SEPARATIONS

Synthesis of Azeotropic Distillation Systems with Recycles

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The systematic generation of process alternatives for multicomponent heterogeneous or homogeneous distillation systems is described. Alternatives based on distillation and decanting alone must generally be expanded by mixing and occasionally by recycling to provide high-purity products. For azeotropic mixtures, systematic considerations of recycles further expand those alternatives to meet the additional goal of high recoveries. The latter generates many potential alternatives, and new necessary conditions given here for feasible recycle destinations eliminate as many as 90% of the infeasible alternatives without the need for a complete converged material balance simulation. The physical meaning of this recycle reachability rule is that there must be an exit point for each component not only for the entire process system, but also within each recycle loop. The recycling of pure components is also identified as a useful and sometimes essential feature in developing alternatives. Selected results are reported for a ternary mixture of ethanol, benzene, and water and also for a quaternary mixture of water, *n*-butanol, acetic acid, and *n*-butyl acetate.

Introduction and Background

Conceptual design seeks feasible flowsheet alternatives for a wide variety of tasks. This often includes heterogeneous and homogeneous azeotropic distillations, which are common and economical techniques for separating azeotropic mixtures. We report results from studies of the synthesis of azeotropic separation systems to yield high-purity products with high recoveries using decanters, distillation, mixing, and recycling. The algorithms and rules in this paper address process feasibility, especially the issues raised by recycles.

As for many problems in process synthesis, this class of problems requires the identification and specification of various equipment units and their interconnections. The problems in heterogeneous azeotropic mixtures are typically characterized by a large number of alternatives,¹ so that systematic methods are useful for generating them. These methods normally include calculations, heuristics, or a combination of the two to generate feasible alternatives within the design space defined by the assumptions concerning the allowed types of units and their interconnections.

Several approaches have been developed to generate liquid separation systems and to identify the recycle streams. These include forward-chaining,² hierarchical procedures,^{3–5} and means–ends analysis.⁵

Wahnschafft et al.⁶ developed a blackboard-based architecture to accommodate different synthesis approaches in an opportunistic problem-solving approach implemented in SPLIT software. Another approach based on graph theory and combinatorial techniques was proposed by Friedler et al.;⁷ a key in this approach is a special directed bipartite graph known as a "process graph" or P-graph.

Rooks et al.⁸ described a feasibility test and algorithms for the generation of distillation systems for homogeneous azeotropic mixtures. Such methods have been implemented for ternary and multicomponent systems to generate a large number of alternative flowsheets. However, this approach did not include a systematic study of recycles or a treatment of heterogeneous liquid–liquid behavior. Both are often found in systems for the separation of nonideal mixtures and can be used to effect certain separations that are otherwise infeasible.

Recycling of impure cuts, or sometimes even pure components, has been used to improve the overall separation process for a particular mixture, e.g., recycling a pure component in exactly the required amount to intentionally form an azeotrope with the entire flow of another component.^{9–11} Although the use of recycles to close material balances has been studied in many papers, we know of no systematic study of recycles to develop process alternatives. This paper describes the results of such a study, including new feasibility tests to discriminate among the large number of alternatives that arise.

The approach described here for generating alternatives includes several algorithms. These are based on combinations of target-oriented, forward-chaining, and/ or opportunistic procedures, for which new rules and decisions are developed to treat heterogeneous phase behavior and recycles. The approach is divided into two main parts.

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Figure 1. Residue curve map for ethanol, benzene, and water at 1 atm.

Part I finds alternatives with *feasible product purities* using combinations of traditional process synthesis techniques along with some new heuristics for mixing and recycling. This approach is based primarily on a forward-chaining process in which we study each state in the process. Opportunistic decisions are made for each level, and these decisions are tracked as alternatives until the product requirements are satisfied, i.e., until all product species leave the process in exit streams of the desired purity. A state-task network is used to represent these flowsheets with feasible product purities.

In addition to the desired exit streams, there are often additional streams generated in part I that do not meet any desired product purity. Part II generates alternatives with *high factional recoveries* by considering different decisions for the recycling of these additional streams. New necessary conditions for recycle feasibility are described that can efficiently and quickly eliminate many infeasible alternatives without requiring lengthy closed-loop material balance calculations.

Motivating Example

A ternary mixture of ethanol, benzene, and water can be separated using heterogeneous azeotropic distillation. The residue curve map (RCM) boundaries and the liquid-liquid phase envelope on the boiling surface are shown in Figure 1, and the azeotropic compositions are given in Table 1. The UNIQUAC activity model is used to represent the vapor-liquid-liquid equilibrium phase behavior of ethanol, benzene, and water. The binary parameters between ethanol and water are taken from Stabnikov et al.,¹² and those between ethanol and benzene are taken from Ellis.¹³ The binary parameters between benzene and water are estimated using UNIFAC vapor-liquid equilibrium parameters. This model predicts reasonable solubilities and azeotropic compositions at 1 atm. Gmehling et al.¹⁴ and references therein discuss this particular mixture as well as the importance and difficulty of modeling phase equilibria in heterogeneous mixtures.

 Table 1. Azeotropic Compositions for Ethanol (1),
 Benzene (2), and Water (3) at 1 atm Pressure^a

	temp				
azeotrope	(°C)	<i>X</i> ₁	<i>X</i> ₂	<i>X</i> 3	stability
ternary	64.2	0.2766	0.5248	0.1985	unstable node
benzene + ethanol	68.0	0.4585	0.5415	0.0000	saddle
benzene + water	69.2	0.0000	0.7025	0.2975	saddle
ethanol + water	78.1	0.9074	0.0000	0.0926	saddle

^{*a*} Liquid-phase nonidealities represented by the models discussed in the text. Compositions given as mole fractions x_i for components 1 (ethanol), 2 (benzene), and 3 (water)



Figure 2. State-task network for a mixture of 20% ethanol (A), 40% benzene (B), and 40% water (C). Underlined streams are heterogeneous and can be decanted. Nodes in the STN represent streams, and arcs represent tasks of mixing, decanting, and distillation. Node 1 is feed 1 in Figure 1.

Consider a feed stream containing 20% ethanol, 40% water, and 40% benzene at 1 atm pressure (feed 1 in Figure 1). This heterogeneous mixture is located in distillation region 3 where water can be recovered as a bottoms product at high purity. (For promising alternatives, the fate of trace components must also be considered in a later stage of the design.)

Alternatively, a decanter can be used to split feed 1 into an aqueous stream in region 3 and an organic stream in region 1. For the latter stream, benzene is a feasible high-purity product. The impure distillates from the two columns producing water and benzene can be mixed to generate a stream in region 2, where ethanol is a feasible high-purity product. The corresponding column configuration with high-purity products for the three pure components is shown in Figures 2 (statetask network) and 3a (flowsheet). Several alternatives can be generated by recycles, e.g., stream 9 can be recycled to the decanter, to unit I, or to unit II; this generates Figure 3b-d, respectively (flowsheets with high recoveries). These alternatives differ only in the recycle destination and raise the following questions: (1) How many feasible flowsheets are generated by the different recycle destinations for stream 9? Are there any simple rules for determining them? (2) Would a different feasible process result if feed 1 were distilled to first produce pure water and then the overhead stream were decanted to produce a stream in region 1? If so, how does that alternative compare with others? (3) How can feasible flowsheets be generated systematically? (4) How can mixtures containing more components be treated?

Answers to these questions are the focus of this paper.

Part I. High-Purity Alternatives

Alternatives with the desired high purities are obtained by the following three algorithms. More examples are provided in Tao.¹⁵ We consider only high-purity



Figure 3. Candidate flowsheets for feed 1 in Figure 2. (a) Column structure with feasible purities; stream 9 can be recycled to the decanter, or unit I or II. (b) Case 1: stream 9 is recycled to the decanter. (c) Case 2: stream 9 is recycled to unit I. (d) Case 3: stream 9 is recycled to unit II.

products and consider only feasibility here (feasible alternatives should be ranked and optimized later).

Algorithm 1. Characterize the Mixture. 1. To begin this problem, one is given a phase equilibrium model, the feed composition and flow rate, and the column pressure(s). Note that some of these givens will be design variables when this procedure is used in a larger context, e.g., whole flowsheet synthesis where the feed composition for the separation is determined in part by an optimization of the reactor conditions.

2. Characterize the residue curve map structure as follows:

(a) Compute the compositions and temperatures of all azeotropes and determine the stability of all singular points (azeotropes and pure components).¹⁶

(b) Number the singular points in order of increasing boiling temperature.

Note that these calculations do not require graphical representations and can be done for any number of components for which a model is available.

3. Compute the adjacency and reachability matrices for the residue curve map structure.¹¹ Note that these matrices are completely defined from the singular point structure in the residue curves and depend only on the pressure and the phase equilibrium behavior.

4. Calculate the liquid—liquid phase stability of each azeotrope using, for example, the method of Wasyl-kiewicz et al.¹⁷ For each heterogeneous azeotrope, compute the compositions and relative amounts of the

coexisting liquid phases and determine the distillation region that contains each composition. Note that a liquid—liquid phase separation can sometimes be induced or amplified by lowering the liquid temperature; we do not include this possibility here. Also, if a tie line crosses a distillation boundary, decanting might be advantageous (see algorithm 3). Otherwise, the separations will be based on distillation alone, because the liquid—liquid tie lines cannot be used to cross distillation boundaries to gain advantage.

It is useful to define four classifications for streams in developing alternatives: type 1, product exit streams; type 2, nonproduct exit streams, such as purges, streams to treatment, streams to fuel byproducts, etc.; type 3, intermediate streams, that is, streams in the forward flow path from unit to unit; and type 4, all other streams in the flowsheet. These streams cannot be separated further by decanting or distillation and are resolved in algorithm 3 or in part II.

The desired purities for types 1 and 2 are considered to be known for our purposes. It is also useful in what follows to distinguish between exit streams (types 1 and 2) and nonexit streams (types 3 and 4).

Algorithm 2. Alternatives from Decanting and Distillation. An important part of the procedure is based on the use of decanters and columns. Because we consider a maximum of two liquid phases and simple columns with a single feed and two product streams, the results of this algorithm can be represented in a binary tree structure. Simple distillation sequences for ideal mixtures are a special case and can be completely generated by this algorithm (no decanter will appear). For nonideal mixtures, the situation is more complex, and this algorithm must be combined with other considerations as discussed in algorithm 3.

1. Begin with a list of streams, S_m , and a set of tree structures, T, one for each of the current known alternatives. T will expand as alternatives are generated and each additional alternative will have its own list of streams S_m .

(a) Note that the ultimate size of T (and therefore the range of m) is equal to the total number of alternatives. Except for simple cases such as ideal mixtures, this number is initially unknown and is determined recursively via step 4 of this procedure. (In subsequent steps, the tree structures generated will become parts of larger, more complex alternatives generated by including mixing and recycling; see algorithm 3.)

(b) Also note that the ultimate size of each list S_m is unknown initially. S_1 is initialized with one stream, and new streams are generated in steps 3 and/or 4 of this procedure. The initial stream in step 1 is the original feed or a stream generated by subsequent considerations of mixing and recycling in algorithm 3.

2. If the current stream matches a desired exit purity, classify it as type 1 (for products) or type 2 (for nonproducts) and go to step 6.

3. If the current stream is heterogeneous, calculate the coexisting equilibrium liquid compositions and flows. If the compositions are in different distillation regions from one another, then classify the current stream as type 3, use a decanter to generate two more streams and add them to S_{m} ; then go to step 6.

4. If the current stream is (a) homogeneous or (b) heterogeneous with a tie line that does not cross a distillation boundary, then calculate the feasible splits (direct split and/or indirect split) using the method of Rooks et al.⁸ If the resulting list of feasible product streams is nonzero, then the current stream can be split using distillation. In that case, classify the current stream as type 3, add the list of feasible product streams found to S_{m} , increment the number of alternatives, and add a new tree in T to describe each one; then go to step 6. Otherwise, continue with step 5.

5. The current stream cannot be split by distillation or decanting and is not a desired exit stream. These are streams with compositions at (within a small tolerance of) a homogeneous binary or ternary azeotrope or a homogeneous composition at a distillation boundary. Classify the current stream as type 4.

6. If S_m is not empty, repeat from step 2 for the next entry in S_m . If no alternative remains with unclassified streams, finish; otherwise increment m and repeat this algorithm from step 2 for the next alternative.

Algorithm 2 is used first to generate alternatives for the original feed. These will all be binary trees. One or more of them might meet the desired purities, and those are alternatives desired for the first part of this study. Other alternatives generated in algorithm 2 (perhaps all of them) will not meet the desired purities, but it might be possible to modify them to develop alternatives that will.

These modifications rely on the mixing of streams with different compositions to create compositions in distillation regions that are not accessible by other means. Such mixing is counter to the intuitive view that streams with different compositions should not be mixed as part of a separation system; *this intuition is incorrect for nonideal mixtures*.

Two different aspects of the distillation region structure can be exploited. The first is to mix two or more streams already created that cannot be separated further by distillation or decanting, i.e., type 4 streams that result from algorithm 2. This is useful if the type 4 streams have compositions that lie in different distillation regions and the stream produced by mixing them lies in another region. A separation scheme for the resulting stream can be generated by an additional application of algorithm 2. This adds a mixer (which destroys the tree structure) and other downstream units to the flowsheet but does not add recycle streams.

A second use of mixing combines a single homogeneous stream of type 4 with parts of one or more exit streams. This is advantageous if the resulting stream is heterogeneous with coexisting liquid phases that lie in different distillation regions, and if one or both of those regions are not otherwise accessible. This also destroys the binary tree structure of the flowsheet and introduces a recycle.

Algorithm 3. Alternatives from Mixing and Recycling. First, we sort the alternatives from algorithm 2 into two lists, according to whether the desired purities are feasible (list F) or not (list L). If L is empty and F is not, then F gives the alternatives sought and algorithm 3 is not needed. If L is not empty, we process the entries as follows:

1. Set the current alternative to the first entry of *L*.

2. If more than one stream of type 4 is present in the current alternative, test to see whether the mixtures of two or more of those streams have compositions in a liquid-liquid region. If not, go to step 4. Otherwise, create a new stream by mixing the streams of type 4. Test whether the mixed stream lies in a distillation region different from the first two, or whether the stream is heterogeneous and has coexisting liquid phases with compositions in one or more regions different from the first two. If not, go to step 4.

3. (a) Reclassify the type 4 streams mixed in step 1 as type 3 streams.

(b) Add the new mixed stream to the list of streams for the current alternative. Use algorithm 2 to generate one or more binary trees with additional decanters, columns, and streams to separate this new stream.

(c) Expand the current alternative (and create additional new alternatives if necessary) by including the binary trees generated in the previous step. Add these new alternatives to F or L, depending on whether they produce feasible purities, and go to step 5.

4. Attempt to create a feasible alternative by recycling a portion of one or more exit streams. This is done in the following steps for each type 4 stream.

(a) Test each heterogeneous binary azeotrope to determine whether one or both of the coexisting liquid phases at the azeotrope lie in distillation regions different from the one containing the type 4 stream. (Note: If none are found, higher-order azeotropes, ternary, quaternary, etc., could be tested, but we have not found this necessary.) If none are found, go to step 5.

(b) For each such heterogeneous binary azeotrope found, add to the current alternative by introducing a mixer to combine the type 4 stream being examined with either (i) a portion of an exit stream containing the heterogeneous binary azeotrope found in step 4a, if such an exit stream exists, or (ii) portions of the two pure product streams containing the components that make up that heterogeneous binary azeotrope. Choose the ratio of flows for these two recycle streams equal to the ratio of the component compositions in the binary azeotrope.

Find the minimum flow rates of the recycle streams needed to produce a mixed stream that is heterogeneous and which has coexisting compositions in the same distillation regions as the binary heterogeneous azeotrope. This introduces a decanter following the mixer. Set the flows to be 50% larger than the minimum, provided that the resulting mixed stream remains heterogeneous with coexisting compositions in the desired regions. Otherwise, reduce the flows until this is true.

The composition and flow(s) of the recycle stream(s) are new degrees of freedom in the design. These should be optimized later along with several other design variables. Depending on the details of a particular problem, it might be possible to reduce the flows for one of these recycle streams to 0.

(c) Process the two exit streams from the decanter using algorithm 2. Add the results as additional alternatives to L or F as appropriate.

5. If L is not empty, increment the current alternative and repeat from step 2. Otherwise, either alternatives with feasible purities (but not necessarily high recoveries) are contained in F, or else no feasible alternative can be found. In the latter case, a new pressure, an additional component, a relaxation of the desired purities, or the use of different technology is required to achieve the desired purities.

Two strategic uses of recycles are employed in algorithm 3 to generate a flowsheet with feasible product purities. The first use is employed to replace an infeasible split with a related feasible split. In Figure 3a, two distillate streams (4 and 6) are mixed to create stream 8, which lies in distillation region 2 of Figure 1, where ethanol is a feasible product. A second use is exemplified in a novel method of purifying diethoxymethane (DEM) in U.S. Patent 4,740,273;18 also see Doherty and Malone,¹⁹ Figure 8.22, for the residue curve map. There, a portion of one or more desired product streams (water or a mixture of water with DEM) is recycled and mixed with a ternary homogeneous stream within the flowsheet. This generates a mixed stream in the heterogeneous liquid-liquid region that is decanted to create two streams in different distillation regions where new splits are possible. After decanting, DEM is easily purified from the organic phase by an additional column requiring no additional entrainer or solvents.

Part II. High-Recovery Alternatives Using Recycles

Many or all of the alternatives generated in part I will not achieve high recoveries because one or more type 4 streams are not resolved. Modified alternatives with high recoveries can be generated by identifying feasible recycle destinations for such streams.

Recycling is generally a powerful alternative to performing additional processing.² However, the application of recycling can also affect feasibility for a number of reasons discussed next. As mentioned earlier, a recycle can be used to provide the internal flow of one component to form an azeotrope with a second component in an amount such that all of the second component appears in only one product from a distillation. This "azeotroping" via recycles can generate alternatives with fewer units, as shown later in example 3.

A more complex use of recycling is to cross distillation boundaries. This approach was studied by Doherty and Caldarola²⁰ for homogeneous ternary mixtures. The concept is to devise internal recycles within the flowsheet to "jump" across boundaries at recycle mixing points. Doherty and Caldarola showed that this technique can lead to infeasible designs on account of material balance constraints, and they suggest the following alternative: "For mixtures with distillation boundaries, choose product compositions from each column that lie within the feasible separation regions and on the same side of the simple distillation boundary (or on the same side of the infinite reflux boundary in the distillation line map); do not attempt to cross a simple distillation boundary unless all other alternatives have been explored, and then do so with caution." Also beware of the limitations imposed by the finite reflux distillation boundaries (also see Doherty and Malone,¹⁹ section 5.4).

Recycles can also cause a process to become infeasible for other reasons. For example, a recycle might cause a column feed composition to move into a new distillation region where the desired product is no longer feasible, or it might move a decanter composition from a heterogeneous into a homogeneous liquid region.

A common practice is to identify recycle alternatives by intuition and check feasibility by performing closedloop material balance calculations using simulations. Thus, the definitive test for feasibility is a converged set of closed-loop material balances. However, it is timeconsuming to perform such simulations for all of the recycle alternatives, and consequently, alternatives often go unexplored. (Furthermore, an unconverged material balance calculation provides no definite conclusion about feasibility, because the lack of convergence might be for other reasons, e.g., numerical procedures or tolerances.)

Our strategy is to examine recycle destinations systematically. This can be done effectively with an efficient test to screen out infeasible alternatives which we describe below. Closed-loop material balances for high recoveries are required only for those alternatives that are not eliminated.

A Simple Rule for Infeasibility of Recycles. The following rule is a necessary condition for the feasibility of recycle streams.

Recycle Reachability Rule: For feasibility, the recycle destination should be chosen so that an exit point for each component is reachable from the recycle mixing point. (Reachability is defined precisely below.) A useful special case is the following: If each recycle and each intermediate stream in a flowsheet with feasible purities contains all components present in the fresh feed, then the recycle destinations must be chosen so that all of the nonexit streams in the flowsheet can reach all of the exit streams. Ternary mixtures often fall into this class.

This is a simple but powerful rule that follows from steady-state material balances of all species within each recycle loop. The physical meaning of the recycle reach-



Figure 4. State-task network, adjacency matrix, and reachability matrix for Figure 3b with recycling to the decanter. Node 1 is feed 1 in Figure 1.



Figure 5. State-task network, adjacency matrix, and reachability matrix for Figure 3c with recycling to unit I.

ability rule is that there must be an exit point for each component *not only for the entire process system, but also within each recycle loop.* For example, Figures 3b and 4 show a flowsheet that satisfies the necessary condition and turns out to be a feasible flowsheet to meet high recoveries, as confirmed by closed-loop mass balance. In contrast, some components in certain streams for the alternatives in Figures 3c,d, 5, and 6 cannot reach an exit stream, and we can quickly conclude that these two alternatives are infeasible. For example, in Figure 3c (also see Figure 5), stream 4 cannot reach exit stream 7. Because stream 4 contains all three components and cannot reach an exit point for water (component C), this alternative is infeasible. A similar situation is found for streams 2, 6, 8, and 9.

The recycle reachability rule is a necessary condition for feasibility; it is not sufficient because there are several additional potential reasons for infeasibility.

The state-task network (STN), introduced by Kondili



Figure 6. State-task network, adjacency matrix, and reachability matrix for Figure 3d with recycling to unit II.

et al.,²¹ is a useful tool for representing the implementation of this simple rule, as well as for representing alternatives in general. In an STN, streams are vertices, and tasks are lines. Agrawal²² used an STN to represent alternatives for the separation of near-ideal multicomponent mixtures, and Sargent²³ proposed a general framework for systematic implicit enumeration and evaluation of feasible designs using an STN. In distillation using simple columns, the basic tasks are rectifying in the upper section of a column and stripping in the lower section to produce two states corresponding to the distillate and bottom streams. In a decanter, the task is the liquid—liquid phase separation to produce an organic phase and an aqueous phase.

There is a direct correspondence between the STN and the adjacency and reachability matrices (**A** and **R**, respectively) and also between the STN and a conventional flowsheet representation (where streams are lines and tasks are boxes or "vertices") shown schematically below.

flowsheet
$$\Leftrightarrow$$
 STN \rightarrow **A** \rightarrow **R** (1)

It is convenient to use the adjacency and reachability matrices as a data structure in algorithmic approaches to represent feasibility for the flowsheet in the implementation of the recycle reachability rule. To do this, we calculate the adjacency and reachability matrices for each component in the fresh feed. For instance, a five-component feed will need five pairs of adjacency and reachability matrices each with dimensions $M \times M$, where M is the total number of streams in the flowsheet resulting from part I. The adjacency matrix of a flow-sheet for component k is defined by

 $\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ if streams *i* and *j* both contain component *k* and

 $A_{i,i}^{\kappa} =$

 $\begin{cases} stream j is an output from a unit where i is an input, \\ 0 otherwise \end{cases}$

(2)

We say that *j* is *reachable* from *i*, if there is a path from *i* to *j*. The reachability matrix of a flowsheet for component *k* is defined by

 $R_{i,i}^k =$

 $\int 1$ if stream *j* is reachable from stream *i* by any path,

0 otherwise

(3)

By definition, the singleton *j* defines a path, so each vertex *j* is reachable from itself (Roberts,²⁴ p 53), and $R_{i,i}^{k} = 1$. Note that there might be more than one path from stream *i* to *j*.

The adjacency matrix can be obtained from the structure of the flowsheet, whereas the reachability matrix can be calculated directly from the adjacency matrix using the Boolean function (e.g., Roberts,²⁴ p 6)

$$\mathbf{R} = \text{Boolean}[\mathbf{A} + \mathbf{I}]^{n-1}$$
(4)

where *n* is the number of vertices and **I** is the identity matrix.

Rooks et al.⁸ used the general idea of adjacency and reachability matrices, but in their work, the elements in the adjacency and reachability matrices refer to singular points in the residue curve map. Here, the elements in the adjacency and reachability matrices refer to the streams in the flowsheet. It is this algebraic representation that is crucial for application to higherdimensional problems.

The STN and the adjacency and reachability matrices corresponding to Figure 3b-d are shown in Figures 4-6, respectively. The ternary example is a special application of the recycle reachability rule, because the recycle streams and all of the intermediate streams in this alternative contain all three components. We need only one adjacency matrix and one reachability matrix for this example, because the adjacency matrices corresponding to each component are identical.

An exit stream is identified by a row of 0's in the adjacency matrix, because an exit stream can reach no state except itself. The corresponding row of the reachability matrix will have null entries except for the diagonal, which will be unity.

For a feasible alternative, it is necessary that all nonexit streams (intermediate streams and recycle streams) reach all exit streams. This can be checked by inspecting columns of the reachability matrix. For general cases, the recycle reachability rule is implemented by using the reachability matrix for each component k, because some nonexit streams might not contain all components. For each matrix \mathbf{R}^{k} , we test the column corresponding to the exit stream containing component k. If any of the values are 0, other than entries in the rows corresponding to the other exit streams, the recycle reachability rule is violated, and the flowsheet is infeasible. (Alternatively, if all of the values other than the rows corresponding to the other exit streams are unity, the recycle reachability rule is satisfied.)

This rule excludes a large of number of alternatives generated by potential recycles and greatly reduces the number of closed-loop material balance calculations.

The recycle reachability rule does not apply to captive solvents that have inventory but never leave the process. We accommodate this fact by omitting such solvents from the list of components, and we represent separation subsystems that use captive solvents by a single subsystem without the solvent explicitly represented. For example, extractive distillation is represented as a subsystem with a single feed stream (a



Figure 7. Geometry of the lever-rule feasibility illustrated for a ternary composition space.

binary azeotropic mixture) and two exit streams (each containing a pure component).

Further Screening of Alternatives. Particularly for mixtures with more components, the number of alternatives can grow substantially and it is useful to screen these further before a more detailed evaluation.

Two practical rules, though not necessary, are useful to limit the number of alternatives generated.

Recycle Composition Heuristic. Recycle only to intermediate streams that contain all components in the stream being recycled. For example, if a type 4 stream contains components A, B, and C, do not recycle it to an intermediate stream containing A, B, and D. Without this rule, the downstream devices beyond the recycle mixing point might become infeasible for the required splits. (An alternative to this heuristic is to repeat part I for the portion of the flowsheet effected.)

Recycle Flow Heuristic. Do not recycle streams with flows less than a certain tolerance (say, some small fraction of the fresh feed flow rate). Instead generate additional alternatives with exit streams for waste treatment, fuel byproducts, etc.

For each flowsheet and each subflowsheet, application of the lever rule gives further useful mass balance constraints that eliminate additional infeasible recycle alternatives. Figure 7 shows the geometry of these constraints in composition space for a ternary system. In every flowsheet and subflowsheet, the feed composition must lie inside a polygon formed by the compositions of the output streams. In Figure 7, this is a tetrahedron for streams 1-4. If one of these four output streams is subsequently considered for a recycle, then, no matter what the internal destination, the flowsheet is infeasible unless the feed is located within the triangle defined by the composition of the other three product streams. For the feed shown in Figure 7, recycling of streams 1 or 3 is infeasible, but recycling of streams 2 or 4 will not violate the lever rule. In each iteration during solution of the material balances, this lever rule is tested.

In the calculation of closed-loop material balances, other conditions for separation feasibility might be violated. For example, the recycled stream might cause an upstream composition to move into another distillation region, making a previously feasible distillation now impossible. This infeasibility is due to the constraints on distillation feasibility and not to material balances alone. There are several separation feasibility tests that must also be satisfied and that we apply at each iteration of the flowsheet material balance calculations:

(1) Test for two liquid phases in each decanter. The feed to a decanter might become homogeneous because of changes in the amount or composition of a recycle stream(s) (Wasylkiewicz et al.¹⁷).

(2) Test for the distillation region. The composition of the feed to a distillation column might move into a different distillation region because of recycling. We test the location of the feed to each distillation column for each iteration of the overall material balance calculation.

(3) Test for a common saddle point within each distillation region. For each individual distillation column, a sufficient condition for a feasible split is the common saddle test.⁸ This is tested for each column feed.

(4) Test for positive flows and feasible mole fractions in material balance calculations. The mole fractions of each stream must sum to unity and must lie in the feasible composition space of nonnegative mole fractions.

Example 1: One Recycle Stream. There is a single potential recycle stream (9) for the structure with feasible purities in Figure 3a, which has three possible destinations. A summary of the feasibility tests using the reachability rule is as follows.

Case 1 (Figures 3b and 4). The flowsheet is not infeasible by the recycle reachability rule. Streams 5, 7, and 10 are exit streams and are reachable by all nonexit streams in the flowsheet. This is represented algebraically in the reachability matrix in Figure 4. In column 5, only the entries in rows 7 and 10 are 0, so only the exit streams 7 and 10 cannot reach stream 5 (all streams can reach themselves, so the fifth entry in column 5 is unity). Similarly, only the entries in rows 5 and 10 and in rows 5 and 7 are 0 for columns 7 and 10, respectively. The compositions also satisfy all lever-rule material balance constraints. That is, no infeasibility test is violated, and the complete material balances are easily calculated; the alternative is feasible.

Case 2 (Figures 3c and 5). The flowsheet is infeasible because it violates the recycle reachability rule. Recycling of stream 9, containing all three components, would cause the accumulation of water (component C) in the upper recycle loop. The infeasibility is seen in the STN or in the reachability matrix shown in Figure 5. Exit streams 5 and 10 are reachable from all of the nonexit streams. However, exit stream 7 is not reachable from five of the nonexit streams (2, 4, 6, 8, and 9). This is represented algebraically by the 0's in the corresponding rows of column 7 in the reachability matrix.

Case 3 (Figures 3d and 6). The flowsheet also violates the recycle reachability rule and is infeasible. In this case, component B would accumulation if stream 9 were recycled via stream 3 to unit II. The STN together with the adjacency and reachability matrices are shown in Figure 6.

This example answers some of the questions posed earlier and shows that material balances must be carefully considered for feasibility. Unit operations that work in a flowsheet with feasible purities might no longer function in the same manner or might become infeasible after a recycle loop is closed. The recycle reachability rule can be used to determine infeasibility in this case and to exclude alternatives that violate either overall or local mass balances. The material balance calculation for high recoveries can be carried out on a smaller number of alternative flowsheets. This is especially important for multicomponent systems because the number of candidate flowsheet alternatives with high recoveries can be large.

Example 2: Two Recycle Streams. Example 1 showed that recycling can be employed to improve separations and exploited the fact that the feed formed two liquid phases. In this example, we consider the same ternary mixture, but with a homogeneous feed containing 42.55% ethanol (A), 50% benzene (B), and 7.45% water (C), shown as feed 2 in Figure 1.

One alternative meeting the desired purities is shown in Figure 8a. There are two potential recycle streams (7 and 9) to resolve, as well as two recycle streams for pure components. The distillate from column I (stream 2) is a ternary mixture with a composition near the ternary azeotrope. This stream is homogeneous. A feed composition slightly lower in ethanol will produce a heterogeneous distillate, but even that might not have an equilibrium tie line that crosses the critical distillation boundary between regions 1 and 3. Algorithm 3 generates recycle streams of water and benzene that are mixed with stream 2. The result is stream 4, which is guaranteed to be heterogeneous and to have an equilibrium liquid-liquid tie line that crosses the distillation boundary between regions 1 and 3. The streams from the decanter (5 and 6) can be distilled to obtain pure benzene from one column and pure water from the other.

Note that, if the feed composition were chosen in a distillation region where benzene or water were the stable node, the algorithm would use the same method to find alternatives with feasible product purities.

The high-purity alternative shown in Figure 8a can be used to generate six recycle alternatives, according to the destinations for streams 7 and 9. The results of feasibility tests using the recycle reachability rule, the lever rule, and separation feasibility rules are listed in Table 2. Only one of the alternatives is feasible, where streams 7 and 9 are recycled to unit I; the corresponding feasible alternative with high recoveries is shown in Figure 8b. (The others are not shown here in detail.)

This alternative has the desired high purities and recoveries, and once the recycle loops for streams 7 and 9 are closed, the pure-component recycles are not necessary, as shown in Figure 8b. This alternative was also simulated using HYSYS, and material balances calculated by the algorithms in this paper and by the HYSYS simulations are provided in the Supporting Information. The pure-component recycle streams are not strictly necessary for this example. However, this



Figure 8. Candidate column structures for feed 2 generated from algorithm 3. (a) column structure with feasible purities. (b) Feasible structure with high recoveries. (c) Feasible structure with high recoveries including recycling of pure components.

alternative is also feasible when such recycles are retained, as shown in Figure 8c. These recycles move

 Table 2. Feasibility Tests for Six Recycle Alternatives in

 Example 2

destination of R1, R2	recycle reachability rule	lever rule	separation feasibility tests	mass balance satisfied?
unit I, I	satisfied	satisfied	satisfied	yes
unit I, II	satisfied	satisfied	feed to decanter	no
unit I, III	satisfied	satisfied	is homogeneous feed to unit III is in wrong distillation region	no
unit II, I	satisfied	satisfied	feed to decanter is homogeneous	no
unit II, II	violated	violated	-	no
unit II, IV	violated	violated	-	no

Table 3. Boiling Temperatures and AzeotropicCompositions for the Mixture Water (A), *n*-Butanol (B),Acetic Acid (C), and *n*-Butyl Acetate (D) at 1 atmPressure^a

component or azeotrope	temp (°C)	XA	ХB	XC	ХD	stability
A + B + D	90.90	0.7119	0.0786	0.0000	0.2095	unstable node
A + B	92.93	0.7588	0.2412	0.0000	0.0000	saddle
Α	100.00	1.0000	0.0000	0.0000	0.0000	saddle
$\mathbf{B} + \mathbf{D}$	116.94	0.0000	0.7878	0.0000	0.2122	saddle
В	117.7	0.0000	1.0000	0.0000	0.0000	saddle
С	118.1	0.0000	0.0000	1.0000	0.0000	saddle
B + C + D	121.54	0.0000	0.2448	0.4167	0.3385	saddle
B + C	123.14	0.0000	0.4656	0.5344	0.0000	stable node
D	125.9	0.0000	0.0000	0.0000	1.0000	stable node

 $^{a}\,\mathrm{Liquid}\text{-phase}$ nonidealities represented by the model discussed in the text.

the composition of stream 4 deeper into the heterogeneous region.

We found that simulations for the alternative in Figure 8c were significantly easier to converge than those for the alternative shown in Figure 8b. This type of recycle can be useful when the feed composition is uncertain or when the heterogeneous region near the ternary azeotrope is small, because it provides additional degrees of freedom that can be used to ensure a liquid—liquid phase split.

For other mixtures, such as ethanol and water with DEM,¹⁸ alternatives without some pure-component recycle might be infeasible because the ternary azeo-trope is homogeneous.

Éxample 3: Four-Component Mixture. The approach described here is particularly useful when applied to multicomponent systems, for which the number of alternatives is much greater than for ternary mixtures and for which graphical techniques are difficult to apply. As an example, consider a quaternary mixture of water, *n*-butanol, acetic acid, and *n*-butyl acetate.

The UNIQUAC model is used to represent the liquidphase nonidealities, while the vapor phase is treated as ideal, except for acetic acid dimerization.²⁵ The compositions, temperatures, and stabilities of the pure components and azeotropes are shown in Table 3. There are two stable nodes, pure *n*-butyl acetate or the maximum-boiling azeotrope between *n*-butanol and acetic acid, so there are two distillation regions.

We consider a feed mixture containing 60% water (A), 10% *n*-butanol (B), 10% acetic acid (C), and 20% *n*-butyl acetate (D), and the goal is to split this mixture into components with high purity. Using algorithms 1-3, we generate eight feasible alternatives with high purities summarized in Table 4. All of these together generate more than 20 000 potential recycle alternatives.

Alternative 1 shown in Figure 9 results from the algorithms in part I; another seven alternatives with



Figure 9. Alternative 1 with feasible purities for a fourcomponent mixture. Unit VII is an extractive distillation subsystem.

Table 4. Eight Alternatives with Feasible Purities forExample 3

alternative	number of devices	number of recycles	number of recycle alternatives
1	8	3	343
2	8	4	2401
3	9	2	64
4	9	3	512
5	9	4	4096
6	10	3	729
7	10	4	6561
8	11	4	10 000

feasible purities are reported in Tao.¹⁵ Figure 9 has one decanter, six distillation columns, and one extractive distillation subsystem (block VII). Following decanter I, stream 2 is rich in water and stream 3 is rich in butyl acetate. The distillation in unit II is a direct split that leaves only water, butanol, and acetic acid in the bottom (stream 5). Unit III gives butyl acetate as a bottoms product and leaves water, butanol, and acetic acid as the distillate (stream 6). Streams 5 and 6 are separated in two distillation columns.

Figure 9 has three potential recycle streams (4, 8, and 16), and 343 alternatives can be developed when the recycle destinations are any of the eight units other than the source of the recycle stream. It would be a tremendous amount of work to determine the feasibility of all 343 recycle alternatives by carrying out the closed-loop mass balance calculations. Application of the recycle reachability rule eliminates 237 alternatives, and the recycle composition heuristic eliminates 86, leaving 30 alternatives for further screening. The calculations required in these feasibility tests are much simpler than the full mass balances, because only the adjacency and reachability matrices are used. It is practical to perform the mass balance calculations for the 30 remaining recycle alternatives to determine their feasibilities (each takes several minutes of CPU time). Six alternatives survive these calculations (Table 5), and two of these six feasible alternatives are shown in Figures 10 and 11. In Figure 10, streams 4, 8, and 16 are recycled to units I, I, and IV, respectively. In Figure 11, the corresponding recycle destinations are units I, III, and



Figure 10. Feasible recycle alternative generated from the alternative shown in Figure 9.



Figure 11. Second feasible recycle alternative generated from alternative shown in Figure 9 using alternative recycle destinations.

Table 5. Feasible Flowsheets with High Recoveries forAlternative 1 in Example 3

	-		
alternative	destination	destination	destination
	of R1	of R2	of R3
1-1	unit I	unit I	unit IV
1-2	unit I	unit III	unit IV
1-3	unit I	unit V	unit IV
1-4	unit I	unit VII	unit IV
1-5	unit III	unit I	unit II
1-6	unit III	unit I	unit VI

IV. Additional details including the stream flow rates are given in Tao.¹⁵

There are several opportunities for additional alternatives and optimization. Because the same mixture can be separated in more than one device, giving rise to multiple streams containing the same components, it is useful to consider eliminating some of those devices, for example, in favor of multiple-feed columns. That is



Figure 12. Alternative with feasible purities generated from Figure 9 with pure component C recycled in stream 16.

not always possible, for example, on account of distillation boundaries, but there are other aspects of azeotropic behavior that can be exploited. For example, Figure 9 can actually have fewer separation devices if some of the *pure products* are recycled for the purposes of azeotroping with another component, thereby allowing complete removal of that component, as illustrated in Figure 12. There, component C (acetic acid) produced from unit VII is partially recycled to unit V so that only pure A (water) appears in the distillate stream 10, while all of the component B (*n*-butanol) in stream 6 is removed as part of the binary B-C azeotrope in the bottoms stream 11. The distillation in unit VIII of Figure 9 is thereby eliminated. This approach generates a total of 36 recycle alternatives instead of 343 for the alternative in Figure 9. Application of the recycle reachability rule and recycle composition heuristic rules out 27 of the 36 alternatives as infeasible, leaving 9 to be checked using detailed material balances. The three surviving feasible recycle alternatives are shown in Figure 13a-c.

Summary and Conclusions

The method described here for generating separation flowsheets decomposes the problem into two parts. First, a tree structure of feasible alternatives with high purities is generated with decanting and distillation (algorithm 2) and additional mixing or recycling (algorithm 3) if necessary. Destinations for potential recycle streams remaining after part I are then enumerated using combinatorial techniques in part II, so that every possible recycle scheme is considered.

Many of these potential recycle alternatives are infeasible. Using the recycle reachability rule, recycle composition heuristic, and recycle flow heuristic, we can screen out a large fraction of the infeasible alternatives, without a complete mass balance calculation. An efficient way of implementing the recycle reachability rule is with the reachability matrix for the flowsheet. Example calculations show that up to 90% of the alternatives with high recoveries can be eliminated quickly using this approach. The full mass balance calculation is applied only to a small fraction of the



Figure 13. Three feasible recycle alternatives (a, b, c) generated from Figure 12 using different recycle destinations.

possible alternatives that have a chance of being feasible. Here, we use a revised Wegstein's method for the full material balances. The number of flowsheet options generated by this approach grows rapidly with the number of separation methods taken into account, the number of components to be separated, and the number of recycle streams. This approach gives many feasible alternatives, some of which cannot be easily obtained by intuition or heuristics (such as Figures 10, 11, and 13). Even for ternary mixtures, systematic study suggests new alternatives, such as including a recycle of pure components for mixtures with a ternary heterogeneous azeotrope.

The approach demonstrated here is not restricted to distillation separations and can be applied with little or no modification to include other devices whose individual feasibilities are understood. The number of flowsheet alternatives is expected to increase by using more complex separators such as side-stream or multiplefeed devices. Devices with multiple functionalities, such as simultaneous reaction and separation, cannot be handled without some modifications to the methodology.

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Nomenclature

 $\mathbf{A} = adjacency matrix$

 \mathbf{A}^{k} = adjacency matrix of a flowsheet for component k

- $A_{i,j}^{k}$ = element of the adjacency matrix
- F''= set of feasible flowsheet alternatives with feasible product purities
- L = set of flowsheet alternatives that do not meet all feasible product purities
- $\mathbf{I} = \text{identity matrix}$

 \mathbf{R} = reachability matrix

- \mathbf{R}^{k} = reachability matrix of a flowsheet for component k
- $R_{i,i}^{k}$ = element of the adjacency matrix
- $T \stackrel{\scriptscriptstyle \cup}{=}$ set of tree structures
- $T_m = m$ th tree structure
- S = set of streams

 S_m = list of streams corresponding to the *m*th tree structure

Subscripts and Superscripts

- *i* = streams
- j = streams
- k =components
- m = counter for the number of tree structures
- M = total number of streams for an alternative generated in part I

Supporting Information Available: Tables listing component and total flows for streams in Figures 3a,b; 8a–c; 9–12; and 13a–c, including HYSYS simulation results for the streams in Figure 8b and for the column design. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Siirola, J. J. Strategic Process Synthesis: Advances in the Hierarchical Approach. *Comput. Chem. Eng.* **1996**, 20, S1637–S1643.

(2) Siirola, J. J.; Rudd, D. F. Computer-Aided Synthesis of Chemical Process Designs. *Ind. Eng. Chem. Fundam.* **1971**, *10*, 353–362.

(3) Douglas, J. M. Synthesis of Separation System Flowsheets. *AIChE J.* **1995**, *41*, 2522–2536.

(4) Barnicki, S. D.; Fair, J. R. Separation System Synthesis: A Knowledge-Based Approach. 1. Liquid Mixture Separations. *Ind. Eng. Chem. Res.* **1990**, *29*, 421–432.

(5) Sirrola, J. J. Industrial Applications of Chemical Process Synthesis. *Adv. Chem. Eng.* **1996b**, *23*, 1–62.

(6) Wahnschafft, O. M.; Jurain, T. P.; Westerberg, A. W. SPLIT: A Separation Process Designer. *Comput. Chem. Eng.* **1991**, *15*, 565–581.

(7) Friedler, F.; Tarjan, K.; Huang, Y. W.; Fan, L. T. Graph-Theoretic Approach to Process Synthesis: Axioms and Theorems. *Chem. Eng. Sci.* **1992**, *47*, 1973–1988.

(8) Rooks, R. E. Feasibility and Column Sequencing for the Distillation of Homogeneous Multicomponent Azeotropic Mixtures. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1997.

(9) Ewell, R. H.; Harrison, J. M.; Berg, L. Azeotropic Distillation. Ind. Eng. Chem. Res. 1944, 36, 871-875.

(10) Safrit, B T.; Westerberg, A. W. Synthesis of Azeotropic Batch Distillation Separation Systems. *Ind. Eng. Chem. Res.* **1997**, *36*, 1841–1854.

(11) Rooks, R. E.; Julka, V.; Doherty, M. F.; Malone, M. F. Structure of Distillation Regions for Multicomponent Azeotropic Mixtures. *AIChE J.* **1998**, *44*, 1382–1391.

(12) Stabnikov, V. N.; Matyushev B. Z.; Protsyuk T. B.; Yushchenko N. M. Equilibrium in the Ethyl Alcohol–Water System at Atmospheric Pressure. *Pishch. Promst. (Kiev)* **1972**, *15*, 49–56.

(13) Ellis, S. R. Equilibrium Still and Binary Equilibrium Data. *Trans. Inst. Chem. Eng.* **1952**, *30*, 58–64.

(14) Gmehling, J.; Steinigeweg, S.; Popken, T. To the Editor. AIChE J. 2001, 48, 2848-2849.

(15) Tao, L. Feasibility and Synthesis of Reaction–Separation Systems with Recycles. Ph.D. Thesis, University of Massachusetts, Amherst, 2003.

(16) Fidkowski, Z. T.; Malone, M. F.; Doherty, M. F. Computing Azeotropes in Multicomponent Mixtures. *Comput. Chem. Eng.* **1993**, *17*, 1141–1155.

(17) Wasylkiewicz, S. K.; Sridhar, L. N.; Doherty, M. F.; Malone, M. F. Global Stability Analysis and Calculation of Liquid–Liquid Equilibrium in Multicomponent Mixtures. *Ind. Eng. Chem. Res.* **1996**, *35*, 1395–1408.

(18) Martin, D. L.; Raynolds, P. W. (Eastman Kodak Company). Process for the Purification of Diethoxymethane from a Mixture with Ethanol and Water. U.S. Patent 4,740,273, 1988.

(19) Doherty, M. F.; Malone, M. F. Conceptual Design of Distillation Systems; McGraw-Hill: New York, 2001.

(20) Doherty, M. F.; Caldarola, G. A. Design and Synthesis of Homogeneous Azeotropic Distillation. 3. The Sequencing of Columns for Azeotropic and Extractive Distillations. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 474–485.

(21) Kondili, E.; Pantelides, C. C.; Sargent, R. W. H. A General Algorithm for Short-Term Scheduling of Batch Operations I. MILP Formulation. *Comput. Chem. Eng.* **1993**, *17*, 211–227.

(22) Agrawal, R. Synthesis of Distillation Column Configurations for a Multicomponent Separation. *Ind. Eng. Chem. Res.* **1996**, *35*, 1059–1071.

(23) Sargent, R. W. H. A Functional Approach to Process Synthesis and Its Application to Distillation Systems. *Comput. Chem. Eng.* **1998**, *22*, 31–45.

(24) Roberts, F. S. *Discrete Mathematical Models*; Prentice-Hall: Englewood Cliffs, NJ, 1976.

(25) Venimadhavan, G.; Malone, M. F.; Doherty, M. F. A Novel Distillate Policy for Batch Reactive Distillation with Application to the Production of Butyl Acetate. *Ind. Eng. Chem. Res.* **1999**, *38*, 714–722.

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