Batch Heteroazeotropic Rectification of a Low Relative Volatility Mixture under Continuous Entrainer Feeding

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ABSTRACT
For the assessment of the feasibility of the heteroazeotropic distillation in a batch rectifier a new method is presented extending the former methods published for the batch homoazeotropic distillation. The method is based on the analysis of the map of the possible overall liquid composition profiles containing also the heterogeneous liquid boiling envelope with the tie-lines. By this method the separation of a low relative volatility, zeotropic mixture with an entrainer forming a binary heteroazeotrope with one of the components is studied. The calculation results are presented for the mixture dichloro-methane – acetone by using water as heterogeneous entrainer. The continuous feeding of the entrainer is also studied and the results are compared with those of the usual batch addition of the entrainer.

1. INTRODUCTION
For the separation of such mixtures where the two components (A and B) form an azeotrope or the relative volatility ($\alpha_{A,B}$) is near to the unity a special distillation method must be applied such as the extractive/homoazeotropic (ED) or the heteroazeotropic distillation (AD). In both cases a third component (entrainer E) is added to the mixture which makes the separation of A and B possible without the formation of new azeotropes (ED) or by the formation of at least one heteroazeotrope (AD).

Batch distillation has always been an important part of seasonal, uncertain or low capacity and high-purity chemicals production. It is a very frequent separation process in the pharmaceutical industry and in the wastewater units.

The simplest and most frequently used bath distillation configuration is the rectifier. For the more sophisticated configurations such as the middle vessel column very few experimental results have been published. To our knowledge so far batch extractive distillation (BED) experimental results have been published only for the rectifier (e.g. Yatim et al. (1993), Lelkes et al. (1998a), Milani (1999)). By our former BED experiences with continuous E-feeding much better results (Lang et al. (1994), Lang et al. (2000b)) can be obtained than by the batch addition of E.

The batch heteroazeotropic distillation (BAD) is a well-known separation method. The entrainer is added to the charge in batch, at once before the start of the distillation. On the basis of our former favourable experiences obtained with the continuous entrainer feeding we studied its feasibility and characteristics for the batch heteroazeotropic distillation, as well.

Bernot et al. (1990,1991) developed a simple method to predict the behaviour, the feasibility and the separation sequence of multicomponent batch distillation. Lelkes et al. (1998) suggested a method for the assessment of the feasibility of the BED when applying continuous feeding of the homogeneous entrainer for the separation of minimum azeotropes. This method was extended for the BED separation of maximum azeotropes by Lang et al. (2000a).

The aim of this paper is to extend the above feasibility method for a heterogeneous entrainer and study the continuous heterogeneous entrainer feeding for the separation of a low relative volatility (close boiling) mixture by feasibility calculations. The method will be presented for the separation of the mixture dichloro-methane (DCM,A)-acetone (B) using water as heterogeneous entrainer (E) forming a binary heteroazeotrope with component A. The results obtained by the batch addition (BA) and the continuous (CF) of the entrainer are compared. The influence of the most important operational parameters (reflux ratio (R), molar flow rate (F) and quantity (SF) of the entrainer) are also presented.
2. FEASIBILITY STUDIES
First the method applied for the assessment of the feasibility is presented then the results of the feasibility calculation are shown.

2.1 Feasibility method
The feasibility method of Lelkes et al. (1998b) elaborated for the BED separation of minimum azeotropes and applied for maximum azeotropes by Lang et al. (2000a) is extended.

The batch heteroazeotropic distillation is usually performed in a batch rectifier (Fig. 1.a) consisting of three main parts: the condenser with the decanter (LLE-separator), the rectifying section (all stages of the column) and the still. The whole quantity of entrainer (E) is added in batch to the binary charge (A-B) before the start of the distillation.

The overhead vapour $y_2$ is totally condensed into two equilibrium liquid phases: an entrainer-lean phase of composition $x_{1,1}'$ and an entrainer-rich phase of composition $x_{1,1}''$. The molar ratio of the liquid phases in the decanter is given by the lever rule ($i$ is the component index)

$$
\phi = \frac{L''+D''}{L'+D'} = \frac{x_{1,1}'' - y_{2,i}}{y_{2,i} - x_{1,1}'},
$$

The overall reflux ratio is given by

$$
R = \frac{L'}{D'} = \frac{L'+L''}{D'+D''},
$$

The distillate is usually withdrawn only from one of the two liquid phases. If the distillate consists of pure entrainer-lean phase ($'$), in this case $D''=0$ and $x_{0,i}'=x_{0,i}''$.

The overall reflux composition becomes fixed if the value of $R$ is specified and $x_{0,i}''$ can be calculated by the lever rule. If a high enough reflux ratio can be ensured by returning all the entrainer-rich phase onto the top tray of the column as reflux, one-phase reflux is applied, that is $L'=0$, $L''=L'$ and $D'=D''$. In this case $R=\phi$ and the composition of the reflux is $x_{0,i}''=x_{0,i}'$. If the entrainer-rich phase does not provide a sufficient reflux flow one part of the entrainer-lean phase is also returned as reflux, that is $L'>0$, $L''=L'+L''$. In this case $R>\phi$ and the overall reflux composition $x_{0,i}''$ lies between $x_{1,1}'$ and $y_2$ on the tie-line.

In the limiting case of $R=\infty$ the reflux composition equals to that of the top vapour ($x_{0,i}''=y_2$) and the overall liquid composition ($x^o_0$) profile of the column follows a residue-curve. When calculating the residue-curve...
map for a ternary heterogeneous mixture we have to calculate the trajectory of the overall composition \((x^o)\) of all coexisting liquid phases for the simple distillation still (Pham and Doherty, 1990). The residue-curve is calculated by

\[
\frac{dx^o}{d\xi} = (x^o - y^*)
\]  

(3)

If we apply continuous entrainer feeding the column (Fig. 1.b) contains two different sections: stages above the feed stage (rectifying section) and stages from the feed plate to the lowest plate of the column named extractive section.

The feasibility method is based on the analysis of the still path on the map of possible column section profiles. The profile map contains the heterogeneous liquid boiling envelope (with the tie-lines), as well, since the liquid-liquid phase split must be taken into consideration at the assessment of the feasibility.

The method involves the following simplifying assumptions:

- negligible tray hold-up,
- quasi-steady state in the column,
- constant molar overflow,
- boiling point liquid entrainer feeding
- LLE-separation at the boiling point of the condensate.

Feasibility means that starting from the charge of given composition \((x_{\text{ch}})\) under the given operating conditions \((R, F/V)\) the specified distillate composition \((x_{D,\text{spec}})\) can be obtained. The necessary and sufficient condition of the feasibility is to have at least one possible column profile connecting the still path

- with the point \(x_{D,\text{spec}}\) if \(x_{D,\text{spec}}\) is located outside the hlbe (in the homogeneous region) or
- with the tie-line passing through \(x_{D,\text{spec}}\) if \(x_{D,\text{spec}}\) is within the heterogeneous region.

For the assessment of the feasibility the liquid composition profiles of the sections must be calculated. Taking into consideration the possibility of the presence of two liquid phases when we write the material balances around an inner stage \(j\) of the given section we get

\[
x^0_{j-1} = V/L^0 (y^* - y) + x^0_j
\]  

(4)

where \(V\) the molar flow rate of vapour,
\(L^0\) the overall liquid flow rate in the given section,
\(y^*\) is the vapour composition being in equilibrium
- in the homogeneous region with \(x^0\) \((x^0 = x)\)
- in the heterogeneous region with \(x'\) and \(x''\),
\(y\) the vapour composition calculated from the material balance written around the stage \(j\) and stage 1 (consisting of the condenser and the decanter).

The rectifying and extractive profiles are calculated with the following simple differential equations obtained from the above material balance equations:

\[
\frac{dx^o}{dh} = \frac{V}{L^0} (y^* - y^*)
\]  

(5)

In the above equation the value of the ratio \(V/L^0\) and that of the function \(y(x^0)\) can be calculated for the different sections in the following way.

- rectifying section:

\[
\frac{V}{L^0} = \frac{R + 1}{R} \quad \text{and} \quad y = \frac{R}{R + 1} x^0 + \frac{1}{R + 1} x_{D,\text{spec}}
\]  

(6) and (7)

- extractive section:

\[
\frac{V}{L^0} = \frac{R + 1}{R + (R + 1)F/V} \quad \text{and} \quad y = \left( \frac{R}{R + 1} + \frac{F}{V} \right) x^0 + \frac{1}{R + 1} x_{D,\text{spec}} - \frac{F}{V} z
\]  

(8) and (9)

For each composition \(x^0\) we have to decide whether the liquid is homogeneous or heterogeneous (that is the given point is in a stable or in a meta-stable region of the triangle). For the heterogeneous region instead of simple VLE calculation we have to perform VLLE-calculation for the determination of \(y^*\) starting from the given overall liquid composition \(x^0\). The VLLE-calculation involves the determination of the boiling point, the composition of the two liquid phases \((x', x'')\) and the relative amount of the two liquid phases \((\phi = L'/L')\). The equilibrium calculations are performed by the method of Bril et al. (1974) involving also a reliable stability check.

The variation of the overall still composition \((x^0)\) with the time can be calculated from the material balances:
\[
\frac{d(H_0^x D^x)}{dt} = F \cdot z - D^0 x_D^0
\]

where \(H_0^x\) is the overall molar hold-up in the still and the initial condition is defined by the charge composition.

If \(R=\infty\) the rectifying profile follows a simple distillation residue curve and the overall composition of the reflux equals to the top vapour composition \((x^0 = y^0 = y_2)\).

### 2.2 Feasibility calculations

#### 2.2.1 The map of the possible concentration profiles

If for the separation of a low relative volatility (close boiling) mixture we apply an entrainer (E) forming only one azeotrope, a binary heteroazeotrope with the more volatile component (A) the following residue curve map can be obtained (Fig. 2) if we superimpose also the heterogeneous liquid boiling envelope (hlebe).

The heterogeneous liquid boiling envelope contains the compositions of the equilibrium liquid phases \((x', x'')\) at the boiling point of a heterogeneous mixture of given overall composition \((x_o)\). The points \(x_o, x', x''\) are located on a tie line whose end-points are on the heterogeneous liquid boiling envelope.

In the above figure the vapour line and the critical point (CR, where the second liquid phase disappears) are also given. The intersection of the tangent of a heterogeneous residue curve (drawn from \(x^0\)) with the vapour line gives the composition of the vapour phase \((y')\) for \(x^0\). To all points of a tie line only one equilibrium vapour point \((y')\) belongs on the vapour line. The stable node of the residue curves is vertex E. The unstable node is the azeotropic point \((AZ)\) located on the A-E edge within the heterogeneous region. The point AZ is one of the end-points of the vapour line. (The other end point of the vapour line is the point being in equilibrium with the point CR.) The liquid mixture of composition AZ splits into two equilibrium liquid phases \((AZ', AZ'')\). There are two saddle points: vertex A and B. On the residue curve map there are two distillation regions, separated by an unstable separatrix (rbu); in both regions the first cut is the A-E azeotrope.

At finite reflux ratios the possible concentration profiles of the rectifying section must be determined for the specified reflux ratio and the overall product composition \((x_D^0)\). In Fig. 3 a rectifying profile map is shown for \(R=10\) when the prescribed distillate composition is \(AZ'\) (one-phase distillate (point D) is withdrawn from the entrainer-lean phase of the azeotrope).

The stable node of the rectifying profiles (SNr) is assigned by the overall reflux composition located between AZ and AZ'' on the A-E edge since the given reflux ratio cannot be ensured by returning only the entrainer-rich (') phase of the condensate to the column and one part of the entrainer-lean phase must be also returned (two phase reflux). In this case on several plates of the column two liquid phases may appear. In our case SN,
is very close to the azeotropic point. In the rectifying profile map a saddle point ($S_r$) appears (originated from vertex B).

![Rectifying Profile Map](image)

Figure 3: The rectifying profile map at a finite reflux ratio ($R=10, x_D=[0.97, 0.00, 0.03]$)

There is a new boundary (rb) separating the feasible (FR₁, FR₂) and infeasible regions (IR₁, IR₂). This boundary limits the recovery of component A, when the still composition $x_s$ reaches this boundary the specified distillate composition (point D) can not be maintained any longer. In our case rb is located in the homogeneous region, it runs further from D than the hlbe.

If we would apply only one-phase reflux (of composition $AZ''$) the specified distillate composition could not be reached from anywhere and the whole area of the triangle would be infeasible.

On the basis of the analysis of rectifying profile map, we conclude that the following separation steps must be performed in the case of batch addition of the entrainer:

0. Addition of the whole quantity of E (SF) to the binary charge A-B.
1. Start up ($R=\infty$).
2. Production of A (in composition of $AZ'$), two-phase reflux and one-phase distillate.

In the case of continuous feeding of the entrainer the extractive profile map must be studied. The extractive profile map for a finite reflux ratio is shown in Fig 4.

![Extractive Profile Map](image)
Figure 4: The extractive profile map at a finite reflux ratio (R=10, F/V=1/4).

The stable node of the extractive profiles (SN_e) is located on the A-E edge. Though the stable node is farther from D than in the case of F/V=0 (Fig. 3) but it remains in the heterogeneous region. Hence the distillate composition D can be reached on the tie-line without a rectifying section. There is a saddle point (S_s) (originated from vertex B). There is a boundary (eb) separating the feasible (FR_1, FR_2) and infeasible regions (IR_1, IR_2). This extractive boundary limiting the recovery of A is located in the homogeneous region in our case.

On the basis of the analysis of extractive profile map, we conclude that the following separation steps must be performed in the case of continuous entrainer feeding:
0. Addition of a small quantity of E (SF_0) to the binary charge A-B (optional).
1. Start up (R=∞, F=0).
2. Production of A (in composition of AZ’) under continuous feeding of E (R<∞, F>0; two-phase reflux and one-phase distillate).

We can conclude that the separation can be feasible by both batch addition and continuous feeding of E. In order to compare the maximum recoveries of A we must compare the location of the boundaries of extractive and rectifying profiles for the given operating conditions.

Before this comparison we investigate the influence of the operational parameters.

2.2.2. Influence of the operational parameters

The influence of the most important operational parameters is investigated for both batch addition and continuous feeding of the entrainer.

Batch addition of the entrainer

In this case we have to study the effect of the variation of reflux ratio and the amount of the entrainer added.

![Figure 5: The influence of the reflux ratio on the rectifying boundary.](image)

On the decrease of the reflux ratio the rectifying boundary gets closer to the specified distillate composition so the feasibility region decreases. The stable node of the rectifying profiles gets further from the azeotropic point according to the change of $x^*_0$ by the lever rule, this is indicated by the movement of rbu. Under a certain reflux ratio (in our case R<10) the rectifying boundary enters the heterogeneous region. If at the end of Step 2 $x^*_0$ is located in the heterogeneous region on rb the composition of the E-rich phase ($x^{*+}$) is found further from D than rb. However even in this latter case the recovery of A is limited by rb.

If we add a small quantity of entrainer (SF) to the charge the mixture point (M) remains in the homogeneous region. In this case we have a minimum reflux ratio at which the rectifying boundary passes through the point M (Lang et al 2000a).
By the addition of a greater quantity of entrainer the mixture point (M°) may enter the heterogeneous region (Fig. 6.). In this case the mixture can be separated into two phases (M’, M’’). To the A–rich phase (M’) a smaller R_{min} belongs than to the E-rich one (M’’). We have to remark that in the E-rich phase the concentration of A is smaller than it was in the charge.

![Figure 6: The effect of phase splitting in the case of batch addition of a great quantity of entrainer.](image)

For a given reflux ratio and charge composition by the increase of the quantity of the entrainer we can get into the feasible region even if the charge composition is in the infeasible region. On the basis of this fact a minimum amount of entrainer (SF_{min}) can be determined (Lang et al. 2000a).

**Continuous feeding of the entrainer**

In this case we study the effect of the variation of the
- reflux ratio under F/V=constant,
- flow rate of the entrainer (F/V ratio),
- reflux ratio under constant entrainer consumption (SF=const.),

The influence of the variation of the reflux ratio is shown in Fig. 7.

![Figure 7: The influence of the reflux ratio on the extractive boundary (F/V=0.25).](image)
On the decrease of $R$ the extractive boundary approaches to specified distillate point $D$ and under a certain value of $R$ it gets into the heterogeneous region. (The stable node gets somewhat further from the azeotropic point.)

![Diagram](image-url)

**Figure 8**: The influence of the $F/V$ ratio on the extractive boundary ($R=20$).

On the increase of the flow rate of the entrainer (Fig. 8) the feasibility region rises since the extractive boundary is removing from the point $D$. The stable node gets significantly further from the azeotropic point. At a higher value of $F/V$ the stable node can reach the point $E$ and can even leave the ternary diagram, there is a maximum $F/V$ ratio.

When we decrease the reflux ratio under constant entrainer consumption (Fig. 9) we have to simultaneously increase the value of $F/V$.

![Diagram](image-url)

**Figure 9**: The influence of the variation of $R$ on the extractive boundary under $SF=constant$.

The extractive boundary is moving as a resultant of two opposite effects. It would approach to point $D$ on the effect of the decrease of $R$, it would get further from $D$ due to the increase of $F/V$. In our case the influence of the decrease of $R$ is dominant so the extractive boundary is getting closer to $D$ and the feasibility region decreases. On the contrary in the moving of ebu the increase of $F/V$ has dominant effect therefore the stable node is getting further from the azeotropic point.
### 2.3 Comparison of the continuous feeding and batch addition of the entrainer

The continuous feeding (under SF₀=0) and batch addition of the entrainer will be compared under constant entrainer consumption (Fig. 10). The extractive boundary is located further from the specified distillate point D in the region of the entrainer to charge ratios having practical importance. (It can be also seen that the extractive profile (ep) crosses the rectifying boundary even at the end of the production step (Step 2).) The end point of the still-path in the case of continuous feeding (P₂) is further from D than in the case of batch addition (P₁). Hence greater recovery of A can be reached by the continuous feeding.

![Comparison of the CF and BA of the entrainer under SF=const.](image)

### 3. RIGOROUS SIMULATION RESULTS

The feasibility method is based on several simplifying assumptions (such as negligible tray hold-up, constant distillate composition) making the description of the process less accurate. Therefore the feasibility calculations must be usually completed by rigorous simulation calculations. When making the rigorous simulation the usual simplifying assumptions were applied:

- theoretical trays,
- negligible vapour hold-up,
- constant volume of liquid hold-up,
- negligible fluid dynamic lags.

The model equations to be solved are well-known:

a. Non-linear differential equations (material balances, heat balances)

b. Algebraic equations (VLE, VLLE relationships, summation equations, hold-up equivalence, physical property models).

For the solution of the above equations we used the BATCHCOLUMN module of the CHEMCAD 5.0 professional simulator applying the simultaneous correction method. The solution method is based on quasi-steady state approximation.

#### 3.1 Example

In the example studied the aim of the separation to remove 99% of component A in Step 2 from beside B from the charge of composition: \( x_{ch} = [0.05, 0.95, 0] \). (In Step 3 B can easily purified from E.) The quantity of the charge: \( U_{ch} = 100 \) moles \( (U_{ch}^{vol} = 7.23 \text{ dm}^3) \). The column contains 22 theoretical plates including the reboiler (plate 22) and the total condenser with the decanter (plate 1). The volumetric liquid hold-up: 50 ml/plate. The heat duty of the reboiler: \( Q_{n+1} = 1.5 \) kW. Pure entrainer of boiling point liquid is used.

*Binary batch distillation*
First conventional batch rectification was simulated without the application of entrainer. It was not possible to remove component A from beside B to the prescribed extent even if a very high reflux ratio (R=40) was applied. We were able to remove only the 98.1% of A with unacceptably high loss of B (85.8%).

Even at the end of the start-up period under R=∞ the concentration of A was not high enough (35%). In spite of the fact that there is no azeotrope under the given number of stages and hold-up high x_{D,A} can not be obtained because of the low relative volatility. (We were not able to obtain A of great purity under R=∞ even if the hold-up was neglected, a distillate of 82% was then received.)

In the moment when the concentration of A in the distillate decreased below its concentration in the charge (the condition of x_{D,A}<x_{ch,A} was first satisfied) only the 71.2% of A was removed with a loss of B of 34.4%. We concluded that the separation cannot be performed by binary batch distillation due to the unfavourable VLE-conditions and the application of separating agent is necessary. First the traditional batch addition of the entrainer then its continuous feeding was studied.

**Batch heteroazeotropic distillation (batch addition of the entrainer)**

Since the simple binary separation was not sufficient we applied an entrainer for promoting the separation. First Step 1 was studied.

a. Start-up under R=∞ (Step 1)

By the addition of the entrainer the volume of the mixture to be distilled increases. (If we apply 200 moles of E, (SF/U_{ch}=2.0) it increases to 10.83 dm³.) If we supply the condenser with a decanter (with a volume ensuring convenient residence time for the separation of the condensate) the hold-up also rises, e. g. in the case of a decanter of 150 ml U_{vol}=200 ml.

With the above parameters at the end of Step 1 the condensate is heterogeneous, x_{1}^{0}=[0.790,0.168,0.042] but on the plates of the column there is only one liquid phase because of the considerable concentration of B (e.g. x_{2}=[0.634,0.320,0.046].)
The composition of the condensate at the end of Step 1 depends on the quantity of the entrainer (Table 1) and the hold-up (Table 2)

<table>
<thead>
<tr>
<th>SF/U_{ch}</th>
<th>0.5, 0.75,1,2, 3, 5</th>
<th>x_{1}^{0} hetero.plates</th>
</tr>
</thead>
</table>

Table 1. The influence of the quantity of the entrainer on the condensate composition at the end of Step 1 (U_{vol}=200 ml)

On the increase of the amount of E the separation becomes better, the mole fraction of A and that of E rise in the condensate to the detriment of the content of B. Under the given conditions we had to apply more than 10 moles of E for each mole of A of the charge to have heterogeneous condensate.

<table>
<thead>
<tr>
<th>U_{vol}</th>
<th>50,100,150,200,250,300</th>
<th>x_{1}^{0} hetero.plates</th>
</tr>
</thead>
</table>

Table 2. The influence of the decanter hold-up on the condensate composition at the end of Step 1 (SF/U_{ch}=2.0)

x_{1}^{0} depends strongly on the decanter hold-up. On the increase of the decanter hold-up the separation becomes worse, the mole fraction of B strongly rises in the condensate to the detriment of the two other components. The number of the heterogeneous plates is decreasing and at U_{vol}=250 ml the second liquid phase disappears even in the decanter.

According to the above experiences the minimum amount of entrainer (SF_{min}) necessary to attain with the condensate composition x_{1}^{0} the heterogeneous region also strongly depends on the hold-up. For example for U_{vol}=50 ml already at SF/U_{ch}=0.5 the upper three plates are heterogeneous and the condensate composition is: x_{1}^{0}=[0.894,0.032,0.074].

b. Step2 with phase separation
After the start-up period Step 2 was studied. First we tried to perform the removal of A with one phase reflux (E-rich phase) and distillate (E-lean phase). In this way the reflux ratio obtained was very low (R<0.05) and already at the beginning of Step 2 the condensate became homogeneous indicating that liquid-liquid phase separation can be ensured only by refluxing not only the total quantity of the E-rich phase but also one part of the E-lean phase.

The results obtained with two-phase reflux for the different ratios withdrawn of the E-lean phase (β) as distillate are shown in Table 3, where the quantity of the components gained in the decanter during the heterogeneous part of Step 2 can be seen (sd)

<table>
<thead>
<tr>
<th>Case</th>
<th>β</th>
<th>1-β</th>
<th>sdₐ, sd₉, sdₑ, moles</th>
<th>ηₐ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>0</td>
<td>0.33</td>
<td>1.438 0.540 0.114</td>
<td>0.510</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1.458 0.510 0.114</td>
<td>0.510</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.67</td>
<td>1.582 0.300 0.164</td>
<td>0.510</td>
</tr>
</tbody>
</table>

Table 3. The influence of the ratio refluxed of the E-lean phase on the removal of A

We can see that even if a very great part of the E-lean phase was refluxed (Case 3, where the reflux ratio was around 39) only less than 1/3 of A was removed while the condensate remained heterogeneous. This means that in the greater, remaining part of Step 2 the decanter is unnecessary. Hence we investigated the case where the decanter was omitted.

c. Step 2 without phase-separation

First we studied the first, shorter part of Step 2 where the condensate is heterogeneous. We applied a reflux ratio of 9, which is near to the average reflux ratio of Case 2. The duration of the distillation and so the energy consumption were the same as in Case 2.

Without phase separation - letting unchanged the decanter hold-up (U₁vol=200 ml)- we obtained practically the same quantity of distillate as before with the following composition sd=[1.431, 0.540, 0.124 moles]. Comparing this result with that obtained with phase separation we can state that the change is very small.

The quantity of A slightly decreased, that of B and E slightly increased in the product. (The quantity of A slightly decreased, that of B and E slightly increased in the product). When we took into consideration that without decanter the hold-up decreases (U₁vol=50 ml) we obtained sd=[1.813, 0.110, 0.160 moles], that is, the gain of A significantly increased and the loss of B considerably decreased. (The loss of E slightly rose.) This means that in the first part of Step 2 the separation is significantly better without decanter thanks to the diminution of the hold-up. The condensate composition was already much more favourable at the end of Step 1: x₁⁰=[0.92, 0.01, 0.07] against x₁⁰=[0.76, 0.17, 0.07] obtained with decanter.

On the basis of the results of the above comparison the further calculations for the whole Step 2 were carried out without separating the condensate into two liquid phases. The prescribed removal of A (under R=9) was achieved within 1.60 h with the following distillate composition: sd=[4.95, 23.67, 0.41 moles], that means a loss of B of 24.9 %. (In the instantaneous distillate the ratio of components A and B (xₑₐ / xₑ₉) decreased for the first time below their ratio in the charge (xₙₐ / xₙ₉) at t=0.83 h when the composition of the distillate product: sd=[4.68, 10.04, 0.37 moles]).

The evolution of the distillate composition x₀ with the time is shown in Figure

Figure The evolution of the distillate composition x₀ with the time (batch addition, SF/U₉=2, R=9)

At the beginning of Step 2 for a very short time (~0.15 h) the distillate is heterogeneous as it can be seen in Figure where two concentration profiles are depicted in the triangular diagram. Just after the end of Step 1 (t=0) on 4 plates two liquid phases occur. Later, at t=0.15 h only the condensate is heterogeneous.
Figure The concentration profile in the first part of Step 2 with heterogeneous distillate

In the remaining part of Step 2 there is only one liquid phase in the whole column (Figure ).

Figure The concentration profile in Step 2 with homogeneous distillate

**Batch heteroazeotropic distillation with continuous feeding of the entrainer**

On the basis of the promising results of the feasibility studies the continuous feeding of the entrainer was also investigated. In the first calculation the entrainer feeding arrived at the 7-th plate (the length of the rectifying section is the half of that of the extraction section) with a molar flow rate of 100 mole/h. The decanter was omitted. The 99 % of A (under R=9) was removed within 1.51 h with the following distillate composition: $\text{sd}=[4.95,22.19,1.21\text{ moles}]$, that means a loss of B of 23.4 %. (In the instantaneous distillate the ratio of components A and B ($x_{D,A}/x_{D,B}$) decreased for the first time below their ratio in the charge ($x_{ch,A}/x_{ch,B}$) at $t=1.27$ h when the composition of the distillate product: $\text{sd}=[4.83,17.93,1.13\text{ moles}]$).

The evolution of the distillate composition $x^0_{D}$ with the time is shown in Figure

At the end of Step 1 before the start of the entrainer feeding the distillate had the same composition as it was in the case of binary distillation, that is, $x_{D,A}$ was not high enough. For a short period ($\Delta t=0.07$ h) $x_{D,A}$ was increasing and $x_{D,B}$ is decreasing. Then $x_{D,A}$ took its maximal and $x_{D,B}$ its minimal value, respectively. During the whole Step 2 $x_{D,B}$ was relatively high therefore the condensate remained always homogeneous. The evolution of the concentration profile of the column in the time is shown in triangular diagram (Figure ).

During the whole Step 2 the whole concentration profile remained in the homogeneous region.

Comparing the above results with those obtained for the batch addition we can conclude that the continuous feeding is competitive with the traditional batch addition and in the given case it gave even better results the same removal of A was achieved besides somewhat smaller loss of B and lower entrainer and energy consumption.

Before making a comparison more complete between the batch addition and continuous feeding of the entrainer the influence of the most important operational parameters was investigated for both methods.

### 3.2 Influence of the operational parameters

The influence of the most important operational parameters is investigated for both batch addition and continuous feeding of the entrainer. The following input data were always kept constant: $N=22$, $Q_{N+1}=1500$ W and $U_{j}^{vol}=50$ ml/plate $(j=1,\ldots,N)$.

**Batch addition of the entrainer**

In this case the whole quantity of E is added to the charge at once and there is no continuous feeding ($F/V=0$). We studied the effect of the variation of

- the reflux ratio and
- the amount of the entrainer added.

Step 2 is finished when for the instantaneous distillate composition the following criterion is satisfied: $x_{D,A}\leq 0.005$.

The influence of the variation of R was studied for 4 different amounts of entrainer (SF=10, 100, 200 and 400 moles). On the increase of the reflux ratio the distillate withdrawal rate D decreases, the length of Step 2 ($\Delta t_2$) and proportionally to $\Delta t_2$ the energy consumption (SQ) increase (Table 1a-c).
Table 1. The influence of the variation of the reflux ratio (BA)

a. SF=10 moles

b. SF=100 moles c. SF=200 moles

The variation of the relative loss of B \( (\eta_B) \) is depicted in Fig. 13.

Figure 13. The influence of the reflux ratio on the relative loss of B (BA; SF/U_ch=0.1, 1.0, 2.0, 4.0)

Studying the curves obtained for the different amount of E we can conclude that
- When a very small amount of E is applied (curve B1) though the loss of B decreases in a monotone way on the increase of R the loss remains very great (\( \eta_B > 0.65 \)) even if R is very high.
- In the case of SF/U_ch=1.0 first (when R \( \leq 10 \)) the loss significantly decreases on the increase of R (curve B2) then it hardly changes.
- In the third case (SF/U_ch=2.0, curve B3) there is an optimum reflux ratio (\( R_{opt} = 5 \)) where \( \eta_B \) has a minimal value. Above \( R_{opt} \) the increase of R has detrimental effect, the loss of B rises.
- In the case of SF/U_ch=4.0 (curve B4) the value of \( R_{opt} \) is still lower (\( R_{opt} = 3 \)).

The loss of entrainer decreased in a monotone way on the increase of R in each case.

The influence of the amount of the entrainer (SF) was investigated (Fig. 14, Table ) under three different reflux ratios (R=1,4,10).

Figure 14. The influence of the amount of entrainer on the relative loss of B (BA; R=1,4,10)

On the increase of SF the duration of Step 2, the amount of the distillate (SD) decreased in a monotone way in each case. The loss of B also fell but less and less sharply. The \( \eta_B \)- SF curve is the steepest for the lowest R (R=1) and it is the least steep for the highest R (R=10). For the smallest amount of E (SF=50 moles) the best separation is achieved for the highest R whilst for the greatest amount of E the lowest R provided the best separation. However for the medium SF values there is a region where the medium R (R=4) gave the best separation, that is in this region there is an optimum reflux ratio (\( R_{opt} \), whose value is not far from 4). The loss of E decreases with increasing SF due to the strong decrease of SD but the E-content of the distillate \( (x_{D,E,av}) \) increases.

Continuous feeding of the entrainer

First the whole quantity of E was introduced to the column continuously (SF_0/SF=0). We studied the effect of the variation of the
- reflux ratio (under constant entrainer flow rate, F=const.),
- flow rate of the entrainer,
- entrainer feed plate.

In the above cases Step 2 was finished applying the criterion used for the batch addition. In these cases since the duration of Step 2 changes the quantity of entrainer is not kept constant. We also investigated the influence of the variation of
- R under constant entrainer consumption and constant amount of distillate (SF=const., SD=const.)
- R under constant entrainer and consumption (SF=const., SQ=const.)

Finally we studied the influence of the variation of the
- ratio of the entrainer quantity added in batch (SF_0/SF).

The influence of the reflux ratio under F=const. (Fig. 15, Tables a,b,c ) was investigated for three different flow rates of E (F=10,100,250 moles/h).

Figure 15. The influence of the reflux ratio on the relative loss of B under F=constant (CF; F= 10,100,250 moles/h).

On the raise of R the duration of Step 2 increases so both the entrainer and the energy consumptions increase considerably. The loss of B falls in each case but less and less sharply. The loss of E also diminishes.

The influence of the feed flow rate of the entrainer (Fig. 16, Tables a,b,c ) was investigated for three different reflux ratios (R=4,10,20).

Figure 16. The influence of feed flow rate of the entrainer on the relative loss of B (CF; R=4,10,20).
When raising the value of F the loss of B gets smaller and the stopping criterion is fulfilled earlier (Δt₂ decreases) in each case. Though the entrainer content of the distillate (x_{D,E,av}) increases the loss of E (d_{E}) due to the diminution of the amount of distillate decreases.

In the case of continuous feeding of E the feed stage location provides an additional degree of freedom compared with the batch addition. The influence of the feed stage location was investigated for three different reflux ratios (R=10,4,20; Fig. 17 a, Tables a,b,c) and for three different entrainer flow rates (F=100,50,250 moles/h; Fig. 17 b, Tables a,d,e).

Figure 17 a. The influence of feed stage location on the relative loss of B (CF; F=100 moles/h, R=10,4,20).

Figure 17 b. The influence of feed stage location on the relative loss of B (CF; R=10, F=100,50,250 moles/h).

On the increase of the length of the rectifying section to the detriment of the extractive section the loss of B rose and the duration of Step 2 and the loss of entrainer decreased. From the point of view of the separation of A/B in each case the optimum feed stage was the upper plate of the column (f_{opt}=2).

So far when investigating the influence of the reflux ratio the entrainer consumption (SF) was not kept constant. The effects of the variation of R were also studied under SF=const. First besides SF the quantity of the distillate remained unchanged (SD=const.) With the increase of R the time necessary for obtaining the same quantity of distillate increases since

\[ \Delta t_{2,new} = SD \times (R_{new} + 1) / V_{2} \]  

where V₂ is the vapour molar flow rate arriving at the condenser.

The energy consumption increases proportionally to Δt₂ since SQ= Q * Δt₂  and Q is unchanged. Since the heat balances are taken into consideration V₂ does not remain constant when varying R. Therefore we had to ensure the simultaneous constancy of SF and SD in an iterative manner. First we calculated the new value of F by the assumption of unchanged V₂ by

\[ F_{new} = F \times (R + 1) / (R_{new} + 1) \]

and we determined with the first simulation calculation the time (Δt₂,corr) necessary for obtaining SD moles of distillate. Then for the second simulation calculation F_{new} was so corrected that the SF=const. condition be satisfied (F_{new,corr} = SF / Δt₂,corr). In the majority of the cases Δt₂ did not change more and so one correction of F_{new} was enough. The results are shown in Fig. 18 and Table .

Figure 18. The influence of the reflux ratio on the relative loss of B under constant entrainer consumption and amount of distillate (CF; SF = 205 moles, SD = 15 moles).

On the raise of R the recovery of A increased and the loss of B decreased in a monotone way and the loss of E remained almost constant. In this case there was no optimum reflux ratio contrary to the extractive batch distillation separation of maximum azeotropes (Lang et al. 2000a, 2000b) where above a certain reflux ratio (R_{opt}) the separation became worse and η_{A} decreased.

Then the influence of the reflux ratio was investigated under the simultaneous constancy of entrainer and heat consumption. These conditions can be ensured in the easiest way by keeping the duration of Step 2 constant (Δt₂ = 1 h). In this case with the raise of R the amount of distillate decreases by Eq. 1. In Fig. 19 the variation of η_{A} and η_{B} are depicted in the function of R for three different entrainer flow rates (F=10, 100, 250 moles/h).

Figure 19. The influence of the reflux ratio on the recovery of A and the relative loss of B under constant entrainer and heat consumption (CF; Δt₂ = 1 h, F=10, 100, 250 moles/h).

On the increase of the reflux ratio the concentration of A in the distillate (x_{D,A,av}) increased that of B decreased. The entrainer concentration of the distillate (x_{D,E,av}) had a minimum value in each case (e.g. in the case of F=250 moles/h at R=4). Both η_{A} and η_{B} diminished in a monotone way. The extent of the decrease of η_{B} gets smaller and smaller (|dη_{B}/dR| diminishes). The entrainer flow rate had slight influence on the η_{B}-
R curves. However it had very significant effect on the $\eta_A$-R curves. At the highest value of F (F=250 moles/h) $\eta_A$ remained in a large region (between R=1 and R=10) high whilst in this $\eta_B$ strongly decreased. This fact suggests that there is an optimum reflux ratio ($R_{\text{opt}}$) where $\eta_A$ is still high and $\eta_B$ is already low.

**Mixed addition of the entrainer.**

So far when making rigorous calculations all the quantity of the entrainer was introduced continuously to the column (SF$_0$/SF=0). In this case Step 2 begins with a the distillate of relatively low content of A as it was shown before (Fig. ). On the other hand the batch addition of the entrainer provided higher content of A at the beginning of Step 2. Therefore we investigated the combination of the batch addition and continuous feeding of the entrainer. We added one part of E to the charge in Step 0 (SF$_0$) and the other part continuously during Step 2 (SF$_2$). For the mixed addition of E we studied the influence of the variation of the ratio SF$_0$/SF (where SF=SF$_0$+SF$_2$). When changing SF$_0$/SF SF was kept constant and duration of Step 2 was also unchanged ($\Delta t_2$=1 h). This study (Fig. 20, Table ) was performed for two different entrainer to charge ratio (SF/$_{\text{Uch}}$=1 and 2).

Figure 20. The influence of SF$_0$/SF on the recovery of A and the relative loss of B under constant entrainer and heat consumption (mixed addition; f= 2, $\Delta t_2$ = 1 h, R=10, SF=100 and 200 moles).

The recovery of A had a maximum at SF$_0$/SF=0.6 (around this maximum not sharp there was a plateau) for both SF values. The loss of B had a minimum in both cases (for SF= 100 at SF$_0$/SF=0.4 and for SF= 200 at SF$_0$/SF=0.7).

In both cases at the medium values of SF$_0$/SF (e.g. at SF$_0$/SF=0.5) both the recovery of A and the loss of B was significantly more favourable than at the very low (e.g. SF$_0$/SF=0.1) and very high (e.g. SF$_0$/SF=0.9) values of SF$_0$/SF. These results suggest that there must be an optimum SF$_0$/SF ratio (where $\eta_A$ is high and simultaneously $\eta_B$ is low). By all means in our case SF$_0$/SF=0.5 provided an efficient separation and probably it is not far from the optimum. The evolution of the distillate composition for this case is shown in Fig. 21.

Figure 21 The evolution of the distillate composition in the case of the mixed addition of the entrainer (f= 2, $\Delta t_2$ = 1 h, R=10, SF= 200 moles ?)

**3.3 Comparison of the different entrainer addition methods**

We compared the traditional batch as well as the newly proposed mixed addition (SF$_0$/SF=0.5) and continuous feeding of the entrainer under constant entrainer and heat consumption. The duration of Step 2 was fixed. The comparison was performed for four different entrainer quantities (SF/$_{\text{Uch}}$=0.5,1,1.5,2) and two different reflux ratios (R=4 and 10). The duration of Step 2 was fixed (for R=10 $\Delta t_2$ = 1 h and for R=4 $\Delta t_2$ = 28 min) so SF and SQ remained unchanged when varying R?). Fig. 22 and Table show the results.

Figure 22. Comparison of the different entrainer addition methods (??)

The best separation (highest recovery of A, lowest loss of B) was obtained by the mixed addition in all 8 cases. The continuous feeding was competitive with the batch addition. It resulted in lower loss of B in all 8 cases than the batch addition. Regarding the recovery of A for the higher reflux ratio (R=10) it provided higher values for the higher entrainer quantities (SF/$_{\text{Uch}}>1$). For the lower reflux ratio (R=4) the continuous feeding yielded lower recovery of A for the whole region of SF/$_{\text{Uch}}$ studied.

**4. CONCLUSION**

The method of Lelkes et al. was extended for the assessment of the feasibility of the heteroazeotropic distillation in a batch rectifier. By this method the separation of a low relative volatility, zeotropic mixture with an entrainer forming a binary heteroazeotrope with one of the components was studied. The calculations were performed for the mixture dichloro-methane – acetone using water as heterogeneous entrainer. For the vapour-liquid-liquid equilibrium calculations the method of Bril et al. was applied. The possibility of continuous feeding of the entrainer besides its usual batch addition was also studied. Comparing the continuous feeding and the batch addition of the entrainer we conclude that the feasibility region of the
continuous feeding can be greater under the same entrainer and energy consumption than in the case of the batch addition. The rigorous simulation results to be published elsewhere also verified the feasibility and potential benefits of the continuous entrainer feeding.

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