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# Practical residue curve map analysis applied to solvent recovery in non ideal binary mixtures by batch distillation processes

Gerbaud Vincent<sup>1</sup>, Joulia Xavier<sup>1</sup>, Rodriguez-Donis Ivonne<sup>2</sup>, Baudouin Olivier<sup>3\*</sup>, Rosemain Olivier<sup>3</sup>,  
Vacher Alain<sup>3</sup>, Castelain Pierre<sup>3</sup>.

<sup>1</sup> Laboratoire de Génie Chimique, UMR CNRS 5503, ENSIACET – UPS – CNRS, BP1301, 5 rue Paulin Talabot, F-31106 Toulouse Cedex 1, France

<sup>2</sup> Centro de Quimica Farmaceutica, Ave. 200 y 21 Atabey Apdo. 16042, Playa, C. Habana, Cuba.

<sup>3</sup> Prosim SA, Rue Ampère, Imm. Stratège A, BP2738, F-31312 Labège Cedex

\*Corresponding author. Email: [Vincent.Gerbaud@ensiacet.fr](mailto:Vincent.Gerbaud@ensiacet.fr), Tel: (33) 5 62 88 58 44

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## Abstract

Batch distillation inherent advantages has initiated recent search for process feasibility rules enabling the separation of azeotropic or difficult zeotropic binary mixtures thanks to the addition of an entrainer. A systematic procedure enabling to find suitable process and eventually suitable entrainer for the separation of zeotropic or azeotropic binary mixture is described. It brings together into practical use batch distillation process feasibility rules, chemical affinity insight and thermodynamic data analysis available in the literature. The procedure has been implemented in a wizard computer tool and is illustrated on the separation of the water – acetonitrile binary homoazeotrope. Through this tool, all possible 224 feasibility rules and 326 batch distillation sequence processes are checked systematically for each entrainer.

## 1. Introduction

Batch distillation is an important separation technique in chemical industries. In particular, it is widely used in pharmaceutical and specialty chemical manufacturing to recover valuable components from liquid waste and solvent mixtures. But, the frequent presence of multicomponent azeotropes in these streams can delimit distillation regions where the types of feasible separations are restricted. Therefore, products generated by a separation process like batch distillation are highly dependent on the initial mixture composition. Even for zeotropic mixtures, distillation can be cost prohibitive when a pinch in the vapor – liquid equilibrium diagram exists. In general, to split a mixture into its pure components a sequence of batch processes may be required and several different configurations of columns may have to be used. This has led to the study of novel and hybrid batch processes to separate azeotropic mixtures since the 90's. In particular, stripper, middle vessel and extractive distillation column configurations have been studied in addition to the classical rectification column. Recent textbooks on distillation reflect this novel interest /1, 2, 3/.

A general statement is that in a ternary distillation region where there is always a low boiling, a heavy boiling and an intermediate boiling component, a rectifier configuration enables to purify the low boiling in a distillate cut, a stripper configuration enables to get the high boiling in a residue cut, an extractive configuration enables to get the intermediate boiling in the distillate thanks to the continuous feeding of an entrainer during part of the operation. A middle vessel configuration may enable to get at the same time the high boiling in the residue and the low boiling in the distillate (or the intermediate boiling in an extractive middle vessel configuration) while keeping the intermediate boiling in the middle vessel.

Most processes for the separation of azeotropic or difficult zeotropic mixtures involve the addition of an entrainer. Recently, exhaustive selection rules for homogeneous and heterogeneous batch distillation in rectifier and stripper configurations for the separation of binary mixtures either minimum boiling azeotropic, maximum boiling azeotropic or zeotropic mixtures with pinch or low relative volatility have expanded the industrial application range of batch distillation /4, 5, 6, 7/.

In this paper, we present a procedure to systematize the search for a suitable process enabling the separation of binary mixtures by batch distillation. A major work has been the adaptation of the scientifically correct distillation rules and principles to solve real cases. In particular, rules devised for topologically correct ternary diagrams but with no occurrence reported in the literature were discarded. Two aims are focused on, first to systematically find entrainers in databases that would eventually

satisfy published feasibility rules; and second to devise the process sequence associated with each feasible entrainer.

The feasibility analysis uses residue curve map analysis which can be readily systematized for ternary systems only. As a consequence, one should identify the two major components A and B in any industrial mixture to be split into pure components using the procedure described. Adding an entrainer E defines a ternary mixture A-B-E suited for residue curve map analysis.

Implementation of the methodology in a ready-to-use tool imposed itself from the beginning but together with the published rules, it limited us to consider only rectifier and stripper configurations. On the other hand it enables to keep record of any entrainer during the whole procedure. Indeed, a bottleneck of any systematic search in databases is the availability of experimental data or of predictive models. A first reasonable choice is to use UNIFAC-like contribution group methods to estimate physico-chemical properties. Within the RegSolExpert® tool used for illustration, Simulis®, a CAPE-OPEN compliant thermodynamic property server is used and further thermodynamic model refinement can be made easily when needed. In this work, thermodynamic models and eventual binary interaction coefficients are presumably known.

The paper is organized as follow: the algorithm is detailed with some background information given when needed and each step is illustrated using the same example. The illustrative example concerns the separation of the water – acetonitrile homoazeotropic mixture under 1 atm. It is a waste stream of chromatographic processes that exhibits experimentally a minimum boiling temperature homoazeotrope near  $x_{\text{acetonitrile}}=0.67$ . Molar units are used through the paper.

## **2. Binary mixture separation by batch distillation process**

The step by step procedure is described in figure 1.

INSERT Figure 1.

INSERT Figure 2.

### **2.1. Step 1 – Analysis of the binary mixture A-B to be split.**

The first step consists in analyzing the binary mixture to be separated at a given operating pressure  $P_{\text{op}}$ . Azeotropes reflect non ideal behaviour of mixture components that deviate from Raoult's law. Minimum (resp. maximum) boiling temperature azeotropes indicate a positive (resp. negative) deviation from Raoult's law [+] (resp. [-]). Figure 2 displays four binary azeotropic mixtures along with

three zeotropic mixtures that are suited for the procedure of figure 1 and an ideal mixture easy to separate by classical distillation.

- Azeotropic mixtures (cases b,c,d,e) are readily found by computing equilibrium constants

$$K_A = \frac{x_A}{y_A} \text{ at } x_A \approx 0 \text{ and at } x_A \approx 1, \text{ component A being the most volatile. Then,}$$

- if  $K_A^{x_A \approx 0} > 1$  and  $K_A^{x_A \approx 1} < 1$ , there exists a minimum boiling temperature azeotrope,
- if  $K_A^{x_A \approx 0} < 1$  and  $K_A^{x_A \approx 1} > 1$ , there exists a maximum boiling temperature azeotrope,
- else no binary azeotrope exists.

At this stage, no difference is made between minimum homoazeotropes and heteroazeotropes.

- Difficult zeotropic mixtures (cases f,g,h) can be assessed by computing a mean relative volatility  $\alpha_{AB}^m$  which is compared to a limit value. From our experience, graphical representation is mandatory but for computation, a 1.2 limit value indicates a close boiling mixture (case f) while a 1.5 limit value *may* indicate a pinch mixture (cases g,h) that a precise computation of the equilibrium curve could confirm. g and h cases are distinguished on a formal point of view as h can also be called a “tangential azeotrope” mixture, that is a mixture easy to separate in most of the composition domain, but behaving like an azeotropic mixture near pure component composition. The mean relative volatility  $\alpha_{AB}^m$  is computed as:

$$\alpha_{AB}^m = \sqrt{\alpha_{AB}^{x_A \approx 0} \cdot \alpha_{AB}^{x_A \approx 1}} \quad [1]$$

Graphical validation is always welcome in this case and is done easily within the RegSolExpert® tool used for illustration using Simulis® implemented thermodynamic routines (boiling and dew curve calculation and graphics for a binary mixture).

Figure 3 displays suitable batch distillation processes for all binary mixtures shown on figure 1. Classical batch distillation (no entrainer added to the mixture) and pressure-swing batch distillation (for pressure sensitive azeotropes) are well described in textbooks /1, 2, 3/. A hybrid classical distillation process combining a batch distillation column with a decanter at the top can be also used to separate heteroazeotropic binary mixtures without the addition of any entrainer. Azeotropic distillation implies addition of an entrainer and is also described in a review paper in its continuous operation mode /13/. When the resulting ternary system displays no liquid phase separation, the process is called homoazeotropic distillation; otherwise it is called heteroazeotropic distillation. This later case can be

done either by adding to a binary heteroazeotropic mixture any entrainer, or by adding to a binary homoazeotropic mixture an entrainer inducing a liquid phase separation in the ternary mixture. A single binary heteroazeotrope must exist to apply heteroazeotropic batch distillation rules describes by Rodriguez-Donis *et al.* /6/, Skouras *et al.* /7/, Modla *et al.* /8/. The batch heteroazeotropic distillation process uses the same column configuration as in a hybrid classical distillation process. When the entrainer Batch extractive distillation, not considered in this paper, is another process of choice especially for azeotropic binary mixture A–B which azeotrope becomes a saddle point of the ternary mixture A–B–E. Homogeneous batch extractive or heterogeneous batch extractive distillation can be devised and the process feasibility is readily evaluated computing equivolatility curve for the azeotrope to be separated /9, 10, 11, 12/.

INSERT Figure 3.

### Illustration of step 1: Acetonitrile – Water separation.

As acetonitrile is the light component A of the Acetonitrile – Water binary mixture,  $K_A^{x_A=0} > 1$ . Using an NRTL thermodynamic model with parameters taken from the DECHEMA tables /14/ (see table 3), calculation shows that  $K_A^{x_A=1} = 0.998514$  which is lower than unity. Hence a minimum boiling azeotrope is predicted.

### 2.2. Step 2 – Accurate determination of eventual A-B azeotrope.

Computing accurately azeotrope composition, type and stability can be done through the integration of a residue curve equation:

$$\frac{dx_i}{d\xi} = x_i - y_i \quad [2]$$

The distillation driving force  $(x_i - y_i)$  is the difference of the liquid phase  $x_i$  and vapor phase  $y_i$  compositions. At the azeotrope, the driving force is null, explaining why azeotropes cannot be split by classical distillation. Integration in the  $+\xi$  (resp.  $-\xi$ ) direction will evaporate light (resp. heavy) components and will end at the maximum (resp. minimum) boiling temperature azeotrope. Initial point could be a 50-50% mixture of A and B at boiling point or more efficiently its equilibrium vapour after a flash calculation. For calculation in homogeneous systems, any simple numerical method, such as Euler's integration scheme is suitable provided that the equilibrium relation between  $x_i$  and  $y_i$  is taken into account. However in the case of a heteroazeotrope, the number of phases in equilibrium may

change during the residue curve integration from the V-L region to the V-L-L one or vice-versa. Either a phase stability test should be used to evaluate the number of coexisting phases /13/ or a versatile dynamic multiphase equilibrium model should be used /16/. Such a model handles inherently the number of phases through pseudo phase composition vectors and is also useful to detect case e diagram (binary homoazeotrope with VLL region) for which no feasibility rule has been published so far. Besides the integration method should be robust so as to handle phase number changes during the integration. We use an in-house integration scheme with a gear corrector – predictor numerical algorithm.

As a result from this step, the eventual binary A-B azeotrope is calculated and distinction is made between maximum boiling temperature homoazeotropes, minimum boiling temperature homoazeotrope with or without VLL region and minimum boiling temperature heteroazeotrope at the pressure chosen by the user. Several commercial tools exist to compute azeotropes. Validation of the azeotropes calculated by comparison with existing experimental data compiled in azeotropic database and literature /14, 15/ is strongly recommended.

### **Illustration of step 2: Acetonitrile – Water separation.**

Precise calculation of the azeotrope composition and temperature at  $P = 1$  atm is performed using the residue curve integration in the  $-\xi$  direction and gives:  $T_{Azeo}=349.94K$  and  $x_{acetonitrile,azeo}=0.676$ , well in accordance with experimental data /14, 15/ that ranges  $T_{Azeo} \in [349.15K; 349.95K]$  and  $x_{acetonitrile,azeo} \in [0.681; 0.726]$ . It is a minimum boiling homoazeotrope without VLL region in the mixture composition range.

### **2.3. Step 3 – Pressure swing process evaluation**

Pressure swing distillation process exploits the fact that azeotrope composition may vary with pressure. The more the composition changes with pressure, the better. Therefore, using two columns at different pressure will enable to split the binary azeotropic mixture into pure components as sought. In our procedure, as this process does not require any entrainer addition that will inevitably pollute the original binary mixture, the azeotrope pressure dependency is systematically explored before any entrainer search. In addition, the binary equilibrium diagram should be computed and looked at to detect any pinch that would make pressure swing distillation process cost prohibitive.

### Illustration of step 3: Acetonitrile – Water separation.

Pressure dependency of the Acetonitrile – Water homoazeotrope composition requires step 1 and step 2 calculations at different pressures. As shown in Table 1, it does not lead to its disappearance and even a VLL region appears at very low pressure. So, the pressure operating range for pressure swing batch distillation is narrow below 1 atm and does not induce large changes in composition. It would hint at a pressure swing process with a high pressure greater than 1 atm.

INSERT Table 1.

### 2.4. Step 4 – Entrainer broad screening

Process feasibility rules for the separation of binary mixtures with the addition of an entrainer are based on ternary diagram A – B – E properties: existence and stability of azeotropes, curvature of distillation boundaries. This will require intensive calculation. As a consequence, a systematic search of databases may rapidly become fastidious unless a broad screening scheme is used /17/.

INSERT Table 2.

First, solid or hardly condensable components are put aside. Criteria for rejecting an entrainer are displayed in table 1. For illustration, among the ~1700 components of the DIPPR database that was available through the CAPE-OPEN thermodynamic property server connected to RegSolExpert, sodium and methane satisfy respectively criteria 1 (solid) and 2 (uncondensable).

Second is the usual classification of the entrainer versus the two original components in terms of boiling point temperature. Indeed, any process feasibility rules for the separation of binary mixtures with the addition of an entrainer are set according to the entrainer boiling point temperature  $T_{bE}$  relative to A and B boiling point temperature  $T_{bA}$  and  $T_{bB}$ . Each entrainer is listed either as light ( $T_{bE} < \{ T_{bA}, T_{bB} \}$ ) or intermediate ( $T_{bA} < T_{bE} < T_{bB}$ ) or heavy ( $\{ T_{bA}, T_{bB} \} < T_{bE}$ ).

Third, in order to hint at the residue curve integration direction  $+\xi$  or  $-\xi$  and to avoid inutile computation when searching for eventual azeotropes, the possible deviation from Raoult's law between A and B with each entrainer E is evaluated. Indeed, azeotropy reflects non ideal behaviour that arises from interaction between molecules, among which is hydrogen bonding capacity, polarity and boiling point temperature difference. Perry *et al.* /17/ have summarized general criteria predicting deviation from Raoult's law. Positive, negative and null deviation may lead to the appearance of minimum boiling, maximum boiling and no azeotrope respectively (Figure 2). Notice that a small deviation may not lead systematically to azeotropy. Those general criteria are based on deviation

tendencies between components belonging to chemical families. They are related to boiling temperature differences  $\Delta T_{\text{boiling}}$ . Mixtures with small deviations from Raoult's law may form an azeotrope only if the components are close boiling. As the boiling temperature difference increases, the azeotrope composition shifts towards the lowest boiling (resp. highest boiling) pure component if the azeotrope is minimum boiling (resp. maximum boiling). A 50°C limit value for  $\Delta T_{\text{boiling}}$  is considered in the illustrative example. Therefore, all entrainers with  $\Delta T_{\text{boiling}} > 50^\circ\text{C}$  versus A (resp. B) are set in the null deviation entrainer group for A (resp. B) because even though they may form an azeotrope with either A or B, its composition is likely to be too close from a pure component to lead to an economically efficient separation process. Below that threshold, positive or negative deviation is expected. Some chemical families may induce either positive or negative deviation depending on their molecular weight, etc. As the systematic procedure in step 5 first checks positive deviation, then negative deviation and null deviation, some entrainers that could display at first both positive and negative deviation are always assigned to the positive deviation entrainer group.

#### **Illustration of step 4: Acetonitrile – Water separation.**

Being a member of the nitrile chemical family, acetonitrile belongs to both group 1 and 2 of Perry's classification whereas water belongs to group 1 only. Group 1 concerns polar components containing C atoms bonded to acceptor chemical residue (O, N, aromatic cycle) with active hydrogen. Hydrogen bonds can be formed with molecules from any groups. Group 2 concerns polar components containing C atoms bonded to acceptor chemical residue (O, N, aromatic cycle) with non active hydrogen. It includes some chemical families from group 1 where the active hydrogen is replaced by organic groups R ( $\text{CH}_3$ ,  $\text{CH}_3\text{-CH}_2$ , etc). Heavy molecular weight R chains can lead to partial miscibility in the binary system.

For illustration, 53 entrainers are selected from the DIPPR database. For all entrainers, a preliminary search is done using a predictive model, in our case Dortmund modified UNIFAC model. Notice that any use of such a predictive thermodynamic model should be considered with care: methyl acetate is predicted with no azeotrope and a VLL region whereas there is experimentally a homoazeotrope methyl-acetate with a VLL region. Such a case is far from isolated. Indeed for acrylonitrile, the entrainer we retained at last, the predictive model leads also to erroneous prediction of azeotropes, whereas NRTL or UNIQUAC model with binary parameters from the DECHEMA tables /14/ give the correct trend. Despite the invaluable usefulness of the predictive approach for a first checking, we recommend for a precise entrainer search using validated thermodynamic model with binary interaction parameters based on experimental data /18/ whenever they exist. Such was the case for

all entrainers considered in this study where NRTL or UNIQUAC model with binary parameters from the DECHEMA tables /14/ was used but for a few cases when some binary were not available. Whatever the thermodynamic model, all predicted VLL features (azeotrope existence, type and composition) of the ternary diagrams where systematically validated against experimental azeotropic and equilibrium data /14, 15/.

Using RegSolExpert® tool, preliminary checking of the 53 entrainers rejected 14 of them because they are considered as solids (criterion n°1), are difficult to condensate (criterion n°2) or are close boiling with water or acetonitrile (criterion n°3).  $T_{\text{melting}}$  limit value was set to 298.15K and  $T_{\text{boiling}}$  limit value was set to 303.15K and  $\alpha_{ij}^m$  limit value was set to 1.5. Choosing a right  $\alpha_{ij}^m$  limit value is difficult as it does not enable at this step to reject acetone ( $\alpha_{\text{water,acetone}}^m > 5 \gg \alpha_{ij,\text{limit}}^m$ ) which forms a well known pinch mixture with water (diagram h in figure 2).

INSERT Table 3.

## 2.5. Step 5 – A B E ternary system analysis

Process feasibility rules for the separation of binary mixtures A B with the addition of an entrainer E are based on ternary diagram A – B – E properties: existence and stability of azeotropes, curvature of distillation boundaries. This is called residue curve map analysis and it has proven to be the most significant concept for the design of distillation processes /2/.

First, Raoult's law deviation classification of step 4 is confirmed for each entrainer by running step 1 azeotrope fast checking procedure for each A-E and B-E binary system, first for positive Raoult's deviation, then for negative Raoult's deviation and finally for null Raoult's deviation. Any refutation for an entrainer in the positive deviation list moves it in the negative deviation list. Any refutation for an entrainer in the negative deviation list moves it in the null deviation list.

Second, precise determination of the eventual A-E or B-E azeotrope composition and temperature is performed using the residue curve integration procedure described in step 2.

Third, for each ternary system, the stability of each unary and binary singular point is checked by computing the associated eigenvalues /19/. Within a residue curve map, a singular point can be stable or unstable node or saddle, depending on the sign of the eigenvalues related to the residue curve equation set (equation 2). Assuming that no system with two ternary azeotropes exists, we check the topology equation valid for a ternary system:

$$2 \cdot N_3 - 2 \cdot S_3 + N_2 - S_2 + N_1 = 2$$

where  $N_3$  and  $S_3$  are the number of ternary node and saddle respectively,  $N_2$  and  $S_2$  are the number of binary node and saddle respectively and  $N_1$  is the number of unary node. Result of  $N_2 - S_2 + N_1 - 2$  equal to 0, -2 or 2 indicates respectively no ternary azeotrope, a ternary node or a ternary saddle.

Fourth, the eventual ternary unstable or stable node is sought using residue curve integration similar to step 2. For a ternary saddle, the procedure of Doherty /20/ which follows the temperature ridges towards the saddle is used. In both cases, accurate ternary azeotrope composition and temperature are obtained.

Fifth, knowing all singular points enables to know precisely the number of distillation boundaries from Serafimov's classification /21/. Those boundaries are computed and the ternary diagram is displayed so as to check the curvature crucial for feasibility rules.

### **Illustration of step 5: Acetonitrile – Water separation.**

Analysis of the 39 remaining entrainers leads to a mixed result:

Twelve are rejected according to Table 1 criterion number 4 to 6: five for criterion n<sup>4</sup> (2 heteroazeotrope or 2 VLL with A and B), seven for criterion n<sup>5</sup> (homoazeotrope with VLL region), none for criterion n<sup>6</sup> (no azeotrope with A or B but VLL region, this criterion would hold for methyl acetate if UNIFAC model was mistakenly used).

27 entrainers are considered valid and should be checked upon feasibility rules.

Figure 4 displays the ternary diagram for the acetonitrile – water – acrylonitrile system showing residue curves, VLLE envelope, LLE at 298K envelope, vapour line, distillation boundaries, singular points drawn with ProSim Ternary Diagram, a freeware tool for drawing versatile ternary diagrams /22/. The distillation boundary shows not significant curvature and is almost coincident with the vapour line in the shaded VLLE region. The striped LLE at 25°C region will hold in the heteroazeotropic process decanter of the column. As often, it is wider than the VLLE region.

INSERT Figure 4.

### **2.6. Step 6 – Batch distillation process feasibility rule checking**

An exhaustive but somewhat expert sets of feasibility rules has been published by Rodriguez-Donis *et al.* /4, 5/ which consider rectifier and stripper column configuration for the separation of minimum boiling, maximum boiling and zeotropic binary mixtures to which is added a light, an intermediate or a heavy entrainer leading to ternary systems displaying straight or curved distillation boundaries.

Considering only ternary systems known to occur, Skouras *et al.* /7/ also give a comprehensive review of feasibility rules.

For the present procedure, we have gone through both approaches and discarded rules related to ternary systems for which no occurrence is known /21/ or for which process is too complex. This has reduced them to a still impressive set of 224 feasibility rules, fortunately coded into RegSolExpert®. Figure 5 displays an example of feasibility rule 6a for a homogeneous ternary system with a concave boundary curvature. There, curvature is critical to separate A and B. Depending on the curvature (convex or concave) and on the process (a sequence of three stripper columns or a sequence of two stripper columns and one rectifier column can be used), rule 6 declines into four processes 6a, 6b, 6c and 6d. Overall, the 224 feasibility rules give rise to 326 different processes summarized on sheets like figure 5 /23/. In addition to the system classification in all useful classification /17, 21/, Figure 5 displays the relevant three batch stripper sequence process main features (feed region, products, batch transitions, batch task ending criteria ...).

INSERT Figure 5.

#### **Illustration of step 6: Acetonitrile – Water separation.**

Among the 27 valid entrainers after step 5, 5 fail to satisfy any feasibility rule (table 3). The 22 remaining feasible entrainer candidates are listed in table 4 (12 low boiling entrainers) and in table 5 (6 intermediate boiling entrainers and 4 heavy boiling entrainers). Table 4 and 5 detail for each valid entrainer, its formula, name, and CAS number; the ternary diagram with all calculated azeotropes, distillation boundaries and eventual LLE at 298 K and LLVE; the ternary diagram classification M; P; S; Z according respectively Matsuyama /21/, Perry's Chemical Engineer's Handbook /17/, Serafimov /21/ and Zharov /21/. The feasibility rule according to RegSolExpert®'s numbering is also displayed along with the feed region, the relevant batch distillation sequence to operate with all cuts, reflux and recycles. F, D<sub>n</sub>, P<sub>n</sub>, recycl<sub>n</sub> stand respectively for the feed, the distillate of the n<sup>th</sup> rectifier task, the bottom product of the n<sup>th</sup> stripper task, the recycled decanter phase of the n<sup>th</sup> task. The thermodynamic model used in calculation with eventual binary interaction coefficient that has been validated against experimental data is also provided. The same binary coefficients have been used to compute both LLE at 298 K and LLVE, even though it is better to use specific binary parameters regressed on LLE data to compute LLE. Notice that, for some A-B-E mixtures (cited in the table), some binary and ternary azeotropes predicted by the thermodynamic model are not reported in the literature, which is far from exhaustive but they are reasonably assumed to occur until later experimental validation is done.

INSERT Table 4.

INSERT Table 5.

Only nine different rules are obeyed by the 22 valid entrainers. Not surprisingly, these rules give rise to ternary diagrams A-B-E with a high occurrence among known diagrams /21/: Following Serafimov's classification and quoting Reshetov's statistics /21/, the 3.1-2 diagram (statistical occurrence: 26.0%) is predominantly found (rules 17 and 59 for light boiling entrainers; rules 29 and 76 for intermediate boiling entrainers; rule 89 for heavy boiling entrainers). The 2.0-2b diagram (statistical occurrence: 21.0%) (rules 9 and 46) and the 1.0-2 diagram (statistical occurrence: 8.5%) (rule 6) are also found for light boiling entrainers. The 2.1-2b diagram (statistical occurrence: 4.0%) is found for heavy boiling entrainers (rule 88).

Several rules lead to more than one process depending on the distillation boundary curvature and process: rules 6, 9, 17 and 29 lead to four different processes each, with either SSS or SSR sequence and whether E (for rule 9) or A (for rule 6, 17 and 29) is in the concave or in the convex region; rules 59, 76 and 89 are not boundary curvature dependent but are related either to the RS or the SS sequence. Only one sequence process is displayed for each entrainer.

For heterogeneous batch distillation processes where the column top is fed to a subcooled decanter before reflux, the composition of the distillate and reflux is set by the LLE at the subcooled temperature (we choose arbitrarily a 298 K value for the calculations) and thus, the LLE at 298 K is displayed on the relevant diagrams. The LLE can be either of type I or of type II without any incidence on the process operation.

Many candidate entrainers are not interesting: For example, all listed processes involving no LLV region (e.g. with methanol) (rules 6, 9, 17 and 29) require at least three batch distillation columns to be operated sequentially. Such processes lead to several offcuts to be recycled, one of them being the original AB azeotrope. So separation efficiency is quite low for these processes. On the other hand, heterogeneous batch distillation processes (rule 46, 59, 76, 88 and 89) where the entrainer is partially miscible with either A or B are much more efficient. The only drawback is that if the A-rich or B-rich phase of the partially miscible mixture is not pure enough, a purification step is further required. LLE tie line precise calculation is therefore important to assess the exact purity of each liquid phase and should be verified against experimental data before implementing effectively the recommended process. Further purification is never considered in the heterogeneous batch distillation processes we are concerned with. As shown in the literature and validated experimentally /6, 7, 24/, heterogeneous

batch distillation is a flexible process as several reflux policies can be thought of to drive effectively the still composition in the composition space towards pure component vertexes. It also greatly enlarges the feasible region for the feed composition [7, 25]. Furthermore, contrary to homogeneous batch distillation, still paths are not compelled to move straight away from the distillate composition, thanks to the potential accumulation (operation mode B in Skouras *et al.* [7]) or depletion of phases in the decanter [6]. But, some heterogeneous batch distillation processes can be operated without taking benefit from the decanter. This is the case with rule 59 and a process sequence RS where the top of the first rectification column should lie at the ternary heteroazeotrope and the reflux should be set at this ternary heterogeneous composition, like in a homogeneous batch distillation process (operation mode A in Skouras *et al.* [7]).

Another cause to discard an entrainer may come from thermodynamic features of the ternary mixture like a particular shape of the distillation boundaries, the slope and intersection of the LLE tie lines versus the distillation boundary as discussed in Skouras *et al.* [7]. For example, ethyl acetate leads to a strong pinch of the AB-ABE and AE-ABE boundaries near the ternary heteroazeotrope. As a consequence for the prescribed RS process, it may be difficult to get the ternary heteroazeotrope at the column top unless very large stage number and reflux are used. Furthermore, the LLE envelope intersection with the recommended feed region is so small that there may not even be a LL split at the top. This would also hold for the RS process with isopropyl acetate or with 1,2-dichloroethane where two boundaries pinch near the ternary heteroazeotrope for each entrainer. But fortunately, in the case of 1,2-dichloroethane, the LLE region is larger, so a SS sequence can be implemented.

For several rules where different sequences are eligible (e.g. rule 76: RS or SS), selecting the right sequence is governed by expertise. For instance we told above why RS is not recommended for 1,2-dichloroethane obeying rule 76 and SS should rather be chosen, enabling to locate the feed composition in the A – intersection of the LLE with the AE-ABE boundary – ABE – intersection of the LLE with the AB-ABE boundary region. For 1,4-cyclohexadiene the process sequence related to rule 76 displayed in Table 5 is RS. But in fact, if the first rectification task is operated according operation mode A (reflux of the heteroazeotropic composition) rather than according operation mode B (reflux policy taking advantage of the LLE), it may require to set the feed composition exactly on the heteroazeotropic – pur acetonitrile straight line. For that reason a SS sequence would offer far less constraint on the feed location. On the other hand, if the first rectification task is operated according operation mode B, the feed composition initial location choice is greater as the reflux policy will enable to drive the still composition towards pure A. The same holds for rule 59 with RS or SS sequences.

A typical example of an efficient heterogeneous batch distillation processes is the use of dichloromethane or of acrylonitrile to separate the water – acetonitrile homoazeotropic mixture. The relevant process, obeying rule 46, is performed in a single step using a single batch distillation column with a decanter at the top (heterogeneous batch distillation). The process with acrylonitrile was simulated and experimentally validated in Rodriguez-Donis *et al.* /6/. Operated according mode B, with reflux of the acrylonitrile-rich decanter phase only, it showed excellent performances with a final distillate tank content 94.6 molar% water rich; a final still content 99.5 molar% acetonitrile rich and an overall 91.8 mass % of acetonitrile recovered.

### **2.7. Step 7 – Feasible batch process simulation**

At this step of the entrainer selection procedure, the process information associated to any single feasibility rule (see Figure 5 and Tables 4 and 5) should be used to simulate and optimize the operating parameters of the batch sequence /24/. Calculated thermodynamic data, in particular LLE tie line slope and compositions should be validated by experimental data. This step is critical for heterogeneous batch distillation processes in order to devise the best reflux policy enabling to drive the main tank composition path towards pure vertexes /6, 7, 24/. Implementing robust controller of such reflux policies has also been discussed in the literature /26/.

### **3. Conclusions**

Batch distillation inherent advantages has initiated recent search for process feasibility rules enabling the separation of azeotropic or difficult zeotropic binary mixtures thanks to the addition of an entrainer. A systematic procedure enabling to find a suitable non extractive batch distillation process and eventually a suitable entrainer for the separation of zeotropic or azeotropic binary mixture is described. It brings together into practical use batch distillation process feasibility rules, chemical affinity insight and thermodynamic data analysis available in the literature. The procedure has been implemented in a wizard computer tool and is illustrated on the separation of the water – acetonitrile binary homoazeotrope. Through this tool, all possible 224 feasibility rules and 326 batch distillation sequence processes are checked systematically for each entrainer. The graphical tools enables to compare efficiently the entrainer and select the candidates needing further investigation.

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## **Figure Caption**

Figure 1. Batch distillation process finding procedure for the separation of binary mixtures

Figure 2. Binary mixtures requiring non classical batch distillation processes

Figure 3. Batch distillation processes for the binary mixtures shown in figure 1

Figure 4. Ternary diagram for the acetonitrile – water – acrylonitrile system

Figure 5. Example of feasibility rule and process for batch homogeneous distillation

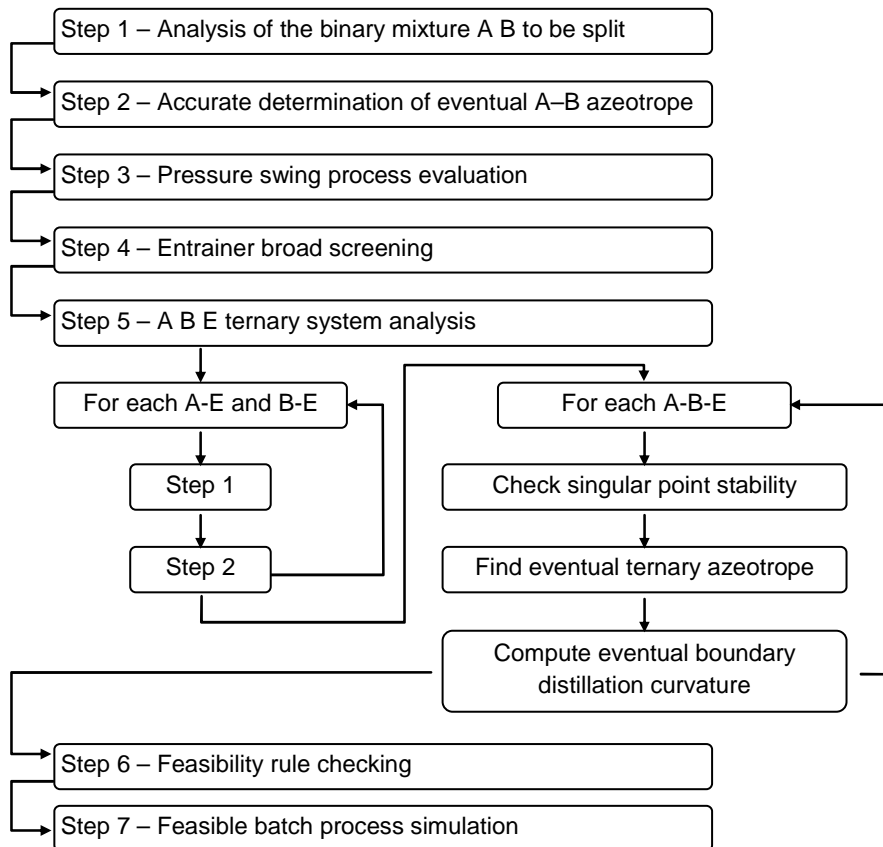
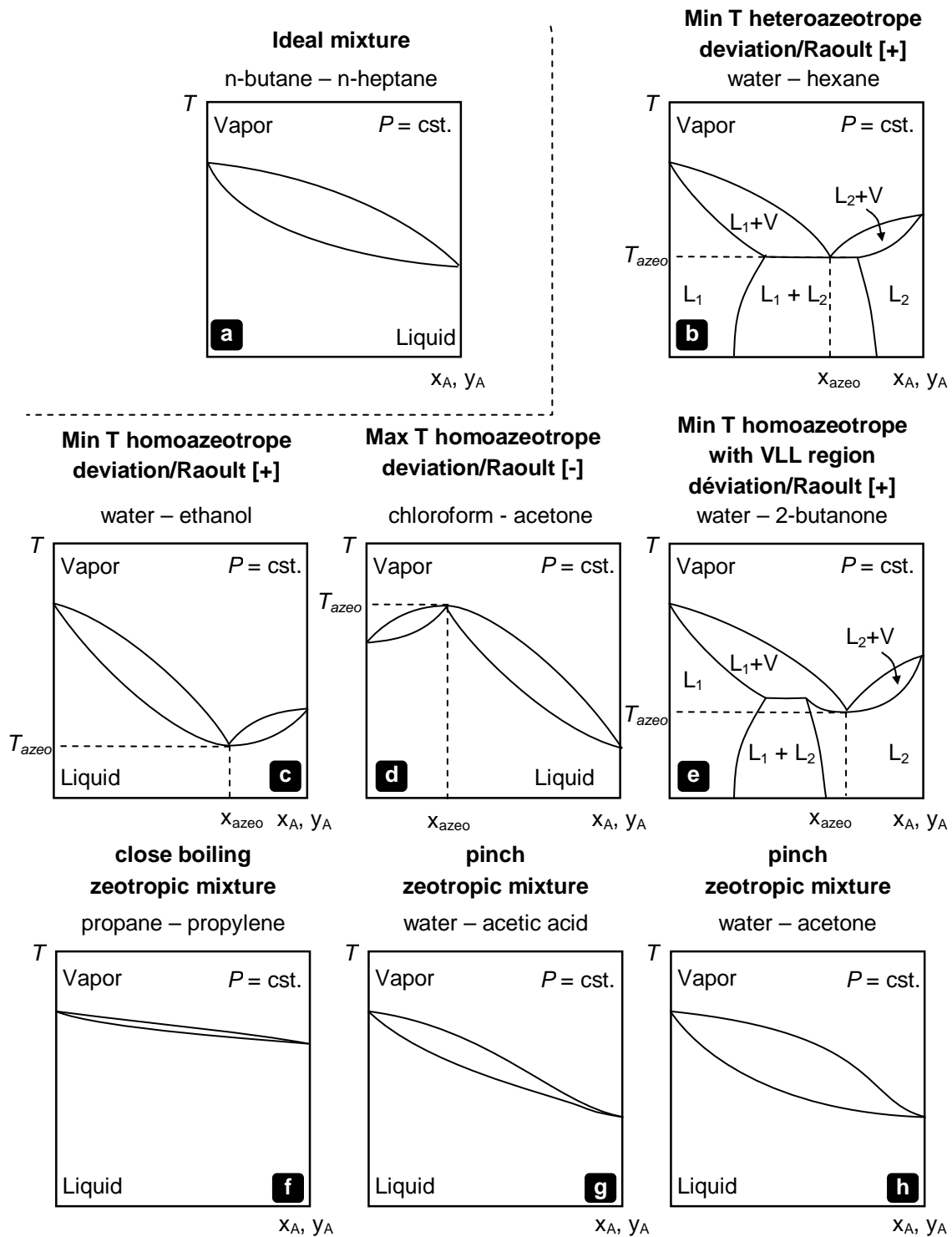


Figure 1. Batch distillation process finding procedure for the separation of binary mixtures



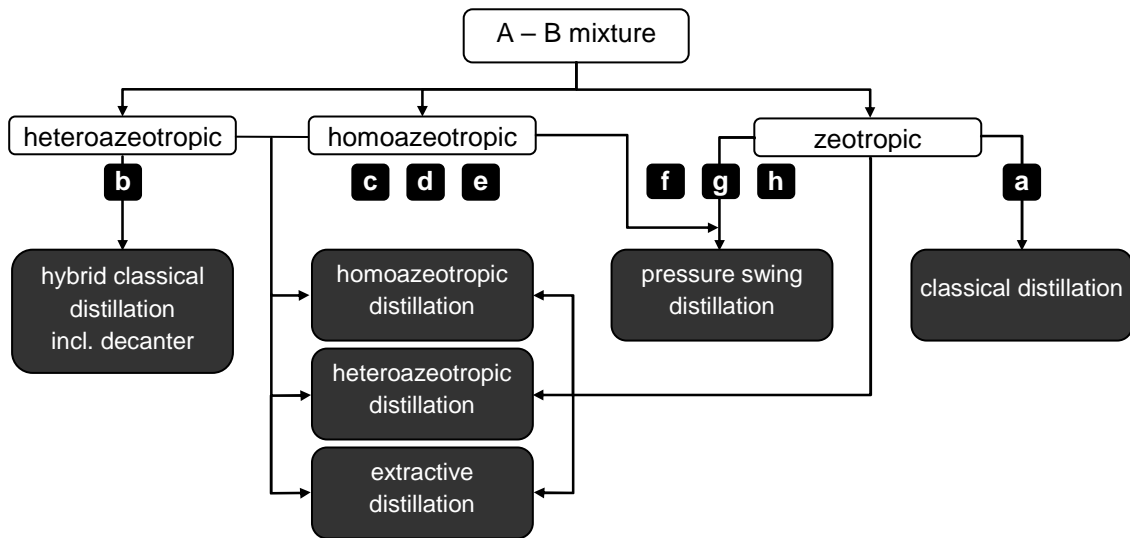


Figure 3. Batch distillation processes for the binary mixtures shown in figure 1.

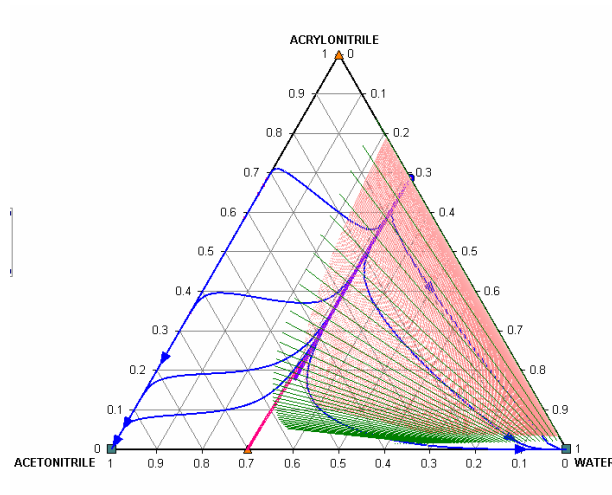


Figure 4. Ternary diagram for the acetonitrile – water – acrylonitrile system

Rule 6a

Sequence rule	Batch sequence	Separatrix	Diagram
8a	S-S-S	cutved	
Type azeo AB	Entrainer case	Entrainer type	
cutMol	homogeneous	light	
Rodriguez-Dona's article rule (Rodriguez et al., 2001)			
1 (AB sa)			
Matsumura's class (Matsumura & et al., 1977)	Perry's handbook class	Perry's number	See affinity / Zhang or classes (Woo et al., 2003)
020	1435	#004	1.0-2 / 4 Occurrence : 85 %
Batch 1 product sequence			Stripper S1
Feed region	Feed composition	Product location : P <sub>1</sub>	Remain
A+B+E	A+B+E top and still	Sill : A	Top : A+B+E
Suggested criteria for batch task end			
A purity in the bottom outlet			
Batch 2 product sequence			Stripper S2
Inlet transition	Feed composition	Product location : P <sub>1</sub>	Remain
22 - InCondPart	A+B+E top and still	Sill : A+B	Top : E
Suggested criteria for batch task end			
E purity in the condenser			
No more E in the still			
Batch 3 product sequence			Stripper S3
Inlet transition	Feed composition	Product location : P <sub>1</sub>	Remain
22 - InCondPart	A+B top and still	Sill : B	Top : AB
Suggested criteria for batch task end			
B purity in the bottom outlet			
No more A in the still			
Remarks	<ul style="list-style-type: none"> <li>Region containing A is concave</li> <li>At the end of batch 2, the bottom outlet is split between condenser and boiler of batch 3</li> </ul>		
<p>▲ : [sa] = saddle node    ○ : [un] = unstable node    ■ : [sn] = stable node  X... pure component    XY : azeotrope X-Y    X+Y : mixture X+Y  — : main tank composition path</p>			
<p>12 - OutCondTot: all the content of the condenser is get out  19 - OutBoTol: all the content of the bottom outlet is remove to a batch  22 - InCondPart: repartition of the mixture between the boiler and the condenser</p>			

Figure 5. Example of feasibility rule and process for batch homogeneous distillation

### **Table Caption**

- Table 1. Pressure dependency of the Acetonitrile – Water azeotrope calculated with the NRTL model
- Table 2. Entrainer rejection criteria
- Table 3. Entrainer rejected for the separation of water – acetonitrile homoazeotropic mixture
- Table 4. Valid light boiling candidate entrainers for the separation of water – acetonitrile homoazeotropic mixture
- Table 5. Valid intermediate and heavy boiling candidate entrainers for the separation of water – acetonitrile homoazeotropic mixture

Table 1. Pressure dependency of the Acetonitrile – Water azeotrope calculated with the NRTL model

Pressure (atm)	Temperature (K)	A Acetonitrile	B Water	$K_A^{x_A=0}$	$K_A^{x_A=1}$	Azeotrope type
0.0131579	256.828	0.999652	0.000348	78.9082	0.999999	Homogeneous LLV
0.210526	309.737	0.795693	0.204307	27.8671	0.999214	Homogeneous LLV
0.407895	325.616	0.743285	0.256715	21.7085	0.998931	Homogeneous LLV
0.605263	335.889	0.713067	0.286933	18.7116	0.998752	Homogeneous
0.802632	343.643	0.691933	0.308067	16.8314	0.998619	Homogeneous
1.000000	349.939	0.675739	0.324261	15.5027	0.998514	Homogeneous

Table 2. Entrainer rejection criteria

Criterion	Entrainer rejection criteria	Additional information
1	$T_{\text{melting}} > T_{\text{melting}} \text{ limit value}$	entrainer is considered as a solid
2	$T_{\text{boiling}} < T_{\text{boiling}} \text{ limit value}$	entrainer condensation is difficult
3	$\alpha_{AE}^m \text{ or } \alpha_{BE}^m < \alpha_{ij}^m \text{ limit value}$	entrainer is close-boiling with A or B
4	E forms two binary heteroazeotropes or two VLL region with A and B	
5	E forms one binary homo azeotrope with VLL region with either A or B	
6	E doesn't form any binary azeotrope but a VLL region with either A or B exists	
7	no feasible rule found	
8	numerical failure during calculation	
9	A-B forms a homoazeotrope with VLL region.	

Table 3. Entrainer rejected for the separation of water – acetonitrile homoazeotropic mixture

<b>Entrainer rejected</b>	<b>Rejection criterion</b>	<b>Entrainer rejected</b>	<b>Rejection criterion</b>
2-methyl-2-propanol C <sub>4</sub> H <sub>10</sub> O	1	n-pentane C <sub>5</sub> H <sub>12</sub>	4
naphthalene C <sub>10</sub> H <sub>8</sub>	1	cyclohexane C <sub>6</sub> H <sub>12</sub>	4
methanethiol CH <sub>4</sub> S	2	hexane C <sub>6</sub> H <sub>14</sub>	4
vinyl chloride C <sub>2</sub> H <sub>3</sub> Cl	2	2-butanol C <sub>4</sub> H <sub>10</sub> O	5
propane C <sub>3</sub> H <sub>8</sub>	2	ethyl iodide C <sub>2</sub> H <sub>5</sub> I	5
ethyl acetylene C <sub>4</sub> H <sub>6</sub>	2	methyl acetate C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	5
1,3-butadiene C <sub>4</sub> H <sub>6</sub>	2	methyl ethyl ketone C <sub>4</sub> H <sub>8</sub> O	5
1-butene C <sub>4</sub> H <sub>8</sub>	2	isobutyl chloride C <sub>4</sub> H <sub>9</sub> Cl	5
butane C <sub>4</sub> H <sub>10</sub>	2	n-decane C <sub>10</sub> H <sub>22</sub>	5
3-methyl-1-butyne C <sub>5</sub> H <sub>8</sub>	2	undecane C <sub>11</sub> H <sub>24</sub>	5
1-pentene C <sub>5</sub> H <sub>10</sub>	2	diethyl amine C <sub>4</sub> H <sub>11</sub> N	No feasible rule
isopentane C <sub>5</sub> H <sub>12</sub>	2	1-propanol C <sub>3</sub> H <sub>8</sub> O	No feasible rule
acetic acid C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	3	1,4 dioxane C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	No feasible rule
oxazole C <sub>3</sub> H <sub>3</sub> NO	3	2 methoxyethanol C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	No feasible rule
octane C <sub>8</sub> H <sub>18</sub>	4	1-butanol C <sub>4</sub> H <sub>10</sub> O	No feasible rule
2-methyl-1-butene C <sub>5</sub> H <sub>10</sub>	4		

FOR QUALITY, ENLARGED VERSION OF EACH TERNARY DIAGRAM IS PROVIDED IN ANOTHER FILE.

Table 4. Valid light boiling candidate entrainers for the separation of water – acetonitrile homoazeotropic mixture

<p><b>CCl<sub>4</sub> / Carbon tetrachlorure / CAS 56-23-5</b></p> <p>NRTL      <math>A_{ij}</math>      <math>A_{ji}</math>      <math>\alpha_{ij}</math>  A-B      364.836      1321.73      0.2858  B-E      4470.1659      3202.7976      0.2  A-E      563.9473      1323.8907      0.465</p> <p>Rule 59 SS</p> <p>A [sn] (354.6 K)  M 222-m  P #058  S 3.1-2  Z 23</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)  E [sn] (349.8 K)</p> <p>AE [sa] (344.5 K)  BE [sa] (340.0 K)  ABE [un] (337.0 K)</p> <p>recycl<sub>2</sub>  recycl<sub>1</sub></p> <p>LLE 298K  LLVE  S1  S2  F  D1  P2  P1</p>	<p><b>CHCl<sub>3</sub> / Chloroform / CAS 67-66-3</b></p> <p>NRTL      <math>A_{ij}</math>      <math>A_{ji}</math>      <math>\alpha_{ij}</math>  A-B      364.836      1321.73      0.2858  B-E      829.8500      1456.6787      0.2  A-E      723.051      -388.4718      0.3041</p> <p>Rule 46 R</p> <p>A [sn] (354.6 K)  M 021  P #006  S 2.0-2b  Z 11a</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)  E [sa] (334.2 K)</p> <p>BE [un] (330.4 K)  AE [sa] (334.2 K)</p> <p>reflux</p> <p>LLE 298K  LLVE  R1  F  D1</p>	<p><b>CH<sub>2</sub>Cl<sub>2</sub> / Dichloromethane / CAS 75-09-2</b></p> <p>UNIFAC</p> <p>A [sn] (354.6 K)  M 021  P #006  S 2.0-2b  Z 11a</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)  E [sa] (312.8 K)</p> <p>BE [un] (311.2 K)  AE [sa] (312.8 K)</p> <p>reflux</p> <p>LLE 298K  LLVE  R1  F  D1</p>
<p><b>CH<sub>4</sub>O / Methanol / CAS 67-56-1</b></p> <p>NRTL      <math>A_{ij}</math>      <math>A_{ji}</math>      <math>\alpha_{ij}</math>  A-B      364.836      1321.73      0.2858  B-E      -48.6725      610.4032      0.3001  A-E      50.6506      603.3091      0.2979</p> <p>Rule 9 SSS</p> <p>A [sn] (354.6 K)  M 120  P #009  S 2.0-2b  Z 11a</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)  E [sa] (337.6 K)</p> <p>AE [un] (336.8 K)</p> <p>recycl<sub>3</sub>  recycl<sub>2</sub></p> <p>LLE 298K  LLVE  S1  S2  S3  F  P2  P3</p>	<p><b>C<sub>2</sub>H<sub>6</sub>O / Ethanol / CAS 64-17-5</b></p> <p>UNIQUAC      <math>A_{ij}(A_{ij}(T))</math>      <math>A_{ji}(A_{ij}(T))</math>  A-B      266.311      332.599  B-E      -96.473 (0.6843)      -31.629 (0.4759)  A-E      1047.39 (-3.0701)      -119.468 (1.6298)</p> <p>Rule 17 SSR</p> <p>A [sn] (354.6 K)  M 222m  P #058  S 3.1-2  Z 23</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)</p> <p>AE [sa] (346.1 K)  ABE [un] (346.0 K)  BE [sa] (351.2 K)  E [un] (351.5 K)</p> <p>recycl<sub>3</sub>  recycl<sub>2</sub></p> <p>LLE 298K  LLVE  R1  R2  R3  F  S1  S2  P1  P2  P3</p>	<p><b>C<sub>3</sub>H<sub>3</sub>N / Acrylonitrile / CAS 107-13-1</b></p> <p>NRTL      <math>A_{ij}</math>      <math>A_{ji}</math>      <math>\alpha_{ij}</math>  A-B      364.836      1321.73      0.2858  B-E      2133.3077      584.6434      0.2960  A-E      475.621      -336.251      0.3042</p> <p>Rule 46 R</p> <p>A [sn] (354.6 K)  M 021  P #006  S 2.0-2b  Z 11a</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)  E [sa] (350.8 K)</p> <p>BE [un] (344.3 K)  AE [sa] (350.8 K)</p> <p>reflux</p> <p>LLE 298K  LLVE  R1  F  D1</p>
<p><b>CCl<sub>4</sub> / Acetone / CAS 67-64-1</b></p> <p>UNIQUAC      <math>A_{ij}</math>      <math>A_{ji}</math>  A-B      266.311      332.599  B-E      356.554      86.598  A-E      200.43      -162.767</p> <p>Rule 6 SSS</p> <p>A [sn] (354.6 K)  M 020  P #004  S 1.0-2  Z 4</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)  E [un] (329.2 K)</p> <p>recycl<sub>3</sub>  recycl<sub>2</sub></p> <p>LLE 298K  LLVE  S1  S2  S3  F  P2  P3</p>	<p><b>C<sub>3</sub>H<sub>7</sub>Br / 1-Bromopropane / CAS 106-94-5</b></p> <p>UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 59 RS</p> <p>A [sn] (354.6 K)  M 222-m  P #058  S 3.1-2  Z 23</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)</p> <p>AE [sa] (339.8 K)  ABE [un] (335.3 K)  BE [sa] (337.4 K)  E [sn] (344.1 K)</p> <p>recycl<sub>2</sub>  B/E recycl<sub>2</sub></p> <p>LLE 298K  LLVE  R1  F  S1  S2  D1</p>	<p><b>C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> / Ethyl acetate / CAS 141-78-6</b></p> <p>UNIQUAC      <math>A_{ij}(A_{ij}(T))</math>      <math>A_{ji}(A_{ij}(T))</math>  A-B      266.311      332.599  B-E      -9.6725      945.6148  A-E      -159.8897      405.2521</p> <p>Rule 59 RS</p> <p>A [sn] (354.6 K)  M 222-m  P #058  S 3.1-2  Z 23</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)</p> <p>AE [sa] (348.9 K)  ABE [un] (344.3 K)  BE [sa] (344.4 K)  E [sn] (350.2 K)</p> <p>recycl<sub>2</sub>  B-rich to S2  E-rich recycl<sub>1</sub></p> <p>LLE 298K  LLVE  R1  F  S1  S2  D1</p>
<p><b>C<sub>4</sub>H<sub>9</sub>Cl / n-Butyl chloride / CAS 109-69-3</b></p> <p>UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 59 RS</p> <p>A [sn] (354.6 K)  M 222-m  P #058  S 3.1-2  Z 23</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)</p> <p>AE [sa] (344.1 K)  ABE [un] (338.3 K)  BE [sa] (341.9 K)  E [sn] (352.6 K)</p> <p>recycl<sub>2</sub>  B-rich to S2  E-rich recycl<sub>1</sub></p> <p>LLE 298K  LLVE  R1  F  S1  S2  D1</p>	<p><b>C<sub>5</sub>H<sub>8</sub> / trans 1,3-Pentadiene / CAS 2004-70-8</b></p> <p>UNIFAC * (calculated binary BE and ternary ABE azeotropes are not reported experimentally)</p> <p>Rule 59 RS</p> <p>A [sn] (354.6 K)  M 222-m  P #058  S 3.1-2  Z 23</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)</p> <p>AE [sa] (313.8 K)  ABE [un] (312.3 K)  BE [sa] (313.2 K)  E [sn] (315.1 K)</p> <p>B/E recycl<sub>2</sub>  B-rich to S2  E-rich recycl<sub>1</sub></p> <p>LLE 298K  LLVE  R1  F  S1  S2  D1</p>	<p><b>C<sub>6</sub>H<sub>6</sub> / Benzene / CAS 71-43-2</b></p> <p>UNIFAC</p> <p>A [sn] (354.6 K)  M 222-m  P #058  S 3.1-2  Z 23</p> <p>AB [sa] (349.9 K)  B [sn] (373.1 K)</p> <p>AE [sa] (346.5 K)  ABE [un] (339.7 K)  BE [sa] (342.7 K)  E [sn] (353.3 K)</p> <p>recycl<sub>2</sub>  B-rich to S2  E-rich recycl<sub>1</sub></p> <p>LLE 298K  LLVE  R1  F  S1  S2  D1</p>
<p>Legend: same as table 5</p>		

Table 5. Valid intermediate and heavy boiling candidate entrainers for the separation of water – acetonitrile homoazeotropic mixture

<p><b>C<sub>2</sub>HCl<sub>3</sub> / Trichloroethylene / CAS 79-01-6</b>                      UNIQUAC                      A-B 266.311 332.599                      B-E 474.727 3469.349                      A-E -55.546 598.082</p> <p>Rule 76                      SS                      M 222-m P #058                      S 3.1-2 Z 23</p>	<p><b>C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> / 1,2-Dichloroethane / CAS 107-06-1</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 76                      SS                      M 222-m P #058                      S 3.1-2 Z 23</p>	<p><b>C<sub>3</sub>H<sub>8</sub>O / Isopropanol / CAS 67-63-0</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 29                      SSR                      M 222-m P #058                      S 3.1-2 Z 23</p>
<p><b>C<sub>5</sub>H<sub>10</sub>O<sub>2</sub> / 1,4-cyclohexadiene / CAS 628-41-1</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 76                      RS                      M 222-m P #058                      S 3.1-2 Z 23</p>	<p><b>C<sub>5</sub>H<sub>10</sub>O<sub>2</sub> / isopropyl acetate / CAS 108-21-4</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 76                      SS                      M 222-m P #058                      S 3.1-2 Z 23</p>	<p><b>C<sub>6</sub>H<sub>10</sub> / Cyclohexene / CAS 110-83-8</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 76                      SS                      M 222-m P #058                      S 3.1-2 Z 23</p>
<p><b>C<sub>8</sub>H<sub>14</sub> / 1-Octene / CAS 629-05-0</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 88                      RS                      M 220-m P #053                      S 2.1-2b Z 10</p>	<p><b>C<sub>4</sub>H<sub>9</sub>Br / 1-Bromobutane / CAS 109-65-09</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 89                      SS                      M 222-m P #058                      S 3.1-2 Z 23</p>	<p><b>C<sub>7</sub>H<sub>8</sub> / Toluene / CAS 108-88-3</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 89                      SS                      M 222-m P #058                      S 3.1-2 Z 23</p>
<p><b>C<sub>8</sub>H<sub>10</sub> / Ethylbenzene / CAS 100-41-4</b>                      UNIFAC * (calculated ternary ABE azeotrope is not reported experimentally)</p> <p>Rule 88                      RS                      M 220-m P #053                      S 2.1-2b Z 10</p>	<p><b>Legend:</b> see text and the following notations</p> <p> <math>\Delta</math> : [sa] = saddle    <math>\bullet</math> : [un] = unstable node    <math>\blacksquare</math> : [sn] = stable node                      X: pure X    XY: XY azeotrope    <math>\overline{XY}</math>: XY heteroazeotrope  <math>\underline{X}</math>-rich: X rich heterogeneous mixture    <math>\overline{X/Y}</math>: mixture of X-rich and Y-rich  <math>\rightarrow</math> : main tank composition path (Rn: n<sup>th</sup> rectifier; Sn: n<sup>th</sup> stripper)                      ..... : LLE at 298K tie line                      P<sub>n</sub>, D<sub>n</sub>, recycl<sub>n</sub>: bottom heavy product, distillate light product, recycled stream of the n<sup>th</sup> batch task.                 </p>	