Graph-Theoretic Method for the Algorithmic Synthesis of Azeotropic-Distillation Systems

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A highly effective algorithmic method is proposed for optimally synthesizing an azeotropic-distillation system from an extensive set of candidate operating units, i.e., functional units. The method has been derived by resorting to the graph-theoretic approach to process-network synthesis based on process graphs (P-graphs); it also resorts to the methodology established in our previous contribution for dividing the residue curve map (RCM) of a material system, i.e., mixture, to be separated into partitioned materials. This allows the entire space of the RCM to be taken into account in composing networks of candidate operating units, thereby preventing the localization of search. Moreover, the RCM is transformed into the flow-rate map, where any material is quantitatively defined by the molar flow rates of its components instead of the concentrations as in the RCM. This renders it possible to eliminate the nonlinearity in the governing equations of the candidate operating units. The efficacy of the method is amply demonstrated through the well-known example of separating ethanol from its aqueous solution with toluene as the entrainer. The method is applicable to other complex processes with phase transition, and/or phase separation, e.g., crystallization, extraction, reactive distillation, and their combinations.

Introduction

The current contribution is concerned with the optimal synthesis of azeotropic-distillation systems. Specifically, it aims at developing an algorithmic and systematic method for synthesizing an azeotropic-distillation system from an extensive set of candidate operating, i.e., functional, units. It is a sequel to our contribution in this journal, in which a methodology is proposed for identifying plausible operating units for either algorithmic or heuristic synthesis.[1]

Analyzing an azeotropic-distillation system is exceedingly difficult because of its severe nonlinearity. This complexity is profoundly compounded in design, i.e., synthesis, by the combinatorial complexity involved. The majority of existing azeotropic-distillation processes have been developed and designed through heuristic methods: relatively little was known about the fundamental aspects of such processes until approximately 2 decades ago. Since then, rapid progress has been made on the analyses of azeotropic-distillation systems.[2−9] The majority of the available approaches, often termed analysis-driven syntheses, are essentially based on the first principles and/or heuristic rules derived from analyzing the residue curve map (RCM) of the system of interest.[3−8] For instance, the method proposed by Malone and Doherty[3] comprises a series of steps derived from a comprehensive set of rules or heuristics. These methods have been widely adopted in industry and have led to significant improvement in various processes involving azeotropic-distillation systems. The analysis-driven or heuristic methods are applicable to both homogeneous and heterogeneous systems. The algorithmic syntheses of azeotropic-distillation systems, mainly resorting to mixed-integer-nonlinear programming (MINLP), however, have apparently been confined hitherto to homogeneous systems;[9−11] moreover, these syntheses have involved relatively simple RCMs of three-component systems. The combinatorial complexity is not excessive, and only a limited number of flowsheets or network structures are obtainable. Despite the encouraging progress made to date, much remains to be addressed for establishing a systematic and comprehensive methodology for algorithmically synthesizing heterogeneous as well as homogeneous azeotropic-distillation systems.

Unlike relatively ideal distillation systems, the physical/chemical intricacy of azeotropic-distillation systems leads to extraordinary combinatorial complexities. These complexities tend to give rise to an exceedingly large number of plausible or candidate operating units that should be taken into account in synthesis. In our earlier work, an extensive analysis of the azeotropic-distillation system for separating ethanol from its aqueous solution with toluene as the entrainer has demonstrated that hundreds of operating units are plausible even for such a relatively simple system.[1] As a result, the number of combinatorially feasible flowsheets that can be generated from these plausible operating units easily exceeds 100 000. Naturally, a heuristic method can search through only a minute segment of this vast solution space. It also prevents the implementation of a conventional MINLP method because of the exponential nature of any algorithm based on it; a nonconventional approach is indeed needed.

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In the current algorithmic method for synthesizing azeotropic-distillation systems based on process graphs (P-graphs),[13-16] the mathematical models are derived for the operating units involved, i.e., distillation columns, mixers, and decanters, through the application of RCMs and analytical geometry. The boundaries on the RCMs, i.e., distillation boundaries and liquid−liquid equilibrium envelopes, are linearized piecewisely for simplicity. This is followed by the algorithmic generation of the operating units and their synthesis. The efficacy of the method has been amply demonstrated by synthesizing optimal and near-optimal flowsheets producing pure ethanol from its aqueous solution via azeotropic distillation.

Graph-Theoretic Approach to Process-Network Synthesis

The three major facets of the current graph-theoretic approach to process-network synthesis involving the solution of a MINLP or MILP problem are the representation of the process structure by unique directed bipartite graphs, termed P-graphs, a set of axioms describing the main features and characteristics of a combinatorially feasible structure of the process as depicted by the P-graphs, and a set of the algorithms derived by virtue of the axioms for implementing the approach. These three facets are fully delineated in the earlier publications.[13-16] It has been ascertained that the current graph-theoretic approach to process-network synthesis gives rise to a rigorous and inordinately efficient method for solving a MINLP or MILP problem; apparently, no comparable method is available.

Method

A method for the optimal synthesis of an azeotropic-distillation system is framed by prudently adapting the graph-theoretic approach to process-network synthesis based on P-graphs.

Representation of the System. The thermodynamic pinches/boundaries, e.g., azeotropes, distillation boundaries, and boundaries of liquid−liquid equilibrium envelopes, which are of critical importance for azeotropic distillation, can readily be represented by RCMs;[3,4] it is natural that the current work resorts to the RCMs for representing azeotropic-distillation systems; the RCM of the ethanol−water−toluene system is illustrated in Figure 1.[1]

(a) Piecewise Linearization of Boundaries on RCMs. As will be delineated subsequently, the nonlinearity of boundaries of RCMs will lead to the nonlinearity of the constraints involved in the MINLP problem that need be solved for optimal synthesis. This nonlinearity usually gives rise to inordinate difficulty in the solution. To circumvent such difficulty, the boundaries are linearized or sectionally linearized. As an example, distillation boundaries XH, YH, and ZH and the boundary of the liquid−liquid equilibrium envelope, WQRT, in Figure 1 are linearized or sectionally linearized, thereby resulting in Figure 2. The accuracy of the representation can be modulated as desired by varying the number of linear sections.

(b) Partitioning Materials. A countless number of plausible materials may be identified even for a system containing as few as three components: The RCM of such a system is a two-dimensional plane, i.e., area, or higher dimensional space. For exhaustive inclusion of all plausible alternatives, therefore, a need exists to partition all of the materials within each of the two-dimensional areas or higher dimensional spaces, defined by various boundaries in the RCM. Any heuristic method can take into account only a minute portion of the RCM of interest.[1]

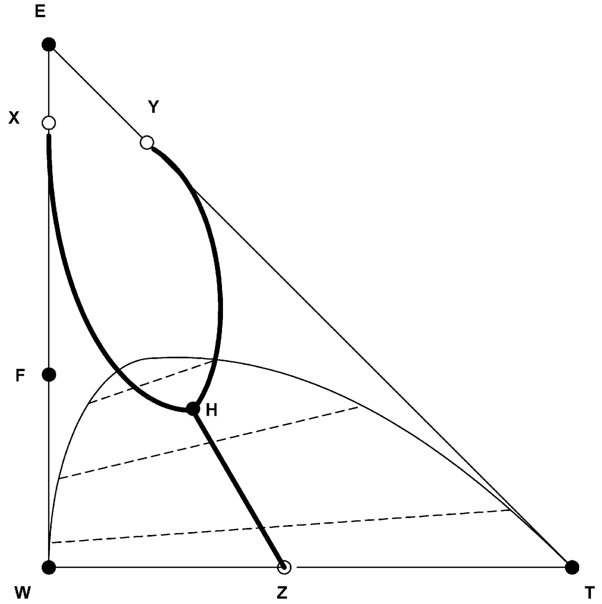

Figure 1. RCM of the ethanol (E)−water (W)−toluene (T) system: F, feed; X, Y, Z, binary azeotropes; H, ternary azeotrope.

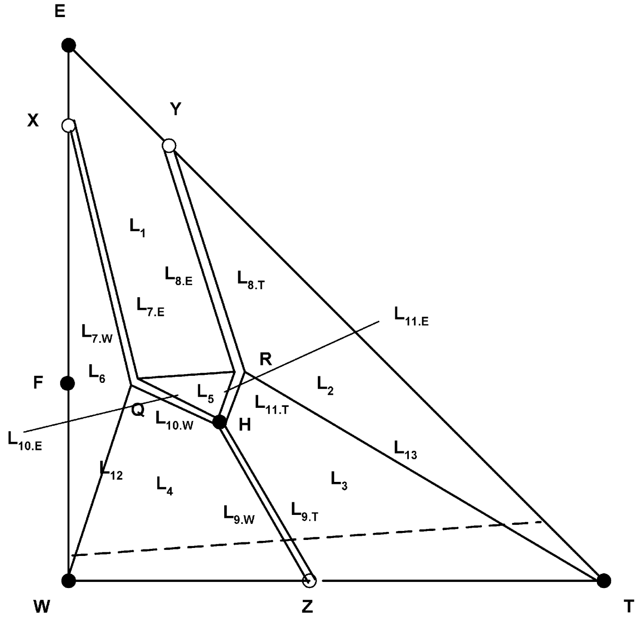

Figure 2. Linearized RCM of the ethanol (E)−water (W)−toluene (T) system illustrating the partitioned materials.

Generally, the products and feed for any distillation column should be in a single region created by distillation boundaries. When the significant curvature of a distillation boundary is exploited, however, the products and feeds can be in the two distinct regions straddling this boundary. Nevertheless, in this situation, the design and operation of the distillation columns exploiting the significant curvature are severely affected, often negatively, by the reliability of thermodynamic data, many of which contain appreciable error. In addition, large amounts of recycling streams frequently are needed to cross distillation boundaries when exploiting

Table 1. List of Partitioned Materials

index	partitioned materials	areas represented	operating unit type producing material[a]
1	E	E	S
2	W	W	S
3	F	F	
4	T	T	S
5	L_1	EYRQXE	M
6	L_2	YTRY	M
7	L_3	RTZHR	M
8	L_4	QHZWQ	M
9	L_5	QRHQ	M
10	L_6	XQWX	M
11	$L_{7.W}$	XQ on the XQWX side	S
12	$L_{7.E}$	XQ on the EYRQXE side	S
13	$L_{8.E}$	YR on the EYRQXE side	S
14	$L_{8.T}$	YR on the YTRY SIDE	S
15	$L_{9.T}$	HZ on the RTZHR side	S
16	$L_{9.W}$	HZ on the QHZWQ side	S
17	$L_{10.W}$	QH on the QHZWQ side	S
18	$L_{10.E}$	QH on the QRHQ side	S
19	$L_{11.T}$	RH on the RTZHR side	S
20	$L_{11.W}$	RT	S
21	L_{12}	line QW	D
22	L_{13}	line RT	D

[a] D: decanter. M: mixer. S: separator.

the curvatures. Because this tends to lead to both high capital cost and energy consumption, it is often advisable to avoid the situation when alternative approaches for crossing distillation boundaries are available, e.g., those taking advantage of phase splitting.

Unlike in our previous work,[1] the materials are partitioned only according to the critical curves and lines in the current work; the uniqueness of the intermediate products from separation of any partitioned material can be guaranteed by the pertinent constraints, as will be delineated in a subsequent section. For the example in Figure 2, the entire area of the RCM is classified into those materials occupying the points, i.e., E, W, T, and F; those occupying the lines, i.e., L_{12}, $L_{7.W}$, $L_{7.E}$, $L_{8.E}$, $L_{8.T}$, $L_{9.T}$, $L_{9.W}$, $L_{10.W}$, $L_{10.E}$, $L_{11.E}$, and $L_{11.T}$; and those occupying the areas, i.e., L_1, L_2, L_3, L_4, L_5, and L_6. The resultant partitioned materials are listed in Table 1.

Mathematical Models of Operating Units. Representation by RCMs is inordinately effective for distillation systems.[3,5] Nevertheless, each coordinate of any RCM signifies the concentration of a component in the mixture or material of interest, thereby resulting in nonlinear mathematical models of the operating units. For instance, the most frequently encountered expression for such models is

$$\sum_{j=1}^{s}(M^{j}c_{i}^{j}) = \sum_{k=1}^{t}(M^{k}c_{i}^{k}), \quad i = 1, 2, ..., n \tag{1}$$

which is the mass balance equation for component i ($i = 1, 2, ..., n$). In this expression, n is the number of components; c_i^j and c_i^k, the molar concentrations of component i; and M^j ($j = 1, 2, ..., s$) and M^k ($k = 1, 2, ..., t$) the total molar flow rates in input stream j ($j = 1, 2, ..., s$) to and output stream k ($k = 1, 2, ..., t$) from any operating unit with s inputs and t outputs, respectively. These expressions are obviously nonlinear when every M^j, c_i^j, M^k, and c_i^k is a free variable. Such nonlinearity leads to the nonlinearity of the constraints involved in the MINLP problem that need be solved for optimal synthesis; consequently, almost unsurmountable difficulty arises in solution. In contrast, the flow-rate-based representation, in which a stream of material is expressed in terms of the molar flow rates of the components in the stream, eliminates the constraints in terms of the molar concentration and total molar flow rate expressed by eq 1, thereby liberating us from the difficulty arising from nonlinearity, as will be demonstrated subsequently. For convenience, the diagram for the flow-rate-based representation is termed the flow-rate map, or the FRM, analogous to the RCM. Naturally, the coordinates of the FRM are the molar flow rates, M_i's, of individual components in the material.

(a) Quantitative Definition of Materials. The models of partitioned materials need be quantitatively represented prior to constructing the models of operating units. For clarity and simplicity, the focus at the outset will be on three-component systems.

Any material at point A^1 on the RCM, termed material A^1 in short and characterized by its compositions, is represented in the corresponding FRM as

$$M = (M_1, M_2, M_3) \tag{2}$$

$$M_i = v^1 c_i^1, \quad i = 1-3 \tag{3}$$

$$v^1 \geq 0 \tag{4}$$

where M is the point in the FRM whose coordinates M_1, M_2, and M_3 are expressed in terms of the molar flow rates of components in material A^1; v^1, the total molar flow rate of material A^1; and c_i^1, the concentration, and M_i, the molar flow rate of component i in the partitioned material. Because v^1 is a free variable, a point on the RCM is transformed into a straight line in the corresponding FRM.

Any partitioned material on a straight line determined by two points, one for material $A^1(c_1^1,c_2^1,c_3^1)$ and the other for material $A^2(c_1^2,c_2^2,c_3^2)$, in the RCM is represented in the corresponding FRM as

$$M = (M_1, M_2, M_3) \tag{5}$$

$$M_i = v^1 c_i^1 + v^2 c_i^2, \quad i = 1-3 \tag{6}$$

$$v^1 \geq 0; \quad v^2 \geq 0 \tag{7}$$

where v^1 and v^2 are the total molar flow rates of materials A^1 and A^2, respectively; c_i^1 and c_i^2, the concentrations of component i in materials A^1 and A^2, respectively; and M_i, the molar flow rate of component i in the partitioned material. Because both v^1 and v^2 are free variables, a straight line on the RCM is transformed into part of a convex area in the corresponding FRM.

Any partitioned material in a convex area enclosed by the straight lines, each connecting two successive ones of points A^1-A^m in the RCM, can be represented in the corresponding FRM as

$$M = (M_1, M_2, M_3) \tag{8}$$

$$M_i = \sum_{j=1}^{m} v^j c_i^j, \quad i = 1-3;\ m \geq 3 \tag{9}$$

$$v^j \geq 0, \quad j = 1, 2, ..., m \tag{10}$$

where v^j is the total molar flow rate of material A^j; and c_i^j, the molar concentration, and M_i, the molar flow

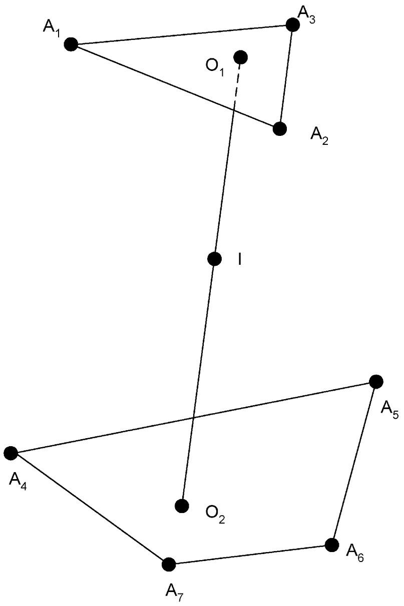

Figure 3. Representation of a separator in the RCM with input I and outputs O_1 and O_2, which are on the bounding planes, $A_1A_2A_3$ and $A_4A_5A_6A_7$, respectively.

rate, of component *i* in the partitioned material. Because every v^j is a free variable, a convex area in the RCM is transformed into part of a convex volume in the corresponding FRM.

By generalizing for the system with four or more components, we obtain

$$M = (M_1, M_2, ..., M_i, ..., M_n), \quad n \geq 4 \tag{11}$$

$$M_i = \sum_{j=1}^{m} v^j c_i^j, \quad i = 1, 2, ..., n \tag{12}$$

$$v^j \geq 0, \quad j = 1, 2, ..., m \tag{13}$$

Naturally, the FRM is a hyperspace for such a system.

Any partitioned material, at a point for which $m = 1$, on a straight line for which $m = 2$, or in a convex area for which $m \geq 3$, in the RCM of a three-component system, i.e., $n = 3$, is represented as a straight line, part of a convex area, or part of a convex volume, respectively, in the corresponding FRM. Similarly, any partitioned material at a point for which $m = 1$, on a straight line for which $m = 2$, in a convex area for which $m = 3$, in a convex volume with $m = 4$, or in a convex hyperspace with $m \geq 5$ in the RCM of a four or more component system, i.e., $n \geq 4$, is represented as a straight line, part of a convex area, part of a convex volume, part of a four-dimensional convex hyperspace, or part of a convex hyperspace with five or more dimensions, respectively, in the corresponding FRM.

(b) Models of Operating Units. With the models of partitioned materials in terms of the molar flow rates of their respective components presented above, the mathematical models of operating units can be derived. To circumvent nonlinearity, these models are derived in terms of molar balances. The derivation of the equations except those for the mixers, however, needs to rely on various thermodynamic information provided by the corresponding RCM, e.g., distillation boundaries, and liquid−liquid equilibrium envelopes.

A. Mixer. A mixer with two inputs and one output can be represented on the FRM as

$$I_i^1 + I_i^2 = O_i, \quad i = 1, 2, ..., n \tag{14}$$

where I_i^1, I_i^2, and O_i are the molar flow rates of component *i* in input material I^1, input material I^2, and output material O, respectively.

B. Separator. For simplicity, it is assumed that any separation leads to two products, each on a boundary or bounding plane on the RCM. Naturally, any boundary is either a distillation boundary or a natural boundary which is one of the coordinates of the RCM, and any bounding plane is determined by distillation boundaries and/or natural boundaries. As a result, a separator can be represented in the FRM as follows:

$$I_i = O_i^1 + O_i^2, \quad i = 1, 2, ..., n \tag{15}$$

$$O_i^1 = \sum_{j=1}^{k} v^j c_i^j, \quad i = 1, 2, ..., n \tag{16}$$

$$O_i^2 = \sum_{j=k+1}^{m} v^j c_i^j, \quad i = 1, 2, ..., n \tag{17}$$

$$v^j \geq 0, \quad j = 1, 2, ..., m \tag{18}$$

where I_i, O_i^1, and O_i^2 are the molar flow rates of component *i* in input material I, output material O^1, and output material O^2, respectively. The bounding boundary or plane on the corresponding RCM containing partitioned material O^1 is determined by the *k* bounding points, $A^1(c_1^1,c_2^1,...,c_n^1)$ through $A^k(c_1^k,c_2^k,...,c_n^k)$, while the bounding boundary or plane containing partitioned material O^2 is determined by the $m - k$ bounding points, $A^{k+1}(c_1^{k+1},c_2^{k+1},...,c_n^{k+1})$ through $A^m(c_1^m,c_2^m,...,c_n^m)$; see Figure 3. Note that obviously the sum of the concentrations of any material A^j is equal to 1, i.e., $\sum_{i=1}^{n} c_i^j = 1$, where $j = 1, 2, ..., m$.

C. Decanter. By definition, decanting yields two products, each on the bounding boundary or plane of the liquid−liquid equilibrium envelope in the RCM. This envelope is sectionally linearized; see Figure 2. Each segment of the sectionalized envelope can be part of a convex area, convex volume, or convex hyperspace in the corresponding FRM depending on the number of components in the system, *n*. It is part of a convex area for $n = 3$; part of a convex volume for $n = 4$; and part of a convex hyperspace for *n* equal to or greater than 5.

For clarity and simplicity, the model for a decanter of the three-component system, producing pure ethanol from its aqueous solution with toluene as the entrainer, is established in the FRM first; see Figure 4. Note that the corresponding RCM is defined by points E, W, and T with straight lines EW, ET, and WT as its coordinates as well as the boundaries in the figure. Consequently,

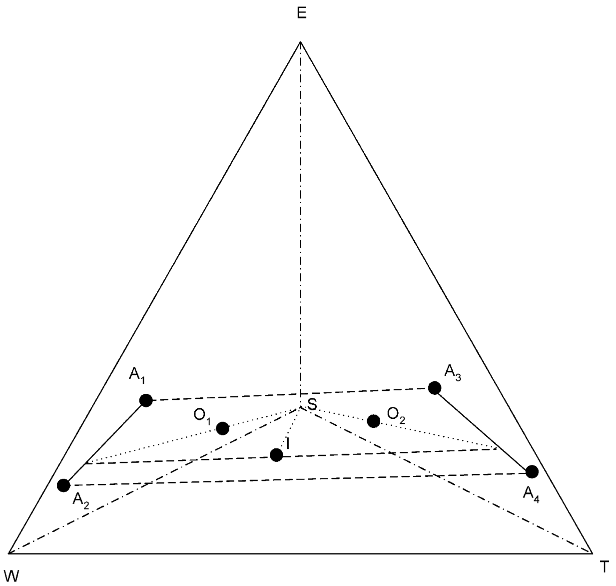

Figure 4. of the ethanol (E)−water (W)−toluene (T) system for illustrating the derivation of the governing equations for decanter $I = O_1 + O_2$: lines SE, SW, and ST are the coordinates of the FRM, and EW, ET, and WT are the coordinates and boundaries of the RCM.

the decanter for the three-component system can be represented in the FRM as follows:

$$I_i = O_i^1 + O_i^2, \quad i = 1{-}3 \tag{19}$$

$$O_i^1 = \sum_{j=1}^{2} v^j c_i^j, \quad i = 1{-}3 \tag{20}$$

$$O_i^2 = \sum_{j=3}^{4} v^j c_i^j, \quad i = 1{-}3 \tag{21}$$

In the above expressions, I_i, O_i^1, and O_i^2 are the molar flow rates of component i in input material I, output material O^1, and output material O^2, respectively.

For a system with four or more components, the bounding boundary or plane on the RCM containing partitioned material O^1 is determined by the k bounding points, $A^1(c_1^1,c_2^1,...,c_n^1)$ through $A^k(c_1^k,c_2^k,...,c_n^k)$, while the bounding boundary or plane containing partitioned material O_2 is determined by the $m - k$ bounding points, $A^{k+1}(c_1^{k+1},c_2^{k+1},...,c_n^{k+1})$ through $A^m(c_1^m,c_2^m,...,c_n^m)$; see Figure 5. Note that obviously the sum of the concentrations of any material A^j is equal to 1, i.e., $\sum_{i=1}^{n} c_i^j = 1$, $j = 1, 2, ..., m$. As a result, the governing equations for the decanter in the FRM are

$$I_i = O_i^1 + O_i^2, \quad i = 1, 2, ..., n \tag{22}$$

$$O_i^1 = \sum_{j=1}^{k} v^j c_i^j, \quad i = 1, 2, ..., n \tag{23}$$

$$O_i^2 = \sum_{j=k+1}^{m} v^j c_i^j, \quad i = 1, 2, ..., n \tag{24}$$

Identification of Plausible Operating Units and the Pertinent Materials. The following constraints are imposed in identifying candidate/plausible operating units according to the methodology delineated in our previous work.

1. Any distillation column yields two products from a single feed, with each product being located at a singular point, on a distillation boundary, or on a bounding surface.
2. No materials in the same region are mixed.
3. No mixer yields any partitioned material occupying a singular point, distillation boundary, liquid−liquid equilibrium envelope, or bounding surface.

Constraint 1 represents rational simplification at the conceptualization stage of process design, i.e., process synthesis. Options such as complex columns with two or more feeds and three or more products are better left for consideration in the later stage of design. Moreover, the nearer the products to the thermodynamic pinches, the higher the degree of their separation achievable through distillation, thereby lowering the cost provided that the products are not exceedingly close to the thermodynamic pinches. Constraint 2 is valid: The partitioned materials are bounded by distillation boundaries and/or liquid−liquid equilibrium envelopes, and thus the materials in the same region are identical from the standpoint of serving as the feed to an operating unit; no advantage is gained from blending the identical materials. Constraint 3 is also valid: Although possible, it is impractical to generate a partitioned material occupying a singular point, a distillation boundary, or a bounding surface because it is extremely difficult, if not impossible, to control the operation of the mixer so that the blended product is exactly at such geometrically singular locations.

In addition to the first three constraints, the following constraints are imposed specifically in the illustration of producing pure ethanol (E) from its aqueous solution to further simplify the problem.

4. The product from any mixer is not fed to any other mixers.
5. Only two materials are fed to a mixer.
6. A desired product is not mixed with any other materials.

Constraint 4 is logical: Mixing leads to an increase in entropy or dissipation of available energy; the larger the number of repetitions of mixing, the greater the loss of available energy. Moreover, any resultant gain from repetitive mixing tends to be nullified by accompanying mechanical and operational complications. Constraints 5 and 6 may be regarded as reasonable simplifications. Note that these three additional constraints can be relaxed; in fact, it may be advantageous to relax one or more of them. For instance, three-stream mixing and mixing a desired product with one or more intermediate materials have been practiced to generate a series of innovative and superior flowsheets for purifying diethoxymethane from a mixture with ethanol and water.[17]

(a) 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. 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 an error may make the design and operation impossible or extremely difficult. The operating units producing the desired products can be identified by examining the topology of the RCM of the corresponding system.[18−20]

In the example illustrated in Figure 2, the two products, ethanol (E) and water (W), are situated in regions EYRHQXE and XQHZWX, 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 linking 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 operating unit yielding product E must be located in region EYRHQXE. Similarly, both the feed to and the intermediate products from any operating unit producing water (W) must be situated in region XQHZWX. These indispensable operating units are identified below in terms of the partitioned materials indicated in Figure 2.

According to the topology of the RCM, the plausible operating units for producing ethanol (E) are distillation columns ({L_1}, {E, $L_{7.E}$}); ({L_1}, {E, $L_{8.E}$}); ({L_1}, {E, $L_{10.E}$}); and ({L_1}, {E, $L_{11.E}$}). Note that, in contrast with the methodology delineated in our previous work for identifying plausible operating units and materials,[1] material L_1 is not further partitioned into subpartitioned materials according to the uniqueness of the intermediate products from the separation of L_1, i.e., $L_{7.E}$, $L_{8.E}$, $L_{10.E}$, and $L_{11.E}$. Similarly, the plausible operating units for producing water (W) are distillation columns ({F}, {W, $L_{7.W}$}); ({L_6}, {W, $L_{7.W}$}); ({L_4}, {W, $L_{9.W}$}); ({L_4}, {W, $L_{10.W}$}); ({L_{12}}, {W, $L_{7.W}$}); and ({L_{12}}, {W, $L_{10.W}$}).

To elude thermodynamic pinches, another class of operating units is indispensable. As mentioned earlier, these operating units in terms of the partitioned materials for the system can be identified in Figure 2. They include decanters ({L_3}, {L_{12}, L_{13}}); ({L_4}, {L_{12}, L_{13}}); ({L_5}, {L_{12}, L_{13}}); ({$L_{9.W}$}, {L_{12}, L_{13}}); ({$L_{9.T}$}, {L_{12}, L_{13}}); ({$L_{10.E}$}, {L_{12}, L_{13}}); ({$L_{10.W}$}, {L_{12}, L_{13}}); ({$L_{11.E}$}, {L_{12}, L_{13}}); and ({$L_{11.T}$}, {L_{12}, L_{13}}).

Similarly, a separator is effective for eluding the thermodynamic pinch when the separation is performed in a space with at least one more dimension than the space in which the thermodynamic pinch is located; in fact, it is indispensable. Because such a separator does not exist in the system illustrated in Figure 2, this is demonstrated with a simple system in Figure 6 where binary azeotrope X can be eluded with separators ({L_2}, {A, L_3}), ({L_2}, {B, L_1}), and ({L_2}, { L_1, L_3}). Note that azeotrope X is located on the one-dimensional line, AB, while the three separations identified are performed in the two-dimensional area encircled by points A−C.

(b) Operating Units for Generating the Feeds to the Indispensable Operating Units. 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 desired product, therefore, can be fed into the corresponding indispensable operating unit, yielding the desired product. Naturally, the raw material or any intermediate material 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 desired products.

In the example illustrated in Figure 2, the feeds to the indispensable operating units selected are L_1, L_4, L_5, L_6, L_{12}, $L_{9.W}$, $L_{9.T}$, $L_{10.E}$, $L_{10.W}$, $L_{11.E}$, and $L_{11.T}$. Obviously, partitioned materials $L_{9.W}$, $L_{9.T}$, $L_{10.E}$, $L_{10.W}$, $L_{11.E}$, and $L_{11.T}$ can be generated by the pertinent separators producing pure materials E, W, and T; partitioned material L_{12} can be produced by the decanters already identified; partitioned materials L_1, L_4, L_5, and L_6 need to be generated by mixers because each of

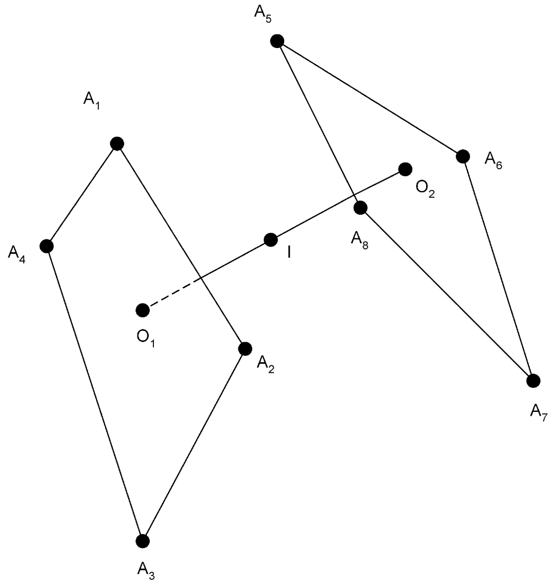

Figure 5. Representation of a decanter in the RCM with input I and outputs O_1 and O_2, which are on the bounding planes, $A_1A_2A_3A_4$ and $A_5A_6A_7A_8$, of the corresponding liquid−liquid equilibrium envelope, respectively.

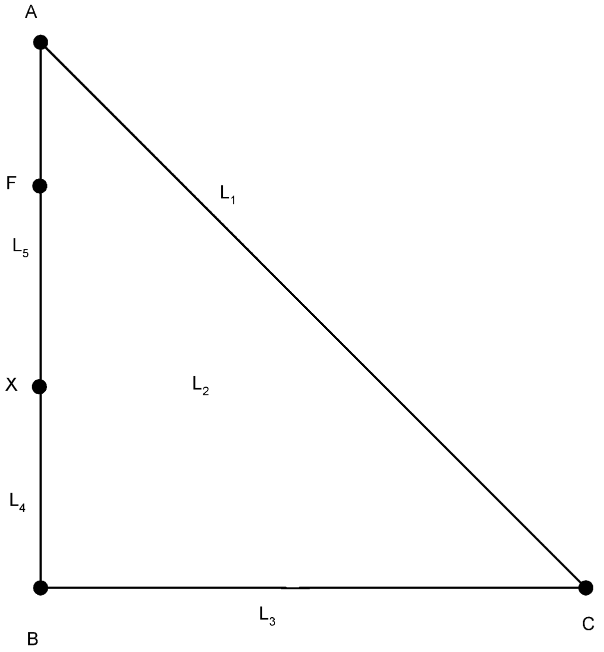

Figure 6. Simple system illustrating the identification of separators for eluding the thermodynamic pinches: A and B, desired products; F, feed; X, binary azeotrope of A and B; L_1, lumped material occupying line AC; L_2, lumped material occupying area ABC; L_3, lumped material occupying line BC; L_4, lumped material occupying line AX; L_5, lumped material occupying line XB.

these partitioned materials occupies a convex area. Consequently, all of these partitioned materials can be represented by eqs 8−10.

Constraints 4−6 are intended for mixers in general. Naturally, it should be applicable to any mixer preparing the feed to an indispensable operating unit. By taking into account constraints 4−6, the candidate feeds to the plausible mixers in the example illustrated in Figure 2 are F, T, $L_{7.E}$, $L_{7.W}$, $L_{8.E}$, $L_{8.T}$, $L_{9.W}$, $L_{9.T}$, $L_{10.E}$, $L_{10.W}$, $L_{11.E}$, $L_{11.T}$, L_{12}, and L_{13}. The intermediate materials resulting from mixing are partitioned materials, L_1, L_3, L_4, L_5, and L_6.

The mixers for generating the feeds to the indispensable operating units are algorithmically generated by exhaustively assessing the possible product from mixing every pair of the candidate feeds identified. Mathematically, a mixer is feasible if there is a solution for the series of equations including mathematical models of the two feeds and the product as well as the governing equations of the mixer. In what follows, the methodology for algorithmically assessing the feasibility of a plausible mixer is illustrated through the generation of mixer ($\{L_{7.W}, L_{13}\}, \{L_1\}$).

Partitioned material $L_{7.W}$ occupies the straight line, XQ, linking points X and Q. According to eqs 5−7, this partitioned material can be represented as

$$L_{(7.W)} = (L_{(7.W)1,}\ L_{(7.W)2},\ L_{(7.W)3}) \tag{25}$$

$$L_{(7.W)i} = v_X c_{Xi} + v_Q c_{Qi}, \quad i = 1-3 \tag{26}$$

$$v_X \geq 0, \quad v_Q \geq 0 \tag{27}$$

where v_X and v_Q are the total molar flow rates of materials X and Q, respectively; c_{Xi} and c_{Qi}, the concentrations of component i in materials X and Q, respectively; and $L_{(7.W)i}$, the molar flow rate of component i in the partitioned material. Similarly, partitioned material L_{13} occupies the straight line, RT, linking points R and T, and can be represented as

$$L_{13} = (L_{(13)1,}\ L_{(13)2},\ L_{(13)3}) \tag{28}$$

$$L_{(13)i} = v_R c_{Ri} + v_T c_{Ti}, \quad i = 1-3 \tag{29}$$

$$v_R \geq 0, \quad v_T \geq 0 \tag{30}$$

Partitioned material L_1 occupies the concave area EYRQXE encircled by a series of straight lines connecting points E, Y, R, Q, and X. According to eqs 8−10, this partitioned material L_1 can be represented as

$$L_1 = (L_{(1)1,}\ L_{(1)2},\ L_{(1)3}) \tag{31}$$

$$L_{(1)i} = v_E c_{Ei} + v_Y c_{Yi} + v_R c_{Ri} + v_Q c_{Qi} + v_X c_{Xi}, \quad i = 1-3 \tag{32}$$

$$v_E \geq 0, \quad v_Y \geq 0, \quad v_R \geq 0, \quad v_Q \geq 0, \quad v_X \geq 0 \tag{33}$$

The overall molar balance around the mixer yields

$$L_{(7.W)i} + L_{(13)i} = L_{(1)i}, \quad i = 1-3 \tag{34}$$

The feasibility of mixer ($\{L_{7.W}, L_{13}\}, \{L_1\}$) is ascertained by the existence of a solution from simultaneously solving eqs 25−34.

(c) Other Operating Units Facilitating Separation. Usually, the pure entrainers are recycled in a feasible flowsheet. Thus, any separator regenerating the pure entrainers should be selected. Consequently, any operating units producing the feed to separators regenerating the pure entrainers should also be selected. In the example illustrated in Figure 2, the operating units, separators, regenerating the entrainer, T, are ($\{L_2\}$, $\{L_{8.T}, T\}$); ($\{L_3\}$, $\{L_{9.T}, T\}$); ($\{L_3\}$, $\{L_{8,T}, T\}$), ($\{L_{13}\}$; $\{L_{8.T}, T\}$); and ($\{L_{13}\}$, $\{L_{8.T}, T\}$). L_{13} can be produced by decanters ($\{L_3\}$, $\{L_{12}, L_{13}\}$); ($\{L_4\}$, $\{L_{12}, L_{13}\}$); ($\{L_5\}$, $\{L_{12}, L_{13}\}$); ($\{L_{9.T}\}$, $\{L_{12}, L_{13}\}$); ($\{L_{9.W}\}$, $\{L_{12}, L_{13}\}$); ($\{L_{10.E}\}$, $\{L_{12}, L_{13}\}$); ($\{L_{10.W}\}$, $\{L_{12}, L_{13}\}$); ($\{L_{11.E}\}$, $\{L_{12}, L_{13}\}$); and ($\{L_{11.T}\}$, $\{L_{12}, L_{13}\}$); L_2. Moreover, L_3 can be produced by the corresponding mixers that can be readily identified by the aforementioned method.

Generation of Feasible and Optimal Flowsheets. The maximal structure is generated by resorting to algorithm MSG, with the operating units identified in the preceding subsection as the inputs. Subsequently, algorithm SSG yields all combinatorially feasible structures, i.e., flowsheets, from the maximal structure.

Combinatorially feasible structures or flowsheets, however, may often turn out to be infeasible. This is especially the case for a system containing a relatively large number of operating units. These operating units should be excluded from further consideration.

The causes that render a combinatorially feasible flowsheet infeasible are the following.

1. Generating one or more byproducts, i.e., product not included in the designated product set, e.g., any product which is neither ethanol (E) nor water (W) in the example of producing pure ethanol from its aqueous solution.

2. Not satisfying mass balance around at least one cycle in the flowsheet.

The infeasibility due to the first one can be readily remedied in the P-graph method: those generating byproducts are simply eliminated by assessing every product generated. As to the second one, the infeasibility is addressed by imposing the pertinent mass balance equations for every cycle as constraints in the optimization; this will be delineated later.

Upon elimination of the structures generating byproducts, the remainder of the combinatorially feasible structures can be optimized individually by formulating the following optimization problem.

Minimize

$$C = \sum_{i=1}^{\mathrm{op}} \mathrm{cost}_i(F_{11}^{\mathrm{IN},i}, F_{12}^{\mathrm{IN},i}, ..., F_{1n}^{\mathrm{IN},i}; F_{21}^{\mathrm{IN},i}, F_{22}^{\mathrm{IN},i}, ..., F_{2n}^{\mathrm{IN},i}; ..., F_{11}^{\mathrm{OUT},i}, F_{12}^{\mathrm{OUT},i}, ..., F_{1n}^{\mathrm{OUT},i}; F_{21}^{\mathrm{OUT},i}, F_{22}^{\mathrm{OUT},i}, ..., F_{2n}^{\mathrm{OUT},i}; ...) \tag{35}$$

subject to the following four categories of constraints: (1) the equations representing each material in the structure, i.e., eqs 11−13; (2) the governing equation for each mixer in the structure, i.e., eq 14; (3) the governing equations for each separator in the structure, i.e., eqs 15−18; and (4) the governing equations for each decanter in the structure, i.e., eqs 22−24. Note that governing equations for the operating units tacitly require that the mass balance around each cycle in the structure must be satisfied. In eq 35, C stands for the total cost of the structure; i, $i = 1, 2, ...,$ op, the index for the operating units in the structure, whose total number is op; cost_i, the cost of operating unit i; $F_{jk}^{\text{IN},i}$, the flow rate of component k in input or feed stream j to operating unit i; and $F_{jk}^{\text{OUT},i}$, the molar flow rate of component k in output stream j from operating unit i. Note that the constraints in categories 2−4 prevent the structures, in which at least one cycle violates mass balance, from further consideration in the optimization.

Equation 35 can be either linear or nonlinear while all of the constraints are linear. Naturally, the linearity of the constraints drastically reduces the computational complexities involved in optimization. For simplicity, all cost_i's are regarded as linear in F_{ij}'s, thereby giving rise to a LP problem, which is solvable by any effective LP algorithm.

Application. Hitherto, the various facets of the current method have been separately illustrated with the well-established example of producing pure ethanol from its aqueous solution via azeotropic distillation with toluene as the entrainer. Herein, the method is illustrated in totality with the same example; recall that the RCM of the system is depicted in Figure 1. As an initial screening, the cost function in eq 35 is taken as the sum of the molar flow rates of the input or feed streams to all separators, which signify their capacities: the cost of a decanter or mixer is negligible compared to that of a separator. Consequently, eq 35 is simplified as

$$C = \sum_{i=1}^{\text{op}} \Big(\sum_{j=1}^{n} S_j^{\text{IN},i} \Big) \qquad (36)$$

where $S_j^{\text{IN},i}$ denotes the molar flow rate of component j in the input or feed stream to separator i. Naturally, $S_j^{\text{IN},i} = F_{1j}^{\text{IN},i}$ if operating unit i is a separator; otherwise, $S_j^{\text{IN},i} = 0$.

It has been found that any feasible structure resulting from the final step comprises five or more operating units. Our preliminary exploration, however, has indicated that any structure with an exceedingly large number of operating units is highly unlikely to be optimal; thus, the upper bound of the total number of operating units in each structure is considered to be seven. In addition, it is assumed for simplicity that the feed or each intermediate material can be consumed only by a single operating unit, while each product or intermediate material can also be produced only by a single operating unit.

The method entails that the synthesis be carried out according to the following procedure; see Figure 2. First, the boundaries on the RCM are linearized. Second, the entire domain of the RCM is divided into a set of partitioned materials. Third, all plausible operating units, including 13 separators, 6 decanters, and 256 mixers are identified according to the procedure depicted in the Identification of Plausible Operating Units and the Pertinent Materials section. Fourth, the mathematical models, i.e., governing equations, of these operating units are derived systematically and algorithmically according to the governing equations of the operating units presented in the Mathematical Modeling of Operating Units section. Fifth, the maximal structure is generated via algorithm MSG. Sixth, all of the combinatorially feasible structures with seven or fewer operating units are generated from the maximal structure via algorithm SSG; the limitation on the number of operating units is imposed to drastically reduce the computational time. Seventh, any cominatorially feasible structure generating byproducts, i.e., the products other than pure ethanol (E) and water (W), is discarded. Finally, the cost of each of the structures surviving the elimination, numbering 3789 in total, is minimized with respect to the molar flow rates of each component in the feeds to and the products from every operating unit, i.e., the design variables, in light of eq 36 by linear programming subject to mass balance constraints. Only six structures turn out to satisfy these constraints. They are structures 2294, 2645, 2649, 2684, 2721, and 2732. The results are summarized and ranked in Table 2; obviously, structures 2684 and 2721 are identical and optimal, while structures 2645, 2649, and 2732 are suboptimal. Figure 7 exhibits the optimal structure, i.e., flowsheet, corresponding to structures 2684 and 2721 in the RCM; Figure 8 shows the same structure as a P-graph. The synthesis, executed on a PC (Celeron 366 MHz), has consumed a total of 4 min and 2 s.

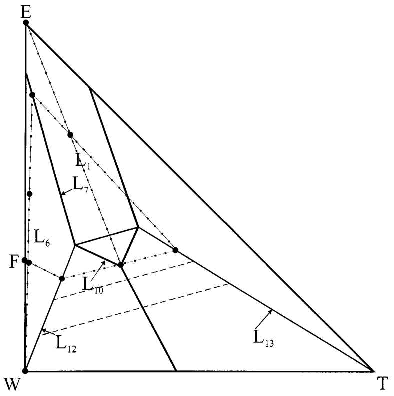

Figure 7. Structures 2684 and 2721, which are feasible as well as optimal, represented on the RCM.

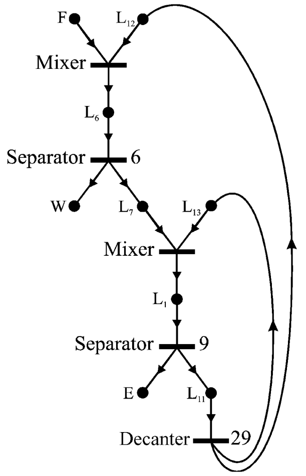

Figure 8. Structures 2684 and 2721, which are feasible and optimal, represented by a P-graph.

Table 2. List of Feasible Structures

no.	cost	total number of operating units in the structure	ranking
2294	1628.672	7	3
2645	200.631	7	2
2649	200.631	7	2
2684	172.743	5	1
2721	172.743	5	1
2732	200.631	7	2

Discussion

It is well known that the major and often insurmountable difficulty encountered in process synthesis is its profound combinatorial complexity. For example, to synthesize a system with n plausible operating units, a conventional MINLP approach needs to search a space comprising $2^n - 1$ possible combinations or structures; by any measure, this number is huge whenever n is relatively large. For instance, it is $2^{275} - 1 = 6.07 \times 10^{82}$ in the example of the current work for producing ethanol from its aqueous solution where 13 separators, 6 decanters, and 256 mixers are identified to be plausible. Naturally, even a severalfold improvement in the efficiency of the conventional MINLP approach would do little in circumventing the combinatorial complexity of this magnitude. Moreover, any enhancement in the approach would prematurely exclude the optimal and even near-optimal structures if not done rigorously.[20,21]

In contrast, the proposed method is combinatorially highly efficient and robust: Both algorithms MSG and SSG are based on the five axioms generated by mathematically and rigorously distilling the unique structural features of the process systems. In fact, algorithm MSG is a polynomial algorithm which eliminates with dispatch all of the combinatorially infeasible operating units and their concomitant linkages.[13] For the example of the current work, algorithm MSG composes the maximal structure in approximately $n(n + 1)/2 = 275(275 + 1)/2 = 37\,950$ steps. Although not polynomial, algorithm SSG is far more efficient than a typical all-purpose algorithm, e.g., MINLP. The solution structures are generated from the maximal structure containing only the combinatorially feasible networks whose number tends to be a minute fraction of the total number of possible networks when n is not exceedingly small; moreover, the implementation of algorithm SSG is facilitated by a unique mathematical function, termed decision mapping, conceived by exploiting the unique features of a process network expressed in the five axioms.[15] Consequently, the entire synthesis of the example system of the current work has consumed only 4 min and 2 s on a PC (Celeron 366 MHz), thereby demonstrating the efficacy of the proposed method. The algorithm is implemented by incorporating LINX, a simplex-based routine collection written in C++, as the LP solver.[22]

The proposed method is capable of rapidly screening a large number of potentially feasible structures, eliminating the infeasible ones, and ranking the feasible ones. In practice, this prevents the search involved from being trapped at a locally optimal solution. The real optimal structure can be identified by comparing the ranked optimal and near-optimal structures, as given in Table 2 for the example, through detailed simulation via a commercial simulator. The ranking of the optimal and near-optimal structures also renders it possible to replace immediately the optimal with the next best when the former is deemed undesirable from the standpoint of its stability and controllability or in view of environmental, societal, regulatory, and other pertinent constraints. This replacement can be repeated as needed.

Conclusions

A highly efficient and robust method has been established for algorithmically synthesizing optimal as well as near-optimal flowsheets of an azeotropic-distillation system. This has been rendered possible by resorting to the methodology of classifying the entire space of a RCM into partitioned materials, thus preventing the localization of search; by judiciously adapting the graph-theoretic algorithmic approach to process-network synthesis based on P-graphs, thus circumventing the enormous combinatorial complexities; and by introducing the notion of the FRM to complement the RCM, thus eliminating the nonlinearity of the governing equations of operating units to be incorporated into the system. The proposed method should be applicable to other complex processes with phase transition and/or separation, e.g., crystallization, extraction, reactive distillation, and their combinations.

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