Batch Extractive Distillation of Maximal Azeotrope with Middle Boiling Entrainer

Z. Lelkes, E. Rev, C. Steger, and Z. Fonyo
Chemical Engineering Dept., Budapest University of Technology and Economics, H-1521 Budapest, Hungary

Separation of maximum boiling azeotropes using batch extractive distillation (BED) is feasible in a rectifying column with intermediate boiling entrainer. The main difference between BED and solvent-enhanced batch distillation (SBD) is the application of continuous entrainer feeding to the column or still. Finding a well-working intermediate boiling entrainer is more difficult than finding a heavy or light entrainer. The test mixture, selected according to didactic viewpoints, is chloroform and ethyl acetate with 2-chlorobutane. Operation steps (sequencing), limiting flows, and limiting stage numbers are determined by a feasibility study, based on profile maps; the design is validated by rigorous simulation. Results of parametric studies and comparison of SBD and BED, according to effectiveness, are presented. Separation of maximum boiling azeotropes in SBD and BED is feasible with an intermediate boiling entrainer, but the application of continuous feeding (characteristic to BED) makes the process more efficient. Pure-component A cannot be produced in SBD or BED, but producing component A mixed with entrainer and free of component B is feasible in both processes. The operation steps are similar in the two processes except for continuous feeding of the entrainer in step 2 of BED. With identical specification and comparable operation parameters, BED produces the same products in a shorter time and with a significantly smaller amount of maximum holdup in the still.

Introduction

Several suggestions can be found in the literature for batch separation of minimum or maximum boiling binary azeotropes using an entrainer. According to Laroche et al. (1991), the entrainer for homoazeotropic distillation can be the lightest, the heaviest, or even the intermediate boiling component in the system. Even heteroazeotropic distillation can be used; see, for example, Rodriguez et al. (2001).

Finding a well-working intermediate boiling entrainer is more difficult than finding either a heavy or a light entrainer and, consequently, the intermediate boiling entrainer actually found might be inferior to the others. On the other hand, a good intermediate boiling entrainer also has merits compared to the others. The most significant reason to study intermediate boiling entrainers is the opportunity of having an intermediate boiling component in the mixture to be separated. In that case, the intermediate boiling component may be the best choice because no other, foreign, component is then applied.

The use of an intermediate boiling entrainer in the batch is discussed by Bernot et al. (1991). According to their suggestions, maximum-boiling azeotropes can be separated in a batch rectifier (Figure 1), after mixing an intermediate boiling entrainer with the charge.

In the case of a maximum boiling azeotrope, the full composition triangle constitutes a single distillation region in the sense of simple distillation (Figure 2); thus, the mixture can, in principle, be separated. The first fraction is (the lighter) component A, the second one is the (intermediate boiling) entrainer E, and the third product is (the heavier) component B in the residue in the case of applying infinite reflux ratio and an infinite number of stages. However, as those extreme conditions are not satisfied, the third fraction is pure B, and the residue contains an azeotropic mixture.

The suggestions of Bernot et al. (1991) are based on analysis of the residue curve map (RCM). This analysis involves the assumptions of the infinite reflux ratio (equivalent to zero product flow rate in the case of batch distillation) and an infinite number of theoretical stages. No particular mixture is mentioned.

Correspondence concerning this article should be addressed to E. Rev.

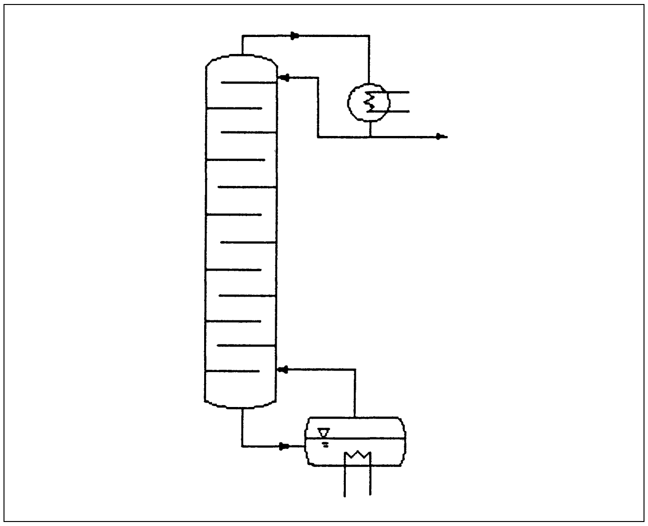


Figure 1. Batch rectifier.

Batch extractive distillation (BED) is another batch process using entrainer for separating azeotropes. The entrainer is continuously fed to the unit, either to the column or to the still (or other vessel); thus, BED is a semicontinuous or semibatch process, see Figure 3. In contrast, the genuine batch distillation schemes that mix the entrainer with the charge in advance, like those suggested by Bernot et al. (1991), here will be called Solvent-enhanced batch distillation (SBD). Depending on the application of the rectifier, stripper, or a middle vessel column (Safrit et al., 1995; Cheong and Barton, 1999; Warter and Stichlmair, 1999; Phimister and Seider, 2000) versions of BED can also be distinguished; however, here we will simply use the term BED for batch extractive distillation in a rectifier.

Several versions of BED have already been studied and published. Separation of both minimum and maximum boiling azeotropes with BED using a heavy entrainer is studied by Lang et al. (1994), Lelkes et al. (1998a,b), Lang et al. (2000a,b). Separation of minimum boiling azeotropes with BED using a light entrainer was studied by Lelkes et al. (1998c) and Lang et al. (1999). The simulations and experimental work include the following mixtures and entrainers in BED: with a heavy entrainer, minimum boiling azeotrope: acetone and methanol with either water, isopropanol, ethanol, or chlorobenzene; low relative volatility mixture: benzene and toluene with phenol; maximum boiling azeotrope: acetone and chloroform with either benzene or toluene; minimum boiling azeotrope in BED with a light entrainer: ethanol and water with methanol. Additionally, minimum boiling azeotropes with a light entrainer in batch extractive stripper have also been studied: ethanol and water with methanol, and *n*-butanol and *n*-butyl acetate with *n*-propyl formate or di-propylether.

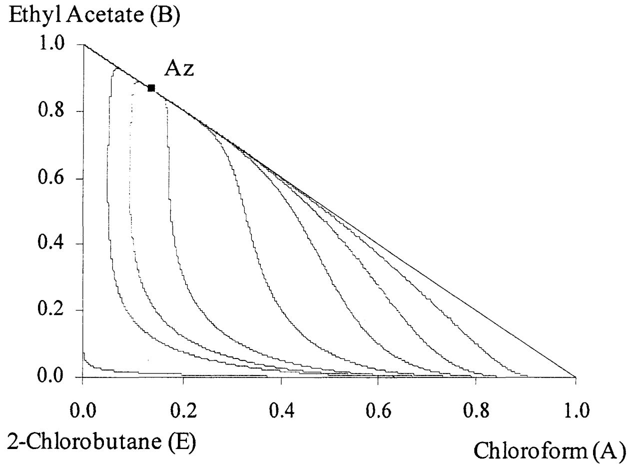


Figure 2. Residue curve map of the studied system: a maximum boiling azeotrope with intermediate boiling entrainer.

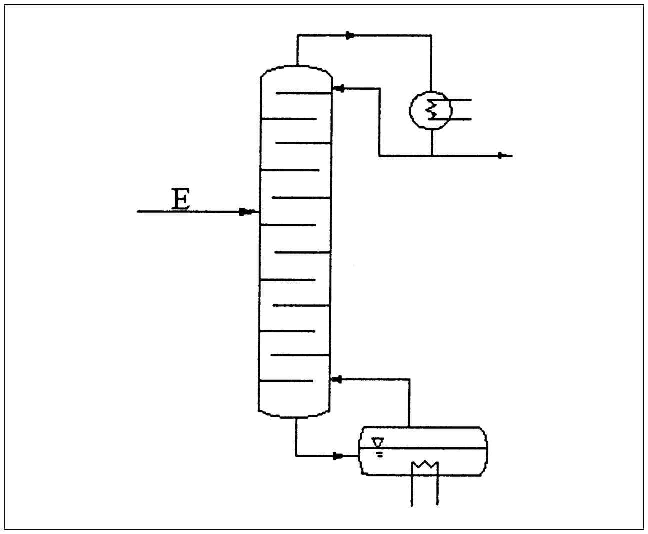


Figure 3. Batch extractive distillation (BED) in a rectifier.

According to our best knowledge, BED with an intermediate boiling entrainer has not been studied or published yet. In this article, separation of maximum boiling azeotropes in BED using an intermediate boiling entrainer is analyzed. The mixture studied is chloroform and ethyl acetate with 2-chlorobutane. Operation steps (sequencing), limiting flows, and limiting stage numbers are determined by a feasibility study; the design is checked by rigorous simulation; the effects of the design parameters are plotted; and SBD and BED are compared according to effectiveness.

Separation of minimum boiling azeotropes in BED with an intermediate boiling entrainer, namely methyl acetate and cyclohexane with carbon tetrachloride, is also studied and will be published elsewhere (Lelkes et al., 2002).

Methodology

Feasibility method

The first step in studying the opportunity of applying an entrainer in BED is testing its feasibility using the simplified tools developed by Lelkes et al. (1998b). Here we reiterate the essential steps and ideas of the feasibility method, because they are applied in the subsequent sections.

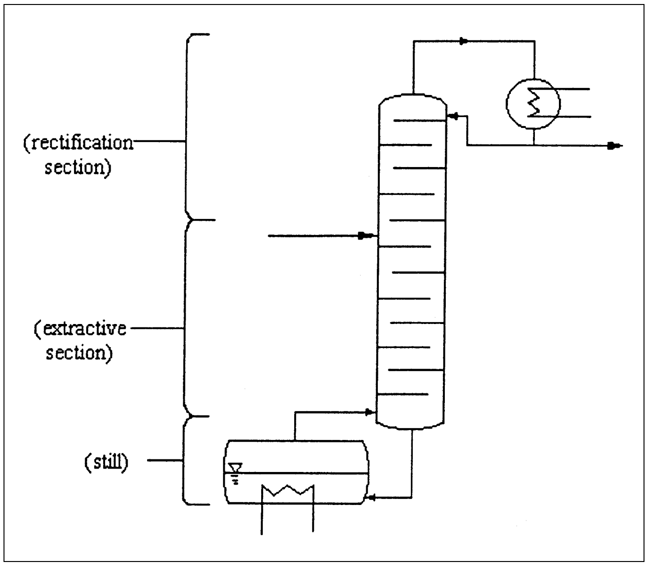


Figure 4. Sections of BED.

The batch rectifier is divided into three main sections (Figure 4). From the bottom up, these are (1) the still; (2) the extractive section, including all the stages above the still up to and including the feed stage; and (3) the rectification section, which consists of all the stages above the feed and the condenser with the reflux divider.

The feasibility analysis is based on calculating and analyzing the instantaneous concentration profile maps of the column's rectification and extractive sections, plus analysis of the still path. The still path is the trajectory (that is, projection to the composition triangle) of the still composition in time. Throughout this analysis, the following simplification is applied:

- No holdup is taken into account (that is, zero holdup is considered).
- Column dynamics are approached via steady states.
- Constant molar overflow is applied in the model.
- The feed and the reflux streams are at the boiling point.
- No pressure drop along the column or in the condenser is taken into account.

Composition profiles in the column sections are computed by solving the following differential equation:

$$\frac{dx}{dh} = \pm \frac{V}{L}[y(x) - y^*(x)] \tag{1}$$

where h is dimensionless column height; y is computed according to the component balances, that is, the so-called operating lines, whereas y^* is the equilibrium vapor composition belonging to the liquid composition x. The vapor-to-liquid ratio (V/L) is determined from the molar balance in the corresponding column section.

The operating line of the rectification section is identical to the conventional "upper operating line" of the continuous distillation

$$y = \frac{(V - D)x + Dx_D}{V} \tag{2}$$

whereas the component balance called "operating line" of the extractive section involves the feed-component flow rates that are all considered in the liquid flow

$$y = \frac{(V + F - D)x - Fz + Dx_D}{V} \tag{3}$$

Equation 1 is an initial-value problem. Computation of any rectification profile starts at some specified distillate flow composition (x_D) as an initial condition. Computation of any extractive profile starts at some specified still composition (x_S) as an initial condition. Thus, computation of the two profiles is performed in opposite directions. Integration along the column height is performed with the appropriate sign, accordingly. The actual composition along the column height is not recorded, but the composition trajectories are analyzed.

The still path is computed by solving the following differential component balance (initial-value problem)

$$\frac{d(H_S x_S)}{dt} = Fz - Dx_D \tag{4}$$

where the initial condition is $x_S(t_0) = x_{Ch}$. The composition trajectory is analyzed. However, some periods belonging to reaching at some feasibility boundary or other characteristic composition is recorded and applied in the design.

Feasibility of BED or SBD, as a notion, can be defined in two different but related senses.

In the principal (or marginal) sense, the separation is feasible if the specified product compositions can be reached, irrespective of the recovery ratio or the product flow rate. Thus, the separation is feasible in the principal or marginal sense even if the product composition can be reached with no more than zero recovery and a zero product flow rate (that is, infinite reflux ratio) and, perhaps, an infinite number of stages. In some cases, an infinite amount of entrainer or infinite operating time is needed to produce the specified product composition. According to this idea, the necessary and sufficient condition of feasibility is the existence of a steady-state column profile connecting a point of the still path to the specified distillate composition. The column profile may consist of just a rectification profile or it may consist of an extractive profile extended by a rectification profile.

In this principal or marginal sense, all the BED and SBD configurations are feasible unless there is a perfectly straight separatrix in the system. By applying this definition, however, we can determine the limiting design and/or operating parameters.

In a practical sense, however, the separation is feasible if a range of design and operational parameters exists in such a way that the product specifications can be reached with reasonable or justifiable recovery, time, amount of entrainer, number of stages, and reflux ratio. This range can also be explored by analyzing the profile maps and the still path computed with various reflux ratios, feed-to-vapor flow-rate ratios, and, in some cases, entrainer premix ratios.

Marginal feasibility, together with a preliminary suggestion of the operational steps (product sequencing) is determined by analyzing the profile maps calculated with the infinite re-

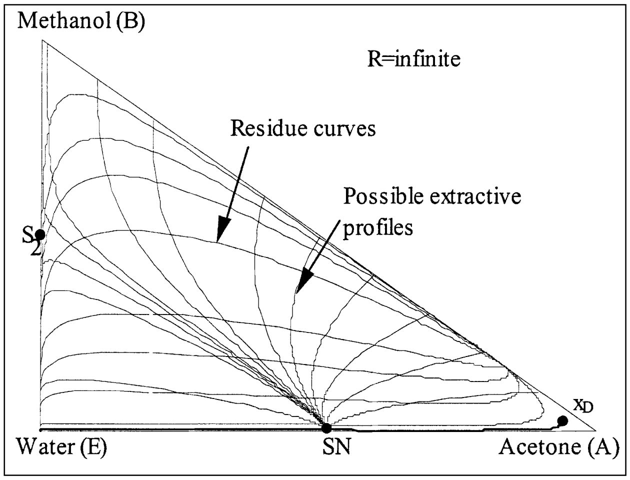


Figure 5. Profile maps of a minimum boiling azeotropic system with heavy entrainer, at total reflux.

flux ratio. In that case, the rectification profile map is identical to the residue curve map of the system.

For example, profile maps with the infinite reflux ratio ($R = \infty$), $V = 0.048$ mol/s vapor flow rate, $F = 30$ cm^3/s pure entrainer feed flow rate, and specified distillate composition $\boldsymbol{x}_D = [0.94,\ 0.025,\ 0.035]$, are shown in Figure 5 for an atmospheric system of acetone and methanol, forming a minimum boiling azeotrope, with the heavy boiling water as the entrainer. The separation is feasible with the listed parameters, including $R = \infty$ and $F/V \approx 0.5$, because all the extractive profiles run to the neighborhood of SN, and there is a rectification profile crossing $\boldsymbol{x}_D$ and crossing practically all the extractive profiles near SN. According to the preceding profile map, the operation steps of this separation may be the following

(1) Heatup, $R = \infty$, $F = 0$

(2) Runup, $R = \infty$, $F > 0$

(3) Production of component A, $R < \infty$, $F > 0$

(4) Production of component B, and regeneration of the entrainer, $R < \infty$, $F = 0$.

In the spirit of Safrit et al. (1995), the feasible region of the separation is the set of feasible still compositions, according to the definition of Lelkes et al. (1998b).

Equilibrium model

The vapor–liquid equilibria are calculated using the modified Raoult–Dalton equation

$$y_i^* p = \gamma_i(T,\boldsymbol{x}) x_i p_i^o(T) \tag{5}$$

Neither the Poynting correction or vapor-phase nonideality is taken into account.

The vapor pressure $p^o(T)$ of pure components is calculated using the three-parameter Antoine equation

$$\log p^o = A - \frac{B}{T + C} \tag{6}$$

with a 10-base logarithm, mercury millimeter (Hgmm) (that is, torr) for pressure, and centigrade (C) for temperature.

The liquid-phase activity coefficients $\gamma_i(T,\boldsymbol{x})$ ($i \in$ A,B,E) are calculated using the NRTL model (Renon and Prausnitz, 1968)

$$\ln \gamma_i = \frac{\sum\limits_j \tau_{ji} G_{ji} x_j}{\sum\limits_k G_{ki} x_k} + \sum_j \frac{G_{ij} x_j}{\sum\limits_k G_{kj} x_k} \left[\tau_{ij} - \frac{\sum\limits_m \tau_{mj} G_{mj} x_m}{\sum\limits_k G_{kj} x_k} \right] \tag{7a}$$

$$\tau_{ij} \equiv \frac{A_{ij}}{RT} \tag{7b}$$

$$G_{ij} \equiv \exp\left(- \alpha_{ij} \frac{A_{ij}}{RT} \right) \tag{7c}$$

where the $\alpha_{ij} = \alpha_{ji}$ nonrandomness parameters are dimensionless, whereas the binary interaction parameters, A_{ij}, have a dimension of cal/mol. The Regnault constant (general gas constant) is taken with the value $R = 1.98721$ cal/(mol K).

Rigorous simulation

Simulations for testing the validity of the feasibility study, and the corresponding design and operating parameters for testing the effect of column holdup and simplified dynamics, as well as for comparing the effectiveness of different separation structures, have been performed using the Batch Distillation Unit, Simultaneous Correction model of the ChemCAD simulator, version 5.06. Results of the ChemCAD simulations were compared to results of test runs with the Batchfrac component of the AspenPlus simulator, version 10.2 (Batch Plus 2.2) when any doubt emerged about the numerical stability of the simulation. ChemCAD computes the process history as a series of steady states, whereas realistic dynamics are computed by AspenPlus.

Sample System

It is rather difficult to find an appropriate entrainer for maximum boiling azeotropes. The entrainer should have a similar interaction with one of the components like the two components to be separated have. However, such systems rarely occur, and two binary systems of such behavior are looked for.

The system of chloroform and ethyl acetate with 2-chlorobutane as the entrainer seems to be an appropriate example, although the entrainer is not as good as usually expected. The atmospheric boiling points are listed in Table 1. The interaction parameters are taken from Gmehling and Onken (1977), except for the binary mixture of chloroform and 2-chlorobutane, for which the vapor–liquid equilibrium mea-

Table 1. Atmospheric Boiling Points of Chloroform, Ethyl Acetate, and 2-Chlorobutane

	Boiling Point [C]
Chloroform (A)	61.7
2-Chlorobutane (E)	68.1
Ethyl acetate (B)	77.1
Azeotrope (A–B)	77.8

Table 2. Antoine Coefficients

	A	*B*	*C*
Chloroform (A)	6.95465	1170.966	226.232
2-Chlorobutane (E)	6.88177	1190.334	229.068
Ethyl acetate (B)	7.10179	1244.950	217.881

surement data are not found in the literature. NRTL binary interaction parameters for that pair are fitted to UNIFAC (Skjold-Jørgensen et al., 1979) estimations at atmospheric pressure. The Antoine coefficients and the NRTL parameters are listed in Tables 2 and 3.

Feasibility of Solvent-Enhanced Batch Distillation Providing Pure A

SBD is a simpler process than BED, so it might be preferred. In the case of SBD, determination of the separation sequence is based on the residue curve map. The residue curve map of the system studied is shown in Figure 2. There is no separatrix in the map; each curve connects the corner point of the lightest component A to the highest boiling point azeotropic composition. With an infinite reflux ratio and infinite number of stages, any internal point can be considered as a still composition and can be connected to A with a feasible column profile. Therefore, the SBD process is feasible. Based on the residue curve map, the following operation steps can be suggested:

Step 0. Mixing entrainer to the charge.

Step 1. Heatup.

Step 2. Producing pure A in the distillate.

Step 3. Regenerating pure E in the distillate; obtaining pure B in the still (residue).

The imagined process is illustrated in Figure 6. Suppose the azeotropic mixture in the charge, the composition obtained by mixing the entrainer with it (step 0) provides a new composition along the straight line connecting the azeotrope with corner E. After heating up the column (step 1), production of A can start. Step 2 is finished when the total amount of A is removed from the still, at which point, the still composition is somewhere on the B–E edge. Finally, (in step 3) the entrainer is distilled out, and component B is obtained as the residue. If, somehow, some component A remains in the still, then B can be distilled out, and the residue contains a small amount of the azeotrope (Bernot et al., 1991).

Rigorous simulations with ChemCAD have been performed to validate this process. However, moderately pure chloroform ($x_{AD} \geq 0.9$) could not be produced, even with a large number of theoretical stages and an unacceptably large reflux ratio. Two column profiles, one with $x_S = [0.1;\ 0.635;\ 0.265]$, and the other with $x_S = [0.05;\ 0.3175;\ 0.6325]$, are shown in Figure 7. In both cases, the column has $N = 100$ stages, $R = 70$ reflux ratio, and $Q = 1.5$ kW boil-up power. The molfractions of A in the distillate are 0.86 and 0.71, respectively. We concluded that pure product cannot be achieved in this way.

Table 3. NRTL Parameters

i-j	A_{ij}	A_{ji}	α_{ij}
A–E	857.97	−595.47	0.2216
A–B	375.569	−619.982	0.8704
E–B	118.613	16.088	0.3007

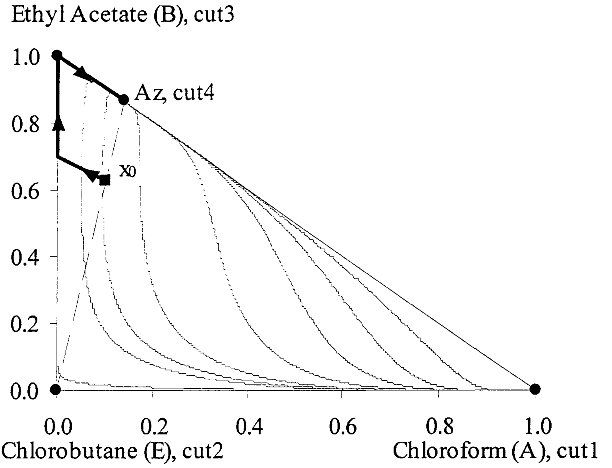


Figure 6. Sequencing of SBD, according to Bernot et al. (1991).

Feasibility of Batch Extractive Distillation Providing Pure A

According to the general feasibility methodology, the extractive profiles for a specified distillate composition, total reflux, and several feed ratios, are also computed, and are visualized together with the residue curve map. With an appropriate feed ratio, for example, $F/V = 0.2$, all the extractive profiles run into the same SN, as shown in Figure 8. The rectification profile started at some composition near pure A crosses these extractive profiles; therefore, pure A can be produced. According to this map, the separation is marginally feasible with the following operation steps:

Step 0. Mixing some entrainer to the charge.

Step 1. Heat-up.

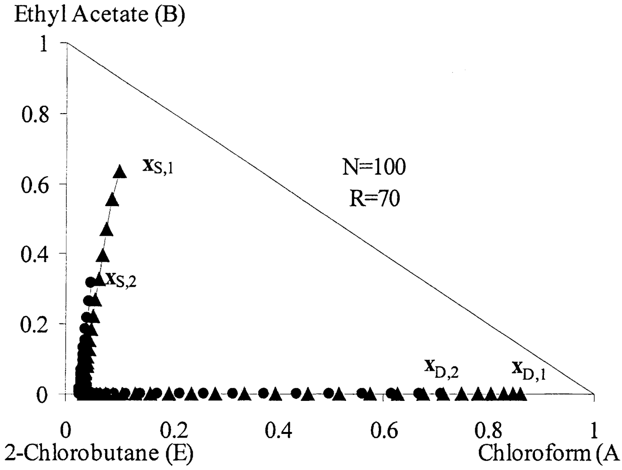


Figure 7. Two simulated column profiles of SBD, with extreme reflux ratio and column length.

The distillate is not pure enough.

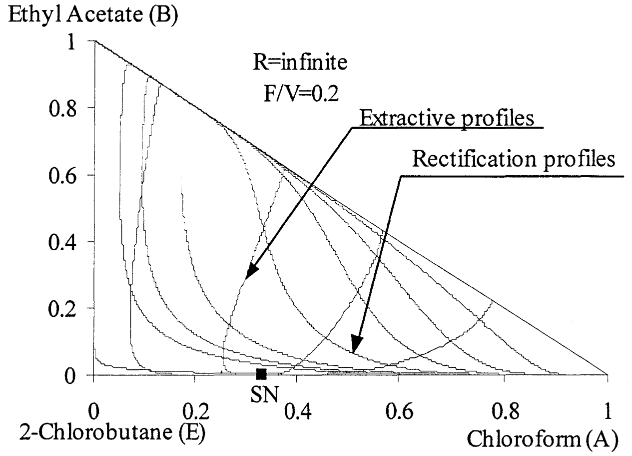


Figure 8. Profile maps of BED.

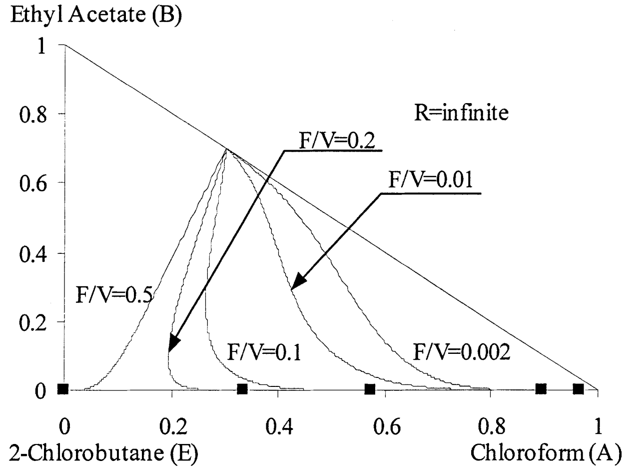


Figure 9. Single extractive profiles at different F/V ratios; there is no minimal F/V.

Step 2. Producing pure A in the distillate, with continuous feeding of E.

Step 3. Regenerating pure E in the distillate; obtaining pure B in the still (residue).

Effect of feed ratio

Single extractive profiles with different F/V ratios, but all with the same x_S, are shown in Figure 9. It can be seen that there is no minimal value of F/V; the process is (marginally) feasible without continuous feeding, as was already stated in the previous section and earlier by Bernot et al. (1991). The stable node moves on the A−E edge. The stable node is situated near corner E at higher feed ratios, whereas it is situated near corner A at lower ratios. The process is (marginally) feasible at any of these values. For a preliminary design, one has to make a trade-off between two high extractive sections and two high rectification sections; a value is to be selected so that SN is situated somewhere in the middle of the A−E edge. Therefore $F/V = 0.1$ or $F/V = 0.2$ seem to be appropriate choices.

Effect of reflux ratio

A series of figures (Figure 10) shows the effect of the reflux ratio on the extractive profiles at a given feed ratio. At decreasing reflux ratios, and a moderate feed ratio, an SN moves approximately along edge A−E. There is also an unstable node originating at the corner E and moving to the right. Both nodes move out of the composition triangle with decreasing R; the extractive profiles become increasingly parallel to the A−E edge. However, the process may be feasible even at low reflux ratios.

On the other hand, the rectification profiles are highly sensitive to the locus of the specified distillate composition. Three rectification profiles, each with a 0.95 molfraction of A in the distillate, are shown in Figure 11. Contamination of the distillate with component B is almost zero in all three cases, but a little bit different. Molfractions of B are, in turn, 10^{-4}, 10^{-14}, and 10^{-24}; the shapes of the rectification profiles are significantly different.

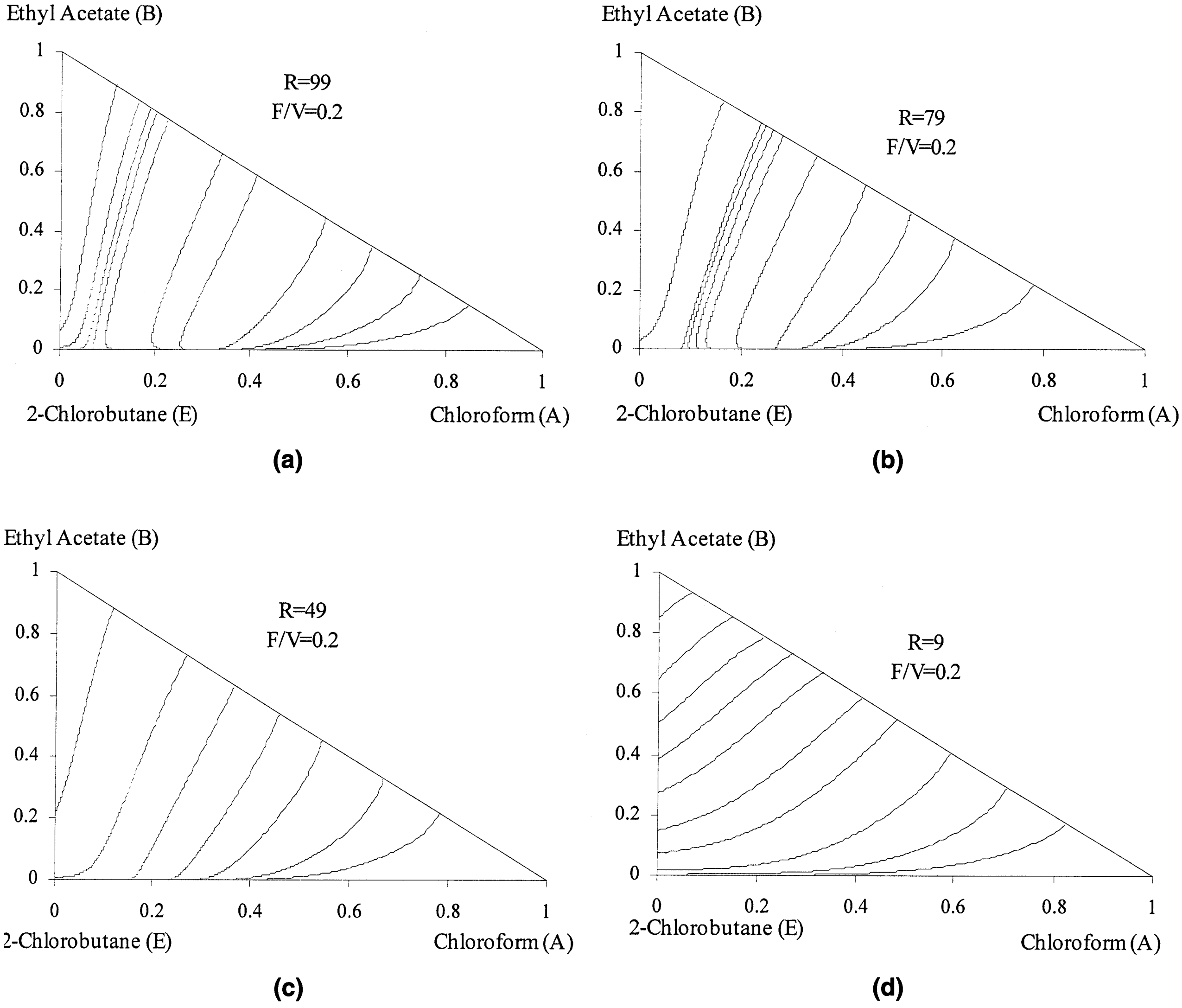
In order to explore the feasibility region even in this case of extreme sensitivity, a less strict specification is applied. Instead of specifying a single composition, a minimal molfraction of component A in the distillate is specified. This specification assigns a small triangle of acceptable distillate composition in the composition triangle, near corner A, as shown in Figure 12 at a rather high reflux ratio ($R = 49$) and $F/V = 0.2$. With this specification, the rectification profiles bundle assigns a region that can be reached by the rectifying section alone. Therefore, this is a feasible region of SBD. This means that the feasible still compositions should be situated inside, or on the border of, this region in order to reach the specified product purity with SBD.

The rectification profiles run to an almost common point, S_R in the A−B edge. By approximating the A−E edge with x_D, the rectification profiles approach a limit profile, also shown in Figure 12. The corresponding extractive profile tangent to this limit rectification profile is also shown in the figure. Compositions between the two lines and at the smaller E-content side of the tangent point (meeting point of the two curves) are also feasible still compositions in the case of BED, because each extractive profile that started from those points crosses some feasible rectification profile. However, compared to SBD, this is a rather small area within which BED increases the feasible region.

The feasible region shown in Figure 12 is valid at $R = 49$. Pure A can be produced only if the still composition is inside the feasible region. However, in this case the $B/(A+B)$ ratio in the still is under the azeotropic composition, even at this high reflux ratio. As a consequence, no still path can reach the B−E edge; pure B cannot be produced, and the entrainer cannot be regenerated. With lower reflux ratios, the feasible region is even smaller. We have to conclude that the specified purity cannot be achieved in a practical way, even if applying batch extractive distillation.

Feasibility of SBD and BED Providing Pure Products With an Extra Operation Step

Although pure A cannot be produced in the first production step, a mixture of A and E (chloroform and 2-chlorobutane) can be produced, and later separated. Product purity specification in this production step is to be defined accord-



(a) (b) (c) (d)

Figure 10. Extractive profiles at: (a) $R = 99$, (b) $R = 79$, (c) $R = 49$, and (d) $R = 9$.

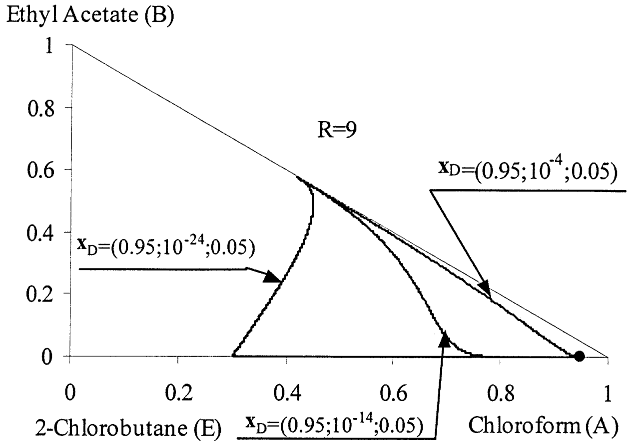


Figure 11. Three rectification profiles started almost from the same distillate composition.

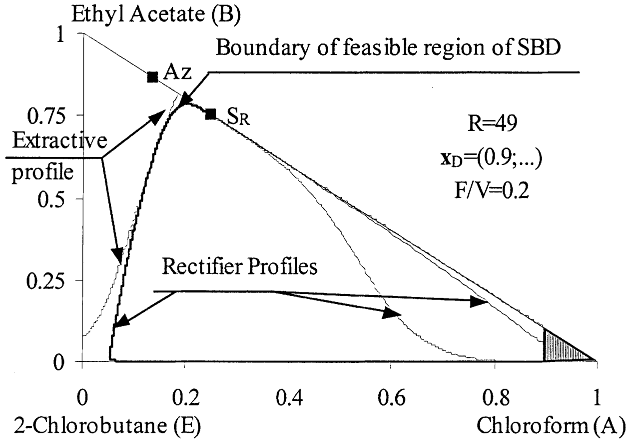


Figure 12. Feasible regions of SBD and BED for pure A as distillate.

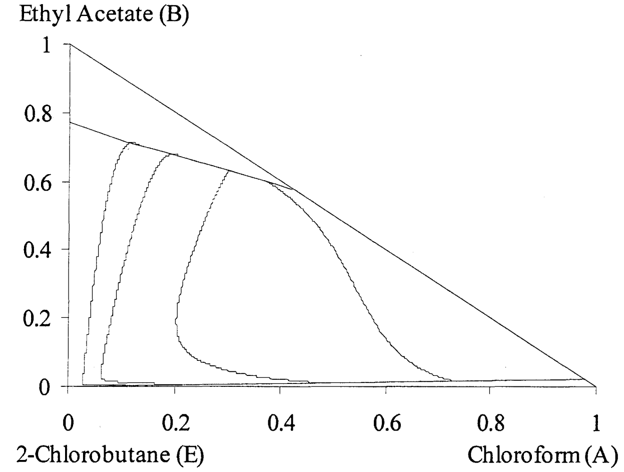


Figure 13. Rectification profiles and approximating boundary of the feasible region of SBD for mixed A + E as distillate.

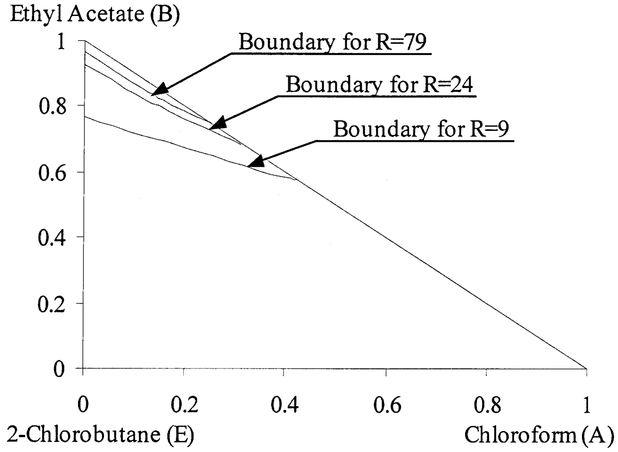


Figure 14. Feasibility boundaries of SBD depending on *R*.

ingly. In order to be able to obtain pure A in a later step, a reduced molfraction of A in the distillate is specified: $x_{AR} \equiv x_A/(x_A + x_B)$ in the distillate is to be greater than or equal to a specified value. With a high enough value, such as, $x_{AR} = 0.98$, this designates a narrow triangle along the A–E edge, as the range of acceptable distillate compositions. Definition of feasibility also has to be updated, accordingly. A composition (a point in the composition triangle) is considered feasible still composition if there is a column profile connecting it to the specified product purity region assigned by x_{AR}.

Feasibility of SBD

Depending on the actual distillate compositions, the rectification profiles run along different paths and run into different pinch points. The set of points touched by the rectification profiles constitutes a feasible region, as is shown in Figure 13. The set of pinch points is a good approximation of the feasibility boundary, because the profile curvatures do not pass very far beyond this approximating line. The feasible region reaches the B–E edge, and the separation is practically feasible with the following operation steps, applying SBD:

Step 0. Mixing some entrainer to the charge.

Step 1. Heatup.

Step 2. Producing A–E mixture in the distillate.

Step 3. Separating E from B.

Step 4. Changing the content of the still and separating A from E.

The feasible region increases with an increasing reflux ratio, as is shown in Figure 14. At very high reflux ratios the infeasible region is very small or disappears.

Clearly, there is a minimum entrainer amount to be mixed with the charge in order to reach the feasible region, if the charge composition is situated in the infeasible region. If the charge composition is situated in the feasible region, then any infinitesimal amount of entrainer is marginally feasible. In order to get an SBD process with reasonable recovery, however, it is necessary to use a larger amount of entrainer. The reason for this increased entrainer usage is shown in Figure 15. The still composition moves in the opposite direction to the actual distillate composition. If the mixed charge composition is not well inside the feasible region, the still path crosses the feasibility boundary. Therefore, a greater amount of entrainer has to be premixed with the charge in order to achieve a reasonable recovery.

Feasibility of BED

Based on Figure 13, the operation steps of BED can also be determined:

Step 0. Mixing some entrainer to the charge.

Step 1. Heat-up. $R = \alpha$, $F = 0$.

Step 2. Producing A–E mixture in the distillate, $F > 0$.

Step 3. Separating E from B, $F = 0$.

Step 4. Changing the content of the still and separating A from E, $F = 0$.

The principal merit of applying continuous feeding is explained in Figure 16. Distillation in step 2 with the same re-

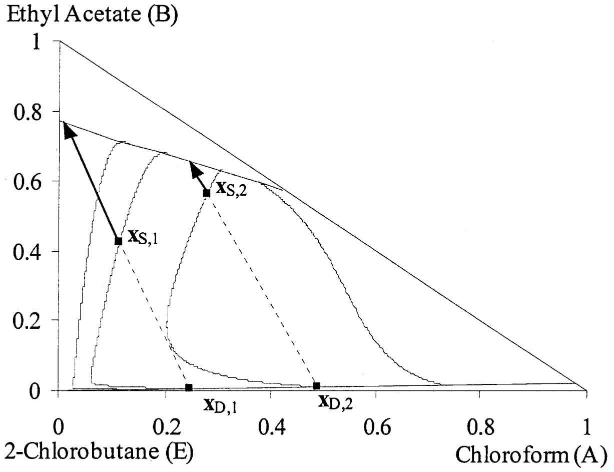


Figure 15. Expected still-path directions depending on the still composition, for SBD.

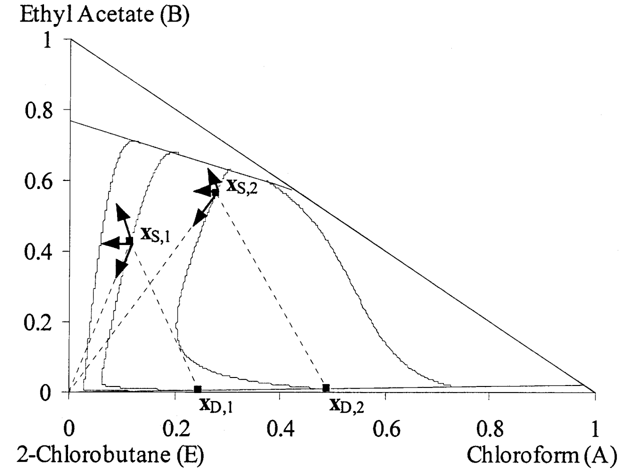


Figure 16. Expected still-path directions for BED (continuous feeding).

covery specification can be started with a smaller amount of pre-mixed entrainer, because the continuous feeding of the entrainer turns the still path more toward edge B–E. Applying the appropriate feed ratio, the direction of the still path can be made horizontal, or even to decreasing x_B.

Since the feasibility region that is valid for SBD reaches edge B–E, no feeding to the column is necessary; continuous feeding to the still is sufficient. However, feeding to the column is possible, and its expected effect is also studied. The extractive profiles depend on the specified distillate composition. With an increasing molfraction of E in the distillate, the extractive profiles become less steep, but they keep running into edge B–E. At a given F/V ratio and reflux ratio, that is, $R = 9$ and $F/V = 0.2$, an envelope of the extractive profiles crossing feasible rectification profiles can be given, as is shown in Figure 17. (This envelope fixes the boundary.) This figure also shows how the application of BED increases the feasibility region compared to SBD, at the given F/V ratio. This increase does not seem significant, because the still composition can be shifted toward the feasibility region simply by premixing more entrainer with the charge. However, this is a question of economy, and will be subject of a later study.

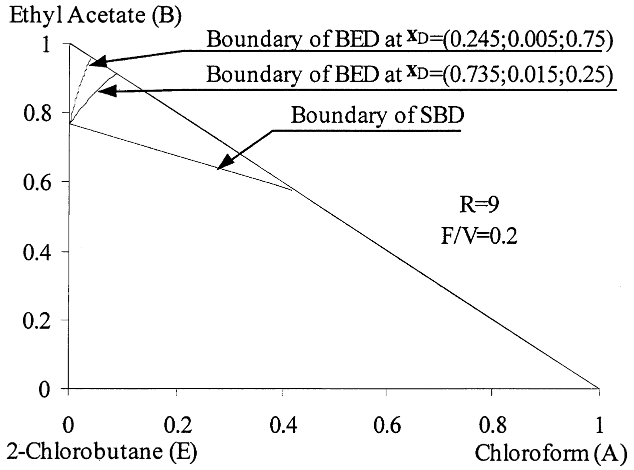


Figure 17. Feasibility boundaries of BED.

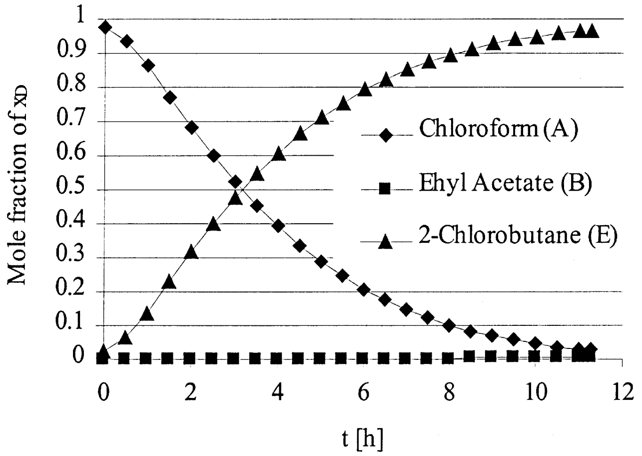


Figure 18. Simulated column history of SBD (step 2).

Simulation Results

Comparison of SBD and BED, with the first product being A–E mixture

The history of the molfractions in the distillate stream in step 2 of SBD is shown in Figure 18, with the column and operation parameters as follow: $N = 45$, $Q = 1.5$ kW, $R = 20.0$, $x_{Ch} = [0.5; 0.5; 0.0]$, $H = 6$ L ≈ 0.068 kmol, $x_{S,t0} = [0.215; 0.215; 0.57]$, $H_0 = 15.46$ L ≈ 0.158 kmol. The amount of entrainer consumed is 0.09 kmol. The still path, together with two composition profiles (one at $t = 0$ h, the other at $t = 5$ h), are shown in Figure 19. The results are in good agreement with the approximating profile map. The purity $x_{AR} \equiv x_A/(x_A + x_B)$ achieved in the accumulator is 0.995; the time of step 2 is 11.29 h; the recovery is $\eta = 91.59\%$; the productivity is $\Sigma D/t = 8.77$ mol/h.

Simulation with the same specifications, but continuous feeding to the still is also performed. The history of the distillate stream molfractions in step 2 of BED is shown in Figure 20, with the column and operation parameters as follow: $N_{\text{extr}} = 0$, $N_{\text{rect}} = 45$, $Q = 1.5$ kW, $F = 0.009$ kmol/h, $R = 20.0$, $x_{Ch} = [0.5; 0.5; 0.0]$, $H = 6$ L ≈ 0.068 kmol. The given feed flow rate and boiling power roughly correspond to a feed ratio of

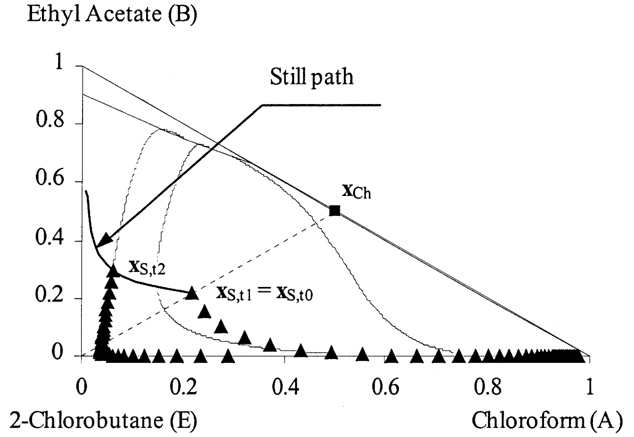


Figure 19. Two simulated column profiles and the still path of SBD over the background of the shortcut-calculated profile maps.

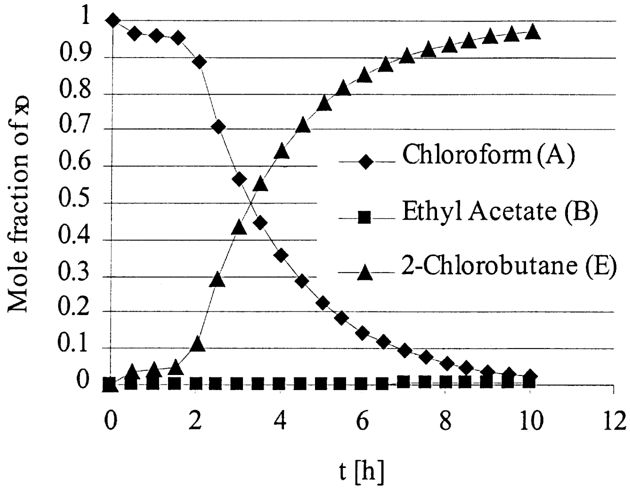


Figure 20. Simulated column history of BED (step 2).

$F/V \approx 0.05$. The still path, together with two composition profiles (one at $t = 1$ h, the other at $t = 5$ h) are shown in Figure 21. The purity $x_{AR} \equiv x_A/(x_A + x_B)$ achieved in the accumulator is 0.995; the time of step 2 is 10.0 h; the recovery is $\eta = 91.96\%$; the productivity is $\Sigma D/t = 8.13$ mol/h. The results are in good agreement with the approximating profile map.

The two simulation runs are given in such a way that they provide the same purity in the accumulator and consume the same amount of entrainer. The results are summarized and compared in Table 4.

According to the results, batch extractive distillation (BED) provides the same products in a *shorter time and at a significantly smaller still holdup* as does solvent-enhanced batch distillation (SBD), with identical purity and slightly greater productivity. Holdup of SBD is approximately twice as great as that of BED. In our case, at an industrial site with given vessel dimensions, the capacity of BED is approximately twice that of the SBD.

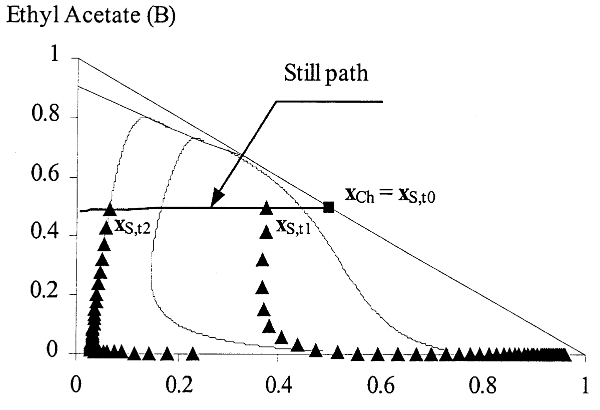


Figure 21. Two simulated column profiles and the still path of BED over the background of the shortcut-calculated profile maps.

Table 4. Comparison of SBD and BED

	SBD	BED
Charge, L	6	6
Charge composition, mol/mol	[0.5; 0.5; 0.0]	[0.5; 0.5; 0.0]
Charge, mol	68	68
$x_A/(x_A + x_B)$ in accumulator	0.995	0.995
Reflux ratio	20	20
Amount of entrainer, mol	90	90
Feed flow rate, kmol/h	0	0.009
Init. still composition, mol/mol	[0.215; 0.215; 0.57]	[0.5; 0.5; 0.0]
Init. still holdup, mol	158	68
Recovery, %	91.59	91.96
Productivity, mol/h	8.77	8.13
Time of producing A + E, h	11.29	10.0
Max. still holdup, mol	158	70.2
Max. still holdup, L	15.5	7.1
Entrainer in accumulator, mol	65.33	54.13
Entrainer in residue, mol	24.67	35.87

Application of BED results in significantly less entrainer in the product, but leaves more entrainer in the residue. Separation of A from E, and separation of E from B are two subsequent production steps. Which version is preferable from the point of view of these subsequent separations depends on the relative difficulty of these separation tasks. In order to make an economic decision, these separations ought to be simulated and evaluated as well.

Parametric study on BED

The results of a parametric study are shown in the following five figures. Recovery ratio η (moles of component A in the accumulator per that in the charge), and productivity $\Sigma D/t_2$ (product moles per step operation time, step 2) are shown in all the figures as a function of a selected parameter. In all cases, the basis of comparison is $N_{\text{rect}} = 50$, $N_{\text{extr}} = 0$, $Q = 1.5$ kW, $F = 0.072$ kmol/h ($F/V \approx 0.04$), $R = 24.0$, the charge is $\mathbf{x}_{Ch} = [0.136; 0.864; 0.0]$, the azeotropic composition being inside the infeasible region, $H_{Ch} = 4.3$ L ≈ 45.2 mol, $\mathbf{x}_{S,t0} = [0.1; 0.635; 0.265]$, $H_0 = 6$ L ≈ 61.5 mol, no holdup in the column, the specified purity is 0.98 reduced mole fraction $x_A/(x_A + x_B)$ in the accumulator.

The effect of R has a contradictory effect on η and $\Sigma D/t_2$, as shown in Figure 22. This is the shape of change usual at

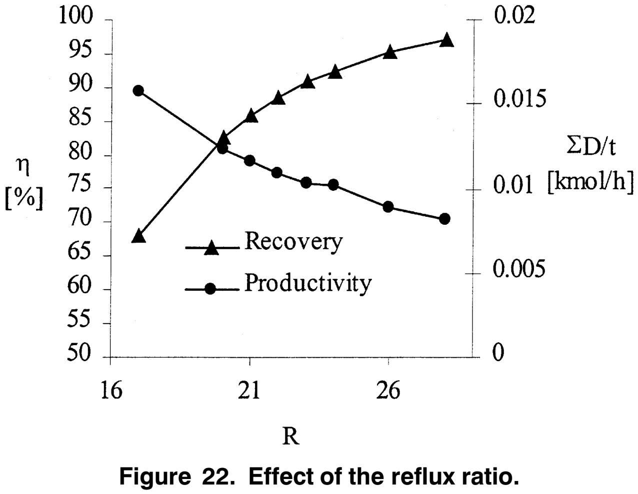


Figure 22. Effect of the reflux ratio.

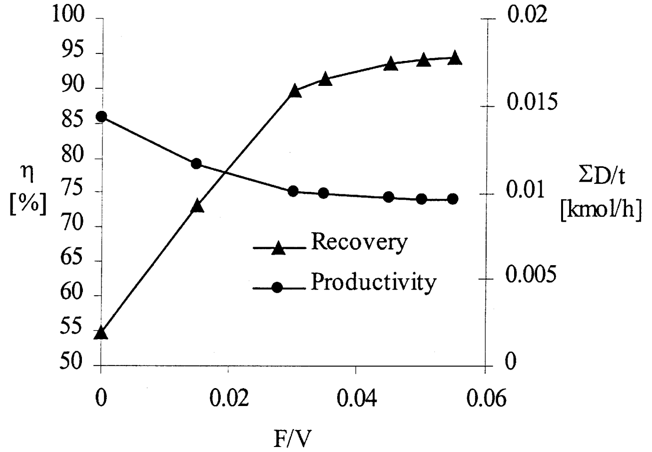


Figure 23. Effect of the feed ratio.

batch distillation. There must be an optimal reflux ratio. The effect of the feed ratio *F/V* is shown in Figure 23. Recovery steeply decreases below *F/V* ≈ 0.03, while productivity increases slightly with a decreasing feed ratio. Above this value, however, a decrease in productivity is not significant, while a significant, although not very steep, increase in recovery can be observed. At very low values of *F/V*, the still path goes in the wrong direction (cf. Figures 15 and 16), involving decreasing recovery. On the other hand, increasing *F/V* can be used to make the still path avoid the feasibility boundary.

The number of rectification stages (Figure 24) has only a small effect on the productivity; but the recovery ratio increases steeply with it. This is the usual shape of change at batch distillation. Feeding some stages above the still does not have much effect, but some decrease in productivity and some increase in recovery are seen in Figure 25. We see so little effect because the charge composition is far from the region where it would matter.

For the sake of simplicity, all the results hitherto shown are computed with zero holdup. The effect of the holdup, as is shown in Figure 26, is neglectable on recovery and productivity. The column holdup is expressed in the figure as a percentage of the initial holdup in the still.

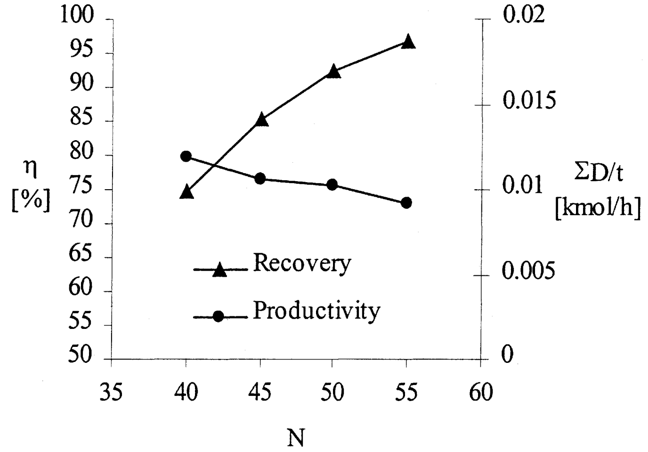


Figure 24. Effect of the number of stages.

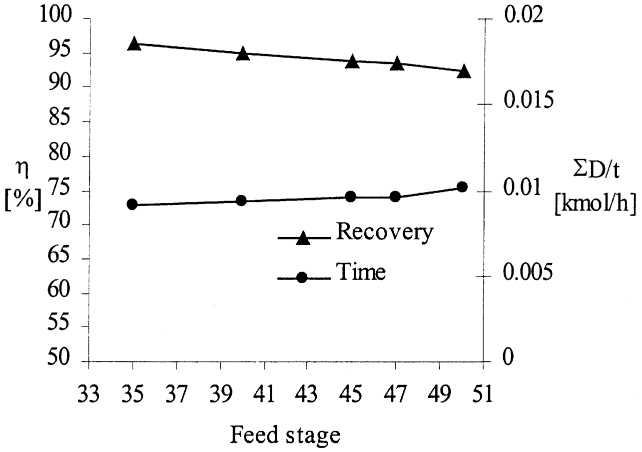


Figure 25. Effect of the feed location.

Conclusion

Separation of the maximum boiling azeotropes is feasible using batch extractive distillation (BED) in a rectifier column with an intermediate boiling entrainer. The main difference in BED compared with solvent-enhanced batch distillation (SBD) is that the entrainer is fed continuously to the column or the still.

BED with light or heavy entrainers was studied earlier. Finding a well-working intermediate boiling entrainer is more difficult than finding either a heavy or a light entrainer and, as a result, the intermediate boiling entrainer actually found might be inferior to the others. On the other hand, a good intermediate boiling entrainer also has merits compared to the others. However, the most significant reason for studying intermediate boiling entrainers is the opportunity of having an intermediate boiling component in the mixture to be separated. In that case, the intermediate boiling component may be the best choice, because no other, foreign, component is then applied.

Separation of the maximum boiling azeotropes in both SBD and BED is feasible with an intermediate boiling entrainer,

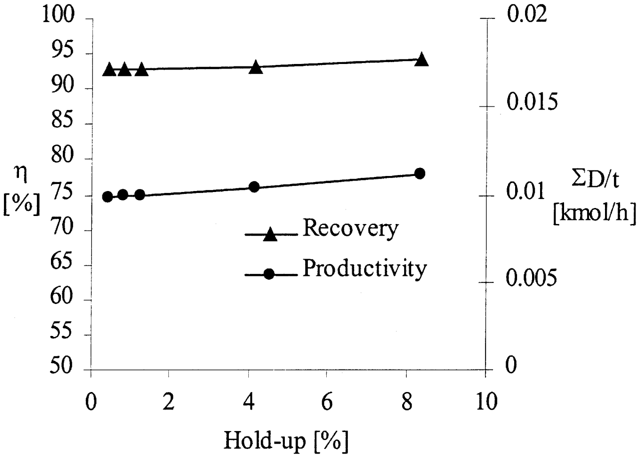


Figure 26. Effect of the column holdup (in percent of the still).

Table 5. Operation Steps of SBD and BED for Maximum Boiling Azeotrope

	SBD	BED
Step 0	Mixing some entrainer to the charge	Mixing some entrainer to the charge
Step 1	Heatup	Heatup, $F = 0$
Step 2	Producing A–E in the distillate	Producing A–E in the distillate, $F > 0$
Step 3	Separating E from B	Separating E from B, $F = 0$
Step 4	Separating A from E	Separating A from E, $F = 0$

and the application of continuous feeding (a characteristic of BED) makes the process more efficient. Our test mixture is chloroform and ethyl acetate with 2-chlorobutane as the entrainer.

According to the feasibility study, pure component A cannot be produced in either SBD or BED. On the other hand, producing component A mixed with an entrainer and free of component B is feasible in both processes. The operation steps are rather similar in the two processes, as shown in Table 5.

The only difference between the operation steps is the continuous feeding in step 2. In practice, much less entrainer has to be premixed with the charge in the case of BED, whereas the entrainer is continuously fed to the still (or to some area near the still) during step 2.

SBD and BED are compared with the simulation results (ChemCAD) in Table 4. With identical specification and comparable operation parameters, BED produces the same recovery in a shorter time and with significantly less holdup in the still. This is because continuous feeding is applied to lead the still path in a more preferable direction.

A parametric study on the recovery and productivity of the process, involving studying the effect of reflux ratio, feed ratio, stage numbers, and column hold-up, is also performed. The conclusions based on the feasibility analysis are confirmed by rigorous simulation results.

Acknowledgment

This work was partially supported by Hungarian grants OTKA F035085 and AKP 2001-112.

Notation

A, B, C = dimension-dependent parameters of Antoine equation, Eq. 6
A = binary interaction parameter in NRTL equation, Eq. 7
A = light component
B = heavy component
BED = batch extractive distillation
E = entrainer component
F = feed flow rate
G = Boltzmann-factor in NRTL equation, Eq. 7
H = holdup
N = number of theoretical stages
p = pressure
p^o = vapor tension of pure component
R = Regnault's universal gas constant in Eq. 7
R = reflux ratio
Q = boiling power
SBD = solvent-enhanced batch distillation
SN = stable node
T = temperature
t = time
UN = unstable node
V = vapor flow rate
$\mathbf{x}$ = liquid composition: array of mole fractions
x = liquid mole fraction
$\mathbf{y}$ = vapor composition: array of mole fractions
y = vapor mole fraction

Greek letters

α = nonrandomness parameter in NRTL equation, Eq. 7
γ = activity coefficient
η = recovery: amount of A in the collector related to that in the charge
$\Sigma D/t$ = productivity: product amount collected per time
τ = parameter in NRTL equation, Eq. 7

Subscripts

A = component A (light component)
B = component B (heavy component)
Ch = charge
D = distillate stream
E = entrainer (intermediate boiling component)
F = feed
i, j, k, m = running indices of components
min = minimum
max = maximum
rect = rectification section
extr = extractive section
S = still
t_1 = time at the end of operation step 1
t_2 = time at the end of operation step 2
t_3 = time at the end of operation step 3

Literature Cited

Bernot, C., M. F. Doherty, and M. F. Malone, "Feasibility and Separation Sequencing in Multicomponent Batch Distillation," *Chem. Eng. Sci.*, **46**, 1331 (1991).

Cheong, W., and P. I. Barton, "Azeotropic Distillation in a Middle Vessel Column," *Ind. Eng. Chem. Res.*, **38**, 1504 (1999).

Gmehling, J., and U. Onken, "Vapour-Liquid Equilibrium Data Collection," *DECHEMA*, Frankfurt (1977).

Lang, P., H. Yatim, P. Moszkowicz, and M. Otterbein, "Batch Extractive Distillation Under Constant Reflux Ratio," *Comput. Chem. Eng.*, **18**, 1057 (1994).

Lang, P., Z. Lelkes, M. Otterbein, B. Benadda, and G. Modla, "Feasibility Studies for Batch Extractive Distillation with a Light Entrainer," *Comput. Chem. Eng.*, **23**(Suppl.), S93 (1999).

Lang, P., G. Modla, B. Kotai, Z. Lelkes, and P. Moszkowitz, "Homoazeotropic Distillation of Maximum Azeotropes in a Batch Rectifier with Continuous Entrainer Feeding: II. Rigorous Simulation Results," *Comput. Chem. Eng.*, **24**, 1429 (2000a).

Lang, P., G. Modla, B. Benadda, and Z. Lelkes, "Homoazeotropic Distillation of Maximum Azeotropes in a Batch Rectifier with Continuous Entrainer Feeding: I. Feasibility Studies," *Comput. Chem. Eng.*, **24**, 1665 (2000b).

Laroche, L., N. Bekiaris, H. W. Andersen, and M. Morari, "Homogeneous Azeotropic Distillation: Comparing Entrainers," *Can. J. Chem. Eng.*, **69**, 1302 (1991).

Lelkes, Z., P. Lang, P. Moszkowicz, B. Benadda, and M. Otterbein, "Batch Extractive Distillation: The Process and the Operational Policies," *Chem. Eng. Sci.*, **53**, 1331 (1998a).

Lelkes, Z., P. Lang, B. Benadda, and P. Moszkowicz, "Feasibility of Extractive Distillation in a Batch Rectifier," *AIChE J.*, **44**, 810 (1998b).

Lelkes, Z., P. Lang, and M. Otterbein, "Feasibility and Sequencing for Homoazeotropic Distillation in a Batch Rectifier with Continuous Entrainer Feeding," *Comput. Chem. Eng.*, **22**, S653 (1998c).

Lelkes, Z., E. Rev, V. Varga, C. Steger, and Z. Fonyo, "Separation of Minimum Boiling Azeotrope in Batch Extractive Rectifier with Intermediate Boiling Entrainer," *Ind. Eng. Chem. Res.*, in press (2002).

Phimister, J. R., and W. D. Seider, "Semicontinuous, Middle-Vessel, Extractive Distillation," *Comput. Chem. Eng.*, **24**, 879 (2000).

Renon, H., and J. M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures," *AIChE J.*, **14**, 135 (1968).

Rodriguez, D. I., V. Gerbaud, and X. Joulia, "Heterogeneous Entrainer Selection for the Separation of Azeotropic and Close Boiling Temperature Mixtures by Heterogeneous Batch Distillation," *Ind. Eng. Chem. Res.*, **40**, 4935 (2001).

Safrit, B. T., A. W. Westerberg, U. Diwekar, and O. M. Wahnschafft, "Extending Continuous Conventional Extractive Distillation Feasibility Insights to Batch Distillation," *Ind. Eng. Chem. Res.*, **34**, 3257 (1995).

Skjold-Jørgensen, S., B. Kolbe, J. Gmehling, and P. Rasmussen, "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension," *Ind. Eng. Chem. Process Des. Dev.*, **18**, 714 (1979).

Warter, M., and J. Stichlmair, "Batchwise Extractive Distillation in a Column with a Middle Vessel," *Comput. Chem. Eng.*, **23**, S915 (1999).

Manuscript received Jan. 28, 2002, and revision received July 10, 2002.