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Systematic Generation of the Optimal and Alternative Flowsheets for Azeotropic-Distillation Systems

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ABSTRACT

A systematic and rigorous method for synthesizing azeotropic-distillation systems, which is of utmost practical importance, is yet to be fully established. The available methods are based mainly on heuristics and graphical procedures. Our experience indicates that even in synthesizing a simple separation network, the structure of the optimal solution may be counterintuitive. For synthesizing a complex network structure necessary for an azeotropic-distillation system, therefore, the probability is very high that the solution generated would be far from the optimal one unless the method is systematic and rigorous.

The proposed method is capable of algorithmically synthesizing optimal, near optimal, and other feasible structures for an azeotropic-distillation system from a set of candidate operating units. Initially, the residue curve map of the system is transformed to a unique multidimensional representation to facilitate the systematic partitioning of the feasible regions into lumped materials bounded by the thermodynamic boundaries and pinches. This renders it possible to derive analytical expressions of the resultant materials in terms of the coordinates of these boundaries and to automatically identify with dispatch the candidate operating units, such as separators, mixers, and decanters, for possible inclusion in the system. The process-graph (P-graph) representation of these operating units serves as a basis for the synthesis procedure including combinatorial algorithms. The method is equally applicable to various other complex processes with phase transition and/or phase separation with any number of components. Crystallization, extraction, reactive distillation, and their combinations are examples of such processes. A case study in which ethanol is separated from its aqueous solution with toluene as the entrainer demonstrates amply the efficacy of the method.

1. INTRODUCTION

The current contribution is concerned with the synthesis of feasible alternative flowsheets of azeotropic-distillation systems. Specifically, it aims at developing an algorithmic and systematic method for synthesizing azeotropic-distillation systems from an extensive set of candidate operating units, i.e., functional units.

Azeotropic distillation is ubiquitous in chemical and allied industries. The majority of existing azeotropic-distillation processes were developed and designed through extensive try-and-error based on past experiences. Consequently, questions largely remain unanswered as to

what potential benefit there might be for improving existing processes as well as what methodologies are to be adopted for devising new processes.

In contrast to the rapid progress that has been made on the analysis of azeotropic-distillation systems since the mid-1980's (see, e.g., Van Dongen and Doherty, 1985; Siirola, 1996; Widagdo and Seider, 1996), success achieved for the synthesis of azeotropic-distillation systems has been rather modest. The majority of the available approaches, often termed analysis-driven synthesis, are essentially based on the first principles and/or heuristic rules derived from the analysis of the residue curve map (RCM) of the system of interest (see, e.g., Siirola, 1996; Westerberg and Wahnschafft, 1996).

In spite of the progress made to date, much remains to be resolved for establishing a systematic and comprehensive methodology for synthesizing azeotropic-distillation systems. In fact, some critical issues are yet to be resolved: For example, how can be feasible alternative flowsheets systematically and inclusively generated for the analysis-driven synthesis approach (see, e.g., Siirola, 1996).

The difficulty of synthesizing an azotropic-distillation system is attributable to its physical/chemical intricacy, which inevitably leads to enormous combinatorial complexity in synthesis (Feng *et al.*, 2000). In other words, it may result in an inordinately large number of plausible or candidate operating units, the possibility of which being included in a feasible structure must de determined in synthesis. The magnitude of the solution space renders it extremely difficult, if not impossible, to adopt a conventional MINLP method. Hence, the development of a combinatorially effective method is deemed highly desirable. Such a method is proposed here; it is based on the process graph (P-graph), an innovative mathematical system, which has been conceived for process synthesis by incorporating the specificities of process systems (see, e.g., Friedler *et al.*, 1992; Friedler *et al.*, 1993; Friedler *et al.*, 1995).

2. DEFINITION OF THE SYNTHESIS PROBLEM

The thermodynamic pinches or boundaries, e.g., azeotropes, distillation boundaries, and the boundaries of liquid-liquid equilibrium envelopes, are of critical importance for azeotropic distillation. Moreover, the composition of the feed- and product-streams must be specified to define the synthesis problem for an azeotropic-distillation system. Such information can be represented by RCM's. For illustration, the RCM of the ethanol-water-toluene system is depicted in Figure 1. The points F, E, W, and T, represent the feed, product, byproduct, and the entrainer, respectively.

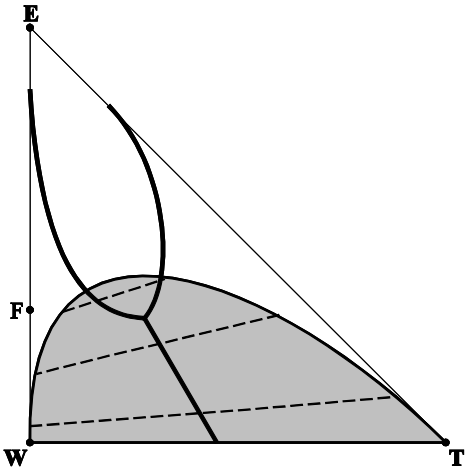

Fig. 1. RCM of the ethanol(E)-water(W)-toluene(T) system.

The materials and operating units are the essential building blocks of a chemical process system. In what follows, the materials and operating units will be defined first. Naturally, the materials concomitant with plausible or candidate operating units, i.e., the input and output materials to each of them, are also simultaneously identified as required by the P-graph approach.

A countless number of plausible materials or mixtures may be identified for a systems of three or more components. For exhaustive inclusion of every plausible alternative, therefore, a need exists to partition all the materials within each of the areas defined by various boundaries in the RCM.

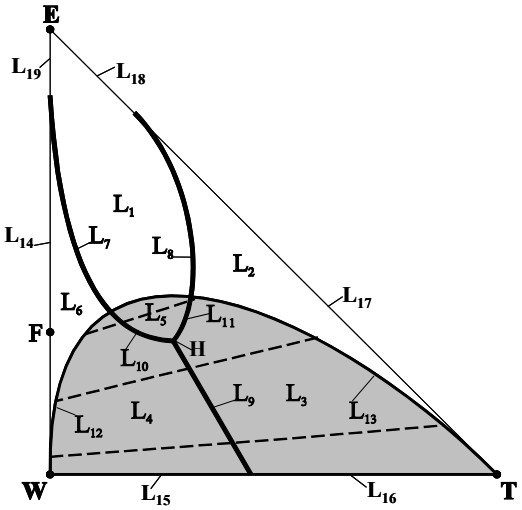

Fig. 2. Lumped materials (L_1, L_2, …, L_{13}).

Any RCM occupying an area or space comprises an infinite number of points; as a result, the number of plausible operations is also infinite. Feng *et al.* (2000) have proposed that the RCM be partitioned into a finite number of lumped materials covering the entire are as illustrated in what follows.

In Figure 2, the whole RCM is partitioned into materials occupying the points, i.e., E, W, T, H, and F; those occupying the areas, i.e., L_1 through L_6; and those occupying the lines, i.e., L_7 through L_{19}.

According to the topology of the RCM, the plausible operating units are the distillation columns producing ethanol (operating units 1 through 6 in Table 1); water (operating units 7 through 10); toluene (operating units 11, 12, and 13); ternary azeotrop H (operating units 14 through 23), decantors (operating units 24 through 30); and mixers.

The set of products, raw materials, and operating units serve as the input to the process-network-synthesis algorithms.

3. AZEOTROPIC DISTILLATION DESCRIBED BY P-GRAPHS

A set of operating units can be represented in a P-graph, where the operating units are denoted by horizontal bars, and their input and output materials by solid circles. The P-graph is a directed graph; the direction of the arcs representing a process network is the direction of the material flows in the network; it is directed to an operating unit from its input materials and from an operating unit to its output materials. For example, distillation columns 6 and 9, decantor 29, and two mixers are represented by P-graph in Figure 3. A P-graph is said to be a combinatorially feasible process structure or solution structure if it satisfies the five

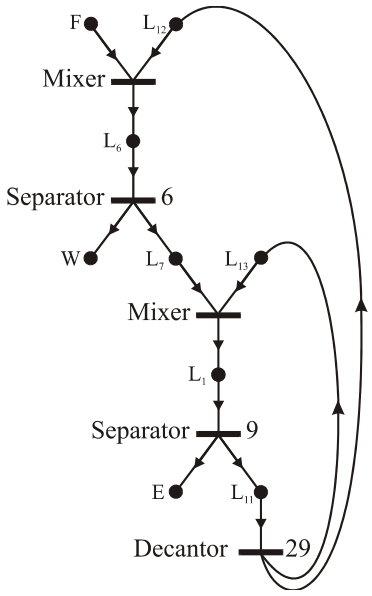

Fig. 3. P-graph representation of a process structure.

axioms (S1) through (S5) of the combinatorially feasible process structures (see, e.g., Friedler *et al.*, 1992 and 1993). Axiom (S1) implies that each product is produced by at least one of the operating units of the system; axiom (S2), a material is not produced by any operating unit of the system if and only if this material is a raw material; axiom (S3), only the plausible operating units of the problem are taken into account in the synthesis; axiom (S4), any operating unit of the system has a series of connections eventually leading to the operating unit generating at least one of the products; and axiom (S5), each material appearing in the system is an input to or an output from at least one operating unit of the system.

The union of all combinatorially feasible process structures is defined to be the maximal structure. The maximal structure of a synthesis problem comprises all the feasible structures capable of yielding the specified products from the specified raw materials. Naturally, the optimal network or structure is among the feasible structures generated from the maximum structure, which is the complete and yet simplest super-structure rigorously defined mathematically. The maximal structure is constructed via algorithm MSG (Friedler *et al.*, 1993). The complete set of the combinatorially feasible process structures or solution structures can be generated by algorithm SSG (Friedler *et al.*, 1995).

To facilitate algorithmic synthesis, the mathematical models are derived for the various operating units involved, i.e., distillation columns, mixers, and decantors, based on RCM's and analytical geometry.

Table 1
Operating units for production of pure ethanol from its aqueous solution with toluene as the entrainer.

#	Type	Input	Outputs
1	distillation	L_1	E, L_7
2	distillation	L_1	E, L_8
3	distillation	L_1	E, L_{10}
4	distillation	L_1	E, L_{11}
5	distillation	L_5	E, L_{10}
6	distillation	L_5	E, L_{11}
7	distillation	L_4	W, L_{10}
8	distillation	L_4	W, L_9
9	distillation	L_6	W, L_7
10	distillation	F	W, L_7
11	distillation	L_2	T, L_8
12	distillation	L_3	T, L_9
13	distillation	L_3	T, L_{11}
14	distillation	L_1	H, L_{18}
15	distillation	L_1	H, L_{19}
16	distillation	L_5	H, L_{18}
17	distillation	L_5	H, L_{19}
18	distillation	L_6	H, L_{14}
19	distillation	L_4	H, L_{14}
20	distillation	L_4	H, L_{15}
21	distillation	L_3	H, L_{16}
22	distillation	L_3	H, L_{17}
23	distillation	L_2	H, L_{17}
24	decanting	L_3	L_{12}, L_{13}
25	decanting	L_4	L_{12}, L_{13}
26	decanting	L_5	L_{12}, L_{13}
27	decanting	L_9	L_{12}, L_{13}
28	decanting	L_{10}	L_{12}, L_{13}
29	decanting	L_{11}	L_{12}, L_{13}
30	decanting	H	L_{12}, L_{13}

The boundaries on RCM's, i.e., the distillation boundaries and the boundaries of liquid-liquid equilibrium envelopes, are often non-linear. The non-linearity of these boundaries leads to the non-linearity of the constraints involved in the mathematical programming problem that need be solved for optimal synthesis. This non-linearity usually gives rise to inordinate difficulty in solution. To circumvent such difficulty, the boundaries are linearized or sectionally-linearized. Note that distillation boundaries and the boundary of liquid-liquid equilibrium envelope in Figure 2 are linearized or sectionally linearized, thereby resulting in Figure 4. The linearized models serve for the structure generation but not for the analysis of

individual structures which need to be evaluated on the basis of the rigorous models to ensure optimality.

The linearized RCM and flow-rate-based representation conceived for separation-network synthesis (Kovacs *et al.*, 2000) render the mathematical models of mixers and separators linear. Moreover, the mathematical models of decantors can be made sufficiently linear. In the flow-rate-based representation, the materials are represented by the flow rates of their components, e.g., M = (M_1, M_2, M_3), where M_1, M_2, and M_3 are the flow rates of the first, second and third components, respectively. The total flow rate is the sum of the flow rates of the components. The mass-balance constraints for the input and output materials of operating units can be written in the form of a simple sum of the vectors representing the materials, e.g., A = B + C or (A_1, A_2, A_3) = (B_1, B_2, B_3) + (C_1, C_2, C_3). If any material M is inside a convex partitioned region, M can be written as a nonnegative linear combination of the vectors of the concentrations of the points, which are at the intersections of the boundaries of the region. For example, $L_6 = v_1w + v_2q + v_3x$, where v_1, v_2, and v_3 are the nonnegative variables (v_1, v_2, $v_3 \geq 0$); and w, q, and x are the constant vectors of the concentrations of points W, Q, and X in Figure 3, respectively. The mathematical model for any operating unit involves the mass-balance constraint and the constraints for its input and output materials. For example, the mathematical model of distillation column 9 consuming L_6 and producing W and L_7 is given in Table 2.

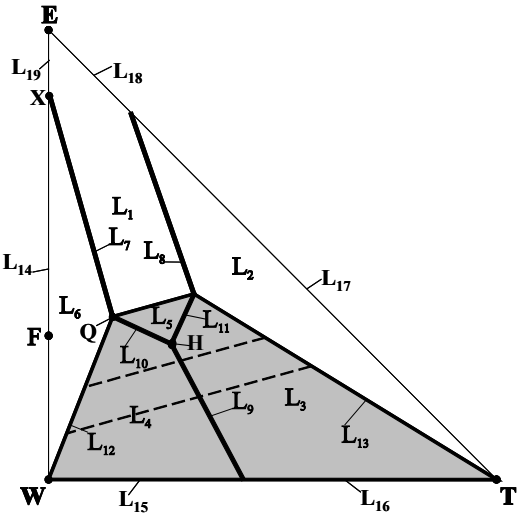

Fig. 4. Linearized RCM.

Table 2
Mathematical model of distillation column 9.

$L_7 = v_1q + v_2x$
$L_6 = v_3w + v_4q + v_5x$
$W = v_6w$
$v_1, v_2, \ldots, v_6 \geq 0$
$W + L_7 = L_6$

The mathematical programming model of a process network includes the constraints for the operating units, e.g., the mathematical models of the operating units, and those for the materials, e.g., the mass-balance constraints or constraints for the products or raw materials. The mathematical models of the operating units defined in the preceding section, i.e., mixers, separators, and decantors are linear, and the flow-rate-based representations of the mass-balance constraints are also linear. Thus, the mathematical-programming model gives rise to a MILP problem which can be solved effectively by the algorithms developed for the P-graph approach.

4. SOLUTION OF THE SYNTHESIS PROBLEM OF PRODUCTION OF PURE ETHANOL FROM ITS AQUEOUS SOLUTION WITH TOLUENE AS THE ENTRAINER

To demonstrate the efficacy of the proposed method, the systematic synthesis of the feasible flowsheets for the 3 component system of ethanol-water-toluene given in Figure 1 has

been solved at the level of linearization given in Figure 3. The resultant synthesis problem is defined on the basis of 24 partitioned regions denoted in Figure 2; it involves 23 separators, 7 decantors, and 593 mixers, thereby yielding altogether 623 operating units. The resultant synthesis problem, however, is extremely complex because of this huge number of candidate operating units. Under the constraint that each process structure contains at most 7 operating units, the implementation of the algorithm has resulted in 15 feasible flowsheets in 130 minutes on a PC (Pentium II. Celeron 366 MHz). One of the feasible structures is represented on RCM in Figure 5 and by P-graph in Figure 3.

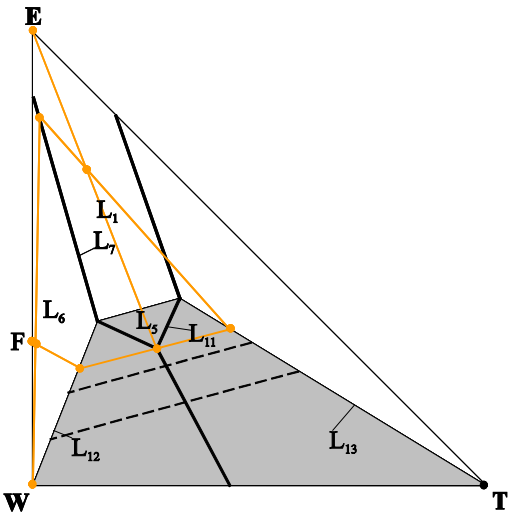

Fig. 5. Feasible structure.

5. CONCLUSION

A systematic method based on the first principles and minimal heuristics has been developed for the algorithmic synthesis of azeotropic-distillation systems. The method is capable of generating the complete set of feasible flowsheets for an azeotropic-distillation system, from which optimal and near-optimal flowsheets emerge once the cost of operating units are appropriately assigned.

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