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Separation of ethyl acetate–isooctane mixture by heteroazeotropic batch distillation

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A B S T R A C T

This paper studies the separation of an ethyl acetate–isooctane mixture by heterogeneous azeotropic distillation in a batch rectifying column. An initial list of 60 candidates was studied but only methanol and acetonitrile were obtained as potential heterogeneous entrainers. These entrainers form a low boiling heterogeneous azeotrope with isooctane. Experimental verification of the miscibility gap with isooctane was performed at 25 °C for each entrainer giving a smaller region for methanol than for acetonitrile. Feasibility of the heterogeneous azeotropic batch distillation was carried out experimentally in a laboratory batch distillation column having 44 theoretical equilibrium stages and using a high reflux ratio. Several distillate fractions were taken as a function of the temperature at the top of the column. For both methanol and acetonitrile, the main fraction was defined by the condensed vapor providing a liquid–liquid split of the isooctane/entrainer heteroazeotrope into the decanter. Ethyl acetate impurity was detected in both decanted phases, but in much lower amount when using acetonitrile as entrainer. The process with acetonitrile also resulted in a shorter operating time and higher purity and recovery yield of isooctane as the main distillate product. Pure ethyl acetate remained into the boiler at the end of each process.

Keywords: Heteroazeotropic distillation; Solvent recovery; Batch distillation; Ethyl acetate–isooctane mixture; Entrainer selection; Methanol; Acetonitrile

1. Introduction

Solvent recovery is becoming a major issue in the pharmaceutical and specialty chemical industries. As waste regulations are becoming stricter, the economic benefits of having recovery systems for the reuse of solvents in processes are significant. Recovery of organic solvents is generally practiced because of increased solvent cost and potential solvent shortages. Pharmaceutical and chemical industries are using large amounts of solvents for production and cleaning operation that may end up as waste streams (Whim and Johnson, 1996;

Stoye, 2000; Seyler et al., 2006). Batch processes have been the preferred operating mode in the manufacturing of high-value added chemicals, since the demand for high-value chemicals are seasonal and low in volume (Halim and Srinivasan, 2007).

Among all separation techniques, distillation is by far the most used technique for the separation of waste streams in their individual components. Unfortunately the use of conventional batch distillation is often limited by the frequent presence of azeotropes. Therefore, nowadays waste streams are often incinerated when azeotropes are involved (Van Baelen et al., 2010). Reducing incineration and increasing the

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recovery of these solvents by distillation will decrease emissions of greenhouse gasses in the air, lower the cost of waste incineration and will lead to a more efficient and sustainable use of raw materials (Seyler et al., 2006).

Advanced distillation techniques, like heteroazeotropic batch distillation on which we focus here, have to be applied to recover solvents from waste streams containing azeotropes. Although distillation requires also a lot of energy, there is still a benefit expected from an ecologic and economic point of view, especially in mixtures containing expensive solvents, like isooctane.

Most processes for the separation of azeotropic or low relative volatility zeotropic mixtures AB involve the addition of an entrainer E, leading to a homogeneous ternary mixture ABE or exhibiting a binary heterogeneous miscibility gap (Doherty and Malone, 2001). Simulation and experimental results have shown key differences between homogeneous and heterogeneous batch distillation and led to the publication of general feasibility rules (Rodriguez-Donis et al., 2001a,b; Skouras et al., 2005). 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) depending on the reflux policy, the typical unstable separatrices of residue curve map are not a limit anymore for the separation of components located in different basic distillation regions (Lang and Modla, 2006; Hegely et al., 2013).

In this study we are concerned with the separation of an organic waste composed of ethyl acetate (bp=77.2 °C) and isooctane (bp=99.1 °C), commonly used in the pharmaceutical industry. This binary mixture exhibits a minimum boiling temperature azeotrope at 76.3 °C under atmospheric pressure with 0.844 of ethyl acetate molar composition (Gmehling et al., 2004). According to the feasibility rules for batch azeotropic distillation (Rodriguez-Donis et al., 2001b; Skouras et al., 2005), non-conventional distillation processes such as heterogeneous azeotropic batch distillation (HABD) can be feasible to separate both components into high purity fractions. It requires the addition of an entrainer which has to form a heterogeneous binary azeotrope with one of the key components and having the lowest boiling temperature of the resulting ternary mixture. The formation of a ternary azeotrope should be avoided as it pollutes the main product distillate with unwanted compounds. However, good performance of the heteroazeotropic batch distillation is not limited by the presence of extra homogeneous binary azeotropes. Hence, feasible ternary diagrams for minimum boiling azeotropes are the 2.0-2b, 2.0-2c and 3.0-2 class diagrams according to Serafimov's classification having a physical occurrence of 21.1%, 0.9% and 8.4%, respectively (Hilmen et al., 2002; Kiva et al., 2003).

In this paper, the choice of the entrainer is first discussed in order to find the best entrainer option for heterogeneous azeotropic batch distillation. Second, the topological and thermodynamics properties of the ethyl acetate–isooctane–entrainer mixture residue curve map are described. Feasibility of the heterogeneous azeotropic batch distillation (HABD) process is evaluated taking into account the extend of the liquid–liquid vapour equilibrium region

into the residue curve map, the liquid–liquid split ratio at the binary heteroazeotrope and the purity of both decanted phases. Finally, experiments are run in a packed laboratory batch distillation column under high reflux ratio to validate the feasibility of the separation of ethyl acetate–isooctane mixture by heterogeneous batch azeotropic distillation. The purities of isooctane as distillate product and ethyl acetate as boiler product are then compared to the preliminary results given by the residue curve map analysis.

2. Entrainer selection for the separation of ethyl acetate–isooctane mixture

The overall performance of non-ideal mixtures separation strongly relies on the choice of a suitable entrainer E. Assessing feasibility requires the evaluation of the ability of E to form binary and ternary azeotropes with A or B. Azeotropic tendency can be approximately estimated via the study of chemical interactions (homologous series, polarity, hydrogen bonding aptitude) together with heuristics on boiling temperature differences (Berg, 1969; Perry et al., 1997; Doherty and Knapp, 1993; Gerbaud et al., 2006). Accurate prediction of azeotropic composition and temperature under the operating pressure requires either experimental data (Gmehling et al., 2004; Gmehling and Onken, 1982) or calculation using thermodynamic models of vapor–liquid and vapor–liquid–liquid phase equilibria, like activity coefficient models or equation of states or group contribution methods (Bossen et al., 1993; Gmehling and Möllmann, 1998; Thery et al., 2004).

First, the selection of potential feasible entrainers (E) for the separation of the minimum temperature boiling azeotropic mixture ethyl acetate (A)–isooctane (B) is performed using the RegsolExpert® wizard tool which combines chemical insight and thermodynamic calculations to find suitable entrainers (Gerbaud et al., 2006). A set of 60 components was selected as candidate entrainers belonging to several chemical families and having boiling temperature lower than ethyl acetate (light E), higher than isooctane (heavy E) and intermediate between both original components (intermediate E). The modified UNI-FAC Dortmund version 1993 (Gmehling et al., 1993) was used for estimating the existence of binary azeotropic mixtures (A)–(E) and (B)–(E) and, also, the eventual occurrence of ternary azeotrope ABE. Predicted azeotrope occurrence was further verified against experimental evidence (Gmehling et al., 2004, this work).

Analysing all possible generic mixtures A–B separation with any entrainer E, Rodriguez-Donis et al. derived a completed set of necessary entrainer selection rules for batch azeotropic distillation were elucidated (Rodriguez-Donis et al., 2001a,b). Those rules were implemented into the decision making software RegSolExpert® for Regenerating Solvents by batch distillation, along with feasibility rules for classical and pressure swing batch distillation (Prosim S.A., 2012). In the batch rectification (resp. stripping) process, that usually starts with an infinite reflux (resp. reboil) operation followed by distillate (resp. bottom product) removal, the column overhead (resp. bottom) composition under infinite reflux (resp. reboil) is the least (resp. most) volatile component; an unstable (resp. stable) node; of the distillation region where the global mixture composition lies, enabling to recover it as distillate (resp. bottom product) (Bernot et al., 1990, 1991). Separation of minimum boiling azeotropic mixtures with homogeneous or heterogeneous entrainer is only feasible if:

Table 1 – Candidate entrainer (E) for separating ethyl acetate (A)–isooctane (B) by batch azeotropic distillation. Azeotropic data predicted with the modified Dortmund UNIFAC model.

Entrainer	Type	Azeo AE	Azeo BE	Azeo ABE	Sequence
Diethyl ether	Light	None	None	None	SSS
Acetone	Light	None	HomPmin [un]	None	SSS
Ethyl formate	Light	None	HomPmin [un]	None	SSS
Methanol	Light	HetPmin [un]	HomPmin [s]	None	R
Ethanol	Light	HomPmin [s]	HomPmin [s]	HomPmin [un]	SSS
1-Butanal	Light	None	HomPmin [un]	None	SSS
1-Pentyne	Light	None	None	None	SSS
n-Hexane	Light	HomPmin [un]	None	None	SSS
Acetonitrile	Intermediate	HetPmin [un]	HomPmin [s]	None	R
n-Butylamine	Intermediate	HomPmin [un]	None	None	SSS
3-Methylpentane	Intermediate	HomPmin [un]	None	None	SSS
Acrylonitrile	Intermediate	HomPmin [s]	HomPmin [s]	HomPmin [un]	SSS
Water	Heavy	HetPmin [s]	HetPmin [s]	HetPmin [un]	RRR
Nitromethane	Heavy	None	HetPmin [s]	None	Extractive

- (1) By introducing light and intermediate entrainers and requiring the use of two consecutive batch stripping column configuration (S–S). (1.a) the simplest case is given by an intermediate entrainer forming no azeotrope with either (A) or (B). (1.b) The remaining cases impose the formation of a ternary azeotrope or a maximum boiling azeotrope, more difficult to find in practice.
- (2) A heavy homogeneous entrainer can be also used if the boundaries in the ternary residue curve map exhibit some curvature and, in this case, the separation requires three consecutive batch distillation tasks, all involving stripping column configuration (SSS).
- (3) Heterogeneous entrainers (light, intermediate and heavy) increase the separation alternatives and can be used with a batch rectification column with a top decanter. (3.a) The simplest alternative is given by the formation of a heterogeneous binary azeotrope (A–E) or (B–E) being the sole unstable node of the residue curve as it was pointed out by [Rodríguez-Donis et al. \(2001b\)](#). After condensation the heteroazeotropic gives rise to a liquid–liquid split in the decanter from which the product-rich phase is withdrawn as distillate. In this case, separation of (A) and (B) can be reached using only one batch separation task in a rectifying column configuration (R). (3.b) A sequence of several batch distillation tasks is used in the presence of a ternary heteroazeotrope.

The criterion (3.a) governs the search of a feasible entrainer for the separation ethyl acetate–isooctane mixture. As a result of the entrainer screening, 13 of the 60 preselected entrainers were found suitable for the separation of the ethyl acetate–isooctane mixture and are reported in [Table 1](#) along with the suitable batch distillation process sequence, with rectifier (R) or stripper (S) column configuration. No homogeneous entrainer could match the simplest alternative (1.a). Most of them make feasible the separation using a sequence of three batch stripper column where the recovery yield of the components depends strongly on the curvature degree of the residue curve map boundaries.

Regarding heavy entrainers, water forms three heterogeneous azeotropic mixtures: two binaries and one ternary giving a very complex scenario of the resulting ternary residue curve map. Nitromethane is also mentioned in [Table 1](#) as it lead to the formation of a heteroazeotrope with isooctane but, being a saddle point azeotrope, the feasible process is not

heteroazeotropic distillation, but heterogeneous extractive distillation ([Rodríguez-Donis et al., 2003a,b](#)).

Two heterogeneous entrainers were found matching with the criterion (3.a), a light component (methanol) and an intermediate component (acetonitrile). Methanol and acetonitrile were then selected for more detailed design of the heterogeneous azeotropic batch distillation process in a batch rectifier with a decanter.

3. Design of heterogeneous batch distillation using residue curve map analysis

[Figs. 1 and 2](#) show the residue curve map for methanol and acetonitrile, respectively. Calculation of the azeotropic mixtures and the liquid–liquid envelope were done using Aspen Plus® software and the original UNIFAC as thermodynamic model ([Fredenslund et al., 1975](#)). The modified Dortmund UNIFAC model used in RegSolExpert® (ProSim S.A.) uses temperature dependent parameters and fitted atomic radius and volume whereas the original UNIFAC model has no temperature dependency and uses Bondi's method for the radius and volume ([Bondi, 1964](#); [Gmehling et al., 1993](#)). Although they also have different parameter values for the group contributions, the predicted value are close in the system we studied and consistent with the experimental data available.

Both methanol and acetonitrile entrainers form one homogeneous azeotrope with ethyl acetate and one heterogeneous azeotrope with isooctane. As the ternary mixture involves three binary azeotropic mixtures and no ternary azeotrope, the resulting residue curve map corresponds to the 3.0-2 class according to Serafimov's classification, with an estimated statistic occurrence of 8.4% among reported ternary azeotropic mixtures ([Kiva et al., 2003](#)). The residue curve map exhibits two unstable boundaries connecting the binary heteroazeotrope to each homogeneous binary azeotrope and dividing the composition space in three basic distillation regions. These boundaries usually restrict the separation of the components by homogeneous azeotropic distillation, but not anymore in the case of heterogeneous entrainers ([Rodríguez-Donis et al., 2002](#); [Lang and Modla, 2006](#)). The efficiency of heterogeneous azeotropic distillation is largely determined by the temperature and composition of the binary heteroazeotrope and by the composition of each liquid phase after decantation. [Table 2](#) displays the boiling temperature and the composition of each azeotropic mixture along with the purity of each liquid phase after decantation at 25 °C computed by the original UNIFAC

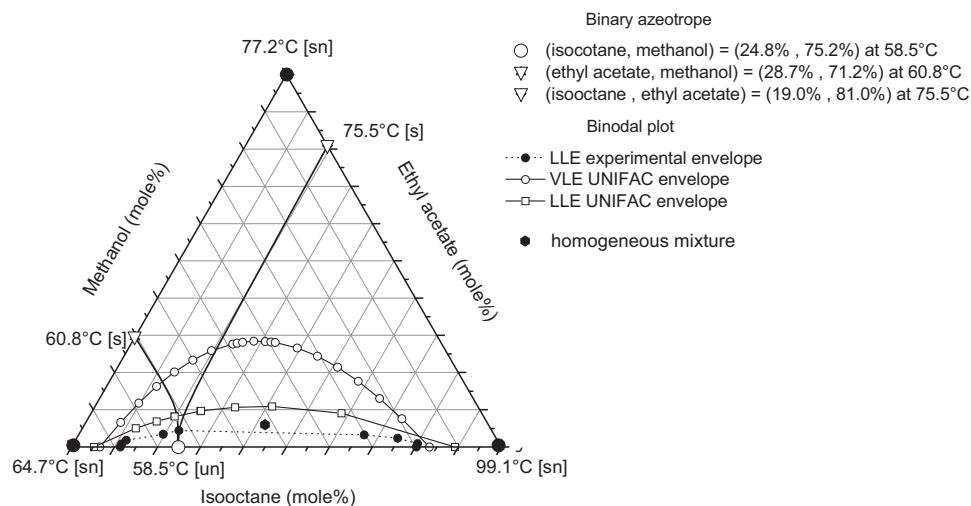


Fig. 1 – Methanol–ethyl acetate–isooctane 3.0-2 class ternary diagram and liquid–liquid and liquid–liquid–vapour equilibrium envelopes estimated by the original UNIFAC model.

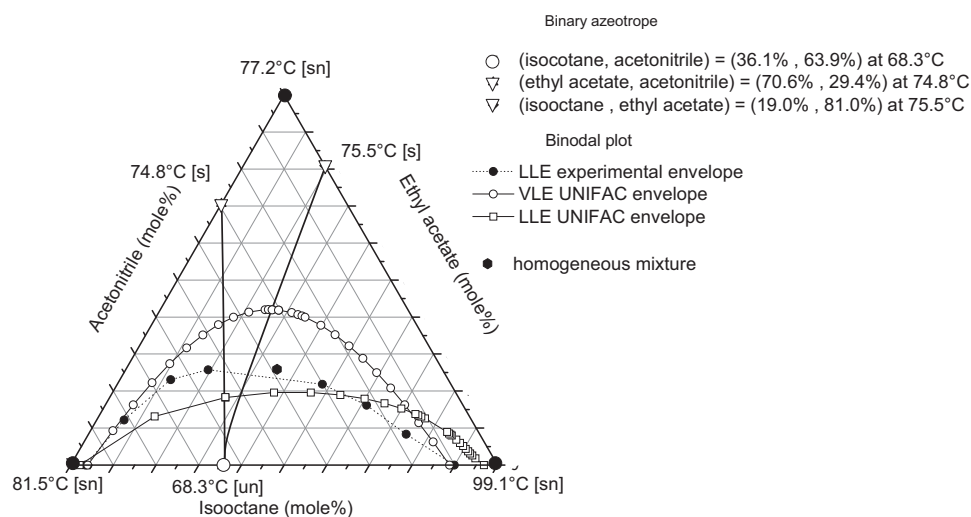


Fig. 2 – Acetonitrile–ethyl acetate–isooctane 3.0-2 class ternary diagram and liquid–liquid and liquid–liquid–vapour equilibrium envelopes estimated by the original UNIFAC model.

Table 2 – Predicted temperature and composition of binary heterogeneous azeotropic mixture and liquid–liquid equilibrium data at 25 °C.

Entrainer (E)	Heteroazeotrope isooctane (B)–entrainer (E)		Entrainer heavy phase	Isooctane light phase	(Heavy/light) mole ratio
Methanol (64.7 °C)	$x_E = 0.7523$	$T = 58.5 \text{ °C}$	$x_E = 0.9476$	$x_B = 0.8924$	3.30
Acetonitrile (81.5 °C)	$x_E = 0.6382$	$T = 68.3 \text{ °C}$	$x_E = 0.9788$	$x_B = 0.9682$	1.78

model and represented in Figs. 1 and 2. Similar data (not shown) were obtained with the modified Dortmund UNIFAC model used in RegsolExpert® (ProSim S.A.).

The heterogeneous binary azeotrope has the lowest boiling point in the mixture for both entrainers. For a HABD process, mixing a given amount of the entrainer into the initial charge allows the withdrawal of a binary heteroazeotrope as vapour top product using the required number of equilibrium plates into the column. After condensation of this vapour, two liquid phases are decanted. The entrainer-rich phase is the heavy liquid phase and it can be directly sent back at the top of the column as liquid reflux. The isooctane-rich light phase is kept as distillate product.

Comparison of methanol and acetonitrile can be performed from analysis of Figs. 1 and 2 along with Table 2. Some important remarks can be done as following:

- The size of the immiscibility gap together with the purity of isooctane-rich light phase determines the easiness of the HABD process and the distillate purity. Comparing Figs. 1 and 2, acetonitrile provides the largest immiscibility region and the best purity, 0.9682 compared to 0.8924 given by methanol (see Table 2). However, a further purification of isooctane is expected to be done by an additional batch distillation step if a purer isooctane is sought.

- (b) When the composition of the binary heteroazeotrope is close to the entrainer apex, the lever rule underlying the phase split into the decanter hints that less amount of the distillate phase can be drawn, providing a prohibited operating time. This is displayed in [Table 2](#) by the (heavy/light) mole phase ratio, representing the liquid–liquid split ratio into the decanter. A value of the liquid–liquid split ratio approaching to unity is recommended in order to provide at the same time enough entrainer-rich phase as a liquid reflux towards the column top and an adequate distillate flow rate of the isooctane-rich phase. In this sense acetonitrile shows the most promising value.
- (c) A lower boiling temperature of the binary heteroazeotrope may provide a separation with less energy demand. Methanol as a light entrainer displays a lower temperature value of the binary heteroazeotrope with isooctane. However, it is very close to the boiling temperature of the homogeneous azeotrope methanol–ethyl acetate (see [Fig. 1](#)). On the other hand, acetonitrile leads to a larger difference between the boiling temperature of its heteroazeotropic mixture with isooctane and the homogeneous azeotrope with ethyl acetate (see [Fig. 2](#)). As a compromise, acetonitrile is preferable.
- (d) Ethyl acetate remains into the boiler at the end of the batch distillation process for both entrainers. It can be obtained with a very high molar purity, depending on the initial charge of the entrainer and the rigorous control of reflux policy ([Rodríguez-Donis et al., 2002](#); [Skouras et al., 2005](#)). However, if the still content is finally polluted with the entrainer, the recovery yield of ethyl acetate will be better if the overall composition of the homogeneous binary azeotrope is closer to entrainer apex. It happens for methanol (compare [Figs. 1 and 2](#)).
- (e) The overall composition of the homogeneous binary azeotrope entrainer–ethyl acetate may prevent the concentration of ethyl acetate into the still during batch operation. Indeed, once isooctane is completely distilled out, it may happen that the still composition reaches the binary side entrainer–ethyl acetate on the segment limited by the entrainer apex and the homogeneous binary azeotrope. In this segment the ethyl acetate is not the stable node anymore, but it is the entrainer. Hence, the entrainer is then concentrated into the still whereas ethyl acetate is fully taken out of the column as distillate given by the minimum boiling azeotropic mixture entrainer–ethyl acetate. In that case, methanol offers the best option like in (d).

As a whole, those arguments point out acetonitrile as a better entrainer than methanol for separating ethyl acetate–isooctane by heterogeneous azeotropic batch distillation.

4. Experimental validation of the separation of ethyl acetate–isooctane by heterogeneous azeotropic batch distillation

The heterogeneous azeotropic distillation is feasible when the binary heteroazeotrope, being the sole unstable node of the residue curve map, is obtained at the column top and further undergoes a liquid–liquid splitting into the decanter after condensation.

Regarding the choice of methanol and acetonitrile as candidate entrainers, the lack of the liquid–liquid–vapour and

liquid–liquid equilibrium experimental data for the studied mixtures prompted us to measure the immiscibility gap before running heteroazeotropic batch distillation process experiments.

4.1. Materials and sample analysis

99.0 mass% grade ethyl acetate (Fisher Scientific) and isooctane (2,2,4-trimethylpentane) (Sigma–Aldrich) and 99.9 mass% acetonitrile, methanol and 1-propanol (VWR Prolabo) were used. All samples were analysed in triplicate by gas chromatography (Chromopack 9002) equipped with a flame ionisation detector (FID) using a CP-Sil 5 CB column of 25 m length, 0.32 mm internal diameter and 5 μ m film thickness. The temperature of the injector and detector were set at 200 °C. The injection volume was 0.1 μ l. For the samples obtained by the distillation experiment with acetonitrile as entrainer the temperature of the GC oven was set at 80 °C, raised for 4 min at a rate of 10 °C/min and held for 2 min at 120 °C. The internal standard was 1-propanol and samples were diluted in methanol. For the samples obtained by the distillation experiment with methanol as entrainer, the temperature of the GC oven was set at 80 °C for 4 min, and raised for 2 min at a rate of 20 °C/min. The internal standard was acetonitrile and samples were diluted in 1-propanol.

The standard deviation between the three replicates of the same sample was always lower than 2.5%.

For each sample the sum of volume% of entrainer, isooctane and ethyl acetate was 100% \pm 2.5%. All results were normalised to 100.0%.

4.2. Experimental verification of heterogeneous azeotropic distillation

4.2.1. Determination of the immiscibility gap for each ternary mixture

Experimental determination of the liquid–liquid phase envelope of each ternary mixture was done and compared to the calculated liquid–liquid phase envelope at 25 °C displayed in [Figs. 1 and 2](#). Several ternary mixtures with different total concentrations were made by mixing the pure products. Therefore each time a fixed amount of ethyl acetate, isooctane and entrainer (methanol or acetonitrile) was agitated with a magnetic stirrer in a closed thermostated vessel for 4 h. After the agitation, the mixture was left for decantation for 12 h. Samples were taken from each liquid phase and analysed following the methodology described in [Section 4.1](#). Finally, to verify the extent of the liquid–liquid phase splitting, we also report one homogenous sample. Here the liquid–liquid separation just disappeared. So this sample represents an upper limit for ethyl acetate content before phase separation disappears. The experimental data are reported in [Tables 3 and 4](#) and plotted in [Fig. 2](#).

We compared those measured LLE values at 25 °C with predicted ones by the same UNIFAC model than the one used during the entrainer selection step.

In the case of methanol, [Fig. 2](#) shows some differences between the measurements and the liquid–liquid equilibrium computed using the UNIFAC model. The two phase region span is smaller than the one predicted and the maximum concentration of ethyl acetate is smaller in the experiments. Also, the isooctane concentration of the isooctane-rich phase (light) and the methanol concentration of the methanol-rich (heavy)

Table 3 – Experimental composition of the heavy and light phase of the samples used for liquid–liquid equilibrium data at 25 °C for the ethyl acetate–isooctane–methanol system (mole%).

Sample	Ethyl acetate	Isooctane	Methanol
Sample 1	$x_A = 0.0000$	$x_B = 0.2690$	$x_E = 0.7310$
Heavy phase 1	$x_A = 0.0000$	$x_B = 0.1131$	$x_E = 0.8869$
Light phase 1	$x_A = 0.0000$	$x_B = 0.8026$	$x_E = 0.1974$
Sample 2	$x_A = 0.0083$	$x_B = 0.2360$	$x_E = 0.7556$
Heavy phase 2	$x_A = 0.0082$	$x_B = 0.1124$	$x_E = 0.8794$
Light phase 2	$x_A = 0.0090$	$x_B = 0.8005$	$x_E = 0.1905$
Sample 3	$x_A = 0.0196$	$x_B = 0.2370$	$x_E = 0.7434$
Heavy phase 3	$x_A = 0.0186$	$x_B = 0.1178$	$x_E = 0.8636$
Light phase 3	$x_A = 0.0240$	$x_B = 0.7468$	$x_E = 0.2293$
Sample 4	$x_A = 0.0299$	$x_B = 0.2395$	$x_E = 0.7307$
Heavy phase 4	$x_A = 0.0296$	$x_B = 0.1980$	$x_E = 0.7724$
Light phase 4	$x_A = 0.0324$	$x_B = 0.6648$	$x_E = 0.3028$
Homogenous	$x_A = 0.0613$	$x_B = 0.4212$	$x_E = 0.5175$

phase were smaller than those calculated using the UNIFAC model.

In the case of acetonitrile, the calculated liquid–liquid envelope lies under the experimental one and extends farther towards the isooctane vertex compared to our measurements. Nevertheless, the experimental isooctane concentration of the isooctane-rich phase is larger when using acetonitrile compared to the one using methanol. However, the maximum molar composition of isooctane in the light phase is near to 90%. An additional distillation step will be required for more pure product.

These experimental results confirm the selection of acetonitrile as an adequate heterogeneous entrainer as was elucidated above from Table 2 predictions.

4.2.2. Experimental validation of heterogeneous azeotropic distillation in a laboratory batch distillation column

Fig. 3 shows the batch distillation column used for the separation of the mixture acetonitrile–ethyl acetate–isooctane and the mixture methanol–ethyl acetate–isooctane. This distillation column is designed to have a maximal amount of theoretical plates within the available lab space. It has a length of 1.50 m and an inner diameter of 0.03 m. To minimise heat losses the column has a radiation screen and a vacuum mantle. The column is filled with 3 cm × 3 cm raschig rings meaning about 44 theoretical plates. The HETP (height equivalent to a theoretical plate) of the packed column and the

Table 4 – Experimental composition of the heavy and light phase of the samples used for liquid–liquid equilibrium data at 25 °C for the ethyl acetate–isooctane–acetonitrile system (mole%).

Sample	Ethyl acetate	Isooctane	Acetonitrile
Sample 1	$x_A = 0.0000$	$x_B = 0.2330$	$x_E = 0.6770$
Heavy phase 1	$x_A = 0.0000$	$x_B = 0.0348$	$x_E = 0.9652$
Light phase 1	$x_A = 0.0000$	$x_B = 0.8991$	$x_E = 0.1009$
Sample 2	$x_A = 0.1010$	$x_B = 0.4338$	$x_E = 0.4652$
Heavy phase 2	$x_A = 0.1221$	$x_B = 0.0642$	$x_E = 0.8137$
Light phase 2	$x_A = 0.0833$	$x_B = 0.7443$	$x_E = 0.1724$
Sample 3	$x_A = 0.1945$	$x_B = 0.3793$	$x_E = 0.4262$
Heavy phase 3	$x_A = 0.2310$	$x_B = 0.1186$	$x_E = 0.6503$
Light phase 3	$x_A = 0.1618$	$x_B = 0.6124$	$x_E = 0.2258$
Sample 4	$x_A = 0.2274$	$x_B = 0.3676$	$x_E = 0.4050$
Heavy phase 4	$x_A = 0.2573$	$x_B = 0.1935$	$x_E = 0.5492$
Light phase 4	$x_A = 0.2186$	$x_B = 0.4803$	$x_E = 0.3010$
Homogenous	$x_A = 0.2588$	$x_B = 0.3542$	$x_E = 0.3870$



Fig. 3 – Batch distillation column configuration at laboratory scale.

associated plate number was experimentally defined by running the separation of a heptane–methylcyclohexane mixture (Herington et al., 1979). The boiler was heated with an electrical heating jacket of 0.6 kW at about 40% of its maximum heating capacity. The condenser was cooled with tap water of about 10–15 °C until the condensate was at room temperature (25 °C) and the liquid reflux was controlled through the open/close time of a solenoid valve. Temperature was measured with a Pt-100 temperature data logger at the top of

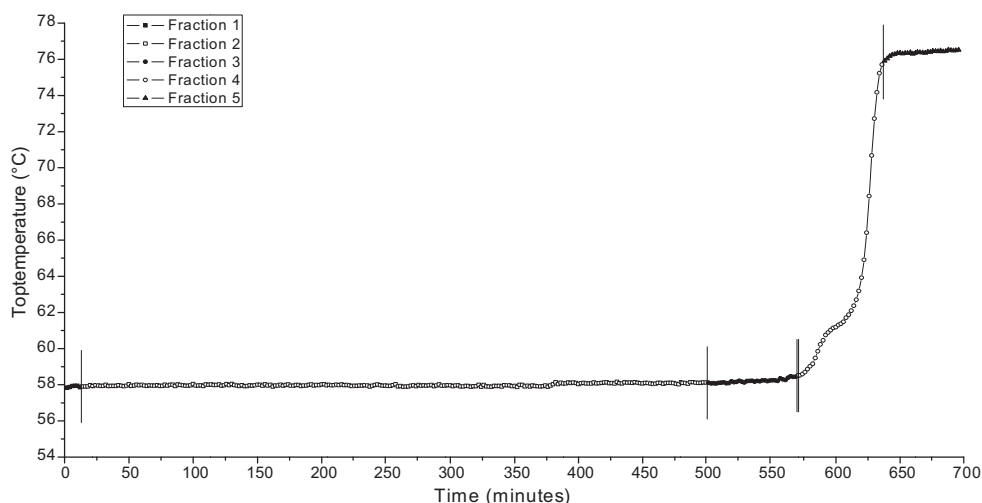


Fig. 4 – Evolution of the top temperature with operation time during the HABD process with methanol as entrainer.

the column. In all experiments total reflux was applied until the column reaches the steady state determined by unvarying temperature at the top of the column. Then the distillate was drawn under a fixed reflux ratio. Several fractions were collected according to the temperature variation at the top and further analysed by GC-FID. The distillation was stopped when the top temperature reached the boiling temperature of ethyl acetate.

4.2.2.1. Experimental validation of the separation of ethyl acetate–isooctane with methanol as entrainer. The total amount of initial ternary mixture fed having a total composition of $x_F = \{0.550/0.283/0.167\}$ (methanol/ethyl acetate/isooctane) into the boiler was 0.841 L (10.811 mol). The amount of entrainer was calculated by taking 5% of entrainer volume more than the theoretical composition of the binary heteroazeotrope with isooctane computed by the original UNIFAC model (Table 2) in order to make sure that isooctane can be distilled by this heteroazeotrope, taking in account the total liquid holdup of the column. The heterogeneous azeotropic distillation process was carried out under a constant reflux ratio of 20, to ensure that the heteroazeotrope is obtained in the vapour overhead, as the theoretical feasibility criterion 3.a requests. Smaller reflux ratio values were not tested but would be needed in industrial operation.

Fig. 4 shows the variation of the temperature at the top of the column during the batch operation and the five distillate fractions that were taken. The temperature at the top of the column was very stable during the distillation experiment for nearly 8 h near to 58 °C, close to the targeted boiling temperature of the binary heteroazeotrope predicted by both UNIFAC models (58.5 °C).

Table 5 shows the five distillate fractions that were taken depending on the top temperature. The first fraction (only 0.012 L) was homogeneous, because of the high content of ethyl acetate. Fraction 2 corresponded to a heterogeneous top vapour composition and constituted the main distillate fraction having 0.435 L. The next fractions 3, 4 and 5 were the transition cuts towards pure ethyl acetate into the boiler. The whole process took 11 h and 36 min until pure ethyl acetate was obtained in the residue (Fig. 5).

Table 6 shows the overhead vapour composition computed from the composition of heavy and light phase of fraction 2. This fraction 2 was decanted at 25 °C. The methanol-rich phase contains almost 15 mole% of isooctane and the isooctane-rich phase exhibits only 67.5 mole% of isooctane, significantly lower than the predicted value for binary heteroazeotrope (see Table 2). This is mainly due to the fact that the condensed vapour drawn at the top of the column also contained 4.6 mole% of ethyl acetate (Table 6), indicating that a better separation requires a higher number of equilibrium stages. So both liquid phases have a lower purity than expected as well and the mole ratio of both phases (4.96) is higher than predicted (3.3). All these experimental results confirm that methanol is not a favourable entrainer as predicted from the analysis of Fig. 1 and Table 2.

Table 7 shows the molar mass balance of the distillation experiment. The residue contains 100 mole% of pure ethyl acetate at the end of the distillation process. Except fraction 2, all other fractions were homogeneous and were taken together in the mass balance. The distillation experiment was done in duplicate and the solvent losses in the mass balance in both tests were nearly constant and therefore not only due to experimental errors. The solvent losses in the mass balance are

Table 5 – Volume, time and top temperature for each distillate fraction.

Fraction	Volume (L)	Time (hours:minutes)		Top temperature (°C)	
		Begin	End	Begin	End
Fraction 1	0.012	0:00	0:12	57.8	57.9
Heavy fraction 2	0.305	0:12	8:20	57.9	58.1
Light fraction 2	0.130				
Fraction 3	0.050	8:20	9:30	58.1	58.4
Fraction 4	0.050	9:30	10:37	58.4	75.7
Fraction 5	0.050	10:37	11:36	75.7	76.5
Residue	0.178	11:36	–	76.5	–

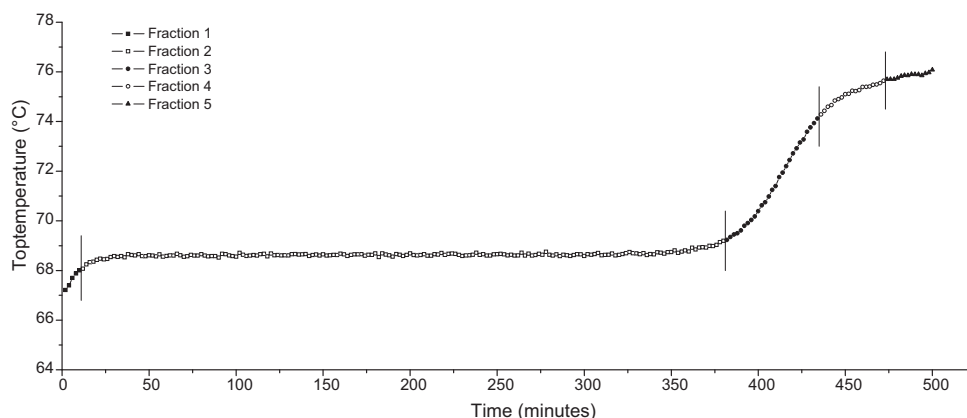


Fig. 5 – Evolution of the top temperature with operation time during the HABD process with acetonitrile as entrainer.

Table 6 – Experimental liquid–liquid splitting for fraction 2 at 25 °C.

Component	Overhead vapor (mole%)	Heavy phase (mole%)	Light phase (mole%)	heavy/light phase (mole ratio)
Methanol	71.9	81.3	25.3	4.96
Ethyl acetate	4.6	4.0	7.2	
Isooctane	23.5	14.7	67.5	

mainly due to the liquid retention in the column as well as to evaporation losses to the atmosphere at the solenoid valve and sample points of the column, although all possible actions were undertaken to minimise these solvent losses. The recovery yield of methanol during the main fraction 2 was 72.3% and 78.0% for isooctane. According to Table 7, the recovery yield of ethyl acetate was 59.3%. It could be improved by avoiding the withdrawal of fraction 5, as the top temperature vs time curve displayed in Fig. 4 shows a boiling temperature near pure the ethyl acetate value for this fraction.

4.2.2.2. *Experimental validation of the separation of ethyl acetate–isooctane with acetonitrile as entrainer.* For the separation of ethyl acetate–isooctane mixture with acetonitrile, 0.772 L (8.154 mol) of initial ternary mixture were fed into the boiler having a composition of $x_F = \{0.404/0.375/0.221\}$ (acetonitrile/ethyl acetate/isooctane). The amount of entrainer was again calculated by taking 5% of the entrainer volume in excess as well. Fig. 4 shows the temperature evolution at the top of the column as a function of the operating time and the five distillate fractions that were taken. Table 8 shows the volume of these five distillate fractions and their related temperature and operating time.

Table 9 shows the overhead vapour composition during fraction 2 and the composition of the related phases after decantation at 25 °C.

Unlike to the methanol case, liquid–liquid splitting into the decanter appears from the beginning of the batch operation, which is not surprising as Fig. 2 shows that the LLE region is much larger, compared to the one with methanol (see

Fig. 1). Besides, the composition of ethyl acetate in the overhead vapour (1.5% in Table 9) is lower than the experimental value reported in Table 6 for methanol. Hence, the same distillation column with the same reflux ratio performs a better separation when using acetonitrile.

Fraction 2 represents the main distillate product. The temperature of fraction 2 is nearby 68.0 °C, very close to the predicted value of the binary heteroazeotrope by UNIFAC (Table 2). No experimental data of the binary heterazeotrope acetonitrile–isooctane were found in the usual literature (Gmehling et al., 2004) but it can be assumed that the real temperature value lies slightly below the fraction 2 temperature because the overhead vapour composition has a small content in ethyl acetate (1.5 mole% in Table 9). The next fractions 3–5 contain the transition to pure ethyl acetate. The whole process took 8 h and 20 min until pure ethyl acetate was obtained in the residue into the boiler.

Fraction 2 is considered as the main product. The overall composition of fraction 2 and the corresponding heavy and light phase composition along with the mole ratio of both phases are close to the theoretical composition predicted by the original UNIFAC model (Table 2).

As seen in Table 9, the heavy and the light phase have a high content of acetonitrile and isooctane, respectively. Both phases also contain less ethyl acetate than when using methanol as entrainer. Those experimental results confirm that acetonitrile is the preferred entrainer for the heteroazeotropic batch distillation process.

Table 10 shows the molar mass balance of the distillation experiment. Fractions 1 and 2 were heterogeneous and were

Table 7 – Molar mass balance of HABD with methanol as entrainer.

Component	Input	Output streams			Balance		
		Heterogeneous fraction	Homogeneous fraction	Residue	Total-IN	Total-OUT	Deviation (%)
Methanol	5.950	4.305	0.960	0.000	5.950	5.265	–11.5
Ethyl acetate	3.054	0.272	0.894	1.812	3.054	2.979	–2.5
Isooctane	1.807	1.409	0.213	0.000	1.807	1.621	–10.3
Total	10.811	5.986	2.067	1.812	10.811	9.864	–8.8

Table 8 – Volume, time and top temperature range of the distillate fractions.

Fraction	Volume (L)	Time (hours:minutes)		Top temperature (°C)	
		Begin	End	Begin	End
Heavy fraction 1	0.004	0:00	0:10	67.2	68.0
Light fraction 1	0.006				
Heavy fraction 2	0.161	0:10	6:20	68.0	69.2
Light fraction 2	0.247				
Fraction 3	0.050	6:20	7:15	69.2	74.1
Fraction 4	0.030	7:15	7:52	74.1	75.6
Fraction 5	0.020	7:52	8:20	75.6	76.1
Residue	0.202	8:20	–	76.1	–

Table 9 – Experimental liquid–liquid splitting for fraction 2 at 25 °C.

Component	Overhead vapor (mole%)	Heavy phase (mole%)	Light phase (mole%)	Heavy/light phase (mole ratio)
Acetonitrile	63.6	94.6	8.9	1.77
Ethyl acetate	1.5	1.8	0.9	
Isooctane	34.9	3.6	90.2	

Table 10 – Molar mass balance of HABD with acetonitrile.

Component	Input	Output streams			Balance		
		Heterogeneous fraction	Homogeneous fraction	Residue	Total-IN	Total-OUT	Deviation (%)
Acetonitrile	3.293	2.874	0.236	0.000	3.293	3.110	–5.6
Ethyl acetate	3.054	0.067	0.620	2.056	3.054	2.744	–10.1
Isooctane	1.807	1.574	0.161	0.000	1.807	1.735	–4.0
Total	8.154	4.515	1.020	2.056	8.154	7.589	–6.9

combined together in the mass balance. Also the homogenous fractions 3, 4 and 5 were taken together in the mass balance. The negative sign in the column deviation indicates solvent losses. The reasons for these solvent losses were explained above for the experiments with methanol. Again the distillation was done in duplicate, with nearly constant solvent losses. The recovery yield of acetonitrile from the heterogeneous fractions 1 and 2 was 87.3% and 87.1% for isooctane, within experimental uncertainty. The recovery yield of the ethyl acetate remained into the still was 67.3%. All recovery yields are higher 10% than those obtained with methanol.

In conclusion, acetonitrile performs the separation of ethyl acetate–isooctane mixture in a shorter operating time (8.2 h) than methanol (11.36 h) and with better purities and recovery yields for both original components and the heterogeneous entrainer. This was anticipated from the entrainer choice step and later confirmed by the experiments.

5. Conclusions

The separation of an ethyl acetate–isooctane mixture cannot be achieved by conventional distillation process, because a minimum boiling homogenous azeotrope exists. Therefore the use of HABD for the separation of this binary mixture was investigated. Acetonitrile and methanol were selected as the best entrainers, using the RegSolExpert® software from an initial list containing 60 candidates belonging to different chemical families. Later, the feasibility of HABD was assessed, based on the computation of the residue curve map for both entrainers where UNIFAC was used as a thermodynamic model. Both heterogeneous entrainers provide a ternary diagram matching to the 3.0-2 class diagram according to Serafimov's classification. Analysis of the residue curve map and the liquid–liquid envelope pointed out that acetonitrile was a more promising candidate than methanol

because of the entrainer composition in the heteroazeotropic isooctane–entrainer, a wider immiscibility gap with a higher composition of isooctane in the light phase and the high temperature difference respecting to other involved azeotropic mixtures. Experimental assessment of the ternary immiscibility gap under 25 °C was carried out in agreement with the predictions by UNIFAC. Experimental verification of the HABD process showed that acetonitrile is a better heterogeneous entrainer because it performs the separation of the azeotropic components in a shorter operating time and provides higher purity and recovery yield for all components. Further optimisation of the heterogeneous azeotropic distillation is now compulsory in order to improve the column design so as to reduce the solvent losses and to establish the optimal values for the essential operating parameters such as the reflux ratio, initial amount of the entrainer, heat duty to the boiler, etc. According to our knowledge, this is first contribution of the separation of ethyl acetate–isooctane mixture using heterogeneous azeotropic distillation process.

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