Separation of n-hexane - ethyl acetate mixtures by azeotropic batch distillation with heterogeneous entrainers.

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Abstract.

In this article, a systematic study of the separation of the n-hexane - ethyl acetate mixture with an entrainer by heterogeneous azeotropic batch distillation is performed. Based upon the thermodynamic behaviour of the ternary mixtures, potential entrainers partially miscible with one or two original azeotropic components are chosen. In all cases, the entrainer adds a heterogeneous binary or ternary azeotrope that is the lowest boiling point in the ternary diagram. Therefore, it leaves the column by the overhead stream which is subcooled to get two liquid phases in the decanter. The phase with the highest amount of the original component is removed as distillate product whereas the entrainer – rich phase is continuously refluxed to the column. Considering methanol, acetonitrile, water and nitromethane as heterogeneous entrainers, screening was performed based on the composition of the unstable heteroazeotropic mixture, the ratio of both liquid phases in the condensed top vapour and the purity of the distillate product determined by the liquid – liquid envelope at the decanter temperature. The process feasibility analysis is validated by using rigorous simulation with the batch process simulator ProSimBatch. Simulation results are then corroborated in a bench experimental column for the selected entrainer, showing several advantages of heterogeneous batch distillation compared to homogeneous systems.

Keywords: batch distillation, heterogeneous entrainer, azeotropic distillation

1. Introduction

Batch processes are again becoming important because of recent expansion of the pharmaceutical and speciality chemical industries in many developing countries. Besides, recycling of liquid waste streams is becoming a key issue in all processing plants to meet stricter environmental regulations. Batch distillation is a widely used separation method in batch processes because of its inherent operational flexibility due to some extent to its time dependent operation. The separation of azeotropic mixtures or close boiling components is a challenging task in many chemical processes as it is impossible using a single conventional column or as a pressure swing distillation is an uneconomical process. Alternative techniques based on the addition of an auxiliary substance in the original mixture have been developed and are usually known as azeotropic and extractive distillation.

Process synthesis and design of these non-conventional distillation processes proceed in two steps. The first step - process synthesis - is the selection of one or more candidate entrainers along with the computation of thermodynamic properties like residue curve maps that help assess many column features such as the adequate column configuration and the corresponding product cuts sequence. The second step - process design - involves the search for optimal values of batch distillation parameters such as the entrainer amount, reflux ratio, boiler duty and number of stages. The complexity of the second step depends on the solutions obtained at the previous level, because efficiency in azeotropic and extractive distillation is largely determined by the mixture thermodynamic properties that are closely linked to the nature of the entrainer. Hence, we have established a complete set of rules for the selection of feasible entrainers for the separation of non ideal mixtures by homogeneous azeotropic batch distillation [1]. In contrast to batch homogeneous distillation processes, studies on heterogeneous batch distillation were scarce [2-4] until a new method for the synthesis of heterogeneous distillation in a batch rectifier was defined and a complete set of rules for the selection of heterogeneous entrainers for the separation of non-ideal mixtures was established [5,6].

Simulation and experimental results have shown key differences between homogeneous and heterogeneous batch distillation [6]. Indeed, some advantages of heterogeneous batch processes compared to homogeneous systems are : i) more suitable candidate entrainers and hence, more design alternatives for the separation of non-ideal mixtures, ii) simplified distillation sequences thanks to the liquid – liquid phase split occurring in some parts of the column and in the decanter, iii) the addition of a smaller amount of entrainer to the original mixture, iv) the use of more flexible reflux policies through any combination of the entrainer – rich phase and the distillate – rich phase, v) the still path can cross unstable separatrices allowing the separation of components located in different basic distillation regions. The overall cost reduction generated by these advantages makes heterogeneous batch distillation an attractive option for the separation of non-ideal mixture generated by specialty industries.

The aim of this paper is to study the performance of heterogeneous batch distillation (HBD) for the separation of the mixture n-hexane – ethyl acetate. This azeotropic mixture is often used in pharmaceutical industries for separating bioactive substances by liquid chromatographic processes. The separation of this mixture by batch distillation was first studied by Rodriguez-Donis *et al.* [7], by using acetone as a homogeneous entrainer. As the separation by using a single batch distillation process with acetone was not possible, a hybrid process was proposed involving a homogeneous azeotropic distillation column with acetone and a liquid – liquid extraction column with water. To circumvent this complex process, we propose in this paper a simpler process by using heterogeneous azeotropic batch distillation. Based on entrainer selection rules established by Rodriguez-Donis et al. [5], which consider the thermodynamic behaviour of multicomponent mixtures, an initial list of potential entrainers partially miscible with one or both original azeotropic components are selected. From the analysis of residue curve map features, in particular the decanter phases composition and the distillation region separatrices curvature, the sequence of products to be drawn from the rectifier column can be predicted. The number of distillation tasks in the whole process is set by the products targeted purity.

2. Selection of a suitable entrainer for the separation of n-hexane - ethyl acetate mixtures by heterogeneous azeotropic batch distillation.

Liquid – vapour equilibrium data for the binary mixture n-hexane – ethyl acetate have been scarcely reported in the scientific literature [8]. Those authors reported a minimum boiling temperature azeotrope with an average mole fraction of n-hexane equal to 0.6565 and a temperature of 65.15°C at 101.3 kPa. A more detailed experimental study, at atmospheric pressure, of liquid - vapour equilibrium was performed by Acosta et al. [9]. Their estimation of the azeotropic mixture corresponds to a temperature of 64.85°C with a molar fraction of n-hexane of 0.657 with an average experimental error for the temperature and composition measurements of 0.02 °C and 0.003 mole fraction, respectively.

The candidate homogeneous and heterogeneous entrainers are investigated applying the rules reported by Rodriguez-Donis et al. [1,5]. The existence of binary and ternary azeotropes is sought by using literature data [8] and by simulating liquid – vapour and liquid – liquid – vapour equilibrium by using the BibPhyAddIn Macro in an Excel spreadsheet [10]. Confirming the need for a complex hybrid process in case a homogeneous entrainer like acetone is used [7], no homogeneous entrainer matching the reported rules has been found whereas some suitable heterogeneous entrainers have been identified; the composition and temperature of their azeotropic mixtures with the original components are displayed in Table 1 [8].

As seen in Table 1, the boiling temperature of the possible entrainers is either lower or higher than that of the original components. All candidates form a binary heterogeneous azeotrope with n-hexane. Methanol and acetonitrile add a homogeneous minimum boiling azeotrope with ethyl acetate. Nitromethane forms a zeotropic mixture with ethyl acetate, whereas water is the only component that forms an additional heterogeneous azeotrope with ethyl acetate and also adds a heterogeneous ternary azeotrope to the resulting mixture. Experimental liquid – vapour equilibrium data are available for all binary entrainer- ethyl acetate mixtures [11]. However, for the binary system entrainer – n-hexane that exhibits a significant miscibility gap, the only experimental thermodynamic information is given in Table 1, except for methanol for which liquid – vapour equilibrium data were reported by Gmehling et al. [11]. All previous experimental data are used to regress binary interaction parameters for the UNIQUAC and NRTL models with ChemCAD IV minimizing the mean square deviation between the experimental and calculated mole fraction in the liquid – phase (Table 2). Then, ternary liquid – liquid – vapour equilibrium is determined by using these binary coefficients with BibPhyAddIn [10]. As a result of the use of these binary interaction parameters regressed on binary systems to predict the behavior of a ternary system, we have detected the existence of the experimental heterogeneous ternary azeotrope in the mixture n-hexane – ethyl acetate – water, which has the lower boiling point in the system (unstable node).

For the synthesis of heterogeneous batch distillation the liquid – liquid envelope at the decanter temperature is considered in addition to the residue curve map. Therefore, the binary interaction parameters used in predicting liquid – liquid equilibrium are estimated from binary heterogeneous azeotrope or liquid – liquid equilibrium data [8,10]. Table 3 shows the calculated purity of original components in each phase split at 25°C for all heterogeneous azeotropes reported in Table 1. The thermodynamic models and binary coefficients used in the calculation of the liquid – liquid – vapour equilibrium, liquid – liquid equilibrium at 25°C and the separatrices are reported in Table 2.

From the thermodynamic information given in Table 1, Table 2 and Table 3, the residue curve maps are drawn in figure 1 for each entrainer and the batch distillation task sequence required to perform the separation of the original components is deduced using published rules [5]. The residue curve maps of the ternary mixture n-hexane – ethyl acetate – entrainer displayed in Figure 1 indicate the temperature and the topological stability of all singular points. As the heteroazeotropes are unstable nodes, they are recovered in the decanter where the phase rich in one of the original components L_W is removed as distillate, whereas the other original component is retained into the still at the process end. In some cases, the composition of the phase rich in original component defined by the liquid – liquid equilibrium at the decanter temperature may not meet purity requirements; then, further distillation tasks are needed.

One of the key thermodynamic parameter in heterogeneous batch distillation is the decanter split ratio ω. It is defined by the position of the heteroazeotrope composition on its liquid – liquid tie line at the decanter temperature or alternatively by the mole ratio of the entrainer – rich phase L_R to the overall liquid phase $L°$ into the decanter as follows:

$$L_R = \omega \cdot L^o \tag{1}$$

Then, the molar quantity of entrainer-weak / original component – rich phase L_W is given by equation (2):

$$L_W = (1-\omega) \cdot L^o \tag{2}$$

As stated by Rodriguez-Donis et al. [6], the reflux policy to be used is strongly influenced by the split ratio ω at the decanter. If the liquid reflux needed at the top of the column is lower than L_R, then the distillation can be performed by using only the reflux of entrainer – rich phase. Otherwise, the separation of original components requires the reflux of a combination of both decanted phases.

Nitromethane shows the simplest residue curve map with one unstable curved separatrix dividing the triangle in two basic distillation regions. Methanol and acetonitrile give rise two binary azeotropic mixtures and three distillation regions that are bounded by two unstable curved separatrices. Water shows the most complicated residue curve maps, due to the presence of a ternary azeotrope and a miscibility gap with both the n-hexane and the ethyl acetate component. In all four cases, the heteroazeotrope (binary or ternary) has the lowest boiling temperature of the system. As it can be seen in Table 3, all entrainers except water provide the n-hexane – rich phase L_W as distillate product with a purity better than 0.91. Water is not a desirable entrainer because of the existence of ternary azeotrope whose n-hexane – rich phase has a water purity much lower (0.70). Considering in Table 3 the split ratio ω at the decanter (inside the range 0.3-0.6) and the purity of both liquid phases at 25°C, methanol and acetonitrile are better entrainers than nitromethane. Methanol is a light entrainer that would result in a ternary system with a low boiling temperature that in turn will likely increase the cost of the condenser cooling system and the make-up of fresh entrainer to be added in the next batch. Besides, the mole ratio of the product-to-be n-hexane in the methanol rich phase ($x^{II}_{n\text{-hexane}}$ in Table 3) is higher than the one calculated for the acetonitrile. Therefore, acetonitrile seems the best entrainer for the separation of n-hexane – ethyl acetate by heterogeneous azeotropic batch distillation.

3. Simulation of the separation of the mixture n-hexane – ethyl acetate by heteroazeotropic batch distillation using acetonitrile.

We study the separation of n-hexane – ethyl acetate mixture by using acetonitrile as a heavy heterogeneous entrainer. The simulation of the process is performed with the batch process simulator ProSimBatch [10]. It enables to evaluate operational parameters like the entrainer amount that are not provided by the feasibility and synthesis analysis The column model consists of usual plate by plate 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 phase split. Numerical treatment of the Differential Algebraic Equation (DAE) system and discrete events handling is performed with DISCo, a numerical package for hybrid systems with a DAE solver based on Gear’s method. The column technical features and operating conditions are shown in Table 4. A sequence of two operational batch steps, namely an infinite reflux step and a distillate removal step described in detail below are simulated.

The amount of heterogeneous entrainer to be added to the original binary mixture is established from material balances considering that the entrainer composition in the still should be less than 0.01 at the end of infinite reflux batch step 1. Simulation shows that this composition is reached after two hours, which is the end of batch step 1. It should be noted that the initial ternary composition F is placed in distillation region I that is not limited by the vertex of ethyl acetate (see Figure 2). Therefore, in order to reach the vertex of ethyl acetate located in region II at the end of the distillation process, the still path must cross the unstable separatrix connecting the heteroazeotrope with the homoazeotrope n-hexane – ethyl acetate. As established by Rodriguez – Donis et al. [6], such a crossing is possible with different reflux policies, either the reflux of entrainer – rich phase or a combination of both decanted liquid phases. In this example, the distillate removal step (batch step 2) is performed refluxing a combination of entrainer – rich L_R and entrainer-weak L_W phases coming from the decanter, the reflux policy 2.3 of Rodriguez-Donis et al. [6]. As in Rodriguez-Donis et al. [6] the acetonitrile – rich phase L'_R and n-hexane – rich phase L'_W reflux flow rates are a fraction θ and φ of the amount of each phase (L_R and L_W) contained in $L°$, the condensed vapour flow rate entering the decanter. Table 4 displays the θ and φ values that enable to withdraw the binary heterogeneous azeotrope during the whole distillation process. The process requires that the reflux of the acetonitrile – rich phase is larger (θ >1) than the acetonitrile quantity in the vapour flow rate leaving the column top $L°$, while the amount of n-hexane to be recycled at the top of the column is determined by the calculated φ value. $\theta > 1$ means that drying of the acetonitrile – rich phase in the decanter during operation can occur and care should be taken to avoid it in the definition of an optimal reflux policy.

Figure 2 shows the simulation results, the still path and the column liquid profile, at the end of batch step 1 (infinite reflux) and at the beginning and end of batch step 2 (distillate removal). Table 5 displays significant process values. As can be seen in Figure 2 and Table 5, only 12.2% of acetonitrile is added to the initial azeotropic binary mixture and the resulting ternary mixture lies in the distillation region I. it has been observed [6] that heterogeneous batch distillation requires less entrainer than homogeneous batch distillation. The liquid profile in the column at the end of the infinite reflux operation links the still composition $F_{R\infty}$ to the binary heteroazeotrope n-hexane – acetonitrile in the first top tray of the column through the vapour line. Then, applying the reflux policy detailed in Table 4, distillate removal starts. Five minutes after the beginning of the distillation step, the column liquid profile changes suddenly and crosses the unstable separatrix due to the recycle of both decanted liquid phases. The reason is that the liquid phase leaving the first tray of the column top has a composition (x_T) inbetween the heteroazeotrope and the acetonitrile – rich phase composition and is located in a distillation region (III) different from region (I) which contains the still composition at infinite reflux $F_{R\infty}$. Consequently, the simulated still path crosses the unstable separatrix separating distillation regions I and II (full black line in Figure 2). At the end of batch step 2, the still path reaches the ethyl acetate vertex when all n-hexane is drawn as distillate product. The operating parameters θ and φ are set to obtain the binary heteroazeotrope at the column top during the whole step 2. Therefore, the split ratio ω is kept constant. The n-hexane – rich phase is drawn as distillate product whereas the acetonitrile – rich phase can be recovered at the decanter at the end of the step 2. Table 5 reports the simulated purity and recovery yield of all components. Simulation computation time is typically less than 4 minutes on a Pentium III – based computer.

4. Experimental verification of the separation of the mixture n-hexane – ethyl acetate by heteroazeotropic batch distillation in a bench scale rectification column.

The technical features of the column and the operating conditions are similar for the experiments and the simulations. The glass SCHOTT distillation column has a total height of 1.7 m and an internal diameter of 0.026 m. The total height is packed with stainless steel wire mesh rings of 3x3 mm. The total packed height is considered to be equivalent to 45 theoretical plates and the total liquid hold goes up of 52.5 ml. The condenser is subcooled at 25°C and total liquid reflux is provided at the top of the column by a solenoid valve. The open/close time of the solenoid valve is defined considering that 70% of the condensed vapour is returned to the column. The 30% remaining condensed vapour is collected into the decanter (70 ml.) where the light phase is drawn as distillate (n-hexane – rich phase) whereas a portion of the heavy entrainer – rich phase is recycled to the top of the column with a peristaltic pump.

Experiments taking into account these operating conditions (Table 4) are carried out in the bench distillation column and the results are presented in Figure 2 and Table 5. Analysis of the still composition is performed every 0.5 hours. The analysis of purity of the light and heavy phases in the decanter and of the distillate product is made at the end of the process (4.8 h). The acetonitrile, n-hexane and ethyl acetate compositions are determined using a FISONS HRGC chromatograph with a FID detector and with a column HP INNOWax (30 m x 0.53 mm, 0.25μm film). The injector and detector temperature are held at 180°C while the column temperature is set equal to 65°C. Prior calibration is done using internal standards; the samples were prepared by weighing on a SARTORIUS BP 211D balance with a precision of 10 μg. The standard accuracy and reproducibility in the composition for all components are found to be ± 0.1% and 0.3% respectively.

As shown in Figure 2, the still path obtained experimentally (circles) is in excellent agreement with the still trajectory calculated by simulation. The selected reflux policy permits the still path to cross the separatrix into another distillation region than the initial feed region. Hence, the still path is able to reach the ethyl acetate vertex and this component remains pure into the still at the end of the distillate removal step. Such a behavior is not possible with a homogeneous entrainer that gives rise to a similar residue curve map because the distillation process is restricted to the distillation region where the initial composition of the mixture is located. In this case, ethyl acetate could not be obtained as an isolated product.

Table 5 displays the quantity and composition of the main streams of the process. N-hexane is drawn of as distillate product with a molar purity of 96.8%. Another binary batch distillation step is required to obtain n-hexane with a highest purity. Ethyl acetate with 99.6% of purity is recovered in the still at the end of the process, while the acetonitrile – rich phase obtained from decanter can be reused in the next batch distillation process. The make-up of fresh entrainer for the next cycle of n-hexane – ethyl acetate separation is approximately 52 %.

5. Conclusions

Acetonitrile was chosen as a suitable heterogeneous entrainer for the separation of the azeotropic mixture n-hexane – ethyl acetate by heteroazeotropic batch distillation from the comparison of the residue curve maps of several candidate entrainers. We have confirmed the feasibility of the heteroazeotropic batch distillation via simulation and by experimentation in a bench batch distillation column. Good agreement was obtained between simulation and experimental results. The novel process with a single heterogeneous distillation column shows a great potential over a reported hybrid process with a homogeneous distillation column and a liquid – liquid extraction column. Indeed, the consumption of entrainer is low and the separation of all three components can be performed in a single batch distillation step using the defined reflux policy. The ethyl acetate purity is high enough to enable its recycling in a chromatography process whereas the n-hexane – rich phase must be purified in a simple non azeotropic batch distillation process.

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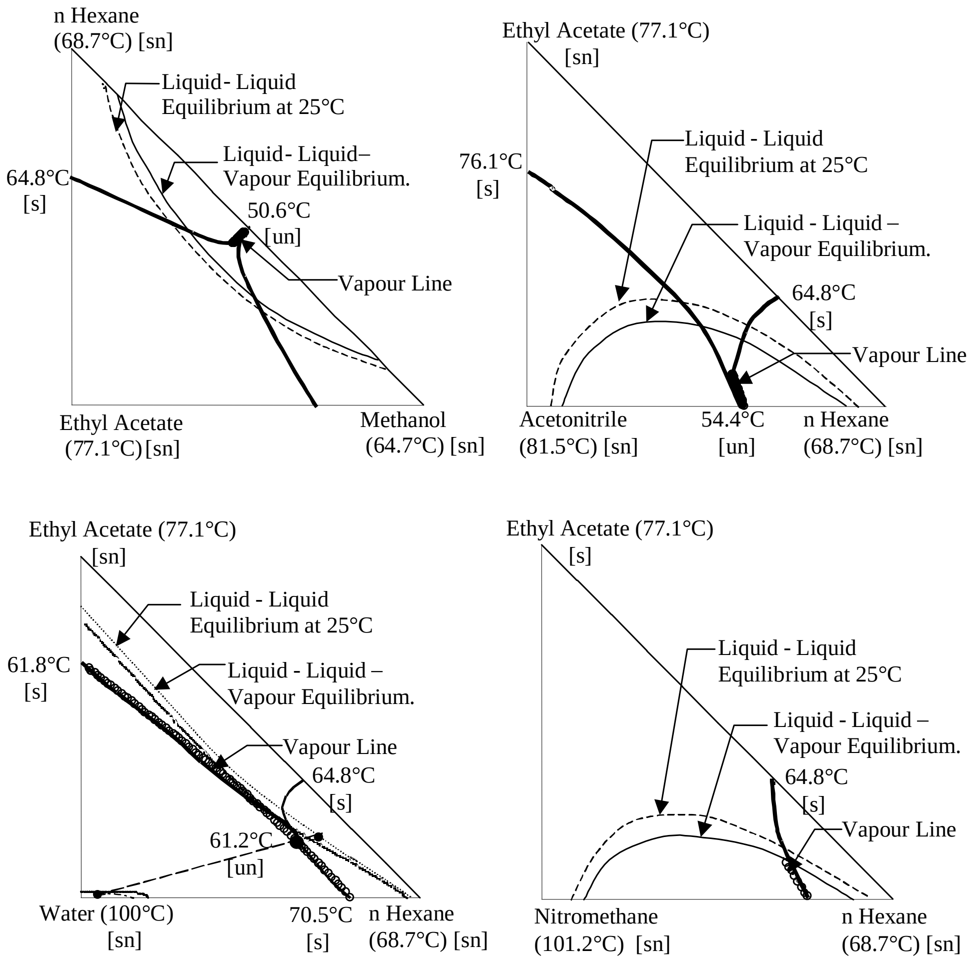
FIGURE CAPTION

Figure 1. Residue curve maps of ternary systems n hexane – ethyl acetate – heterogeneous entrainer

Figure 2. Simulation and experimental results of the separation of n hexane – ethyl acetate by using batch distillation with acetonitrile as a heavy heterogeneous entrainer



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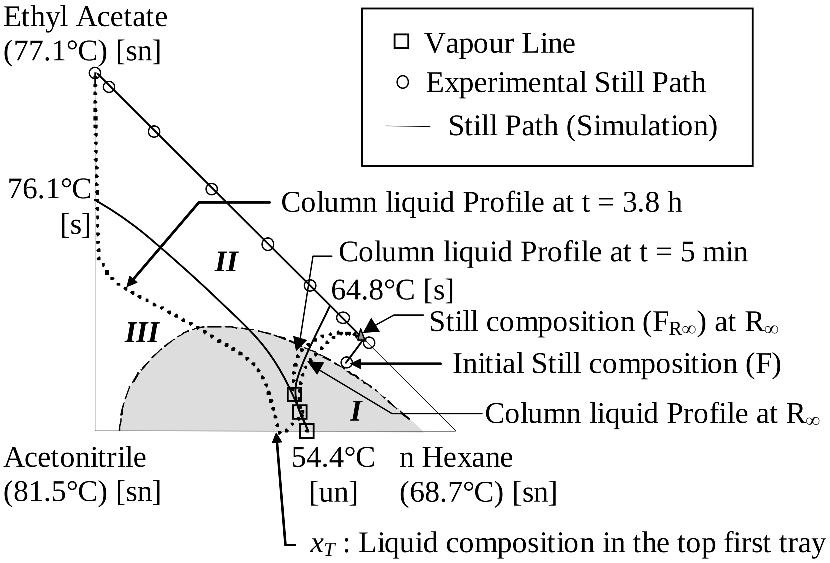

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TABLE CAPTION

Table 1. Potential heterogeneous entrainers for the separation of n-hexane- ethyl acetate mixture with thermodynamics data from Gmehling et al. (1994).

Table 2. Binary interaction parameters for NRTL and UNIQUAC models.

Table 3. Purity of n-hexane – rich phase (x^I) and entrainer – rich phase (x^{II}) at 25°C.

Table 4. Operating conditions of heteroazeotropic batch distillation with acetonitrile

Table 5. Simulation and experimental results (x1: n-hexane; x2: ethyl acetate; x3: acetonitrile)

Entrainer	b.p	Binary azeotrope with n-hexane (68.7°C)		Binary azeotrope with ethyl acetate (77.1°C)		Ternary azeotrope	
	$(°C)$	x_{molar} *	$T(°C)$	x_{molar} *	$T(°C)$	x_{molar} *	$T(°C)$
Methanol	64.7	0.5100**	50.6	0.708	62.05	-	-
Acetonitrile	81.5	0.5755**	54.4	0.6730	76.1	-	-
Water	100.0	0.7860**	61.8	0.7000**	70.5	0.5764** 0.2558	60.7
Nitromethane	101.2	0.7271**	62.0	zeotropic		-	-

* The mole fraction indicated is that of the lightest component in the mixture
** Heteroazeotrope

Table 1. Potential heterogeneous entrainers for the separation of n-hexane- ethyl acetate mixture with thermodynamics data from Gmehling et al. (1994).

Binary coefficients for NRTL model (cal/mol)			
Binary parameters	A_{ij}	A_{ji}	α_{ij}
n-hexane – ethyl acetate	720.731	-33.844	0.1521
n-hexane - acetonitrile	924.616	1212.64	0.2000
ethyl acetate - acetonitrile	580.783	-253.247	0.1997
Binary coefficients for UNIQUAC model (cal/mol)			
Binary parameters	A_{ij}	A_{ji}	
n-hexane – ethyl acetate	371.892	-133.73	-
n-hexane - methanol	1451.225	7.831	-
ethyl acetate - methanol	770.688	-147.777	-
n-hexane - water	2292.190	-324.669	-
ethyl acetate - water	768.058	214.271	-
n-hexane - nitromethane	1080.270	7.335	-
ethyl acetate - nitromethane	181.416	-42.973	-

Table 2. Binary interaction parameters for NRTL and UNIQUAC models

Entrainer	Binary azeotrope with n-hexane			Ternary azeotrope		
	$x^{I}_{nhexane}$	$x^{II}_{nhexane}$	ω	x^{I}	x^{II}	ω
Methanol	0.9152	0.1198	0.5346	-	-	-
Acetonitrile	0.9176	0.0605	0.3991	-	-	-
Water	-	-	-	0.7028 0.1754	0.2481 0.0324	0.1265
Nitromethane	0.9356	0.0893	0.2464	-	-	-

Table 3. Purity of n-hexane – rich phase (x^{I}) and entrainer – rich phase (x^{II}) at 25°C.

Parameters	Value
Initial charge (mol)	12.2
Initial composition (molar)	0.705/0.173/0.122
Number of theoretical trays	50
Operating Pressure (atm)	1
Holdup on the trays (mol)	0.0072
Tray Efficiency	1
Vapour flowrate (mol/hr)	from 9.7 to 7.5
Extra entrainer – rich phase (mol/hr)	1.2
Decanter holdup (mol)	3.4
Decanter temperature (°C)	25
Distillation time (h)	4.8
ω	0.3991
θ	1.01
φ	0.7

Table 4. Operating conditions of heteroazeotropic batch distillation with acetonitrile.

	Simulation Results		Experimental Results	
	quantity (mol)	molar fraction	quantity (mol)	molar fraction
Initial mixture	12.2	x_1 0.705 x_2 0.173 x_3 0.122	12.2	x_1 0.705 x_2 0.173 x_3 0.122
n-hexane – rich phase (Distillate + Decanter)	8.6	x_1 0.951 x_2 0.002 x_3 0.047	8.4	x_1 0.968 x_2 0.001 x_3 0.031
Acetonitrile – rich phase (Decanter)	1.1	x_1 0.107 x_2 0.157 x_3 0.736	0.99	x_1 0.082 x_2 0.190 x_3 0.728
Final Still Content (ethyl acetate)	1.7	x_1 0.001 x_2 0.992 x_3 0.007	1.6	x_1 0.001 x_2 0.991 x_3 0.008
Ethyl acetate recovery yield	81.04 %		75.1 %	
n-hexane recovery yield	95.1 %		94.5 %	
Acetonitrile recovery yield	54.5 %		48.4 %	

Table 5. Simulation and experimental results (x_1: n-hexane; x_2: ethyl acetate; x_3: acetonitrile)