



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>
Eprints ID : 15857

To link to this article : DOI : 10.1515/revce-2014-0031

URL : <https://www.degruyter.com/view/j/revce.2015.31.issue-1/revce-2014-0031/revce-2014-0031.xml>

| |
|---|
| <p>To cite this version : Shen, Weifeng and Benyounes, Hassiba and Gerbaud, Vincent <i>Extractive distillation: recent advances in operation strategies</i>. (2014) Reviews in Chemical Engineering, vol. 31 (n° 1). pp. 13-26. ISSN 0167-8299</p> |
|---|

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Weifeng Shen, Hassiba Benyounes and Vincent Gerbaud*

Extractive distillation: recent advances in operation strategies

Abstract: Extractive distillation is one of the efficient techniques for separating azeotropic and low-relative-volatility mixtures in various chemical industries. This paper first provides an overview of thermodynamic insight covering residue curve map analysis, the application of univolatility and unidistribution curves, and thermodynamic feasibility study. The pinch-point analysis method combining bifurcation shortcut presents another branch of study, and several achievements have been realized by the identification of possible product cut under the following key parameters: reflux ratio, reboil ratio, and entrainer-feed flow rate ratio. Process operation policies and strategy concerning batch extractive distillation processes are summarized in four operation steps. Several configurations and technological alternatives can be used when extractive distillation processes take place in a continuous or batch column, depending on the strategy selected for the recycle streams and for the main azeotropic feeds.

Keywords: batch; bifurcation theory; continuous; extractive distillation; operation strategies; thermodynamic analysis.

DOI 10.1515/revce-2014-0031

***Corresponding author: Vincent Gerbaud**, Université de Toulouse, INP, UPS, LGC (Laboratoire de Génie Chimique), 4 allée Emile Monso, F-31432 Toulouse Cedex 04, France, e-mail: Vincent.Gerbaud@ensiacet.fr; and CNRS, LGC (Laboratoire de Génie Chimique), F-31432 Toulouse Cedex 04, France
Weifeng Shen: Université de Toulouse, INP, UPS, LGC (Laboratoire de Génie Chimique), 4 allée Emile Monso, F-31432 Toulouse Cedex 04, France; CNRS, LGC (Laboratoire de Génie Chimique), F-31432 Toulouse Cedex 04, France; and Chemical and Biomolecular Engineering, Clarkson University, Potsdam, NY, USA
Hassiba Benyounes: U.S.T. Oran, Laboratoire de Chimie Physique des Matériaux, Catalyse et Environnement, Oran, Algérie

1 Introduction

In most separation systems, the predominant nonideality occurs in the liquid phase because of molecular interactions. Azeotropic and low-relative-volatility mixtures are often present in the separating industry, and their separation cannot be realized by conventional distillation. Extractive distillation is then a suitable widely used technique for separating azeotropic and low-relative-volatility mixtures in the pharmaceutical and chemical industries. Given an azeotropic mixture A-B (with A having a lower boiling temperature than B does), an entrainer E is added to interact selectively with the original components and alter their relative volatility, thus enhancing the original separation. Extractive distillation differs from azeotropic distillation by the fact that the third-body solvent E is fed continuously in another column position than the feed mixture. Extractive distillation has been studied for many decades, with a rich body of literature. Some main subjects studied include column with all possible configurations; process operation policies and strategy; process design, synthesis, and optimization; determination of separation sequencing; entrainer design and selection; feasibility studies; and so on. Among these topics, feasibility is always a critical issue, as it is necessary to assess process feasibility before making design specifications. Feasibility studies also contribute to a better understanding of complex unit operations such as batch extractive distillation (BED).

2 Thermodynamic topologic insights

The design of distillation processes is connected to thermodynamics, in particular to the boiling point of each compound and azeotrope. The initial feasibility study relates to well-known design tools: residue curve map (RCM) analysis and liquid phase diagrams, since they represent close approximations to actual equilibrium behavior and can be used to predict composition changes in separation processes under infinite reflux ratio conditions.

2.1 Residue curve map

The RCM technique is considered as a powerful tool for flow-sheet development and preliminary design of conventional multicomponent separation processes. RCM is a collection of the liquid residue curves in a simple one-stage batch distillation originating from different initial compositions. Using the theory of differential equations, the study of the topological properties of RCMs is summarized in two published articles (Hilmen et al. 2003, Kiva et al. 2003). The simple RCM was modeled by the following differential equation:

$$\frac{dx_i}{dh} = x_i - y_i^* \quad (1)$$

where h is a dimensionless time describing the relative loss of the liquid in the still-pot, x_i is the mole fraction of species i in the liquid phase, and y_i is the mole fraction of species i in the vapor phase. The y_i values are related with the x_i values using equilibrium constant K_i . The singular points of the differential equation are checked by computing the associated eigenvalues. Within a nonreactive RCM, a singular point can be a stable or an unstable node or a saddle, depending on the sign of the eigenvalues related to the residue curve equation. For nonreactive mixtures, there are three stabilities: unstable node, stable node, and saddle point (Figure 1A). The residue curves move away from the unstable node to the stable node with increasing temperatures. Some residue curves move away from a saddle point with decreasing temperatures, and others, with increasing temperatures (Figure 1B).

A past review article (Fien and Liu 1994) presented the use of ternary diagrams including RCMs for feasibility analysis, flow sheet development, and preliminary design of both homogeneous and heterogeneous azeotropic system separation processes. RCMs of reactive and extractive distillation units were used by Jiménez et al. (2001) for a simultaneous analysis. This graphical technique reveals the sensitivity of design options by

offering a visual representation over the whole composition space and assisting the engineer to detect separation constraints. Pham and Doherty (1990) conducted an RCM analysis for ternary heterogeneous mixtures to aid in the sequencing of heterogeneous distillation columns. However, distillation runs under finite reflux ratio (reboil ratio in reverse extractive distillation) conditions, to determine which products are achievable and the location of the suitable feed composition region, are more complicated (Wahnschafft et al. 1992, Poellmann and Blass 1994) because the dependency of the composition profile on the reflux ratio (reboil ratio) needs to be considered. This affects the range of composition available to each section profiles due to the occurrence of pinch points, which differ from the singular points of the RCM (Doherty and Caldarola 1985, Levy et al. 1985, Bausa et al. 1998, Urdaneta et al. 2002).

2.2 Unidistribution curve and relative volatility

The distribution coefficient and relative volatility are well-known characteristics of the vapor-liquid equilibrium. The distribution coefficient K_i is defined by:

$$K_i = \frac{y_i}{x_i} \quad (2)$$

K_i characterizes the distribution of component i between the vapor and liquid phases in equilibrium. $K_i=1$ defines the unidistribution curve. The vapor is enriched with component i if $K_i>1$ and is impoverished with component i if $K_i<1$ compared to the liquid. The higher the K_i , the greater the driving force (y_i-x_i) is given and the easier the distillation will be. The ratio of the distribution coefficient of components i and j gives the relative volatility. The relative volatility is a very convenient measure of the ease or difficulty of separation in distillation. The volatility of component i relative to component j is defined as

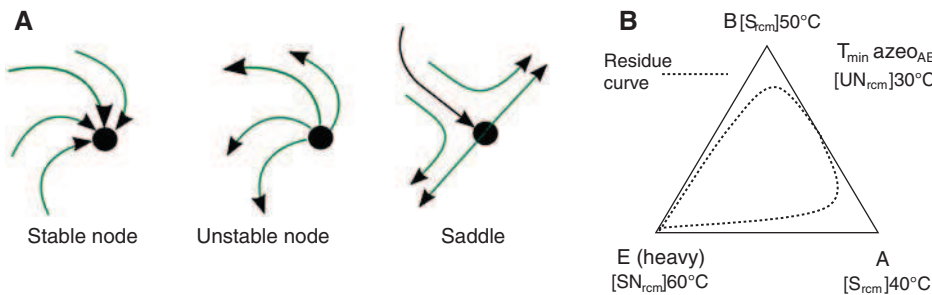


Figure 1 Features of (A) singular point and (B) RCM.

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j} \quad (3)$$

The relative volatility characterizes the ability of component i to transfer (evaporate) into the vapor phase compared to the ability of component j . Component i is more volatile than component j if $\alpha_{ij} > 1$ and less volatile if $\alpha_{ij} < 1$. For ideal and nearly ideal mixtures, the relative volatilities for all pairs of components are nearly constant in the whole composition space. The situation is different for nonideal and in particular azeotropic mixtures where the composition dependence can be complex.

Unidistribution and univolatility line diagrams can be used to sketch the VLE (vapor–liquid equilibrium) diagrams and represent the topologic features of the simple phase transformation trajectories. The qualitative characteristics of the distribution coefficient and relative volatility functions are typical approaches for the thermodynamic topological analysis. Kiva et al. (2003) considered the behavior of these functions for ternary mixtures. The composition dependency of the distribution coefficients is the qualitative and quantitative characteristics of the VLE for the given mixture. In a similar way to the distribution coefficient, relative volatility features can be represented by isovolatility lines. Then, the system of univolatility lines where $\alpha_{ij} = 1$ was proposed. It is evident that the point of a binary azeotrope gives rise to the univolatility line and that the point of a ternary azeotrope gives rise to the three univolatility lines. These features, related to the diagram of unidistribution and univolatility lines, are represented in Figure 2 for the most probable classes. They can characterize the VLE for any given mixture and enable us to sketch residue curves and distillation lines maps without any computation. As shown in Figure 2, unidistribution lines are named using the component where they started (e.g., a in class 1.0-1a), while univolatility lines are never started from pure component, and they are named by two letters (e.g., ab in class 1.0-1a). The existence of a binary azeotrope gives rise to two unidistribution lines, and the existence of a ternary azeotrope gives rise to three unidistribution lines. The figures in Figure 2 are classified by Serafimov's (1996) classification; Serafimov denotes a structure class by the symbol "MT," where M can take the values 0, 1, 2, or 3 and T can take the values 0 or 1. These classes are further divided into types and subtypes denoted by a number and a letter (Serafimov 1996). Recently, Rodriguez-Donis et al. (2009a) and Lang and Modla (2006) studied how univolatility lines split the composition triangle into regions of certain order of volatility of components and defined a general feasibility criterion for extractive distillation under the infinite

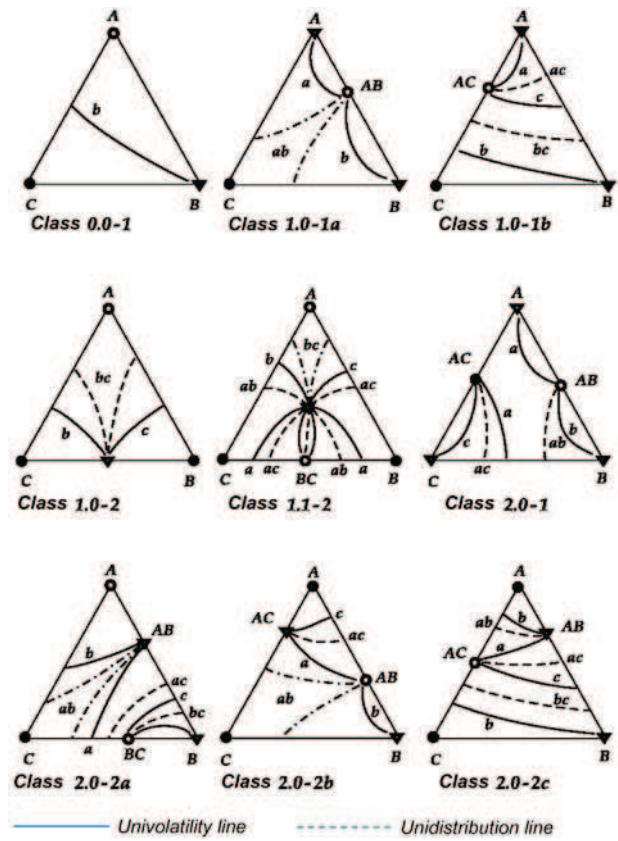


Figure 2 Unidistribution and univolatility line diagrams for the most probable classes of ternary mixtures (adapted from Kiva et al. 2003).

reflux ratio. In this work, we consider unidistribution and univolatility line diagrams for the purpose of sketching volatility order regions and thus of assessing the feasible structures that will give possible products and offer information related to possible limitations of entrainer feeds.

2.3 Thermodynamic feasibility insight

The maximum efficiency of extractive distillation is not necessarily improved by increasing the reflux ratio (Knapp and Doherty 1994), and BED studies further demonstrate the importance of selecting a suitable entrainer-feed flow rate ratio (Lelkes et al. 1998a). Feasibility study, the design of conventional and azeotropic distillation, is connected to thermodynamics, in particular the volatility of each compound and azeotrope. Considering a ternary diagram A-B-E formed by a binary mixture A-B with the addition of an entrainer E, the total number of binary azeotropes M and the number of ternary azeotropes T are applied as classification parameters. These classes are further

divided into types and subtypes denoted by a number and a letter. Serafimov (1996) has proposed a theoretical classification of 26 classes. The corresponding Serafimov classification is detailed in Kiva et al. (2003). As Laroche et al. (1992) showed for the 1.0-1a class, knowledge of the RCM and of the location of the univolatility curve $\alpha_{AB}=1$ can help assess which product is removed in the distillate when using a light, intermediate, or heavy entrainer. Combining knowledge of RCMs and of the univolatility and unidistribution curve location, Rodriguez-Donis et al. (2009a,b, 2010, 2012a,b) published a general feasibility criterion for extractive distillation under the infinite reflux ratio: “Homogeneous extractive distillation of a A-B mixture with entrainer E feeding is feasible if there exists a residue curve connecting E to either A or B following a decreasing (a) or increasing (b) temperature direction inside the region where A or B are the most volatile (a) or the heaviest (b) component of the mixture.” The volatility order is set by the univolatility curves. Using illustrative examples covering all subcases, but exclusively operated in BED, these authors found that Serafimov’s classes covering up to 53% of azeotropic mixtures were suited for extractive distillation: 0.0-1 (low-relative-volatility mixtures), 1.0-1a, 1.0-1b, 1.0-2 (azeotropic mixtures with light, intermediate, or heavy entrainers forming no new azeotrope), 2.0-1, 2.0-2a, 2.0-2b, and 2.0-2c (azeotropic mixtures with an entrainer forming one new azeotrope). For all suitable classes, the general criterion under the infinite reflux ratio could explain the product to be recovered and the possible existence of limiting values for the entrainer-feed flow rate ratio for batch operations: a minimum value for the class 1.0-1a, a maximum value for the class 1.0-2, etc. The behavior at the finite reflux ratio could be deduced from the infinite behavior and properties of the RCMs, and some limits on the reflux ratio were found. However, precise determination of the limiting values of the reflux ratio or of the entrainer-feed flow rate ratio required other techniques.

Continuous extractive distillation studies have always considered a heavy entrainer to split a minimum boiling azeotrope. There are some cases when its use is not recommended, such as when a heat-sensitive or a high-boiling-component mixture has to be separated. Besides, different entrainers can cause different components to be recovered as first cut in extractive distillation. Therefore, finding potential entrainers is critical since an economically optimal design made with an average design using the best entrainer can be much less costly. Theoretically, any candidate entrainer satisfying the feasibility and optimal criteria can be used whether it is a heavy, light, or intermediate entrainer. Literature studies on intermediate

entrainer or light entrainer validate this assumption (Lang et al. 1999, Lelkes et al. 2002, Rodriguez-Donis et al. 2012a, Shen and Gerbaud 2013). Tables 1 and 2 summarize the information on the literature for the typical ternary systems.

3 Extractive distillation pinch-point analysis

The identification of possible cuts under key parameters reflux ratio, reboil ratio, and entrainer-feed flow rate ratio has been the main challenge for an efficient separation of azeotropic mixtures. Several achievements have been realized by the use of an algebraic criterion (Levy and Doherty 1986) or mathematical approaches either by using bifurcation theory (Knapp and Doherty 1994), by interval arithmetic (Frits et al. 2006), or by a combined bifurcation-shortcut rectification body method (RBM) (Brügge-mann and Marquardt 2008). Extending their method for single-feed azeotropic distillations (Levy et al. 1985), Levy and Doherty (1986) proposed an algebraic trial-and-error tangent pinch-point procedure for determining the minimum reflux ratio without the necessity of lengthy iteration schemes involving column profile calculations. The method consisted of finding the value of the reflux ratio, which makes the feed pinch point, the saddle pinch point, and the controlling feed composition collinear, but was restricted to ternary mixtures. After studying the sequence extractive column and entrainer regeneration column for the separation of acetone-methanol azeotrope with water (Knapp and Doherty 1990), Knapp and Doherty (1994) used bifurcation theory to analyze the 1.0-1a class behavior and related the feasibility to the appearance of saddle-node bifurcation points and branching points. Feasible processes required that a ternary saddle originating from a pure component exist, whereas the appearance of a ternary unstable node on the pinch branch originating at the azeotrope led to an unfeasible separation. They also proposed some heuristics to set the operational values of R and F_E , once their minimal value was known. These authors also published more general diagrams, issued from bifurcation theory, without providing illustrative examples for each. Frits et al. (2006) used an interval arithmetic-based branch-and-bound optimizer to find limiting flows based on the existence and location of singular points and separatrices in profile maps and applied it to the same 1.0-1a mixture as Knapp and Doherty (acetone-methanol-water), but for BED. Agreeing with the findings of Knapp and Doherty (1994), they found

Table 1 Most important literature concerning extractive distillation separation of binary azeotropic and low-relative-volatility mixtures in a batch rectifier with light, intermediate, or heavy entrainer.

| Entrainer type | Azeotrope type | Serafimov class | Volatility order | References |
|----------------|----------------|-----------------|------------------|---|
| Heavy | Minimum | 1.0-1a | Az>A>B>E | Yatim et al. 1993 Laroche et al. 1992 Lang et al. 1994 Knapp and Doherty 1994 Lelkes et al. 1998a,b Brüggemann and Marquardt 2004 Luyben 2008a,b Rodriguez-Donis et al. 2009a Shen et al. 2013 Benyounes et al. 2014 Benyahia et al. 2014 |
| | Maximum | 1.0-2 | A>B>Az>E | Lang et al. 2000a,b Rodriguez-Donis et al. 2009a Shen et al. 2013 Benyounes et al. 2014 |
| | Low alpha | 0.0-1 | A>B>E | Lang et al. 1994 Rodriguez-Donis et al. 2009b |
| Intermediate | Minimum | 1.0-1b | Az>A>E>B | Rév et al. 2003 Varga 2006a Rodriguez-Donis et al. 2012b |
| | Maximum | 1.0-1b | A>E>B>Az | Bernot et al. 1990 Lelkes et al. 2002 Rodriguez-Donis et al. 2012b |
| Light | Minimum | 1.0-2 | E>Az>A>B | Hunek et al. 1989 Laroche et al. 1992 Lelkes et al. 1998a,b Lang et al. 1999 Varga et al. 2006b Rodriguez-Donis et al. 2012a Shen and Gerbaud 2013 |
| | Maximum | 1.0-1a | E>A>B>Az | Varga et al. 2006b Rodriguez-Donis et al. 2012a Shen and Gerbaud 2013 |
| | Low alpha | 0.0-1 | E>A>B | Varga et al. 2006b Rodriguez-Donis et al. 2012a |

a feasible process under the infinite reflux ratio above a minimal entrainer-feed flow rate ratio, which corresponded to the merging of a stable pinch point originating from the azeotrope, with a saddle point originating from a pure component. Finite reflux ratio analysis showed that the pinch points moved inside the composition triangle and brought unfeasible regions, which are described later. Kossack et al. (2008) exploited a fully automated shortcut design procedure to determine the limit values. The method is based on the approximation of all column profiles by the so-called RBM, which is constructed from nonlinear analysis of the pinches of each section (Bausa et al. 1998). Like Knapp and Doherty (1994), Kossack et al. also set some operational constraints to determine the

quasi-optimal values once the minimal values of R and F_E are known. The constraints were incorporated into a general algorithm for the determination of the optimal values of the entrainer-feed flow rate ratio and the reflux ratio. Several ternary mixtures were used for illustration, all of them belonging to the 1.0-1a class, but a quaternary mixture with two azeotropes and an entrainer forming no new azeotrope was shown. Kossack et al. (2008) then used the RBM method as a second screening criterion for evaluating the extractive distillation entrainer candidates. Fast and efficient, the method bears some critiques when the profiles are highly curved because each rectification body has straight boundaries (Lucia et al. 2008). Finally, one should notice the recent publication of a unique

Table 2 Study case related to extractive distillation separation of binary azeotropic and low-relative-volatility mixture in a batch rectifier with light, intermediate, or heavy entrainer.

| Entrainer type | Azeotrope type | Class | Volatility order | Case study | | |
|----------------|----------------|---------|------------------|---------------------|------------------|-----------------|
| Heavy | Minimum | 1.0-1a | Az>A>B>E | Acetone | Methanol | Water |
| | | | | Acetone | Methanol | Isopropanol |
| | | | | Acetone | Methanol | Ethanol |
| | | | | Acetone | Methanol | Chlorobenzene |
| | Maximum | 1.0-2 | A>B>Az>E | Acetone | Chloroform | Benzene |
| | | | | Acetone | Chloroform | Toluene |
| | | | | Vinyl acetate | Butyl acetate | Chloroform |
| | Low alpha | 0.0-1 | A>B>E | Ethyl acetate | Benzene | Butanol |
| | | | | Heptane | Toluene | Phenol |
| | | | | Heptane | Toluene | Chlorobenzene |
| | | | | Ethyl acetate | Benzene | Hexanol |
| | Intermediate | Minimum | 1.0-1b | Az>A>E>B | Methyl acetate | Cyclohexane |
| Methanol | | | | | Toluene | Triethylamine |
| Chloroform | | | | | Ethyl acetate | 2-chlorobutane |
| Light | Minimum | 1.0-2 | E>Az>A>B | Ethanol | Water | Methanol |
| | Maximum | 1.0-1a | E>A>B>Az | Ethanol | Toluene | Acetone |
| | | | | Methyl ethyl ketone | Benzene | Acetone |
| | | | | Water | Ethylene diamine | Methanol |
| | | | | Acetone | Chloroform | DCM |
| | Low alpha | 0.0-1 | E>A>B | Propanoic acid | DMF | MIBK |
| | | | | Chlorobenzene | Ethylebenzene | 4-methylheptane |

noniterative method for finding the possible splits at finite reflux ratio of azeotropic distillation based on the identification of the common terminal points of pinch branches in each column section (Petlyuk et al. 2011, 2012). Its extension to extractive distillation is in preparation.

4 Batch process operation policies and strategies

Process operation policies and strategies concern BED processes. The BED realization and the role played by the different steps in the process are analyzed and are presented by Lelkes et al. (1998) on the basis of the analysis of several operational policies. Usually, BED proceeds in four operation steps: (1) infinite reflux ratio operation to reach steady state inside the column, (2) infinite reflux ratio operation with continuous entrainer feeding, (3) finite reflux ratio, leading to the distillation of one of the original components while feeding continuously the entrainer, and (4) conventional distillation for the separation of the zeotropic binary mixture retained into the still. The original $R=\text{const.}$ policy is modified by shortening the second preparatory step of the BED ($R=\infty$,

$F>0$). The possibilities of performing a constant distillate composition ($x_{D,A}=\text{const.}$) policy are discussed. In their article about improved operational policies for BED columns, Safrit and Westerberg (1997) studied the sensitivities to various column operation parameters, in particular the entrainer-feed flow rate ratio policy, bottom flow rate ratio policy, and the switching time between operational steps. They showed that these variables do have a large effect on the final solution and should be solved as in an optimal process. While the optimal policies for the entrainer and bottom flow rate ratio were not obvious, the value of the switching time that maximized the final profit for the simulations run was very near to the value of the time in which the accumulated profit was maximized in the main operational step (distillate recovery step). The problem solution was very sensitive to assumed product value and operational costs. These authors also found that the still path steering algorithm provides a good first approximation to the bottom flow rate ratio policy for certain types of objective functions. Demicoli and Stichlmair (2003) presented an experimental investigation of the separation of a zeotropic ternary mixture via total reflux ratio operation and of the separation of an azeotropic binary mixture via batch-wise extractive distillation. Lang et al. (2006) proposed a

new operational policy, which was successfully applied in the industry as well. They started the continuous E feeding during the heating up of the column. Düssel and Stichlmair (1995) proposed the so-called hybrid method (absorption+distillation) for the separation of minimum azeotropes with a heavy entrainer. By this method, in step 3 (absorption), one component is produced under a zero reflux ratio with a high flow rate of entrainer fed at the top plate of the column. (In step 4, the remaining component is separated from the entrainer by distillation without entrainer feeding and under finite R.) Stichlmair and Fair (1998) suggested this method in their book. Kotai et al. (2007) studied this process in detail and stated its limits. Lang et al. (2010) conducted successful laboratory experiments for the recovery of tetrahydrofurane from a pharmaceutical multicomponent waste solvent mixture both by the BED and hybrid processes.

Step 1 feasibility obeys the RCM analysis results because the residue curve then describes the liquid composition in the column. Steps 2 and 3 are the extractive steps, and their feasibility is determined by the existence of an extractive composition profile that links the

rectifying profile to the instantaneous still composition, following Lelkes' model. Under feasible operating parameters, both profiles intersect close to the extractive stable node (SN_{extr}) that, under a sufficiently high entrainer-vapor flow rate ratio and number of extractive trays, is commonly located near the binary side of the entrainer and the original component, which is drawn as distillate product. The other azeotropic component remains in the still with the entrainer at the end of step 3. This intersection-finding methodology has been used to study the separation of minimum and maximum azeotropic mixtures and that of close-boiling mixtures by feeding a heavy, light, and intermediate entrainer in extractive distillation (Rodriguez-Donis et al. 2009a,b, 2010, 2012a,b). The necessary operating steps of the process and the limiting operating parameters in a batch rectifier or a batch stripper with intermediate entrainer feeding are determined and compared in Tables 3 and 4. These results can be useful in other separation problems. The limiting parameters include the reflux ratio R, the entrainer-feed flow rate ratio F/V, and the number of theoretical stages in rectifying and extractive section.

Table 3 Operating steps and limiting parameters of extractive distillation in configuration BED-I separating binary azeotropic and low-relative-volatility mixture in a batch rectifier with light, intermediate, or heavy entrainer (adapted from Stéger et al. 2005, Shen 2012).

| Extractive distillation of ternary mixture systems | | | | | | | | |
|--|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Entrainer type | Heavy | | | Intermediate | | Light | | |
| Mixture | Minimum | Maximum | Low alpha | Minimum | Maximum | Minimum | Maximum | Low alpha |
| Serafimov class | 1.0-1a | 1.0-2 | 0.0-1 | 1.0-1b | 1.0-1b | 1.0-2 | 1.0-1a | 0.0-1 |
| Volatility Order | Az>A>B>E | A>B>Az>E | A>B>E | Az>A>E>B | A>E>B>Az | E>Az>A>B | E>A>B>Az | E>A>B |
| Analysis of operating steps with configuration BED-I | | | | | | | | |
| Adding entrainer in advance | – | – | – | – | Necessary | Necessary | Necessary | Necessary |
| Startup | R=∞; F=0 | R=∞; F=0 | R=∞; F=0 | R=∞; F=0 | R=∞; F=0 | R=∞; F=0 | R=∞; F=0 | R=∞; F=0 |
| Purification | R=∞; F>0 | R=∞; F>0 | R=∞; F>0 | R=∞; F>0 | – | – | – | – |
| First product | R<∞; F>0 {A} | R<∞; F>0 {A} | R<∞; F>0 {A} | R<∞; F>0 {A} | R<∞; F>0 {AE} | R<∞; F>0 {EA} | R<∞; F>0 {EA} | R<∞; F>0 {EA} |
| Second product | R<∞; F=0 {B} | R<∞; F=0 {B} | R<∞; F=0 {B} | R<∞; F=0 {E} | R<∞; F=0 {E} | R<∞; F=0 {E} | R<∞; F=0 {E} | R<∞; F=0 {E} |
| Third product | Remainder: {E} | Remainder: {E} | Remainder: {E} | Remainder: {B} | Remainder: {B} | Remainder: {B} | Remainder: {B} | Remainder: {B} |
| Reloading | | | | | {AE} | {EA} | {EA} | {EA} |
| Fourth product | | | | | R<∞; F=0 {A} | R<∞; F=0 {E} | R<∞; F=0 {E} | R<∞; F=0 {E} |
| Fifth product | | | | | Remainder: {E} | Remainder: {A} | Remainder: {A} | Remainder: {A} |
| Limitation parameters | | | | | | | | |
| Reflux ratio | Min | Min | Min | Min | Min | Min; max | Min; max | Min |
| N _{Rect} (rect. stage) | Min; max | Min | Min | Min; max | Min | Min; max | Min; max | Min; max |
| N _{Extr} (extr. stage) | Min | Min; max | Min | Min | – | Max | Max | Max |
| F/V (entrainer-feed flow rate ratio) | Min | Max | Min | Min | Min | Max | Min | – |

Table 4 Operating stages and limiting parameters of azeotropic extractive distillation in configuration BES-I separating binary azeotropic and low-relative-volatility mixture in a batch rectifier with light, intermediate, or heavy entrainer (adapted from Stéger et al. 2005, Shen 2012).

| Extractive distillation of ternary mixture systems | | | | | | | | |
|---|--------------------------|--------------------------|--------------------------|--------------------------|------------------------|----------|------------------------|------------------------|
| Entrainer type | Heavy | | | Intermediate | | Light | | |
| Mixture | Minimum | Maximum | Low alpha | Minimum | Maximum | Minimum | Maximum | Low alpha |
| Volatility order | Az>A>B>E | A>B>Az>E | A>B>E | Az>A>E>B | A>E>B>Az | E>Az>A>B | E>A>B>Az | E>A>B |
| Analysis of operating steps with configuration BES-I | | | | | | | | |
| Operating steps – BES-I | | | | | | | | |
| 1. Startup | $s=\infty; +F$ | $s=\infty; +F$ | $s=\infty; +F$ | $s=\infty; +F$ | $s=\infty; F=0$ | – | $s=\infty; F=0$ | $s=\infty; +F$ |
| 2. Purification | – | – | – | – | $s=\infty; F>0$ | – | $s=\infty; F>0$ | – |
| 3. Production | $s<\infty; F>0$ {B/E} | $s<\infty; F>0$ {B/E} | $s<\infty; F>0$ {B/E} | $s<\infty; F>0$ {B/E} | $s<\infty; F>0$ {B} | – | $s<\infty; F>0$ {B} | $s<\infty; F>0$ {B} |
| 4. Cutting | $s<\infty; F>0$ | $s<\infty; F>0$ | $s<\infty; F>0$ | $s<\infty; F=0$ | $s<\infty; F=0$ | – | $s<\infty; F=0$ | $s<\infty; F=0$ |
| 5. Production | $s<\infty; F=0$ {E} | $s<\infty; F=0$ {E} | $s<\infty; F=0$ {E} | $s<\infty; F=0$ {E} | $s<\infty; F=0$ {E} | – | $s<\infty; F=0$ {A} | $s<\infty; F=0$ {A} |
| Reloading | Remainder: A {B/E} | Remainder: A {B/E} | Remainder: A {B/E} | Remainder: A {B/E} | Remainder: A – | – | Remainder: E – | Remainder: E – |
| 6. Production | $s<\infty; F=0$ {E} | $s<\infty; F=0$ {E} | $s<\infty; F=0$ {E} | $s<\infty; F=0$ {B} | – | – | – | – |
| | Remainder: B | Remainder: B | Remainder: B | Remainder: E | | | | |

5 Different configurations of operation strategies

Azeotropic and extractive distillation can be carried out in a continuous or batch distillation column. Several configurations and technological alternatives can be used when azeotropic and extractive distillation processes take place in a continuous or batch column depending on the strategy selected for recycle streams and the main azeotropic feed.

5.1 Continuous process configurations

The synthesis and design of azeotropic or extractive distillation processes first depend on the miscibility of the entrainer with one of the azeotropic components. The

entrainer is regarded as heterogeneous if its introduction resulted in phase split over a range of compositions. Otherwise, the entrainer is homogeneous. Homogeneous entrainers allow only in a single feasible region unless that ternary system contains distillation boundaries with a significant curvature. Shen (2012) presents a typical flow sheet for extractive distillation with heavy entrainer and light entrainer. As shown in Figure 3, it includes an extractive distillation column where the solute, A, is obtained as the distillate and the mixture of raffinate, B, and solvent exists from the bottom. A solvent recovery column comes next, where the purified raffinate, B, is obtained as distillate and the solvent is recovered from the bottom and recycled to the extractive distillation column. Unlike the homogeneous distillation process, heterogeneous entrainers provide a simple technique to cross a basic distillation boundary, and the overall mass balance line

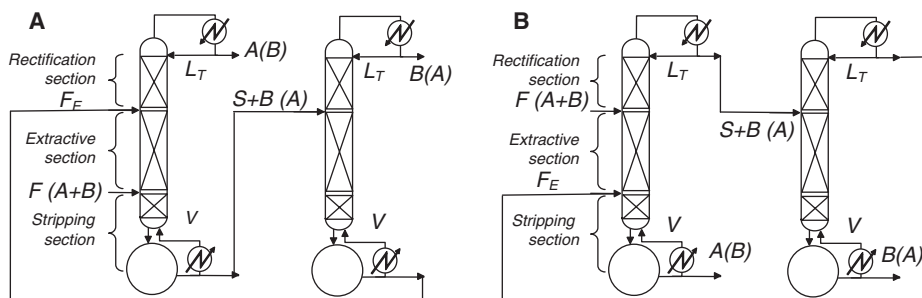


Figure 3 Flow sheet of typical extractive distillation with (A) heavy entrainer and (B) light entrainer (adapted from Shen 2012).

can connect two streams located in different distillation regions (Rodriguez-Donis et al. 2007).

Usually, a sequence of three connected continuous columns are used where the heterogeneous column and its decanter are the target of the design and synthesis analysis. An entrainer recovery column and a preconcentrator are commonly associated with the heteroazeotropic column. Rodriguez-Donis et al. (2007) investigated the feasibility of heterogeneous extractive distillation processes in a continuous column considering several feed point strategies for the entrainer recycle stream and for the main azeotropic feed (Figure 4). Depending on these choices, the heterogeneous distillation column is composed of one, two, or three column sections. Unlike homogeneous extractive distillation, a reflux policy composed of single or dual decanted liquid phases is considered. The authors also looked at the impact of the external feeding influence on the composition of the top column liquid stream, the knowledge of which was required to assess feasibility. Figure 4 displays the superstructure for the extractive distillation column considering all possibilities for both the entrainer recycle and the main azeotropic feed (Rodriguez-Donis et al. 2007). Each type of configuration is indicated by a number from 1 to 7. Considering a high boiling entrainer, seven main configurations can be set for the heteroazeotropic continuous column as follows: (1) the recycled entrainer feed, F_E , is mixed to the azeotropic stream, following the direction of stream 1 from F_E , and fed at the same intermediate tray of the column, following the direction of stream 1 from F ; (2) the entrainer stream is fed to an intermediate tray of the column, following the direction of stream 2 from F_E , as is commonly used in the homogeneous extractive distillation process; (3) F_E is sent at the first top tray as a single external stream or mixed

with the liquid reflux stream; (4) both F_E and F are introduced at the first top tray of the column; (5) the entrainer F_E is sent to the decanter; (6) similar to 5, but a part of the distillate product, D , is also recycled to the decanter in order to ensure a liquid-liquid split in this vessel; and (7) the main azeotropic feed F is fed at the first top tray of the column or mixed into the liquid reflux, and F_E is returned directly to the decanter.

Figure 5 presents a drawing illustrating the internal and external configuration of heterogeneous distillation column parts. In each stage of the distillation tower, a vapor phase is contacted with a liquid phase, and mass transfers from vapor to liquid and from liquid to vapor (Figure 5A). The liquid falls toward the bottom of the tower. At the bottom of the tower, in general, more heat is added to the liquid by a “reboiler,” which may be heated by steam or fuel-fired furnace (see industrial reboiler in Figure 5D). The heat added to the mixture before entering the tower partially vaporizes the mixture, and the vapors rise up the tower and begin to cool in a condenser (see industrial condenser in Figure 5C). There are two main categories of condenser: In the first category of total condenser, all of the vapor leaving the top of the column is condensed. Consequently, the composition of the vapor leaving the top tray is the same as that of the liquid distillate product. In a partial condenser, the vapor is only partially liquefied. The liquid produced is returned to the column as liquid, and a vapor product stream is removed. A partial condenser functions as an equilibrium separation stage. Reboilers take several forms: they may be “thermosiphon” types, which rely on the thermal effects on density to draw liquid through the heat exchanger; “forced circulation” types, which use a pump to force liquid through; or even “stab-in” types, which come through the side of the column into the liquid reservoir. In large, complex columns, sidestream reboilers can be used. These draw liquid off a tray, heat it, and then return the vapor liquid mixture to the same or similar trays. Typically, a horizontal two-phase decanter is used in the heteroazeotropic continuous column, as shown in Figure 5B. After being captured by a spray catcher, the remaining gas is sent out by a gas outlet. The stratification of two or more immiscible liquids occurs by gravity, and then they are removed by different liquid outlets separately. A level controller is used for monitoring the stratification level for different purposes.

An entrainer is always loaded into the still at the beginning of the azeotropic distillation process while in continuous extractive distillation, and the entrainer must be fed continuously at some tray of the column or into the still during the whole operation (Lang et al. 1999, Lelkes

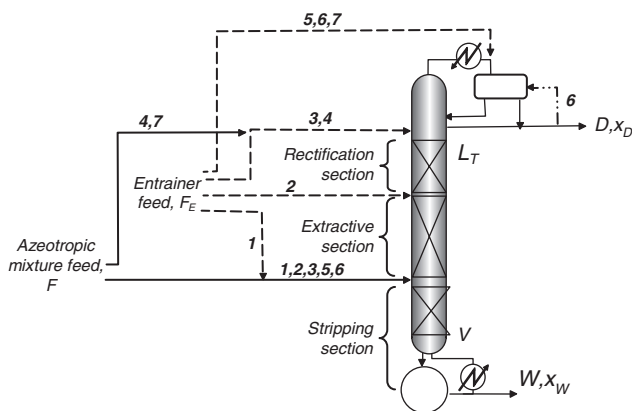


Figure 4 Configurations for the heterogeneous distillation column considering all possibilities for both the entrainer recycle and the main azeotropic feed (adapted from Rodriguez-Donis et al. 2007).

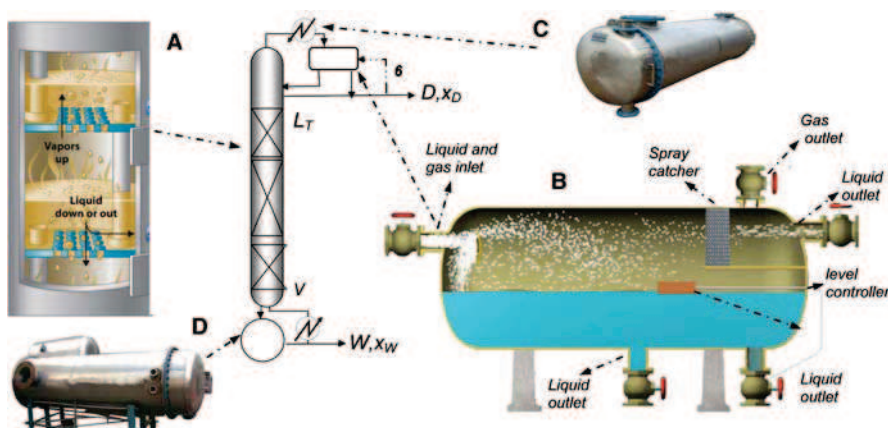


Figure 5 Drawing illustrating a heterogeneous distillation column: internal configuration of (A) distillation tower and (B) decanter and external configuration of (C) industrial condenser and (D) industrial reboiler.

et al. 1998a,b, 2002). Doherty and coworkers made a critical analysis of the heterogeneous azeotropic distillation process with different entrainer recycle strategies because the feasibility of this process depends heavily on where the entrainer recycle stream returns to the heteroazeotropic column (Ryan and Doherty 1989, Pham and Doherty 1990). More recently, Marquardt and coworkers presented a shortcut design method based on the RBM to design heterogeneous azeotropic distillation processes and extractive distillation columns (Bausa et al. 1998, Urdaneta et al. 2002, Brüggemann and Marquardt 2004).

An innovative solution to overcome the drawback of energy-intensive extractive distillation is using advanced process intensification and integration techniques, such as thermally coupled distillation columns, dividing-wall columns (DWCs), heat-integrated distillation columns, or cyclic distillation. Extractive DWC (EDWC) has had great appeal in the chemical process industry recently because it can separate more components in a single distillation unit, thereby saving the cost of building two columns and cutting the operating costs by using a single condenser and reboiler. Kiss and Suszwalak (2012) demonstrated the potential use of novel distillation alternatives based on extractive and azeotropic DWC for enhanced bioethanol dehydration. The proposed processes are technically feasible, allowing the separation with high-purity bioethanol. Bravo-Bravo et al. (2010) proposed a constrained stochastic multiobjective optimization technique for the extractive dividing-wall distillation column. The simulation results show the effect of the main variables on the complex extractive distillation process. Sun et al. (2014) proposed three control strategies for extractive dividing

wall distillation column: the basic control strategy uses four composition controllers, and two improved control strategies, with and without vapor split ratio, use temperature controllers that are more practical in application than the basic control strategy. Zhang et al. (2014) established three control structures for the EDWC, and they revealed that it is useful to adjust the entrainer flow rate or vapor split ratio to hold the purity specifications. Xia et al. (2012, 2013) explored two effective composition control structures for the stabilization of the EDWC and proposed temperature control structures with an adjustable vapor split, and they also confirmed feasibility and proved that the structure can handle feed disturbances effectively.

5.2 Batch process configurations

Several column configurations can be used for extractive distillation both in batch and continuous processes. In batch mode, the entrainer is always loaded into the still at the beginning of the azeotropic distillation process, while in extractive distillation, the entrainer must be fed continuously at some tray of the column or into the still during the whole operation. In batch process configurations, both BED and simple batch distillation (SBD) processes can be performed either in a rectifier, in a middle-vessel column, or in a stripping column. In Figure 6, the symbols -T, -I, or -B are introduced to represent that the feed is added at the top, intermediate, or bottom of the column, respectively. According to the position of the entrainer feed, four configurations in a rectifier can be considered: (1) there is a single rectifying section that exists: SBD configuration is

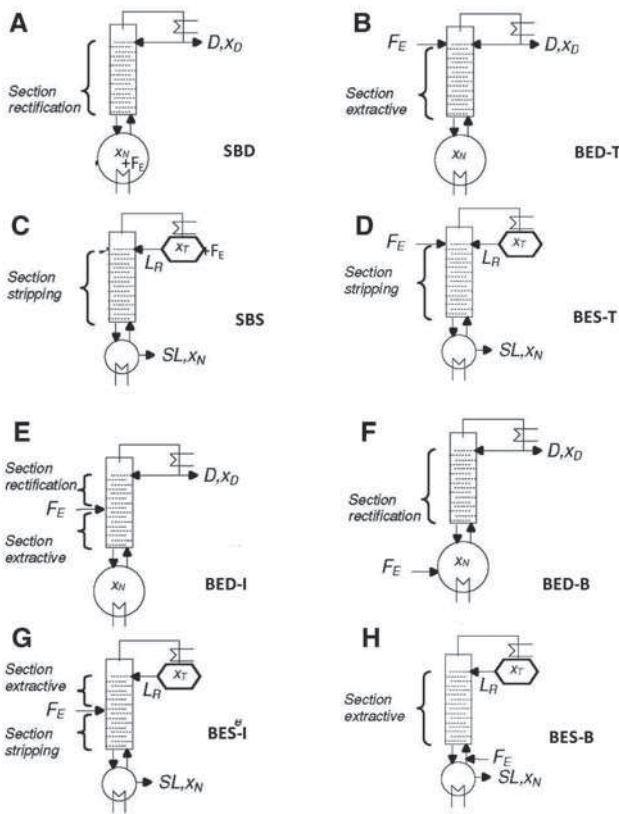


Figure 6 Configurations of extractive batch distillation columns in rectifier and stripper (adapted from Shen 2012).

the case when both the entrainer and feed are premixed to the boiler in batch mode (see Figure 6A) and BED-B configuration occurs when the entrainer is fed to the boiler continuously (see Figure 6B); (2) there are existing extractive and rectifying sections while the entrainer is fed to the intermediate section in continuous mode, which is named configuration BED-I (Figure 6E); and (3) only a single extractive section exists, and the entrainer is fed to the condenser in continuous mode (see Figure 6F of BED-T configuration). On the other hand, depending on the location of the feed configurations in a stripper, another four configurations can be considered: (1) a single stripping section exists: SBS configuration is the situation when both the entrainer and feed are premixed to the condenser (Figure 6C), and BES-T configuration is defined when both the feed and the entrainer are fed to the condenser and the entrainer is fed continuously (Figure 6D); (2) configuration BES-I has extractive and rectifying sections, and the entrainer is fed to the intermediate section in continuous mode (see Figure 6G); and (3) a single extractive section exists, the feed is fed to the condenser, and the entrainer is fed to the boiler in continuous mode see (Figure 6H for configuration BES-B). Stéger et al. (2005) emphasize that

the most commonly applied configuration is the rectifier, as controlling a batch rectifier is less complex than controlling a stripper.

Although batch process generally is less energy efficient than continuous distillation, it has received increased attention in the last few years because of its simplicity of operation, flexibility, and lower capital cost. In order to make the column more energy efficient, some attempts were carried out to improve the batch configurations. Warter et al. (2004) presented an experimental investigation of azeotropic mixtures using batch distillation in a column with a middle vessel. It can easily be operated in a “total reflux operation with constant hold-up” mode for the removal of light and heavy boiling impurities from an intermediate boiling product. The results prove that batch distillation with a middle vessel offers many practical advantages such as a reduction in both the temperature in the feed vessel and the contact time with the hot surface of the reboiler, as well as in the duration of the process start-up. It also offers the possibility to reduce the size of the reboiler. Wittgens et al. (1996) proposed a simple feedback control strategy for total reflux operation of a multivessel column. Total reflux operation with constant vessel holdup is carried out until the compositions in all vessels satisfy their specifications. It had been validated that the proposed control scheme is feasible and easy to implement and operate by simulations and experiment.

6 Conclusions

This paper has focused on reviewing key operation policies and strategies, including thermodynamic insight, pinch-point analysis, and several configurations, depending on the strategy selected for the recycle streams and for the main azeotropic feeds. The thermodynamic insight study relates well-known design tools: RCM analysis, univolatility and undistribution curves, and some topological character analysis. Pinch-point analysis concerns the knowledge of bifurcation theory, and the key parameters reflux ratio, reboil ratio, and entrainer-feed flow rate ratio are the targets. The necessary operating steps of the process and the limiting operating parameters in a batch rectifier or a batch stripper with intermediate entrainer feeding are determined, which can be useful in other separation problems. Taking into account the seven configurations combining the entrainer recycle stream and the main azeotropic feed, several configurations and technological alternatives for both continuous and batch can

be used and illustrated; this could give clear guidance for different design circumstances and aims.

The studies performed to date show a diverse field of current popular extractive distillation design methodology research. It is apparent that interest in general areas of operation strategy study rests on feasibility design and has the potential to be, perhaps, a more sustainable technique than are current comparable commercial technologies for extractive separation. However, there are very few detailed economic studies on extractive separation technologies. It should be noted that one of the significant factors in decision making for alternative technologies is the economical evaluation. It is imperative that novel proposed techniques consider the design sustainability of extractive distillation process when they are used to replace the traditional technologies.

References

- Bausa J, Watzdorf R, Marquardt W. Shortcut methods for non ideal multicomponent distillation: I. Simple columns. *AIChE J* 1998; 44: 2181–2198.
- Benyahia K, Benyounes H, Shen WF. Energy evaluation of ethanol dehydration with glycol mixture as entrainer. *Chem Eng Technol* 2014; 37: 987–994.
- Benyounes H, Shen WF, Gerbaud V. Entropy flow and energy efficiency analysis of extractive distillation with a heavy entrainer. *Ind Eng Chem Res* 2014; 53: 4778–4791.
- Bernot C, Doherty MF, Malone MF. Patterns of composition change in multicomponent batch distillation. *Chem Eng Sci* 1990; 45: 1207–1221.
- Bravo-Bravo C, Segovia-Hernández JG, Gutiérrez-Antonio C, Durán AL, Bonilla-Petriciolet A, Briones-Ramírez A. Extractive dividing wall column: design and optimization. *Ind Eng Chem Res* 2010; 49: 3672–3688.
- Brüggemann S, Marquardt W. Shortcut methods for nonideal multicomponent distillation: 3. Extractive distillation columns. *AIChE J* 2004; 50: 1129–1149.
- Demicoli D, Stichlmair J. Novel operational strategy for the separation of ternary mixtures via cyclic operation of a batch distillation column with side withdrawal. *Comput Aided Chem Eng* 2003; 14: 629–634.
- Doherty MF, Calderola GA. Design and synthesis of homogeneous azeotropic distillations. 3. The sequencing of columns for azeotropic and extractive distillations. *Ind Eng Chem Fundam* 1985; 24: 474–485.
- Düssel R, Stichlmair J. Separation of azeotropic mixtures by batch distillation using an entrainer. *Comput Chem Eng* 1995; 19: 113–118.
- Fien G-JAF, Liu YA. Heuristic synthesis and shortcut design of separation processes using residue curve maps: a review. *Ind Eng Chem Res* 1994; 33: 2505–2522.
- Frits ER, Lelkes Z, Fonyó Z, Rév E, Markót MC, Csédes T. Finding limiting flows of batch extractive distillation with interval arithmetic. *AIChE J* 2006; 52: 3100–3108.
- Hilmen E, Kiva V, Skogestad S. Topology of ternary VLE diagrams: elementary cells. *AIChE J* 2003; 48: 752–759.
- Hunek J, Gal S, Posel F, Glavič P. Separation of an azeotropic mixture by reverse extractive distillation. *AIChE J* 1989; 35: 1207–1210.
- Jiménez L, Wanhshafft O, Julka V. Analysis of residue curve maps of reactive and extractive distillation units. *Comp Chem Eng* 2001; 25: 635–642.
- Kiss AA, Suszwalak DJ. Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing-wall columns. *Sep Purif Technol* 2012; 86: 70–78.
- Kiva V, Hilmen E, Skogestad S. Azeotropic phase equilibrium diagrams: a survey. *Chem Eng Sci* 2003; 58: 1903–1953.
- Knapp JP, Doherty MF. Thermal integration of homogeneous azeotropic distillation sequences. *AIChE J* 1990; 36: 969–983.
- Knapp JP, Doherty MF. Minimum entrainer-feed flows for extractive distillation: a bifurcation theoretic approach. *AIChE J* 1994; 40: 243–268.
- Kossack, S, Kraemer K, Gani R, Marquardt W. A systematic synthesis framework for extractive distillation processes. *Chem Eng Res* 2008; 86: 781–792.
- Kotai B, Lang P, Modla G. Batch extractive distillation as a hybrid process: separation of minimum boiling azeotropes. *Chem Eng Sci* 2007; 62: 6816–6826.
- Lang P, Modla G. Generalised method for the determination of heterogeneous batch distillation regions. *Chem Eng Sci* 2006; 61: 4262–4270.
- Lang P, Yatim H, Moszkowicz P, Otterbein M. Batch extractive distillation under constant reflux ratio. *Comput Chem Eng* 1994; 18: 1057–1069.
- Lang P, Lelkes Z, Otterbein M, Benadda B, Modla G. Feasibility studies for batch extractive distillation with a light entrainer. *Comput Chem Eng* 1999; 23: S93–S96.
- Lang P, Modla G, Benadda B, Lelkes Z. Homoazeotropic distillation of maximum azeotropes in a batch rectifier with continuous entrainer feeding I. Feasibility studies. *Comput Chem Eng* 2000a; 24: 1665–1671.
- Lang P, Modla G, Kotai B, Lelkes Z, Moszkowicz P. Homoazeotropic distillation of maximum azeotropes in a batch rectifier with continuous entrainer feeding II. Rigorous simulation results. *Comput Chem Eng* 2000b; 24: 1429–1435.
- Lang P, Kovacs GY, Kotai B, Gaal-Szilagyi J, G, Modla G. Industrial application of a new batch extractive distillation operational policy. *Distillation & Absorption, IChemE Symposium*, 2006.
- Lang P, Hegely L, Kovacs GY, Gaal-Szilagyi J, Kotai B. Solvent recovery from a multicomponent mixture by batch extractive distillation and hybrid process. In *Proceedings of Distillation & absorption 2010, Eindhoven, The Netherlands, 2010; September 12-15*, 295–300.
- Laroche L, Bekiaris N, Andersen HW, Morari M. The curious behavior of homogeneous azeotropic distillation – implications for entrainer selection. *AIChE J* 1992; 38: 1309–1328.
- Lelkes Z, Lang P, Benadda B, Moszkowicz P. Feasibility of extractive distillation in a batch rectifier. *AIChE J* 1998a; 44: 810–822.
- Lelkes Z, Lang P, Moszkowicz P, Benadda B, Otterbein M. Batch extractive distillation: the process and the operational policies. *Chem Eng Sci* 1998b; 53: 1331–1348.
- Lelkes Z, Rev E, Steger C, Fonyo Z. Batch extractive distillation of maximal azeotrope with middle boiling entrainer. *AIChE J* 2002; 48: 2524–2536.

- Levy SG, Doherty MF. Design and synthesis of homogeneous azeotropic distillations. 4. Minimum reflux ratio calculations for multiple-feed columns. *Ind Eng Chem Fundam* 1986; 25: 269–279.
- Levy SG, Van Dongen DB, Doherty MF. Design and synthesis of homogeneous azeotropic distillations. 2. Minimum reflux ratio calculations for non ideal and azeotropic columns. *Ind Eng Chem Fundam* 1985; 24: 463–474.
- Lucia A, Amale A, Taylor R. Distillation pinch points and more. *Comp Chem Eng* 2008; 32: 1342–1364.
- Luyben WL. Effect of solvent on controllability in extractive distillation. *Ind Eng Chem Res* 2008a; 47: 4425–4439.
- Luyben WL. Comparison of extractive distillation and pressure-swing distillation for acetone-methanol separation. *Ind Eng Chem Res* 2008b; 47: 2696–2707.
- Petlyuk F, Danilov R, Skouras S, Skogestad S. Identification and analysis of possible splits for azeotropic mixtures. 2. Method for column sections. *Chem Eng Sci* 2011; 66: 2512–2522.
- Petlyuk F, Danilov R, Skouras S, Skogestad S. Identification and analysis of possible splits for azeotropic mixtures. 2. Method for simple columns. *Chem Eng Sci* 2012; 69: 159–169.
- Pham HN, Doherty MF. Design and synthesis of heterogeneous azeotropic distillations – III. Column sequences. *Chem Eng Sci* 1990; 4: 1845–1854.
- Poellmann P, Blass E. Best products of homogeneous azeotropic distillations. *Gas Sep Purif* 1994; 8: 194–228.
- Rév E, Lelkes Z, Varga V, Stéger C, Fonyo Z. Separation of a minimum-boiling azeotrope in a batch extractive rectifier with an intermediate-boiling entrainer. *Ind Eng Chem Res* 2003; 42: 162–174.
- Rodriguez-Donis I, Papp K, Rev E, Lelkes Z, Gerbaud V, Joulia X. Column configurations of continuous heterogeneous extractive distillation. *AIChE J* 2007; 53: 1982–1993.
- Rodriguez-Donis I, Gerbaud V, Joulia X. Thermodynamic insights on the feasibility of homogeneous batch extractive distillation, 1. Azeotropic mixtures with a heavy entrainer. *Ind Eng Chem Res* 2009a; 48: 3544–3559.
- Rodriguez-Donis I, Gerbaud V, Joulia X. Thermodynamic insights on the feasibility of homogeneous batch extractive distillation, 2. Low-relative-volatility binary mixtures with a heavy entrainer. *Ind Eng Chem Res* 2009b; 4: 3560–3572.
- Rodriguez-Donis I, Gerbaud V, Joulia X. Thermodynamic insight on extractive distillation with entrainer forming new azeotropes. In *Proceedings of Distillation & absorption 2010*, Eindhoven, The Netherlands, 2010; September 12–15, 431–436.
- Rodriguez-Donis I, Gerbaud V, Joulia X. Thermodynamic Insights on the feasibility of homogeneous batch extractive distillation. 3. Azeotropic mixtures with light entrainer. *Ind Eng Chem Res* 2012a; 51: 4643–4660.
- Rodriguez-Donis I, Gerbaud V, Joulia X. Thermodynamic insights on the feasibility of homogeneous. batch extractive distillation. 4. Azeotropic mixtures with intermediate boiling entrainer. *Ind Eng Chem Res* 2012b; 51: 6489–6501.
- Ryan PJ, Doherty MF. Design optimization of ternary heterogeneous azeotropic distillation sequences. *AIChE J* 1989; 35: 1592–1601.
- Safrit BT, Westerberg AW. Improved operational policies for batch extractive distillation columns. *Ind Eng Chem Res* 1997; 36(2): 436–443.
- Serafimov LA. Thermodynamic and Topological Analysis of Liquid-Vapor Phase Equilibrium Diagrams and Problems of Rectification of Multicomponent Mixtures. *Mathematical Methods in Contemporary Chemistry*, S.I. Kuchanov (Ed.) Gordon and Breach Publishers, Amsterdam 1996; 557–605.
- Shen WF, Gerbaud V. Extension of thermodynamic insights on batch extractive distillation to continuous operation. 2. Azeotropic mixtures with a light entrainer. *Ind Eng Chem Res* 2013; 52: 4623–4637.
- Shen WF. Extension of thermodynamic insights on batch extractive distillation to continuous operation. PhD Thesis, Institut National Polytechnique de Toulouse, 2012.
- Shen WF, Benyounes H, Gerbaud V. Extension of thermodynamic insights on batch extractive distillation to continuous operation. 1. Azeotropic mixtures with a heavy entrainer. *Ind Eng Chem Res* 2013; 52: 4606–4622.
- Stéger C, Vargaa V, Horvath L, Rév E, Fonyo Z, Meyerc M, Lelkes Z. Feasibility of extractive distillation process variants in batch rectifier column. *Chem Eng Process* 2005; 44: 1237–1256.
- Stichlmair JG, Fair JR. *Distillation Principles and Practices*. New York: Wiley-VCH, 1998.
- Sun L, Wang Q, Li L, Zhai J, Liu Y. Design and control of extractive dividing wall column for separating benzene/cyclohexane mixtures. *Ind Eng Chem Res* 2014; 53: 8120–8131.
- Urdaneta RY, Bausa J, Brüggemann S, Marquardt W. Analysis and conceptual design of ternary heterogeneous azeotropic distillation processes. *Ind Eng Chem Res* 2002; 41: 3849–3866.
- Varga V, Fritts ER, Gerbaud V, Fonyo Z, Joulia X, Lelkes Z, Rev E. Separation of azeotropes in batch extractive stripper with intermediate entrainer. 16th European Symposium on Computer Aided Process Engineering and 9th International Symposium on Process Systems Engineering Garmisch-Partenkirchen, Germany, Elsevier, 2006; 21: 793–797.
- Varga V, Rev E, Gerbaud V, Fonyo Z, Joulia X. Batch extractive distillation with light entrainer. *Chem Biochem Eng Q* 2006; 20: 1–23.
- Wahnschafft OM, Koehler J, Blass E, Westerberg AW. The product composition regions of single-feed azeotropic distillation columns. *Ind Eng Chem Res* 1992; 31: 2345–2362.
- Warter M, Demicoli D, Stichlmair J. Operation of a batch distillation column with a middle vessel: experimental results for the separation of zeotropic and azeotropic mixtures. *Chem Eng Process* 2004; 43: 263–272.
- Wittgens B, Litto R, Sørensen E, Skogestad S. Total reflux operation of multivessel batch distillation. *Comput Chem Eng* 1996; 20: S1041–S1046.
- Xia M, Yu B, Wang Q, Jiao H, Xu C. Design and control of extractive dividing-wall column for separating methylal/methanol mixture. *Ind Eng Chem Res* 2012; 51: 16016–16033.
- Xia M, Xin Y, Luo J, Li W, Shi L, Min Y, Xu C. Temperature control for extractive dividing-wall column with an adjustable vapor split: methylal/methanol azeotrope separation. *Ind Eng Chem Res* 2013; 52: 17996–18013.
- Yatim H, Moszkowicz P, Otterbein M, Lang P. Dynamic simulation of a batch extractive distillation process. *Comput Chem Eng* 1993; 17: 57–62.
- Zhang H, Ye Q, Qin J, Xu H, Li N. Design and control of extractive dividing-wall column for separating ethyl acetate-isopropyl alcohol mixture. *Ind Eng Chem Res* 2014; 53: 1189–1205.

Bionotes



Weifeng Shen

Université de Toulouse, INP, UPS, LGC (Laboratoire de Génie Chimique), 4 allée Emile Monso, F-31432 Toulouse Cedex 04, France; CNRS, LGC (Laboratoire de Génie Chimique), F-31432 Toulouse Cedex 04, France; and Chemical and Biomolecular Engineering, Clarkson University, Potsdam, NY, USA

Weifeng Shen obtained his PhD in 2012 with a focus on extractive distillation at University of Toulouse, France, funded by National Natural Science Foundation of China. He has been working in the group of Prof. Ross Taylor at Clarkson University as a research associate since 2012. He received his master's degree in chemical engineering at Chongqing University, China. His current research interests focus on modeling, simulation, design, optimization of extractive distillation, reactive distillation, DWC, and natural gas treating.



Hassiba Benyounes

U.S.T. Oran, Laboratoire de Chimie Physique des Matériaux, Catalyse et Environnement, Oran, Algérie

Hassiba Benyounes has been an assistant professor at the Department of Chemical Engineering of University of Science and Technology of Oran, Algeria, since 2004. She received her PhD degree in chemical engineering in 2003 from State Academy of Fine Chemical Technology M.V. Lomonossov, Moscow, Russia. Her main research fields are distillation, extractive distillation, thermodynamics, computer-aided simulation, and design of chemical processes. She is a member of Laboratory of Physical Chemistry, Material, and Environnement in Algeria and collaborates with the research group of Prof. Xavier Joulia at the Laboratory of Chemical Engineering of Toulouse.



Vincent Gerbaud

Université de Toulouse, INP, UPS, LGC (Laboratoire de Génie Chimique), 4 allée Emile Monso, F-31432 Toulouse Cedex 04, France; and CNRS, LGC (Laboratoire de Génie Chimique), F-31432 Toulouse Cedex 04, France

Vincent.Gerbaud@ensiacet.fr

Vincent Gerbaud is a research director at the French National Scientific Research Center CNRS at Laboratoire de Génie Chimique in Toulouse. His research field concerns modeling and simulation in process system engineering, with a strong interest in small-scale modeling: molecular simulation, thermodynamics, computer-aided molecular and mixture design. At the process scale, he has published over 25 articles related to the design and synthesis of extractive and azeotropic distillation for nonideal mixture purification, with a particular interest in thermodynamic insight useful for the design of these processes.

Graphical abstract

Weifeng Shen, Hassiba Benyounes
and Vincent Gerbaud

**Extractive distillation: recent
advances in operation strategies**

DOI 10.1515/revce-2014-0031

Review: This paper provides an overview of thermodynamic insight, pinch-point analysis, process operation policies, and different configuration strategies in continuous or batch extractive distillation columns.

Keywords: batch; bifurcation theory; continuous; extractive distillation; operation strategies; thermodynamic analysis.

