

FEASIBILITY OF BATCH EXTRACTIVE DISTILLATION WITH MIDDLE-BOILING ENTRAINER IN RECTIFIER

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ABSTRACT

Feasibility of batch extractive distillation in rectifying column with a middle boiling entrainer is theoretically and experimentally studied. These processes are preferable when the entrainer is already present in the mixture to be separated. Separation of methyl acetate and cyclohexane (forming minimum boiling azeotrope) using carbon tetrachloride, and separation of chloroform and ethyl acetate (forming maximum boiling azeotrope) using 2-chlorobutane are theoretically studied based on profile maps and rigorous simulation. Non-extractive distillation with pre-mixing the entrainer to the charge is also studied in both cases. Feasibility of the processes is demonstrated experimentally in a laboratory scale packed column.

INTRODUCTION

Several suggestions can be found in the literature for batch separation of minimum or maximum boiling binary azeotropes using entrainer. According to [1], the entrainer for homoazeotropic distillation can be either the lightest, the heaviest, or even the intermediate boiling component in the system. The most significant reason to study intermediate boiling entrainers is the opportunity of having such a component in the mixture to be separated. This may be the best choice because no other, foreign, component is then applied. According to [2], maximum boiling azeotropes can be separated in a batch rectifier, and minimum-boiling azeotropes can be separated in a batch stripper, after mixing intermediate boiling entrainer to the charge. In case of a maximum boiling azeotrope, the full composition triangle constitutes a single distillation region in the sense of simple distillation (**Fig 1**); 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 case of applying infinite reflux ratio and infinite number of stages. If that extreme conditions are not satisfied then the third fraction is pure B, and the residue contains azeotropic mixture. In case of a minimum boiling azeotrope, the full composition triangle similarly constitutes a single distillation region in the

sense of simple distillation (**Fig 2**); thus the mixture can, in principle, be separated in a stripper. The first fraction is (the heavier) component B, the second one is the (intermediate boiling) entrainer E, and the third product is (the lighter) component A remaining in the upper vessel in case of extreme conditions, or is removed as the third fraction leaving azeotropic composition in the vessel. Suggestions of [2] are based on analysis of the residue curve map (RCM). This analysis involves the assumptions of infinite reflux ratio and infinite number of theoretical stages.

Batch Extractive Distillation (BED) is another entrainer-using batch process for separating azeotropes. 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 **Fig 3**. In contrast, the genuine batch distillation schemes with mixing the entrainer to the charge in advance, like those suggested in [2], will be called in this article 'Solvent-enhanced Batch Distillation' (SBD). Versions of BED in a rectifier, a stripper, or a middle vessel column [3] 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 heavy entrainer has been studied [4-8]. Separation of minimum boiling azeotropes with BED using light entrainer has also been studied [9,10]. According to our best knowledge, BED with intermediate boiling entrainer has not yet been studied or published.

METHODOLOGY OF THEORETICAL ANALYSIS

Feasibility Method

The first step in studying the opportunity of applying an entrainer in BED is testing its feasibility by simplified tools [6]. Here we re-iterate the essential steps and ideas of the feasibility method, because they are applied in the subsequent sections. The batch rectifier is divided into 3 main sections (**Fig 3**), from bottom up: (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 consisting of all the stages above the feed and the condenser with the reflux divider. The feasibility analysis is based on calculating and analysing the steady state concentration profile maps of the column's rectification and extractive sections, together with analysing the still path. The still path is the trajectory (i.e. projection to the composition triangle) of the still composition in time. Throughout this analysis, the usual simplifications are applied. Composition profiles in the column sections are computed by solving the following differential equation:

$$\frac{dx}{dh} = \pm \frac{V}{L} \left(y(x) - y^*(x) \right) \quad (1)$$

where h is dimensionless column height; y is computed according to the component balances, i.e. the so-called operating lines; whereas y^* is the corresponding equilibrium vapour composition of the liquid composition x . V/L is determined according to the molar balance in the corresponding column section (operating line). The still path is computed by solving the following differential component balance

$$\frac{d(H_S x_S)}{dt} = F x_F - D x_D \quad (2)$$

where F is feed, D is distillate, H is hold-up, and index S refers to the still. The feasible region of the separation, according to the definition [6] and in spirit of [3], is the set of feasible still compositions.

Equilibrium Model and Rigorous Simulation

Vapour-liquid equilibria are calculated using the modified *Raoult-Dalton* equation; the vapour pressure of pure components is calculated using three parameter *Antoine* equation with 10-base logarithm, Hgmm for pressure, and centigrade [C] for temperature. The liquid phase activity coefficients are calculated using NRTL model [11]. Simulations have been performed using Batch Distillation Unit, Simultaneous Correction model of ChemCAD[®] simulator, version 5.06. Boiling points and model parameters [12, 13] of the studied systems are listed in **Tables A1-A3**.

MINIMUM BOILING AZEOTROPE - THEORY

Separation of the methyl acetate from cyclohexane with carbon tetrachloride as an entrainer is selected as an example mixture to demonstrate the properties of this process.

Feasibility of SBD

SBD is a simpler process than BED; therefore it might be preferred. Determination of the separation sequence is based on RCM, shown in **Fig 4**. I and II are batch distillation regions. Assuming infinite reflux ratio and infinite number of stages, the first distillate product is the azeotrope. Thus, the products of operation steps, according to which region contains the initial still composition, would be those listed in the upper and the middle rows of **Table 1**. With lower 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 the upper and lower rows of **Table 1**.

Producing almost pure A is marginally feasible from both regions by applying huge amount of entrainer and *finite* number of theoretical stages, so that the residue curve crossing the mixed charge composition runs arbitrarily near to pure A, and the composition profile stops (or starts) at the specified purity. Then the operation steps and the products would be the following: 1st cut (distillate): pure A; 2nd cut (distillate): pure E; 3rd cut (residue): pure B. However, the product purity in the first step cannot be maintained with changing still composition in a column operated at constant number of stages and reasonable reflux ratio. Nevertheless test simulations were run, but the results confirmed the practical infeasibility of this process. In order to reach reasonable purity, approximately 13 times more entrainer than the charge is needed; involving unacceptable column and still dimensions.

Table 1: Would-be products of SBD with $N=\infty$

Operation step	Initial still composition is situated in	
	Region I	Region II
1 st cut (distillate)	A-B azeotrope	A-B azeotrope
2 nd cut (distillate)	pure A	pure E
If $R=\infty$:		
residue	pure E	pure B
If $R<\infty$:		
3 rd cut	pure E	-
residue	pure B	pure B

Feasibility of BED

Profile maps and separation sequencing

Rectification profiles and extractive profiles at $F/V=0.5$, both at infinite reflux ratio, are simultaneously shown in **Fig 5**. At this modest feed ratio, there is a stable node (SN) near the A-E edge, and this makes possible to reach high purity product even if the still composition is in the middle of the composition triangle. A feasible rectification profile is also shown in the figure by bold line. The feasible operation steps can be determined according to this figure.

First the charge is loaded to the still, and the column is heated up (step 1) without entrainer feeding and with total reflux. The column composition profile lies on the A-B edge. 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 to extractive distillation is forming in the column. The still composition moves from the charge inside the triangle in the direction of the feed composition. The feed tray composition is situated near SN. Separation of A from E happens practically in the rectification section, whereas the extractive section serves as to wash down component B. The still path can be calculated, according to **eq 2**, with zero distillate flow rate. After reaching the desired composition in the top, distillate product removal and collection is started in step 3. As a result of removing the product, the still path turns sharply to the opposite edge of the triangle, as is also shown in **Fig 6**. Step 3 may be ended when either component A is removed from the still or some boundary is reached, depending on the finite reflux ratio. According to the information available based on the profile maps with infinite reflux ratio, this step ends when the still path reaches the B-E edge. The B-E mixture in the still is separated in step 4 without entrainer feeding. The operation steps can be summarised as follows:

- Step 1. Heat-up, $R=\infty$, $F=0$
- Step 2. Run-up (reaching pure product composition in the top), $R=\infty$, $F>0$
- Step 3. Production of the 1st product, $R<\infty$, $F>0$
- Step 4. Entrainer regeneration (distillate), 2nd product in the residue, $R<\infty$, $F=0$

Profile maps, limiting values, effects

Some consequences of having profile maps shown in **Fig 5** are that the feasible number of extractive stages should have a minimal value; the feasible number of rectification stages should have both minimal and maximal value; and there is a minimal F/V ratio, at infinite reflux ratio. A minimum number of extractive stages are needed to reach the neighbourhood of SN from all the points of the still path. A minimum number of rectification stages are also needed to reach the extractive profile, near SN, from the specified \mathbf{x}_D composition. On the other hand, the rectification profile starting from the feed composition up to the top bends near pure A and turns in the direction of the azeotrope if too many stages are used. Two profile maps, belonging to two different feed flow rates, at total reflux, are shown in **Fig 7**. At $F/V=0.05$ (**Fig 7a**) the stable node SN is situated in the very inside of the composition triangle. The separation is infeasible in this case; therefore, the feed flow rate is smaller than the minimum. The feed flow rate is minimal if SN is situated on the rectification profile belonging to the specified distillate composition. Further increase in flow rate of F leads to a further shifting of SN, see **Fig 7b**, with $F/V=0.5$. A series of extractive profiles with different (F/V) ratios is shown in **Fig 8**. The pinch point reaches the A-E edge at about $(F/V)_{\min} \approx 0.166$. However, this is not an absolute minimum; smaller ratios may be applied with finite reflux ratios.

The profile maps may drastically change with changing reflux ratio. For the sake of simplicity, the effect of R is studied at a feed ratio F/V greater than 0.166. There is a drastic change in the length of the rectification profile as R decreases from 3.1 to 3.0, as is shown in **Figs 9a** and **9b**. The short rectification profile cannot cross appropriate extractive profiles; thus the separation is infeasible at $R_{\min}=3.0$. As a conclusion, minimum reflux ratio is situated between these two values: $3.0 < R_{\min} < 3.1$. Direction of the still path from $\mathbf{x}_{S,12}$ in step 2 is determined as $F\mathbf{x}_F - D\mathbf{x}_D$, see **Fig 10**. The rectification profile constitutes a boundary of the feasible still compositions.

Simulation Results

Simulation of steps 2 and 3 is performed with $N_{\text{extr}}=15$, $N_{\text{rect}}=15$, $Q=1.5$ kW, $F=0.085$ kmol/h, $R=10.0$, $\mathbf{x}_{\text{Ch}}=[0.5; 0.5; 0.0]$, $H=6$ liter ≈ 0.0645 kmol. The given feed flow rate and boil-up duty roughly correspond to a feed ratio $F/V \approx 0.5$. The still path together with two composition profiles (one at $t=41.4$ min, the other at $t=75.6$ min) are shown in **Fig 11**. The time of finishing step 3 is $t_3 \approx 1.98$ h ≈ 118.8 min.

Results of a parametric study are shown in **Figs 12-15**. Recovery ratio η (moles of component A in the accumulator per that in the charge), and productivity $\Sigma D/(t_2+t_3)$ (product moles per step operation time, step 2 and step 3 together) are shown in all the figures as function of a selected parameter. The basis run for the study is given as $N_{\text{extr}}=15$, $N_{\text{rect}}=15$, $Q=1.5$ kW, $F=0.085$ kmol/h ($F/V \approx 0.5$), $R=10.0$. The charge is $\mathbf{x}_{\text{Ch}}=[0.5; 0.5; 0.0]$, $H=6$ liter ≈ 0.0645 kmol, the specified purity is 0.9 mole fraction of A in the accumulator, at the end of step 3, in all the cases. The specified purity cannot be achieved at $R=4.0$, in agreement to the existence of R_{\min} . The pre-calculated $R_{\min} < 3.1$ is valid at $N=\infty$, whereas R has a greater limit at a specified finite number of stages. The specified purity cannot be achieved at or below $F/V \approx 0.11$. This is in good agreement with our earlier conclusion of having a minimal F/V . Its value was about 0.166 at total reflux, but can be smaller at $R < \infty$. The simulation

could not produce the specified purity at $N_{\text{rect}} \leq 5$ or $N_{\text{rect}} \geq 19$ in agreement to the existence of minimal and maximal stage numbers. The effect of too few extractive stage numbers on the recovery, as expected, can also be observed.

MAXIMUM BOILING AZEOTROPE - THEORY

It is rather difficult to find entrainer for maximum boiling azeotropes. The system of chloroform and ethyl acetate with 2-chlorobutane (**Fig 2**) seems to be an appropriate example, although the entrainer is not so good as usually expected.

Feasibility of SBD Producing Pure A

SBD is a simpler process than BED; therefore it might be preferred. The proposed process [2], based on RCM, is illustrated in **Fig 16**. Rigorous simulations have been performed to validate this process. However, moderately pure chloroform ($x_{\text{AD}} \geq 0.9$) could not be produced even with a great number of theoretical stages and unacceptable great reflux ratio. Two column profiles, one with $x_{\text{S}} = [0.1; 0.635; 0.626]$, and the other with $x_{\text{S}} = [0.05; 0.3175; 0.6325]$, are shown in **Fig 17**. In both cases, the column has $N=100$ stages, $R=70$ reflux ratio, and $Q=1.5$ kW boil-up duty. 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.

Feasibility of BED Producing Pure A

According to the general feasibility methodology, extractive profiles for a specified distillate composition, total reflux, and several feed ratios are also computed, and visualised together with RCM. With an appropriate feed ratio, e.g. $F/V=0.2$, all the extractive profiles run into the same stable node SN, as shown in **Fig 18**. 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.
- 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.

Single extractive profiles with different F/V ratios but all with the same x_{S} are shown in **Fig 19**. It can be seen that there is not minimal value of F/V ; the process is (marginally) feasible without continuous feeding. The rectification profiles are highly sensitive on the locus of the specified distillate composition. Therefore, a minimal molfraction of component A in the distillate is specified. The feasible region of BED is shown in **Fig 20** at $R=49$. Even at this high reflux ratio, the still path cannot reach the B-E edge; the entrainer cannot be regenerated; the specified purity cannot be achieved even with BED.

Feasibility of SBD and BED Producing A+E Mixture

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. In order to obtain pure A in a later step, reduced molfraction of A, $x_{\text{AR}} = x_{\text{A}} / (x_{\text{A}} + x_{\text{B}})$, in the distillate is specified. With a high enough value, e.g. $x_{\text{AR}} = 0.98$, this assigns a narrow triangle along the A-E edge, as a range of acceptable distillate compositions.

SBD

The feasible region, shown in **Fig 21**, reaches the B-E edge ($N=\infty$), and the separation is practically feasible with the following operation steps:

- Step 0. Mixing some entrainer to the charge.
- Step 1. Heat-up.
- 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.

There is a minimum entrainer amount to be mixed to the charge in order to get into the feasible region, if the charge composition is situated in the infeasible region. In order to get an SBD process with reasonable recovery, however, use of a higher amount of entrainer is necessary. If the mixed charge composition is not well inside the feasible region, the still path crosses into the feasibility boundary, see **Fig 22**.

BED

Based of **Fig 21**, the operation steps of BED can also be determined:

- Step 0. Mixing some entrainer to the charge.
- Step 1. Heat-up.
- 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 significant merit of applying continuous feeding is illustrated in **Fig 23**. Distillation in step 2 with the same recovery specification can be started with less amount of pre-mixed entrainer, because the continuous feeding of the entrainer turns the still path more in the direction toward edge B-E. Since the feasibility region valid for SBD reaches edge B-E, feeding to the still is sufficient.

Simulation Results

Simulation of step 2 of SBD is performed with $N=45$, $Q=1.5$ kW, $R=20.0$, $\mathbf{x}_{Ch}=[0.5; 0.5; 0.0]$, $H=6$ liter ≈ 0.068 kmol, $\mathbf{x}_{S,t0}=[0.215; 0.215; 0.57]$, $H_0=15.46$ liter ≈ 0.158 kmol. The amount of the consumed entrainer 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 **Fig 24**. The results are in good agreement with the approximating profile map. The achieved purity $x_{AR} \equiv x_A/(x_A+x_B)$ 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 (BED) is also performed with $N_{extr}=0$ (feed to the still), $N_{rect}=45$, $Q=1.5$ kW, $F=0.009$ kmol/h, $R=20.0$, $\mathbf{x}_{Ch}=[0.5; 0.5; 0.0]$, $H=6$ liter ≈ 0.068 kmol. The given feed flow rate and boil-up duty roughly correspond to a feed ratio $F/V \approx 0.05$. The still path together with two composition profiles (one at $t=1$ h, the other at $t=5$ h) are shown in **Fig 25**. The achieved purity $x_{AR} \equiv x_A/(x_A+x_B)$ 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 specified in a way that they provide the same purity in the accumulator and consuming the same amount of entrainer. According to the

results, BED produces the same products in shorter time (10.0 h vs. 11.3 h) and half of the still hold-up (7.1 liter vs. 15.5 liter) with identical purity and productivity. Thus, BED may be preferred over SBD.

Table 2: Comparison of SBD and BED

	SBD	BED
Charge, liter	6	6
Amount of entrainer, mol	90	90
Time of producing A+E, hour	11.29	10.0
Maximum still hold-up, liter	15.5	7.1

Results of a parametric study on BED are shown in **Figs 26-29**. 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 function of a selected parameter. $N_{\text{rect}}=50$, $N_{\text{extr}}=0$, $Q=1.5$ kW, $F=0.072$ kmol/h ($F/V \approx 0.04$), $R=24.0$, the charge is $\mathbf{x}_{\text{Ch}}=[0.136; 0.864; 0.0]$ azeotropic composition being inside the infeasibility region, $H_{\text{Ch}}=4.3$ liter ≈ 45.2 mol, $\mathbf{x}_{\text{S},t_0}=[0.1; 0.635; 0.265]$, $H_0=6$ liter ≈ 61.5 mol, no hold-up in the column, the specified purity is 0.98 reduced mol fraction $x_A/(x_A+x_B)$ in the accumulator, at the end of step 2, in all the cases. The trends are generally the same as usual in conventional batch distillation. On the other hand, the unfavourable effect of too low feed ratio (F/V) can be observed. At low feed ratio the recovery (and/or product purity) sharply decreases.

EXPERIMENTAL RESULTS

Distillation apparatus

A 5 cm diameter packed glass column with two feed junctions, one is just at the bottom, the other one is at the upper third length, is built over a 1 liter, three-neck, glass still. A cooler with reflux distributor is fitted on the top of the column, according to **Fig 30**. Oil bath with electric heater controlled by a two-state automatic switch is applied to boil up the column. A two-state magnetic device with time-switch electric controller is applied to maintain the specified reflux ratio. The still is equipped with a sampler. The approximate number of theoretical stages in the whole column is 16 at system Methyl acetate / Cyclohexane / Carbon tetrachloride, and is 12 at system Chloroform / Ethyl acetate / 2-Chlorobutane.

Materials and analysis

Materials are obtained from REANAL (cyclohexane, ethyl acetate, chloroform) and MERCK (2-chlorobutane, methyl acetate, carbon tetrachloride). Composition was determined by a PerkinElmer AutoSystem XL gas chromatograph equipped with TCD. Samples were run through a 2 m column filled with PEG 1540.

BED of Methyl acetate and Cyclohexane with Carbon tetrachloride

The aim of the experiment was to check the feasibility of the process. The process is considered feasible if the distillate composition path can cross the isovolatility line during the run-up step. The isovolatility line is an extension of the azeotrope inside the composition triangle. Therefore; the experiment were started with a binary charge composition $[0.5; 0.5; 0]$ situated between pure cyclohexane and the azeotrope. The

distillate composition at total reflux is situated on the same side of the azeotrope. According to the measurement, it was $\mathbf{x}_D(R=\infty)=[0.757; 0.245; 0]$. In order to accelerate the experiment and to decrease the effects of column hold-up, the run-up was performed with finite reflux ratio ($R=10$). The distillate composition path is shown in **Fig 31**. The isovolatility curve started from the azeotrope is also indicated in the figure. The composition path crosses the isovolatility line, steadily approaches the A-E binary edge, and thus it demonstrates the feasibility of the process. The actual number of theoretical stages is not sufficient to produce purer product.

SBD of Chloroform and Ethyl acetate with 2-Chlorobutane

The aim of the experiment was to check the feasibility and the applicability of the process. According to our best knowledge, such an experiment has not yet been published. Charge pre-mixed with entrainer was loaded to the still. The distillate and the still compositions at total reflux were found as $\mathbf{x}_D(R=\infty)=[0.6247; 0.0110; 0.3643]$ and $\mathbf{x}_S(R=\infty)=[0.3363; 0.6276; 0.0361]$. The distillate composition is far from being pure, but is pure enough in the sense of relative molfraction. The distillate composition path and the still composition path at $R=18$ are shown in **Fig 32**. The distillate initially moves along the A-E edge but then it sharply turns away. This happens because the still composition approaches and crosses the feasibility border (also indicated in the figure). That is, the process is feasible for producing A-E mixture free of B, but the recovery is limited, as it was expected.

BED of Chloroform and Ethyl acetate with 2-Chlorobutane

The aim of the experiment was to check the feasibility of keeping the distillate composition along the A-E edge with continuous entrainer feeding. Charge pre-mixed with entrainer was again loaded to the still. The distillate and the still compositions at total reflux were found as $\mathbf{x}_D(R=\infty)=[0.6384; 0.0198; 0.3418]$ and $\mathbf{x}_S(R=\infty)=[0.3376; 0.6302; 0.0322]$. Thus, a column state similar to that found in the SBD experiment is reached. The distillate contains more of the heavy component than at the SBD experiment. The distillate composition path and the still composition path at $R=18$ are shown in **Fig 32**. The two distillate composition paths (one for the SBD experiment, the other for the BED experiment) cross each other. In spite of the worse initial composition, the distillate is kept along the A-E edge for a similar period as was traced at SBD. The direction of the still path in the BED experiment keeps the still composition inside the feasible region. Thus, the experimental results demonstrate the feasibility of the process.

CONCLUSION

Separation of both minimum and maximum boiling azeotropes are feasible using Batch Extractive Distillation (BED) in a rectifier column with intermediate boiling entrainer. The main difference of BED comparing to Solvent-enhanced Batch Distillation (SBD) is application of continuous entrainer feeding either to the column or to the still.

Separation of minimum boiling azeotropes in SBD with intermediate boiling entrainer is practically infeasible. Application of continuous feeding (characteristic to BED) makes the process feasible with the following operation steps:

1. Heat-up, $R=\infty$, $F=0$
2. Run-up (reaching pure product composition in the top), $R=\infty$, $F>0$
3. Production of the 1st product, $R<\infty$, $F>0$
4. Entrainer regeneration (distillate), 2nd product in the residue, $R<\infty$, $F=0$

Our test mixture is methyl acetate and cyclohexane with carbon tetrachloride as entrainer. Rigorous simulation provides results in good agreement with the estimated values. Experimental results demonstrate the feasibility of the new process.

Separation of maximum boiling azeotropes in both SBD and BED is feasible with intermediate boiling entrainer, but application of continuous feeding (characteristic to BED) makes the process more efficient. Our test mixture is chloroform and ethyl acetate with 2-chlorobutane as entrainer. Pure component A cannot be produced in either SBD or BED. Producing component A mixed with entrainer and free of component B is, on the other hand, feasible in both processes. The operation steps are rather similar in the two processes. The only difference in the operation steps is the continuous feeding in step 2. In practice, much less entrainer is to be pre-mixed with the charge in the case of BED, whereas entrainer is continuously fed to the still (or to some stage near the still) during step 2. With identical specification, equal amount of entrainer, and comparable operation parameters, BED produces the same recovery in shorter time and significantly less hold-up in the still. Experimental results demonstrate the feasibility of both processes.

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APPENDIX

Table A1: Normal boiling points of the pure materials and the azeotropes

	Boiling point [C]		Boiling point [C]
Azeotrope (A-B)	54.5	Chloroform (A)	61.7
Methyl acetate (A)	56.7	2-Chlorobutane (E)	68.1
Carbon tetrachloride (E)	76.3	Ethyl acetate (B)	77.1
Cyclohexane (B)	80.3	Azeotrope (A-B)	77.8

Table A2: Antoine coefficients

	A	B	C
Methyl acetate (A)	7.41791	1386.51	247.853
Carbon tetrachloride (E)	6.87926	1212.021	226.409
Cyclohexane (B)	6.85146	1206.47	223.136
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

Table A3: NRTL parameters

i-j	MeOAc, CCl ₄ , Cyclohexane			CHCl ₃ , 2Cl-Butane, EtOAc		
	A _{ij}	A _{ji}	α_{ij}	A _{ij}	A _{ji}	α_{ij}
A-E	173.3082	175.3669	0.3013	857.97	-595.47	0.2216
A-B	588.5211	455.9006	0.2953	375.569	-619.982	0.8704
E-B	696.57	-570.815	0.3048	118.613	16.088	0.3007

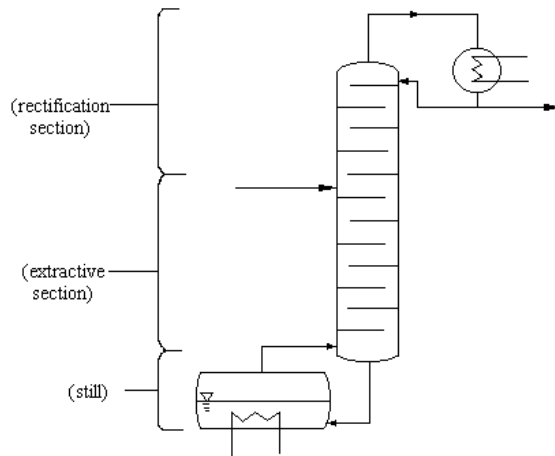


Figure 3. Sections of BED

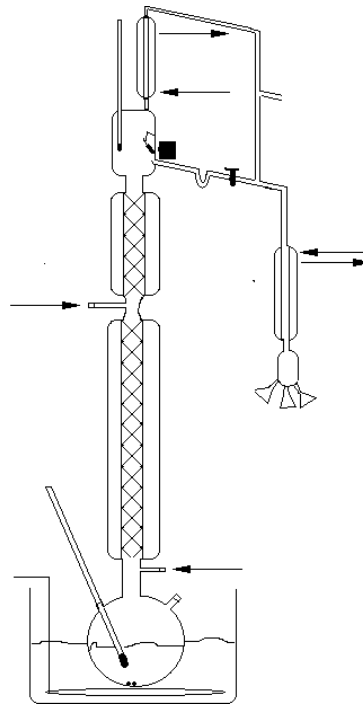


Figure 30. Experimental setup

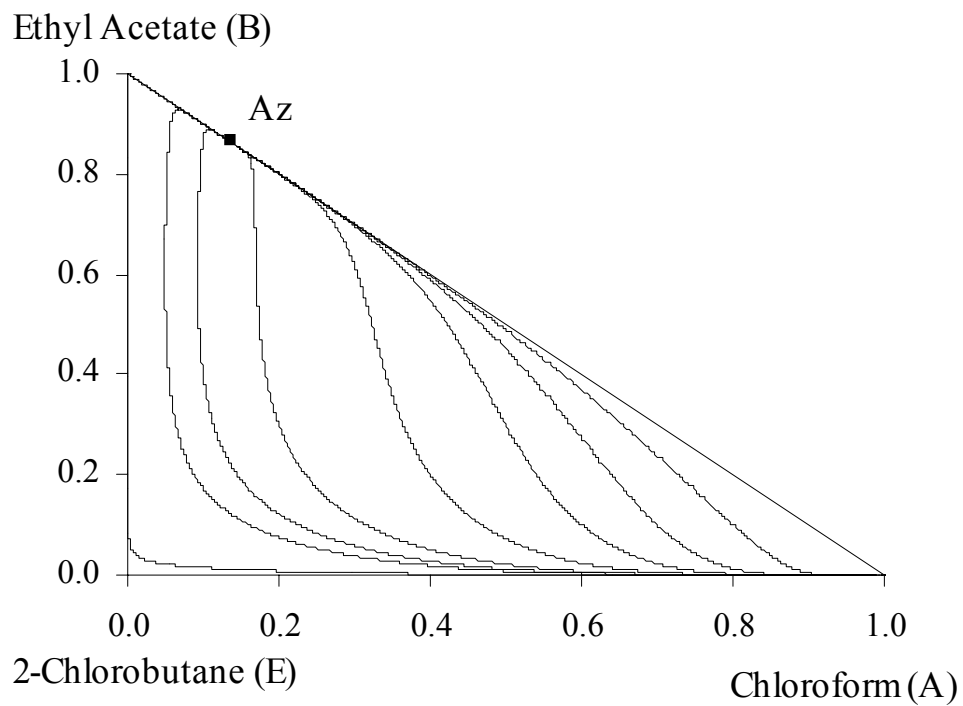


Figure 1. RCM of a maximum boiling azeotrope with middle boiling entrainer

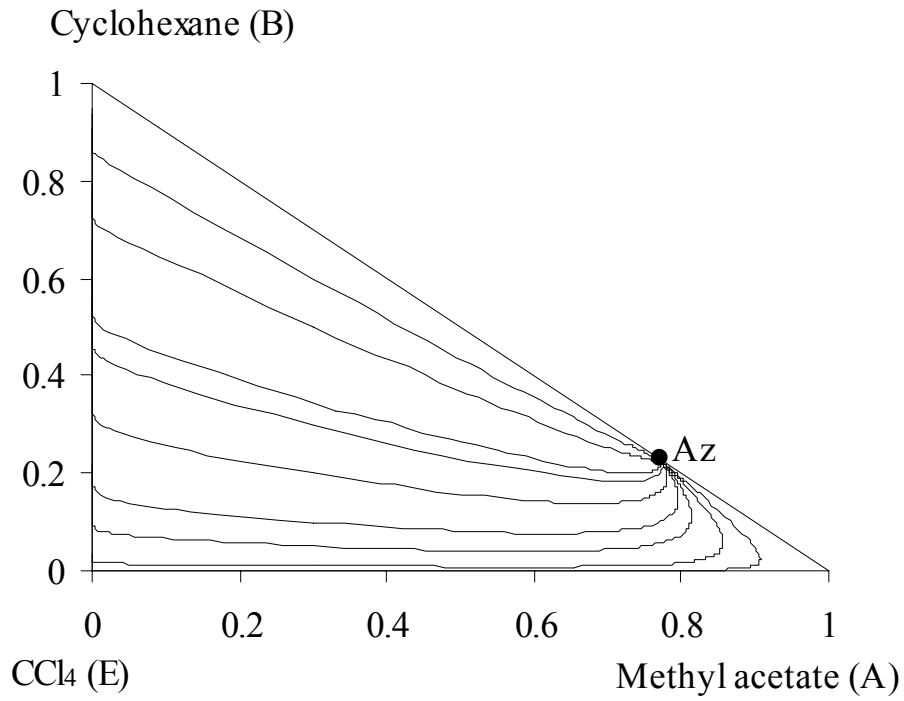


Figure 2. RCM of a minimum boiling azeotrope with middle boiling entrainer

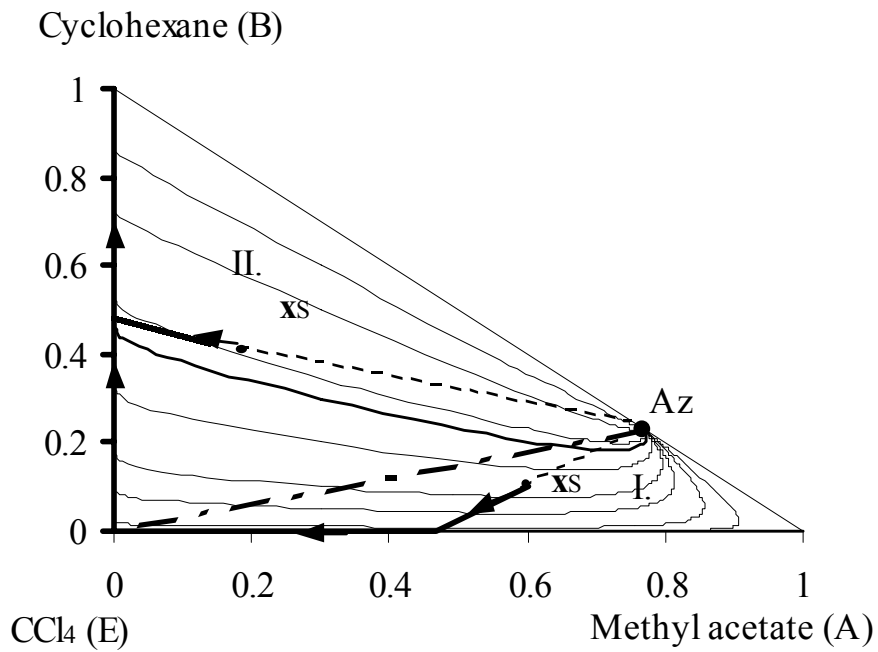


Figure 4. Still paths of SBD

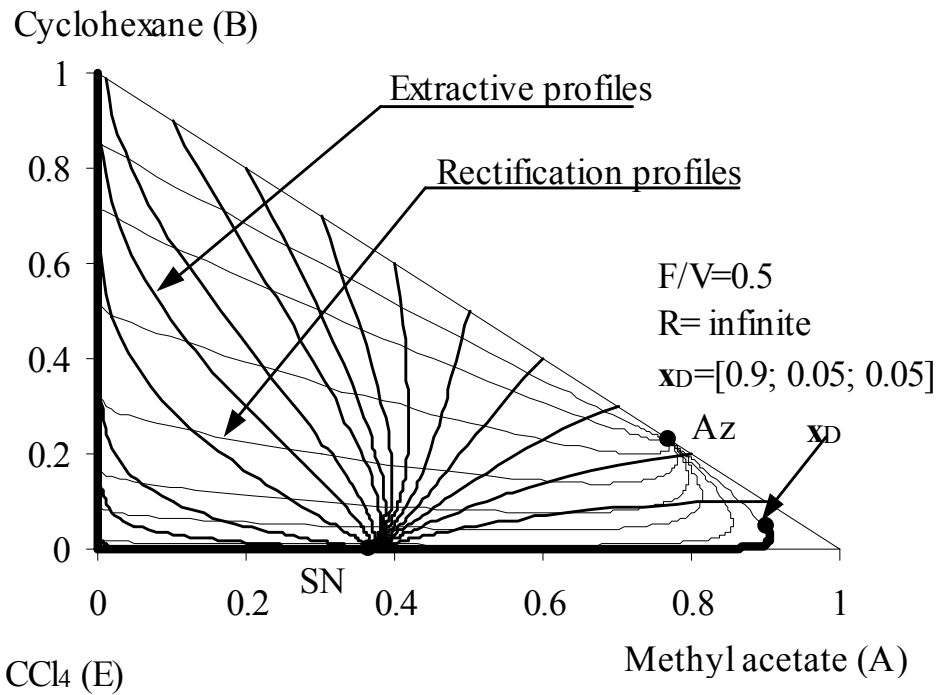


Figure 5. Extractive and rectification profile maps at infinite reflux ratio and $F/V=0.5$.

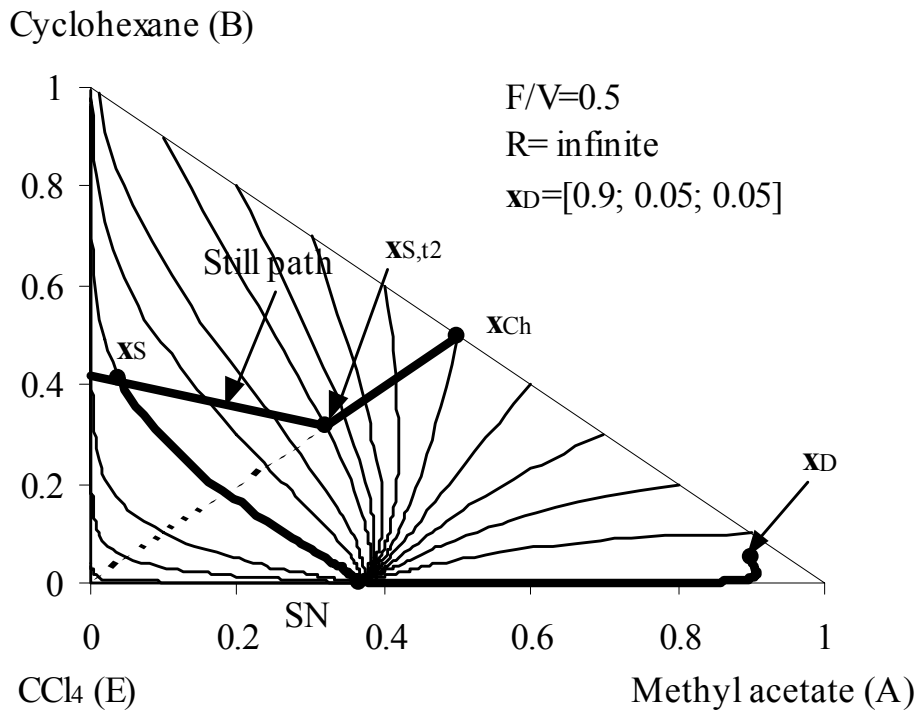


Figure 6. Step 3: Production of component A. The profiles are calculated with infinite reflux ratio (short-cut). The still path is estimated for finite reflux ratio.

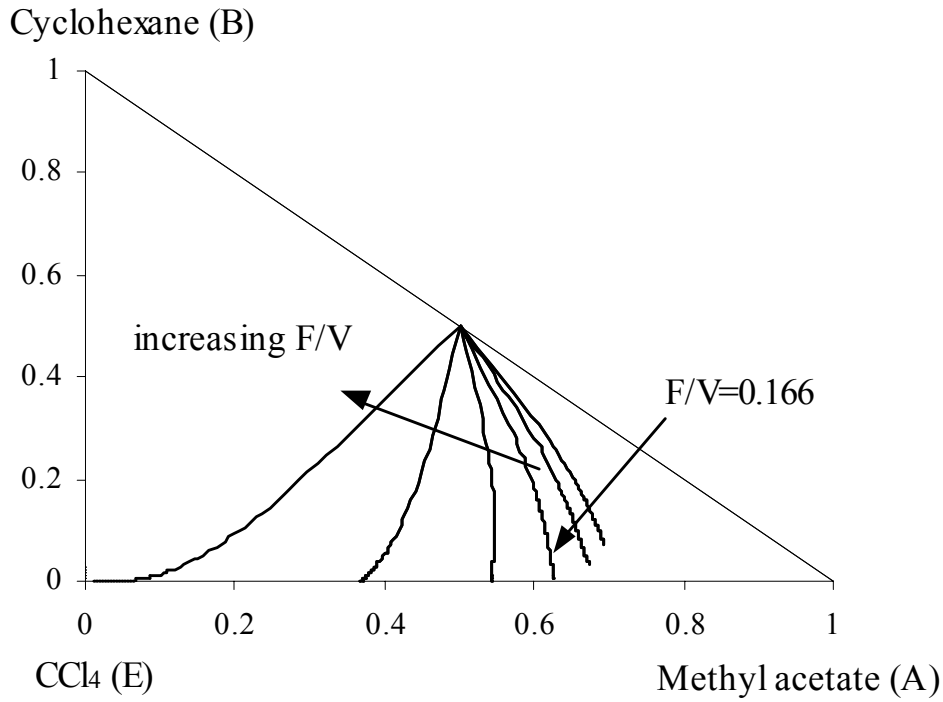


Figure 8. Extractive profiles at increasing feed ratios. The profiles reach the A-E edge approximately at the minimal F/V value.

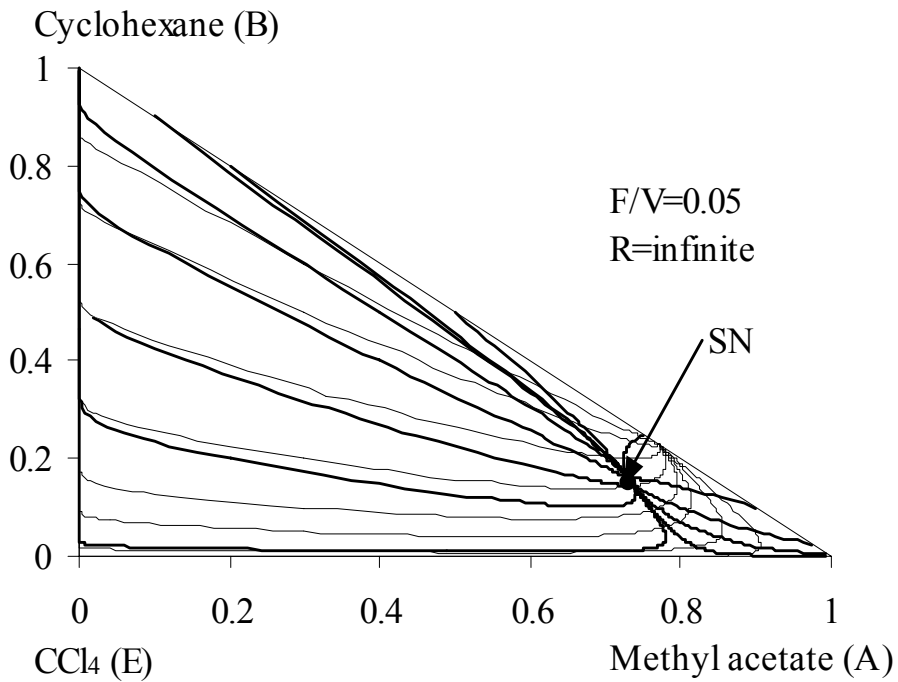


Figure 7a. Stable node SN is situated inside the triangle. Therefore, F/V is smaller than the minimum. Pure A cannot be produced in this case.

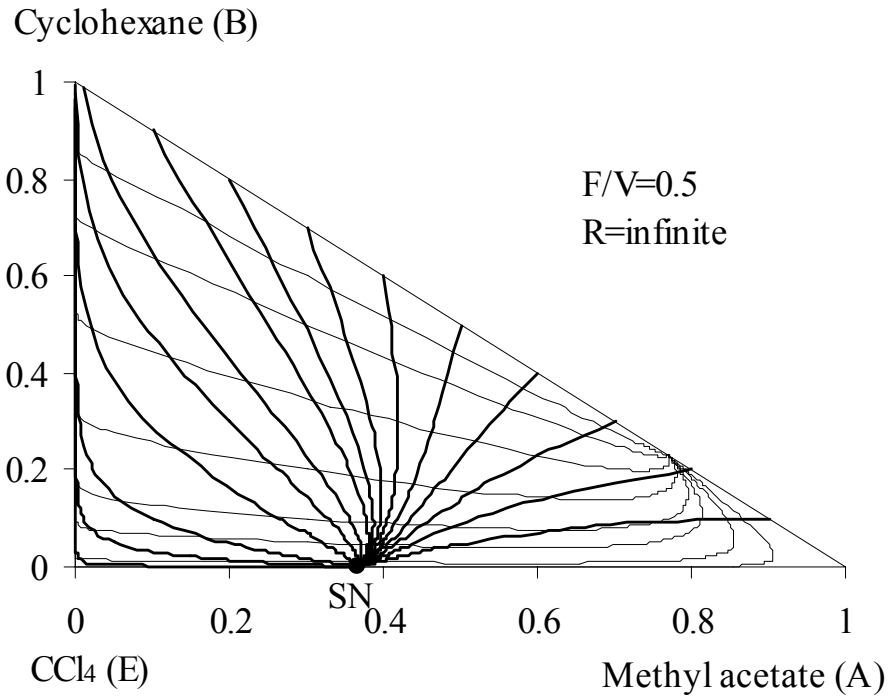


Figure 7b. Stable node SN moves down to and approximately along edge AE.

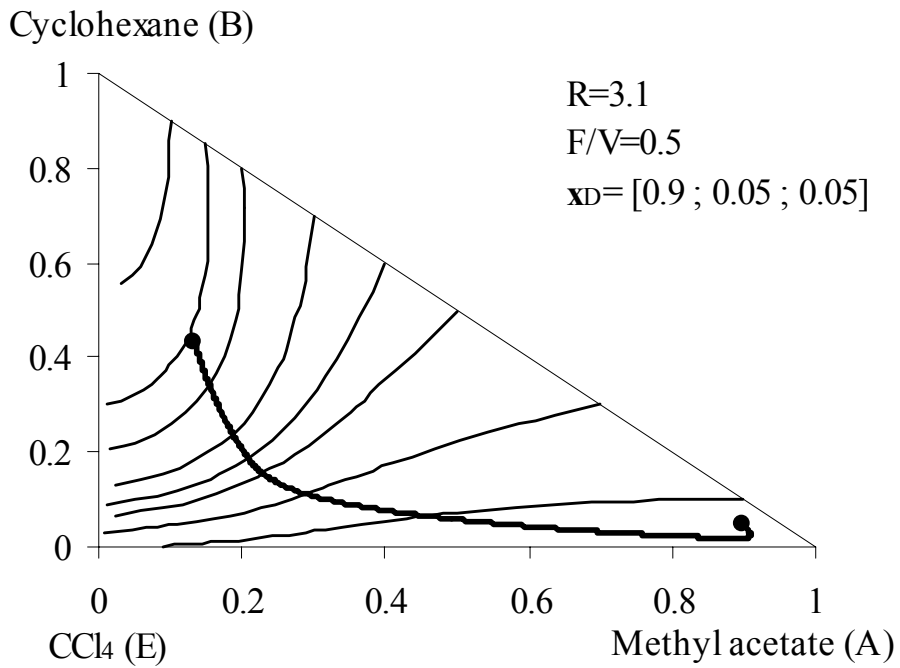


Figure 9a. Extractive profiles and rectification profile at $R=3.1$.

Cyclohexane (B)

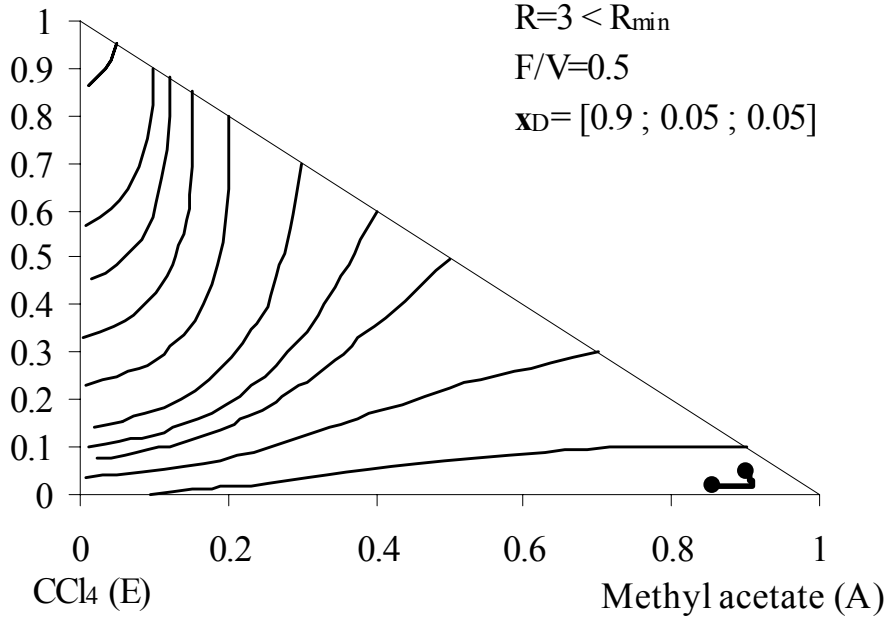


Figure 9b. Extractive profiles and rectification profile at $R=3.0$.

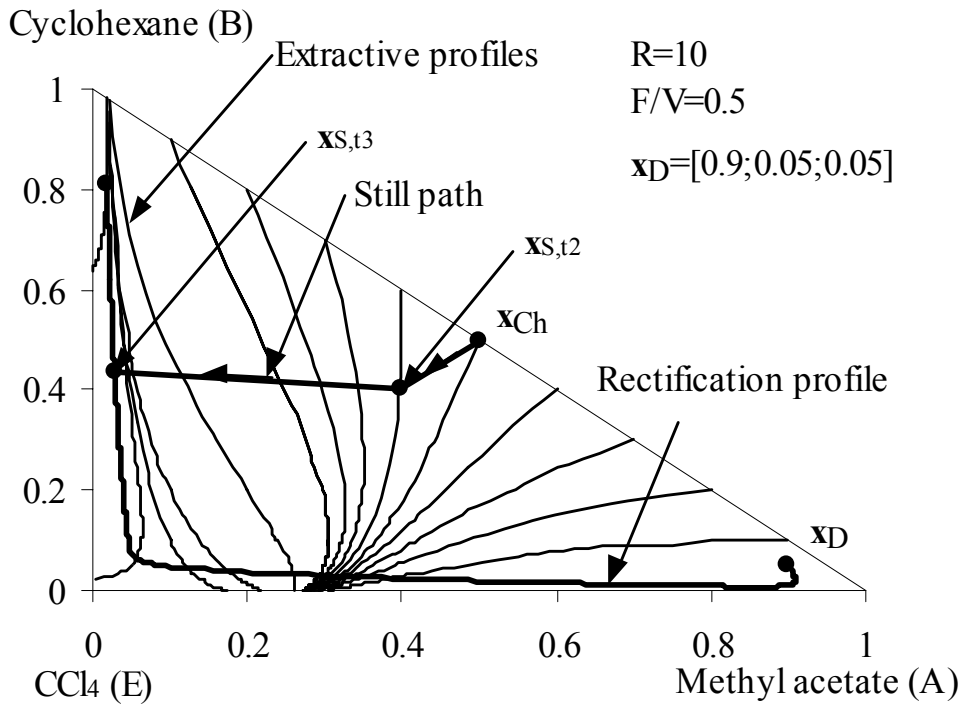


Figure 10. Estimation of the still path. The still path is to be ended at the calculated rectification profile belonging to x_D .

Cyclohexane (B)

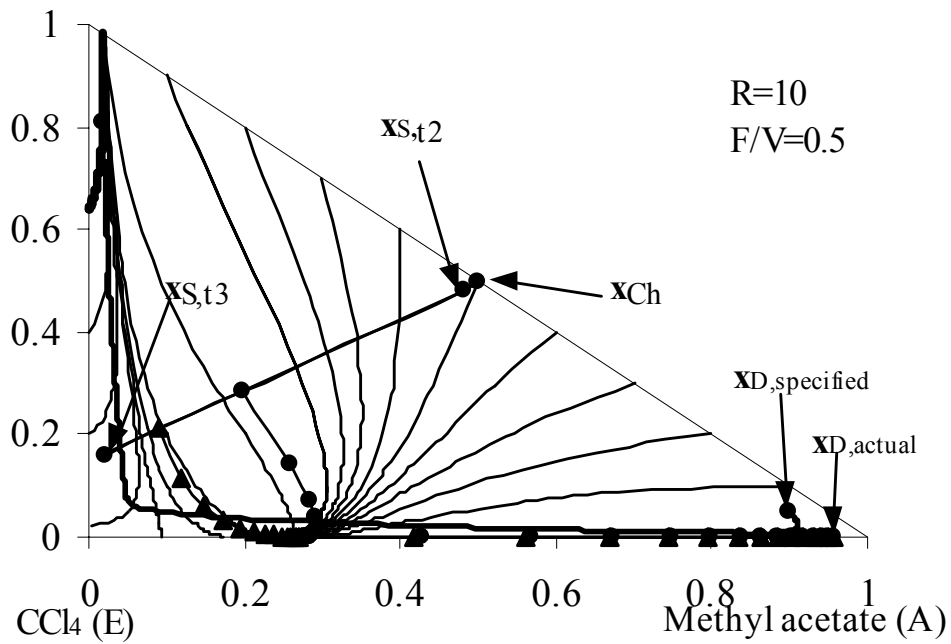


Figure 11. Two simulated column profiles over the background of the short-cut calculated profile maps. The still path ends on the profile of the actual distillate composition.

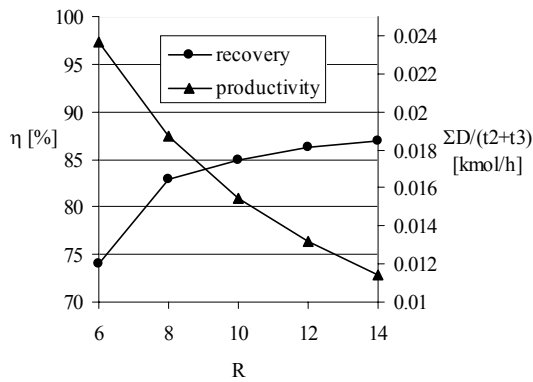


Figure 12. Effect of the reflux ratio

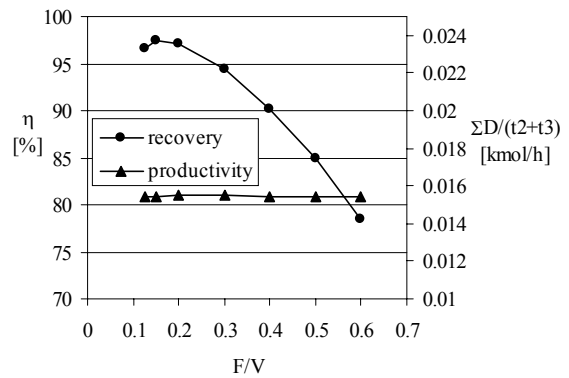


Figure 13. Effect of the feed ratio

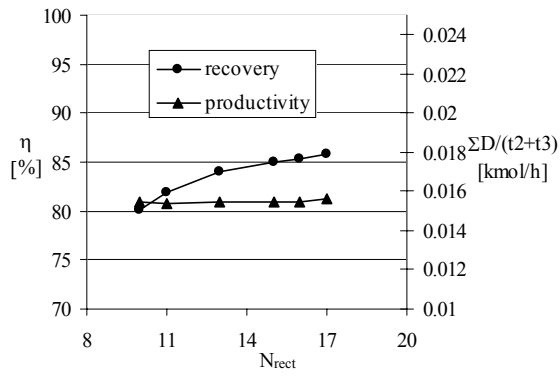


Figure 14. Effect of the number of rectification stages

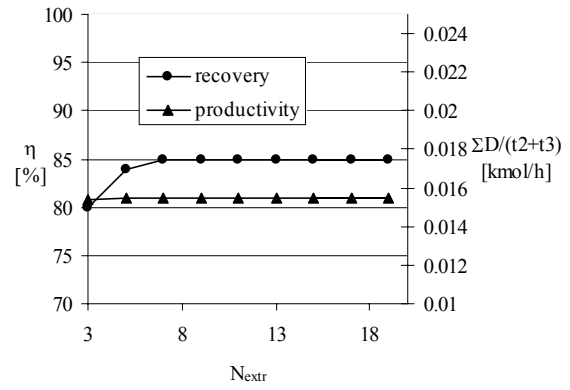


Figure 15. Effect of the number of the extractive stages.

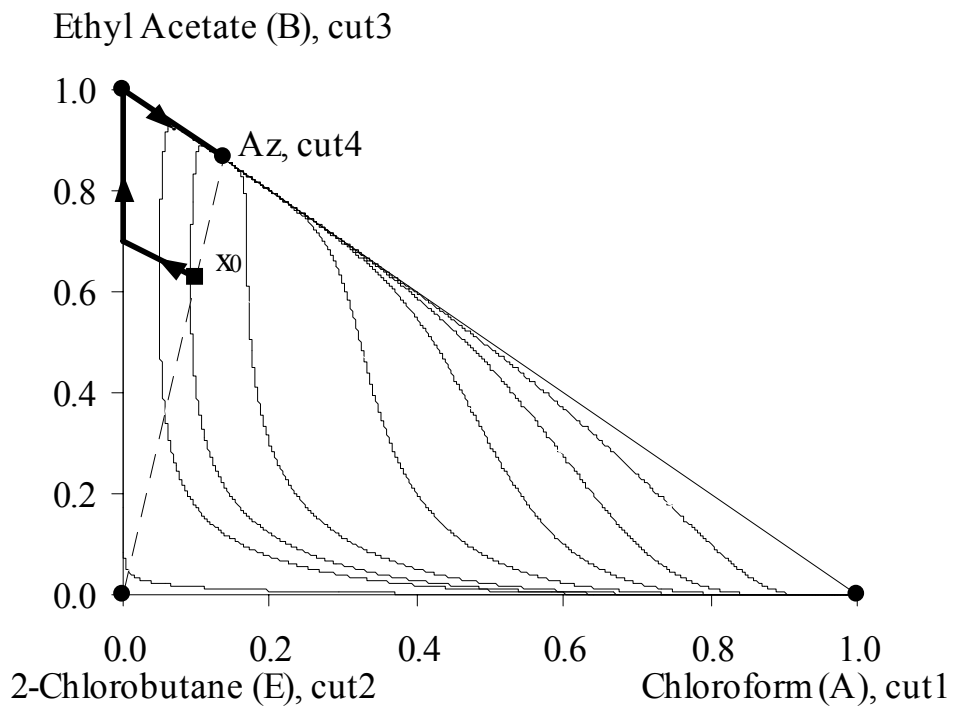


Figure 16. Sequencing of SBD, according to [2]

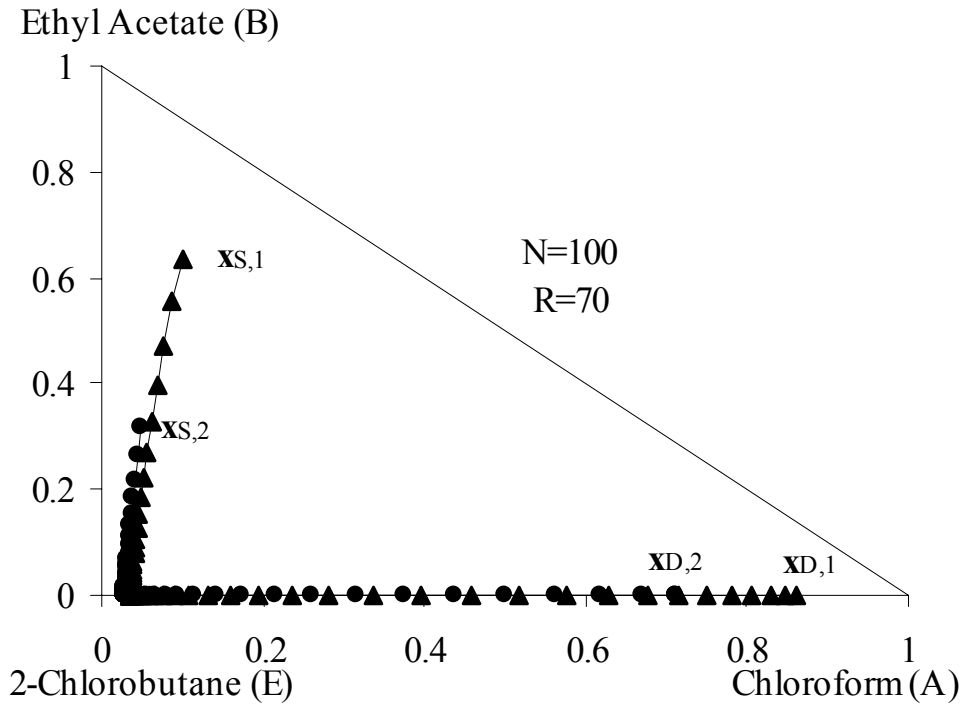


Figure 17. Two simulated column profiles of SBD, with extreme reflux ratio and column length. The distillate is not pure enough.

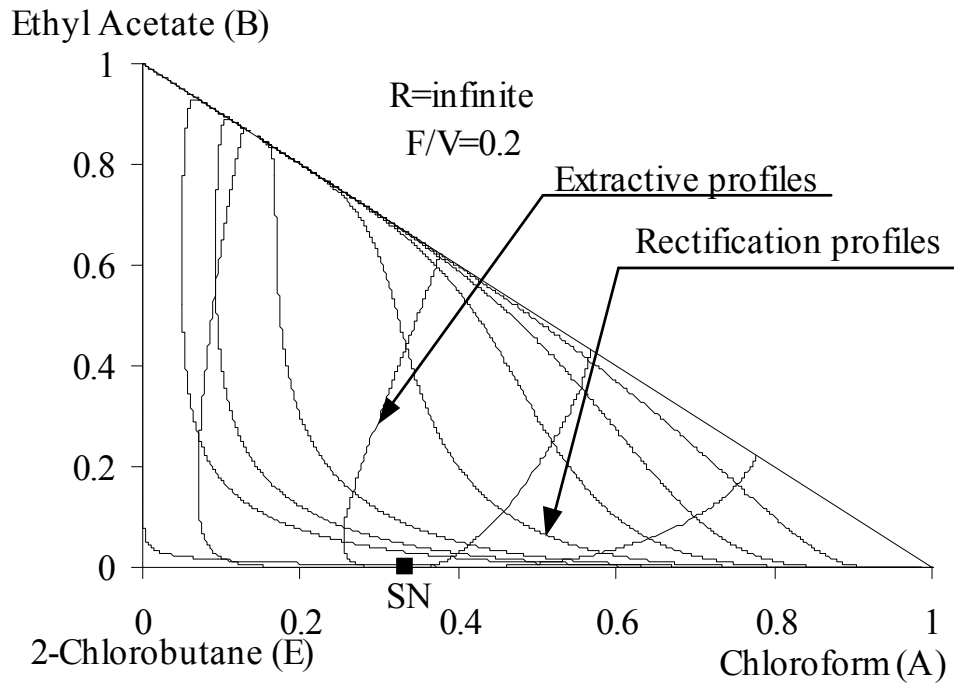


Figure 18. Profile maps of BED

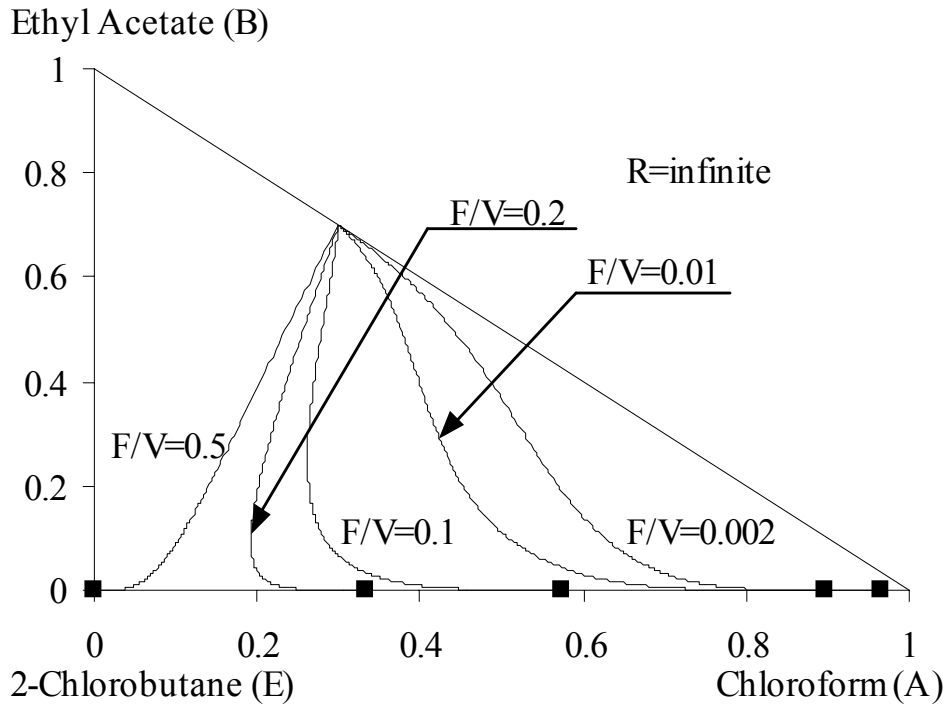


Figure 19. Single extractive profiles at different F/V ratios.

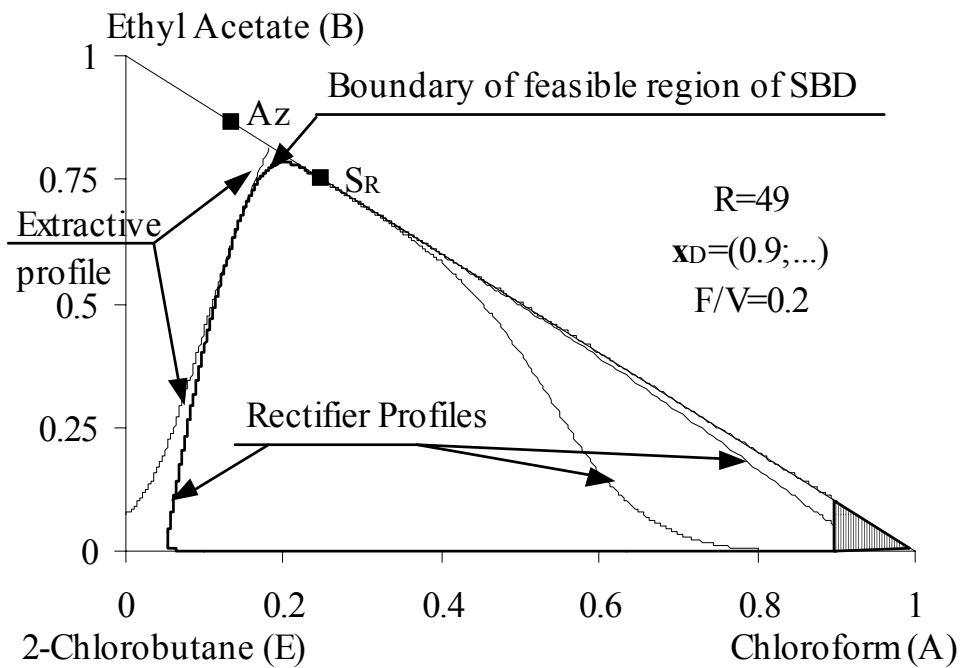


Figure 20. Feasible regions of SBD and BED for pure A as distillate

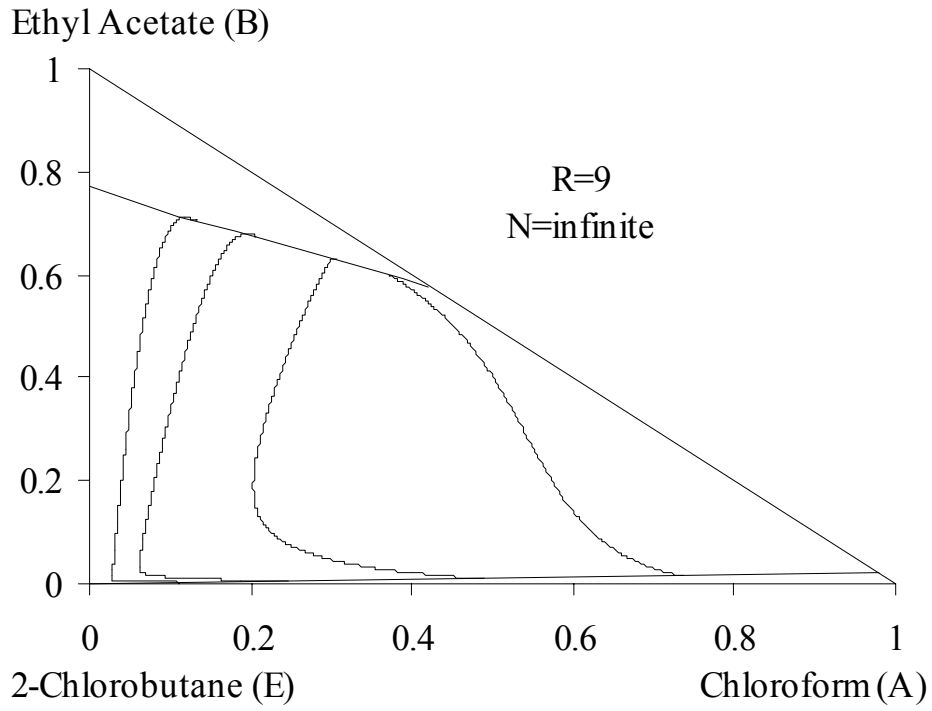


Figure 21. Feasible region of SBD for mixed A+E as distillate

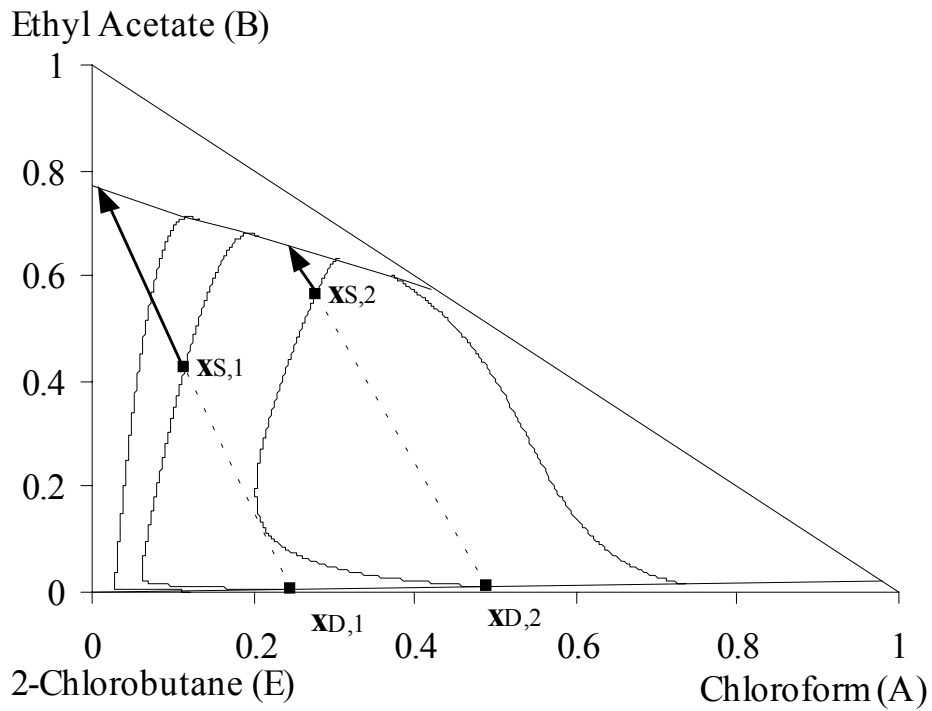


Figure 22. Expected still path directions depending on the still composition, for SBD

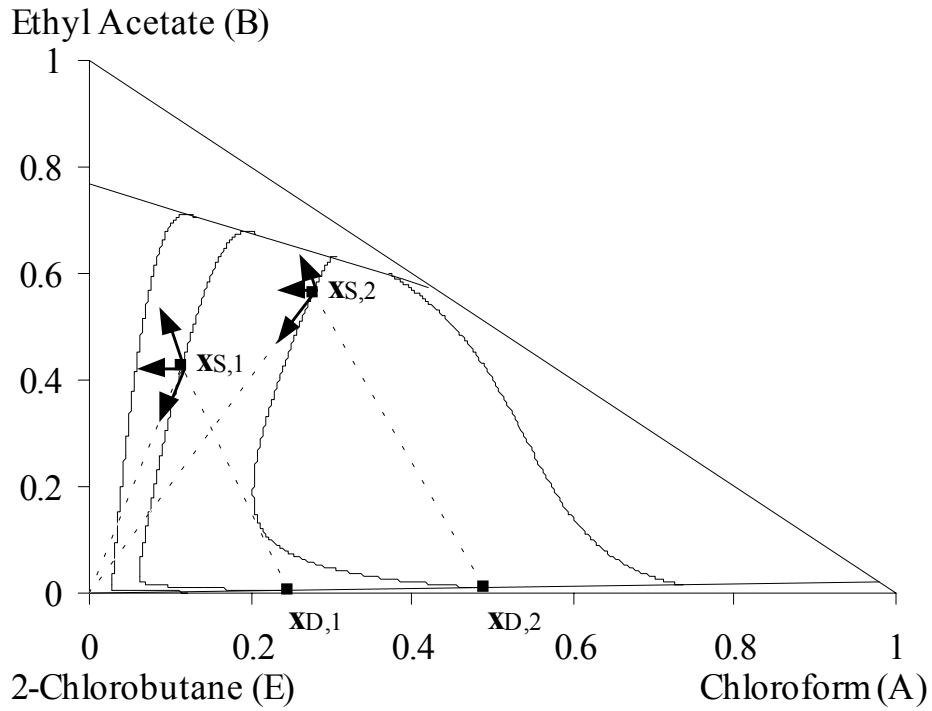


Figure 23. Expected still path directions for BED (continuous feeding)

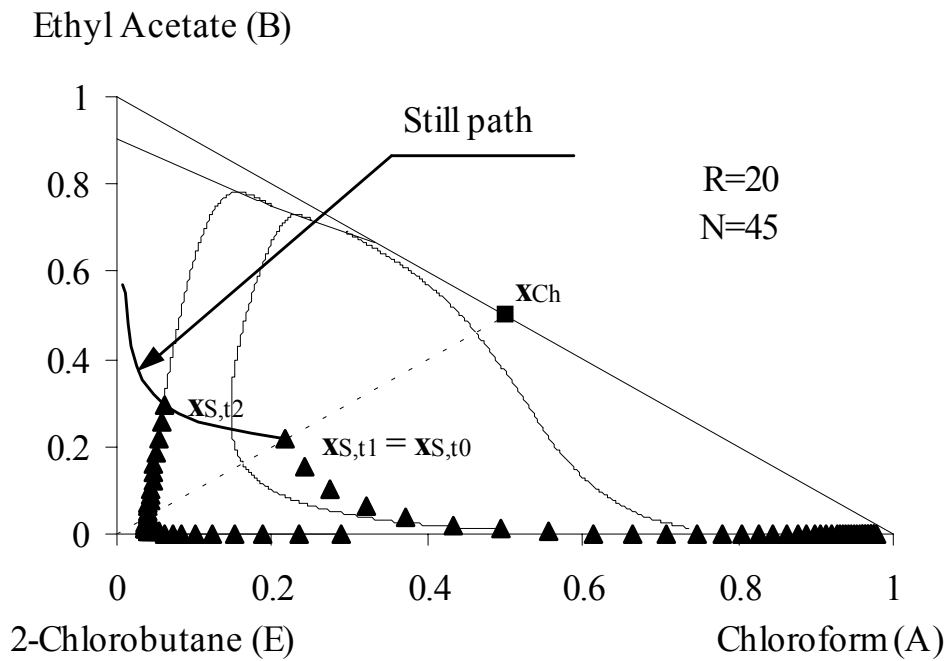


Figure 24. Two simulated column profiles (triangles) and the still path of SBD. Short-cut calculated profiles are also indicated for comparison.

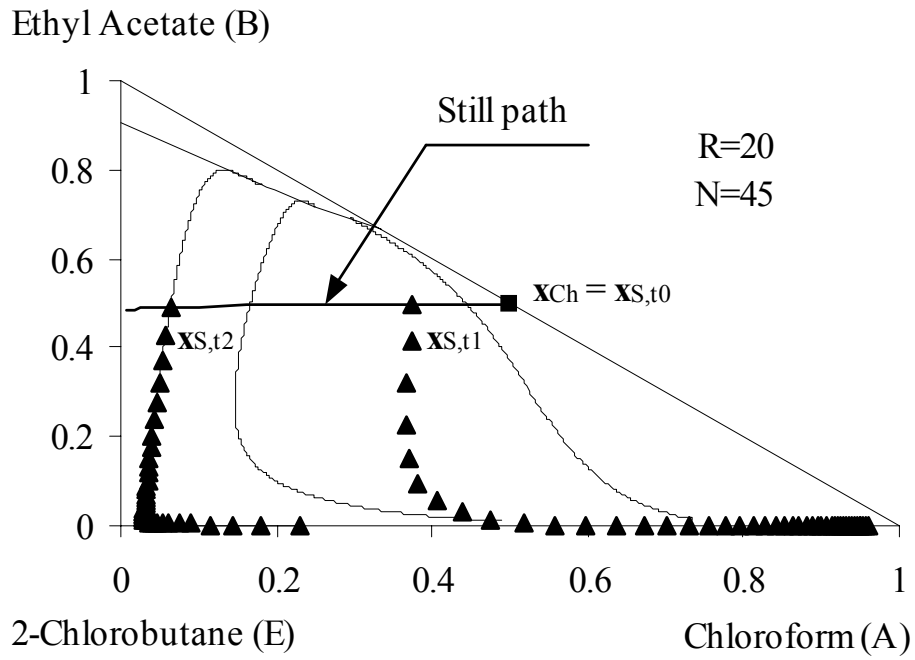


Figure 25. Two simulated column profiles and the still path of BED. Short-cut calculated profiles are also indicated for comparison.

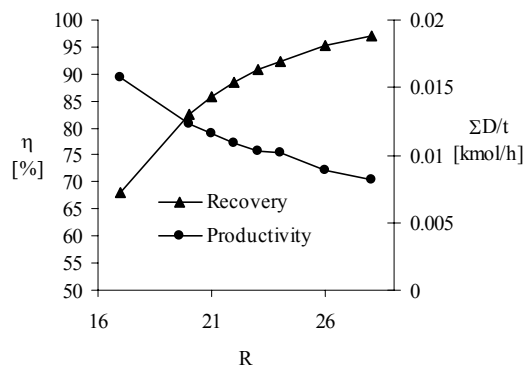


Figure 26. Effect of the reflux ratio

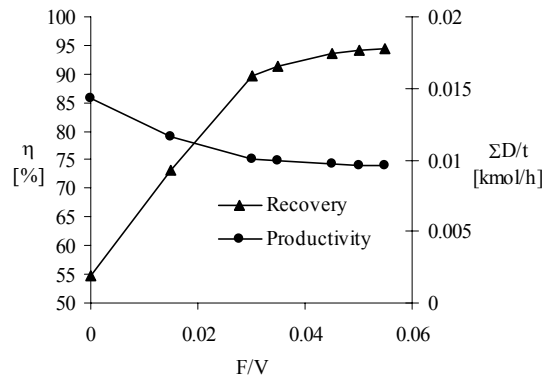


Figure 27. Effect of the feed ratio

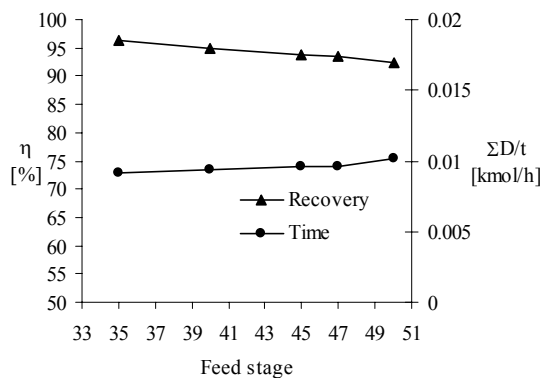


Figure 28. Effect of the feed location

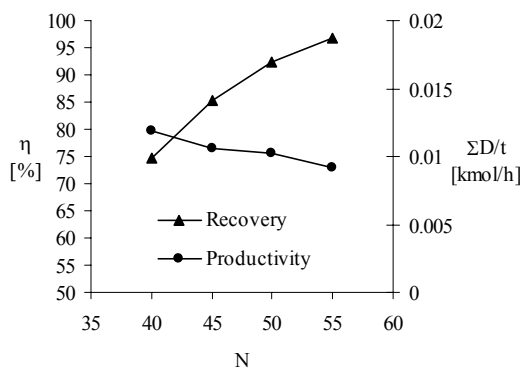


Figure 29. Effect of the number of stages

Cyclohexane (B)

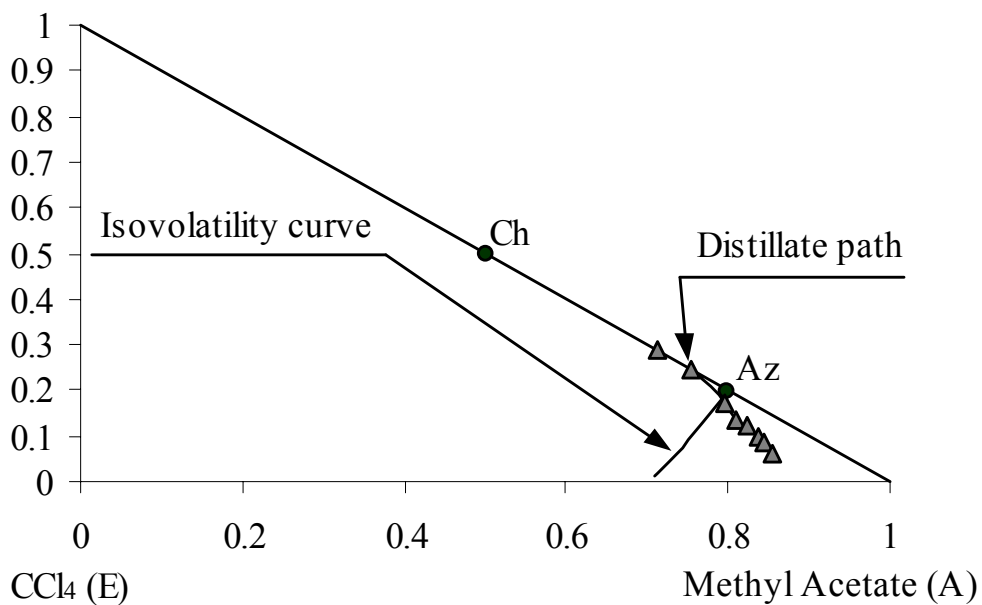


Figure 31. BED of minimum boiling azeotrope with middle boiling entrainer. Distillate composition path during run-up.

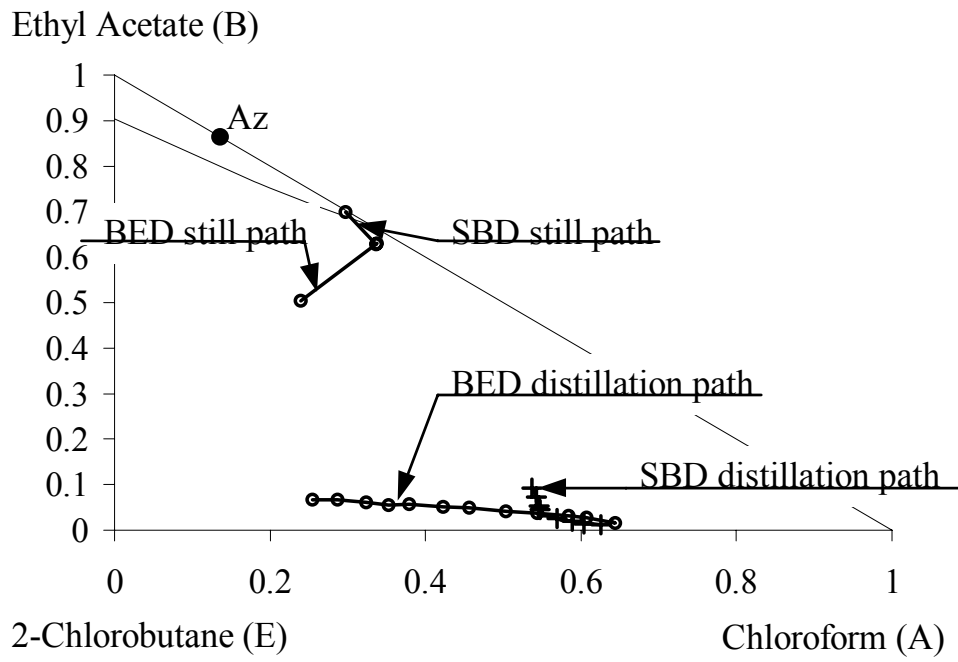


Figure 32. SBD and BED of maximum boiling azeotrope with middle boiling entrainer. Distillate composition paths and still paths.