Identifying Operating Units for the Design and Synthesis of Azeotropic-Distillation Systems

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A highly effective method has been established to identify processing or operating units necessary for the design or synthesis of azeotropic-distillation systems by resorting to the first principles and logical sequencing of such units. The materials represented in the space of the residue curve map are partitioned into lumped materials bounded by the thermodynamic boundaries and pinches. Subsequently, the operating units are identified on the basis of these lumped materials. The efficacy of the method has been amply illustrated by generating some feasible flowsheets with a set of relatively simple heuristics for the process of producing pure ethanol from its aqueous solution via azeotropic distillation, which is a typical complex process involving thermodynamic pinches, such as azeotropes, phase transition, and/or phase separation. The method is applicable to other complex processes, e.g., crystallization, extraction, reactive distillation, and their combinations. It is highly likely that the method can be an integral part of any conventional heuristic or algorithmic flowsheeting procedure because selecting plausible or candidate operating units is essential for synthesizing a flowsheet by any procedure.

Introduction

This work aims at developing a systematic and efficient method to identify processing or operating units required in establishing the flowsheets of azeotropic-distillation systems which are ubiquitous in chemical and allied industries.[1−8] Rapid progress has been made on the analysis of azeotropic-distillation systems since the mid-1980s.[3,7,9−11] For example, effective methods have been developed for determining feasible regions of product compositions and the existence and corresponding compositions of azeotropes; computing minimum reflux ratios and entrainer flows; and identifying multiplicity.[2,11−14] In contrast, much remains to be done in synthesizing azeotropic-distillation systems despite the fact that some notable accomplishments, predominantly based on heuristic methods, have been reported.[4,8,9,11] Indeed, a few critical questions are yet to be resolved, e.g., how systematically to generate feasible alternative flowsheets and/or how systematically to construct a superstructure linking all conceivable processing equipment, i.e., operating units.

A set of plausible or candidate operating units must be available prior to synthesizing any process. Hence, to identify operating units need be the first and essential task for synthesizing, i.e., developing the flowsheet of an azeotropic-distillation system or, for that matter, any process system. In fact, without the set of candidate operating units, neither a superstructure nor alternative flowsheets can be generated. Undertaking the task of generating the candidate operating units, however, is far more daunting for a separation system involving azeotropic distillation than for a relatively ideal separation system: The existence of thermodynamic pinches, e.g., azeotropes and distillation boundaries, always magnifies substantially the chemical/physical complexity of the system. This complexity, in turn, imposes significant restrictions on selecting candidate operating units. It may hinder us from adopting various operating units seemingly feasible to generate the desired products because they yield intermediate materials which cannot be processed further because of the thermodynamic pinches. On the other hand, certain operating units must be conceived to overcome thermodynamic pinches.

Obviously, the physical/chemical intricacy of azeotropic-distillation systems leads to enormous combinatorial complexity. In other words, it may result in a large number of plausible or candidate operating units, which may further increase the number of possible combinations or flowsheets comprising these operating units. The existing methods, mainly based on heuristics, can only take into account a fraction of these operating units. Naturally, this limitation of the existing methods often prevents the real optimal flowsheet from being synthesized. Thus, a systematic method for identifying the candidate operating units is deemed highly desirable for azeotropic-distillation systems.

To cope with the situation mentioned above, substantial domain knowledge of the system and various mathematical techniques need be incorporated into the method to deal with the system specificity. For example, residue curve maps (RCMs) serve to represent the system,[9,11] and materials partitioning, classification of operating units, and numerical curve fitting come into play to systematize and automate the method. To facilitate the presentation, each major step of the proposed method is delineated with a well-known example of the azeotropic-distillation system, i.e., the

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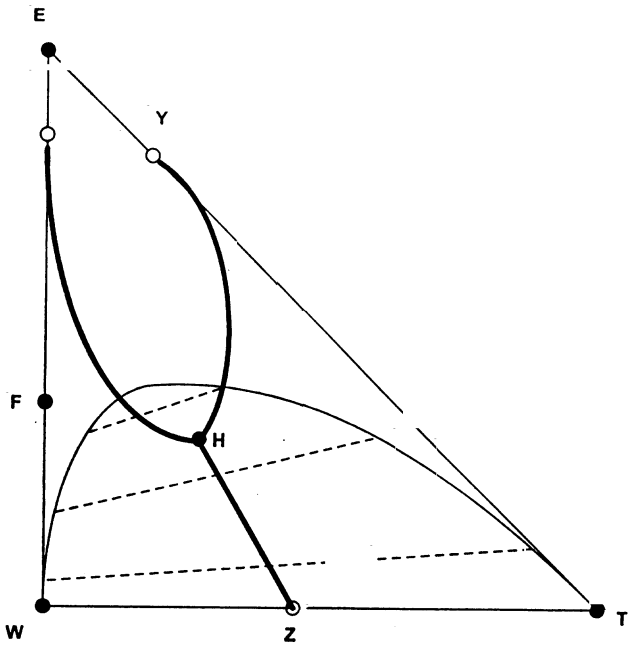

Figure 1. RCM of the ethanol (E)–water (W)–toluene (T) system with pertinent materials and operating units (see, e.g., ref 24): X, Y, Z, binary azeotropes; H, ternary azeotrope.

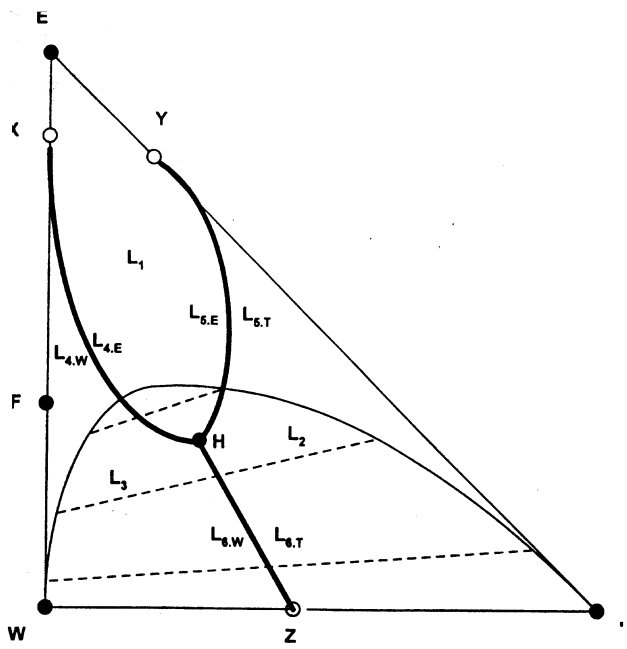

Figure 2. RCM of the ethanol (E)–water (W)–toluene (T) system illustrating the partitioning of materials via the distillation boundaries.

production of pure ethanol from its aqueous solution with toluene as the entrainer.

Overcoming Thermodynamic Pinches and/or Crossing Distillation Boundaries

In identifying candidate operating units with the concomitant flows of materials, thermodynamic pinches demand special attention because they constitute major obstacles in synthesizing azeotropic-distillation systems. Various means have been proposed to overcome such obstacles, either heuristically or based on the first principles.[4,5,9] What follows lists some means of dealing with a special type of thermodynamic pinches, i.e., distillation boundaries, which should be of particular concern in azeotropic distillation.[4,5,9]

a. Crossing a distillation boundary by exploiting the liquid–liquid equilibrium (LLE) with decantation or extraction; solid–liquid equilibrium (SLE) with crystallization or adsorption; or kinetic phenomena with membrane separation.

b. Reaching a new region by adding a mass separating agent (MSA) or other materials. Nevertheless, reaching a new region by introducing materials through recycling alone cannot be effective for crossing a distillation boundary.

c. Expanding the dimensionality of the RCM by adding an MSA so that the original boundary does not extend into a new residue curve map; this results in extractive distillation.

d. Shifting the position of a distillation boundary by varying the system pressure, thereby resulting in pressure-swing distillation.

e. Exploiting the extreme boundary curvature so that both the distillate and bottom are obtained in a region away from the region where the feed is situated.

Any means of crossing distillation boundaries gives rise to a specific RCM. Obviously, toluene (T) is the MSA, i.e., entrainer, in the RCM for producing pure ethanol from its aquatic solution, as illustrated in Figure 1. Naturally, other means can be adopted.

To facilitate the development and presentation, the procedures for generating candidate operating units and pertinent materials are illustrated with this example. Note that the addition of toluene leads to a two-phase region to be exploited for overcoming the ethanol–water azeotrope.

Partitioning Materials

A countless number of plausible materials may be identified for a three or more component system: the RCM of such a system is a two-dimensional plane, i.e., area or higher dimensional space. For generalization, therefore, a need exists to partition all of the materials within each of the two-dimensional areas or higher dimensional space defined by various boundaries in the RCM.

Generally, the products and feed for any distillation column should be in the same region created by distillation boundaries. When the extreme curvature of a distillation boundary is exploited, however, the products and feeds can be in the two different regions straddling this boundary.[15] Nevertheless, in this situation, the design and operation of the distillation columns exploiting such extreme curvature are severely affected, often negatively, by the reliability of thermodynamic data which often tend to contain appreciable error. It is, therefore, advisable to avoid the situation.

Partitioning Materials According to the Critical Curves and Lines. As can be discerned in Figure 2, distillation boundaries XH, YH, and ZH divide the entire RCM into three regions which cannot be crossed by simple distillation; in other words, i.e., simple distillation can only be implemented inside a single region. With the exception of those located infinitesimally close to each of the three boundaries and the singular points, E, W, T, and F, the materials in the RCM are partitioned into three classes, i.e., lumped materials L_1, L_2, and L_3. On the other hand, azeotropes X, Y, Z, and H are not classified as separate classes of materials because they are the terminal points of the distillation

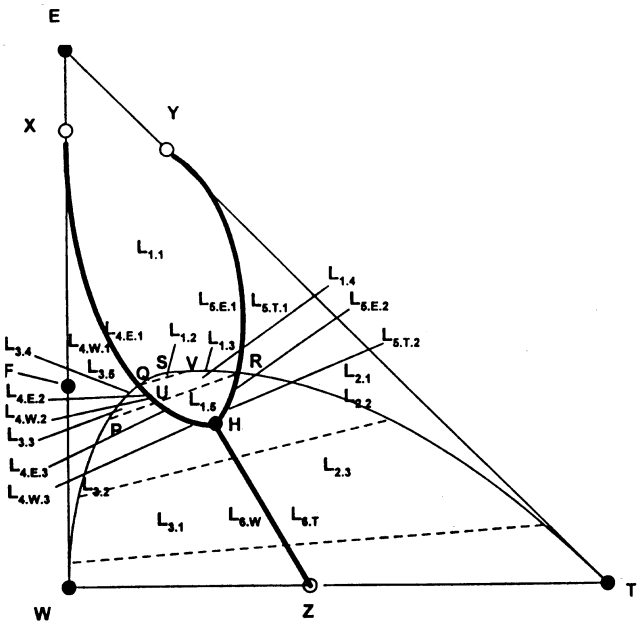

Figure 3. RCM of the ethanol (E)–water (W)–toluene (T) system illustrating the further partitioning of the lumped materials via phase splitting.

boundaries. Note that the materials situated infinitesimally close to a boundary can only be produced by distillation columns, each with an infinite number of trays under total reflux. The materials along distillation boundary XH on the sides of regions XHZWX and EYHXE are classified as lumped materials $L_{4.W}$ and $L_{4.E}$, respectively, because any of the former and that of the latter can be generated by distillation columns producing water (W) and ethanol (E), respectively. Similarly, the materials along distillation boundary YH on the sides of regions EYHXE and YTZHY are classified as lumped materials $L_{5.E}$ and $L_{5.T}$, respectively, and the materials along distillation boundary ZH on the sides of regions YTZHY and XHZWX, as lumped materials $L_{6.T}$ and $L_{6.W}$, respectively.

Further partitioning of lumped materials according to phase splitting is desirable because it may facilitate overcoming the thermodynamic pinch attributable to the ethanol–water azeotrope. For this purpose, it is deemed essential to identify the following additional critical points in the RCM. In Figure 3, they are point S, where the two branches of the LLE envelope merge; points Q and V, which are the terminal points of the first tie line totally located in region EYHXE; points P and R, which are the two terminal points of the first tie line with a single terminal point, i.e., the latter, located in region EYHXE; and point U, where distillation boundary XH and tie line PR cross each other at point Q. Note that distillation boundary XH and liquid–liquid envelope WST cross each other at point Q while distillation boundary YH and liquid–liquid envelope WST intercept each other at point R. The further partitioning of the lumped materials is accomplished as follows:

Lumped material L_1 is partitioned into lumped material $L_{1.1}$ in homogeneous region ERSQE; lumped material $L_{1.2}$ on curve QSV which is part of LLE envelope WST and in heterogeneous region QSVQ where phase splitting leads to the crossover of neither distillation boundary XH nor distillation boundary YH; lumped material $L_{1.3}$ on distillation boundary VR; lumped material $L_{1.4}$ in heterogeneous region QVRUQ where phase splitting leads to the crossover of distillation boundaries XH; and lumped material $L_{1.5}$ in heterogeneous region URHU where phase splitting leads to the crossover of both distillation boundary XH and distillation boundary YH. Lumped material L_2 is partitioned into lumped material $L_{2.1}$ in homogeneous region YTRY; lumped material $L_{2.2}$ on curve RT which is part of LLE envelope WQSRT; and lumped material $L_{2.3}$ in region RTZHR. Lumped material L_3 is partitioned into lumped material $L_{3.1}$ in region HZWPUH; lumped material $L_{3.2}$ on curve WP which is part of LLE envelope WQSRT; lumped material $L_{3.3}$ in region QUPQ; lumped material $L_{3.4}$ on curve PQ which is part of LLE envelope WQSRT; and lumped material $L_{3.5}$, in region XQWX. Note that in contrast to the situation of distillation boundaries curves RT and WQ are not classified further because the materials on both sides of either of these curves are situated in identical regions bounded by the distillation boundaries.

Lumped material $L_{4.E}$ is partitioned into lumped material $L_{4.E.1}$ along curve XQ, which is the homogeneous part of distillation boundary XH and on the side of region EYHXE; lumped material $L_{4.E.2}$ along curve QU, which is one of the two heterogeneous parts of distillation boundary XH and on the side of region EYHXE; and lumped material $L_{4.E.3}$ along curve UH, which is another portion of the heterogeneous part of distillation boundary XH and on the side of region EYHXE. Note that lumped material $L_{4.E.2}$ splits into lumped materials $L_{3.4}$ and $L_{1.3}$ while lumped material $L_{4.E.3}$ splits into lumped materials $L_{2.2}$ and $L_{3.2}$. Similarly, lumped material $L_{4.W}$ is further partitioned into lumped materials $L_{4.W.1}$, $L_{4.W.2}$, and $L_{4.W.3}$; lumped material $L_{5.E}$, into lumped materials $L_{5.E.1}$ and $L_{5.E.2}$; and lumped material $L_{5.T}$, into lumped materials $L_{5.T.1}$ and $L_{5.T.2}$ (see Table 1). Similar to partitioning lumped material L_1, lumped material L_2 is partitioned into lumped materials $L_{2.1}$, $L_{2.2}$, and $L_{2.3}$; and lumped material L_3, into lumped materials $L_{3.1}$, $L_{3.2}$, $L_{3.3}$, $L_{3.4}$, and $L_{3.5}$ (see Figure 3).

Products E and W, entrainer T, and feed F comprise singular points of the RCM. Each of these materials possesses unique properties; therefore, each is regarded as a separate class of its own.

It is worth noting that the partitioned materials are bounded by the natural boundaries, i.e., the boundaries of the RCM, distillation boundaries, LLE envelope, and critical tie lines. In other words, the partitioning of the materials is based solely on the first principles; no heuristics is involved.

Further Partitioning of the Lumped Materials According to the Uniqueness of Intermediate Products from Separation. The materials in an area-occupying or curve-occupying subregion, indicated by a double subscript in Figure 3, may not yield a unique intermediate lumped material upon separation. For instance, besides product E, the materials in region EYRHUQXE, i.e., the region representing lumped material $L_{1.1}$, may yield intermediate lumped materials $L_{4.E.1}$, $L_{4.E.2}$, $L_{4.E.3}$, $L_{5.E.1}$, or $L_{5.E.2}$ depending on the locations or compositions of the materials. It is, therefore, deemed desirable to further partition the materials in some area-occupying subregions. As clearly discernible in Figure 4, this has been accomplished by supplying additional boundaries, i.e., the dot-dashed lines, thus giving rise to the area-occupying lumped materials, each indicated by a triple subscript, as elaborated in the succeeding paragraphs. Nevertheless, some of the nota-

Table 1. List of Lumped Materials

index	partitioned materials	area represented	no. of phases	types of operating units employed to produce it[a]
1	E	E	1	S
2	W	W	1	S
3	F	F	1	
4	T	T	1	S
5	$L_{1.1.1}$	EQXE	1	M
6	$L_{1.1.2}$	EDQE	1	M
7	$L_{1.1.3}$	EBVSDE	1	M
8	$L_{1.1.4}$	ERBE	1	M
9	$L_{1.1.5}$	EYRE	1	M
10	$L_{1.2.1}$	DGQD	1/2	D/M
11	$L_{1.2.2}$	SVBGDS	1/2	D/M
12	$L_{1.3.1}$	VB	1	D
13	$L_{1.3.2}$	BR	1	D
14	$L_{1.4.1}$	GUQG	2	M
15	$L_{1.4.2}$	VBCUGV	2	M
16	$L_{1.4.3}$	BRCB	2	M
17	$L_{1.5.1}$	UCHU	2	M
18	$L_{1.5.2}$	CRHC	2	M
19	$L_{2.1}$	YTRY	1	M
20	$L_{2.2}$	RT	1	D
21	$L_{2.3.1}$	RTR	2	M
22	$L_{2.3.2}$	RTHR	2	M
23	$L_{2.3.3}$	HTZH	2	M
24	$L_{3.1.1}$	HZWH	2	M
25	$L_{3.1.2}$	UHWU	2	M
26	$L_{3.1.3}$	AUWA	2	M
27	$L_{3.1.4}$	QAWPQ	2	M
28	$L_{3.2}$	WP	1	D
29	$L_{3.3.1}$	QAPQ	2	M
30	$L_{3.3.2}$	QUAQ	2	M
31	$L_{3.4}$	PQ	1	D
32	$L_{3.5}$	XQWX	1	M
33	$L_{4.E.1}$	XQ on EYHXE side	1	S
34	$L_{4.E.2}$	QU on EYHXE side	2	S
35	$L_{4.E.3}$	UH on EYHXE side	2	S
36	$L_{4.W.1}$	XQ on XHZWX side	1	S
37	$L_{4.W.2}$	QU on XHZWX side	2	S
38	$L_{4.W.3}$	UH on XHZWX side	2	S
39	$L_{5.E.1}$	YR on EYHXE side	1	S
40	$L_{5.E.2}$	RH on EYHXE side	2	S
41	$L_{5.T.1}$	YR on YTZHY side	1	S
42	$L_{5.T.2}$	RH on YTZHY side	2	S
43	$L_{6.T}$	HZ on YTZHY side	2	S
44	$L_{6.W}$	HZ on XHZWX side	2	S

[a] D, decantor; M, mixer; S, separator.

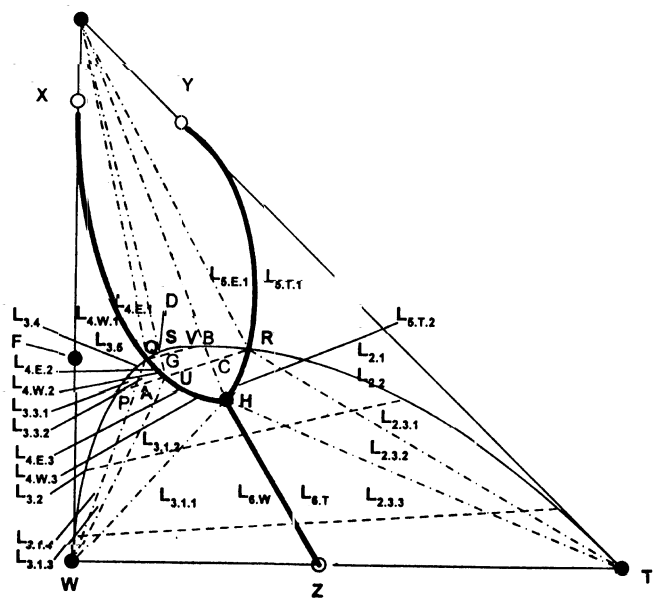

Figure 4. RCM of the ethanol (E)–water (W)–toluene (T) system illustrating the further partitioning of the lumped materials according to the intermediate products from separation.

tions representing such lumped materials, e.g., $L_{1.1.1}$, are omitted from the figure to avoid overcrowding.

Lumped material $L_{1.1}$ is partitioned into lumped material $L_{1.1.1}$ in region EQXE; lumped material $L_{1.1.2}$ in region EDQE; lumped material $L_{1.1.3}$ in region EBVSDE; lumped material $L_{1.1.4}$ in region ERBE; and lumped material $L_{1.1.5}$ in region EYRE. Lumped material $L_{1.2}$ is partitioned into lumped material $L_{1.2.1}$ in region DGQD and lumped material $L_{1.2.2}$ in region SVBGDS. Lumped material $L_{1.3}$ is partitioned into lumped material $L_{1.3.1}$ on curve VB and lumped material $L_{1.3.2}$ in curve BR. Lumped material $L_{1.4}$ is partitioned into lumped material $L_{1.4.1}$ in region GUQG, lumped material $L_{1.4.2}$ in region VBCUGV, and lumped material $L_{1.4.3}$ in region BRCB. Finally, lumped material $L_{1.5}$ is partitioned into lumped material $L_{1.5.1}$ in region UCHU and lumped material $L_{1.5.2}$ in region CRHC. The lumped materials resulting from partitioning lumped materials $L_{1.1}$ through $L_{1.5}$ are listed in Table 1. Similarly, lumped materials $L_{2.3}$, $L_{3.1}$, and $L_{3.3}$ are partitioned; the results are also listed in the same table. Note that Table 1 contains 40 lumped materials identified in the table besides the four materials, E, W, T, and F, each occupying only a single point on the RCM.

Identifying the Plausible Operating Units and Concomitant Materials

The candidate operating units will be identified along with the concomitant materials that have been lumped. In what follows, the convention of process graphs, i.e., P-graphs, is adopted for representing operating units.[16–20] In this convention, any operating unit is represented by symbol ({...}, {...}) in which the first {...} represents the set comprising all of the input material and the second {...} represents all of the output material.

Identifying the Indispensable Operating Units. The operating units necessary for producing the desired products need be identified at the outset. Generally, the products and feed for any distillation column should be in the same region created by distillation boundaries. When the extreme curvature of a distillation boundary is exploited, however, the products and feed can be in different regions, i.e., one on either side of this boundary.[15] Nevertheless, in this situation, the effectiveness of the design and operation of the identified operating unit depends strongly on the reliability of thermodynamic data; often, these data contain appreciable error. It is, therefore, advisable to avoid the situation because such error may render the design and operation impossible or extremely difficult.

In the illustration of Figure 4, the two products, ethanol (E) and water (W), are situated in regions EYHXE and XHZWX, respectively. Because each of these regions contains a portion of the heterogeneous region, phase splitting by decanting or other similar mechanical means such as liquid–liquid centrifugation appears to be viable to circumvent distillation boundaries XH, YH, and ZH including the terminal points, i.e., azeotropes X, Y, Z, and H. Probably, there is no need to exploit the appreciable curvature of distillation boundaries XH and YH. Hence, both the feed to and the intermediate product from any of operating units yielding product E must be located in region EXHYE. Similarly, both the feed to and the intermediate product from any operating unit producing water (W) must be situated in region XHZWX. These indispensable operating units are identified below in terms of the lumped materials indicated in Figure 4.

The candidate operating units for producing E are distillation columns ({$L_{1.1.1}$}, {E, $L_{4.E.1}$}); ({$L_{1.1.2}$}, {E,

$L_{4.E.2}$}); ({$L_{1.1.3}$}, {E, $L_{4.E.3}$}); ({$L_{1.1.4}$}, {E, $L_{5.E.2}$}); ({$L_{1.1.5}$}, {E, $L_{5.E.2}$}); ({$L_{1.2.1}$}, {E, $L_{4.E.2}$}); ({$L_{1.2.2}$}, {E, $L_{4.E.2}$}); ({$L_{1.3.1}$}, {E, $L_{4.E.2}$}); ({$L_{1.3.2}$}, {E, $L_{5.E.2}$}); ({$L_{1.4.1}$}, {E, $L_{4.E.2}$}); ({$L_{1.4.2}$}, {E, $L_{4.E.3}$}); ({$L_{1.4.3}$}, {E, $L_{5.E.2}$}); ({$L_{1.5.1}$}, {E, $L_{4.E.3}$}); and ({$L_{1.5.2}$}, {E, $L_{5.E.2}$}). The candidate operating units for producing W are distillation columns ({F}, {W, $L_{4.W.1}$}); ({$L_{3.1.1}$}, {W, $L_{6.W}$}); ({$L_{3.1.2}$}, {W, $L_{4.W.3}$}); ({$L_{3.1.3}$}, {W, $L_{4.W.2}$}); ({$L_{3.1.4}$}, {W, $L_{4.W.1}$}); ({$L_{3.2}$}, {W, $L_{4.W.1}$}); ({$L_{3.3.1}$}, {W, $L_{4.W.1}$}); ({$L_{3.3.2}$}, {W, $L_{4.W.2}$}); ({$L_{3.4}$}, {W, $L_{4.W.1}$}); and ({$L_{3.5}$}, {W, $L_{4.W.1}$}).

To avoid or overcome thermodynamic pinches, another class of operating units is indispensable. As indicated earlier, these operating units in terms of the lumped materials for the system are illustrated in Figure 4. They include decantors ({$L_{1.4.1}$}, {$L_{1.3.2}$, $L_{3.4}$}); ({$L_{1.4.2}$}, {$L_{1.3.2}$, $L_{3.4}$}); ({$L_{1.4.3}$}, {$L_{1.3.2}$, $L_{3.4}$}); ({$L_{4.E.2}$}, {$L_{1.3.2}$, $L_{3.4}$}); ({$L_{4.W.2}$}, {$L_{1.3.2}$, $L_{3.4}$}); ({$L_{3.3.1}$}, {$L_{1.3.2}$, $L_{3.4}$}); ({$L_{3.3.2}$}, {$L_{1.3.2}$, $L_{3.4}$}); ({$L_{1.5.1}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{1.5.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{4.E.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{4.W.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{5.E.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{5.T.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{2.3.1}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{2.3.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{2.3.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{3.1.1}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{3.1.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{3.1.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{3.1.4}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{6.W}$}, {$L_{2.2}$, $L_{3.2}$}); and ({$L_{6.T}$}, {$L_{2.2}$, $L_{3.2}$}). Naturally, these operating units can be substituted with similar operating units, such as those for performing facilitated decanting by liquid–liquid centrifugation, whenever deemed practical.

The present method is predicated on the two assumptions often imposed explicitly or implicitly in dealing with azeotropic distillation.[14,21] One is that the maximum degree of separation is attained by any distillation column containing an infinite number of trays under the conditions of total reflux, and the other is that each distillation column yields the two products, distillate and residue. As a result, the materials or lumped materials on the RCM representing the two products from any distillation column must be located infinitesimally close to either a distillation boundary, including the concomitant terminal points, or a boundary of the phase diagram, including the two terminal points representing the corresponding two pure components. An example is operating unit ({$L_{1.1.1}$}, {E, $L_{4.E.1}$}) in Figure 4, which is a distillation column.

The two assumptions on which the present method is based significantly reduce the complexity of system representation. With these assumptions, the intermediate product from any distillation column producing ethanol (E) is $L_{4.E.1}$, $L_{4.E.2}$, $L_{4.E.3}$, $L_{5.E.1}$, or $L_{5.E.2}$. Similarly, the intermediate product resulting from any distillation column producing water (W) is $L_{4.W.1}$, $L_{4.W.2}$, $L_{4.W.3}$, or $L_{6.W}$.

Identifying the Operating Units for Generating the Feeds to the Indispensable Operating Units Selected. The feed to and the products from a distillation column must be in the same region created by distillation boundaries. Any material located in a region containing a product, therefore, can be fed into the corresponding indispensable operating unit yielding the product. Naturally, the raw material or any intermediate product from an indispensable operating unit can be such a feed provided that it is located in a region of the RCM containing one of the products.

Mixing and decanting are the principal means for producing the feeds for indispensable operating units because one or more products may be located in a region segregated by distillation boundaries, in which no raw material or feed to the entire process, i.e., feed F, is situated. An example is product E in region EYHXY. In what follows, any lumped material representing an area cannot be the feed to any mixer, which, in turn, produces the feed to an indispensable operating unit becauase such a lumped material itself can only be generated by one or more mixers. In other words, only the feed and the lumped materials representing the curves and lines are fed into the mixers producing the feeds to the indispensable operating units. In addition, dividers are needed when a material stream is fed into more than one operating unit.

The materials capable of serving as the feeds to candidate operating units yielding product E are lumped materials $L_{1.1.1}$, $L_{1.1.2}$, $L_{1.1.3}$, $L_{1.1.4}$, $L_{1.1.5}$, $L_{1.2.1}$, $L_{1.2.2}$, $L_{1.3.1}$, $L_{1.3.2}$, $L_{1.4.1}$, $L_{1.4.2}$, $L_{1.4.3}$, $L_{1.5.1}$, and $L_{1.5.2}$. Naturally, these lumped materials can be generated by the operating units performing physical processes, i.e., mixers and decantors; these materials are described in the succeeding paragraphs.

Lumped material $L_{1.1.1}$ can be produced by mixers ({F, $L_{5.T.1}$}, {$L_{1.1.1}$}); ({$L_{4.W.1}$, T}, {$L_{1.1.1}$}); ({$L_{4.W.1}$, $L_{5.T.1}$}, {$L_{1.1.1}$}); ({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.1.1}$}); ({$L_{3.2}$, $L_{5.T.1}$}, {$L_{1.1.1}$}); and ({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.1}$}) as listed in Table 2. Similar to lumped materials $L_{1.1.1}$, lumped materials $L_{1.1.2}$, $L_{1.1.3}$, $L_{1.1.4}$, $L_{1.1.5}$, $L_{1.2.1}$, $L_{1.2.2}$, $L_{1.4.1}$, $L_{1.4.2}$, $L_{1.4.3}$, $L_{1.5.1}$, and $L_{1.5.2}$ can be produced by the mixers as given in the same table.

Lumped material $L_{1.3.1}$ can be created by decantors ({$L_{1.4.1}$}, {$L_{3.4}$, $L_{1.3.1}$}) and ({$L_{1.4.2}$}, {$L_{3.4}$, $L_{1.3.1}$}). Lumped material $L_{1.3.2}$ can be created by decantors ({$L_{1.4.1}$}, {$L_{3.4}$, $L_{1.3.2}$}); ({$L_{1.4.2}$}, {$L_{3.4}$, $L_{1.3.2}$}); and ({$L_{1.4.3}$}, {$L_{3.4}$, $L_{1.3.2}$}).

While the mixers and decantors for generating the feeds to candidate operating units yielding product E can be readily identified according to the lever rule as demonstrated in the preceding paragraphs, some of them may not function if the materials in certain regions of the RCM serve as the feeds. For example, mixer ({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.3}$}) is invalid if the material at point Q or in its vicinity and that at point T or in its vicinity are selected for $L_{4.W.1}$ and $L_{2.2}$, respectively, because the mixing will not lead to any material located in the region represented by lumped material $L_{1.1.3}$. Thus, iterative fine-tuning by means of the lever rule may be required after the initial synthesis as will be elaborated later.

The materials capable of serving as the feeds to candidate operating units generating product W are material F, i.e., the raw material, and lumped materials $L_{3.1.1}$, $L_{3.1.2}$, $L_{3.1.3}$, $L_{3.1.4}$, $L_{3.2}$, $L_{3.3.1}$, $L_{3.3.2}$, $L_{3.4}$, and $L_{3.5}$. Naturally, these lumped materials can also be generated by the operating units performing physical processes, i.e., mixers and decantors, described in the succeeding paragraphs.

Lumped material $L_{3.1.1}$ can be produced by mixer ({F, $L_{6.T}$}, {$L_{3.1.1}$}); ({$L_{4.E.1}$, $L_{6.T}$}, {$L_{3.1.1}$}); ({$L_{4.E.2}$, $L_{6.T}$}, {$L_{3.1.1}$}); and ({$L_{4.E.3}$, $L_{6.T}$}, {$L_{3.1.1}$}) as listed in Table 2. Similar to lumped material $L_{3.1.1}$, lumped materials $L_{3.1.2}$, $L_{3.1.3}$, $L_{3.1.4}$, $L_{3.3.1}$, $L_{3.3.4}$, and $L_{3.5}$ can be generated by the mixers as given in the same table.

Lumped material $L_{3.2}$ can be formed by decantors ({$L_{1.5.1}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{1.5.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{4.E.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{4.W.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{5.E.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{5.T.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{2.3.1}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{2.3.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{2.3.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{3.1.1}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{3.1.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{3.1.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{3.1.4}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{6.W}$}, {$L_{2.2}$, $L_{3.2}$}); and ({$L_{6.T}$}, {$L_{2.2}$, $L_{3.2}$}) as listed in Table

Table 2. List of Plausible Operating Units

index	operating unit	type	index	operating unit	type
1	({$L_{1.1.1}$}, {E, $L_{4.E.1}$})	distillation column	76	({F, $L_{5.T.1}$}, {$L_{1.1.3}$})	mixer
2	({$L_{1.1.2}$}, {E, $L_{4.E.2}$})	distillation column	77	({$L_{4.W.1}$, $L_{5.T.1}$}, {$L_{1.1.3}$})	mixer
3	({$L_{1.1.3}$}, {E, $L_{4.E.3}$})	distillation column	78	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.1.3}$})	mixer
4	({$L_{1.1.4}$}, {E, $L_{5.E.2}$})	distillation column	79	({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.3}$})	mixer
5	({$L_{1.1.5}$}, {E, $L_{5.E.1}$})	distillation column	80	({$L_{4.W.1}$, T}, {$L_{1.1.3}$})	mixer
6	({$L_{1.2.1}$}, {E, $L_{4.E.2}$})	distillation column	81	({$L_{4.W.2}$, $L_{5.T.1}$}, {$L_{1.1.3}$})	mixer
7	({$L_{1.2.2}$}, {E, $L_{4.E.3}$})	distillation column	82	({$L_{3.2}$, $L_{5.T.1}$}, {$L_{1.1.3}$})	mixer
8	({$L_{1.3.1}$}, {E, $L_{4.E.3}$})	distillation column	83	({$L_{3.4}$, $L_{5.T.1}$}, {$L_{1.1.3}$})	mixer
9	({$L_{1.3.2}$}, {E, $L_{5.E.2}$})	distillation column	84	({F, $L_{5.T.1}$}, {$L_{1.1.4}$})	mixer
10	({$L_{1.4.1}$}, {E, $L_{4.E.2}$})	distillation column	85	({$L_{4.W.1}$, T}, {$L_{1.1.4}$})	mixer
11	({$L_{1.4.2}$}, {E, $L_{4.E.3}$})	distillation column	86	({$L_{4.W.1}$, $L_{5.T.1}$}, {$L_{1.1.4}$})	mixer
12	({$L_{1.4.3}$}, {E, $L_{5.E.2}$})	distillation column	87	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.1.4}$})	mixer
13	({$L_{1.5.1}$}, {E, $L_{4.E.3}$})	distillation column	88	({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.4}$})	mixer
14	({$L_{1.5.2}$}, {E, $L_{5.E.2}$})	distillation column	89	({$L_{4.W.2}$, $L_{5.T.1}$}, {$L_{1.1.4}$})	mixer
15	({F}, {W, $L_{4.W.1}$})	distillation column	90	({$L_{4.W.3}$, $L_{5.T.1}$}, {$L_{1.1.4}$})	mixer
16	({$L_{3.1.1}$}, {W, $L_{6.W}$})	distillation column	91	({$L_{3.2}$, $L_{5.T.1}$}, {$L_{1.1.4}$})	mixer
17	({$L_{3.1.2}$}, {W, $L_{4.W.3}$})	distillation column	92	({$L_{3.4}$, $L_{5.T.1}$}, {$L_{1.1.4}$})	mixer
18	({$L_{3.1.3}$}, {W, $L_{4.W.2}$})	distillation column	93	({F, $L_{5.T.1}$}, {$L_{1.1.5}$})	mixer
19	({$L_{3.1.4}$}, {W, $L_{4.W.1}$})	distillation column	94	({$L_{4.W.1}$, $L_{5.T.1}$}, {$L_{1.1.5}$})	mixer
20	({$L_{3.2}$}, {W, $L_{4.W.1}$})	distillation column	95	({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.5}$})	mixer
21	({$L_{3.3.1}$}, {W, $L_{4.W.1}$})	distillation column	96	({$L_{4.W.1}$, T}, {$L_{1.1.5}$})	mixer
22	({$L_{3.3.2}$}, {W, $L_{4.W.2}$})	distillation column	97	({$L_{4.W.2}$, T}, {$L_{1.1.5}$})	mixer
23	({$L_{3.4}$}, {W, $L_{4.W.1}$})	distillation column	98	({$L_{4.W.3}$, T}, {$L_{1.1.5}$})	mixer
24	({$L_{3.5}$}, {W, $L_{4.W.1}$})	distillation column	99	({$L_{3.2}$, $L_{5.T.1}$}, {$L_{1.1.5}$})	mixer
25	({$L_{2.1}$}, {T, $L_{5.T.1}$})	distillation column	100	({$L_{3.4}$, $L_{5.T.1}$}, {$L_{1.1.5}$})	mixer
26	({$L_{2.2}$}, {T, $L_{5.T.1}$})	distillation column	101	({$L_{4.W.2}$, $L_{5.T.1}$}, {$L_{1.2.1}$})	mixer
27	({$L_{2.3.1}$}, {T, $L_{5.T.1}$})	distillation column	102	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.2.1}$})	mixer
28	({$L_{2.3.2}$}, {T, $L_{5.T.2}$})	distillation column	103	({$L_{4.W.2}$, $L_{5.T.1}$}, {$L_{1.2.2}$})	mixer
29	({$L_{2.3.3}$}, {T, $L_{6.T}$})	distillation column	104	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.2.2}$})	mixer
30	({$L_{1.4.1}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	105	({F, $L_{5.T.2}$}, {$L_{1.4.1}$})	mixer
31	({$L_{1.4.1}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	106	({$L_{4.W.2}$, $L_{5.T.1}$}, {$L_{1.4.1}$})	mixer
32	({$L_{1.4.2}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	107	({$L_{4.W.2}$, $L_{5.T.2}$}, {$L_{1.4.1}$})	mixer
33	({$L_{1.4.2}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	108	({F, $L_{5.T.2}$}, {$L_{1.4.2}$})	mixer
34	({$L_{1.4.3}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	109	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.4.2}$})	mixer
35	({$L_{1.4.3}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	110	({$L_{4.W.2}$, $L_{5.T.1}$}, {$L_{1.4.2}$})	mixer
36	({$L_{1.5.1}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	111	({$L_{4.W.2}$, $L_{5.T.2}$}, {$L_{1.4.2}$})	mixer
37	({$L_{1.5.2}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	112	({$L_{4.W.3}$, $L_{5.T.1}$}, {$L_{1.4.2}$})	mixer
38	({$L_{4.E.2}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	113	({F, $L_{5.T.2}$}, {$L_{1.4.3}$})	mixer
39	({$L_{4.E.2}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	114	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.4.3}$})	mixer
40	({$L_{4.W.2}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	115	({$L_{4.W.2}$, $L_{5.T.1}$}, {$L_{1.4.3}$})	mixer
41	({$L_{4.W.2}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	116	({$L_{4.W.2}$, $L_{5.T.2}$}, {$L_{1.4.3}$})	mixer
42	({$L_{2.3.1}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	117	({$L_{4.W.3}$, $L_{5.T.1}$}, {$L_{1.4.3}$})	mixer
43	({$L_{2.3.2}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	118	({F, $L_{5.T.2}$}, {$L_{1.5.1}$})	mixer
44	({$L_{2.3.3}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	119	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.5.1}$})	mixer
45	({$L_{3.1.1}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	120	({$L_{4.W.2}$, $L_{5.T.2}$}, {$L_{1.5.1}$})	mixer
46	({$L_{3.1.2}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	121	({$L_{4.W.3}$, $L_{5.T.1}$}, {$L_{1.5.1}$})	mixer
47	({$L_{3.1.3}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	122	({$L_{4.W.3}$, $L_{5.T.2}$}, {$L_{1.5.1}$})	mixer
48	({$L_{3.1.4}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	123	({$L_{4.W.3}$, $L_{2.2}$}, {$L_{1.5.1}$})	mixer
49	({$L_{3.3.1}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	124	({$L_{3.2}$, $L_{5.T.2}$}, {$L_{1.5.1}$})	mixer
50	({$L_{3.3.1}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	125	({F, $L_{5.T.2}$}, {$L_{1.5.2}$})	mixer
51	({$L_{3.3.2}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	126	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.5.2}$})	mixer
52	({$L_{3.3.2}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	127	({$L_{4.W.2}$, $L_{5.T.2}$}, {$L_{1.5.2}$})	mixer
53	({$L_{4.E.2}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	128	({$L_{4.W.3}$, $L_{5.T.1}$}, {$L_{1.5.2}$})	mixer
54	({$L_{4.E.2}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	129	({$L_{4.W.3}$, $L_{5.T.2}$}, {$L_{1.5.2}$})	mixer
55	({$L_{4.W.2}$}, {$L_{3.4}$, $L_{1.3.1}$})	decantor	130	({$L_{4.W.3}$, $L_{2.2}$}, {$L_{1.5.2}$})	mixer
56	({$L_{4.W.2}$}, {$L_{3.4}$, $L_{1.3.2}$})	decantor	131	({$L_{3.2}$, $L_{5.T.2}$}, {$L_{1.5.2}$})	mixer
57	({$L_{4.E.3}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	132	({F, $L_{5.T.2}$}, {$L_{1.5.2}$})	mixer
58	({$L_{4.W.3}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	133	({F, $L_{6.T}$}, {$L_{3.1.1}$})	mixer
59	({$L_{5.E.2}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	134	({$L_{4.E.1}$, $L_{6.T}$}, {$L_{3.1.1}$})	mixer
60	({$L_{5.T.2}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	135	({$L_{4.E.2}$, $L_{6.T}$}, {$L_{3.1.1}$})	mixer
61	({$L_{6.T}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	136	({$L_{4.E.3}$, $L_{6.T}$}, {$L_{3.1.1}$})	mixer
62	({$L_{6.W}$}, {$L_{2.2}$, $L_{3.2}$})	decantor	137	({F, $L_{6.T}$}, {$L_{3.1.2}$})	mixer
63	({F, $L_{5.T.1}$}, {$L_{1.1.1}$})	mixer	138	({$L_{4.E.1}$, $L_{6.T}$}, {$L_{3.1.2}$})	mixer
64	({$L_{4.W.1}$, $L_{5.T.1}$}, {$L_{1.1.1}$})	mixer	139	({$L_{4.E.2}$, $L_{6.T}$}, {$L_{3.1.2}$})	mixer
65	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.1.1}$})	mixer	140	({$L_{4.E.3}$, $L_{6.T}$}, {$L_{3.1.2}$})	mixer
66	({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.1}$})	mixer	141	({F, T}, {$L_{3.1.3}$})	mixer
67	({$L_{4.W.1}$, T}, {$L_{1.1.1}$})	mixer	142	({F, $L_{6.T}$}, {$L_{3.1.3}$})	mixer
68	({$L_{3.2}$, $L_{5.T.1}$}, {$L_{1.1.1}$})	mixer	143	({$L_{4.E.1}$, $L_{6.T}$}, {$L_{3.1.3}$})	mixer
69	({F, $L_{5.T.1}$}, {$L_{1.1.2}$})	mixer	144	({$L_{4.E.2}$, $L_{6.T}$}, {$L_{3.1.3}$})	mixer
70	({$L_{4.W.1}$, $L_{5.T.1}$}, {$L_{1.1.2}$})	mixer	145	({F, T}, {$L_{3.1.4}$})	mixer
71	({$L_{4.W.1}$, $L_{5.T.2}$}, {$L_{1.1.2}$})	mixer	146	({F, $L_{6.T}$}, {$L_{3.1.4}$})	mixer
72	({$L_{3.2}$, $L_{5.T.1}$}, {$L_{1.1.2}$})	mixer	147	({F, $L_{4.E.2}$}, {$L_{3.3.1}$})	mixer
73	({$L_{3.4}$, $L_{5.T.1}$}, {$L_{1.1.2}$})	mixer	148	({F, $L_{4.E.2}$}, {$L_{3.3.2}$})	mixer
74	({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.2}$})	mixer	149	({F, $L_{4.E.1}$}, {$L_{3.5}$})	mixer
75	({$L_{4.W.1}$, T}, {$L_{1.1.2}$})	mixer	150	({F, $L_{4.E.2}$}, {$L_{3.5}$})	mixer

Table 2 (Continued)

index	operating unit	type	index	operating unit	type
151	({F, $L_{4.E.4}$}, {$L_{3.5}$})	mixer	167	({$L_{4.W.3}$, $L_{2.2}$}, {$L_{2.3.1}$})	mixer
152	({F, $L_{5.E.1}$}, {$L_{3.5}$})	mixer	168	({$L_{4.E.3}$, $L_{2.2}$}, {$L_{2.3.1}$})	mixer
153	({F, $L_{5.E.2}$}, {$L_{3.5}$})	mixer	169	({$L_{6.W}$, $L_{2.2}$}, {$L_{2.3.1}$})	mixer
154	({F, $L_{5.T.1}$}, {$L_{3.5}$})	mixer	170	({F, $L_{2.2}$}, {$L_{2.3.2}$})	mixer
155	({F, $L_{5.T.2}$}, {$L_{3.5}$})	mixer	171	({$L_{4.W.1}$, $L_{2.2}$}, {$L_{2.3.2}$})	mixer
156	({F, $L_{2.2}$}, {$L_{3.5}$})	mixer	172	({$L_{4.E.1}$, $L_{2.2}$}, {$L_{2.3.2}$})	mixer
157	({F, T}, {$L_{3.5}$})	mixer	173	({$L_{4.W.2}$, $L_{2.2}$}, {$L_{2.3.2}$})	mixer
158	({F, $L_{6.T}$}, {$L_{3.5}$})	mixer	174	({$L_{4.E.2}$, $L_{2.2}$}, {$L_{2.3.2}$})	mixer
159	({$L_{4.W.1}$, $L_{2.2}$}, {$L_{2.1}$})	mixer	175	({$L_{4.W.3}$, $L_{2.2}$}, {$L_{2.3.2}$})	mixer
160	({$L_{4.E.1}$, $L_{2.2}$}, {$L_{2.1}$})	mixer	176	({$L_{4.E.3}$, $L_{2.2}$}, {$L_{2.3.2}$})	mixer
161	({$L_{5.E.1}$, $L_{2.2}$}, {$L_{2.1}$})	mixer	177	({$L_{6.W}$, $L_{2.2}$}, {$L_{2.3.2}$})	mixer
162	({F, $L_{2.2}$}, {$L_{2.3.1}$})	mixer	178	({$L_{5.E.1}$, $L_{6.W}$}, {$L_{2.3.2}$})	mixer
163	({$L_{4.W.1}$, $L_{2.2}$}, {$L_{2.3.1}$})	mixer	179	({$L_{5.E.2}$, $L_{6.W}$}, {$L_{2.3.2}$})	mixer
164	({$L_{4.E.1}$, $L_{2.2}$}, {$L_{2.3.1}$})	mixer	180	({$L_{6.W}$, $L_{2.2}$}, {$L_{2.3.3}$})	mixer
165	({$L_{4.W.2}$, $L_{2.2}$}, {$L_{2.3.1}$})	mixer	181	({$L_{5.E.1}$, $L_{6.W}$}, {$L_{2.3.3}$})	mixer
166	({$L_{4.E.2}$, $L_{2.2}$}, {$L_{2.3.1}$})	mixer	182	({$L_{5.E.2}$, $L_{6.W}$}, {$L_{2.3.3}$})	mixer

2. Similar to lumped material $L_{3.2}$, lumped material $L_{3.4}$ can be generated by the decantors as given in the same table.

Note that any lumped material along a distillation boundary and located in the same region as the intermediate material to be produced cannot be fed into any mixer generating the intermediate material. An example is lumped material $L_{6.W}$, which should not be fed to any mixer generating intermediate lumped materials $L_{3.1.1}$, $L_{3.1.2}$, $L_{3.1.3}$, $L_{3.1.4}$, $L_{3.2}$, $L_{3.3.1}$, $L_{3.3.2}$, $L_{3.4}$, or $L_{3.5}$.

Identifying Other Candidate Operating Units Facilitating Separation. Usually, the pure entrainer is recycled in a feasible sequence or flowsheet. Thus, any operating unit capable of regenerating the entrainer should not be ignored. Naturally, every feed to such an operating unit must be located in the region of the RCM created by distillation boundaries, which contains entrainer T; the intermediate product from an indispensable operating unit can be such a feed. As illustrated in Figure 4, the operating units, specifically distillation columns, that can regenerate entrainer T are ({$L_{2.1}$}, {$L_{5.T.1}$, T}); ({$L_{2.2}$}, {$L_{5.T.1}$, T}); ({$L_{2.3.1}$}, {$L_{5.T.1}$, T}); ({$L_{2.3.2}$}, {$L_{5.T.2}$, T}); and ({$L_{2.3.3}$}, {$L_{6.T}$, T}). In other words, lumped materials $L_{2.1}$, $L_{2.2}$, $L_{2.3.1}$, $L_{2.3.2}$, and $L_{2.3.3}$ are needed as the intermediate materials to be fed into these distillation columns.

Lumped intermediate material $L_{2.1}$ can be produced by mixers ({$L_{4.W.1}$, $L_{2.2}$}, {$L_{2.1}$}); ({$L_{4.E.1}$, $L_{2.2}$}, {$L_{2.1}$}); and ({$L_{5.E.1}$, $L_{2.2}$}, {$L_{2.1}$}) as listed in Table 2. Similar to intermediate lumped material $L_{2.1}$, intermediate lumped material $L_{2.3.1}$, $L_{2.3.2}$, and $L_{2.3.3}$ can be produced by the mixers as listed in the same table. In contrast, intermediate lumped material $L_{2.2}$ can be produced by decantors ({$L_{4.W.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{4.E.3}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{5.E.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{5.T.2}$}, {$L_{2.2}$, $L_{3.2}$}); ({$L_{6.W}$}, {$L_{2.2}$, $L_{3.2}$}); and ({$L_{6.T}$}, {$L_{2.2}$, $L_{3.2}$}) listed in the same table.

The proposed method for classifying the materials and identifying the operating units appears to be concocted and complicated. In reality, however, the method is highly systematic and logical, the results of which can be presented in compact tabular form to facilitate its application; see Tables 1 and 2.

Application

Obviously, the present method is applicable to the flowsheeting or synthesis of azeotropic distillation or similar processes in conjunction with a conventional method heavily guided by heuristics. Such a method can often be effective at least in generating some feasible flowsheets. A set of simple, ordered heuristics is developed here to demonstrate the application.

Simple, Ordered Heuristics for Synthesis. This set of simple, ordered heuristics consists of the following rules arranged sequentially.

1. Select the operating units from which all of the desired products can be generated.

2. Select the operating units yielding the intermediate materials which are to be fed into the operating units generating the desired products.

3. Select recursively the operating units generating all other intermediate

materials serving as the feeds to the operating units already selected until at

least one designated feed is consumed and no unacceptable byproducts are

generated.

If any of the heuristic rules is inapplicable or of trivial consequence, the succeeding one is activated.

Heuristic rule 1 indicates that the procedure is backward in nature; specifically, it is initiated at the products and proceeds backward. As in dynamic programming, this approach should be substantially more efficient than those starting from raw materials and proceeding forward for the synthesis problems with the desired products known or specified a priori. Otherwise, a forward procedure starting from the raw materials, e.g., the state-space method, should be employed.[21,22] For instance, this situation arises in composing the flowsheets of a process to recover chemicals from waste streams.

Heuristic rule 2 renders possible to proceed backward one additional step in the synthesis. This is naturally advantageous.

Heuristic rule 3 is valid: logically, at least one raw material needs be totally consumed to produce the designated products. In addition, the generation of byproducts is not permitted and, therefore, synthesis should proceed until no unacceptable byproduct is produced.

Generation of Feasible Flowsheets. The proposed method is demonstrated with a well-established process, i.e., pure ethanol production from its aqueous solution via azeotropic distillation; the two products to be produced are ethanol (E) and water (W).[23,24] For illustration, the composition of the feed is fixed at 37% ethanol on the molar basis in this example; see Figure 1. The three ordered heuristic rules are applied sequentially as follows:

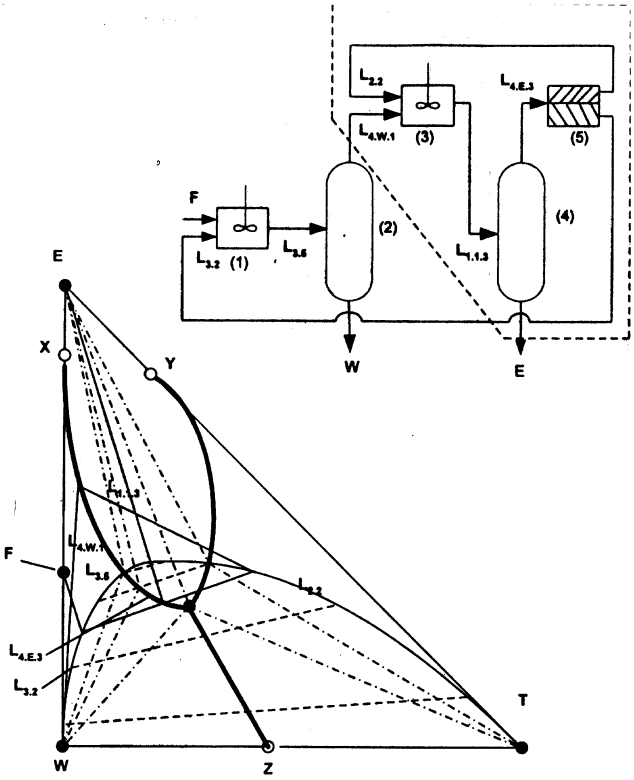

Figure 5. RCM of the ethanol (E)–water (W)–toluene (T) system to generate the flowsheet for the example: (1) mixer; (2) distillation column; (3) mixer; (4) distillation column; (5) decantor.

1. Heuristic rule 1 leads to the selection of distillation column ({$L_{1.1.3}$}, {E, $L_{4.E.3}$}) yielding product E, i.e., ethanol, and distillation column ({$L_{3.5}$}, {W, $L_{4.W.1}$}) yielding product W, i.e., water.

2. Heuristic rule 2 leads to the selection of mixer ({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.3}$}) for producing intermediate material $L_{1.1.3}$ fed into distillation column ({$L_{1.1.3}$}, {E, $L_{4.E.3}$}) selected by applying heuristic rule 1, and mixer ({F, $L_{3.2}$}, {$L_{3.5}$}) for producing intermediate material $L_{3.5}$ fed into distillation column ({$L_{3.5}$}, {W, $L_{4.W.1}$}) selected by applying heuristic rule 1.

3. Heuristic rule 3 leads to the selection of decantor ({$L_{4.E.3}$}; {$L_{2.2}$, $L_{3.2}$}) generating intermediate material $L_{2.2}$ fed to mixer ({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.3}$}) selected by applying heuristic rule 2. The decantor selected also yields intermediate material $L_{3.2}$ fed to mixer ({F, $L_{3.2}$}, {$L_{3.5}$}) selected by applying heuristic rule 2. Intermediate material $L_{4.W.1}$ has already been generated by distillation column ({$L_{3.5}$}, {W, $L_{4.W.1}$}) selected by applying heuristic rule 1. In addition, feed F is consumed by mixer ({F, $L_{3.2}$}, {$L_{3.5}$}) selected by applying heuristic rule 2.

Th resultant feasible flowsheet is illustrated in Figure 5. It comprises distillation columns ({$L_{1.1.3}$}, {E, $L_{4.E.3}$}) and ({$L_{3.5}$}, {W, $L_{4.W.1}$}), mixers ({$L_{4.W.1}$, $L_{2.2}$}, {$L_{1.1.3}$}) and ({F, $L_{3.2}$}, {$L_{3.5}$}), and decantor ({$L_{4.E.3}$}, {$L_{2.2}$, $L_{3.2}$}).

Similarly, other feasible flowsheets are readily identified; two of them are summarized below.

Flowsheet 2, as illustrated in Figure 6, comprises distillation columns ({$L_{1.1.3}$}, {E, $L_{4.E.3}$}), ({$L_{3.5}$}, {W, $L_{4.W.1}$}), and ({$L_{2.2}$}, {$L_{5.T.1}$, T}), mixers ({$L_{4.W.1}$, T}, {$L_{1.1.3}$}), ({F, $L_{3.2}$}, {$L_{3.5}$}), and ({$L_{4.W.1}$, $L_{5.T.1}$}, {$L_{1.1.3}$}), and decantor ({$L_{4.E.3}$}, {$L_{2.2}$, $L_{3.2}$}).

Flowsheet 3, as illustrated in Figure 7, comprises distillation columns ({$L_{1.1.3}$}, {E, $L_{4.E.3}$}), ({$L_{3.2}$}, {W, $L_{4.W.1}$}), and ({$L_{2.2}$}, {$L_{5.T.1}$, T}), mixers ({F, T}, {$L_{3.1.2}$})

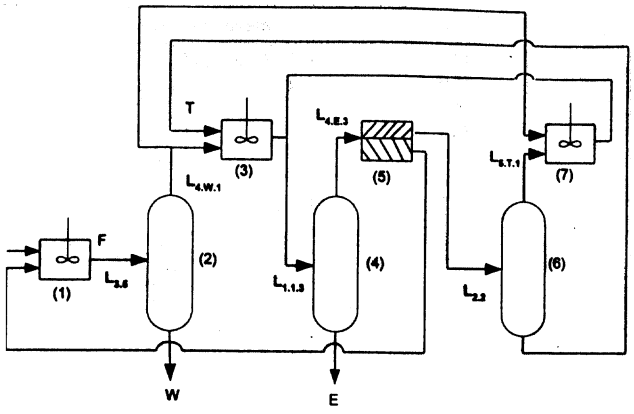

Figure 6. Flowsheet 2 for the ethanol (E)–water (W)–toluene T) system: (1) mixer; (2) distillation column; (3) mixer; (4) listillation column; (5) decantor; (6) distillation column; (7) mixer.

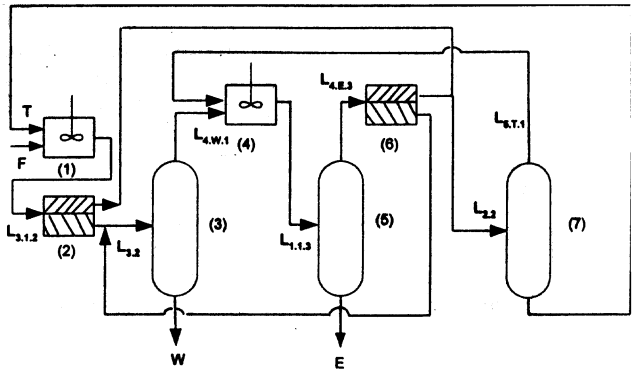

Figure 7. Flowsheet 3 for the ethanol (E)–water (W)–toluene (T) system: (1) mixer; (2) decantor; (3) distillation column; (4) mixer; (5) distillation column; (6) decantor; (7) distillation column.

and ({$L_{4.W.1}$, $L_{5.T.1}$}, {$L_{1.1.3}$}), and decantors ({$L_{4.E.3}$}, {$L_{2.2}$, $L_{3.2}$}) and ({$L_{3.1.2}$}, {$L_{2.2}$, $L_{3.2}$}).

Note that for a flowsheet to be indeed feasible mass balance must be satisfied around every loop in it. An example of such a loop is indicated in Figure 5; it is encircled by the dashed line. Graphically, the input material, lumped material $L_{4.W.1}$, and the output materials, lumped materials E and $L_{3.2}$, must be on a single straight line.

It is worth noting that the mixers in flowsheets 1–3 are simply for conceptual illustration. In practice, these mixers can be eliminated; instead, the two feeds can be directly fed into the succeeding distillation column. In general, processing equipment and piping networks linking them embody the functions of mixing or division to achieve the appropriate extent of homogenization or segregation.

Discussion

The method established in the current work to identify and select operating units for the design and synthesis of azeotropic-distillation systems appears to be inordinately complex, because it generates a multitude of such units. Nevertheless, an efficient and user-friendly table-look-up or computer-aided procedure can be developed because the method is immensely systematic and logically structured. In addition, heuristics can be easily introduced to eliminate certain candidate but undesirable operating units.

Naturally, the proposed method can be used in conjunction with a conventional or heuristic-based

process flowsheeting, i.e., process synthesis, by partially adopting the vast number of operating units identified. In fact, a set of simple, ordered heuristics has specifically been proposed here for generating or synthesizing feasible sequences on the basis of the candidate operating units identified. A robust and effective algorithmic approach for sequencing or synthesizing, however, is required to take full advantage of the method; such an approach is indeed available.[16-20]

The method is illustrated in detail with the well-known process of production of pure ethanol from its aqueous solution by azeotropic distillation; the process possesses traits, such as the existence of distillation boundaries, the formation of azeotropes, of a complex process involving phase transition and/or phase separation. The method, therefore, is capable of being part of designs and syntheses of various other complex processes. Examples are extraction, crystallization, extractive distillation, extractive crystallization, reactive distillation, extractive reaction, and reactive crystallization. The production of butanol and other chemicals from the broth of corn fermentation[25-29] and the extractive crystallization separation of the mixture of *p*-, *m*-, and *o*-xylene with butane as the solvent[30] involves one or more of these complex processes.

It is worth noting that certain types of complex operating units, e.g., those adopting products as entrainers for azeotropic distillation and/or mixers with three or more feeds,[31] can be highly useful in certain circumstances. For simplicity, such operating units are not taken into account in this work; they can be readily incorporated into the system according to the proposed approach.

The proposed methodology is applicable to a system with four or more components although it is illustrated in this work with a system having three components. The graphical representation of a system with five or more components, however, would be extremely convoluted even if it is possible. Fortunately, the mathematical expressions of the boundaries, either curved or linear, on the RCM can be rigorously derived by resorting to analytical geometry regardless of the dimension of the RCM; consequently, any lumped material can be analytically represented independent of the number of components in it. In addition, the governing equations of the operating units involved, i.e., the separators, mixers, and decantors, are linear because every equation satisfies the lever rule. What is described hitherto renders it possible to exhaustively generate algorithmically lumped materials, operating units, and eventually feasible flowsheets satisfying various constraints, e.g., mass balance, which will be the subject of a sequel to the current work.

Concluding Remarks

An immensely effective method has been established to identify processing or operating units necessary for the design or synthesis of azeotropic-distillation systems. The efficacy of this method has been amply demonstrated by generating flowsheets of the process for azeotropic distillation of pure ethanol from its aqueous solution. The method can be readily extended to complex processes involving phase transition and/or phase separation. The method also possesses great potential to become an integral part of any conventional or heuristic flowsheeting. Nevertheless, its full potential can probably be realized only when applied in conjunction with a robust algorithmic approach to process design and flowsheeting, i.e., process synthesis.

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