distillation process and of the vocabulary that describes it, to help

readers not familiar with chemical engineering processes to follow the ensuing discussion. In the process of distillation the degradation of heat is used to drive a chemical separation.⁴ To achieve separation by distillation or other equilibrium countercurrent exchange processes a minimum quantity of internally circulating fluid is required. In distillation the vapor-liquid countercurrent flows are typically established by a continuous reflux.⁴ A flow (moles per unit time) of liquid (*L*) maintained at its boiling point and of vapor (*V*) are circulated between stages in order to purify a quantity of feed per unit time (*F*) into products.

Figure 1 depicts this purification of the feed flow (*F*) into the product flows, the distillate (*D*) being enriched in the volatile component and the bottoms (*B*) being enriched in the less volatile component. In distillation heat is added below the feed point, that is, to the stripping section of the column, to drive off the volatile materials and in the descending liquid stream. Similarly, heat is removed above the feed point, that is, to the rectifying section of the column, to condense the less volatile materials out of the ascending vapor stream.

In a distillation column the liquid (*L*) and vapor (*V*) flows are often nearly constant in a subsection containing no heat exchangers or side-stream inputs or outputs. By assuming constant flows and considering mass balance, one can obtain linear relations, called operating lines, for the components' concentrations in the flow streams passing between adjacent stages.⁴ Equilibrium curves limit the concentrations of flow streams leaving a given stage. Thus, concentration differences in the flow streams at any point in the column are bounded by the operating lines and the equilibrium curve. The McCabe-Thiele diagrams (Figure 2) graphically depict the distillation process.⁴ Figure 2a corresponds to a column with no intermediate heat exchangers while Figure 2b corresponds to a column with two intermediate heat exchangers. Irreversibilities which arise from mixing of flow streams with components at different chemical potentials are reduced when the operating lines are constructed to lie closer to the equilibrium

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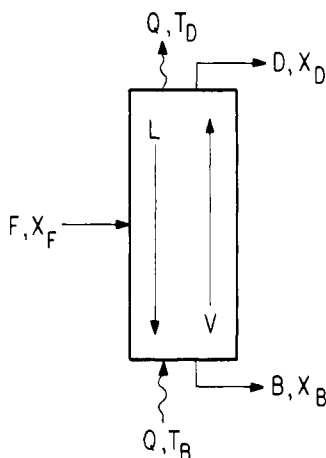


Figure 1. Purification of a quantity of feed per unit time (F) of mole fraction x_F into bottoms (B) and distillate (D) of mole fractions x_B and x_D , respectively. Note the countercurrent flows of ascending vapor (V) and descending liquid (L) which are maintained by the degradation of heat (Q) through the temperature gradient $T_B - T_D$.

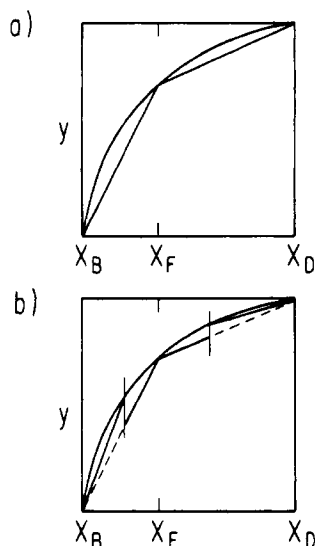


Figure 2. McCabe-Thiele diagrams relating the mole fraction of the volatile component in the vapor (y) and liquid (x) phases for the equilibrium curves and the distillation operating lines. The subscripts F , B , and D correspond to feed, bottoms, and distillate, respectively. These diagrams represent total purification. (a) For a distillation column with no intermediate heat exchangers. (b) For a distillation column with two intermediate heat exchangers.

curves. In the following analysis only binary distillation will be considered.

From mass-balance considerations expressions for the minimum liquid flows (L_m) can be obtained.

$$L_m(x_p) = \frac{F(x_F - x_B)(y_D - y_p)}{(\alpha - 1)(y_D - x_B)x_p(1 - y_p)} \quad (\text{rectifying section}) \quad (1)$$

$$L_m(x_p) = \frac{F(y_D - x_F)(y_p - x_B)}{(\alpha - 1)(y_D - x_B)x_p(1 - y_p)} \quad (\text{stripping section}) \quad (2)$$

for a liquid feed.^{4,5} y and x refer to the mole fraction of the more volatile component in the vapor and liquid flow streams and p refers to stage p . The separation factor $\alpha \equiv [y_p/x_p]/\{(1 - y_p)/(1 - x_p)\}$ is often constant for a given separation.^{4,5} As we are interested in the entropy production per unit feed, F will be set

equal to unity. Larger values of L than L_m can be employed but result in irreversible entropy production. L_m is a continuously varying function of x_p and, for constant α , L_m is a monotonic function of x_p which is maximized at x_F . Therefore, in distillation irreversible entropy production occurs unless a continuous adjustment of L can be made throughout the column.

Optimization of Distillation

General Considerations. Binary distillation is conventionally performed by using one column in which all heating occurs at the highest temperature region of the column, the lowest point of the stripping section, and all cooling occurs at the lowest temperature region of the column, the highest point of the rectifying section (neglecting possible thermal adjustment of the feed).⁴ This simple method of distillation is highly irreversible because all heat supplied to the column unnecessarily suffers the largest possible degradation in the column.

Several methods exist for reducing irreversibilities in distillation. In multi-effect distillation the distillate of one column is used to heat the bottoms of a second column, this being accomplished by operating the columns at different pressures.^{4,6,7} Large pressure differences can also be maintained between two column subsections allowing the transfer of heat from the rectifying section to the stripping section.⁷⁻¹⁰ The total quantity of heat necessary for separation is reduced but higher quality heat is often required at the high-temperature stripper and additionally the expenditure of work is often necessary to maintain the pressure differential.

Heat pumps can also reduce irreversibilities in distillation by allowing heat to be transferred from the distillate to the bottoms.^{4,6,7,10-13} Again, the heat requirement for the column is reduced compared to the conventional case but at the expense of draining a work reservoir.

Irreversibilities in distillation can be reduced through the use of intermediate heat exchangers^{3-6,9,14-16} or "exchange points". In this case the total heat requirement of the column is equivalent to the conventional case but the degradation of the heat is reduced. It is the utility of exchange points which we will examine.

Numerical analyses have been performed which illustrated both the technical improvement and the economic impact of the use of exchange points.^{6,14} General expressions describing the impact of exchange points on the net work consumption have been given^{15,16} as have applications to specific examples.¹⁶ Kayihan¹⁵ also found an analytical solution for the optimal location of exchange points for the special case of total separation of an ideal binary mixture for which $\alpha \rightarrow 1$. Using the analytic solutions for exchange point locations he graphically illustrated the decrease in net work consumption for varying numbers of exchange points as a function of feed composition.¹⁵

We have found a general perturbative analytical solution for the optimized location of exchange points for partial purification and for separations where α is as large as 3. The effect of exchange points on the relative and absolute entropy production has been considered particularly as a function of the feed composition. Entropy production for the limiting case of an infinite number of exchange points is considered. The effectiveness of multiple columns for a binary separation is compared with that of exchange points in a single column.

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We assume that heat reservoirs which drive the distillation are available at arbitrary temperatures. We also assume that the enthalpies of the feed and products are equal, so that no net transfer of heat occurs. (This is done to avoid the unnecessary complications of mandatory heat transfer, which may be treated separately.)

It is our interest to minimize the entropy production in the heat reservoirs associated with a given separation. Here, we consider the entropy production to result from the degradation of heat in the column and not from the transport of heat across boundaries. Sufficient heat must be transferred to the column at appropriate locations to guarantee an adequate reflux (L_m) at all points in the column. Thus, to reduce irreversibilities through an altered process design, the heat degradation must be minimized subject to the constraining equations 1 and 2. If there were no limit to the allowable process alterations, the reversible entropy production should result (for binary distillation). The product of the entropy production (ΔS) and the ambient temperature (T_0) gives the net work consumption of the heat reservoirs. Thus, minimizing the entropy production is equivalent to minimizing the net work consumption.

A very common method of performing distillation is to maintain a constant reflux ratio (L/D) throughout the column⁴ where, from eq 1 and 2, $L = L_m(x_F)$. In an actual distillation column the reflux ratio is greater than $L_m(x_F)$ by a constant factor, typically 1.25, due to the finite number of plates and nonidealities in the distillation.⁴ This constant multiplicative factor does not affect the optimal exchange point locations but does affect the heat loads at the exchange points where the heat loads scale with L . We would like to describe distillation with the minimum of irreversibilities so we will ignore the multiplicative factor. To maintain a constant reflux ratio throughout the column a quantity of heat is added at the bottom of the column and removed at the top of the column. The corresponding entropy production is

$$\Delta S = \lambda_F L_m(x_F) (-1/T_B + 1/T_D) \quad (3)$$

where λ_F is the heat of vaporization of the mixture with composition x_F .

Kayihan's Result

Introducing exchange points reduces the entropy production for a given flow of feed by reducing the degradation of heat.^{3-6,9,14-16} That is, by increasing the variety of temperatures at which heat is exchanged with reservoirs, one reduces entropy production. Note that the total quantity of heat supplied to the column is not diminished by the addition of heat exchangers. If the heat of vaporization is constant, an expression can be written for the entropy production for M intermediate reboilers at x_j and temperature T_j' and N intermediate condensers at x_i and temperature T_i .

$$\begin{aligned} \Delta S_M^N = & \lambda L_m(x_1) \left(-\frac{1}{T_B'} + \frac{1}{T_1'} \right) + \\ & \sum_{j=2}^M \lambda L_m(x_j) \left(-\frac{1}{T_{j-1}'} + \frac{1}{T_j'} \right) + \lambda L_m(x_F) \left(-\frac{1}{T_M'} + \frac{1}{T_N} \right) + \\ & \sum_{i=2}^N \lambda L(x_i) \left(-\frac{1}{T_i} + \frac{1}{T_{i-1}} \right) + \lambda L_m(x_1) \left(-\frac{1}{T_1} + \frac{1}{T_D} \right) \quad (4) \end{aligned}$$

where the primed temperatures correspond to the stripping section and the unprimed to the rectifying section. For the limiting case of pure separation of an ideal binary mixture with $\alpha \rightarrow 1$ ($T_B - T_D \rightarrow 0$) Kayihan obtained an analytical solution.¹⁵ For $\alpha \rightarrow 1$ a symmetry appears for the two L_m equations 1 and 2. From the Calusius-Clapeyron equation an expression for $\alpha - 1$ results:^{3,15}

$$\alpha - 1 \sim \ln \alpha = \ln \frac{P_a(T_B)}{P_b(T_B)} \sim \frac{\lambda}{R} \left(-\frac{1}{T_B} + \frac{1}{T_D} \right) \quad (5)$$

where P_k is the vapor pressure of component k and R is the ideal gas constant. The lower case subscripts a and b refer to the more and less volatile components, respectively. An approximation can

be obtained for the temperature of the refluxing solution as a function of composition.^{3,15}

$$T_p = T_B - c \frac{\ln [1 + (\alpha - 1)x_p]}{\ln \alpha} \sim T_B - cx_p \quad (6)$$

where $c = T_B - T_D$ and x_p represents the mole fraction at some arbitrary location in the column. In the case of total separation, eq 4 can be simplified by using eq 5 and 6:

$$\begin{aligned} \frac{\Delta S_M^N}{R} = & \frac{x_{bF}}{x_{b1}} (1 - x_{b1}) + \frac{x_{bF}}{x_{b2}} (x_{b1} - x_{b2}) + \dots + \\ & \frac{x_{bF}}{x_{bM}} (x_{bM-1} - x_{bM}) + (x_{bM} + x_1 - 1) + \frac{x_F}{x_N} (x_{N-1} - x_N) + \\ & \frac{x_F}{x_{N-1}} (x_{N-2} - x_{N-1}) + \dots + \frac{x_F}{x_1} (1 - x_1) \quad (7) \end{aligned}$$

x_{bj} refers to the mole fraction of the less volatile component for the stripping section exchange points and x_i refers to the mole fraction of the volatile component for the rectifying section exchange points. As was shown the optimal location of the exchange points can now be obtained.¹⁵

$$x_i = x_F^{j/(N+1)} \quad (\text{rectifying section exchange points}) \quad (8)$$

$$x_{bj} = x_{bF}^{j/(M+1)} \quad (\text{stripping section exchange points}) \quad (9)$$

The corresponding heat removal at the rectifying section exchange points and heat input at the stripping section exchange points are¹⁵

$$Q_i = \frac{\lambda x_F}{\alpha - 1} \left(\frac{1}{x_{i+1}} - \frac{1}{x_i} \right) \quad \text{rectifying section} \quad (10)$$

$$Q_j = \frac{\alpha \lambda x_{bF}}{\alpha - 1} \left(\frac{1}{x_{bj+1}} - \frac{1}{x_{bj}} \right) \quad \text{stripping section} \quad (11)$$

Using Kayihan's results the entropy production for M stripping section exchange points and N rectifying section exchange points is

$$\begin{aligned} \Delta S_M^N / R = & x_{bF} (M + 1) [x_{bF}^{-1/(M+1)} - 1] + x_F (N + 1) [x_F^{-1/(N+1)} - 1] \quad (12) \end{aligned}$$

It is interesting that for this special case minimum entropy production corresponds to equivalent entropy production for column subsections between two exchange points. The correspondence of minimum entropy production and equal entropy production has been found to apply to a much different system.¹⁷

Reversibility

In the limit of an infinite number of optimally located exchange points above and below the feed, the expression for the reversible entropy production should emerge from eq 12; in that limit, the reflux ratio is continuously and optimally adjusted throughout the column. Expanding the appropriate terms in eq 12, we have

$$\lim_{\substack{M \rightarrow \infty \\ N \rightarrow \infty}} \Delta S_M^N = -R(x_{bF} \ln x_{bF} + x_F \ln x_F) \quad (13)$$

This is the well-known expression for the reversible entropy of mixing for two ideal components. Thus, as expected, for $M, N \rightarrow \infty$ the entropy production in the heat reservoirs (eq 13) is equivalent to the entropy decrease associated with the separation of the feed into pure components. With the assumption that $\alpha \rightarrow 1$ the isolated products and the feed have the same temperature. Relaxing this assumption would give products at different temperatures and lead to an additional contribution to the entropy decrease in the transformation of feed into products.

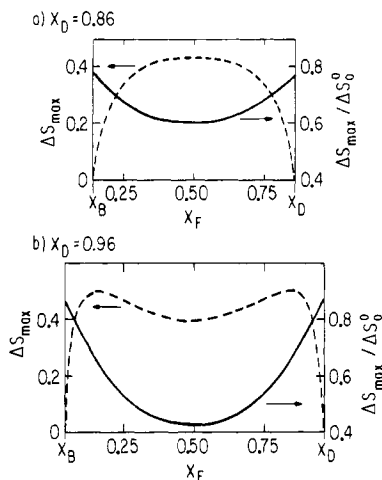


Figure 3. Maximum absolute (ΔS_{\max} (---)) and relative ($\Delta S_{\max}/\Delta S_0^0$ (—)) entropy production decrease in distillation through the use of exchange points as a function of x_F . $x_B = 1 - x_D$. ΔS_{\max} is in units of R , the ideal gas constant, where $F = 1$ and $\alpha \rightarrow 1$. (a) $x_D = 0.86$. (b) $x_D = 0.96$.

The More General Solution

In the case of partial purification an analytic solution for the optimal location of the exchange points cannot be obtained even with all assumptions (except total purification) used to obtain eq 7. However, with these assumptions and with the use of perturbation methods the approximate solutions for the location of exchange points are found. For $\alpha \rightarrow 1$ eq 1 and 2 for the minimum reflux can be rewritten

$$(\alpha - 1)L_m(x_p) = \frac{x_F - x_B}{x_D - x_B} \frac{1}{x_p} (1 - \delta_p) \quad (\text{rectifying section}) \quad (14)$$

where

$$\delta_p = \frac{1 - x_D}{1 - x_p} \quad (15)$$

and

$$\frac{(\alpha - 1)}{\alpha} L_m(x_p) = \frac{x_D - x_F}{x_D - x_B} \frac{1}{x_{bp}} (1 - \gamma_{bp}) \quad (\text{stripping section}) \quad (16)$$

where

$$\gamma_{bp} = \frac{1 - x_{bB}}{1 - x_{bp}} \quad (17)$$

The entropy production can be expressed in a format similar to eq 7 and the optimal locations of the exchange points can be solved. The zeroth-order solutions are

$$x_i = x_D (x_F/x_D)^{i/(N+1)} \quad (\text{rectifying section exchange points}) \quad (18)$$

$$x_{bj} = x_{bB} (x_{bF}/x_{bB})^{j/(M+1)} \quad (\text{stripping section exchange points}) \quad (19)$$

Note that for total purification the perturbation factors δ and γ are identically zero and eq 18 and 19 reduce to the exact solutions of eq 8 and 9. The optimal location of heat exchangers can be found iteratively by using eq 20 and 21,

$$x_i^2 = \left\{ 1 + \frac{1}{1 - \delta_{i+1}} \left[\frac{x_i}{x_{i-1}} \left(\frac{1 - x_{i-1}}{1 - x_i} \right) (\delta_{i-1} - \delta_i) - (\delta_i - \delta_{i+1}) \right] \right\} \quad (\text{rectifying section}) \quad (20)$$

$$x_{bj}^2 = \left\{ 1 + \frac{1}{1 - \gamma_{j+1}} \left[\frac{x_{bj}}{x_{bj-1}} \left(\frac{1 - x_{bj-1}}{1 - x_{bj}} \right) (\gamma_{j-1} - \gamma_j) - (\gamma_j - \gamma_{j+1}) \right] \right\} \quad (\text{stripping section}) \quad (21)$$

A numerical examination shows that the zeroth-order and iterated solutions often differ by only a few percent even when $x_D, x_{bB} \ll 1$ and for small M, N .

The heat load at the exchange points k can be obtained by accounting for the change of $L_m(x_k)$ resulting in equations similar to eq 10 and 11.

Using the approximate exchange point locations of eq 18 and 19 we find the entropy production for M stripping section exchange points and N rectifying section exchange points to be

$$\frac{\Delta S_M^N}{R} = \left(\frac{x_D - x_F}{x_D - x_B} \right) \left[\left(\frac{x_{bF}}{x_{bB}} \right)^{-1/(M+1)} - 1 \right] \left[(M+1) - (1 - x_{bB}) \sum_{j=1}^{M+1} \frac{1}{1 - x_{bB} (x_{bF}/x_{bB})^{j/(M+1)}} \right] + \left(\frac{x_F - x_B}{x_D - x_B} \right) \left[\left(\frac{x_F}{x_D} \right)^{-1/(N+1)} - 1 \right] \left[(N+1) - (1 - x_D) \sum_{i=1}^{N+1} \frac{1}{1 - x_D (x_F/x_D)^{i/(N+1)}} \right] \quad (22)$$

Additional exchange points have a diminished effect on reducing the entropy production. For pure separation eq 22 reduces to eq 12. As the number of exchange points grows, the perturbation terms used to solve for exchange point locations (in eq 20 and 21) vanish. Thus, as the number of optimally placed exchange points becomes infinite, eq 18 and 19 and therefore eq 22 become exact. For very large N eq 23 applies.

$$\lim_{N \rightarrow \infty} \sum_{i=1}^{N+1} \frac{1/(N+1)}{1 - x_D (x_F/x_D)^{i/(N+1)}} = \int_0^1 \frac{dn}{1 - x_D (x_F/x_D)^n} \quad (23)$$

In the limit of infinite N and M the entropy production becomes

$$\frac{\Delta S_{\infty}^{\infty}}{R} = \left(\frac{x_D - x_F}{x_D - x_B} \right) \left[x_{bB} \ln \left(\frac{x_{bB}}{x_{bF}} \right) + (1 - x_{bB}) \ln \left(\frac{1 - x_{bB}}{1 - x_{bF}} \right) \right] + \left(\frac{x_F - x_B}{x_D - x_B} \right) \left[x_D \ln \left(\frac{x_D}{x_F} \right) + (1 - x_D) \ln \left(\frac{1 - x_D}{1 - x_F} \right) \right] \quad (24)$$

The entropy production is equal to the decrease in entropy of the partially purified feed so once again reversible separation is achieved with an infinite number of optimally located exchange points above and below the feed.

The quantitative advantage of exchange points can be expressed in terms of either the resulting absolute or the fractional decrease in entropy production for a given flow of feed. Depending on circumstances either of these two indices could be the more significant measure of performance. We will continue to consider $\alpha \rightarrow 1$ and constant λ for the following discussion concerning different performance goals. The maximum absolute decrease in ΔS for a given separation is obtained by subtracting the reversible entropy production (ΔS_{rev}) from that obtained for a column with no exchange points (ΔS_0^0), $\Delta S_{\max} = \Delta S_0^0 - \Delta S_{\text{rev}}$. The maximum fractional decrease in ΔS is $\Delta S_{\max}/\Delta S_0^0$. As the products approach purity, ΔS_0^0 becomes insensitive to the value of x_F until for pure separation ΔS_0^0 is a constant. The criteria of maximizing ΔS_{\max} and $\Delta S_{\max}/\Delta S_0^0$ become increasingly similar as $x_D \rightarrow 1$ and are necessarily equivalent only for the case of pure separation.

To illustrate the distinction between these two performance indices, their behavior as a function of x_F will be examined for

the case when $x_D = 1 - x_B$. When additionally $x_D < 1$ both ΔS_{rev} and ΔS_0^0 are maximized at $x_F = 1/2$ and decrease monotonically to zero as $x_F \rightarrow x_D$ or x_B . The absolute difference function of eq 25

$$\Delta S_{\text{max}} = \frac{(x_D - x_F)(x_F + x_D - 1)}{(2x_D - 1)x_F(1 - x_F)} - [x_D \ln x_D + (1 - x_D) \ln (1 - x_D) - x_F \ln x_F - (1 - x_F) \ln (1 - x_F)] \quad (25)$$

where the entropy is in units of R , is extremized at $x_F = 1/2$. This function undergoes a bifurcation at $x_D = (3 + 17^{1/2})/8$ such that, for small values of x_D , ΔS_{max} is a maximum at $x_F = 1/2$ while, for larger values of x_D , ΔS_{max} is maximized by two values of x_F which are symmetrically spaced about $1/2$. The spacing between the two optimal values of x_F widens as x_D increases until for pure separation eq 25 is maximized for $x_F = 0$ or 1 . However, only for total purification is eq 25 maximized for $x_F = x_D$. It is interesting that, for separations where $x_D < 0.89$, $x_F = 1/2$ corresponds to a global maximum of eq 25 while for total separation $x_F = 1/2$ corresponds to the global minimum of this function.

The maximum fractional decrease of entropy production is

$$\frac{\Delta S_{\text{max}}}{\Delta S_0^0} = 1 + \{x_F \ln x_F + (1 - x_F) \ln (1 - x_F) - x_D \ln x_D - (1 - x_D) \ln (1 - x_D)\} / \left\{ \frac{1}{2x_D - 1} \left(1 - \frac{x_D(1 - x_D)}{x_F(1 - x_F)} \right) \right\} \quad (26)$$

By examining second and higher order derivatives of eq 26, one can show that the fractional entropy decrease grows monotonically as x_F goes from $1/2$ to x_D (or x_B). Figure 3 illustrates the behavior of ΔS_{max} and $\Delta S_{\text{max}}/\Delta S_0^0$ as functions of x_F where $x_D = 1 - x_B$ for two values of x_D . In Figure 3a note that, for $x_F = 1/2$, the value of ΔS_{max} corresponds to the global maximum while the value of $\Delta S_{\text{max}}/\Delta S_0^0$ corresponds to the global minimum. Similar conclusions are drawn if the extremal decrease in entropy production is evaluated for a fixed number of exchange points.

Thus, if $\Delta S_{\text{max}}/\Delta S_0^0$ is the criterion, then exchange points are most advantageous for feeds where x_F approaches x_D or x_B . However, if ΔS_{max} is the criterion for a separation where $x_D < 0.89$, then the use of exchange points is most advantageous for $x_F = 1/2$. In other words, the magnitude of the benefits of exchange points depends on the criterion for performance. Different criteria can produce opposite conclusions regarding the desirability of exchange points as a function of the molar composition of the feed.

Applicability of the Simple Distillation Model

In order to obtain the optimal locations of the exchange points several simplifying assumptions were made. The effect on exchange point location of relaxing some of these assumptions will now be examined. The assumption that the components form an ideal mixture is not overly restrictive, particularly for mixtures of organic solvents; therefore, this assumption will be retained. The value of α was constrained to be small so it is important to examine how robust the result is if α is allowed to grow. A temperature-insensitive value of α would only introduce a constant factor in the minimum reflux equations 1 and 2 so the optimal location of the exchange points obtained from eq 4 would remain unaffected. However, including the temperature dependence of α may shift the optimal location of the exchange points.

From Raoult's law, the Clausius-Clapeyron equation, and Trouton's rule, α can be obtained from a first-order expansion:

$$\alpha(T) = \frac{P_a^0(T)}{P_b^0(T)} \approx \exp \left[10 \left(\frac{T_B - T_D}{T} \right) \right] \times \exp \left\{ \frac{(\Delta c_p)}{R} \left[\frac{T_B - T_D}{T} - \ln \frac{T_B}{T_D} \right] \right\} \approx \alpha_0 \left(1 + \frac{c}{T_B} x_p \right) \approx \alpha_0' \left(1 - \frac{c}{T_D} x_{bp} \right) \quad (27)$$

where Δc_p gives an effective difference of the heat capacities of the liquid and vapor phases for the mixture, $c = T_B - T_D$, $\alpha_0 = e^{10c/T_B}$, and $\alpha_0' = e^{10c/T_D}$. The first-order expansions of temperature and the exponential do not introduce significant error for values of c/T_B up to 0.1. This permits the use of α 's such that $\alpha \leq 3$, which is satisfactory for modeling many real systems. For pure separation eq 1 and 2 can be expressed as

$$L_m(x_p) = \frac{x_F}{\alpha_0 - 1} \left[\frac{1}{x_p} - \frac{\alpha_0}{(\alpha_0 - 1)} \frac{c}{T_B} \right] \quad (\text{rectifying section}) \quad (28)$$

$$L_m(x_p) = \frac{\alpha_0' x_{bF}}{\alpha_0' - 1} \left[\frac{1}{x_{bp}} + \frac{1}{(\alpha_0' - 1)} \frac{c}{T_D} \right] \quad (\text{stripping section}) \quad (29)$$

Equations 28 and 29 show that including the temperature dependence of α to first order introduces a constant additive term to the minimum reflux equation. Thus, the optimal locations of the exchange points are not directly influenced by the inclusion to first order of the temperature dependence of α .

With the use of values of α much larger than 1 a first-order correction is needed for the difference of two reciprocal temperatures. This requires a second-order correction for the inverse temperature. Expanding and dividing the logarithms in the expression for temperature (eq 6), we obtain a modified temperature expression:

$$T_p \approx T_B - cx_p - c \frac{\alpha - 1}{2} (x_p - x_p^2) \quad (30)$$

With the crude approximation $\alpha - 1 \sim 10c/T_D$ for the second-order coefficient the inverse temperature is obtained for a mixture with mole fraction x_p .

$$\frac{1}{T_p} \approx \frac{c}{T_B^2} \left[\frac{T_B}{c} + x_p + x_p \frac{c}{T_B} (5 - 4x_p) \right] \approx \frac{c}{T_D^2} \left[\frac{T_D}{c} - x_{bp} + x_{bp} \frac{c}{T_B} (5 - 4x_{bp}) \right] \quad (31)$$

The correction terms can be quite significant and may influence the exchange point location. The temperature correction term can be treated as a perturbation on the zeroth-order exchange point position. Substitution of eq 31 into eq 4 gives the perturbation factors. For a column with $N + M$ exchange points

$$x_i = x_{i0}(1 + \epsilon_r) \quad (\text{rectifying section}) \quad (32)$$

where

$$\epsilon_r = (c/T_B)[-2 + 2x_F^{1/(N+1)} + 2x_F^{N/(N+1)} - 2x_F] \quad (33)$$

and x_{i0} is given in eq 8.

$$x_{bj} = x_{bj0}(1 + \epsilon_s) \quad (\text{stripping section}) \quad (34)$$

where

$$\epsilon_s = (c/T_D)[2 - 2x_{bF}^{1/(M+1)} - 2x_{bF}^{M/(M+1)} + 2x_{bF}] \quad (35)$$

and x_{bj0} is given in eq 9.

The perturbation terms of eq 33 and 35 vanish for $M, N \rightarrow \infty$ but the optimal location of exchange points is not determined exactly. The correction terms are small for $c/T \leq 0.1$ and always move the exchange points to lower positions in the column and therefore to higher temperatures. Examination of eq 31 shows that the rate of change of the corrected inverse temperature is largest for small x_p and monotonically diminishes with the growth of x_p , in contrast to the previously used linear dependence of $1/T_p$ on x_p . The correction of the exchange point location is such that smaller values of L_m are required in regions of rapidly changing temperature (stripping section) or that for the same values of L_m the temperature gradient is reduced (rectifying section). The difference in description occurs because in the stripping section

the location of the higher exchange point determines the value of L_m while in the rectifying section the location of the lower exchange point determines the value of L_m .

The effect of the dependence of heats of vaporization on composition was examined for an ideal mixture. Because the heats of vaporization of the refluxing liquid for two column sections adjacent to an exchange point differ at most by a few percent for $c/T \leq 0.1$, the impact on exchange point location is negligible.

The results obtained for optimizing a simple system ($\alpha \sim 1$) are seen to generalize to many systems of interest. The inclusion of large, temperature-dependent separation factors and of significant temperature corrections do not appreciably alter the optimized exchange point locations. Although the conclusions concerning various corrections were drawn for the case of total purification, they are generally valid for partial purification.

As the value of α increases, the optimal distribution of exchange points between the rectifying and stripping sections is changed. The more rapidly varying temperatures in the high-temperature region of the column tend to favor location of exchange points in the stripping section. Furthermore, the symmetry of the expressions for L_m for the two sections is broken for $\alpha > 1$. An additional factor of α for the stripping section L_m appears and produces large absolute differences in the value of L_m between various points in the stripping section. Again, the growth of α biases the exchange point distribution in favor of the stripping section. The actual number and distribution of exchange points for a process depends on process parameters and operation goals.

Binary Distillation with Multiple Columns

The entropy production in distillation can be reduced by a method similar to exchange points in concept but different in design. For a given separation the use of additional columns can reduce the degradation of heat. All columns are considered to be operating at the same working pressure so split column distillation is not being considered here. Each additional column requires one or two additional heat exchangers. Therefore, a comparison can be made of the two methods for reducing ΔS , additional exchange points or additional columns. The expressions for entropy production for these two cases are of the same general form but additional mass-balance equations must be satisfied in the case of multiple columns. For the multiple-column design reversible separation can be achieved only with an infinite number of columns each doing an infinitesimal separation. For any column performing a finite separation the entropy production can be reduced by the inclusion of exchange points.

Some generalities hold for any arrangement of columns which individually have no exchange points. The derivations of eq 1 and 2 are valid for any arbitrary distillation apparatus. Therefore, as with exchange points, the use of multiple columns cannot reduce the minimum reflux, L_m , at any position in the column. L_m is largest at x_F and this determines the minimum quantity of heat necessary to perform the distillation. To minimize irreversibilities within the column and in the transfer of heat to the column, the value $L_m(x_F)$ should not be exceeded. For a multiple-column arrangement the total reflux at x_F , $L_{TOT}(x_F)$, is given by the sum of the refluxes, L_i , for the individual columns which contain a section corresponding to x_F .

$$L_m(x_F) = L_{TOT}(x_F) = \sum_i L_i(x_F) \quad (36)$$

But each column i must have a reflux at least equal to $L_{mi}(x_F)$, the minimum reflux at x_F for column i . The sum of all $L_{mi}(x_F)$ equals $L_m(x_F)$ so the conclusion is reached that each column i containing a section at x_F must have a reflux corresponding to $L_{mi}(x_F)$.

It is useful to optimize a simple column design and compare the result with exchange point optimization. For simplicity it will be assumed that $\alpha \rightarrow 1$ and that total purification is being performed. Consider the binary separation depicted in Figure 4. The initial feed is divided into two components F_I and F_{II} . F_I is fed into column I, which acts to produce totally pure bottoms ($x_B = 0$) and a partially purified distillate ($x_{F1} < 1$). Column II has

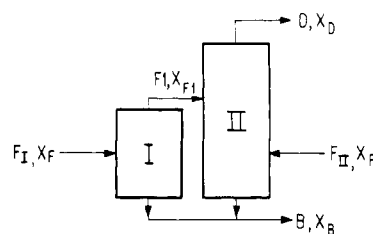


Figure 4. Two-column binary distillation.

two feed inputs of different composition F_I and F_{II} and acts to produce pure products. As previously stated the reflux in column II must be equal to $L_{mII}(x_F)$, which depends on the division of the feed. Furthermore, for minimum entropy production

$$L_{mII}(x_F) = L_m(x_{F1}) \quad (37)$$

where $L_m(x_{F1})$ is given by eq 1. If $L_{mII}(x_F) > L_m(x_{F1})$, then F_{II} could be decreased and F_I increased until $L_{mII}(x_F) = L_m(x_{F1})$. This redistribution of the feed results in a decreased ΔS in column II, an increased ΔS in column I, and a net decrease in ΔS .

The optimal values of x_{F1} , F_I , and F_{II} can now be found. The total entropy production for the two columns can be expressed as

$$\Delta S = \lambda L_m(x_F) \left(-\frac{1}{T_B} + \frac{1}{T_{F1}} \right) + \lambda L_m(x_{F1}) \left(-\frac{1}{T_{F1}} + \frac{1}{T_D} \right) \quad (38)$$

which is seen to be identical with the entropy production for one column with a rectifying section exchange point (see eq 4). Thus, the two columns of Figure 4 give an entropy production equal to that of one column with one exchange point. The value of x_{F1} is obtained by minimizing the entropy production (eq 38) as done previously and the value of F_I can be found by solving eq 37.

The two-column design depicted in Figure 4 is indeed a special case. Several other multiple-column designs were optimized and found to be less effective than exchange points at reducing irreversibilities because of the greater number of mass-balance restrictions. Nevertheless, there may be cases where only one exchange point is desired so the use of two columns as in Figure 4 provides a viable alternative especially if the same reboiler can be used for both columns.

Summary

Distillation has illustrated the optimization of a process whose output is chemical work, achieved by minimizing the irreversibilities of that process. The irreversible mass transfers and heat transfers in a distillation column result in the excess degradation of heat in heat reservoirs used to drive distillation. A simple model is employed to analyze the decrease of entropy production in distillation through the use of exchange points and multiple columns. This model is accurate for $\Delta T/T \leq 0.1$ in the distillation column and thus can be used to represent many real systems. For $\alpha \rightarrow 1$ the location of exchange points is solved by perturbation methods for the more general case of partial purification. As the number of exchange points becomes infinite, the solution for their location becomes exact and the entropy production in distillation becomes equal to the reversible entropy of mixing. A comparison is made between the use of exchange points and multiple columns for a binary separation. The effectiveness of multiple columns can match that of exchange points for only a few specific cases. The effectiveness of process modification is seen to depend heavily on the definition of performance goals.

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