Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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F. P. McCandless[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, MONTANA STATE UNIVERSITY BOZEMAN, MONTANA

To cite this Article McCandless, F. P.(1996) 'The Role of Recycle in Countercurrent Recycle Distillation Cascades. II. Extractive Distillation and Hybrid Cascades', Separation Science and Technology, 31: 5, 605 — 628
To link to this Article: DOI: 10.1080/01496399608000707
URL: http://dx.doi.org/10.1080/01496399608000707

SEPARATION SCIENCE AND TECHNOLOGY, 31(5), pp. 605–628, 1996

The Role of Recycle in Countercurrent Recycle Distillation Cascades. II. Extractive Distillation and Hybrid Cascades

F. P. McCANDLESS
DEPARTMENT OF CHEMICAL ENGINEERING
MONTANA STATE UNIVERSITY
BOZEMAN, MONTANA 57717-0266

ABSTRACT

Stage recycle requirements for a specified separation in a countercurrent recycle cascade vary with local (stage) composition and local α in a complex manner. The amount of stagewise recycle necessary to maintain stage separation is lower for higher values of α, and also decreases as the local stage compositions in the separation cascade approach desired product compositions. In Part I of this paper it was shown how this latter behavior can be used to design ideal and/or "squared-off" cascades which minimize total interstage flow and equipment size. In addition, α can be significantly increased for some systems, by use of a suitable extractive agent, that is, by using extractive distillation. Part II of this paper discusses some of the possible benefits of using extractive distillation with respect to reducing the number of theoretical stages required and also greatly reducing the required recycle ratio (and thus energy) requirements for a specified separation relative to ordinary distillation. It is also shown that it is theoretically possible to design an extractive-ordinary hybrid distillation cascade which could offer some advantages over extractive distillation for some systems. The proposed hybrid cascade would use the same (low) reflux ratio necessary in the center of the extractive distillation section (where α is high) throughout the cascade, including the two ordinary distillation sections (where α is low without agent). This is possible because, in the ordinary distillation sections, stage compositions are closer to the required product compositions. Depending on the specific system and equipment design, the hybrid cascade could reduce the number of extractive distillation stages required for a specified separation, require less inventory of extractive agent, and require less total interstage flow and/or fewer actual stages than that required for straight extractive distillation. Results of some preliminary calculations are presented for some hybrid cascades for systems with $\alpha = 1.1/1.2$ and $\alpha = 1.4/2.1$, for ordinary and extractive distillation, respectively. Calculations for a system with $\alpha = 1.5/3.5$ suggest that a hybrid cascade may not be suitable for that system, but shows the possible benefits of using extractive distillation for such a system. These applications further illustrate the consequences of the stagewise dependence of minimum reflux ratio in countercurrent recycle cascades.

INTRODUCTION AND BACKGROUND

Part I of this study illustrated how minimum recycle ratio varies with stage α, stage composition, and product compositions, and emphasized and illustrated this dependence by comparing constant reflux, ideal, and squared-off cascade designs in terms of the number of stages, total interstage flow, and relative energy requirements to make a specified separation for constant α. The squared-off and ideal cascade designs utilize different reflux ratios in different parts of the cascade. Part II explores the consequences of the dependence of minimum recycle ratio on α and stage composition with respect to extractive distillation where α can be increased by the presence of a suitable *extractive agent.*

In extractive distillation (ED) the relative volatility of a binary mixture is altered by the presence of a third compound or extractive agent. The relative volatility usually increases with increasing concentration of agent. An increase in relative volatility means fewer theoretical stages, and smaller reflux ratios are required to make a specified separation compared with conventional (ordinary) distillation (OD), with possible concomitant savings in distillation tower costs and energy requirements. However, the presence of the extractive agent may decrease ordinary tray efficiency, and so, for this case, more actual stages may be required using ED than for OD, depending on the amount α is increased and tray efficiency is decreased. Although trays may be designed that have high efficiency for ED, the ED trays would probably cost more, and with extractive agent present the column would probably have to be larger than for the same liquid rates in OD. Thus, when the dependence of $(R_i)_{\min}$ on α and composition (together with the adverse effects of agent on tray efficiency and column size) is considered, it appears that there may be the possibility of utilizing an OD/ED hybrid cascade to advantage for some systems. Again, this will depend on specific system behavior, i.e., on the increase in α and decrease in tray efficiency for a given extractive agent.

Basis for Increased α in Extractive Distillation

At low to moderate pressures, the following equation adequately describes vapor–liquid equilibrium for many systems (1):

$$y_iP = x_i\gamma_iP_i^{\text{sat}} \tag{1}$$

where y_i and x_i are the equilibrium compositions of vapor and liquid phases, respectively, P is the total pressure of the system, γ_i are liquid phase activity coefficients, and P_i^{sat} are the vapor pressures of pure i. For a binary mixture of compounds A and B, the expression for relative volatility (assuming compound A is the more volatile component) becomes

$$\alpha_{\text{AB}} = \frac{y_{\text{A}}/x_{\text{A}}}{y_{\text{B}}/x_{\text{B}}} = \left(\frac{\gamma_{\text{A}}}{\gamma_{\text{B}}}\right)\left(\frac{P_{\text{A}}^{\text{sat}}}{P_{\text{B}}^{\text{sat}}}\right) \tag{2}$$

Thus, it is seen that α may be altered by either a change in the ratio of activity coefficients or vapor pressures. The vapor pressure ratio may sometimes vary slightly with temperature, but usually not enough to increase α_{AB} significantly. However, many liquid mixtures form nonideal solutions and, as a result, the ratio of activity coefficients can sometimes be significantly increased by adding a liquid that selectively interacts with one of the components of the mixture to be separated, thus increasing the magnitude of $(\gamma_{\text{A}}/\gamma_{\text{B}})$. A "good" extractive agent is usually thought of as being a compound that forms a near-ideal solution with the heavier component and a highly nonideal solution with the lighter one (2, p. 93). This will increase the activity coefficient of the lighter compound with a large increase in apparent relative volatility. Since the basis for increased relative volatility is a phenomenon that occurs entirely in the liquid phase, a good agent should be substantially less volatile than either of the compounds to be separated. This means that very little of the extractive agent will be present in the vapor phase, and thus will not increase the vapor rate in the column. It also assures that the agent can be readily separated from the bottoms product.

Engineering Design of an Extractive Distillation System

The design of an ED system is more complex than for ordinary distillation because of the presence of the extractive agent. Some important considerations have recently been discussed by Sucksmith (2).

The apparent relative volatility $(\alpha_{\text{AB}})_{\text{EXT}}$ is usually a function of the amount of extractive agent present, increasing with extractive agent concentration (3–5). As a result, a high concentration of extractive agent usually must be present in the liquid phase to significantly increase α. If the feed to the ED system is liquid, agent must be added with the feed stream to maintain constant agent concentration in the liquid phase below the feed tray. The agent must be heated in both the ED and agent recovery columns, therefore more energy is required at higher agent flow rates. This energy requirement is closely tied to the reflux ratio that is used. Just as in OD, higher reflux ratios lead to better separations with fewer stages. Thus, it is obvious that reflux ratio and agent concentration require optimization. In addition, and probably equally important, the presence of the required high concentration of extractive agent in the liquid phase may require innovative equipment design to eliminate low tray efficiencies due to increased liquid viscosity, less efficient vapor–liquid contacting, etc.

A search of the literature reveals that very little has been published concerning stage (tray or plate) efficiency for extractive distillation. Sucksmith (2), in a study of the separation of *n*-heptane–toluene using phenol as the solvent, assumed a tray efficiency of 25% for ED, compared with 65% for OD, without giving a basis for the assumption. Atkins and Boyer (9), in a plant study of ED for the recovery of butylene from butanes using a solvent of 85% acetone, 15% water, reported plate efficiencies of 63.2% above the feed plate and 63.5% below the feed plate, while laboratory work indicated 50–63%. Individual plate samples indicated efficiencies as low as 34%. A study by Dunn et al. (10) for the recovery of toluene from "nontoluenes" using 60–65% phenol assumed a "conservative" estimate of 50% tray efficiency.

Typically, liquid flows in ED will be 50–90% extractive agent, with 10–50% of the components being separated. The extractive agent is usually nonvolatile ("heavier" with respect to boiling point) and probably more viscous. Since the extractive agent is nonvolatile, the up-flowing vapor rate will be small relative to the total liquid rate. On a molar basis the vapor rate will only be greater than the solvent free liquid rate by an amount equal to the overhead product rate in the enriching section of the column. Intuitively, it would seem that conventional vapor–liquid contactors (trays) would be less efficient for these ED systems than for OD. On the other hand, it may be possible to design trays for ED that would have efficiencies comparable to OD. Personal communications with Glitsch Technology Corp. personnel indicates that, with proper design of trays and packings, the tray efficiency can be maintained in the presence of solvents (11). However, the distillation business appears to be highly competitive with new tray design and innovation viewed as proprietary, and thus design details and efficiencies have not been discussed in the open literature. In all probability, the increased tray efficiency results from more complicated (and expensive) designs. In any case, equipment size for ED probably must be larger than for OD. Thus, Benedict and Rubin (4) analyzed the separation process of ED, and concluded that:

> . . . the high solvent rate increases the size of the extractive tower, and the solvent stripping tower and, therefore, has an optimum value in practice.

Although the design and analysis of ED can be complex, in the limiting case of an extractive agent with low volatility the design problem with respect to the number of ideal stages reduces to a standard problem except for the modification of the relative volatility (6). Atkins and Boyer concluded that plant test data agreed closely with calculated data, which indicated that the extractive distillation system lends itself readily to fundamental distillation calculation using the McCabe–Thiele method on a solvent-free basis (9). After the number of theoretical stages is determined, appropriate stage efficiencies must be applied to determine the required number of actual trays.

A schematic diagram of an extractive distillation cascade is shown in Fig. 1.

The increase in relative volatility can vary widely for different systems as shown in Table 1, which presents four arbitrary examples from the literature.

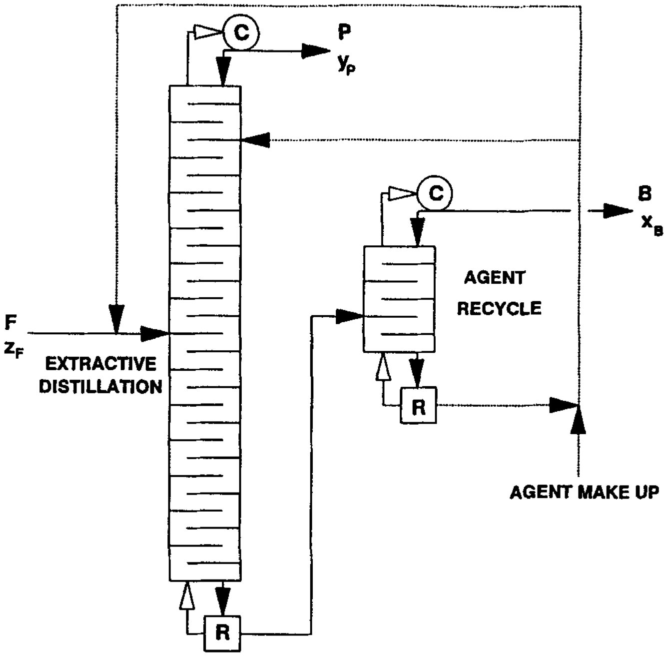


FIG. 1 Schematic diagram of an extractive distillation cascade.

TABLE 1
Increased Relative Volatility Due to Extractive Agents

System	α_{AB}	$(\alpha_{AB})_{EXT}$	Extractive agent	Ref.
o-Xylene–*m*-xylene	1.1	1.2	Hexylacetate Ethylacetoacetate	7
Isobutane–1-butene	1.16	2.00	Furfural	8
n-Hexane–benzene	1.37	2.09	Phenol	2
Heptane–toluene	1.50	3.50	Phenol	3

MINIMUM RECYCLE AS APPLIED TO EXTRACTIVE DISTILLATION

The following equations which give minimum recycle rates as a function of product and stage compositions, and stage α were derived and discussed in Part I of this paper, but are again presented here to aid in the discussions that follow regarding their consequences for ED.

$$\text{Enriching section} \qquad \left[\frac{N_{i+1}}{P}\right]_{\min} = \frac{(y_P - y_i)[y_i + \alpha(1 - y_i)]}{(\alpha - 1)(y_i)(1 - y_i)} \tag{3}$$

$$\text{Stripping section} \qquad \left[\frac{N_{j+1}}{B}\right]_{\min} = \frac{\alpha x_j - x_B[1 + (\alpha - 1)x_j]}{(\alpha - 1)(x_j)(1 - x_j)} \tag{4}$$

The recycle ratios for both enriching and stripping sections can be put on the same basis by

$$\left[\frac{N_{j+1}}{P}\right]_{\min} = \left[\frac{N_{j+1}}{B}\right]_{\min} \left[\frac{B}{P}\right] \tag{5}$$

The precursors to these equations come from a consideration of material balance and stage equilibrium requirements around individual stages, and the entire enriching or stripping section of a distillation cascade. Equations (3) and (4) result from a consideration of what happens to the separation that occurs between *adjacent* stages as the liquid flow rate entering a stage is reduced. Note that N_{i+1} and N_{j+1} are the liquid flow rates entering a stage from the stage above it and that the stage liquid compositions leaving the adjacent stages approach each other as N_{i+1} or N_{j+1} is reduced, thus requiring more and more stages to reach the "critical" composition. In the limit, $[N_{i+1}]_{\min}$ or $[N_{j+1}]_{\min}$ results in an infinite number of stages being required to reach the critical composition where separation ceases between these adjacent stages. These equations are important to the development and discussions that follow, and show that:

1. Minimum recycle is a stage-composition phenomenon; its value depends on the composition of equilibrium vapor or liquid, and on the value of α on a given stage.
2. Minimum recycle ratios are higher at stages where stage compositions depart more and more from product compositions, thus, it is a maximum at the feed stage, and, at constant α, "tapers" to smaller values toward both product ends of the separation cascade.
3. Higher values of α result in lower recycle requirements, and hence lower energy input needs.

The general advantages of using ED over OD can be conveniently illustrated by comparing the minimum number of theoretical stages required (calculated by the Fenske–Underwood equation), and the maximum minimum reflux ratio (calculated from Eq. 3), for a specified separation. This was done for the three hypothetical systems investigated in this paper (vide infra). The results of the calculations are presented in Table 2.

$[(R_i)_{\min}]_{\max}$ can take on values in the indicated range, since y_i at the feed stage will be different depending on the actual R_i used, which can vary from minimum to "total" reflux. As can be seen for these systems, for ED, $N_{\min}$ is about 35 to 52% and $[(R_i)_{\min}]_{\max}$ is about 20 to 48% of that required for the corresponding OD, depending on the magnitude of the αs and the increase in α due to the presence of the extractive agent. Thus, from this it would appear that ED would require smaller equipment (fewer stages) and less energy input for a specified separation. The latter is probably the main incentive for using ED over OD. However, the increase in separation efficiency using ED will be, in all cases, partially

TABLE 2

Minimum Number of Stages, and $[(R_i)_{\min}]_{\max}$ for $y_P = 0.99$, $x_W = 0.01$, and $z_F = 0.5$ for Several Different OD and ED αs

	Ordinary distillation		Extractive distillation	
System	$N_{\min}$	$[(R_i)_{\min}]_{\max}$	$N_{\min}$	$[(R_i)_{\min}]_{\max}$
α = 1.1, 1.2	97	20.6–20.6	51	9.8–10.8
α = 1.4, 2.1	28	4.8–5.8	13	1.8–2.8
α = 1.5, 3.5	23	3.9–4.9	8	0.8–1.8

offset by increased separation cascade complexity and additional energy requirements due to the presence of the extractive agent in the system. As a result, there are ample opportunities for optimization in an ED cascade.

CONCEPT OF A HYBRID CASCADE USING BOTH ED AND OD

Typically, distillation columns are designed for a constant reflux ratio on the order of 1.1 to 1.5 times $(R_i)_{\min}$ at the feed point, which means that $(R_i)/(R_i)_{\min}$ is greater than this value everywhere else in the column. The presence of a suitable extraction agent increases α with a concomitant decrease in required recycle ratio. However, as discussed above, since minimum recycle ratio also depends on stage α and stage and product compositions, smaller recycle ratios can be utilized toward the two product ends compared with stages near the feed point. As a result of this decrease in recycle requirements as product compositions are approached, it is possible to design a cascade in which ED is used in the "center" section, while OD will still further the separation toward the two product ends while using the same reflux ratio throughout the cascade, provided care is taken in choosing where the change is made between ED and OD. Figure 2 illustrates the feasible regions for ED and OD when a constant recycle ratio is used for such a *hybrid* cascade. As can be seen, there are two pinch points where the operating lines cross the equilibrium curve for the smaller α. In order for the hybrid cascade to be feasible, ED must be used to get "past" these pinch points before switching to OD. The actual compositions where the transition is made could be an important variable in the design since more and more stages would be required to make the separation as the transition compositions approach the pinch compositions.

Thus, as shown above, it is theoretically possible to design a hybrid extractive–ordinary distillation cascade which would take advantage of the smaller recycle requirements accompanying the higher $(\alpha_{AB})_{EXT}$ in the portion of the composition range "near" the feed point, while this same low recycle ratio would be adequate to further the separation toward both product ends *without* extractive agent being present, that is, when the relative volatility is α_{AB}.

A conceptual schematic diagram for such a hybrid system is shown in Fig. 3. In the proposed cascade the "center" section is an ED column which contains parts of both stripping and enriching sections of the cascade. In this section, extractive agent is present in the liquid phase at concentrations necessary to maintain the relative volatility everywhere in the ED section at $(\alpha_{AB})_{EXT}$. The feed (which also contains recycled

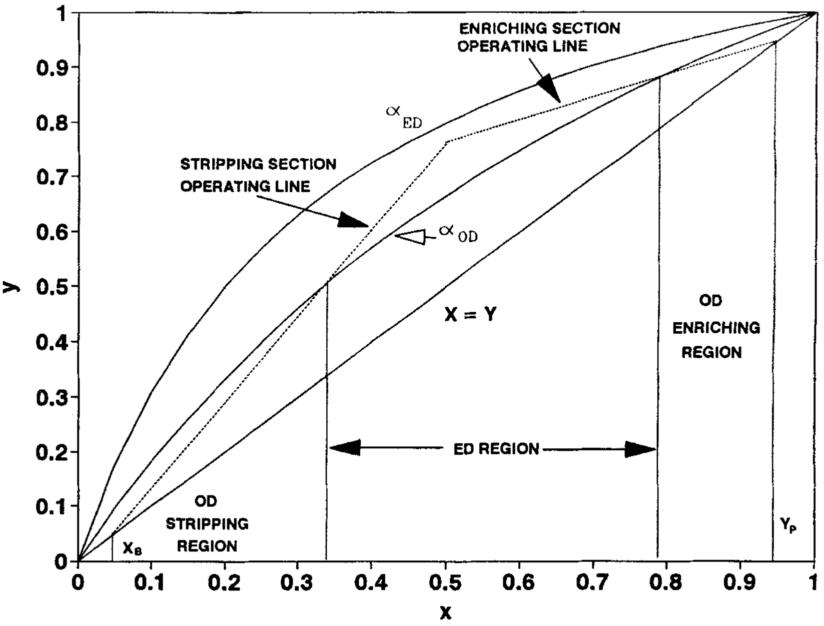


FIG. 2 McCabe–Thiele plot showing feasible hybrid regions for ED and OD.

extractive agent) is introduced at the proper location in this section. The portion of the cascade above (and including) the feed stage is the enriching section, while that below the feed stage is the stripping section. The feed is stripped and enriched in this section at $(\alpha_{AB})_{EXT}$ to produce heads and tails streams leaving this section which represents some intermediate separation. In the design of the hybrid cascade, the extent of separation occurring in the ED section (and hence the required number of stages) would ultimately be chosen by some optimization scheme.

The tails stream from the ED section (which contains all of the extractive agent) is sent to an extractive agent recycle column which produces nearly pure agent as bottoms for recycle to the top of the ED section and to the feed stream. The overhead from the recycle column is condensed and becomes the liquid reflux required for the (OD) stripping section. In this section the more volatile component is further stripped from the reflux liquid at relative volatility α_{AB} to produce the desired bottoms product, x_B. The vapor stream leaving the top of the OD stripping section provides the "reboil" vapor necessary for the operation of the ED section and the OD enriching section.

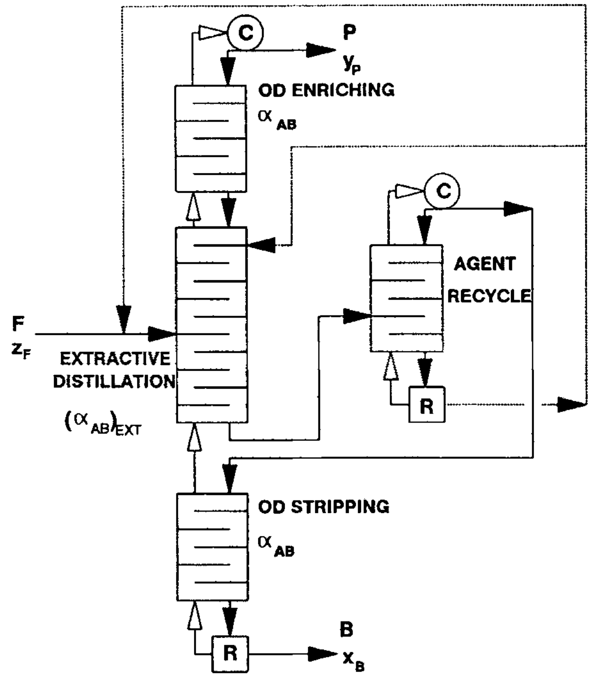


FIG. 3 Conceptual flow diagram of an ED, OD hybrid cascade.

The vapor (heads) stream leaving the top of the ED section (which should contain very little of the heavier extraction agent) provides the "reboil" vapor required for the OD enriching section which continues to enrich the vapor stream up to the desired product composition, y_P, while the tails stream leaving this section provides the reflux to the top of the ED section.

When the need for a high concentration of extractive agent in the liquid phase is considered (coupled with the possible detrimental effects of the presence of extractive agent on tray efficiency) and which is also coupled with the dependence of the required recycle ratios on stage α, stage compositions, and product compositions, it seems reasonable that a system similar to the hybrid system discussed above may, in some cases, offer some advantages over straight ED or OD. In such a system there would be many opportunities for optimization since the extent of separation and the reflux ratio can be varied within limits. For the system above, it is assumed that one "reflux ratio" is used throughout the cascade and hence the reflux ratio chosen for the ED section, together with the extent of separation in the ED section, must be consistent with recycle requirements in the OD sections which operate at lower α. It would also be possible to design hybrid cascades which would utilize different reflux ratios in each section, but this would require additional reboilers and/or condensers and add to the complexity of the cascade. Some of the possible advantages for the ED–OD hybrid system discussed above are summarized below:

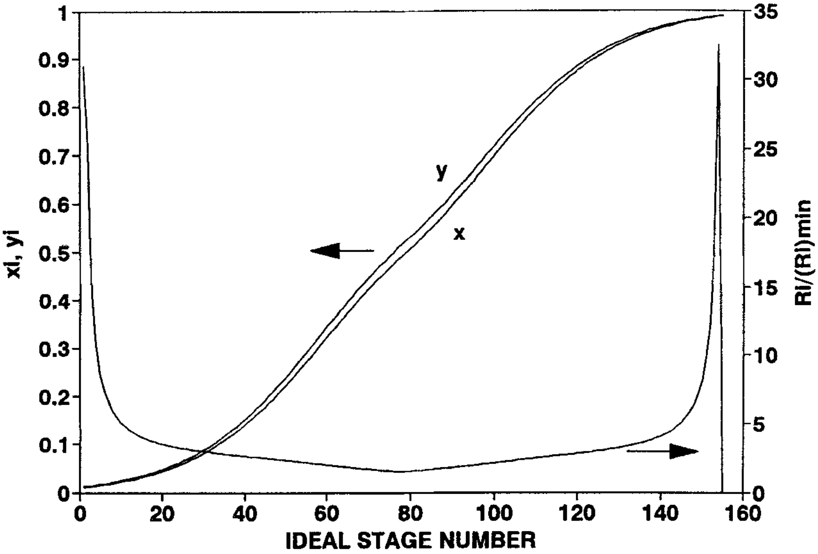
1. Fewer actual stages may be required compared with pure ED if tray efficiencies are much lower for ED than for OD.
2. Less total solvent-free interstage flow will be required than for OD, and in some cases less than for pure ED. In addition, less total interstage flow (and inventory) of extractive agent may be required compared with pure ED.
3. The energy input required for the separation (which, to a large extent, is dictated by the maximum recycle ratio in the cascade) will certainly be less than for ordinary distillation, and when Item 2 is considered, it may be less than for pure ED.

EXAMPLES AND CALCULATIONS

Design calculations were made to show the advantages of ED over OD and to illustrate the concept of a hybrid ED–OD cascade. A spreadsheet computer program was used for these calculations, as discussed in Part I. In all cases, calculations started at the feed stage and progressed to the two product ends, using appropriate stage equilibrium and stripping and enriching material balances; and for the hybrid case, changing from $(\alpha_{AB})_{EXT}$ to α_{AB} at appropriate (though rather arbitrary) stage compositions. Specific compositions for this change cannot be specified, but only approximate ones, because of the nature of the engineering design calculations for these systems. Specific stage compositions cannot be determined before calculations are made. The results are used only to illustrate the possible technical feasibility of the concept with no real effort to optimize the systems. For this study three hypothetical systems were studied:

α_{AB}	$(\alpha_{AB})_{EXT}$
1.1	1.2
1.4	2.1
1.5	3.5

(a) ORDINARY DISTILLATION
α = 1.1, REFLUX RATIO = 29



(b) EXTRACTIVE DISTILLATION
α = 1.2, REFLUX RATIO = 15

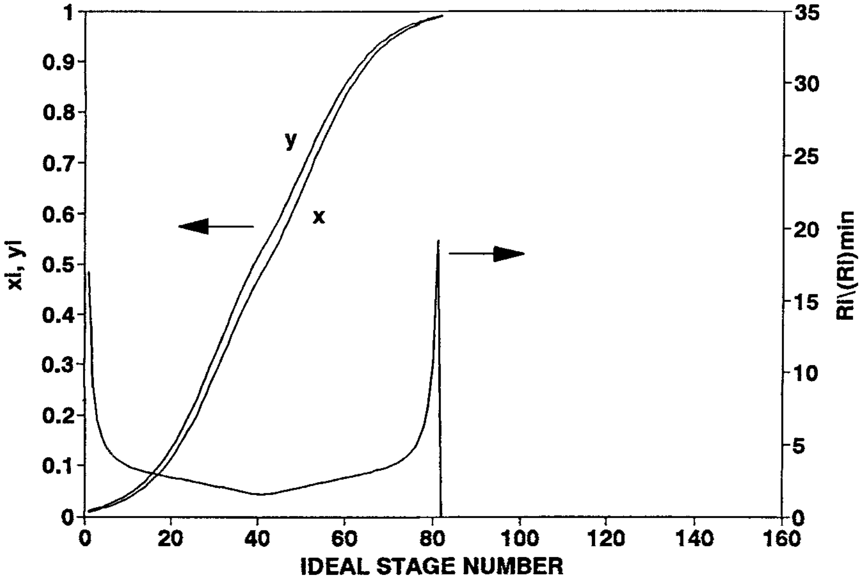
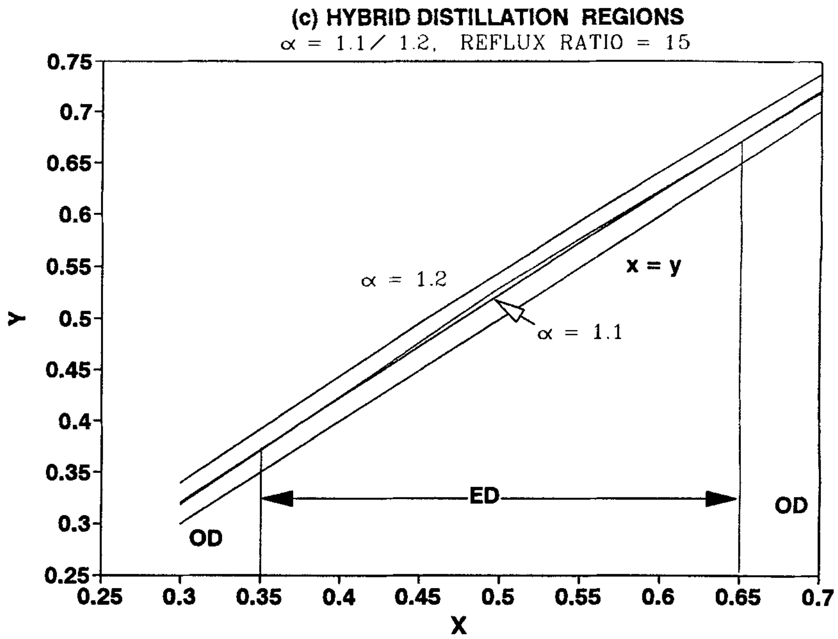
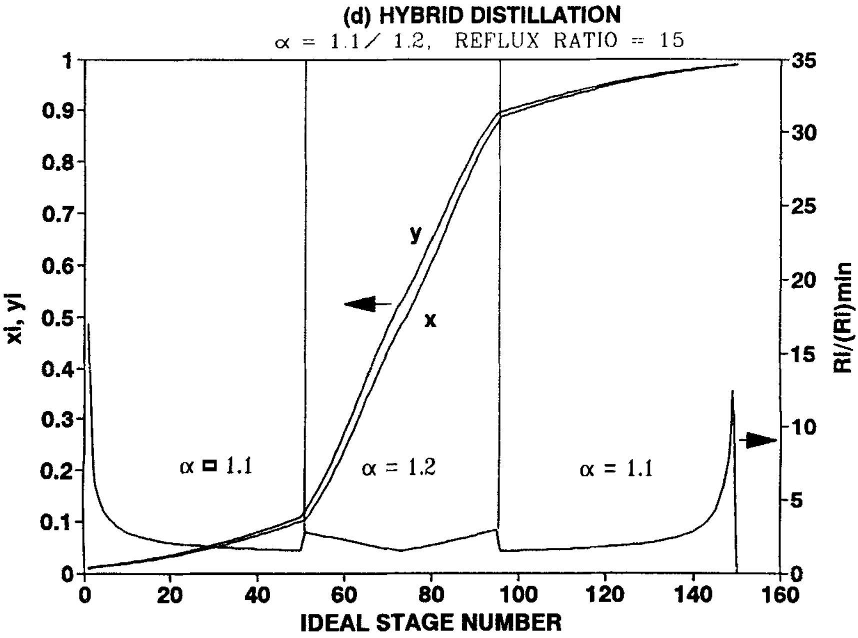


FIG. 4 Comparison of OD, ED, and hybrid cascades, $\alpha = 1.1, 1.2$; flows relative to $P = 1$.


(c) HYBRID DISTILLATION REGIONS

α = 1.1/ 1.2, REFLUX RATIO = 15


(d) HYBRID DISTILLATION

α = 1.1/ 1.2, REFLUX RATIO = 15

FIG. 4 Continued

In all cases the following values for the external variables were assumed:

$$z_F = 0.5, \qquad y_P \approx 0.99, x_B \approx 0.01$$

$$\text{Reflux ratio} \approx 1.5 \times (R_i)_{\min} \text{ at the feed point for ED}$$

Calculations were made for pure OD, pure ED, and for rather arbitrary hybrid cascades for comparison. The results of the calculations for the different cascade designs are presented below.

Results

$\alpha = 1.1/1.2$

Figure 4 and Table 3 present the results of calculations for $\alpha = 1.1$ for OD and 1.2 for ED. This might represent the separation of meta- and ortho-xylene using hexylacetate or ethylacetoacetate as the extractive agent (7). Shown are figures which present compositions and $R_i/(R_i)_{\min}$ in the various cascade configurations as a function of ideal stage number, together with a McCabe–Thiele plot showing feasible regions for ED and OD. Also, the table presents a comparison of the cascades with respect to the actual stages, total interstage flow (relative to $P = 1$), and reflux ratios for the assumed cascades. Two cases were considered: Case 1, with tray efficiencies of 25 and 65% for ED and OD, respectively, and Case 2, with equal tray efficiencies of 65% for both ED and OD. In both cases it was assumed that the liquid phase in the ED sections is 80% extractive agent. The following conclusions can be made, based on the results of the calculations presented in Fig. 4.

TABLE 3

Comparison of OD, ED, and Hybrid Cascades, $\alpha = 1.1, 1.2$; Flows Relative to $P = 1$. Cascade to Produce 99% Products from 50% Feed

OD, ED, η[a]	System	Total ideal stages	Number of actual stages			Total interstage flow $\times 10^{-3}$		
			OD	ED	Total	$V = L$	EA[b]	RR
Case 1:	OD, $\alpha = 1.1$	155	238	—	238	7.1	0	29
.65	ED, $\alpha = 1.2$	82	—	325	325	5.2	20.7	15
.25	Hybrid	150	161	180	341	5.4	11.6	15
Case 2:	OD, $\alpha = 1.1$	155	238	—	238	7.1	0	29
.65	ED, $\alpha = 1.2$	82	—	126	126	2.0	8.0	15
.65	Hybrid	150	161	70	231	3.7	4.4	15

[a] η = tray efficiency.

[b] Extractive agent, assumes ED liquid is 80% agent.

Figure 4, Case 1 (25% ED, 65% OD efficiencies). (a) OD with α = 1.1 would require the least number of actual stages (239) compared with 325 for ED and 341 for the hybrid cascade for the specified separation, but would require a solvent-free reflux ratio of 29 compared with 15 for ED, a 93% increase. Or, alternatively, ED would require only about 52% of the solvent-free reflux required for OD.

(b) The assumed hybrid cascade would require only about 4% more actual stages than for pure ED but, significantly, would require only about 56% of the total interstage flow of extractive agent and use the same low (solvent-free) reflux ratio required for ED.

Figure 4, Case 2 (65% ED, 65% OD efficiencies). (a) Pure ED would require only about 53% of the actual stages required for pure OD with (again) the solvent-free reflux ratio being only about 52% of that required for OD.

(b) For the case with equal (65%) tray efficiencies, the total interstage flow of extractive agent would be only about 39% of that required if tray efficiency for ED were 25%.

(c) The hybrid cascade would need a total of 231 actual stages compared with 126 for pure ED, but would require only 70 ED stages. As a result, the required total interstage flow of extractive agent in the hybrid cascade would be only about 55% of that required for pure ED.

(d) The Case 2 hybrid cascade would require only about 21% of the total interstage flow of extractive agent of that for pure ED, and about 38% of that for the Case 1 hybrid cascade.

α = 1.4/2.1

Figure 5 and Table 4 present the same information for a system with α = 1.4 for OD and 2.1 for ED. This might represent the separation of *n*-hexane from benzene using phenol as the solvent (2). The following conclusions can be made based on the results of the calculations presented in Fig. 5.

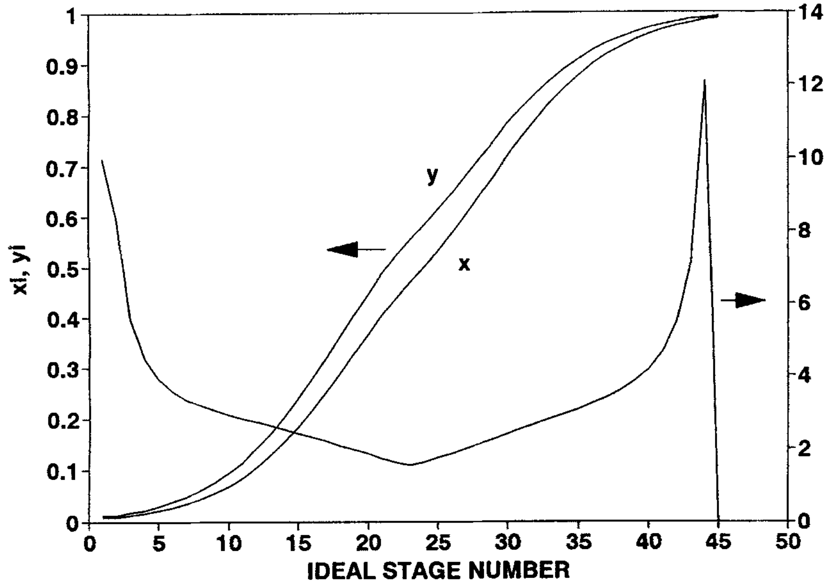
Figure 5, Case 1 (25% ED, 65% OD efficiencies). (a) OD would require the fewest number of actual stages, with pure ED requiring about 16% more, but OD would require a reflux ratio of 8 compared with 3.2 for ED, a 150% increase (40% of that required for OD).

(b) The assumed hybrid cascade would require about 14% more stages than for pure ED and about 31% more than for pure OD, but, significantly, would use the same low solvent-free reflux ratio throughout the cascade as required for pure ED.

Figure 5, Case 2 (65% efficiency for both ED and OD). (a) Pure ED would require only about 45% of the stages required for pure OD,

(a) ORDINARY DISTILLATION

α = 1.4, REFLUX RATIO = 8.0



(b) EXTRACTIVE DISTILLATION

α = 2.1, REFLUX RATIO = 3.2

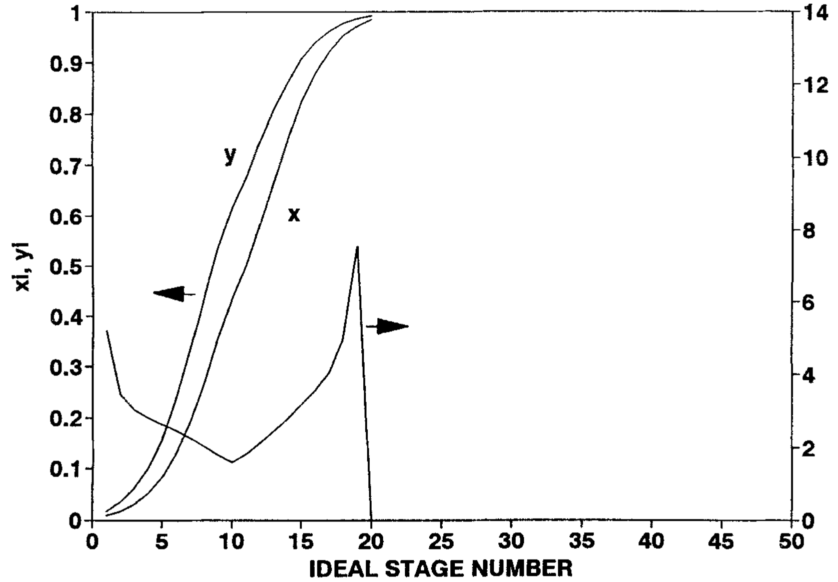
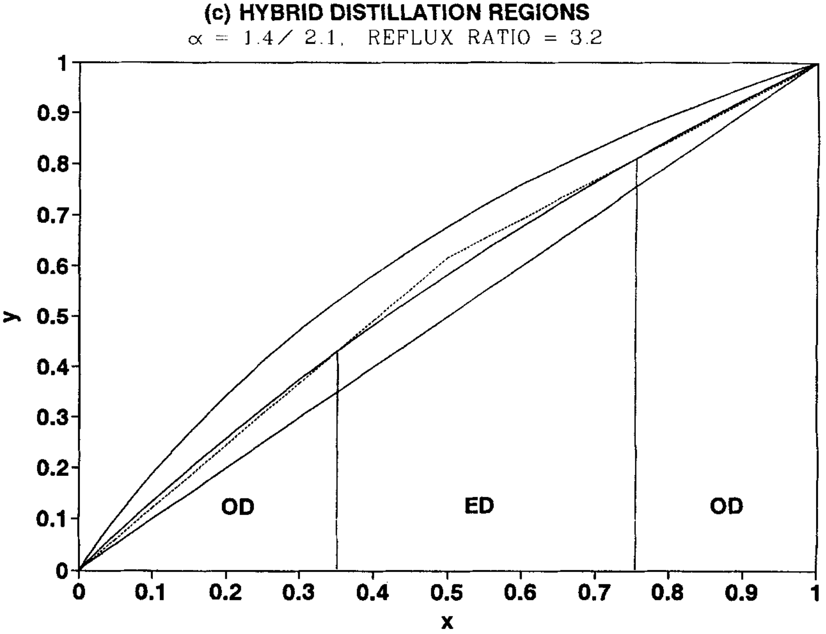
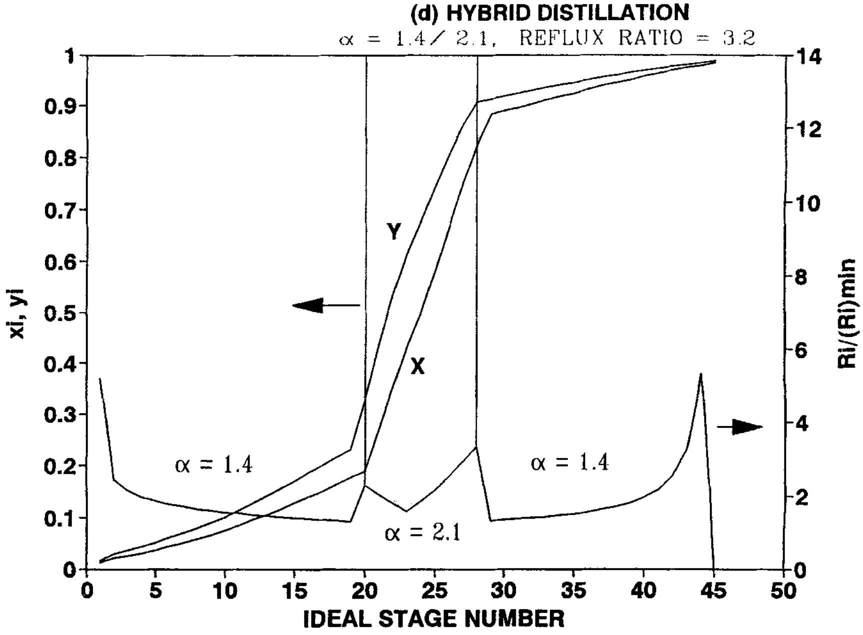


FIG. 5 Comparison of OD, ED, and hybrid cascades, α = 1.4, 2.1; flows relative to P = 1.



(c) HYBRID DISTILLATION REGIONS

α = 1.4/ 2.1, REFLUX RATIO = 3.2



(d) HYBRID DISTILLATION

α = 1.4/ 2.1, REFLUX RATIO = 3.2

FIG. 5 Continued

TABLE 4
Comparison of OD, ED, and Hybrid Cascades, $\alpha = 1.4, 2.1$; Flows Relative to $P = 1$. Cascade to Produce 99% Products from 50% Feed

OD, ED, η[a]	System	Total ideal stages	Number of actual stages OD	ED	Total	Total interstage flow × 10^{-3} $V = L$	EA[b]	RR
Case 1:	OD, $\alpha = 1.4$	45	69	—	69	.62	0	8
.65	ED, $\alpha = 2.1$	20	—	80	80	.34	1.34	3.2
.25	Hybrid	45	55	36	91	.39	.59	3.2
Case 2:	OD, $\alpha = 1.4$	45	69	—	69	.62	0	8
.65	ED, $\alpha = 2.1$	20	—	31	31	.13	.54	3.2
.65	Hybrid	45	56	14	70	.29	.25	3.2

[a] η = tray efficiency.

[b] Extractive agent, assumes ED liquid is 80% agent.

with (again) the solvent-free reflux ratio being only about 40% of that required for OD.

(b) With equal tray (65%) efficiencies for ED and OD, the total interstage flow of extractive agent would be only about 40% of that required if the tray efficiency for ED were 25%.

(c) The hybrid cascade would need about the same number of actual stages as for OD, but the ED section in the hybrid cascade would contain only about 45% of the trays that would be required for pure ED. As a result, the required total interstage flow of extractive agent in the hybrid cascade would be less than half of that required for pure OD.

(d) The Case 2 hybrid cascade would require only about 19% of the total interstage flow of extractive agent required for pure ED, and only about 42% of that for the Case 1 hybrid cascade.

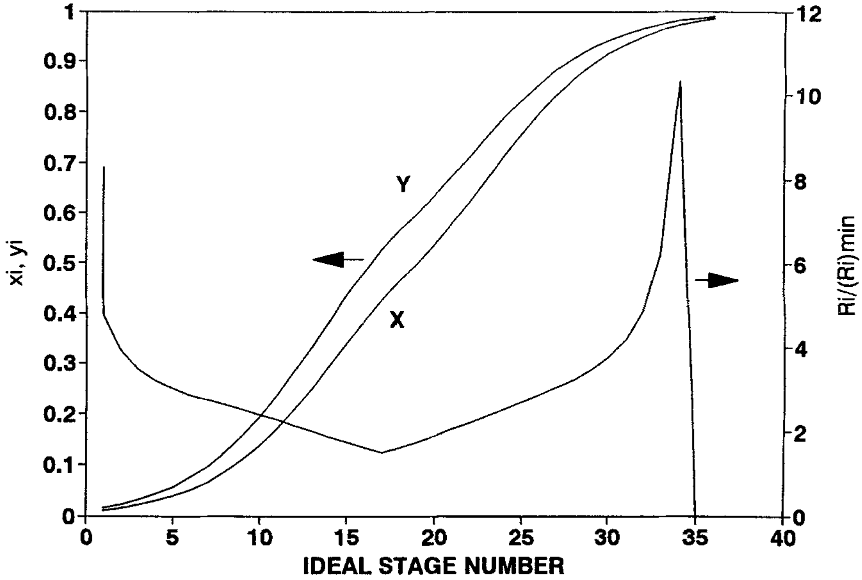
$\alpha = 1.5/3.5$

Figure 6 and Table 5 present the results of calculations with $\alpha = 1.5$ for OD and 3.5 for ED. This might represent the separation of *n*-heptane and toluene; for example, Ref. 3. As can be seen from Fig. 6(c), it is doubtful that a hybrid cascade would be suitable for this system because of the small possible OD zones, but the results of calculations for OD and ED clearly show the possible benefits of ED. The following conclusions can be made from the results of the calculations presented in Fig. 6.

Figure 6, Case 1 (25% ED, 65% OD Efficiencies). (a) The pure ED separation would require about 93% of the actual trays required for OD but only about 23% of the solvent-free reflux ratio.

(a) ORDINARY DISTILLATION

α = 1.5, REFLUX RATIO = 6.3



(b) EXTRACTIVE DISTILLATION

α = 3.5, REFLUX RATIO = 1.45

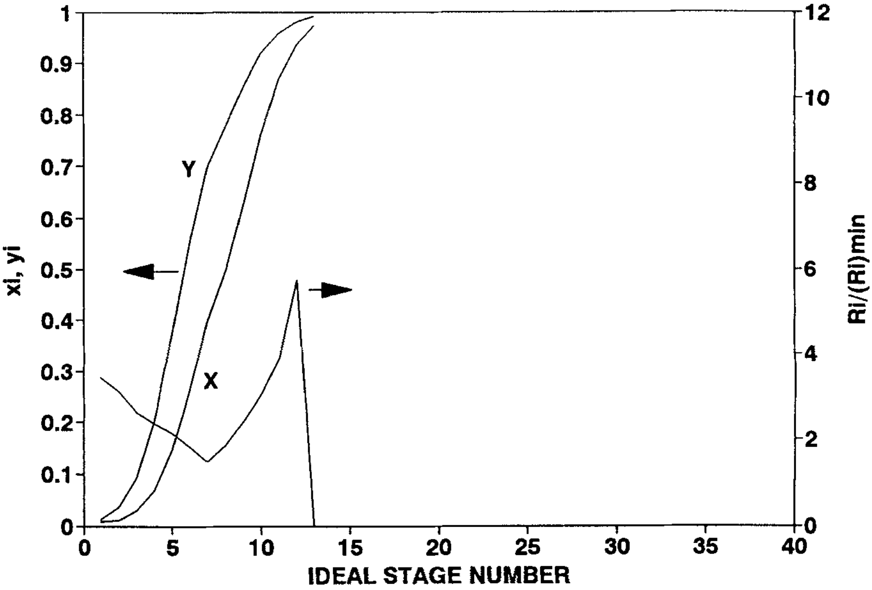
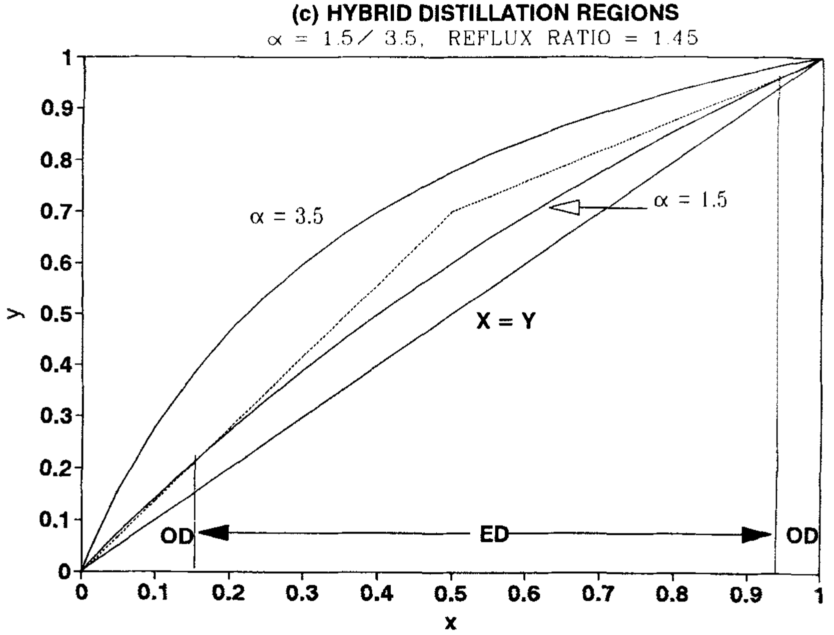


FIG. 6 Comparison of OD and ED cascades, α = 1.5, 3.5; flows relative to P = 1.

(continued)


(c) HYBRID DISTILLATION REGIONS

α = 1.5/ 3.5, REFLUX RATIO = 1.45

FIG. 6 Continued

Figure 6, Case 2 (65% Efficiencies for Both ED and OD). (a) The pure ED cascade would require about 36% of the actual number of trays required for OD, with the same decrease in required reflux ratio as in Case 1.

(b) The Case 2 ED cascade would require only about 37% of the total interstage flow of extractive agent compared with Case 1.

TABLE 5

Comparison of OD and ED Cascades, α = 1.5, 3.5; Flows Relative to $P = 1$. Cascade to Produce 99% Products from 50% Feed

OD, ED, η[a]	System	Total ideal stages	Number of actual stages			Total interstage flow			
			OD	ED	Total	V	L	EA[b]	RR
.65	OD, α = 1.5	36	56	—	56	402	404	0	6.3
.25	ED, α = 3.5	13	—	52	52	120	131	526	1.45
.65	OD, α = 1.5	36	56	—	56	402	404	0	6.3
.65	ED, α = 3.5	13	—	20	20	49	48	192	1.45

[a] η = tray efficiency.

[b] Extractive agent, assumes that ED liquid is 80% agent.

GENERAL DISCUSSION

The fact that $(R_i)_{\min}$ depends on product compositions, stagewise (equilibrium) compositions, and on *stagewise* values of α has not been adequately discussed in the popular textbooks on countercurrent stage separation, and, as a result, the full significance of this phenomenon is apparently not generally understood. The functional dependence of $(R_i)_{\min}$ on α and x_i or y_i for fixed y_P and x_B means that it is possible to use different reflux ratios in different parts of a cascade; and also that a reflux ratio that is adequate in the composition range near the feed point composition with a "high" value of α may also be adequate for lower values of α in a composition range closer to either y_P or x_B.

The use of a suitable extractive agent can increase α for some separations, but typically a high concentration of agent must be present in the liquid phase. The presence of large quantities of extractive agent could result in a greatly decreased tray efficiency for ordinary distillation tray design, or require special tray design or column packing to maintain tray efficiency at levels possible in ordinary distillation for some solvent systems.

Tables 3–5 and Figs. 4–6 clearly show the potential benefits of using ED for systems where ED is effective. ED can require significantly fewer stages, and probably more important, much lower reflux ratios are required compared with the same separation using OD. Certainly lower reflux means that less energy input is required. However, the benefits of using an extractive agent does not come without cost. The ED column will probably have to be larger to accommodate the increased flow due to the presence of the agent, and, probably, special tray designs must be used to result in high vapor–liquid contacting efficiency. In addition, as shown in Fig. 1, a separate agent recovery/recycle column must be used to separate the bottoms product from the agent so it can be recycled back to the ED column. For some extractive agents, degradation may be expected as it is recycled over a long period of time, thus requiring a solvent make-up stream and possibly even a solvent purification facility to remove degradation products. Thus, total agent inventory must also be an economic factor, since some of the possible extractive agents tend to be exotic and expensive.

As a result of the functional dependence of minimum recycle ratio, it is certainly theoretically possible to design a hybrid OD/ED cascade, and considering the disadvantages of ED discussed above, in some cases a hybrid cascade could offer some economic advantages over pure ED. The economic hybrid design could probably best be determined through optimization of the several factors which control the number of actual stages and the required total interstage flow of vapor–liquid and extractive agent. The total inventory of extractive agent that must be on hand (which will be related to required total interstage flow of agent) may also be an important optimization variable since, as indicated above, some agents are expensive and/or environmentally objectionable.

The conceptual designs discussed in this paper are very simplified but do tend to show the technical feasibility of the hybrid cascade concept. In reality, each candidate system would have to be studied in detail, taking into account the variation in α and tray efficiency with agent and system concentration, coupled with cascade reflux ratio and agent recycle column requirements. Stage compositions where the switch is made from ED to OD would be an important optimization variable since the number of OD stages required to further the separation can be greatly increased if the switch is made too "close" to the pinch points. Energy requirements for the separation (which to a large extent depends on reflux ratio and rate of extractive agent recycle) would be a very important part of any optimization study. Cascade size (and cost) will be a function of total interstage flow of vapor, liquid, and extractive agent. Technical and economic feasibility may be different for different feed compositions since the required R_i increases with more dilute feeds and decreases for more concentrated feeds. The same is true for the required purity of products: the R_i required decreases as y_P decreases and x_B increases.

The present study indicates that hybrid cascades might better be adapted to systems with low to moderate increases in α with use of an extractive agent, but, as discussed above, each system would have to be judged on its own merits until trends from detailed studies are established. Optimization studies were beyond the scope (and resources) of this preliminary conceptual study.

Finally, as a reminder, the main purpose of this paper is to illustrate some of the consequences of the stage dependence of $(R_i)_{\min}$ on separation cascade design. Hopefully, the examples of this paper have accomplished that goal and may result in the design of more efficient extractive distillation systems.

NOMENCLATURE

B	rate of bottoms (waste) product
ED	extractive distillation
L	total interstage liquid flow
N	liquid (recycle) rate entering or leaving a distillation stage
OD	ordinary distillation

P	rate of distillate or top product
R_i	enriching stage recycle ratio = $[N_{i+1}/P]$
R_j	stripping stage recycle ratio = $[N_{j+1}/B]$
RR	reflux ratio = R_i
V	total interstage vapor flow
x	mole fraction in liquid stream
y	mole fraction in vapor stream

Greek Letters

α	relative volatility
γ	liquid phase activity coefficient

Subscripts

A	compound A in a binary mixture
AB	binary mixture of compounds A and B
B	bottoms composition, compound B in a binary mixture
EXT	α_{AB} in the presence of extractive agent
i	general stage in enriching section, compound i in mixture
j	general stage in stripping section
min	minimum recycle ratio
P	distillate (top) product

Superscript

sat	saturation (vapor) pressure of pure compound in a mixture

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Received by editor June 26, 1995