

Entrainer Selection Approach for Distillation Column

Onkar A. Deorukhkar^{1*}, Tamini B. Rahangdale¹,
Yogesh S. Mahajan¹

¹*Dr. Babasaheb Ambedkar Technological University,
Lonere-Raigad-402103, Maharashtra, India.*

**corresponding author: onkar_506@rediffmail.com*

Abstract

This paper represents an overview regarding selection procedure of entrainer, which is very important in separation processes like azeotropic/extractive distillation. Screening of entrainer plays an important role in synthesis and design of these processes. Addition of entrainer is used to break azeotrope of binary mixture which introducing it into a pure component. This paper gives an idea about different types of entrainer, entrainer addition distillation methods, selection process, and vapour liquid equilibrium and RCM technique. There are three types of entrainer heavy, intermediate and light entrainer which based on the boiling point of the entrainer. A selection process of entrainer is different for different processes and which is dominantly based on the type of entrainer used for operation and distillation process. Different selection criteria are given to screen entrainer for all types (i.e. maximum, minimum and close boiling) of azeotropic binary mixture in both homogenous and heterogeneous distillation and also in reactive distillation. The feasibility of entrainer is determined by residue curve map (RCM) technique. To determine feasibility using RCM, vapour liquid diagram is necessary to understand.

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

1.1 INTRODUCTION

Entrainer is very important in distillation separation process. It plays a vital role in making a boiling point difference in the components whereas a criterion for entrainer selection is dependent on the behaviour of the system. For today's importance in separation point of view many researchers are working in distillation field.

Entrainer refers to the separating agent used to enhance the separation of close boilers or azeotrope by azeotropic or extractive distillation. Entrainer is added to the

azeotropic mixture which is difficult to separate. The entrainer are specific to the mixture, benzene is used as entrainer for separating ethanol and water mixture but not for ethanol and ethyl methyl ketone mixture ^[1].

Distillation of azeotropic close boiling mixture consist of two or more component, in which entrainer is added, enhances the separation of component. Application of entrainer is different for different type of distillation. In extractive distillation, entrainer is added continuously in top section of the column for enhancing relative volatility of mixture. When entrainer forms azeotrope with one or more component of the mixture, at this condition entrainer is added batch wise to the distillation column, this process is called azeotropic batch distillation. Various types of techniques are currently used to break azeotrope using entrainer. These techniques are classified as homogenous azeotropic distillation, heterogeneous azeotropic distillation, reactive distillation and salted distillation which are discussed below ^[2, 3].

Depending on the boiling point of entrainer, three types of entrainer are observed which are described below.

- ✓ Heavy entrainer: entrainer which have higher boiling point as compared to both the component of azeotropic mixture.
- ✓ Intermediate entrainer: the boiling point of entrainer is in between boiling point of both the component of mixture.
- ✓ Light entrainer: this type of entrainer have low boiling point with respect to the both the component of mixture. Application of light entrainer is more favourable in batch stripper than batch stripper ^[3].

1.2 LITERATURE SURVEY

A decade ago, Pham and Doherty (1990) ^[4] studied rules for entrainer selection and updated in the books of Fair and Stichlmair ^[5] and Doherty and Malone ^[6]. In 1977, Matsuyama and Nishimura ^[7] first assumed that each binary face has no more than one azeotrope and that the ternary system possesses at most one ternary azeotrope. They show that only 113 different and independent residue curve maps are possible. In 1991, Bernot et. al. ^[8] describes the feasibility and separation sequencing in multi-component batch distillation. Dussel et. al. ^[9] Investigate the azeotropic separation technique using an entrainer by homogenous batch distillation. Because their rules do not cover all possible cases, Rodriguez et. al. ^[2, 10] established a complete set of rules for entrainer selection for the separation of azeotropic mixture by both homogenous and heterogeneous batch distillation. Laroche et al. (1991) ^[3] discussed comparatively three types of entrainers (light, intermediate, and heavy) and their feasibility for the separation of homogenous azeotropic distillation on the basis of equivolatility curve, isovolatility curve, and local volatility order. By analyzing different entrainers, Laroche and his coworkers observed that each class of entrainer has specific strength and weakness. So they concluded that comparison of candidate entrainer should be takes place in same class of entrainer and from that the best candidate is selected by designing, costing and optimizing feasible separation sequences. There are number of research paper in which entrainer feasibility was discussed for specific type of

separation process for specific system of the component. Here we will review entrainer criteria for different type distillation process and determination methods of their feasibility.

1.3 ENTRAINER ADDITION DISTILLATION METHODS

Based on the properties and role of the entrainer, distillation is divided in three main groups which are given below.

a) Homogenous azeotropic distillation:

Entrainer used in distillation which is completely miscible with component in original mixture. It forms homogenous azeotrope with component in the original mixture, this carried out in single feed column.

b) Heterogeneous azeotropic distillation

Entrainer forms heterogeneous azeotrope with one or more components in the original mixture which is carried out distillation column with a decanter.

c) Extractive distillation

This process is carried out in two feed column in which entrainer is introduced above the original mixture feed point and largely removed as bottom product. Entrainer is used to enhance the relative volatility of low volatility component to precede the separation of mixture. Entrainer has high boiling point (heavy entrainer) as compared to the original mixture component. It does not form any type of azeotrope.

Other than above distillation techniques some more are used now a day which are listed below:

d) Reactive distillation

Entrainer reacts with one or more component from original mixture. The non-reacting component is produce as a distillate and the entrainer is recovered from reverse reaction. Jong et. al. investigate the selection criteria for entrainer based reactive distillation for esterification with iso-propanol.

e) Salt distillation

It is the one type of extractive distillation in which relative volatility is altered by addition of salt as an entrainer in the top reflux ^[2, 3].

1.4 ENTRAINER SELECTION CRITERIA

Previously, several authors studied the different technique for entrainer selection for various types of distillation which are discussed above. To break azeotrope to its pure component; the design of distillation requires two steps. First step is selection of entrainer and second is synthesizing a separation sequence for selected entrainer. Suitable entrainer is to be selected which leads to feasible separation of azeotropic mixture. Small quantity of entrainer is able to enhance the relative volatility of given component reduces the cost of separation.

Bernot et. al. ^[8] proposed the criteria depending upon the type of azeotropic mixture A-B (i.e. maximum, minimum and close boiling) involved in the process.

Application of feasibility criteria defines the four general conditions to screen entrainer for separation of minimum, maximum and close-boiling azeotropic binary mixture for batch distillation ^[2].

- a) No additional azeotrope is introduced.
- b) A minimum-temperature binary azeotrope exists between Entrainer (E) and either A or B component.
- c) A maximum-temperature binary azeotrope exists between Entrainer (E) and either A or B component.
- d) There might be a ternary azeotrope.
- e) Above four rules are applied for homogenous batch distillation but for heterogeneous batch distillation additional two rules are suggested by Rodriguez et. al.(2001) ^[10] which are listed below.
- f) E is not miscible with one of component of the original mixture (either A or B).
- g) E forms minimum temperature heteroazeotrope with A or B.

The above rules are established by some scheme which is briefly explained by Rodriguez et. al.(2001) ^[10].

For esterification reaction in reactive distillation, Jong et. al. ^[11] concluded that the entrainer used in the process should fulfil the following criteria,

- (a) It should increase the relative volatility of water compare to alcohol; water removed from the top and reaction equilibrium shifts to product side.
- (b) It should be insoluble with water, then the distillate can easily separated using decanter in two phases (i.e. as entrainer phase and aqueous phase)
- (c) It should have low solubility of entrainer in water, such that no further purification is necessary.
- (d) It should have low solubility of water in entrainer, such that entrainer can be used as a recycle.

Above criteria is applied only for specific esterification process but we can also follow this criteria in which water is used as reactant. Effects of various entrainers on different polarity can be investigated using above criteria.

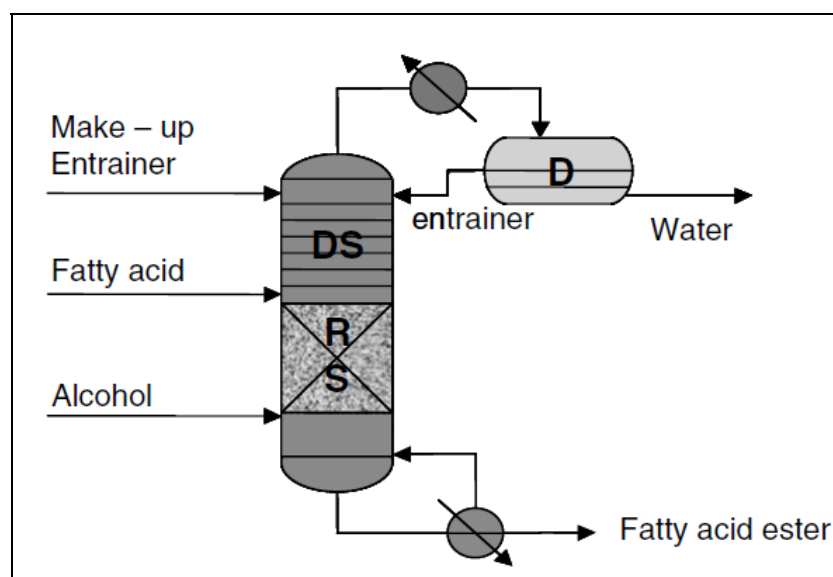


Figure 1.1: Entrainer based reactive distillation (Jong et.al. 2006)

1.5 CONCEPT OF VAPOUR LIQUID EQUILIBRIUM

When entrainer is added to binary mixture, ternary mixture results, for this vapour liquid equilibrium is necessary to consider for predicting composition of overhead and bottom product. VLE diagram is used to solve problems related to separation. VLE is used identify and evaluate thermodynamic state, properties of mixture and composition of the liquid and vapour in that mixture. The vapour liquid equilibrium diagrams are constructed at either constant pressure or at constant temperature ^[12]. The low boiling component at high temperature forms superheated vapour and at low temperature it forms sub-cooled liquid. In between that vapour and liquid both are present which are in equilibrium with each other. The general vapour liquid equilibrium diagram of binary mixture at constant pressure is illustrated in below fig 1.2 ^[12]. Vapour-liquid equilibrium is also constructed as X-Y diagram. The X-Y diagram of binary mixture which forms azeotrope is differs from the ideal binary mixture diagram ^[13].

A liquid can split into two different partially miscible or immiscible phases. Two separate phases are formed to lower the Gibbs free energy of the system and this leads to liquid-liquid equilibrium. Vapour liquid-liquid equilibrium occurs when pressure of the system decreased with both liquid-liquid (LL) equilibrium and vapour-liquid-liquid (VLL) equilibrium. The VLLE diagram has same properties as that of LLE diagram.

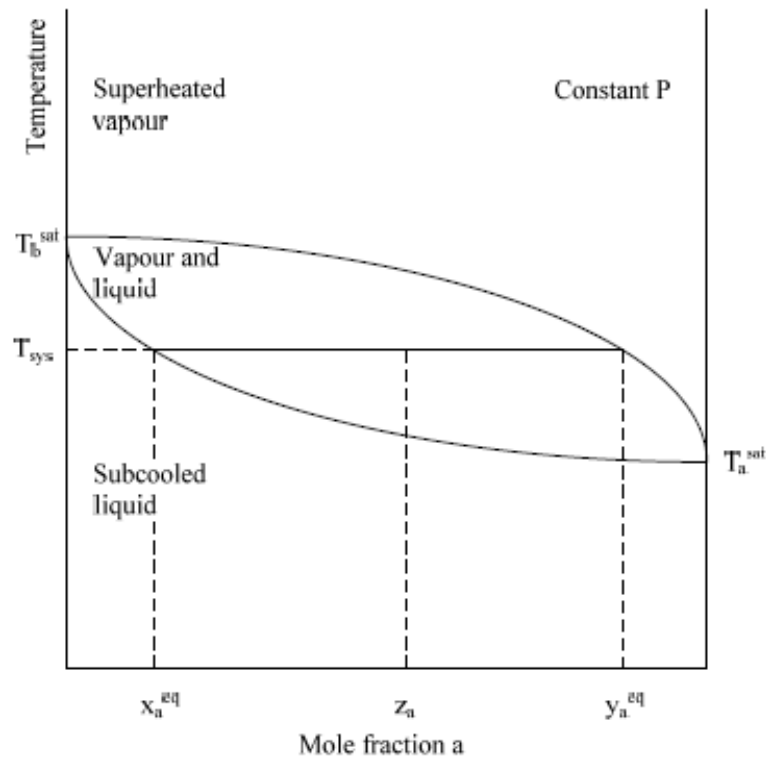


Figure 1.2: Vapour liquid equilibrium T-x-y phase diagram (koretsky 2004)

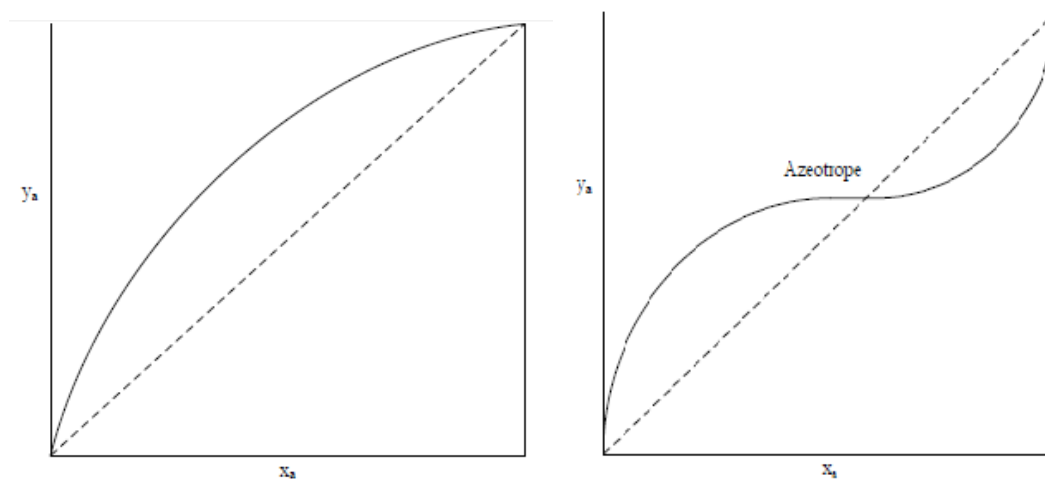


Figure 1.3: (a) vapour-liquid x-y diagram for ideal binary mixture (b) vapour-liquid x-y diagram for binary mixture that forms an azeotrope. (Seader and Henley 2006)

1.6 RESIDUE CURVE MAPS

Residue curve map (RCM) analysis is useful for the selection of entrainer for azeotropic and extractive distillation. RCM is geometric representation of vapour liquid equilibrium (VLE) phase behaviour of multi-component mixture which consists

of collection of residue curve and trajectories compositions of components with respect to time. The boiling points of pure components, binary, ternary or multi-component mixture indicated on the diagram. The composition trajectories move from lightest component to the heavy component i.e. the temperature continually increases to as the liquid gets richer in heavier component. Temperature indicated by arrow on residue curve from lighter component to heavier component. The nature of RCM changes with extent of reaction i.e. depending upon the reaction kinetics. These curves can be determined either experimentally or by mathematical simulation of the experiment. The rules and construction of residue curve map is already described^[14].

Consider a ternary mixture of component A, B, C forms two binary azeotrope and no ternary azeotrope. The pure component and their temperature are marked on vertices; azeotrope (binary or ternary) and their temperature are also marked on residue curve. The residue curve originates at lightest boiler (azeotrope AB) which goes in the direction of heavier component B or C creating imaginary boundary connecting the two binary azeotropes. The dividing curve is called a distillation boundary^[14].

The presence of azeotrope dividing composition space into distillation regions by distillation boundary such that residue curve in different regions go toward different components. For multi-component mixture, multiple distillation boundaries may exist. These distillation boundaries begin at same point but end at different points (i.e. different regions) and vice versa.

Evolution of Feasibility of entrainer using RCM technique consists of step wise procedure which is explained briefly. First construct the RCM for given multi-component mixture consisting of azeotropic component and the given candidate entrainer. Next, check the phase behaviour of the system, whether it is liquid-liquid or vapour-liquid phase. The tie-lines indicate the two phase compositions. Then draw an envelope over the RCM composition space, superimposing the composition scale rather than temperature scale.

There are some criteria to evaluate the feasibility of entrainer using RCM techniques which are given below^[1].

1. Arrange the list of components and candidate entrainer
2. Prepare an RCM for each candidate entrainer: To construct RCM for the system of A, B, and the candidate entrainer, requires thermodynamic physical property.
 - a. If it is not available then modelled using UNIFAC, provided the predictions are in agreement with available azeotrope data.
 - b. If no physical property model is available, then construct RCM using available azeotropic temperature, composition (approximate), and solubility (approximate) data.
 - c. If neither physical property nor azeotropic data available then required information can be calculated using guessing or calculated experimentally.

3. Determine the feasibility of candidate entrainer from the structure of the RCM:-
 - a) The entrainer does not divide components (A and B) to be separated into different distillation regions.
 - b) The entrainer induces liquid-liquid phase separation; there exists liquid-liquid equilibrium tie line crossing distillation boundary.
4. Evaluate all separation sequences: - number of distillation column with decanters and also their interconnections from the RCM of system for all feasible entrainer.
5. Determine the most promising entrainer for given feasibility conditions.
6. Design, stimulate and optimize separation sequences.

We have mentioned one example for understanding the RCM plot for dimethoxyethane /ethanol mixture separation using water as an entrainer.

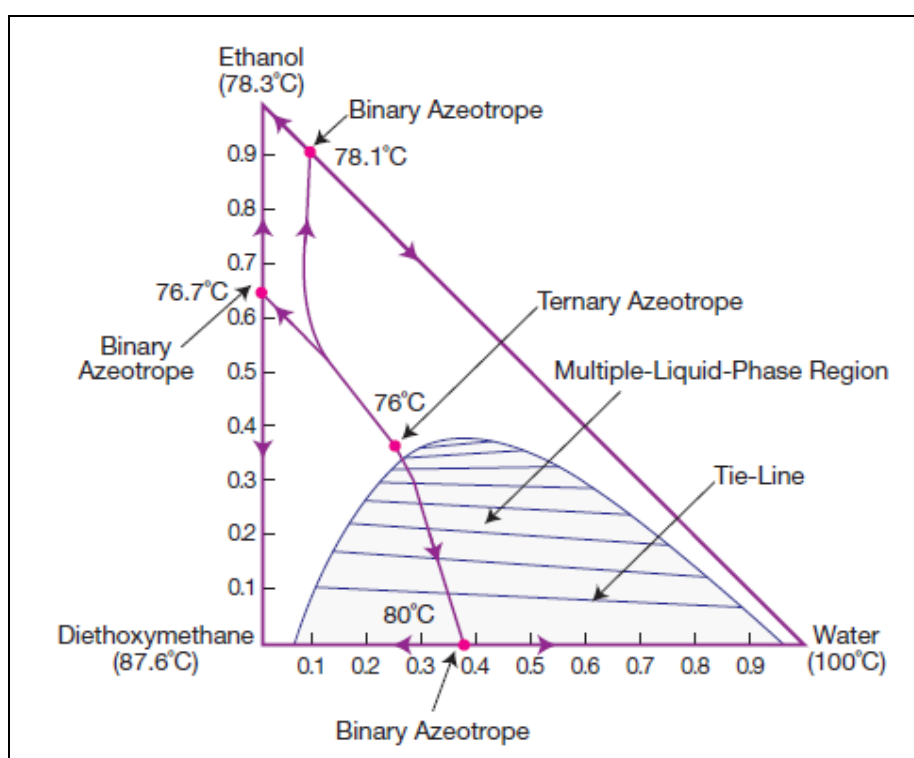


Figure 1.4: RCM plot for water-ethanol-DEM system^[1].

Here, they have assumed 50:50 mol percentages of DEM and ethanol in the process. The system consists of three binaries azeotropes and a ternary azeotrope with three distillation boundaries and multiple liquid phase regions. In this process, a minimum boiling homogeneous azeotrope is breakdown by means of water. Ternary azeotrope does not lie in the multiple liquid phase region, because of this the separation is not that much feasible to that extent of the maximum separation. So here, RCM gives a significant approach towards separation with water with more number of distillation sequences^[1].

CONCLUSION

To understand the behaviour of the separation process of any reaction system, it is very important to know the VLE and RCM strategy for the screening of entrainer. In this paper we focus on the different procedures for selection of entrainer for different distillation methods. For a good separation, knowledge of distillation regions, boundaries and tie line plays a vital role. With VLE, VLLE is also necessary to predict the nature of the curvature of the residue maps. For a good design of distillation process, a selection criterion of entrainer / solvent is the main step, which is involved in this review paper.

REFERENCES

- [1] Julka V., Chiplunkar M., O'Young L., 2009, "Selecting Entrainers for Azeotropic Distillation", *AICHE*, pp. 47-53
- [2] Rodriguez-Donis I., Gerbaud V., and Joulia X., 2001, "Entrainer Selection Rules For the Separation of Azeotropic and Close-Boiling Temperature Mixtures by Homogeneous Batch Distillation Process", *Ind. Eng. Chem. Res.*, pp. 2729-2741.
- [3] Laroche L., Bekiaris N., Andersent W. And Moraris M., 1991 "Homogenous Azeotropic Distillation: Comparing Entrainers", *Canadian Journal of Chemical Engineering*, Vol 69, pp. 1302-1329.
- [4] Pham H. N. and Doherty M. F., 1990, "Design and Synthesis of Heterogeneous Azeotropic Distillations-II, Residue Curve Maps, *Chemical Engineering Science*, Vol 45, pp. 1837-1843.
- [5] Stichlmair J. G., Fair J. R., 1998 "Distillation: Principles and Practices"
- [6] Doherty M. F. and Malone M. F., 2001 "Conceptual Design of Distillation System", *Mcgraw-Hill*, New York, pp. 568
- [7] Matsuyama H. and Nishimura H., 1977, "Topological And Thermodynamic Classification Of Ternary Vapour-Liquid Equilibria", *Journal Of Chemical Engineering of Japan*, Vol 10(3) , pp. 181-187
- [8] Bernot C., Doherty M., and Malone M., 1992 "Feasibility and Separation Sequences in Multicomponent Batch Distillation", *Chemical Engineering Science*, Vol. 46(5, 6), pp. 1311-1326.
- [9] Dussel R. and Stichlmair J., 1995, "Seperation of Azeotropic Mixtures by Batch Distillation Using an Entrainer", *Computer and Chemical Engineering*, Vol. 19(1), pp. 113-118.
- [10] Rodriguez-Donis I., Gerbaud V., and Joulia X., 2001, "Heterogeneous Entrainer Selection for the Separation of Azeotropic and Close Boiling Temperature Mixtures by Heterogeneous Batch Distillation", *Ind. Eng. Chem. Res.*, pp. 4935-4950.
- [11] De Jong M. C., Dimian A. C., Kuipers N. J. M. and De Haan A. B., 2006, "Entrainer Selection for the Synthesis of Fatty Acid Esters by Entrainer Based Reactive Distillation", *IchemE , Symposium Series No. 152*, pp. 678-688

- [12] Koretsky, M.D. 2004, "Engineering and chemical thermodynamics", Wiley.
- [13] Seader, J.D. & Henley, E.J. 2006, "Separation Process Principles", John Wiley & Sons, USA.
- [14] Raut N.B. and Sakpal V. S., 2014, "Optimization of Design And Operation In Reactive Distillation" Shodhganga, pp. 65-75.