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MODELING AND SIMULATION OF A BATCH DISTILLATION COLUMN FOR RECOVERING LIMONENE EPOXIDE

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ABSTRACT

Aspen Plus and MATLAB software simulation tools were employed for modeling, simulation and optimization of a distillation process to recover limonene epoxide from a liquid mixture containing limonene + acetonitrile + water + limonene epoxide. This mixture is obtained from limonene epoxidation over PW-Amberlite using aqueous hydrogen peroxide as oxidant and acetonitrile as solvent. Analyses of residue curve maps indicate that batch distillation columns of inverse configuration are adequate to separate limonene epoxide. The model parameters, i.e., the number of stages (8) and the reflux ratio (3,1) were determined by steady state simulations with short-cut models and rigorous models from Aspen Plus. Aspen Plus simulation of the batch distillation operation showed that it is possible to recover up to 95 % limonene epoxide with a molar fraction of 0,97 after 7,5 h. For comparison purposes, the batch distillation operation was also simulated with a semi-rigorous MATLAB model and similar results were obtained.

KEY WORDS: batch distillation; modeling and simulation; residue curve maps; limonene epoxide.

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MODELADO Y SIMULACIÓN DE UNA COLUMNA DE DESTILACIÓN POR LOTES PARA RECUPERAR EPÓXIDO DE LIMONENO

RESUMEN

Se emplearon herramientas de software de simulación como Aspen Plus y MATLAB para el modelado, simulación y optimización de un proceso de destilación para recuperar epóxido de limoneno a partir de una mezcla líquida que contiene limoneno + acetonitrilo + agua + epóxido de limoneno. Esta mezcla se obtiene de la epoxidación de limoneno sobre PW-Amberlita utilizando peróxido de hidrógeno acuoso como oxidante y acetonitrilo como disolvente. Los análisis de curvas de composición residual indicaron que las columnas de destilación por lotes de configuración inversa son adecuadas para separar el epóxido de limoneno. Los parámetros del modelo, como el número de etapas (8) y la relación de reflujo (3,1) se determinaron mediante simulaciones de estado estacionario con modelos cortos y rigurosos de Aspen Plus. La simulación del equipo por lotes en Aspen Plus mostró que es posible recuperar hasta el 95 % del epóxido de limoneno con una fracción molar de 0,97 después de 7,5 h. Con fines comparativos, la destilación por lotes también se simuló con un modelo semirriguroso construido en MATLAB, con el cual se lograron resultados similares.

PALABRAS CLAVE: destilación por lotes; modelado y simulación; curvas de composición residual; epóxido de limoneno.

MODELAGEM E SIMULAÇÃO DE UMA COLUNA DE DESTILAÇÃO POR LOTES PARA RECUPERAR EPÓXIDO DE LIMONENO

RESUMO

Empregaram-se ferramentas de software de simulação como Aspen Plus e MATLAB para a modelagem, simulação e otimização de um processo de destilação para recuperar epóxido de limoneno a partir de uma mistura líquida que contém limoneno + acetonitrilo + água + epóxido de limoneno. Esta mistura obtém-se da epoxidação de limoneno sobre PW-Amberlita utilizando peróxido de hidrogênio aquoso como oxidante e acetonitrilo como disolvente. As análises de curvas de composição residual indicaram que as colunas de destilação por lotes de configuração inversa são adequadas para separar o epóxido de limoneno. Os parâmetros do modelo, como o número de etapas (8) e a relação de refluxo (3,1), se determinaram mediante simulações de estado estacionário com modelos curtos e rigorosos de Aspen Plus. A simulação da equipe por lotes em Aspen Plus mostrou que é possível recuperar até o 95 % do epóxido de limoneno com uma fração molar de 0,97 após 7,5 h. Com fins comparativos, a destilação por lotes também se simulou com um modelo semirrigoroso construído em MATLAB, com o qual se conseguiram resultados similares.

PALAVRAS-CHAVE: destilação por lotes; modelagem e simulação; curvas de composição residual; epóxido de limoneno.

1. INTRODUCTION

Batch distillation is a widely used process for the separation of liquid mixtures in the fine chemical industry, such as pharmaceutical, biochemical, and food production. Batch distillation is commonly preferred for separation of liquid mixtures when: i) relatively small amounts of compounds are involved; ii) there are rapid changes in market needs; and iii) the mixtures must be purified under various operating conditions (Mujtaba and Macchietto, 1996; Seider, Seader and Lewin, 2003; Mujtaba, 2004; Low and Sørensen, 2004; Bai *et al.*, 2005; Kaewpradit *et al.*, 2008). One of the most interesting attributes of batch distillation is its flexibility when compared with continuous distillation. Separation of a multicomponent mixture with n_c compounds can be achieved in a single batch distillation column by drawing the distillate product to accumulation tanks at specific times; in contrast, n_c-1 columns will be required to separate all the components of the mixture in continuous distillation (Seider, Seader and Lewin, 2003; Mujtaba, 2004). In addition, batch operations facilitate the identification of production lots, which is essential in several food and pharmaceutical industries where product tracking and quality control are required (Mujtaba, 2004).

Limonene epoxide, a high value-added product obtained from limonene, is used in fragrance, flavour, and agrochemical industries. Furthermore, limonene epoxide can be copolymerized with CO_2 for the production of biodegradable plastics (Byrne *et al.*, 2004). Limonene conversions above 80 % and selectivities to limonene epoxide higher than 90 % can be obtained under mild reaction conditions in the catalytic system PW-Amberlite/aqueous hydrogen peroxide/acetonitrile (Barrera, Villa and Montes, 2006, 2009a). The kinetics and mechanistic pathway of PW-Amberlite catalyzed reaction (Barrera, Villa and Montes, 2006, 2009a) as well as detailed dynamic modeling, simulation, and optimization of the reaction system, i.e., a batch reactor, has been also reported (Barrera *et al.*, 2010). After a given batch reaction time the mixture will essentially contain limonene, acetonitrile, water and limonene epoxide. Modeling and simulation of the reactor allowed us to size the reactor, as well as to determine the operation parameters for a desired limonene epoxide yield (Barrera *et al.*, 2010). To the best of our knowledge, no studies regarding the separation of liquid mixtures have been reported. Thus, the objective of the present study deals with modeling and simulation of the separation of limonene epoxide from a liquid mixture containing limonene + acetonitrile + water + limonene epoxide using specialized batch distillation software tools. The results of this work could be useful for designing separation experiments of this liquid mixture and its further implementation for industrial production of limonene epoxide.

This paper is organized as follows: first, some insights of possible separation sequences are presented from the analysis of residue curve maps obtained from Aspen Plus; then, the steady state separation process is simulated in Aspen Plus using short-cut methods and rigorous methods aiming to estimate design and operation parameters of the distillation unit. Next, the batch distillation process is simulated using Aspen Plus. Results are compared with a semi-rigorous batch distillation model built in MATLAB and finally, the conclusions of this work are presented.

A key novelty on this work is the sequential use of simulation software tools proposed for modeling and simulation of the limonene + acetonitrile + water + limonene epoxide system. To the best of our knowledge, this is the first report about the separation of mixtures containing limonene epoxide. Thus, the results of this work could be used for designing experiments aiming limonene epoxide isolation from limonene + water + acetonitrile + limonene epoxide mixtures.

2. METHODOLOGY

The residue curve maps were obtained with the computational Aspen Plus tool SPLIT. These maps were useful to evaluate the feasibility of separation and possible sequences of operation for recovering

limonene epoxide from the liquid mixture limonene + acetonitrile + water + limonene epoxide. The initial value of the parameters required for modeling and simulating the batch distillation column, i.e., reflux ratio, distillate rate and operating temperature, were estimated by simulating the separation process at steady-state (continuous distillation) using Aspen Plus (AspenTech, 2010) short-cut methods (DSTWU) and rigorous methods (RadFrac). The batch distillation column was simulated with the Aspen Plus BatchFrac model that considers the full dynamics of the column from rigorous mathematical methods (AspenTech, 2010). The physicochemical properties of pure substances and mixtures required were obtained from the database "Pure 22" of Aspen Plus. Limonene epoxide properties as well as physicochemical and thermodynamic properties of the liquid mixture were estimated from their molecular structure, using the group contribution method UNIFAC-DMD (Lohmann, Joh and Gmehling, 2001). The molecular group distribution for the compounds present in the liquid mixture was taken from Barrera, Villa and Montes (2009b) (table 1).

Table 1. UNIFAC-DMD groups used to estimate the properties of limonene epoxide and the multicomponent liquid mixture (Barrera, Villa and Montes, 2009b)

UNIFAC-DMD group No.	Acetonitrile	Water	Limonene	Limonene epoxide
1000	0	0	2	2
1005	0	0	2	1
1010	0	0	4	4
1015	0	0	2	2
1300	0	1	0	0
1605	0	0	0	1
1905	1	0	0	0

Additionally, for comparison purposes, a batch distillation column was simulated with a semi-rigorous mathematical model developed in MATLAB R2008 software (Mathworks, 2010). Table 2 summarizes the computational tools used in this work, their application and the main findings.

Table 2. Objectives of the computational tools used in this work

Computational tool	Uses	Findings
1. Aspen analysis tools	Evaluate feasibility of mixture separation	The convenience of using a distillation tower of inverse configuration for the initial separation of limonene epoxide, i.e., the heavier compound of the mixture
2. Aspen Plus short-cut model (DSTWU)	Simulate steady-state distillation	Initial values for simulation parameters, such as number of stages, reflux ratio, and distillation rate
3. Aspen Plus rigorous model (RadFrac)	Simulate steady-state distillation	Operation parameters used in further simulations
4. Aspen Plus batch model (BatchFrac)	Simulate batch distillation	Recovering of limonene epoxide with 0,97 molar fraction in 7.5 h
5. MATLAB semi-rigorous model	Compare results with Aspen Plus batch simulations	Recovering of limonene epoxide with 0,93 molar fraction in 7.5 h

3. RESULTS AND DISCUSSION

3.1 Analysis of residue curve maps using Aspen SPLIT

The residue curve maps of a mixture can be used to develop preliminary designs of separation units, determine the most appropriate sequence of operation, predict changes in composition of the mixture during the separation process and determine the feasibility of specific separation processes (Doherty and Malone, 2001; Tapp *et al.*, 2003; Gerbaud *et al.*, 2006; Lang and Modla, 2006). The Aspen SPLIT tool of Aspen Plus was used in this work to build the residue curve maps of four possible ternary systems, i.e., limonene + acetonitrile + water, limonene epoxide + acetonitrile + water, limonene epoxide +

limonene + water and limonene epoxide + limonene + acetonitrile. The simulations were performed with the software Aspen Plus V7.1.

The azeotrope search with Aspen Plus software predicts the formation of three unstable nodes (azeotropes), i.e., water + acetonitrile, water + limonene and water + limonene epoxide (table 3). Therefore, through ordinary distillation the complete separation of the four mixture components is not possible.

Table 3. Azeotrope prediction for the multicomponent liquid mixture

Azeotrope	Binary i,k	temperature °C	mol fraction i	mol fraction k
1	water + acetonitrile	76,68	0,3165	0,6835
2	water + limonene epoxide	85,98	0,8342	0,1658
3	water + limonene	76,57	0,7636	0,2364

Figure 1 shows the residue curve maps of the ternary mixtures: limonene + acetonitrile + water (figure 1a), limonene epoxide + acetonitrile + water (figure 1b), limonene epoxide + limonene + water (figure 1c) and limonene epoxide + limonene + acetonitrile (figure 1d). The presence of azeotropic points in the water containing mixtures (table 3) does not allow complete separation of these mixtures by continuous ordinary distillation or by conventional batch distillation using sequential separation of lighter components to obtain limonene epoxide as the bottom product, i.e., the compound with the higher boiling point of the mixture. However, distillation lines on the residue curve maps predict that it is possible to use distillation for recovering limonene epoxide from the mixture without a complete separation of the other compounds (figures 1b-1d), i.e., the mixture acetonitrile + water + limonene would remain in the column. This separation is possible in a batch distillation column of inverse configuration (Sørensen and Skogestad, 1996; Mujtaba, 2004) where the heaviest product is initially recovered from the bottom of the column. Once limonene epoxide is separated from the mixture, alternative separation techniques could be used for separating remaining acetonitrile + water + limonene mixture, that forms a type-1 ELL (Barrera, Villa and Montes, 2005), with the possibility of recycling the mixture limonene + acetonitrile (Barrera *et al.*, 2010).

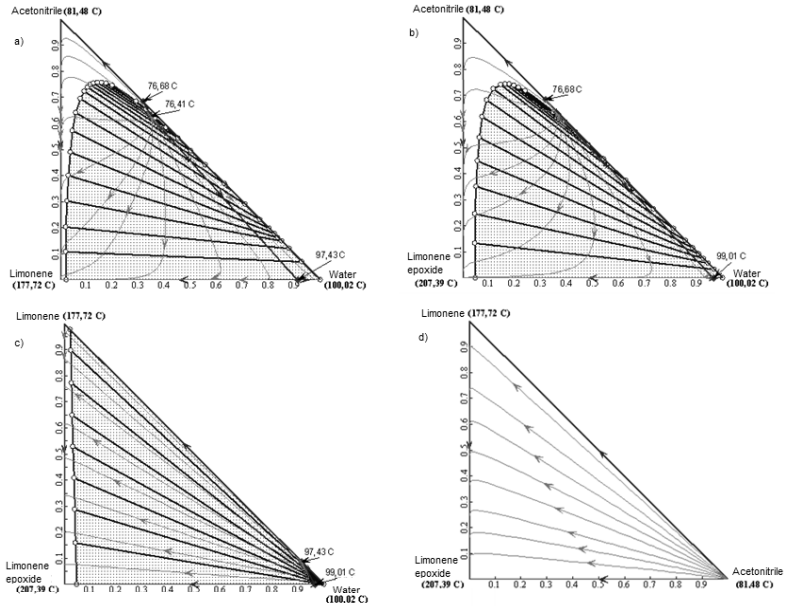

Figure 1. Residue curve maps obtained from Aspen Plus for the ternary mixtures: (a) acetonitrile + water + limonene, (b) limonene epoxide + acetonitrile + water, (c) limonene epoxide + limonene + water and (d) limonene epoxide + limonene + acetonitrile

3.2 Simulation of the steady-state distillation

To the best of our knowledge, the separation of mixtures containing limonene epoxide has not been reported in the open literature; thus, the initial values for the number of theoretical plates or stages required for the separation, reflux ratio, distillate rate, rate of vaporization, and operating temperature were determined from Aspen Plus steady state simulations using short-cut and rigorous methods. First, the DSTWU model of Aspen Plus was used. It only requires the desired separation for the key compounds (AspenTech, 2010) and uses the simplified short method of Winn-Underwood-Gilliland (Mujtaba and Macchietto, 1996; Seader and Henley, 1998). The data found with this model were used as a first estimation for determining the operating conditions of the column. Subsequently, the results of the simulation with the model DSTWU (table 4) were used to specify the required parameters in a rigorous model that includes material balances, energy and equilibrium relationships in all the stages inside the column to simulate the separation process, i.e., the Aspen Plus RadFrac model (AspenTech, 2010), (figure 2). The feeding mixture composition was taken from the literature (Barrera *et al.*, 2010); it was assumed a limonene conversion of 80 % for the PW-Amberlite/aqueous hydrogen peroxide/acetonitrile catalytic system.

Table 4. Feed and operation conditions in the continuous distillation tower

Condition	Value
Total flow (Kmol s^{-1})	390
Limonene mol fraction	0,010
Acetonitrile mol fraction	0,642
Limonene epoxide mol fraction	0,021
Water mol fraction	0,327
Feed temperature, °C	77
Pressure, atm	1
Total stages (including condenser and reboiler)	8
Plates	6
Condenser (stage 1)	Total
Pressure fall	0 (isobaric)
Distillate rate (Kmol s^{-1})	354,8
Reflux ratio	3,1

According to the RadFrac simulation results, the molar flow of the bottom stream (figure 2) is 35,43 kmol s^{-1} and the limonene epoxide molar fraction is 0,97 (table 5). The stage by stage composition profiles, (figure 3), show that the conditions stated for the separation process (table 4), i.e., results from the DSTWU Model are appropriate, since limonene epoxide is recovered. The residue curve maps (figure 1) and the simulation results of the continuous column (table 5) indicate that the distillate stream corresponds to a ternary mixture composed of acetonitrile + water + limonene. The presence of azeotropes in the mixture (figure 1a) suggests that neither acetonitrile nor limonene may be recovered by ordinary distillation of the mixture

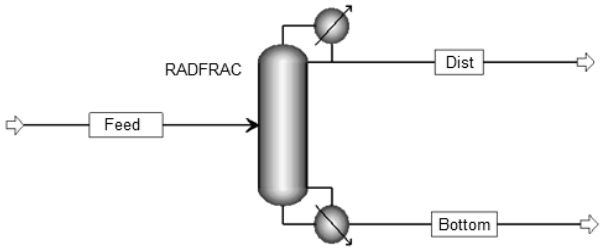

Figure 2. Aspen Plus flowsheet diagram for continuous distillation of the mixture limonene + acetonitrile + water + limonene epoxide

Table 5. Results of Aspen Plus RadFrac simulation for distillate and bottom streams in the continuous distillation (figure 2)

	Stream (Figure 2)		
Estimated parameter	Distillate	Feed	Bottoms
Water, Kmol s^{-1}	62,44	62,44	$3,8x10^{-8}$
Acetonitrile, Kmol s^{-1}	279,8	279,8	$8,5x10^{-5}$
Limonene epoxide, Kmol s^{-1}	1,519	35,90	34,38
Limonene, Kmol s^{-1}	11,05	12,09	1,047
Water mol fraction	0,176	0,160	$1,0x10^{-9}$
Acetonitrile mol fraction	0,788	0,717	$2,4x10^{-6}$
Limonene epoxide mol fraction	$4,3x10^{-3}$	0,092	0,970
Limonene mol fraction	0,031	0,031	0,029
Total flow, Kmol s^{-1}	354,8	390,2	35,43
Total flow, Kg s^{-1}	14 348	19 725	5 377
Temperature, K	350,1	350,1	479,3
Pressure, atm	1,0	1,0	1,0
Vapor fraction	0	0	0
Liquid fraction	1	1	1
Enthlapy, J $Kmol^{-1}$	$-1,4x10^{7}$	$-4,6x10^{7}$	$-2,6x10^{8}$
Enthropy, J $Kmol^{-1}K^{-1}$	$-1,5x10^{5}$	$-2,3x10^{5}$	$-7,8x10^{5}$
Density, Kmol m^3	18,03	17,09	5,132
Average molecular weight	40,44	50,55	151,8

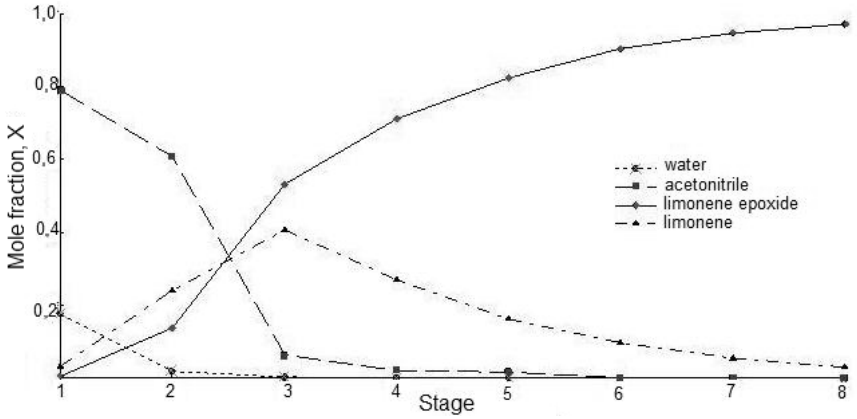

Figure 3. Stage by stage composition profiles of the continuous distillation unit; stage 1: condenser; stage 8: reboiler

3.3 Modeling and simulation of a batch distillation column using Aspen Plus

Modeling and simulation of a batch distillation column for recovering limonene epoxide from limonene + acetonitrile + water + limonene epoxide mixture, was performed with the Aspen Plus BatchFrac model (AspenTech, 2010), which considers the full dynamics of the column by rigorous mathematical methods. The assumed operating parameters of the column were the values obtained from the simulation of the continuous columns (table 5). Eight separation stages, including condenser and reboiler, were considered. The initial loading was 390 mol (77 °C, 1 atm) with the molar composition described in table 4. The amount of liquid retained in the accumulator and in either plate was considered constant at 2 % of the initial loading (7,8 mol). The column operation was simulated at constant internal reflux of 3,1 (table 4). The stopping criterion was either a 0,97 limonene epoxide mol fraction in reboiler or a batch operation time of 12 hours.

BatchFrac simulation results showed that after 7,5 h of operation the mixture in the reboiler corresponds to about 1 kg of limonene epoxide (i.e., 95,6 % of limonene epoxide in the feed mixture) with a molar fraction of 0,97. The estimated temperatures for condenser and reboiler were 77 °C and 185 °C, respectively. Figure 4 shows the instantaneous composition of the liquid phase in either column plate at 7,5 h of operation, which is the time required to achieve the desired limonene epoxide molar fraction of 0,97 at stage 8 (reboiler).

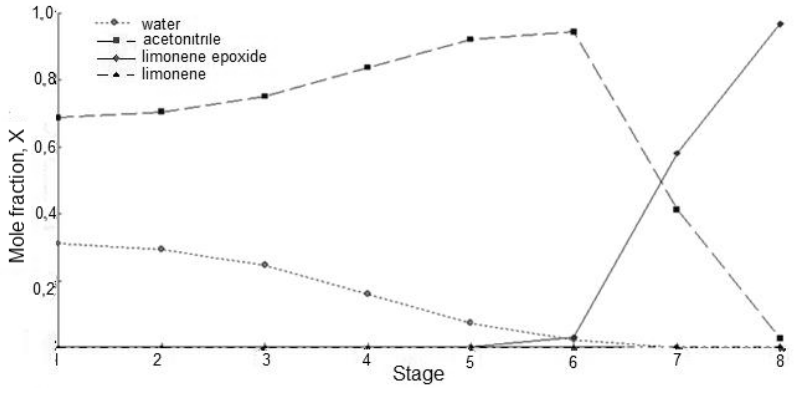

Figure 4. Instantaneous stage composition in the batch distillation unit. Batch time, 7,5 h. Data acquired from Aspen Plus BatchFrac

3.4 Modeling and simulation of a batch distillation column using semi-rigorous methods in MATLAB

In order to confirm the above results, a semi-rigorous mathematical model (Domenech and Enjalbert, 1981; Luyben, 1988; Quintero-Marmol and Luyben, 1990; Mujtaba, 2004) of a batch distillation column of inverse configuration (figure 5) was developed to simulate such separation. The mathematical model performed in MATLAB (Mathworks, 2010) was based on Mujtaba's work (Mujtaba, 2004) and includes stage by stage molar balance calculations (figure 6) considering the following assumptions: i) constant relative volatility, ii) constant accumulated liquid (molar) in the condenser and the inner plates, iii) negligible vapor accumulation, iv) perfect mixing between the liquid and vapor in the plates, v) adiabatic column, vi) feeding at boiling temperature of the mixture, and vii) no pressure drop in the column. The same parameter values used in the BatchFrac simulation were used for the MATLAB model, i.e, initial charge, 390 mol; initial composition (mol fraction), 0,01; 0,021; 0,327 and 0,642 for limonene, limonene epoxide, water and acetonitrile, respectively; number of stages, j = 8; and 7,5 moles of constant fluid accumulated in the condenser A_C and in the plates A_j. The initial composition in the condenser and in the plates was assumed similar to the feed composition. The estimation of relative volatility of limonene, water and acetonitrile with respect to limonene epoxide, $\alpha_{i,epoxy}$, was based on the activity coefficients, γ_i, and the saturation pressure, P_i^S, of each component in the mixture (Barrera, Villa and Montes, 2009b), using equation 1.

$$\alpha_{i,epox} = \frac{\gamma_i P_i^S}{\gamma_{epox} P_{epox}^S} \quad (1)$$

Activity coefficients γ_i were estimated with the Aspen Plus UNIFAC-DMD model considering the concentration profiles for each compound of the mixture through the column at steady-state (figure 3). When modeling the batch distillation column, the average values of $\alpha_{i,epox}$ for limonene (2.77), acetonitrile (29.12) and water (151) were assumed to be constant.

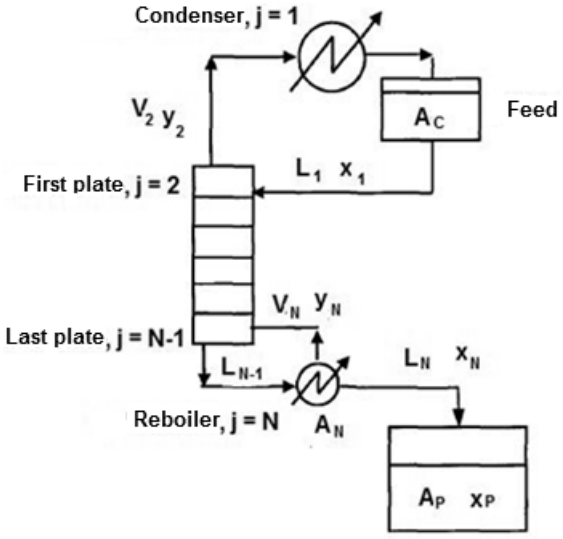

Figure 5. Scheme of a inverse configuration batch distillation column (Mujtaba, 2004)

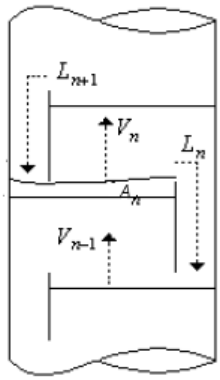

Figure 6. Scheme of a generic plate (stage n)

Although the semi-rigorous model proposed (equations 2-12), does not include energy balances in the plates or in the reboiler (Quintero-Marmol and Luyben, 1990; Mujtaba, 2004), the temperatures at each stage can be obtained from the Antoine equation (Manca, 2007). The mathematical model (equations 2-12) was solved with the 4th order Runge-Kutta formula with the MATLAB ode45 (Mathworks, 2010) algorithm for solution of differential equations

Condenser (j = 1; i = 1 to n_c-1)

$$\frac{dx_{1(i)}}{dt} = \frac{\left(Vy_{2(i)} - Lx_{1(i)}\right)}{A_C} \quad (2)$$

Internal plates (j = 2 to 7; i = 1 to n_c-1)

$$\frac{dx_{j(i)}}{dt} = \frac{V}{A_j}\left(y_{j+1(i)} - y_{j(i)}\right) + \frac{L}{A_j}\left(x_{j-1(i)} - x_{j(i)}\right) \quad (3)$$

Reboiler and product accumulator (j=N; i=1 to n_c-1)

$$\frac{dA_P}{dt} = L_N \quad (4)$$

$$\frac{dx_{P(i)}}{dt} = \frac{L_N}{A_P}\left(x_{N(i)} - x_{P(i)}\right) \quad (5)$$

$$\frac{dx_{N(i)}}{dt} = \frac{\left(Lx_{N-1(i)} - L_N x_{N(i)} - Vy_{N(i)}\right)}{A_N} \quad (6)$$

Equilibrium ratio (j = 2 to N; i = 1 to n_c-1)

$$y_{j(i)} = \frac{\alpha_{i,epox} x_{j(i)}}{\sum_{k=1}^{n_c} \alpha_{k,epox} x_{j(k)}} \quad (7)$$

Normalization (j = 1 to N; i = 1 to n_c)

$$\sum_{i=1}^{n_c} x_{j(i)} = 1 \quad (8)$$

$$\sum_{i=1}^{n_c} y_{j(i)} = 1 \quad (9)$$

Other ratios

$$r = \frac{V}{L} \quad (10)$$

$$L_1 = L_N = L_{N-1} = L \quad (11)$$

$$V_2 = V_N = V \quad (12)$$

The MATLAB simulation results (figure 7) indicate that a limonene epoxide molar fraction of 0,95 can be achieved in the reboiler after 8 h or a molar fraction of 0,93 after 7,5 h of operation. Although these results differ from the values obtained with Aspen Plus (limonene epoxide molar fraction of 0,97 in 7,5 h), the MATLAB developed model predicts the feasibility of limonene epoxide recovery from limonene + acetonitrile + water + limonene epoxide mixture using a batch distillation column of inverse configuration. It is expected that the model can be used in different optimization strategies for studying the system improvement (Bahri, Bandoni and Romagnoli, 1997; Farhat *et al.,* 1990; Venkateswarlu and Avantika, 2001; Jiménez *et al.,* 2002; Schlegel *et al.,* 2005; Pommier *et al.,* 2008).

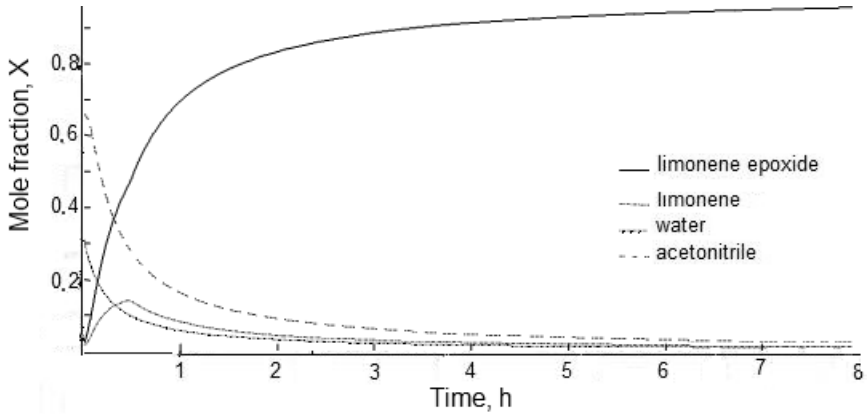

Figure 7. Composition (molar fraction) profiles in the reboiler for the inverse configuration batch distillation unit. Data from MATLAB simulations (equations 2-12)

4. CONCLUSIONS

The distillation columns can be used for recovering limonene epoxide from a mixture of limonene + acetonitrile + water + limonene epoxide. Due to the presence of azeotropes, it is convenient to initially separate limonene epoxide, even though this is the heavier compound of the mixture. According to Aspen Plus and MATLAB simulations, it is concluded that batch distillation columns of inverse configuration are a viable alternative to separate limonene epoxide from the mixture. Limonene epoxide can be recovered with a molar fraction of 0,97 after 7,5 h using this type of columns. Results from this work are useful for designing separation experiments of this mixture that lead to the large-scale implementation of limonene epoxide production from limonene.

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NOMENCLATURE

A	accumulated liquid
L	liquid flow
n_c	number of compounds
P^S	saturation pressure
r	reflux ratio (internal)
V	vapor flow
x_i	liquid composition of component i
y	vapor composition
	Greek letters
α	relative volatility
γ	activity coeficient
	Subscripts
C	condenser
D	distillate
j = 1	condenser
j = 1,2,…N	stages
j = 2,3,….N-1	plates
j = N	reboiler
P	product

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