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Mixing and Work of Separation in Countercurrent Recycle Cascades

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ABSTRACT

The increased work of separation due to remixing partially separated streams within countercurrent recycle cascades, W_{unmix}, was calculated and compared with the absolute minimum thermodynamic work, W_{min}, required to effect a given separation. Remixing can occur in all countercurrent constant recycle cascades regardless of whether a separation process is potentially reversible, partially reversible, or irreversible in nature, or whether the cascade is composed of double entry or single entry stages. In an ideal cascade (IC), the remixing of materials with different compositions is eliminated and the sum of the stagewise separative work, W_{sep}, is identically equal to W_{min} based on the overall separation occurring across the cascade, or $W_{\mathrm{sep}} = W_{\mathrm{min}}$. However, in the constant recycle cascade (CRC) the work of separation is greater than the thermodynamic minimum by an amount equal to W_{mix} due to remixing of partially separated streams, or $W_{\mathrm{sep}} = W_{\mathrm{min}} + W_{\mathrm{unmix}}$. By comparison, the separative work due to remixing is *lost* or *wasted* in the CRC. The lost work, W_{unmix}, can be a significant contribution to the energy requirements of countercurrent recycle cascades since it becomes infinite at both extremes of reflux; the minimum recycle ratio, $\mathrm{RR}_{\mathrm{min}}$, and total recycle, $\mathrm{RR}_{\mathrm{total}}$. Consequently, W_{unmix} goes through a minimum at some point in between the two limiting extremes of recycle ratio in a constant recycle cascade. For the examples considered in this analysis, W_{unmix} in the CRCs goes through

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a minimum at recycle ratios of 1.32, 1.35, and 1.53 times the minimum recycle (RR_{min}) for separation factors of $\alpha = 1.027$, 1.067, and 1.20, respectively. At these "optimal" recycle ratios (i.e., minimum W_{unmix}), the work of separation is increased by about 28 to 31% over the thermodynamic minimum. Finally, many of the perceived differences in the analysis of separation cascades for the partially reversible, potentially reversible, and irreversible processes disappear when mixing within the CRC is taken into account.

INTRODUCTION AND BACKGROUND

All fractionation processes require an input of energy (work) to drive the separation. The minimum work required for a prescribed separation in a reversible process is easily calculated from methods of classical thermodynamics. For binary component systems which form ideal solutions, this minimum work requirement is given by

$$\begin{aligned} W_{min} = & -RT\{P[y_P \ln y_P + (1 - y_P)\ln(1 - y_P)] \\ & + W[x_W \ln x_W + (1 - x_W)\ln(1 - x_W) \\ & - F[z_F \ln z_F + (1 - z_F)\ln(1 - z_F)]\} \end{aligned} \tag{1}$$

The quantities F, P, and W are the feed, product, and waste stream flow rates in moles/hour; z_F, y_P, and x_W are the mole fractions of the desired components in these streams, respectively. It is assumed that the separation is carried out at constant temperature, T. Obviously, the minimum work as given by Eq. (1) is dependent only on the feed, product, and waste stream flow rates and compositions and is independent of the particular process used to effect the separation. Furthermore, W_{min} is a strong function of feed composition since more concentrated feeds require less separation. For mixtures that do not form ideal solutions, the compositions in the logarithmic terms of Eq. (1) must be multiplied by the appropriate activity coefficients or a similar measure of nonideality. The energy input and work requirements measured in terms of available energy is typically many times greater than this minimum in practical separation devices due to irreversibilities and energy losses within the system.

Separation processes have been classified according to the perception of whether or not the process can be theoretically designed to approach the minimum required by thermodynamics (1). *Potentially reversible processes* (binary distillation is the common example) are those in which the net work can theoretically be reduced to the minimum required by thermodynamics, W_{min}. *Partially reversible processes* (examples are extractive distillation and chemical exchange columns used in isotope separations) contain some steps in the process which are inherently irreversible, while the remaining steps are theoretically reversible. In *irreversible* *processes* (such as gaseous diffusion or membrane permeation), every step in the process requires an irreversible input of energy to effect the separation.

Irreversibilities inherent to each of these processes commonly involve the remixing of partially separated streams within the cascade; the magnitude of this effect depends largely on engineering design. This remixing of streams with different compositions results in an entropy increase in the feed streams to the individual stages, thereby requiring additional work in excess of $W_{\min}$ to effect the desired overall separation. Although various authors have suggested that mixing is detrimental to separation processes (1, 2), apparently none have accounted for its effect on the overall separation. Examination and quantification of this *lost* or *wasted* work, W_{unmix}, is the topic of this paper.

COUNTERCURRENT RECYCLE CASCADES

Many types of separations are carried out in multistage separation processes in order to obtain the desired amount and purity of product. This is necessary since the single-stage separation factor may not be large enough to accomplish the specified separation in a single step or stage. Experience has shown that the countercurrent recycle cascades provide an effective means of achieving the desired product purity in stagewise contacting systems. Consequently, the countercurrent recycle flow scheme is commonly encountered in large-scale commercial operations. It is closely approximated in many types of separation equipment such as distillation columns and isotope separation cascades (1). A schematic of a typical countercurrent cascade and the associated nomenclature for a binary component system is indicated in Fig. 1.

The recycle cascade in Fig. 1 consists of a number of stages connected in series. The function of each stage is to separate a feed stream with flow rate F_i and molar composition z_i into a heads stream enriched in the desired component with flow rate M_i and composition y_i, and a tails stream (flow rate N_i; composition x_i) which is depleted in the desired component. Consequently, each stage functions to provide a small fraction of the overall separation. The cascaded arrangement of stages functions to separate a fresh feed stream of flow rate F and composition z_F into an enriched product stream flowing at rate P with composition y_P and a depleted waste or tails stream with composition x_W and flow rate W. The fresh feed, waste, and product flow rates and molar compositions define the *external variables* and establish the overall separation produced within the cascade. The molar flow rates and compositions associated with individual stages in the cascade are termed the *internal variables*. Note that the

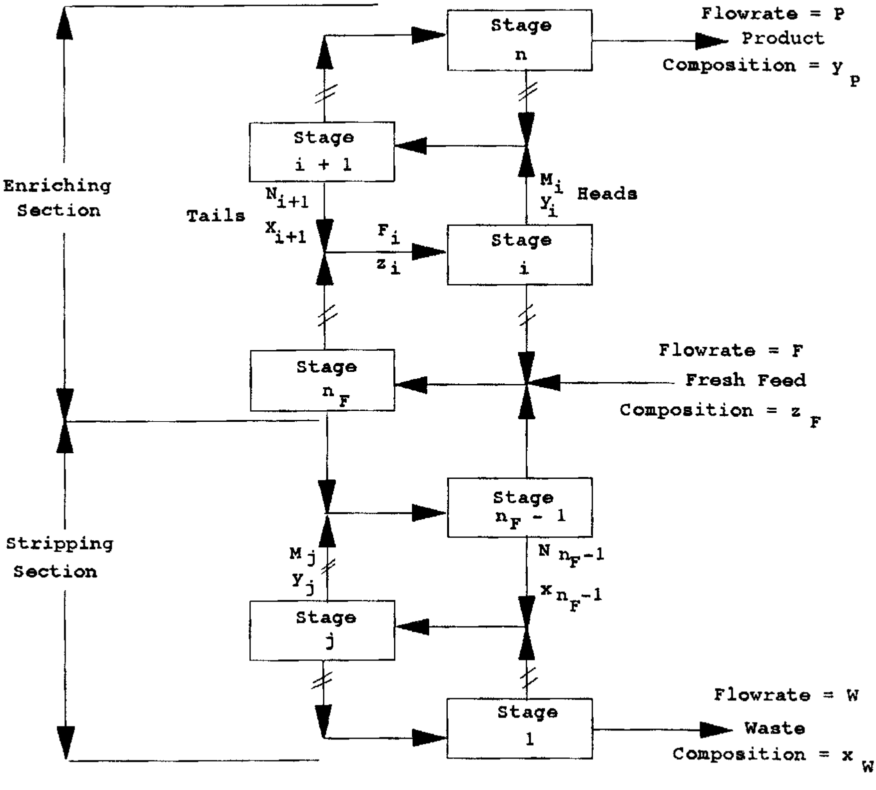

FIG. 1 Flow schematic of a generalized countercurrent recycle cascade.

internal variables are subscripted to indicate the particular stage with which each is associated.

That portion of the cascade from the product stage up to and including the feed stage is referred to as the *enriching section*. That portion of the cascade from the waste end up to (but not including) the feed stage is termed the *stripping section*. The purpose of the enriching section is to produce material of the desired composition; it is therefore required for proper cascade operation. The stripping section functions to recover or "strip" the desired component from the feed stream. Therefore, the stripping section serves only to reduce the amount of fresh feed necessary to make a specified amount of product.

For the engineering analysis of separation cascades it is convenient to define the following stage separation factors based on binary component systems:

$$\text{Stage separation factor, } \alpha = \frac{y_i/(1 - y_i)}{x_i/(1 - x_i)} \tag{2}$$

$$\text{Heads separation factor, } \beta = \frac{y_i/(1 - y_i)}{z_i/(1 - z_i)} \tag{3}$$

$$\text{Tails separation factor, } \gamma = \frac{z_i/(1 - z_i)}{x_i/(1 - x_i)} \tag{4}$$

The ideal single stage separation factor, α, is particularly useful in cascade calculations since it is typically independent of compositions for many binary systems and its functional relationship is generally known or readily determined from experiment.

In a countercurrent recycle cascade the feed to a given stage (except for the feed, waste, and product stages) consists of the heads stream from the next lower stage and the waste stream from the next higher stage in the cascade. *Recycle* or *reflux* is required in order for the cascade to operate properly. It is convenient to define the recycle ratio at a given stage as the ratio of the stagewise tails stream flow rate to that of the product stream:

$$\text{Recycle ratio, } \mathrm{RR}_i \equiv N_{i+1}/P \tag{5}$$

CONSTANT RECYCLE CASCADES

In a constant recycle cascade (CRC), reflux is typically maintained at a constant value for each stage within the cascade. Note that it is possible for different, but constant, values of the recycle ratio to occur in the stripping and enriching sections, depending upon the condition of the feed and the manner in which the recycle ratio is defined. Thus, $\mathrm{RR}_i = (\mathrm{RR})_{\mathrm{enricher}}$ and $\mathrm{RR}_j = (\mathrm{RR})_{\mathrm{stripper}}$ may differ in the enriching and stripping sections, i and j, respectively. The recycle ratio within a CRC, $(\mathrm{RR})_{\mathrm{CRC}}$, is typically defined in accord with Eq. (5). This definition assumes the tails stream flow rate exiting each stage is constant across the entire cascade if the recycle ratio is to be constant at each stage.

In the CRC, it is known that there exists a minimum recycle ratio, $\mathrm{RR}_{\mathrm{min}}$, where the separation just ceases to occur at some point within the cascade. This *pinch point* is generally associated with the feed stage and occurs under conditions where separation at that point just ceases ($y_i = y_{i+1}$). As a consequence of minimum recycle, as $\mathrm{RR}_{\mathrm{CRC}}$ approaches $\mathrm{RR}_{\mathrm{min}}$ the required number of stages to make the separation becomes infinitely large. At the other extreme, the recycle ratio approaches infinitely large values, a condition known as total recycle, $\mathrm{RR}_{\mathrm{total}}$, the number of ideal stages required to make the separation approach some theoretical minimum value. The "optimum" recycle ratio for a CRC is generally chosen based on economic considerations, but is generally close to the minimum recycle ratio.

The total interstage flow (TIF) through a cascade is defined as the sum of the flow rates of all heads and tails streams for each stage across the cascade:

$$\mathrm{TIF} = \sum_i [M_i + N_i] \tag{6}$$

The TIF becomes infinite at conditions of both total and minimum reflux and is a minimum at some value in between. The required conditions for a constant recycle cascade can be met in isotope separation cascades, gas permeation cascades, and continuous distillation columns with systems which result in constant molar overflow.

IDEAL CASCADES

An ideal cascade (IC) is characterized by the following criteria:

1. The heads and tails streams forming the feed to any stage have the same composition. This assumption is typically referred to as the *no-mix criteria*, or mathematically:

$$y_{i-1} = x_{i+1} = z_i \tag{7}$$

2. The single stage heads and tails separation factors are constant and equal to the square root of the single stage overall separation factor, α:

$$\beta = \alpha^{0.5} = \gamma \tag{8}$$

The above criteria insure there is no remixing of streams with different levels of separation within the cascade, and that the total interstage flow (a measure of cascade size) will be a minimum. It should be noted that the no-mix criteria can be satisfied even though the relationship for the second criteria as given by Eq. (8) is not met. However, for this case the design would not result in the minimum total interstage flow (3).

A salient feature of the IC, and one that is mandated by the no-mix criteria, is that the recycle ratio is different for each stage in an ideal cascade. Consequently, each stage in an ideal cascade is of a different size or volume to accommodate the variations in recycle ratio. The largest amount of recycle is necessary at the feed stage, and "tapers" to smaller values through both the enriching and stripping sections as the product and waste stages, respectively, are approached. Theoretically, the ideal cascade requires about twice the number of stages as a CRC operated under conditions of total reflux to perform the same separation (4).

MIXING IN SEPARATION STAGES

In an IC, the heads and tails streams which make up the feed to each stage are of the same composition. If the process is otherwise reversible, the sum of the stagewise work of separation will be $W_{\min}$. However, in the CRC, these streams are of different compositions (different levels of separation), and the remixing of these streams to form the feed to a stage must result in an increase in entropy within the stage. Therefore, the sum of the stagewise work terms across the entire cascade (for an otherwise reversible process) must necessarily be greater than $W_{\min}$.

Pratt (5) has identified two types of separation elements or stages, termed single-entry and double-entry stages, as shown in Fig. 2. A countercurrent recycle cascade can be devised from stages of either type, depending on the particular system. In a single-entry stage, the heads and tails streams (F_1 and F_2) are mixed prior to entering the stage. In the double-entry stage, the two streams enter the stage separately, and mixing occurs within the stage.

A single-entry stage is fed a single one-phase stream that is then split into a fraction θ of enriched product (heads) and a fraction $(1 - \theta)$ of depleted product (tails). The fraction θ is the *stage cut* or simply *cut*. Generally, in a single-entry stage the feed, heads, and tails streams are of the same phase and contained within two regions required to make the separation. Typically, these regions are at different pressures and sepa-

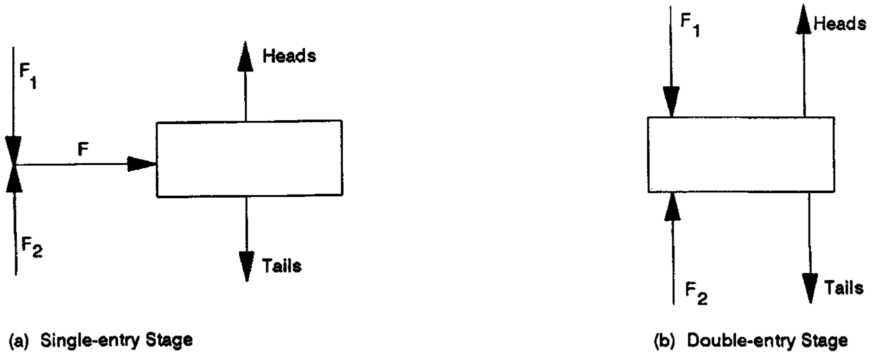

FIG. 2 Types of separation stages.

rated by a barrier. Single-entry examples include gas diffusion stages or permeation cells where a portion of the feed mixture is separated because the different components diffuse or permeate through porous or nonporous membranes at different rates.

In separation cascades containing single-entry stages, the two streams (F_1 and F_2) forming the feed to the stage are assumed to be intimately mixed prior to entry. If these streams are of different compositions, the entropy increase due to mixing is given by:

$$\begin{aligned}\Delta S = -R\{&F[x_F \ln x_F + (1 - x_F) \ln(1 - x_F)] \\ &- F_1[x_{F1} \ln x_{F1} + (1 - x_{F1}) \ln(1 - x_{F1})] \\ &- F_2[x_{F2} \ln x_{F2} + (1 - x_{F2}) \ln(1 - x_{F2})]\}\end{aligned} \tag{9}$$

where

$$x_F = (x_{F1}F_1 + x_{F2}F_2)/(F_1 = F_2) \qquad \text{and} \qquad F = F_1 + F_2 \tag{10}$$

Of course, these relationships assume ideal solution behavior and that F_1 and F_2 are at the same pressure.

For double-entry stages, the two feed streams are of different phases and separation usually occurs as a result of phase or chemical equilibrium. Double-entry stages are encountered in distillation and isotopic separations by chemical exchange reactions where equilibrium occurs between a liquid phase and a vapor or gaseous phase.

In a typical double-entry separation stage, *light* and *heavy* phases are contacted, mixed, and disengaged to form the heads and tails streams exiting the stage. Flow and mixing, as well as heat and mass transport between phases within the stage, is complex. Stage efficiency is usually defined in terms of how closely equilibrium conditions between heads and tails streams are approximated. However, simple mass and energy balance calculations show that intimate contacting of F_1 and F_2 *must* occur; indeed, the assumption that each feed stream is individually separated into the respective equilibrium product streams without intimate contacting *cannot* be consistent with mass and energy balance requirements around the individual stages. Hence, in this study it is assumed that the stagewise feed streams are perfectly mixed to form two phases of the same composition. Ideal or equilibrium stage conditions are achieved between the two phases due to mass transfer. This assumption results in the maximum entropy increase due to mixing of the partially separated feed streams. Under these conditions, the stage entropy increase due to mixing is given by Eqs. (9) and (10), and is the same as for the single-entry stage.

The traditional engineering analysis of separation cascades containing either type of stage is essentially the same. Both rely on the concept of ideal stages together with the material and energy balances around individual stages and the entire cascade. Pratt (5) has suggested that the McCabe–Thiele analysis of separation cascades using either single-entry or double-entry stages is virtually identical. Slight differences exist only in the mixing method of the heads and tails streams as represented and interpreted on the McCabe–Thiele diagram.

Thus, the stagewise mixing of streams with different compositions, or different levels of separation, results in an increase in entropy within the cascade. This is true regardless of the type of separation element used, and additional work over $W_{\min}$ is necessary to counteract this mixing. The work associated with the unmixing process for stage i is given by:

$$(W_i)_{\text{unmix}} = -T\Delta S \tag{11}$$

where ΔS is given by Eq. (9). The total work of unmixing across the entire cascade is the sum of the stagewise work terms:

$$W_{\text{unmix}} = \sum_i (W_i)_{\text{unmix}} \tag{12}$$

These concepts can be viewed as increasing the minimum work of separation in CRCs above the minimum required by thermodynamics:

$$(W_{\text{sep}})_{\text{CRC}} = W_{\min} + W_{\text{unmix}} \tag{13}$$

Here $W_{\min}$ is the minimum thermodynamic work as given by Eq. (1), and W_{unmix} is given by Eq. (12).

Different cascade configurations (IC or CRC) can easily be modeled by solving the appropriate ideal stage and cascade material and energy balance equations on a digital computer. The different work terms ($W_{\min}$ and W_{unmix}) can be evaluated for various values of α and the recycle ratio. Some interesting results of such calculations are presented in the following sections.

CALCULATIONS

Mixing of partially separated streams will occur in all countercurrent recycle cascades that do not meet the no-mix criteria of Eq. (7) regardless of the actual separation process involved. Basic engineering analysis is the same regardless of whether the process is potentially reversible, partially reversible, or irreversible in nature. It is convenient to use examples for a specific separation to illustrate the magnitude of W_{unmix}.

Herbst (3) investigated the separation of boron isotopes utilizing the isotopic exchange reaction between gaseous BF_3, and the liquid BF_3·donor complexes according to the reaction

$$^{11}BF_3 \cdot \text{Donor(l)} + {}^{10}BF_3(g) \rightleftharpoons {}^{10}BF_3 \cdot \text{Donor(l)} + {}^{11}BF_3(g) \quad (14)$$

The separation factor is defined as the equilibrium constant for Reaction (14):

$$\alpha = K_{eq} = \frac{[^{10}B/^{11}B](l)}{[^{10}B/^{11}B](g)} \quad (15)$$

Different cascade configurations were modeled and the pertinent quantities calculated for each case. The external variables for each cascade were fixed such the different types of cascades were performing the same overall separation:

$$y_P \geq 0.950$$

$$z_F = 0.198$$

$$x_W \leq 0.050$$

$$P = 2 \text{ mol/h}$$

$$T = 303.15 \text{ K}$$

Using the above variables with a feed flow rate of $F = 12$ mol/h and a waste flow rate of $W = 10$ mol/h, an external material balance indicates a waste stream composition of $x_W = 0.0476$. Using these flow rates and compositions in Eq. (1) as the *base case separation*, the thermodynamic minimum work of separation is calculated to be $W_{min} = 9.228$ kJ/h.

Separation factors for specific donors at a temperature of $T = 303.15$ K are

$$\alpha = 1.027$$

$$\alpha = 1.067$$

These values of α were assumed constant for constant temperature and not to vary with composition. Although this study was originally initiated to investigate boron isotope separation systems, it became apparent that the calculational methods would apply to *any* system with the specified α's and external variables. Hence, a value of $\alpha = 1.2$ for a hypothetical system has been included in these calculations to show trends expected for larger separation factors. Note that there is no known donor species which gives an $\alpha = 1.2$ for the chemical exchange separation of boron isotopes.

With the above external variables, the feed and waste stream flow rates (F and W, respectively) are fixed for each case by material balance relationships. Note that slight variations are expected in y_P, x_W, F, and W for different values of α since the cascades considered were limited to those containing a discrete number of stages as opposed to a differential formulation. However, in all cases the cascades perform essentially the same overall separation. Therefore, a valid comparison of W_{sep}, total interstage flow, and number of ideal separation stages can be made as functions of α, cascade configuration, and recycle ratio. The isotopic system will approximate that of the "ideal case," therefore activity coefficients were not required to calculate W_{min} and W_{unmix}. The details of the calculational procedure can be found in Reference 3.

RESULTS AND DISCUSSION

Calculational results for the ideal cascades are presented in Table 1 for different values of α. In the ideal cascades, the sum of the individual work terms for each stage, $\sum(W_i)_{sep}$, is identical to the thermodynamic minimum, W_{min}, as given by Eq. (1) for the specified temperature, external flow rates, and compositions. Despite variations in W_{min} due to small differences in the external variables, these values are comparable to the base case separation of $W_{min} = 9.228$ kJ/h. The energy of unmixing, W_{unmix}, is, of course, zero by definition for the ideal cascades.

The total interstage flow was evaluated by summing the heads and tails flow rates exiting each stage across the entire cascade in accord with Eq. (6). Note that both the total interstage flow and required number of ideal stages in the ideal cascades decrease dramatically as the separation factor,

TABLE 1
Requirements for Ideal Cascades

	Separation factor, α		
	1.027	1.067	1.200
$W_{min} = \sum(W_i)_{sep}$ (kJ/h)	9.198	9.183	9.211
W_{unmix} (kJ/h)	0	0	0
Total interstage flow (mol/h)	248,837	41,902	5320
Number of ideal stages	433	181	64
Maximum recycle ratio, $(RR_i)_{max}$	357.2	147.5	53.5
Feed flow rate, F (mol/h)	12.13	12.13	12.17
Product composition, y_P	0.9506	0.9500	0.9517
Waste composition, x_W	0.0490	0.0495	0.0498

α, increases. This trend simply reflects the fact that the separation is easier for larger values of α.

The maximum reflux, $(RR_i)_{max}$, is associated with the feed stage in the ICs. The recycle ratio decreases from the maximum value as both ends of the cascade are approached, and is identically zero for the product and waste stages in the ideal cascade (4).

Results of calculations similar to those for ICs are shown in Table 2 for constant recycle cascades with the same α's. For the CRCs, the selected recycle ratio minimizes the total interstage flow and work of unmixing, W_{unmix}, at the specified separation factor. The minimum thermodynamic work in the CRCs, W_{min}, is approximately constant and consistent with the base case of $W_{min} = 9.228$ kJ/h. This is expected since the CRCs (and ICs) are all performing approximately the same overall separation. Again, the small variations in W_{min} are due to slight differences in the external cascade variables as a consequence of using a discrete number of separation stages. Note that the summation of the stagewise work across the cascade, W_{sep}, is the combination of the minimum energy and the work of unmixing in accord with Eq. (13). As expected, the required number of ideal stages and the total interstage flows in the CRCs decrease as α increases.

For a given separation factor, the recycle ratio in the CRCs is smaller than the maximum reflux in the corresponding ICs. Furthermore, the required number of ideal stages in the CRCs is substantially less than for the ICs. On the other hand, the total interstage flow in the ICs is much smaller than in the corresponding CRCs. The work of separation in the ICs is identical to W_{min}; however, W_{sep} is greater for a specified α in the corresponding CRC. In fact, the work of separation for the CRCs is 28 to 31% greater than for the ICs considered in this study. This increased

TABLE 2
CRC Requirements Designed for Minimum Total Interstage Flow and W_{unmix}

	Separation factor, α		
	1.027	1.067	1.200
$W_{sep} = \sum(W_i)_{sep}$ (kJ/h)	11.78	11.83	12.04
W_{unmix} (kJ/h)	2.59	2.64	2.81
W_{min} (kJ/h)	9.19	9.19	9.23
Total interstage flow (mol/h)	336,893	57,198	7404
Number of ideal stages	362	152	52
Recycle ratio (constant)	233	94.6	36.1
RR/RR_{min}	1.32	1.35	1.53

work of separation is due to the unmixing process prevalent in the CRCs. The above-described contrasts between ICs and CRCs are expected and consistent with cascade theory.

Figure 3 indicates variations in the different work terms for the CRCs as a function of recycle ratio and α. The minimum work of separation, W_{min}, is constant regardless of separation factor or recycle ratio. This behavior reflects the fact that the external process variables are essentially constant; thus, each cascade is performing the same overall separation. The work of separation in the CRCs, W_{sep}, (shown only for $\alpha = 1.067$) is simply the sum of W_{unmix} and W_{min}; thus, the W_{unmix} curve is shifted upward by a constant amount corresponding to W_{min}. Note that the work of unmixing goes through a minimum in the vicinity of the minimum recycle ratio, RR_{min}, and becomes infinite as both RR_{min} and RR_{total} are approached. As discussed subsequently, W_{unmix} *must* become infinite as both limits of reflux are approached. The minimum in W_{unmix} corresponds to the optimum recycle ratio for a specified α. The value of RR/RR_{min} at which these minima occur are listed in Table 2 for the different separation

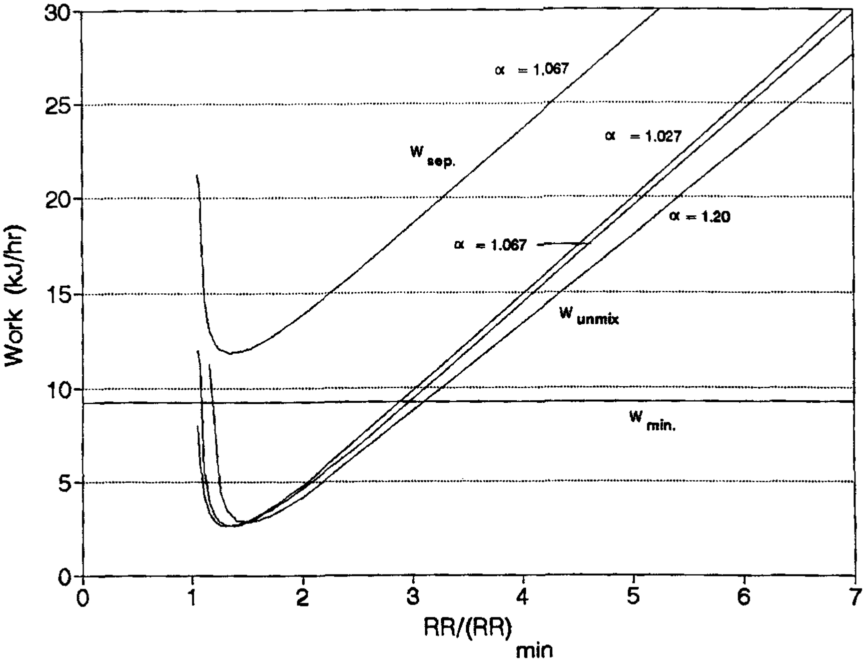

FIG. 3 Various cascade work terms as a function of recycle ratio and separation factor, α. Note that $W_{total} = W_{unmix} + W_{min}$.

factors. Furthermore, W_{unmix} is less than W_{min} in the vicinity of optimum reflux but becomes greater than W_{min} at RR/RR_{min} values of approximately 1 and 2.8.

Figure 4 indicates the variations in total interstage flow (TIF) and required number of ideal stages as a function of reflux and α for the CRCs. As with W_{unmix} and W_{min}, TIF goes through a minimum at the optimum recycle ratio and becomes infinite as the limits of reflux are approached. Note that the ideal stage requirements increase slightly as the recycle ratio is decreased, begin rapidly rising in the vicinity of optimum reflux, and become infinite as minimum recycle is approached. Consequently, a CRC designed for optimal recycle requires *more* ideal stages than if somewhat larger values or reflux are used. The trade-off is, of course, the larger total interstage flow and the increased work of unmixing at larger (and smaller) recycle ratios. In accord with theory, Fig. 4 indicates the minimum number of ideal stages required in a CRC operated at total reflux.

Finally, Fig. 5 is a plot of W_{unmix} as a function of total interstage flow for each value of α in the CRCs. As indicated, W_{unmix} is directly proportional to TIF at constant α. Differences in the slopes of these curves are

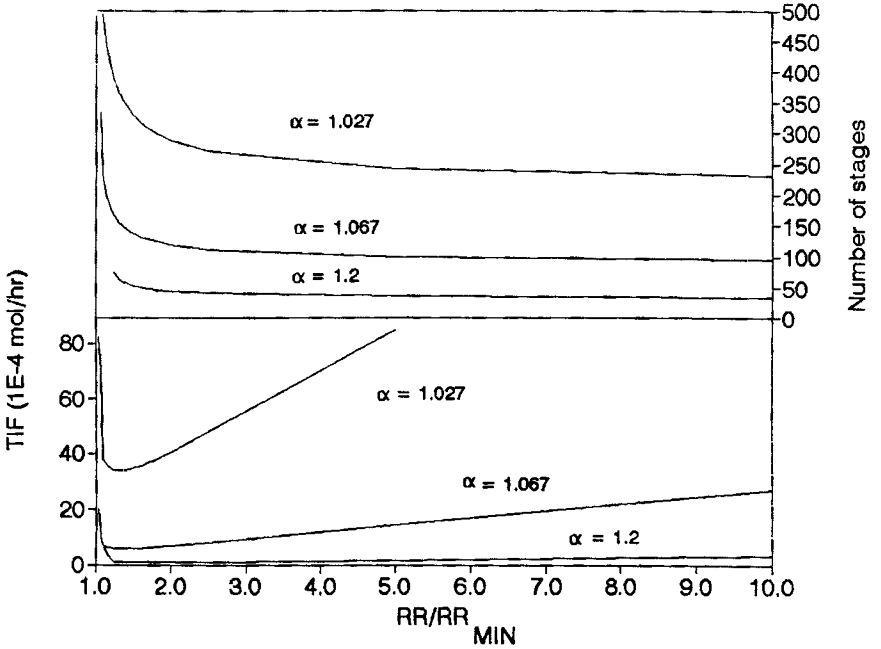

FIG. 4 Total interstage flow and number of ideal stages as a function of recycle ratio and separation factor in a CRC.

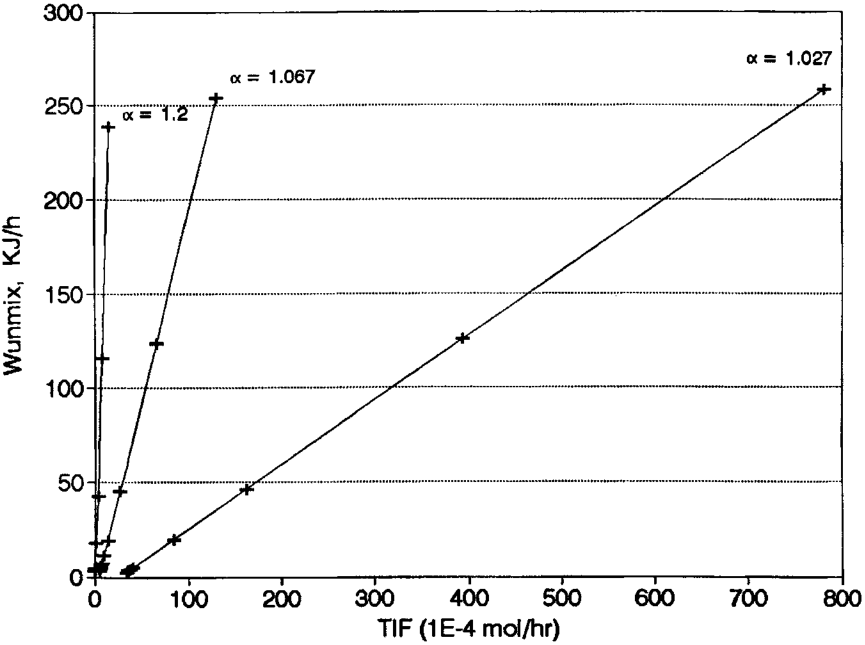

FIG. 5 Work of unmixing, W_{unmix}, as a function of total interstage flow, TIF, for various separation factors, α, in CRCs.

a direct indication that substantially more mixing is present per unit of interstage flow (and therefore per stage) at larger values of α.

GENERAL DISCUSSION AND CONCLUSIONS

There is no question regarding the maximum amount of mixing between heads and tails streams making up the feed to a single-entry stage. The two streams are of the same phase, and mixing must occur when streams of different compositions are brought together. With perfect mixing, the resulting feed stream is homogeneous and the maximum entropy increase associated with the mixing process will be given by Eqs. (9) and (10).

However, in double-entry stages, the amount of mixing associated with intimately contacting the two feed streams is not as clear. The heads and tails streams making up the feed to double-entry stages are usually immiscible or, at best, partially miscible (i.e., are of different phases) and a homogeneous mixture cannot result by intimate contact of the two phases. Intuitively, more work should be required when two immiscible feed streams of different compositions are mixed than if they were miscible and of the same composition. This is apparent since the contacting of streams of unequal compositions is precisely the reverse of the process taking place in the stage itself. Pratt (5) suggests an equivalent to the no-mix criteria for a cascade comprised of double-entry stages to minimize the total interstage flow and cascade volume. This would also eliminate the entropy increase resulting from contacting partially separated streams. Attempts to calculate actual entropy increases due to contact of two immiscible streams with unequal compositions have thus far been fruitless. However, this effect is certainly not negligible, and may be as large as given by Eqs. (9) and (10). Thus, perfect mixing is a reasonable assumption and is preferable to assuming the two immiscible feed streams in the double-entry stages are individually separated into streams of equilibrium composition. As previously mentioned, the latter alternative cannot be consistent with stagewise mass and energy balance requirements.

The thermodynamic minimum work of separation, W_{min}, is a strong function of feed composition and is greatest for $z_F = 0.5$ and pure products (6). For the case of pure products, and with $z_F = 0.5$, $F = 12.0$ mol/h, and $T = 303.15$ K, the maximum value the thermodynamic work can assume is $W_{\text{min}} = 20.96$ kJ/h. If the feed composition is lowered to $z_F = 0.198$, the minimum work of separation is reduced to $W_{\text{min}} = 15.05$ kJ/h. In the boron isotope separation, the minimum thermodynamic work required is even less ($W_{\text{min}} = 9.23$ kJ/h for the base case) since pure products are not produced in the cascades. Note that the inefficiencies due to mixing will be present regardless of W_{min}.

The wasted work, W_{unmix}, becomes infinitely large as conditions of minimum and total recycle are approached in the CRCs. This behavior occurs in both single-entry and double-entry stages when stagewise mixing, equilibrium relationships, and material balance equations are simultaneously taken into account. In the case of minimum recycle, infinite W_{unmix} is due to the infinite number of ideal separation stages required to get past the pinch point in the vicinity of the feed stage. In the classic McCabe–Thiele analysis, the pinch point occurs where the operating and equilibrium lines become coincident. At total reflux, W_{unmix} also becomes infinite. However, this behavior is due to the infinite flow rates of streams exiting and entering each stage in the limit of total reflux. The condition of total recycle implies that material neither enters at the feed point nor exits from the product or waste ends of the cascade. Consequently, the interstage flow rates become infinite and W_{unmix} becomes unbounded on *each* of the ideal separation stages, even though the required number of stages is at a minimum.

Table 2 and Figs. 3 and 4 indicate that both total interstage flow and W_{unmix} go through minimum values in the CRCs at recycle ratios varying from $1.32(\mathrm{RR})_{\min}$ to $1.53(\mathrm{RR})_{\min}$. These values are comparable to "economically optimum" recycle ratios of 1.05 to 1.3 times $(\mathrm{RR})_{\min}$ reported in the literature (7). The number of ideal stages and the volume of each stage are measures of the size of a cascade, and both are directly related to the total interstage flow. Furthermore, the energy input and size of equipment necessary to provide recycle in a cascade are also related to the total interstage flow. However, the total interstage flow is also a function of the recycle ratio. Thus, the economic optimum recycle ratio in a CRC should approximate that necessary to minimize total interstage flow. Conversely, if conditions of minimum total interstage flow exist, the work of unmixing, W_{unmix}, will also be a minimum.

Figure 5 indicates that there is a greater amount of mixing per unit of total interstage flow for larger values of α. Consequently, CRCs become more irreversible as the separation factor *and* recycle ratio increase. These observations are consistent with the requirements for increasing the reversibility of binary distillation. Thus, King (6, p. 701) states:

> In order to reduce the net work consumption of a binary distillation it is necessary to lessen the driving force for heat and mass transfer within the individual stages. This reduces to a problem of making the operating and equilibrium curves more nearly coincident.

These requirements are approached with smaller separation factors and recycle ratios that minimize W_{unmix}. In ICs there is no mixing; however, this removes only one potential source of irreversibilities since other driving forces will be finite throughout the ideal cascade.

Comparison of thermodynamic efficiency for CRCs with different separation factors and recycle ratios, and between CRCs and ICs is complicated when W_{unmix} is taken into account. In ideal cascades, $(\mathrm{RR}_i)_{\max}$ fixes the energy input required to provide recycle throughout the cascade to make the separation. Likewise, in the constant recycle cascade, $(\mathrm{RR})_{\mathrm{CRC}}$ determines the energy required to provide reflux (3). This is true for potentially reversible and partially reversible processes with the separating agent reused from stage to stage. The work of separation (except possibly at the extremes of recycle in CRCs) is small compared with the energy requirements of providing recycle. Assuming that the required energy input to provide reflux is directly proportional to the recycle ratio, about 6.45 times more energy would be necessary to provide reflux with $\alpha = 1.027$ than for $\alpha = 1.20$ in a CRC designed for minimum W_{unmix}. About 1.5 times more recycle energy would be required for ICs over that for CRCs at the same separation factor. This indicates CRCs are more energy efficient than corresponding ICs from the standpoint of the first law for potentially reversible and partially reversible processes. However, the second law compares the loss of *available* energy with W_{min} as the input energy travels though the cascade. Since W_{min} is less in the IC because mixing does not occur, careful second law analysis should indicate the IC could *potentially* have a higher thermodynamic efficiency than the CRC regardless of the type of process.

Most of the above discussions revolve about processes where the separating agent (energy and the donor material in isotope separations) is reused from stage to stage; the so-called potentially and partially reversible processes. In irreversible processes, energy must be added at each stage in proportion to interstage flow. As a result, energy consumption must become infinite at both extremes of recycle for irreversible processes: minimum stages and infinite interstage flow at total reflux; and an infinite number of stages with infinite total interstage flow at RR_{min} (7). However, the present CRC analysis has shown W_{unmix} to be infinite at both of these extremes regardless of the type of process. Therefore, in an irreversible process *both* W_{unmix} *and the sum of the stagewise energy inputs required to produce interstage flow become infinite at both extremes of recycle*. Consequently, the most efficient CRC design for irreversible processes will be at the recycle ratio which results in a minimum total interstage flow and minimum W_{unmix}. Furthermore, the IC will be the most efficient of any design for an irreversible process since the total interstage flow will be an absolute minimum and there is no W_{unmix}.

It is apparent that when stagewise mixing is taken into account in the analysis of CRCs, many of the perceived differences between process types disappear. In all cases, an infinite energy consumption is required at the extremes of recycle ratio, and there is an "optimum" recycle ratio which results in a minimum W_{unmix} and total interstage flow. Although proof from a calculational standpoint is lacking, it appears this recycle ratio would result in a minimum consumption of available energy to produce the desired separation in a CRC. Since $W_{\text{unmix}} = 0$ and total interstage flow is an absolute minimum in ICs, this design could potentially be the most efficient regardless of the process type short of approaching total reversibility by eliminating all finite driving forces within the individual stages of the separation cascade. Total reversibility in countercurrent recycle cascades may be impossible to achieve when mixing is incorporated into the analysis.

Based on the results of this study, it is concluded that:

1. The work required to counteract remixing of streams with different compositions within countercurrent recycle cascades, W_{unmix}, in-

creases the minimum work required for a specified separation. Mixing is completely eliminated in ideal cascades.

2. In CRCs, W_{unmix} goes through a minimum at some point between the limiting extremes of minimum recycle ratio and total recycle. At these extremes of recycle ratio, W_{unmix} becomes infinite.
3. For the examples considered, W_{unmix} in the CRCs goes through a minimum at recycle ratios of 1.32, 1.35, and 1.52 times $(\text{RR})_{\text{min}}$ for separation factors of $\alpha = 1.027$, 1.067, and 1.20, respectively. At these minimum values, W_{min} is increased by about 28 to 31% over the thermodynamic minimum work of separation. For these cases, W_{unmix} becomes larger than W_{mix} at recycle ratios greater than about $3(\text{RR})_{\text{min}}$ and lower than about $1.2(\text{RR})_{\text{min}}$.
4. W_{unmix} is very close to being directly proportional to total interstage flow within a CRC. The constant of proportionality increases with increasing separation factor, α, and recycle ratio.
5. Many of the perceived differences in the analysis of stagewise separation cascades for potentially reversible, partially reversible, and irreversible processes disappear when mixing within the CRC is taken into account.

It will be of interest to further explore the thermodynamic consequences of internal mixing in separation processes by making parametric studies examining variations in W_{unmix} with α, z_F, and the extent of separation.

NOMENCLATURE

CRC	constant recycle cascade
F	feed flow rate (mol/h)
IC	ideal cascade
K_{eq}	equilibrium constant for isotope exchange reaction ($= \alpha$)
M	flow rate of heads stream (mol/h)
N	flow rate of tails stream (mol/h)
n	nth stage in a cascade
P	enriched product flow rate (mol/h)
R	universal gas constant (kJ/mol·K)
RR	recycle ratio (dimensionless)
S	entropy (kJ/mol·K)
T	absolute temperature (K)
TIF	total interstage flow (mol/h)
W	depleted product (waste) flow rate (mol/h)
W	work (kJ/h)
x	composition of liquid phase or tails stream (mole fraction)

y	composition of vapor phase or heads stream (mole fraction)
z	composition of feed stream (mole fraction)

Greek Letters

α	stage separation factor
β	heads separation factor
γ	tails separation factor
θ	stage cut = N/F

Subscripts

CRC	constant recycle cascade
cascade	refers to reflux or recycle ratio of CRC
F	feed stage
F1, F2	feed stream to a stage
g	gas phase in isotope exchange reaction
i	stage number in enriching section
j	stage number in stripping section
l	liquid phase in isotope exchange reaction
max	maximum
min	minimum, minimum thermodynamic work
P	product stage
sep	separation
total	refers to condition of total reflux in a CRC
unmix	unmixing, excess work required due to mixing
W	waste or depleted product stage

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