

Synthesis, experiments and simulation of heterogeneous batch distillation processes

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Abstract

The presence of azeotropes in multicomponent mixtures complicates the design of batch distillation separation processes widely used in pharmaceutical and speciality chemical industries. Most of those processes include the use of a homogeneous entrainer to ease the separation. We describe novel methods to break azeotropes using an entrainer that is partially miscible with one of the initial binary mixture components. We depict some of the advantages of heterogeneous batch distillation processes: more design alternatives for the separation of an azeotropic binary mixture than with homogeneous batch distillation, batch distillation boundary crossing thanks to a controlled reflux of the entrainer-rich phase, simplified distillation sequences as a consequence of less distillation tasks. Three examples based on the separation of non-ideal azeotropic or close boiling point binary mixtures through heterogeneous batch distillation are simulated using a commercial batch distillation package. Experiments validate the simulated separation of a minimum boiling azeotropic mixture. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Heterogeneous batch distillation; Azeotropic mixture; Close boiling mixture; Heterogeneous entrainer

1. Introduction

Batch distillation is a common solvent recovery technology in pharmaceutical and speciality chemical industries and help deal with increasing economic incentives and environmental regulations. Azeotropes in waste-solvent streams complicates both synthesis and design steps of batch distillation processes. Azeotropic ternary diagrams may display distillation boundaries. As those boundaries outline distillation regions, the batch distillation products sequence depends on the initial feed composition in the still (Bernot, Doherty, & Malone, 1990, 1991) and separation of an azeotropic mixture into its pure components may require several batch distillation tasks. The complexity of azeotropic batch distillation synthesis and design steps has implicitly restricted the choice of an entrainer miscible with the azeotropic binary mixture to which it is added to. We suspect that the use of a heterogeneous entrainer intro-

ducing a phase split with one of the binary mixture component will likely increase the number of process alternatives and even achieve azeotropic separations impossible with homogeneous systems. The scarcity of published work on heterogeneous batch distillation (Düssel & Stichlmair, 1995; Köhler, Haverkamp, & Schadler, 1995) and industrial interests prompted us to address the feasibility of batch distillation using a heterogeneous entrainer for the separation of azeotropic and close boiling binary mixtures.

Design and synthesis tools for heterogeneous distillation were first introduced by Pham and Doherty (1990a,b,c). They showed that synthesis of heterogeneous continuous distillation processes for the separation of non-ideal mixtures using a heterogeneous entrainer involves the analysis of residue curve maps as in the homogeneous system case. Residue curve maps can first be used to select feasible entrainers and then to establish the associated distillation column sequence. Then process parameter optimal values are looked at. But they depend on the entrainer choice because it largely determines the azeotropic distillation process efficiency.

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Thermodynamics, product sequence and batch tasks assessment tools are already available for batch distillation process. Batch distillation regions that determine the product sequences may be obtained with the algorithm developed by Ahmad, Zhang, and Barton (1998) for homogeneous mixtures and the heterogeneous liquid boiling envelope can be determined from liquid–liquid–vapour equilibrium data (Pham & Doherty, 1990a). Then, a State-Task Network (Safrit & Westerberg, 1997) relating product cuts to column configuration can be established. In our work, only regular and inverted batch column configurations are considered.

The entrainer screening issue for homogeneous batch azeotropic distillation has been looked at (Bernot, Doherty, & Malone, 1991; Düssel & Stichlmair, 1995) but was incomplete until a recent paper addressed the topic and that of heterogeneous batch distillation (Rodriguez-Donis, Gerbaud, & Joulia, 2000a,b). In this paper, we intend to demonstrate a few advantages of heterogeneous batch distillation (HBD) processes through several examples in which feasibility and synthesis is assessed and demonstrated through experiments and simulation with a batch process simulator, ProSimBATCH® (ProSim SA (France)). HBD synthesis is in particular shown to differ significantly from homogeneous batch distillation synthesis.

2. Interest of heterogeneous batch distillation

Rodriguez-Donis, Gerbaud, and Joulia (2000b,c) set up HBD process synthesis key points:

- A complete set of rules for the selection of entrainers can be defined from the analysis of all feasible ternary diagrams. As a general rule, a potential entrainer is defined as a component partially miscible with one of the initial mixture component and which generates a ternary diagram where the heterogeneous azeotrope (binary or ternary) or one of original component vertex is a node. There are some cases where it is possible to obtain a feasible batch distillation process even though the liquid–liquid–vapour envelope does not transverse the distillation boundary dividing the regions that contain both original components.
- Comparison of heterogeneous versus homogeneous systems shows that the number of ternary diagrams suitable for a separation is about three times higher for the heterogeneous case. Hence, design alternatives are increased. Besides, the liquid–liquid phase split may reduce the number of distillation tasks. Assuming a complete phase split, the separation of the original mixture components can always be carried out considering one to three batch distillation tasks involving either a single column configuration

(regular or inverted) or a combination of both column types.

- A small amount of entrainer needs to be added to the initial binary mixture if the heterogeneous azeotrope (binary or ternary) is located in the same distillation region than the binary azeotrope to be separated. The separation of both original components can be performed using a single batch regular column where the component immiscible with the entrainer is recovered in the distillate while the miscible component is obtained in the still at the end of the process. The synthesis method employed in homogeneous systems considering total reflux and high number or trays to determine the still path and distillate cut sequences can not be extended right away to heterogeneous batch distillation process.
- Reflux ratio can be composed either by the entrainer-rich phase or by a combination of the two liquid phases contained in the decanter, depending whether or not the entrainer vertex limits the distillation region where both heterogeneous azeotropic point and miscible component vertex are located. In both cases an appropriate initial entrainer composition and reflux ratio policy allow the still path to cross batch distillation boundaries if the initial ternary composition is placed in a batch region which is not limited by the miscible component vertex.

3. Minimum boiling temperature mixture separation with a heterogeneous entrainer

Feasibility of HBD is first illustrated with the separation of the water–acetonitrile azeotropic binary mixture with the addition of acrylonitrile as a heterogeneous entrainer. Experiments and simulations are carried out to validate the product sequence and the predicted still path.

A water–acetonitrile minimum temperature azeotrope is to be separated using acrylonitrile as an entrainer (Fig. 1). Acrylonitrile forms a heteroazeotrope with water. Singular points stability and boiling temperature are shown on the ternary diagram on Fig. 1. [sn] stands for stable nodes; [sa] for saddle and [un] for unstable nodes. Two batch distillation boundaries join the heteroazeotrope to the acetonitrile vertex and to the homoazeotrope. Three batch distillation regions overlapping the liquid–liquid–vapour zone are defined where the product sequence is unique.

3.1. Feasibility analysis

The feasibility analysis tells us that either an inverted batch column or a regular batch column — can be thought up to separate the water–acetonitrile azeotropic mixture.

- The inverted column (Fig. 1a) is fed in the decanter with mixture A (usually the water–acetonitrile homoazeotrope) plus organic phase L_1 and acrylonitrile. The resulting ternary feed F rests in the batch region containing the entrainer vertex. While processing, pure acetonitrile is completely removed as bottom product P_1 . At the end of the single batch task, two liquid phases stay in the distillate drum. Phase L_2 containing water ($x = 95\%$) and acrylonitrile but no acetonitrile is removed as a product P_2 , to undergo further purification if needed. The entrainer-rich phase L_1 may stay in the decanter for a new cycle of separation water–acetonitrile. Entrainer make-up could compensate losses during P_2 removal.
- The regular column (Fig. 1b) is fed in the still with a ternary mixture located in a batch region different from the stripping one. Aqueous phase L_2 is removed during the operation as product P_1 from the decanter whereas the entrainer rich phase L_1 is refluxed. After the single batch task, the still contains pure acetonitrile taken as product P_2 . The phase L_1 is then put back in the still for a new cycle.

The lowest amount of entrainer added to the water–acetonitrile mixture is obtained for the regular column case as seen on Fig. 1 diagrams with feed F position. This happens because the binary azeotrope acetonitrile–water is placed in the same batch distillation region than the heterogeneous azeotropic point. Notice that using a homogeneous entrainer inducing the same residue curve diagram without the dual liquid phase zone is impossible. Such a distillation would leave an entrainer–water azeotropic mixture after the first distillation task that would have to be separated again. This readily proves that HBD increases the number of process alternatives for the separation of azeotropic mixtures.

3.2. Methods and tools

Batch distillation is simulated using ProPhyPlus[®] (properties server) and ProSimBATCH[®] (batch process simulator). Column technological features and operating conditions described below are put into the simulator. The UNIQUAC (minimum azeotrope separation example) or NRTL model (maximum azeotrope and close boiling separation examples) is used to represent the phase equilibrium with binary parameters taken from the DECHEMA tables. Calculated equilibrium consistency is checked with ProPhyPlus[®] against experimental data available in the DECHEMA tables. A slight curvature of the heteroazeotrope–homoazeotrope boundary is noticed, in particular near the homoazeotrope point (see Fig. 3 below). The temperature dependent liquid–liquid–vapour envelope applies to the column trays and the liquid–liquid envelope at 25°C to the subcooled condenser and to the decanter. The column model consists of usual tray by tray MESH (Material balance, Equilibrium, Summation of fractions and Heat balance) equations which are solved for the whole column, decanter included and taking into account the liquid–liquid demixing. Numerical treatment of the Differential Algebraic Equation (DAE) system and discrete events handling is performed with DISCO, a numerical package for hybrid systems with DAE solver based on Gear's method (Sargousse, Lelann, Joulia, & Jourda, 1999). Reflux ratio is set to six at the beginning of the distillation step. Afterwards, it gradually increases to keep a constant interface level in the decanter, as in the experiments.

Simulated operating conditions are as follows: column geometrical parameters match the laboratory column ones used afterwards; total reflux operation step duration is set to 1 h and is followed by a heterogeneous distillation step, during which aqueous

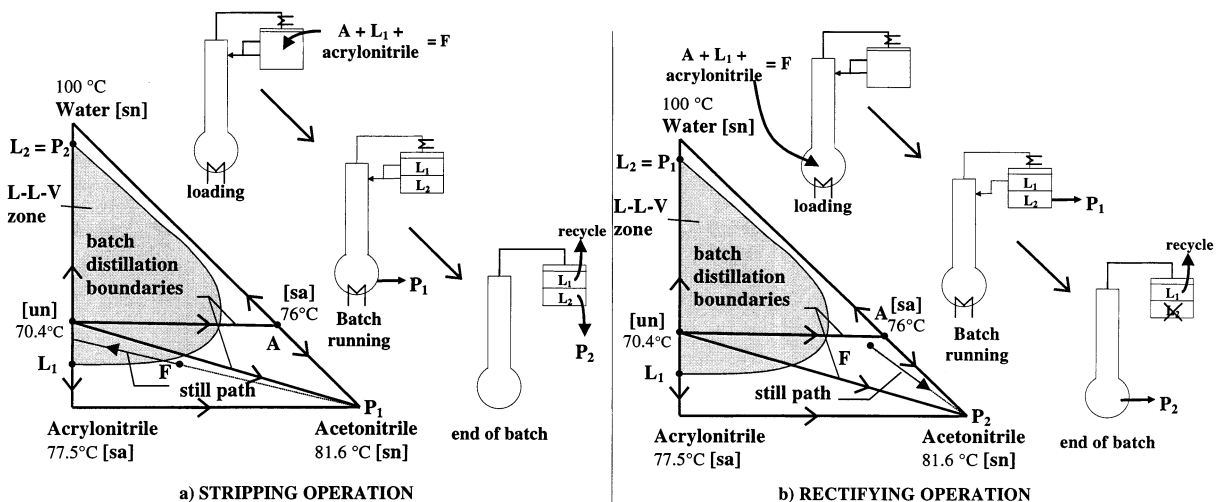


Fig. 1. Heterogeneous batch distillation feasibility (water–acetonitrile–acrylonitrile system).

Table 1
Experimental and calculated molar compositions and quantities during heterogeneous regular column batch operation of a water–acetonitrile–acrylonitrile ternary mixture

| | Simulation results | | | Experimental results | | |
|--|--------------------|---------------------------------|--------------------|----------------------|---------------------------------|--------|
| | Quantity (g) | Molar fraction | | Quantity (g) | Molar fraction | |
| Initial still content | 672.85 | H ₂ O | 0.262 | 672.85 | H ₂ O | 0.262 |
| | | C ₂ H ₃ N | 0.673 | | C ₂ H ₃ N | 0.673 |
| | | C ₃ H ₃ N | 0.065 | | C ₃ H ₃ N | 0.065 |
| Heavy aqueous phase (P ₂) Distillate + Decanter $T_{\text{overhead}} = 72\text{--}74^\circ\text{C}$ | 96.2 | H ₂ O | 0.948 | 108.3 | H ₂ O | 0.918 |
| | | C ₂ H ₃ N | 0.033 | | C ₂ H ₃ N | 0.051 |
| | | C ₃ H ₃ N | 0.019 | | C ₃ H ₃ N | 0.031 |
| Light phase (reflux) Decanter (+ pipes during experiments) $T_{\text{overhead}} = 72\text{--}74^\circ\text{C}$ | 60.2 | H ₂ O | 0.174 | 70.3 | H ₂ O | 0.076 |
| | | C ₂ H ₃ N | 0.204 | | C ₂ H ₃ N | 0.356 |
| | | C ₃ H ₃ N | 0.622 | | C ₃ H ₃ N | 0.568 |
| Distillate 2nd cut $T_{\text{overhead}} = 74\text{--}81^\circ\text{C}$ | 38.6 | H ₂ O | 0.032 | 35.6 | H ₂ O | 0.014 |
| | | C ₂ H ₃ N | 0.600 | | C ₂ H ₃ N | 0.663 |
| | | C ₃ H ₃ N | 0.368 | | C ₃ H ₃ N | 0.323 |
| Trays hold-up | 42.76 | H ₂ O | 3×10^{-8} | Not measured | | |
| | | C ₂ H ₃ N | 0.994 | | | |
| | | C ₃ H ₃ N | 0.006 | | | |
| Final still content (product P ₁) | 435.1 | H ₂ O | 3×10^{-5} | 408.6 | H ₂ O | 0.0010 |
| | | C ₂ H ₃ N | 0.994 | | C ₂ H ₃ N | 0.9985 |
| | | C ₃ H ₃ N | 0.006 | | C ₃ H ₃ N | 0.0005 |
| C ₂ H ₃ N mass recovery yield | 83.2% | | | 78.7% | | |

phase is removed as distillate, is undertaken until the molar fraction of water into the still is less than 0.001. The time calculated for this step equals to 2.5 h. Later, a second batch homogeneous distillation step is performed without reflux to recover the remaining acrylonitrile into the column. It is ended when the column overhead temperature reaches 81°C. The second batch step duration is calculated to be 3 min and leads to the final mole fraction of acetonitrile in the still, $x = 0.994$.

Batch experiments are carried out in a small laboratory column made of 50 trays (including still and condenser) to evaluate the relevancy of the synthesis and simulation achieved so far. Liquid tray hold-up amounts to 1.25 and to 50 ml in the decanter. Condenser is subcooled to 25°C. A phase split can occur in the column and in the decanter where the aqueous phase is removed while the organic phase is refluxed into the column. Pressure equals to 1 and a 0.05 atm pressure drop is estimated. Boiler heat flow rate equals to 205 W.

After 1 h of total reflux operation, distillation starts. To match the simulation, it is ended after 2.5 h. At this time the column overhead condensed vapour has become homogeneous. Overhead vapour temperature stays around 72–74°C. The decanter heavy phase is

poured into the aqueous distillate tank before analysis. Decanter, reflux pipe and condenser pipes light phases are mixed together and analysed as well. Distillation is then continued without reflux to recover as much entrainer as possible in shortest operation time. This new distillate cut is related to an overhead vapour temperature between 74 and 81°C and is obtained in less than 5 min. Finally, the still content is weighted.

Analysis of the still composition is performed every 15 min. Analysis of the decanter content is made at the end of the first distillation step. Gas chromatography is used to measure the acetonitrile and acrylonitrile contents. Karl Fisher technique is used for the water content determination. Compositions results are in mole fractions and quantities are in mass.

3.3. Comparison of experimental and simulated results

The mean value obtained from three experiments are shown in Table 1. Fig. 2 shows the evolution of the still composition with time during the first distillation step. Water is quickly removed from the still and almost pure acetonitrile remains. A more detailed analysis of the results is given below in comparison with the simulation results.

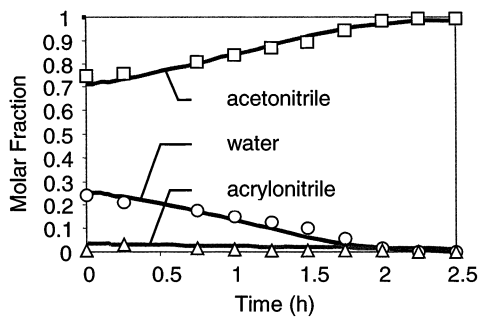


Fig. 2. Time evolution of the still molar liquid compositions during the heterogeneous regular column batch operation of a water–acetonitrile–acrylonitrile ternary mixture. Calculated values: (—), Experimental points; (□), acetonitrile; (△), acrylonitrile; (○), water.

Simulation results are displayed in Table 1 and on Fig. 2 and Fig. 3. Fig. 3 displays the ternary diagram main features and the column liquid profile evolution during the distillation step operation. As predicted, the still path moves from its initial position towards the acetonitrile vertex. At $t = 0$ h, the feed into the column is close to the unstable separatrix and several tray compositions are inside the liquid–liquid–vapour envelope. When batch distillation begins, the liquid composition profile changes suddenly due to the reflux of the acrylonitrile-rich phase. In this particular example, only the reflux of the entrainer-rich phase is needed to ensure feasibility of the separation intended because the acrylonitrile vertex is located in the same distillation region than both azeotropic points and acetonitrile vertex. The azeotropic mixture acrylonitrile–water composition is not reached at the column top because of a too small number of trays. However, it lies inside the 25°C liquid–liquid envelope close to the entrainer-rich side. Distillate is almost pure water. Application of the lever rule tells us that the aqueous phase volume in the decanter is always lower than the entrainer-rich phase one. A look at the condensed vapour path shows

that this feature is enhanced as distillation proceeds. With the condition of a constant volume decanter, the distillate flowrate decreases while the reflux flowrate increases along the distillation. The peculiar twist of the condensed vapour path is related to a overhead temperature that decreases slightly from 72.4 to 72.1°C during the first 2 h of distillation when the acetonitrile that filled the trays after the total reflux operation moves down to the still. Then overhead temperature increases to 74.2°C.

Comparison of Table 1 and Fig. 2 demonstrates that the experimental and simulation results agree well with and that no major discrepancy is noticed. The following remarks are made:

- Experimental and simulated product streams compositions exhibit the same features after equivalent duration. The experimental acetonitrile recovery yield also agrees with the simulated value. This validates the feasibility predictions that acetonitrile and water can be split in two high purity phases using a heterogeneous entrainer. It also proves the capacity of the simulation model to describe the batch distillation process.
- Experimental and simulated quantities and compositions of the heavy aqueous phase removed as product P_1 are similar. This validates the liquid–liquid equilibrium thermodynamics prevailing in the decanter.
- The experimental quantity of light phase obtained in the decanter at the end of heterogeneous batch distillation and the distillate cut rich in entrainer are similar to the simulated values. One notices also that less than 10% of the initial acrylonitrile amount leaves the column with the heavy phase P_1 and none with the product P_2 . This points the amount of entrainer make-up that should be added before each stage of a cycle of batch water–acetonitrile separations performed sequentially in the column.

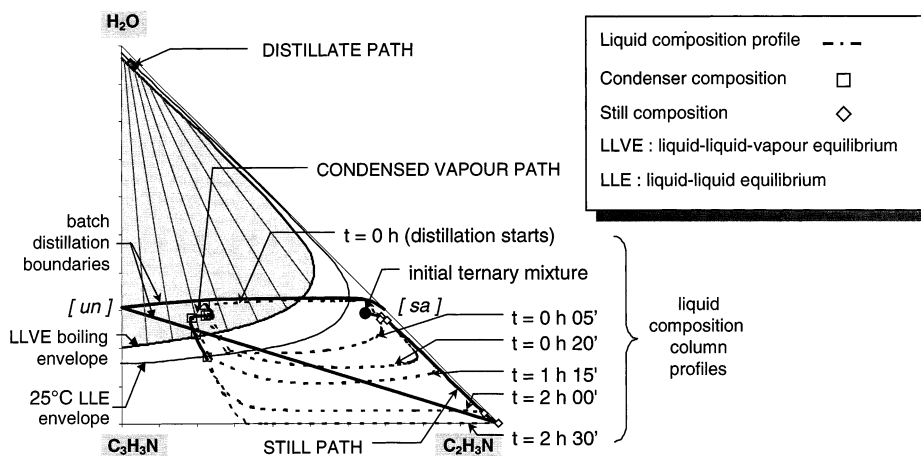


Fig. 3. Calculated liquid composition profiles for the heterogeneous regular column batch operation of a water–acetonitrile–acrylonitrile ternary mixture.

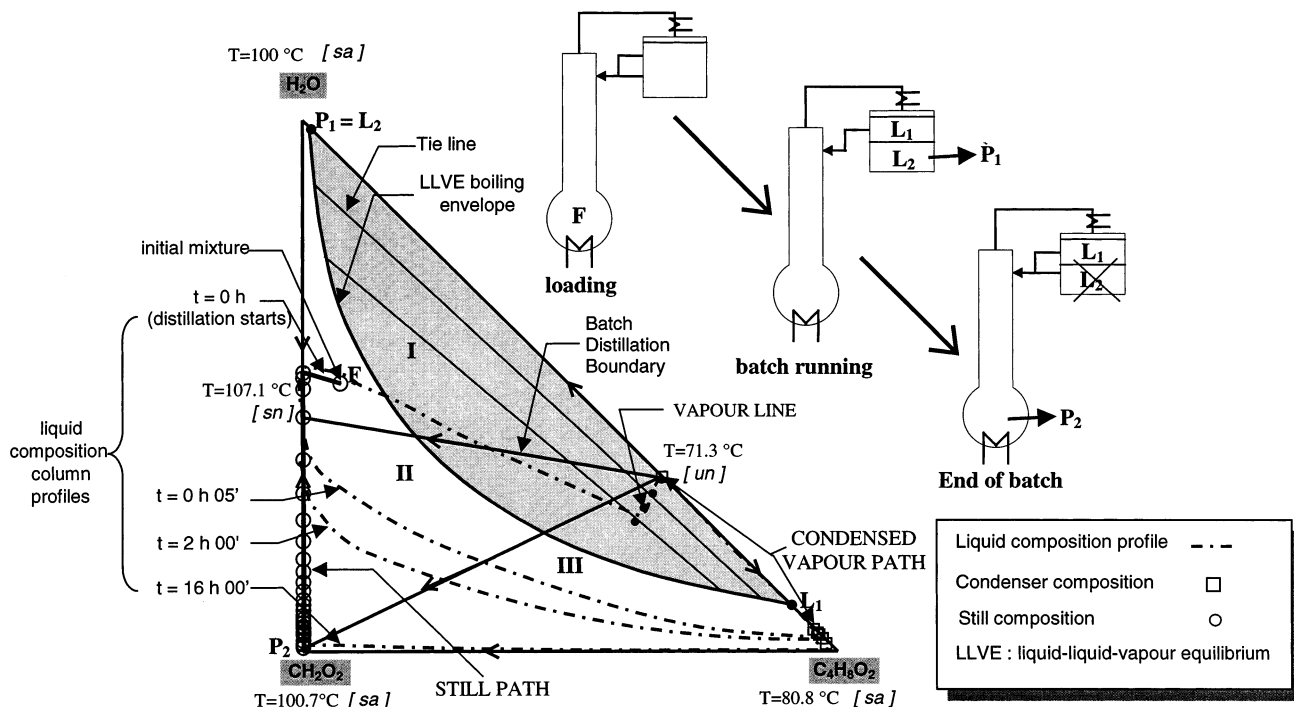


Fig. 4. Simulation results for the separation of maximum boiling temperature azeotrope water–formic acid by using propyl formate as heterogeneous entrainer.

- The experimental acetonitrile recovery yields agrees with the calculated value by simulation, but it is far from 100% because the 2nd distillate cut rich in acrylonitrile takes some acetonitrile from the still and acrylonitrile is replaced on the tray by acetonitrile. It will likely improve if a cycle of batch water–acetonitrile separations is performed sequentially, as the trays are not emptied at the end of each cycle stage.

In conclusion, both simulation and experiments validate the predictions of the feasibility study and shows that for this particular example, acetonitrile and water can be separated in two product phases with a significant purity by regular column batch operation. The amount of entrainer needed for this operation is low and the make-up for a cycle of water–acetonitrile separation is reasonable.

4. Maximum boiling temperature mixture separation with a heterogeneous entrainer

Maximum boiling temperature azeotropes are less frequent than minimum boiling temperature ones. However, a large percentage of such mixtures have an important industrial application. This is the case of the water–formic acid mixture. Heterogeneous batch distillation with the addition of propyl formate enables the separation of both components with a single regular column batch task (Fig. 4). Azeotropic points, fixed

points stability, boiling temperature, liquid–liquid–vapour envelope and simulation results (still path, condensed vapour path, liquid composition profiles) are shown on the ternary diagram in Fig. 4.

The simulation if performed with ProSimBATCH® using a 50 equilibrium stages batch column. Similarly to the previous case, a small quantity of entrainer is used in the process and the initial composition ($x_{C_4H_8O_2} = 0.07$, $x_{H_2O} = 0.5$, initial charge = 0.5 kg) is located in batch distillation region I containing the saddle water vertex. Column liquid profile at total reflux ($t = 0$ h) joins the still composition to the heteroazeotropic point and crosses the batch distillation boundary because the vapour line is located in batch distillation region III and therefore moves the liquid composition on the column top trays away from region I (see Fig. 4). When distillation begins, reflux of the propyl formate-rich phase at the column top changes abruptly the liquid composition profile now located in both batch distillation region II and III. The still path crosses the batch distillation boundary between region I and II because of the reflux of the entrainer-rich phase. The calculated initial reflux ratio equals to 2.62 and increases with time to keep a constant interface level into the decanter. The separation is more difficult as time proceeds in particular when the condensed vapour becomes homogeneous. Notice that the condensed vapour path could be maintained into the heterogeneous batch region if the liquid reflux at the column top combined by both decanting phases (aqueous and or-

ganic). However, the control of this operational parameter would be more complex. Simulation indicates that after 35.8 h, 96.2% of water and 97.0% of formic acid are recovered. The saddle formic acid vertex P_2 is obtained in the still at the end of the process with a high purity ($x_{\text{mean}} = 0.9948$). Water is removed as distillate P_1 ($x_{\text{mean}} = 0.9943$). The organic phase contained in the decanter represents 48.5% of total amount of propyl formate ($x = 0.9289$). Only 3.3% of the initial propyl formate is lost with both products P_1 and P_2 because the rest of the entrainer remains on the column trays.

5. Close-boiling point mixture separation with a heterogeneous entrainer

Separation of binary mixtures that have a low relative volatility can be as tedious as azeotropic binary mixture separation. Indeed, pinches of the liquid–vapour equilibrium curve can cause a direct distillation process to become uneconomical because of a number of stages too large. Such is the case of the water–acetic acid system. Heterogeneous batch distillation with the addition of vinyl acetate provides a simple way to ease the separation. The ternary diagram with boiling temperature and stability of the singular points is displayed in Fig. 5 along with a sketch of the process. Vinyl acetate and water form a heteroazeotrope. The liquid–liquid demixing enables us to recover an aqueous phase free of acetic acid and containing a reasonable amount

of vinyl acetate. A batch distillation boundary joins the acetic acid vertex to the heteroazeotrope. Its shape is assumed straight.

The simulation if performed with ProSimBATCH[®]. The ternary system exhibits two batch distillation regions. Fig. 5 displays the simulation results. The separation of the initial ternary mixture ($x_{\text{C}_4\text{H}_6\text{O}_2} = 0.1$, $x_{\text{H}_2\text{O}} = 0.5$, initial charge = 0.5 kg) requires 10 ideal equilibrium stages. Unlike the previous case, the liquid profile changes gradually due to the reflux of the entrainer-rich phase after the total reflux operation. This is due to three reasons. First, the acetic acid vertex is a stable node of both batch distillation regions; second, the initial ternary mixture and the vapour line are placed in the same batch distillation region; third the entrainer content of the organic phase refluxed at top of the column is not very high and has a low attractive power on the column top liquid compositions towards the vinyl acetate vertex. The calculated initial reflux ratio is 4.38 and gradually increases to keep a constant interface level into the decanter. Afterwards, the reflux ratio increases because the condensed vapour becomes homogeneous. During 2.5 h of batch distillation, water is removed as distillate product P_1 with a time average molar composition equal to 0.9984. In the meanwhile, high purity acetic acid is obtained in the still ($x = 0.9964$). The molar recovery yields of water and formic acid reaches 94.52 and 95.97%, respectively. 72.1% of the entrainer is recovered at the end in the organic phase resting in the decanter ($x = 0.912$). Water is the main impurity of the en-

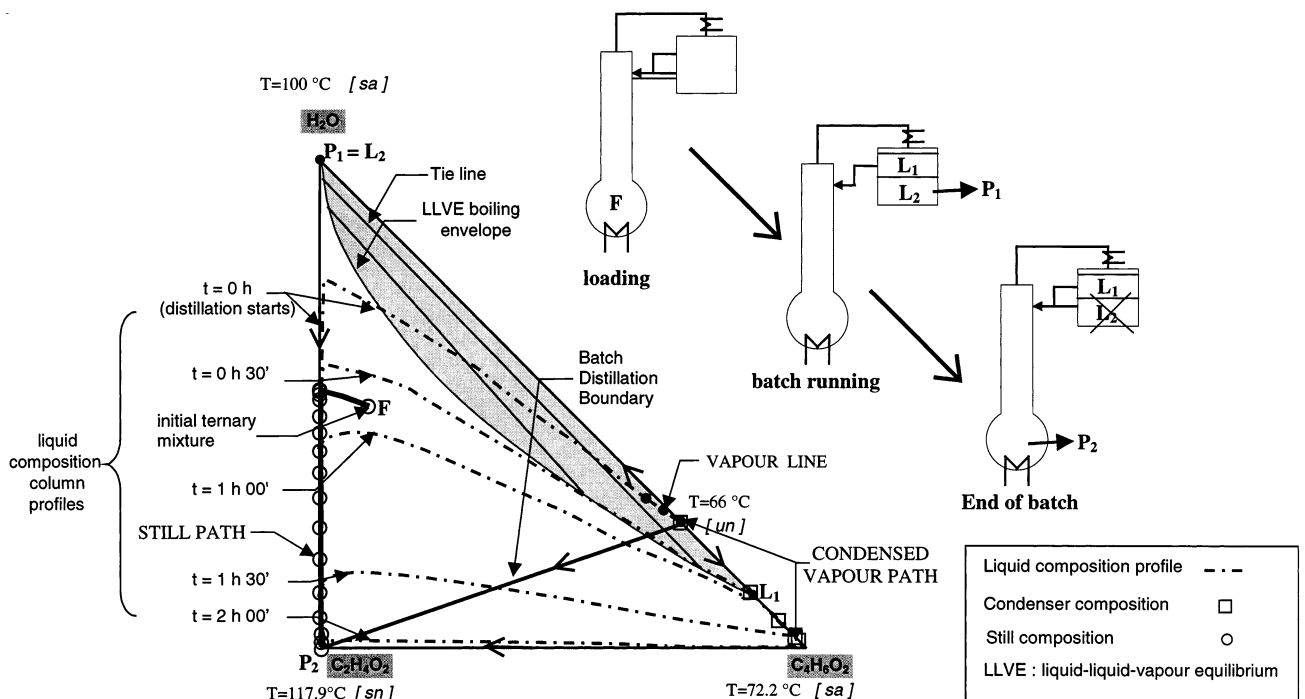


Fig. 5. Simulation results for the separation of the close boiling water–acetic acid mixture by using vinyl acetate as a heterogeneous entrainer.

trainer-rich phase. The rest of the entrainer is mostly retained on the column trays. Finally, notice that if the entrainer was homogeneous, the batch distillation could be performed with a single inverted column but with two distillation tasks instead of one for the HBD process.

6. Conclusions

The use of a heterogeneous entrainer increases the interest and the number of alternatives of batch distillation processes. Several applications to the separation of solvent–waste mixtures using the heterogeneous batch distillation are presented. The first example concerns the separation of the water–acetonitrile azeotropic binary mixture with the addition of acrylonitrile as a heterogeneous entrainer. Experiments and simulations are carried out. They are both well in accordance and validate the predictions of the feasibility study. The second and third examples involve the separation of a maximum boiling temperature mixture and close-boiling point mixture, namely water–formic acid using propyl formate as entrainer and water–acetic acid using vinyl acetate, respectively. Simulation results are presented in both examples. All examples show that both original components can be separated in two product phases with a significant purity during a single regular column batch task. Feasibility analysis shows that in some cases two batch stripper tasks would be required if a homogeneous entrainer was used. For a regular column operation the amount of entrainer needed is low and can be recycled. Simulation results show that the still path can cross batch distillation boundaries when an appropriate initial entrainer composition and reflux ratio policy, sometimes combining both decanting phases, are chosen.

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