BATCH DISTILLATION: SIMULATION AND EXPERIMENTAL VALIDATION

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ABSTRACT

Batch industries, specially the fine chemical industry, need rapid and robust mathematical models that can easily predict the degree of separation of mixtures like volatile organic compounds. Otherwise, in the study of on line production scheduling and planning of fine chemical plants, there is a lack of quick but reliable and more accurate than black box models in batch distillation. In this work, a robust and rapid mathematical model has been developed, based on mass balance and relative volatility. The model has been extensively tested in a variety of scenarios using a batch distillation pilot plant that has been constructed adhoc. The satisfactory results obtained allows to use the model in real time for a better control and management of batch distillation, resulting in an improved production scheduling/rescheduling of batch processes.

INTRODUCTION

Environmental constraints force industries to have rapid and contrasted models in batch distillation for solving the recovery of volatile organic compounds. The European Community has developed a directive in order to restrict the industrial emissions of this kind of solvents [1].

The fine chemical industry works with a high variety of chemical products with a high added value, that are changing continuously following market fluctuations and have a small lifetime. This implies that batch distillation must be a flexible unit operation and must be able to separate the changing mixtures efficiently. This is an important challenge in batch distillation. Rapid but reliable mathematical models contribute to this objective.

Luyben [2] and Al-Tuwain and Luyben [3] studied a short-cut method based on mass balances and mathematical correlations to design batch distillation columns. Diwekar and Madhavan [4] also presented a rapid method to design batch distillation columns, based on the equations of Fenske-Underwood-Gilliland (FUG). Barolo and Botteon [5] worked with a column at infinite reflux ratio in order to obtain theoretically pure components in a binary mixture. Galindez and Fredenslund [6] studied a model based on the program Unidist applied to continuous columns. Their results are compared with the experimental data of Domenech and Enjalbert [7]. Stewart et al.[8] and Hitch and Rousseau [9] presented a parametric study based on mass and energy balances that was experimentally validated.

Diwekar et al.[10], Diwekar [11] and Noda et al.[12] have studied optimization problems in batch distillation. Their work conclude that optimal reflux ratio is comparable with constant reflux ratio for batch distillation columns.

In this work a mathematical model based on mass balances and the equilibrium vapor-liquid equations has been developed. The industry needs rapid models like this one presented in this work. The vapor-liquid equilibrium will be studied with constant and variable relative volatility. This is a new aspect presented in this work for the first time. All the work in the past has been based on the use of constant relative volatility.

In batch distillation only a few research works are experimentally validated. Most of them uses the experimental works of Domenech and Enjalbert [7] and Nad and Spiegel [13]. There is a lack of experimental studies in batch distillation. In this work the model has been extensively validated experimentally. Firstly, it has been applied to the methanol-water mixture, that has served for the start-up and fine tuning of the pilot plant. Then, the ternary mixture cyclohexane-toluene-chlorobenzene has been studied with the model and experimentally validated. This mixture hasn't been referenced in the bibliography, and only experimental data of a ternary mixture have been published for Nad and Spiegel [13].

Azeotropic mixtures present a barrier in the recovery of solvents in batch chemical plants. The rapid model developed in this work has also been applied to the study of binary azeotropic mixtures. The interest of this part of the work is that only a few short-cut methods for azeotropic mixtures are published, and also there is a lack in experimental data. Toluene-n-butanol, with a minimum boiling point is the mixture studied. The last part of the work emphasizes in the resolution of this binary azeotropic mixture by adding a solvent, n-octanol.

All the work presented has an important objective which is the application to the scheduling of batch chemical plants, specially fine chemical plants. In production scheduling, batch distillation is treated like a black box model, where the actual distillation time is not contemplated. The proposed model permits to accurate modeling at the scheduling level and offers an improved on line operation facilitating eventual rescheduling.

MATHEMATICAL MODEL

The mathematical model presented in this work is based on mass balances and the equilibrium vapor-liquid equations. It can be applied to multicomponent mixtures and also binary azeotropic mixtures. Figure 1 represents a schematic representation of the batch distillation column used.
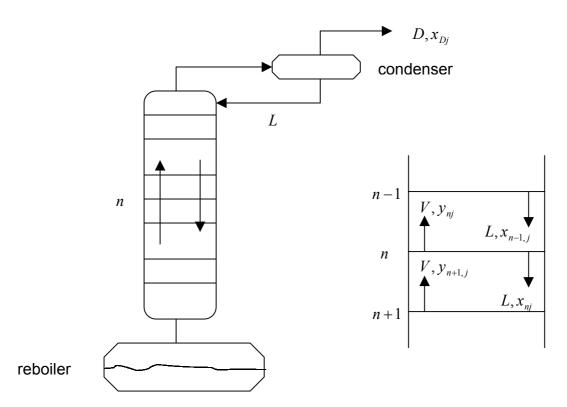

Figure 1. Schematic representation of a batch distillation column for the simplified mathematical model.

The model is based on the assumptions of constant flowrate for the liquid and the vapor, constant holdup for the liquid, negligible vapor holdup, total condenser, adiabatic column and theoretical trays.

The mathematical model can be described by the following equations:

Overall mass balance around the column

$$\frac{dM_B}{dt} = -D \tag{1}$$

Mass balance of component j at tray n

$$H_n \frac{dx_{nj}}{dt} = L\left(x_{n-1,j} - x_{nj}\right) + V\left(y_{n+1,j} - y_{nj}\right) \tag{2}$$

Overall mass balance around the condenser

$$L = V - D \tag{3}$$

Mass balance of component j for the condenser

$$H_D \frac{dx_{Dj}}{dt} = Vy_{1j} - \left(L + D\right)x_{Dj} \tag{4}$$

Mass balance of component j for the reboiler

$$\frac{d\left(M_B x_{Bj}\right)}{dt} = Lx_{Nj} - Vy_{Bj} \tag{5}$$

Vapor-liquid equilibrium at tray n

$$y_{nj} = \frac{\alpha_j x_{nj}}{\sum\limits_{k=1}^{NC} \alpha_k x_{nk}} \tag{6}$$

Vapor-liquid equilibrium for the reboiler

$$y_{Bj} = \frac{\alpha_j x_{Bj}}{\sum\limits_{k=1}^{NC} \alpha_k x_{Bk}} \tag{7}$$

Antoine's equation for component j

$$\log P_j^o = A_j - \frac{B_j}{C_j + T} \tag{8}$$

Dalton's law for vapor phase

$$p_j = Py_j \tag{9}$$

Raoult's law for the liquid phase

$$p_j = \gamma_j P_j^o x_j \tag{10}$$

Equilibrium relations for a binary azeotropic mixture

$$y_1' = \frac{\alpha \, x_1'}{1 + x_1'(\alpha - 1)} \tag{11}$$

Region A:

$$x_1' = \frac{x_1}{x_1^{az}} \qquad x_2' = 1 - x_1' \tag{12}$$

$$y_1' = \frac{y_1}{y_1^{az}} \qquad y_2' = 1 - y_1' \tag{13}$$

Region B:

$$x_1' = \frac{x_1 - x_1^{az}}{1 - x_1^{az}} \qquad x_2' = 1 - x_1' \tag{14}$$

$$y_1' = \frac{y_1 - y_1^{az}}{1 - y_1^{az}} \qquad y_2' = 1 - y_1' \tag{15}$$

The model uses the approach of Anderson and Doherty [14] who transformed the variables of binary vapor-liquid equilibrium calculations by splitting the equilibrium curve into two regions. Region A is the zone with a mole fraction of more volatile component between zero and the azeotropic composition. Region B is the zone between the azeotropic composition and the unit, also for the more volatile component. This approach permits the study of the vapor-liquid equilibrium for binary azeotropic mixtures.

Equations from (1) to (10) permit the study of multicomponent mixtures without azeotropes. For binary azeotropic mixtures the model takes into account equations from (1) to (5) and equations (8), (9), (10), (12), (13), (14), (15).

The model has been implemented in Fortran language. The simulations for knowing the goodness of the model have been made at constant reflux ratio because this kind of reflux is comparable with the optimum reflux ratio, according to Diwekar [10,11]. The differential equations have been solved with the fourth order Runge-Kutta method.

PILOT PLANT

One of the objectives of the present work is to validate experimentally the model results obtained by simulation in a variety of scenarios. For this reason, an experimental and flexible pilot plant has been constructed. The first experiments realized in this plant are presented in this work.

Figure 2 shows the pilot plant. The column is 3.75 m height, 50 mm and 90 mm inner and outer diameter respectively, and has 15 oldershaw trays. It is made of glass with a heated insulation jacket in order to reduce heat losses. The column has a reboiler (6 l) with a maximum heat duty of 1400 W and a total condenser. Temperatures can be measured on-line at 7 different locations, 5 at trays and 2 at the condenser. Compositions are measured off-line along the time at 4 trays. Flowrate distillate is also measured off-line. During the experiences, concentration profiles of the liquid phase, temperature profiles and distillate profiles were measured. For the determination of the liquid phase compositions, samples were taken out of the column and were analyzed by gas chromatography.

First the column works at infinite reflux ratio in order to stabilize it, and then with a finite reflux ratio.

The mixtures that have been experimented are:
- Methanol-water, that has been important for the start-up of the column.
- Cyclohexane -toluene -chlorobenzene.
- Toluene-n-butanol.
- Toluene-n-butanol-n-octanol.

Figure 2. Batch distillation pilot plant.

Many experiments have been made in the pilot plant. In this work we present a resume of the results obtained in 29 experiments that implies 3540 samples analyzed.

RESULTS AND DISCUSSION

Many simulations have been made with all the mixtures in order to know the behavior of the model. In the simulations, the vapor-liquid equilibrium data have been obtained through the bibliography for the methanol-water mixture. The other mixtures have been studied by the Wilson method, because the parameters of this method have been found in the bibliography for all the mixtures. Once the vapor-liquid equilibrium data are obtained, basically the vapor and liquid mole fraction of each component, the relative volatility constant or variable could be calculated. In all the simulations the number of theoretical trays is 13.

The simulations have been compared with experimental results obtained in the pilot plant. The experimental total reflux time for each experiment must be introduced in the simulation. A realistic operation in a batch operation needs of experimental values.

Experimental and simulated results have also been compared with the results obtained with the commercial simulator Batchsim of Pro/II. Pro/II has been chosen because it is a rigorous and recognized simulator in industrial distillation. For the vapor-liquid equilibrium, Batchsim uses always the NRTL method.

The mathematic correlation between the results have been made by least squares.

Methanol-Water Mixture

Experimental data

Experiments with methanol and water mixtures have been made with a heat duty of 466.7 W and 933.3 W. For each heating rate, the column has worked at a constant reflux ratio of 1, 1.5, 2, 2.5 and 3 respectively. The initial volume of the mixture was 4 l and all the mixtures methanol-water have the same initial composition, 20% mole of methanol and 80% mole of water. The column works at atmospheric pressure with 15 trays. In all the experiments the distillation still was charged and heated up under total reflux until steady-state conditions were achieved. After, the reflux ratio was turned from infinity to finite reflux ratio and product was withdrawn at the top of the column. During the column operations, the distillate flowrate profile, the concentration profiles of the liquid phase along the column and the temperature profiles were measured. For the determination of the liquid phase composition, samples were taken and two methods of analysis were applied. Samples with a composition of methanol between 0% mole and 50% mole were analyzed by gas chromatography and samples with a composition of water higher than 50% mole were analyzed by Karl-Fisher method.
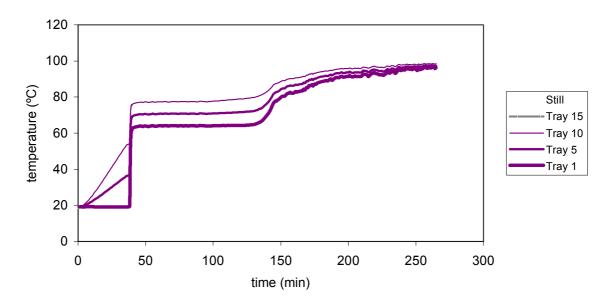

Figure 3. Temperature profiles for the trays of the column. Re = 3. Q = 933.3 W.

Figure 3 and figure 4 show the temperature and concentration profiles for methanol along the column for a reflux ratio of 3 and a heat duty of 933.3 W. After 35 minutes the column has been stabilized. The temperature profiles agree with the concentration profiles along the column. In the distillate (tray 1) the temperature remains at 64.3ºC about 105 minutes. This temperature indicates that pure methanol is obtained; after this time, the temperature rises to 100ºC, and mixtures enriched in water are obtained.

This experiment permits to obtain 79.7% mole of pure methanol in the distillate, the maximum quantity of methanol in all experiments that have been made. Figure 5 shows the distillate flowrate profile.
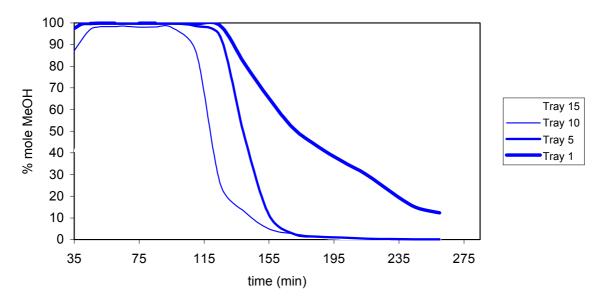

Figure 4. Concentration profiles in the trays of the column. Re = 3. Q = 933.3 W.
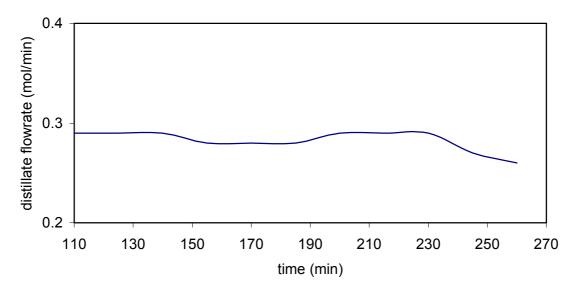*Number of samples analyzed = 84.*

Figure 5. Distillate flowrate profile. $\bar{D}$ = 0.28 mol/min. Re = 3. Q = 933.3 W.
Number of weight measures = 11.

Table 1 and table 2 summarizes the experimental results obtained with a heat duty of 466.7 W and 933.3.W respectively. When the value of the heat duty is doubled, from 466.7 W to 933.3 W, the time at total reflux decreases nearly a half, from 75 minutes to 35 minutes.

For a fixed heat duty, when the reflux ratio increases, also increases the time of the experience and the amount of pure methanol obtained in the distillate. The distillate flowrate decreases.

Table 1. Experimental results with a heat duty of 466.7 W. Total reflux time = 75 min.

Re	Time of the experiment	D (mol/min)	% mole of pure methanol recovered in the distillate
1	5 h 15 min	0.23	46.8
1.5	5 h 30 min	0.20	48.8
2	5 h 45 min	0.17	50.7
2.5	6 h	0.16	56.4
3	6 h 30 min	0.15	59.1

The experiments made at higher value of heat duty, 933.3 W, permit to obtain more distillate flowrate and higher recovery of pure methanol, when we compare them with the experiments at 466.7 W. It can be seen that the experiment at Re=3 and Q=933.3 W permits the maximum recovery of pure methanol.

Table 2. Experimental results with a heat duty of 933.3 W. Total reflux time = 35 min.

Re	Time of the experiment	D (mol/min)	% mole of pure methanol recovered in the distillate
1	3 h 35 min	0.44	71.6
1.5	3 h 35 min	0.38	72.2
2	3 h 35 min	0.35	76.0
2.5	3 h 40 min	0.30	77.3
3	4 h 25 min	0.28	79.7

Validation of the model

The results obtained by simulation with the mathematical model used in this work have been compared with those obtained in the pilot plant and with those obtained by simulation with the commercial simulator Batchsim of Pro/II. Many validations have been made and a few of them are presented. The simulations take into account de variability of relative volatility. This aspect hasn't been referenced in the bibliography. For the methanol-water mixture, the relative volatility from methanol (1) to water(2) used in the simulation is:

$$\alpha_{12} = 4.02 \ \text{(constant value)} \qquad \ln \alpha_{12} = 1.90 - 1.12 \, x_1 \ \text{(variable value)}$$

where x_1 is the mole fraction of methanol in liquid phase.

Figure 6 shows the concentration profiles obtained by simulation of the model with constant and variable relative volatility, for Re=1. These profiles are compared with those obtained with Batchsim and with experimental concentration profiles obtained in the pilot plant.
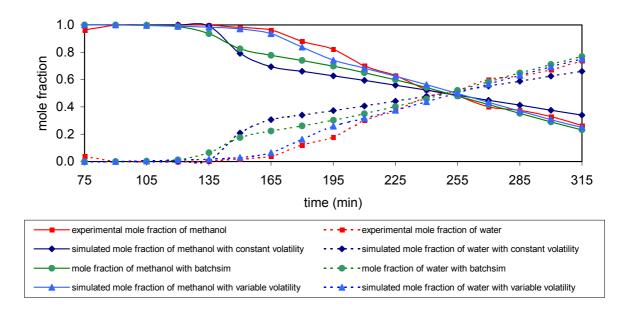

Figure 6. Concentrations profile in the distillate. Re = 1. Total reflux time = 75 min. Experimental heat duty (Q) = 466.7 W.

The mathematic correlation between simulated and experimental results is:

methanol: $x_{1,simulated\ (\alpha=cte)} = 0.920\ x_{1,experimental}$ $r = 0.922$
water: $x_{2,simulated\ (\alpha=cte)} = 0.996\ x_{2,experimental}$ $r = 0.922$

methanol: $x_{1,simulated\ (\alpha\neq cte)} = 0.989\ x_{1,experimental}$ $r = 0.995$
water: $x_{2,simulated\ (\alpha\neq cte)} = 1.004\ x_{2,experimental}$ $r = 0.995$

methanol: $x_{1,experimental} = 1.063\ x_{1,batchsim}$ $r = 0.971$
water: $x_{2,experimental} = 0.921\ x_{2,batchsim}$ $r = 0.971$

The model simulated with variable relative volatility presents the best correlation. All the simulations that have been made with low values of reflux ratio (1, 1.5) with a head duty of 466.7 W and 933.3 W respectively, have the same behavior in the concentration profiles.

Figure 7 shows the concentration profile in the distillate for a reflux ratio Re= 3 and Q=933.3 W.
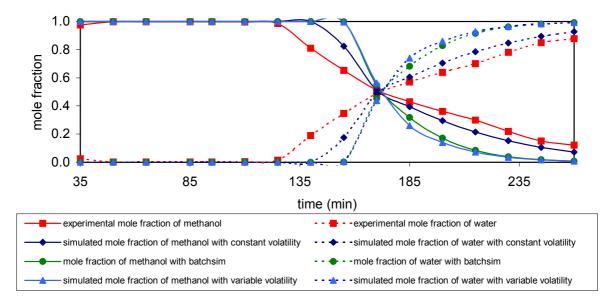
Figure 7. Concentrations profile in the distillate. Re = 3. Total reflux time = 35 min. Experimental heat duty (Q) = 933.3 W.

Now the mathematic correlations show that the mathematic model with constant relative volatility describes better the concentration profile:

methanol: $x_{1,simulated\ (\alpha=cte)} = 1.025\ x_{1,experimental}$ r = 0.984

water: $x_{2,simulated\ (\alpha=cte)} = 1.043\ x_{2,experimental}$ r = 0.984

methanol: $x_{1,simulated\ (\alpha\neq cte)} = 1.017\ x_{1,experimental}$ r = 0.960

water: $x_{2,simulated\ (\alpha\neq cte)} = 1.154\ x_{2,experimental}$ r = 0.960

methanol: $x_{1,experimental} = 0.946\ x_{1,batchsim}$ r = 0.960

water: $x_{2,experimental} = 0.835\ x_{2,batchsim}$ r = 0.960

All the validations that have been made at higher reflux ratio with a heat duty of 466.7 W and 933.3 W indicate that at high reflux ratio the mathematic model with constant relative volatility is a good model.

The results obtained with the concentration profiles agree with those obtained in the temperature profiles. We can conclude that working with low reflux ratio the model with variable relative volatility is better than the model with constant relative volatility. At high reflux ratio the best model is with constant relative volatility.

Cyclohexane-Toluene-Chlorobenzene

Experimental data

Experiments with this mixture have been made with a heat duty of 414 W and 681.3 W. For each heating rate, the column has worked at a constant reflux ratio of 1, 1.5, 2.34 and 4 respectively. The initial volume of the mixture is 6 l and all the mixtures are equimolar. The column works at atmospheric pressure and the start-up is the same as that for the mixture methanol-water. During the column operations, the distillate flowrate profile, the concentration profiles of the liquid phase along the

column and the temperature profiles were measured. For the determination of the liquid phase composition, samples were taken and analyzed by gas chromatography.

The experiments made demonstrate that this mixture doesn't present a good degree of separation for the three components. Figure 8 shows the temperature profiles for the mixture along the column for a reflux ratio of 4 and a heat duty of 681.3 W. After 30 minutes the column has been stabilized.
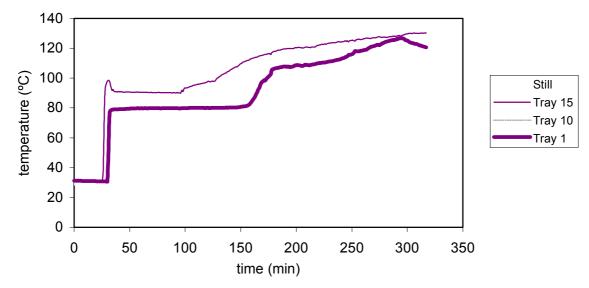

Figure 8. Temperature profiles for the trays of the column. Re = 4. Q = 681.3 W. The boiling temperatures for cyclohexane, toluene and chlorobenzene are 80.7ºC, 111 ºC and 132ºC respectively.

This experiment is the best of all that have been made. Figure 9 and 10 show the concentration profiles at tray 10 and in the distillate for this experiment. It is possible to obtain in the distillate pure cyclohexane with a 99.6% of recovery. Toluene has a higher purity than 93% with a 18.7% of recovery and chlorobenzene can be obtained with a higher purity than 91% with 18.2% recovered.
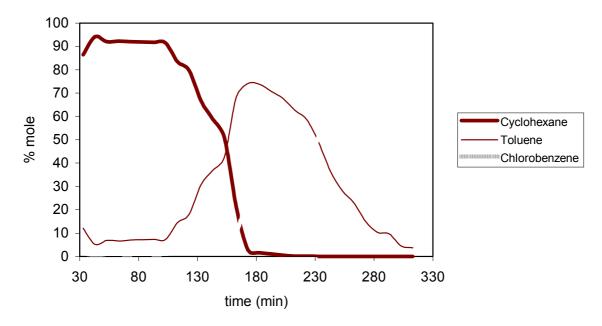
Figure 9. Concentration profile at tray 10. Re = 4. Q = 681.3 W. Number of samples analyzed = 45.
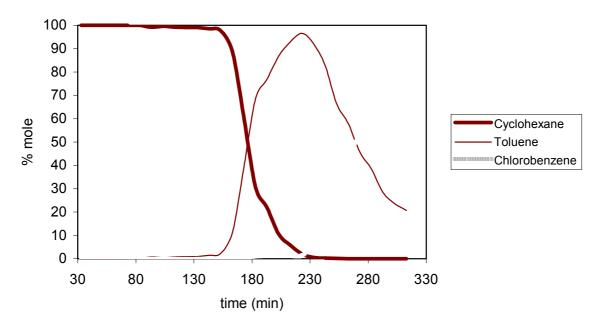

Figure 10. Concentration profile in the distillate. Re = 4. Q = 681.3 W. Number of samples analyzed = 45.

Table 3 summarizes the experimental results obtained with a heat duty of 681.3 W, for a reflux ratio of 1, 1.5, 2.34 and 4, and table 4 compares the distillate flowrate at different heat duties.

Table 3. Experimental results with a heat duty of 681.3 W. Total reflux time=30 min.

Re	Time of the experiment	D (mol/min)	% pure cyclohexane recovered in the distillate	% toluene (>93%) recovered in the distillate	% chlorobenzene (>91%) recovered in the distillate
1	3 h 30 min	0.35	91.8	-	-
1.5	3 h 40 min	0.28	92.5	-	-
2.34	4 h 20 min	0.26	95.4	-	-
4	5 h 10 min	0.19	99.6	18.7	18.2

Table 4. Experimental distillate flowrate for different heat duties.

	414 W	681.3 W
Re	D(mol/min)	D (mol/min)
1	0.30	0.35
1.5	0.20	0.28
2.34	0.19	0.26
4	0.17	0.19

In the experiments made with a heat duty of 414 W, it is not possible to obtain toluene at high concentration.

Validation of the model

A lot of validations have been made and figure 11 shows one of them. A simulation made with a reflux ratio of 1 and total reflux time of 60 minutes is compared with Batchsim and with the experimental results obtained in the pilot plant.

The relative volatilities of the components cyclohexane (1), toluene (2) and chlorobenzene (3) used in the simulation are:

$$\alpha_{13} = 5.51 \qquad \alpha_{23} = 1.77 \qquad \alpha_{33} = 1$$

The mathematic correlation between the simulated results with the rapid and simplified model, and those experimentally obtained are:

Cyclohexane: $\qquad x_{1,\ simulated} = 0.994\ x_{1,\ experimental} \qquad r = 0.991$

Toluene: $\qquad x_{2,\ simulated} = 1.035\ x_{2,\ experimental} \qquad r = 0.989$

Chlorobenzene: $\qquad x_{3, simulated} = 1.002\ x_{3,\ experimental} \qquad r = 0.993$
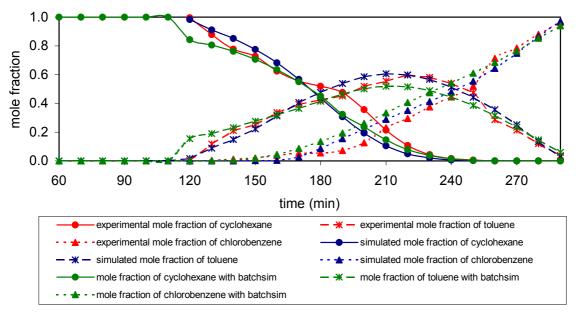
Figure 11. Concentrations profile in the distillate. Re = 1. Total reflux time = 60 min. Experimental heat duty (Q) = 933.3 W.

For the three components of the mixture, the correlation is good and that confirms that the simplified model is a good model for simulating the concentration profiles at Re=1.

If we compare the experimental results with those obtained by simulation with the more rigorous model of Batchsim, the mathematic correlation is:

Cyclohexane: $x_{1, experimental} = 1.093 \, x_{1, batchsim}$ r = 0.993

Toluene: $x_{2, experimental} = 1.058 \, x_{2, batchsim}$ r = 0.977

Chlorobenzene: $x_{3, experimental} = 0.943 \, x_{3, batchsim}$ r = 0.985

The correlation is also good though for toluene and chlorobenzene is lightly lower.

The results obtained in this validation are similar to the other validations made, working with all kinds of profiles, temperature, composition and distillate flowrate. Always in the distillate the results of the validation are more accurate than those obtained on the trays. The reason could be the consideration of constant liquid hold-up. It could be interesting the study of this effect in future work.

Toluene-n-Butanol
After the simplified model has been applied to binary and ternary mixtures with good results, next step is to study if the model can predict the behavior of a binary azeotropic mixture. For a binary azeotropic mixture we must consider if the mixture has a composition in zone A or in zone B. Toluene-n-butanol is a binary azeotropic mixture with a minimum boiling point that has been chosen for studying the model. It's azeotropic composition is 62.5% mole of toluene and 37.5% mole of n-butanol. Toluene is the more volatile component of the mixture. Mixtures in zone A will have a

composition between 0 and 0.625 in mole fraction of toluene. Mixtures in zone B will have a composition between 0.625 and 1 in mole fraction of toluene. For binary mixtures it is easy to introduce the variability of the relative volatility along the column. This aspect has been contemplated in the binary azeotropic mixture. Many simulations have been made for mixtures in zone A and B respectively, with constant and variable relative volatility.

Experimental data

Experiments for mixtures in zone A with a constant reflux ratio of 1, 2 and 3 have been made with a heat duty of 1400 W and 933.3 W respectively. For mixtures in zone B the experiments have been made with a heat duty of 933.3 W and with a constant reflux ratio of 1, 2 and 3. Samples were analyzed by gas chromatography. Figure 12 shows the experimental concentration profiles in the distillate for a mixture of 21% mole of toluene and 79% mole of n-butanol (mixture zone A).
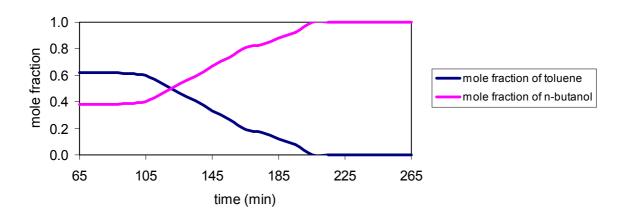

Figure 12. Concentration profiles in the distillate. Mixture zone A. Re = 2. Q = 933.3 W. Number of samples analyzed = 30.

The total reflux time is 60 minutes. For this mixture only pure n-butanol is possible to obtain, but not pure toluene. Figure 13 shows the experimental concentration profiles in the distillate for a mixture of 79% mole of toluene and 21% mole of n-butanol (mixture zone B).

For this mixture, it could be possible to obtain pure toluene but not pure n-butanol, only azeotropic composition of n-butanol.
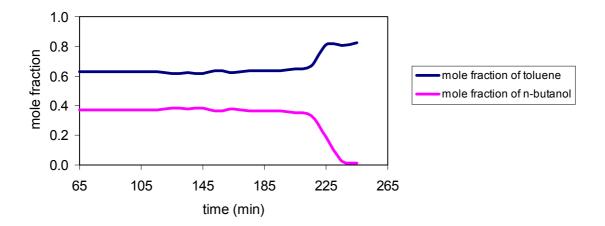
Figure 13. Concentration profiles in the distillate. Mixture zone B. Re = 2. Q = 933.3 W. Number of samples analyzed = 30.

Validation of the model

Figure 14 shows one of the validations that have been made for the concentrations profile in the distillate, for a mixture in zone A with a reflux ratio of 2.
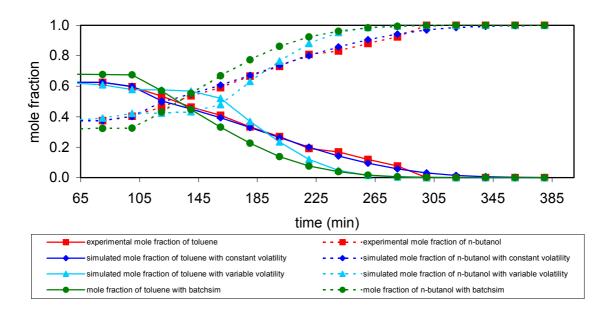

Figure 14. Concentrations profile in the distillate. Mixture zone A. Re = 2. Total reflux time = 65 min. Experimental heat duty (Q) = 933.3 W.

The best mathematic correlation between the experimental results and those simulated with the rapid model is:

Toluene: $x_{1, \text{simulated } (\alpha = \text{cte.})} = 0.969 \, x_{1, \text{experimental}}$ $r = 0.997$

n-Butanol: $x_{2, \text{simulated } (\alpha = \text{cte.})} = 1.004 \, x_{2, \text{experimental}}$ $r = 0.997$

Also the correlations between the experimental results and those obtained with Batchsim are so good:

Toluene: $x_{1, batchsim} = 0.917\ x_{1, experimental}$ $r = 0.959$

n-Butanol: $x_{2, batchsim} = 1.053\ x_{2, experimental}$ $r = 0.959$

Similar results have been obtained with other validations with mixtures in zone A. We can conclude that the mathematical model used with constant relative volatility permits to study binary azeotropic mixtures in zone A.

For mixtures in zone A, the relative volatility from toluene (1) to n-butanol (2) used in the simulation is:

$\alpha_{12} = 2.32$ (constant value) $\alpha_{12} = \exp(1.57 - 2.20x_1)$

where x_1 is the mole fraction of toluene in the liquid phase.

For mixtures in zone B:

$\alpha_{12} = 0.64$ (constant value) $\alpha_{12} = \exp(1.80 - 2.84x_1)$

Figure 15 shows a validation of the concentrations profile for a mixture in zone B, with a reflux ratio of 2.
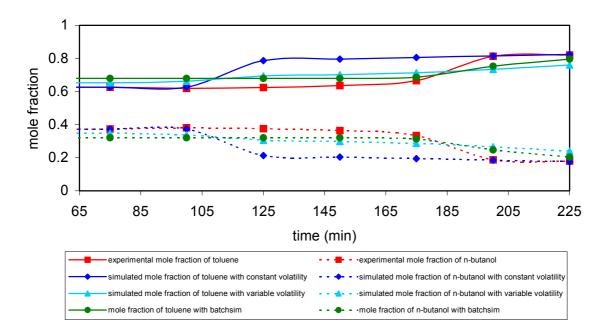

Figure 15. Concentrations profile in the distillate. Mixture zone B. Re = 2. Total reflux time = 65 min. Experimental heat duty (Q) = 933.3 W.

The best correlation between experimental data and simulation results with the rapid model is:

Toluene: $x_{1,\ simulated\ (\alpha \neq cte.)} = 1.014\ x_{1,\ experimental}$ r = 0.867

n-Butanol: $x_{2,\ simulated\ (\alpha \neq cte.)} = 0.9091\ x_{2,\ experimental}$ r = 0.867

We can conclude that the mathematical model with variable relative volatility, presented in this work, permits to study the behavior of binary azeotropic mixtures in zone B.

Toluene-n-Butanol-n-Octanol

Next step in this work is to study the resolution of the binary azeotrope toluene-n-butanol, by adding a solvent. Among all the solvents studied through the data base of Pro/II simulator, n-octanol seems to be a possible solvent to break the azeotrope. Simulations with the ternary mixture toluene-n-butanol-n-octanol have been made and also simulations with Batchsim.

The simulations have been compared with the experimental data obtained in the pilot plant. The azeotrope is broken with the addition of small quantities of n-octanol, for binary azeotropic mixtures in zone B. For mixtures in zone A, the addition of n-octanol doesn't offer a resolution. Figure 16 shows one of the validations that have been made for a mixture of 70% mole of toluene, 25% mole of n-butanol and 5% mole of n-octanol.
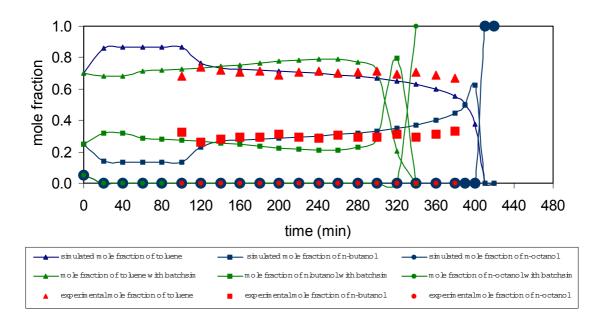

Figure 16. Concentrations profile in the distillate. Re = 1.

The relative volatilities of the three components of the mixture, toluene (1), n-butanol (2) and n-octanol (3) used in the simulations are:

$$\alpha_{13} = 18.38 \qquad \alpha_{23} = 15.50$$

The results obtained by simulation with the model used in this work have the same behavior of the experimental data. The rapid model and the rigorous of Batchsim present a difference in the stabilization time of the column, but the behavior is also comparable. These results obtained are a preliminary study for the industrial resolution of the binary azeotropic mixture toluene-n-butanol.

FINAL CONSIDERATIONS

The model developed based on mass balances and the equilibrium vapor-liquid equations is a rapid and reliable model that has been extensively validated, with satisfactory results. It can be applied to multicomponent mixtures and also binary azeotropic mixtures. This model is being implemented in the planning of multiproduct/multipurpose batch chemical plants at the scheduling model level, specifically, it is being successfully applied in the recovery of solvents, where rapid models are necessary for solving the problems associated to industrial environmental constraints.

NOMENCLATURE

A_j, B_j, C_j	Antoine's equation constants for component j	
D	distillate flowrate	[mol/min]
H_n	holdup at tray n	[mol]
H_D	holdup in the condenser	[mol]
L	liquid flowrate	[mol/min]
M_B	holdup at the reboiler	[mol]
N	number of trays in the column	
n	tray	
NC	number of components	
P	total pressure	[mm Hg]
p_j	partial pressure for component j	[mm Hg]
P_j^o	vapor pressure for component j	[mm Hg]
Q	heat duty	W
Re	reflux ratio	
t	time	[min]
T	temperature	[ºC]
V	vapor flowrate	[mol/min]
x_j	liquid composition of component j	[mole fraction]
x_{Bj}	liquid composition of component j in the reboiler	mole fraction]

x_{Bk}	liquid composition of component k in the reboiler	[mole fraction]
x_{Dj}	liquid composition of component j in the distillate	[mole fraction]
x_{nj}	liquid composition of component j on tray n	[mole fraction]
$x_{n-1,j}$	liquid composition of component j on tray n-1	[mole fraction]
x_{nk}	liquid composition of component k on tray n	[mole fraction]
x_{Nj}	liquid composition of component j on tray N	[mole fraction]
x_1'	liquid composition of component 1 in a binary azeotropic mixture	[mole fraction]
x_2'	liquid composition of component 2 in a binary azeotropic mixture	[mole fraction]
x_1^{az}	azeotropic liquid composition of component 1	[mole fraction]
y_j	vapor composition of component j	[fracción molar]
y_{Bj}	vapor composition of component j in the reboiler	[mole fraction]
y_{nj}	vapor composition of component j on tray n	[mole fraction]
$y_{n+1,j}$	vapor composition of component j on tray n+1	[mole fraction]
y_{1j}	vapor composition of component j on tray 1	[mole fraction]
y_1'	vapor composition of component 1 in a binary azeotropic mixture	[mole fraction]
y_2'	vapor composition of component 2 in a binary azeotropic mixture	[mole fraction]
y_1^{az}	azeotropic vapor composition of component 2	[mole fraction]
α	relative volatility in a binary mixture	
α_j	relative volatility of component j	
α_k	relative volatility of component k	
γ_j	activity coefficient of component j	

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