Batch Extractive Distillation with Light Entrainer

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Use of a light entrainer in batch extractive distillation is justified when the mixture boils at a high temperature, or when an appropriate heavy or intermediate entrainer cannot be found. Feasibility of batch extractive distillation with light entrainer for separating minimum and maximum boiling azeotropes and close boiling mixtures is studied in this article. Our test mixtures are: ethanol/water (minimum boiling azeotrope) with methanol, water/ethylene diamine (maximum boiling azeotrope) with methanol, and chlorobenzene/ethylbenzene (close boiling mixture) with 4-methylheptane. Feasibility, operating steps, limiting entrainer flows, limiting reflux ratios, and limiting number of theoretical stages are determined by parametric study on profiles maps, and verified by rigorous simulation. The effects of reflux ratio, feed ratio, feed stage, number of stages, and thermodynamic state of the entrainer are also examined. It can be established, as a result, that processes separating either minimum or maximum boiling azeotropes, or close boiling mixtures, in batch extractive distillation using a light entrainer are feasible.

Key words:
Batch distillation, extractive distillation, azeotrope, light entrainer

Introduction

Separation of liquid mixtures into pure components is an important industrial task, involving both environmental and economical issues. Liquid mixtures are commonly separated with batch or continuous rectification. However, azeotropes cannot be separated in a simple rectification process. Separation of low relative volatility components is possible but difficult. Extractive distillation is an option for separating azeotropes and mixtures of low relative volatility components.[1,2] In this method an entrainer is fed continuously to the unit (either to the still, or to the column, or to the top) for enhancing the relative volatility of the mixture. Such an entrainer (E) is selected, that forms a single homogeneous liquid phase with the key components (the lighter component A and the heavier component B, to be separated), and does not form any new azeotrope with them. The entrainer is conventionally chosen as a high boiling ('heavy') component.[3,4,5,6] Application of a heavy entrainer is rather favourable; however, there are some cases when its use is not recommended, e.g. if heat sensitive, high boiling components are present. Fortunately, low boiling ('light') components[7,8,9] and even intermediate boiling ('middle') components can also be used.[10,11,12] Already *Laroche* et al.[8,9] pointed out that all three kinds of entrainer can serve well. In the present article we study the applicability of light entrainers.

The separation can be performed either in a continuous or in a batch process. The latter is usually the method-of-choice for separating small quantities of mixtures of varying compositions. In this paper the batch case is studied. The genuine batch process is practically not applicable, as will be shown, but a fed-batch process called batch extractive distillation is useful.

Besides the conventional batch rectifier, batch strippers[12,13] and middle vessel columns[8,14,15] have also been suggested and discussed in the literature. The separation in a middle vessel column can also be performed in a closed vessel operation cycle.[16]

Although it seems obvious that application of light entrainer is more favourable in batch stripper than in batch rectifier, here we confine ourselves to applying batch rectifier only. We have two essential reasons for this decision. First, the rectifier and its operation is well known and applied in the industry, whereas no industrial experience about designing and operating batch strippers is yet available. Second, our group has systematically performed the feasibility study of several variants of BED in rectifier.[17] Before we started studying the feasibility of

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[+] to whom the correspondence and proofs should be addressed the stripper variants, we had completed our research on applying the rectifier for BED with all the possible volatility combinations. We report our results to the research community in the present article.

Considering a batch rectifier unit, the following three cases can be distinguished (Figure 1). (1) Solvent-enhanced Batch Distillation (SBD, Figure 1a). In this case the entrainer is premixed to the charge in the still before distillation; this is a genuine batch process. All the subsequent cases are fed-batch, i.e. semi-batch or semi-continuous processes. (2) Batch Extractive Distillation with feeding to the Bottom of the column, or directly to the still (BED-B, Figure 1b). In this case the entrainer is continuously fed to the bottom part during the distillation. (3) Batch Extractive Distillation with feeding to an intermediate point of the column (BED, Figure 1c). This is the general BED process with an extractive section below the feed and an enriching (rectifying) section above it. One extreme of the feed location is just BED-B. The other extreme of the feed location is feeding to the top of the column; however, this is senseless if light entrainer is applied, because the entrainer would at once leave the column at the top without exerting its extractive effect.

The objective of this study was to analyse systematically the feasibility of applying light entrainer for separating binary mixtures, either in a batch process SBD, or in a fed-batch process BED.

Methodology

Feasibility study of the batch extractive processes is based on short-cut calculated column profiles, as introduced by *Lelkes*.[18–20]

Derivation of the differential equation (1) for calculating the extractive and rectifying profiles of BED is published by *Lelkes* et al.[18,19] Their model also includes a differential equation (2) for predicting the still-path.

$$\frac{\mathrm{d}x}{\mathrm{d}h} = \pm \frac{V_\mathrm{V}}{F_\mathrm{L}} (\boldsymbol{y} - \boldsymbol{y}^*) \tag{1}$$

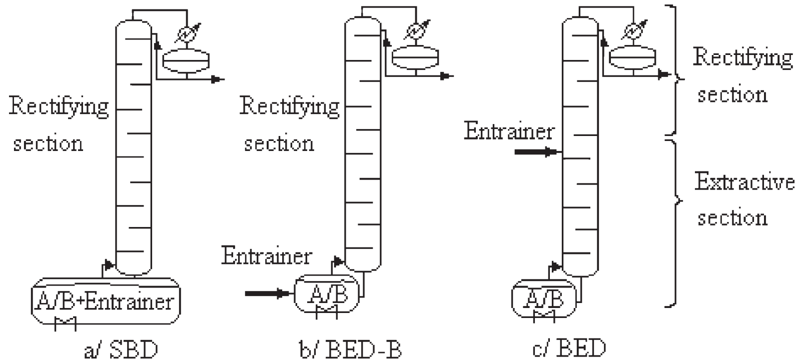


Fig. 1 – *a) – Solvent-enhanced Batch Distillation (SBD); b) Batch Extractive Distillation with feeding to the Bottom, or to the still (BED-B); c) General case of Batch Extractive Distillation (BED)*

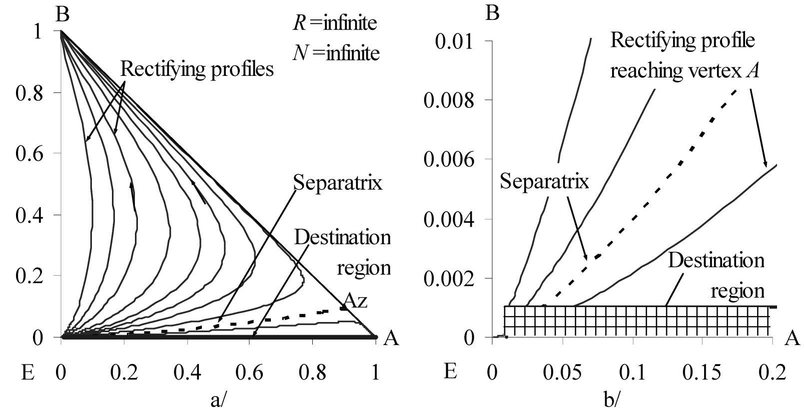


Fig. 2 – *Residue curves map (RCM) of the ethanol/water/methanol system*

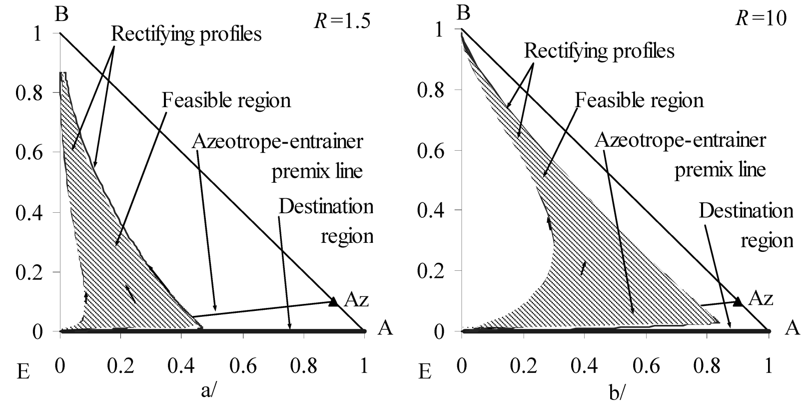


Fig. 3 – *Ethanol/water/methanol system: feasible regions for different reflux ratios: a) R = 1.5; b) R = 10*

$$\frac{\mathrm{d}(U\boldsymbol{x}_\mathrm{S})}{\mathrm{d}t} = F_\mathrm{z} \cdot \boldsymbol{x}_\mathrm{z} - F_\mathrm{D} \cdot \boldsymbol{x}_\mathrm{D} \tag{2}$$

Equations (1) and (2) 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 equation (1) 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 equation (1) is more similar to the differential equations applied in the component transfer and driving force models.

The differential equations (1) and (2) 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 equation (1) depends on the direction of the calculation; it is (–) for the rectifying, and (+) for the extractive profiles. The still path is determined by integrating equation (2).

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, $R = (F_V - F_D)/F_D$. Equation (3) describes the operating line in the rectifying section, and equation (4) in the extractive section, assuming boiling point feed state.

$$\boldsymbol{y} = \frac{(F_V - F_D)\cdot \boldsymbol{x} + F_D \cdot \boldsymbol{x}_D}{F_V} \tag{3}$$

$$\boldsymbol{y} = \frac{(F_V - F_D + F_F)\cdot \boldsymbol{x} - F \cdot \boldsymbol{x}_z + F_D \cdot \boldsymbol{x}_D}{F_V} \tag{4}$$

Equation (5) is an integrated form of equation (2) with constant F_F, F_D, x_Z, x_D. If the final still composition is known, the operating time can be determined with equation (5); equation (6) provides with the recovery ratio of component *A*.

$$\boldsymbol{x}_{S,\,\mathrm{final}} = \frac{U_0 \boldsymbol{x}_{S,0} - F_D \cdot \boldsymbol{x}_D \cdot t + F_F \cdot \boldsymbol{x}_z \cdot t}{U_0 - F_D \cdot t + F_F \cdot t} \tag{5}$$

$$\eta_A = 1 - \frac{(U_0 - F_D \cdot t + F_F \cdot t)\cdot \boldsymbol{x}_{S,\,\mathrm{final}}}{U_0 \cdot \boldsymbol{x}_{S,0,A}} \tag{6}$$

The appropriate operation steps (i.e. the separation sequence) of the feasible processes are also determined according to the short-cut calculated profiles maps. The still path, together with the effects of feed ratio and reflux ratio on the feasibility, is also examined with this tool. The results are verified by rigorous simulation, using ChemCAD® process simulator. The same tools are applied for studying the effect of various process parameters, such as reflux ratio (*R*), entrainer flow rate (F_F), feed location (N_F), and number of theoretical rectifying and extractive stages (N_R, N_E). All these parameters have some effect on product purity and operation time. Boiling liquid entrainer feed stream is considered all over this study, unless otherwise stated. In some cases, the effect of the thermodynamic state of the entrainer feed is also studied.

Feasible region is a central notion of the feasibility methodology; *destination region* is an auxiliary notion for analysing feasibility of SBD and BED with light entrainer. These notions are defined in this paragraph. In case of applying heavy entrainer, a single distillation composition may be specified because approximately pure component can be produced as a first main product. However, this is impossible when light entrainer is applied. Instead, a region of acceptable distillate compositions is specified; this is called '*destination region*'. Any composition is considered 'feasible still composition' if there is such a combination of process parameters (reflux ratio, and feed ratio in case of BED process) that an instantaneous column profile connects this composition to the destination region. The set of feasible still compositions is called '*feasible region*'. However, feasible region is also defined in a narrower sense in some cases. For example, we will speak about feasible region belonging to a given reflux ratio, and will analyse how feasible region changes with process parameters.

The direction of the computation of profiles is not indicated in every map. It is a characteristic feature of our feasibility methodology that rectifying profiles are computed by numerically solving an initial value problem started from a specified distillate composition $\mathbf{x}_D$; thus, the rectifying profiles are directed downward from the top of the column. The extractive profiles, on the other hand, are usually computed by solving another initial value problem started from a supposed still composition x_S; thus, the extractive profiles are directed upward from the bottom of the column. The reason of the upward computation is that usually a rectifying section is situated above the extractive one and, thus, the upper composition end of the extractive section is not known. The only exception is the case of a single extractive section (feeding entrainer to the top of the column), but its use is meaningless in case of applying light entrainer.

Both SBD (case 1) and BED-B (case 2) processes are characterised by having a single enriching (rectifying) section above the still, and not having extractive section. Thus, their feasibility can be studied together, by analysing merely the rectifying profiles. On the other hand, the map of possible extractive profiles is also to be taken into account in analysing the feasibility of the general BED process (case 3).

Separation of minimum boiling azeotropes

Our example is separation of ethanol (A) from water (B) with methanol (E). The model parameters are listed in the Appendix. The residue curve map (RCM) of this ternary system at atmospheric pressure is shown in Figure 2. Methanol (E) vertex is the lightest point in the system; all the curves start here. One bundle of curves arrives at water; another bundle arrives at ethanol; the two bundles are separated by a separatrix curve running from the methanol vertex to the azeotropic composition. Thus, the top composition in a rectifier column is attracted to methanol; the distillate will be rather dilute in methanol.

The charge to be separated is either of azeotropic composition (approximately 9:1 molar ratio of ethanol to water), or dilute ethanol in water; we want to produce pure ethanol at the end. This is possible if some ethanol – water mixture on the ethanol side is produced; this mixture product can be purified further by removing azeotrope.

The process makes sense if the ethanol to water ratio in the product is greater than 9:1. We specify a small maximum water content in the distillate, $x_{\mathrm{D,Water}} \leq 0.001$. For practical reasons, namely for considering the separation of methanol and dry ethanol in a subsequent step, a minimum ethanol concentration in the distillate is also specified; this is $x_{\mathrm{D,EtOH,min}} \geq 0.01$. These two specifications assign a narrow stripe along the ethanol – methanol edge, excluding the leftmost one percent of the edge; this is the destination region in the present separation problem.

Feasibility of systems without extractive section (SBD and BED-B)

Since the residue curves well approximate the rectifying profiles at total reflux and infinite number of stages, it follows from the map that both SBD and BED-B are infeasible at total reflux. However, the curvature of the rectifying profiles increases with decreasing reflux ratio, as is well known, and the profiles cross the separatrix (see, for example[21]). Thus, these processes may become feasible at finite reflux ratio.

Decreasing reflux ratio has also an additional effect on the rectifying profiles computed from a specified distillate composition. This is demonstrated in Figure 3. A profile started from distillate composition specified near the AE edge (i.e., near the binary ethanol – methanol mixture) turns sharply to run along the AB edge, and then turns again to fit to the BE edge. The profile section running along the AB edge gets farther from it at lower reflux ratio. In order to reach the destination region from the still by a rectifying section, some entrainer E should be pre-mixed to the charge in the still. The minimum premix ratio is determined by the reflux ratio, according to Figure 3. The smaller the reflux ratio is, the greater amount of entrainer should be premixed.

The process starts with premixing appropriate amount of entrainer to the charge in the still (step 1), and then warming up the column with total reflux (step 2). Production, i.e. removal of distillate, is started in step 3.

If the genuine batch process SBD is applied in step 3, then the still composition moves in a direction opposite to the composition of the distillate. Since $\boldsymbol{x}_{\mathrm{D}}$ is rather near the pure entrainer vertex, the still composition moves approximately along the straight line connecting the entrainer vertex to the charge (azeotropic) composition. Thus, the still composition moves approximately back along the premixing line. Consequently, the distillate composition also moves off the entrainer vertex, and in a direction off the region of specified purity, because the number of stages cannot be adjusted during distillation.

A simulation run with $N = 30$ theoretical stages (including the still) is shown in Figure 4. Other process data are: $R = 1.5$; $Q_{\mathrm{d}} = 1.5$ kW; $n_{\mathrm{ch}} = 200$ mol; $x_{\mathrm{ch}} = [0.2;\ 0.0222;\ 0.7778]$. The simulation was stopped when $\boldsymbol{x}_{\mathrm{D,Water}}$ increased above 0.001. The final operating time was 4.07 h. The product composition is $\boldsymbol{x}_{\mathrm{P}} = [0.049;\ 0.000124;\ 0.951]$ with an ethanol / water ratio 394. The still path moves approximately along the premixing line. The point of starting the removal of distillate is shown by an open circle on the still composition. Three column profiles, one at t_0, i.e. the time moment of starting the production, one $t_1 = 2.67$ h, and one at $t_2 = 3.78$ h, are shown. The path of the distillate composition is also shown in the figure. Since the distillate path leaves the destination region, no more than 13.5 % of ethanol can be recovered.

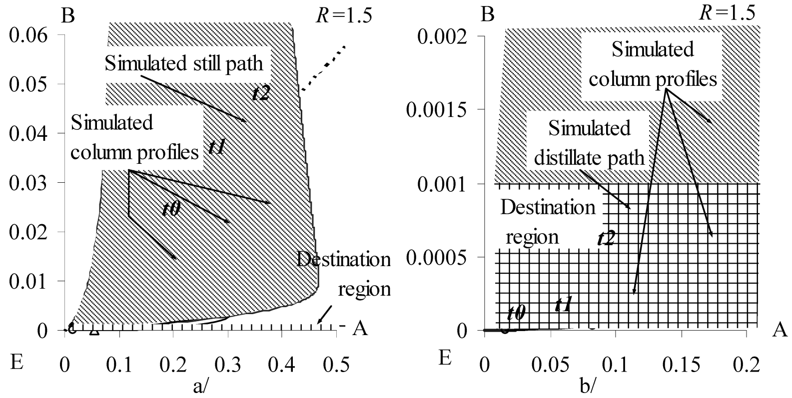


Fig. 4 – *Ethanol/water/methanol system. Separation of the azeotrope is feasible with SBD*

If the number of stages is increased, then the top composition can be kept inside the destination region when the still composition is far away from the entrainer vertex. In this case, however, the distillate contains too much entrainer at the beginning of the process.

Thus, SBD cannot be considered an appropriate alternative for this separation.

On the other hand, the still composition can be kept in the appropriate region if entrainer is continuously fed to the still, i.e. by applying the fed-batch process BED. This case had earlier been studied.[17,18–20] According to the methodology detailed there, the still path can be well estimated for a given feed to vapour ratio or, on the other hand, the appropriate feed ratio can be determined for a pre-specified still path.

Consider, for example, the feasible region at R=1.5, as is shown in Figure 5a. The charge in the still should be pre-mixed with an appropriate amount of entrainer in order to get inside the feasible region. Based on an appropriate premix ratio, and an estimated average distillate composition, feed ratio F_F/F_V = 0.306 provides us with a still path moving toward the BE edge (water – methanol edge), that remains in the feasible region over a long path section.

A simulation run with parameters N = 30, Q_d = 1.5 kW, R = 1.5, F_F = 48.96 mol h^{-1}, $\boldsymbol{x}_F$ = [0;0;1], n_{ch} = 200 mol, $\boldsymbol{x}_{ch}$ = [0.4; 0.0444; 0.5556] is performed to verify the short-cut theory. The simulated still path and three instantaneous column profiles, including the initial one, are shown in Figure 5a. The distillate composition history is shown in Figure 5b. The simulated still path is not straight, because the distillate composition is slightly shifted during the separation step. However, the still composition remains in the feasible region, and reaches the water – methanol edge, resulting in a good recovery ratio, namely η = 93 %, whereas the final product composition is $\boldsymbol{x}_P$ = [0.081; 0.000485; 0.9186], with an ethanol/water ratio of 167.

Thus, BED with feeding entrainer to the still (BED-B) is an appropriate process to separate minimum boiling azeotrope with light entrainer, although a great amount of entrainer should be applied in order to carry out the process.

The operating steps, according to the above considerations, are summarised in Table 1.

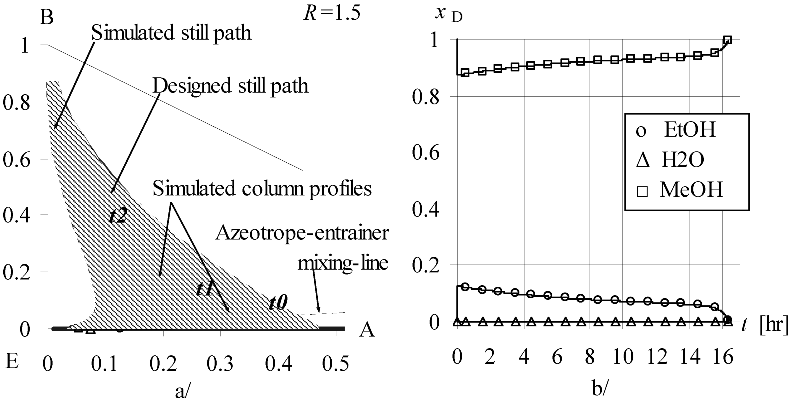


Fig. 5 – *Ethanol/water/methanol system, BED-B: a) still path; b) distillate history*

Table 1 – *Operating steps in case of BED-B process for separating minimum boiling azeotropes*

0	charging	A+B in
1	premixing with entrainer	E in
2	heat-up	$R = \infty$, $F_F = 0$
3	distillation of E+A	$R < \infty$ (low), $F_F > 0$
4	recovery of E from E/B	$R < \infty$, $F_F = 0$
5	change of the still content	B off, E/A in
6	recovery of E from E/A	$R < \infty$, $F_F = 0$
7	removal of pure A	A off

First, premixing the binary charge with methanol is necessary to get the still composition into the feasible region (step 1). Then, after heat-up (step 2), mixture of A and E is distilled out, while entrainer is continuously fed to the still (step 3). When the distillate composition cannot be maintained any more, feeding of E to the still is stopped, and pure E is distilled out in a conventional batch distillation process (step 4). At the end of this step, pure B remains in the still. Then the pure B as a product is removed from the still, and the still is filled with the distillate product of step 3 (step 5). Finally, in step 6, pure E is distilled out in a conventional batch process, and pure A remains in the still.

Feasibility of BED with extractive section

To analyse the feasibility of the general BED process, the extractive and the rectifying profiles should be considered simultaneously because both column sections exist. The rectifying profile computed from a specified distillate composition downward the column should meet the extractive profile computed from the actual still composition upward the column, with the same R, F_F/F_V, and x_D. (The specified $\boldsymbol{x}_D$ is an important parameter of the extractive profiles, as well.) In practice, a single rectifying profile is computed and compared to the extractive profiles map with the same parameters, as is shown in Figure 6. Those still compositions constitute the feasible region from which the extractive profile reaches or crosses the specified rectifying profile. This region is shaded in Figure 6.

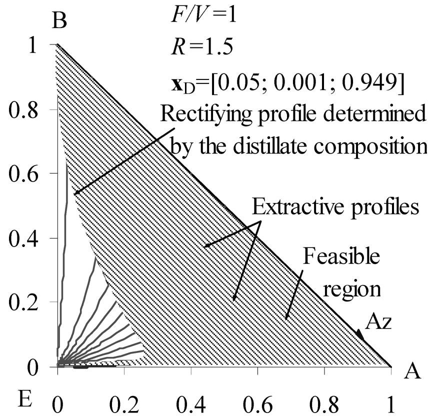


Fig. 6 – *Ethanol/water/methanol system. A map of a rectifying and extractive profiles*

To cope with the existence of a destination region instead of a single $\boldsymbol{x}_D$ composition, and to take into account the expected change of $\boldsymbol{x}_D$ during the production step, a series of extractive maps ought to be computed and taken into account. However, as our computation has demonstrated, a small change of $\boldsymbol{x}_D$ along the AE edge does not seriously alter the shape of the extractive profiles, as is shown in Figure 7a for a high feed ratio. A series of extractive profiles valid at two, slightly different, distillate compositions, are shown in this figure. Separatrices appear in the map at low feed ratios, as is shown in Figure 7b. We suspect that the entrainer's effect on the profile is not high enough at low feed ratio, and this is why the map is similar to the residue curves map shown in Figure 2a. The exact reason of why these separatrices occur is not known; but such low reflux ratio will be avoided for practical reasons.

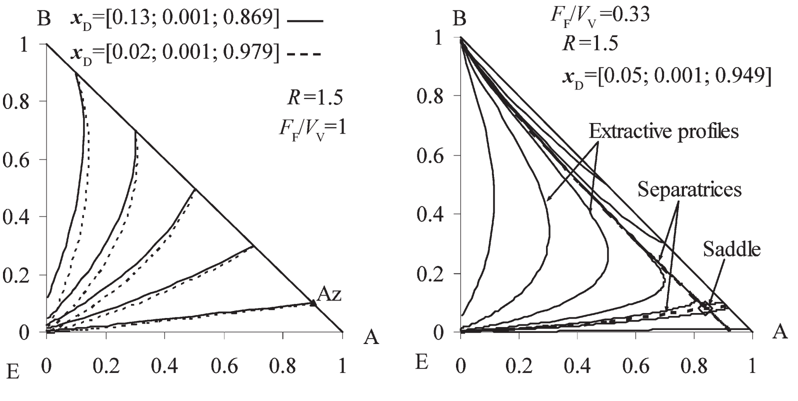


Fig. 7 – *Ethanol/water/methanol system; effect of $\boldsymbol{x}_D$ on the extractive profiles map: a) high F_F/F_V; b) low F_F/F_V*

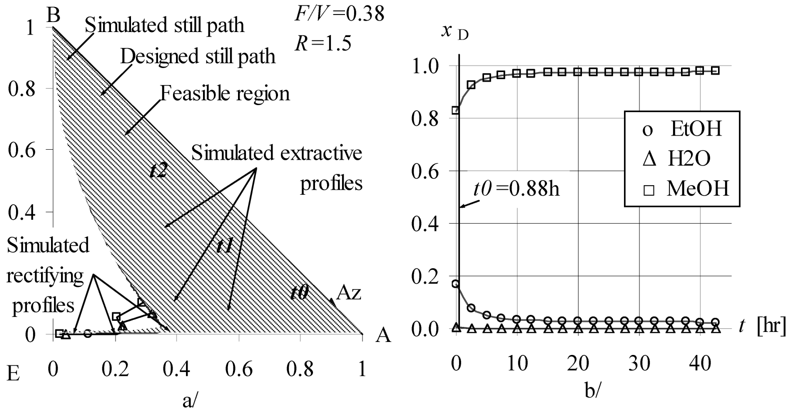
Since the feasible region reaches the AB edge at high enough feed ratio, theoretically no entrainer pre-mixing to the charge is needed. However, because the top composition is attracted by vertex E, some entrainer is suggested to be premixed to the charge instead of slowly pumping in during a run-up period. Thus, the steps shown in Table 2 are recommended for this separation process.

Table 2 – *Operating steps in case of the general BED process for separating minimum boiling azeotropes*

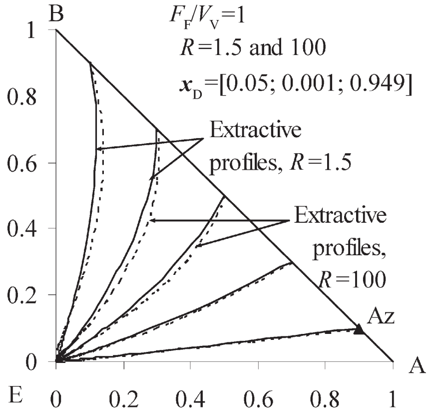
0	charging	A+B in
1	small amount premix	+E small
2	heat-up	$R = \infty$, $F_F = 0$
3	production of A+E	$R < \infty$, $F_F > 0$
4	recovery of E from E/B	$R < \infty$, $F_F = 0$
5	change of the still content	B off, A+E in
6	recovery of E from E/A	$R < \infty$, $F_F = 0$
7	removal of pure A	A off

To check the validity of step 3, the production step, a still path that runs along and near the AB (ethanol – water) edge of the triangle, was designed with R = 1.5 and $\boldsymbol{x}_D$ = [0.08;0.001; 0.919]. We governed the still path near the AB edge in order to apply as small amount of entrainer as possible. Such a still path can be designed with feed ratio F_F/F_V = 0.38; thus, this feed ratio was selected. Simulation was then performed with the following quantities: N = 30, N_F = 26, Q_d = 1.5 kW, R = 1.5, F_F = 58.9 mol h^{-1}, $\boldsymbol{x}_F$ = [0;0;1], n_{ch} = 100 mol, x_{ch} = [0.9; 0.1; 0]. Note, that no entrainer premix is applied in this particular run. Both, the designed and the simulated still paths are shown in Figure 8a.

The feasible region is also shaded in this figure. The distillate composition history is shown in Figure 8b. Three column profiles, one at t_0, one denoted by triangles at t_1 = 30.1 *h*, and one denoted by squares at t_2 = 39.13 *h*, are shown in the figure. Product composition $\boldsymbol{x}_P$ = [0.0814; 0.00035; 0.9182] can be reached with ethanol/water ratio of 230, and 14.5 % of ethanol recovery, if the production step is finished at t =



F i g . 8 – *Ethanol/water/methanol system; general BED: a) still path; b) distillate history*



F i g . 9 – *Ethanol/water/methanol system. Effect of the reflux ratio on the extractive profiles map. Solid lines: R = 1.5; dashed lines: R = 100.*

3.52 h, including the 0.88 h run-up period during which the distillate was not pure enough. Greater recovery can be achieved with smaller water fraction in the product if longer production period is acceptable. For example, η = 69.9 % recovery, $\boldsymbol{x}_P$ = [0.03533; 0.00005; 0.96462], and 679 ethanol / water ratio can be achieved with t_1 = 30.1 h; and $\boldsymbol{\eta}$ = 85.1 % recovery, $\boldsymbol{x}_P$ = [0.03287; 0.00004; 0.96708], and 821 ethanol/water ratio can be achieved with t_2 = 39.13 h. As is well seen in the figure, the simulated path deviates from the designed one. This is mainly due to the time needed for the entrainer to accumulate in the column for achieving the destination region with $\boldsymbol{x}_D$. Premixing some entrainer is useful because it decreases both the process time and the amount of the off-cut.

Thus, the general BED with feeding entrainer to an intermediate point of the column is also an appropriate process to separate minimum boiling azeotrope with light entrainer.

Concluding analysis on the basis of short-cut study

SBD is practically infeasible, but BED is a feasible process for separating minimum boiling azeotrope with light entrainer. Whether the entrainer is to be continuously fed to the still (BED-B) or to a higher point in the column (general BED), cannot be decided without performing a parametric study.

Effect of the reflux ratio on the rectifying profiles had been studied earlier.[18–20] The shape of the calculated rectifying profiles does not guarantee an appropriate distillate product at high R, whereas the destination region can be reached by decreasing R. Effect of R on the extractive profiles map can be neglected. We have found only a small difference in the curvature of the extractive profiles between R = 1.5 and R = 100, see Figure 9.

Effects of the feed flow rate and of the heat duty are combined in the parameter feed ratio F_F/F_V. There is a saddle point of the extractive profiles at low feed ratio, as is clear from the curves shown in Figure 7b. The separatrix connecting vertex B to this saddle point is a border of the feasible region. This separatrix gets closer to the AB edge with a higher feed ratio, and disappears at about $F_F/F_V \approx 0.4$ in our example. At and above this value, all the extractive profiles starting from the ethanol/water edge reach and cross the rectifying profile. Premixing of the entrainer is, in principle, not needed above this feed ratio.

At high feed ratio more entrainer is carried into the system with the feed than carried out of it with the distillate. The excess accumulates in the still. Capacity of the still, or an upper limit of the entrainer concentration in the still, may imply a practical upper limit on the feed ratio.

As is clear from Figures 6 and 8, the number of extractive stages has a maximum, over which the fraction on the feed stage is behind the left hand (lower) side of the feasible region. No minimum number of extractive stages exists. Extractive section is not needed; BED-B can be applied as is shown above, but premixing of entrainer to the charge is necessary in that case.[20]

Both minimum and maximum number of rectifying stages exist for meeting the product purity specifications. If the rectifying section is too long, the distillate is too concentrated in entrainer (methanol).

Parametric study with rigorous simulation

Rigorous parametric study, for exploring the effect of process parameters R, F_F/F_V, N_R, and N_E, as well as the enthalpy state of the feed, is performed simultaneously for the general BED arrangement and its limit case BED-B. In order to make the various simulation results comparable, recovery of 85 mol (94.4 %) ethanol was considered in all the simulation runs. Operation time (t) till the end of step 3, and the achieved separation purity (both ethanol mole fraction and the ethanol to water ratio), are monitored and compared.

As a basis of comparison, the parameter set selected for this case is: N = 34, N_E = 2, 4.5 cm^3 hold-up on each theoretical stage, n_{ch} = 100 mol, Q_d = 1.5 kW, $\boldsymbol{x}_{ch}$ = [0.9; 0.1; 0], $\boldsymbol{x}_F$ = [0;0;1], F_F = 45 mol h^{-1}, R = 2, 22.5 mol of entrainer premix, 0.7 h duration of the preliminary steps, before product removal is started. This is applied because N, N_E, R, and F_F/F_V are approximately optimal around this set of parameters. Sometimes, however, different specified parameters are applied in order to enhance the effect of the varied parameter. Characteristic results are shown in the following charts.

The effect of reflux ratio R is shown in Figure 10. Operation time increases with R, as is evident at constant heat duty. Mole fraction of water in the accumulated product decreases with a higher slope than that of ethanol, as R increases; thus, the ethanol to water ratio increases with R.

The effect of entrainer ratio F_F/F_V is shown in Figure 11. As is expected, a greater feed ratio involves a greater mole fraction of the entrainer in the stages and, by turn, implies an enhanced separation that can be felt in a greater ethanol to water ratio in the product. On the other hand, the more entrainer pumped to the column, more of it accumulates in the distillate; thus, the ethanol mole fraction decreases with F_F/F_V. The same effect implies a slower production of ethanol; that is why operation time increases with the feed ratio.

The effect of the number of rectifying stages N_R is shown in Figure 12, while N_E is kept constant, with N_E = 4. The more rectifying stages are used, the purer product is obtained, as is expected. Both ethanol and water mole fractions change in a favourable way with N_R. The operation time slightly decreases, because ethanol becomes more concentrated in the distillate stream with increasing N_R.

The effect of the number of extractive stages N_E is shown in Figure 13, while N_R is kept constant, with N_R=50. Ethanol mole fraction in the product does not change sensibly with N_E. If only a few extractive stages are applied, the water mole fraction decreases (with a consequential increase of the entrainer mole fraction) in the distillate, implying a sharp increase in the ethanol to water ratio. With more extractive stages, however, this effect turns

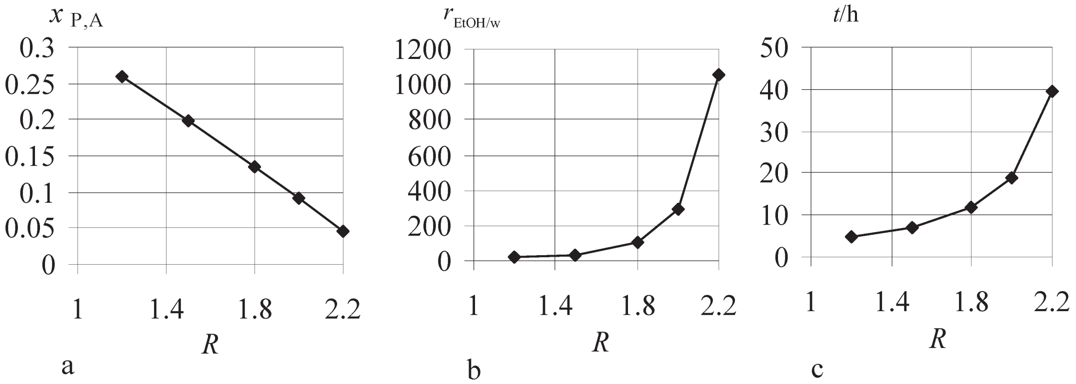


Fig. 10 – *Ethanol/water/methanol system. Effect of the reflux ratio R on: a) mole fraction of ethanol; b) ethanol/water mole ratio; c) operation time.*

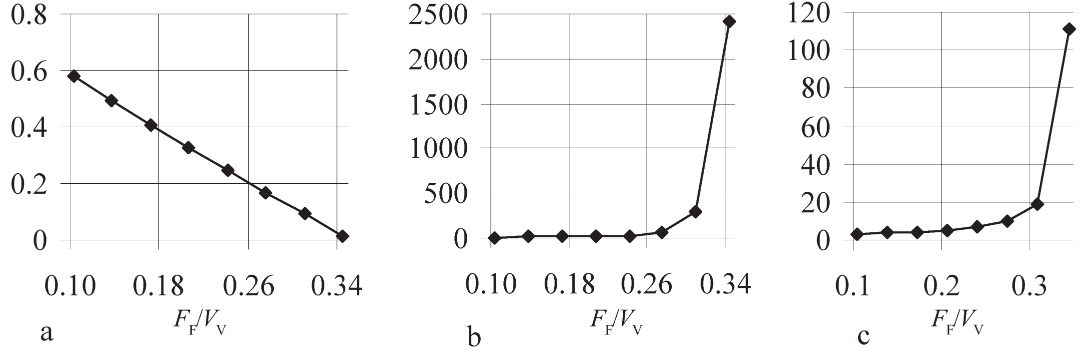


Fig. 11 – *Ethanol/water/methanol system. Effect of the entrainer ratio F_F/F_V on: a) mole fraction of ethanol; b) ethanol/water mole ratio; c) operation time.*

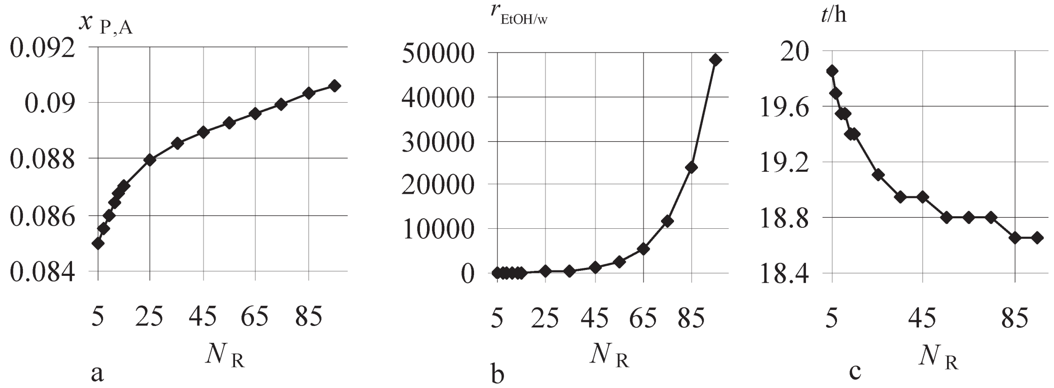


Fig. 12 – *Ethanol/water/methanol system. Effect of the number of rectifying stages N_R on: a) mole fraction of ethanol; b) ethanol/water mole ratio; c) operation time.*

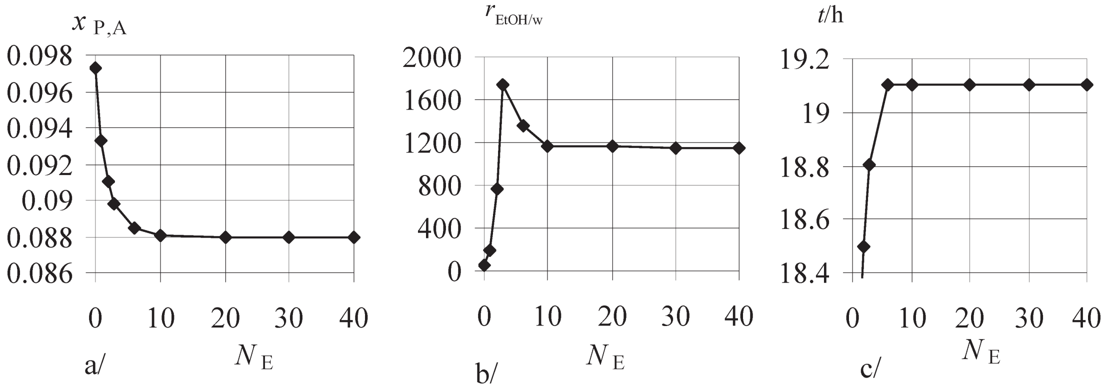


Fig. 13 – *Ethanol/water/methanol system. Effect of the number of extractive stages N_E on: a) mole fraction of ethanol; b) ethanol/water mole ratio; c) operation time.*

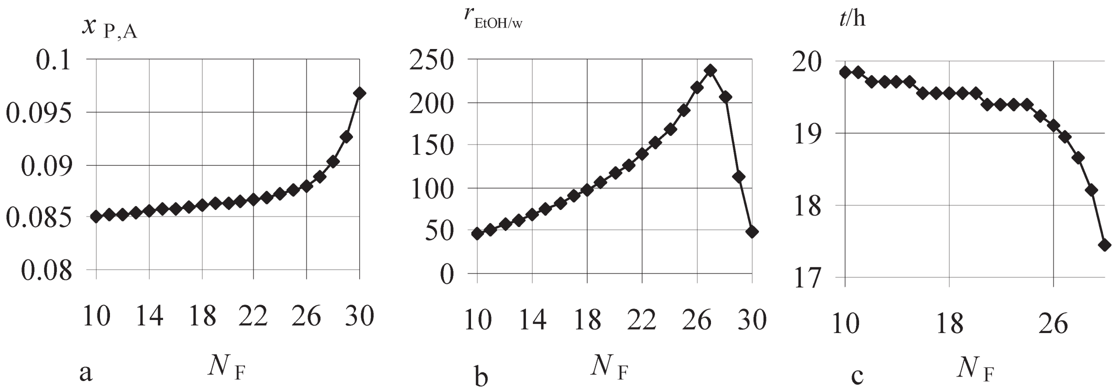


Fig. 14 – *Ethanol/water/methanol system. Effect of the feed location N_F on: a) mole fraction of ethanol; b) ethanol/water mole ratio; c) operation time.*

back a little at first, and then stagnation can be observed in both purity and operation time because the light entrainer simply does not reach down the still from the feed stage, a high point of the column. Thus, the entrainer exerts its effect on a limited number of stages counted down from the feed stage, irrespectively of how many more stages are there below.

Effect of the feed location N_F is shown in Figure 14, while the total number of stages N is kept constant with $N = 29$. (Both column sections are complementary adjusted in this part of the study.) While ethanol fraction slightly increases as the feed stage gets closer to the still (i.e. as N_F is increased), the water mole fraction goes through a minimum at about 2 or 3 stages above the still. The ethanol to water ratio has a maximum at the same value. Operation time has a monotonic decrease in function of N_F because the lower the entrainer is fed to the column, the less of it gets into the top vapour and the distillate stream. Thus, although BED is feasible with or without extractive section, applying 1 to 3 extractive stages may be preferable.

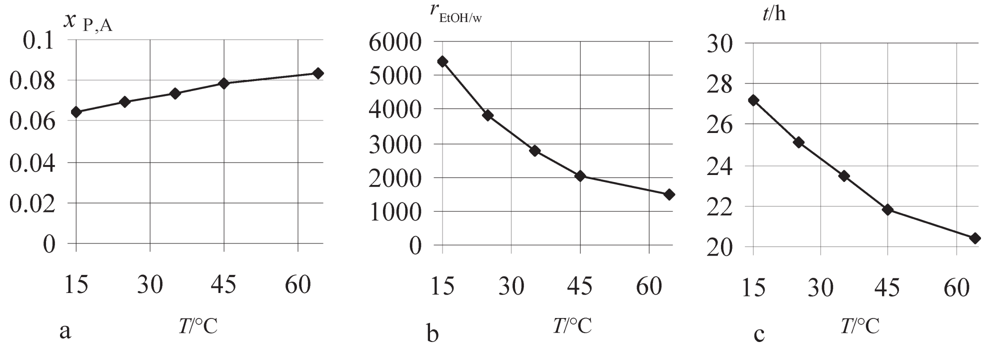


Fig. 15 – *Ethanol/water/methanol system. Effect of the entrainer feed temperature T on: a) mole fraction of ethanol; b) ethanol/water mole ratio; c) operation time.*

Applying cold (subcooled) entrainer instead of feeding it at boiling point is expected to have the effect of enhanced retaining of the entrainer in the column. Therefore, this option is also studied. The effect of feed temperature T is shown in Figure 15, with constant heat duty, and with $N_E = 30$. Lower feed temperature goes with better separation, less water in the product, as is expected. From the viewpoint of product purity, it is worth using subcooled entrainer. On the other hand, operation time increases because a part of the heat duty is consumed for boiling up the entrainer.

Conclusion on SBD and BED of minimum boiling azeotropes with light entrainer

Light entrainer can be successfully applied to separate minimum boiling azeotrope charge in a batch rectifier unit if the entrainer is continuously fed either to the still (to the bottom of the column), or to an intermediate point of the column, a few stages above the still. SDB (a batch process with premixing only, without continuous feeding) is practically useless because of the too small recovery ratio.

As small reflux ratio as possible should be preliminary selected, because operation time increases sharply with R. On the other hand, the ethanol to water ratio in the product of step 3 increases with R; thus, in principle, R ought to be determined according to economic optimization. However, the optimal R is expected to be small.

Design of the BED-B and the general BED processes are slightly different. Once R is fixed, the necessary premix for BED-B is determined according to the feasible region *without extractive profiles* at the given reflux ratio (see Figures 3 and 5a). On the other hand, the premixing ratio in case of the general BED process (feeding to an intermediate point of the column) is rather determined according to the expected hold-up of the column, and the expected liquid composition profile, because the feasible region extends to the AB edge (see Figure 8a).

In either case, once the composition in the still after premixing is known, an expected final still composition is to be specified by the designer. This should be a point on the BE edge (B – E mixture, free of A). This specification assigns an imaginary straight still path from the starting still composition to the expected final still composition, as is shown in Figure 8a. Appropriate feed ratio F_F/F_V can be determined according to material balance because R, together with a constant vapour flow rate, assigns a known distillate flow rate F_D. If entrainer is fed to a stage higher than the still, i.e. when extractive section exists in the column, the feed ratio determined in this way may need to be corrected, because a saddle point and a separatrix appear in the map at low feed ratio (see Figure 7b). This separatrix is shifted toward the AB edge, and out of the triangle, with higher F_F/F_V. Higher feed ratio will involve the expected final still composition becoming richer in E and poorer in B.

The simulated still path will, most probably, deviate from the above straight line; however, it will be sensible.

Since the optimal feed location is either the still (the bottom of the column) or a few stages above, it is expedient to start the design with BED-B, and then gradually increase the feed stage to find the optimal configuration.

Separation of maximum boiling azeotropes

Separation of maximum boiling azeotropes in batch extractive distillation with a light entrainer, according to our knowledge, has not been published yet. There are several well-known mixtures forming maximum boiling azeotropes, that are found in the chemical industry, such as methanol/toluene, pyridine/phenol or water/ethylene diamine.

Our example is separation of water from ethylene diamine (EDA), using methanol (MeOH) as a light entrainer. The model parameters are listed in the Appendix.

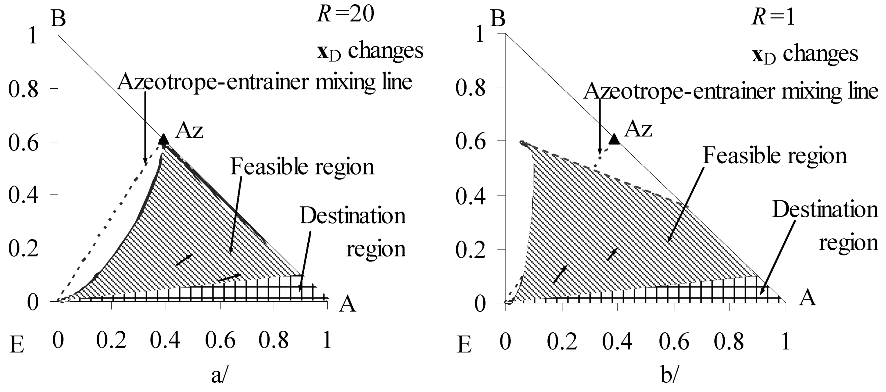


Fig. 17 – *Water/ethylene diamine/methanol system. Feasible regions at different reflux ratios: a) R = 20; b) R = 1.*

The residue curves map was calculated first, in order to approximate the rectifying profiles at total reflux, and is shown in Figure 16. Both key component vertices are saddle points; the entrainer vertex is an unstable node; the azeotropic point is a stable node of the residue curves. The entrainer is an attractor of the column's top composition; none of the key components can be obtained in high purity, free of the entrainer. Consequently, a maximum entrainer fraction in the product, 99 %, is specified. The minimum separation ratio of water/ethylene diamine in the distillate is specified as 9 to 1. (The azeotropic ratio is 0.645.) The above two specifications assign a destination region with a shape of a truncated triangle along the AE edge (water – methanol edge), as is also shown in Figure 16.

Feasibility of systems without extractive section (SBD and BED-B)

If the entrainer is premixed to the still or is fed continuously to the still, a single rectifying section exists in the column. In that case, only the rectifying profiles map needs to be analysed.

According to the map shown in Figure 16, separation of the azeotropic mixture is not feasible in case of total reflux, because none of the rectifying profiles, starting from the destination region, reaches the mixing line.

The feasible region extends approximately to half of the triangle at high R, as is shown in Figure 16 and Figure 17a. The feasible region does not reach the azeotropic composition. We cannot get in the feasible region from the azeotrope even by premixing, because the mixing line lies to the left of the leftmost feasible rectifying profile.

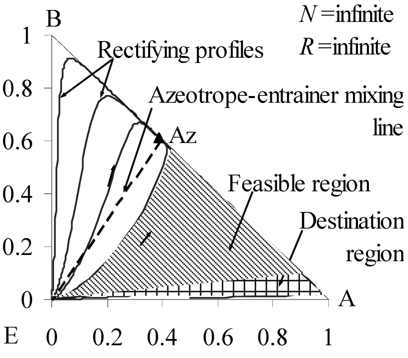


Fig. 16 – *Residue curves map (RCM) of the water/ethylene diamine/methanol system*

The line of pinch points runs very near the AB (water/ethylene diamine) edge in this case, so much that it is difficult to see the difference. This situation changes a lot with lower reflux ratios, as is shown in Figure 17b. The profiles have greater curvature, with two consequences. First, the leftmost profiles cross the mixing line; thus, the feasible region becomes reachable by premixing. Second, the line of the pinch points in this case comes to the very inside of the triangle. If follows that that there is a maximum reflux ratio above which the separation is infeasible with premixing. In our case its value is approximately $R \approx 10$.

A minimum reflux ratio $R_{\min}$ theoretically exists, as well; it is that value at which the rectifying profiles become too short, and they do not reach the premix line. $R_{\min}$ in our case is below 0.005; thus, we neglect its existence in the following analysis.

The operation steps, assigned according to Figure 17, are listed in Table 3 for both SBD and BED-B processes. Both processes start (step 1) with premixing appropriate amount of entrainer to the charge in order to get the still composition in the feasible region. This is followed by a heat-up step (step 2) with total reflux and no feeding, resulting in an appropriate column profile with satisfactory purity in the top of the column. Production, i.e. removal of distillate, is started in step 3.

In the SBD process, the still composition moves in a direction opposite to the composition of the distillate. As a result, the still composition moves out from the feasible region through the line of pinch points. Once the still is outside the feasible region, the distillate composition is also outside the specified destination region. The distillate composition will slip out from the destination region even earlier because a finite and constant number of stages is ap-

Table 3 – *Operating steps in case of SBD or BED-B processes for separating maximum boiling azeotropes*

	SBD	BED-B
0 charging	A+B in	
1 premixing with entrainer	+ E in	
2 heat-up	$F_D = 0$, $F_F = 0$	
3 distillation of E+A	$F_D > 0$, $F_F = 0$	$F_D > 0$, $F_F > 0$
4 recovery of E from E/A/B	$F_D > 0$, $F_F = 0$	
5 recovery of B from A/B	$F_D > 0$, $F_F = 0$	
Azeotropic mixture remains in the still		
6 change of the still content	Azeotrope off, A+E in	
7 recovery of E from A/E	$R < \infty$, $F_F = 0$	
8 removal of pure A	A off	

plied in practice. The entrainer fraction in the distillate decreases during step 3 because the still composition moves farther from the destination region.

To confirm the feasibility of the SBD process, a simulation run with N=7 (including the still), R = 0.5, Q_d = 1.5 kW, n_{ch} = 780 mol, and x_{ch} = [0.05; 0.078205; 0.871795], has been performed. The results are shown in Figure 18. The simulation is stopped when the entrainer fraction in the distillate increased above 99 %, i.e., when $\boldsymbol{x}_D$ left the destination region.

The point of starting the removal of distillate is shown by an open circle on the actual still composition. Three column profiles are shown, one at starting the production (t_0), one at t_1 = 3.95 h, and one at t_2 = 5.75 h. The path of the distillate composition is also shown in the figure. The still composition was yet inside the feasible region, when the distillate composition had already left the destination region, because of the finite number of stages. The final still composition is denoted by a full circle in Figure 18a. When the still composition reached this point, the actual distillate composition suddenly jumped out of the destination region, to a point denoted by a full circle in Figure 18b. The final product composition is $\boldsymbol{x}_P$ = [0.018749; 1.8E-8; 0.9813] (a very small, hardly 2% water fraction in the binary product). The water to EDA ratio is 1E+6 in the accumulator, a very high value, but no more than 15.9 % of water is recovered.

If the number of stages is increased, the top composition can be kept inside the destination region, when the still composition is far away from the entrainer vertex. However, the distillate contains too much entrainer in this case at the beginning of the process.

Thus, the separation with SBD is feasible, but practically useless because of the low recovery and the high entrainer contamination together.

In the BED process, on the other hand, the still composition can be kept inside the feasible region by continuously feeding entrainer to the still in step 3 (refer to Table 3). A simulation run with the same parameters (N = 7, N_F = 7, Q_d = 1.5 kW, R = 0.5, F_F = 100 mol h^{-1}, $\boldsymbol{x}_F$ = [0;0;1], n_{ch} = 144.5 mol, and $\boldsymbol{x}_{ch}$ = [0.27; 0.4223; 0.3077]) has been performed in order to demonstrate the feasibility of BED, and to compare the two processes.

The resulted still path is shown in Figure 19a, together with three instantaneous column profiles (t_0 = 0, t_1 = 1.25 h and t_2 = 4.7 h). The distillate composition history is shown in Figure 19b. Just contrary to what is observed in the SBD process, both the still composition and the distillate composition move approximately parallel with the AE edge (the water – methanol edge), toward smaller water fraction. 78 % of water can be recovered in this way, with product composition $\boldsymbol{x}_P$ = [0.03; 4E-4; 0.97] (a very small, 3 % water fraction). The water to EDA ratio in the product is 67.7, a high enough value.

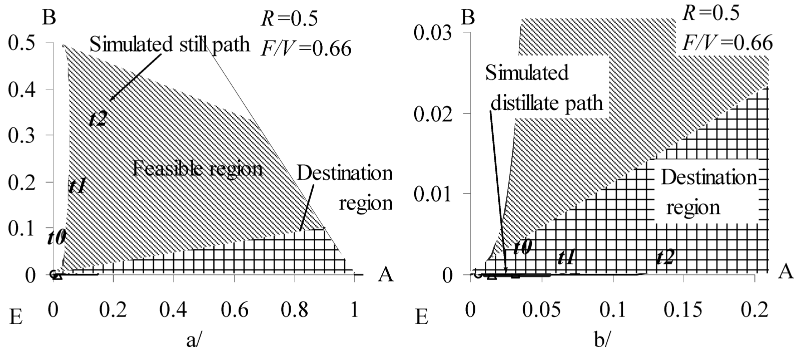


Fig. 18 – *Water/ethylene diamine/methanol system. Separation of the azeotrope is feasible with SBD, but the distillate composition jumps out of the destination region.*

The last steps are also identical to both processes. When the distillate composition cannot be maintained any more, feeding entrainer to the still is stopped, and pure E is distilled out in a conventional batch distillation manner (step 4). At the end of this step, A/B mixture rich in B remains in the still. Then pure B as a distillate is produced in a conventional batch distillation process (step 5), and mixture with approximately azeotropic composition remains in the still. This residue can then be added to the next charge.

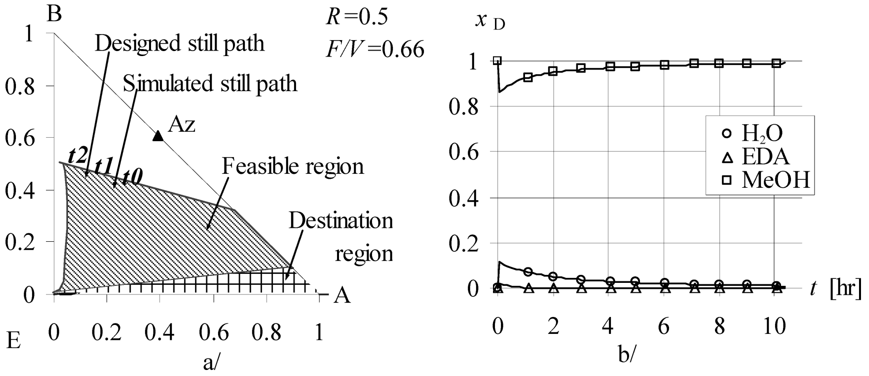


Fig. 19 – *Water/ethylene diamine/methanol system, BED-B: a) still path; b) distillate history*

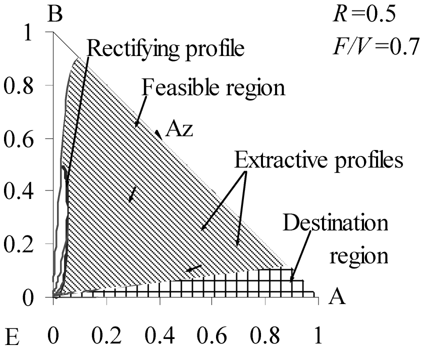


Fig. 20 – *Water/ethylene diamine/methanol system. Map of a rectifying and several extractive profiles.*

Feasibility of BED with extractive section

If the entrainer is fed to the column some stages above the still, an extractive section forms between the feed stage and the still. This extractive section may extend the feasible region compared to that based on the rectifying section only. The destination region might be reachable from the water/ethylene diamine edge of the triangle with the help of an extractive section.

Just like in cases discussed earlier, the still composition should be connected by an extractive profile to a rectifying profile started from the destination region. In practice, a single rectifying profile is drawn and compared to the extractive profiles map computed with the same parameters. The feasible region consists of those still compositions from which the extractive profile reaches or crosses the specified rectifying profile; such a region is shaded in Figure 20. The rectifying profile is reachable from almost any still composition if high enough feed ratio is applied. The extractive profiles run away from the leftmost rectifying profile in the unshaded region.

Since the distillate composition will change during the production step, a series of profiles maps ought to be computed and analysed in order to have an exact feasible region. Figure 21 demonstrates how the rectifying profile, and the leftmost extracting profile reaching it, change with $\boldsymbol{x}_D$ at a given parameter pair of R and F_F/F_V. These leftmost profiles do not cross each other. Thus, the feasible region can be well estimated with the extractive profile belonging to the poorest distillate composition and to the leftmost extracting profile reaching it.

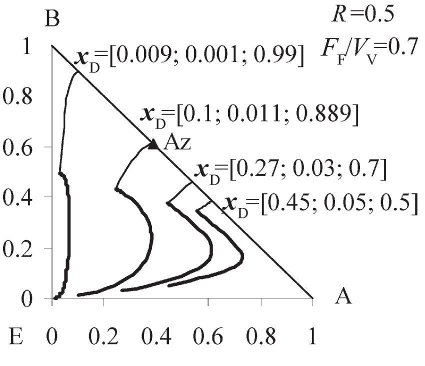


Fig. 21 – *Water/ethylene diamine/methanol system. Evolution of the feasible region with x_D, for the general case of BED.*

The feasible region at high enough feed ratio reaches the AB edge; no entrainer is to be premixed to the charge. However, a small amount premix of entrainer is suggested in order to get to the inside of the composition triangle, if the charge composition lies on the component B side of the azeotrope. Such a premix is not needed if the charge composition lies on the other side, because the top composition approaches the destination region in this latter case. The recommended steps for the separation process are collected in Table 4.

To check the feasibility of this process, a still path that runs along and near the AB (water – EDA) edge of the triangle was designed with

Table 4 – *Operating steps in case of the general BED process for separating maximum boiling azeotropes*

0	charging	A+B in
1	optional small premix of E	+E small; optional
2	heat-up	$R = \infty$, $F_F = 0$
3	production of A+E	$R < \infty$, $F_F > 0$
4	production of E	$R < \infty$, $F_F = 0$
5	production of B	$R < \infty$, $F_F = 0$
	Azeotrope remains in the still	
6	change of the still content	Azeotrope off, A+E in
7	recovery of E from A/E	$R < \infty$, F = 0
8	removal of pure A	A off

R=0.5, F_F/F_V = 0.64 and $\boldsymbol{x}_D$ = [0.02;0.001; 0.979]. We governed the still path near the AB edge in order to apply as small amount of entrainer as possible, during the separation. A simulation run has been performed to verify this assignment. Input data are: N = 7, N_F = 5, Q_d = 1.5 kW, R = 0.5, F_F = 100.5 mol h^{-1}, $\boldsymbol{x}_F$ = [0;0;1], n_{ch} = 100 mol, $\boldsymbol{x}_{ch}$ = [0.39; 0,61; 0]. The results are shown in Figure 22. The feasible region is also shaded in this figure. Approximately 55.8 % water recovery is reached in this way with product composition $\boldsymbol{x}_P$ = [0.01918; 3.6E-6; 0.98082], i.e. a very small (below 2 %) water fraction, and high 53.07 water to EDA ratio.

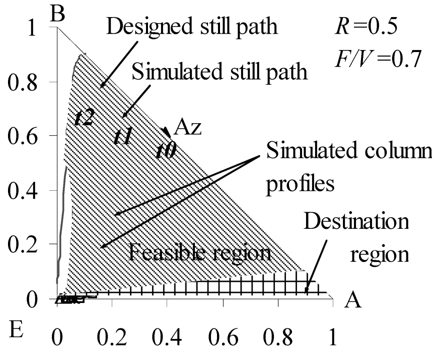


Fig. 22 – *Water/ethylene diamine/methanol system, general case of BED. Still path and column profiles.*

The simulated still path differs significantly from the designed one, mainly because constant distillate composition cannot be maintained.

As the still composition gets closer to the ethylene diamine/methanol edge, the distillate becomes too rich in methanol, i.e. the product composition slips out of the specified domain (destination region). This could be overcome by decreasing R; however, another map ought to be computed for a different R.

Concluding analysis on the basis of short-cut study

SBD is practically infeasible because both the water fraction in the first product and the recovery of water are low.

In spite of the low water content of the first product, that involves a high cost for separating water from the entrainer in a later step, BED with feeding light entrainer to the still or to the column is a candidate for separating water from EDA, because of the high water to EDA ratio and the reasonable recovery ratio.

Effect of R on the rectifying profiles has already been discussed above. The rectifying profiles have greater curvature, and are stretched more toward the BE edge, at lower R. There is a maximum R above which feasible single rectifying profile (for BED-B) cannot be reached by entrainer premixing. Since the extractive profiles run approximately in opposite direction, there must be a maximum R for the general BED process, as well; at this maximum the bundle of feasible column profiles (including both the rectifying and extractive parts) just touches the mixing line between the azeotropic composition and the entrainer vertex.

Both minimum and maximum number of rectifying stages exist. Below or above these limits, the distillate composition lies outside the destination region because the rectifying profile is too short or too long, respectively.

Effect of R on the extractive profiles map is shown in Figure 23. The extractive profiles map seems practically independent of R.

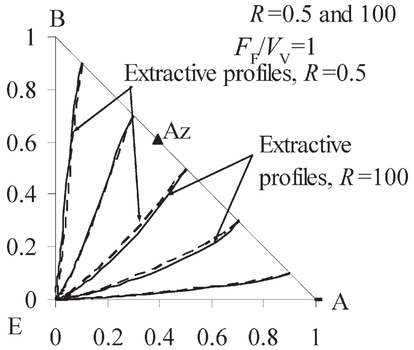


Fig. 23 – *Water/ethylene diamine/methanol system. Effect of the reflux ratio on the extractive profiles map: a) Solid lines: R = 100; b) Dashed lines: R = 0.5.*

There is an unstable node in the extractive profiles at low entrainer feed ratio, see Figure 24. It prevents the separation of azeotropic charge from being feasible without premixing. This unstable node moves out of the triangle with increasing F_F/F_V. Above some feed ratio ($F_F/F_V \approx 0.66$ in our case), the unstable node and the separatrix are outside the triangle, and distillate of appropriate purity

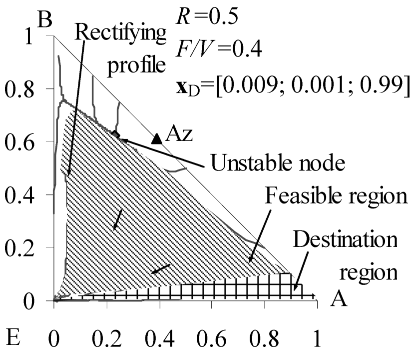


Fig. 24 – *Water/ethylene diamine/methanol system. Map of a rectifying and extractive profiles at a low F_F/F_V-value. Note the existence of an unstable point inside the triangle.*

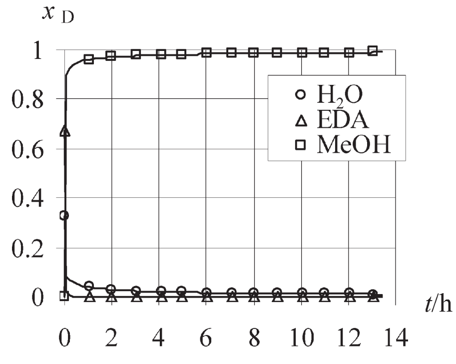
can be produced from almost any still composition. Such a situation is shown in Figure 22.

A minimum and a maximum number of extractive stages exist. If less extractive stages are used than the minimum, the extractive profile does not reach the rectifying profile. With more stages than the maximum, the extractive profile runs over and behind the leftmost rectifying profile.

Parametric study with rigorous simulation

Results of a rigorous parametric study are presented in this section. The model parameters are listed in Appendix. Operation time, product purity, separation ratio (water to EDA), and recovery are observed and compared, applying the same purity specifications that were used during the feasibility study, such as minimum separation mole ratio in the distillate ($r_{\mathrm{w/EDA}} \geq 9:1$) and maximum entrainer fraction in the distillate ($x_{\mathrm{D,MeOH}} \leq 0.99$).

A characteristic simulation history is shown in Figure 25 with $N = 7$, $N_F = 5$, $Q_{\mathrm{g}} = 1.5$ kW, $R = 0.5$, $F_{\mathrm{F}} = 100.5$ mol h^{-1}, $\boldsymbol{x}_{\mathrm{F}} = [0;0;1]$, $n_{\mathrm{ch}} = 100$ mol, and $\boldsymbol{x}_{\mathrm{ch}} = [0.39;\ 0.61;\ 0]$. The main production step (Step 3) starts very near the beginning of the process. There must be a small amount of mixed transient product between Step 4 (recovery of methanol) and Step 5 (production of ethylene diamine). A very small amount of azeotrope remains in the still.



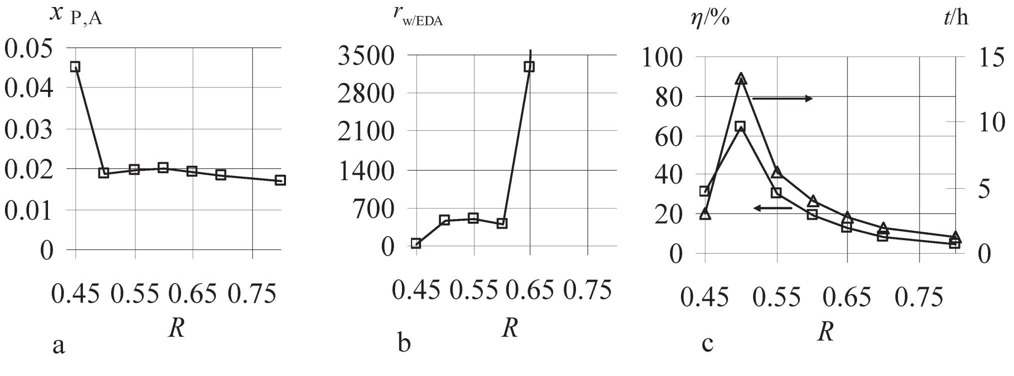
F i g . 2 5 – *Water/ethylene diamine/methanol system, general case of BED. Distillate composition history.*

Effect of the reflux ratio is studied first; see Figure 26. The process is very sensitive to R. The higher R is used, the better separation is obtained; at the same time, the higher entrainer concentration is obtained in the distillate. This involves a decrease in operation time and recovery ratio, as well. Below a minimum reflux ratio, $R = 0.4$, the separation ratio is not high enough to fulfil the purity criteria. (Separation ratio not higher than 4.3 could be reached in this latter case.) There is also a maximum reflux ratio $R = 1.6$, not shown in the figure, above which the distillate contains too much entrainer. The figures show the effect of R up to 0.75 only, because no more than 4 % recovery can be achieved already at $R = 0.8$.

Effect of the entrainer ratio is shown in Figure 27. A better water/ethylene diamine ratio is achieved with a greater $F_{\mathrm{F}}/F_{\mathrm{V}}$, but more entrainer gets into the vapour; thus, the water concentration and the recovery decrease. A minimum feed ratio, $F_{\mathrm{F}}/\mathrm{F}_{\mathrm{Vmin}} = 0.605$, is observed below which the specified separation ratio cannot be achieved. The distillate composition cannot be kept inside the specifications if the feed ratio is above $F_{\mathrm{F}}/\mathrm{F}_{\mathrm{Vmax}} = 1.37$, not shown in the figure. The figures show the effect of $F_{\mathrm{F}}/\mathrm{F}_{\mathrm{V}}$ up to 0.76 only, because the recovery, that can be achieved above this feed ratio, is too low.

Effect of the feed location is shown in Figure 28. If the entrainer is fed to the bottom of the column, the specified purity cannot be achieved without premixing entrainer at the given reflux ratio (see also Figure 17b). Rectifying stages are necessary to reach the specified separation ratio. The figure shows that some extractive stages are also needed for the separation. Maximum recovery can be achieved with feeding the entrainer two stages above the still.

Effect of the number of rectifying stages is shown in Figure 29 with $N_E = 3$. The more rectifying stages are applied, the less pure product is obtained. The separation ratio is very bad with few stages.



F i g . 2 6 – *Water/ethylene diamine/methanol system. Effect of the reflux ratio R on: a) mole fraction of water; b) water / ethylene diamine mole ratio; c) operation time t, and recovery ratio η.*

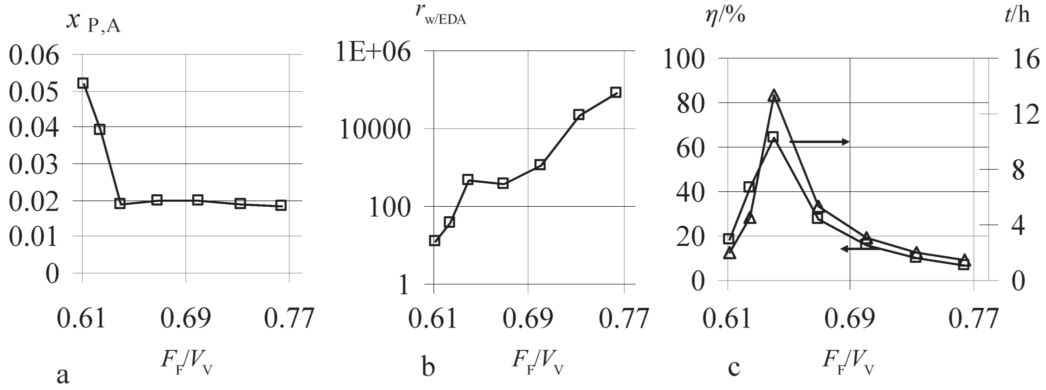


Fig. 27 – *Water/ethylene diamine/methanol system. Effect of the entrainer feed ratio F_F/V_V on: a) mole fraction of water; b) water / ethylene diamine mole ratio; c) operation time t, and recovery ratio η.*

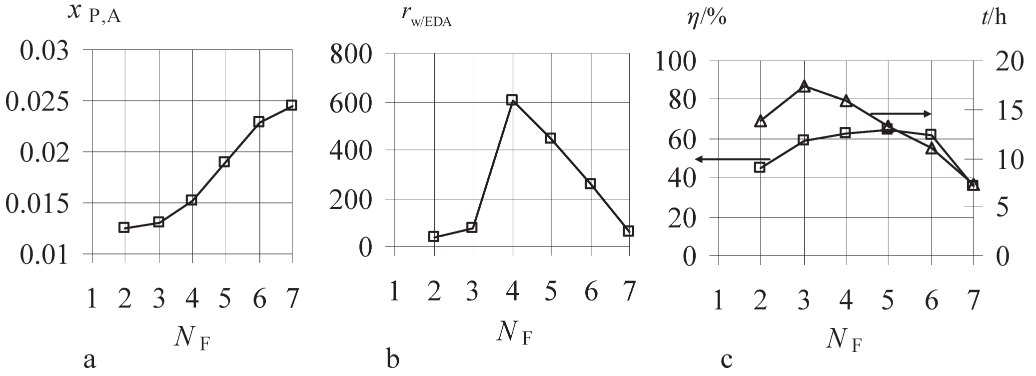


Fig. 28 – *Water/ethylene diamine/methanol system. Effect of the feed location N_F on: a) mole fraction of water; b) water / ethylene diamine mole ratio; c) operation time t, and recovery ratio η.*

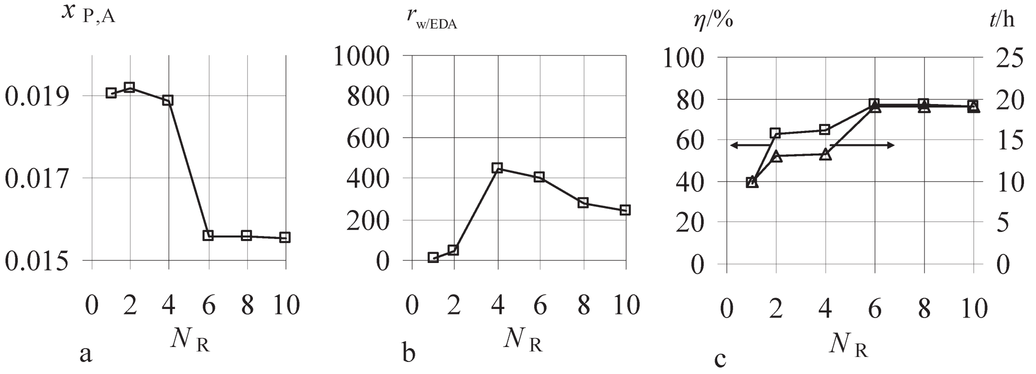


Fig. 29 – *Water/ethylene diamine/methanol system. Effect of the number of rectifying stages N_R on: a) mole fraction of water; b) water / ethylene diamine mole ratio; c) operation time t, and recovery ratio η. The number of extractive stages is N_E = 3.*

Both the water and the ethylene diamine fractions decrease in the product with increasing N_R, if $N_R < 8$. Above this value, the water mole fraction in the accumulator increases, while that of ethylene diamine does not change significantly.

Effect of the number of extractive stages with $N_R = 4$ is shown in Figure 30.

The operation time has maximum value at $N_E = 4$; thus, recovery is the highest at that column configuration. Since the distillation composition gets poorer in water with time, the separation ratio is not the highest at maximum operation time.

The effect of applying cold entrainer feed is shown in Figure 31. Instead of boiling methanol (approximately 64.15 °C at 1 bar), the process is simulated with cold methanol feed. The higher temperature (*T*) the entrainer has, the longer operation time and the better recovery it goes with.

Since the distillate composition is not constant during the process, the design and the estimation of

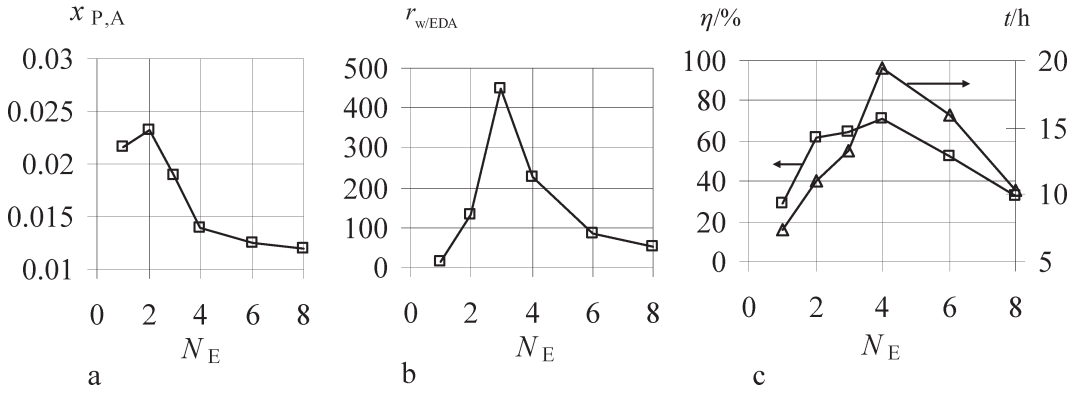


Fig. 30 – *Water/ethylene diamine/methanol system. The effect of the number of extractive stages N_E on: a) mole fraction of water; b) water/ethylene diamine mole ratio; c) operation time t, and recovery ratio η. The number of rectifying stages is N_R = 4.*

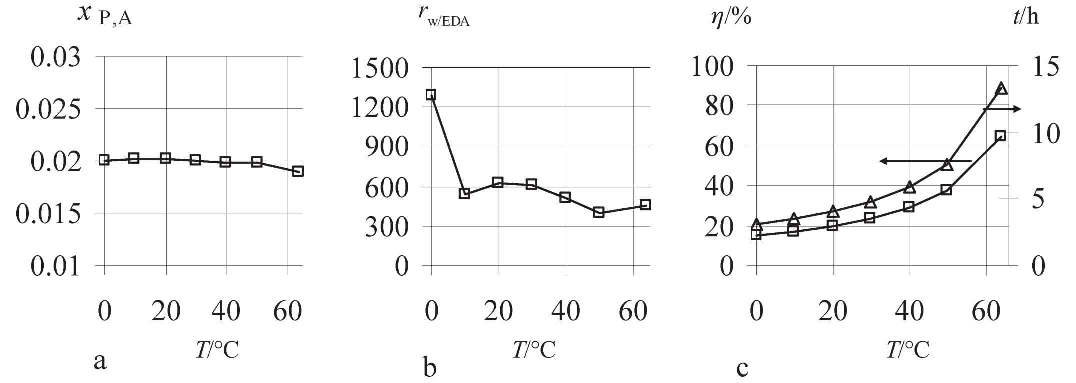


Fig. 31 – *Water/ethylene diamine/methanol system. Effect of the entrainer feed temperature T on: a) mole fraction of water; b) water/ethylene diamine mole ratio; c) operation time t, and recovery ratio η.*

the process parameters are less reliable than in the cases of applying heavy or intermediate boiling entrainer. From the viewpoint of design, we accordingly propose using either heavy or intermediate boiling entrainer, if possible.

Separation of close boiling mixtures

Separation of close boiling mixtures is, in principle, feasible but rather expensive with conventional batch rectification. Both a great number of theoretical stages and great reflux ratio are required to achieve high purity with reasonable recovery. The closer the relative volatility is to one, the more expensive process is needed for the separation. Batch extractive distillation might provide us with more favourable conditions.

The first (binary) product will contain a great percentage of the entrainer, and only a few percent of the key component, if light entrainer is applied. However, separating it from the entrainer may be so much easier that it compensates for the expenses of applying much amount of entrainer. Therefore, at least the theoretical availability of this process is studied here.

A study has been performed on the chlorobenzene (ClB)/ethylbenzene (EtB) mixture with 4-methylheptane (4-MeH) as light entrainer. The key components form an almost ideal liquid mixture; therefore, really efficient entrainer cannot be found.

The residue curves map of the system is shown in Figure 32. The curves run from the 4-methylheptane vertex to the ethylbenzene vertex. The heavy key component vertex is a stable node; the

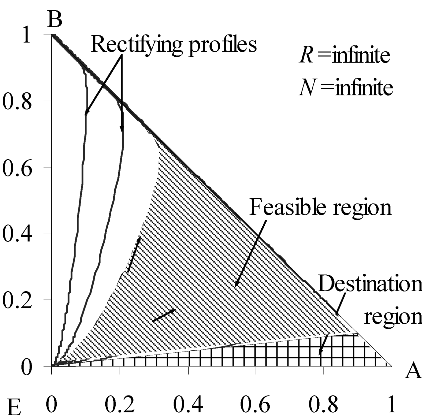


Fig. 32 – *Residue curves map (RCM) of the chlorobenzene/ethylbenzene/4-methylheptane system.*

entrainer vertex is an unstable node; the lighter key component vertex is a saddle point. Therefore, ethylbenzene can, in principle, be obtained in the residue at the end of the separation with infinite reflux ratio and infinite number of theoretical stages. This map is rather similar to one of the simple distillation regions formed in the case of maximum azeotrope with light entrainer. The shaded area of Figure 16 is topologically equivalent to the RCM shown in Figure 32. Thus, the behaviour of SBD or BED with light entrainer applied to close boiling mixtures is expected to be similar to the effects found in maximum boiling azeotropes.

Equimolar chlorobenzene/ethylbenzene mixture charge is considered, and at least 9 to 1 chlorobenzene to ethylbenzene ratio in the distillate is specified with the constraint that the 4-methylheptane mole fraction in the product should not be higher than 0.99. (The entrainer will be present in the product with a great fraction, and its separation is planned in a subsequent step.) Therefore, a destination region is formed along the chlorobenzene/4-methylheptane edge, see Figure 32.

Feasibility of systems without extractive section (SBD and BED-B)

If the entrainer is fed to the still, or premixed with the charge, the feasible region is determined by the rectifying profiles. This is shown with infinite reflux ratio in Figure 32. The separation is practically unfeasible above a certain ethylbenzene content of the charge if R is high, because too many rectifying stages would be required. This practical limit in our case is approximately $x_{\mathrm{EtB}} \approx 0.7$. If we had infinitely many stages, no extractive methodology would be needed.

How the feasible region changes with R is shown in Figure 33. The profiles are calculated with three different reflux ratios ($R = 1$, $R = 2$, and $R = 50$), and three different distillate compositions (x_{D} = [0.01; 0.0011; 0.9889]; x_{D} = [0.2; 0.0222; 0.7778] and $\boldsymbol{x}_{\mathrm{D}}$ = [0.5; 0.0555; 0.4445]). The rectifying profiles become shorter with decreasing R, and their pinch points get closer to $\mathbf{x}_{\mathrm{D}}$. Thus, the feasible region becomes smaller if R is decreased, and $\mathbf{x}_{\mathrm{D}}$ can be reached from a smaller region of still compositions, as is shown in Figure 34.

Separation of a mixture with high ethylbenzene content becomes feasible with applying low R only, but the still composition should first be moved into the feasible region by premixing entrainer in that case. Use of low R is also motivated by economic considerations.

As it is clear from Figure 34, the left hand side border of the feasible region is always the rectifying profile belonging to the poorest x_{D}, here x_{D} = [0.01; 0.0011;0.9889]. The lower the applied R is, the closer this border gets to the ethylbenzene/4-methylheptane edge of the triangle, and smaller amount of chlorobenzene may remain in the still at the end of the first production step. On the other hand, the gap between the feasible region and the chlorobenzene/ethylbenzene edge becomes wider with decreasing R, and more entrainer need to be mixed to the charge in advance.

In case of SBD, it is worth premixing as much entrainer as possible. If BED-B is applied, on the other hand, adding great amount of entrainer in advance is unnecessary.

Suggested separation steps of BED-B are shown in Table 5. As a preparatory step, an amount of entrainer is added to the charge in order to get the still composition into the feasible region (step 0). This amount is determined from n_{ch} and the map computed to R. This is followed by a heat-up step (step 1) without feeding. In the main production step 2, distillate production is started with finite reflux ratio and continuous entrainer feeding. (The distillate of this step is purified in step 6). When the

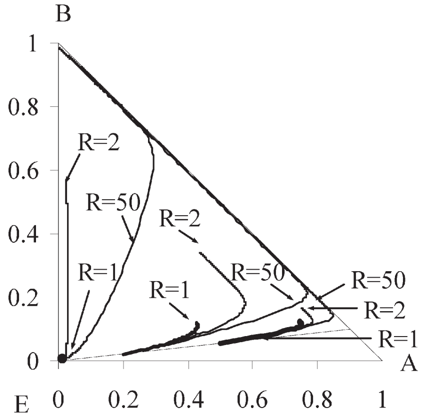


Fig. 33 – *Chlorobenzene/ethylbenzene/4-methylheptane system, SBD or BED-B. Evolution of the rectifying profiles with x_D for different reflux ratios R.*

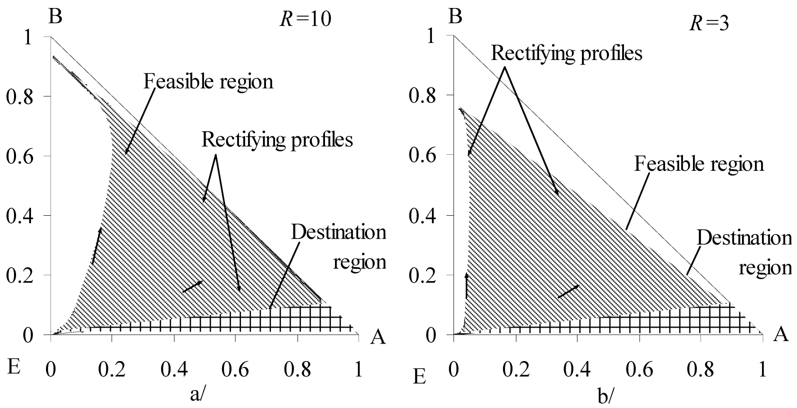


Fig. 34 – *Chlorobenzene/ethylbenzene/4-methylheptane system. Feasible regions with different reflux ratios: a) R = 10; b) R = 3.*

Table 5 – *Operating steps in case of BED-B process for separating close boiling mixtures*

0	charging with entrainer	(A+B) +E in
1	heat-up	$R = \infty$ $F_F = 0$
2	distillation of E+A	$R < \infty$ $F_F > 0$
3	distillation of the rest of A, with E	$R < \infty$ $F_F > 0$
4	recovery of E from E/B	$R < \infty$ F = 0
5	change of the still content	B off, E/A in
6	recovery of E from E/A	$R < \infty$ $F_F = 0$
7	removal of pure A	A off

appropriate distillate purity cannot be maintained further, the receiver is changed, and the rest of lighter key component is evaporated with continuous entrainer feeding (step 3). This cut-off product is almost pure entrainer, and can be used in the next charge. The still composition gets close to the BE edge; thus, the rest of the still can be separated with conventional batch rectification (step 4).

Only a part of component A can be removed with SBD, because the still composition is governed toward the A/B edge instead of the B/E edge. Feeding of entrainer is not applied in step 2, and that process is ended with step 3, also without feeding. In contrast, almost complete separation can be achieved if BED-B is applied.

A designed still path for BED-B is shown in Figure 35a. A minimal entrainer amount is applied to get inside the feasible region, and the path moves toward the BE edge, as a result of continuous entrainer feeding.

According to our calculation, $F_F/F_V = 0.4$ has to be used for the still path to arrive to $\boldsymbol{x}_{S,\text{Final}}$ = [0.039; 0.047; 0.914]. A simulation run is performed with $N = 15$, $N_F = 15$, $Q_d = 1.5$ kW, $R = 3$, $F_F = 61.2$ mol h^{-1}, $\boldsymbol{x}_F$ = [0,0,1], n_{Ch} = 107 mol, and $\boldsymbol{x}_{ch}$ = [0.75; 0.1875;0.0625]. Three column profiles (t_0, $t_1 = 0.65$ h and $t_2 = 3.2$ h) are also shown in Figure 35a. The distillate composition history is presented in Figure 35b. 59 % of chlorobenzene can be recovered with final product composition x_P = [0.1539; 0.011374; 0.834725] at the end of step 2 in less than 8 hours, and with a chlorobenzene to ethylbenzene ratio of 13.5.

The separation process can be quite well estimated with the help of the profiles maps. The appropriate operation parameter values can be determined, as well.

The SBD process is also applicable to separate the mixture. Using $N = 15$, $Q_d = 1.5$ kW, $R = 3$, x_F = [0,0,1], n_{Ch} = 605 mol (the same quantity of entrainer as altogether applied in the BED-B process), 63.5% of chlorobenzene recovery can be achieved in 12.05 h with final product composition $\boldsymbol{x}_P$ = [0.1069; 0.0077; 0.8854], and chlorobenzene to ethylbenzene ratio of 14 (Figure 36). This sort of process gives approximately as good product as BED-B, but with longer time (including greater energy consumption, as well). A simulated column profile (t_1=11.15 h) is also shown in the figure. It follows well the rectifying curves.

The same recovery as we have got with BED-B (59 %) can be achieved with SBD in t=11.45 h, and producing separation ratio of 14.24 with product composition $\boldsymbol{x}_P$ = [0.105828; 0.007431; 0.886741]. If SBD is constrained to the same duration as applied to BED-B, $t = 7.85$ h, only 39 % recovery can be achieved, although, with a little bit better separation ratio (16.23) and product composition $\boldsymbol{x}_P$ = [0.101275; 0.00624; 0.892485]. The maximum purity that we could achieve with SBD with these quantities has been $x_{P,ClB}$ = 0.106872; $x_{P,ClB}$ = 0.15 cannot be achieved in this way.

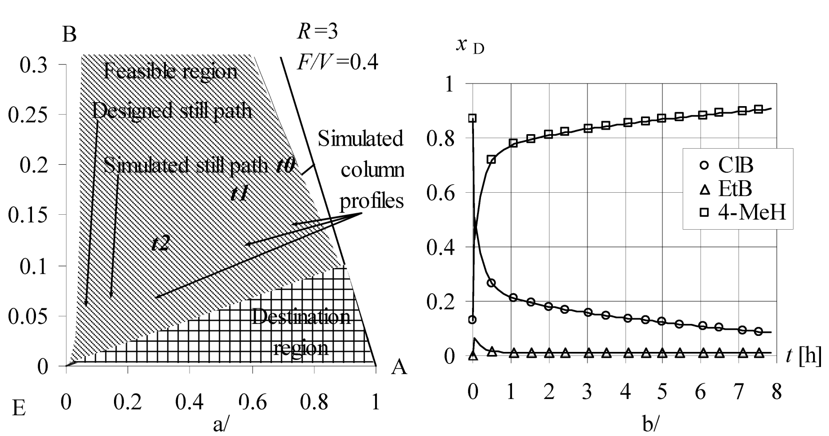


Fig. 35 – *Chlorobenzene/ethylbenzene/4-methylheptane system, BED-B: a) still path; b) distillate history.*

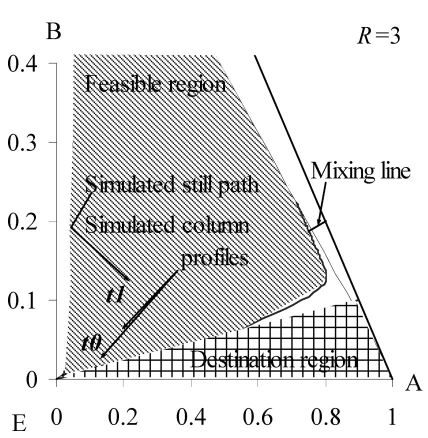


Fig. 36 – *Chlorobenzene/ethylbenzene/4-methylheptane system, general BED. Simulated still path, and a simulated column profile.*

Conventional batch distillation (BD) with the same $N = 15$ and $R = 3$ parameters produces maximum 7.217 ClB to EtB ratio. Product composition $\boldsymbol{x}_P = [0.91135; 0.08865; 0]$, i.e. separation ratio of 10.28, and 34.17 % recovery can be achieved with a much greater reflux ratio $R = 40$.

A greater number of stages would be necessary if a smaller amount of entrainer is premixed to the charge, because the still composition is farther from the distillate composition in that case.

Feasibility of BED with extractive section

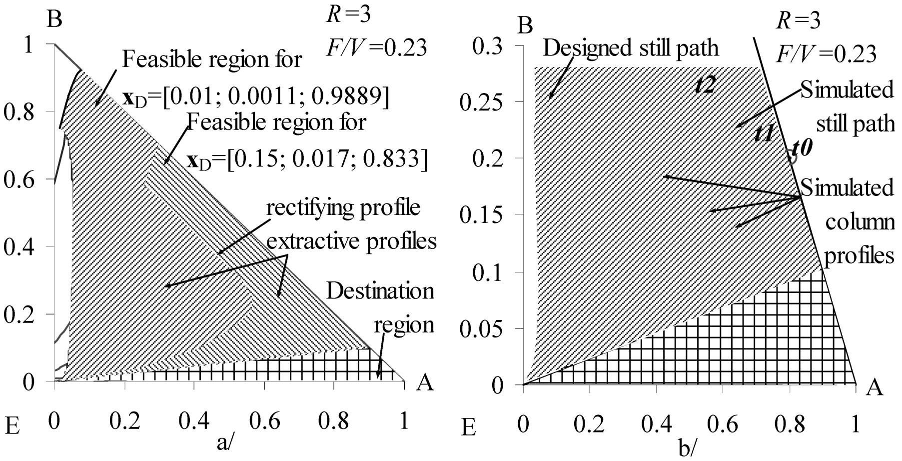
The feasibility study of separating close boiling mixtures is rather similar to that of maximum boiling mixtures, both with light entrainer. The suggested operation steps are collected in Table 6.

How the feasible region changes with the actual distillate composition is shown in Figure 37a. Two rectifying profiles, one with x_{DA}=0.01, and another one with $x_{DA} = 0.015$, delimit two different feasible regions consisting of the points of extractive profiles reaching the actual rectifying profile, both at $R = 3$ and $F_F/F_V = 0.23$. A still path that runs almost parallel to the destination region was designed with the same process parameters $R = 3$, $F_F/F_V = 0.23$, and a supposed average distillate composition $\boldsymbol{x}_D = [0.15; 0.017; 0.833]$. This path is selected with hoping that the separation remains feasible with a constant number of stages, in this case. Then a simulation run is performed with $N = 15$, $N_F = 11$, $Q_d = 1.5$ kW, $R = 3$, $F = 35$ mol h^{-1}, $\boldsymbol{x}_F = [0;0;1]$, $n_{Ch} = 100$ mol, and $\boldsymbol{x}_{ch} = [0.8; 0.2; 0]$. Both the simulated and the designed still paths are shown in Figure 37b. Three column profiles (t_0, $t_1 = 2.15$ h and $t_2 = 6.95$ h) are also drawn in the figure. They show that both the extractive and the rectifying section profiles well follow the pre-calculated profiles map.

There is some deviation between the designed and the simulated still paths. One reason of this differ-

Table 6 – *Operating steps in case of the general BED process for separating close boiling mixtures*

0	charging	A+B in
1	heat-up	$R = \infty$, $F_F = 0$
2	run-up	$R = \infty$, $F_F > 0$
3	production of A+E	$R < \infty$, $F_F > 0$
4	distillation of the rest of A, with E	$R < \infty$ $F_F > 0$
4	recovery of E from E/B	$R < \infty$, $F_F = 0$
5	change of the still content	B off, A+E in
6	recovery of E from E/A	$R < \infty$, $F_F = 0$
7	removal of pure A	A off



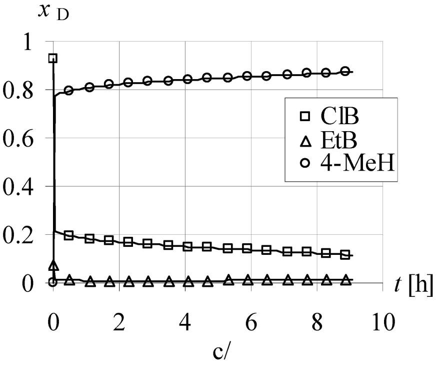


Fig. 37 – *Chlorobenzene/ethylbenzene/4-methylheptane system, general case of BED: a) rectifying and extractive profiles map; b) still path and simulated column profiles; c) distillate history.*

ence may be that constant distillate composition cannot be maintained. Therefore, it is difficult to give a good approximation by pre-calculation. The designed still path is calculated for a supposed average distillate composition. After a certain time, the simulated still path stretches out of the feasible region belonging to $\boldsymbol{x}_D$ = [0.15; 0.017; 0.833], but it still remains inside the feasible region belonging to the whole destination region. The simulation was stopped when the distillate composition left the destination region.

The distillate composition history is shown in Figure 37c. Product composition is $\boldsymbol{x}_P$ = [0.1500; 0.0104; 0.8400]; the chlorobenzene / ethylbenzene ratio is 14.5, with 67 % chlorobenzene recovery.

Thus, BED with feeding entrainer to an intermediate point of the column can also be an appropriate process to separate close boiling components with light entrainer.

Summary and conclusion

Separation of both minimum boiling azeotropes and maximum boiling azeotropes may become feasible, and separation of close boiling mixtures may become less expensive, if entrainer is applied. Batch extractive distillation is one of the appropriate configurations applying entrainer. The entrainer, not forming heterogeneous liquid phase, can be heavy, intermediate, or even light boiling component, according to the volatility rank.

Here we studied the possibility of applying light entrainer (E) for separating A-B mixture that forms minimum boiling azeotrope (A=ethanol, B=water, E=methanol), maximum boiling azeotrope (A=water, B=ethylene diamine, E=methanol), and close boiling mixture (A=chlorobenzene, B=ethylbenzene, E=4-methylheptane), with batch extractive distillation in batch rectifying device.

Feasibility of applying heavy and intermediate boiling entrainer had been systematically studied earlier. Use of light entrainer was earlier also demonstrated. A systematic study on application of light entrainer is presented here.

The entrainer can be (1) preliminary mixed to the charge, or (2) continuously fed to the still, so that the full column over the still constitutes a rectifying section, or (3) continuously fed to the column so that the stages between the still and the feed stage constitute an extractive section, and the stages above the feed constitute a rectifying section. All the three cases are studied here from the viewpoint of feasibility. Feeding the entrainer to the top of the column can be neglected, because the light entrainer leaves the column without serious effect on the separation.

Pure product of component A cannot be produced in any of the above versions, because vertex E is the lightest point in the system. Instead, production of binary mixture A-E, approximately free of B, is targeted by specifying a minimum A to B ratio in the distillate. Pure A can be produced in a later step by recovering E from the binary product. In order to prevent producing too dilute A in E, a maximum mole fraction of E in the distillate is also specified.

Separation of (either minimum or maximum boiling) azeotropes and close boiling mixtures with batch extractive distillation is feasible, and the short-cut feasibility methodology is applicable to all the cases.

Separation of azeotropes with SBD process is theoretically feasible, but practically useless because of low recovery.

Feasibility of the azeotrope-separation processes cannot be decided by studying total reflux operation because these processes are feasible with small reflux ratio only. Although separation of close boiling components is feasible at high reflux ratio, very high number of theoretical stages is required for the process in that case.

If continuous feeding is applied to the still, premixing a finite amount of entrainer to the still in advance is also necessary. In both types of azeotrope, there is a minimum amount to be premixed, and there is a maximum amount over which the feasible region is jumped over by premixing. Naturally, there is a minimum stage number, but there is also a maximum stage number over which the entrainer mole fraction in the distillate becomes too high. There are a minimum feed ratio and a maximum feed ratio between which the still path can be governed inside the feasible region.

The feasible region can be extended by conducting the continuous entrainer feed to the column, and thus using extractive section. Premixing entrainer to the charge is not needed above a minimum feed ratio. This minimum value is not a border of feasibility because the process is feasible even below this value, but with premixing only. However, some premixing is suggested even in the former case, for practical reasons. All the other constraints, existing in the case of feeding to the still, exist in this case, as well. Additionally, there are a minimum number of extractive stages, and a maximum number of extractive stages.

Rigorous parametric study is performed in the cases of separating azeotropes. Effects of changing reflux ratio, feed ratio, stage numbers, and even subcooling the feed below boiling point are studied. When the entrainer is continuously fed to the column, applying cold entrainer seems preferable. Feasibility of the processes, and even the applicable range of the parameter values predicted by the short-cut feasibility study, are verified.

ACKNOWLEDGEMENT

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APPENDIX

All the vapour-liquid equilibria in this article are calculated according to the equality of partial fugacities in the two phases, expressed in the following form of modified *Raoult-Dalton* equation:

$$y_i^* p = \gamma_i x_i p_i^* \tag{A1}$$

The equilibrium vapour pressure is modelled with the three-parameter *Antoine* equation:

$$\lg p_i^\circ = A_i - \frac{B_i}{T - 273.14 + C_i}, \tag{A2}$$

The activity coefficients are modelled with the *NRTL* equation in the following form:

$$\ln \gamma_i = \frac{\sum\limits_j \tau_{ji} G_{ji} x_j}{\sum\limits_l G_{li} x_l} + \sum_j \frac{x_j G_{ij}}{\sum\limits_l G_{lj} x_j} \left(\tau_{ij} - \frac{\sum\limits_n x_n \tau_{nj} H_{nj}}{\sum\limits_k G_{kj} x_j} \right); \tag{A3a}$$

$$\tau_{ij} = \frac{U_{ij}}{R_G T}, \tag{A3b}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}). \tag{A3c}$$

Here A_i, B_i, and C_i are pure component parameters of the *Antoine* equation, U_{ij} are the binary interaction parameters (energy differences), and $\alpha_{ij} = \alpha_{ji}$ are the binary non-randomness parameters of the *NRTL* equation. The actual model parameters[22] are listed in Tables A1 to A3.

Table A1 – *Ethanol/water/methanol system*

A: ethanol, B: water, E: methanol							
Antoine constants*				NRTL parameters			
i	A_i	B_i	C_i	i-j	U_{ij}/R_G [K]	U_{ji}/R_G [K]	α_{ij}
A	8.11220	1592.864	226.184	A-B	–57.7915	692.606	0.2983
B	8.07131	1730.630	233.426	A-E	189.3442	–165.055	0.3057
E	8.08097	1582.271	239.726	B-E	425.323	–127.757	0.2994

*The units of pressure is Hgmm, and the unit of temperature is °C, in the Antoine equation.

Table A2 – *Water/ethylene diamine/methanol system*

A: water, B: ethylene diamine, E: methanol							
Antoine constants*				NRTL parameters			
i	A_i	B_i	C_i	*i-j*	U_{ij}/R_G [K]	U_{ji}/R_G [K]	α_{ij}
A	8.07131	1730.630	233.426	A-B	203.9259	-509.575	0.7773
B	8.09831	1893.720	245.676	A-E	425.323	-127.757	0.2994
E	8.08097	1582.271	239.726	B-E	-649.333	264.0012	0.3087

*The units of pressure is Hgmm, and the unit of temperature is °C, in the Antoine equation.

Table A3 – *Chlorobenzene/Ethylbenzene/4-methylheptane system*

A: chlorobenzene, B: ethylbenzene, E: 4-methylheptane							
Antoine constants*				NRTL parameters			
i	A_i	B_i	C_i	i-j	U_{ij}/R_G [K]	U_{ji}/R_G [K]	α_{ij}
A	7.17294	1549.2	229.26	A-B	185.0373	-154.894	0.3076
B	6.9658	1429.85	213.767	A-E	371.23	-129.569	0.24575
E	6.84909	1285.85	214.6	B-E	169.74	-39.2032	0.28501

*The units of pressure is Hgmm, and the unit of temperature is °C, in the Antoine equation.

Notation

4-MeH – 4-methylheptane
A – lighter main component
Az – azeotropic composition
B – heavier main component
BED – batch extractive distillation
n_{Ch} – amount of charge, mol
ClB – chlorobenzene
F_{D} – distillate flow rate, mol h^{-1}
E – entrainer
EDA – ethylene diamine
EtB – ethylbenzene
EtOH – ethanol
F – molar flow rate, mol h^{-1}
F_{F} – entrainer flow rate, mol h^{-1}
$F_{\mathrm{F}}/\mathrm{F}_{\mathrm{V}}$ – entrainer/vapor flow ratio
h – hold up, 1
H_2O – water
MeOH – methanol
N – number of theoretical stages
p – pressure, bar
Q_{d} – heat duty, kW
$r_{n_{\mathrm{A}}/n_{\mathrm{B}}}$ – mole ratio,
R – reflux ratio
R_{G} – gas constant (*Regnault*)
SBD – solvent-enhanced batch distillation
t – operation time, h
T – temperature; °C in the text; K in the Appendix
U – binary interaction parameter
$\boldsymbol{x}$ – liquid phase composition (mole fractions), 1
$\boldsymbol{y}$ – vapor phase composition (mole fractions) according to material balance, 1
$\mathbf{y}^*$ – equilibrium vapor phase composition (mole fractions), 1

Greek letters

α – non-randomness parameter
η – Recovery ratio, %

Indexes

0 – starting point
ch – charge
D – distillate
E – extractive
F – feed
L – liquid
i,j,k – component indexes
min – minimum, minimal
max – maximum, maximal
P – product
R – rectifying

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