

A Study on Method for Choosing Entrainers for Distillation Columns

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Abstract

An overview of the entrainer selection process, which is crucial for separation procedures like azeotropic/extractive distillation, is provided in this study. Entrainer screening is crucial to the synthesis and design of these procedures. To break the binary mixture's azeotrope and introduce a pure component, entrainer is added. This study provides an overview of various entrainer kinds, RCM approach, vapour liquid equilibrium, selection procedure, and entrainer addition distillation techniques. Based on the entrainer's boiling point, there are three different kinds of entrainers: heavy, moderate, and light. The kind of entrainer utilized for operation and distillation operations determines the selection procedure, which varies for various processes. In both homogeneous and heterogeneous distillation as well as reactive distillation, distinct selection criteria are used to screen entrainers for all kinds (i.e., maximum, minimum, and near boiling) of azeotropic binary mixtures. The residue curve map (RCM) approach is used to assess the viability of entrainers. Understanding the vapour liquid diagram is essential for determining feasibility of RCM.

Keywords: Vapour Liquid Equilibrium, Residue Curve Map (RCM), Entrainer, Distillation

1 INTRODUCTION

In the distillation separation process, the entrainer is crucial. It is essential for determining the components' differences in boiling points, however an entrainer selection criteria depends on the system's behavior. Many academics are engaged in the distillation sector because of the significance of separation from today's perspective.

An entrainer is a separating agent that is used in extractive or azeotropic distillation to improve the separation of nearby boilers or azeotrope. The azeotropic combination, which is hard to separate, is mixed with entrainer. The entrainers are mixture-specific; for example, benzene is employed to separate mixtures of ethanol and water but not ethanol and ethylmethyl ketone.

When an entrainer is introduced to an azeotropic near boiling mixture that contains two or more components, the distillation process improves component separation. various distillation types need various entrainer applications. Entrainer is continually introduced to the upper part of the column during extractive distillation to increase the mixture's relative volatility. Azeotropic batch distillation is the procedure of adding entrainer to the distillation column batch by batch when it creates an azeotrope with one or more of the mixture's components. Currently, entrainers are used in a variety

A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

of methods to break azeotrope. These methods fall into the following categories: reactive distillation, salty distillation, heterogeneous azeotropic distillation, and homogeneous azeotropic distillation. Three sorts of entrainers are detected based on the entrainer's boiling point; they are explained below. Heavy entrainer: an entrainer with a greater boiling point than either of the azeotropic mixture's components. Intermediate entrainer: the entrainer's boiling point is between the boiling points of the two mixture components. Light entrainer: this kind of entrainer has a low boiling point for both combination components. Compared to batch strippers, the use of light entrainers is more advantageous.

1.2 LITERATURE SURVEY

Ten years ago, Pham and Doherty (1990) examined entrainer selection criteria, which were then revised in Fair and Stichlmair's and Doherty and Malone's books. Matsuyama and Nishimura first postulated in 1977 that the ternary system has a maximum of one ternary azeotrope and that each binary face has a maximum of one azeotrope.

They demonstrate that there are only 113 distinct and independent residue curve maps that may be made.

The viability and separation sequencing of multicomponent batch distillation were described by Bernot et al. in 1991. Dussel examined the homogeneous batch distillation method of azeotropic separation using an entrainer. Rodriguez et al. developed a comprehensive set of guidelines for entrainer selection for the separation of azeotropic mixtures by both homogeneous and heterogeneous batch distillation as their guidelines do not account for all potential scenarios. Three entrainer types—light, middle, and heavy—and their viability for the separation of homogeneous azeotropic distillation based on the equivolatility curve, isovolatility curve, and local volatility order were compared by Laroche et al. (1991). Laroche and his colleagues found that every type of entrainer had unique strengths and weaknesses after examining a variety of entrainers. They thus came to the conclusion that candidate entrainers should be compared within the same class, and the best candidate should be chosen by building, estimating, and refining workable separation sequences. Numerous studies have examined the viability of entrainers for certain separation processes for particular component systems. Here, we'll go over the entrainer requirements for various distillation process types and how to assess their viability.

1.3 ENTRAINER ADDITION DISTILLATION METHODS

Distillation is separated into three primary classes, which are listed below, according to the characteristics and function of the entrainer.

a) Azeotropic distillation that is homogenous:

Entrainers that are fully miscible with the components in the original mixture are utilized in

A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

distillation. In a single feed column, it creates a homogeneous azeotrope containing components from the original mixture.

b) Distillation by heterogeneous azeotropic

Using a decanter and a distillation column, the entrainer creates a heterogeneous azeotrope containing one or more of the original mixture's components.

c) Distillation by extraction

Entrainers are inserted above the initial mixture feed point and mostly eliminated as the bottom product in two feed columns used for this operation.

Before the mixture separates, an entrainer is utilized to increase the relative volatility of the low volatility component. Compared to the original combination component, the entrainer has a higher boiling point (heavy entrainer). It doesn't create an azeotrope of any kind. In addition to the distillation methods mentioned above, the following are several more that are currently in use:

d) Distillation by reaction

One or more of the original mixture's components react with the entrainer. The entrainer is recovered from the reverse reaction, while the nonreacting component is produced as a distillate. The selection parameters for entrainer-based reactive distillation for iso-propanol esterification are examined by Jong et al.

e) Distillation of salt

It is the only kind of extractive distillation where adding salt as an entrainer in the top reflux changes relative volatility.

1.4 ENTRAINER SELECTION CRITERIA

A number of writers have already examined the various methods for choosing entrainers for the different kinds of distillation that were previously covered. Two stages are needed in the distillation process in order to break down an azeotrope into its pure component. Choosing an entrainer is the first stage, and creating a separation sequence for the chosen entrainer is the second.

It is necessary to choose an appropriate entrainer that will enable the azeotropic mixture to be separated. The cost of separation may be decreased by using a little amount of entrainer to increase the relative volatility of a particular component.

According to the kind of azeotropic mixture A-B (i.e., maximum, minimum, and near boiling) used in the procedure, Bernot et al. provided the criteria.

The four main requirements for screening an entrainer for the separation of minimum, maximum,

A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

and close-boiling azeotropic binary mixtures for batch distillation are defined by the application of feasibility criteria.

- a) No extra azeotrope is offered.
- b) Between Entrainer (E) and either the A or B component, there is a minimum-temperature binary azeotrope.
- c) There is a maximum-temperature binary azeotrope between the A or B component and the entrainer (E).
- d) There might be a ternary azeotrope.
- e) The four criteria above apply to homogeneous batch distillation; however, Rodriguez et al. (2001) propose two further principles for heterogeneous batch distillation, which are mentioned below.
- f) E is incompatible with either A or B, one of the original mixture's components.
- g) E and A or B create a minimum temperature heteroazeotrope.

The system that produced the aforementioned principles is briefly described by Rodriguez et al. (2001).

According to Jong et al., the entrainer utilized in the esterification reaction in reactive distillation should have the following requirements:

- (a) Water should become more volatile than alcohol in comparison; water will be eliminated from the top and the reaction equilibrium will migrate to the product side.
- (b) If it is insoluble in water, the distillate may be readily split into two phases using a decanter (i.e. as an aqueous phase and an entrainer phase).
- (c) It should be so poorly soluble in water that no further purification is required.
- (d) It must have a low water solubility content so that the entrainer may be recycled.

Although the aforementioned requirements are only applicable to certain esterification processes, we may still apply them when water is employed as a reactant. Using the aforementioned parameters, the effects of different entrainers on different polarities may be examined.

A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

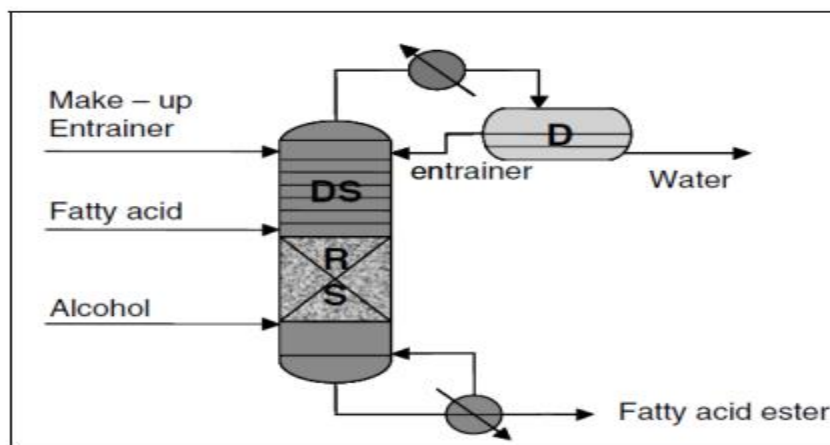


Figure 1: Entrainer based reactive distillation (Jong et.al. 2006)

1.5 VAPOUR LIQUID EQUILIBRIUM CONCEPT

The addition of entrainer to a binary mixture produces a ternary mixture; hence, vapour-liquid equilibrium must be taken into account in order to estimate the makeup of overhead and final product. VLE diagrams are used to tackle separation-related issues. VLE is used to determine and assess the mixture's characteristics, thermodynamic state, and liquid and vapor content. Diagrams of the vapour-liquid equilibrium are created at either constant temperature or constant pressure.

At high temperatures, the low boiling component produces superheated vapor, while at low temperatures, it produces sub-cooled liquid. Between it, there exist both liquid and vapor that are in balance with one another. Figure 2 below shows the typical vapour liquid equilibrium diagram of a binary combination at constant pressure. An X-Y diagram is another way to build vapor-liquid equilibrium. The perfect binary mixture diagram is not the same as the X-Y diagram of a binary mixture that produces an azeotrope.

Two distinct partly miscible or immiscible phases may form from a liquid. In order to reduce the system's Gibbs free energy and achieve liquid-liquid equilibrium, two distinct phases are created. When the system's pressure drops while maintaining both liquid-liquid (LL) and vapour-liquid-liquid (VLL) balance, vapour liquid-liquid equilibrium is reached. The characteristics of the LLE diagram and the VLLE diagram are identical.

A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

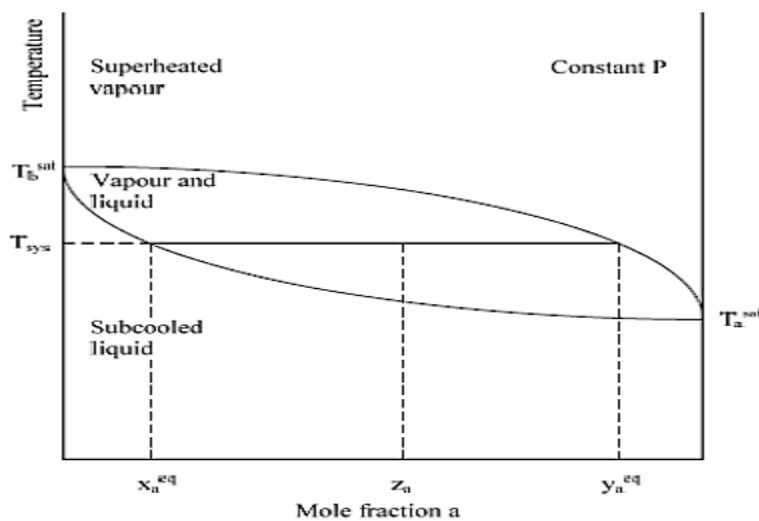


Figure 2: Vapour liquid equilibrium T-x-y phase diagram (koretsky 2004)

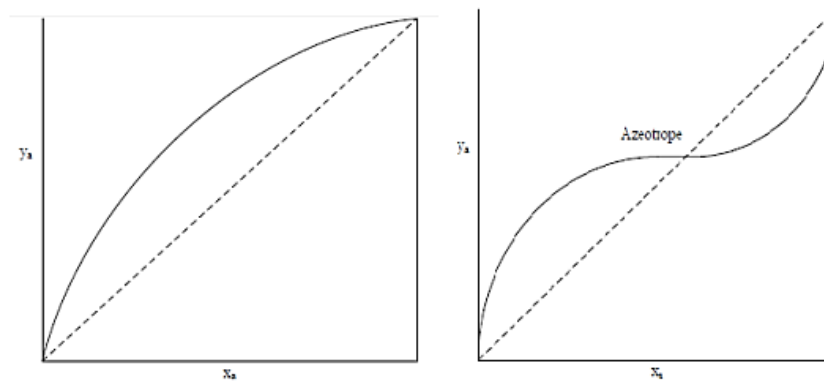


Figure 1.3: (a) vapour-liquid x-y diagram for ideal binary mixture (b) vapour-liquid x-y diagram for binary mixture that forms an azeotrope. (Seader and Henley 2006)

1.6 RESIDUE CURVE MAPS

The examination of residue curve maps (RCMs) is helpful in choosing an entrainer for extractive and azeotropic distillation. RCM, which is a collection of residue curves and component composition trajectories with respect to time, is a geometric depiction of the vapour liquid equilibrium (VLE)

A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

phase behavior of a multi-component mixture. The graphic shows the boiling points of binary, ternary, multicomponent mixtures, and pure components. As the liquid becomes richer in heavier components, the temperature continuously rises as the composition trajectories shift from the lightest component to the heavy component. The arrow on the residue curve from the lighter to the heavier component represents the temperature. Depending on the reaction kinetics, the type of RCM varies with the magnitude of the reaction. These curves may be found by mathematical modeling of the experiment or through experimentation. The residue curve map's structure and regulations have previously been explained.

Two binary azeotropes and no ternary azeotrope are formed by a ternary mixing of components A, B, and C. Vertices display the temperature of the pure component, whereas the residue curve displays the temperature of the binary or ternary azeotrope.

Starting at the lightest boiler (azeotrope AB), the residue curve moves toward the heavier components B or C, forming an imaginary border between the two binary azeotropes. A distillation boundary is the name given to the dividing curve.

Azeotropes are used to divide composition space into distillation regions by distillation boundaries such that the residue curves in those areas point in different directions toward distinct components. There may be more than one distillation boundary for a combination with many components.

These limits of distillation start at the same location but finish at separate locations (i.e., distinct areas), and vice versa.

The step-by-step process of the Evolution of Feasibility of Entrainer utilizing RCM approach is briefly described. First, build the RCM for the specified multicomponent mixture, which includes the proposed entrainer and an azeotropic component. Next, determine if the system is in a liquid-liquid or vapour-liquid phase by looking at its phase behavior. The two phase compositions are shown by the tie-lines. Next, overlay the composition scale—rather than the temperature scale—by drawing an envelope over the RCM composition area.

The following parameters are used to assess the viability of entrainer utilizing RCM methodologies.

1. Put the candidate entrainer and component list in order.
2. Get each applicant entrainer's RCM ready: Thermodynamic physical properties are needed to build RCM for the system of A, B, and the prospective entrainer.

If it is unavailable, UNIFAC will be used to simulate it, as long as the predictions match the azeotrope data that is currently accessible.

- b. Use the available azeotropic temperature, composition (approximate), and solubility (approximate) data to develop RCM if no physical property model is provided.

A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

c. The necessary information may be computed experimentally or by guessing if neither physical property nor azeotropic data are available.

3. Using the RCM's structure, ascertain if the potential entrainer is feasible: - a) The components A and B are not divided into distinct distillation zones by the entrainer.

b) Liquid-liquid phase separation is induced by the entrainer; a liquid-liquid equilibrium tie line crosses the distillation boundary.

4. Assess each and every separation sequence: - the quantity of distillation columns with decanters and the connections between them from the system's RCM for every conceivable entrainer.

5. Based on the specified feasibility requirements, identify the most promising entrainer.

6. Create, encourage, and enhance separation sequences.

We have included an example to help you comprehend the RCM plot for the separation of a dimethoxyethane/ethanol combination with water acting as an entrainer.

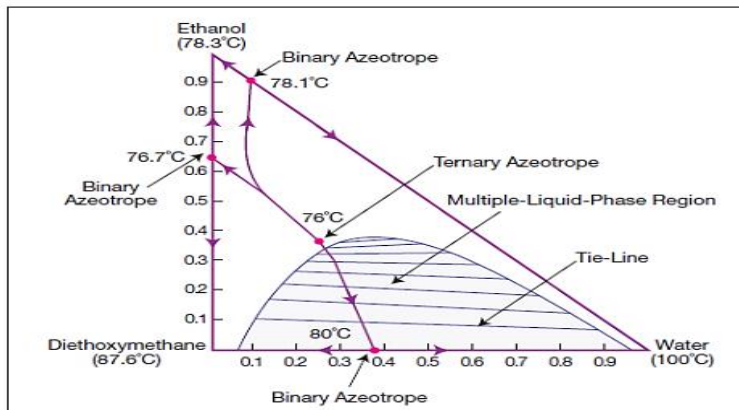


Figure 4: RCM plot for water-ethanol-DEM system.

In this case, they assumed that the ratios of DEM and ethanol in the process were 50:50 mol. Three binary azeotropes and a ternary azeotrope with three distillation borders and many liquid phase areas make up the system. Water is used in this technique to break down a minimal boiling homogenous azeotrope. The separation is not very practicable to the degree of the greatest separation because ternary azeotrope does not reside in the many liquid phase zone. In this case, RCM provides a substantial method for separation using water and a greater number of distillation steps.

A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

CONCLUSION

Understanding the VLE and RCM technique for entrainer screening is crucial to comprehending the behavior of the separation process of any reaction system.

The various processes for choosing an entrainer for various distillation techniques are the main topic of this research. Understanding the borders, tie line, and distillation zones is essential for a successful separation. Predicting the kind of curvature of the residue maps requires VLLE in addition to VLE. The first stage in a well-designed distillation process is choosing an entrainer or solvent, which is what this review article focuses on.

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A Study on Method for Choosing Entrainers for Distillation Columns

Dr. Seema Arora

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