Heterogeneous batch distillation processes for waste solvent recovery in pharmaceutical industry

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Abstract

A summary about our experiences in the introduction of heterogeneous entrainers in azeotropic and extractive batch distillation is presented in this work. Essential advantages of the application of heterogeneous entrainers are showed by rigorous simulation and experimental verification in a bench batch distillation column for separating several azeotropic mixtures such as acetonitrile – water, n hexane – ethyl acetate and chloroform – methanol, commonly found in pharmaceutical industry.

Keywords: heterogeneous entrainer, batch column, azeotropic and extractive distillation

1. Introduction

Batch distillation is widely used in pharmaceutical and specialty chemical industry to recover valuable components from waste of solvent mixtures. The regular presence of azeotropes restricts severely the number of feasible separations. Azeotropic and extractive distillations are the most common alternatives encountered in the industry, requiring the addition of a third component to enhance the volatility of the components.
Synthesis and design of a new batch distillation process is done in two steps: (1) selection of an adequate entrainer along with the column configuration and the corresponding product cut sequence. It can be done using a recent computer tool RegSolExpert® (ProSim SA) including an exhaustive set of rules for selecting both, homogeneous and heterogeneous entrainers and (2) the process design for determining the main operating parameters by using a batch process simulator such as ProSim Batch (ProSim SA). In general, heterogeneous entrainers have a more privileged position than homogeneous because a higher number of ternary diagrams are suitable. Indeed, more than 70% of the feasibility rules included in RegSolExpert® match up to heterogeneous entrainers. In this paper, we present a general procedure to systematize the search for an appropriate azeotropic or extractive distillation process enabling the separation of non-ideal binary mixtures by introducing heterogeneous entrainers.
Primary criteria for selecting feasible heterogeneous entrainer comprise the non pollutant component and the market availability. For the separation of aqueous-organic mixtures, many feasible entrainers could be found among those inducing a liquid-liquid phase split with water and vice versa, water seems to be a promising candidate for organic wastes. Essential features of the application of heterogeneous entrainers are showed by rigorous simulation and experimental verification in a bench batch distillation column for separating three commonly found mixtures: acetonitrile – water, n hexane – ethyl acetate and chloroform – methanol.

2. Heterogeneous entrainers in batch azeotropic distillation (HABD)

Azeotropic distillation in a batch rectifying column is based on the complete addition of an adequate amount of entrainer together with the azeotropic mixture as initial charge in the boiler. One unstable node given by a component or mixture can be drawn as a top product. The general feasibility criterion for selecting a heterogeneous entrainer can be summarized as follows: choose a low, intermediate or high boiling entrainer (E) giving rise to a ternary system in which the heterogeneous azeotrope is an unstable node of the residue curve map. The separation of all components is better if: (a) the heterogeneous azeotrope is binary instead of ternary, (b) the heteroazeotrope composition defines an approx. equal liquid phase split in the decanter and (c) the immiscibility gap is large leading to a high purity of the distillate and the entrainer-rich phase. These features will be analyzed considering two azeotropic mixtures: acetonitrile – water and n hexane – ethyl acetate in a batch rectifier and a quaternary mixture in a middle vessel column.

2.1. Rectifying column configuration

The mixture acetonitrile - water displays a minimum boiling azeotrope with $x_{\text{acetonitrile}} = 0.676$ at 76.8°C. The initial entrainer candidate list included 91 entrainers spanning a wide spectrum of chemical families. According to RegSolExpert®, only 21 entrainers matched with some feasibility criterion (Gerbaud et al., 2006). Four homogeneous entrainers were rejected because the separation was possible due to the curvature of the distillation boundaries and led to complex sequences of operating tasks. From the 17 remains heterogeneous compounds only three light entrainers did not form ternary azeotrope: dichloromethane (39.4°C), chloroform (61°C) and acrylonitrile (77.3°C). Only chloroform and acrylonitrile were tested. Acrylonitrile has been found earlier by manual search (Rodriguez et al. 2002) in an experimental database (Gmehling, J., 1994). Figure 1a and 1b display the residue curve map for chloroform and acrylonitrile, respectively.

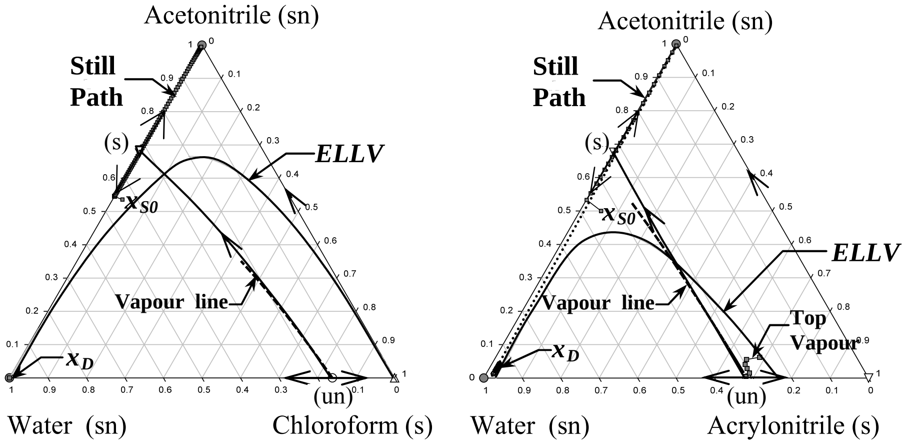


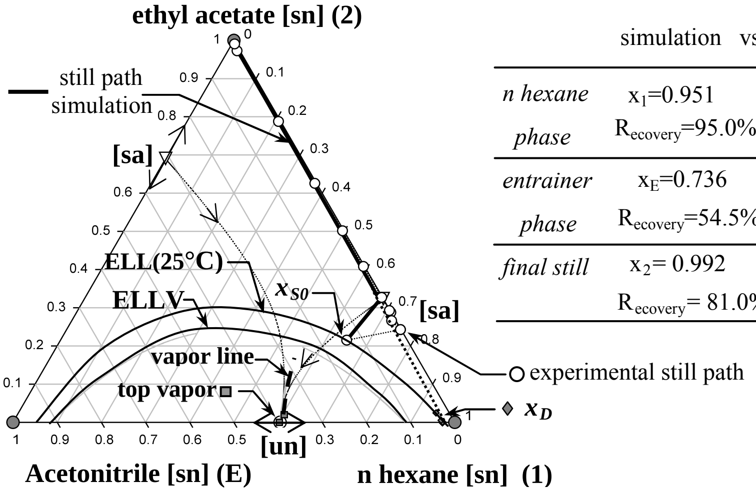
Figure 1. Residue curve map and simulation results of HABD.

Simulation results for both heterogeneous entrainers are reported in Table 1 considering only the reflux of the entrainer-rich phase and showing the superiority of chloroform in recovery and purity of all components. However, the operating times were very similar (about 6.5 hours) because both entrainers lead to a similar phase split ratio into the decanter from the condensed top vapour (about 0.16 in water-rich phase).

Table 1. Simulation results chloroform vs acrylonitrile

	Chloroform	Acrylonitrile (* experimental values)	
Aqueous	x_{Water}=0.9996	x_{Water}=0.947	*x_{Water}=0.946
Phase	$R_{ecovery}$=97.8%	$R_{ecovery}$=92.6%	*$R_{ecovery}$=89.0%
Entrainer	x_E=0.9990	x_E=0.712	*x_E=0.6916
Phase	$R_{ecovery}$=81.0%	$R_{ecovery}$=72.0%	*$R_{ecovery}$=69.0%
Final	$x_{acetonitrile}$= 0.9945	$x_{acetonitrile}$= 0.992	*$x_{acetonitrile}$= 0.995
Still	$R_{ecovery}$= 99.2%	$R_{ecovery}$= 95.6%	*$R_{ecovery}$= 91.8%

Experimental validation of HABD with acrylonitrile were carried out in a SHOTT batch distillation column available in a bench scale (Rodriguez et al., 2002; 2005) considering two reflux policies: case (1) only the reflux of acrylonitrile-rich phase from the decanter for the mixture acetonitrile – water and case (2) an additional reflux given by a portion of the condensed vapour by manipulating the open/close time of the solenoid valve for the separation of n hexane – ethyl acetate using acetonitrile. Experimental values are shown in Figure 1b and Table 1 for case (1) and Figure 2 displays the simulation and experimental results for the case (2) demonstrating the acceptable performance of the HABD process.



	simulation	vs experiments
n hexane phase	x_1=0.951 $R_{ecovery}$=95.0%	x_2=0.968 $R_{ecovery}$=94.5 %
entrainer phase	x_E=0.736 $R_{ecovery}$=54.5%	x_E=0.728 $R_{ecovery}$=48.4%
final still	x_2= 0.992 $R_{ecovery}$= 81.0%	x_2= 0.991 $R_{ecovery}$= 75.1%

Figure 2. Simulation and experimental results for n hexane – ethyl acetate – acetonitrile.

Those two examples bring important insights on HABD:

(a) less entrainer amount is required in the initial charge, compared to azeotropic distillation with a homogeneous entrainer.

(b) the liquid – liquid splitting of the top condensed vapour allows the straightforward withdrawal of one component (water or n hexane) as distillate,

(c) reflux policy can be versatile given by only the reflux of the entrainer-rich phase or by a combined reflux of both decanted phases (Rodriguez-Donis et al., 2002, Skouras et al., 2005),

(d) the adequate reflux policy displaces the typical distillation boundary of the residue curve map close to the binary side of azeotropic components. Therefore, the feasible region is not limited by the typical distillation boundary of the residue curve map anymore (Lang, 2006).

In HABD, the still path moves in a bigger region wherein it is connected to the binary heterogeneous vapour at the column top and the boiler can reach the stable node of acetonitrile at the end of the process (see still path in Figure 1 and 2 starting in x_{S0}). In the case of the sole reflux of the decanted entrainer-rich phase, the boundary of HABD is given by a hypothetical line joining the homogeneous azeotrope to be separated and the composition of the product-rich phase (dotted line in Figure 1b and 2). Although in both cases good agreement was obtained between simulation and experimental results, the reflux policy established in case (2) provided a more stable amount proportion of both liquid phases inside the decanter during the whole process. Theoretically as computed by simulation in Figure 1b and Figure 2, the composition of the top vapour stayed closer to the binary heteroazeotrope composition for case (2). As in continuous heterogeneous azeotropic distillation, liquid – liquid splitting occurred inside the top section in the SCHOTT column and experimental validations went well.

2.2. Middle vessel column configuration (MVC) with light or intermediate entrainer

Analysis of the heterogeneous azeotropic distillation in this column configuration has been made only by using rigorous simulation with ProSim Batch. MVC enable to split quaternary mixtures by a single task like the ternary mixtures using a batch rectifier. The separation of acrylonitrile (light entrainer) – acetonitrile – water – acetic acid mixture was studied elsewhere involving a single basic distillation region in the quaternary composition space (Rodriguez et al., 2001). The binary heteroazeotrope reaches the column top and a suitable reflux policy keep acetonitrile and acetic acid stay into the middle vessel and the boiler at the end of the process, respectively. Now, the use of an intermediate boiling heterogeneous entrainer (isobutyl acetate) is viable for separating a methanol – water – propanoic acid mixture (residue curve map in figure 3).

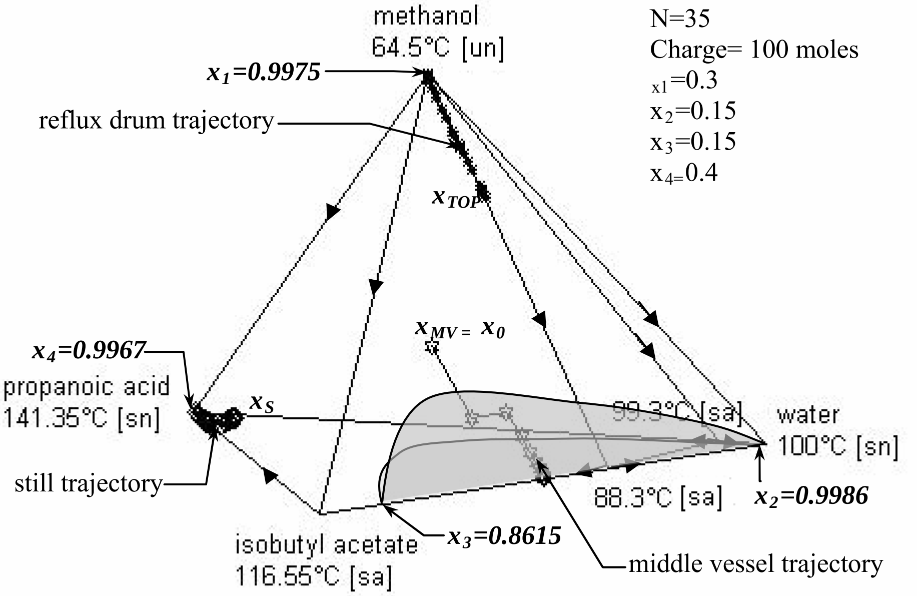


Figure 3. Separation of a quaternary mixture for HABD in a middle vessel column.

The homogeneous mixture methanol – water – propanoic acid exhibits a saddle azeotropic point and it can not be separated by conventional distillation process.

However, separation is feasible in a MVC by HABD with isobutyl acetate. Two binary azeotropes occur but in this case, both are saddle points and the composition space is divided by an unstable distillation boundary in two basic distillation regions. Methanol is the sole unstable node while water and propanoic acid are the stable nodes of their respective regions. The still initial charge into the still and the middle vessel (x_0) has to be located inside the region wherein propanoic acid is the stable node. Figure 3 displays the composition into the boiler (x_S) and the reflux drum (x_{top}) after the heat and liquid filling operation of the whole column. An adequate definition of the liquid holdup inside the reflux drum and the middle vessel allows the separation of four components by one single operating step under infinite reflux ratio. Methanol goes to the top reflux drum (x_1), propanoic acid concentrates in to the boiler (x_4) and the saddle binary heteroazeotrope water (x_2) - isobutyl acetate (x_3) is kept into the middle vessel at the end of the process. Figure 3 shows the final composition and the composition path inside the still, the condenser and the middle vessel along with the column specifications operated under reflux total conditions until steady state is reached (after about 2 hours). Distillate removal or closed operation can start afterwards.

3. Heterogeneous entrainers in batch extractive distillation (HBED)

Extractive distillation is the most used process in the industry due to its operating simplicity. But, the selection of the entrainer is based mainly on a criterion: High boiling homogeneous entrainer forming no additional azeotropes. Despite the criterion simplicity, designing a new extractive distillation process is often complicated. Indeed, many suitable entrainers enhancing significantly the relative volatility of azeotropic components usually give rise to new binary and even ternary heterogeneous azeotropes, that are often saddles. Therefore, these entrainers were always considered as unfeasible although it is not the case using HEBD process (Rodriguez et al., 2003) because a more general criterion rules extractive distillation process feasibility (Rodriguez-Donis et al., 2009a, 2009b). Unlike to azeotropic distillation, the entrainer is fed continuously at some column position, leading to different column sections.

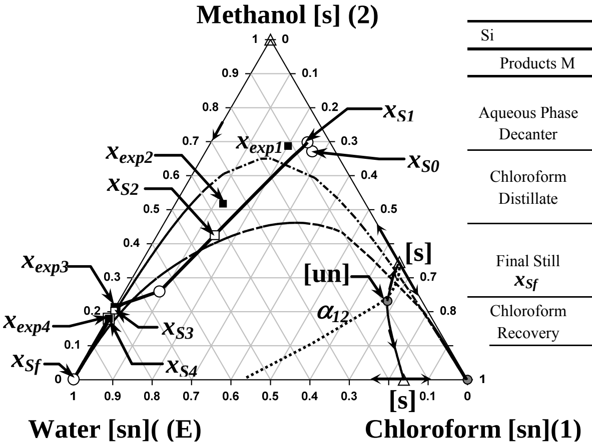
Our precedent works concerned three ternary mixtures: acetonitrile – water with butyl acetate, ethanol – water with ethyl acetate and chloroform – methanol with water (Rodriguez et al., 2003, Van Kaam et al. 2008). HEBD brings a few more advantages:

(1) HEBD in a batch rectifier is simpler than extractive batch distillation using a homogeneous entrainer fed at some intermediate tray, as is usual. Indeed, the heterogeneous entrainer can be fed at the column top leading only to an extractive column section and allowing the withdrawal of the saddle binary heteroazeotrope as top vapor. The further condensation of the top vapor generates two liquid phases similar to the heteroazeotropic distillation process,

(2) Water is often a suitable non pollutant heterogeneous entrainer for organic wastes treatment. And, organic compounds are suited for aqueous-organic wastes split.

(3) HEBD offers more ternary diagrams alternatives than the numerous HABD ones.

Experimental validation in the SCHOTT distillation column was recently performed for the separation of chloroform – methanol – water waste using the inner component, water, as heterogeneous entrainer. Figure 4 displays the simulation results (x_S) and the experimental verification (x_{exp}) of the process. Even if the performance of the process was good and adequate agreement between experiments and prediction was also obtained, extreme care must be taken with the regulation of the heat duty in the boiler. Accumulation of water into the boiler required a continuous increasing of the oil bath temperature wherein the boiler was immersed. However, pollution of methanol in the chloroform-rich phase occurs rapidly if the correct ratio of the water flow rate and the vapor overflow inside the column is surpassed. Indeed, a significant amount of heterogeneous entrainer was required for the separation of all studied ternary system by HEBD given by the interception of the univolatility line α_{12} in the heterogeneous edge close to the entrainer vertex. A better column configuration must be considered such as middle vessel column or those having two boilers as proposed by Hua et al. (2007).



Products	Simulation Results		Experimental Results	
	Mol	x_{MOLAR}	Mol	x_{MOLAR}
Aqueous Phase Decanter	**0.045**	x_1 0.0016	**1.07**	x_1 0.0035
		x_2 0.0027		x_2 0.0211
		x_3 0.9957		**x_3 0.9754**
Chloroform Distillate	**5.2**	**x_1 0.9906**	**4.86**	**x_1 0.9900**
		x_2 0.0048		x_2 0.0044
		x_3 0.0046		x_3 0.0056
Final Still x_{Sf}	**72.3**	**x_1 0.0001**	**69.2**	**x_1 0.0006**
		x_2 0.1795		x_2 0.1800
		x_3 0.8204		x_3 0.8194
Chloroform Recovery		***95.4***		***89.0***

Figure 4. Simulation results and experimental validation of HEBD.

4. Conclusions

Application of heterogeneous entrainer for separating non-ideal mixtures using azeotropic and extractive batch distillation demonstrated important advantages having a straight effect over the economy of the process: more potential candidates reducing the time of the preliminary process synthesis, less amount of entrainer is usually required, heterogeneous entrainer neutralizes the effect of the distillation boundaries of the residue curve map giving a bigger feasible region and allowing the separation of all components in one single operating task. For the separation of aqueous-organic mixtures, many feasible entrainers could be found among those inducing a liquid-liquid phase split with water and vice versa, water seems to be a promising candidate for separating organic wastes. Possibility of the use of non pollutant entrainers is increased.

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