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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

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:

$$\frac{dx_i}{dh} = x_i - y_i^*$$  \hspace{1cm} (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 (Wahnschaft 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:

$$K_i = \frac{y_i}{x_i}$$

(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](image-url) Features of (A) singular point and (B) RCM.
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 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 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 $\alpha_{\text{un}} = 1$ 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) (Brüggemann 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 $F_{\text{p}}$, 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.

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

<table>
<thead>
<tr>
<th>Entrainer type</th>
<th>Azeotrope type</th>
<th>Class</th>
<th>Volatility order</th>
<th>Case study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy</td>
<td>Minimum</td>
<td>1.0-1a</td>
<td>A&gt;B&gt;A&gt;E</td>
<td>Acetone</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>Acetone</td>
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<td>Acetone</td>
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<td></td>
<td></td>
<td>Acetone</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>1.0-2</td>
<td>A&gt;B&gt;A&gt;E</td>
<td>Acetone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Acetone</td>
</tr>
<tr>
<td></td>
<td>Low alpha</td>
<td>0.0-1</td>
<td>A&gt;B&gt;E</td>
<td>Vinyl acetate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Heptane</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td></td>
<td>Intermediate</td>
<td>1.0-1b</td>
<td>A&gt;B&gt;A&gt;E</td>
<td>Methyl acetate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Methanol</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>1.0-1b</td>
<td>A&gt;B&gt;A&gt;E</td>
<td>Chloroform</td>
</tr>
<tr>
<td></td>
<td>Light</td>
<td>1.0-2</td>
<td>E&gt;A&gt;B&gt;A</td>
<td>Ethanol</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ethanol</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Methyl ethyl ketone</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>1.0-1a</td>
<td>E&gt;A&gt;B&gt;A</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Acetone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Propanoic acid</td>
</tr>
<tr>
<td></td>
<td>Low alpha</td>
<td>0.0-1</td>
<td>E&gt;A&gt;B</td>
<td>Chlorobenzene</td>
</tr>
</tbody>
</table>

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=const. policy is modified by shortening the second preparatory step of the BED (R=∞, F>0). The possibilities of performing a constant distillate composition (x_D,A=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 tetrahydrofuran 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_{ext}) 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 azeotrope 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).

<table>
<thead>
<tr>
<th>Extractive distillation of ternary mixture systems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Entrainer type</strong></td>
</tr>
<tr>
<td><strong>Mixture</strong></td>
</tr>
<tr>
<td><strong>Low alpha</strong></td>
</tr>
<tr>
<td><strong>Serafimov class</strong></td>
</tr>
<tr>
<td><strong>Volatility Order</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analysis of operating steps with configuration BED-I</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adding entrainer in advance</strong></td>
</tr>
<tr>
<td><strong>Startup</strong></td>
</tr>
<tr>
<td><strong>Purification</strong></td>
</tr>
<tr>
<td><strong>First product</strong></td>
</tr>
<tr>
<td><strong>Second product</strong></td>
</tr>
<tr>
<td><strong>Third product</strong></td>
</tr>
<tr>
<td><strong>Reloading</strong></td>
</tr>
<tr>
<td><strong>Fourth product</strong></td>
</tr>
<tr>
<td><strong>Fifth product</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Limitation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reflux ratio</strong></td>
</tr>
<tr>
<td><strong>N_{max} (rect. stage)</strong></td>
</tr>
<tr>
<td><strong>N_{min} (extr. stage)</strong></td>
</tr>
<tr>
<td><strong>F/V (entrainer-feed flow rate ratio)</strong></td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Entrainer type</th>
<th>Heavy</th>
<th>Intermediate</th>
<th>Light</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture</td>
<td>Minimum</td>
<td>Maximum</td>
<td>Low alpha</td>
</tr>
</tbody>
</table>

Analysis of operating steps with configuration BES-I

Operating steps – BES-I

1. Startup  s=∞; +F  s=∞; +F  s=∞; +F  s=∞; +F  s=∞; F=0  s=∞; F=0  s=∞; +F
2. Purification – – – – – – –
3. Production  s<∞; F>0  s<∞; F>0  s<∞; F>0  s<∞; F>0  s<∞; F=0  s<∞; F=0  s<∞; F>0  s<∞; F>0  s<∞; F=0
4. Cutting  s<∞; F>0  s<∞; F>0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0
5. Production  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0
6. Production  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0  s<∞; F=0


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 5B). 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

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**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).
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
the case when both the entrainer and feed are premixed to
the boiler in batch mode (see Figure 6A) and BED-B con-
figuration occurs when the entrainer is fed to the boiler
continuously (see Figure 6B); (2) there are existing extrac-
tive 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 loca-
tion 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 con-
trolling 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 configu-
Rations. Warter et al. (2004) presented an experimental
investigation of azeotropic mixtures using batch distil-
lation 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 impu-
rities 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 dura-
tion of the process start-up. It also offers the possibility to
reduce the size of the reboiler. Wittgens et al. (1996) pro-
posed 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 com-
positions in all vessels satisfy their specifications. It had
been validated that the proposed control scheme is fea-
sible and easy to implement and operate by simulations
and experiment.

6 Conclusions

This paper has focused on reviewing key operation poli-
cies and strategies, including thermodynamic insight,
pinch-point analysis, and several configurations, depend-
ing 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,
unvolatility and unidistribution curves, and some topo-
logical character analysis. Pinch-point analysis concerns
the knowledge of bifurcation theory, and the key param-
eters 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 con-
figurations combining the entrainer recycle stream and
the main azeotropic feed, several configurations and tech-
nological 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


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

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**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.