

# Synthesis of Ternary Homogeneous Azeotropic Distillation Sequences: 2. Flowsheet Identification

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This paper presents a systematic methodology for flowsheet generation for separating binary azeotropic mixtures using homogeneous azeotropic distillation. A new classification system for ternary mixtures using 'standard distillation line maps' defined in Sutijan *et al.* (2012) is employed. The new characterisation system is able to link candidate entrainers to flowsheet structures which can facilitate the separation. The sequences considered include pressure-swing distillation, two and three-column flowsheets with or without boundary crossing and the use of single and double-feed columns. For a given ternary mixture, suitable flowsheet structures that can facilitate the separation can be automatically identified. The method is illustrated using examples.

**Keywords:** Azeotropic distillation, Entrainer selection, Residue curve map, Distillation line map, Distillation sequence, Flowsheet structures

## INTRODUCTION

Recent research on ternary azeotropic distillation has addressed entrainer selection, flowsheet synthesis and column design, including that for two-feed columns. An understanding of the applicability and limitations of existing methods allows outstanding problems for flowsheet synthesis to be identified.

Residue curve and distillation line maps are useful for assessing the feasibility of proposed distillation columns and column

sequences and can be used to screen potential entrainers. The two types of maps are qualitatively identical (Widagdo and Seider, 1996). Therefore they provide valuable conceptual tools for process synthesis, that is, for selecting a suitable entrainer, flowsheet configuration and columns designs, to separate a binary mixture in the presence of an entrainer.

Depending on the structure of ternary mixtures, various flowsheet alternatives to separate binary azeotropic mixtures have been proposed. Doherty and Calderola

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(1985) and Foucher *et al.* (1991) have studied the flowsheet for the separation of ternary azeotropic mixtures without distillation boundaries. Knapp and Doherty (1992) apply the concept of pressure swing distillation for the separation of binary azeotropic mixtures by considering the use of entrainers that produce distillation boundaries. Stichlmair and Herguiguera (1992) propose the 'generalised flowsheet' for separating the constituents of minimum or maximum-boiling azeotrope using entrainers that produce distillation boundaries. The generalised flowsheet contains three columns and two recycle streams. Generally, the flowsheet structures proposed are limited to certain class of distillation line maps, and therefore, can miss other promising entrainers.

This work proposed a systematic methodology for generation of feasible flowsheet configuration for separating binary azeotropic mixtures by use of entrainers. The vapour-liquid equilibrium behaviour of ternary homogeneous mixtures is characterised using a 'standard distillation line maps' which can explicitly make a link between proposed entrainers, the feasibility of the desired separation between the binary azeotrope-forming components and the distillation sequence and recycle connections (flowsheet structure) that will facilitate the separation. Associated with each entrainer facilitating the desired separation is one or more flowsheets. A systematic approach to linking proposed entrainers to suitable flowsheets is developed.

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## BACKGROUND

The sequence synthesis problem for separating ternary homogeneous azeotropic mixtures consists of selecting the distillation sequence, the associated recycle structure and the flow rates and compositions of all streams such that the proposed flowsheet and the columns it contains are feasible, and preferably also economically attractive. The flowsheet is feasible if composition profiles of all columns are continuous, *i.e.* there is intersection between rectifying and stripping section composition profiles for a single-feed column.

Rooks *et al.* (1998) propose the 'common saddle criterion' to identify feasible splits using a single-feed column. The feasibility criterion requires the high-reflux or high-reboil liquid composition profiles from both products to approach the same saddle. This criterion is a sufficient (but not necessary) condition for split feasibility that can miss other feasible splits. In particular, when 'continuous distillation regions' (Safrit and Westerberg, 1997), also known as 'compartments' (Thong, 2000) exist, feasible splits can be incorrectly identified as unfeasible splits.

Stichlmair and Herguiguera (1992) propose the 'generalised flowsheet' for separating the constituents of an *a-b* minimum- or maximum-boiling azeotrope using an entrainer. The generalised flowsheet requires the distillation boundary to be curved; one of the columns crosses the distillation boundary. The generalised

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flowsheet contains three columns and two recycle streams. If the boundary is highly curved a two-column flowsheet can be used.

The set of feasible composition profiles of a column section is bounded by the total reflux and minimum reflux (reversible operating) composition profiles (Wahnschafft *et al.*, 1992) *i.e.* the residue curve and pinch point curve passing through the product composition. These regions form the basis of a feasibility test: If the bounds of the composition profiles do not intersect or overlap, the two proposed products cannot be obtained in a single-feed column. This concept is an extension of the one proposed by Levy *et al.* (1985), who uses the intersection of liquid composition profiles for the two proposed products as a criterion for feasibility.

Knapp and Doherty (1992) extend the concept of pressure swing distillation for the separation of binary azeotropic mixtures by considering the use of an entrainer, which is known as 'pressure shifting'. Pressure-insensitive binary azeotropes can be separated using entrainers that produce pressure-sensitive distillation boundaries. The composition space may contain multiple distillation boundaries; as long as only one boundary separates the desired products, a two-column configuration can be used to separate binary mixtures using boundary shifting.

Castillo *et al.* (1998b) propose a sequence of design procedure for ternary azeotropic distillation based on graphical analysis. For a given ternary mixture, flowsheets can be proposed that shift or cross the boundary or exploit finite mass

transfer rates. Feasibility is tested using pinch point curves and distillation lines or residue curves (Wahnschafft *et al.*, 1992); the feasibility test is extended to consider product compositions specified in terms of a desired purity. The recycle composition is selected using a trial and error procedure. No guidance for general flowsheet synthesis is given.

This work presents a systematic method for identifying promising flowsheets for the separation of binary azeotropic mixtures. Promising entrainers are identified using a new classification of ternary mixtures 'standard distillation line maps' developed in Sutijan *et al.* (2012) which is able to link candidate entrainers to flowsheet structures.

## **IDENTIFICATION OF FEASIBLE FLOWSHEET CANDIDATES**

An entrainer is said to be feasible if there is at least one flowsheet structure that can facilitate the separation of a given binary azeotropic mixture. Flowsheet features include boundary shifting or crossing, recycling and mixing, and the use of two-feed columns. Depending on the characteristics of the distillation line map (*i.e.* product stability and the existence of distillation boundaries), one or more flowsheet structures can be associated with each standard distillation line map associated with feasible entrainers.

When an entrainer does not introduce a distillation boundary between the two desired products, recycles in a two-column flowsheet (*i.e.* without boundary shifting or crossing) can generally facilitate the separation. For single-feed column

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**Table 1.** Feasible flowsheets for the separation of a binary azeotrope for which the entrainer does not introduce a distillation boundary between the saddle- and node-type products. A two-column flowsheet with recycle can facilitate the separation.

Azeotrope Type	Direct sequence	Indirect sequence
Maximum-boiling		
Minimum-boiling		

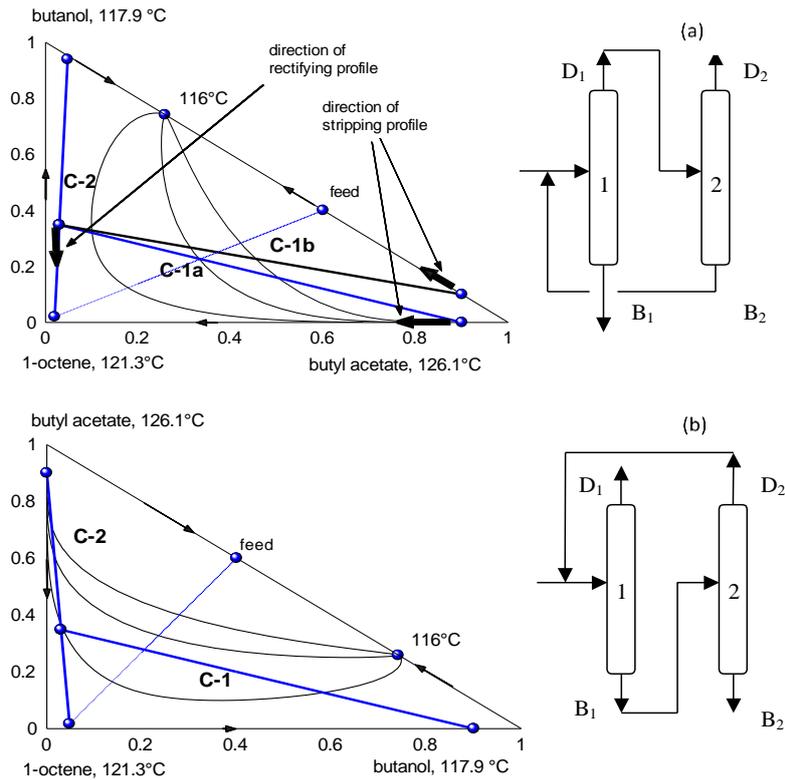
flowsheets, both the direct and the indirect sequence can be used (see Table 1), although both sequences may not be feasible for a given standard distillation line map. The common saddle criterion (Rooks *et al.*, 1998) provides guidance about which specifications are feasible.

Figure 1 shows an example of an entrainer that does not introduce a distillation boundary. A two-column flowsheet with recycles (Fig.1) can facilitate the separation of the minimum-boiling butyl acetate-butanol azeotrope using either the direct or indirect sequence. The specifications of column C-1a (Fig.1a) satisfy the common saddle criterion. At high reflux ratios, the rectifying and stripping profiles approach the same saddle (1-octene). This column is potentially feasible. The specifications of column C-1b (Fig. 1a) do not satisfy the common saddle criterion. At high reflux ratios, the stripping profile approaches the

azeotrope (stable node), so this column is generally unfeasible.

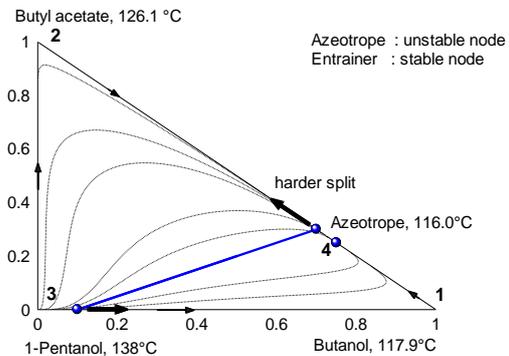
Many entrainers do not introduce a distillation boundary between two saddle products, but cause the composition space to contain two 'continuous distillation regions' (Safrit and Westerberg, 1997) or 'compartments' (Thong, 2000). Fig. 2 illustrates a distillation line map containing two compartments, namely regions 2-3-4 and 1-3-4. The behaviour of residue curves and distillation lines within a compartment is analogous to that of a zeotropic ternary mixture, in which the volatility order is fixed. That is, the compartment represents a relatively well-behaved composition subspace.

It is possible for single-feed columns to cross compartment boundaries – *i.e.* for the two products to lie in different compartments (Thong and Jobson, 2000b). However, the region of feasible product compositions is generally very small. It is



**Fig. 1:** Two-column flowsheet (a) Indirect sequence (primary product is butyl acetate): Column C-1a, which satisfies the common saddle criterion, is feasible, whereas column C-1b is generally unfeasible. ( $P=1$  atm); (b) Direct sequence (primary product is butanol): Both column specifications satisfy the common saddle criterion. ( $P=1$  atm).

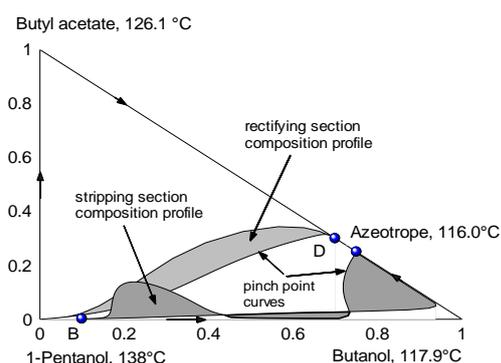
generally only relatively easy to obtain a distillate and a bottom product with compositions close to the stable and unstable nodes, respectively, as illustrated in Fig. 2. This restriction is due to the fact that the composition profiles do not have to traverse far into the adjacent compartment to intersect (Fig. 3). As the products move away from stable and unstable nodes, single-feed columns become unfeasible (Fig. 4). In these cases, a two-feed column can facilitate the separation. The middle-section composition profile can bridge the gap between the stripping and rectifying composition profiles.



**Fig. 2:** Cross-compartment splits in a single-feed column.

Thong (2000b) noted that, in a single-feed column, the intersection of the pinch point curves is a necessary condition for split feasibility. That is, if the products

cannot be produced from a reversible column, these products cannot be produced at all. Thong (2000b) also observed that compartment boundaries can only be crossed in one direction. For example, in Fig. 5, some 24/13 splits are feasible, while 14/23 splits never are. (A 24/13 split is a separation where one product composition lies close to the composition space boundary between singular points 2 (butyl acetate) and 4 (butyl acetate-butanol azeotrope) and the other product composition lies close to the composition space boundary between singular points 1 (butanol) and 3 (1-pentanol) (Thong and Jobson, 2000a). A 24/13 split is analogously defined.)

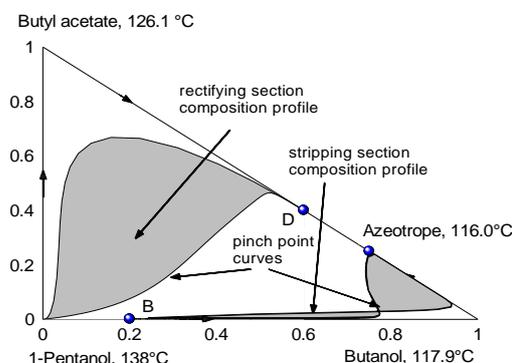


**Fig. 3:** A feasible cross-compartment split in a single-feed column. The compositions of both products are located close to the stable and unstable nodes.

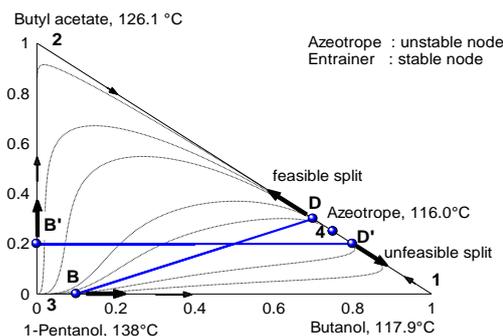
Since some single-feed columns can cross a compartment boundary, flowsheets containing such columns can allow saddle-type final products to be obtained. This result introduces a set of candidate entrainers that are not accommodated by existing entrainer selection criteria.

To employ a single-feed column that crosses a compartment boundary, a three-column flowsheet is generally needed.

Table 2 summarises the flowsheet structures using single-feed columns that can be used to obtain saddle-type final products.



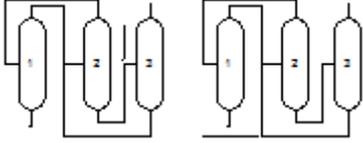
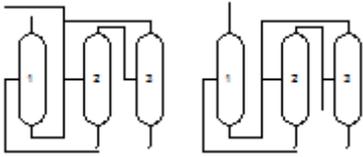
**Fig. 4:** An unfeasible cross-compartment split in a single-feed column. The product compositions are located far from the stable and unstable nodes.

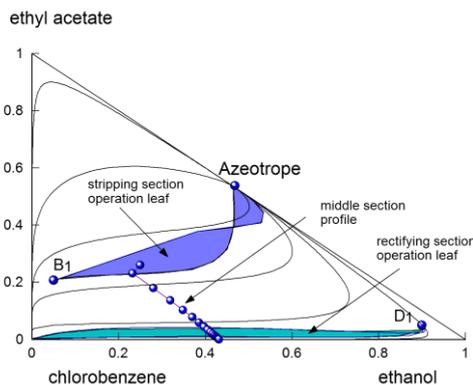


**Fig. 5:** Feasible and unfeasible directions of splits for a single-feed column that crosses a compartment boundary.

Thong (2000b) proposed tests for classes of splits for predicting the feasibility of cross-compartment splits using two-feed columns. These tests were based on the VLE behaviour at the compartment boundary. He also proposed that a given class of split (Thong and Jobson, 2000a) can be performed in a two-feed column if and only if it can also be performed in a single-feed column. That is, whether a class of split is feasible (e.g. 24/13 or 14/23, as

**Table 2.** Feasible flowsheets using single-feed columns for the separation of a binary azeotropic mixture where the entrainer does not introduce a distillation boundary between the two saddle-type products. Column 2 crosses a compartment boundary.

Azeotrope Type	Single-feed column
Maximum boiling	
Minimum boiling	



**Fig. 6:** Two-feed column producing a saddle type product. Middle profile is required to bridge the gap between stripping and rectifying operation leaves. The split is always unfeasible in a single-feed column.

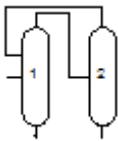
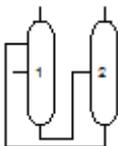
shown in Fig. 12) applies equally to single-feed and double-feed columns. While the product compositions of single-feed columns are constrained to lie close to the unstable and stable nodes, a two-feed column is not similarly constrained. For example, a high-purity ethanol distillate could be obtained from an ethanol-ethyl

acetate-chlorobenzene mixture, as shown in Fig. 6. Because two-feed columns can recover saddle-type final products (e.g. ethanol), two-column flowsheets can facilitate the desired separation, as summarised in Table 3.

Classical extractive distillation is a well-known example of a two-column flowsheet, where the two-feed column produces a saddle-type final product. In this case, a heavy entrainer is used to separate a minimum-boiling azeotrope. The entrainer introduces neither distillation boundaries nor new azeotropes, *i.e.* class OOA type C. Laroche *et al.* (1991) propose a graphical technique to determine the order of recovery of products in the extractive distillation flowsheet. They propose that component A must be recovered first if the A-B isovolatility curve terminates on the A axis. This technique only applies to classical extractive distillation (OOA type C) but not more generally to two-column flowsheets

using a two-feed column that crosses a compartment boundary.

**Table 3.** Feasible flowsheets for the separation of binary azeotrope for which entrainers do not introduce a distillation boundary between two saddle-type products. The two-feed column crosses a compartment boundary.

Azeotrope Type	Double-feed column
Maximum boiling	
Minimum boiling	

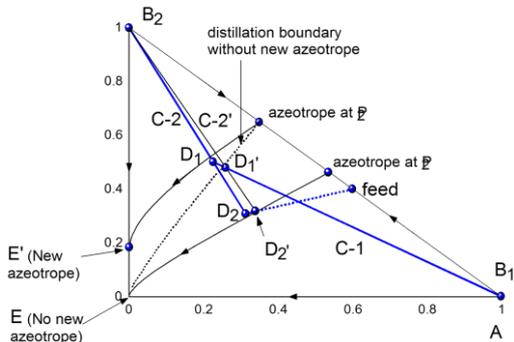
The concept of extractive distillation can be generalised and can allow a new set of candidate entrainers to be defined. These entrainers may introduce new azeotropes with one or both of the components to be separated and may also introduce distillation boundaries in the distillation line map. Fig. 3 presents the set of standard distillation line maps for such entrainers. For separating minimum-boiling azeotropes, entrainers may be low-boiling compounds (*e.g.*, class XXA type C(5) and XXA type C(6)), intermediate-boiling compounds (*e.g.*, class XXA type C(5), XXA type C(6), AOA type C, OAA type C, OAX-Y type C and AOX-Y type C) or high-boiling compounds (*e.g.*, class OOA type C, OOX-Y type C, XXA type C(5) and XXA type C(6)). Intermediate- and low-boiling entrainers can offer economic advantages because of

their relatively low boiling temperatures and latent heats of evaporation.

When a distillation boundary exists between the two components to be separated, the products lie in different distillation regions. In general, two-column flowsheets using only recycle without boundary crossing or boundary shifting cannot recover the desired products since at least one intermediate product must be in the same distillation region as another column. Laroche *et al.* (1992) demonstrate that it is possible to cross a distillation boundary by introducing the feed to a column in one region, and by recovering the products in an adjacent region (boundary crossing). Knapp and Doherty (1992) demonstrate the use of two columns operated at different pressures to recover two products which lie in different distillation regions (boundary shifting). Flowsheets employing boundary crossing, boundary shifting or recycling and mixing can recover pure component products which are separated by a distillation boundary.

Boundary shifting (Knapp and Doherty, 1992) can be applied for both straight and curved boundaries. Pressure-sensitive distillation boundaries can allow relatively low recycle-to-feed ratios to be used, even if new azeotropes appear as a result of the pressure change. Fig. 7 illustrates a feasible two-column flowsheet for such a case. As shown in Fig. 13, if no new azeotrope were formed, a higher recycle-to-feed ratio would be required. The relative flows of recycles  $D_2$  (when a new azeotrope forms) and  $D_2'$  (when no new azeotrope forms) can be determined using the lever-arm rule. Three-column flowsheets exploiting

boundary shifting can benefit from the appearance of a new azeotrope in a similar way.

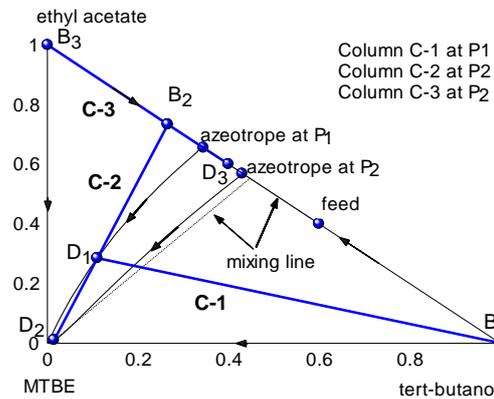


**Fig. 7:** Two-column flowsheet with boundary shifting. An entrainer that introduces a new azeotrope can reduce the recycle-to-feed ratio, relative to the case that no new azeotrope is formed.

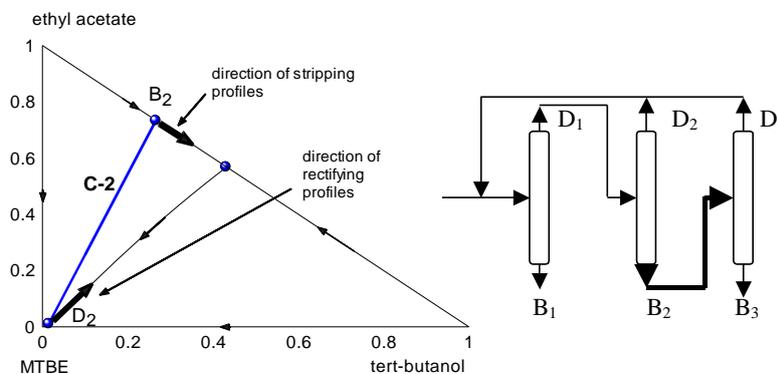
In flowsheets featuring boundary crossing, curvature of the boundary is exploited to allow the products of one column to be located in different distillation region to the feed. More highly curved boundaries can allow lower recycle-to-feed ratios than straighter boundaries (Castillo, 1997). However, reflux ratios and heats of vaporisation can also have a significant impact on the process economics, so entrainer selection on the basis of boundary curvature alone is not adequate.

In distillation line maps with a boundary separating two desired node-type products, two-column flowsheets using boundary shifting or three-column flowsheets using boundary crossing or recycling and mixing can always facilitate the separation of the binary azeotropic mixtures.

Fig. 8 presents the flowsheet mass balance for a three-column flowsheet using boundary shifting. As shown in Fig. 9, when column C-2 is fed to the column C-3, all columns satisfy the common saddle criterion. That is, for high reflux ratios in column C-2, the stripping profile will

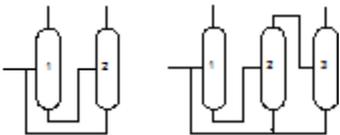
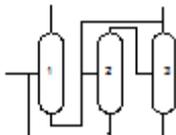
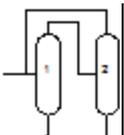
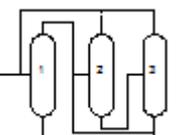


**Fig. 8:** Three-column flowsheet using boundary shifting for the separation of minimum boiling binary azeotrope. The bottom product of column C-2 is fed to the last column.



**Fig. 9:** Direction of stripping and rectifying profiles for column C-2 when the bottom product of column C-2 is fed to the last column. The product specifications satisfy common saddle criterion. Both profiles approach the saddle at high reflux ratio. Flowsheet is feasible.

**Table 4.** Feasible flowsheets for the separation of a binary azeotrope where the entrainer introduces a distillation boundary between the two node-type desired products.

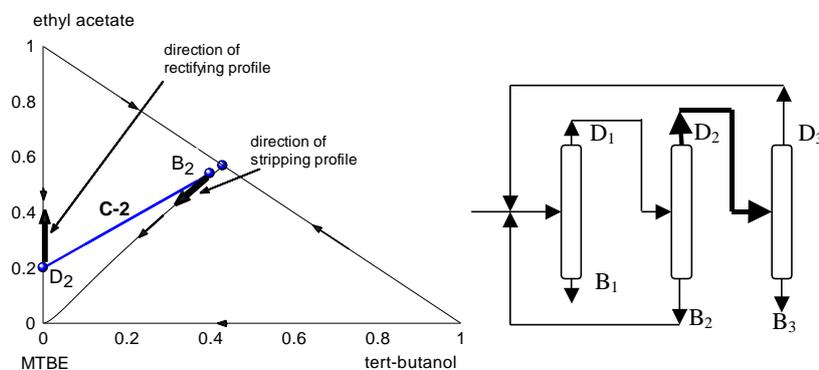
Azeotrope Type	Boundary Shifting/Crossing	Recycling and Mixing
Maximum-boiling		
Minimum-boiling		

approach the saddle (azeotrope at  $P_2$ ), as will the rectifying profile.

When column C-3 is fed by the overhead product of column C-2, on the other hand, column C-2 will not satisfy the common saddle criterion: at high reflux ratios, the stripping profiles will approach the pure entrainer saddle and the rectifying profiles will approach the pure ethyl acetate saddle, as shown in Fig. 10. Such product specifications are generally unfeasible.

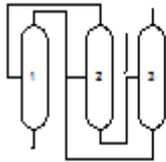
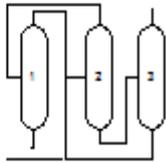
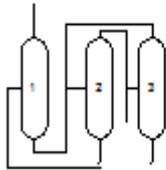
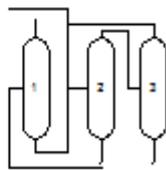
Table 4 summarises the flowsheet alternatives for the classes of distillation

line map where the two desired products are nodes separated by a distillation boundary. The compositions of the feed to the process determine which flowsheets are feasible. If the feed is located on the convex side of the boundary, a three-column flowsheet with boundary crossing cannot perform the separation; a two-column flowsheet with boundary shifting should be used, especially when the boundary is pressure sensitive. When the boundary is not pressure sensitive, the three-column flowsheet with recycling and



**Fig. 10:** Direction of stripping and rectifying profiles for column C-2 when the top product of column C-2 is fed to the last column. The profiles approach the different saddles at high reflux ratio. The flowsheet is unfeasible.

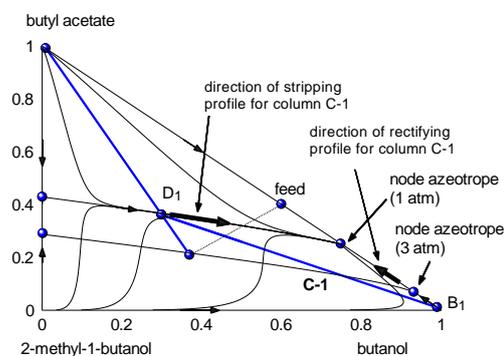
**Table 5.** Feasible flowsheets for producing a node- and a saddle-type pure component product separated by a distillation boundary using single-feed columns. Column C-2 crosses a compartment boundary

Azeotrope Type	Single-feed column	
Maximum boiling		
Minimum boiling		

mixing could be used.

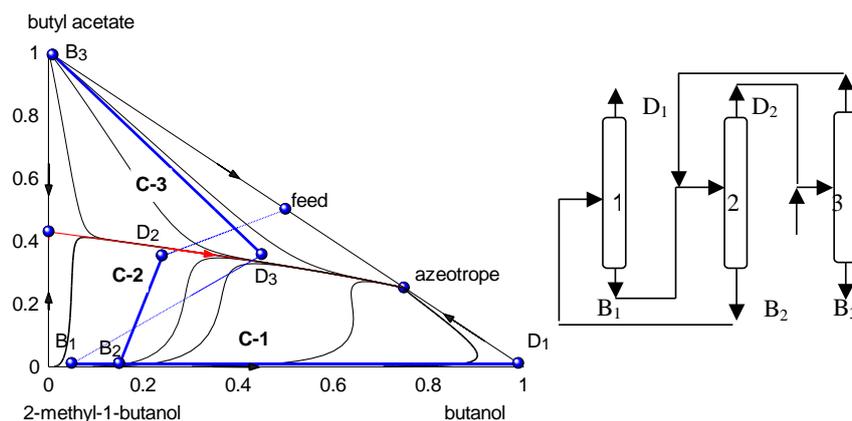
If one of the desired products is a saddle and the other is a node, and a boundary separates the products (classes XOX type A(5) and OXX type B(6)), two compartments will exist in one of the distillation regions. Since the two products are located in different distillation regions, boundary crossing, boundary shifting or recycling and mixing can allow recovery of the products. In general, two single-feed columns with boundary shifting cannot perform the separation, as one of the columns, which has to produce a saddle product, must cross a compartment boundary. As illustrated in Fig. 11, this column (column C-1) is unfeasible since it lies in the direction of unfeasible splits, as discussed previously. However, three-column flowsheets using single-feed columns can perform the separation, as column C-2 can cross the compartment boundary in the direction of feasible splits. Fig. 12 illustrates such a flowsheet. Table 5

summarises the feasible flowsheets containing single-feed columns that can facilitate the separation.



**Fig. 11:** An unfeasible flowsheet of two single-feed columns exploiting boundary shifting. Column C-1 lies in the direction of unfeasible splits and does not satisfy the common saddle criterion. Both profiles approach node type azeotrope at high reflux ratios.

For distillation line maps of class XOX type A(5) and OXX type B(6), flowsheets using a two-feed column and recycling and mixing or boundary shifting can perform

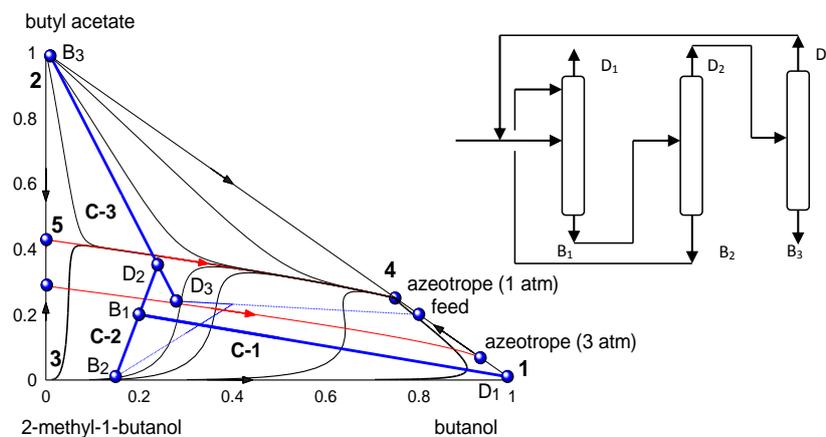


**Fig. 12:** Feasible flowsheet with three single-feed columns using recycling and mixing. Column C-2 lies in the direction of feasible splits.

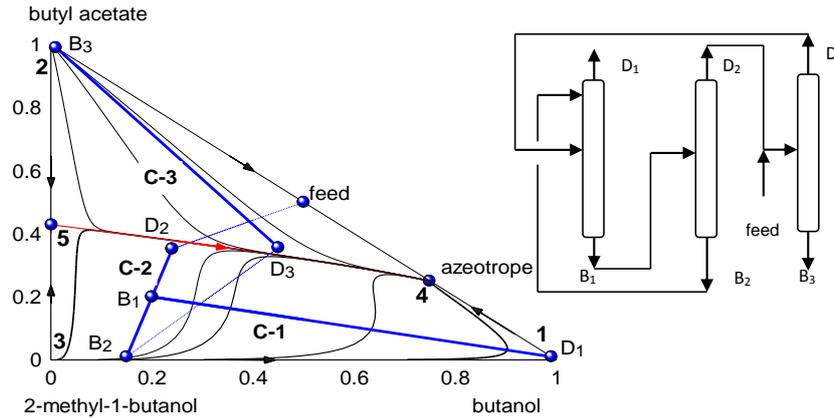
the separation. The composition space contains two distillation regions, one of which is similar to that for classical extractive distillation, *i.e.*; the distillation region contains two non-adjacent saddle singular points. In the distillation region containing compartments (*e.g.* the region 1-3-4-5 in Fig.13), a two-feed column must be used to recover one desired pure product and an intermediate product. The flowsheet uses boundary shifting or recycling and mixing, to recover the other pure component product. Figs. Examples of such flowsheets are presented in Figures 13 and 14. When the feed is located in the

distillation region containing compartments, boundary shifting must be used. Otherwise, boundary shifting or recycling and mixing can be used to facilitate the separation.

The feasible flowsheets for the separation of a maximum-boiling azeotrope are analogous to those for separating a minimum-boiling azeotrope. Table 6 summarises the flowsheets that can be used to recover a saddle-type product and a node-type product using a two-feed column, together with boundary shifting or recycling and mixing.



**Fig. 13:** Three-column flowsheet using a two-feed column and boundary shifting. The feed is located in the distillation region containing compartments (region 1-3-4-5). ( $P_1=1$  atm,  $P_2=1$  atm,  $P_3=3$  atm)



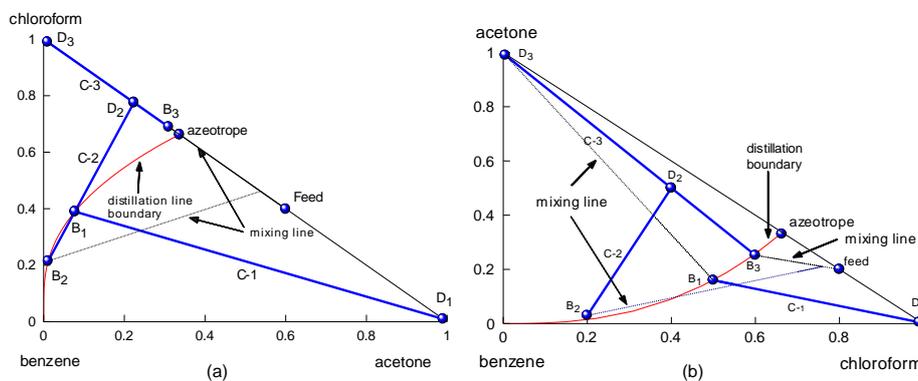
**Fig. 14:** Three-column flowsheet using a two-feed column and recycling and mixing. The feed is located in the distillation region without compartments (region 2-4-5). (P=1 atm).

### DEPENDENCE OF FLOWSHEET STRUCTURES UPON THE CHOICE OF PRIMARY AND SECONDARY PRODUCTS

The new classification system for distillation line maps requires the primary and secondary products to be defined. The order in which the desired products are recovered affects which flowsheet structures are feasible. Figures 15 and 16 illustrate how the choice of primary product can affect which flowsheets are feasible for a given separation requirement. An acetone-chloroform mixture is to be separated using benzene as the entrainer.

When the azeotropic feed is rich in acetone, a three-column flowsheet with boundary crossing or a two-column flowsheet with boundary shifting can facilitate the separation. For the two-column flowsheet, either acetone or chloroform can be recovered as the primary product. However, for the three-column flowsheet, acetone must be recovered as the primary product.

Similarly, when the azeotropic feed is rich in chloroform, a two-column flowsheet with boundary shifting can facilitate the separation. Either acetone or chloroform can be recovered as the primary product. However, a three-column flowsheet with



**Fig. 15:** Three-column flowsheets for the separation of an acetone-chloroform mixture using benzene as the entrainer (P=1 atm). (a) Feed is rich in acetone. Acetone is recovered as the primary product when using boundary crossing. (b) The feed is rich in chloroform. Chloroform is recovered as the primary product when recycling and mixing are used.

boundary crossing cannot perform the separation, but the three-column arrangement using recycling and mixing can (Fig. 15b). In this case, there are three recycled streams, which is likely to be economically unattractive.

The choice of which component is recovered as the primary product should be made to benefit the process economics. The following guidelines are proposed for the selection of the primary product:

- The primary product should be selected to result in a low recycle-to-feed ratio and/or few recycle streams.
- Established heuristics (King, 1980) for sequence selection should be

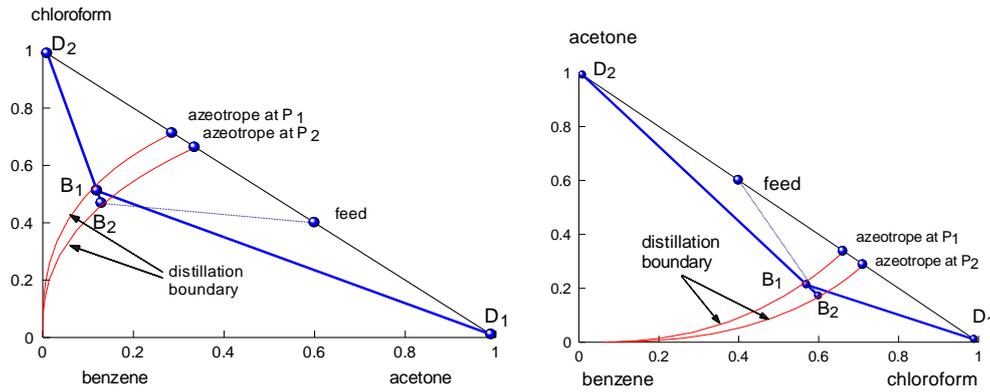
considered; *e.g.* do the most difficult separation last, favour the direct sequence, remove first a component comprising a large fraction of the feed and favour near-equimolar splits between the top and bottom products in a column.

- Practical considerations (*e.g.* hazardous, reactive, heat sensitive and corrosive component must be recovered first) (Smith, 1995) can also suggest which product to recover first.

Since the guidelines are not clearcut, it may be necessary to compare all possible flowsheets for both choices of primary product.

**Table 6.** Feasible flowsheets containing a two-feed column for the separation of a binary azeotropic mixture using an entrainer that introduces a distillation boundary between the saddle-type and node-type desired products

Class	Azeotrope Type	Boundary Shifting	Recycling and Mixing
XOX type A(5)	Minimum		
	Maximum		
OXX type B(6)	Minimum		
	Maximum		



**Fig. 16:** Two-column flowsheet using boundary shifting separates an acetone-chloroform mixture using benzene as the entrainer ( $P_1 = 10$  atm,  $P_2 = 1$  atm). The binary feed is rich in acetone. (a) Acetone is recovered as the primary product. (b) Chloroform is recovered as the primary product.

### ILLUSTRATIVE EXAMPLE

Refer to the case study in Sutijan *et al.* (2012), this example addresses the separation of a mixture of acetone and chloroform, in which components form a maximum-boiling azeotrope. The binary feed mixture, is to be purified using homogeneous azeotropic distillation. Since the azeotrope composition is pressure-insensitive, binary pressure-swing distillation is not a cost-effective design option. An entrainer is needed to facilitate the separation. Promising entrainers and

the associated flowsheets are selected according to the new methodology. Suitable flowsheets for each entrainer are identified directly, given the standard distillation line map classification (see Tables 1 to 6 in Sutijan *et al.* (2012). Figure 8 and Tables 2 (Sutijan *et al.*, 2012) present the eight entrainers to be considered. The set of flowsheets that are suitable for each acceptable entrainer is obtained directly once the ternary mixtures have been classified. Of the candidate entrainers, only methanol is not suitable: in this case the two products would be both saddles

**Table 7.** Feasible and unfeasible flowsheets for the separation of acetone-chloroform mixtures (Y: feasible flowsheets ; N: cannot perform the separation).

Entrainer	Boundary shifting	Boundary crossing	Recycling - mixing	Recycling only	Double-feed (two columns)	Double-feed (three columns)
Acetic acid	Y	N	Y	N	N	N
Acrylic acid	Y	N	Y	N	N	N
Benzene	Y	Y	N	N	N	N
F6 Acetyl acetone	N	N	N	N	Y	N
Methyl ethyl ketone	Y	Y	N	N	N	N
Thio acetic acid	Y	N	Y	N	N	N
Toluene	Y	Y	N	N	N	N

separated by a distillation boundary. Table 7 lists various feasible flowsheet configurations that can separate acetone - chloroform binary azeotropic mixture. Various flowsheet configurations are defined in Table 8.

When the binary feed is located on the convex side of the boundary (entrainer is acetic acid or acrylic acid) only the two-column flowsheet with boundary shifting and the three-column flowsheets with boundary shifting or recycling and mixing can facilitate the separation. The three-column flowsheet with recycling and mixing is expected to require large columns, as the three recycled streams would result in relatively high feed flow rates to the columns, and, in turn, high capital and operating costs for the flowsheet. However, reflux ratio is also an important design parameter, which depends on other parameters such as column pressure, feed quality and sharpness of the split. Therefore, the overall performance of the flowsheet can only be judged after design and optimisation. Two- or three-column

flowsheets with boundary shifting are expected to be an expensive option because the distillation boundaries for these mixtures are not pressure-sensitive and a large pressure difference will be required if the recycle flow rate is not to be excessive.

Thio acetic acid forms a straight distillation boundary. Flowsheets with boundary shifting or recycling and mixing, but not boundary crossing, can facilitate the separation. For this pressure-insensitive distillation boundary, a large pressure difference will be required to provide a low recycle-to-feed ratio. Overall, this entrainer is not expected to be a good entrainer.

F6 acetyl acetone does not introduce a distillation boundary between the two components to be separated. A two-feed column (extractive distillation) and flowsheets with three single-feed columns can perform the separation. When using a two-feed column, recycle-to-feed ratios that can lead to feasible design depend on the vapour-liquid equilibrium behaviour of the system. The distillation line map or

**Table 8.** Key to the definition of flowsheet structures used in this work

Cases	Conditions
Boundary shifting	<ul style="list-style-type: none"> <li>• Boundary exists</li> <li>• Different pressures applied</li> <li>• No column crossing boundary</li> </ul>
Boundary crossing	<ul style="list-style-type: none"> <li>• Boundary exists</li> <li>• No pressure difference</li> <li>• One of columns crossing boundary</li> </ul>
Recycling and mixing	<ul style="list-style-type: none"> <li>• Boundary exists</li> <li>• No pressure difference</li> <li>• No column crossing boundary</li> <li>• Boundary is crossed by mean of mixing between two streams</li> </ul>
Recycling	<ul style="list-style-type: none"> <li>• No boundary exists</li> <li>• No pressure difference</li> <li>• No column crossing boundary</li> <li>• No boundary crossing by mean of mixing between two streams</li> </ul>

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residue curve map alone does not allow the potential of this flowsheet to be evaluated prior to design and optimisation.

Benzene, toluene and methyl ethyl ketone all form a very curved distillation boundary. Boundary crossing can facilitate the separation; low recycle-to-feed ratios at atmospheric pressure can be used. Boundary shifting can also be used; in this case, the gap between the two boundaries can further improve the performance of the flowsheet. For higher pressure differences, the recycle-to-feed ratio is less, but so is the volatility of the light key component, relative to the heavy key component, in the high-pressure column. This trade-offs means that the operating conditions for each entrainer must be optimised before the entrainers can be compared.

## CONCLUSIONS

A systematic method for generating suitable flowsheets for separating a binary azeotropic mixture into its pure component products has been developed. For a given entrainer, potentially feasible flowsheets can be derived directly from the structure of ternary mixtures characterised using the 'standard distillation line maps'.

Flowsheets that can facilitate the desired separation include such features as boundary shifting, boundary crossing, recycling (with or without mixing of recycle streams) and two-feed columns. This set of flowsheets is much broader than that considered in existing systematic approaches to flowsheet synthesis. The structures of suitable flowsheets can be identified directly from the standard distillation line map and the composition of

the azeotropic feed to the process. The approach to flowsheet identification is systematic, providing one or more suitable flowsheets for each promising entrainer.

The entrainer selection and flowsheet identification procedure requires only the small amount of data that is required to determine the structure of the distillation line map. The procedures are suitable for implementation in computer-aided process design software. The methodology is therefore valuable and powerful for the synthesis of ternary homogeneous azeotropic distillation processes.

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