Sequential Approach to Design Batch Distillation Processes for Homogeneous Azeotropic Systems

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By addressing both flowsheeting and scheduling issues, a systematic approach is developed in this work to design batch azeotropic distillation processes for the homogeneous ternary and quaternary systems. The proposed design strategy is implemented sequentially in three stages. First, an integer program (IP) is formulated for producing the optimal structure of state-task network (STN). A nonlinear program (NLP) is then developed to generate the corresponding material-balance constraints. In the final step, a mixed integer linear programming (MILP) model and a mixed integer nonlinear programming (MINLP) model are constructed for stipulating the optimal short-term and cyclic schedules respectively. The conventional concept of event points is adopted to facilitate the continuous-time representation in these model formulations. The implementation procedure is illustrated with two example systems in this paper. Satisfactory process configurations and production schedules can both be produced in all the cases we have studied so far.

1. Introduction

Distillation is one of the most popular separation methods used in the chemical process industries. Since it is accomplished mainly by exploiting the difference between the volatilities of light and heavy keys, it is clearly not possible to break down an azeotrope with a single ordinary distillation operation. In practice, this problem may be overcome by using a pressure-swing column, or by introducing an entrainer, extracting solvent, or ionic salt, that could change the vapor−liquid equilibrium (VLE) properties. To avoid addressing these diversified issues in one study, the scope of present work is limited to those achieved with entrainers. Furthermore, it is assumed that the feed and products of a distillation operation are always located within the same region enclosed by distillation boundaries. Notice that this assumption may not hold if one or more boundary exhibits extreme curvature. However, since the design, operation and control of the corresponding separation processes can be very difficult, such options are therefore excluded in the present study.

The design of azeotropic distillation processes has always been an important research issue. Stichlmair et al.[1] evaluated and developed an entrainer-selection method for any given system. Stichlmair and Herguijuela[2] later exploited the notion of *preferred separation*, which could be used for handling mixtures with several azeotropes and complex boundary structures. It should also be noted that separation techniques other than distillation were also considered in this study. Pham and Doherty[3] proposed a framework for synthesizing azeotropic distillation processes according to estimated minimum reflux ratios. Wahnschafft et al.[4] employed a concept called "operation leaves" to check split feasibility on the basis of residue curves and distillation line maps. Fidkowski et al.[5] developed a calculation procedure to determine the equilibrium compositions of azeotropes. Fien and Liu[6] presented a detailed review concerning the use of ternary composition diagrams and residue curve maps (RCMs) for heuristic synthesis and shortcut design of the multicomponent separation processes. Bauer and Stichlmair[7] formulated a MINLP model to generate the optimal

azeotropic distillation processes. Their model was developed with a superstructure called MESH, in which all thermodynamically preferred columns were embedded. Thong and Jobson[8−10] proposed a systematic design method to generate not only the azeotropic distillation processes but also their detailed equipment specifications. A heuristic synthesis procedure was also proposed in a later study by Thong et al.[11] Feng et al.[12] used a graphical technique to identify all possible operations in an azeotropic distillation system by resorting to the first principles and by logically sequencing such units. Additional works were also carried out to combinatorially generate all feasible sequences via a P-graph-based approach.[13] Finally, advances in the related theories and applications have been thoroughly reviewed by Doherty and Malone.[14]

Since the aforementioned publications are all concerned with the *continuous* azeotropic distillation processes, it is thus desirable to extend the existing design methods for applications in *batch* systems. To this end, it should be first noted that a large number of generalized scheduling models have already been developed. For example, Papageorgaki and Reklaitis[15] proposed a MINLP model to generate the optimal schedules for multiproduct batch processes; Kondili et al.[16] solved this problem with a MILP program; Kim and Moon[17] synthesized the multipurpose schedules with symbolic model verifier (SMV). It is worth noting that the mathematical program reported in Kondili et al.[16] was formulated according to the so-called state-task network (STN) with discrete-time representation. Ierapetritou and Floudas[18,19] later proposed a STN-based MILP model for producing an optimal batch schedule. An equivalent resource task network (RTN) representation was proposed by Pantelides.[20] Zhang and Sargent[21,22] provided a unified mathematical formulation to determine the optimal operating conditions of RTN in continuous-time representation. The STN-based model later became a popular choice for many scheduling applications due to its capability to capture the equipment-sharing possibilities. Various other mathematical programs have also been constructed accordingly, e.g., Shah et al.[23] and Maravelias and Grossmann.[24] An overview of the continuous-time versus discrete-time approaches for scheduling multiproduct and/or multipurpose batch processes was presented by Floudas.[25] Finally, a STN-based cyclic scheduling strategy has also been

proposed by Wu and Ierapetritou.[26] They essentially modified the aforementioned short-term model[18] with additional constraints to accommodate the unique requirements in periodic operations.

From the above discussions, it is obvious that a specific state-task network must be created before constructing the schedule-generating models. There are in fact an extremely large number of alternative means to break up an azeotrope. Since it is impractical to incorporate all of them in a mathematical program, a systematic screening procedure is needed to select an appropriate STN first. To this end, any given azeotrope−entrainer system is divided in this study into a finite number of *lumped materials* according to a modified version of the classification method suggested by Feng et al.[12] On the basis of this classification scheme, all possible operations can then be identified easily by inspection. Although this classification approach can be applied to both homogeneous and heterogeneous systems, the scope in the present paper is limited to the former case for the sake of conciseness. Consequently, there can be only two types of feasible batch operations in each case study discussed in this paper, i.e., distillation and mixing. The former operation splits one material into two (or more), while the latter combines several into one. In fact, a few heuristic search techniques have already been proposed to generate a *continuous* flowsheet on the basis of these feasible operations, e.g., Friedler et al.[27−29] It should be noted that multiple feasible (but not optimal) solutions of a given design problem may be produced with these approaches.[12] To synthesize the "optimal" STN structures for the present applications, the logic-oriented approach suggested by Raman and Grossmann[30,31] has been adopted. In particular, an integer program has been developed to represent the inferential relationship and to determine the best process configuration. In addition, a nonlinear programming model has been formulated on the basis of this configuration for establishing the corresponding material-balance constraints needed in the subsequent scheduling computation. It should be pointed out that this critical step in finalizing STN was usually carried out by hand in an *ad hoc* fashion in the past.

In summary, a sequential synthesis and scheduling approach is followed in the present work to design the batch azeotropic distillation processes. An appropriate STN configuration is first selected with an IP model. The corresponding material-balance data are then generated accordingly with a NLP model. Finally, the optimal short-term (or cyclic) schedule is produced on the basis of the event-point based MILP (or MINLP) model. Details on system classification, STN identification, material-balance specification, and schedule synthesis are discussed in following sections. Two examples are provided to illustrate the model construction procedures and also to demonstrate the benefits of the proposed approach.

2. System Classification

In this study, the residue curve maps (RCMs) and the iso-volatility curves, i.e., the so-called distillation boundaries, are assumed to be available for the homogeneous systems under study. As mentioned previously, since an infinite number of mixtures can be identified in a multicomponent system, there is a need to divide the corresponding RCM into a finite set of regions, areas, lines, and points and treat each of them as a "lumped" materials. The partition approach suggested by Feng et al.[12] has been simplified to reduce the implementation effort. The general principles of this approach are outlined below:

Table 1. Thermophysical Data of the Acetone (A)−Ethanol (E)−Chloroform (C) System

component name	boiling point
acetone unstable node (low-boiling)	55.86 °C
ethanol stable node (high-boiling)	78.02 °C
chloroform saddle point (intermediate)	60.75 °C

Three Azeotropes Sorted by Temperature			
azeotrope number 1	mole-basis	mass-basis	
ethanol	0.141	0.060	59.10 °C
chlf	0.859	0.94	
azeotrope number 2	mole-basis	mass-basis	
acetone	0.341	0.236	62.52 °C
ethanol	0.200	0.110	
chlf	0.459	0.653	
azeotrope number 3	mole-basis	mass-basis	
acetone	0.381	0.230	64.24 °C
chlf	0.619	0.770	

(a) Approximate the critical surfaces and curves, i.e., the distillation boundaries and pseudoboundaries, with flat planes and straight lines.

(b) Divide the ternary or quaternary systems into distinct triangular areas or pyramid regions based on the approximated boundaries.

(c) Carry out further partition to ensure the uniqueness of intermediate products obtained from separation operations.

The specific partitioning steps for typical ternary and quaternary systems are described with specific examples in the sequel.

2.1. Lumped Materials in Ternary Systems. Let us consider the homogeneous mixture of acetone (A), ethanol (E), and chloroform (C). The thermophysical data presented in Table 1 were obtained on the basis of the UNIFAC model and Figure 1a was generated accordingly. The compositions of binary azeotropes are associated with points W and Y, respectively, while that of three-component azeotrope is located at X. The curves AX, EX, WX, and XY are the ASPEN-generated distillation boundaries. In region XYCWX, the lowest and highest bubble temperatures occur at points W (59.10 °C) and Y (64.24 °C), respectively. Since line YW line cannot be crossed with batch distillation, it is thus regarded as a *pseudoboundary*. By approximating these boundaries with straight lines, Figure 1a can be converted to Figure 1b. Notice that five distinct regions, which are labeled respectively as L_1, L_2, $L_{3,1}$, $L_{3,2}$, and L_4, can be identified on the basis of the straight boundary lines. The first subscript of each label denotes a region bounded by the approximated distillation boundaries, while the second subscript (if present) indicates that the region is separated by an additional pseudoboundary.

A total of 30 lumped materials have been identified in this system. The lumped materials corresponding to the above-mentioned regions are listed in rows 18−22 in Table 2. The compositions of first three materials in the same table, i.e., A, E, and C, are located at the three apexes in Figure 1b. The material F represents the feed to the distillation system, which can be placed on the line AY. The next five lumped materials, i.e., AE, AY, CW, CY, and EW, are system boundaries which can be produced with single-cut batch distillation.

It should be noted that the singular points, i.e., W, X, and Y, can only be approached (but not reached) in actual distillation operations. Therefore, to be able to unambiguously represent the lumped materials with compositions approaching that of an azeotrope, an extra index is needed to indicate its origin of
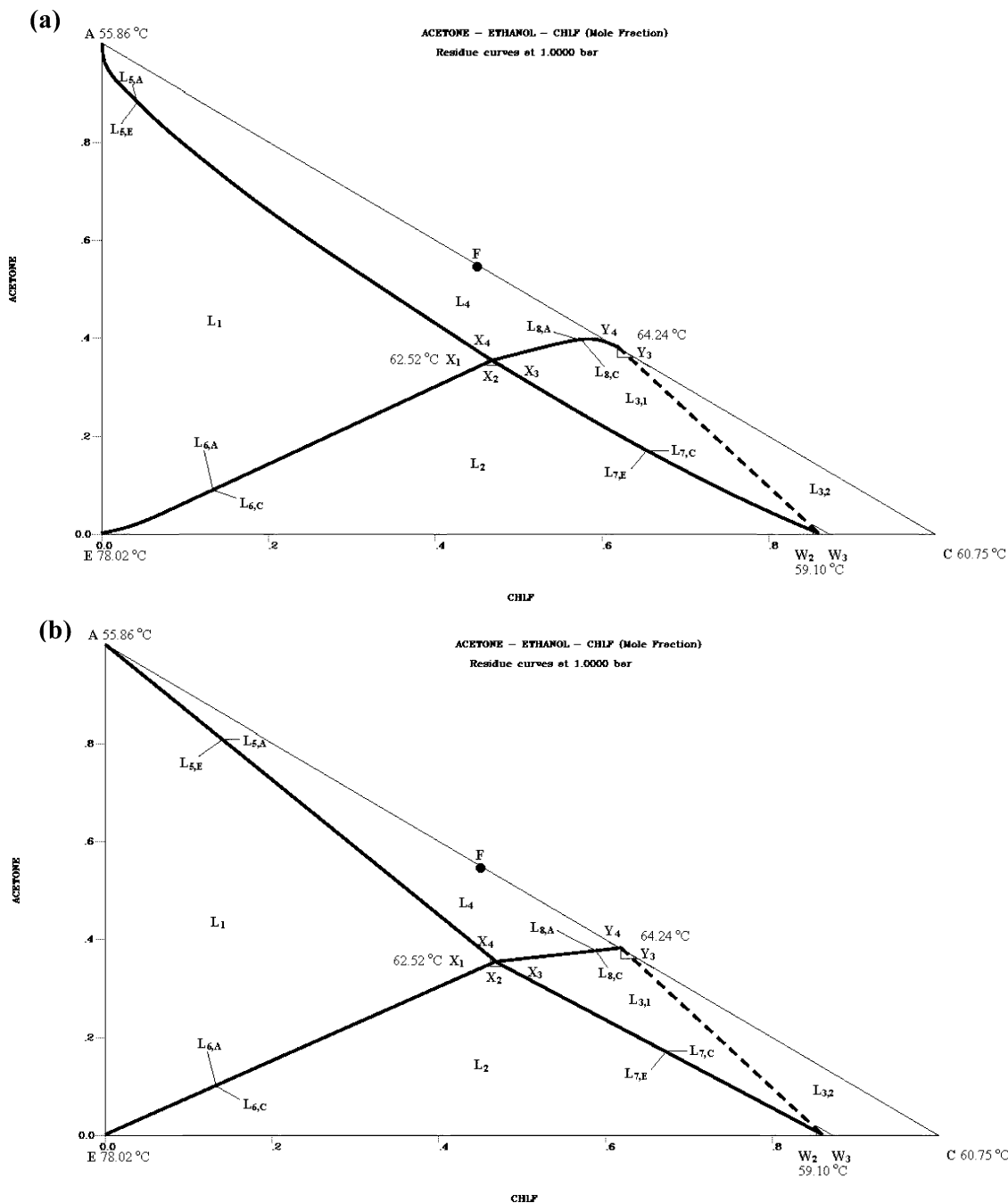
(a)

(b)

Figure 1. (a) RCM of the acetone (A)−ethanol (E)−chloroform (C) system: F, feed; W, Y, binary azeotropes; X, ternary azeotrope. (b) RCM of the acetone (A)−ethanol (E)−chloroform (C) system: F, feed; W, Y, binary azeotropes; X, ternary azeotrope with linear approximation.

production (rows 10−17 in Table 2). More specifically, let us consider azeotrope W as an example. Since the corresponding singular point could be approached in a batch distillation process with a feed located in either region L_2 or region L_3, the corresponding lumped materials are thus denoted as W_2 and W_3, respectively.

Since the compositions on the distillation boundaries are also unreachable in practical operations, the corresponding materials (which could be referred to respectively as L_5, L_6, L_7, and L_8) are not considered in this study as the candidates of inputs and/or outputs of plausible operations. Instead, mixtures with compositions in the neighboring areas of each distillation boundary are treated as possible lumped materials. A second subscript, i.e., A, E, or C, is thus added to the aforementioned boundary labels to reflect their relative positions (see rows

23−30). For example, $L_{6,A}$ in row 25 of Table 2 denotes the area next to boundary EX which is also facing apex A.

2.2. Lumped Materials in Quaternary Systems. The partition method described above can be extended to the quaternary systems. For illustration convenience, let us also consider a specific example in which the homogeneous four-component mixtures are formed with acetone (A), ethanol (E), chloroform (C), and benzene (B). The corresponding thermophysical data (see Table 3) were also obtained on the basis of the UNIFAC model. The simplified quaternary pyramid diagram is presented in Figure 2, while its four different faces are given in Figures 3−6, respectively. The binary azeotropes of ethanol−benzene, acetone−chloroform, and ethanol−chloroform are labeled as W, Y, and Z, respectively, while the ternary azeotrope of acetone−ethanol−chloroform is denoted by X. No quaternary

Table 2. Lumped Materials in the Acetone (A)−Ethanol (E)−Chloroform (C) System

index	partitioned materials	Area represented
1	A	A
2	C	C
3	E	E
4	F	F
5	AE	AE
6	AY	AY
7	CW	CW
8	CY	CY
9	EW	EW
10	W_2	W_2
11	W_3	W_3
12	X_1	X_1
13	X_2	X_2
14	X_3	X_3
15	X_4	X_4
16	Y_3	Y_3
17	Y_4	Y_4
18	L_1	AEXA
19	L_2	EWXE
20	$L_{3,1}$	WXYW
21	$L_{3,2}$	CWYC
22	L_4	AXYA
23	$L_{5,A}$	AX_4
24	$L_{5,E}$	AX_3
25	$L_{6,A}$	EX_1
26	$L_{6,C}$	EX_2
27	$L_{7,C}$	WX_3
28	$L_{7,E}$	WX_2
29	$L_{8,A}$	XY_4
30	$L_{8,C}$	XY_3

Table 3. Thermophysical Data of the Acetone (A)−Ethanol (E)−Chloroform (C)−Benzene (B) System

component name	boiling point
acetone unstable node (low-boiling)	55.86 °C
ethanol stable node (high-boiling)	78.02 °C
chloroform saddle point (intermediate)	60.75 °C
benzene stable node (high-boiling)	79.72 °C

Four Azeotropes Sorted by Temperature:

azeotrope number 1	mole-basis	mass-basis	
ethanol	0.141	0.059	59.10 °C
chlf	0.859	0.941	

azeotrope number 2	mole-basis	mass-basis	
acetone	0.341	0.236	62.52 °C
ethanol	0.200	0.110	
chlf	0.459	0.653	

azeotrope number 3	mole-basis	mass-basis	
acetone	0.381	0.230	64.24 °C
chlf	0.619	0.770	

azeotrope number 4	mole-basis	mass-basis	
ethanol	0.448	0.324	67.10 °C
benzene	0.552	0.676	

Figure 2. RCM of the acetone (A)−ethanol (E)−chloroform (C)−benzene (B) system: W, Y, and Z, binary azeotropes; X, ternary azeotrope.

Figure 3. RCM of the acetone (A)−benzene (B)−chloroform (C) system: Y, binary azeotrope.

Figure 4. RCM of the acetone (A)−benzene (B)−ethanol (E) system: W, binary azeotrope.

azeotropes can be detected with the UNIFAC model. From Figures 3 and 4, it can be observed that lines BY and AW represent the distillation boundaries on faces ABC and ABE respectively. On face AEC of the pyramid (see Figure 5), lines XY, XZ, XA, and XE represent the distillation boundaries, while YZ is a pseudoboundary which cannot be crossed with batch distillation. To be more specific, it should be noted that the bubble points of mixtures at C, X, Y, and Z are 60.75, 62.52, 64.24, and 59.10 °C respectively and, thus, line YZ connects
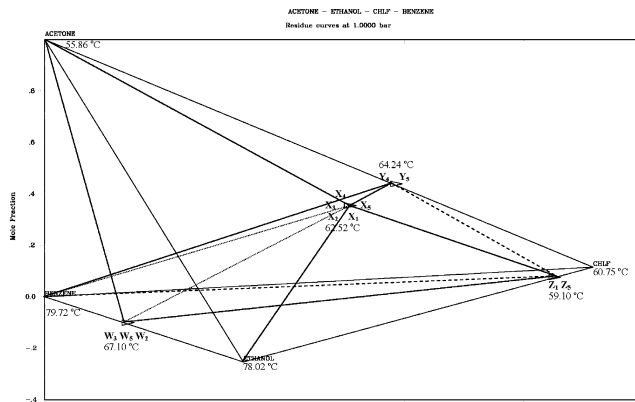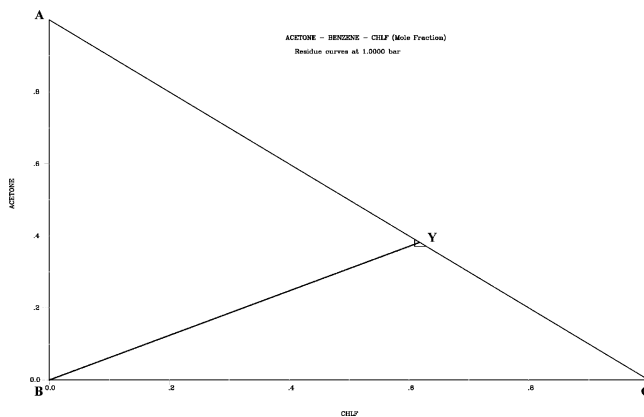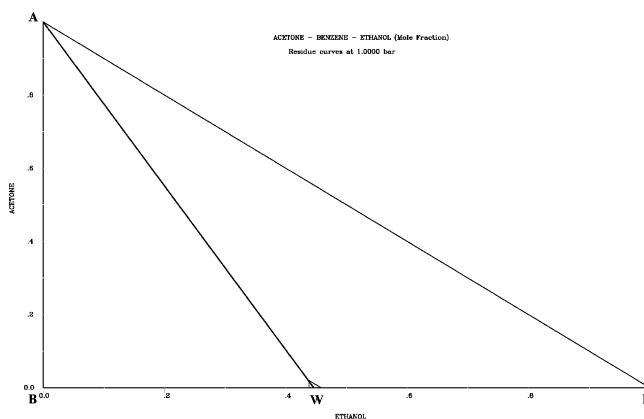
the two points associated with the most extreme temperatures in CXYZ. Notice also that, in each of the two subregions divided by YZ, the mixture at any location can be used to produce the same set of products by batch distillation. Finally, in Figure 6, lines WZ and BZ on face BEC denote respectively the predicted boundary and pseudoboundary.

Since only the distillation boundaries on the four faces of quaternary pyramid can be generated with commercial software, it is postulated in this study that the interior triangular planes ABX, AWX, BWX, BXY, EWX, and WXZ can be treated as the *approximate* locations of three-dimensional distillation boundaries, and BXZ and BYZ can be regarded as the 3D pseudoboundaries. These postulated planes are adopted in such
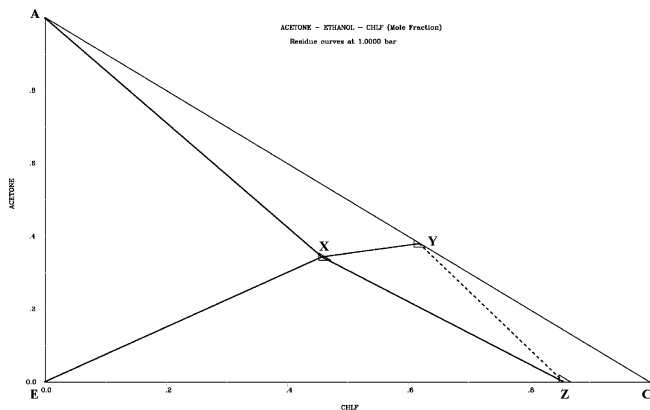
Figure 5. RCM of the acetone (A)−ethanol (E)−chloroform (C) system: Y, and Z, binary azeotropes; X, ternary azeotrope.
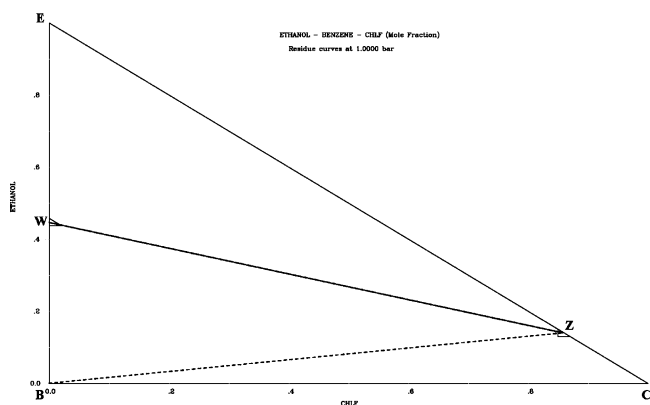

Figure 6. RCM of the ethanol (E)−benzene (B)−chloroform (C) system: W and Z, binary azeotropes.

a way that all ternary distillation boundaries and pseudoboundaries are matched at the four faces of pyramid. Notice that a pseudoboundary plane is defined in this work as a triangular area which is bounded by at least one pseudoboundary line on the pyramid surface. The quaternary system can thus be divided into seven pyramid regions labeled respectively as L_1 (EWXZE), L_2 (AEWXA), L_3 (ABWXA), L_4 (ABXYA), $L_{5,1}$ (BCYZB), $L_{5,2}$ (BXYZB), and $L_{5,3}$ (BWXZB). Notice that a total of five numerical labels, i.e., 1−5, are used as the first subscript to distinguish the regions separated by the postulated distillation boundaries. A second subscript, i.e., 1, 2, or 3, is then introduced to indicate that the region is bounded by at least one pseudoboundary. For example, $L_{5,1}$ denotes the first subregion in L_5 defined by introducing pseudoboundary BYZ.

A total of 55 lumped materials have been identified (see Table 4). Notice that the compositions of the first four materials, i.e., A, E, C, and B, are associated with the four apexes of the system pyramid. Let us assume that ethanol (E) is the entrainer in this example, and thus, feed must be located on face ABC. More specifically, it should be within ABY since it is the only area suitable for ethanol to pull across the interior distillation boundaries.

By adopting the same convention used in the previous subsection, additional subscripts are attached to the labels of azeotropes W, X, Y, and Z to indicate their origins of production. The single-cut distillation operations could obviously be used to produce three-component mixtures on the pyramid surface. These possible products are labeled with three capital alphabets and one or more subscript to denote the originating region. For example, AXY_4 is the lumped material (on plane AXY) produced by single-cut distillation from feed in region

Table 4. Partitioned Materials in Acetone (A)−Ethanol (E)−Chloroform (C)−Benzene (B) System

index	partitioned materials	area represented	index	partitioned materials	area represented
1	A	A	29	XZ_1	XZ_1
2	B	B	30	XZ_5	XZ_5
3	C	C	31	AXY_4	AXY_4
4	E	E	32	BCY_5	BCY_5
5	F	F	33	BXZ	BXZ
6	W_1	W_1	34	BYZ	BYZ
7	W_2	W_2	35	CYZ_5	CYZ_5
8	W_3	W_3	36	XYZ_5	XYZ_5
9	W_5	W_5	37	L_1	EWXZE
10	X_1	X_1	38	L_2	AEWXA
11	X_2	X_2	39	L_3	ABWXA
12	X_3	X_3	40	L_4	ABXYA
13	X_4	X_4	41	$L_{5,1}$	BCYZB
14	X_5	X_5	42	$L_{5,2}$	BXYZB
15	Y_4	Y_4	43	$L_{5,3}$	BWXZB
16	Y_5	Y_5	44	$L_{6,A}$	EWX_2
17	Z_1	Z_1	45	$L_{6,C}$	EWX_1
18	Z_5	Z_5	46	$L_{7,B}$	AWX_3
19	AX_2	AX_2	47	$L_{7,E}$	AWX_2
20	AX_3	AX_3	48	$L_{8,C}$	ABX_4
21	AX_4	AX_4	49	$L_{8,E}$	ABX_3
22	BW_3	BW_3	50	$L_{9,A}$	BWX_3
23	BW_5	BW_5	51	$L_{9,C}$	BWX_5
24	BY_4	BY_4	52	$L_{10,A}$	BXY_4
25	BY_5	BY_5	53	$L_{10,C}$	BXY_5
26	CZ_5	CZ_5	54	$L_{11,C}$	WXZ_5
27	EW_1	EW_1	55	$L_{11,E}$	WXZ_1
28	EW_2	EW_2			

L_4. Notice that some of the surface regions are excluded from Table 4 since they cannot be generated with single-cut distillation. In a similar fashion, the 2-component mixtures produced by the two-cut distillation operations are referred to with two capital alphabets and one or more numerical subscript. For example, AX_2 is the lumped material (on line AX) produced by two-cut distillation from region L_2.

The lumped materials with compositions on the interior distillation boundaries are referred to as L_6, L_7, L_8, L_9, L_{10}, and L_{11}, respectively. A second subscript, i.e., A, B, C, or E, is added to reflect the relative position of a neighboring area. For example, $L_{6,A}$ in row 44 of Table 4 denotes the region close to plane EWX which is also facing apex A.

3. Identification of Plausible Operations

Only two different types of batch operations, i.e., mixing and distillation, are considered for processing the homogeneous mixtures. Since the conventional approach[12,32] was developed primarily for the continuous processes, it is necessary to provide additional options in the present study to facilitate selection of operation type, i.e., rectification or stripping, and also the cut number for every batch distillation operation. To limit the search space, the candidate operations are chosen according to the following criteria:

  (a) The number and compositions of distillation products are dependent upon the selected operation type and cut number. Each product must be located at a singular point, on a distillation boundary, or on a bounding surface.
  (b) The lumped materials in the same region (bounded by the same set of distillation boundaries) are not allowed to be mixed.
  (c) No mixing operation yields any lumped material associated with a singular point, distillation boundary, or bounding surface.

Notice that several alternatives can be considered on the basis of criterion a. Since the distillation products can always be

Table 5. Plausible Operations of the Acetone (A)-ethanol (E)-chloroform (C) system

index	operation	type	index	operation	type
1	$(\{L_1\}, \{A, L_{6,A}\})$	1-cut rectification	27	$(\{L_{5,A}, L_{6,C}\}, \{L_1\})$	mixing
2	$(\{L_1\}, \{E, L_{5,E}\})$	1-cut stripping	28	$(\{L_{5,A}, E\}, \{L_1\})$	mixing
3	$(\{L_1\}, \{A, E, X_1\})$	2-cut rectification/stripping	29	$(\{L_{5,E}, L_{7,E}\}, \{L_{3,1}\})$	mixing
4	$(\{L_2\}, \{W_2, L_{8,C}\})$	1-cut rectification	30	$(\{L_{5,E}, L_{7,E}\}, \{L_4\})$	mixing
5	$(\{L_2\}, \{E, L_{7,E}\})$	1-cut stripping	31	$(\{L_{5,E}, L_{8,C}\}, \{L_4\})$	mixing
6	$(\{L_2\}, \{E, W_2, X_2\})$	2-cut rectification/stripping	32	$(\{L_{5,E}, F\}, \{L_4\})$	mixing
7	$(\{L_{3,1}\}, \{W_3, L_{8,C}\})$	1-cut rectification	33	$(\{L_{5,E}, W_2\}, \{L_{3,1}\})$	mixing
8	$(\{L_{3,1}\}, \{Y_3, L_{7,C}\})$	1-cut stripping	34	$(\{L_{5,E}, W_2\}, \{L_4\})$	mixing
9	$(\{L_{3,1}\}, \{W_3, X_3, Y_3\})$	2-cut rectification/stripping	35	$(\{L_{5,E}, Y_3\}, \{L_4\})$	mixing
10	$(\{L_{3,2}\}, \{W_3, YC\})$	1-cut rectification	36	$(\{L_{6,A}, L_{7,C}\}, \{L_2\})$	mixing
11	$(\{L_{3,2}\}, \{Y_3, WC\})$	1-cut stripping	37	$(\{L_{6,A}, L_{8,A}\}, \{L_2\})$	mixing
12	$(\{L_{3,2}\}, \{C, W_3, Y_3\})$	2-cut rectification/stripping	38	$(\{L_{6,A}, L_{8,A}\}, \{L_{3,1}\})$	mixing
13	$(\{L_4\}, \{A, L_{8,A}\})$	1-cut rectification	39	$(\{L_{6,A}, W_3\}, \{L_2\})$	mixing
14	$(\{L_4\}, \{Y_4, L_{5,A}\})$	1-cut stripping	40	$(\{L_{6,A}, Y_4\}, \{L_2\})$	mixing
15	$(\{L_4\}, \{A, X_4, Y_4\})$	2-cut rectification/stripping	41	$(\{L_{6,A}, Y_4\}, \{L_{3,1}\})$	mixing
16	$(\{E, F\}, \{L_1\})$	mixing	42	$(\{L_{6,C}, F\}, \{L_1\})$	mixing
17	$(\{E, F\}, \{L_4\})$	mixing	43	$(\{L_{6,C}, F\}, \{L_4\})$	mixing
18	$(\{E, Y_4\}, \{L_2\})$	mixing	44	$(\{L_{7,C}, E\}, \{L_2\})$	mixing
19	$(\{E, Y_4\}, \{L_3\})$	mixing	45	$(\{L_{7,E}, L_{8,A}\}, \{L_{3,1}\})$	mixing
20	$(\{F, W_2\}, \{L_{3,1}\})$	mixing	46	$(\{L_{7,E}, F\}, \{L_{3,1}\})$	mixing
21	$(\{F, W_2\}, \{L_4\})$	mixing	47	$(\{L_{7,E}, F\}, \{L_4\})$	mixing
22	$(\{F, X_1\}, \{L_4\})$	mixing	48	$(\{L_{7,E}, Y_4\}, \{L_{3,1}\})$	mixing
23	$(\{F, X_2\}, \{L_4\})$	mixing	49	$(\{L_{8,A}, E\}, \{L_2\})$	mixing
24	$(\{F, X_3\}, \{L_4\})$	mixing	50	$(\{L_{8,A}, E\}, \{L_{3,1}\})$	mixing
25	$(\{F, Y_3\}, \{L_4\})$	mixing	51	$(\{L_{8,A}, W_2\}, \{L_{3,1}\})$	mixing
26	$(\{W_2, Y_4\}, \{L_{3,1}\})$	mixing	52	$(\{L_{8,C}, F\}, \{L_4\})$	mixing

driven closer to the thermodynamic pinches with a larger column, the highest possible degree of separation is therefore assumed at this early stage of process design. On the other hand, since the partitioned regions are bounded by the distillation boundaries, the lumped materials in the same region are considered to be identical from the standpoint of serving as the feed to a mixer. Thus, criterion b is justifiable since no real advantage can be gained by blending the "identical" materials. Finally, criterion c is adopted on the ground that it is extremely difficult, if not impossible, to control the operation of the mixer so that the blended product is exactly at the geometrically singular locations.

In addition to the above-mentioned constraints, three auxiliary selection criteria can also be used to further simplify the search problem:

(d) Exactly two lumped materials are mixable.

(e) A desired product cannot be mixed with any other material.

(f) The product from any mixer is not allowed to be fed to another mixer.

Criteria d and e may be regarded as simplifications needed to avoid unnecessary operation steps. Criterion f is reasonable since mixing inevitably leads to an increase in entropy or dissipation of available energy and, thus, a larger number of such operations should definitely cause a greater loss of available energy. Moreover, any gain from repetitive mixing tends to be nullified by the accompanying mechanical and operational complications.

The plausible operations identified for the two example systems described in section 2 are presented in Tables 5 and 6. In these two tables, every operation is represented by the symbol($\{\cdots\}, \{\cdots\}$), in which the two curly brackets represent sets of inputs and outputs respectively. Notice that the operations listed in each table can be divided into three general categories as follows:

• **Indispensable Operations.** The operations necessary for producing the desired products should be identified at the outset. A distillation operation is used for this purpose in most cases and its products and feed are assumed to be located in the same

subregion created by distillation boundaries and/or pseudoboundaries. Thus, these indispensable operations should be determined by examining the topology of RCM on a case-by-case basis.

It can be observed from Figure 1b that the desired products, i.e., acetone (A) and ethanol–chloroform azeotrope (W), are situated in subregions AEXYA and CEXYC, respectively. Hence, the input and outputs of any batch distillation operation yielding product A must all be located in AEXYA. Similarly, the feed to and the products from any operation producing W must all be located in CEXYC. Thus, the plausible operations for producing acetone (A) are the distillation operations ($\{L_1\}$, $\{A, L_{6,A}\}$), ($\{L_1\}$, $\{A, E, X_1\}$), ($\{L_4\}$, $\{A, L_{8,A}\}$), and ($\{L_4\}$, $\{A, X_4, Y_4\}$). Similarly, the plausible operations for producing the ethanol–chloroform azeotrope (W) are ($\{L_2\}$, $\{W_2, L_{8,C}\}$), ($\{L_2\}$, $\{E, W_2, X_2\}$), ($\{L_{3,1}\}$, $\{W_3, L_{8,C}\}$), ($\{L_{3,1}\}$, $\{W_3, X_3, Y_3\}$), ($\{L_{3,2}\}$, $\{W_3, YC\}$), and ($\{L_{3,2}\}$, $\{C, W_3, Y_3\}$). Notice that the same approach can also be applied to the quaternary system in Figure 2.

• **Operations for Generating the Feeds to the Indispensable Ones.** Mixing is the principal means used in the azeotropic distillation system for producing the feeds to the indispensable operations. This is because the feeds and products of each of these operations can be made to be located in two distinct neighboring regions. Due to criterion f, only the lumped material representing a point, a boundary line, or a boundary plane can be fed into the mixers producing such feeds. It is required in this study that one of the mixer feeds must be associated with an area which is adjacent to the boundary between the aforementioned two neighboring regions. Thus, the mixing product considered here should always be located in the same region where the other feed is also present. To put it differently, the mixing operation that "moves" one of the feeds across the far-side boundary of a region is not permissible in this work. Notice that this restriction is imposed mainly to avoid consuming a unnecessarily large amount of entrainer for the purpose of producing the feeds to the indispensable operations.

For the homogeneous ternary system of acetone–ethanol–chloroform, the feeds to the indispensable operations are L_1, L_2, $L_{3,1}$, $L_{3,2}$, and L_4, and they can only be generated with

Table 6. Plausible Operations of the Acetone (A)−Ethanol (E)−Chloroform (C)−Benzene (B) System

index	operating unit	type	index	operating unit	type
1	$(\{L_1\}, \{Z_1, L_{6,C}\})$	1-cut rectification	167	$(\{Y_5, L_{7,E}\}, \{L_3\})$	mixing
2	$(\{L_1\}, \{Z_1, X_1, EW_1\})$	2-cut rectification	168	$(\{Y_5, L_{9,A}\}, \{L_{5,3}\})$	mixing
3	$(\{L_1\}, \{Z_1, X_1, W_1, E\})$	3-cut rectification/stripping	169	$(\{Y_5, L_{6,A}\}, \{L_1\})$	mixing
4	$(\{L_1\}, \{E, L_{11,E}\})$	1-cut stripping	170	$(\{Y_5, L_{6,A}\}, \{L_{5,3}\})$	mixing
5	$(\{L_1\}, \{E, W_1, XZ_1\})$	2-cut stripping	171	$(\{Y_5, L_{11,E}\}, \{L_{5,3}\})$	mixing
6	$(\{L_2\}, \{A, L_{6,A}\})$	1-cut rectification	172	$(\{AX_2, BW_5\}, \{L_3\})$	mixing
7	$(\{L_2\}, \{A, X_2, EW_2\})$	2-cut rectification	173	$(\{AX_2, BY_5\}, \{L_4\})$	mixing
8	$(\{L_2\}, \{A, X_2, W_2, E\})$	3-cut rectification/stripping	174	$(\{AX_2, BCY_5\}, \{L_4\})$	mixing
9	$(\{L_2\}, \{E, L_{7,E}\})$	1-cut stripping	175	$(\{AX_2, BCY_5\}, \{L_{5,2}\})$	mixing
10	$(\{L_2\}, \{E, W_2, AX_2\})$	2-cut stripping	176	$(\{AX_2, L_{9,C}\}, \{L_3\})$	mixing
11	$(\{L_3\}, \{A, L_{9,A}\})$	1-cut rectification	177	$(\{AX_2, L_{10,C}\}, \{L_4\})$	mixing
12	$(\{L_3\}, \{A, X_3, BW_3\})$	2-cut rectification	178	$(\{AX_2, L_{11,E}\}, \{L_3\})$	mixing
13	$(\{L_3\}, \{A, X_3, W_3, B\})$	3-cut rectification/stripping	179	$(\{AX_2, L_{11,E}\}, \{L_4\})$	mixing
14	$(\{L_3\}, \{B, L_{7,B}\})$	1-cut stripping	180	$(\{AX_2, L_{11,E}\}, \{L_{5,2}\})$	mixing
15	$(\{L_3\}, \{B, W_3, AX_3\})$	2-cut stripping	181	$(\{AX_2, L_{11,E}\}, \{L_{5,3}\})$	mixing
16	$(\{L_4\}, \{A, L_{10,A}\})$	1-cut rectification	182	$(\{AX_3, BY_5\}, \{L_4\})$	mixing
17	$(\{L_4\}, \{A, X_4, BY_4\})$	2-cut rectification	183	$(\{AX_3, EW_1\}, \{L_2\})$	mixing
18	$(\{L_4\}, \{A, X_4, Y_4, B\})$	3-cut rectification/stripping	184	$(\{AX_3, BCY_5\}, \{L_4\})$	mixing
19	$(\{L_4\}, \{B, AXY_4\})$	1-cut stripping	185	$(\{AX_3, BCY_5\}, \{L_{5,2}\})$	mixing
20	$(\{L_4\}, \{B, Y_4, AX_4\})$	2-cut stripping	186	$(\{AX_3, L_{10,C}\}, \{L_4\})$	mixing
21	$(\{L_{5,1}\}, \{Z_5, NCY_5\})$	1-cut rectification	187	$(\{AX_3, L_{6,C}\}, \{L_2\})$	mixing
22	$(\{L_{5,1}\}, \{Z_5, C, BY_5\})$	2-cut rectification	188	$(\{AX_3, L_{11,E}\}, \{L_4\})$	mixing
23	$(\{L_{5,1}\}, \{Z_5, C, Y_5, B\})$	3-cut rectification/stripping	189	$(\{AX_3, L_{11,E}\}, \{L_{5,2}\})$	mixing
24	$(\{L_{5,1}\}, \{B, CYZ_5\})$	1-cut stripping	190	$(\{AX_3, L_{11,E}\}, \{L_{5,3}\})$	mixing
25	$(\{L_{5,1}\}, \{B, Y_5, CZ_5\})$	2-cut stripping	191	$(\{AX_4, BW_5\}, \{L_3\})$	mixing
26	$(\{L_{5,2}\}, \{Z_5, L_{10,C}\})$	1-cut rectification	192	$(\{AX_4, EW_1\}, \{L_2\})$	mixing
27	$(\{L_{5,2}\}, \{Z_5, X_5, BY_5\})$	2-cut rectification	193	$(\{AX_4, BCY_5\}, \{L_{5,2}\})$	mixing
28	$(\{L_{5,2}\}, \{Z_5, X_5, Y_5, B\})$	3-cut rectification/stripping	194	$(\{AX_4, L_{9,C}\}, \{L_3\})$	mixing
29	$(\{L_{5,2}\}, \{B, XYZ_5\})$	1-cut stripping	195	$(\{AX_4, L_{6,C}\}, \{L_2\})$	mixing
30	$(\{L_{5,2}\}, \{B, Y_5, XZ_5\})$	2-cut stripping	196	$(\{AX_4, L_{11,E}\}, \{L_{5,2}\})$	mixing
31	$(\{L_{5,3}\}, \{Z_5, L_{9,C}\})$	1-cut rectification	197	$(\{AX_4, L_{11,E}\}, \{L_{5,3}\})$	mixing
32	$(\{L_{5,3}\}, \{Z_5, X_5, BW_5\})$	2-cut rectification	198	$(\{BW_3, BY_4\}, \{L_{5,2}\})$	mixing
33	$(\{L_{5,3}\}, \{Z_5, X_5, W_5, B\})$	3-cut rectification/stripping	199	$(\{BW_3, BY_4\}, \{L_{5,3}\})$	mixing
34	$(\{L_{5,3}\}, \{B, L_{11,C}\})$	1-cut stripping	200	$(\{BW_3, BY_5\}, \{L_{5,3}\})$	mixing
35	$(\{L_{5,3}\}, \{B, W_5, XZ_5\})$	2-cut stripping	201	$(\{BW_3, BCY_5\}, \{L_4\})$	mixing
36	$(\{A, L_{9,C}\}, \{L_3\})$	mixing	202	$(\{BW_3, CYZ_5\}, \{L_{5,2}\})$	mixing
37	$(\{A, L_{10,C}\}, \{L_4\})$	mixing	203	$(\{BW_3, CYZ_5\}, \{L_{5,3}\})$	mixing
38	$(\{B, F\}, \{L_4\})$	mixing	204	$(\{BW_3, L_{11,E}\}, \{L_{5,3}\})$	mixing
39	$(\{B, AX_4\}, \{L_3\})$	mixing	205	$(\{BW_5, BY_4\}, \{L_{5,2}\})$	mixing
40	$(\{B, L_{7,E}\}, \{L_3\})$	mixing	206	$(\{BW_5, L_{7,E}\}, \{L_3\})$	mixing
41	$(\{B, L_{11,E}\}, \{L_{5,3}\})$	mixing	207	$(\{BW_5, AXY_4\}, \{L_3\})$	mixing
42	$(\{E, F\}, \{L_4\})$	mixing	208	$(\{BW_5, BCY_5\}, \{L_{5,2}\})$	mixing
43	$(\{E, BY_4\}, \{L_1\})$	mixing	209	$(\{BW_5, L_{10,A}\}, \{L_3\})$	mixing
44	$(\{E, BY_4\}, \{L_{5,2}\})$	mixing	210	$(\{BW_5, CYZ_5\}, \{L_{5,2}\})$	mixing
45	$(\{E, BY_4\}, \{L_{5,3}\})$	mixing	211	$(\{BY_4, EW_1\}, \{L_{5,2}\})$	mixing
46	$(\{E, BY_5\}, \{L_1\})$	mixing	212	$(\{BY_4, EW_1\}, \{L_{5,3}\})$	mixing
47	$(\{E, BY_5\}, \{L_{5,3}\})$	mixing	213	$(\{BY_4, EW_2\}, \{L_1\})$	mixing
48	$(\{E, L_{7,B}\}, \{L_2\})$	mixing	214	$(\{BY_4, EW_2\}, \{L_{5,2}\})$	mixing
49	$(\{E, BCY_5\}, \{L_1\})$	mixing	215	$(\{BY_4, EW_2\}, \{L_{5,3}\})$	mixing
50	$(\{E, BCY_5\}, \{L_{5,2}\})$	mixing	216	$(\{BY_4, XZ_1\}, \{L_{5,2}\})$	mixing
51	$(\{E, BCY_5\}, \{L_{5,3}\})$	mixing	217	$(\{BY_4, L_{9,A}\}, \{L_{5,2}\})$	mixing
52	$(\{E, L_{10,A}\}, \{L_1\})$	mixing	218	$(\{BY_4, L_{9,A}\}, \{L_{5,3}\})$	mixing
53	$(\{E, L_{10,A}\}, \{L_{5,2}\})$	mixing	219	$(\{BY_4, L_{6,A}\}, \{L_1\})$	mixing
54	$(\{E, L_{10,A}\}, \{L_{5,3}\})$	mixing	220	$(\{BY_4, L_{6,A}\}, \{L_{5,2}\})$	mixing
55	$(\{E, L_{11,C}\}, \{L_1\})$	mixing	221	$(\{BY_4, L_{6,A}\}, \{L_{5,3}\})$	mixing
56	$(\{E, AXY_4\}, \{L_1\})$	mixing	222	$(\{BY_4, L_{11,E}\}, \{L_{5,2}\})$	mixing
57	$(\{E, Y_4\}, \{L_1\})$	mixing	223	$(\{BY_4, L_{11,E}\}, \{L_{5,3}\})$	mixing
58	$(\{E, X_4\}, \{L_1\})$	mixing	224	$(\{BY_5, EW_1\}, \{L_{5,3}\})$	mixing
59	$(\{F, W_1\}, \{L_3\})$	mixing	225	$(\{BY_5, EW_2\}, \{L_1\})$	mixing
60	$(\{F, W_1\}, \{L_4\})$	mixing	226	$(\{BY_5, EW_2\}, \{L_{5,3}\})$	mixing
61	$(\{F, W_2\}, \{L_3\})$	mixing	227	$(\{BY_5, L_{7,E}\}, \{L_4\})$	mixing
62	$(\{F, W_2\}, \{L_4\})$	mixing	228	$(\{BY_5, L_{9,A}\}, \{L_{5,3}\})$	mixing
63	$(\{F, W_3\}, \{L_4\})$	mixing	229	$(\{BY_5, L_{6,A}\}, \{L_1\})$	mixing
64	$(\{F, W_5\}, \{L_3\})$	mixing	230	$(\{BY_5, L_{6,A}\}, \{L_{5,3}\})$	mixing
65	$(\{F, W_5\}, \{L_4\})$	mixing	231	$(\{BY_5, L_{11,E}\}, \{L_{5,3}\})$	mixing
66	$(\{F, X_1\}, \{L_4\})$	mixing	232	$(\{CZ_5, L_{7,E}\}, \{L_3\})$	mixing
67	$(\{F, X_2\}, \{L_4\})$	mixing	233	$(\{CZ_5, L_{7,E}\}, \{L_4\})$	mixing
68	$(\{F, X_3\}, \{L_4\})$	mixing	234	$(\{CZ_5, L_{7,E}\}, \{L_{5,2}\})$	mixing
69	$(\{F, X_5\}, \{L_4\})$	mixing	235	$(\{CZ_5, L_{7,E}\}, \{L_{5,3}\})$	mixing
70	$(\{F, Z_5\}, \{L_4\})$	mixing	236	$(\{CZ_5, L_{9,A}\}, \{L_{5,2}\})$	mixing
71	$(\{F, AX_2\}, \{L_4\})$	mixing	237	$(\{CZ_5, L_{9,A}\}, \{L_{5,3}\})$	mixing
72	$(\{F, AX_3\}, \{L_4\})$	mixing	238	$(\{CZ_5, L_{6,A}\}, \{L_1\})$	mixing
73	$(\{F, BW_3\}, \{L_4\})$	mixing	239	$(\{CZ_5, L_{6,A}\}, \{L_{5,2}\})$	mixing
74	$(\{F, BW_5\}, \{L_3\})$	mixing	240	$(\{CZ_5, L_{6,A}\}, \{L_{5,3}\})$	mixing
75	$(\{F, BW_5\}, \{L_4\})$	mixing	241	$(\{CZ_5, L_{11,E}\}, \{L_{5,2}\})$	mixing
76	$(\{F, BY_5\}, \{L_4\})$	mixing	242	$(\{CZ_5, L_{11,E}\}, \{L_{5,3}\})$	mixing
77	$(\{F, CZ_5\}, \{L_4\})$	mixing	243	$(\{EW_1, L_{7,B}\}, \{L_2\})$	mixing
78	$(\{F, CZ_5\}, \{L_{5,2}\})$	mixing	244	$(\{EW_1, AXY_4\}, \{L_2\})$	mixing
79	$(\{F, EW_1\}, \{L_2\})$	mixing	245	$(\{EW_1, AXY_4\}, \{L_3\})$	mixing
80	$(\{F, EW_1\}, \{L_4\})$	mixing	246	$(\{EW_1, AXY_4\}, \{L_{5,2}\})$	mixing
81	$(\{F, XZ_1\}, \{L_4\})$	mixing	247	$(\{EW_1, AXY_4\}, \{L_{5,3}\})$	mixing
82	$(\{F, XZ_1\}, \{L_{5,2}\})$	mixing	248	$(\{EW_1, BCY_5\}, \{L_{5,2}\})$	mixing
83	$(\{F, XZ_5\}, \{L_4\})$	mixing	249	$(\{EW_1, BCY_5\}, \{L_{5,3}\})$	mixing

Table 6. Continued

index	operating unit	type	index	operating unit	type
84	$(\{F, L_{7,E}\}, \{L_3\})$	mixing	250	$(\{EW_1, CYZ_5\}, \{L_{5,2}\})$	mixing
85	$(\{F, L_{7,E}\}, \{L_4\})$	mixing	251	$(\{EW_1, CYZ_5\}, \{L_{5,3}\})$	mixing
86	$(\{F, BCY_5\}, \{L_4\})$	mixing	252	$(\{EW_1, XYZ_5\}, \{L_{5,3}\})$	mixing
87	$(\{F, BCY_5\}, \{L_{5,2}\})$	mixing	253	$(\{EW_2, XZ_5\}, \{L_1\})$	mixing
88	$(\{F, L_{9,C}\}, \{L_3\})$	mixing	254	$(\{EW_2, AXY_4\}, \{L_1\})$	mixing
89	$(\{F, L_{9,C}\}, \{L_4\})$	mixing	255	$(\{EW_2, AXY_4\}, \{L_3\})$	mixing
90	$(\{F, L_{10,C}\}, \{L_4\})$	mixing	256	$(\{EW_2, AXY_4\}, \{L_{5,2}\})$	mixing
91	$(\{F, CYZ_5\}, \{L_4\})$	mixing	257	$(\{EW_2, AXY_4\}, \{L_{5,3}\})$	mixing
92	$(\{F, CYZ_5\}, \{L_{5,2}\})$	mixing	258	$(\{EW_2, BCY_5\}, \{L_1\})$	mixing
93	$(\{F, L_{6,C}\}, \{L_2\})$	mixing	259	$(\{EW_2, BCY_5\}, \{L_{5,2}\})$	mixing
94	$(\{F, L_{6,C}\}, \{L_3\})$	mixing	260	$(\{EW_2, BCY_5\}, \{L_{5,3}\})$	mixing
95	$(\{F, L_{6,C}\}, \{L_4\})$	mixing	261	$(\{EW_2, CYZ_5\}, \{L_1\})$	mixing
96	$(\{F, L_{11,E}\}, \{L_3\})$	mixing	262	$(\{EW_2, CYZ_5\}, \{L_{5,2}\})$	mixing
97	$(\{F, L_{11,E}\}, \{L_4\})$	mixing	263	$(\{EW_2, CYZ_5\}, \{L_{5,3}\})$	mixing
98	$(\{F, L_{11,E}\}, \{L_{5,1}\})$	mixing	264	$(\{EW_2, L_{11,C}\}, \{L_1\})$	mixing
99	$(\{F, L_{11,E}\}, \{L_{5,2}\})$	mixing	265	$(\{EW_2, XYZ_5\}, \{L_1\})$	mixing
100	$(\{F, XYZ_5\}, \{L_4\})$	mixing	266	$(\{EW_2, XYZ_5\}, \{L_{5,3}\})$	mixing
101	$(\{W_1, Y_4\}, \{L_{5,2}\})$	mixing	267	$(\{XZ_1, L_{7,E}\}, \{L_3\})$	mixing
102	$(\{W_1, Y_4\}, \{L_{5,3}\})$	mixing	268	$(\{XZ_1, L_{7,E}\}, \{L_4\})$	mixing
103	$(\{W_1, Y_5\}, \{L_{5,3}\})$	mixing	269	$(\{XZ_1, L_{7,E}\}, \{L_{5,2}\})$	mixing
104	$(\{W_1, BY_4\}, \{L_{5,2}\})$	mixing	270	$(\{XZ_1, L_{7,E}\}, \{L_{5,3}\})$	mixing
105	$(\{W_1, BY_4\}, \{L_{5,3}\})$	mixing	271	$(\{XZ_1, BCY_5\}, \{L_{5,2}\})$	mixing
106	$(\{W_1, BY_5\}, \{L_{5,3}\})$	mixing	272	$(\{XZ_1, L_{9,A}\}, \{L_{5,3}\})$	mixing
107	$(\{W_1, AXY_4\}, \{L_{5,2}\})$	mixing	273	$(\{XZ_1, L_{10,A}\}, \{L_{5,2}\})$	mixing
108	$(\{W_1, AXY_4\}, \{L_{5,3}\})$	mixing	274	$(\{XZ_5, L_{7,E}\}, \{L_3\})$	mixing
109	$(\{W_1, BCY_5\}, \{L_{5,2}\})$	mixing	275	$(\{XZ_5, L_{7,E}\}, \{L_4\})$	mixing
110	$(\{W_1, BCY_5\}, \{L_{5,3}\})$	mixing	276	$(\{XZ_5, L_{6,A}\}, \{L_1\})$	mixing
111	$(\{W_1, L_{10,A}\}, \{L_{5,2}\})$	mixing	277	$(\{L_{7,E}, AXY_4\}, \{L_3\})$	mixing
112	$(\{W_1, L_{10,A}\}, \{L_{5,3}\})$	mixing	278	$(\{L_{7,E}, BCY_5\}, \{L_3\})$	mixing
113	$(\{W_1, CYZ_5\}, \{L_{5,2}\})$	mixing	279	$(\{L_{7,E}, BCY_5\}, \{L_4\})$	mixing
114	$(\{W_1, CYZ_5\}, \{L_{5,3}\})$	mixing	280	$(\{L_{7,E}, BCY_5\}, \{L_{5,2}\})$	mixing
115	$(\{W_1, XYZ_5\}, \{L_{5,3}\})$	mixing	281	$(\{L_{7,E}, BCY_5\}, \{L_{5,3}\})$	mixing
116	$(\{W_2, Y_4\}, \{L_{5,2}\})$	mixing	282	$(\{L_{7,E}, L_{9,C}\}, \{L_3\})$	mixing
117	$(\{W_2, Y_4\}, \{L_{5,3}\})$	mixing	283	$(\{L_{7,E}, L_{10,C}\}, \{L_3\})$	mixing
118	$(\{W_2, BY_4\}, \{L_{5,2}\})$	mixing	284	$(\{L_{7,E}, L_{10,C}\}, \{L_4\})$	mixing
119	$(\{W_2, BY_4\}, \{L_{5,3}\})$	mixing	285	$(\{L_{7,E}, CYZ_5\}, \{L_3\})$	mixing
120	$(\{W_2, BY_5\}, \{L_{5,3}\})$	mixing	286	$(\{L_{7,E}, CYZ_5\}, \{L_4\})$	mixing
121	$(\{W_2, AXY_4\}, \{L_{5,2}\})$	mixing	287	$(\{L_{7,E}, CYZ_5\}, \{L_{5,2}\})$	mixing
122	$(\{W_2, AXY_4\}, \{L_{5,3}\})$	mixing	288	$(\{L_{7,E}, CYZ_5\}, \{L_{5,3}\})$	mixing
123	$(\{W_2, BCY_5\}, \{L_{5,2}\})$	mixing	289	$(\{L_{7,E}, L_{11,E}\}, \{L_3\})$	mixing
124	$(\{W_2, BCY_5\}, \{L_{5,3}\})$	mixing	290	$(\{L_{7,E}, L_{11,E}\}, \{L_4\})$	mixing
125	$(\{W_2, L_{10,A}\}, \{L_{5,2}\})$	mixing	291	$(\{L_{7,E}, L_{11,E}\}, \{L_{5,2}\})$	mixing
126	$(\{W_2, L_{10,A}\}, \{L_{5,3}\})$	mixing	292	$(\{L_{7,E}, L_{11,E}\}, \{L_{5,3}\})$	mixing
127	$(\{W_2, CYZ_5\}, \{L_{5,2}\})$	mixing	293	$(\{L_{7,E}, XYZ_5\}, \{L_3\})$	mixing
128	$(\{W_2, CYZ_5\}, \{L_{5,3}\})$	mixing	294	$(\{L_{7,E}, XYZ_5\}, \{L_4\})$	mixing
129	$(\{W_2, XYZ_5\}, \{L_{5,3}\})$	mixing	295	$(\{L_{7,E}, XYZ_5\}, \{L_{5,3}\})$	mixing
130	$(\{W_3, Y_4\}, \{L_{5,2}\})$	mixing	296	$(\{L_{7,B}, L_{6,C}\}, \{L_2\})$	mixing
131	$(\{W_3, Y_4\}, \{L_{5,3}\})$	mixing	297	$(\{AXY_4, BCY_5\}, \{L_{5,2}\})$	mixing
132	$(\{W_3, Y_5\}, \{L_{5,3}\})$	mixing	298	$(\{AXY_4, L_{9,C}\}, \{L_3\})$	mixing
133	$(\{W_3, BY_4\}, \{L_{5,2}\})$	mixing	299	$(\{AXY_4, L_{6,C}\}, \{L_2\})$	mixing
134	$(\{W_3, BY_4\}, \{L_{5,3}\})$	mixing	300	$(\{AXY_4, L_{6,C}\}, \{L_3\})$	mixing
135	$(\{W_3, BY_5\}, \{L_{5,3}\})$	mixing	301	$(\{AXY_4, L_{11,E}\}, \{L_3\})$	mixing
136	$(\{W_3, AXY_4\}, \{L_{5,2}\})$	mixing	302	$(\{AXY_4, L_{11,E}\}, \{L_{5,2}\})$	mixing
137	$(\{W_3, AXY_4\}, \{L_{5,3}\})$	mixing	303	$(\{AXY_4, L_{11,E}\}, \{L_{5,3}\})$	mixing
138	$(\{W_3, BCY_5\}, \{L_{5,2}\})$	mixing	304	$(\{BCY_5, L_{9,A}\}, \{L_{5,2}\})$	mixing
139	$(\{W_3, BCY_5\}, \{L_{5,3}\})$	mixing	305	$(\{BCY_5, L_{9,A}\}, \{L_{5,3}\})$	mixing
140	$(\{W_3, L_{10,A}\}, \{L_{5,2}\})$	mixing	306	$(\{BCY_5, L_{10,A}\}, \{L_{5,2}\})$	mixing
141	$(\{W_3, L_{10,A}\}, \{L_{5,3}\})$	mixing	307	$(\{BCY_5, L_{6,A}\}, \{L_1\})$	mixing
142	$(\{W_3, CYZ_5\}, \{L_{5,2}\})$	mixing	308	$(\{BCY_5, L_{6,A}\}, \{L_{5,2}\})$	mixing
143	$(\{W_3, CYZ_5\}, \{L_{5,3}\})$	mixing	309	$(\{BCY_5, L_{6,A}\}, \{L_{5,3}\})$	mixing
144	$(\{W_3, XYZ_5\}, \{L_{5,3}\})$	mixing	310	$(\{BCY_5, L_{11,E}\}, \{L_{5,2}\})$	mixing
145	$(\{W_5, Y_4\}, \{L_{5,2}\})$	mixing	311	$(\{BCY_5, L_{11,E}\}, \{L_{5,3}\})$	mixing
146	$(\{W_5, Y_5\}, \{L_{5,3}\})$	mixing	312	$(\{L_{9,A}, L_{10,A}\}, \{L_{5,2}\})$	mixing
147	$(\{W_5, BY_4\}, \{L_{5,2}\})$	mixing	313	$(\{L_{9,A}, L_{10,A}\}, \{L_{5,3}\})$	mixing
148	$(\{W_5, AXY_4\}, \{L_{5,2}\})$	mixing	314	$(\{L_{9,A}, CYZ_5\}, \{L_{5,2}\})$	mixing
149	$(\{W_5, BCY_5\}, \{L_{5,2}\})$	mixing	315	$(\{L_{9,A}, CYZ_5\}, \{L_{5,3}\})$	mixing
150	$(\{W_5, L_{10,A}\}, \{L_{5,2}\})$	mixing	316	$(\{L_{9,A}, L_{11,E}\}, \{L_{5,3}\})$	mixing
151	$(\{W_5, CYZ_5\}, \{L_{5,2}\})$	mixing	317	$(\{L_{9,A}, XYZ_5\}, \{L_{5,3}\})$	mixing
152	$(\{Y_4, Z_1\}, \{L_{5,2}\})$	mixing	318	$(\{L_{10,A}, CYZ_5\}, \{L_{5,2}\})$	mixing
153	$(\{Y_4, EW_1\}, \{L_{5,2}\})$	mixing	319	$(\{L_{10,A}, L_{6,A}\}, \{L_1\})$	mixing
154	$(\{Y_4, EW_1\}, \{L_{5,3}\})$	mixing	320	$(\{L_{10,A}, L_{6,A}\}, \{L_{5,2}\})$	mixing
155	$(\{Y_4, EW_2\}, \{L_1\})$	mixing	321	$(\{L_{10,A}, L_{6,A}\}, \{L_{5,3}\})$	mixing
156	$(\{Y_4, EW_2\}, \{L_{5,2}\})$	mixing	322	$(\{L_{10,A}, L_{11,E}\}, \{L_{5,2}\})$	mixing
157	$(\{Y_4, L_{7,E}\}, \{L_3\})$	mixing	323	$(\{L_{10,A}, L_{11,E}\}, \{L_{5,3}\})$	mixing
158	$(\{Y_4, L_{9,A}\}, \{L_{5,2}\})$	mixing	324	$(\{CYZ_5, L_{6,A}\}, \{L_1\})$	mixing
159	$(\{Y_4, L_{9,A}\}, \{L_{5,3}\})$	mixing	325	$(\{CYZ_5, L_{6,A}\}, \{L_{5,2}\})$	mixing
160	$(\{Y_4, L_{6,A}\}, \{L_1\})$	mixing	326	$(\{CYZ_5, L_{6,A}\}, \{L_{5,3}\})$	mixing
161	$(\{Y_4, L_{6,A}\}, \{L_{5,2}\})$	mixing	327	$(\{CYZ_5, L_{11,E}\}, \{L_{5,2}\})$	mixing
162	$(\{Y_4, L_{11,E}\}, \{L_{5,2}\})$	mixing	328	$(\{CYZ_5, L_{11,E}\}, \{L_{5,3}\})$	mixing
163	$(\{Y_4, L_{11,E}\}, \{L_{5,3}\})$	mixing	329	$(\{L_{6,A}, L_{11,C}\}, \{L_1\})$	mixing
164	$(\{Y_5, EW_1\}, \{L_{5,3}\})$	mixing	330	$(\{L_{6,A}, XYZ_5\}, \{L_1\})$	mixing
165	$(\{Y_5, EW_2\}, \{L_1\})$	mixing	331	$(\{L_{11,E}, XYZ_5\}, \{L_{5,3}\})$	mixing
166	$(\{Y_5, EW_2\}, \{L_{5,3}\})$	mixing			

mixers. By taking into account criteria d−f, the plausible mixing operations can be identified and they are listed in rows 16−52 of Table 5. The same approach was adopted to find the plausible mixers for the acetone−ethanol−chloroform−benzene system (see rows 36−331 in Table 6).

• **Other Separation-Facilitating Operations.** Since the entrainers are usually recovered and recycled in the industrial processes, all possible entrainer-regenerating separators should be selected as the plausible operations for a given system. Furthermore, any operation producing the feed to such a separator should also be considered.

In the acetone−ethanol−chloroform system, the distillation operations for producing the entrainer (ethanol) are found to be ($\{L_1\}$, $\{E, L_{5,E}\}$), ($\{L_1\}$, $\{A, E, X_1\}$), ($\{L_2\}$, $\{E, L_{7,E}\}$), and ($\{L_2\}$, $\{E, W_2, X_2\}$). In other words, L_1 and L_2 are needed in these distillation columns (see rows 2, 3, 5, and 6 in Table 5). L_1 and L_2 can be produced with mixing operations which are also listed in rows 16, 18, 27, 28, 36, 37, 39, 40, 42, 44, and 49 of Table 5. The same approach can be applied to find the corresponding operations in the acetone−ethanol−chloroform−benzene system with ethanol as the entrainer (see rows 3−5 and 8−10 for distillation and rows 43, 46, 48, 49, 52, 55−58, 79, 93, 160, 165, 169, 187, 192, 195, 213, 219, 225, 229, 238, 243, 253, 254, 258, 261, 264, 265, 276, 296, 299, 307, 319, 324, 329, and 330 for mixing in Table 6).

4. Synthesis of STN Structure

In this work, the STN configurations are created with an integer programming (IP) model. This model is built on the basis of the formulation used for logic inference. As mentioned before, there can be only two types of operations in the azeotropic distillation system, i.e., mixing and distillation. Let us first consider an operation expressed in the general form ($\{A,B\}$, $\{C\}$). The input−output relation of this operation can be described with the following logic statement

$$A \wedge B \Rightarrow C \qquad (1)$$

which can be rewritten as

$$\neg(A \wedge B) \vee C \qquad (2)$$

where, $\Rightarrow$ is the logic operator for implication; $\neg$ is the logic operator for negation; $\wedge$ denotes "and"; and $\vee$ represents the operation "or". In an IP model, this statement can be translated into an inequality constraint according to Raman and Grossmann:[30]

$$(1 - y_A) + (1 - y_B) + y_C \geq 1 \qquad (3)$$

where, y_A, y_B, and y_C are binary variables denoting the presence (1) or absence (0) of material A, B, and C, respectively.

Notice from Tables 5 and 6 that two or more mixing operations may share the same raw materials, e.g., ($\{E, F\}$, $\{L_1\}$) and ($\{E, F\}$, $\{L_4\}$) in the former case, and ($\{E, BY_5\}$, $\{L_1\}$) and ($\{E, BY_5\}$, $\{L_{5,3}\}$) in the latter. For illustration convenience, let us consider two fictitious mixing operations: ($\{A,B\}$, $\{C\}$) and ($\{A,B\}$, $\{D\}$). By following the aforementioned approach, the logic statement for these two operations can be written as

$$(A \wedge B) \Rightarrow (C \vee D) \qquad (4)$$

The corresponding inequality constraint can then be constructed in a straightforward fashion, i.e.,

$$(1 - y_A) + (1 - y_B) + y_C + y_D \geq 1 \qquad (5)$$

Although logically consistent, the above formulation is still ambiguous. Consequently, the STN configuration generated by the resulting IP model may be suboptimal. To circumvent this drawback, a new binary variable z_i has been introduced in this work to reflect whether the ith operation is selected in STN. Thus, eq 5 can be reformulated as

$$(1 - y_A) + (1 - y_B) + (1 - z_j) + y_C \geq 1$$
$$(1 - y_A) + (1 - y_B) + (1 - z_k) + y_D \geq 1 \qquad (6)$$

In making a selection to produce C or D alone (or both), the following constraint could be adopted:

$$(1 - y_A) + (1 - y_B) + z_j + z_k \geq 1 \qquad (7)$$

On the other hand, a single-cut distillation operation, which can be expressed in a general form as ($\{A\}$, $\{B,C\}$), can be described with the logic statement

$$A \Rightarrow B \wedge C \qquad (8)$$

then the following inequality constraints must *all* be imposed in the integer program

$$(1 - y_A) + (1 - z_m) + y_B \geq 1 \qquad (9)$$

$$(1 - y_A) + (1 - z_m) + y_C \geq 1 \qquad (10)$$

$$(1 - y_A) + z_m \geq 1 \qquad (11)$$

Note that the design options of the multicut distillations can also be considered in this study. For example, let us assume that both the single-cut and two-cut distillations, i.e., ($\{A\}$, $\{B,C\}$) and ($\{A\}$, $\{B,D,E\}$), are allowed in a ternary system. The corresponding inequality constraints should be eqs 9 and 10, and those given below:

$$(1 - y_A) + (1 - z_n) + y_B \geq 1 \qquad (12)$$

$$(1 - y_A) + (1 - z_n) + y_D \geq 1 \qquad (13)$$

$$(1 - y_A) + (1 - z_n) + y_E \geq 1 \qquad (14)$$

$$(1 - y_A) + z_m + z_n = 1 \qquad (15)$$

Again note that this formulation approach can be generalized to any number of multicut distillers sharing the same input.

One of the design objectives used in this work is to minimize the total number of designated operation units in the optimal azeotropic distillation system, i.e.,

$$\min \sum_{j \in \mathcal{O}} z_j \qquad (16)$$

where $\mathcal{O}$ is the set of plausible operations assigned by the designer.

To demonstrate the effectiveness of the above modeling strategy, let us consider the operations listed in Tables 5 and 6 as examples:

• **Process Configuration of the Acetone−Ethanol−Chloroform System.** All operations in Table 5 can be translated into inequality constraints according to the formulation techniques outlined above. It is assumed that (1) the raw material F is always available, (2) the final products are acetone (A) and ethanol−chloroform azeotrope (W_3), and (3) the entrainer is
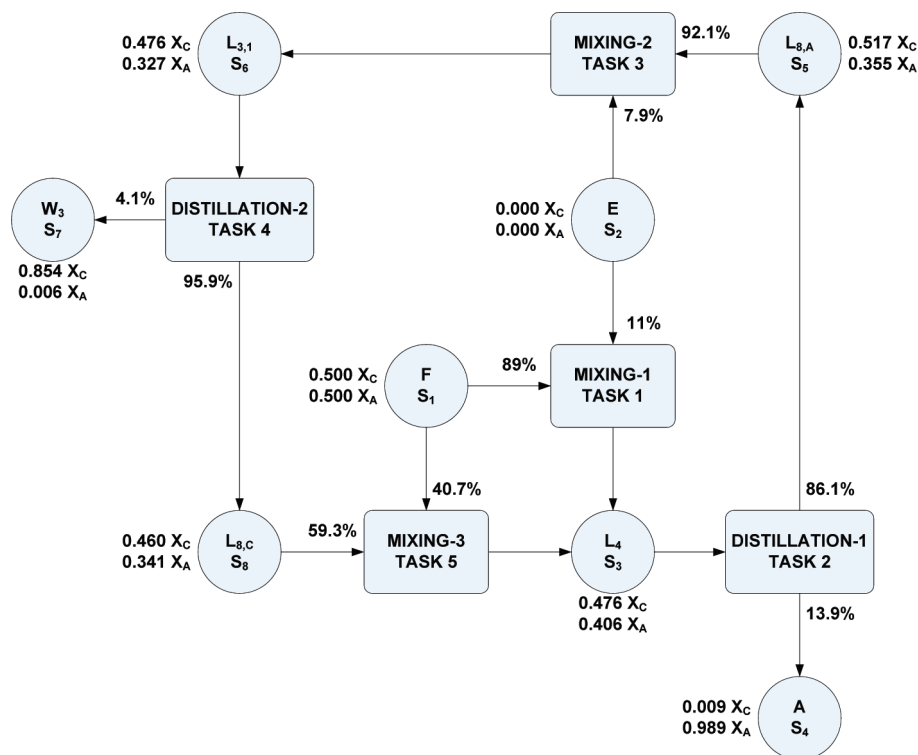
Figure 7. State-task network of the acetone−ethanol−chloroform system.

ethanol (E). Thus, the following equality constraints must also be imposed:

$$y_F = y_A = y_{W_3} = y_E = 1 \qquad (17)$$

By using the objective function in (16), the corresponding IP model can be solved to identify the intermediates and operations needed to minimize the total unit number. In particular, the optimal solution was found to be

$$y_{L_{3,1}} = y_{L_4} = y_{L_{8,A}} = y_{L_{8,C}} = 1$$

$$z_7 = z_{13} = z_{17} = z_{50} = z_{52} = 1$$

The corresponding optimal STN configuration is plotted in Figure 7.

- **Process Configuration of Acetone−Ethanol−Chloroform−Benzene System.** Again the same approach can be adopted to translate the operations listed in Table 6 into inequality constraints. It is assumed in this example that (1) the raw material F is always available, (2) the final products are acetone (A) and ethanol−chloroform azeotrope (Z_1), and (3) the entrainer is ethanol (E). Thus, the following constraints were included in the integer program:

$$y_F = y_A = y_{Z_1} = y_E = 1 \qquad (18)$$

Solving the corresponding IP model yields the following results:

$$y_{L_{6,C}} = y_{L_{10,A}} = y_{L_1} = y_{L_4} = 1$$

$$z_1 = z_{16} = z_{42} = z_{52} = z_{95} = 1$$

The optimal STN configuration in this case is presented in Figure 8.

5. Specification of Material Balance Constraints

The material balance constraints in a STN can be established with a nonlinear programming model. The general model formulation is briefly summarized below.

5.1. Representations of Lumped Materials. According to the classification schemes described previously, a lumped material may be associated with a point, a straight line, a triangular area, or a pyramid region in the RCM. There is thus a need to incorporate their mathematical representations in the NLP model. These items are all characterized with *position vectors* in this paper.

The composition of a specific ternary or quaternary mixture can be considered as a distinct point in the two- or three-dimensional space (say A). The location of this point can be represented with a position vector $\overrightarrow{OA}$ as

$$\overrightarrow{OA} = \begin{cases} [x_1 \quad x_2]^T & \text{in a ternary system} \\ [x_1 \quad x_2 \quad x_3]^T & \text{in a quaternary system} \end{cases} \qquad (19)$$

where $x_i \in [0,1]$ ($i = 1, 2, 3$) denotes the mass fraction of component i in the mixture. Notice that such a position vector always starts at the origin O. According to the definition of mass fraction, it is obvious that the following additional constraints must also be imposed for the ternary and quaternary systems respectively:

$$x_1 + x_2 \leq 1$$
$$x_1 + x_2 + x_3 \leq 1 \qquad (20)$$

Since the compositions of pure components and azeotropes are considered as *given data* in this study, the corresponding position vectors can be determined accordingly.

Any point on the line segment connecting two given points in space (say B and C) can also be expressed with position vectors, i.e.,

$$\overrightarrow{OP}_{BC} = \overrightarrow{OB} + c\overrightarrow{BC} = c\overrightarrow{OC} + (1 - c)\overrightarrow{OB} \qquad (21)$$

where, P_{BC} denotes a point on line BC and $0 \leq c \leq 1$. Similarly, the points in a triangular area (say DEF) and in a pyramid region (say GHIJ) can be respectively expressed as

$$\overrightarrow{OP}_{DEF} = \overrightarrow{OD} + e\overrightarrow{DE} + f\overrightarrow{DF}$$
$$=(1 - e - f)\overrightarrow{OD} + e\overrightarrow{OE} + f\overrightarrow{OF} \tag{22}$$

$$\overrightarrow{OP}_{GHIJ} = \overrightarrow{OG} + h\overrightarrow{GH} + i\overrightarrow{GI} + j\overrightarrow{GJ}$$
$$=(1 - h - i - j)\overrightarrow{OG} + h\overrightarrow{OH} + i\overrightarrow{OI} + j\overrightarrow{OJ} \tag{23}$$

where, P_{DEF} and P_{GHIJ} denote a point in area DEF and in region GHIJ, respectively, and $0 \le e, f, h, i, j \le 1$. In addition, the following inequality constraints should also be imposed:

$$e + f \le 1 \tag{24}$$

$$h + i + j \le 1 \tag{25}$$

In this study, the distillation boundaries and pseudoboundaries are treated as individual lumped materials which are different from those associated with the triangular areas in ternary systems and the pyramid regions in quaternary systems. Such distinctions can be achieved in the NLP formulation by slightly contracting the original triangular areas and pyramid regions. For example, let us consider the triangular area represented by eq 22. Its center of mass X can be determined by

$$\overrightarrow{OX} = \frac{1}{3}(\overrightarrow{OD} + \overrightarrow{OE} + \overrightarrow{OF}) \tag{26}$$

The apexes of a contracted triangle (say D′E′F′) can thus be represented as

$$\overrightarrow{OD'} = \overrightarrow{OX} + (1 - \varepsilon)\overrightarrow{XD} = \varepsilon\overrightarrow{OX} + (1 - \varepsilon)\overrightarrow{OD}$$
$$= \left(1 - \frac{2}{3}\varepsilon\right)\overrightarrow{OD} + \frac{1}{3}\varepsilon\overrightarrow{OE} + \frac{1}{3}\varepsilon\overrightarrow{OF} \tag{27}$$

$$\overrightarrow{OE'} = \overrightarrow{OX} + (1 - \varepsilon)\overrightarrow{XE} = \varepsilon\overrightarrow{OX} + (1 - \varepsilon)\overrightarrow{OE}$$
$$= \frac{1}{3}\varepsilon\overrightarrow{OD} + \left(1 - \frac{2}{3}\varepsilon\right)\overrightarrow{OE} + \frac{1}{3}\varepsilon\overrightarrow{OF} \tag{28}$$

$$\overrightarrow{OF'} = \overrightarrow{OX} + (1 - \varepsilon)\overrightarrow{XF} = \varepsilon\overrightarrow{OX} + (1 - \varepsilon)\overrightarrow{OF}$$
$$= \frac{1}{3}\varepsilon\overrightarrow{OD} + \frac{1}{3}\varepsilon\overrightarrow{OE} + \left(1 - \frac{2}{3}\varepsilon\right)\overrightarrow{OF} \tag{29}$$

where $0 < \varepsilon \ll 1$ is a small positive constant. Thus, points within this contracted triangle can be expressed as

$$\overrightarrow{OP}_{D'E'F'} = (1 - e'-f')\overrightarrow{OD'} + e'\overrightarrow{OE'} + f'\overrightarrow{OF'}$$
$$= \left[\left(1 - \frac{2}{3}\varepsilon\right) + (1 - \varepsilon)e'+(1 - \varepsilon)f'\right]\overrightarrow{OD} +$$
$$= \left[\frac{1}{3}\varepsilon + (1 - \varepsilon)e'\right]\overrightarrow{OE} + \left[\frac{1}{3}\varepsilon + (1 - \varepsilon)f'\right]\overrightarrow{OF} \tag{30}$$

where, $0 \le e', f' \le 1$ and $e' + f' \le 1$.

Similarly, the points within a contracted pyramid can be represented with the same approach. The corresponding formulations are not presented here for the sake of conciseness.

5.2. Descriptions of Feasible Operations. On the basis of the mathematical representations of the lumped materials described above, the feasible operations selected in a STN structure (with the IP model) can then be characterized accurately.

5.2.1. Mixing Operation. For illustration convenience, let us consider a fictitious mixing operation({K,L},{M}). Let us assume that the compositions of feeds K and L are *given*, i.e., the corresponding position vectors $\overrightarrow{OK}$ and $\overrightarrow{OL}$ can be constructed in advance. On the basis of eq 21, the position vector representing the composition of the mixing product can be expressed as

$$\overrightarrow{OM} = (1 - l)\overrightarrow{OK} + l\overrightarrow{OL} \tag{31}$$

where $0 \le l \le 1$. On the other hand, notice that the lumped region for every mixing product in STN has already been selected with
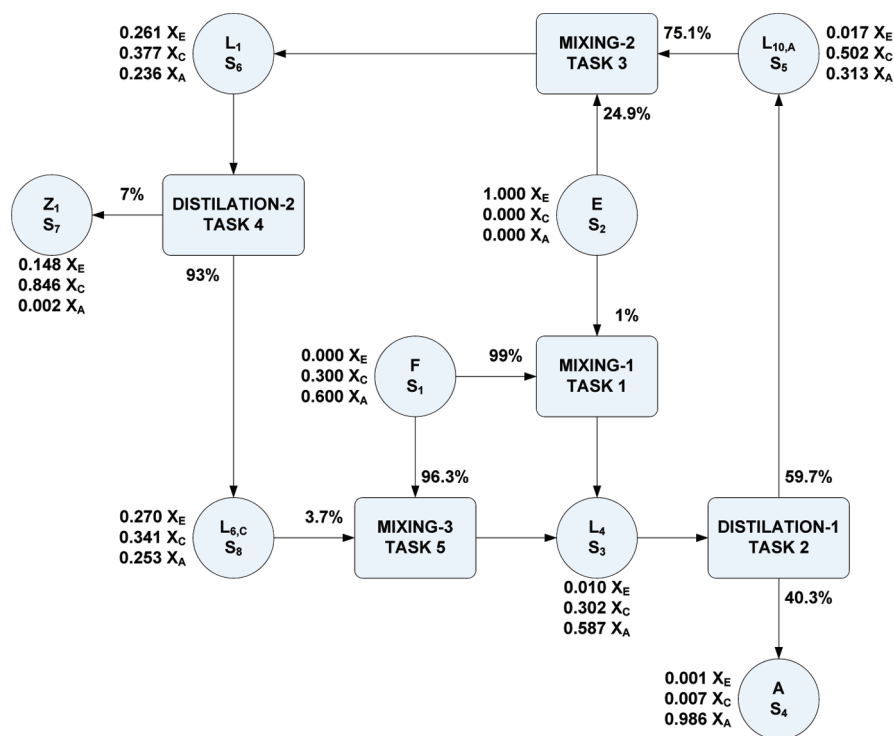

Figure 8. State-task network of the acetone−ethanol−chloroform−benzene system.

integer program. Let us consider the ternary case as an example. By assuming that the mixing product M is located within a *contracted* triangle D'E'F', a set of equality constraints can be established with eq 30, i.e.

$$(1 - l)\overrightarrow{OK} + l\overrightarrow{OL} = \left[\left(1 - \frac{2}{3}\varepsilon\right) + \right.$$
$$\left. (1 - \varepsilon)e' + (1 - \varepsilon)f'\right]\overrightarrow{OD} +$$
$$\left[\frac{1}{3}\varepsilon + (1 - \varepsilon)e'\right]\overrightarrow{OE} + \left[\frac{1}{3}\varepsilon + (1 - \varepsilon)f'\right]\overrightarrow{OF} \quad (32)$$

There are in essence three variables in this formulation, i.e., e', f' and l, while only two equations are embedded since the position vectors in ternary system is only two-dimensional. Although the composition of mixing product is obviously not unique in this situation, the above three variables should still be subject to the inequality constraints given previously, i.e., $0 \leq l, e', f' \leq 1$ and $e' + f' \leq 1$.

It should be noted that the same formulation approach can be extended to the quaternary systems. For the sake of brevity, the corresponding formulations are again omitted in this paper.

5.2.3. Distillation Operations. To separate a given lumped material, more than one batch distillation operation can be performed. For illustration convenience, let us consider a fictitious ternary system as an example.

If a 1-cut rectifier (or stripper) is used, the corresponding operation may be expressed in the form ({N},{D,Q}), where N is located within a triangular region DEF bordered by the original distillation boundaries and/or pseudoboundaries, D is the apex associated with the lowest (or highest) boiling point and Q is at the boundary line opposite to D. In this case, the position vector $\overrightarrow{OQ}$ can be determined according to eq 21, i.e.

$$\overrightarrow{OQ} = \frac{1}{q}\overrightarrow{ON} - \frac{1 - q}{q}\overrightarrow{OD} \quad (33)$$

where, $0 < q \leq 1$. On the basis of the fact that Q is also a point on the straight line EF, the following equality constraints can be established:

$$\frac{1}{q}\overrightarrow{ON} - \frac{1 - q}{q}\overrightarrow{OD} = (1 - f)\overrightarrow{OE} + f\overrightarrow{OF} \quad (34)$$

where, $0 \leq f \leq 1$. Since the position vectors in ternary system are two-dimensional and there are two variables (q and f), a unique location for Q can therefore be identified accordingly.

On the other hand, if a 2-cut distillation is considered, the corresponding operation can be represented as ({N},{D,E,F}), where D, E, and F denote the apexes of a triangular area. With the *given* compositions of the feed and the apexes, it is obvious that the material balance data of 2-cut distillation operation in a ternary system can be uniquely determined according to eq 22.

Finally, it should again be pointed out that the same formulation approach can be extended to the quaternary systems. The corresponding descriptions are also omitted to save space.

5.3. Objective Function. Notice that, by minimizing the total number of designated operation units, more than one task may yield the same state in the optimal STN configuration identified with the proposed IP model. For example, state 3 (L_4) can be created by performing either task 1 (i.e., operation mixing-1) or task 5 (i.e., operation mixing-3) in the STN presented in Figure 7. Although the products of these two operations are regarded as the same lumped materials in STN, their computed compositions may be different if the aforementioned constraints

Table 7. Optimization Results Obtained by Solving NLP Models for Example Systems

system/minimum objective value	operation	input	output
acetone−ethanol− chloroform/obj = 4.775×10^{-20}	mixing-1	F (S_1)−89% E (S_2)−11%	L_4 (S_3)
	distillation-1	L_4 (S_3)	A (S_4)−13.9% $L_{8,A}$ (S_5) − 86.1%
	mixing-2	E (S_2)−7.9% $L_{8,A}$ (S_5)−92.1%	$L_{3,1}$ (S_6)
	distillation-2	$L_{3,1}$ (S_6)	W_3 (S_7)−4.1% $L_{8,C}$ (S_8)−95.9%
	mixing-3	F (S_1)−40.7% $L_{8,C}$ (S_8)−59.3%	L_4 (S_3)
acetone−ethanol− chloroform− benzene/obj = 4.623×10^{-7}	mixing-1	F (S_1)−99% E (S_2)−1%	L_4 (S_3)
	distillation-1	L_4 (S_3)	A (S_4)−40.3% $L_{10,A}$ (S_5)−59.7%
	mixing-2	E (S_2)−24.9% $L_{10,A}$ (S_5)−75.1%	L_1 (S_6)
	distillation-2	L_1 (S_6)	Z_1 (S_7)−7% $L_{6,C}$ (S_8)−93%
	mixing-3	F (S_1)−96.3% $L_{6,C}$ (S_8)−3.7%	L_4 (S_3)

are adopted to specify the material-balance data. Let us denote the locations of lumped materials produced by task 1 and task 5 as $[(x_1^{(1)})_{L_4} (x_2^{(1)})_{L_4}]^T$ and $[(x_1^{(5)})_{L_4} (x_2^{(5)})_{L_4}]^T$, respectively. The objective function used in the NLP model can be expressed as a measure of the difference between the corresponding two compositions, i.e.

$$\text{obj} = ((x_1^{(1)})_{L_4} - (x_1^{(5)})_{L_4})^2 + ((x_2^{(1)})_{L_4} - (x_2^{(5)})_{L_4})^2 \quad (35)$$

If this objective function is minimized, then the resulting material-balance constraints may be made to match the structural features of the given STN as much as possible.

According to the STN presented in Figure 7, the materials produced by task 1 and task 5 must be further processed with a distillation operation, i.e., task 2 (i.e., operation distillation-1). This distillation operation is ({L_4},{A,$L_{8,A}$}), i.e., the 13th feasible operation in Table 5, in which A is the apex associated with the lowest boiling point and $L_{8,A}$ is located at the boundary line opposite to A. It should be noted that, although the distance between $[(x_1^{(1)})_{L_4} (x_2^{(1)})_{L_4}]^T$ and $[(x_1^{(5)})_{L_4} (x_2^{(5)})_{L_4}]^T$ can be made as close as possible by minimizing eq 35, the locations of the corresponding distillation products $L_{8,A}$, denoted respectively here as $[(x_1^{(1)})_{L_{8,A}} (x_2^{(1)})_{L_{8,A}}]^T$ and $[(x_1^{(5)})_{L_{8,A}} (x_2^{(5)})_{L_{8,A}}]^T$, may still be significantly apart. Thus, an alternative approach to generate the material-balance data is to try to align the corresponding distillation tie lines, i.e., the following objective function can be minimized instead:

$$\text{obj} = ((x_1^{(1)})_{L_{8,A}} - (x_1^{(5)})_{L_{8,A}})^2 + ((x_2^{(1)})_{L_{8,A}} - (x_2^{(5)})_{L_{8,A}})^2 \quad (36)$$

By solving NLP models for the two example systems according to the latter objective function, the composition of every state and the mass percentages of inputs (or outputs) of every task in the corresponding STNs can be determined exactly. These data are shown in Table 7 and also in Figures 7 and 8. It can be clearly observed from Table 7 that the minimized objective values are very small in both cases and, for all practical purposes, the corresponding composition differences can be neglected.

6. Generation of Production Schedules

After obtaining the optimal STN and the corresponding material-balance data, several different mathematical pro-

Table 8. Design Parameters of States, Tasks, and Units in the Base Case of the Acetone−Ethanol−Chloroform system

available unit	capacity (rwu/batch)	suitability	mean processing time (h)
mixer-1	100	task 1: mixing-1 ({E, F}, {L$_4$})	1
distiller-1 (rectifier)	100	task 2: distillation-1 ({L$_4$}, {A, L$_{8,A}$})	6
mixer-2	100	task 3: mixing-2 ({L$_{8,A}$, E}, {L$_1$})	1
distiller-2 (rectifier)	100	task 4: distillation-2 ({L$_{3,1}$}, {W$_3$, L$_{8,C}$})	6
mixer-3	100	task 5: mixing-3 ({L$_{8,C}$, F}, {L$_4$})	1

state	storage capacity (rwu)	initial amount (rwu)	price per unit weight (rcu/rwu)
S$_1$ (F)	unlimited	3000	0
S$_2$ (E)	unlimited	1000	50
S$_3$ (L$_4$)	unlimited	0	0
S$_4$ (A)	unlimited	0	85
S$_5$ (L$_{8,A}$)	unlimited	0	0
S$_6$ (L$_{3,1}$)	unlimited	0	0
S$_7$ (W$_3$)	unlimited	0	60
S$_8$ (L$_{8,C}$)	unlimited	0	0

grams can be constructed accordingly for various scheduling purposes. A formal problem statement can be found in Ierapetritou and Floudas,[18] and their continuous-time formulation has been directly adopted in the present work to produce short-term schedules. To create such a model for a particular application, it is necessary to first postulate an enough number of *event points* corresponding to either the initiation of a task and/or the beginning of unit utilization. The locations of these points on time axis are unknown. A trial-and-error procedure has been used for determining the appropriate number of event points needed.

The short-term scheduling model can be reformulated as a MINLP model to generate cyclic (or periodical) schedules.[26]
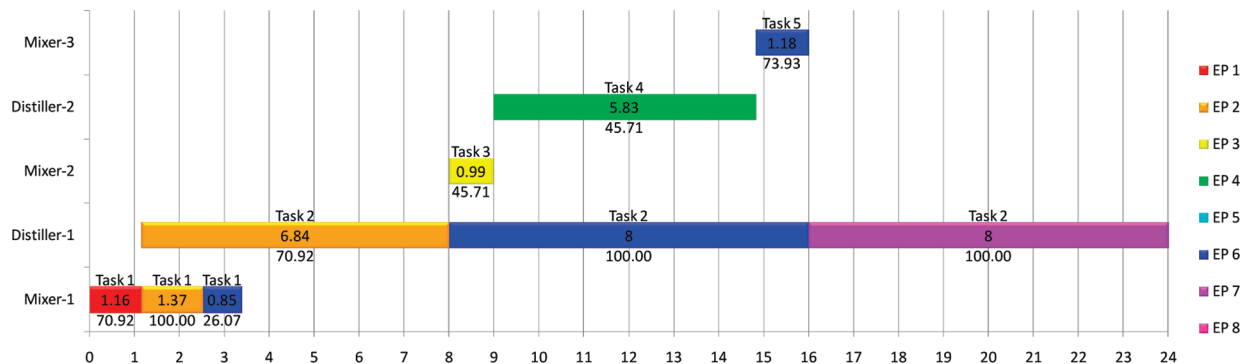
Figure 9. Gantt chart for the base case of acetone−ethanol−chloroform system.

Table 9. State Conditions (rwu) in the Base Case of Acetone−Ethanol−Chloroform System

state	event point							
	1	2	3	4	5	6	7	8
S$_1$ (F)	2936.89	2847.89	2847.89	2847.89	2847.89	2794.59	2794.59	2794.59
S$_2$ (E)	992.20	992.20	977.59	977.59	977.59	974.72	974.72	974.72
S$_3$ (L$_4$)			100.00	100.00	100.00			
S$_4$ (A)			9.86	9.86	9.86	9.86	23.76	37.66
S$_5$ (L$_{8,A}$)			18.96	18.96	18.96	18.96	105.06	191.16
S$_7$ (W$_3$)					1.87	1.87	1.87	1.87
S$_8$ (L$_{8,C}$)					43.84			

Table 10. Design Parameters of States, Tasks, and Units in the Base Case of the Acetone−Ethanol−Chloroform−Benzene System

available unit	capacity (rwu/batch)	suitability	mean processing time (h)
mixer-1	100	task 1: mixing-1 ({E, F}, {L$_4$})	1
distiller-1 (rectifier)	100	task 2: distillation-1 ({L$_4$}, {A, L$_{10,A}$})	6
mixer-2	100	task 3: mixing-2 ({E, L$_{10,A}$}, {L$_1$})	1
distiller-2 (rectifier)	100	task 4: distillation-2 ({L$_1$}, {Z$_1$, L$_{6,C}$})	6
mixer-3	100	task 5: mixing-3 ({F, L$_{6,C}$}, {L$_4$})	1

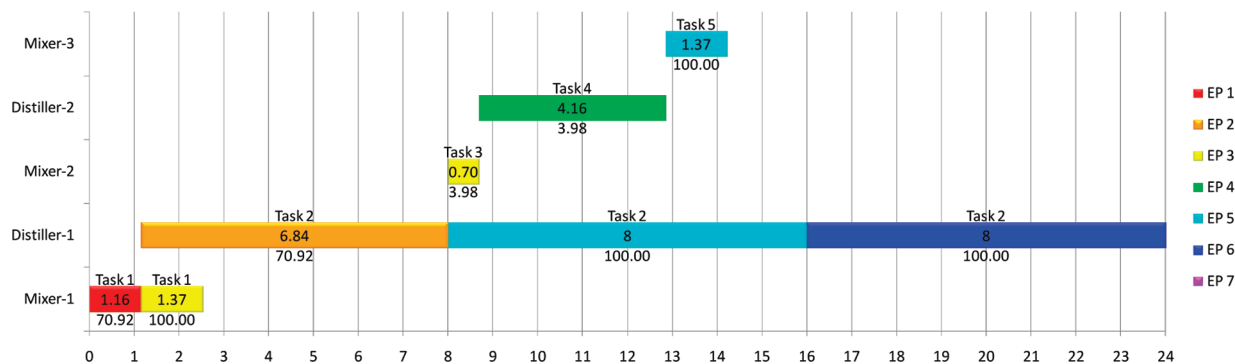| state	storage capacity (rwu)	initial amount (rwu)	price per unit weight (rcu/rwu)
S$_1$ (F)	unlimited	3000	0
S$_2$ (E)	unlimited	1000	50
S$_3$ (L$_4$)	unlimited	0	0
S$_4$ (A)	unlimited	0	85
S$_5$ (L$_{10,A}$)	unlimited	0	0
S$_6$ (L$_1$)	unlimited	0	0
S$_7$ (Z$_1$)	unlimited	0	60
S$_8$ (L$_{6,C}$)	unlimited	0	0

Figure 10. Gantt chart for the base case of the acetone−ethanol−chloroform−benzene system.

Table 11. State Conditions (rwu) in the Base Case of the Acetone−Ethanol−Chloroform−Benzene System

	event point						
state	1	2	3	4	5	6	7
S_1 (F)	2929.79	2929.79	2830.79	2830.79	2734.49	2734.49	2734.49
S_2 (E)	999.29	999.29	997.30	997.30	997.30	997.30	997.30
S_3 (L_4)			100.00				
S_4 (A)			28.58	28.58	28.58	68.88	109.18
S_5 ($L_{10,A}$)			39.35	39.35	39.35	99.05	158.75
S_7 (Z_1)					0.28	0.28	0.28

This scheduling approach is justified primarily due to the following assumption:

For the case that the time horizon is much longer than the durations of individual tasks, a proper time period which is shorter than the entire time horizon exists and, within which, some maximum capacities or other suitable criteria can be reached so that the periodic execution of such schedule will achieve results very close to those obtained by solving the original problem without any periodicity assumption.

As a result, the problem size can be significantly reduced. Besides the obvious advantage in computation, the solution should be more convenient and easier to implement in practice since the same schedule is repeated many times. In this approach, the model variables should include the time length of a cycle as well as the detailed schedule within this period. Unlike short-term scheduling where all intermediates other than those provided initially have to be produced before the beginning of the tasks, each unit schedule can start with certain amounts of intermediates as long as storage capacity constraints are not violated. In this work, the initial and final inventories of every intermediate in each cycle are kept at a fixed level so as to maintain material balance across the cycle boundaries. The excess amounts of intermediates are allowed to be removed at the end of each unit period but are assessed with proper penalties.

Since the existing formulations were applied in a straightforward fashion, the detailed model descriptions are omitted in the present paper for the sake of brevity.

7. Case Studies

The feasibility and effectiveness of the proposed sequential design strategy are demonstrated here with case studies, in which the previously described homogeneous ternary and quaternary systems are considered. The objective function used in all case studies is the overall profit of a production campaign, i.e., the total revenue subtracted by the sum of raw-material costs. A time horizon of 24 h has been adopted for all short-term scheduling problems, while 168 h has been used for generating the cyclic schedules. The former problem
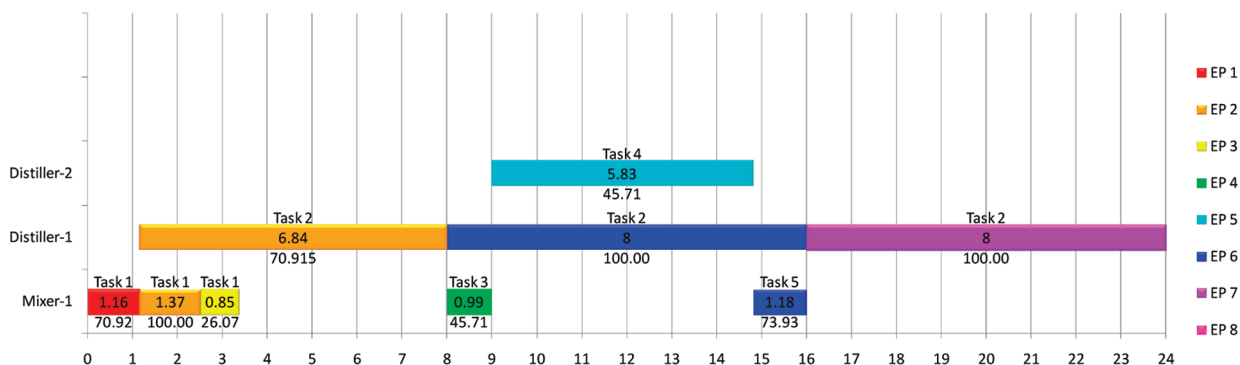

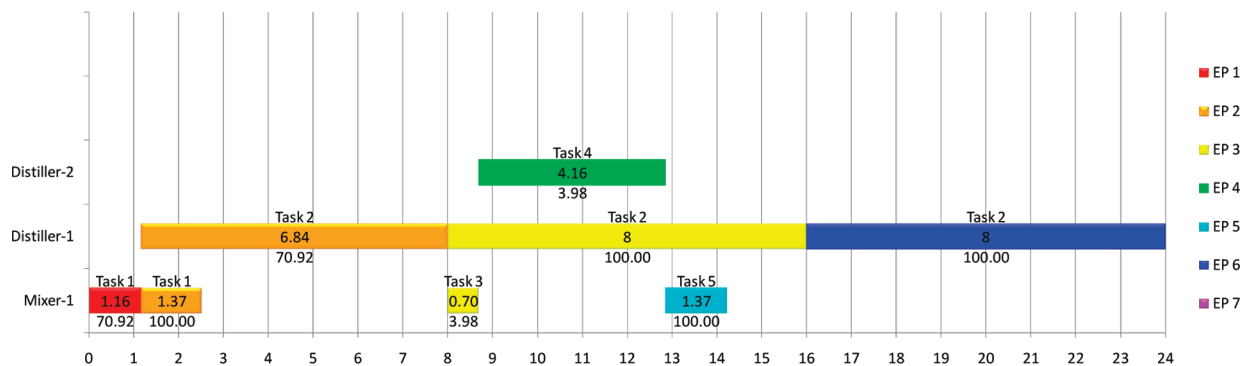**Figure 11.** Gantt chart for case 1 of the acetone−ethanol−chloroform system.

Table 12. State Conditions (rwu) in Case 1 of the Acetone−Ethanol−Chloroform System

	event point							
state	1	2	3	4	5	6	7	8
S_1 (F)	2936.89	2847.89	2824.68	2824.68	2824.68	2794.69	2794.59	2794.59
S_2 (E)	992.20	981.20	978.33	974.72	974.72	974.72	974.72	974.72
S_3 (L_4)			100.00	126.07	126.07	26.07		
S_4 (A)			9.86	9.86	9.86	9.86	23.76	37.66
S_5 ($L_{8,A}$)			61.06	18.96	18.96	18.96	105.06	191.16
S_7 (W_3)						1.87	1.87	1.87

Figure 12. Gantt chart for case 1 of the acetone−ethanol−chloroform−benzene system.

Table 13. State Conditions (rwu) in Case 1 of the Acetone−Ethanol−Chloroform−Benzene System

	event point						
state	1	2	3	4	5	6	7
S_1 (F)	2929.79	2830.79	2830.79	2830.79	2734.49	2734.49	2734.49
S_2 (E)	992.29	998.29	997.30	997.30	997.30	997.30	997.30
S_4 (A)			28.58	68.88	68.88	68.88	109.18
S_5 ($L_{10,A}$)			39.35	99.05	99.05	99.05	158.75
S_7 (Z_1)					0.28	0.28	0.28

was formulated as a MILP model and solved with GAMS/ CPLEX. On the other hand, a MINLP model was used for the cyclic scheduling tasks. The discrete and continuous optimizer (DICOPT) and the branch-and-reduce optimization navigator (BARON) in GAMS were both adopted to solve the MINLP models. Notice that DICOPT was developed on the basis of the outer-approximation algorithm using the equality relaxation strategy.[33] Although it has provisions to handle nonconvexities, a global optimum cannot always be guaranteed. On the other hand, it has been established that BARON implements deterministic search algorithms of the branch-and-bound type which can locate the global optima under fairly general conditions.[34] In all examples reported in this paper, the same solutions were found with both MINLP solvers.

It should also be noted that the examples presented below are used *solely* to highlight various features of the proposed strategy. To this end, the design parameters are chosen primarily for the purpose of facilitating proper trade-off. In particular, all weight and cost data are given in terms of *relative weight unit* (rwu) and *relative cost unit* (rcu) according to the approach suggested by Majozi.[35] The Gantt charts are used to represent the optimal production schedules. In each chart, the vertical axis is used to specify processing units while the horizontal axis represents time. The processing period of each operation (task) is stipulated with a horizontal

bar. The corresponding task number, throughput, and period length are respectively given at locations above, below, and within this bar. The event points are marked with different colors and the event-point labels are given at the right-side of the charts. The inventories of all lumped materials, i.e. state conditions, at various event points are also provided in the various tables below to facilitate representation of the material-balance data identified in the optimal solutions.

7.1. Generation of Short-Term Schedules by Assuming That Dedicated Units Are Available and That There Are No Constraints Concerning Storage Capacities and Product Demands−Base Case. For comparison purposes, let us assume in this base case that every available operation unit is used solely for performing a distinct task in STN and every task can be carried out only in one dedicated unit. The processing time of each task is allowed to vary linearly with the amount of feed within ±33% of the nominal level. The storage capacities of all states are assumed to be unlimited. It is also assumed that, at the end of the given time horizon, (a) there are no specific production targets, (b) the intermediates are not taken out of the system until the end of campaign, and (c) the desired products can be sold completely.

• **Ternary System.** The STN and the corresponding material-balance data in Figure 7 have been used in the present case study. Other design parameters needed for solving the short-term scheduling model are presented in
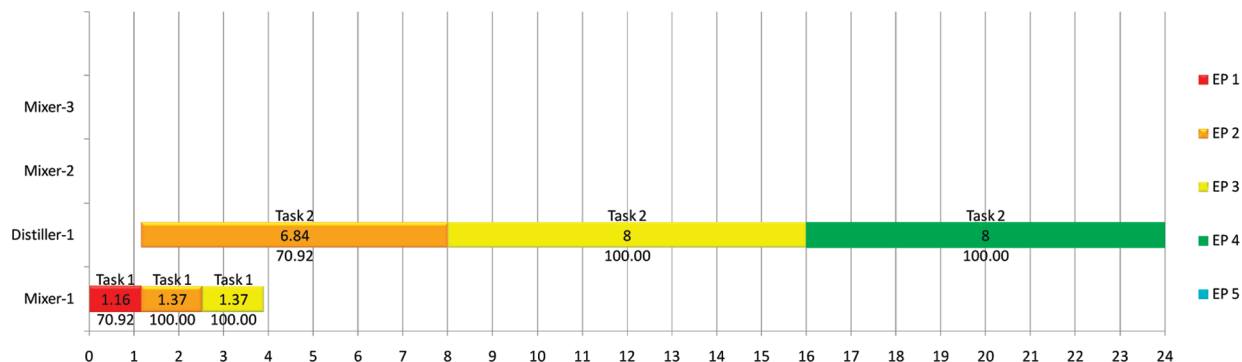

Figure 13. Gantt chart for case 2 of the acetone−ethanol−chloroform system.

Table 14. State Conditions (rwu) for Case 2 of the Acetone−Ethanol−Chloroform System

state	event point				
	1	2	3	4	5
S_1 (F)	2936.89	2847.89	2758.89	2758.89	2758.89
S_2 (E)	992.20	981.20	970.20	970.20	970.20
S_4 (A)			9.86	23.76	37.66
S_5 ($L_{8,A}$)			61.06	147.16	233.25

Table 15. State Conditions (rwu) for Case 2 of the Acetone−Ethanol−Chloroform−Benzene System

state	event point				
	1	2	3	4	5
S_1 (F)	2929.79	2830.79	2731.79	2731.79	2731.79
S_2 (E)	999.29	998.29	997.29	997.29	997.29
S_4 (A)			28.58	68.88	109.18
S_5 ($L_{10,A}$)			42.34	102.04	161.74

Table 8. The most appropriate number of event points is determined through an iterative procedure. The procedure starts by solving the optimization problem with two event points, and this number is then increased one-at-a-time until an additional point does not result in any improvement in the objective function. The optimal number of event points found in this iteration process is 8, and the corresponding profit is 2049.31 rcu. The resulting production schedule and the processing amounts of all tasks can be found in Figure 9. The corresponding state conditions are provided in Table 9. Notice that each empty cell in this table denotes that the corresponding condition is zero rwu. For the sake of conciseness, this table has also been condensed as much as possible. Specifically, if the entries in a row (or column) are all zeros, then this row (or column) is removed from the table completely. Thus, it can be clearly observed that not all possible lumped materials are included in Table 9. From eq 17 and Figure 7, one can see that the desired products should be associated with state 4 (material A) and state 7 (material W_3). Consequently, the corresponding state conditions at event point 7 represent the amounts of acetone (A) and ethanol−chloroform azeotrope (W_3) produced in the production campaign.

• **Quaternary System.** The STN and the corresponding material-balance data in Figure 8 have been adopted for the present case studies. Additional design parameters needed for solving the short-term scheduling model can be found in Table 10. Notice that the optimal number of event points in this case is 7 and the corresponding objective value is 9161.91 rcu. The resulting Gantt chart can be found in Figure 10. The corresponding state conditions are presented in Table 11. Notice that this table has also been condensed. From eq 18 and Figure 8, it is clear that the desired products in this case should be associated with state 4 (material A) and state 7 (material Z_1). Consequently, the corresponding state conditions at event point 7 represent the amounts of acetone (A) and ethanol−chloroform azeotrope (Z_1) produced in the production campaign.

• **Concluding Remarks.** It should be noted that the above results are in some sense impractical. First of all, it can be observe that a large inventory of each intermediate is accumulated in the storage tank at the end of production campaign in both cases. This is of course due to the fact that the penalties for accumulating excess inventories are not assessed in the scheduling model. In addition, it may not be feasible to have a very large storage capacity for every material. Finally, the practice of providing a dedicated unit for every task in STN may not be cost-effective. Equipment sharing should be considered under certain circumstances. To address these practical issues, several different case studies have been performed and their results are presented in the sequel.

7.2. Generation of Short-Term Schedules by Considering Equipment-Sharing Opportunities without Storage and Demand Constraints. The case studies presented here were done with the same assumptions and design parameters adopted in the base cases. Additional constraints were introduced to allow more than one operation to be performed in the shared units. These constraints were formulated according to Ierapetritou and Floudas.[18]

7.2.1. Sharing Mixers−Case 1. It can be observed that multiple mixing operations are present in the STN presented in Figure 7 and also in Figure 8. The effects of sharing mixer are thus examined in the sequel:

• **Ternary System.** In this case, only one mixer (mixer-1) is assumed to be available for task 1, 3, and 5 (i.e., operations mixing-1, mixing-2, and mixing-3) in Figure 7. The optimal number of event points in this case is 8, and the corresponding objective value is exactly the same as that obtained in the base case. This is probably due to that fact the time periods for mixing operations do not overlap in the base-case schedule. However, to solve the present model, more event points are needed to accommodate the operation constraints for sharing mixers. The Gantt chart obtained in the present case is shown in Figure 11. The corresponding state conditions are presented in the condensed Table 12.

• **Quaternary System.** It is assumed that mixer-1 is the only mixer available for carrying out task 1, 3, and 5 (i.e., operations mixing-1, mixing-2, and mixing-3) in the STN in Figure 8. Notice that the optimal number of event points and the corresponding objective value are the same as those obtained in the base case. The resulting Gantt chart is shown
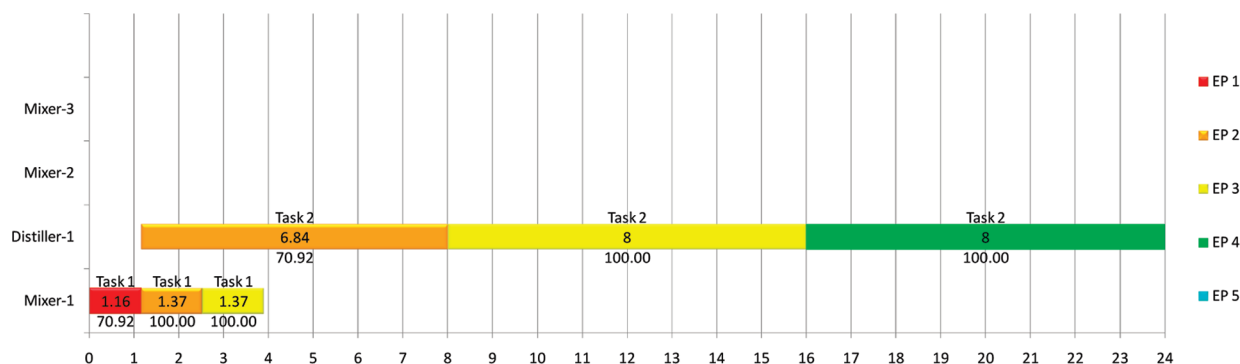
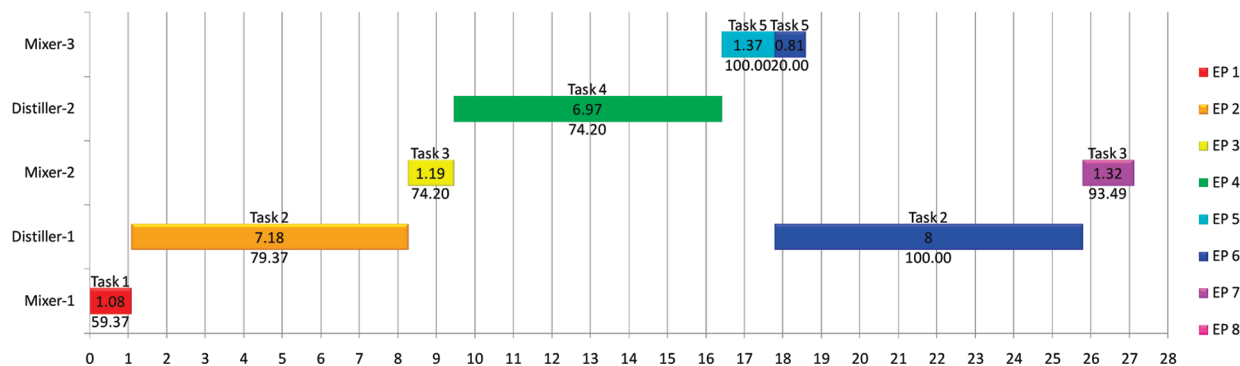**Figure 14.** Gantt chart for case 2 of the acetone−ethanol−chloroform−benzene system.

Figure 15. Gantt chart for a cyclic period in case 3 of the acetone−ethanol−chloroform system.

Table 16. Initial Amounts (rwu) of Lumped Materials in Case 3 of the Acetone−Ethanol−Chloroform System

state	cyclic period	startup period	final period
S_1 (F)	101.68	41.02	130.22
S_2 (E)	19.78	7.00	23.83
S_3 (L_4)	20.00		20.00

Table 17. State Conditions (rwu) during a Cyclic Period in Case 3 of Acetone−Ethanol−Chloroform System

state	event point							
	1	2	3	4	5	6	7	8
S_1 (F)	48.84	48.84	48.84	48.84	8.14			
S_2 (E)	13.25	13.25	7.39	7.39	7.39	7.39		
S_3 (L_4)	20.00						20.00	20.00
S_4 (A)			11.03	11.03	11.03	11.03	24.93	
S_7 (W_3)					3.04	3.04	3.04	
S_8 ($L_{8,C}$)					11.86			

Table 18. Amounts (rwu) of Taken Intermediates and Delivered Products in Case 3 of the Acetone−Ethanol−Chloroform System

periods	cyclic period	startup period		final period		
		event point				
state	8	4	5	6	7	8
S_3 (L_4)						47.44
S_4 (A)	24.93	3.63			24.26	
S_6 ($L_{3,1}$)	93.49			26.55	21.72	51.49
S_7 (W_3)	3.04		1.00		2.60	
S_8 ($L_{8,C}$)		23.39				

in Figure 12. The corresponding state conditions are given in the condensed Table 13.

7.2.2. Sharing Distillers—Case 2. From Figures 7 and 8, one can see that there is more than one rectification and/or stripping operation in each STN. The following case studies were carried out to analyze the impacts of performing these operations in shared distillers.

• Ternary System. It is assumed in this case that distiller-1 is the only available distiller for carrying out both task 2 (distillation-1) and task 4 (distillation-2), but *dedicated* mixers are provided for all mixing operations. The optimal number of event point (5) was found to be lower than that obtained in the base case, and the corresponding objective value (1710.83 rcu) is also smaller. The resulting schedule is presented in Figure 13, and the corresponding state conditions are provided in the condensed Table 14. Note that task 3, 4, and 5 (i.e., operations mixing-2, distillation-2, and mixing-3) are not performed. This is due to the facts that no restriction is set for the demand of state 7 (material W_3) and, also, the selling price of state 7 (material W_3) is lower than that of state 4 (material A).

• Quaternary System. In this case, the processing unit distiller-1 is the only distiller available for performing task 2 (distillation-1) and task 4 (distillation-2), but again, dedicated mixers can be used for all mixing tasks. It was found that the optimal number of event points (5) is lower than that in the base case and the corresponding objective value (9144.73 rcu) is also smaller. The resulting Gantt chart is provided in Figure 14, while the corresponding state conditions are presented in the condensed Table 15. Note that tasks 3, 4, and 5 (i.e., mixing-2, distillation-2, and mixing-3) are not performed at all. This is due to the facts that no restriction is imposed on the demand of state 7 (material Z_1) and also its selling price is lower than of state 4 (material A).

7.2.3. Concluding Remarks. The feasibility and impacts of sharing operating units are discussed in the above examples. It can be concluded that the mixing operations are not critical. The overall profit of a production campaign may still be maintained at the same level as that achieved with dedicated units by sharing the mixers while slightly adjusting the production schedule. On the other hand, sharing distillers inevitably causes a significant reduction in the overall profit. This undesirable outcome usually cannot be circumvented by schedule modification.

7.3. Generation of Cyclic Schedules—Case 3. An expansion of time horizon in short-term scheduling model inevitably results in the incorporation of more decision variables. Consequently, the size of this model may become too large to be solvable. The cyclic scheduling procedure developed by Wu and Ierapetritou[26] has been adopted here to overcome this drawback. Apart of the practical advantage in plant operation management, computationally the problem is limited to a small fraction of the whole time horizon and can be thus solved more efficiently.

It is assumed that every operation unit in this case is dedicated for performing a distinct task in STN, and every task can be carried out only in one available unit. The processing time of each task is allowed to vary between 33% above and below the nominal level. The feeds are assumed to be unlimited. The lowest demand for every product is assumed to be 1 rwu, and for convenience, the upper limits of intermediate inventories in the following cases are all set at 20 rwu. It is also assumed that the intermediates are allowed to be taken out of the system at any time during the given time horizon in case of over production.

• Ternary System. The STN and the corresponding material-balance data in Figure 7 were used in the present case study. Most of the other design parameters in the cyclic scheduling model can be found in Table 8. To impose penalties on the intermediates, the unit cost for state 5
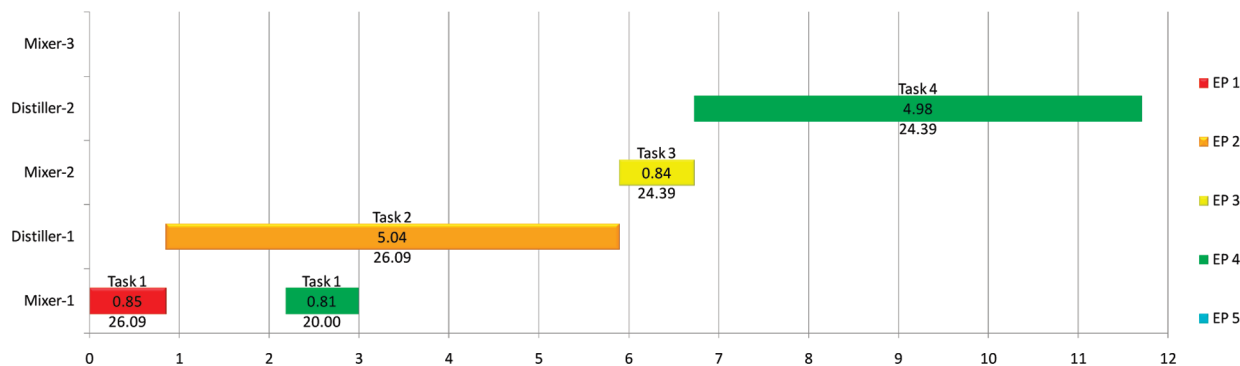
Figure 16. Gantt chart for the startup period in case 3 of the acetone−ethanol−chloroform system.

Table 19. State Conditions (rwu) during the Startup Period in Case 3 of the Acetone−Ethanol−Chloroform System

state	event point			
	1	2	3	5
S_1 (F)	17.80	17.80	17.80	
S_2 (E)	4.13	4.13	2.20	
S_3 (L_4)				20.00
S_4 (A)			3.63	

Table 20. State Conditions (rwu) for Final Period in Case 3 of the Acetone−Ethanol−Chloroform System

state	event point					
	1	2	3	4	5	6
S_1 (F)	115.60	97.80	41.72	41.72	19.31	19.31
S_2 (E)	22.02	19.82	10.20	10.20	5.78	4.07
S_3(L_4)	20.00		20.00			
S_4 (A)			5.06	5.06	16.60	16.60
S_5 ($L_{8,A}$)					20.00	
S_7 (W_3)					1.40	1.40

(lumped material $L_{8,A}$) was changed from 0 (see Table 8) to −15, unit cost for state 8 (lumped material $L_{8,C}$) was changed from 0 to −10, and those of intermediates 3 and 6 (i.e., the lumped materials L_4, and $L_{3,1}$) were also changed from 0 to −1, respectively. A time horizon of 168 h was adopted and it was further divided into three periods according to the solution strategy proposed by Wu and Ierapetritou.[26] A detailed description of the implementation steps is presented in the sequel:

First the repetitive schedule in each cycle was generated. A cycle profit of 42.98 rcu/h with an optimal cycle time of 27.10 h can be identified from the optimal solution. The resulting cyclic schedule can be found in Figure 15. The amounts of raw materials needed for realizing this production schedule are shown in Table 16. Notice that, for the sake of brevity, the initial amounts of states 5 and 6 are not included in this table. These omitted amounts are all zeros. It can also be seen that the final inventories of state 3 (i.e., L_4) is at its upper limit. Additional raw materials at state 1 (material F) and state 2 (material E) are needed in each cycle to provide sufficient intermediates for task 2 (distillation-1) due to these inventory limitations. The corresponding state conditions are presented in Tables 17 and 18. In every cycle, the amounts of produced products, i.e., state 4 (material A) and state 7 (material W_3), were found to be 24.93 and 3.04 rwu,

respectively. A 93.49 rwu portion of state 6 (material $L_{3,1}$) should be removed to maintain steady operation from cycle to cycle.

A total of five cycles should be carried out in this case so as to leave enough time for the initial and final periods. Specifically, the total number of cycles (N_{cycle}) is determined by trial and error to satisfy the following inequality constraint

$$H > CN_{cycle} + MS_0$$

where, MS_0 denotes the minimum make span of the initial period. The time horizon of the final period (MS_f) should then be set at

$$MS_f = H − (CN_{cycle} + MS_0)$$

On the basis of Table 16, it can be observed that the amounts of state 3 (i.e., the intermediate L_4) needed to start the cyclic schedule is 20 rwu. Therefore, this amount must be produced in the initial period. A two-step approach has been taken for this purpose. The short-term scheduling model was first used to solved to minimize the make span of the initial period. The profit of initial period was then maximized with a fixed time horizon calculated from the make-span minimization problem. It was determined that a total of 11.71
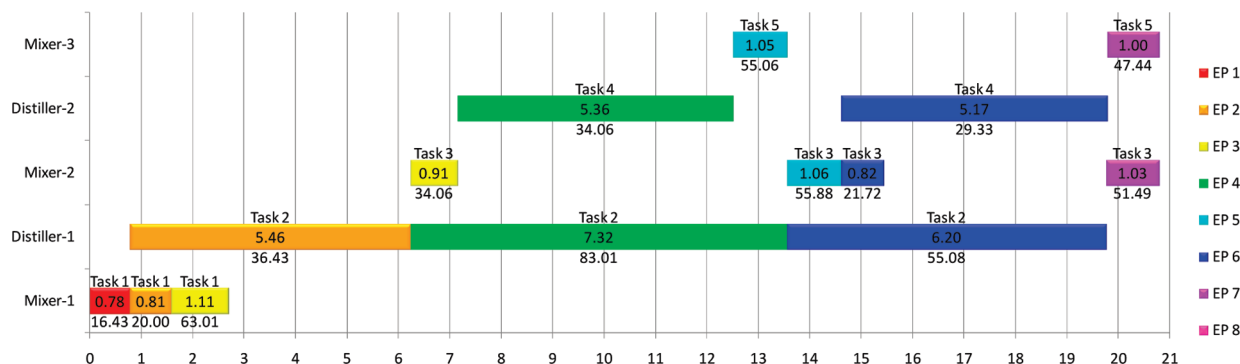

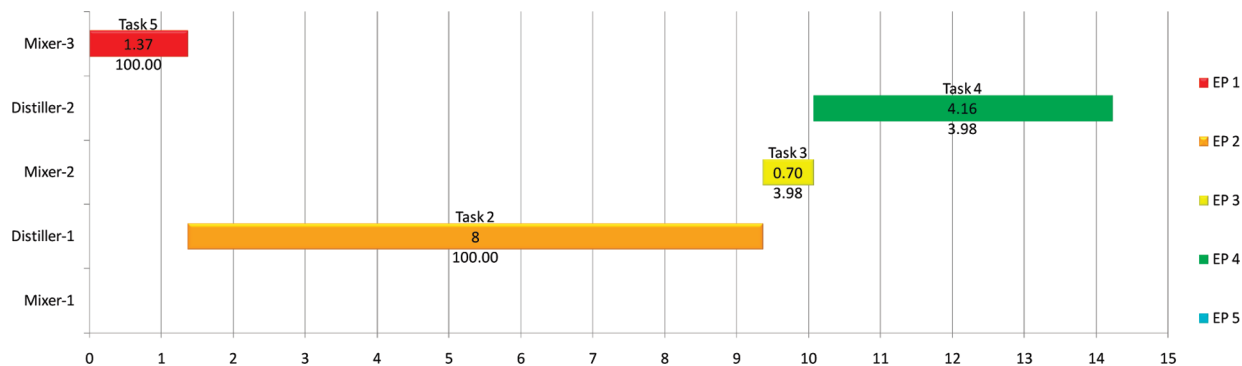**Figure 17.** Gantt chart for the final period in case 3 of the acetone−ethanol−chloroform system.

Figure 18. Gantt chart for a cyclic period in case 3 of the acetone−ethanol−chloroform−benzene system.

Table 21. Initial Amounts (rwu) of Lumped Materials in Case 3 of the Acetone−Ethanol−Chloroform−Benzene System

state	cyclic period	startup period	final period
S_1 (F)	96.30	17.79	148.03
S_2 (E)	0.99	3.74	10.87
S_8 ($L_{6,C}$)	3.70		3.70

Table 22. State Conditions (rwu) during a Cyclic Period in Case 3 of the Acetone−Ethanol−Chloroform−Benzene System

state	event point			
	1	2	3	5
S_2 (E)	0.99	0.99		
S_4 (A)			40.30	
S_8 ($L_{6,C}$)				3.70

Table 23. Amounts (rwu) of Taken Intermediates and Delivered Products in Case 3 of the Acetone−Ethanol−Chloroform−Benzene System

periods	cyclic period		startup period		final period
	event point				
state	4	5	4	5	7
S_4 (A)	40.30		7.24		61.36
S_5 ($L_{10,A}$)		56.71			59.70
S_7 (Z_1)		0.28		1.00	2.91
S_8 ($L_{6,C}$)					38.63

h is needed in the initial period to produce 20 units of state 3 (i.e., L_4) with 5 event points, and the maximum profit is −215.49 rcu. Note that 23.39 rwu of state 8 (i.e., $L_{8,C}$) is removed, and the profit is lower as the removal penalty is imposed. The resulting initial schedule can be found in Figure 16. The amounts of raw materials needed for startup are also shown in Table 16, and the corresponding state conditions are presented in Tables 18 and 19. In this startup period, the amounts of delivered products in state 4 (material A) and state 7 (material W_3) are 3.63 and 1.00 rwu, respectively.

Table 24. State Conditions (rwu) for the Startup Period in Case 3 of the Acetone−Ethanol−Chloroform−Benzene System

state	event point			
	1	2	3	5
S_2 (E)	3.56	3.56		
S_4 (A)			7.24	
S_8 ($L_{6,C}$)				3.70

Notice from Table 17 that the amounts of states 3 (i.e., L_4) at the end of each cycle should be 20 rwu. Thus, the production schedule in the final period should be synthesized to consume these inventories at the end of cyclic schedule. The time horizon for final period was determined by subtracting the total length of the first two periods from the whole horizon, i.e., 20.79 h. The profit in this final period was maximized within this fixed horizon. The optimal number of even point in this case is 8, and the corresponding objective value is 859.31 rcu. The resulting final schedule can be found in Figure 17. The amounts of raw materials needed for final period can be found in Table 16, and the corresponding state conditions are presented in Tables 18 and 20. The overall profit over the entire time horizon was found to be 6640.90 rcu.

• **Quaternary System.** A cycle profit of 178.49 rcu/h with an optimal cycle time of 14.22 h was determined first. The resulting cyclic schedule can be found in Figure 18. The amounts of raw materials needed for realizing this production schedule are shown in Table 21. Notice that the initial amounts of states 3−7 are not included in this table, and these omitted amounts should be all zeros. It can be observed that the final cycle inventory of state 8 (material $L_{6,C}$) is at 3.70 rwu. The corresponding state conditions are presented in Tables 22 and 23. The amounts of produced products, i.e., state 4 (material A) and state 7 (material Z_1), were found to be 40.30 and 0.28 rwu per cycle, respectively. Continuity
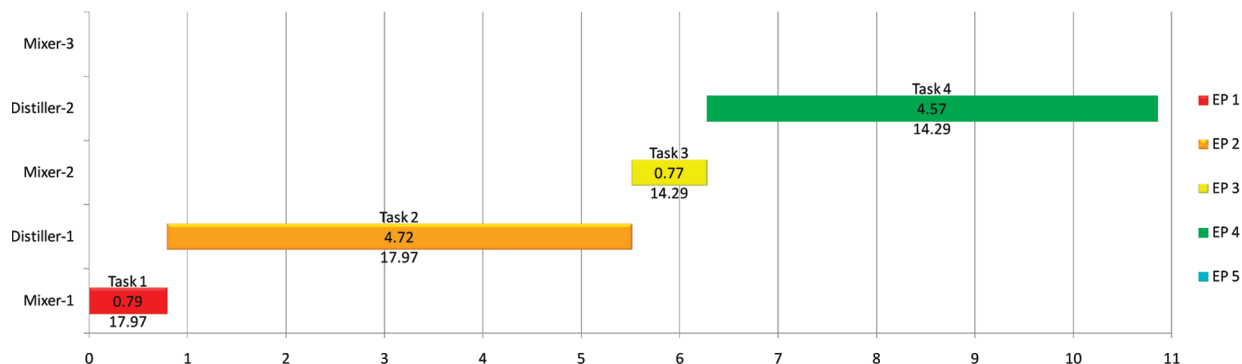

Figure 19. Gantt chart for the startup period in case 3 of the acetone−ethanol−chloroform−benzene system.
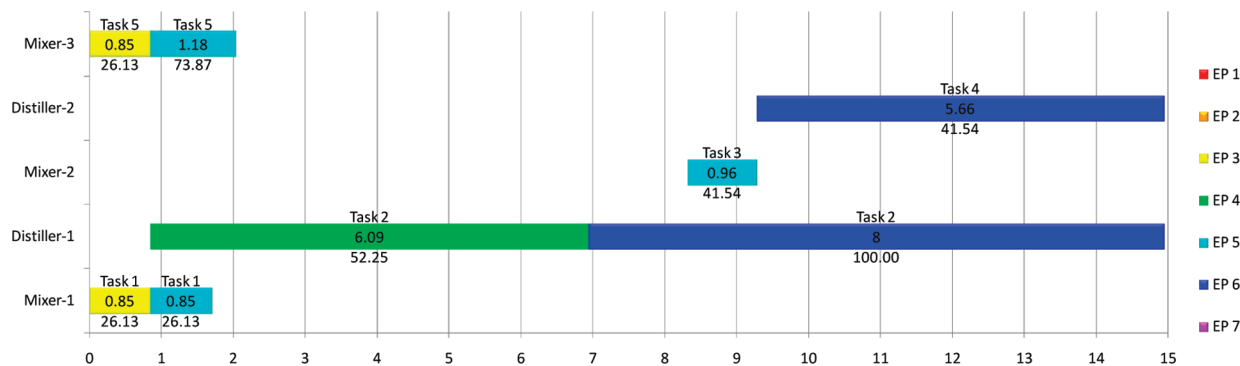
Figure 20. Gantt chart for the final period in case 3 of the acetone−ethanol−chloroform−benzene system.

Table 25. State Conditions (rwu) during the Final Period in Case 3 of the Acetone−Ethanol−Chloroform−Benzene System

state	event point					
	1	2	3	4	5	6
S_1 (F)	148.03	148.03	97.01	97.01		
S_2 (E)	10.87	10.87	10.60	10.60		
S_4 (A)					21.06	21.06
S_8 ($L_{6,C}$)	3.70	3.70	2.73	2.73		

between cycles can be maintained by removing 56.71 rwu of state 5 (material $L_{10,A}$) at the end of every cycle. Ten (10) cycles are needed in this case.

Notice that 3.70 rwu of state 8 (material $L_{6,C}$) must be produced to start the cyclic schedule. A make span of 10.85 h is needed in the initial period to produce this amount of material. The maximum profit in the initial period was found to be 479.16 rcu with five event points. The resulting initial schedule is presented in Figure 19. The amounts of raw materials needed for startup is also shown in Table 21, and the corresponding state conditions are given in Tables 23 and 24. Within this startup period, 7.24 rwu of state 4 (material A) and 1.00 rwu of state 7 (material Z_1) are produced and delivered to customer.

The production schedule in the final period is synthesized mainly for the purpose of consuming the inventory of state 8 (material $L_{6,C}$) at the end of cyclic schedule (i.e., 3.70 rwu). The profit maximization problem for the final period was solved with a fixed time horizon of 14.94 h. The optimal number of event point was found to be 8, and the corresponding objective value was 3908.78 rcu. The resulting final schedule can be found in Figure 20. The amounts of raw materials needed for final period is shown in Table 21, and the corresponding state conditions are presented in Tables 23 and 25. Finally, an overall profit of 29771.03 rcu can be found by summing the profits of individual periods over the entire time horizon.

8. Conclusions

An effective sequential approach is presented in this paper for synthesizing the STNs and the corresponding production schedules of batch azeotropic distillation processes. The proposed STN construction method was rendered possible by resorting to a systematic approach to classify the entire space of a RCM into a finite number of areas, lines, and points and by implementing an integer programming (IP) model for logic inference. A nonlinear program (NLP) was also developed on the basis of this STN structure to generate the material-balance constraints needed for building the scheduling models. Both short-term and cyclic schedules were produced with the conventional continuous-time formulation. The former task was

accomplished by solving a MILP model, while the later a MINLP model. The feasibility of the proposed approach is demonstrated with two specific homogeneous systems. Satisfactory process configurations and production schedules can be obtained in all the cases we have studied so far.

Nomenclature

y_l = binary variable denoting the presence (1) or absence (0) of material l
z_j = binary variable associated with the possible jth operation
x_i = mass fraction of component i in the mixture
H = total production time horizon
C = cyclic period time
N_{cycle} = number of cycles within the time horizon
MS_0 = minimum make span of initial period
MS_f = time horizon of final period

Subscripts
0 = initial
cycle = cycle index
f = final
i = component index
j = unit index
l = lumped material index

Supporting Information Available: Supporting Tables 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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