Feasibility of extractive distillation process variants in batch rectifier column

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Abstract

A systematic comparison is presented about the separation tasks of azeotropic and close-boiling mixtures applying batch extractive distillation (BED) in rectifier. All the eight possible mixture types with at most a single azeotrope (minimum and maximum boiling azeotropes with heavy, light, and intermediate boiling entrainers; and close boiling mixtures with heavy and light entrainers) are compared. The main results of the feasibility studies on the hitherto unpublished cases are presented. All the cases are feasible in batch rectifier, applying BED. The operation steps are determined by the relative position of the azeotropic composition and entrainer in bubble point ranking. The main limiting parameters (F/V, N, E_{premix}) are also determined by the mentioned relative position; only the existence of maximum number of stages in the rectifying section is determined by the type of the azeotrope.

Use of residue curves maps (RCMs) for predicting feasibility is not generally satisfactory, but profiles maps can be used instead. Studying only the *total reflux* case can be misleading, and should be treated with great care.

The theoretical results of separation variants applying intermediate boiling entrainer were proved experimentally.

Keywords: Batch; Extractive; Distillation; Rectifier; Homogeneous; Feasibility

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1. Introduction

Distillation is one of the most widespread separation processes in the chemical industries. Batch distillation is preferred in pharmaceutical and in fine-chemical industries, where either the mixture to be separated is given in small amount, or the charge composition of the mixture fluctuates, or high purity materials must be produced.

Azeotropic mixtures cannot be separated with conventional distillation, and separation of low relative volatility mixtures (having relative volatility near to unity) is also a hard task with conventional distillation. To separate such mixtures with distillation, the relative volatility has to be modified somehow. Extractive distillation is one of the most efficient ways for this purpose. In extractive distillation, an additional component (entrainer) is fed to the distillation equipment. Only high boiling solvent was used for a long time, as entrainer in extractive distillation [1]. A separation scheme with light entrainer was also published, and the process was referred to as reverse extractive distillation, by Hunek et al. [2]. Laroche et al. [3] studied separation of minimum boiling azeotropes with heavy, intermediate boiling, and light entrainers, as well, and called all the three cases extractive distillation, independently of the volatility order.

Only batch and extractive batch distillation processes are discussed in this article, and only in the spirit of feasibility. All the separation processes with continuous entrainer feeding will be called ‘batch extractive distillation’ (BED). In BED, the mixture to be separated (A + B) is charged into the pot,

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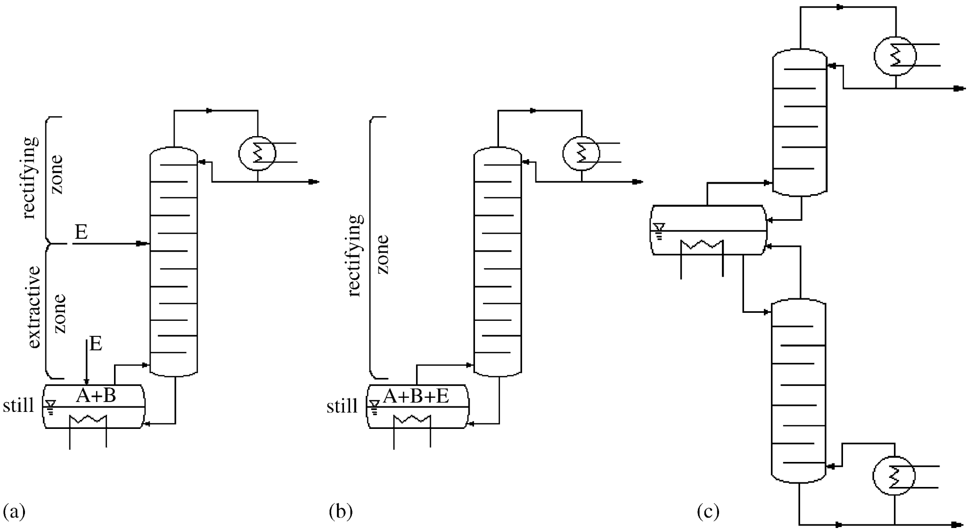


Fig. 1. Schematic draw of: (a) BED configuration, (b) SBD configuration, and (c) the conventional middle-vessel column configuration.

whereas entrainer (E) is fed continuously, during the process, to the column or to the pot (see Fig. 1a); therefore, this process has a semi-batch or semi-continuous character. The chosen entrainer can be applied in genuine batch mode, as well, to modify the relative volatility in the mixture. In this latter case, the entrainer is added to the mixture to be separated at the beginning of the process. This kind of separation will be called 'solvent-enhanced batch distillation' (SBD), in the spirit of [4] (see Fig. 1b). In all the studied cases, the mixture (either azeotropic or close-boiling) to be separated and the chosen entrainer together constitute a homogeneous system. For the entrainer selection rules in batch separation processes, see, e.g. [5].

SBD process can be performed either in rectifier, e.g. [6,7], or in inverted column, e.g. [8], or in middle-vessel column [9–13]. BED can also be performed in all these three configurations. Separation processes in rectifier [4,14–22], in stripper [16], and in middle-vessel column [23–25] have also been studied.

The most commonly applied configuration is the rectifier. Controlling a batch rectifier is less complex task than controlling a stripper. Heavy impurities that usually exist in real systems, and the products of degradations, are concentrated in the bottom, leading to difficulty in producing pure products in batch stripper. There are still a lot of open questions about application of middle-vessel column, although more and more researchers study this topic. Low and Sorensen [26], for example, published that the classical middle-vessel column configuration for the acetone/methanol/water system is less energy-efficient than separation in a batch rectifier. In the classical configuration (see Fig. 1c), the middle vessel acts as a stage of the column with a significant hold-up. Only the industrially most important configuration, i.e. batch rectifier, is discussed in the present article.

BED in rectifier has come to the center of interest in the last decade (see Table 1). Lang et al. [14] deals with separation of minimum boiling azeotrope, and with that of low relative volatility mixture, in batch rectifier with feeding heavy entrainer (I and II) continuously to the column. BED for separating minimum boiling azeotrope has also been studied with heavy entrainer (II) [14,15,19], with intermediate boiling entrainer (III) [22], and with light entrainer (IV) [16,20]. BED for separating maximum boiling azeotrope with heavy

Table 1
Summary of the possible systems for the thorough study

	Minimum boiling azeotrope	Maximum boiling azeotrope	Close boiling mixture
Light entrainer	IV S: 1.0-2 [16,20]	VII S: 1.0-1a First studied here	VIII S: 0.0-1 First studied here
Intermediate boiling entrainer	III S: 1.0-1b [22]	VI S: 1.0-1b [4]	Meaningless system
Heavy entrainer	II S: 1.0-1a [14,15,19]	V S: 1.0-2 [17,18]	I S: 0.0-1 [14]

entrainer (V) [17,18], and with intermediate boiling entrainer (VI) [4], has been published as well.

Although there are a lot of articles published on particular BED variants, not any comprehensive article has yet been published about it, or one that systematically compares separation of the different mixture types. However, this comparison is useful for recognizing the most important properties of these processes from the viewpoint of design. Our team has performed this comparison, and also studied some missing cases to obtain a complete image. For studying the reliability of the feasibility study, some experiments were also performed during the research.

This article has two main aims. First of all, it presents the main results of the feasibility studies for the missing cases, and of the experiments, as well. Second, it presents a systematic comparison of the considered processes according to the properties of the material system, the steps of the feasible separation process, the existence of limiting flows and other limiting parameters, as well as the applicability of different feasibility methodologies. It will turn out that the processes can be sorted into two main classes according to the volatility order of the azeotrope and the entrainer, and these classes can be attributed with separation steps and existence of limiting flows.

2. Considered mixture types

The ternary mixtures formed by the binary mixture to be separated together with the applied entrainer can be classified according to several criteria. The number and type (minimum/maximum boiling) of azeotropes in the mixture as well as the volatility of the components can be taken into consideration. Our team has studied those ternary mixtures that contain no more than one homogeneous azeotrope, and no liquid–liquid phase split.

The two azeotrope types (minimum and maximum boiling) combined with the three possible entrainer positions (light, intermediate boiling, and heavy) in ternary systems give rise to six different cases. There are two additional cases for separating low relative volatility mixtures. Separation of a low relative volatility binary mixture with heavy and with light entrainer is feasible, but its separation with intermediate boiling entrainer is meaningless. These are altogether eight (I–VIII) different cases of BED that can be distinguished and studied (see Table 1). The codes, S: 0.0-1, S: 1.0-1a, S: 1.0-1b, and S: 1.0-2, in this table stand for classifying the studied mixtures according to [27,28].

3. Feasibility methods

The aim of a feasibility method is to quickly and reliably predict the possible product compositions, and to determine the necessary operation steps. Besides these targets, it must be advantageous if the recovery of the components and/or the operation time can also be estimated with the applied model. The models applied in feasibility studies usually contain a set of simplifying assumptions, e.g. constant molar overflow, theoretical stages, negligible hold-up on the stages, constant pressure in the column, etc.

The separation is called feasible by definition if starting from the initial still composition, such state of the column can be reached with which the specified product purity can be produced even if for a very short time only. The column state is given by the composition profile. Both the still composition and the distillate composition lay on the composition profile of the column; therefore, calculation of composition profiles is a possible method for the studies. BED has a batch (semi-batch or fed-batch) character; therefore, the still composition should change in time. Recovery of the components, besides product composition, is also an important point of view in practice. The specified product purity should be maintained for a longer time in order to achieve reasonable recovery. It follows that both prediction of the still path (movement of the still composition) and calculation of different possible composition profiles are necessary for assessing feasibility. Thus, two kinds of feasibility can be distinguished during the feasibility study:

- *Marginal feasibility*: The specified distillate can be produced at least for a moment. This is more exactly defined by the existence of at least one column state connecting a still composition, reachable from the initial charge composition, to the specified product composition. Existence of such a column state may be associated to a single still composition only. As the still composition changes, it may at once be shifted to a point that cannot be connected to the specified distillate composition. Thus, existence of such a single column state is a necessary condition, but is not a guarantee for a longer producibility of the specified distillate and acceptable recovery ratio.
- *Practical feasibility*: The specified distillate can be produced with a considerable recovery. This is more exactly defined by the existence of a contiguous region of points, reachable from the initial still, all being still compositions that can be connected to the specified distillate composition by an appropriate column state. This region is called ‘feasible region’ (FR). How wide FR should be depends on what recovery ratio is to be achieved; this is not well defined generally, but is up to the discretion of the engineer. The process is practically feasible if: (1) it is marginally feasible and (2) the still composition can be kept in the FR during the process. The second condition means that the still can be governed toward compositions of small mole fraction in the main component, and thus achieving its greater recovery.

In this article, only those processes are called feasible that are practically feasible.

Residue curves maps (RCMs) and profiles maps are extensively used in the literature for investigating batch and fed-batch distillation processes. RCMs are generally used for studying SBD. This method is based on the fact that the residue curves, calculated with Eq. (1) describing the movement of the still composition during single-stage (simple) batch distillation [29], almost coincide with the rectifying profiles at high reflux ratio ($R > 7$) [30]. With infinite number of stages, the unstable node of the residue curves can be considered as product composition in batch rectifier.

$$\frac{dx}{d\xi} = x - y^* \tag{1}$$

ξ is a transformed, or 'warped', dimensionless time that gives a more simple formulation for the equation of the residue curves. This transformation is not used in the recent article. See, e.g. [9] for more details.

Studying the possible rectifying profiles is sufficient in the case of SBD because there is only one column section in this case (Fig. 1b); the possible product composition can be predicted for high reflux ratio and infinite number of stages with the method of RCM. Differential equation (2) describes the still path [30]:

$$\frac{d(Ux_S)}{dt} = -Dx_D \tag{2}$$

The feasible region can, in some cases, be partitioned to subsets points of which can serve as starting still compositions for producing the set of specified products with a particular sequence of these products. Such subsets are called 'distillation regions'. This notion is conventionally applied in the literature of batch distillation. This distillation region is not identical to 'simple distillation region' applied in the literature of equilibrium batch distillation, and connected to RCM. Simple distillation regions are separated by separatrices of RCM [31]; distillation regions are usually separated by straight mixing lines connecting the entrainer vertex with a vis-a-vis azeotrope in the triangle. In some cases, however, distillation regions are also separated by separatrices of RCM. The sequences of products obtainable in the distillate are different on the two sides.

The still composition x_S is shifted in a direction assigned by a straight line through the initial still composition $x_{S,0}$, and the distillate composition x_D, and moves away from the latter one, according to Eq. (2). That is, x_S is always on the straight line through $x_{S,0}$ and x_D if x_D and D are constant. Constants x_D and D are assumed in each production step during the feasibility study, in order to simplify the problem.

Use of RCM is not sufficient for studying BED if the entrainer is fed to the column, and not directly to the still, because the column has two sections in that case. Moreover, RCMs do not always give reliable results even for SBD with finite reflux. In some cases, e.g. at separation of maximum boiling azeotrope with intermediate boiling entrainer (see [4]), the rectifying profiles with finite reflux ratio are significantly different from the residue curves; thus, the distillate composition with finite reflux ratio differs from the predicted one with total reflux.

If the entrainer is fed to the column, both a rectifying and an extractive column sections exist (see Fig. 1a). The extractive section includes the feed stage and all the stages below the feed-tray; the rectifying section contains the stages above the feed-tray. Since there are two sections in the column, and thus the composition profile consists of two parts, the RCM is not sufficient for studying the feasibility, even at total reflux.

Derivation of the differential equation (3) for calculating the extractive and rectifying profiles of BED is published by Lelkes et al. [19] (for continuous case, see [32]). Their model also includes a differential equation (4) for predicting the still path.

$$\frac{dx}{dh} = \pm\frac{V}{L}(y - y^*) \tag{3}$$

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

Eqs. (2) and (4) can be derived according to the well-known Rayleigh equation, because the hold-up on the stages is neglected. Although assumption of equilibrium stages was used in its derivation, no equilibrium stages are assumed when Eq. (3) is applied in the feasibility study. The concept of equilibrium stages is meaningless after jumping to the limit of infinitesimal increments, and the physical concept of Eq. (3) is more similar to the differential equations applied in the component transfer and driving force models.

The differential equations (3) and (4) are solved as initial value problems during the feasibility study. Calculation of the rectifying profile is started from the specified distillate composition; extractive profile calculations are started from assumed still compositions. The sign in Eq. (3) depends on the direction of the calculation; it is (−) for the rectifying and (+) for the extractive profiles. The still path is determined by integrating Eq. (4).

This model has a great benefit that it can be used for total reflux as well as for finite reflux ratio. The formulas of the operating lines implicitly include the reflux ratio, $R = (V - D)/D$. Eq. (5) describes the operating line in the rectifying section, and Eq. (6) in the extractive section, assuming boiling point feed state.

$$y = \frac{(V - D)x + Dx_D}{V} \tag{5}$$

$$y = \frac{(V - D + F)x - Fz + Dx_D}{V} \tag{6}$$

Eq. (7) is an integrated form of Eq. (4) with constant F, D, z and x_D. If the final still composition is known, the operating time can be determined with Eq. (7); Eq. (8) provides with the recovery ratio of component A.

$$x_{S,\mathrm{final}} = \frac{U_0 x_{S,0} - Dx_D t + Fzt}{U_0 - Dt + Ft} \tag{7}$$

$$\eta_A = 1 - \frac{(U_0 - Dt + Ft)x_{S,\mathrm{final},A}}{U_0 x_{S,0,A}} \qquad (8)$$

4. Summary of BED and SBD schemes in rectifier

In this part, the separation schemes are concluded for the different cases (mixture classes). Six cases have earlier been studied and published, two cases have not been yet (see Table 1). Separation of minimum boiling azeotropes with heavy, intermediate boiling, and light entrainer, separation of maximum boiling azeotropes with heavy and intermediate boiling entrainer, and even separation of low relative volatility mixtures with heavy entrainer have earlier been studied. Separation of maximum boiling azeotropes and low relative volatility mixtures with light entrainer has not been studied before. Studying these two missing cases makes possible a complete and thorough comparison of the separation variants applying BED. Application of a light entrainer for separating a given mixture can be advantageous either if one of the components is heat-sensitive, and thus the application of a heavy entrainer is not recommended, or if the mixture to be separated already contains a light component that can be applied as entrainer. A thorough comparison provides with facilities to find those properties of the mixture which mainly determine the separation steps and the existence of the most important limiting parameters. Knowledge of the possible operation schemes and the limiting parameters hopefully will make the design of the separation process more reliable, much easier, and faster.

To simplify the task, the charge composition is the azeotrope for azeotrope forming mixtures, and equimolar composition for low relative volatility mixtures in the following examples, when feasibility is in question. Studying the feasibility of separation with azeotropic charge composition is sufficient because it can be approached in all such cases with conventional distillation.

4.1. Separation of minimum boiling azeotrope with heavy entrainer (case II)

Separation of minimum boiling azeotrope with heavy entrainer was studied by several authors [14,15,19,24]. Application of BED in rectifier was suggested by Lang et al. [14], with the operation steps shown in ‘column A’ of Table 2. There is no product withdrawal in the heat-up and run-up steps. The column and the reflux drum are filled up in the heat-up step, without entrainer feeding. The run-up step serves for the evolution of an appropriate extractive profile in the column; thus, continuous entrainer feeding starts in this step. Continuous entrainer feeding and product withdrawal are applied simultaneously in the first production step, and almost pure product can be produced until the still composition reaches a boundary of the separation. One of the unstable separatrices of the extractive profiles serves as separation boundary in Fig. 2. The movement of the still composition is determined by the distillate flow rate, its composition, the entrainer flow rate, and its composition together (see Eq. (4)). The product withdrawal pushes the still composition away from the distillate composition; the entrainer feeding pulls the still composition toward the entrainer composition (to vertex E in our case). The actual direction of the still path is a vectorial sum of these two effects.

The profiles map applied for studying the separation, shown in Fig. 2a, contains a rectifying profile started from the specified distillate composition, $x_D = (0.95; 0.025; 0.035)$. Extractive profiles with the given operating parameters, here $R = 4$ and $F/V = 0.6$, should also be considered because there are two sections in the column.

If the number of extractive stages is in an appropriate range, almost constant composition product can be withdrawn until the still composition reaches one of the unstable separatrices of the extractive profiles. Lelkes et al. [19] performed simulations with 6 rectifying and 12 extractive stages

Table 2
Operation steps for BED separating azeotropic mixtures

Steps	A	B	C	D	E	F
	Heavy entrainer		Intermediate entrainer		Light entrainer	
	Minimum[a]	Maximum[a]	Minimum[a]	Maximum[a]	Minimum[a]	Maximum[a]
Premix				Necessary	Necessary	Necessary
Heat-up	$R = \infty$, $F = 0$	$R = \infty$, $F = 0$	$R = \infty$, $F = 0$	$R = \infty$, $F = 0$	$R = \infty$, $F = 0$	$R = \infty$, $F = 0$
Run-up	$R = \infty$, $F > 0$	$R = \infty$, $F > 0$	$R = \infty$, $F > 0$			
1st cut	$R < \infty$, $F > 0$, A	$R < \infty$, $F > 0$, A	$R < \infty$, $F > 0$, A	$R < \infty$, $F > 0$, AE	$R < \infty$, $F > 0$, EA	$R < \infty$, $F > 0$, EA
2nd cut	$R < \infty$, $F = 0$, B	$R < \infty$, $F = 0$, B	$R < \infty$, $F = 0$, E	$R < \infty$, $F = 0$, E	$R < \infty$, $F = 0$, E	$R < \infty$, $F = 0$, E
3rd cut	Residue: E	Residue: E	Residue: B	Residue: B	Residue: B	Residue: B
Reload				Load AE	Load EA	Load EA
4th cut				$R < \infty$, $F = 0$, A	$R < \infty$, $F = 0$, E	$R < \infty$, $F = 0$, E
5th cut				Residue: E	Residue: A	Residue: A
Main contaminant in A	B	B	E	E	E	E
Bubble point ranking	AB, A, B, E	A, B, AB, E	AB, A, E, B	A, E, B, AB	E, AB, A, B	E, A, B, AB

[a] Azeotrope.

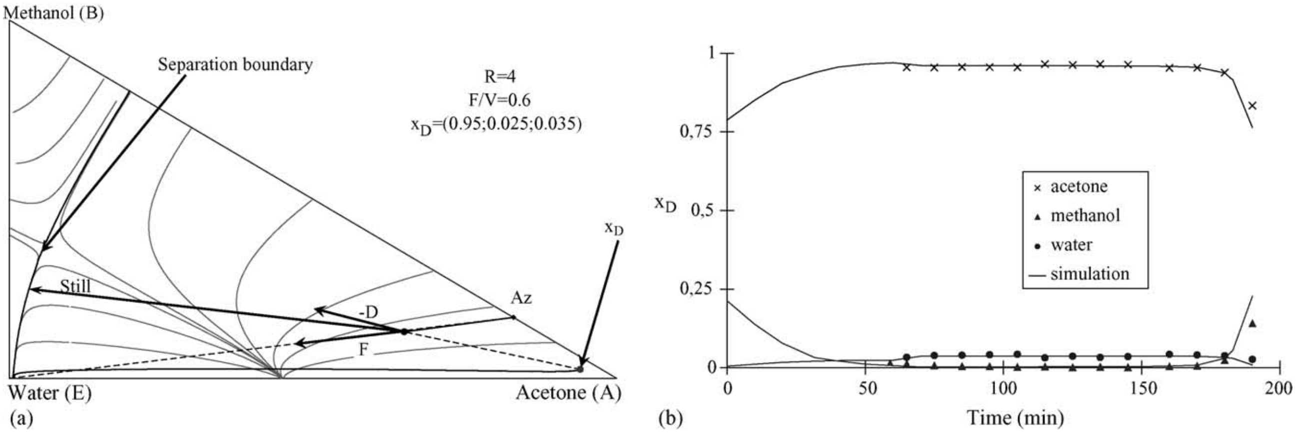


Fig. 2. (a) Profiles map to study the feasibility of separating the acetone/MeOH/H_2O system x_{Ch} = azeotrope and (b) simulated and experimental results for the acetone/MeOH/H_2O system, $x_{Ch} = (0.5; 0.5; 0)$.

on acetone/methanol/water mixture and showed that practically constant product composition can be produced with BED for a long time if the charge is equimolar. The authors published experimental results in another article [21]. The results of the simulations and that of the experiments are in good agreement (see Fig. 2b).

4.2. Separation of maximum boiling azeotrope with heavy entrainer (case V)

Separation of maximum boiling azeotrope with heavy entrainer was studied by Dussel and Stichlmair [7] and Lang et al. [17,18]; they established the feasibility of SBD if the separatrix of the rectifying profiles is highly curved. There are two distillation regions because two unstable nodes (vertices A and B) exist in the RCM. The boundary is a stable separatrix that connects vertex E (stable node of the residue curves) and the azeotropic composition (saddle point of the residue curves). Nearly pure component A can be withdrawn from the convex distillation region in this case, after mixing some entrainer to the mixture (see Fig. 3a).

Lang et al. [17,18] studied the chloroform/acetone/benzene system, and suggested application of BED in rectifier with similar operation steps to those shown in ‘column B’ of Table 2. They have found that separation with BED works with better recovery than that with SBD. The entrainer has to be fed continuously to the column, not directly to the still, so that an extractive section exists. A run-up step serves for the development of an appropriate extractive profile. The entrainer is still fed during the first production step; thus, the shift direction of the still composition is determined by the distillate removal and by the entrainer feeding together (see Eq. (4)).

The profiles map used for studying the separation, see in Fig. 3b, contains a rectifying profile started from the specified distillate composition, $x_D = (0.98; 0.002; 0.018)$, and extractive profiles with the given operating parameters ($R = 25$, $F/V = 0.2$). Almost pure product can be produced until the still composition reaches one of the unstable separatrices of the extractive profiles (separation boundary).

Lelkes and co-workers [18] performed simulations with 15 rectifying and 15 extractive stages and showed that the

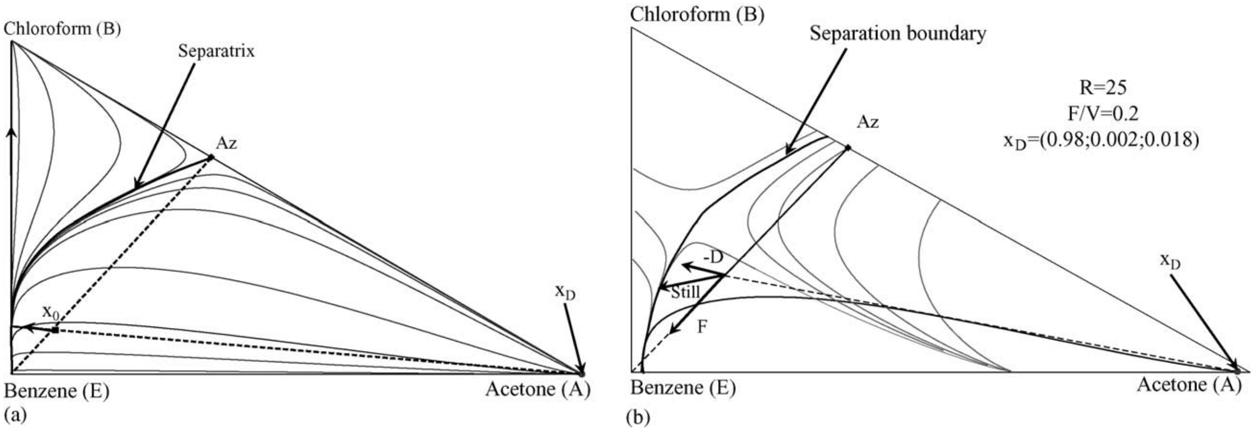


Fig. 3. (a) RCM to study the feasibility of SBD for the acetone/$CHCl_3$/benzene system and (b) profiles map to study the feasibility of BED for the acetone/$CHCl_3$/benzene system.

average distillate composition does not change significantly for a high recovery of acetone (component A).

4.3. *Separation of minimum boiling azeotrope with intermediate boiling entrainer (case III)*

Separation of minimum boiling azeotrope with intermediate boiling entrainer was also studied [6,22]. According to Bernot et al. [6], separation of this type of mixture is feasible only in stripper if SBD is applied; however, Rev et al. [22] demonstrated feasible separation in rectifier when BED is applied. Bernot et al. [6] applied RCMs, but Rev et al. [22] applied profiles maps for the investigation. The determined operation steps are shown in 'column C' of Table 2.

The entrainer is continuously fed to the column in this case, too, in such a way that two (a rectifying and an extractive) sections exist in the column. Since the existence of the extractive section is necessary for the separation, a run-up step appears in the separation process suggested to this system, as well.

The profiles map shown in Fig. 4a contains a rectifying profile started form the specified distillate composition, $x_D = (0.9; 0.05; 0.05)$, and contains extractive profiles belonging to the given operating parameters ($R = 10$, $F/V = 0.5$). Since there is continuous entrainer feeding, the still path is governed both by the distillate removal and by the entrainer feeding in the first production step.

Almost pure product can be produced until the still composition reaches the rectifying profile (separation boundary). The methyl acetate/cyclohexane/CCl_4 system was studied by Rev et al. [22]. The authors performed simulation runs with 15 rectifying and 15 extractive stages, and showed that the distillate composition does not change for a long time if the charge is equimolar (Fig. 4b).

4.3.1. *Experimental results*

The experimental results below, for the present mixture type, have not yet been published in scientific journal, but only at a conference [33]. To support the theoretical results, experiments were performed with the methyl acetate/cyclohexane/CCl_4 system. A glass column of laboratory scale distillation unit had 5 cm inside diameter, 1.6 m height house-made structured packing above the still, and 0.8 m height random packing (ceramic Raschig-ring) in the upper part. The theoretical number of stages was 16 with methyl acetate/cyclohexane mixture. The entrainer was continuously fed between the two packing zones. The still was about 1 l, and heated in oil bath. The sample compositions were determined with gas-chromatograph.

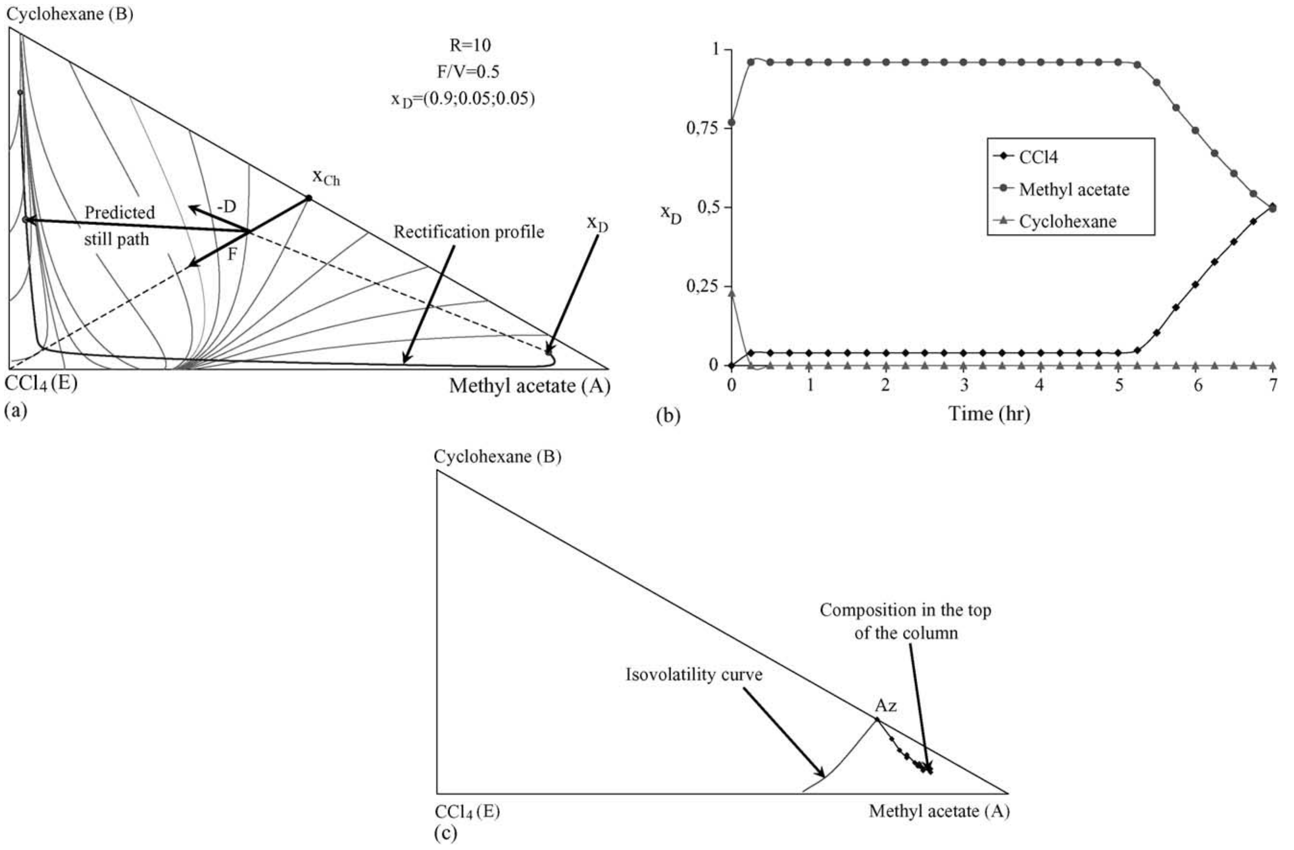


Fig. 4. (a) Profiles map to study the feasibility of BED for the MeOAc/cyclohexane/CCl_4 system; (b) simulated results for the MeOAc/cyclohexane/CCl_4 system; (c) experimental results for the MeOAc/cyclohexane/CCl_4 system.

In the case of minimum boiling azeotrope with intermediate boiling entrainer, the bottleneck of the separation is the run-up step. If the specified distillate composition cannot be achieved with infinite reflux ratio, then it is impossible with finite reflux ratio, as well. Therefore, only the run-up step was investigated experimentally.

After the column had been heated up, the entrainer feeding was started, and the liquid composition in the top was sampled. The composition-path was drawn in the composition triangle (Fig. 4c).

It can be seen in Fig. 4c that the composition in the top of the column starts near the azeotropic composition. This starting composition was expected because the azeotropic composition is the unstable node of the residue curves. Due to entrainer feeding, the top composition moves to the interior of the composition triangle, and runs on the right side of the isovolatility curve, toward pure component A. This movement shows that the azeotropic composition was broken with the continuous entrainer feeding, i.e. production of almost pure component A is possible with intermediate boiling entrainer.

4.4. *Separation of maximum boiling azeotrope with intermediate boiling entrainer (case VI)*

Separation of maximum boiling azeotrope with intermediate boiling entrainer was also studied [4,6]. Bernot et al. [6] dealt with theoretical mixture only, and suggested the SBD process producing pure component A. However, it has been shown for a real system (chloroform/ethyl acetate/2-chlorobutane) by Lelkes et al. [4] that production of pure component A from the azeotropic composition in rectifier is not feasible even with high reflux ratio and large number of stages ($R = 49$, $N = 100$). They suggested an SBD process with a binary product (AE mixture) as a first cut. Separation of the binary mixtures AE (product) and BE (still content after the first production step) is feasible in subsequent steps, since there is not any azeotrope in them. In addition, they suggested a BED process, as well, with the operation steps shown in 'column D' of Table 2. The same idea was used for BED as for SBD, i.e. a binary mixture is produced in the first production step. In the case of BED, the entrainer may be fed to the still, i.e. applying an extractive section is not essential. Irrespectively to whether an extractive section is applied or the entrainer is continuously fed to the still, application of BED is preferable to SBD.

Fig. 5a contains rectifying profiles starting from different compositions satisfying the specification, $x_{\mathrm{AR}} = \frac{x_{\mathrm{DA}}}{x_{\mathrm{DA}}+x_{\mathrm{DB}}} = 0.99$. These rectifying profiles cover a feasible region of the separation with a single rectifying section. Production of the specified distillate is possible until the still composition leaves the feasible region. It can leave the region across the boundary, or across the BE edge. If the still composition leaves the feasible region across the BE edge, then BE mixture remains in the still, which gives a sharper separation (higher recovery) compared to the case of leaving across the boundary. It can be seen in Fig. 5a that the application of BED is more beneficent than SBD. Less entrainer has to be mixed to the azeotropic mixture at the beginning of the process to cross the BE edge with the still path in the case of BED than in the case of SBD. It is so because the movement of the still composition is determined by both the product withdrawal and the entrainer feeding in the case of BED.

Moreover, Lelkes et al. [4] proved with simulations that half of the still volume was sufficient for BED than for SBD, in a particular case actually computed.

4.4.1. *Experimental results*

The experimental results below, for the present mixture type, have not yet been published in scientific journal, but only at a conference [33].

To support the theoretical results, experiments were done with the chloroform/ethyl acetate/2-chlorobutane system. In this separation process, one has to drive the distillate composition along, and keep it near, the AE edge. Therefore, only the first production step was investigated experimentally.

The applied laboratory set was the same as in the separation of minimum boiling azeotrope with intermediate boiling

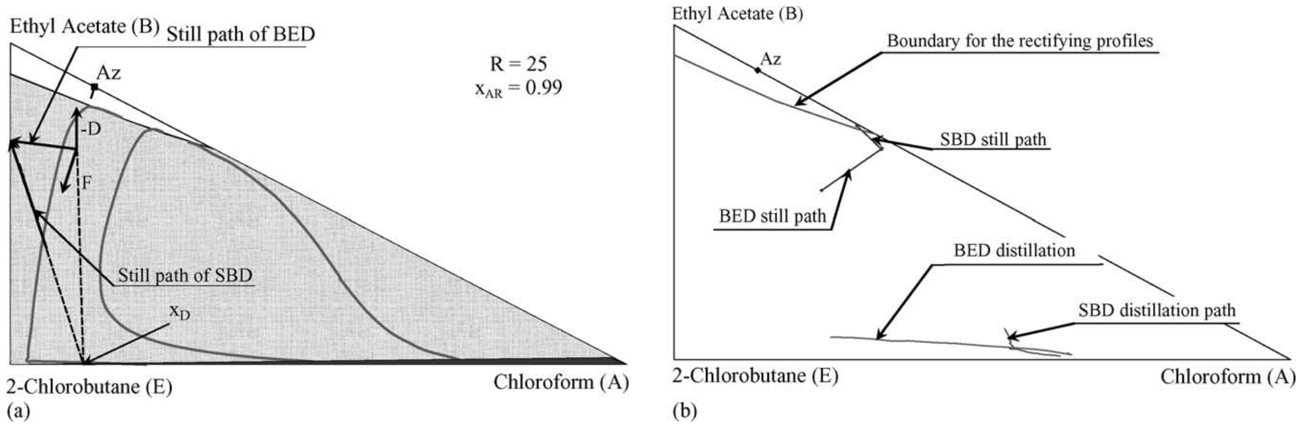


Fig. 5. (a) Profiles map to study the feasibility of BED for the $CHCl_3$/EtOAc/2-chlorobutane system and (b) experimental results for the $CHCl_3$/EtOAc/2-chlorobutane system.

entrainer, described in the previous section. The total number of theoretical stages was 12, instead of the earlier 16, with this mixture.

Two experiments were performed with the same initial still composition. The first experiment was done in the spirit of the SBD process, and the second in that of the BED process. During the operation, samples were taken from the still and from the distillate, as well. Both compositions were analyzed with gas-chromatograph, and the paths were drawn in a composition triangle.

It can be seen in Fig. 5b that the distillate composition was kept along the AE edge due to the continuous entrainer feeding when the BED process was applied. When the whole amount of solvent was added to the charge at the beginning of the process (SBD process), a sharp change in the distillate composition was observed.

4.5. *Separation of minimum boiling azeotrope with light entrainer (case IV)*

Lelkes et al. [16] studied the separation of minimum boiling azeotrope with light entrainer. They suggested application of BED in rectifier with the operation steps shown in 'column E' of Table 2. The first product is a binary mixture in this case, without any azeotrope, so that the separation of this binary mixture is feasible in a later step. The entrainer may be fed to the still, i.e. applying extractive section is not essential. Since the extractive section is not necessary, the separation is also feasible with SBD if the first product is the AE binary mixture. The rectifying profiles started from compositions satisfying the specified distillate purity ($x_{DB} \leq 0.001$ and $x_{DA} \geq 0.01$) form a feasible region (see Fig. 6a). This is the feasible region for SBD and for BED with entrainer feeding directly to the still, as well. This region is situated far from the AB edge, and thus from the azeotropic composition. Therefore, a great amount of entrainer has to be mixed to the charge for separation. In the case of SBD, the still composition moves to the direction of the AB edge, and leaves the feasible region very fast; therefore, the recovery of component A is not significant.

In the case of BED, on the other hand, the still path is determined by both the product withdrawal and the entrainer feeding. This direction is more advantageous than the one determined by distillate removal only. If there is continuous entrainer feeding besides the distillate withdrawal, the still composition can be driven near to the BE edge, which gives rise to better recovery (see Fig. 6a).

The feasible region can be extended with the use of some extractive stages. This possibility has not been investigated in previous papers. The extractive profiles run through the feasible region of rectifying profiles (Fig. 6b), i.e. the extractive section has a maximum length (maximum number of stages). If there are too many stages, the extractive section ends near vertex E (outside of the feasible region of rectifying profiles), and the specified product cannot be produced. Several simulation runs were performed to investigate the effect of the extractive number of stages on recovery ratio and production time. A few extractive stages increase the recovery [34].

Separation of minimum boiling azeotrope with light entrainer is feasible with small reflux ratio (*R*) only. Otherwise, the rectifying profiles do not intersect the separatrix of the residue curves.

4.6. *Separation of maximum boiling azeotrope with light entrainer (case VII)*

Separation of maximum boiling azeotrope with light entrainer has not been studied before. In this paper, only the main results are presented. The thorough study will be published in a separate paper [34].

Separation with light entrainer is not feasible if pure component is to be produced in the first step because the most volatile component, i.e. the pure entrainer, leaves the column first. However, the separation is feasible with the operation steps shown in 'column F' of Table 2. The first product is the AE binary mixture. This binary mixture does not contain any azeotrope; thus, its separation is feasible in a later step.

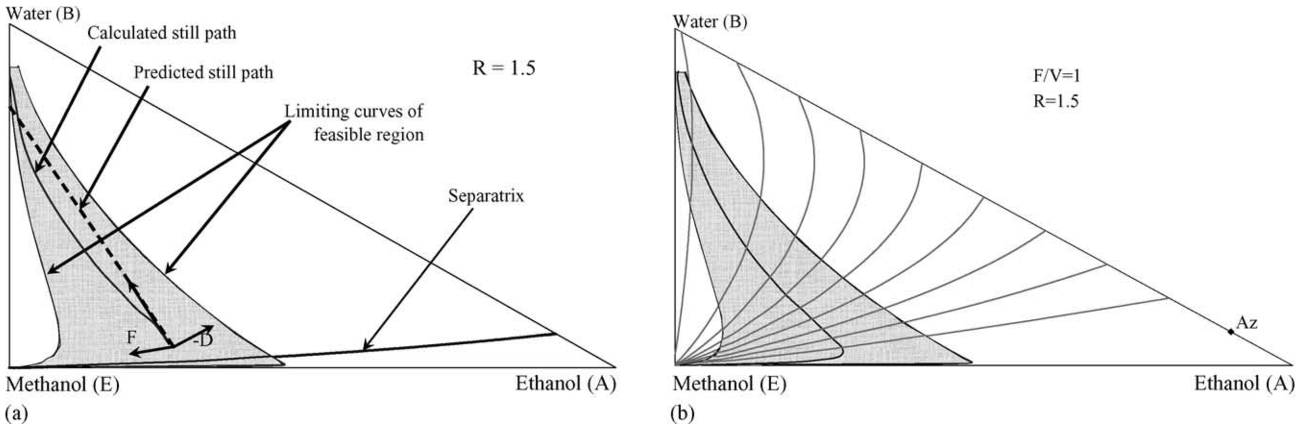


Fig. 6. (a) Rectifying profiles for the EtOH/H_2O/MeOH system and (b) rectifying and extractive profiles for the EtOH/H_2O/MeOH system.

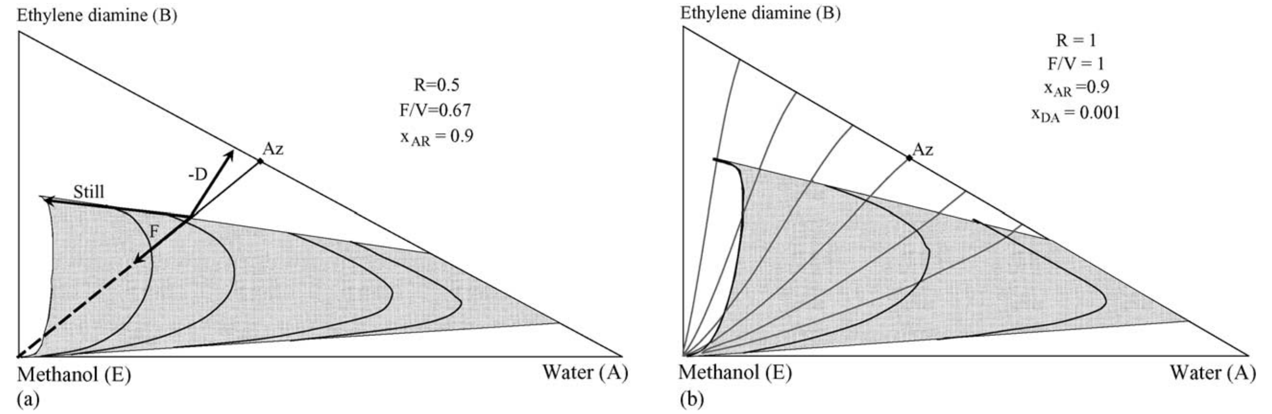


Fig. 7. (a) Rectifying profiles for the H_2O/ethylene diamine/MeOH system and (b) rectifying and extractive profiles for the H_2O/ethylene diamine/MeOH system.

Fig. 7a shows the region of rectifying profiles satisfying the specified distillate purity ($x_{AR} = \frac{x_{DA}}{x_{DA}+x_{DB}} = 0.9$ and $x_{DA} \geq 0.009$). The initial still composition can be shifted into this region with some mixing of the entrainer, so that the specified product can be produced with SBD. However, the still composition moves in the direction of the AB edge in the case of SBD; thus, it leaves the feasible region so fast that the recovery of component A is negligible. The entrainer can be fed directly to the still in the case of BED because the feasible region is large enough even with rectifying profiles only. But, since there is continuous entrainer feeding, the still composition can be directed toward the BE edge. Recovery of component A is higher with BED than with SBD.

Enlargement of the feasible region is expected as a result of applying extractive stages. The length of the extractive section has a limiting value in the same way as in the case of minimum boiling azeotrope with light entrainer because the extractive profiles run through the feasible region of rectifying profiles (Fig. 7b). If the extractive section has too many stages, the separation becomes infeasible.

There is a separatrix, not shown in Fig. 7, of the residue curves very close to the mixing line between the azeotropic composition and the entrainer vertex. Because of the existence of this separatrix, separation of maximum boiling azeotrope with light entrainer is feasible with small reflux ratio (R) only. Otherwise, the rectifying profiles do not intersect the separatrix [34].

4.7. Separation of low relative volatility mixture with heavy entrainer (case I)

Lang et al. [14] studied separation of low relative volatility mixtures with heavy entrainer. Simulation runs were performed for the heptane/toluene/phenol system to prove the feasibility of the separation, but they did not apply or develop a feasibility method.

Since there is not any azeotrope in the system, the separation is feasible with SBD, but it was found that the separation with BED gives better recovery than SBD. They suggested the application of BED in rectifier with the same operation steps as shown in 'column A' of Table 2.

We have studied separation of the heptane/toluene/phenol system with our feasibility method, which makes possible to obtain the boundaries of the separation, estimation of the recovery ratio and the operation time, and to give good initial values to perform reliable simulations.

Fig. 8a contains a rectifying profile started from the specified distillate composition $x_D = (0.94;\ 0.04;\ 0.02)$, and contains the corresponding extractive profiles ($R = 5$, $F/V = 1$). The extractive profiles have a stable node near the AE edge; the rectifying profiles started from the vicinity of pure A also run near the AE edge; thus, a wide bundle of extractive profiles intersect the actual rectifying profile. Therefore, application of an extractive section may be advantageous in this separation task. Nearly pure product can be produced until the still composition reaches one of the unstable separatrices of the extractive profiles. This is the same phenomenon that was found at separation of minimum and maximum boiling azeotropes with heavy entrainer.

Rigorous simulation runs were performed for the heptane/toluene/phenol system with $N_{extr} = 10$, $N_{rect} = 5$, $Q_{reb} = 3\,kW$, $U_0 = 24\,mol = 3\,l$, $x_{ch} = (0.5;\ 0.5;\ 0)$. Fig. 8a shows the predicted rectifying and extractive profiles together. The unstable separatrices of the extractive profiles form a boundary of the BED process. The simulated still path is shown in Fig. 8a. Fig. 8b shows a history of the accumulator composition. A vertical dashed line marks the time when the composition in the accumulator reaches (from above) the specified distillate purity ($x_{D,A} \geq 0.94$). The specified distillate can be withdrawn while the still composition remains in the predicted feasible region.

4.8. Separation of low relative volatility mixture with light entrainer (case VIII)

Separation of close boiling mixture with light entrainer has not been studied before. In this paper, only the main results

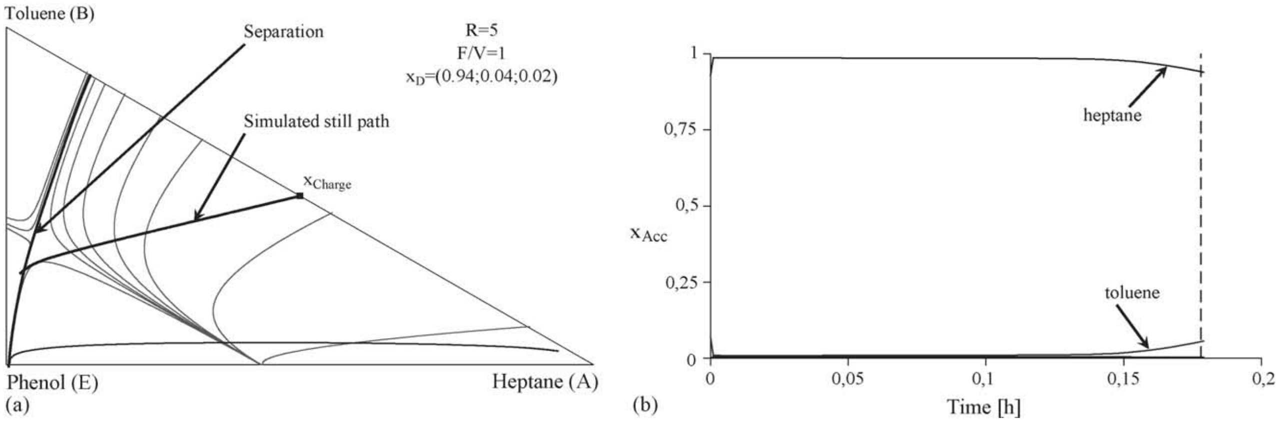


Fig. 8. (a) Profiles map to study the feasibility of BED for the heptane/toluene/phenol system and (b) simulated results with the heptane/toluene/phenol system.

are presented. The thorough study will be published in a later paper [34].

Separation with light entrainer is not beneficent if pure component is to be produced in the first step because the most volatile component, i.e. pure entrainer, leaves the column first, and the low relative volatility mixture remains in the still for the next production step. The separation is feasible with the operation steps shown in 'column E' of Table 2. The first product is the AE binary mixture.

According to the idea of producing binary product, those rectifying profiles form a feasible region which satisfy the specified distillate purity ($x_{\mathrm{AR}} = \frac{x_{\mathrm{DA}}}{x_{\mathrm{DA}}+x_{\mathrm{DB}}} = 0.9$ and $x_{\mathrm{DA}} \geq 0.009$) (see Fig. 9a). This feasible region is appropriate for separating the equimolar mixture with SBD because the initial still composition can be moved into this region with premixing entrainer. However, in the case of SBD, the still composition moves toward AB edge, and leaves the feasible region very soon. Therefore, recovery of component A is negligible. In the case of BED, the entrainer can be fed directly into the still because the feasible region is large enough even with rectifying profiles only. Because of continuous entrainer feeding, the final still composition will be nearer the BE edge.

One would expect that application of extractive stages enlarge the feasible region in this system, too, and the length of the extractive section has a limit because the extractive profiles run through the feasible region of rectifying profiles (Fig. 9b). It has been found by simulation for the ethylbenzene/chlorobenzene/methyl cyclohexane system, however, that the extractive section is longer than needed even if a single extractive stage is applied.

5. Comparison of the separation schemes

5.1. Operation steps of BED

The operation schemes have been summarised in the previous section. It can be established that application of BED is beneficent in each case. If the entrainer is fed to the column, then extractive section exists besides the rectifying one, and an extractive profile is formed that connects the still composition to the rectifying profile. If the feed is fed to the still, then the continuous entrainer feeding provides merely an appropriate still-path direction, to achieve higher recovery.

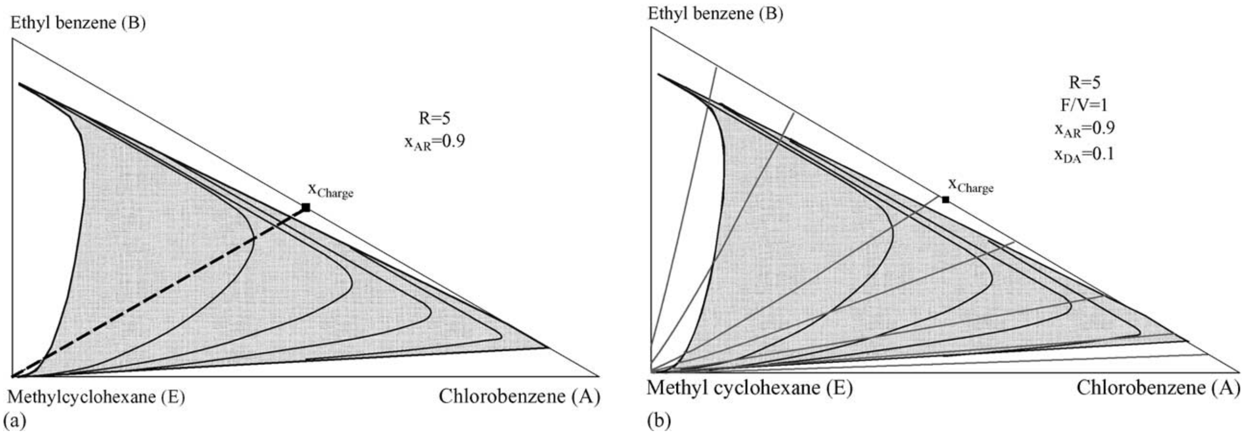


Fig. 9. (a) Rectifying profiles for the ethylbenzene/chlorobenzene/methyl cyclohexane system and (b) rectifying and extractive profiles for the ethylbenzene/chlorobenzene/methyl cyclohexane system.

Separation of an azeotropic mixture is feasible with either heavy, or intermediate boiling, or light entrainer. A low relative volatility mixture can be separated with a light entrainer or with a heavy entrainer, as well. If the applied entrainer is the heaviest component, or it is the intermediate boiling component separating minimum boiling azeotrope, then component A can be produced in pure form in the first production step. If the entrainer is the lightest component, or it is the intermediate boiling component separating maximum boiling azeotrope, then component A can be separated from component B only in a form of binary mixture with the entrainer. This phenomenon is in good accordance with the results of Laroche et al. [3]. They concluded that separation of minimum boiling azeotrope by continuous extractive distillation is feasible with a two-column arrangement. The separation is feasible with a direct split in the first column (producing distillate A) if the applied entrainer is the heaviest component. If the entrainer is the lightest component, the separation is feasible with an indirect split producing AE mixture as distillate in the first column. If the applied entrainer is the intermediate boiling component, the separation is feasible either with a direct split or with an indirect split. Batch distillation can be considered as the time analogue of the continuous multicolumn arrangement, as is also pointed out by Cheong and Barton [10].

The type of the first product (i.e. either nearly pure product or binary mixture) depends on the relative position of component E and the azeotropic composition in the bubble point ranking. If the boiling point of the entrainer is higher than that of the azeotrope, then production of pure A is feasible in the first production step. If the entrainer has a lower boiling point than the azeotrope, then only binary mixture can be withdrawn in the first production step. To ease the use of this rule, the bubble point ranking is also presented in each column of Table 2.

According to this property, the separation tasks can be classified into two groups on the ground of the operation steps shown in Table 2. The operation steps for separating low relative volatility mixture with heavy entrainer, not shown in Table 2, coincide with those cases at which the entrainer has lower boiling point than the azeotrope. The operation steps for separating low relative volatility mixture with light entrainer coincide with those cases at which the entrainer has higher boiling point than the azeotrope. Thus, the operation steps for the separation of low relative volatility mixtures can be discussed together with those shown in Table 2.

If the azeotropic composition is more volatile than the applied entrainer, then a so-called run-up step is needed after the heat-up step. In the run-up step, component A is purified in the top of the column. The most important effect of the run-up step is evolution of the appropriate extractive profile in the column. In these cases, the components can be withdrawn in the order of decreasing volatility, and the least volatile component remains in the still in pure form.

If the azeotropic composition is less volatile than the applied entrainer, then run-up step is not needed because the existence of an extractive profile is not a precondition to the feasible separation. But in these cases, premix of the entrainer is necessary before the heat-up step. The components are not recovered in the order of decreasing volatility because reload of the still with the product of the first cut (AE mixture) is necessary and, thus, the first pure product is the intermediate boiling component in these processes.

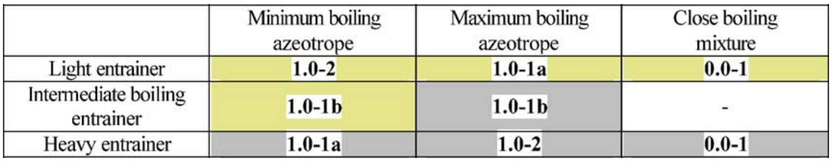
Comparing the results collected in Table 2 to the classification of mixtures according to Serafimov [27,28] as marked in Table 1, it turns out that Serafimov's classes cannot be utilized for predicting feasibility and the separation scheme. All the four groups (S: 0.0-1, S: 1.0-1a, S: 1.0-1b, and S: 1.0-2) of our studied mixtures occur in both significantly different triple columns of Table 2. This is also shown by different shadings in Table 3.

5.2. *Residue curves maps versus profiles maps*

According to the results summarised in Section 4, the operation steps of the feasible separation processes with finite reflux ratio can be determined using profiles maps, but use of RCMs seems satisfactory in some cases only. Considering feasibility with infinite reflux ratio and infinite number of stages is not sufficient to decide whether separation with finite values is feasible or not. Therefore, in addition to RCMs, profiles maps must also be calculated. Some figures containing all the azeotrope separation problems are collected in Figs. 10–13 with different conditions (*R*, *N*, SBD/BED).

Maps calculated with total reflux are collected in Figs. 10 and 11. Feasibility studies presented in the literature usually stop at this point. However, it is worth calculating some maps with finite reflux ratio, as well. These maps, calculated with finite reflux ratio, are collected in Figs. 12 and 13. It will turn out that, depending on the mixture type, the feasibility can change with switching between infinite and finite reflux ratio. Some separation processes seeming feasible with total reflux will prove infeasible at finite reflux ratio. Even

Table 3
Serafimov's classes against separation schemes shown by shading



	Minimum boiling azeotrope	Maximum boiling azeotrope	Close boiling mixture
Light entrainer	**1.0-2**	**1.0-1a**	**0.0-1**
Intermediate boiling entrainer	**1.0-1b**	**1.0-1b**	-
Heavy entrainer	**1.0-1a**	**1.0-2**	**0.0-1**

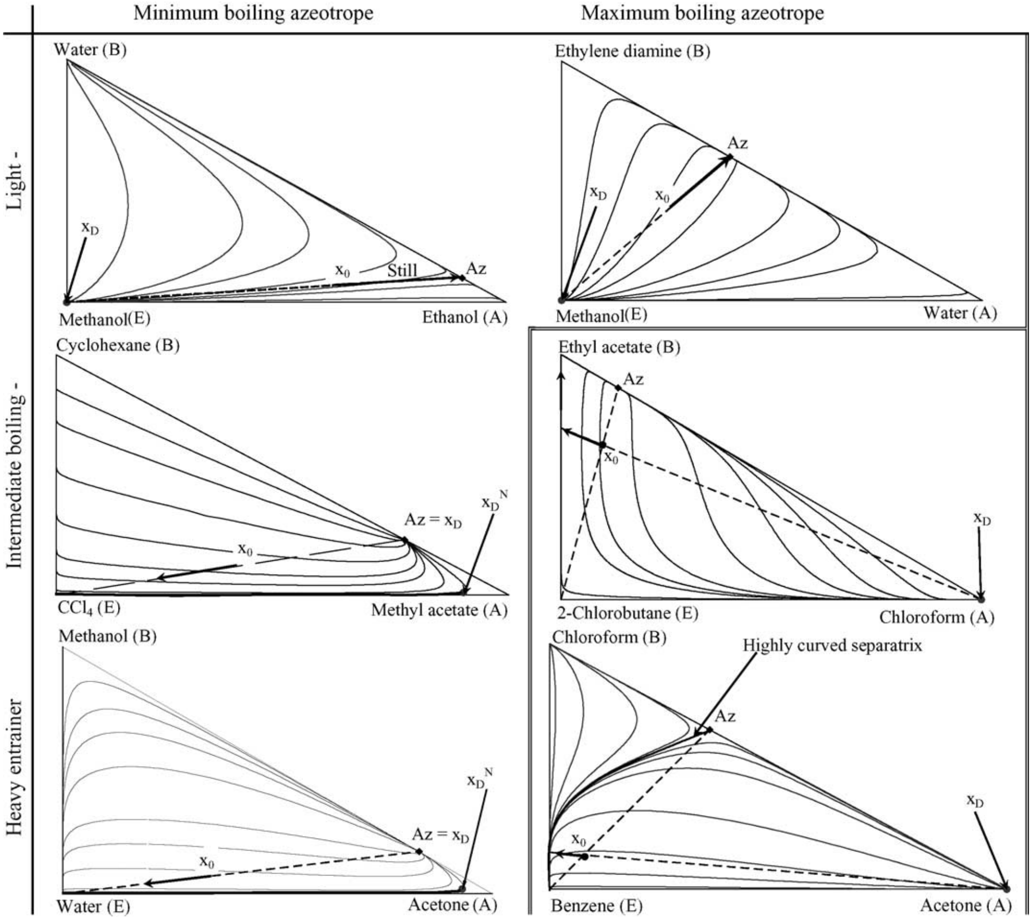


Fig. 10. RCMs (rectifying profiles with $R = \infty$) for studying feasibility of SBD, or that of BED with feeding to the still.

more important are the cases at which the separation process seems infeasible on the base of total reflux, but feasibility is recognized when the process is studied with finite reflux ratio.

5.2.1. *Analysis of the RCMs with $R = \infty$ ($D = 0$): SBD process and BED process with entrainer feeding into the still*

Fig. 10 shows the RCMs for the studied systems. The residue curves can be considered as rectifying profiles at total reflux ($R = \infty$, $D = 0$), and can be applied for studying the feasibility of SBD, or the feasibility of BED with feeding the entrainer to the still, both at total reflux and with infinite or finite number of stages. Concluding feasibility or infeasibility of the process is based on supposing very slow product removal, i.e. almost infinite reflux ratio, and assuming the same rectifying profiles map as obtained with total reflux.

The top composition is pure entrainer in case of applying light entrainer and infinite number of stages, irrespectively to whether minimum or maximum boiling azeotrope ought to be separated, and whether SBD process or BED process (with feeding to the still) is applied. The top composition is near the entrainer vertex even if finite number of stages is applied. After mixing some entrainer to the azeotropic charge, the product is pure or almost pure entrainer, and the still composition moves back toward the azeotropic composition. Thus, these processes seem infeasible.

The specified rectifying profiles are drawn by bold in the maps of minimum boiling azeotrope with intermediate boiling and with heavy entrainer. In both cases, application of finite number of stages would be necessary to produce the needed purity of the light product because azeotropic mixture is the top composition if infinite number of stages are available. Unfortunately, an unacceptable amount of entrainer ought to be mixed (in case of SBD) or premixed (in case of BED with feeding to the still) to the charge in order to obtain a still composition that would lie in the specified rectifying profile. If a smaller amount of entrainer is mixed to the charge, then the specified purity cannot be reached. Thus, these processes also seem infeasible.

Separation of maximum boiling azeotrope with intermediate boiling entrainer, and the same with heavy entrainer if the separatrix has a strong curvature, seem feasible according to the maps. The light component (i.e. A) is the top composition even if only a small amount of entrainer is mixed or premixed to the charge. In the case of intermediate boiling entrainer, removal of product A pushes the still composition toward the BE edge, and great recovery is expected. If the curvature of

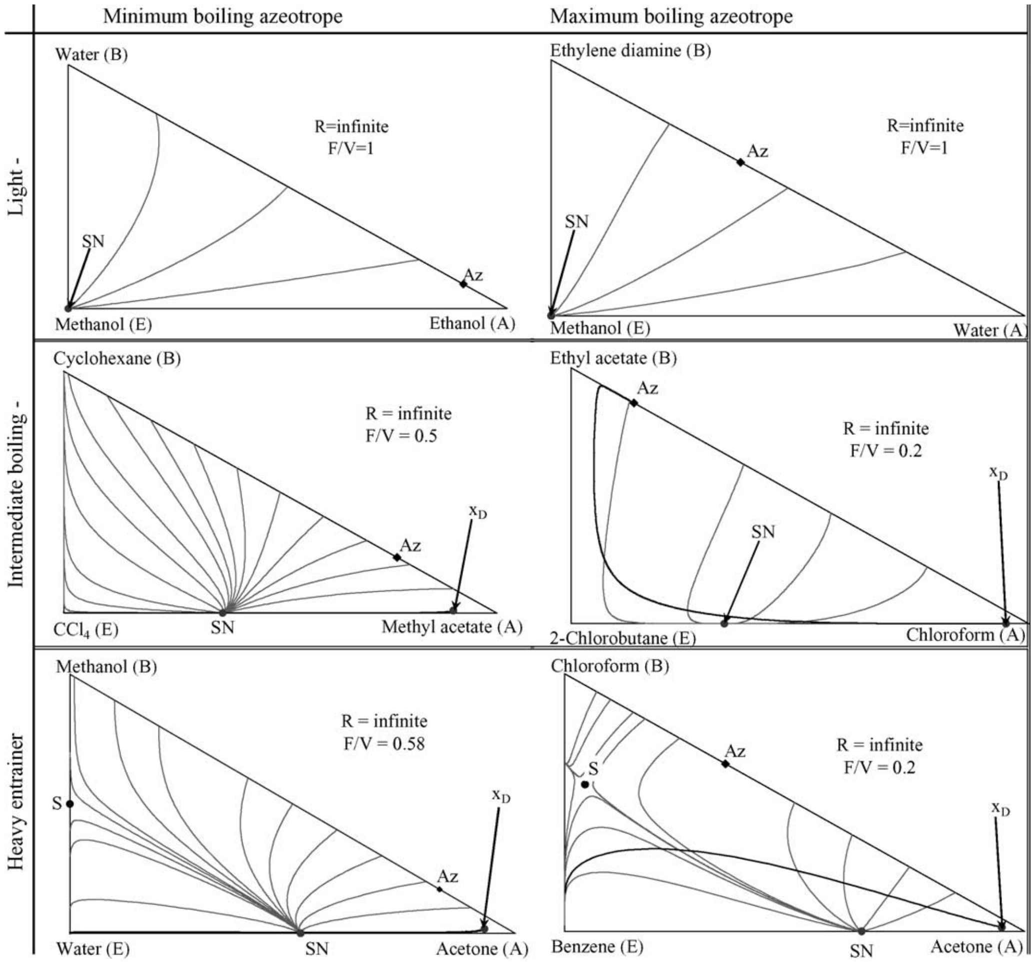


Fig. 11. Extractive profiles with $R = \infty$, used in studying feasibility of BED with feeding to the column.

the separatrix is great enough in the case of applying heavy entrainer, the still composition can be pulled so near to the entrainer vertex that the still path can well approach the BE edge, and great enough recovery is expected for the price of a greater entrainer premix. Note, however, that infinite number of stages seems to be an essential requirement for producing almost pure product in the case of intermediate boiling entrainer, because the length of the rectifying profile changes as the still composition is shifted toward the BE edge.

5.2.2. Analysis of the profiles maps with $R = \infty$ ($D = 0$): BED process with entrainer feeding into the column

The profiles maps shown in Fig. 11 can be used to study BED processes with feeding to the column, i.e. with extractive section. These maps are computed at total reflux ($R = \infty$, $D = 0$), and can be considered as (rough) approximations to the maps with finite (but high) reflux ratio.

Only the extractive profiles are shown in the upper two maps, i.e. in the cases of applying light entrainer. The corresponding rectifying profiles are shown in Fig. 10. The top product in these cases is always the entrainer, or a composition near the entrainer, even if extractive section is applied. Although rectifying profiles running near the AE edge exist, and one would expect producing binary AE product with a short enough rectifying section, these profiles can be reached by extractive profiles from a very narrow composition region only. Thus, the still composition cannot be shifted toward the BE edge, and the process is infeasible.

The extractive profiles maps are shown together with the specified rectifying profiles in all the other maps of Fig. 11. Almost pure product A can be produced in all these cases because the rectifying profile can be reached by extractive profiles from the majority of the compositions.

According to these maps, separation of minimum boiling azeotropes with heavy or intermediate boiling entrainer is predicted feasible with BED, whereas it was predicted infeasible with SBD. The rectifying profiles have a maximum length, i.e. the rectifying section can be characterized with a maximum number of stages; otherwise, the top product is the azeotrope.

The profiles maps regarding to the BED of maximum boiling azeotropes with heavy or intermediate boiling entrainer result in predicting feasibility, the same as with SBD. The specified rectifying profile can be reached by extractive profiles from the majority of the compositions. According to the map shown for the intermediate boiling entrainer, the still

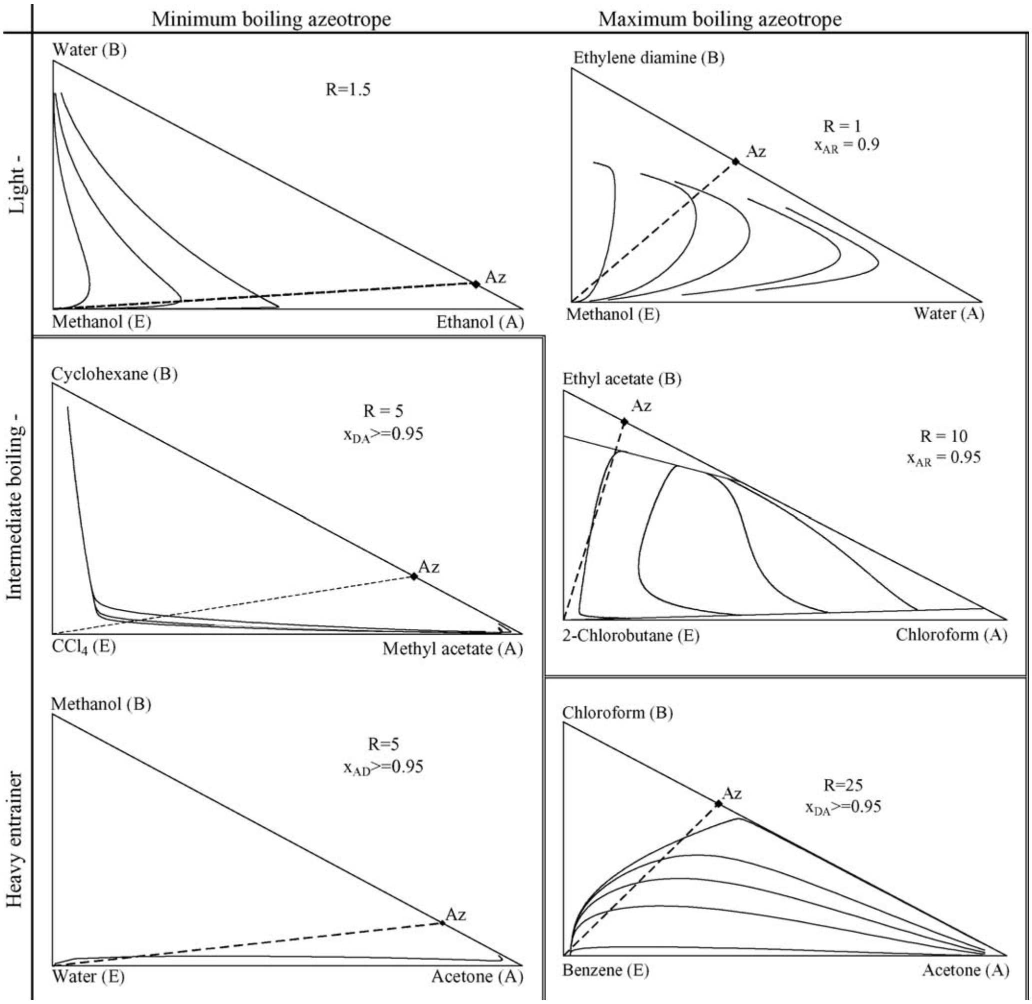


Fig. 12. Rectifying profiles with $R < \infty$ and feasibility regions for SBD, and for BED with feeding to the still.

path cannot be shifted near enough to the BE edge. However, different rectifying profiles may be applied during the separation, and a binary product with increasing amount of E (here: 2-chlorobutane) can be produced, and separated in a subsequent step.

5.2.3. *Analysis of profiles maps with $R < \infty$ ($D > 0$): SBD process and BED process with entrainer feeding into the still*

Fig. 12 collects the rectifying profiles maps with finite reflux ratio. These maps can be used for studying feasibility of SBD, or the feasibility of BED with feeding the entrainer to the still, at finite reflux ratio and with infinite or finite number of stages. This is a counterpart of Fig. 10, which shows the same cases with total reflux.

The rectifying profiles with appropriate finite reflux ratio cover a wide enough region in the interior of the composition triangle in the case of applying light entrainer to either minimum or maximum boiling azeotrope, and they cross the straight line section of mixing balance between the azeotrope and the entrainer. Thus, binary AE product, separable in a subsequent step, can be produced with SBD, until the still composition leaves the feasible region. In case of SBD, x_D and x_S are situated in the composition triangle in such a relative position that the still composition cannot be shifted toward the BE edge; it is shifted toward the AB edge; thus, reasonable recovery cannot be achieved. However, the specified purity can be maintained for a while, and the process is predicted to be feasible, contrary to what was predicted by using RCMs only.

If, on the other hand, entrainer is continuously fed to the still, then the still composition can be, with appropriately designed feed ratio, directed toward the BE edge, and the process becomes feasible with reasonable recovery.

The requirement of mixing unacceptable amount of entrainer to the charge, the conclusion on the base of RCMs in the cases of separating minimum boiling azeotropes with either heavy or intermediate boiling entrainer, is dropped according to the profiles maps. However, the region covered by the rectifying profiles, at an appropriate finite reflux ratio, that cross the mixing line and provides with pure enough distillate, is so narrow that the still path cannot move. Thus, these

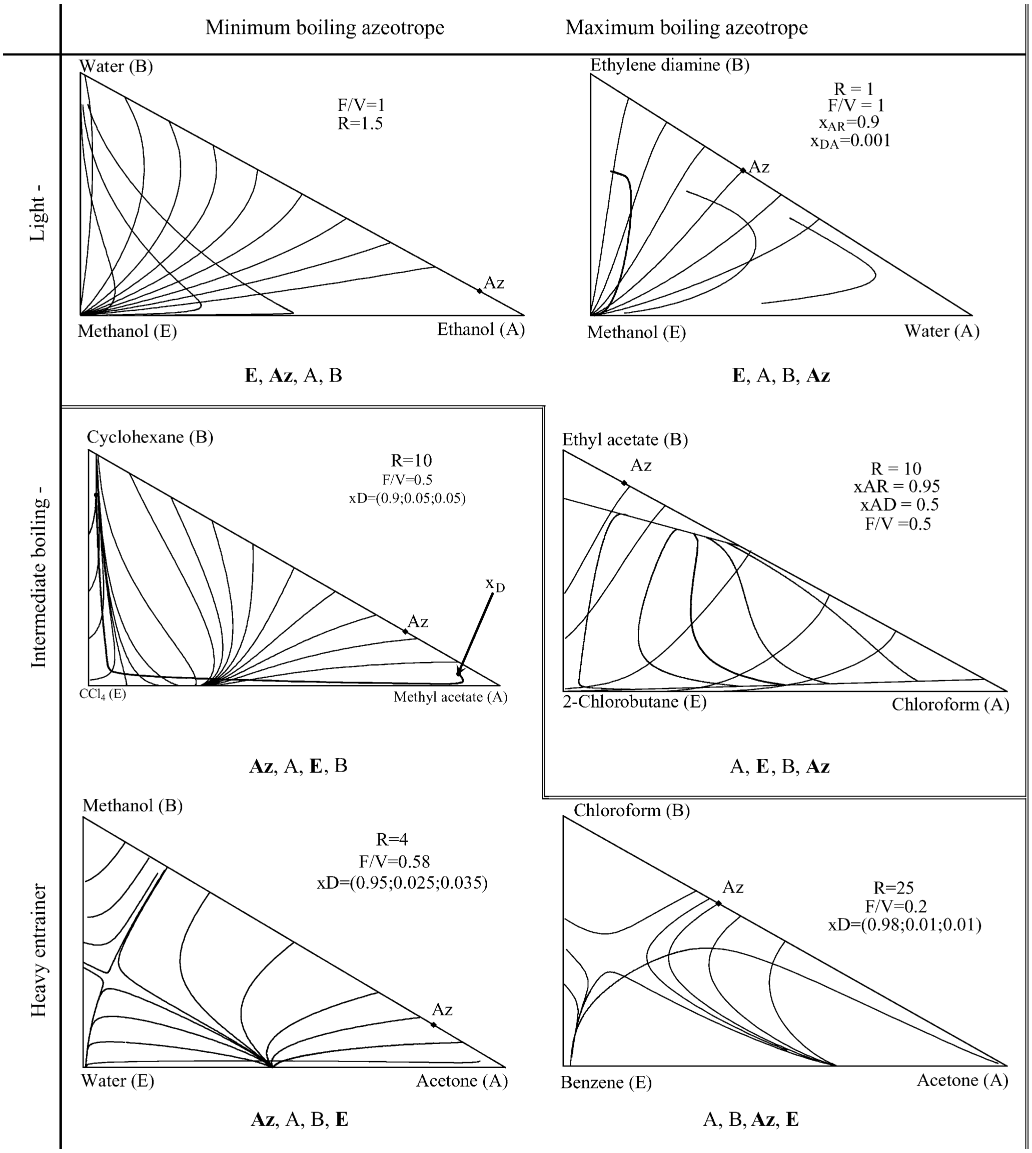


Fig. 13. Profiles maps with $R < \infty$, used in studying feasibility of BED with feeding to the column.

processes are predicted to be infeasible, just as predicted on the base of RCMs.

The feasibility of producing binary product with intermediate boiling entrainer, or almost pure product with heavy entrainer, from a maximum boiling azeotropic mixture with SBD process is maintained even by studying rectifying profiles maps with finite reflux, but the situation is not so promising as it would seem based on studying RCMs only. Almost perfect recovery was predicted by RCMs, whereas the still composition leaves the feasible region very soon in the cases of finite reflux, and the process is feasible with a low recovery ratio only.

5.2.4. Analysis of profiles maps with $R < \infty$ ($D > 0$): BED process with entrainer feeding into the column

The extractive profiles maps with finite reflux ratio, together with the specified rectifying profiles, are collected in Fig. 13. These maps can be used for studying feasibility of BED with feeding the entrainer to the column, i.e. with extractive section, at finite reflux ratio and with infinite or finite number of stages. This is a counterpart of Fig. 11, which shows the same cases with total reflux. Several rectifying profiles are shown in those cases where binary product is produced in the first step, instead of an almost pure one.

The most striking result of switching to finite from infinite reflux ratio is the predicted feasibility of BED processes with light entrainer, contrary to what was predicted with total reflux. Minimum boiling azeotropes can be separated, and the still path can be directed toward the upper part of the BE edge. Separation of maximum boiling azeotropes with light entrainer is not so easy, but is predicted feasible at least with some appreciable recovery.

The predicted feasibility of separating maximum boiling azeotrope with intermediate boiling entrainer is maintained even if the reflux ratio is finite. However, the predicted feasible operation steps are different. While production of almost pure component A is predicted on the base of total reflux, it is excluded according to the profiles maps constructed with finite reflux ratio. Binary AE mixture can be produced in the first step, instead.

Feasibility of the other three cases where almost pure product can be produced, predicted by the maps in Fig. 11 on the base of RCMs, is maintained but with some new restrictions due to applying finite reflux ratio. In all these three cases, some new boundary in the interior of the composition triangle prevents the still path from reaching the BE edge, and thus prevents the process from reaching almost total recovery. The new boundary is the specified rectifying profile itself in the case of separating minimum boiling azeotrope with intermediate boiling entrainer; it is a pair of unstable separatrices in the cases of applying heavy entrainer.

All the separation tasks are feasible if BED is applied with finite reflux ratio. The first product is nearly pure component A if the entrainer has higher bubble point than the azeotrope. The first product is a binary mixture if the entrainer has lower bubble point than the azeotrope (see the bubble point ranking in Fig. 13).

It is clear from the above comparison that application of profiles maps gives more reliable results for a real separation task than the use of RCMs. The benefit of the profiles maps is supported with rigorous simulation and with experimental results, as well.

5.3. *Limiting parameters*

If the task of the engineer is to design a BED process, the knowledge of feasibility or unfeasibility of the separation task is not enough; one needs also a set of information about the limiting parameters. It is an advantage of applying profiles maps that existence of different limiting parameters (N, R, F/V) can be predicted with it, and the appropriate range of some parameters (R, F/V) can even be estimated. In most cases, the expectations are supported with rigorous simulation. Table 4 contains the different limiting parameters together.

5.3.1. *Minimum values*

Reflux ratio and the number of stages in the rectifying section have, naturally, minimum, as is the case in any kind of multistage distillation processes.

Existence of some limiting parameter depends on the relative position of component E and of the azeotrope in the bubble point ranking. If extractive section is necessary for the feasible separation (i.e. when the entrainer is less volatile than the azeotrope), then this section has a minimum length (number of stages). If the separation is feasible without extractive section, then premixing of the entrainer is necessary and the premixed entrainer has a minimum amount.

The shape of the extractive profiles significantly depends on the ratio of entrainer feed rate to vapor rate (F/V). This ratio is a characteristic parameter of batch extractive distillation. The stable node of the extractive profiles moves from the most volatile composition to the feed composition (in our cases to the pure solvent) with increasing F/V (see Fig. 14).

If there is extractive section in the column, then a necessary condition to feasible separation is that the extractive profiles and the specified rectifying profile intersect. The separation is feasible with the given distillate specification if and only if the stable node of the extractive profiles lies on or beyond the rectifying profile started from the specified distillate composition.

Separation of minimum boiling azeotropes with heavy and intermediate boiling entrainers has a minimum F/V value. This is somewhere between 0.05 and 0.1 for the acetone/methanol/water system, and between 0.1 and 0.2 for the acetone/chloroform/benzene system. If a maximum boiling azeotrope is separated with intermediate boiling entrainer, then the separation is feasible with the condition $F/V > 0$. This behavior is noticed in Table 4 with a '+' sign.

The limiting value of the F/V ratio with $R < \infty$ differs from that with total reflux ($R = \infty$). Since the reflux ratio modifies the shape of the extractive profiles as well as that of the rectifying ones, the separation should be feasible even with a smaller F/V ratio if the reflux ratio is finite.

Table 4
Limiting parameters and boundaries of BED process variants

	Heavy entrainer		Intermediate entrainer		Light entrainer	
	Minimum[a]	Maximum[a]	Minimum[a]	Maximum[a]	Minimum[a]	Maximum[a]
R_{min}	y	y	y	y	y	y
$N_{min,rect}$	y	y	y	y	y	y
$N_{min,extr}$	y	y	y	n	n	n
$E_{premix,min}$	n	n	n	y	y	y
F/V_{min} (at $R = \infty$)	y	y	y	+	n	n
$N_{max,rect}$	y	n	y	n	y	y
Boundary	Separatrix of the extractive profiles		Specified rectification profile and the corresponding extractive profile	Envelope of the rectification profiles (this can be marginally extended by extractive profiles)		

Notation: n—no, there is not such a limit; y—yes, there is such a limit; +—the value must be greater than zero.

[a] Azeotrope.

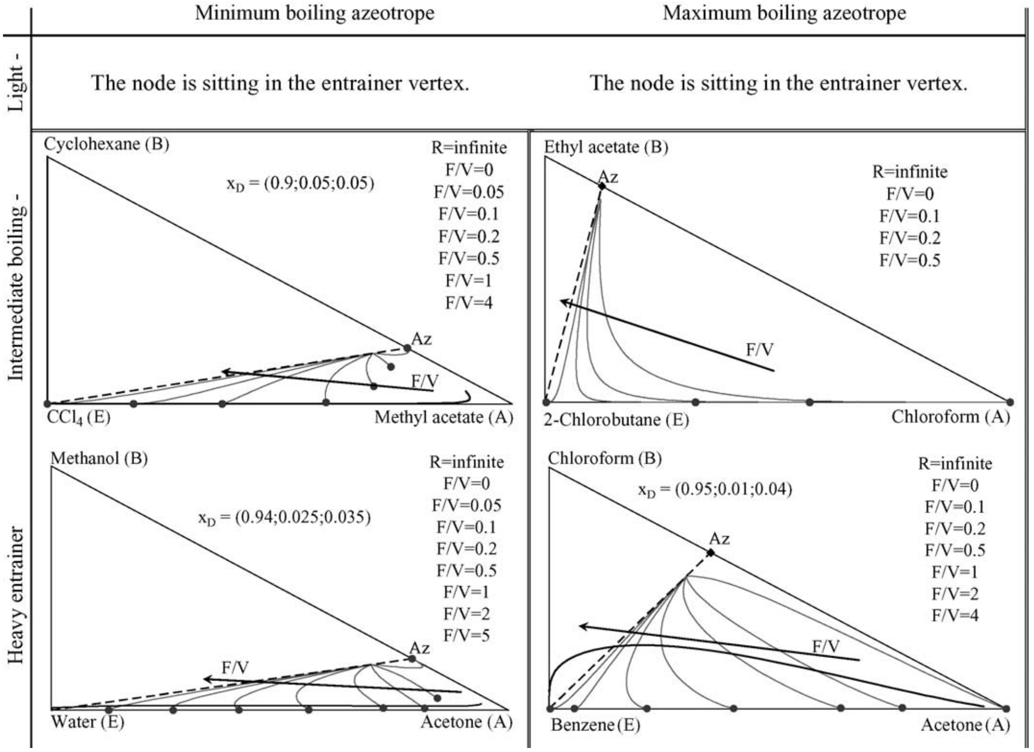


Fig. 14. Path of the stable node of the extractive profiles, with increasing *F*/*V* ratio.

5.3.2. *Maximum values*

Existence of maximum values to the parameters is independent of the existence of the minimum values.

The rectifying section has a maximum length (number of stages) if the unstable node of the rectifying profiles does not coincide with vertex A. This happens at separating minimum boiling azeotropes, or at separation tasks with light entrainer. The extractive section has a maximum length if the extractive profiles cross, and go beyond, the feasible region of rectifying profiles. This happens at separation tasks with light entrainer. The amount of premixed entrainer has a maximum value, in a way similar to the length of the extractive section, if the mixing line crosses, and goes beyond, the feasible region of rectifying profiles. This happens at separating maximum boiling azeotrope with light entrainer.

The reflux ratio has a maximum at separation tasks with light entrainer at separating either minimum or maximum boiling azeotrope (see also [16]).

5.4. *Boundaries*

Recovery ratio can be estimated from the shape and the extension of the feasible region, and from the still path (see Eq. (8)). Therefore, knowledge about the feasible region boundaries is important if the recovery ratio plays an important role, in addition to the product composition, during the separation.

The rules on the occurrence of limiting parameters can be summarised in strict rules collected in Table 4, and on the operation steps shown in Table 2. Similar, but not so strict, rules can also be concluded on the occurrence of feasible region boundaries, as well.

If the applied entrainer is more volatile than the azeotrope, the knowledge on the boundary of the feasible rectifying profiles is enough for a reliable estimation.

If the applied entrainer is less volatile than the azeotropic composition, then any of the two types of profiles (the rectifying or the extractive one) can serve as a boundary. As a general rule, that profile will be the boundary which runs nearer the edge opposite to the separated component and, at the same time, can provide with the specified distillate composition. In the cases of separation with heavy entrainer, the separatrices of the extractive profiles are the boundaries; in the case of separating minimum boiling azeotrope with intermediate boiling entrainer, the rectifying profile is the boundary (Fig. 13).

5.5. *Some other aspects in choosing the entrainer*

Application of BED is advantageous if the entrainer is less volatile than the azeotrope because pure product can be produced in the first step in this case.

However, the processes with more volatile (intermediate boiling or light) entrainer are also important, and can be preferable in some cases. For example, if an impurity is lighter than one of or both the azeotrope-forming components and, at the same time, it is an appropriate entrainer, then its use can be preferable to introducing a fourth, foreign, component. Use of a light entrainer is also preferable if the azeotrope-forming components are prone to degradation or to tar-formation at high temperature.

During the design of a batch separation process, the primary contaminant of the products can be an important aspect. Because of the batch characteristic, there is always a transient state between the different cuts during the separation (see, e.g. the history of the simulation runs for the separation of minimum boiling azeotrope with heavy (Fig. 2b) or intermediate boiling entrainer (Fig. 4b)). In the transient state, the composition of component A sharply decreases, whereas the composition of the second most volatile component (component B in Fig. 2b and the entrainer in Fig. 4b) sharply increases. The second most volatile component acts as impurity. If component B is allowed to contaminate product A, application of a heavy entrainer is appropriate. If component B is not allowed to contaminate product A, then application of a lighter entrainer is suggested; otherwise, the off-cut product (product of the transient state) must be recycled to another charge, which implies decrease in the efficiency of the separation.

6. Summary

Batch extractive distillation has come to the center of interest in the last decade; nevertheless, there is not any comprehensive article about the BED process. A systematic comparison was presented in this article about the separation tasks of azeotropic and close-boiling mixtures applying BED in rectifier. All the eight possible mixture types with at most a single azeotrope (minimum or maximum boiling azeotropes with heavy, light, or intermediate boiling entrainer, and close boiling mixtures with heavy or light entrainer) can be separated by applying BED in rectifier.

The main results of the feasibility studies and rigorous simulation runs on the hitherto unpublished cases – applying light entrainer for separating maximum boiling azeotropes and close boiling mixtures – were presented. Feasibility of separating minimum and maximum boiling azeotropes with intermediate boiling entrainer was experimentally verified.

Use of residue curves maps for predicting feasibility is not generally satisfactory, but profiles maps should be used instead. Use of profiles maps is preferable even if the feasibility can be predicted on the base of RCM, because application of BED with entrainer feeding to the column is usually preferable against SBD, and extractive profiles maps should then also be studied. Studying the $R = \infty$ case can be misleading, and should be treated with great care. The separation may be infeasible even if it is predicted to be feasible on the base of $R = \infty$ curves. Moreover, the separation may be feasible even if it is dropped according to the predicted infeasibility on the base of $R = \infty$ curves.

The operation steps of the feasible processes are determined by the relative position of the azeotropic composition and the entrainer in the bubble point ranking. If the entrainer has higher boiling point than the azeotropic composition, then production of pure component A is possible in one step; otherwise, the first cut gives a binary mixture of components A and E, and this binary product must be separated in a subsequent step. The main limiting parameters (F/V, N, E_{premix}) are also determined by the mentioned relative position; only the existence of maximum number of stages in the rectifying section is given by the type of the azeotrope.

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Appendix A. Nomenclature

D	distillate flow rate
E	entrainer
F	feed flow rate
h	height along the column
L	liquid flow rate
Q	heat duty
N	number of stages
R	reflux ratio
U	still hold-up
V	vapor flow rate
x	liquid composition
y	vapor composition calculated from the operating line
y^*	equilibrium vapor composition
z	feed composition
BED	batch extractive distillation
FR	feasible region
RCM	residue curves map
SBD	solvent-enhanced batch distillation

Greek letters

ξ	warped time
η	recovery of a specified component

Subscripts

A	component A
AR	reduced (entrainer-free) mole fraction of component A in the distillate
B	component B
Ch	charge
D	distillate
extr	extractive
max	maximal, maximum
min	minimal, minimum
premix	premixed
rect	rectifying
S	still
0	initial

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