

SYNTHESIS OF DISTILLATION SEQUENCES FOR SEPARATING MULTICOMPONENT AZEOTROPIC MIXTURES

Dennis Y-C Thong**, Guilian Liu*, Megan Jobson*, Robin Smith*

** Degussa AG, Marl, Germany

* Department of Process Integration, UMIST, Manchester, UK

ABSTRACT

An automatic procedure for the synthesis of sequences of distillation columns for separating homogeneous multicomponent azeotropic mixtures is developed. Key to the approach is the use of sets of compositions, or 'product regions', to specify product compositions. The synthesis procedure is implemented in two stages. The first stage consists of identifying classes of splits. Each class of splits may be characterised as either feasible or potentially feasible. The synthesis procedure systematically combines these classes of splits to generate column sequences that satisfy a pre-determined separation requirement. The second stage of the synthesis procedure assesses the feasibility of a proposed flowsheet once the recycle options have been defined. Preliminary column design for each column in the sequence can be performed. The feasibility assessment procedure will form the basis for systematic flowsheet generation and optimisation.

KEYWORDS: feasibility, product region, manifold, recycle

INTRODUCTION

In azeotropic mixtures, the volatility order depends on the composition of the mixture. Therefore, it is difficult to assess whether a proposed separation is feasible, especially when many components are present in the mixture. In the synthesis of sequences of distillation columns for the separation of azeotropic mixtures, assessing whether proposed separations are feasible is a key challenge. Typically, recycle streams are used to improve the recovery of the desired components. These recycle streams increase the complexity of the problem because of the interactions between columns that they introduce.

A wealth of knowledge has been developed regarding the separation of three- and four-component azeotropic mixtures. Two- and three-dimensional graphical representations have been profitably exploited to assess the feasibility of proposed separations, to generate distillation sequences, to design columns, etc. [e.g. 1, 2].

Multicomponent azeotropic mixtures present a new set of challenges because visual representation is impractical. Recent research has considered the calculation of azeotropes in multicomponent azeotropic mixtures [e.g. 3, 4, 5, 6]. Based on this information, it is now possible to identify the structure of the composition space, *i.e.* the existence and location of distillation regions and boundaries [7, 8, 9]. The systematic generation of distillation sequences for separating azeotropic mixtures has also been an active area of research (9, 10, 11). However, the synthesis problem still presents severe challenges, due to the complex nature of multicomponent azeotropic mixtures.

This work extends knowledge in the area of synthesis of distillation sequences for the separation of multicomponent azeotropic mixtures. It builds on the geometric relationships established for ternary and quaternary azeotropic mixtures and exploits concepts established to characterise multicomponent composition space. It overcomes some of the challenges particular to azeotropic distillation by describing proposed separations in terms of sets of compositions ('product regions'), rather than fully specifying the composition of feed or product streams.

BACKGROUND

Many feasibility tests developed for assessing proposed separations of ternary and quaternary azeotropic mixtures require a continuous composition profile to connect the proposed distillate and bottom product compositions. In ternary mixtures, the set of all liquid composition profiles, for any number of stages and any reflux or reboil ratio, that can lead to a product of a given composition [2] was named the 'operation leaf' [12]. The operation leaf is bounded by the composition profile at total reflux (the residue curve [1] or distillation line [13]) and the pinch point curve, which represents operation at minimum reflux [2]. It is easy to generate the operation leaf for a proposed product pair and easy to see whether a pair of operation leaves overlap. If they do, it may be concluded that a continuous composition profile exists and that the separation is feasible. Fig. 1 illustrates a pair of operation leaves and one corresponding composition profile for the separation of a ternary azeotropic mixture.

In higher-dimensional composition space, those concepts apply in principle, but, in practice, the distribution of impurities or trace components in the proposed products influence strongly whether a continuous composition profile will be found. The rectification body method [14] allows feasibility of a proposed multicomponent separation to be assessed. The rectification body for a column section (for a given reflux or reboil ratio) is constructed from the set of pinch points for a given product composition using linear approximations. Intersection of two rectification bodies indicates that the proposed separation is feasible.

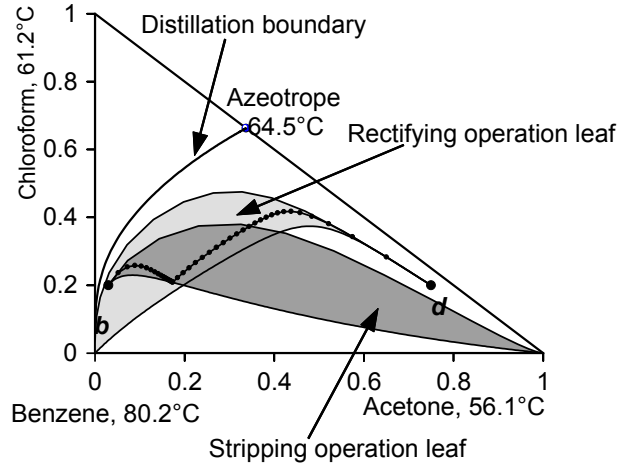


Fig. 1 Operation leaves and a continuous composition profile joining distillate (d) and bottoms (b) compositions in a ternary azeotropic mixture at 1 atm.

Research on ternary and quaternary azeotropic distillation has shown that the presence of distillation boundaries significantly restricts which separations will be feasible. Rooks *et al.* [9] developed an equation-based approach for identifying the presence and location of distillation boundaries in higher-dimensional composition space. When the singular points of the mixture are numbered in order of increasing boiling temperature, the ‘directed adjacency matrix’ and associated ‘reachability matrix’ [15] can be obtained and interpreted to represent the structure of the composition space. Fig. 2 shows the residue curve map and adjacency and reachability matrices for a mixture of acetone, chloroform and methanol at 1 atm.

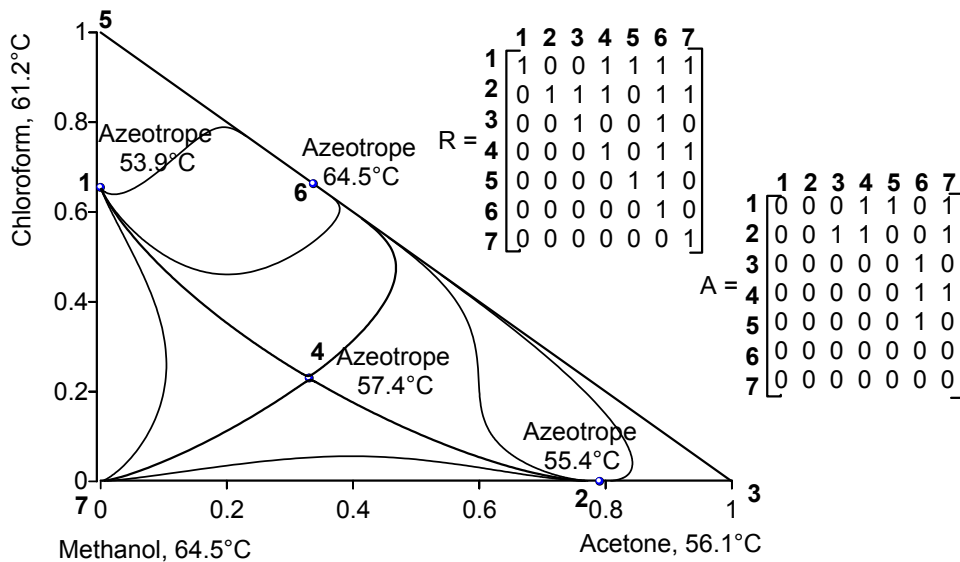


Fig. 2 Residue curve map for the mixture acetone, chloroform and methanol at 1 atm. The mixture forms three binary azeotropes, one ternary azeotrope, four distillation regions and four distillation boundaries. Also shown are the adjacency and reachability matrices.

The objective of distillation sequence synthesis for azeotropic mixtures is to identify sequences of separation tasks and the associated set of recycle streams that will achieve a given separation objective. A methodology for sequence synthesis for

multicomponent mixtures is presented by Wahnschafft *et al.* [10]. A sequential procedure identifies possible column sequences for a given feed composition, allows splits to be combined and assigns recycles. Because recycles affect the feed compositions to proposed separations, some iteration is required. Obtaining the appropriate recycle compositions is difficult; also, the methodology can miss sequences of interest because of the way of generating the separation tasks. Simulation is used to check feasibility of proposed splits at high reflux ratios, which can miss separations only possible at lower reflux ratios.

Bauer and Stichlmair [11] present a superstructure of columns, each of which performs a 'preferred separation' (*i.e.* a thermodynamically ideal separation). Preferred separations are generated sequentially from a fully specified feed composition, which leads to a superstructure that does not necessarily contain all possible splits. The superstructure is optimised using mixed integer non-linear programming, after recycle streams have been determined. That graphical tools assist with identifying recycle options restricts the applicability of the method for multicomponent systems.

The 'common saddle test' [9] for column feasibility requires the composition profiles from both specified product compositions to approach the same saddle at total reflux. Rooks *et al.* [9] use this feature to propose a method, using the reachability matrix, to identify feasible sequences within a distillation region. Recycling is not systematically accommodated and column designs are not obtained during sequence selection. The common saddle test provides a sufficient (but not necessary) condition for a proposed split to be feasible, so excludes some feasible splits [16], as will be shown.

NEW FEASIBILITY TEST

The positions in composition space of composition profiles, like operation leaves, are very sensitive to the relative amount of impurities in the product compositions. Instead of being a disadvantage, this property can be used to develop an approximate feasibility test for multicomponent splits.

As an example, consider the quaternary mixture illustrated in Fig. 3. Six composition profiles are calculated from six, almost identical, distillate compositions at the same reflux ratio. The small differences in the compositions of the impurities (Isobutanol and 1-butanol) in the products cause a large difference in the resulting composition profiles. The resulting composition profiles terminate at the same pinch point and lie in a volume, represented by a shaded region in Fig. 3. This volume is structurally identical to the rectification body of Bausa *et al.* [14].

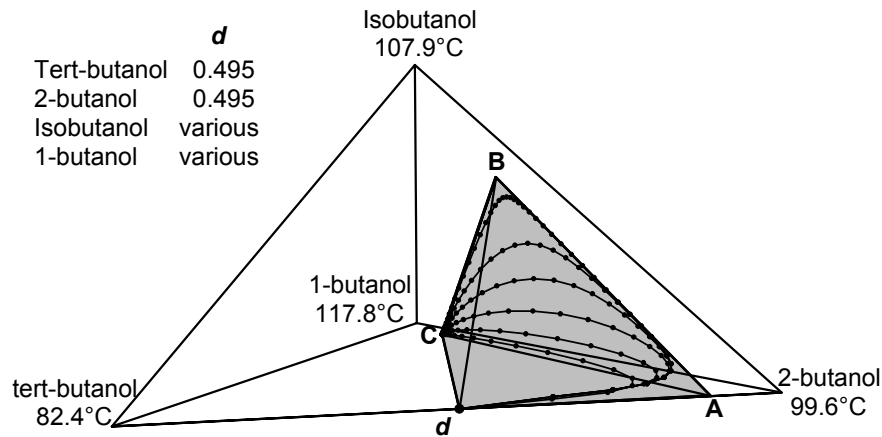


Fig. 3 Region of feasible liquid composition profiles for a range of similar distillate compositions when the reflux ratio is 5. A, B and C are pinch points. The composition profiles approach the plane ABC asymptotically.

When both the reflux ratio and composition of trace components are varied simultaneously, the resulting composition profiles lie in a volume formed by the product composition and three of the component vertices, as shown in Fig. 4. Three pinch point curves from d form three edges of this volume, one of which starts at d and ends at the 2-butanol vertex, tracing the edge of the composition space. In the rest of this work, however, the pinch point curves will be approximated by straight lines. This approximation causes the volume to be inexact, the consequences of which are discussed later in this work. In the early stages of column design, however, a linear approximation of the edges expedites the mathematical description of these volumes. The vertices of the rectifying manifold are obtained directly from the reachability matrix; the vertices are connected by linear curves, surfaces, or higher-dimensional structures. A stripping manifold for a bottoms composition can be constructed in an analogous manner.

Both manifolds contain all the possible composition profiles, at any reflux or boil-up ratio and at for any distribution of impurities, leading to the two product compositions. The intersection of the rectifying and stripping manifolds will therefore indicate product feasibility, subject to the linear approximation used to describe the manifolds. This criterion defines the feasibility test for product compositions. Thong [17] presents a numerical procedure for calculating the intersection between two n -dimensional manifolds.

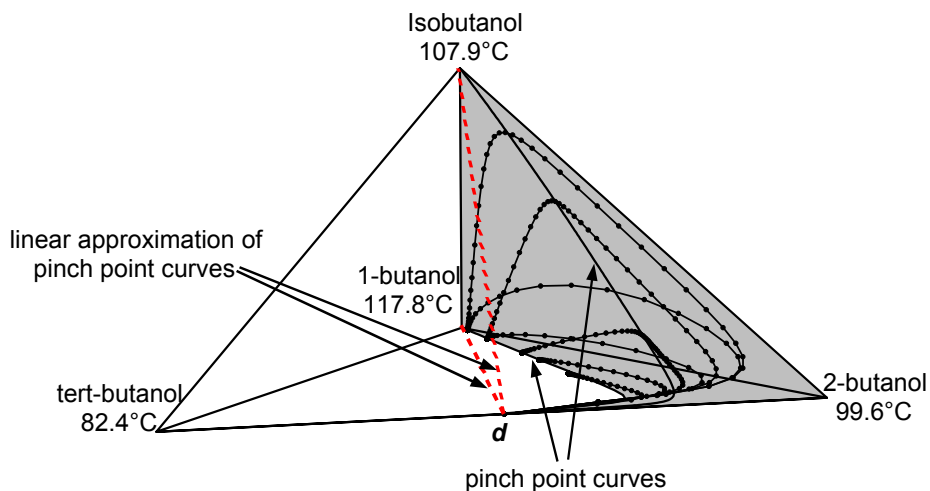


Fig. 4 Rectifying manifold for distillate d , for any number of stages and any reflux ratio.

FEASIBILITY TEST FOR CLASSES OF SPLITS

In this work, we use product regions to specify product compositions. A product region is the set of product compositions that satisfies a certain topological constraint. Fig. 5 illustrates the concept for a quaternary azeotropic mixture. The (1-2) product region is the set of all mixtures lying close to the binary edge between the singular points 1 and 2. Similarly, any bottoms composition close to the ternary (3-4-5) face is a (3-4-5) bottoms product.

Associated with product regions are *classes* of splits; these splits may be feasible, potentially feasible or infeasible. Fig. 5 presents, as an example, a proposed 1-2/3-4-5 class of split. Manifolds can be formed for both product regions, and the procedure for generating a manifold is similar to the one described earlier for product compositions. Fig. 5 shows both manifolds for the 1-2/3-4-5 split; each manifold contains all possible composition profiles leading to the associated product region. The class of split is judged potentially feasible if the manifolds intersect or just touch, as they do in the 1-2/3-4-5 case.

In many mixtures, 'compartments' will form in a distillation region, where in each compartment the volatility order is constant. Saifit and Westerberg [8] term these compartments 'continuous distillation regions'. Fig. 6 shows a ternary distillation region (1-2-3-5) that displays two compartments, (1-2-5) and (1-3-5). The residue curves in each compartment behave in the same manner as residue curves in the composition space of a non-azeotropic mixture. Compartments are simply identified, by identifying subsets of a distillation region which have 'ideal' reachability matrices [16]. It is convenient to use a linear approximation for the compartment boundary (e.g., in Fig. 6, a straight line joining points 1 and 5).

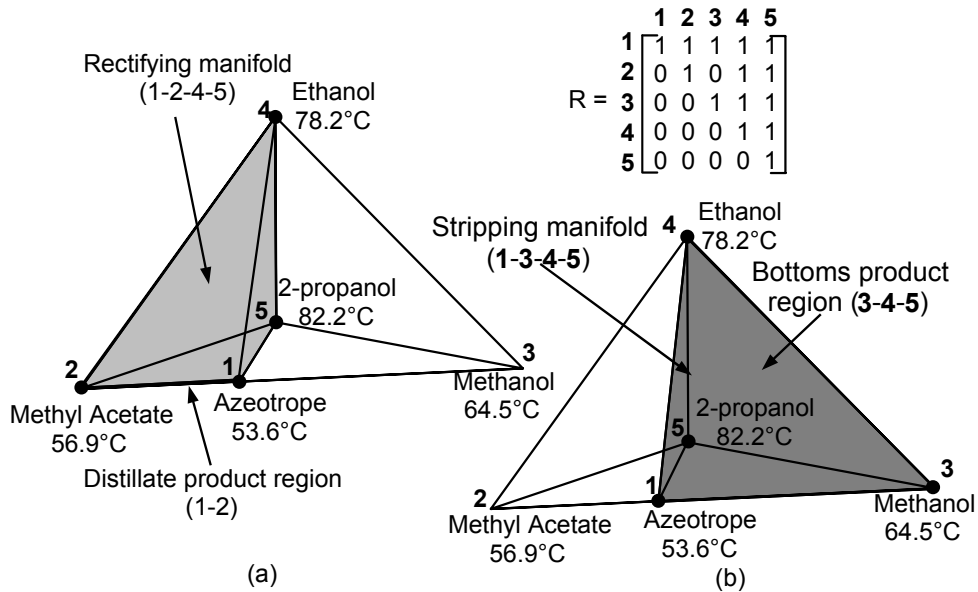


Fig. 5 Product regions and manifolds for a 1-2/3-4-5 class of split. (a) Distillate product region and rectifying manifold. (b) Bottoms product region and stripping manifold. The reachability matrix is also shown.

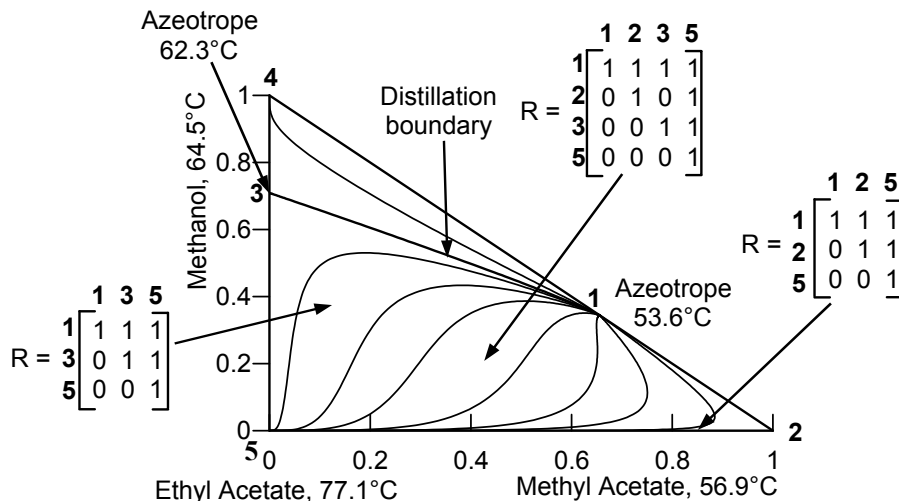


Fig. 6 A ternary azeotropic mixture of methyl acetate, methanol and ethyl acetate. The lower distillation region (1-2-3-5) is divided into two compartments, (1-2-5) and (1-3-5).

The procedure for identifying which classes of splits are potentially feasible depends on whether a distillation region contains exactly one compartment. It is easy to generate the set of all possible splits within a compartment (or a region containing a single compartment). Whether these splits are potentially feasible can be inferred from the reachability matrix without further calculation. It is found that potentially feasible splits either obey the common saddle criterion [9] (Type A splits), or one manifold is a subset of the other (Type B splits), but the common saddle criterion is not obeyed. Type A splits are feasible for all proposed product pairs; Type B splits are always feasible for only some pairs of products.

The mixture in Fig. 2 contains six compartments (in four distillation regions); for this mixture, a total of twenty different feasible classes of splits are identified, as shown in Table 1.

Table 1 Feasible splits for the methanol, acetone, chloroform mixture shown in Fig. 2.

Compartments	C#1	C#2	C#3	C#4	C#5	C#6
Feasible splits	1/6	1/6	1/4-7	2/4-7	2/6	2/6
	1/4-6	1/5-6	1-4/7	2-4/7	2/3-6	2/4-6
	1-4/6	1-5/6	1-4/4-7	2-4/4-7	2-3/6	2-4/6
	1-4/4-6	1-5/5-6			2-3/3-6	2-4/4-6

When a distillation region contains more than one compartment, it is necessary to identify potentially feasible splits that cross the compartmental boundary. This category of split is a Type C split; it does not satisfy the common saddle criterion. Typically, these splits are performed by two-feed columns. A well-known example is the separation of ethanol (distillate) from water-ethylene glycol (bottoms) in a two-feed column [17]. For the remainder of this work, however, only single-feed columns are considered. Fig. 7 illustrates an example of a feasible Type C split carried out in a single-feed column, for the same mixture as shown in Fig. 6. The distillate composition is in the 1-3-5 compartment while the bottoms composition is in the 1-2-5 compartment. The operation leaves, as well as the composition profile corresponding to a feasible separation, are plotted.

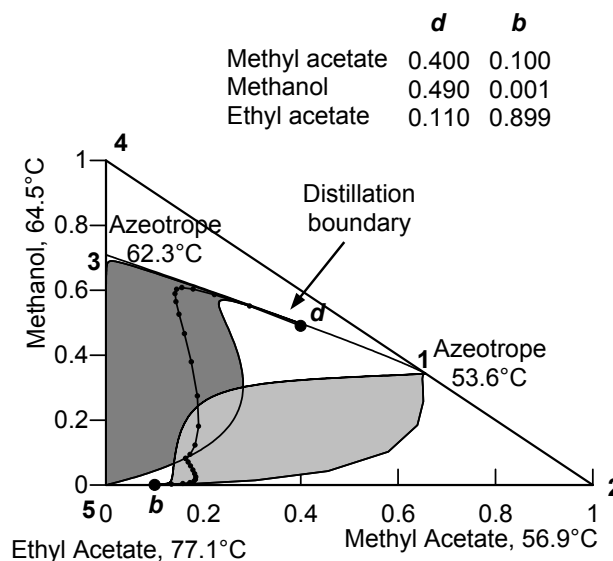


Fig. 7 A cross-compartmental (Type C) split in a ternary azeotropic mixture.

Because a Type C split involves product regions from different compartments whose product manifolds will never intersect, the manifolds have to share a common face, or plane, for feasibility. The procedure for identifying potentially feasible Type C splits is straightforward, requiring only the information contained in the reachability matrix [16].

So far, only splits constrained by distillation boundaries have been discussed. It is also possible to propose splits that lie entirely within a distillation boundary, *i.e.*, both

product regions are on, or close to a distillation boundary. The feasibility of these splits also needs to be assessed. To identify potentially feasible splits on a distillation boundary requires compartments within the boundary to be determined, and then the procedures for classifying proposed splits as Type A, B or C (or infeasible) is carried out as before for product regions lying within the distillation boundary.

The new approach for assessing feasibility of proposed splits, expressed in terms of product regions, avoids the requirement of fully specifying stream compositions. Consequently, constraints on which exact products are feasible for which exact feeds do not need to be considered, which simplifies the sequence synthesis process while simultaneously accommodating the presence of recycle streams, as will be demonstrated. Simple algorithms, together with the information included in the reachability matrix (in turn derived from information about the topology of the residue curve map) allow proposed separations to be categorised as feasible, potentially feasible or infeasible. Separations involving product regions on a distillation boundary can also be assessed for feasibility. The feasibility test outlined here forms the basis of the procedure for generating potentially feasible sequences of distillation columns to separate a multicomponent azeotropic mixture into a set of desired products.

DISTILLATION COLUMN SEQUENCE SYNTHESIS PROCEDURE

The first step in the sequencing procedure is to specify the problem. For a given feed mixture, all the azeotropes that may occur can be computed, and the adjacency and reachability matrices can be calculated [15]. The distillation regions and boundaries can then be identified [9]. For a given set of desired products, it can then be determined whether the feed and products lie in the same or different distillation regions.

The sequence synthesis procedure presented in this work exploits the fact that internal recycle streams allow the manipulation of the feed compositions to any column in the sequence. Exact feed compositions to the various columns do not need to be fixed. Instead, the synthesis procedure generates sequences of columns, each performing a class of split. The type and feasibility of each class of split can be determined as discussed above. The classes of splits are constrained to line within distillation regions or on distillation boundaries, but the ranges of product compositions are not highly constrained, since the splits are defined in terms of product regions.

Once all the feasible and potentially feasible classes of splits for the mixture have been identified, all possible column sequences are generated by recursive searching, starting with $(C-1)$ -dimensional splits and ending with binary splits. The column sequences that recover the desired components are accepted while the others are rejected. Stream compositions, other than the overall feed composition, do not have to be fully specified at this point. No recycling exists at this stage. The full algorithm for generating feasible column sequences is presented in Thong and Jobson [18].

The procedure for generating alternative distillation sequences is illustrated with a quaternary example. An equimolar mixture of methyl acetate, methanol, ethanol and isopropanol is to be separated into its constituent components. Fig. 8 shows the quaternary diagram, adjacency and reachability matrices, and lists the distillation regions, boundaries and compartments. One binary minimum-boiling azeotrope, one distillation region and two compartments exist. All four components are to be recovered, and because no distillation boundary exists in the mixture, no boundary crossing is required. The feed composition lies in the (1-3-4-5) compartment.

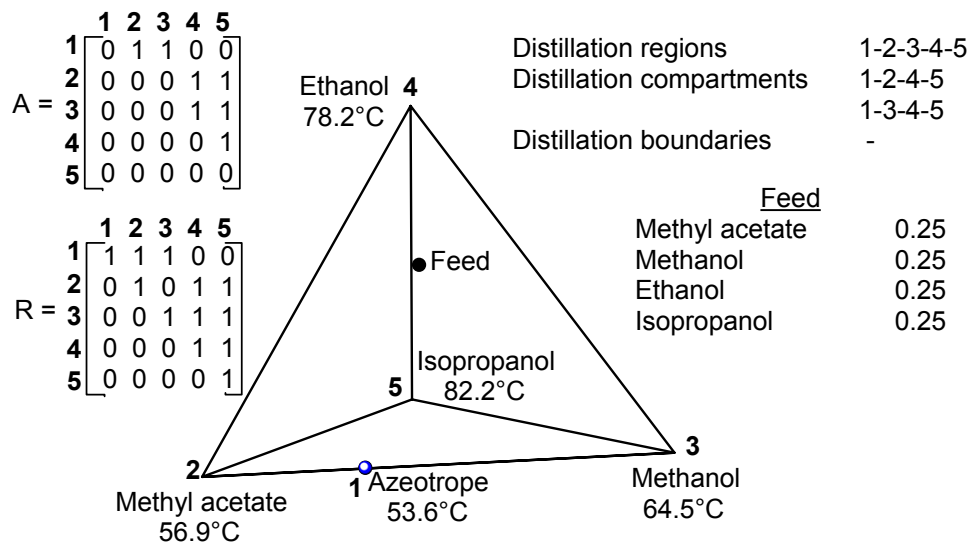


Fig. 8 A quaternary diagram representing the composition space of a four-component azeotropic mixture. Also shown are the adjacency and reachability matrices. The mixture displays one distillation region and two compartments.

Table 2 lists the feasible and potentially feasible classes of splits identified for this quaternary mixture. All quaternary splits (in 4-distillation regions), ternary splits (in 3-distillation regions) and binary splits are listed and labelled according to split type.

To illustrate the sequence generation algorithm, a 1/3-4-5 split is arbitrarily selected. Fig. 9 shows the separation tree corresponding to the 1/3-4-5 split as the first split. None of the options in Fig. 9 lead to the recovery of methyl acetate (2), which is a desired product. As a result, this sequence is rejected. Instead of the 1/3-4-5 split, any of the other quaternary splits in the feed compartment can be selected to be the first split.

Table 2 Feasible and potentially feasible classes of splits for the quaternary mixture in Fig. 8. Superscripts denote the split type.

4-distillation regions	1-2-3-4-5					
Compartments	C#1 (1-2-4-5)			C#2 (1-3-4-5)		
Quaternary Splits (Types A & B)	$1/4-5^A$ $1/2-4-5^A$ $1-2/4-5^A$ $1-2/2-4-5^A$ $1-2-4/5^A$ $1-2-4/4-5^A$ $1-2-4/2-4-5^B$			$1/4-5^A$ $1/3-4-5^A$ $1-3/4-5^A$ $1-3/3-4-5^A$ $1-3-4/5^A$ $1-3-4/4-5^A$ $1-3-4/3-4-5^B$		
Quaternary Splits (Type C)	C#1 x C#2 (cross-compartmental split) $1-2/3-4-5$ $1-3/2-4-5$ $1-2-4/3-4-5$ $1-3-4/2-4-5$					
3-distillation regions	1-2-3-4		1-2-3-5		2-4-5	3-4-5
Compartments	C#1 (1-2-4)	C#2 (1-3-4)	C#3 (1-2-5)	C#4 (1-3-5)	C#5 (2-4-5)	C#6 (3-4-5)
Ternary Splits (Types A & B)	$1/4^A$ $1/2-4^A$ $1-2/4^A$ $1-2/2-4^A$	$1/4^A$ $1/3-4^A$ $1-3/4^A$ $1-3/3-4^A$	$1/5^A$ $1/2-5^A$ $1-2/5^A$ $1-2/2-5^A$	$1/5^A$ $1/3-5^A$ $1-3/5^A$ $1-3/3-5^A$	$2/4-5^A$ $2-4/4-5^A$ $2-4/5^A$	$3/4-5^A$ $3-4/4-5^A$ $3-4/5^A$
Ternary Splits (Type C)	C#1 x C#2 $1-2/3-4$ $1-3/2-4$		C#3 x C#4 $1-2/3-5$ $1-3/2-5$			
Binary splits	$1/2^A$	$1/3^A$	$2/4^A$	$2/5^A$	$3/4^A$	$3/5^A$ $4/5^A$

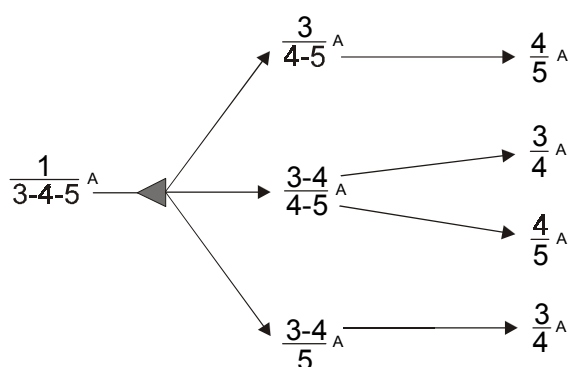


Fig. 9 Separation tree for a $1/3-4-5$ first split. In all cases the methyl acetate-methanol azeotrope (1), methanol (3), ethanol (4) and isopropanol (5) are recovered. Superscripts denote the split type.

It is also possible to synthesise column sequences that include a column that straddles a distillation boundary. In this type of column, the feed lies in one region and the products in an adjacent region. Boundary crossing is possible if the feed

composition is in the concave segment of the distillation boundary. When boundary crossing is being considered, the sequence synthesis procedure is carried out as described previously, until a compartment on a distillation boundary is produced as a product region. If a product region is a compartment on a distillation boundary and the product region contains the desired component(s), all splits in the adjacent region (or compartment) that do not have the boundary as a product region are identified. Only those splits on the boundary where the feed to the split is on the concave side of the boundary are considered. One approach to estimating boundary curvature is presented in Thong and Jobson [16].

The procedure for checking whether the product region on the boundary contains the desired product is illustrated using a quaternary mixture of methyl acetate, ethyl acetate, methanol and ethanol. Fig. 10 represents the composition space for this mixture. If the feed composition is in the (1-2-3-5-6) region and the boundary curves towards the other region, a boundary crossing operation is feasible. If, say, pure methanol (4) is a desired product and ethanol (7) is not, the boundaries of interest are then (1-3), (3-5) and (1-2-3-5). Product regions on the boundary do not contain methanol (4) and are therefore not worth crossing as there is no possibility of recovering methanol in subsequent columns.

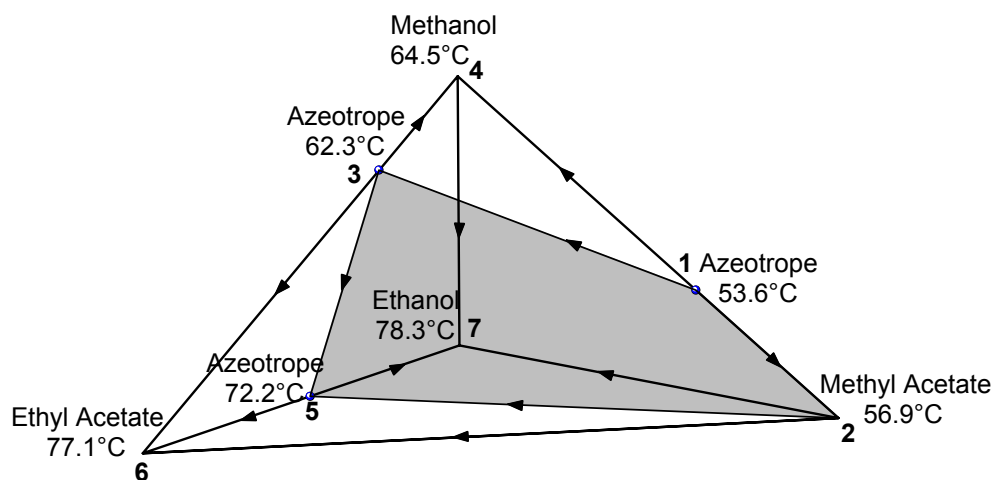


Fig. 10 The 1-2-3-5 surface forms a distillation boundary for the quaternary mixture of methyl acetate, ethyl acetate, methanol and ethanol.

The procedure for identifying splits on a distillation boundary is illustrated using a quaternary mixture of acetone, chloroform, benzene and toluene, which forms a binary azeotrope between acetone and chloroform. The composition space, adjacency and reachability matrices are shown in Fig. 11. Fig. 11 indicates that the distillation boundary curves towards the (2-3-4-5) region. The feed to the column sequence is equimolar in all components. Table 3 lists the feasible splits on the boundary and its lower-dimensional constituents. Fig. 12 lists some sequences that enable the recovery of all the components.

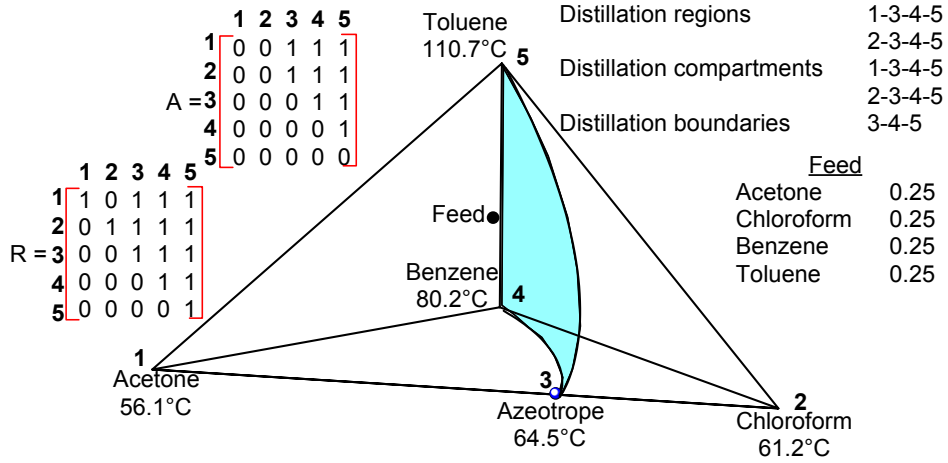


Fig. 11 Composition space, distillation boundary, adjacency and reachability matrices for a quaternary mixture of methyl acetate, ethyl acetate, methanol and ethanol.

Table 3 Feasible classes of splits on the distillation boundary (3-4-5) of the quaternary mixture shown in Fig. 11

4-distillation boundaries	3-4-5	
Compartments	C#1 (3-4-5)	
Quaternary splits (Type A)	3-4/5, 3-4/4-5	
3-distillation boundary	3-4	3-5
Compartments	C#1 (3-4)	C#1 (3-5)
Ternary splits (Type A)	3/4	3/5

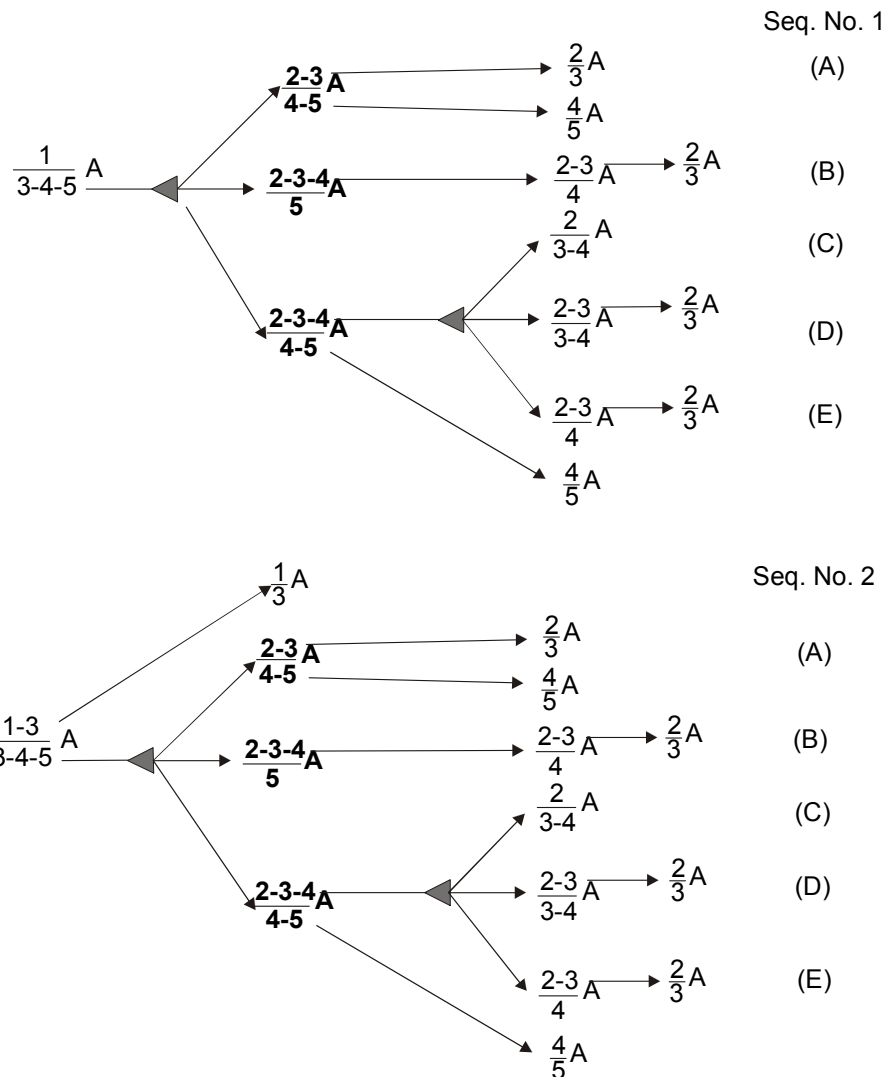


Fig. 12: Potentially feasible sequences for the recovery of all constituent components in the quaternary mixture shown in Fig. 11. Boundary-crossing operations are highlighted in bold.

COLUMN DESIGN USING MANIFOLDS

To evaluate a proposed sequence and recycle structure, each column in the sequence must be checked for feasibility and designed. A method for column design that is useful for this purpose is presented by Thong and Jobson [19]. As discussed previously, fully specifying the composition of all product and intermediate streams in the flowsheet decreases the likelihood of a feasible design being found. This problem is aggravated when recycle options are also considered because of the interactions between columns that are introduced by recycle streams. The design method uses product regions and composition manifolds to describe product specifications and composition profiles in multicomponent composition space and 'representative compositions' to generate manifolds.

A product region is the set of compositions that satisfies the composition constraints of a specified product. The representative compositions are a set of fully specified compositions that can capture the characteristics of the product region. A four-

component example is shown in Fig. 13: the pure-component product is required to contain at least 95% tert-butanol; the distribution of the remaining three components is not specified. The three representative compositions are the three binary mixtures containing 95% tert-butanol and 5% of the other component.

Manifolds represent the set of all liquid compositions that can be obtained within a column section, on any stage, for any reflux or reboil ratio, with a product lying in a given product region. It has been shown how manifolds are useful for identifying the feasibility of a proposed class of split (e.g. Fig. 5). However, these manifolds, generated from the reachability matrix, do not provide information about the feasibility of a separation where the pair of product regions have been more exactly specified.

Manifolds can also be used for column design. In this case, the manifold for each column section can be constructed for a more specific set of operating conditions, e.g. to represent the set of all liquid composition profiles lying on a particular stage and for a particular reflux or reboil ratio, where the product lies in a given product region. Here representative compositions are used to generate the manifolds. To generate the manifolds shown in Fig. 13, the composition on a given stage (in this case, the fifth stage) for a given reflux or reboil ratio is calculated from each of three representative compositions, which, in Fig. 13, are binary mixtures. The rectifying manifold is the linear combination of the three resulting compositions. The two manifolds in Fig. 13 represent all possible compositions on the fifth rectifying stage, for two reflux ratios, corresponding to a distillate product containing 95 % tert-butanol, with the 5 % of impurities present in any proportion.

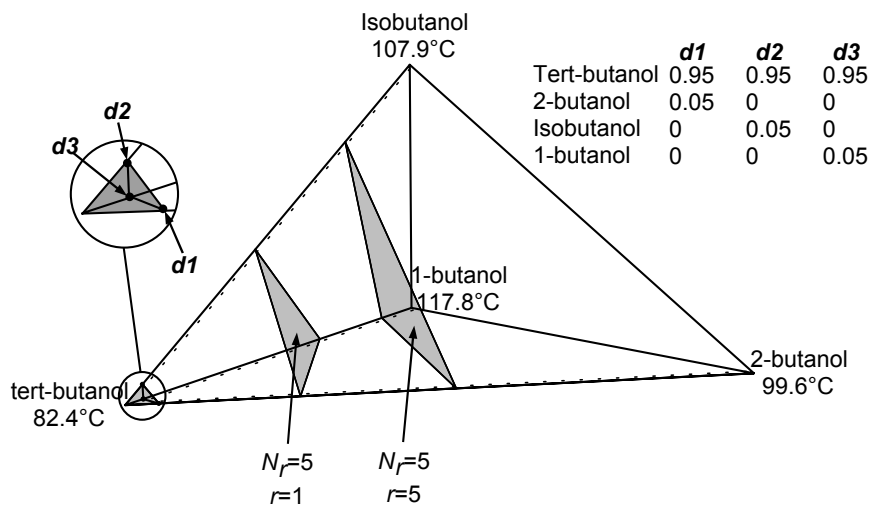


Fig. 13 A 95% tert-butanol distillate product region and two rectifying manifolds calculated from three representative compositions **d1**, **d2** and **d3**. The dashed lines represent the binary composition profiles.

Stripping manifolds can be constructed in a similar way. Where any rectifying manifold intersects any stripping manifold, it may be concluded that the proposed separation is feasible; furthermore, an approximate column design is obtained, since each manifold is associated with a certain number of stages and a certain reflux or reboil ratio. Once a design has been obtained, the column can be evaluated using a simple cost indicator or cost model. Identifying whether a given pair of manifolds intersects is a straightforward matter of using geometrical considerations to decide

whether a pair of linear bodies (lines, surfaces, volumes or higher-dimensional bodies intersect) [19].

That linear approximations are made introduces error into the design procedure. Thong and Jobson [19] present an iterative design procedure to calculate column design parameters more accurately, which is especially valuable in cases that are just feasible or just infeasible.

The concept of a combined manifold has been developed [19] to overcome some of the difficulties of finding higher-dimensional entities that intersect. In this case, the manifold represents all compositions leading to a given product region for a given *range* of reflux or reboil ratio or a given *range* of number of stages. Fig. 14 shows an example where both the reflux ratio and the reboil ratio lie in the range 3 to 4 and there are 15 stages in both column sections. The thermal condition of the feed is taken to be a degree of freedom. The combined manifolds in Fig. 14 are volumes, rather than surfaces, which increases the probability of intersection. Once again, an approximate column design can be obtained when the bodies do intersect. Even such an approximate design provides a very useful starting point for process evaluation, for more detailed studies or for rigorous simulation.

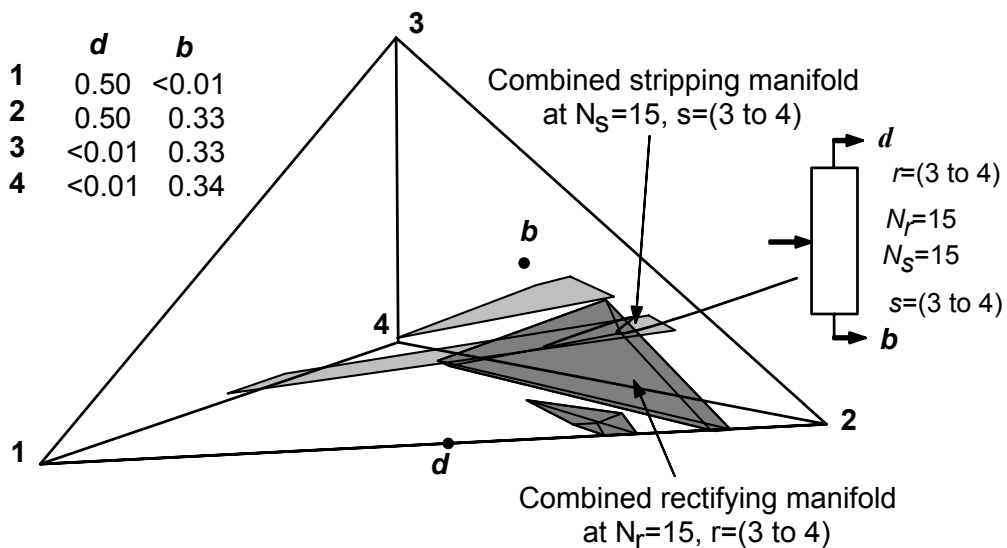


Fig. 14 The intersection of a pair of combined rectifying and stripping manifolds indicates feasible design parameters.

The principle of combined manifolds is extended to include other combinations of the degrees of freedom (e.g. a range of reflux ratios for a fixed number of rectifying stages and a range of stripping stages for a fixed reboil ratio) or to increase further the dimension of the manifolds (e.g. range of reflux ratios *and* range of rectifying stages). By systematically generating all possible combined manifolds and searching for intersections between different combinations of rectifying and stripping manifolds, a concerted effort can be made to find feasible designs (especially for a split known to be of a potentially feasible class). If, for a given pair of product regions, no intersection can be found, it may be concluded that the separation is not feasible.

When combined manifolds are found to intersect, inaccuracies introduced by assuming linear curves, surfaces and bodies may lead to incorrect ranges of design variables being identified or to incorrect diagnosis of a proposed split as being feasible. Nevertheless, the combined manifolds do provide valuable qualitative and quantitative information on the feasibility of and column design for a proposed separation and do provide enough information for an initial evaluation or costing of the distillation process.

RECYCLE SELECTION AND PROCESS EVALUATION

Once all potentially feasible sequences have been identified, suitable recycling options can be identified using a simple procedure. First, a superstructure of recycling options is constructed. Every end product from a column (pure component, azeotrope or a stream with no desired components) is a potential recycle stream. Every feed to a column is a potential destination for every recycle stream. The size of this superstructure is then reduced using a set of logic-based rules, which are as follows:

1. Azeotropes can either be recovered, partially recovered, or recycled completely.
2. Never recycle a stream to the column that produces it.
3. Never mix a recycle stream with a feed to a column performing a split where the recycle stream contains one or more components that are not present in either product stream.
4. Never mix streams with compositions in different compartments. The exception to this is recycle streams to columns performing Type C splits; these streams can lie in either compartment that the split traverses.

The recycling options are generated for Sequence 2(A) shown in Figs. 11 and 12. Fig. 15 shows a four-column sequence with potential recycles indicated by dashed lines. In this sequence, all splits are of Type A; the split 2-3/4-5 crosses the curved distillation boundary.

The synthesis of distillation sequences for separating multicomponent azeotropic mixtures is a sequential task. First, many sequences of potentially feasible splits are generated and the recycle options are identified for each flowsheet. The procedure for generating flowsheets has been developed in such a way that sequences can be generated and recycle options proposed without strict constraints being imposed on the composition of feeds to and products from columns in the sequence. Next, the feasibility of the recycle flowsheets needs to be verified and the columns within the flowsheets need to be designed. Only then is it possible to evaluate and compare the alternative flowsheets. Therefore it is necessary to select recycle connections (using the recycle superstructure discussed previously) and assign values to recycle flow rates. This step fixes the composition of intermediate streams and allows column design and evaluation.

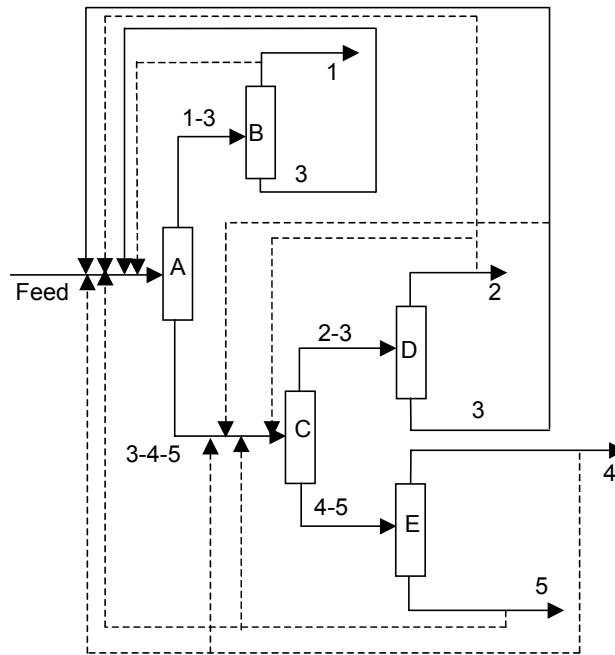


Fig. 15 The recycle superstructure for a potentially feasible four-column sequence to recover all constituent components in a quaternary mixture (Fig. 11). Solid lines represent definite recycles. Dashed lines indicate potential recycles.

A drawback of previous approaches to sequence synthesis has been that only exact compositions of column feeds and products were considered, and that the process for fixing the recycle options meant that splits had to be simulated and evaluated each time the recycle options changed [10] or recycles had to be fixed ahead of feasibility checks [11]. A new, systematic approach to selecting structural and parametric design variables for a fixed sequence with recycles is proposed. The method evaluates the feasibility of a set of proposed separations by considering subsystems within the sequence and allowing various intermediate and product streams to provide recycles, the flow rate of which may vary over a specified range. Flow rates, or ranges of flow rates, of recycles for which all separations in the subsystem are feasible can be identified.

The procedure starts with downstream columns, *i.e.* those producing final products (usually pure components, but sometimes azeotropes). Next, systems of two, then three, etc. adjacent columns are considered. For a proposed recycle flow rate within the range, the mass balance over the subsystem can be closed for the principal components in the subsystem; the presence of minor components is described using representative compositions. In this way, sensitivity of a proposed separation to trace components can be accommodated.

Fig. 16(a) shows a single-column subsystem, from which the bottom product can be partly recycled. From the overall mass balance on the sequence, the flow rate (F) of the distillate and bottom products are known, and the compositions of those streams (C) are partly specified (*i.e.* the distribution of impurities is not specified). If the bottom product is to be recycled, its composition is known; the flow rate of the recycle is allowed to vary from zero to a specified maximum. Thus, the composition and flow rate of the feed to the subsystem can be calculated (without fixing the distribution of

the impurities). The proposed separation can be assessed using representative compositions and combined manifolds. A preliminary column design can also be obtained and evaluated. If, over the entire range of recycle flow rates, the proposed separation is found to be infeasible, then the entire sequence can be eliminated from further consideration (as long as the range of recycle flows being considered is sufficiently wide).

Similarly, Fig. 16(b) shows a three-column subsystem. The subsystem contains two columns producing final products; the feasibility of these separations has been checked in a previous step. Each of the downstream columns potentially provides a recycle stream. The composition of the feed to each of these columns, and hence of the products of the first column in the subsystem, can be determined by mass balance on the main components of the subsystem. For a given pair of recycle flow rates, the feasibility of the first column in the subsystem can be checked and the column can be designed. If the separation in the first column is not feasible for any pair of recycle flow rates (in the range that makes the two downstream separations feasible), then the sequence can be eliminated.

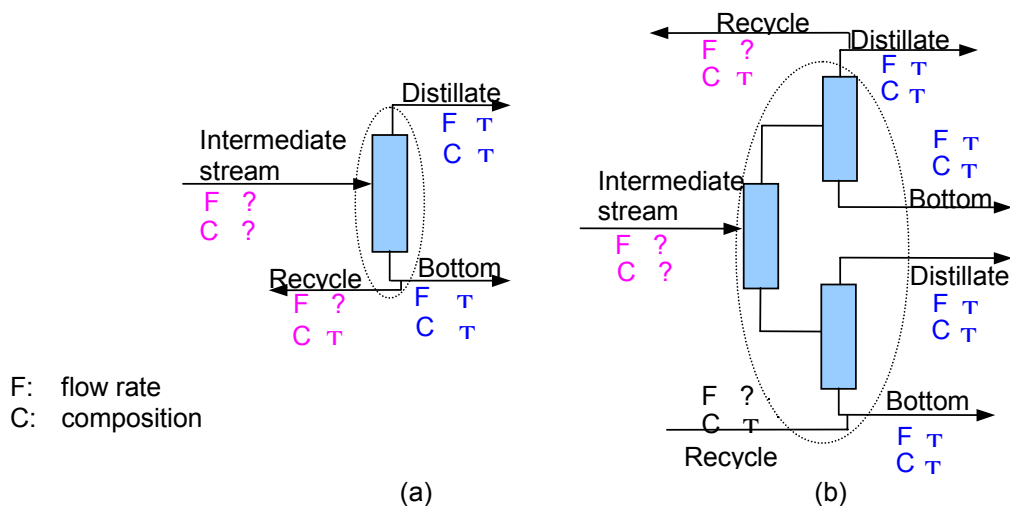


Fig. 16 Calculation of subsystem mass balance. (a) single column; (b) three-column subsystem

The feasibility check for the sequence progressively increases the size of the subsystem until the envelope includes the entire sequence. The number of recycles to be considered also increases as the number of columns in the subsystem increases. At each step, the feasibility of any new separations in the subsystem is checked, and column designs are obtained.

The first benefit of starting the procedure with downstream columns is that downstream separations are easier to evaluate, since there are fewer components present in significant concentrations. Secondly, by considering downstream columns and recycle options simultaneously at the outset, the impact of the recycle stream on the performance of the downstream column is built into the feasibility assessment. This means that fewer iterations are required within the design procedure.

The procedure described above can, in the first instance, be used to check the feasibility of all the columns in a given sequence. If any one of the proposed

separations is infeasible, the sequence can be eliminated. The recycle structure of the flowsheet is obtained from the recycle superstructure. Because the range of flow rates considered for each recycle starts with zero, unnecessary recycles can be detected and deleted. A more sophisticated approach could be adopted to gather additional information (e.g. the range of recycle flow rates for which a given separation is feasible and the range of corresponding column designs). The procedure for assessing feasibility of proposed flowsheets will form the basis for a new approach to optimisation of multicomponent azeotropic distillation flowsheets.

The flowsheet evaluation procedure can be summarised as follows:

1. Fix the sequence to be tested.
2. Generate the recycle superstructure.
3. Specify product purity, composition of azeotropes to be recycled, the range of reflux or reboil ratios to use in every column, and the range of flow rates for every recycle stream.
4. Select a subsystem within the sequence, starting with columns producing final products.
5. Specify the initial flow rate of every recycle stream.
6. Calculate flow rates and compositions of intermediate streams by mass balance.
7. Use combined manifolds to test the feasibility of every split.
8. If all splits are feasible, then the sequence is feasible (go to 10); otherwise, go to 9.
9. Change the flowrates of recycle streams, go to 6.
10. Increase the size of the subsystem by including adjacent columns; go to 6.

Fig. 17 illustrates the results of the recycle selection and flowsheet evaluation procedure applied to Flowsheet 2(A) presented in Figs. 12 and 15. For each column in the sequence, the feasibility was verified and approximate design parameters were obtained. In two cases, a recycle flow rate of zero means that this recycle is not required. To date, flowsheet validation has simply aimed to verify that a given flowsheet is feasible for at least one set of operating conditions, to obtain a consistent set of recycle flow rates and connections and to design the corresponding columns. No attempt has been made to evaluate the solution or optimise flowsheets. However, the feasibility assessment procedure will form the basis for an optimisation approach for flowsheet generation, evaluation and selection.

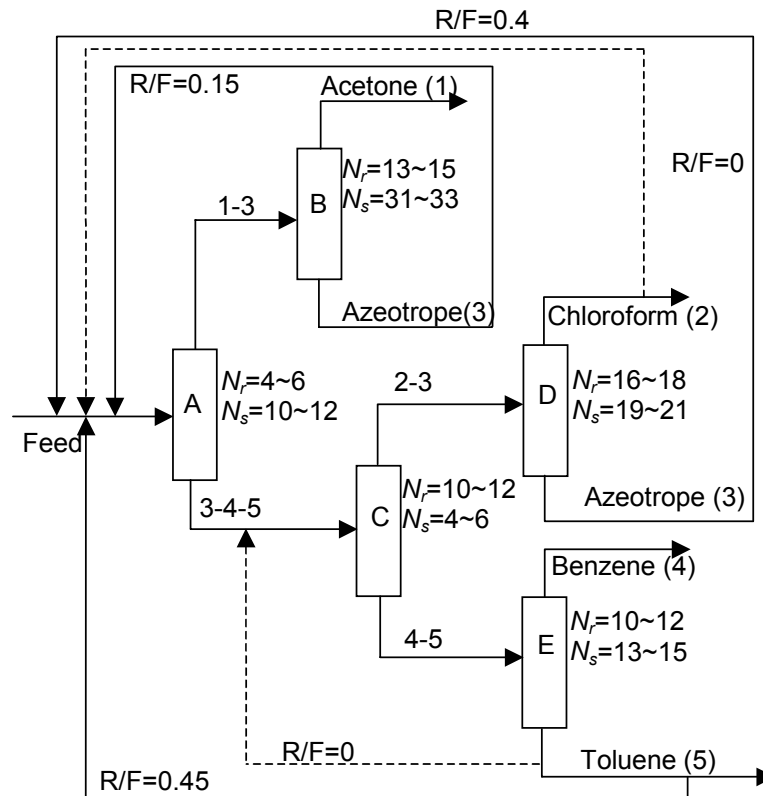


Fig. 17 A feasible flowsheet for Sequence 2(A) shown in Figs. 12 and 15. Feed flow rate is F ; recycle flow rate is R .

CONCLUSIONS

A two-stage procedure for the synthesis of sequences of distillation columns for separating homogeneous multicomponent azeotropic mixtures is presented. The first stage consists of identifying classes of splits. The adjacency and reachability matrices allow feasibility of classes of splits to be assessed; splits may be classified as Type A, B and C. Each type of split may be characterised as feasible or potentially feasible. The sequence generation step systematically combines these classes of splits to satisfy a given separation requirement. No stream compositions need to be fully specified; therefore, the methodology is not subjected to as many constraints as are existing methods. The sequences consider only the main separation tasks to be carried out in each column, and allow a wide range of recycle options, in terms of recycle connections, compositions and flow rates. The algorithms used in this stage require only the reachability matrix, given the existence, nature (stability), composition and boiling temperature of azeotropes in the mixture.

The second stage of the synthesis procedure assesses the feasibility of a proposed flowsheet once the recycle options have been defined. A set of logic-based rules generates a recycle superstructure for every identified sequence. For each possible recycle connection, a range of flow rates is considered. Thus, the flowsheet mass balance can be fixed more precisely, and the feasibility of proposed separations can be assessed more rigorously and quantitatively than in the first stage. The key to the approach is the use of representative compositions to describe product compositions. Sequences containing splits that are not feasible can be rejected; sequences that

contain only feasible splits can be further investigated. Preliminary designs for each column in the sequence can be obtained. The feasibility assessment procedure will form the basis for a systematic approach to flowsheet optimisation.

NOTATION

<i>A</i>	adjacency matrix
<i>b</i>	bottoms mole fraction vector
<i>C</i>	number of components
<i>d</i>	distillate mole fraction vector
N_r	rectifying stage number
N_s	stripping stage number
<i>r</i>	reflux ratio
<i>R</i>	reachability matrix
<i>s</i>	reboil (boil-up) ratio

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