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Csaba Stéger, Endre Rev, Laszlo Horvath, Zsolt Fonyo, Michel Meyer, et al.. New extractive configuration separating azeotropic mixture in semi-batch way. Separation and Purification Technology, 2006, 5 (2), pp.343 -356. 10.1016/j.seppur.2006.05.009 . hal-03597999

HAL Id: hal-03597999

<https://hal.science/hal-03597999>

Submitted on 4 Mar 2022

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New extractive configuration separating azeotropic mixture in semi-batch way

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Abstract

A new variant of batch extractive distillation, the so-called inverse-fed batch extractive distillation is presented. The total amount of the entrainer is pre-loaded to the boiler, and the mixture charge to be separated is continuously fed to the column in this novel configuration.

The feasibility study of conventional extractive distillation was extended and a thorough study was performed to separate a maximum boiling azeotrope with intermediate boiling entrainer. The new configuration was found more efficient than the conventional one. The results of the feasibility study was validated and completed with a sensitivity analysis performed with commercial simulator software.

Keywords: Batch extractive distillation; Feasibility study; Batch rectifier

1. Introduction

Extractive variants of multistage distillation are well known processes for separating liquid components, which form minimum or maximum boiling azeotrope, or for separating close boiling components.

Original meaning of *extractive distillation* is applying a third component (entrainer) that selectively interacts with one of the key components in such a way as “pulling” that component with itself to the bottom of the column, and thus letting the other key component be produced at the top [1]. The usual practice is feeding a low volatility entrainer above the azeotropic feed in case of continuous distillation, almost near the top, and thus washing down one of the key components. No new azeotrope is usually formed, and no heterogeneous liquid phase is usually formed.

If the applied entrainer forms heterogeneous phase in the system, the process is called heteroazeotropic distillation. Rules for selecting entrainer for heterogeneous azeotropic distillation were studied, e.g., by Rodriguez-Donis et al. [2] and by Skouras et al. [3].

Several variants of extractive distillation have been suggested and analysed in the last 15–20 years (see, e.g., a review by Widagdo and Seider [4]). We apply the term *extractive distillation* (ED) for those cases only where the entrainer is fed to the column at a stage different from the feed stage of feeding the key components. If the entrainer is directly mixed to the key components, or the entrainer stream and the main feed are directed to the same stage, the process is called *solvent-enhanced distillation* (SD).

The conventional practice of applying a high boiling entrainer has been relaxed; e.g., Hunek et al. [5] applied low boiling entrainer. According to Laroche et al. [6] the entrainer can be either the lightest, or the intermediate boiling, or the heaviest component in the system, in the case of continuous extractive distillation. Since then, this statement has proven valid even for batch distillation. Entrainer selection is also discussed in Rodriguez-Donis et al. [7].

The conventional practice of applying rectifier apparatus for a batch process has also been relaxed. *Solvent-enhanced batch distillation* (SBD) and *batch extractive distillation* (BED) can also be performed in middle vessel column (e.g. [8–11]), in inverted batch distillation column (batch stripper, see e.g. [12,13]) or in batch multivessel column (e.g. [14–16]). Both non-conventional configurations (batch stripper and middle vessel column) are studied in the literature but not applied in the chemical indus-

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Nomenclature

| | |
|----------------|--|
| A | light component |
| Az | azeotropic composition |
| B | heavy component |
| BED | batch extractive distillation |
| D | distillate flow rate |
| E | entrainer component |
| ED | extractive distillation |
| F | feed flow rate |
| h | height along the column |
| $IBED$ | inverse batch extractive distillation |
| L | liquid flow rate |
| MER | mixture/entrainer ratio |
| N | number of theoretical stages |
| R | reflux ratio |
| RCM | residue curve map |
| S | saddle |
| SBD | solvent-enhanced batch distillation |
| SD | solvent-enhanced distillation |
| SN | stable node |
| U | molar hold-up |
| UN | unstable node |
| V | vapour flow rate |
| \mathbf{V} | direction vector of the still path |
| \mathbf{x} | liquid composition: array of the mole fractions |
| \mathbf{y} | vapour composition: array of the mole fractions |
| \mathbf{y}^* | vapour composition in equilibrium with the liquid: array of mole fractions |
| \mathbf{z} | feed composition: array of the mole fractions |

Greek symbol

| | |
|--------|----------------|
| η | recovery ratio |
|--------|----------------|

Subscripts

| | |
|--------|-------------------------|
| A | light component |
| Acc | accumulator |
| AR | reduced light component |
| Az | azeotrope |
| B | heavy component |
| Ch | charge |
| D | distillate |
| $extr$ | extractive section |
| E | entrainer component |
| f | feed |
| S | still |
| $rect$ | rectifying section |

distillation (SBD). In this case, the entrainer, as a solvent, is charged to the still together with the mixture to be separated (Fig. 1a). Bernot et al. [13] published their feasibility studies about separating minimum and maximum boiling azeotropes with SBD. The second possibility is *batch extractive distillation* (BED). In this case, the mixture to be separated is charged to the still, and the entrainer is fed continuously to the column (Fig. 1b). This configuration is studied for separating minimum or maximum boiling azeotropes, or close boiling mixtures, with light, or intermediate boiling, or heavy entrainer [17–25]. A comprehensive study of the different separation tasks performed in batch rectifier has also been published [26]; according to the results presented by that article, the most important property in designing a BED process is the relative position of the azeotropic composition and the entrainer in the bubble point ranking. This property determines the proper operation steps, and the existence of the main limiting parameters, as well.

In the novel case introduced in the present article, the entrainer is charged to the still as solvent, and the mixture to be separated is fed continuously to the column (Fig. 1c). The places where the azeotropic mixture and the entrainer feed enter the system are swapped, compared to BED; thus, this configuration will here be called *inverse-fed batch extractive distillation* (IBED). According to the results of Steger et al. [26], IBED seems more advantageous to SBD or BED if the chosen entrainer has a lower bubble point than the azeotropic composition.

How feasibility of the new process IBED is to be studied is presented in this article, and demonstrated on the problem of separating maximum boiling azeotrope ($\text{CHCl}_3/\text{EtOAc}$) with intermediate boiling entrainer (2CIBu). To validate the results of the feasibility study, commercial simulator software (ChemCAD) is applied. A thorough study of BED with the same mixture, using the same software tools, has been published by Lelkes et al. [23]. This allows us to make a reliable comparison of the two configurations.

2. Approach

Studying a new configuration is worth to organize in consecutive steps. A *feasibility study* based on essential simplifying model assumptions is the first step; *validation* of the promising results (if they exist) with so-called *rigorous simulation* is the second one; and *experimental validation* is the third step.

Feasibility study always works with a simplified model. Theoretical stages, constant molar overflow (CMO), negligible hold-up in the column, and saturated liquid feed are the most general assumptions. Constant product composition during the production step is another important assumption in the case of batch extractive processes. (Such an assumption is usually not applied in conventional, i.e., non-extractive, batch distillation processes.) Because of the numerous assumptions, the simplified model can be solved in a short time, and one can decide very soon whether the studied separation is feasible or not. In addition, the main limiting parameters of the separation (reflux ratio, number of stages, entrainer feed flow rate, etc.) can also be estimated.

tries. Studying feasibility of extractive distillation in batch stripper apparatus, and extractive/reactive distillation in batch MVC apparatus is being studied by our research group, and preliminary results are going to be published shortly.

If batch separation is performed in a conventional batch rectifier apparatus, the entrainer can be applied in three different ways. The first studied possibility is *solvent-enhanced batch*

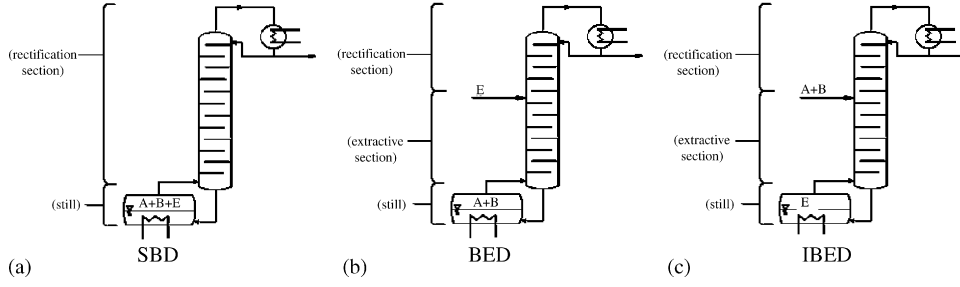


Fig. 1. Schemes of batch configurations in batch rectifier.

Most of these assumptions are dropped in the so-called ‘rigorous’ simulation step. For example, no CMO is assumed; hold-up is taken into account, etc. However, some approximations are usually applied for enabling fast computation; thus, the simulation is not really rigorous. Usually a simplified dynamic is taken into account that cannot cope with the details of the real process. Moreover, even approximating the dynamics through quasi steady states is yet a usual design practice. Really rigorous dynamics are computed for modelling start-up and shut-down processes only, e.g., Wang et al. [27]. However, even this simplified simulation can be successfully applied to perform a thorough sensitivity analysis for studying the main effects of the process parameters. The sensitivity analysis gives a more exact picture about the limiting parameters, and provides us with a good basis for the third step.

There are always effects that cannot be explored even with the most rigorous available simulation tools. Thus, the experimental work cannot be neglected in the engineering practice.

However, the necessary time, work and money for performing the above three steps increases, whereas, the number of simplifying assumptions and the number of candidate configurations to study decreases, as we proceed from feasibility study toward experiments.

Our targets in this article are (1) providing the reader with a feasibility methodology applicable to IBED, and (2) comparing IBED to BED for the studied mixture. Thus, results of the first two steps are presented in this article. Comparison of IBED and BED would be much more reliable if the two processes were first optimized on the same basis. On the other hand, even a preliminary comparison based on feasibility study can convince us about preference of one of the processes against the other one.

The numerical results may (and, of course, will) be different for other mixtures of the same type, but the main conclusions (feasibility considerations, existence of limiting parameters, comparison of IBED and BED) cannot change.

3. Feasibility methodology

The feasibility methodology proposed by Lelkes et al. [21] has been extended for the new configuration. The same model equations can be applied for the new process, but the values of the concentration parameters are different, even if the same mixture is separated with the same operation parameters. In this chapter, the main elements of the original feasibility study and the modifications are presented.

The method published by Lelkes et al. [21] divides the batch rectifier into three zones. It distinguishes (1) a rectifier section (the column section above the feed), (2) an extractive section (the column section below the feed), and (3) the still vessel. They proposed differential equations to investigate each of them as follow, respectively:

$$\frac{dx}{dh} = \frac{V}{L}(y - y^*) \quad \text{where } y = \frac{(V - D)x + Dx_D}{V} \quad (1)$$

$$\frac{dx}{dh} = \frac{V}{L}(y - y^*) \quad \text{where } y = \frac{(V + F - D)x - Fz + Dx_D}{V} \quad (2)$$

$$\frac{d(Ux_S)}{dt} = -Dx_D + Fz \quad (3)$$

The differential Eqs. (1)–(3) can be solved as initial point problems. Integration of the Eqs. (1) and (2) as long as possible along the height of an infinitely long column provides us with the information on the possible liquid compositions formed in the rectifying and the extractive column sections (respectively) at a given time instant. The resulted composition paths are called the rectifying and the extractive profiles, respectively. Integrating Eq. (3) in time provides us with information how the still composition evolves during the process. The evolution of the still composition is called the *still path*.

The assumed or specified distillate composition, x_D , is taken as initial value for integrating Eq. (1) top down, and thus computing a rectifying profile. If the effect of specifying different distillate compositions is to be studied, then Eq. (1) is to be integrated from several initial composition points. In this way, a map of rectifying profiles is computed.

The assumed momentary still composition, x_S , is taken as initial value for integrating Eq. (2), and thus computing an extractive profile bottom up. Since the still composition is not a constant point, a map of extractive profiles is usually computed by integrating Eq. (2) from several initial composition points.

The actual length of the extractive section, i.e., the section below the feed, may be longer or shorter in practice. If the entrainer is fed to the still, there is no extractive section; there is no need to compute extractive profiles in that case. This is a variant of BED, with feeding to the still (to the bottom of the column), called BED-B. BED-B is not identical to SBD. The total amount of the entrainer is mixed to the charge, i.e., charged to the still, before starting the production in the case of SBD; whereas, the entrainer is continuously fed to the bottom of the

column (to the still) during the production step, in the case of BED-B. Thus, the still paths are different.

Any point of a rectifying profile can be considered as such a still composition from which the specified distillate composition can at least momentarily be produced in an SBD or a BED-B process, i.e., with a rectifying section only. If a composition point does not lie on the rectifying profile, but an extractive profile computed from that composition with the same process parameters (first of all distillate composition \mathbf{x}_D , and reflux ratio R) intersect the rectifying profile, then the specified distillate composition can at least momentarily be produced from the actual still composition with two column sections, i.e., with feeding to the column (either BED or IBED). In this case, the point of intersection is the expected composition of the feed stage.

In either case, we speak about a *feasible column profile*. This is a feasible rectifying profile in case of SBD or BED-B, and is a pair of intersecting rectifying and extractive profiles in case of BED or IBED. Only the utilized sections of the profiles are considered; i.e., a rectifying profile section from \mathbf{x}_D to \mathbf{x}_S in case of SBD or BED-B; and a rectifying profile section from \mathbf{x}_D to the intersection point, and an extractive profile section from \mathbf{x}_S to the intersection point if the feed is led to the column.

Those composition points which can serve as a still composition of a feasible column profile, and which can be achieved by some still path, including mixing the charge with the entrainer, constitute a *feasible region* of still compositions. If this region consists of only a single point, or is a very small region, then the recovery of component A is negligible. This kind of feasibility is called *marginal feasibility*. If this region is of a considerable extension, then we speak about *practical feasibility* because a non-negligible recovery of component A can be achieved.

The model equations published in [21] for BED can be used for the new configuration IBED as well, but the composition parameters are swapped. In the new configuration the initial still composition ($\mathbf{x}_S(0)$) is equal to that of the entrainer (\mathbf{x}_E), instead of \mathbf{x}_{Ch} , because the entrainer is charged to the still; and the feed composition is the composition of mixture to be separated (\mathbf{x}_{Ch}), instead of \mathbf{x}_E , because the charge is pumped to the column during the process.

4. Feasibility of SBD and BED

Bernot et al. [13] studied the feasibility of separating a maximum boiling azeotrope with intermediate boiling entrainer in batch rectifier. An academic example is the maximum boiling azeotropic mixture of ethyl acetate and chloroform with the intermediate boiling 2-chloro-butane as entrainer. The characteristic bubble points are listed in Table 1.

According to [13], this type of system can be separated with the following operation steps (see also Fig. 2):

1. Mixing the entrainer to the charge; and charging this ternary mixture into the still; and heating up the column.
2. Distilling out component A until the still composition reaches the BE edge.
3. Distilling out component E until the still composition reaches vertex B.

Table 1
Bubble points in the studied system

| | T (°C) |
|--------------------|----------|
| Chloroform (A) | 61.7 |
| Ethyl acetate (B) | 68.1 |
| 2-Chlorobutane (E) | 77.1 |
| Azeotrope (AB) | 77.8 |

For obtaining the above sequence, Bernot et al. [13] applied only residue curve maps [28], of a theoretical mixture; thus, their reasoning is acceptable with total reflux only. Lelkes et al. [23] studied the feasibility of applying SBD for the same type of mixture with finite reflux ratio, and on a real system. Here we recall the main conclusions.

The points of the rectifying profiles integrated from different composition points of the specified distillate region (a small triangle at vertex A) constitute a feasible region (Fig. 3). The feasible region belonging to the product purity specification $\mathbf{x}_{D,A} \geq 0.95$, and reflux ratio $R=49$ is shown in Fig. 3a; the feasible region with the same purity but reflux ratio $R=75$ is shown in Fig. 3b.

SBD is feasible if the still composition can be managed into the feasible region by mixing the charge with entrainer. Thus, the process is feasible if the mixing line between the charge composition and the entrainer composition intersects the feasible region. The mixing line is just tangent to the border of the feasible region at minimum reflux ratio; in our case, $R_{\min} \approx 75$. Even at this very high reflux ratio, SBD cannot produce pure A with significant recovery because the still path leaves the feasible region very soon.

Lelkes et al. [23] suggested a modified SBD process producing first a binary AE mixture that can later be easily separated. The distillate purity is specified as $\mathbf{x}_{D,AR} \equiv \mathbf{x}_{D,A}/(\mathbf{x}_{D,A} + \mathbf{x}_{D,B}) \approx 1$ (entrainer-free, or *reduced* mole fraction). A rectifying profiles map is shown in Fig. 4 with the specifications $\mathbf{x}_{D,AR} \geq 0.95$, and $R=9$. The feasible region extends well toward the BE edge; thus, a great recovery of component A is expected,

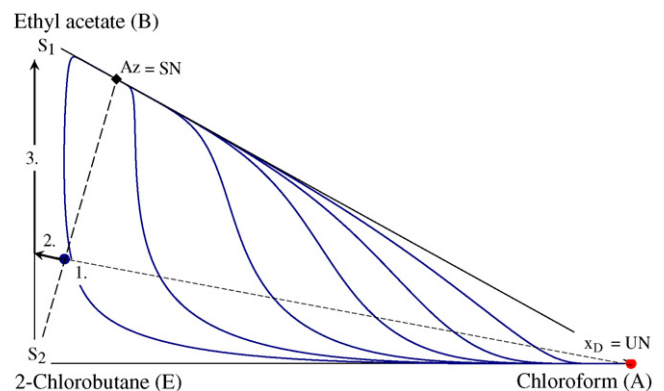


Fig. 2. Residue curve map of the studied mixture and the still path during the separation proposed by Bernot et al. [13].

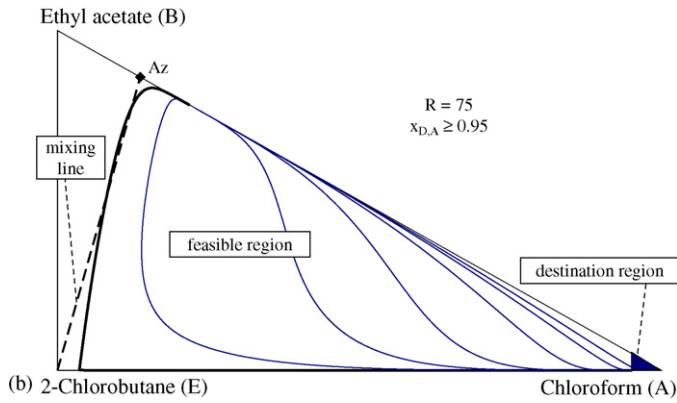
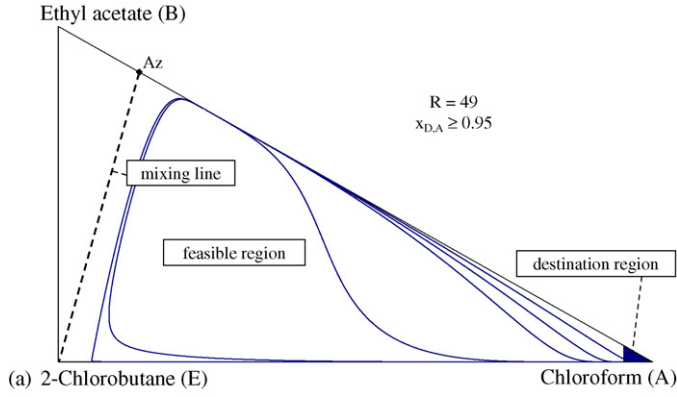


Fig. 3. Rectifying profiles maps of the $\text{CHCl}_3/\text{EtOAc}/2\text{-Cl-butane}$: (a) $R = 49 < R_{\min}$; (b) $R = 75 \approx R_{\min}$.

and can really be achieved, by producing the AE binary mixture.

According to Lelkes et al. [23], separation of the studied mixture is feasible with BED. The product of the first operation step is a binary mixture AE . As follows from the rectifying profiles map, shown in Fig. 4, the entrainer need not be fed above the still; it may be fed to the bottom, i.e., to the still (BED-B). The role of the entrainer is merely steering the still path in an appropriate direction.

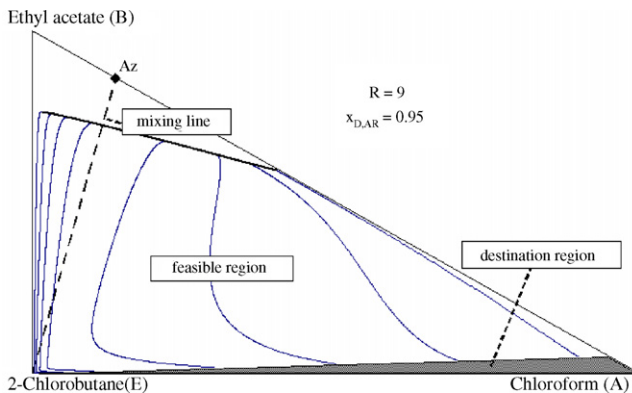


Fig. 4. Rectifying profiles maps of the $\text{CHCl}_3/\text{EtOAc}/2\text{-Cl-butane}$ with binary product.

The separation consists of the following operation steps:

1. Charging the azeotropic composition to the still, and premixing it with a designed amount of entrainer.
2. Distilling out binary mixture AE with continuous entrainer feeding to the still.
3. Distilling out pure entrainer (component E), while there is no feeding.
4. Removal of pure component B from the still, and recharging the still with the first binary product AE .
5. Distilling out pure component A .

As is shown by Lelkes et al. [23], BED-B has better operation properties than SBD. BED-B provides the same products in shorter time and at a significantly smaller still hold-up as does SBD, with identical purity and slightly greater productivity.

5. Feasibility of the new process (IBED)

The entrainer is charged to the still in the new configuration (IBED), and the charge to be separated is fed continuously to the column. This arrangement provides a more effective contact between the uprising solvent and the down coming mixture; thus, this may give rise to a more effective process. The same mixture of CHCl_3 and EtOAc , forming maximum boiling azeotrope, and the same, intermediate boiling, entrainer 2ClBu is applied here for studying this configuration. Results of the feasibility study, including studying the effects of process parameters (reflux ratio, distillate specification, feed flow rate, feed position, etc.), are presented in this chapter.

Since our target is separating component A (CHCl_3) from component B (EtOAc), we prefer producing pure A in the first production step. This is studied with total reflux in Section 5.1, and then with finite reflux ratio in Section 5.2. It turns out in Section 5.2 that this process version is infeasible. However, producing $A-E$ ($\text{CHCl}_3-2\text{ClBu}$) mixture in the first production step is feasible with finite reflux ratio as is shown in Section 5.3. The $A-E$ binary mixture can then be easily separated in a later step. What kind of limiting parameters in this (feasible) process exists is discussed in Sections 5.4 and 5.5. Based on feasibility analysis, a preliminary comparison of BED and IBED is provided in Section 5.6; this is followed by a short conclusion of the feasibility study, in Section 5.7.

5.1. Total reflux analysis

The case of total reflux is easier studied, and can be considered as limit case to great reflux ratios; therefore, this case is studied first.

It follows from the residue curves map shown in Fig. 2 that, in the same way as both SBD and BED-B is feasible irrespectively to how the still path evolves, the new configuration without extractive section (IBED-B) is also feasible according to the total reflux approximation.

When the process starts, the still vessel contains pure entrainer if there is no premix ($\mathbf{x}_{S,0} = \mathbf{x}_E$). The still path ($\mathbf{x}_S(t)$) is determined by both the distillate withdrawal ($-D\mathbf{x}_D$) and the

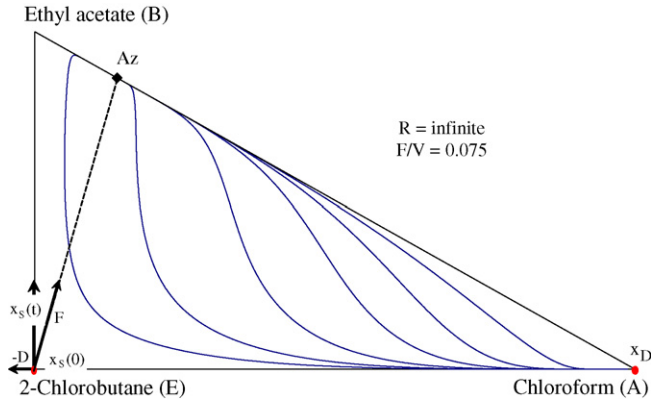


Fig. 5. Residue curve map of the studied mixture and the still path during the separation applying the novel configuration.

charge feed (Fx_{Ch}); thus, the still path can be driven along the BE edge by applying appropriate F/D ratio. This is shown in Fig. 5.

The presence of an extractive section does not annul the feasibility; thus, the IBED process with feeding to the column is also feasible based on the total reflux approximation.

There is a single residue curve crossing any composition different from the singular points. Such a residue curve is a good approximation of the unique rectifying profile started from that specific distillate composition x_D , with total reflux. Beside such a rectifying profile, a map of extractive profiles with total reflux, feed ratio $F/V=0.075$, and the specified x_D near vertex A, are shown in Fig. 6. The rectifying profile is shown by bold; a part of it is labelled with '2', and other part with '3'. The point labelled with x_S is supposed to be an actual still composition.

An extractive profile computed bottom up from point x_S ends in point SN. A part of this profile is shown by bold with wide dots over it. SN is a stable node of all the extractive profiles computed inside the triangle, with the actual x_D , R , and F/V parameters. The presence of this stable node explains why a pair of separatrices can be seen in the extractive profiles map (Fig. 6).

Points x_S and x_D can be connected in two different ways. One is a single rectifying section from x_D to x_S , including both the

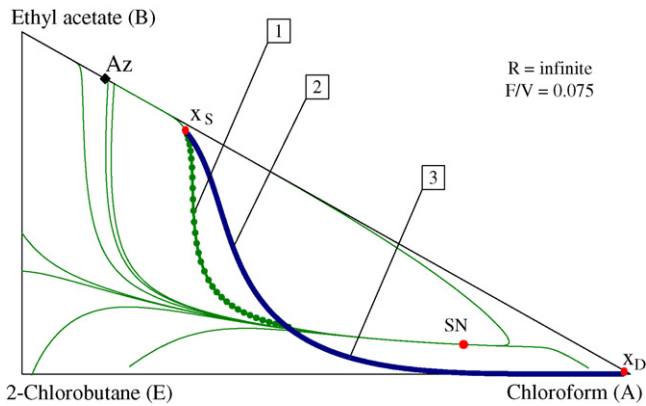


Fig. 6. Different composition profiles to withdraw the same product from the same still composition but with different column configuration and number of stages.

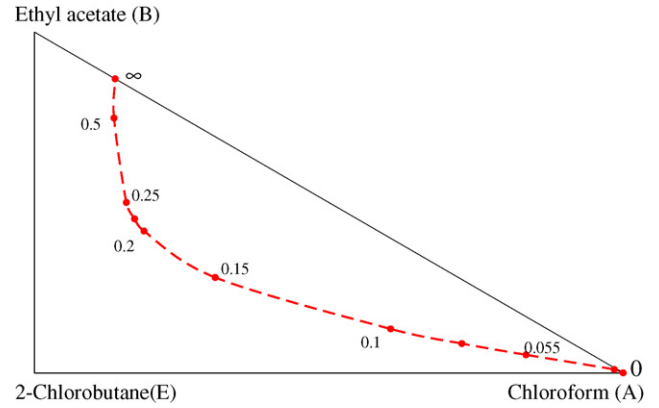


Fig. 7. Position of the stable node SN depending on feed ratio.

parts labelled by '3' and '2'. The other one is a two-section column; the lower (extractive) section from x_S to the intersection, this is labelled by '1', and the upper (rectifying) section from the intersection to x_D , this is labelled by '3'. The two configurations can correspond to different stage numbers; the configuration with less number of stages may be preferable. The number of stages is an important factor in estimating the efficiency of the process, but it does not have any effect on the feasibility.

The existence and position of the stable node SN does not annul or constrain the feasibility of the separation with infinite reflux ratio, but it makes possible the same production from the same still composition with different column states. The dependence of the stable node location on the F/V ratio is shown in Fig. 7. SN starts, with zero feed, from the most volatile vertex A, and is shifted toward to the feed composition (the azeotropic composition in this case) with increasing feed ratio.

5.2. Finite reflux ratio, pure A as product

Feasibility with total reflux does not involve feasibility with finite reflux ratio of extractive distillation. We have to check how the feasibility changes with decreasing R .

We hope that the same product purity can be maintained with small reflux ratios; this assumption is checked in the present subsection.

Product purity is specified as earlier, $x_{D,A} \geq 0.95$; the rectifying profiles belonging to $R=49$ and $R=75$ are shown in Fig. 3. Since the mixing line does not intersect the feasible region of rectifying profiles below $R_{min} \approx 75$, a rather great value, the separation is practically infeasible without feeding above the still. If, however, the mixture to be separated is fed above the still, an extractive section appears in the column; thus, extractive profiles maps must also be computed and studied. The location and the type of the singular points and separatrices provide us with significant information about the feasibility of the process.

Extractive profiles maps with different reflux ratios are shown in Fig. 8. There is an unstable node UN, a stable node SN, and a saddle point S_1 in the maps with high R ; a saddle point S_2 must also be presented somewhere inside or outside the triangle, as is clear from the curvature of the profiles. The unstable separatrix pair of S_1 is running almost parallel to the mixing line; position

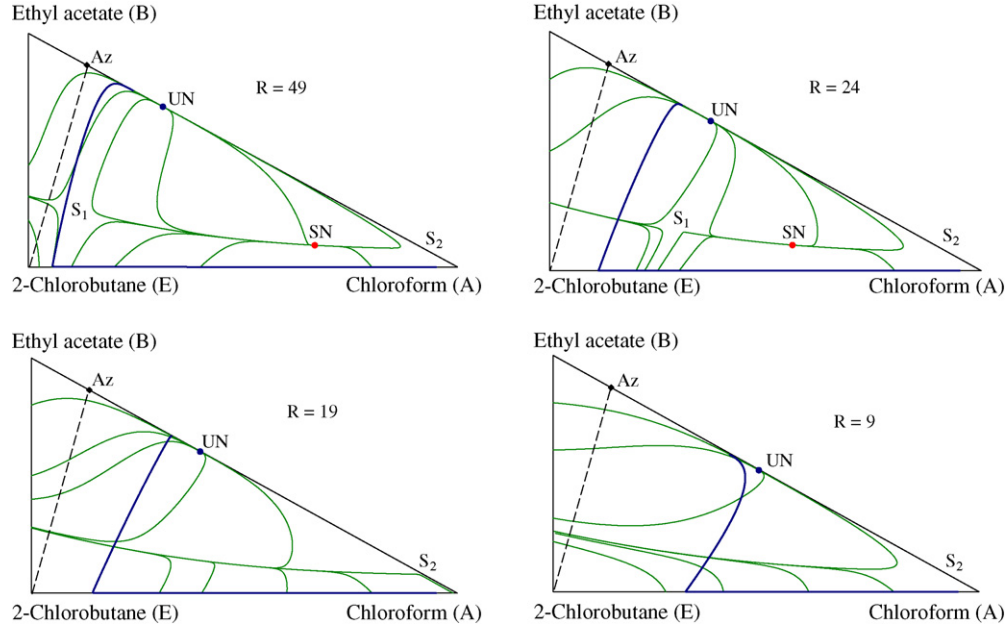


Fig. 8. Extractive profiles maps with finite reflux ratio, $F/V=0.075$.

of this pair is mainly determined by the applied reflux ratio R . One of the stable separatrices of S_1 is running along the line connecting S_1 to the stable node SN ; position of the stable separatrix pair is mainly determined by the feed ratio F/V . S_1 and SN approach each other with decreasing R ; they disappear at a reflux ratio between 19 and 24, if the feed ratio is $F/V=0.075$. S_2 does not move significantly; at lower R , the stable separatrix of S_2 is situated at the same line as the separatrix chain along S_2 – SN – S_1 at higher R .

The boundary of feasible region with rectifying profiles, i.e., the leftmost rectifying profile, and the mixing line between the azeotrope and the entrainer, are also drawn in the figures. The feasible region originally covered by the feasible rectifying profiles could be expanded if some extractive profiles started outside, and crossing the mixing line, moved into the original feasible region. Unfortunately, all the extractive profiles crossing the mixing line run toward edge BE , i.e., away from the feasible region of rectifying profiles; thus, the extractive profiles do not enlarge the feasible region. Pure component A cannot be produced this way; this process version is infeasible.

5.3. Finite reflux ratio, binary mixture as product

Producing pure A in the first production step, as is shown in the previous subsection, is infeasible with realistic (finite) reflux ratio. There is, however, another possibility: producing A – E mixture first; this binary mixture can be easily separated in a later step. Feasibility of this process version is studied in the present subsection.

Instead of a sharp cut, a sloppy separation can be also specified in batch way. It means that the first cut is a binary non-azeotropic mixture that can be separated in a subsequent step. In our case this binary product is the mixture of the entrainer (E) and the lightest component (A). Its purity is characterized with

the reduced molfraction of $x_{D,AR} = \frac{x_{D,A}}{x_{D,A} + x_{D,B}}$. The new specification means that the destination region is a narrow triangle along the edge AE instead of the small triangle on the vertex A . The distillate purity is specified as $x_{D,AR} \geq 0.95$. Rectifying profiles map similar to that shown in Fig. 4 are computed by starting the rectifying profiles from the boundary of the specified region of acceptable distillate.

The specified purity can be produced, i.e., components A and B can be separated, in a batch rectifier with a really great recovery of A . At $R = 10$, the feasible region, with considering rectifying profiles only, extends up to the BE edge (Fig. 9). Thus, the initial composition in the still, i.e., x_E , is situated in the border of the feasible region. However, it is worth to premix a small quantity of the azeotropic mixture to the entrainer in order to get the still composition to the inside of the triangle and thus reach the specified purity of the binary product at once when distillate withdrawal is started.

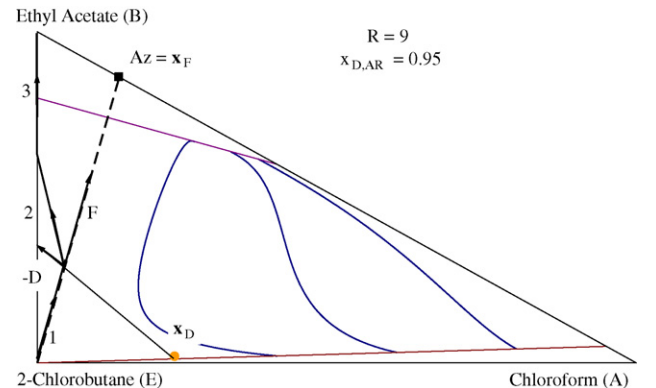


Fig. 9. Rectifying profiles map for binary product specification and the still path of the novel configuration applying some pre-mix of the mixture to be separated.

The specified binary mixture can be produced with IBED-B process until the still path crosses a border of the feasible region. If the still composition leaves the feasible region by crossing the BE edge, a total recovery of component A is achieved. Some amount of component A remains in the still if the still path cannot be governed to the BE edge.

When the process starts, the still contains a mixture of the total amount of entrainer and a premixed part of the charge to be separated. The still path ($\mathbf{x}_S(t)$) is determined by both the distillate withdrawal ($-D\mathbf{x}_D$) and the charge feed ($F\mathbf{x}_{Ch}$). The distillate withdraw pushes the still composition toward the BE edge; the azeotrope feed pulls it toward the azeotropic composition. If the “push-effect” is greater than the “pull-effect”, the still path can be driven toward the BE edge. This is shown in Fig. 9. With smaller distillate flow rate, and greater feed flow rate, the still composition would move more upward, and would leave the feasible region through its upper borderline.

In order to check if the feasible region can be extended by applying extractive section, i.e., by feeding the azeotropic charge to an intermediate point of the column (IBED process), extractive profiles should also be calculated and visualized. Since the distillate composition is not fixed to a single point, but rather to a wider region, several \mathbf{x}_D compositions should be studied along the boundary of the specified distillate region. An extractive profiles map ought to be computed to each pair of R and \mathbf{x}_D .

Three examples of extractive profiles maps are shown in Fig. 10, together with the corresponding rectifying profiles. The region from where the actual rectifying profile is reachable is shaded in each figure. Unfortunately, an unstable node (UN), together with separatrices, appears in the map in such a location that the extractive profiles do not enlarge the feasible region; compare this to Fig. 9. From the feasibility point of view, the application of extractive stages is not prohibited, but unnecessary. Thus, application of IBED-B is suggested.

The following operation steps can be proposed for separating the studied mixture with IBED:

1. Charging the designed amount of entrainer to the still, pre-mixing a small part of the azeotropic charge, and heating up the column.
2. Distilling out AE binary mixture, with continuously feeding the main part of the azeotropic charge to the still.
3. Distilling out pure entrainer (component E).
4. Removal of pure component B from the still, recharging the still with the AE binary mixture produced in step 2, and distilling out pure component A.

5.4. Limiting parameters

Not only the operation steps but the existence, and rough estimation to the limiting values, of the most important operation parameters can also be determined with the feasibility methodology. Results related to the existence and estimated limiting values are presented in this section.

Separation with total reflux ratio is feasible because vertex A is the only unstable node in the system (Fig. 2). Therefore, the feasibility is not constrained by reflux ratio from above. The feasible region decreases with the reflux ratio, as is shown in Fig. 11. Therefore, the feasibility is constrained by the reflux ratio from below. In other words, a minimum reflux ratio, R_{\min} exists. For example, its value is $R_{\min} \approx 5$ at specification $\mathbf{x}_{D,AR} \geq 0.95$ if the mixture to be separated is azeotropic, as is shown in Fig. 11. The minimum value depends on the specified distillate purity and on the charge composition.

We have pure entrainer at the beginning, but a small amount of the azeotropic charge is suggested to mix to the entrainer either before or after charging it to the still. Anyhow, there is not any minimum of the ratio of azeotropic mixture premixed to the entrainer. On the other hand, there is a maximum azeotropic mixture to entrainer ratio, as is shown in Fig. 12 for the case

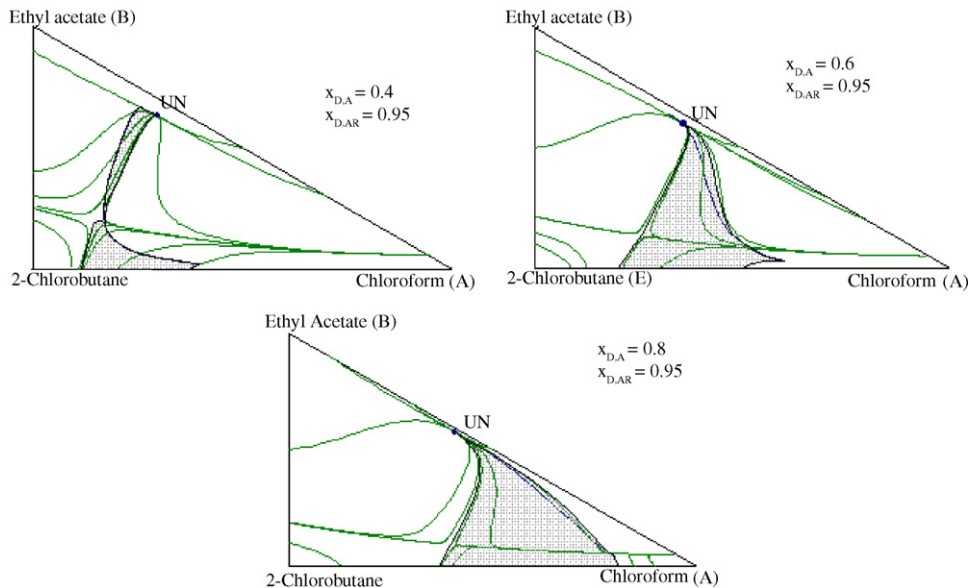


Fig. 10. Extractive profile maps and the regions covered by those crossing the actual rectifying profiles, producing binary product $R = 10$, $F/V = 0.05$.

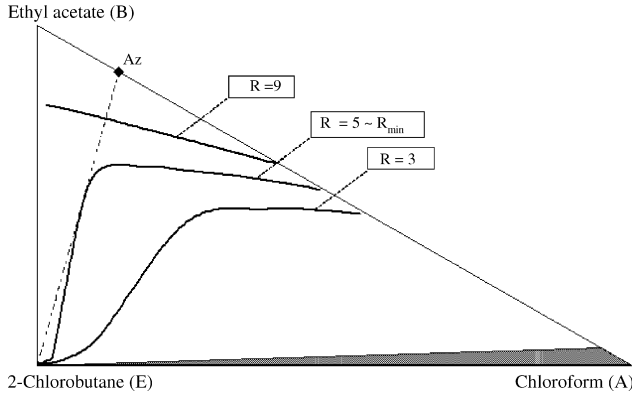


Fig. 11. Boundaries of the rectifying profiles region with finite reflux ratios for binary product specification.

of $R = 9$ and $x_{D,AR} \geq 0.95$. Pre-mixing ratio $PMR \approx 1$ is feasible because the obtained composition (point M1 in the figure) is yet inside the feasible region, whereas, ratio $PMR \approx 10$ is infeasible because the obtained composition (point M2 in the figure) is already behind the upper boundary. The pre-mix ratio belonging to the limit point (point M3 in the figure) is the maximum: $PMR_{max} \approx 5$. Determining the optimal pre-mixing ratio is not a task to be performed in the frame of feasibility study.

The only unstable node of the residue curves map is vertex A, and this remains the only unstable point in the rectifying profiles maps at finite reflux ratios, as well. The top composition is always attracted by vertex A; the longer rectifying section is used, the top composition is nearer to pure A. Therefore, the length of the rectifying section is not constrained from above. There is, however, a minimum length of the rectifying section, as usual, needed to reach the specified purity.

Since the process is feasible with feeding to the still (or to the bottom of the column), no minimum length of the extractive section exists. Since application of an extractive section does not influence the feasibility of the process (see above, Fig. 10), the extractive section can also be of any length. Although the length of the extractive section has no limit, use of some extractive stages may be advantageous, and an optimal length may exist, depending on the actual curvature of the extractive profiles (see Fig. 6).

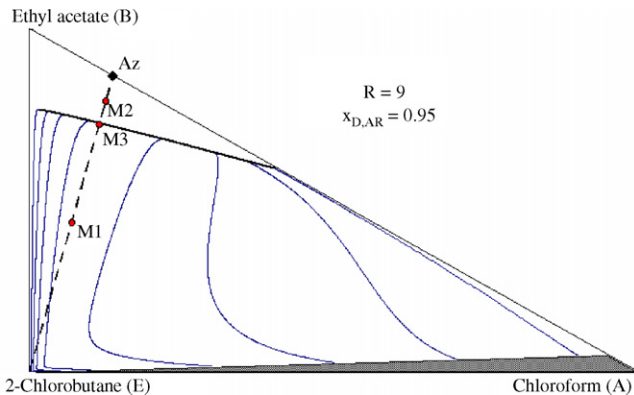


Fig. 12. Feasible and infeasible premix ratios, and the limit ratio. M1: $PMR = 1$; M2: $PMR = 10$; M3: $PMR = 5$.

Table 2
Existence of limiting values in IBED

| Parameter | Minimum | Maximum |
|--------------------|---------|---------|
| Reflux ratio, R | Yes | No |
| Pre-mix ratio, M | 0+ | Yes |
| F/V | 0 (no) | No |
| N_{rect} | Yes | No |
| N_{extr} | 0 (no) | No |

Results on the existence of limiting parameters are collected in Table 2.

5.5. Recovery dependence on feed ratio

As it has been recalled in Chapter 4, the separation is feasible with the SBD producing binary AE mixture as first product; thus, the process is feasible with no entrainer feed, but with mixing the total charge to the entrainer in the still. So much entrainer may then be applied as not to exceed the PMR_{max} explained in the previous paragraph. Thus, no positive lower bound to F/V exists. There is, on the other hand, a specific feed ratio $(F/V)^*$, belonging to a given premix ratio PMR , that seems sharply restricting the reachable recovery of component A. The recovery can, in theory, reach 100% if the still path can reach the $B-E$ edge below the intersection of this edge with the boundary of the feasible region. If the still path crosses the boundary of the feasible region then it does not reach the $B-E$ edge and, thus, a part of component A remains in the still vessel at the end of the production step.

Which direction the still path evolve in from an instantaneous position x_S is determined by the feed flow rate (F) and the feed composition ($z = x_{Ch}$), and by the distillate flow rate (D), and the instantaneous distillate composition (x_D) together according to a vectorial sum: $V = F(z - x_S) + D(x_D - x_S)$. This is demonstrated in Fig. 13. At too high feed flow rate (F), the vectorial sum V points toward the upper borderline of the feasible region. Thus, there is a specific $(F/V)^*$ above which the recovery cannot be 100% even in an ideal case. Below this value, however, the still composition can be directed toward the $B-E$ edge and, thus, perfect recovery can be reached in theory. For example, this specific value is $(F/V)^* \approx 0.042$ if $R = 9$, $x_S(0) = [0.03, 0.2, 0.77]$, $x_D = [0.01, 0.0053, 0.9847]$, and $z = x_{Az}$.

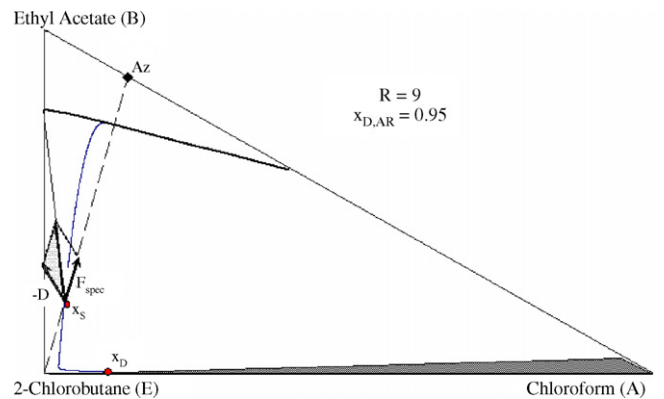


Fig. 13. Still path direction is determined by x_S , D , x_D , F , and $z = x_{Ch}$ together.

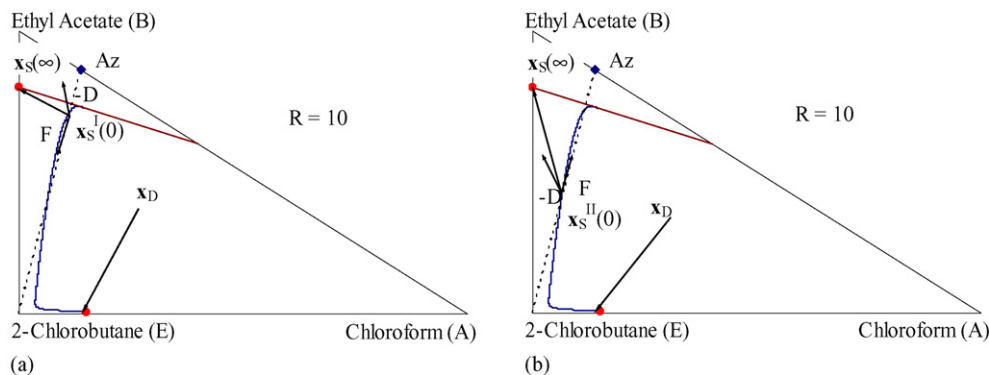


Fig. 14. Conceptual comparison of (a) BED and (b) IBED.

5.6. Comparison of BED and IBED

Binary AE product is to be produced in both BED and IBED processes, and no extractive stages are needed in either case. A main difference is that pre-mixing is necessary in BED, whereas, IBED can be performed without it.

The same separation task is feasible with both configurations; therefore, it is worth comparing them. Such a comparison performed with the tools of the feasibility study is necessarily of conceptual nature, based on simplifying assumptions and estimations. This kind of comparison is presented in this section; a rigorous comparison will be presented in a later section.

The conceptual comparison is based on the fact that some rectifying profiles have two intersections with the mixing line. Such a rectifying profile is shown in Fig. 15. The mixing line is shown by a dotted line; the upper borderline of the feasible region is also shown. The intersection point nearer the azeotropic composition is chosen as initial still composition for BED (Fig. 14a); the intersection point farther from the azeotropic composition is chosen as initial still composition for IBED (Fig. 14b). This is the logical selection because we want as small ratio of entrainer in the still as possible in the case of BED, and as small ratio of the key components in the still as possible in the case of IBED.

The nearer the still composition at the end of the production step to vertex B, the smaller amount of entrainer is used and to be distilled out from the residue. Thus, we would like to direct the still toward the corner of the feasible region; this is possible with an appropriate feed flow rate, in both cases. Suppose that both processes end in the same still composition x_{final} , and then the still path intersects the same set of rectifying profiles in the two processes. In this way, the instantaneous product compositions can also be the same, with appropriately tailored column lengths. The same product is produced with applying a shorter section of each rectifying profile intersected by the still paths; i.e., a smaller column length is applied in the IBED process. Thus, better product purity is expected with IBED than with BED if the same column length is used.

5.7. Conclusions of the feasibility study

The conclusions of the feasibility study are:

- Separation of maximum boiling azeotrope with intermediate boiling entrainer is feasible with IBED.
- The operation steps are determined as listed above.
- The existence of the main limiting parameters is determined according to Table 2.
- IBED should be more effective than BED because it can produce the same product with less number of stages, or better product purity with the same number of stages.

6. Validation by rigorous simulation

Results of the feasibility study should be validated by rigorous simulation. Such simulation has been performed, using ChemCAD, and the results of this validation are presented in this chapter.

6.1. BED versus IBED

The main parameters of the simulation runs are taken from an earlier publication [23], to ease the comparison of the two configurations. The applied parameters and the results are collected in Table 3. In order to compare the two processes, not only the column but the distillate purity and the recovery are also tried to be kept equal. In both cases the batch column does not have any extractive stages. In the case of BED, the entrainer is fed directly to the boiler; in the case of IBED, the mixture to be separated is fed directly to the boiler.

The product compositions are nearly the same in both cases, and both configurations provide with high recovery ratio of component A (CHCl_3). A great advantage of IBED is that it needs less solvent to separate the same amount of mixture. More than 20% of the entrainer (70 mol instead of 90 mol) can be saved with the new configuration (IBED), compared to that in BED.

Table 3
Simulation parameters and results of comparing BED and IBED

| | BED | IBED |
|------------------------------------|-------|-------|
| N | | 45 |
| N_f | | 45 |
| R | | 20 |
| Q (kWh) | 15 | 14985 |
| Amount to be separated (mol) | | 68 |
| Initial content of the still (mol) | | |
| CHCl_3 | 34 | 21 |
| EtOAc | 34 | 21 |
| 2-ClBu | 0 | 70 |
| Applied amount of entrainer (mol) | 90 | 70 |
| $x_{\text{AR,Acc}}$ | 0.995 | 0.997 |
| F (mol/h) | 9 | 7.8 |
| Length of the production step (s) | 36000 | 12000 |
| η_{CHCl_3} | 92.0% | 91.2% |

6.2. Sensitivity analysis

In order to explore the effects of the process parameters, to validate the existence of limiting values, and to find if there are extremal values, a sensitivity analysis is performed with rigorous simulation for the novel configuration (IBED). The configuration shown in Table 3, with the parameters $Q = 4.5$ kW and hold-up = 0, are applied as a base case; when parameters are varied one by one, the other parameters of the base case are kept constant. The stop criterion is $x_{\text{AR,Acc}} = 0.997$.

Two properties were investigated in each configuration; the recovery ratio of chloroform (η_A), and the mixture/entrainer ratio (MER), i.e., a mole ratio of the separated mixture to the applied entrainer, are monitored. MER is the charge size that can be worked up with one mole entrainer. The higher value involves the more effective separation, for both monitored properties.

6.2.1. Effect of the reflux ratio

Both recovery and MER increase monotonically; the recovery ratio has a plateau over $R = 20$ (Fig. 15). It follows that there is no upper value of the reflux ratio from the viewpoint of feasibility, even if there must be an optimal value depending on the objective function. A minimum reflux ratio was predicted with the feasibility study ($R \approx 5$ in Fig. 11) if the mixture to be separated is azeotropic.

In the simulation step the mixture to be separated is equimolar thus the minimum reflux ratio must be determined again applying the new parameters ($x_F = [0.5, 0.5, 0]$ and $x_{\text{AR}} = 0.997$).

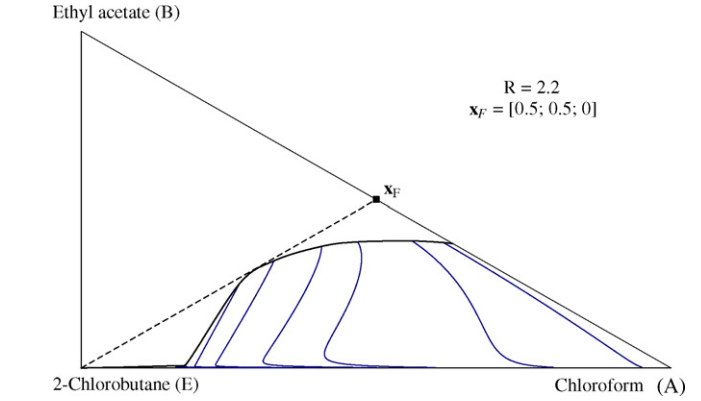
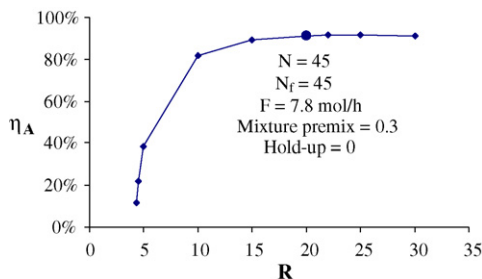


Fig. 16. Minimum reflux ratio with equimolar charge.

The minimum value of the reflux ratio, applying the feasibility study with the above-mentioned parameters, is about $R \approx 2.2$ (see Fig. 16).

Really, a minimum value is found at about $R \approx 4.3$ applying the rigorous model. This value is the double to the predicted one; the difference originates from the different numbers of theoretical stages in the two steps. The feasibility study works with the infinite number of theoretical stages assumption, whereas, our rigorous model consists of only 45 stages.

6.2.2. Effect of the feed flow rate

The recovery steadily decreases, but MER increases, with increasing feed flow rate (Fig. 17). The MER increases because the greater feed flow rate involves more mixture (key components) mixed to the entrainer. Constant distillate composition and infinite number of stages were assumed in predicting the still path in the feasibility study. None of these assumptions hold in the rigorous simulation; this is why the recovery ratio of the lightest component does not reach unity, and there is no sudden decrease in the recovery ratio.

6.2.3. Effect of pre-mixing ratio

Pre-mixing ratio PMR has a significant effect on the process, according to the results of the feasibility study. Since the two properties change in opposite directions (Fig. 18), there should be an optimal value. Determining this optimal premix ratio is not a target of the present article.

A maximum value of the pre-mix ratio was predicted in the feasibility study, as is shown in Fig. 12. This maximum value cannot be found in Fig. 18 because the charge composition is

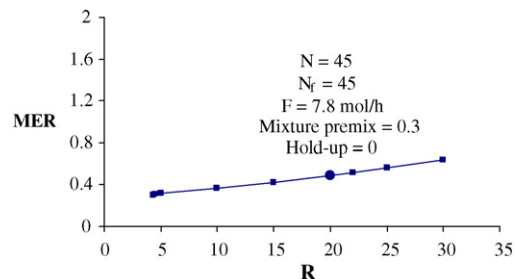


Fig. 15. Effect of the reflux ratio.

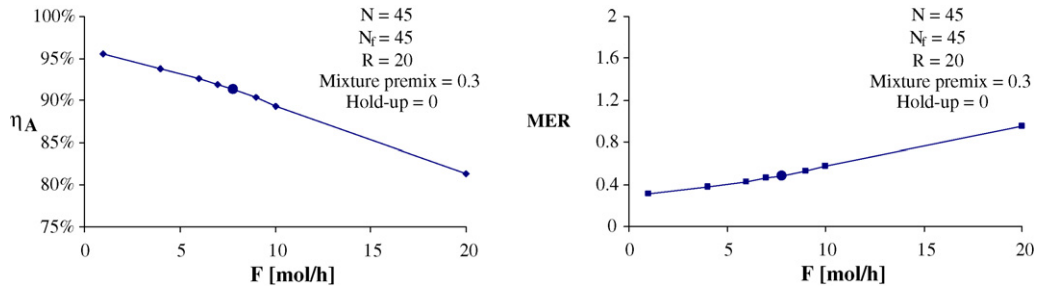


Fig. 17. Effect of the feed flow rate.

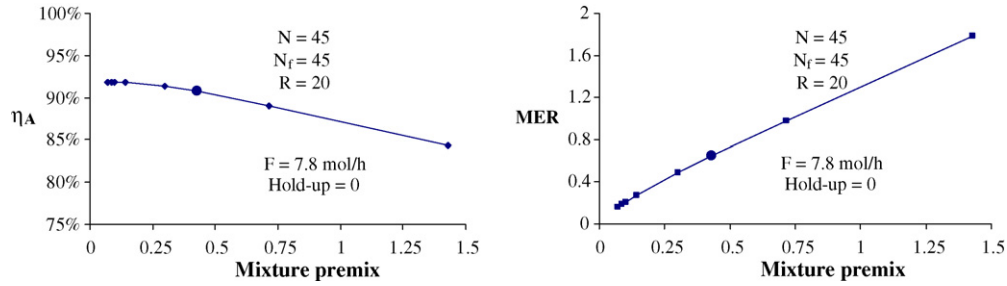


Fig. 18. Effect of the pre-mix of the equimolar mixture.

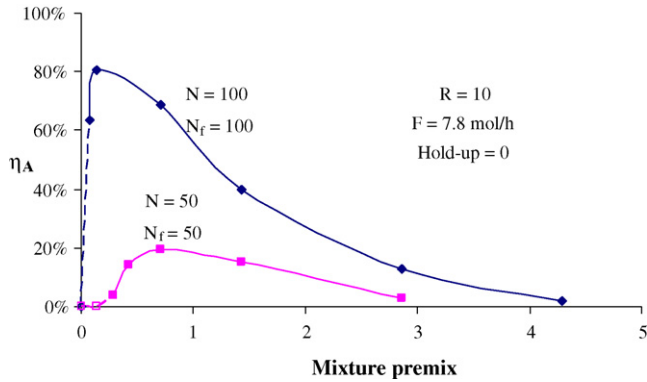


Fig. 19. Effect of the pre-mix of the azeotropic mixture.

equimolar. Such a composition is situated just at the border of the feasible region, and no maximum exists in that case (see Fig. 12 again). The maximum was established when the azeotropic composition was considered to separate.

To check the existence of the maximum PMR, additional simulation runs were performed with the specifications: $N = 50$ (100); $R = 10$; $Q = 4.5$ kW; $F = 7.8$ mol/h; $z = [0.137, 0.863, 0]$;

$N_f = 50$ (100); hold-up = 0. The stop criterion was $x_{AR,Acc} = 0.95$ in order to be consistent with Fig. 12.

The results are shown in Fig. 19. The predicted value for the maximum premix ratio was about 5, with the assumption of infinite number of stages. The simulation runs computed smaller values in both series. The critical value is nearer to the predicted one in the case of higher number of stages. Thus, the difference can be explained with the difference in the numbers of theoretical stages.

6.2.4. Effect of the number of stages in the rectifying section

Both recovery ratio and MER increase first, and then have plateau (Fig. 20). Thus, the number of theoretical stages in the rectifying section does not have maximum value in the viewpoint of feasibility, even if there must be an optimal length from economic point of view. There is a minimum number of stages at the given parameters, as usual.

6.2.5. Effect of the number of stages in the extractive section

The recovery increases up to 100%, whereas, the MER does not change significantly, when the number of rectifying stages

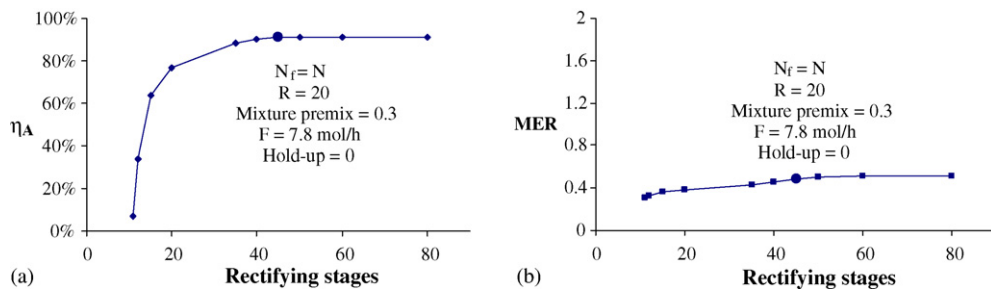


Fig. 20. Effect of the length of the rectifying section.

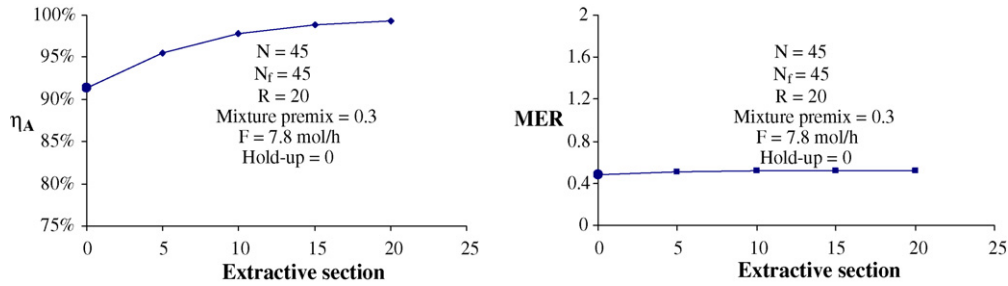


Fig. 21. Effect of the length of the extractive section.

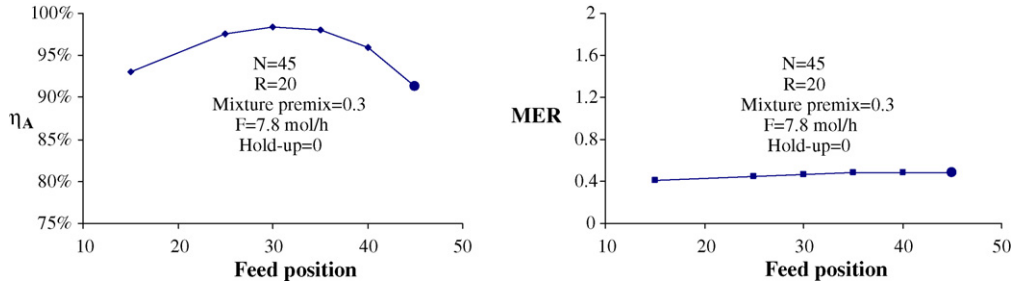


Fig. 22. Effect of the feed location.

is kept constant (45), and the number of extractive stages is increased (Fig. 21). It follows that neither a positive lower, nor an upper limit to the number extractive stages exist. Although the increase of the efficiency could be an effect of increasing the total number of stages, 100% recovery cannot be achieved by merely applying a great number of rectifying stages (see the plateau in Fig. 20a). Thus, application of some extractive stages increases the efficiency of the process.

Fig. 6 shows how the same product composition can be reached with two different column profiles starting from the same still composition. The column profile curvatures are different; thus, different stage numbers are needed in the two cases.

6.2.6. Effect of the feed location

The feed location is the only parameter that recovery ratio and MER exhibits an extremum in (Fig. 22).

This phenomenon can also be explained with the different curvature of extractive and rectifying profiles (Fig. 6). From feasibility (not necessarily economic) point of view, optimal feed location can be read from this figure. The maximum in the recovery of component A is a consequence of the two last explained phenomena. While the feed position is put higher, then the num-

ber of extractive stages increases, and the number of rectifying stages decreases.

6.2.7. Effect of the column hold-up

The hold-up on the stages has a negative effect for both monitored properties (Fig. 23) because the higher the hold-up the more material remains on the stages.

6.3. Conclusions of the sensitivity analysis

The followings can be concluded:

- Existence of the predicted limiting parameters is confirmed with rigorous simulation runs.
- Most of the limiting parameters can be calculated in the feasibility step, and in the sensitivity analysis step, as well. The two values are usually close to each other, but they are different. This difference can be explained with the application of a more precise model in the simulation runs and with the different numbers of theoretical stages. Infinite number of stages is assumed in the feasibility study, whereas, finite stage numbers are taken into account in the simulation runs.

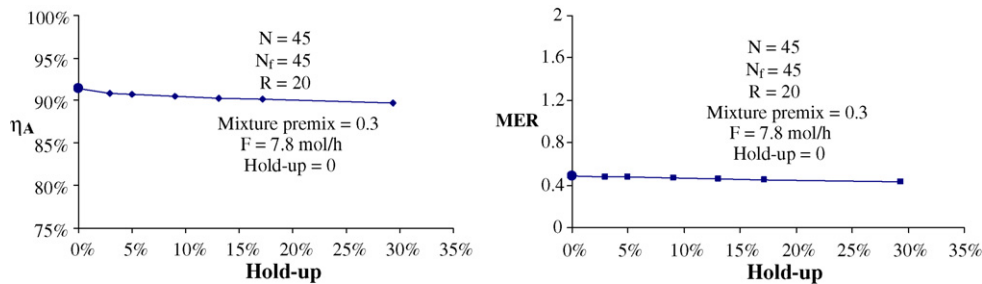


Fig. 23. Effect of the hold-up.

7. Summary

A new variant of batch extractive distillation (BED), the so-called inverse-fed batch extractive distillation (IBED) is presented. The total amount of the entrainer is pre-loaded to the boiler, and the mixture charge to be separated is continuously fed to the column in this novel configuration. The feasibility study developed for studying conventional batch extractive distillation (Lelkes et al. [21]) is extended for studying the novel configuration, as well. A thorough study is performed on the separation of a maximum boiling azeotrope (chloroform/ethyl acetate) with intermediate boiling entrainer (2-chlorobutane). We found the new configuration more efficient than the conventional one. According to the results of the feasibility study, IBED is expected to be more effective than BED because it can produce the same product with less number of stages, or better product purity with the same number of stages.

The results of the feasibility study are validated, and the study is completed, with a sensitivity analysis using commercial simulator software (ChemCAD). The existence of the predicted limiting parameters is confirmed with rigorous simulation runs. Most of the limiting parameters can be well estimated in the feasibility step, and can be determined with a slightly greater accuracy in the sensitivity analysis step. The improvement in accuracy can be explained with the application of realistic theoretical stage numbers in the analysis step, whereas, the number of stages is not taken into account in the feasibility step.

The main results of the feasibility study presented in this article remain valid for any homogeneous mixture that includes a maximal boiling azeotrope and an intermediate boiling entrainer. The separation is feasible in the same way, but the limiting parameters and the optimal operation parameters are different for each particular mixture.

Acknowledgements

This work was partially supported by Hungarian grants OTKA F046282 and OTKA T037191 and by the French Government grant. This publication is offered to the memory of Prof. Zsolt Fonyó.

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