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Synthesis of Ternary Homogeneous Azeotropic Distillation Sequences: Entrainer Selection

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This paper presents a methodology for automatic selection of entrainers for separating binary azeotropic mixtures using homogeneous azeotropic distillation. A new classification system for ternary mixtures based on the termini of distillation boundaries and the type (stability) of products and azeotropes is proposed. The new characterisation system is able to link candidate entrainers to flowsheet structures which can facilitate the separation. Existing entrainer selection criteria are extended to accommodate other promising entrainers, including light, intermediate and heavy-boiling entrainers.

Keyword: Azeotropic Distillation, Distillation Line Map, Distillation Sequence, Entrainer Selection, Residue Curve Map, Ternary

INTRODUCTION

A third component, or entrainer, can often allow the separation of a binary azeotropic mixture into two pure components using homogeneous distillation. The vapour-liquid equilibrium behaviour of the resulting ternary mixture can be characterised using residue curve maps (RCM) or distillation line maps (DLM). These two maps contain sets of feasible liquid composition profiles for staged and packed columns, respectively, operating at total reflux. 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.

Doherty and Caldarola (1985) suggest a conservative entrainer selection criterion for the separation of a binary azeotrope-forming mixture (*a*-*b*) – an entrainer is suitable if both desired products lie in the same distillation region. Laroche *et al.* (1992) develop entrainer selection criteria that accept entrainers that form curved boundaries. This enables the use of a column crossing the boundary (*i.e.* with the feed lying in one distillation region and both products in another adjacent region) and leads to a longer list of potential entrainers. Stichlmair and Herguijuela (1992) and Stichlmair and Fair (1998) propose another strategy for entrainer selection, which can accept an entrainer that produces new azeotropes with one or two of the components of the binary azeotropic feed mixture.

However, existing classification systems for the vapour-liquid equilibrium behaviour of ternary homogeneous mixtures cannot 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. In this work, a new classification system is proposed for this purpose. This classification method characterises ternary mixtures based on the existence and termini (*i.e.* end points) of distillation boundaries in the composition space diagram and the type (stability) of binary azeotropes and of the desired products. Associated with each entrainer facilitating the desired separation is one or more flowsheets. A systematic approach to linking proposed entrainers to suitable flowsheets will be presented in a further work.

BACKGROUND

The existing classification systems for ternary mixtures (Matsuyama and Nishimura, 1977, and extended by Stichlmair and Herguijuela, 1992) use singular point properties to characterise the vapour-liquid equilibrium behaviour of a ternary mixture. All residue curve maps and distillation line maps can be classified. However, the classification system results in a relatively large number of classes of residue curve maps or distillation line maps. Furthermore, the classification system cannot indicate whether or not an entrainer will facilitate the desired separation. Therefore, it is difficult to draw general guidelines for the selection of promising entrainers based on the existing characterisation systems. Unless stated otherwise, this work uses distillation line maps and the classification system of Stichlmair *et al.* (1989).

It is usually possible to separate binary azeotropic mixtures into their pure constituents by addition of an entrainer. The choice of the entrainer must permit easy separation of the azeotrope-forming components and the recovery of the entrainer, which will be recycled within the process.

Wahnschafft *et al.* (1992) and Wahnschafft and Westerberg (1993) suggest a simple method to identify promising entrainers. The equilibrium constants of the azeotropic components at infinite dilution in an entrainer reflect the impact of the entrainer on the relative volatilities of the azeotrope-forming species. Based on the equilibrium constant at infinite dilution, Bauer and Stichlmair (1995) and Gmehling and Möllmann (1998) use the selectivity of the azeotropic components at infinite dilution in the entrainer to guide entrainer selection. However, neither of the proposed indicators provides information about vapour-liquid equilibrium behaviour over the whole of the composition space.

Two sets of criteria for entrainer selection based on residue curve maps and distillation line maps have been proposed. The first approach selects an entrainer that produces no boundary between the two azeotropic constituents (Doherty and Caldarola, 1985; Foucher *et al.*, 1991). In this case, the binary azeotrope *a-b*, *i.e.* the azeotrope formed between components *a* and *b*, must be either an origin or a terminus of distillation lines. Van Dongen and Doherty (1985) and Levy *et al.* (1985) observe that the entrainer selection strategy of Doherty and Caldarola (1985) is conservative and can miss many potentially suitable entrainers.

In the second approach, the entrainer is selected so that the two constituents (desired products) of the binary feed mixture are origins or termini of distillation lines (Stichlmair and Herguijuela, 1992; Stichlmair and Fair, 1998). Such systems always have distillation boundaries. Additional azeotropes and even ternary azeotropes may exist. Based on these criteria, Stichlmair and Herguijuela (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 flowsheet contains three columns and two recycle streams. If the boundary is highly curved a two-column flowsheet can be used.

The entrainer selection criteria of Doherty and Caldarola (1985) and Stichlmair and Herguijuila (1992) are adopted and extended in this work. As will be shown, many entrainers which violate the existing criteria can facilitate the desired separation of an *a-b* mixture to product pure component products *a* and *b*. Also adopted and extended in this work are the entrainer selection criteria of Knapp and Doherty (1992) which include entrainers that produce pressure-sensitive distillation boundaries.

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. A compartment is a subspace within the composition space which contains one stable node, an adjacent saddle and an adjacent unstable node. Within a compartment the volatility order is constant. The compartment is bounded by a compartment boundary, although no rigorous definition of the concept exists; in this work the boundary is approximated by a straight line connecting the unstable and stable nodes.

The set of feasibile 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.

This work presents a systematic method for identifying promising entrainers for the separation of binary azeotropic mixtures. Promising entrainers are identified using a new classification of ternary mixtures which is able to link candidate entrainers to flowsheet structures.

NEW CLASSIFICATION SYSTEM FOR TERNARY MIXTURES

It is assumed that, in ternary mixtures, only one binary azeotrope can be formed in each binary system and only one ternary azeotrope can be formed. Although counter examples have been reported in the literature (Gaw and Swinton, 1966), these cases are quite rare. These assumptions restrict the number of potential residue curve maps or distillation line maps for a ternary system to 125 (Doherty and Perkins, 1979).

In this work, ternary mixtures are characterised using a 'standard distillation line map', which is a characterisation system for ternary mixtures based on the existence and termini (beginning or end points) of distillation boundaries and the stability of singular points. This classification system enables one to link candidate entrainers directly to flowsheets facilitating the desired separation between azeotrope-forming components *a* and *b*.

Singular points, which are pure components and azeotropes, are labelled according to the convention shown in Fig. 1.

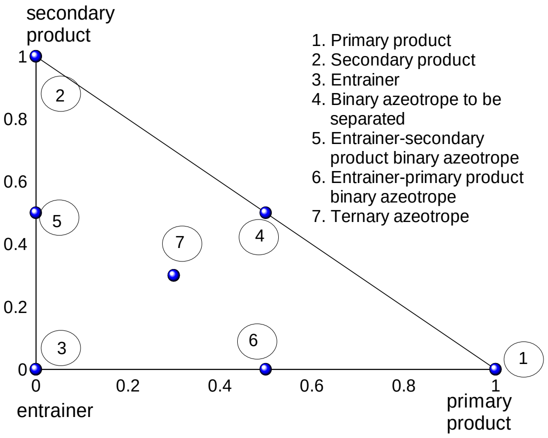


Fig. 1: Convention for labelling singular points in the standard distillation line map.

The primary product is the first azeotropic constituent to be produced as a pure component product in the flowsheet. Which azeotropic constituent is selected to be the primary product affects which flowsheets will be feasible and the performance of feasible flowsheets. Therefore, part of the synthesis problem is the selection of primary and secondary products.

This work assumes that the composition and temperature of all azeotropes at a given system pressure can be reliably calculated, and that the structure of the resulting distillation line map can be characterised in a consistent fashion (stability of singular points, origins and termini of boundaries, *etc*). Distillation boundaries can be conveniently approximated using distillation lines starting from the vicinity of saddle type azeotropes. The distillation boundary always connects saddle- and node-type singular points and separates two distillation regions (Doherty and Perkins, 1979).

The standard distillation line maps is defined in this work in terms of class (related to the termini of distillation boundaries in the composition space), and type (related to the stability of the products' singular points). The standard distillation line map is classified using the general term:

i j k (l) – z Type p (q)

where Table 1 defines the indices. The classification system is applied to a number of systems later in the paper.

All distillation line maps identified in previous work (Stichlmair and Herguijuela, 1992) can be classified using the new system. The new classification system allows identification of which categories of standard distillation line maps to lead to feasible separations. Which flowsheets can be used to facilitate the desired separation can be derived directly from the classification.

ENTRAINER SELECTION

The mixture to be separated into its pure component products is assumed to be a binary azeotropic mixture, but not necessarily the azeotrope itself. Two approaches to entrainer selection presented in the literature form the basis for the new selection criteria. The first approach requires both products to be located in the same distillation region (Doherty and Caldarola, 1985). In the second approach (Stichlmair and Herguijuela, 1992), entrainers are selected such that both products are termini

Table 1. Key to standard distillation line map classification – ijk (l) – z Type p (q)

Index	Singular point referred to	Character	Key
i	5	O	Binary azeotrope does not exist
j	6	A	Binary azeotrope is not terminus of distillation boundary
k	4		
		X	Binary azeotrope is terminus of distillation boundary
z	7	Y	Ternary azeotrope is a terminus of distillation boundary (blank otherwise)
l	1,2,3	1,2,3,12,13,23,123	List of all pure component singular points lying on distillation boundaries (blank otherwise)
p	1,2	O	Both products are nodes
		A	Primary product is saddle; secondary product is node
		B	Primary product is node; secondary product is saddle
		C	Both products are saddles
q	5,6	5,6,56	List all saddle-type binary azeotropes (blank otherwise)

of distillation lines (*i.e.* nodes in the distillation line map) and are separated by a distillation boundary. When entrainers introduce a ternary azeotrope, the azeotrope must be the same type (*i.e.* maximum or minimum boiling) as the azeotrope of interest. In this work, both approaches are adopted and extended to accommodate other entrainers.

An entrainer which does not introduce a distillation boundary between the two components to be separated is a promising entrainer (Doherty and Caldarola, 1985). In this case, both products and the binary azeotropic feed are located within the same distillation region. The feed mixture can be separated using recycle streams in the distillation flowsheet (*i.e.* without boundary shifting or crossing). All standard distillation line maps satisfying the criteria of Doherty and Caldarola (1985) are listed in Figs. 2 and 3.

Fig. 2 shows standard distillation line maps in which one of the products is a saddle and no boundary separates the desired products. The maps are ordered according to the number of binary azeotropes present in the mixture. For simplicity, all distillation boundaries are drawn using straight lines. All standard distillation line maps in which no boundary separates the desired products and where both products are saddles (type C) are presented in Figure 3.

Many entrainers introduce a distillation boundary between the two components to be separated. In this case, the two products are located in different distillation regions. Separation cannot be achieved using only distillation and recycle streams. In order to be able to recover the products, the distillation boundary must be crossed or relocated ('shifted'). The feed of a boundary-crossing column is located in one distillation region, and both products are located in another adjacent distillation region (Laroche *et al.*, 1992). Boundary crossing requires the boundary to be curved. As the curvature of the boundary decreases, the flow rates of recycled streams will increase, by the lever arm rule, leading to economically unattractive flowsheets.

Flowsheets employing boundary shifting (Knapp and Doherty, 1992) exploit the pressure-sensitivity of azeotrope composition and the location and curvature of the boundary. At least two columns in the flowsheet operate at different operating pressures; two different boundaries constrain the two columns. Both straight and curved boundaries can be shifted to good effect. The introduction of new azeotropes in the mixture with a change in operating pressure has previously not been accommodated. As will be shown, this phenomenon can even enhance the separation when the existing azeotropes are pressure-sensitive.

Fig. 4 presents the standard distillation line maps for entrainers that introduce a boundary between the components to be separated and which adhere to the entrainer selection criteria of Stichlmair and Herguijuela (1992). These criteria stipulate that the ternary azeotrope must be of the same type (*i.e.* maximum or minimum boiling) as the azeotrope of interest. In this work, this criterion is relaxed in the case that both desired products are nodes in the distillation line map. In the presence of a ternary azeotrope, the only requirement for an entrainer to be feasible is that both

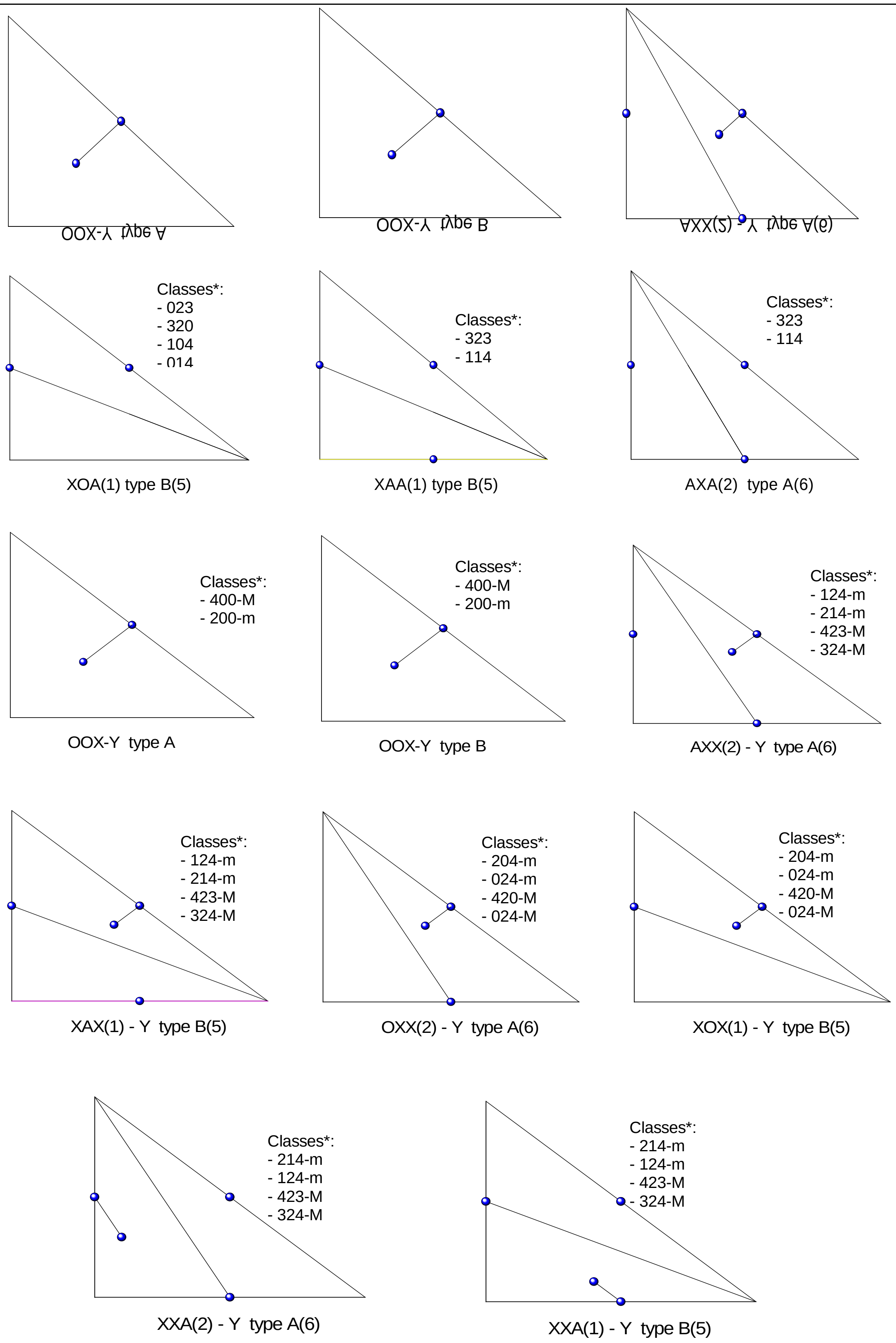


Fig. 2: Standard distillation line maps corresponding to feasible entrainers for which the two pure products are located in the same distillation region. One of the products is a saddle. (*: Existing classification of Stichlmair and Herguijuela, 1992)

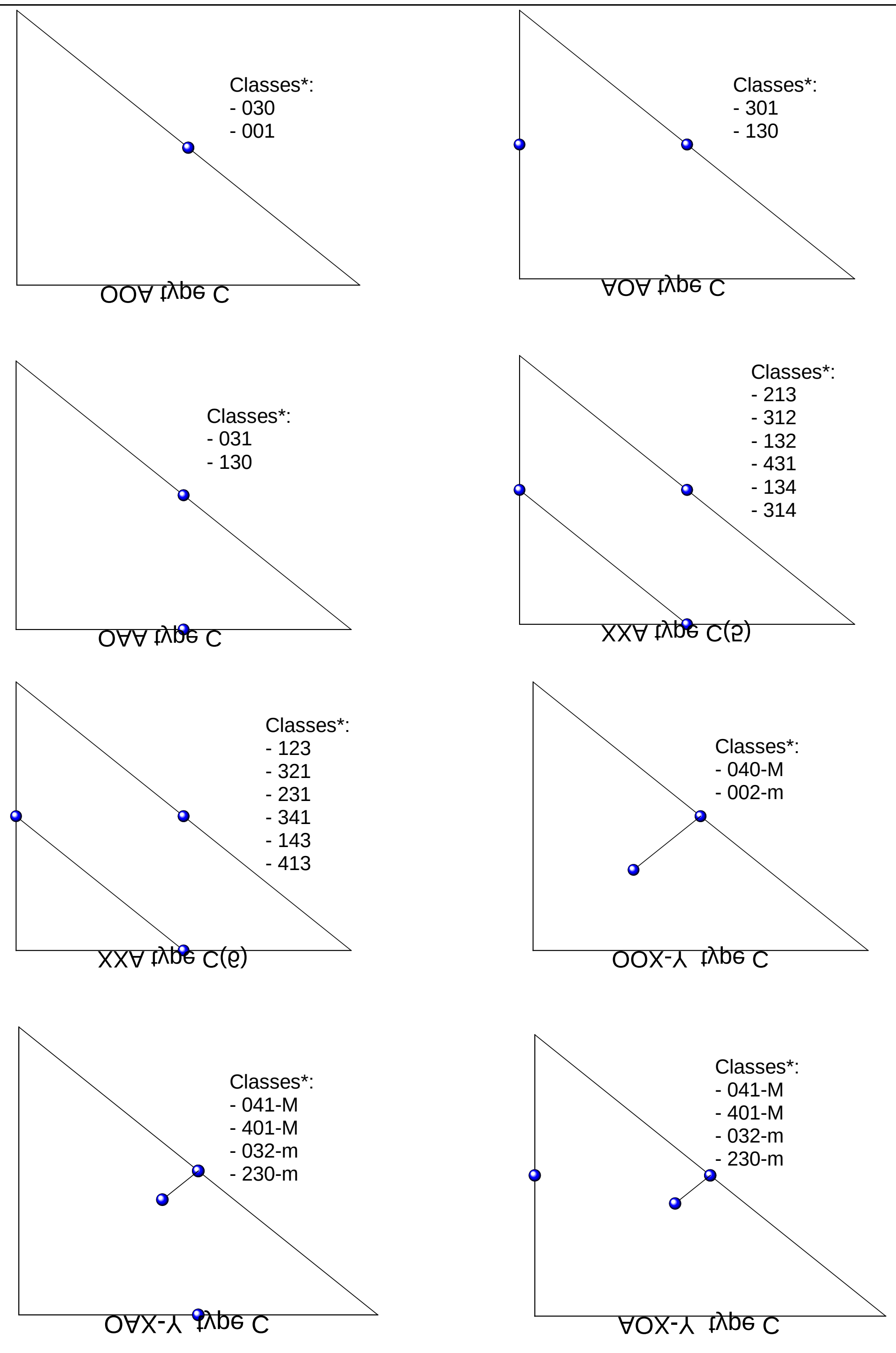
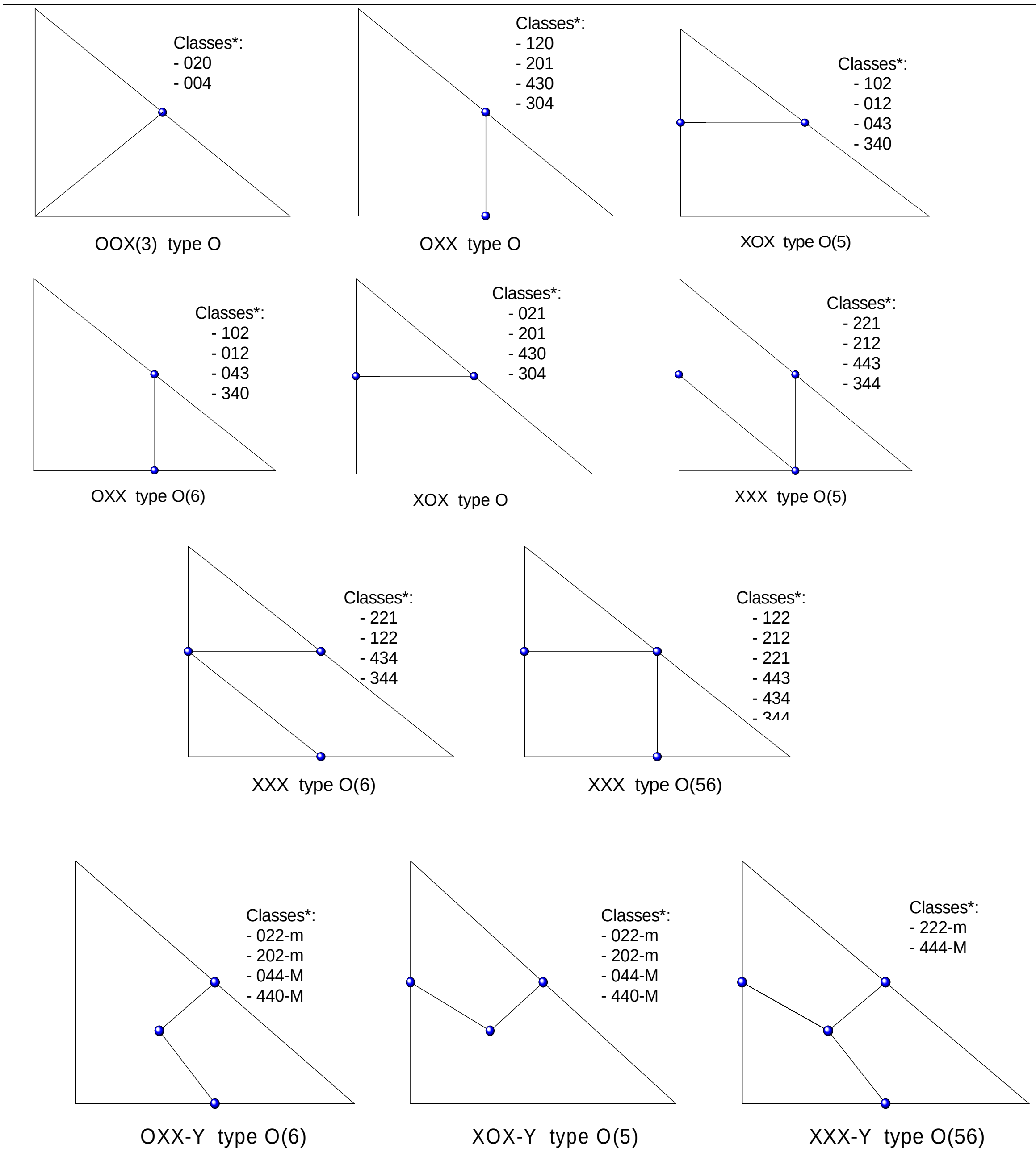


Fig. 3: Standard distillation line maps for entrainers for which two pure products are located within the same distillation region. Both products are saddles. (*: Existing classification of Stichlmair and Herguijuela, 1992)

products are nodes and are connected by distillation boundaries or composition-space boundaries via a saddle-type ternary or binary azeotrope. For these entrainers, two-column or three-column flowsheets can be generated so that all column specifications satisfy the common saddle criterion, which indicates column feasibility (Rooks *et al.*, 1998; Thong, 2000). An example of an entrainer of this



OOX(3) type O
OXX type O
XOX type O(5)
OXX type O(6)
XOX type O
XXX type O(5)
XXX type O(6)
XXX type O(56)
OXX-Y type O(6)
XOX-Y type O(5)
XXX-Y type O(56)

Fig. 4: Standard distillation line maps for promising entrainers where the two node-type desired products are located in different distillation regions. (*:Existing classification of Stichlmair and Herguijuela, 1992)

type and a feasible flowsheet not previously identified as suitable, is shown in Fig. 5. Fig. 6 represents standard distillation line maps for feasible entrainers where the ternary azeotrope is not of the same type as the binary azeotrope of interest.

The criteria of Stichlmair and Herguijuela (1992) always reject entrainers which result in one or both desired products being saddles in the distillation line map. Using a combination of a double-feed column and boundary shifting, or recycling and mixing, entrainers which introduce a distillation boundary between the two components to be separated, one of which is a saddle, can still facilitate the desired separation. Such

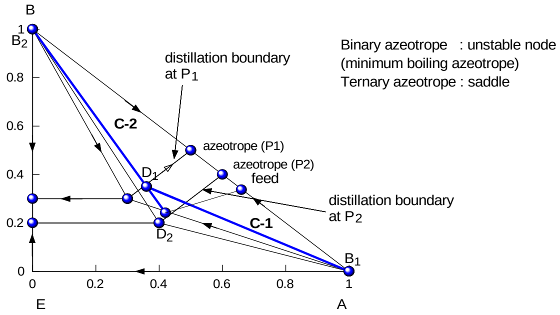


Fig. 5: Example of a distillation line map XOX(12) type O for an entrainer that introduces a ternary azeotrope of a different type to the binary azeotrope of interest. A two-column flowsheet with boundary shifting can facilitate the separation.

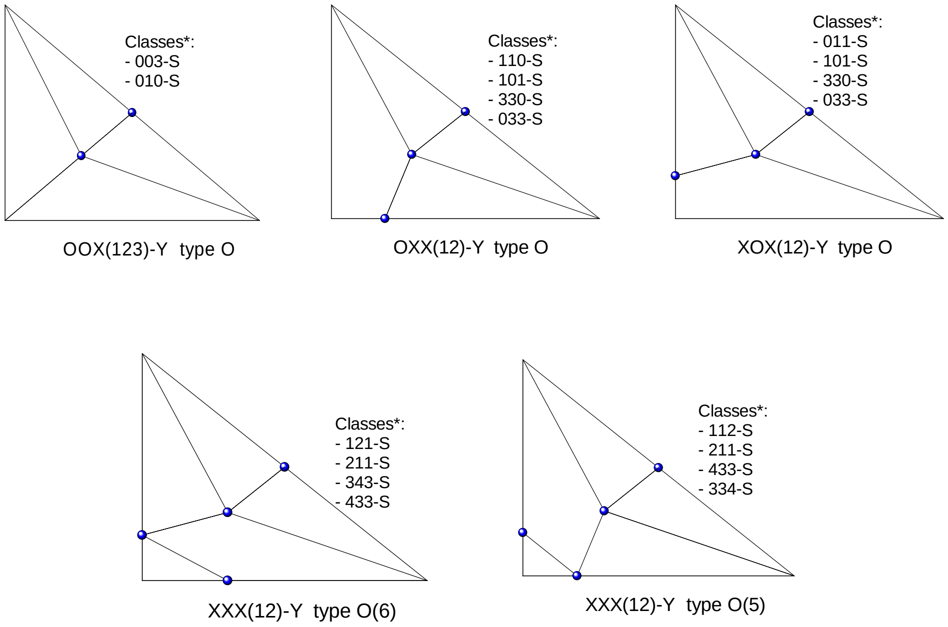


Fig. 6: Standard distillation line maps for promising entrainers in which the two node-type desired products are located in different distillation regions. The entrainer introduces a ternary azeotrope of a different type (*i.e.* maximum, intermediate or minimum boiling) to the azeotrope of interest. (*: Existing classification of Stichlmair and Herguijuela, 1992)

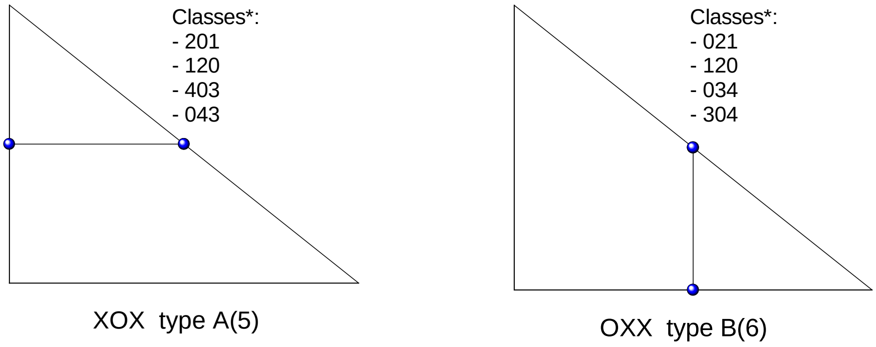


Fig. 7: Standard distillation line maps for promising entrainers for which the two desired products are located in different distillation regions and one of which is a saddle. (*: Existing classification of Stichlmair and Herguijuela, 1992)

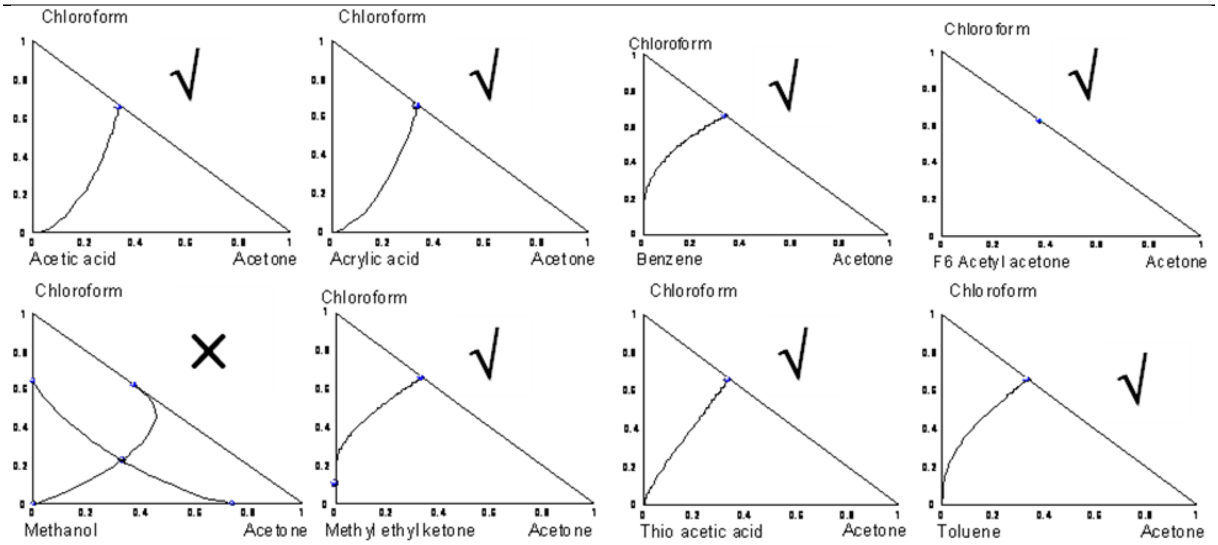


Fig. 8: Distillation line maps of entrainers considered for the separation of an acetone-chloroform mixture. Acetone is the primary product. (√ : promising, × : not promising)

entrainers violate the criteria of both Doherty and Caldarola (1985) and Stichlmair and Herguijuela (1992). Standard distillation line maps for this type of candidate entrainer are presented in Fig. 7. Identification of feasible flowsheets for given standard distillation line maps will be presented in a further work.

CASE STUDY

This example addresses the separation of a mixture of acetone and chloroform, in which components form a maximum-boiling azeotrope. Promising entrainers and the associated flowsheets are selected according to the new methodology.

The binary feed mixture, which contains 60 mole % acetone and 40 mole % chloroform, is to be purified using homogeneous azeotropic distillation. Acetone and chloroform form a maximum-boiling azeotrope. 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. Since the binary feed is richer in acetone than chloroform, acetone is selected as the primary product. The composition, temperature and stability of singular points and existence and termini of distillation boundaries are calculated at atmospheric pressure using the methods of Fidkowski *et al.* (1993). The distillation line maps is classified based on the stability of singular points and the existence and termini of distillation boundaries. Suitable flowsheets for each entrainer are identified directly, given the standard distillation line map classification (from Figures 2 to 7).

Figure 8 and Tables 2 present the eight entrainers to be considered. The physical properties of the pure compounds are obtained from Reid *et al.* (1987) and vapour-liquid equilibrium behaviour is calculated using the Wilson model and the default model parameters from Hysys. The set of flowsheets that are suitable for each acceptable entrainer is obtained directly

Table 2. Some physical properties, distillation line map characteristics and corresponding feasible flowsheets of candidate entrainers for the separation of an acetone-chloroform mixture.
(BS: boundary shifting, BC: boundary crossing, RM: recycling and mixing, DF: double feed column)

Entrainer	Formula	BP, °C	Boundary	Classification	Primary product	Secondary product	Accept?	Flowsheet Structures
Acetic acid	C2H4O2	117.95	Exists	OOX(3) type O	Node	Node	Yes	BS, RM
Acrylic acid	C3H4O2	141	Exists	OOX(3) type O	Node	Node	Yes	BS, RM
Benzene	C6H6	80.09	Exists	OOX(3) type O	Node	Node	Yes	BS, BC
F6 acetyl acetone	C3F6O	54.15	No	OOA type C	Saddle	Saddle	Yes	DF
Methanol	CH4O	64.65	Exists	XX(3)-Y type C	Saddle	Saddle	No	None
Methyl ethyl ketone	C4H8O	79.55	Exists	XOX type O	Node	Node	Yes	BS, BC
Thio acetic acid	C2H4OS	87.05	Exists	OOX(3) type O	Node	Node	Yes	BS, RM
Toluene	C7H8	110.65	Exists	OOX(3) type O	Node	Node	Yes	BS,BC

once the ternary mixtures have been classified (see Table 2). Of the candidate entrainers, only methanol is not suitable: in this case the two products would be both saddles separated by a distillation boundary. For this class of distillation line maps, there is no feasible flowsheet that can be generated. Detailed discussion on feasible flowsheet identification will be presented in a further work.

CONCLUSIONS

A new classification system for homogeneous ternary azeotropic mixtures has been developed for the purposes of screening candidate entrainers for separating a binary azeotropic mixture into its pure component products. The 'standard distillation line map' is classified according to the presence and termini of distillation boundaries and the type (stability) of binary azeotropes and products. Entrainers that induce liquid-phase splitting are not addressed in this work. The key advantage of the new characterisation system is that suitable flowsheets can be identified immediately. A new set of entrainer selection criteria is defined; it expands significantly the set of previously published criteria by accepting many candidate entrainers that violate existing entrainer screening criteria.

This new classification system allows promising entrainers to be identified easily and potentially feasible flowsheets to be derived directly. The methodology is therefore valuable and powerful for the synthesis of ternary homogeneous azeotropic distillation processes.

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