

# Separation of a Minimum-Boiling Azeotrope in a Batch Extractive Rectifier with an Intermediate-Boiling Entrainer

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The separation of minimum-boiling azeotropes is feasible using batch extractive distillation (BED) in a rectifying column with an intermediate-boiling entrainer. The main difference between BED and solvent-enhanced batch distillation (SBD) is the application of continuous entrainer feeding either to the column or to the still. Our test mixture, selected according to didactic viewpoints, is methyl acetate and cyclohexane with carbon tetrachloride. Operation steps (sequencing), limiting flows, and limiting numbers of stages are determined by a feasibility study based on profile maps; the design is validated by rigorous simulation. Results of parametric studies and a comparison of SBD and BED in terms of effectiveness are presented. The studied parameters are the numbers of stages, the reflux ratio, the feed ratio, and the column hold-up. The separation of minimum-boiling azeotropes in SBD with an intermediate-boiling entrainer is practically infeasible. The application of continuous feeding (characteristic of BED) makes the process feasible. Our test entrainer is thermodynamically rather well behaved.

## Introduction

Several suggestions can be found in the literature for separating minimum-boiling binary azeotropes using an entrainer. According to Laroche et al.,<sup>1</sup> the entrainer for homoazeotropic distillation can be the lightest, the heaviest, or even the intermediate-boiling component in the system. For homoazeotropic batch distillation, Bernot et al.<sup>2</sup> and Rodriguez-Donis et al.<sup>3</sup> discussed the selection of appropriate entrainers. Even heteroazeotropic distillation can be used; see, for example, Rodriguez-Donis et al.<sup>4</sup>

Finding an intermediate-boiling entrainer that works well is more difficult than finding either a heavy or a light entrainer, and as a result, the intermediate-boiling entrainer that is actually found might be inferior to the others. On the other hand, a good intermediate-boiling entrainer 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 might be the best choice because no other, foreign, component is applied in that case.

The use of intermediate-boiling entrainers in batch distillations is discussed by Bernot et al.<sup>2</sup> According to their suggestions, minimum-boiling azeotropes can be separated in batch strippers (Figure 1) after an intermediate-boiling entrainer has been mixed into the charge.

In the case of a minimum-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 in a stripper. The first fraction is (the heavier) component B; the second is the (intermediate-boiling) entrainer E; and the third is (the lighter) component A, which remains in the

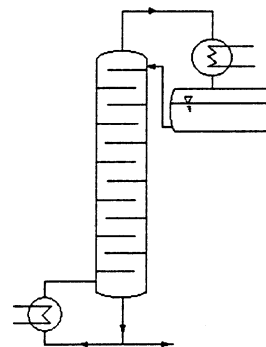


Figure 1. Batch stripper.

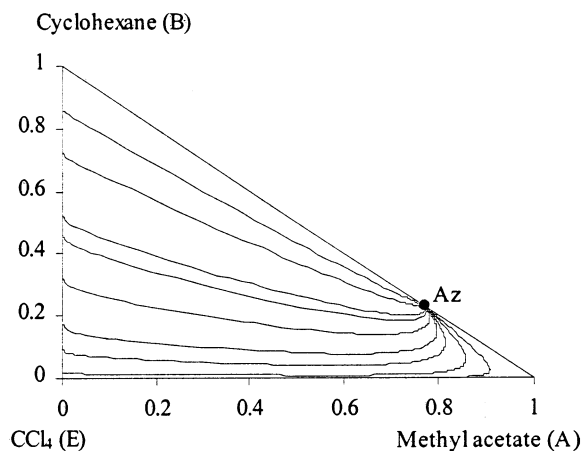
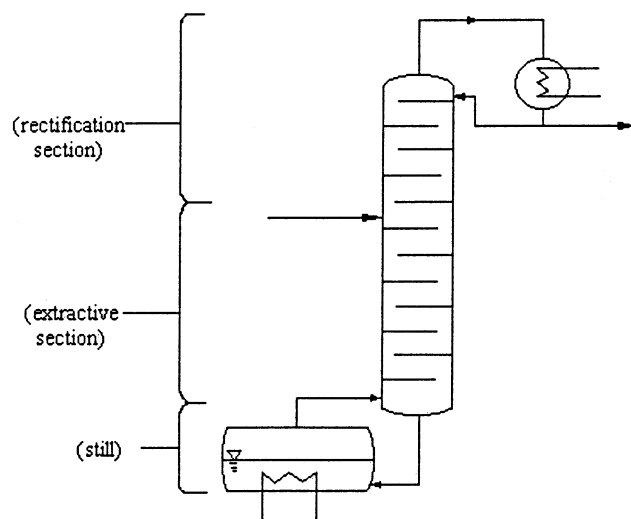


Figure 2. Residue curve map of a minimum-boiling azeotrope with an intermediate-boiling entrainer.

upper vessel in the case of extreme conditions or is removed as the third fraction, leaving the azeotropic composition in the vessel.

The suggestions of Bernot et al.<sup>3</sup> are based on an analysis of the residue curve map (RCM). This analysis involves the assumptions of infinite reflux ratio (equivalent to zero product flow rate in the case of batch distillation) and infinite number of theoretical stages.

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**Figure 3.** Batch extractive distillation (BED) in a rectifier with the rectifier sections.

No particular mixture is mentioned. According to their suggestions, batch strippers can be used to separate mixtures forming minimum-boiling azeotropes. However, rectifiers are the usual construction available and conventionally applied in the industry, and the staff generally has no experience in operating batch strippers. The separation of minimum-boiling azeotropes in batch rectifiers is a process that would be warmly welcomed by the industry.

Batch extractive distillation (BED) is another entrainer-using batch process for the separation of azeotropes. In BED, 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, genuine batch distillation schemes in which the entrainer is mixed into the charge in advance, such as those suggested by Bernot et al.,<sup>3</sup> will be called in this article "solvent-enhanced batch distillation" (SBD). Versions of BED can also be distinguished according to the use of a rectifier, stripper, or a middle vessel column;<sup>5–8</sup> 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. The separation of both minimum- and maximum-boiling azeotropes with BED using heavy entrainers was studied by Lang et al.<sup>9–11</sup> and Lelkes et al.<sup>12,13</sup> The separation of minimum-boiling azeotropes with BED using light entrainers was studied by Lelkes et al.<sup>14</sup> and Lang et al.<sup>15</sup> Their simulations and experimental work included the following mixtures and entrainers in BED: heavy entrainer with minimum-boiling azeotrope, acetone and methanol with either water, 2-propanol, ethanol, or chlorobenzene; low relative volatility mixture, heptane and toluene with phenol; maximum-boiling azeotrope, acetone and chloroform with either benzene or toluene; light entrainer with minimum-boiling azeotrope, ethanol and water with methanol. Additionally, minimum-boiling azeotropes with light entrainers in batch extractive strippers have also been studied, including ethanol and water with methanol, as well as *n*-butanol and *n*-butyl acetate with *n*-propyl formate or dipropyl ether.

According to our best knowledge, BED with intermediate-boiling entrainers has not yet been studied or published. In this article, the separation of minimum-boiling azeotropes in BED using an intermediate-boiling

entrainer not forming a new azeotrope is analyzed. The mixture studied is methyl acetate and cyclohexane with carbon tetrachloride. The entrainer is not selected according to practical (industrial) aspects, such as toxicity and economics; it is selected because it demonstrates well the characteristic effects of BED with intermediate-boiling entrainers. Operation steps (sequencing), limiting flows, and limiting numbers of stages 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.

The separation of a maximum-boiling azeotrope in BED with an intermediate-boiling entrainer, namely, chloroform and ethyl acetate with 2-chlorobutane, has also been studied and is published elsewhere (Lelkes et al.<sup>16</sup>).

## Methodology

**Feasibility Method.** The first step in studying the possibility of applying an entrainer in BED is testing its feasibility by simplified tools, developed by Lelkes et al.<sup>12</sup> Here, we reiterate the essential steps and ideas of the feasibility method, because they are applied in the subsequent sections.

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

The feasibility analysis is based on calculation and analysis of the steady-state concentration profile maps of the column rectification and extractive sections, together with analysis of the still path. The still path is the trajectory (i.e., projection onto the composition triangle) of the still composition in time. Throughout this analysis, the following simplifications are applied: (1) No column hold-up is taken into account (i.e., zero hold-up is considered). (2) Column dynamics are approached via steady states. (3) Constant molar overflow is applied in the model. (4) The feed and reflux streams are at their boiling points. (5) No pressure drop along the column or in the condenser is taken into account.

The composition profiles in the column sections are computed by solving the following differential equation

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

where  $h$  is the dimensionless column height;  $\mathbf{y}$  is computed according to the component balances, i.e., the so-called operating lines; and  $\mathbf{y}^*$  is the equilibrium vapor composition characterizing the liquid composition  $\mathbf{x}$ . The vapor–liquid ratio ( $V/L$ ) is determined according to the molar balance in the corresponding column section.

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

$$\mathbf{y} = \frac{(V - D)\mathbf{x} + D\mathbf{x}_D}{V} \quad (2)$$

whereas the component balance, called the operating line of the extractive section, involves the feed component flow rates, all considered in the liquid flow

$$\mathbf{y} = \frac{(V + F - D)\mathbf{x} - F\mathbf{z} + D\mathbf{x}_D}{V} \quad (3)$$

Equation 1 is an initial value problem. Computation of any rectification profile starts at some specified distillate flow composition ( $\mathbf{x}_D$ ) as the initial condition. The computation of any extractive profile starts at some specified still composition ( $\mathbf{x}_S$ ) as the initial condition. Thus, the computation of the two profiles is performed in opposite directions. Integration along the column height is accordingly performed with appropriate sign. 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)

$$\frac{d(H_S \mathbf{x}_S)}{dt} = F\mathbf{z} - D\mathbf{x}_D \quad (4)$$

where the initial condition is  $\mathbf{x}_S(t_0) = \mathbf{x}_{ch}$ . The composition trajectory is analyzed. However, some periods involving the attainment of some feasibility boundary or other characteristic composition are recorded and applied in the design.

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

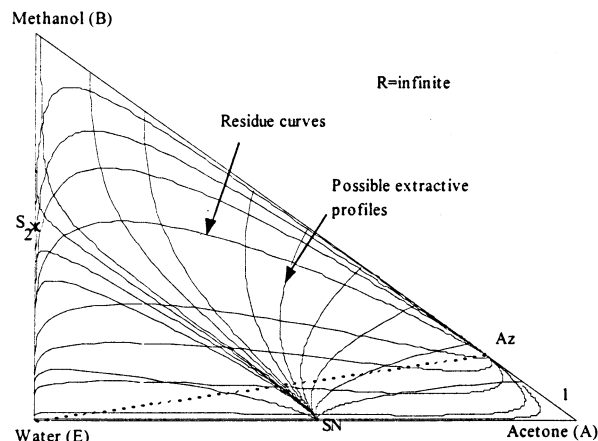
In principle (or in a marginal sense), the separation is feasible if the specified product compositions can be reached, irrespective of the recovery ratio or the product flow rate. Thus, the separation is feasible in principle (or is marginally feasible) even if the product composition can be reached with no more than zero recovery and zero product flow rate (i.e., infinite reflux ratio) and, perhaps, an infinite number of stages. In some cases, an infinite amount of entrainer or an 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 on the still path to the specified distillate composition. The column profile might consist of just a rectification profile, or it might consist of an extractive profile continued by a rectification profile.

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

In a practical sense, however, the separation is feasible if a range of design and operating parameters exist in such a way that the product specifications can be reached with a 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 preload ratios.

Marginal feasibility, together with a preliminary suggestion of operating steps (product sequencing), is determined by analyzing the profile maps calculated with an infinite reflux ratio. In that case, the rectification profile map is identical to the residue curve map of the system.

For example, Figure 4 displays profile maps of an atmospheric system of acetone and methanol, forming a minimum-boiling azeotrope with the heavy-boiling component water as the entrainer, for an infinite reflux



**Figure 4.** Profile maps of a minimum-boiling azeotropic system with a heavy entrainer at total reflux.

ratio ( $R = \infty$ ), a vapor flow rate of  $V = 0.048$  mol/s, a pure entrainer feed flow rate of  $F = 30$  cm<sup>3</sup>/s, and a specified distillate composition of  $\mathbf{x}_D = (0.94, 0.025, 0.035)$ . The separation is feasible with the listed parameters, including  $R = \infty$  and  $F/V \approx 0.5$ , because all of the extractive profiles run to the neighborhood of SN (stable node), and there is a rectification profile crossing  $\mathbf{x}_D$  and crossing practically all of the extractive profiles near SN. According to the profile map in this figure, the operation steps of this separation might be the following: (1) heat-up,  $R = \infty$ ,  $F = 0$ ; (2) run-up,  $R = \infty$ ,  $F > 0$ ; (3) production of component A,  $R < \infty$ ,  $F > 0$ ; and (4) production of component B and regeneration of the entrainer,  $R < \infty$ ,  $F = 0$ . The feasible region of the separation, in the spirit of Safrit et al.,<sup>4</sup> is the set of feasible still compositions, according to the definition of Lelkes et al.<sup>12</sup>

### Equilibrium Model

Vapor-liquid equilibrium is calculated using the modified Raoult-Dalton equation

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

Neither the Poynting correction nor vapor-phase non-ideality is taken into account.

The vapor pressures  $p_i^o(T)$  of the pure components are calculated using the three-parameter Antoine equation

$$\log p_i^o = A - \frac{B}{T + C} \quad (6)$$

with the base-10 logarithm, millimeters of mercury (mmHg) (i.e., Torr) for the pressure, and degrees centigrade (°C) for the temperature.

The liquid-phase activity coefficients  $\gamma_i(T, \mathbf{x})$  ( $i \in A, B, E$ ) are calculated using the NRTL model (Renon and Prausnitz<sup>17</sup>)

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{G_{ij} x_j}{\sum_k G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_m \tau_{mj} G_{mj} x_m}{\sum_k G_{kj} x_k} \right) \quad (7a)$$

$$\tau_{ij} \equiv \frac{A_{ij}}{RT} \quad (7b)$$

**Table 1. Atmospheric Boiling Points of the Methyl Acetate, Carbon Tetrachloride, Cyclohexane System**

	boiling point (°C)
azeotrope (A-B)	54.5
methyl acetate (A)	56.7
carbon tetrachloride (E)	76.3
cyclohexane (B)	80.3

**Table 2. Antoine Coefficients**

	A	B	C
methyl acetate (A)	7.417 91	1386.51	247.853
carbon tetrachloride (E)	6.879 26	1212.021	226.409
cyclohexane (B)	6.851 46	1206.47	223.136

**Table 3. NRTL Parameters**

<i>i-j</i>	<i>A<sub>ij</sub></i>	<i>A<sub>ji</sub></i>	$\alpha_{ij}$
A-E	173.3082	175.3669	0.3013
A-B	588.5211	455.9006	0.2953
E-B	696.57	-570.815	0.3048

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

where the  $\alpha_{ij} = \alpha_{ji}$  nonrandomness parameters are dimensionless, whereas the binary interaction parameters  $A_{ij}$  have units of calories per mole. The Regnault constant (general gas constant) is taken with the value  $R = 1.987 \text{ 21 cal/(mol K)}$ .

**Rigorous Simulation.** Simulations for testing the validity of the feasibility study and of the corresponding design and operating parameters, for testing the effect of column hold-up and of simplified dynamics, as well as for comparing the effectiveness of different separation structures were performed using the batch distillation unit with simultaneous correction model of ChemCAD simulator, version 5.06. The latent heat model was used to take the enthalpy balance into account. The results of the ChemCAD simulations were compared to the 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. The process history was computed as a series of steady states by ChemCAD, whereas realistic dynamics were computed by AspenPlus.

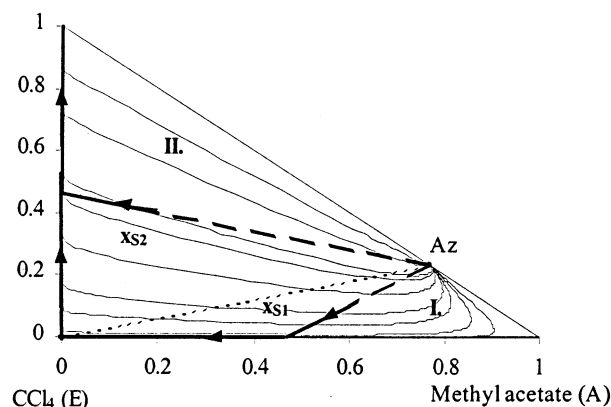
### Sample System

The separation of methyl acetate from cyclohexane with carbon tetrachloride as the entrainer was selected as an example mixture to demonstrate the properties of this process. Other entrainers were also considered, but they involved essential uncertainty in modeling vapor-liquid equilibrium. The boiling points of the investigated components at atmospheric pressure are shown in Table 1. Their Antoine coefficients are listed in Table 2, and NRTL model parameters, taken from Gmehling and Onken,<sup>18</sup> are listed in Table 3.

### Feasibility of Solvent-Enhanced Batch Distillation

SBD is a simpler process than BED; therefore, it might be preferred. In the case of SBD, the separation sequence is determined on the basis of the residue curve map. The residue curve map of the studied system is shown in Figure 5. There is no separatrix in this system; each residue curve connects the azeotropic point to

Cyclohexane (B)

**Figure 5.** Still paths of SBD.**Table 4. Would-Be Products of SBD**

(a) $R = \infty$ and $N = \infty$		
operation step	initial still composition situated in	
	region I	region II
first cut (distillate)	A-B azeotrope	A-B azeotrope
second cut (distillate)	pure A	pure E
residue	pure E	pure B
(b) $R < \infty$ and $N = \infty$		
operation step	initial still composition situated in	
	region I	region II
first cut (distillate)	A-B azeotrope	A-B azeotrope
second cut (distillate)	A	E
third cut	E	-
residue	B	B

**Table 5. Would-Be Products of SBD with  $R < \infty$  and  $N \ll \infty$  and a Great Deal of E in the Still**

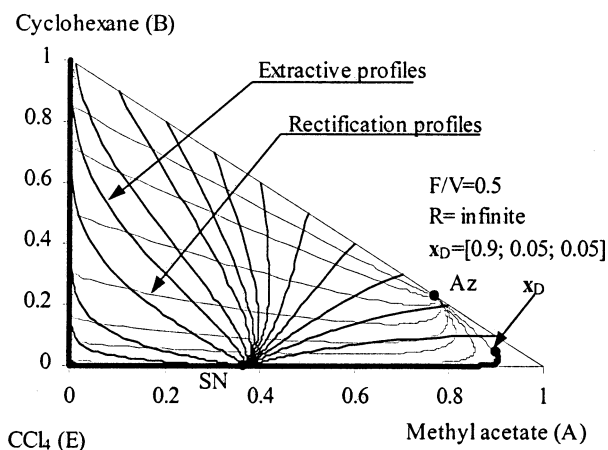
operation step	product
first cut (distillate)	A
second cut (distillate)	E
residue	B

component B. The regions (denoted by I and II) separated by a straight line connecting the azeotrope to E are not simple distillation regions but batch rectification regions. Both the corners of pure A and pure E are saddle points. For an infinite reflux ratio and an infinite number of stages, the distillate product is the azeotrope. Thus, the products of the operation steps, according to the region containing the initial still composition, would be those listed in Table 4a. With a realistic reflux ratio, however, the still path cannot exactly reach the edges; therefore, some contamination remains in the still, and the products would be those listed in Table 4b.

The production of almost pure A is marginally feasible from both regions if a huge (or infinite) amount of entrainer and a *finite* number of theoretical stages are applied, so that the residue curve crossing the mixed charge composition runs arbitrarily near pure A and the composition profile stops (or starts) at the specified purity. Then, the operation steps and the products would be those listed in Table 5.

In the first step, during the production of pure component A, the still path would move approximately along a straight line directed toward the B-E edge. This is a consequence of the component balance obtained upon removal of almost pure A. Once all of component A had been removed from the still, the distillate





**Figure 6.** Extractive and rectification profile maps at infinite reflux ratio and  $F/V = 0.5$ . The potential rectification profile characterizing the specified distillate composition is emphasized with the bold line. All of the extractive profiles run to SN (stable node).

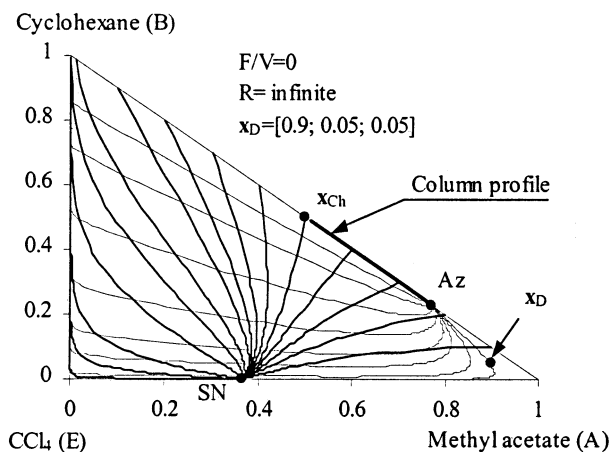
composition would quickly change to a binary composition on the B–E edge. In the second step, the B–E mixture would be separated.

However, the product purity in the first step cannot be maintained with changing still composition in a column operated at a constant number of stages and a reasonable reflux ratio. Therefore, the separation process expressed in the steps of Table 5 is practically infeasible. Nevertheless, test simulations were run (using the ChemCAD simulator), but the results confirmed the practical unfeasibility of this process. With a column of  $N = 20$  theoretical stages operated with a reflux ratio of  $R = 15$ , no hold-up in the trays or in the reflux drum, equimolar ( $x_A = x_B = 0.5$ ) charges of 11 mol each plus 140 mol of the entrainer mixed with the charge, and the pot heated at  $Q = 1.5$  kW, the computed initial distillate concentration (0.95, 0.025, 0.025) can be maintained for no longer than 0.1 h; then, the purity decreases. To reach a reasonable purity ( $x_{D,A} \geq 0.9$ ), an amount of entrainer approximately 13 times greater than the charge itself (in terms of moles) would be needed; this is an unacceptable ratio. It would also require unacceptable column and still dimensions.

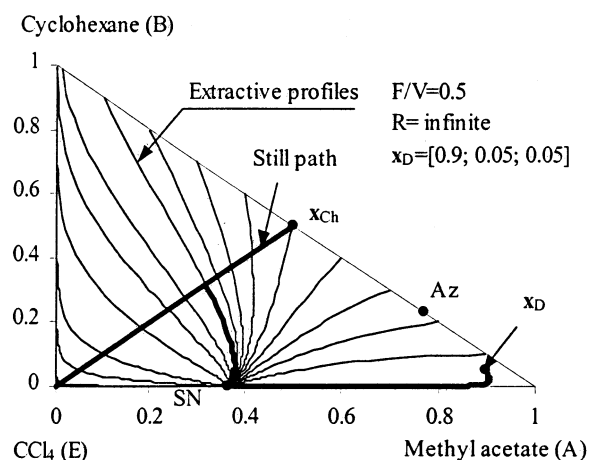
### Feasibility of Batch Extractive Distillation

**Profile Maps and Separation Sequencing.** The introduction of a continuous feed of entrainer into the column involves a radical change in the profile maps. Rectification profiles (residue curves) and extractive profiles at  $F/V = 0.5$ , both at an infinite reflux ratio, are simultaneously shown in Figure 6. All of the residue curves run from the azeotrope to the stable node B; all of the extractive profiles run from any point in the triangle to the point denoted by SN. Although much higher purity can be achieved with BED, as will be seen later, moderate purity ( $x_{D,A} \geq 0.9$ ) is specified here so that the shape of the concentration profiles and the still path can be better seen and the effects can be better demonstrated.

At this modest feed ratio, there is a stable node (SN) near the A–E edge, and this makes it possible to reach a high-purity product even if the still composition is in the middle of the composition triangle. From any point in the triangle (in the case of an infinite reflux ratio), the extractive profile leads to the neighborhood of SN,



**Figure 7.** Effect of heat-up before feeding entrainer (step 1). The column profile before feeding is situated along the A–B edge and is shown with the bold line.



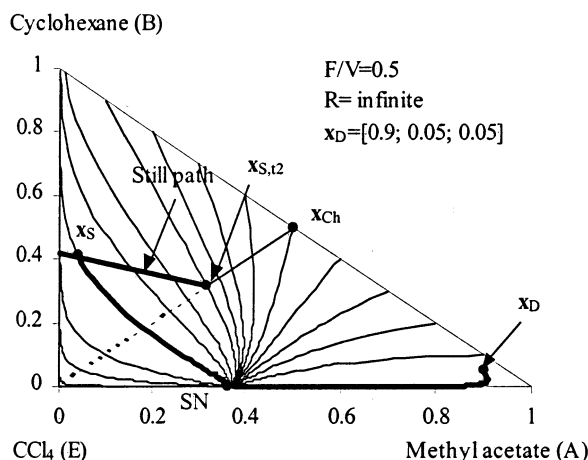
**Figure 8.** Step 2: Effect of feeding pure entrainer at total reflux (run-up). The potential still path and a particular column profile are shown with bold lines.

and thus to the neighborhood of the A–E edge, and there is a rectification profile crossing the extractive profiles and some point  $x_D$  near pure A. Such a feasible rectification profile is also shown in the figure by a bold line.

The feasible operation steps can be determined according to this figure.

First, the charge is loaded into the still, and the column is heated (step 1) without entrainer feeding and with an infinite reflux ratio i.e., without product removal. At the end of this step, the composition in the top of the column is near that of the azeotrope, whereas the still composition remains at the charge composition. Assuming an infinite number of stages, the end compositions are identical to the azeotrope and charge compositions. The column composition profile lies on the A–B edge, between the two mentioned end compositions. Such a profile is shown in Figure 7 for the case of a charge composition between the azeotrope and pure B.

Total reflux is maintained in step 2, the run-up step, while pure entrainer is continuously fed to the column. In this step, a composition profile characteristic of extractive distillation forms in the column. Such a profile is shown with the bold line in Figure 8. As a consequence of the feeding of entrainer, the still composition moves from the charge inside the triangle, along



**Figure 9.** Step 3: Production of component A. The profiles are calculated with infinite reflux ratio (short-cut). The still path is estimated for finite reflux ratio.

the still path, in the direction of the feed composition. In our simplified analysis, the feed is pure entrainer. Regardless of how far the still composition has moved inside the triangle, there is an extractive profile crossing the still composition and leading to SN. There is also a rectification profile connecting the extractive profile to the specified distillate composition. The feed tray composition is near SN. The separation of A from E occurs practically in the rectification section, whereas the extractive section serves to wash down component B, so that it does not appear in the rectification section at a significant concentration.

The above-explained situation arises in our mixture. The occurrence of another ternary system with SN situated along the B–E edge, rather than along the A–E edge, cannot be excluded. In that case, the entrainer is enriched in the top; therefore, the separation is infeasible. It follows that the entrainer should be selected to prefer the removal of component A and the retention component B. The roles of components A and B cannot be swapped. This is a distinctive feature of this process, as role swapping is enabled when heavy and light entrainers are applied.

The still path can be calculated, according to eq 4, by a simplified equation

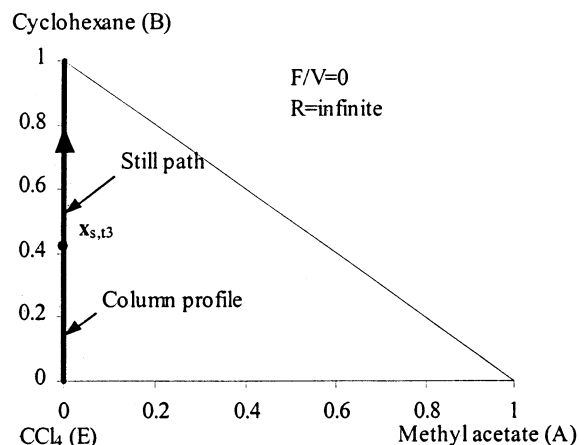
$$\frac{d(H_S \mathbf{x}_S)}{dt} = F \mathbf{z} \quad (8)$$

that takes into account the zero distillate flow rate. The initial values are the charge composition  $\mathbf{x}_{Ch}$  and the charge amount  $H_{Ch}$ .

After the desired composition in the top is reached, removal and collection of the distillate product is started in step 3. Continuous feeding of the entrainer keeps the feed stage composition near SN, thus making it possible to produce the desired purity product in the distillate via the rectification profile.

The still path can be calculated using eq 4, with the initial value  $\mathbf{x}_{S,t2}$  being the still composition and the still hold-up  $H_{S,t2}$  at the beginning of step 3, i.e., at the end of step 2. As a result of product removal, the still path turns sharply to the opposite edge of the triangle, as is also shown in Figure 9.

Step 3 can be ended either when component A is removed from the still or when some boundary is reached, depending on the finite reflux ratio. In the



**Figure 10.** Step 4: Separation of E from B.

present stage of feasibility analysis, the effect of the finite reflux ratio is not known, but will be analyzed later. According to the information available from the infinite-reflux-ratio profile maps, the step ends when the still path reaches the B–E edge.

The B–E mixture in the still at the end of step 3 is separated in step 4 without feeding, i.e., by applying conventional batch distillation. The composition profiles connect the still composition with a point near pure E (distillate), while the still path moves in the opposite direction. Both lines lie on the B–E edge (see Figure 10).

The operation steps can be summarized as follows: (1) heat-up,  $R = \infty$ ,  $F = 0$ ; (2) run-up (reaching the pure product composition in the top),  $R = \infty$ ,  $F > 0$ ; (3) production of the first product,  $R < \infty$ ,  $F > 0$ ; and (4) production of the second product in the residue and regeneration of the entrainer (distillate),  $R < \infty$ ,  $F = 0$ .

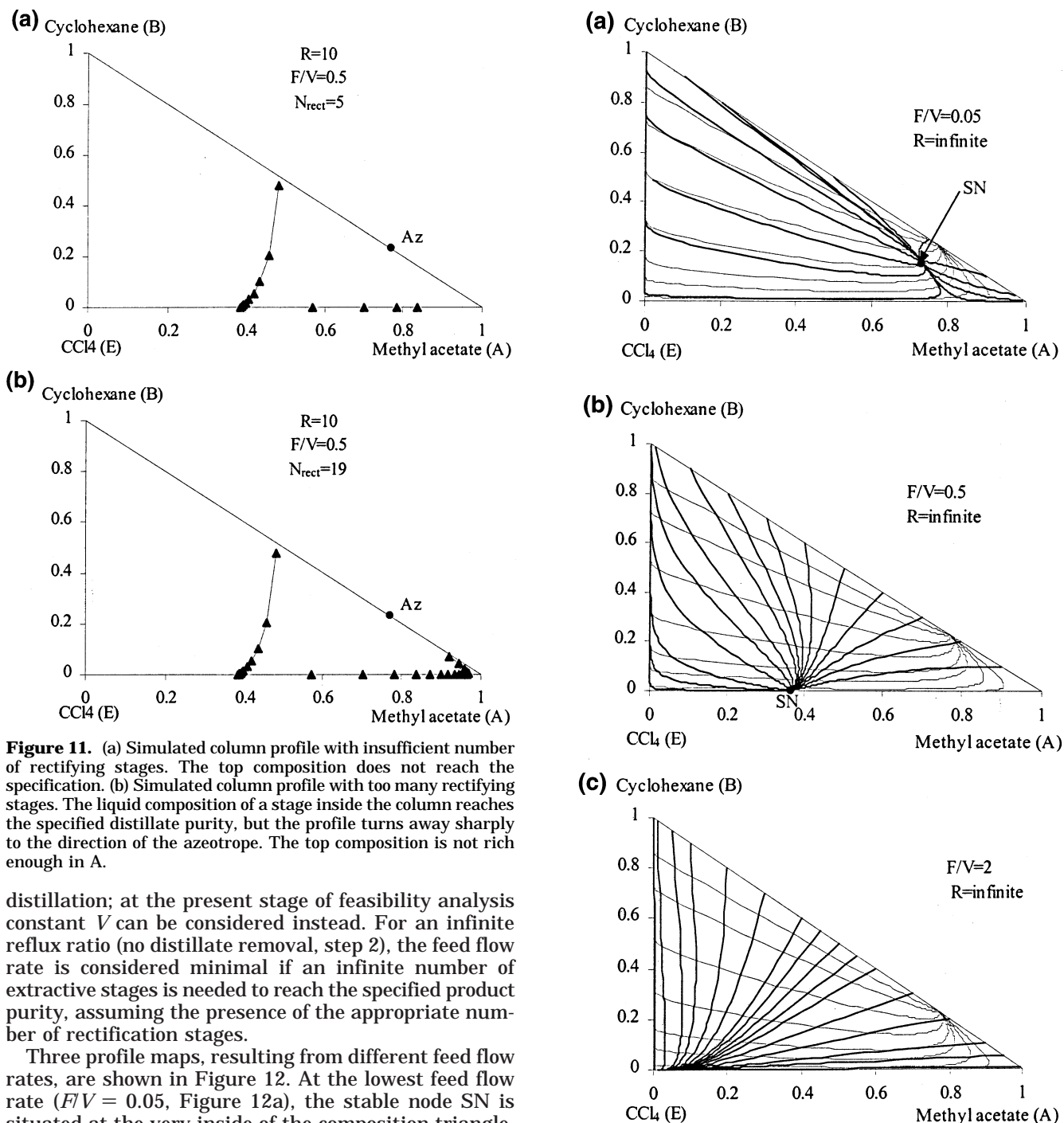
**Profile Maps and Existence of Limiting Values at Infinite Reflux Ratio.** Some consequences of having the profile maps shown in Figure 6 are that the feasible number of extractive stages should have a minimum value; the feasible number of rectification stages should have both minimum and maximum values; and the  $F/V$  ratio should have a minimum value at infinite reflux ratio.

A minimum number of extractive stages is needed to reach the neighborhood of SN from all the points of the still path. The crucial points of the still path, in this sense, are the initial charge composition and the final composition, because they are the farthest from SN.

A minimum number of rectification stages is also needed to reach the extractive profile near SN from the specified composition  $\mathbf{x}_D$ . On the other hand, the rectification profile starting from the feed composition going to the top bends near pure A and turns in the direction of the azeotrope if too many stages are used. These effects are shown in Figure 11a,b. In both parts of this figure, the number of stages in the extractive profile is sufficiently large. (The steady states at 18 min after the start of step 2 are shown.) The distillate is contaminated with entrainer if the number of rectification stages is too low, and it is contaminated with component B if the number of rectification stages is too high.

Because the separation is infeasible without continuous feeding, there should also be a minimum feed flow rate at given vapor flow rate with an infinite reflux ratio.

**Effect of the Feed Ratio with Infinite Reflux Ratio.** Heating power is usually kept constant in batch



**Figure 11.** (a) Simulated column profile with insufficient number of rectifying stages. The top composition does not reach the specification. (b) Simulated column profile with too many rectifying stages. The liquid composition of a stage inside the column reaches the specified distillate purity, but the profile turns away sharply to the direction of the azeotrope. The top composition is not rich enough in A.

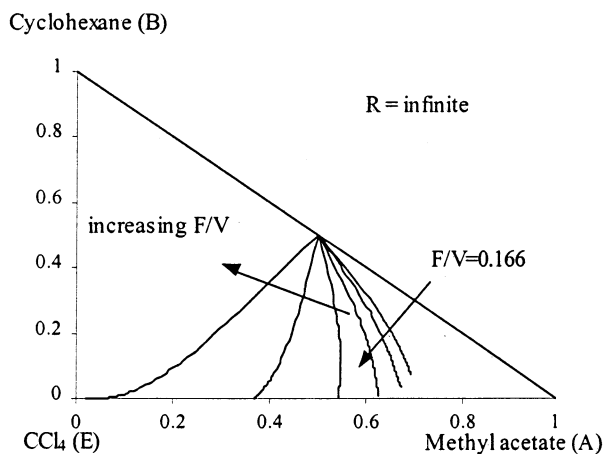
distillation; at the present stage of feasibility analysis constant  $V$  can be considered instead. For an infinite reflux ratio (no distillate removal, step 2), the feed flow rate is considered minimal if an infinite number of extractive stages is needed to reach the specified product purity, assuming the presence of the appropriate number of rectification stages.

Three profile maps, resulting from different feed flow rates, are shown in Figure 12. At the lowest feed flow rate ( $F/V = 0.05$ , Figure 12a), the stable node SN is situated at the very inside of the composition triangle. The extractive profiles crossed by the rectification profile of the specified product composition cover just a small area near the corner of pure A. In that area, the extractive profiles crossing the possible rectification profiles arrive from compositions richer in A than the points that can be reached with the rectifying profile itself. After crossing the possible rectification profiles, the extractive profiles run to SN. Thus, the separation is infeasible in this case; therefore, the feed flow rate is smaller than the minimum. With increasing feed flow rate, the locus of SN is continuously shifted nearer to the A-E edge while also being shifted farther from A. The feed flow rate is minimal if SN is just situated on the rectification profile characterizing the specified distillate composition. A further increase in flow rate of  $F$  leads to a further shifting of SN. Such a situation is shown in Figure 12b for  $F/V = 0.5$ . The stable node

**Figure 12.** (a) Stable node SN is situated inside the triangle. Therefore,  $F/V$  is less than the minimum. Pure A cannot be produced in this case. (b) Stable node SN moves down to and approximately along edge A-E. (c) Stable node SN moves out of the triangle.

can even be shifted outside the composition triangle, as shown in Figure 12c for  $F/V = 2.0$ . In either of the latter cases, the separation remains feasible.

$(F/V)_{min}$  at  $R = \infty$  can be approximately determined by finding the ratio at which SN reaches the A-E edge. To find the locus of SN, the computation of the whole profile map is not needed; the computation of a single extractive profile is enough. Any initial composition, e.g., the charge composition, can be used. A series of such single extractive profiles with different  $F/V$  ratios is shown in Figure 13. The pinch point reaches the A-E edge at about  $F/V = 0.166$ ; this rather modest value can



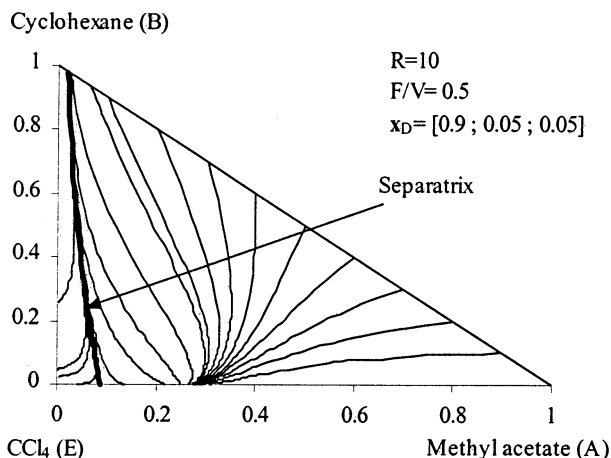
**Figure 13.** Extractive profiles at increasing feed ratios. The profiles reach the A–E edge approximately at the minimum  $F/V$  value.

be considered as the approximate minimum feed ratio:  $(F/V)_{\min} \approx 0.166$ . This is not an absolute minimum, as smaller ratios can be applied with finite reflux ratios, but a value higher than this one is suggested for the preliminary design. Considering also Figure 12b,c, the feed ratio ought to be kept under  $F/V = 2.0$ . Selecting such a value, or one even greater, would involve a larger number of rectifying stages than is necessary at  $F/V = 0.5$ , because the feed stage composition moves away from corner A. In most cases, the extractive section also needs more stages at higher  $F/V$ . Therefore,  $F/V = 0.5$  is suggested for a trial run.

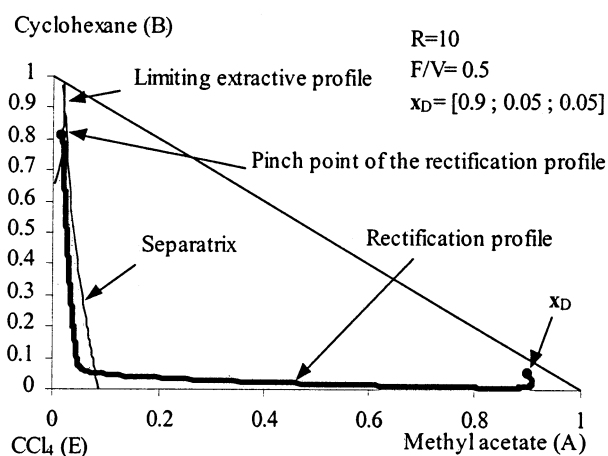
**Effect of the Reflux Ratio at Constant  $F/V$ .** The separation is feasible with infinite reflux ratio, as was shown in the previous sections. On the other hand, the profile maps might drastically change with changing reflux ratio; thus, its effect on feasibility must also be studied. For the sake of simplicity, the effect of  $R$  was studied at a feed ratio  $F/V$  greater than 0.166. At feed ratios under that value, the effect of  $R$  is more complicated.

If  $F/V$  is zero, there is no extractive section. At very small  $F/V$  ratios, the extractive profiles do not differ very much from the rectification profiles. Thus, the rectification profile map can be considered as a limiting case of the extractive profile map for  $F/V \rightarrow 0$ . Accordingly, at  $R = \infty$  and  $F/V = 0$ , corner B is an unstable node ( $UN^-$ ) of the extractive profiles, corner E is a saddle ( $UN$ , a notation compatible with the notation applied in our earlier publications; see Lelkes et al.<sup>12</sup> and Knapp and Doherty<sup>19</sup>), and the azeotropic composition is a stable node ( $SN$ ). As  $F/V$  is increased,  $SN$  moves into the triangle. As  $R$  is decreased from infinity to finite values at  $F/V > 0.166$ ,  $UN^-$  and  $UN$  move to the right, and a separatrix connecting them is formed. We do not indicate the exact positions of these points, in the same way that we do not indicate the exact position of  $SN$  in Figure 12c, because these points do not have physical meanings outside the composition triangle. However, the existence of the  $UN$  and  $UN^-$  points and the separatrix connecting them can be concluded from the shape of the profile map in Figure 14.

Several profile maps were computed with different reflux ratios  $R$ , all at the same feed ratio ( $F/V = 0.5$ ). The locations of the singular points of the extractive profile map strongly depend on  $R$ .  $SN$  is located along the A–E edge at high enough  $R$ , and the existence of



**Figure 14.** Extractive profiles at  $R = 10$ . There is a separatrix along edge E–B.



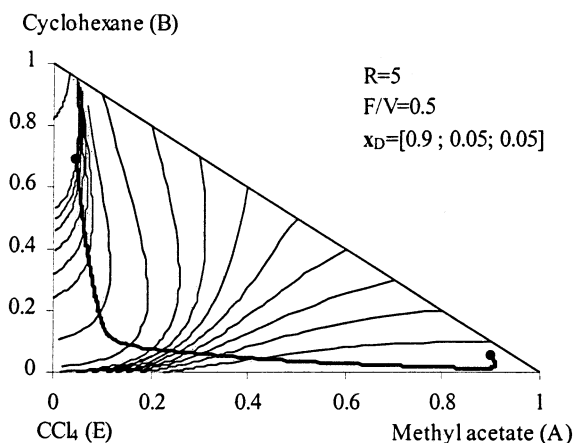
**Figure 15.** Rectification profile at  $R = 10$ . The limiting extractive profile goes through the pinch point of the rectification profile.

the separatrix can also be concluded, as is shown in Figure 14. The separatrix connecting the two nodes does not constitute a distillation boundary, because the rectification profiles cross it (cf. Figure 15).

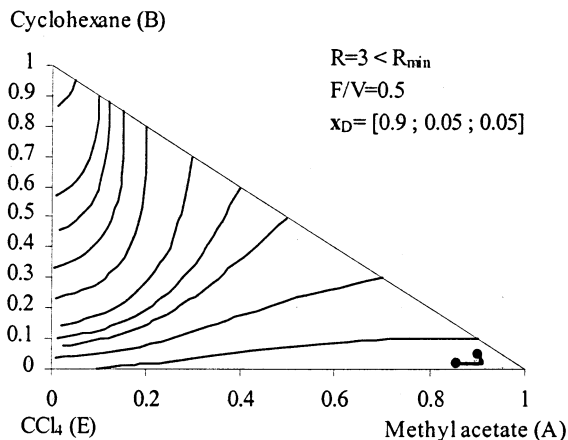
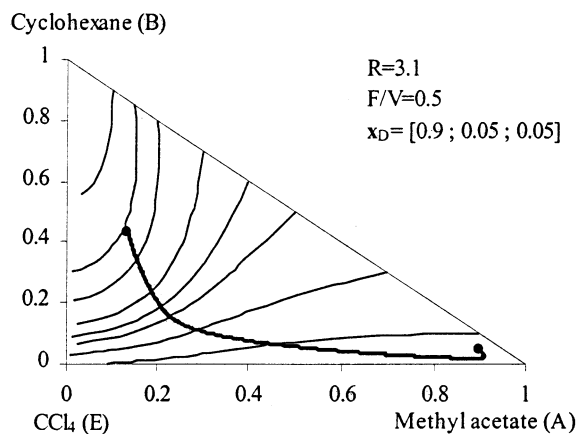
There are, however, a feasible region and an unfeasible region at this reflux ratio ( $R = 10$ ) and feed ratio ( $F/V = 0.5$ ). A feasible rectification profile characterizing the specified product composition is shown as a bold line in Figure 15. The extractive profile crossing the end point (pinch point) of the feasible rectification profile together with the feasible rectification profile itself is the boundary of the feasible region. Any point to the right of the boundary is a feasible still composition, whereas the points on to the left are infeasible. Extractive profiles computed from the points below or to the left of the boundary do not cross the feasible rectification profile. Points to the right of the boundary and to the left of the separatrix are also feasible, although the extractive profiles crossing them do not approach  $SN$  but lead to the B–E edge. These points are feasible because the feasible rectification profile crosses the extractive profiles starting from them.

As the reflux ratio is decreased further, the saddle node  $UN$  moves to the right, while  $SN$  moves left. As  $SN$  and  $UN$  approach each other, they move out of the triangle, and a map similar to that shown in Figure 16 ( $R = 5$ ) forms. The existence of the two (feasible and infeasible) regions is not affected by this radical change,





**Figure 16.** Extractive profiles and rectification profile at  $R = 5$ .

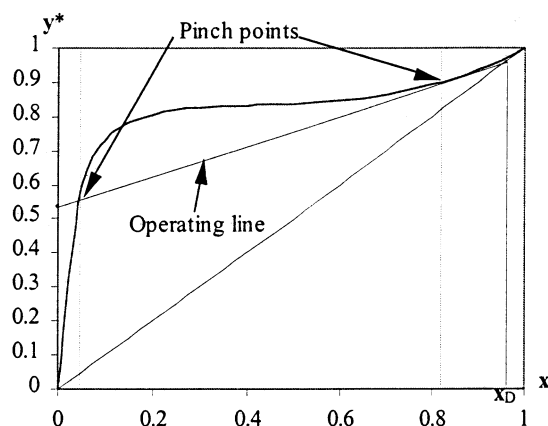


**Figure 17.** Extractive profiles and rectification profile at (a)  $R = 3.1$  and (b)  $R = 3.0$ .

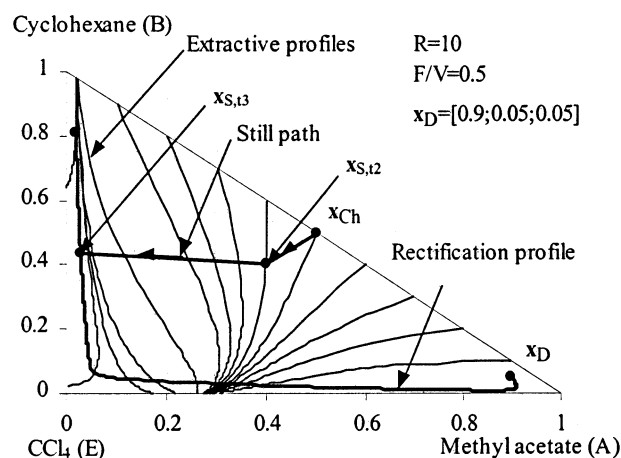
as the feasible rectification profile crosses appropriate extractive profiles.

However, decreasing  $R$  involves decreasing the length of the rectification profile. There is a sudden change in the length of the rectification profile (valid at the given product purity specification) as  $R$  decreases from 3.1 to 3.0, as is shown in Figure 17a,b. The short rectification profile cannot cross appropriate extractive profiles; thus, the separation is infeasible at  $R = 3.0$ . Consequently, the minimum reflux ratio is situated between these two values:  $3.0 < R_{\min} < 3.1$ .

The reason for the sudden change in the length of the rectification profile is the high curvature of the residue curves; there is a bifurcation of the pinch points. This



**Figure 18.** Tangential operating line at minimum reflux ratio in the case of a highly curved equilibrium line of a binary mixture.

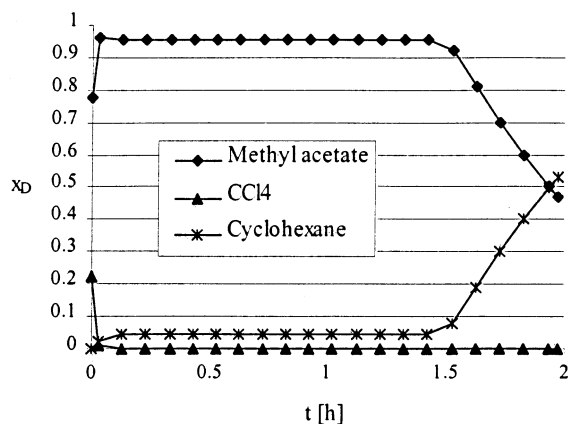


**Figure 19.** Estimation of the still path. The still path is to be ended at the calculated rectification profile characterizing  $x_D$ .

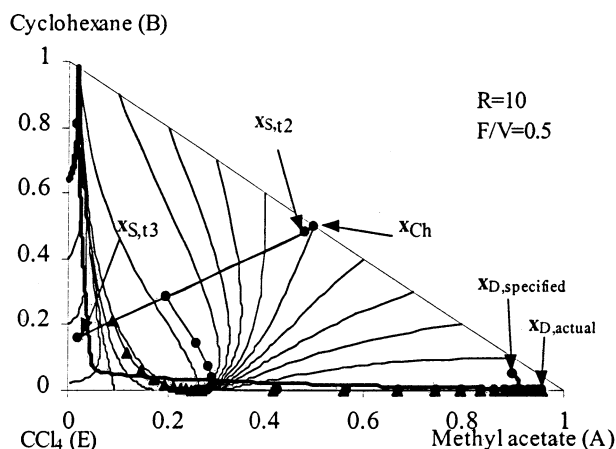
phenomenon is analogous to the assignment of a minimum reflux ratio in binary systems with an upper operating line tangential to the equilibrium line, as is illustrated in Figure 18.

**Estimation of Operating Time, Recovery, and Appropriate Numbers of Stages.** The necessary time for step 2 (run-up) cannot be estimated on the basis of the profile maps, but must be determined from hold-ups. Once this time is estimated, the still composition  $x_{S,t_2}$  at the end of step 2 can also be calculated by material balance. This is the starting point of step 3. The extreme end of step 3 is determined by the situation that the still path meets the boundary, very probably the rectification profile itself (see Figure 19). Although this situation cannot exactly be reached, it was chosen to approximate the operating time and the product recovery ratio.

The direction of the still path in step 3 is determined by a vectorial summation of the velocities assigned by the feed and the product removal. That is, the direction of the still path from  $x_{S,t_2}$  is  $Fx_F - Dx_D$ . The still path in this section is a straight line if the distillate composition and flow rate are constant. With a constant reflux ratio policy, the flow rate is constant. The composition changes slightly with constant reflux ratio, but for this preliminary estimation, the still path can be considered straight. The composition of the crossing point,  $x_{S,t_3}$ , can be read from the figure. Comparing this result to  $x_{S,t_2}$  and taking the feed flow rate into account, the operating time  $t_3 - t_2$  can be calculated. The recovery of component



**Figure 20.** Simulated column history (steps 2 and 3). The run ends when the accumulator composition reaches the specification. The actual distillate composition is plotted.



**Figure 21.** Two simulated column profiles over the background of the short-cut calculated profile maps. The still path ends on the profile of the actual distillate composition.

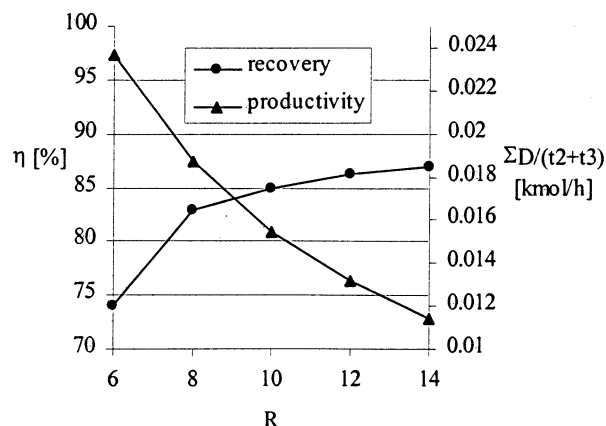
A can also be determined from the difference between  $x_{Ch}$  and  $x_{S,t3}$  and taking into account the amount of entrainer fed to the column in steps 2 and 3 together.

The appropriate number of equilibrium (ideal) stages can be simply determined using stage-by-stage calculations starting from  $x_D$  for the rectification section and starting from extreme points ( $x_{S,t2}$  and  $x_{S,t3}$ ) of the estimated still path for the extractive section.

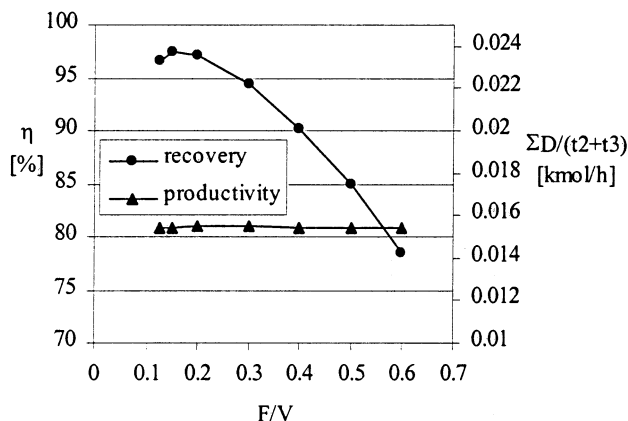
### Rigorous Simulation Results

The history of the mole fractions in the distillate stream in steps 2 and 3 is shown in Figure 20 for the following column and operating parameters:  $N_{extr} = 15$ ,  $N_{rect} = 15$ ,  $Q = 1.5$  kW,  $F = 0.085$  kmol/h,  $R = 10.0$ ,  $x_{Ch} = (0.5, 0.5, 0.0)$ , and  $H = 6$  L  $\approx 0.0645$  kmol. The given feed flow rate and boiling power roughly correspond to a feed ratio of  $F/V \approx 0.5$ . The still path together with two composition profiles (one at  $t = 41.4$  min and the other at  $t = 75.6$  min) are shown in Figure 21. The ending time of step 3 is  $t_3 \approx 1.98$  h  $\approx 118.8$  min.

The results are in good agreement with the estimated profiles and still path. The rectification profile shown with a bold line in the figure is calculated and valid at the specified  $x_D$  composition. However, the actual distillate composition of the real run is different; it is situated nearer to the corner point A. This situation is typical, because the limiting values are determined according to the specification, whereas the runs are performed at



**Figure 22.** Effect of the reflux ratio.



**Figure 23.** Effect of the feed ratio.

design parameters better than the minimum or maximum. In that case, the actual rectification profile runs nearer to the A–E edge; thus, the actual still path crosses the rectification profile calculated at the specified  $x_D$ .

The results of a parametric study are shown in the next five figures. The recovery ratio  $\eta$  (number of moles of component A in the accumulator per number of moles of component A in the charge) and productivity  $\Sigma D/(t_2 + t_3)$  (number of moles of product per step operating time for steps 2 and 3 together) are shown in all of these figures as functions of a selected parameter. The basis run for the study is given by the following data:  $N_{extr} = 15$ ,  $N_{rect} = 15$ ,  $Q = 1.5$  kW,  $F = 0.085$  kmol/h ( $F/V \approx 0.5$ ),  $R = 10.0$ , and no hold-up in the column. The charge is  $x_{Ch} = (0.5, 0.5, 0.0)$ ,  $H = 6$  L  $\approx 0.0645$  kmol, and the specified purity is 0.9 mole fraction of A in the accumulator at the end of step 3 in all cases.

The effect of  $R$  is shown in Figure 22. The specified purity cannot be achieved at  $R = 4.0$ , in agreement with the existence of  $R_{min}$ . The precalculated value of  $R_{min} < 3.1$  is valid at  $N = \infty$ , whereas  $R$  has a greater limit at a specified finite number of stages. The recovery ratio breaks down suddenly at low reflux ratios. With increasing reflux ratio, the recovery increases slightly, but the productivity decreases sharply. An optimum reflux ratio must be located somewhere in between.

The effect of the feed ratio  $F/V$  is shown in Figure 23.  $F/V$  does not significantly affect the productivity. The recovery ratio goes through a maximum and sharply decreases with decreasing feed ratio below the maximum point. The specified purity cannot be achieved at or below  $F/V \approx 0.11$ . This is in good agreement with

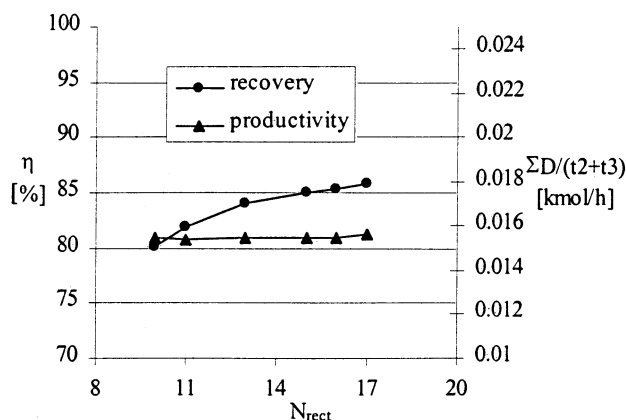


Figure 24. Effect of the number of rectification stages

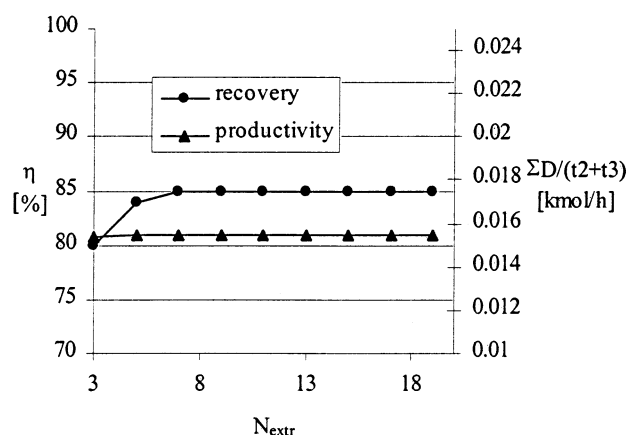


Figure 25. Effect of the number of the extractive stages.

our earlier conclusion that a minimum  $F/V$  exists. Its value is about 0.166 at total reflux ( $R = \infty$ , cf. Figure 12a) but can be smaller at finite reflux ratios ( $R < \infty$ ). The recovery ratio also decreases with increasing feed ratio above the maximum point because SN move to the left (cf. Figure 12b,c); this involves an increase in the number of necessary theoretical stages, but the actual number of stages is constant.

The number of rectification stages does not have any significant effect on the productivity, but the recovery ratio slightly increases with  $N_{\text{rect}}$ ; see Figure 24. There are both a minimum and a maximum number of rectifying stages (cf. Figure 11a,b). Accordingly, the simulation could not produce the specified purity at  $N_{\text{rect}} = 5$  (it was too low) or  $N_{\text{rect}} = 19$  (it was too high).

The number of extractive stages also has no significant effect on the productivity; however, after a steep increase in the recovery from 80 to 85% with an increase in  $N_{\text{extr}}$  from 4 to 6, the recovery does not increase significantly (see Figure 25). Therefore, five or perhaps six extractive stages are sufficient. This sudden increase in recovery and the subsequent stagnation can be explained by observing the corresponding change in composition at the top of the extractive section, i.e., the composition of the feed stage. As  $N_{\text{extr}}$  increases, this composition approaches SN (the pinch point), and once reaching a small neighborhood of SN, the composition does not change significantly (cf. Figure 19).

All of the results hitherto shown were computed with zero hold-up for the sake of simplicity. The column hold-up is expressed as a percentage of the initial hold-up in the still in Figure 26. The effect of the hold-up on the run-up time, shown in Figure 26a, is enormous if one

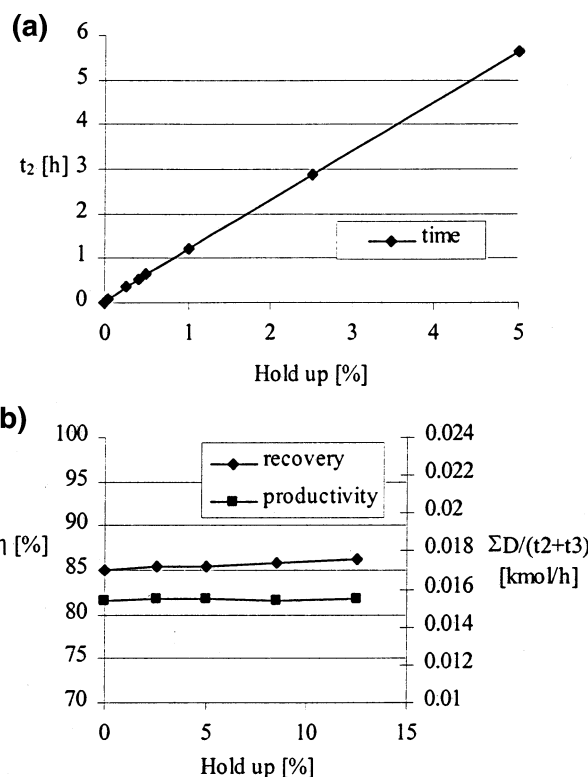


Figure 26. Effect of the column hold-up (in percent of the still) obtained (a) for step 2 and (b) by starting step 3 after a 0.03-h period of step 2.

insists on reaching the same purity in the top as specified with zero hold-up. The specified purity can be reached much faster, however, by starting step 3 before reaching the specified purity in step 2. The results shown in Figure 26b, obtained by starting step 3 after a 0.03-h period of step 2, indicate that hold-up has no significant effect on the recovery and productivity with this strategy.

## Conclusion

The separation of minimum-boiling azeotropes is feasible using batch extractive distillation (BED) in a rectifier column with an intermediate-boiling entrainer. The main difference between BED and solvent-enhanced batch distillation (SBD) is the application of continuous entrainer feeding either to the column or to the still.

BED processes with light or heavy entrainers were studied earlier. Finding an intermediate-boiling entrainer that works well 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 intermediate-boiling entrainer applied in our test example behaves as a very good entrainer, not considering its toxicity. The most significant reason for studying intermediate-boiling entrainers, however, is the opportunity of having an intermediate-boiling component in the mixture to be separated. In that case, the intermediate-boiling component might be the best choice because then no other, foreign, component needs to be applied.

The separation of minimum-boiling azeotropes in SBD with an intermediate-boiling entrainer is practically

infeasible. The application of continuous entrainer feeding (characteristic of BED) makes the process feasible. Our test mixture was methyl acetate and cyclohexane with carbon tetrachloride as the entrainer. This entrainer is toxic, but its application has didactic merits in presenting characteristic behavior of the studied process. According to a feasibility analysis based on profile maps, with infinite reflux ratio, the operation steps are as follows: (1) heat-up,  $R = \infty$ ,  $F = 0$ ; (2) run-up (reaching the pure product composition in the top),  $R = \infty$ ,  $F > 0$ ; (3) production of the first product,  $R < \infty$ ,  $F > 0$ ; and (4) production of the second product in the residue and regeneration of the entrainer (distillate),  $R < \infty$ ,  $F = 0$ .

The following limiting values constrain the design and operating parameters of the process:  $(F/V)_{\min}$  at constant  $R$ ;  $N_{\min, \text{extr}}$ ,  $N_{\min, \text{rect}}$ , and  $N_{\max, \text{rect}}$  all at constant  $R$  and given  $F/V$ ; as well as  $R_{\min}$  at given  $F/V$ .

Feasibility analysis includes the exploration, using profile maps, of the effects of parameters on the feasible region. Thus, the minimum feed ratio at total reflux (in our case  $F/V_{\min} \approx 0.166$ ), minimum reflux ratio at given feed ratio (e.g.,  $R_{\min} \approx 3.0\text{--}3.1$  at  $F/V \approx 0.5$ ), reasonable numbers of stages, and expected recovery and operating time can be determined. (The above numerical data are for specified purity  $x_{D,A} = 0.9$ .)

A rigorous simulation with ChemCAD provided results in good agreement with the estimated values. A parametric study was also performed, involving a study of the effects of the reflux ratio, feed ratio, numbers of stages, and column hold-up on the recovery and productivity of the process. The results of this parametric study support the conclusions drawn from the feasibility analysis.

## Acknowledgment

This work has been partially supported by Hungarian grants OTKA T037191 and OTKA F035085.

## Notation

$A, B, C$  = dimension-dependent parameters of the Antoine equation, eq 6  
 $A$  = binary interaction parameter in the 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 the NRTL equation, eq 7  
 $H$  = hold-up  
 $N$  = number of theoretical stages  
 $p$  = pressure  
 $p^\circ$  = vapor pressure of pure component  
 $R$  = Regnault's universal gas constant in eq 7  
 $R$  = reflux ratio  
 $Q$  = boiling power  
 $SBD$  = solvent-enhanced batch distillation  
 $\Sigma D/t$  = productivity (amount of product collected per unit time)  
 $SN$  = 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

$\alpha$  = nonrandomness parameter in the NRTL equation, eq 7

$\gamma$  = activity coefficient

$\eta$  = recovery (amount of A in the collector compared to amount of A in the charge)

$\tau$  = parameter in the 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

$\text{rect}$  = rectification section

$\text{extr}$  = 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

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*Received for review* January 28, 2002

*Revised manuscript received* October 18, 2002

*Accepted* October 18, 2002

IE020080A