Heterogeneous Extractive Batch Distillation of Chloroform - Methanol – Water: Feasibility and Experiments.

R. Van Kaam [a,b], I. Rodriguez-Donis [a], V. Gerbaud [b,*]

[a] *Centro de Quimica Farmacéutica, Ave 200 y 21, Playa Apdo 16042, Ciudad de la Habana, Cuba.*

[b] *Université de Toulouse, LGC (Laboratoire de Génie Chimique), CNRS, INP, UPS, 5 rue Paulin Talabot - BP 1301, 31106, Toulouse, France*

accepted for publication in

Chemical engineering science, 63, 78-94, 2008

doi:10.1016/j.ces.2007.09.005

* corresponding author. Vincent.Gerbaud@ensiacet.fr

Abstract

A novel heterogeneous extractive distillation process is considered for separating the azeotropic mixture chloroform – methanol in a batch rectifying column, including for the first time an experimental validation of the process. Heterogeneous heavy entrainer water is selected inducing an unstable ternary heteroazeotrope and a saddle binary heteroazeotrope with chloroform (ternary diagram class 2.1-2b). Unlike to well-known heterogeneous azeotropic distillation process and thanks to continuous water feeding at the column top, the saddle binary heteroazeotrope chloroform – water is obtained at the column top, condensed and further split into the liquid – liquid decanter where the chloroform-rich phase is drawn as distillate. First, feasibility analysis is carried out by using a simplified differential model in the extractive section for determining the proper range of the entrainer flowrate and the reflux ratio. The operating conditions and reflux policy are validated by rigorous simulation with ProSim Batch Column® where technical features of a bench scale distillation column have been described. Six reproducible experiments are run in the bench scale column matching the simulated operating conditions with two sequentially increasing reflux ratio values. Simulation and experiments agree well. With an average molar purity higher than 99%, more than 85% of recovery yield was obtained for chloroform and methanol.

Keywords: Heterogeneous extractive distillation; Batch rectifying column; Feasibility study; Distillation simulation; Distillation experiments

1. Introduction

Batch processes are again becoming important because of the recent expansion of the pharmaceutical and speciality chemical industries. Besides, recycling of liquid waste streams is a must in the compliance of all processing plants to novel and stricter environmental regulations. For its inherent ability to achieve high product purity and recovery, distillation is a recommended process. However, its economic contribution to an industrial plant operating costs is significant because of the need to vaporize partially the boiler content and this justifies improvement of distillation processes. Liquid waste streams are often non ideal mixtures where interactions between their components lead to azeotropic mixtures or to mixtures with a low relative volatility. The separation of such mixtures by using a conventional column or a pressure swing distillation is not a feasible alternative or it can be expensive because of a high reflux or a large column requirements. Alternative techniques usually known as azeotropic and extractive distillation process have been developed having in common the addition of an auxiliary compound in the original mixture. Furthermore, batch operation adds flexibility as composition paths can be steered changing the reflux policy.

Considering the separation of a binary mixture A-B, the addition of an entrainer E forms a so-called ternary diagram A-B-E which belongs to a finite set of 26 topologically feasible structures according to Serafimov's classification (Kiva *et al.*, 2003). So far, only 16 of the 26 theoretically possible classes have been matched by real ternary mixtures with significant different occurrences among ternary azeotropic mixtures (Hilmen, 2000). Batch azeotropic distillation has been evaluated for all 26 structures (Rodriguez-Donis *et al.*, 2001a,b) but batch extractive distillation with continuous entrainer feeding has been mainly studied for homogeneous entrainers inducing no new azeotrope with the original mixture A-B. It encompasses Serafimov's structures 0.0-1; 1.0-1a; 1.0-1b and 1.0-2, representing approximately one third of occurring azeotropic mixtures (Kiva *et al.*, 2003). Processes and operating parameters for batch homogeneous extractive distillation were reviewed in rectifying (Steger *et al.*, 2005) and stripping column (Varga, 2006). For heterogeneous entrainers, feasibility analysis was first proposed by Rodriguez-Donis *et al.* (2003a) through the separation of water – acetonitrile by using butyl acetate or n-hexylamine, both cases matching Serafimov's class 2.0-2b. An industrial case reported by Köhler *et al.* (1995) involving the separation of ethanol – ethyl acetate mixture with water entrainer matching Serafimov's class 3.1-2 was also analyzed by Rodriguez-Donis *et al.* (2003a).

Experimental verification of batch extractive distillation is still very limited even in the most studied case including the separation of minimum boiling azeotropes with a homogeneous heavy entrainer in a batch rectifying column. Therefore, the purpose of this paper is first to assess the feasibility of the separation of a minimum azeotropic mixture using a heavy heterogeneous entrainer, matching Serafimov's class 2.1-2b not studied before, and second to corroborate it by simulation in order to set operating parameters for the final experimental validation in a bench batch rectifying column.

We are concerned in this study by the separation of an organic waste composed mainly by chloroform and methanol, a widely used effective solvent for bioactive substances extraction from biological sources in pharmaceutical and biotechnology industry (Schengrund and Kovac, 1999; Stark *et al.*, 1999; Row and Jin, 2006). This binary mixture exhibits a minimum boiling temperature azeotrope with 0.65 of chloroform molar composition at 53.5°C under atmospheric pressure (Gmehling *et al.*, 1994). Then, non-conventional distillation processes such as extractive or azeotropic distillation are required to separate both components. After discussing the choice of the entrainer, water is chosen as it adds no extra difficulty because it is the main impurity detected in the original organic waste. Besides, water produces a notable increasing of the relative volatility of the original components, which can be estimated from the activity coefficient ratio of chloroform (1) and methanol (2) at infinite dilution in water (see Table 1 and text). The addition of water to the chloroform – methanol mixture leads to a ternary mixture matching Serafimov’s class 2.1-2b (approximate occurrence 4% among ternary azeotropic mixtures, see Kiva *et al.*, 2003).

The manuscript is organized as follow. First the choice of the entrainer is discussed in order to find the best entrainer option. Second, the topological and thermodynamics properties of the Chloroform – Methanol – Water mixture residue curve map are described. Third, feasibility of the heterogeneous batch extractive distillation process is evaluated for all process operating steps after defining the feasibility criteria according to the distillate target, the corresponding column configuration and the limiting operating condition for each step. Fourth, rigorous simulation of the process is performed to enable computing the operating parameter values. Fifth, experimental validation is done in a bench scale column. Overall it is shown that a heterogeneous batch extractive distillation process is suited for the separation of a minimum boiling azeotropic mixture with the addition of a heterogeneous entrainer inducing a new binary azeotrope and ternary azeotrope, matching Serafimov’s class 2.1-2b.

2. Entrainer selection for the separation of chloroform – methanol mixture

Non ideal mixtures separation overall performance heavily relies on the choice of a suitable entrainer E. This issue has been frequently considered for a non ideal binary mixture A-B separation under continuous operation (Berg, 1969; Doherty and Caldarola, 1985; Laroche *et al.*, 1991, 1992; Pöllmann and Blass, 1994; Perry *et al.*, 1997) or under batch operation (Lang *et al.*, 1994; Safrit *et al.*, 1995; Lelkes, 1998; Rodriguez-Donis *et al.*, 2001a,b, 2003a,b; Skouras *et al.*, 2005; Gerbaud *et al.*, 2006; Kotai *et al.*, 2007). Apart from being market available, inexpensive, stable, non toxic, non-flammable or non corrosive, the most awaited feature of the entrainer E is selectivity, through preferential interaction with either A or B. Recycling of E is also preferable and so it should have a high relative volatility with the non preferentially interacting compound B or A. It should be miscible in the case of homogeneous distillation or as immiscible as possible with either A or B in the case of heterogeneous distillation where heteroazeotropic mixtures occurrence doesn't provide any additional inconvenient. Other properties may influence the process efficiency: a low molar volume is sought especially in batch extractive distillation as the entrainer accumulates in the column; low heat capacity and vaporization enthalpy will attenuate the energy demand increase.

Entrainers are commonly classified as heavy, intermediate or light if their boiling temperature is respectively higher, intermediate or lower than A and B's boiling temperature. Process feasibility has been evaluated for continuous (Widagdo and Seader, 1996) and batch (Rodriguez-Donis *et al.*, 2001a,b, Skouras *et al.* 2005) azeotropic distillation for all significant Serafimov's classes and led to major industrial applications in the continuous operation mode. For homogeneous extractive distillation, class 1.0-1a has been thoroughly investigated for a continuous column (Knapp and Doherty, 1994; Hilmen, 2000; Brüggemann and Marquardt, 2004) and only 0.0-1; 1.0-1a; 1.0-1b and 1.0-2 classes for a batch rectifier or stripper column (Steger *et al.*, 2005, Varga, 2006). For heterogeneous batch extractive distillation, only 2.0-2b class has been studied in detail (Rodriguez-Donis *et al.*, 2003a; Varga *et al.,* 2005). We contribute in this paper to assess the feasibility of heterogeneous batch extractive distillation for Serafimov's class 2.1-2b.

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; Doherty and Knapp, 1993; Perry *et* *al.*, 1997; Rodriguez-Donis *et al.*, 2003a; Gerbaud *et al.*, 2006). Accurate prediction of azeotropic composition and temperature under the operating pressure requires either experimental data (Gmehling and Onken, 1982; Gmehling *et al.* 1994) or calculation using thermodynamic models of vapor – liquid phase equilibrium, like activity coefficient models or equation of states or group contribution methods (Bossen *et al.*, 1993; Thery *et al.*, 2004). Entrainer selectivity through preferential interactions with either A or B is assessed using several complementary quantitative indices, namely the relative volatility $\alpha_{A,B}$ and the activity coefficient ratio under infinite dilution in the entrainer $\gamma_A^\infty / \gamma_B^\infty$. In particular, the higher the relative volatility $\alpha_{A,B}$ increase or the infinite dilution activity coefficient ratio the better the selectivity. Process operation efficiency also depends on the entrainer due to the existence of minimum values for the entrainer flowrate and the reflux ratio. They are both related to the topology of the extractive profile maps, in particular to the univolatility line $\alpha_{A,B}$ =1 and the product composition x_P at its intersection point with the edge E – distillate product (A or B) (Knapp and Doherty, 1994; Hilmen, 2000; Steger *et al.*, 2005; Frits *et al.*, 2006).

For the most studied homogeneous case, 1.0-1a class, the minimum entrainer feed flowrate value corresponds to the value where the extractive profile stable node matches with the location where the univolatility line intersects the E-A (resp. E-B) edge at x_P, so as to cross the rectification profile leading to the desired distillate A (resp. B). Considering A (resp. B) as distillate, the minimum entrainer flowrate will be lower if the univolatility line intersects the E-A (resp. E-B) edge closer to A (resp. B) (Laroche *et al.*, 1991). The residue curve inflection point line behaves similarly to the univolatility line to assess the entrainer selectivity (Laroche *et al.*, 1991; Pöllmann and Blass, 1994; Kiva *et al.*, 2003). Based on the analysis of operating continuous extractive distillation processes, Knapp and Doherty (1994) have suggested a heuristic to set the optimal entrainer flowrate value at 2.0 to 4.0 the minimum entrainer flowrate value so as to get a minimum separation cost. As usual in continuous extractive distillation, this cost concerns a sequence of columns with regeneration of the entrainer. For batch extractive distillation, an increasing factor of 1.2 – 1.5 was suggested by Lelkes (1998). The effect of reflux is complex because it induces major topological changes on the extractive profile map with the occurrence of extractive boundaries crossing at extractive saddle points and reducing the feasibility composition region (Knapp and Doherty, 1994; Lelkes *et al.*, 1998a; Brüggemann and Marquardt, 2004). Hence, $\gamma_A^\infty / \gamma_B^\infty$ must be sufficiently large to achieve the desired purity with a moderate reflux and a minimum number of trays in the rectifying section (Hilmen, 2000).

Unfortunately, homogeneous entrainers with high selectivity have usually shown a limited miscibility with at least one of original components (Lee and Gentry, 1997; Lee, 1998) and are then qualified as heterogeneous entrainers. Unlike in heterogeneous azeotropic batch distillation where the unstable binary heteroazeotrope is obtained in the vapor overhead (Rodriguez-Donis *et al.*, 2002), in heterogeneous batch extractive distillation, either the saddle miscible primary component (case 1) or the saddle binary heteroazeotrope (case 2) can be obtained in the vapor overhead of the rectifying column thanks to the feed of the heterogeneous entrainer at some tray near the column top (Rodriguez-Donis *et al.*, 2003a). For case 1, the process works in a way similar to homogeneous batch extractive distillation but the x_P value is usually lower, producing higher entrainer consumption. For case 2, significant operation differences exist compared to the classic process because the univolatility line always intercepts the heterogeneous binary side. $\gamma_A^\infty / \gamma_B^\infty$ is greater (resp. lower) than unity if the entrainer forms a heteroazeotropic mixture with the most (resp. least) volatile original component A (resp. B). In all cases, x_P lies between the heteroazeotrope and the high boiling temperature entrainer vertex. This is not the case in homogeneous system where the univolatility curve always arrives to the zeotropic binary side either AE or BE.

First, the selection of potential feasible entrainers (E) for the separation of the minimum temperature boiling azeotropic mixture chloroform (A) – methanol (B) is defined by using the RegsolExpert® program which combines chemical insight and thermodynamic calculations to find suitable entrainers (Gerbaud *et al.*, 2006). A set of 54 entrainers with experimentally reported azeotropic behaviour with chloroform and methanol (Gmehling *et al.*, 1994) was classified according to their boiling temperature: 14 entrainers were light, one intermediate and 39 heavy. UNIQUAC or NRTL thermodynamic model were used when binary coefficients were reported in Gmehling and Onken (1982). Otherwise, the modified UNIFAC Dortmund version 1993 (Gmehling *et al.*, 1993), afterwards simply called UNIFAC, was used as it predicted azeotropic data matching the experimental data (Van Kaam, 2006). As a result of the entrainer screening, the 14 heavy entrainers reported in Table 1 were found relevant for the separation of chloroform – methanol mixture in a batch rectifying configuration, 12 by the well settled homogeneous extractive distillation process (BED) and only two heterogeneous entrainers (water and methyl cyclohexane) by using an heterogeneous extractive distillation process (HBED).

The first six homogeneous entrainers and water reported in Table 1 provide the separation of chloroform as the first distillate cut because $\gamma_A^\infty / \gamma_B^\infty$ is higher than unity and the univolatility line arrives at the binary side chloroform-entrainer. Otherwise, methanol is the first distillate cut for the remaining seven entrainers including methyl cyclohexane. Costly or toxic entrainers were rejected. Separation by homogeneous batch extractive distillation using n-butyl acetate was compared to separation by heterogeneous batch extractive distillation using water by Van Kaam *et al.* (2006) that concluded on the superiority of water related to the total consumption of the entrainer. Furthermore, the industrial waste stream chloroform – methanol is polluted by a few percent of water. Adding n-butyl acetate as an entrainer would induce the formation of a quaternary mixture with a two side VLLE region complicating the process. So, water is finally selected as the best entrainer for the separation of chloroform – methanol.

3. Topological and thermodynamic properties of chloroform-methanol-water.

In Fig. 1 the ternary residue curve map for the mixture chloroform – methanol – water is shown. Phase equilibria were determined by the modified Raoult-Dalton equation with ideal vapor phase and non ideal liquid phase represented with activity coefficients using NRTL model. Binary coefficients for chloroform – methanol and methanol – water were taken from the specialized literature (Gmehling and Onken, 1982). Binary coefficients of the NRTL model for chloroform-water were computed from the ternary liquid – liquid – vapor equilibrium data estimated by UNIFAC. Table 2 shows the NRTL binary parameters applied for the calculation of the vapor – liquid – liquid (VLLE) equilibrium of the ternary mixture chloroform – methanol – water and the calculated binary and ternary azeotropes are reported in Table 3.

NRTL using the binary coefficient of the liquid – liquid – vapor equilibrium (Table 2) underestimated and poorly represented the scarce experimental LLE ternary data tie line at 0°C (Sörensen and Arlt, 1980) as confirmed by the experimental decanter measurements. On the other hand, calculated LLE data with UNIFAC agree better with experimental data at 0°C (Fig. 1), giving the right inclination of the LL tie lines but overestimating the LLE region size. So, UNIFAC was used as the thermodynamic model for the estimation of LLE in the decanter. Thermodynamic and topological features of the resulting ternary system are shown in Fig. 1 including the univolatility curve chloroform – methanol (α_{12}) and both calculated liquid – liquid – vapor and the liquid – liquid phase envelopes. Thermodynamic calculations were done by using Simulis Thermodynamics®, a thermodynamic property server available in Microsoft Excel (ProSim S.A., 2000) and figures were drawn using a freeware ternary diagram drawing tool (Prosim SA., 2005).

Matching Serafimov's class 2.1-2b, the ternary system exhibits an unstable ternary heteroazeotrope [UN_{rcm}] that is linked to two binary saddle points by two unstable separatrices dividing the composition space in two basic distillation regions. One saddle point is the original homoazeotrope chloroform – methanol [S_{rcm}] and the other saddle point is the heteroazeotrope chloroform – water [S_{rcm}]. Chloroform and water vertices are stable nodes (SN_{rcm}) of their respective distillation regions while methanol is a saddle point [S_{rcm}]. The vapor line of the heterogeneous region is located close to the unstable separatrix passing through both heterogeneous azeotropes. The process for a 2.1-2b mixture behaves similarly to the process for a 2.0-2b mixture (Rodriguez-Donis *et al.*, 2003a): the chloroform – methanol univolatility line ($\alpha_{AB} = 1$) starts from the original homogeneous azeotrope, goes through the ternary heteroazeotrope. Because the univolatility line ends at the heterogeneous binary side chloroform – water, the chloroform – water saddle binary heteroazeotrope can be drawn as vapor overhead at the column top generating two liquid – liquid phases into the decanter after condensation (Rodriguez-Donis *et al.*, 2003a). The heavy chloroform-rich phase ($\boldsymbol{x^I = x_D}$) can be withdrawn as a distillate product whereas the water – rich phase ($\boldsymbol{x^{II}}$) or a mixture composed by both decanted liquid phases can be refluxed toward the column top.

4. Feasibility methodology of the batch extractive distillation process involving heavy heterogeneous entrainers

4.1 Distillate target and feasibility criteria

Assessing the feasibility implies choosing first a column configuration, a distillate objective and a process operating policy, then finding the limiting parameters enabling the process for the entrainer/vapor flowrate and reflux ratio.

The configuration for the batch heterogeneous distillation column is shown in Fig 2, considering that the entrainer is fed at the column top along with the liquid reflux coming from the decanter. The heterogeneous batch column is the aggregation of several parts among which (1) a condenser and a decanter together, (2) an extractive section from the entrainer feed at the column top down to the upper part of the reboiler and (3) the reboiler where the charge is initially fed. Figure 2b shows how the entrainer recycle $\boldsymbol{F_E}$ affects the liquid reflux. This batch column configuration is simpler than those commonly used in homogeneous batch extractive distillation where the entrainer is fed at intermediate tray dividing the column in two, rectifying and extractive, sections (Lelkes et al, 1998). Depending on the entrainer feed position, other column configurations exists for heterogeneous batch extractive distillation (Rodriguez-Donis *et al.*, 2005; Varga *et al.*, 2005).

The separation of the chloroform-methanol mixture using water as heavy heterogeneous entrainer by batch extractive distillation process involves the following operating steps:

- Step 1: initial charge of the binary mixture into the still and infinite reflux operation so as to obtain the steady state inside the column and the unstable ternary heteroazeotrope is settled at the column top.

- Step 2: infinite reflux operation with continuous feeding of the heterogeneous entrainer at the column top inducing the replacement of the ternary unstable heteroazeotrope by the binary saddle heteroazeotrope chloroform – water in the vapor overhead.

- Step 3: distillation under a given reflux policy while continuously feeding the entrainer in order to remove the chloroform-rich phase as distillate product with average chloroform purity equal or higher than the specified minimum value. At the end of this step, the chloroform content into the still must be as low as possible.

-Step 4: Separation of the zeotropic mixture methanol – water remained into the still under a defined reflux policy where methanol is drawn as the second distillate cut.

At the end of step I, the still composition is labeled $\boldsymbol{x_{Si}}$.

Once a distillate objective in terms of purity or recovery is set, the range of operating parameters (entrainer/vapor flowrate ratio $\boldsymbol{F_E/V}$ and reflux ratio $\boldsymbol{R} = \boldsymbol{L}/\boldsymbol{D}$) are determined for each operating step so as to match a general feasibility criterion. In our case, we would like to achieve a minimum mean purity of 99% molar chloroform in the distillate withdrawn from the decanter. Figure 1 displays the relevant liquid - liquid tie line $\boldsymbol{x_{Dmin}} = \boldsymbol{x^I}$=[0.9900, 0.0092, 0.0008] and $\boldsymbol{x^{II}}$=[0.0010, 0.0288, 0.9702]. This composition vector is written in decreasing order of volatility of the pure components [chloroform, methanol, water]. The top destination region (TDR) is then delimited by the selected liquid – liquid tie line, the heterogeneous binary side chloroform – water and the liquid – liquid envelope at decanter temperature and it is also shown in Fig 1. The original component-rich phase can be taken out as distillate product with purity equal or higher than the fixed minimum limiting value ($\boldsymbol{x_{Dmin}}$).

In the well-known homogeneous case, feasibility is assessed by the interception of the extractive profile to the rectifying profile giving one original component as distillate product. The extractive liquid composition profile is computed by using the differential model of Lelkes *et al.* (1998a) from a punctual still composition $\boldsymbol{x_S}$ as initial value. In that case, the liquid reflux composition x_0 coincides with the distillate composition $\boldsymbol{x_D}$ because the entrainer is fed at an intermediate column point. In heterogeneous batch distillation as shown in Fig 2, $\boldsymbol{x_0}$ and $\boldsymbol{x_D}$ are dissimilar. $\boldsymbol{x_0}$ is determined by a mass balance between the entrainer flowrate $\boldsymbol{x_E}$ and the liquid reflux $\boldsymbol{x_R}$ that also depends on the reflux policy and on the decanter split ratio (Varga, 2006). According to the criterion enounced by Varga *et al.* (2005), the heterogeneous extractive batch distillation is feasible if the vapor top composition $\boldsymbol{y_T}$ is located on the selected liquid – liquid tie line or inside the TDR. Therefore, total condensation of $\boldsymbol{y_T}$ provides two liquid phases into the decanter and the composition of distillate will be equal or higher than the minimal specified value (x_{Dmin}). The vapor extractive profile can be computed using a similar differential equation that those proposed for the homogeneous case for the liquid profile (Lelkes *et al.*, 1998a). Whatever the reflux policy, x_R and y_T are located on the same liquid-liquid tie line. However, the additional mixing of the entrainer to the liquid reflux coming from the decanter sets a new x_0 line between the selected liquid – liquid tie line and the entrainer vertex (Rodriguez-Donis *et al.* 2007). The x_0 line has to be computed for a fixed F_E/V and R and feasibility is now assessed by the existence of the extractive liquid profile connecting x_S to any point located on this new x_0 line. Figure 4 shows the x_0 line { (0.4500, 0.0042, 0.5458); (0.0004, 0.0130, 0.9864)} for F_E/V=1.2 and infinite reflux. In order to simplify the feasibility analysis, we perform the computation of the extractive liquid profile from x_S for several values of F_E/V and R. Feasibility is then accomplished if the ending point of the extractive liquid profile lies on the heterogeneous binary side chloroform – water because it implies the previous obligatory interception of the x_0 line. This assumption doesn't affect the aim of the preliminary feasibility analysis in determining limiting values for F_E/V and R that are further used as initial values for the rigorous simulation of the process.

With the column configuration defined (Fig. 2), the minimal distillate purity (x_{Dmin} in Fig. 1) and the general feasibility criterion, the next section describes the equations implicated in the simplified model for the preliminary feasibility analysis purpose. All retained assumptions will not affect the aim of the preliminary feasibility analysis in determining limiting values for F_E/V and R that are further used as initial values for the rigorous simulation of the process.

4.2 Extractive profile equation and topological analysis

The successful feasibility methodology of Lelkes *et al.* (1998a) proposed for batch homogeneous extractive process has been extended for the heterogeneous process as well (Modla *et al.*, 2001; Rodriguez-Donis *et al.*, 2003a; Rodriguez-Donis *et al.*, 2005). Under the assumption of constant molar overflow $\boldsymbol{V}$ and $\boldsymbol{L}$, negligible liquid holdup inside the column and infinite column height, the liquid composition variation in the extractive section is:

$$\frac{d\boldsymbol{x}_i}{d\boldsymbol{h}} = \frac{\boldsymbol{V}}{\boldsymbol{L}}(\boldsymbol{y}_i - \boldsymbol{y}_i{}^*) \tag{1}$$

where $\boldsymbol{h}$ is the dimensionless column height; $\boldsymbol{V}$ and $\boldsymbol{L}$ are the vapor and liquid flowrates, respectively; $\boldsymbol{y_i*}$ is the vapor composition in equilibrium with the liquid composition $\boldsymbol{x_i}$ and $\boldsymbol{y_i}$ is the actual vapor composition according to the component mole balance (Eq. 2) around any position inside the column and involving the external streams: entrainer supply $\boldsymbol{F_E}$ and distillate withdrawal $\boldsymbol{D}$ (Varga, 2006).

$$\begin{aligned}
\frac{\boldsymbol{V}}{\boldsymbol{L}} &= \frac{\boldsymbol{V}}{\boldsymbol{V}+\boldsymbol{F_E}-\boldsymbol{D}} = \frac{\boldsymbol{R}+1}{\boldsymbol{R}+(\boldsymbol{R}+1)\cdot(\boldsymbol{F_E}/\boldsymbol{V})}\\
\boldsymbol{y}_i &= \frac{(\boldsymbol{V}+\boldsymbol{F_E}-\boldsymbol{D})\boldsymbol{x}_i+\boldsymbol{D}\boldsymbol{x_D}-\boldsymbol{F_E}\boldsymbol{x_E}}{\boldsymbol{V}} = \left(\frac{\boldsymbol{R}}{\boldsymbol{R}+1}+(\boldsymbol{F_E}/\boldsymbol{V})\right)\boldsymbol{x}_i+\frac{1}{\boldsymbol{R}+1}\boldsymbol{x_D}-(\boldsymbol{F_E}/\boldsymbol{V})\boldsymbol{x_E}
\end{aligned} \tag{2}$$

Eq. (1) is an initial value problem forming a differential-algebraic equations system with the component mass balance (Eq. 2) including the internal column overflows $\boldsymbol{V}$ and $\boldsymbol{L}$ and the external $\boldsymbol{D}$ and $\boldsymbol{F_E}$ streams. The liquid profile inside the extractive column is computed bottom up from different still compositions $\boldsymbol{x_S}$ in order to obtain the map of extractive liquid profiles for given operating parameters $\boldsymbol{F_E/V}$, $\boldsymbol{x_E}$, $\boldsymbol{x_D}$ and $\boldsymbol{R}$. During a real process operation or simulation, the $\boldsymbol{V}$ value is set by the boiler heat duty and by the heat capacity and vaporization enthalpy of the boiler mixture which vary during the whole process. This is a possible cause of discrepancy between the feasibility predictions and the simulations and experiments. Past works have shown that is was never significant if an adequate control of the boiler heat duty is kept during the experimental validation (Rodriguez-Donis *et al.*, 2002; Rodriguez-Donis *et al.*, 2005).

Due to the non stationary nature of batch distillation process, the feasibility condition enounced above must be kept during all process steps. Therefore, the change of the still composition $\boldsymbol{x_S}$ from which extractive profiles are computed is given by Eq. (3) (Varga, 2006).

$$\frac{d(\boldsymbol{H_S}\boldsymbol{x_S})}{dt} = \boldsymbol{F_E}\boldsymbol{x_E} - \boldsymbol{D}\boldsymbol{x_D} \tag{3}$$

Similarly to residue curve map (rcm) analysis, the extractive profile map analysis enables to identify feasible and unfeasible regions for the composition in the extractive section of the column. Those regions are bounded by extractive stable and unstable separatrices crossing at saddle extractive singular points (Knapp and Doherty, 1994). As demonstrated for the 1.0-1a class mixture by Knapp and Doherty (1994) for a stage by stage model of the extractive profiles and Frits *et al.* (2006) for the differential model cited above, the pinch point of the extractive profiles are a stable extractive node SN_{extr} issued from the original minimum boiling azeotrope and saddle extractive points $S_{i,extr}$ are issued from the rcm saddle points (A and B vertex for 1.0-1a class). An unstable extractive node UN_{extr} is located at the entrainer vertex for the 1.0-1a class.

At infinite reflux while the entrainer feed ratio $\boldsymbol{F_E/V}$ increases, SN_{extr} moves along the univolatility line and the $S_{i,extr}$ move along the binary edges AE and BE towards the E vertex. Extractive stable separatrices between SN_{extr} and $S_{i,extr}$ move inside the composition triangle with no effect on feasibility. On the other hand, at finite reflux ratio while $\boldsymbol{F_E/V}$ increases, both a $S_{i,extr}$ and the UN_{extr} move inside the composition triangle, along with an extractive unstable separatrix between $S_{i,extr}$ and UN_{extr}. This unstable separatrix is responsible for the occurrence of an unfeasible composition region inside the extractive section of the column. As seen below, those features are also observed for the 2.1-2b class mixture.

According to the operating steps described above for heterogeneous extractive batch distillation, the feasibility analysis is only performed for steps 2 and 3. Step 1 serves for heating up and establishes the initial steady state in the column while step 4 is a conventional separation of a binary zeotropic mixture methanol – water once chloroform is exhausted from the still.

4.3 Feasibility analysis of Step 2: Operation at infinite R and $F_E > 0$

Table 4 displays the initial charge molar composition into the still $\boldsymbol{x_{S0}}$, showing that water is present in the original waste as impurity. The reflux ratio being infinite, step 2 feasibility depends primarily on the entrainer flowrate $\boldsymbol{F_E}$ value enabling to substitute the unstable ternary heteroazeotrope, refluxed at the column at the end of step 1, by the saddle binary heterogeneous azeotrope chloroform – water at the top of the column. Following the works of Laroche *et al.* (1992) and Knapp and Doherty (1994) for continuous extractive distillation, Lelkes *et al.* (1998b) showed that the minimum entrainer flowrate $\boldsymbol{F_{E}}_{\min}$ for batch extractive distillation is the value required for the extractive liquid profile end (SN_{extr}) to reach the intersection of the univolatility line α_{AB} with the rectification profile enabling to reach the desired distillate composition. In the case of heterogeneous batch distillation, $\boldsymbol{F_{E}}_{\min}$ is here defined by the interception of the extractive liquid profile and the selected liquid – liquid tie line neglecting the existence of the x_0 line as stated above. The process $\boldsymbol{F_E}$ is always higher than its minimum value (Lelkes, 1998).

As all extractive profiles within a given extractive region reach the same stable node, Frits *et al.* (2006) suggest the computing of several extractive profiles displayed in Fig. 3 from the initial charge composition $\boldsymbol{x_{S0}}$ for different ratio $\boldsymbol{F_E/V}$ (0.01, 0.5, 1.0 and 1.2) at infinite reflux. Strictly, we should compute the profiles from the still composition $\boldsymbol{x_{S1}}$ at the end of step 1 (infinite reflux, no entrainer), right before starting the feeding of the entrainer, but under feasibility analysis assumptions (no holdup, infinite column length), $\boldsymbol{x_{S0}}$ equals $\boldsymbol{x_{S1}}$ and

$\boldsymbol{x_{S0}}$ is used in Fig. 3 to 7. On the other hand, during rigorous simulation and experiments, $\boldsymbol{x_{S0}}$ will be different from $\boldsymbol{x_{S1}}$ (see below and Fig. 8 and 9).

When $(\boldsymbol{F_E/V})$ goes to 0, SN_{extr} ends on the univolatility line in the infinitesimal surrounding of the ternary heteroazeotrope that, as $\mathrm{UN_{rcm}}$, is the location of the overhead vapor composition under infinite reflux. If $(\boldsymbol{F_E/V}) < (\boldsymbol{F_E/V})_{\mathrm{min}}$, SN_{extr} moves on the univolatility line. In our case, $(\boldsymbol{F_E/V})_{\mathrm{min}}=1.0$ as the corresponding extractive liquid profile from $\boldsymbol{x_{S0}}$ finishes on the univolatility curve at the $SN_{extr,min}$ point, intercepting the top destination region precisely on the selected liquid – liquid tie line which enables to withdraw from the decanter the chloroform-rich phase ($\boldsymbol{x_{Dmin}}$) with the desired 99% molar purity in chloroform. If $(\boldsymbol{F_E/V}) > (\boldsymbol{F_E/V})_{\mathrm{min}}$, SN_{extr} moves inside the top destination region enabling to withdraw a distillate with a chloroform purity higher than the specified limit value. Such is the case of the extractive liquid profile computed for $\boldsymbol{F_E/V}=1.2$. At some particular value $(\boldsymbol{F_E/V})=1.09 > (\boldsymbol{F_E/V})_{\mathrm{min}}$ (not shown on Fig 3), SN_{extr} reaches the binary edge E-A and merges with a $S_{i,extr}$ that has moved away from the rectification saddle binary heteroazeotrope E-A as $(\boldsymbol{F_E/V})$ increased. A similar behavior was demonstrated for 1.0-1a class mixture by Knapp and Doherty (1994) with a stage by stage model and Frits *et al.*, (2006) with a differential model. For higher values of $(\boldsymbol{F_E/V})$, the SN_{extr} point moves towards the entrainer vertex keeping the process feasible. At infinite $(\boldsymbol{F_E/V})$, SN_{extr} reaches the vicinity of the entrainer vertex.

Figure 4 displays the extractive liquid profiles map for $(\boldsymbol{F_E/V})=1.2$ under infinite reflux during step 2. A stable extractive separatrix joins the end point of the extractive profiles SN_{extr} to the saddle extractive $S_{1,extr}$ emerged from the methanol vertex S_{rcm} while a UN_{extr} lies at the entrainer vertex. The existence of the stable extractive separatrix does not affect the feasibility as would do an unstable extractive separatrix: any composition is linked to the TDR by an extractive profile ending at SN_{extr} located on the binary side chloroform – water. This is true for the still composition that, because the process is performed at infinite reflux, starts at the initial ternary composition $\boldsymbol{x_{S0}} = \boldsymbol{x_{S1}}$ and moves towards the entrainer vertex due to the sole continuous feeding of water at the column top without any distillate withdrawal ($\boldsymbol{D}$=0 in Eq. 3). At the end of this operating step, the punctual still composition $\boldsymbol{x_{S2}}$ is located on the straight line going from $\boldsymbol{x_{S0}}= \boldsymbol{x_{S1}}$ to the vertex *E*. Hypothetical position of $\boldsymbol{x_{S2}}$ is indicated in Fig. 4. Besides, $\boldsymbol{x_{S2}}$ is connected by an extractive liquid profile to the stable node S_{Nextr} and the heterogeneous binary azeotropic mixture is established at the column top. Theoretically, step 2 duration is determined by the substitution of the unstable UN_{rcm} ternary heterogeneous azeotrope by SN_{extr} in the TDR region. It mainly depends on the effect of water on the relative volatility between chloroform and methanol. This operating time is further computed by rigorous simulation.

4.4 Feasibility analyses of Step 3: Operation with F_E > 0 at finite R

In step 2, the extractive liquid profile ends at SN_{extr} in the TDR and the liquid – liquid splitting occurs into the decanter enabling to withdraw the chloroform – rich phase as the first distillate product. However, a reflux policy has to be determined in order to obtain the maximum recovery of chloroform with an average molar purity higher than the minimum specified value ($\boldsymbol{x_{Dmin}}$ in Fig 4). Therefore, a map of extractive profile is computed for ($\boldsymbol{F_E/V}$)=1.2 and at fixed reflux ratio $\boldsymbol{R}$ considering the minimum distillate purity in Eq. 2. The still path must be located in feasible region and connected by an extractive profile to any liquid composition belonging to the TDR.

Figure 5 displays the extractive liquid profiles map for $\boldsymbol{R}$=1 and ($\boldsymbol{F_E/V}$)=1.2. Compared to Fig 4, $S_{1,extr}$ and UN_{extr} have moved inside the composition triangle ($S_{1,extr}$=[0.022, 0.129, 0.849] and UN_{extr}=[0.006, 0.000, 0.994]). It results into the occurrence of an unstable extractive separatrix linking UN_{extr} *to* $S_{1,extr}$ and to an unphysical SN'_{extr} outside the triangle.

The upper region above the unstable extractive separatrix is not feasible because extractive profiles are ending at an unphysical SN'_{extr} outside the triangle and thus reach the homogeneous side methanol – water instead of the TDR.

The still path must remain inside this feasible region located below the unstable extractive separatrix during the whole operating step 3. Regarding Eq. 3, the still path is influenced by both the feeding of entrainer $\boldsymbol{F_E}$ and the distillate withdrawal $\boldsymbol{D}$ and the still composition motion $\boldsymbol{x_S}$ is restricted by the cone vector limited by $\boldsymbol{x_E}$ and $\boldsymbol{x_D}$. Figure 5 shows that it might cross the unstable extractive separatrix into the unfeasible region at some time. Consequently, complete recovery of chloroform is not possible for this reflux value. This indicates that $\boldsymbol{R}$=1 can be selected as an initial value for simulation purpose but that increasing the reflux ratio is necessary in order to deplete chloroform in the still at the end of this operating step.

Note in Fig 5 that for $(\boldsymbol{F_E}/\boldsymbol{V})$=1.2, the stable node SN_{extr} is closer ($x_{E,SNextr}$=0.798) to the entrainer vertex when $\boldsymbol{R}$ decreases (Fig 4 $x_{E,SNextr}$=0.619). A lower reflux ratio means that less amount of liquid reflux is sent from the decanter to the column top and the concentration of the entrainer increases in this column section. It implies that at finite reflux ratio, less entrainer is required and the minimum value $(\boldsymbol{F_E}/\boldsymbol{V})_{\text{min, finite R}}$ is lower than the $(\boldsymbol{F_E}/\boldsymbol{V})_{\text{min,R}\,\infty} = 1.0$ at infinite R.

However, diminishing $\boldsymbol{R}$ also increases the unfeasible region size until the process is no longer feasible whatever the composition. The minimum reflux ratio $\boldsymbol{R_{min}}$ is obtained when the infinite reflux still path $\{\boldsymbol{x_{S0}}, \boldsymbol{x_E}\}$ is tangent to the unstable extractive separatrix. Below $\boldsymbol{R_{min}}$, the whole infinite reflux still path will lie in the unfeasible region. Figure 6 shows that this happens for $\boldsymbol{R_{min}} = 0.38$ with the given conditions $(\boldsymbol{F_E}/\boldsymbol{V})$ and $\boldsymbol{x_E}$ (here pure water), whatever the step 2 duration. At an even lower $\boldsymbol{R}$ value, the whole composition triangle is unfeasible as the stable node SN_{extr} moves out of the triangle on the left of the composition space and the entire ternary diagram become unfeasible. Figure 7 displays such an extractive profiles map computed for $\boldsymbol{R}$=0.17.

In summary, reducing the reflux ratio concentrates the entrainer into the column and so reduces the minimum amount of entrainer compared to $(\boldsymbol{F_E/V})_{\text{min}}$ at infinite $\boldsymbol{R}$. But it also lowers the recovery yield of chloroform in the distillate and may even prevent the feasibility of the process. To cope at best with these constraints, we recommend to select $(\boldsymbol{F_E/V}) > (\boldsymbol{F_E/V})_{\text{min,R}\,\infty} = 1.0$ and keep it for both steps 2 and 3. From Figs 3 and 4, we choose $(\boldsymbol{F_E/V}) = 1.2$. The reflux ratio value for step 3 is set from the influence of $\boldsymbol{R}$ on the shape of the extractive separatrix and on the feasible region size. At the beginning of step 3, the reflux ratio can be kept low (we choose $\boldsymbol{R} = 1$ from Fig 5) because $\boldsymbol{x_{S0}}$ is inside the feasible region. As distillate removal proceeds, $\boldsymbol{x_S}$ will come closer to the unstable separatrix. Therefore, the reflux ratio must be increased (we choose $\boldsymbol{R} = 10$) enabling to move the unstable separatrix away from the still composition and keeping $\boldsymbol{x_S}$ into the feasible region to continue distillate withdrawal until the still reaches the binary side methanol – water. Overall, the reflux policy has to be selected in order to shift the still composition from x_{S1} to a final value x_{S2} located as close as possible to the binary side methanol – water, thus enabling to recover a maximum of chloroform. Besides, the average purity of chloroform in the distillate has to be always kept higher than the minimal set value x_{Dmin} for accomplishing the goal of the extractive distillation process.

5. Rigorous simulation of the separation of the chloroform – methanol mixture with water by heterogeneous extractive distillation process in a batch rectifier

Simulation of the heterogeneous batch extractive distillation of chloroform – methanol by using water as a heterogeneous heavy entrainer is performed with two sequential reflux ratio values in step 3. Operating times for each reflux ratio are computed with a constraint of obtaining an average molar purity of chloroform in the distillate product higher than 99%.

BatchColumn® software (Prosim, 2000) describes a batch distillation column by a model with usual plate by plate MESH set of differential algebraic equations (Material balance, Equilibrium, Summation of fractions and Heat balance) which are solved for the whole column, decanter included and taking into account the liquid-liquid phase splitting. Thermodynamic models are identical to those used in the feasibility analysis. Column technical features and operating conditions of a real bench batch distillation column are described in Table 3. The total packed height of the column was determined from past experiments to be equivalent to 45 theoretical plates. The top vapor goes to the total condenser and the resulting liquid flowrate is retained into a subcooled decanter at 25°C. No heat loss and no pressure drop are considered in the whole column. The reflux policy was set so that no decanter accumulation is allowed and overall, all the entrainer-rich phase is refluxed with part of the product-rich phase. This option was defined in the software by means of the recycle of a portion of the condensed vapor at its boiling temperature. The remaining condensed vapor is sent to the decanter where the liquid – liquid splitting takes place and the heavy phase (chloroform-rich phase) is drawn as distillate. Besides, additional reflux of the water-rich phase was also defined and its flowrate is determined automatically to keep a constant level into the decanter.

Rigorous simulation of the heterogeneous extractive distillation process in a batch rectifying column is performed for the four operating batch steps described in section 3 considering that the organic waste mixture is charged initially into the still at room temperature (x_{S0} in Fig 7, Table 4). The following results were obtained:

Step (1): After loading the still with x_{S0} composition mixture, heating the still and filling with boiling liquid the distillation column, including the condenser and decanter holdup, takes

12 minutes. Then, the column is operated under infinite reflux during two hours in order to reach steady state conditions: that is the residue curve unstable ternary heteroazeotrope is obtained at the column top (condenser and decanter) and is connected by a liquid profile to the still composition $\boldsymbol{x_{S1}}$ as it is shown in Fig 8.

Step (2): Proceeds under infinite reflux operation while feeding 20 mol/h of 25°C pure water at the column top. Following the feasibility analysis, such a water flowrate corresponds to 1.2 times the vapor flowrate generated by the reboiler with the specified heat duty in Table 4 at infinite reflux ratio. With water fed during 100 minutes, the vapor overhead composition moves along the vapor line from the unstable ternary heteroazeotrope to the saddle binary heteroazeotrope chloroform – water at $\boldsymbol{y_T}$ point (Fig 8). Besides, starting at $\boldsymbol{x_{S1}}$, the still composition runs in a straight line towards the water vertex, ending after 100 min at $\boldsymbol{x_{S2}}$ that is connected by an extractive liquid profile to the $\boldsymbol{x_T}$ point inside the TDR. $\boldsymbol{x_T}$ is close to the theoretical stable extractive node SN_{extr} on the binary edge chloroform – water displayed in Fig 3. The liquid - liquid tie line corresponding to $\boldsymbol{y_T}$ gives two liquid phases are $\boldsymbol{x^I}$=[0.9949, 0.0044, 0.0007] and $\boldsymbol{x^{II}}$=[0.0006, 0.0134, 0.9859]. The potential distillate $\boldsymbol{x^I}$ matches the purity objective for the distillate.

Step (3): The chloroform-rich phase is withdrawn as distillate product while continuously feeding pure water. Following the feasibility analysis, $\boldsymbol{R}$=1.4 and $\boldsymbol{R}$=10 are set during 60 and 20 minutes to achieve both a significant recovery of chloroform until $\boldsymbol{x_{S,chloroform}} < 0.0001$ in the still and an average distillate composition of 99% in chloroform. This reflux policy corresponds to 50 and 90 percent of the condensed vapor recycled at the column top for $\boldsymbol{R}$=1.4 and $\boldsymbol{R}$=10, respectively. The remainder goes to the decanter where an additional amount of the water-rich phase has to be sent from the decanter to the column top to maintain a constant level of the light phase into the decanter. Figure 8 shows the still path during the step 3 with its end point $\boldsymbol{x_{S3}}$ located close to the binary side methanol – water as the still contains less than 0.01% of chloroform (see Table 5). In the meanwhile, the distillate composition $\boldsymbol{x_D}$ moves closer to the chloroform vertex.

Step (4): as the still is almost depleted from chloroform, homogeneous conventional distillation process is carried out in step 4 without feeding of water, enabling to recover methanol as distillate. Two reflux ratios, namely $\boldsymbol{R}$=1.5 and $\boldsymbol{R}$=10, are set during 1.65 h and 2.51 h. The final still composition $\boldsymbol{x_{s4}}$ almost matches with the water vertex.

Table 5 displays the molar purity and the recovery yield of the main products of this process: the aqueous phase retained into the decanter at the end of the step 3, the still content at the end of the steps 3 and 4 ($\boldsymbol{x_{S3}}$ and $\boldsymbol{x_{S4}}$), the chloroform-rich phase as the first distillate cut drawn during the step 3 and the methanol as the second distillate product in the step 4. Overall, the reflux policy established in step 3 allows the recovery of 95.4 % of chloroform with a molar purity of 0.9906 where we have considered the total amount of the collected distillate also mixed with the heavy phase retained into the decanter at the end of the step 3. Besides, methanol can be recovered as a second distillate product with a molar purity of 0.9982 and 91.6% of recovery yield. At the end of the step 4, a 0.9988 water-rich mixture remains essentially in the still. Validation of this novel batch distillation process by experimentation in the real bench column is now presented.

6. Experimental verification of the heterogeneous extractive distillation process in a batch rectifying column

6.1 Experimental conditions of the batch rectifying column

The column technical features and operating conditions are similar for the simulation and all six experiments. The glass SHOTT 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 representing 45 equilibrium trays. One litre of the organic waste is initially added into a 2 L capacity glass balloon. The balloon is submerged into a heating oil bath and the vapor flowrate is settled by controlling the oil temperature. Initial oil temperature is calibrated to provide the computed condensed vapor at the column top under zero liquid reflux. Later, increment of the oil temperature was required during distillation step 3 to keep the distillate flowrate determined by simulation. The column has a total condenser and the decanter is subcooled at 25°C. A binary mixture ethanol – water (50:50 mass) at 5°C is used as a cooling medium in the condenser-decanter system. The liquid reflux is provided at the column top by a solenoid valve. The open/close time of the solenoid valve is defined considering the specified value of the condensed vapor to be returned to the column during the distillation step. As the entrainer, bi-distillated pure water at 25°C is supplied at the column top by a peristaltic pump. Due to the complexity of the recycle of water-rich phase from the decanter to the top of the column, this reflux is also provided as bi-distillated pure water by the peristaltic pump. Therefore, the total flowrate given by the peristaltic pump comprises the requirements of water as the fresh entrainer and the reflux of the light phase in order to guarantee a more stable operation of the distillation column.

6.2 Experimental replicates and analytical methods

Six replicas of the experiments were performed under the same operating conditions determined by simulation and described in the preceding section. Only the heterogeneous extractive distillation process involving the steps 1, 2 and 3 were corroborated experimentally because step 4 corresponds to a well-known conventional distillation process for separating the zeotropic binary mixture methanol - water. Each step (1, 2 and 3) was carried out considering the computed time and the reflux ratio as the main operating conditions while keeping a constant water flowrate at the column top. The experimental reflux policy for the step 3 is indicated in Fig. 10 corresponding to those determined by simulation in the previous section. The still composition and the distillate quantity and purity were verified experimentally. Several samples were taken from the still at the end of step 1 (infinite reflux operation) and at 20 minutes of step 2 (infinite reflux along with the continuous water feeding). After about 30 minutes of step 2, liquid – liquid demixtion was visually detected into the still and no more samples could be taken off. Samples into the still at the end of the $\boldsymbol{R}$=1.4 duration in step 3 and at the end of step 3 were also taken. The amount and composition of all collected chloroform – rich phase as distillate product, the aqueous phase accumulated into the decanter, the intermediate distillate cut and the mixture retained into the still at the end of the distillation process were also determined.

Purity was checked for all still samples $\boldsymbol{x_{Si}}$ and for the final mean distillate product along with the heavy phase retained into the decanter at the end of the process. The chloroform and methanol compositions in all samples were determined using a FISONS HRGC as gas chromatography equipment configured with a FID detector and with a column HP INNOWax (30 m x 0.53 mm, 0.25µm film). The injector and detector temperature were held at 250°C and 150°C, respectively and the column temperature was assigned to be constant at 65°C. Preliminary calibration of the gas chromatography technique was done using butanol as an internal standard in samples prepared by mass on a SARTORIUS BP 211D balance with a precision of 0.01 mg. The water composition in the experimental samples was determined using the well established Karl Fischer method. Composition of all components in each sample (calibration or experimental) was determined three times where the standard error was always less than ± 0.1 %.

6.3 Experimental results of the extractive distillation in a batch column

6.3.1 Still composition variation in the different operating steps

Figure 9 shows the average experimental (black squares) and simulated (white squares and continuous line) composition into the still at the following times of the process: end of the infinite reflux operation $\boldsymbol{x_{exp1}}$ (step 1), at 20 minutes of step 2 $\boldsymbol{x_{exp2}}$ (infinite reflux along with continuously water feeding) and during the distillation step 3 with $\boldsymbol{R}=1.4$ ($\boldsymbol{x_{exp3}}$) and $\boldsymbol{R}=10$ ($\boldsymbol{x_{exp4}}$), respectively. The largest deviation between experimental and calculated value was obtained for the punctual still composition at 20 minutes of the step 2 ($\boldsymbol{x_{exp2}}$ and $\boldsymbol{x_{S2'}}$). Note in Fig 9 that this point is close to the vapor – liquid – liquid equilibrium envelope calculated with the NRTL model. Experimentally, VLLE event was detected visually 10 minutes after the sample was taken from the still. Better agreement between experimental ($\boldsymbol{x_{exp3}}$ and $\boldsymbol{x_{exp4}}$) and simulation ($\boldsymbol{x_{S3'}}$ and $\boldsymbol{x_{S3}}$) results was obtained for the samples taken at the end of the distillation step with $\boldsymbol{R}=1.4$ and $\boldsymbol{R}=10$, where the amount of chloroform into the still is very low (see Fig 9). Finally, a homogeneous mixture very close to the methanol – water is left into the still at the end of the heterogeneous extractive distillation process using this column configuration.

6.3.2 Temperature behaviour of the top condensed vapour.

Figure 10 displays the mean experimental temperature evolution of the condensed vapor at the column top during steps 2 and 3 for the six replicates. The precision of the thermometer located at the column top was 1°C. The experimental temperatures of the ternary and binary heteroazeotropes (Gmehling *et al.*, 1994) are also displayed in Fig.10. A small deviation between the reported boiling temperature for the heteroazeotropic points and those determined by simulation is attributed to the calculation of the vapor – liquid – liquid equilibrium by using estimated binary coefficients.

The initial position in Fig 10 ($\boldsymbol{t}=0$) corresponds to the end of step 1 where the column reached the steady state operation and the top temperature shows its minimum value corresponding to the ternary heteroazeotrope boiling temperature (53°C). For $\boldsymbol{t} > 0$, water is fed at the column top keeping the infinite reflux operation during 100 minutes (step 2). For all replicates, the top temperature reaches up the 56 - 57 °C level corresponding to the saddle binary heteroazeotrope chloroform – water boiling temperature within experimental temperature precision. This top temperature level is also maintained when the chloroform-rich phase is withdrawn from the decanter by using a reflux ratio of $\boldsymbol{R}$=1.4 during 60 minutes. After that, the distillation step proceeds at reflux ratio $\boldsymbol{R}$=10 during 20 minutes and the top temperature drops, indicating that the top vapor composition goes back towards the ternary heteroazeotrope. It indicates that some chloroform is still retained inside the column affecting the overall recovery of this component. Therefore, an intermediate cut is expected to be drawn before the top temperature reaches the methanol boiling temperature as is shown in Fig 10. During the whole distillation withdrawal step 3, the heating oil temperature was controlled to maintain the distillate flowrate determined by simulation. Once the computed time for the step 3 is over, the experimental distillation column required more than 10 minutes to overcome 60°C at the column top and an additional cut of heterogeneous condensed vapor was collected keeping $\boldsymbol{R} = 1$ without water feeding. Total amount and composition of this intermediate distillation cut is reported in Table 5. Due to its low chloroform purity, this cut is not mixed to the distillate product obtained during the step 3. This fraction could be added to the initial charge in the next batch distillation process. Finally, chloroform is depleted of the column when the top temperature is higher than 64.5°C corresponding to the boiling temperature of methanol.

This behaviour was not predicted by simulation where the simulated sharp separation of chloroform from the ternary mixture does not occur in a real batch distillation column. Some simplifying assumptions retained in rigorous simulation are hardly accomplished in practice: equivalence between equilibrium trays and packed column, adiabatic column and no pressure drop, ideal controller of the liquid reflux at the top and the heating in the reboiler, etc.

Additional time keeping the water feeding at ***R*** = 10 could avoid the top temperature drop and passing directly to the boiling point of methanol in a shorter time.

6.3.3 Purity and amount of the main product streams

Table 5 and 6 show the average molar amount and composition of the main streams drawn of the column for the six experimental replicates at the end of the heterogeneous extractive batch distillate process (approximately 200 minutes with origin at step 2 start). These streams are:

- Distillate Cut Step 3: Total amount of the heavy phase collected into the decanter during the step 3 ending at 180 minutes of the operating time.
- Aqueous Phase Decanter: Total amount of the light phase accumulated into the decanter during the whole step 3.
- Side Cut: Amount of distillate taken from the column after step 3 is over (between 180 - 200 minutes of operating time).
- Final Still Step 3: Amount of liquid phase retained into the still at the end of the distillation process when the column reached the room temperature.

Experimental error in determining the composition of the main streams was evaluated by computing the average absolute error (AAE) and it is reported in Table 5. The experimental total output was 75.85 moles with an average absolute error of 3.2 moles. Note that the theoretical total input is 80 moles (20 moles of initial charge into the still and 60 of moles of water are introduced into the column during the operation steps 2 and 3). Hence, good reproducibility of the distillation process under the same experimental operating conditions was obtained for the six replicates. The amount and composition of the liquid holdup retained inside the column at the end of the process could not be measured. It can be estimated to 4.15 ± 3.2 moles from the difference between the mean total output (75.85 ± 3.20 moles) and the total input (80.00 moles). The simulation were done with a volumetric liquid holdup experimentally determined from past tests for the bench column (67.5 mL see Table 3) and that corresponds to 2.3 moles at the process end.

Table 6 reports the molar component balance computed from the average value for the amount and composition of the main output streams. Deviation of the molar amount of each component between input and output streams is negligible compared to the total molar amount involved in the initial charge into the still or in the external feeding as in the water case.

6.3.4 Final considerations about the experimental validation

Therefore, Table 5 and 6 show that all six experiments ran satisfactorily and the average values agreed well with the simulations. As we have already validated the thermodynamic model, this corroborate the heterogeneous batch extractive distillation process ability to separate efficiently the chloroform – methanol minimum boiling azeotrope feeding water at the column top. Further differences between simulation and experiments (see Table 5) are worth mentioning:

- Chloroform was separated as distillate product with a molar purity of 0.9914 and this component was practically removed from the initial organic mixture with a recovery yield of 89.1%. The residual chloroform is mostly contained in the side cut because only 0.02% is lost in the aqueous phase.
- Chloroform was not detected experimentally in the liquid mixture drawn from the still after the whole column was cooled. The corresponding simulated value at the end of the step 3 in Table 5 concerns the mixture into the still while the whole column is operated at (hot) equilibrium condition.
- The liquid mixture extracted from still contained 86 % of initial methanol and only 0.3% of methanol is lost in the aqueous phase and distillate (Table 6). Side cut

contains only 0.5% of methanol and we assume that the methanol leftover was retained inside the column. Therefore, 99.4% of the methanol not withdrawn with distillate or lost in the decanter aqueous phase can be separated in further batch conventional distillation step considering the operating conditions previously determined by simulation.

- As explained before, the experimental decanter aqueous phase comprises the totality of the water-rich phase retained into the decanter during the whole distillation step 3. The additional reflux of water-rich phase was provided by the peristaltic pump. This experimental operating strategy didn’t affect the efficiency of the separation of the azeotropic components chloroform and methanol.

These good experimental results encourage the performance of this novel batch distillation process in a higher scale technology for treatment of this organic waste.

7. Conclusion

Reproducible experimental results showed that water is an effective entrainer for the separation of the organic waste chloroform – methanol mixture by heterogeneous extractive distillation in a batch rectifying column fed at the column top. This distillation process for the separation of a minimum boiling azeotrope with a heavy entrainer (mixture class 2.1-2b) was first analyzed for feasibility, then validated via rigorous simulation where the values of essential operating parameters such as the entrainer flowrate and the reflux ratio were obtained considering the technical features of a real bench rectifying column. A sequentially increasing reflux ratio policy could also be proposed from the feasibility analysis. The binary heteroazeotrope chloroform – water that is a saddle point of the ternary system can be drawn as condensed vapor thanks to the continuous feeding of water at the column top. Then, a liquid – liquid phase splitting takes place into a subcooled decanter and the chloroform-rich phase is withdrawal as distillate product. Chloroform molar purity in the distillate reached 0.9914 with a recovery yield 89.1%. Methanol and water were the major components retained into the still mixture at the end of the extractive process for further separation demonstrated by rigorous simulation considering a conventional distillation process.

Notations

Roman letters

D	distillate flowrate (mol.s^{-1})
F	entrainer feed flowrate (mol.s^{-1})
h	column height (m)
H	liquid holdup (mol)
L	internal liquid flowrate (mol.s^{-1})
R	reflux ratio (-)
S	saddle singular point (-)
SN	stable node singular point (-)
t	time (s)
UN	unstable node singular point (-)
V	internal vapor flowrate (mol.s^{-1})
x	liquid molar fraction (-)
y	vapor molar fraction (-)
y^*	vapor molar fraction in vapor liquid equilibrium with x (-)

Greek letters

α_{AB}	A – B relative volatility
$\gamma_A^\infty / \gamma_B^\infty$	infinite dilution activity coefficient ratio

Superscript

I	refers to entrainer lean phase in the decanter
II	refers to entrainer rich phase in the decanter

Subscript

0	refers to the top liquid stream
1	refers to the top vapor stream
A	refers to component A
B	refers to component B
D	refers to the decanter
dec	refers to the decanter
extr	refers to extractive profile map
E	refers to the entrainer
i	refers to component i
min	refers to minimum condition value
P	refers to univolatility line intersection with binary edge.
rcm	refers to residue curve map
R	refers to the reflux stream
s	refers to the still
T	refers to the column top

References

Berg, L. (1969). Azeotropic and extractive distillation: Selecting the agent for distillation. *Chemical Engineering Progress*, 65, 52-57.

Bossen, B.S., Jorgensen, S.B., & Gani, R. (1993). Simulation, design and analysis of azeotropic distillation Oderations. *Industrial & Engineering Chemistry Research*, 32, 620-633.

Brüggemann, S., & Marquardt, W. (2004). Shortcut methods for nonideal multicomponent distillation: 3. Extractive distillation columns. *AIChE Journal*, 50, 1129-1149.

Doherty, M. F., & Knapp, J. F., (1993) *Distillation, Azeotropic and Extractive* (Vol. 8) (4th ed.), Kirk-Othmer Encyclopedia of Chemical Technology.

Doherty, M.F., & Caldarola, G.A. (1985). Design and synthesis of homogeneous azeotropic distillation - III. The sequencing of columns for azeotropic and extractive distillations. *Industrial & Engineering Chemistry, Fundamentals*, 24(4), 474-485.

Frits, E.R, Lelkes, Z., Fonyo, Z., Rev, E., & Markot, M.Cs. (2006). Finding limiting flows of batch extractive distsillation with interval arithmetics. *AIChE Journal*, 52(9), 3100-3108.

Gerbaud, V., Joulia, X., Rodriguez-Donis, I., Baudouin, O., Rosemain, O., Vacher, A., & Castelain, P. (2006). Practical residue curve map analysis applied to solvent recovery in non-ideal binary mixtures by batch distillation processes. *Chemical Engineering & Processing*, 45(8), 672-683.

Gmehling, J., Menke, J., Krafczyk, J., & Fischer, K. (1994). *Azeotropic Data*. VCH Editor: Weinheim.

Gmehling J., & Onken, U. (1982). *Vapor-Liquid Equilibrium Data Collection*. DECHEMA Chemistry Data Series. Vol. 1 DECHEMA: Frankfurt am Main.

Gmehling, J., Li, J., & Schiller, M. A. (1993). Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Industrial & Engineering Chemistry Research*, 32, 178-193.

Hilmen, E. K. (2000). *Separation of azeotropic mixtures: Tools for analysis and studies on batch distillation operation*. Ph.D. thesis. Norwegian University of Science and Technology, Trondheim, Norway.

Kiva, V.N., Hilmen, E.K., & Skogestad, S. (2003). Azeotropic phase equilibrium diagrams: a survey. *Chemical Engineering Science*, 58, 1903-1953.

Knapp, J. P., & Doherty, M. F.(1994). Minimum entrainer flow for extractive distillation: a bifurcation theoretic approach. *AIChE Journal*, 40(2), 243-268.

Kotai, B., Lang, P., & Modla, G. (2007). Batch extractive distillation as a hybrid process: Separation of minimum boiling azeotropes, *Chemical Engineering Science*, In Press, Accepted Manuscript available online, 2007.

Köhler, J., Haverkamp, H., & Schadler, N. (1995). Discontinuous Rectification of Azeotropic Mixtures with Auxiliary Substances. *Chemie Ingenieur Technik*, 67 (8), 967-971.

Lang, P., Yatim, H., Moszkowicz, P., & Otterbein, M. (1994). Batch extractive distillation under constant reflux ratio. *Computers & Chemical Engineering*, 18, 1057-1069.

Laroche, L., Bekiaris, N., Andersen, H.W., & Morari, M. (1991). Homogeneous azeotropic distillation: comparing entrainers. *The Canadian Journal of Chemical Engineering*, 69, 1302-1319.

Laroche, L., Bekiaris, N., Andersen, H.W., & Morari, M. (1992). The curious behavior of homogeneous azeotropic distillation – implications for entrainer selection. *AIChE Journal.*, 38 (9) 1309-1328.

Lee, F.M., & Gentry J.C. (1997). Don’t Overlook Extractive Distillation. *Chemical Engineering Progress*, 10, 56-64.

Lee, F.M. (1998). Extractive Distillation: Separating Close – Boiling – Point Mixtures. *Chemical Engineering*, 105(12), 112-121.

Lelkes, Z. (1998). *Etude de la distillation homoazéotropique et extractive discontinue*. Ph.D. thesis n°98 ISAL 0051, Lyon.

Lelkes, Z., Lang, P., Benadda B., & Moszkowicz P. (1998a). Feasibility of extractive distillation in batch rectification. *AIChE Journal*, 44(4), 810-822.

Lelkes, Z., Lang, P., Moszkowicz, P., Benadda, B., & Otterbein, M. (1998b). Batch extractive distillation: the process and the operational policies. *Chemical Engineering Science*. 53(7), 1331-1348.

Modla, G., Lang, P., & Molnar, K. (2001). Batch heteroazeotropic rectification of a low relative volatility mixture under continuous entrainer feeding: feasibility studies. *Proceedings of 6th World Congress of Chemical Engineering*, Melbourne, Australia.

Perry, R.H., Green, D.W., & Maloney J.O. (1997). *Perry's Chemical Engineer's Handbook*. (7th ed.). McGraw Hill: New York.

Pöllmann, P., & Blass, E. (1994). Best products of homogeneous azeotropic distillations. *Gas Separation and Purification*, 8, 194-228.

ProSim S.A. http://www.prosim.net. *Reference Manual* (2000) and *Ternary Diagram Tool* (2005).

Rodríguez-Donis, I., Gerbaud, V., & Joulia, X. (2001a). Entrainer selection rules for the separation of azeotropic and close boiling point mixtures by homogeneous batch distillation. *Industrial & Engineering Chemistry Research*, 40(12), 2729-2741.

Rodríguez-Donis, I., Gerbaud, V., & Joulia, X. (2001b). Heterogeneous entrainer selection rules for the separation of azeotropic and close boiling point mixtures by heterogeneous batch distillation. Industrial & Engineering Chemistry Research, 40(22), 4935-4950.

Rodriguez-Donis, I., Gerbaud, V., & Joulia, X. (2002). Feasibility of Heterogeneous Batch Distillation. *AIChE Journal*. 48 (6), 1168-1178.

Rodríguez-Donis, I;, Acosta-Esquijarosa, J., Gerbaud, V., & Joulia, X. (2003a). Heterogeneous Batch Extractive Distillation of Minimum Boiling Azeotropic Mixtures. *AIChE Journal*, 49(12), 3074-3083.

Rodriguez-Donis, I., Gerbaud, V., Lelkes, Z., Acosta-Esquijarosa, J., Papp, K., Rev, E., Joulia, X., & Fonyo, Z. (2003b). Separation of an Azeotropic Mixture by Heterogeneous Extractive Continuous Distillation. *Chemical Engineering Transactions*, 3, 355-360.

Rodríguez-Donis, I., Vargas, V., Gerbaud, V., Lelkes, Z., Rév, E., Fonyó, Z., & Joulia, X. (2005). Feasibility Study of Heterogeneous Batch Extractive Distillation. *ESCAPE-15* Proceedings, Computer Aided Chemical Engineering 20 part B, 895-900, L. Puigjaner & A. Espuña (Eds), Elsevier B.V., ISBN 0-444-51991-2.

Rodríguez-Donis, I., Acosta-Esquijarosa I., Gerbaud V., Pardillo-Fondevila E., Joulia, X. (2005), Separation of n hexane – ethyl acetate mixture by azeotropic batch distillation with heterogeneous entrainers. *Chemical Engineering and Processing.* 44, 131-137.

Rodriguez-Donis, I., Papp, K., Gerbaud, V., Joulia, X., Rev, E., & Lelkes, Z. (2007) Column Configurations of Continuous Heterogeneous Extractive Distillation. *AIChE Journal*. In Press, Accepted Manuscript available online, 2007.

Row, K.H., & Jin, Y. (2006). Recovery of catechin compounds from Korean tea by solvent extraction. *Bioresource Technology*, 97(5), 790-793.

Safrit, B.T., Westerberg, A.W., Diwekar, U.M., & Wahnschafft, O.M. (1995). Extending continuous conventional and extractive distillation feasibility insights to batch distillation. *Industrial & Engineering Chemistry Research*, 34, 3257-3264.

Schengrund, C.L., & Kovac, P. (1999). A simple, nonenzymatic method for desialylating polysialylated ganglio-N-tetraose series gangliosides to produce GM1. *The Journal of Lipid Research*, 40, 160-163.

Skouras, S., Kiva, V., & Skogestad S. (2005). Feasible separations and entrainer selection rules for heteroazeotropic batch distillation. *Chemical Engineering Science*, 60, 2895-2909.

Sörensen, J.M., & Arlt, W. (1980). *Liquid – Liquid Equilibrium Data Collection*, Dechema Chemistry Series, Vol. 5. DECHEMA: Frankfurt am Main.

Stark, M., Jörnvall, H., & Johansson, J. (1999). Isolation and characterization of hydrophobic polypeptides in human bile. *European Journal of Biochemistry*, 266, 209-214.

Steger, C., Varga, V., Horvath, L., Rev, E., Fonyo, Z., Meyer, M., & Lelkes, Z. (2005). Feasibility of extractive distillation process variants in batch colonne de rectification column. *Chemical Engineering & Processing*, 44, 1237-1256.

Thery, R., Llovell, F., Meyer, X., Gerbaud ,V., & Joulia, X. (2004). Modelling of a dynamic multiphase flash: the positive flash. Application to the calculation of ternary diagrams. *Computer & Chemical Engineering*, 28(12), 2469-2480.

Varga, V., Rodriguez-Donis, I ., Gerbaud, V., Lelkes, Z., Rev, E., Fonyo, Z., & Joulia, X. (2005). Feasibility study of batch heterogeneous extractive distillation process. *Proceedings of 7th world congress of Chemical Engineering 2005*, Glasgow, UK, 07/10-14/05.

Varga V. (2006). *Distillation extractive discontinue dans une colonne de rectification et dans une colonne inverse*. Ph.D. thesis, INP-Toulouse, France. http://ethesis.inp-toulouse.fr

Van Kaam, R., Rodriguez-Donis, I., Labrada-Fernandez, Y., Acosta-Esquijarosa, J., & Gerbaud, V. (2006). Synthesis of non-conventional distillation processes for the separation of chloroform – methanol mixture. *Revista Cubana de Química*. ISBN 959-282-27-X.

Van Kaam, R. (2006). Intermediate Report of the FIPHARIAA ALFA II-400-FA project. Available from the corresponding author.

Widagdo, S., & Seider, W. D. (1996). Azeotropic Distillation, *AIChE Journal*, 42(1), 96-146.

FIGURE CAPTION

Fig. 1. Chloroform (A) – Methanol (B) – Water (E) residue curve map (class 2.1-2b).

Fig. 2. Batch rectifying column configuration for heterogeneous extractive distillation. (a) column. (b) column top and decanter details.

Fig. 3. Extractive liquid profiles for various (F/V) ratios under infinite reflux (step 2).

Fig. 4. Extractive liquid profiles map ((F_E/V)=1.2 ; infinite reflux) (step 2).

Fig. 5. Feasible regions for the still path during the step 3 ((F_E/V)=1.2; R=1).

Fig. 6. Extractive liquid profiles map ((F_E/V)=1.2 ; R_{min}=0.38).

Fig. 7. Extractive liquid profiles map ((F_E/V)=1.2 ; R=0.17). Unfeasible region matches the whole triangle.

Fig. 8. Simulation results of the separation of chloroform – methanol with water by heterogeneous extractive batch distillation process.

Fig. 9. Simulation and experimental results of the separation of chloroform – methanol with water by heterogeneous extractive distillation process in a batch rectifying column.

Fig. 10. Top temperature evolution for the six experimental replicates and simulation results of the heterogeneous extractive distillation process in a batch rectifying column. Experimental results (●). Simulation results (┈○┈)

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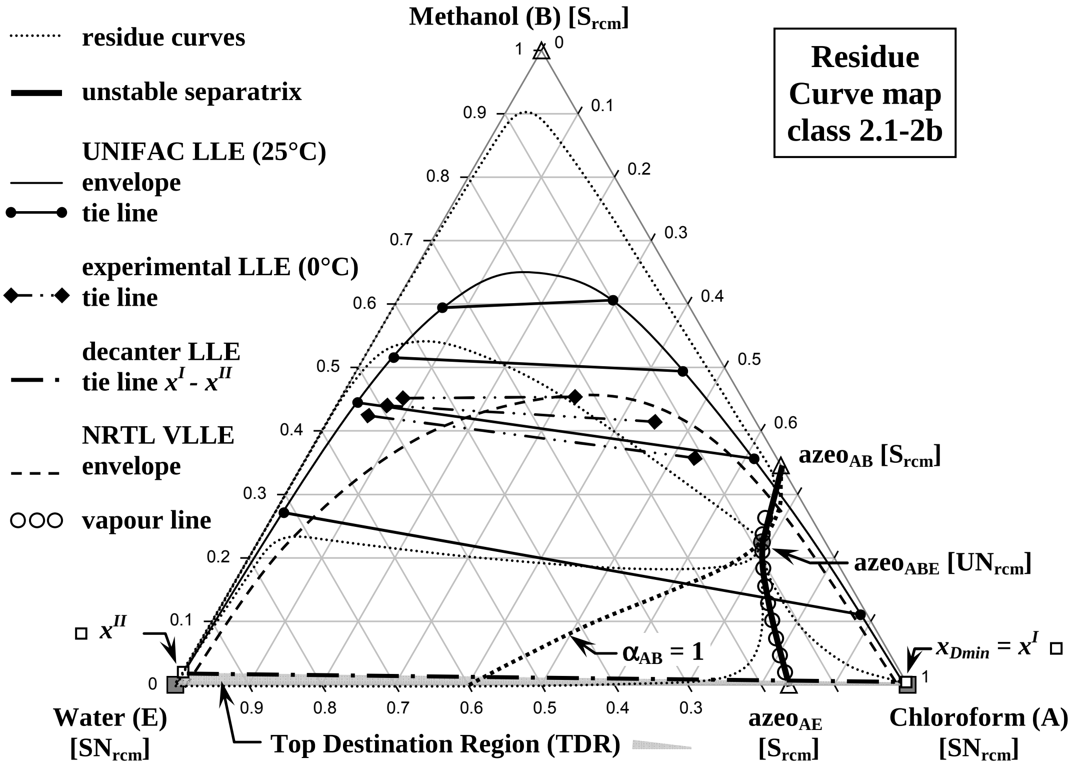
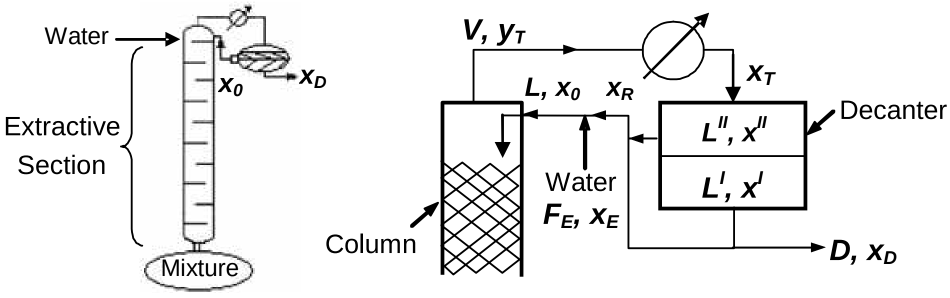


Fig. 1. Chloroform (A) – Methanol (B) – Water (E) residue curve map (class 2.1-2b)



(a) (b)

Fig. 2. Batch rectifying column configuration for heterogeneous extractive distillation (a) column. (b) column top and decanter details.

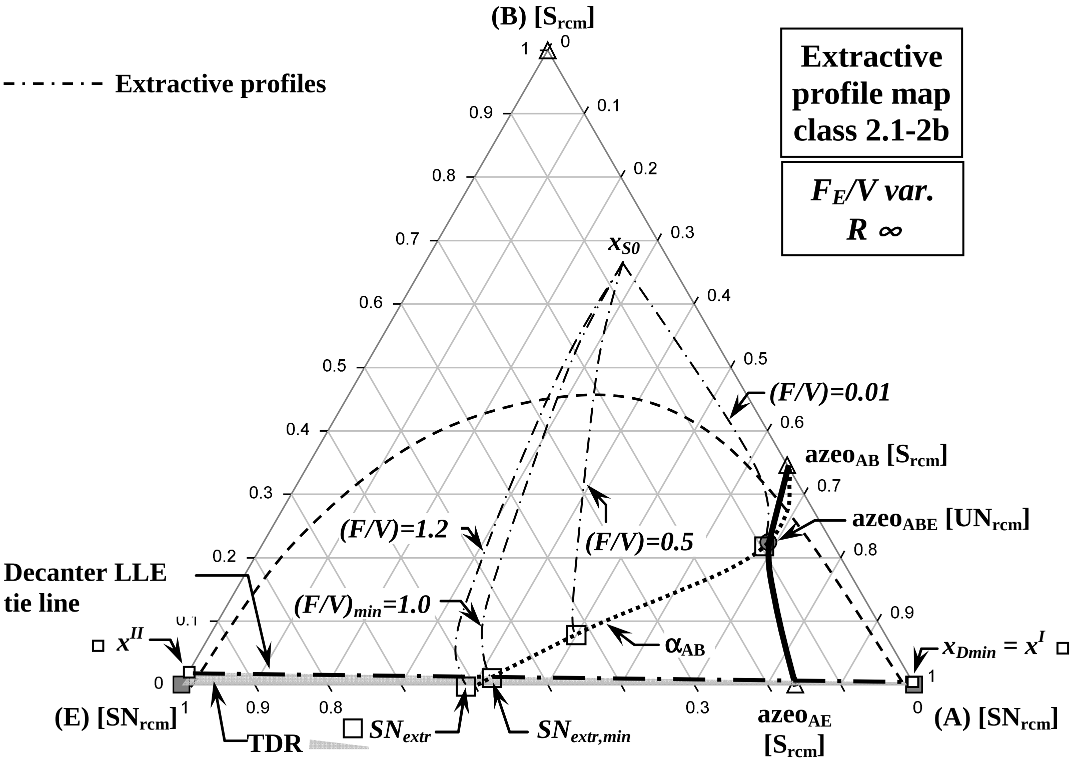


Fig. 3. Extractive liquid profiles for various (*F/V*) ratios under infinite reflux (step 2).

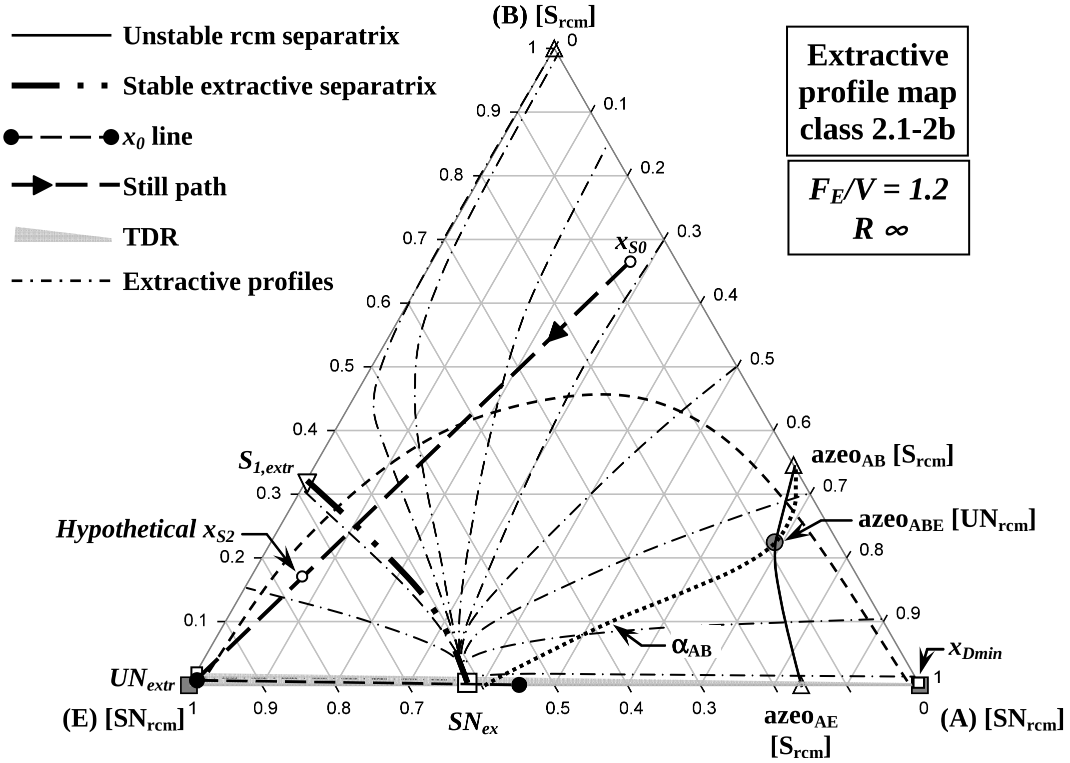


Fig. 4. Extractive liquid profiles map ((F_E/V)=1.2; infinite reflux) (step 2).

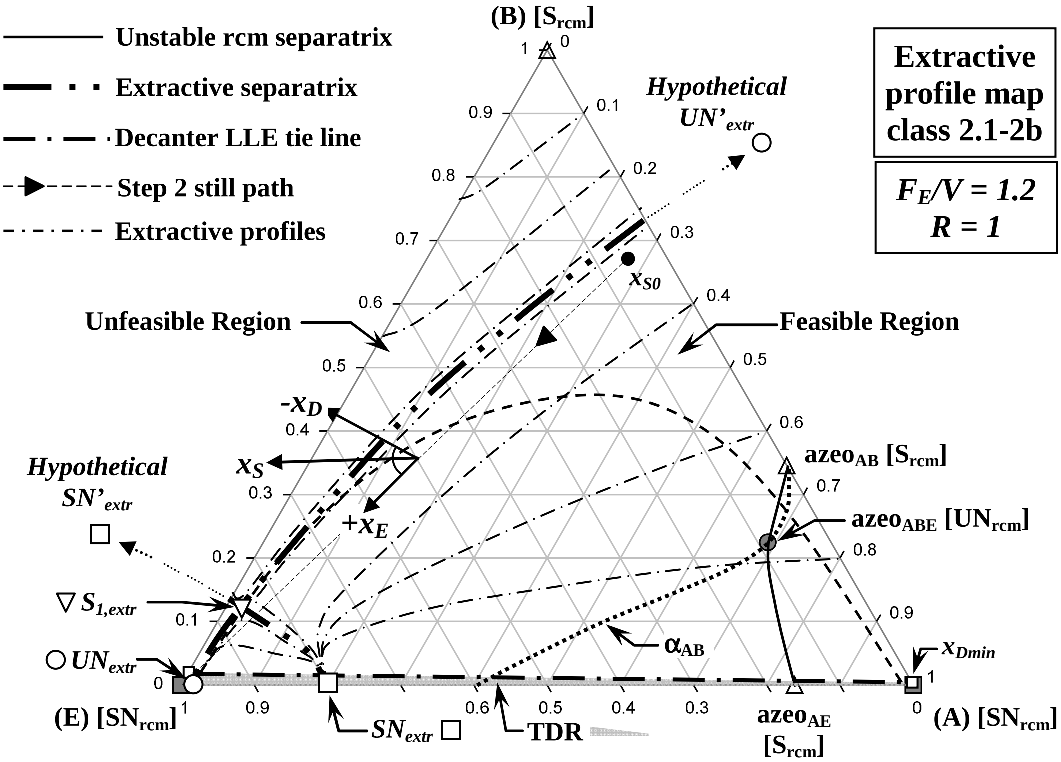


Fig. 5. Feasible regions for the still path during the step 3 ((F_E/V)=1.2 ; R=1).

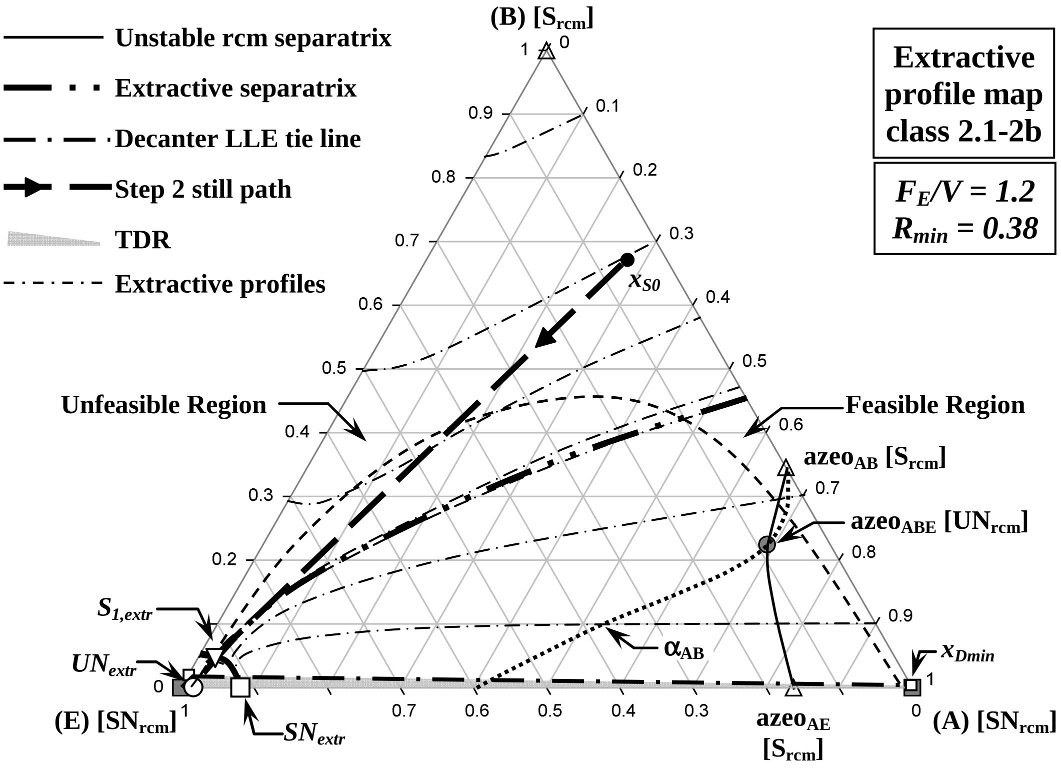


Fig. 6. Extractive liquid profiles map ((F_E/V)=1.2 ; R_{min}=0.38).

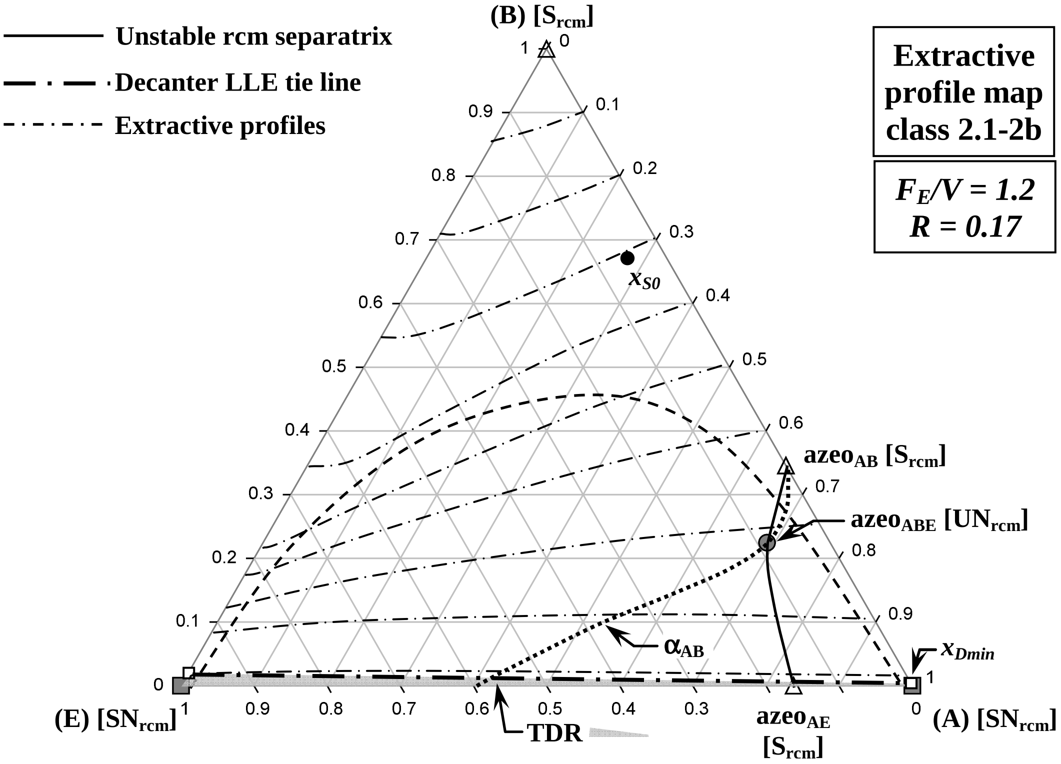


Fig. 7. Extractive liquid profiles map ((F_E/V)=1.2 ; R=0.17). Unfeasible region matches the whole triangle.

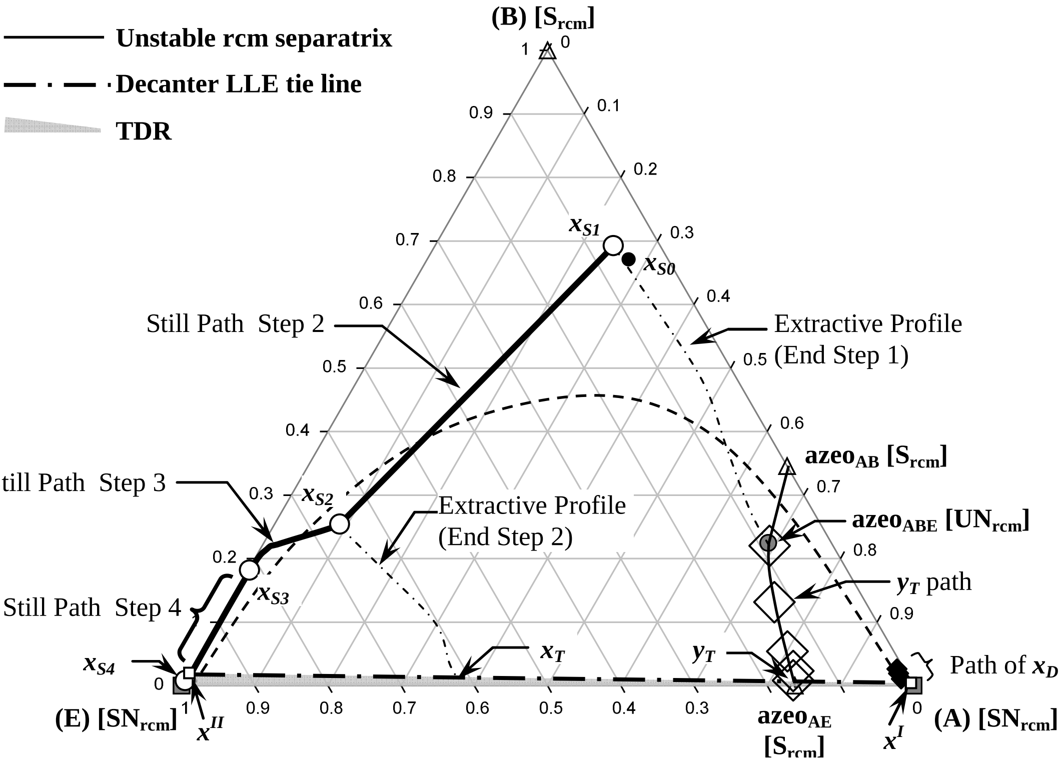


Fig. 8. Simulation results of the separation of chloroform – methanol with water by heterogeneous extractive batch distillation process.

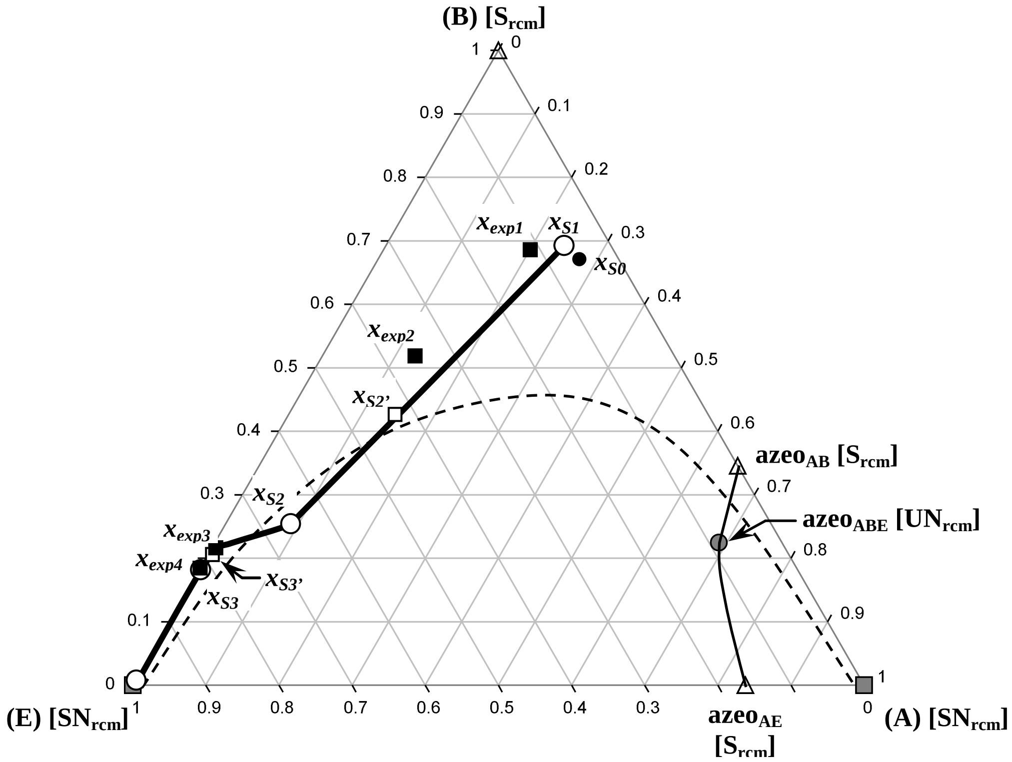


Fig. 9. Simulation and experimental results of the separation of chloroform – methanol with water by heterogeneous extractive distillation process in a batch rectifying column.

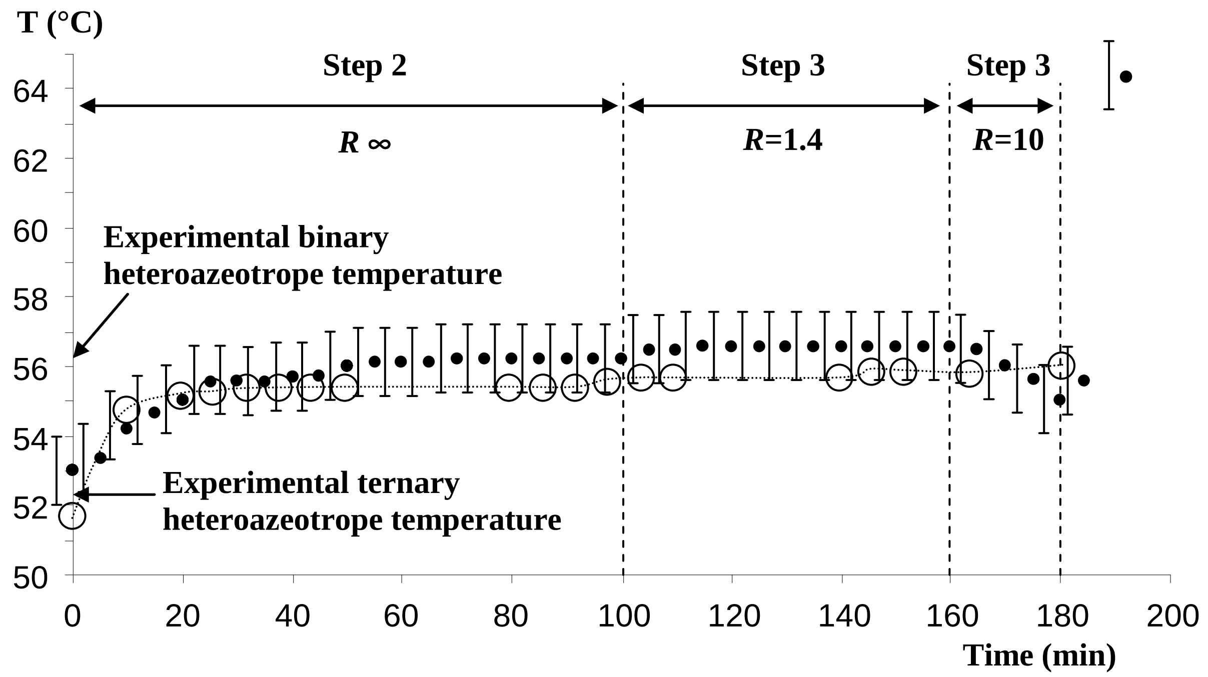


Fig. 10. Top temperature evolution for the six experimental replicates and simulation results of the heterogeneous extractive distillation process in a batch rectifying column. Experimental results (●). Simulation results (···○···)

TABLE CAPTION

Table 1. Candidate entrainers for the separation of chloroform (A) – methanol (B)

Table 2. Thermodynamic model parameters

Table 3. Experimental and computed azeotropes with NRTL model Chloroform (A) – Methanol (B) – Water (E)

Table 4. Bench scale batch distillation column technical features and operating conditions

Table 5. Simulation results of the heterogeneous extractive distillation process in a batch rectifier

Table 6. Component molar mass balance of the main streams of the process

Table 1

Candidate entrainers for the separation of chloroform (A) – methanol (B)

Entrainer (E)	**$T_{Boiling}$ (°C)**	**ABE class**	γ_A^∞	γ_B^∞	$\gamma_A^\infty / \gamma_B^\infty$	**process**	x_P	**Rejection ****
chloroform (A)	61.1		2.26	-	0,19			
methanol (B)	64.5		-	11,77				
Acetic acid	118.0	1.0-1a	1.85	0.99	1.87	BED	0.42 (A)	1,3
Allyl alcohol	96.9	1.0-1a	1.22	0.99	1.23	BED	0.54 (A)	1, 2, 3
1-Propanol	97.4	1.0-1a	1.61	1.07	1.50	BED	0.43 (A)	3
1-Butanol	117.8	1.0-1a	1.52	1.15	1.32	BED	0.22 (A)	3
2-Methyl-1-Propanol	107.6	1.0-1a	1.52	1.15	1.32	BED	0,29 (A)	3
2-butanol	99.5	1.0-1a	1.48	1.19	1.24	BED	0.24 (A)	3
Water	100.0	2.1-2b *	665.03	1.67	398.22	HBED	0.42 (A)	-
n-Butyl acetate	126.5	1.0-1a	0.41	3.74	0.11	BED	0.66 (B)	3
Furfural	161.4	1.0-1a	1.07	2.56	0.42	BED	0,60 (B)	1, 2, 3
Pyridine	115.2	1.0-1a	0.43	0.83	0.52	BED	0,46 (B)	2, 3
Nitrobenzene	210.6	1.0-1a	0.14	2.54	0.05	BED	0.70 (B)	1, 2, 3
4-methyl-2-pentanone	116.7	1.0-1a	0.43	2.42	0.18	BED	0.61 (B)	2, 3
1,4 dioxane	101.3	1.0-1a	0.23	1.80	0.13	BED	0.73 (B)	1, 2, 3
Methyl cyclohexane	101.0	2.0-2b *	1.42	68.15	0.02	HBED	0.55 (B)	2, 3

* heterogeneous entrainer ** Rejection criteria: 1 – toxic; 2 – pollution; 3 – cost vs water.

Table 2

Thermodynamic model parameters

Vapor – Liquid – Liquid equilibrium			
Binary Coefficients for NRTL model	A_{ij} [cal/mol]	A_{ji} [cal/mol]	α_{ij}
chloroform – methanol	2736.86	-1244.030	0.0950
chloroform - water	3303.40	3533.100	0.2000
methanol - water	-253.80	845.206	0.2994
Liquid – Liquid equilibrium			
UNIFAC Dortmund 1993			

Table 3

Experimental and computed azeotropes with the NRTL model Chloroform (A) – Methanol (B) – Water (E) cited in Table 2.

	Experimental (Gmehling *et al.*, 1994).		**NRTL**	
Mixtures	**Temperature (°C)**	**Molar Fraction**	**Temperature (°C)**	**Molar Fraction**
AB	53.5	$x_A = 0.650$	53.3	$x_A = 0.654$
AE	56.2	$x_A = 0.850$	56.3	$x_A = 0.838$
ABE	53.1	$x_A = 0.700$ $x_B = 0.235$	52.3	$x_A = 0.689$ $x_B = 0.224$

Table 4

Bench scale batch distillation column technical features and operating conditions

Parameter	Value
Initial Charge Step 1 (mol)	20
Initial Composition Step 1 (molar)*	0.2704/0.6714/0.0582
Initial Charge Step 4 (mol)	72.3
Initial Composition Step 4 (molar)*	0.0001 / 0.1795 / 0.8204
N° of Equilibrium Trays	45
Operating Pressure (atm)	1
Total Liquid Holdup per Tray (L)	0.0015
Total Liquid Holdup (Condenser+Decanter) (L)	0.020+0.050
Heat Duty at the reboiler (Watt)	150
Water Flowrate at 25°C (mol/h)	20

*(chloroform/methanol/water)

Table 5

Simulation results of the heterogeneous extractive distillation process in a batch rectifier

Products	Simulation Results		Experimental Results			
	Amount (Mol)	Molar fraction	Amount (Mol)	AAE (moles)	Molar fraction	AAE
Aqueous Phase Decanter	0.045	x_A 0.0016	1.07	0.11	x_A 0.0010	0.0007
		x_B 0.0027			x_B 0.0300	0.0072
		x_E 0.9957			**x_E 0.9690**	0.0067
Distillate Cut STEP 3	5.2	x_A 0.9906	4.86	0.09	**x_A 0.9914**	0.0064
		x_B 0.0048			x_B 0.0029	0.0045
		x_E 0.0046			x_E 0.0057	0.0060
Chloroform Recovery Yield STEP 3 (%)	95.4		**89.1**			
Final Still STEP 3	72.3	x_A 0.0001	69.20	1.30	**x_A 0.0000**	0.0000
		x_B 0.1795			x_B 0.1664	0.0260
		x_E 0.8204			x_E 0.8336	0.0259
Intermediate Distillate Cut	0		0.72	0.11	x_A 0.8280	0.0565
					x_B 0.1199	0.0223
					x_E 0.0521	0.0468
Distillate Cut STEP 4	12.3	x_A 0.0017	N.A.		N.A.	
		x_B 0.9982				
		x_E 0.0001				
Methanol Recovery Yield STEP 4 (%)	91.6		N.A.			
Final Still STEP 4	56.2	x_A 0.0000	N.A.		N.A.	
		x_B 0.0012				
		x_E 0.9988				

(x_A: chloroform; x_B: methanol; x_E: water)

AAE: Average Absolute Error

Table 6

Component molar mass balance of the main streams of the process

component	**Input Streams**		**Output Streams**				**Balances**		**Deviation**
	Initial Charge	**Water Feeding**	**Aqueous Phase**	**Distillate**	**Interm. Cut**	**Final Still**	**Total Entry**	**Total Exit**	
$CHCl_3$	5.408	0.0	0.0011	4.8184	0.6213	0.0000	5.4080	5.4408	-0.0328
CH_3OH	13.428	0.0	0.0321	0.0141	0.0618	11.5147	13.4280	11.6226	1.8054
H_2O	1.164	60.0	1.0368	0.0275	0.0369	57.6853	61.1640	58.7866	2.3774
Total	20.000	60.0	1.0700	4.8600	0.7200	69.2000	80.0000	75.8500	4.1500