Evaluation of the Dynamics of a Distillation Column with Two Liquid Phases

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Distillation is one of the oldest and most important separation processes used in chemical process industry. On the other hand, it presents extremely low thermodynamic efficiency, accounting for the largest percentage of the overall energy consumption of a plant. In this sense, distillation is the most referred process when it comes to energy consumption. The present work was initiated with a search for the reduction in the energy consumption in a distillation train of 1,2-dichloroethane (EDC) of a commercial plant for producing vinyl monochloride (MVC), which involves azeotropic distillation. The results obtained using the commercial simulator Aspen[TM] show that the reduction in the reboiler heat duty caused significant changes in both concentration and temperature profiles throughout the column due to the formation of two liquid phases. This fact is an indication that the occurrence of this 2nd liquid phase causes significant changes in the operation of the column as well as on the separation to be obtained. The results also show that the operation of the column with two liquid phases throughout some stages still satisfies bottom product specification (mass fraction of H_2O), and also consume less energy. The formation of two liquid phases occurs even with a reduced amount of H_2O present in the feed stream. Therefore, it is necessary to verify the feasibility of operating such a column with the presence of two liquid phases, requiring, therefore, the evaluation of the dynamics of the process which will also be useful for controllability purposes. The results indicate that the temperature of some of the stages of the column can act as an indicator about the formation of the 2nd liquid phase. Therefore, controllers that maintain the parameters of the processes at acceptable levels must be proposed avoiding controlling the temperature of stages with two liquid phases.

1. Introduction

Distillation is one of the oldest and most important separation processes used in chemical process industry. On the other hand, it presents extremely low thermodynamic efficiency, accounting for the largest percentage of the overall energy consumption of a plant. In this sense, distillation is the most referred of the processes when it comes to energy consumption.

The distillation column considered in this paper presents the characteristics of an azeotropic distillation column, since there is the formation of two liquid phases in the reflux vessel, and depending on the operational condition, in some stages throughout the column. Another feature that makes the system unconventional is that the feeds are held at the reflux vessel. Such column is part of the 1,2-dichloroethane (EDC) purification train of a commercial plant that produces vinyl monochloride (MVC). The process of obtaining the EDC occurs through direct chlorination of ethylene (C_2H_4), according to the reaction: $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$. The product EDC (high purity) leaves the reactor and flows to the purification system, which includes an aqueous washing, which is conducted in the settler vessel (or reflux vessel), shown in Figure 1.

After the top condenser, as well as the reflux vessel, there are two liquid phases: H_2O saturated organic phase, and an organic saturated aqueous phase. The organic phase gives rise to reflux of the column,

while the aqueous phase is discarded. Although less volatile than EDC, H_2O leaves through the top of the column because of the inversion on the value of the equilibrium constant K, a consequence of the fact that H_2O forms a minimum azeotrope, not only with EDC, but virtually with all organic compounds in the process. In the industry, despite the degree of freedom analysis points two variables to be manipulated, only the heat duty of the reboiler is used. The work from *Guedes et al.* (2007) aimed to reduce the energy consumption of the azeotropic column. In this sense, by performing tests on the industrial plant, the heat duty of the reboiler was gradually reduced, which resulted in temperatures of the stages (top, middle and bottom) much lower than those observed historically. Although the value of moisture in the bottom stream of the column was below the specification (10ppm), the tests were suspended after 07 hours of operation, and a new operating condition (lowest heat duty) was established. However, the simulations were performed without the formal definition of an objective function and constraints (optimization). Further, no study to control the operating conditions (with and without two liquid phases throughout the column) was performed. Thus, this study aimed to: formalize the optimization of energy consumption and evaluate the control of the column under both operating conditions (with and without two liquid phases inside the column) study using the Singular Value Decomposition (SVD).

2. Modeling and Simulation

At steady state, the simulation was performed using the commercial simulator Aspen Plus™ (version 7.2). The column was modeled using RadFrac™ routine, which detects the possible formation of a second liquid phase (whose main component is H_2O) at any stage, it also assumes equilibrium stages and uses specified values for stage efficiencies. These efficiencies can be manipulated to adapt to plant data. To adjust the data generated by Aspen Plus ™ to the plant data, it was used Murphree efficiency (Eff) equal to 64% for all stages and 100% for the reboiler. Industrially, the column has 25 stages (numbered from top to bottom) and a thermosyphon reboiler. On Aspen Plus ™, the pressure on each stage of the column, as well as the other equipments, is kept constant. To represent the equilibrium between the vapor-liquid-liquid (VLLE) phases, it was used a γ-φ approach. Even the column operating at low pressure, the vapor phase was represented by the Redlich-Kwong equation of state (EOS). The activity coefficient γ was determined from the NRTL model. A comparison between the plant data (historical operating condition - Base Case) and those provided by the simulation is presented on Table 1.

To determine the optimal energy consumption, the objective function to be minimized was defined as theheat duty of the reboiler (Qr). The constraint was the mass fraction of H_2O in the liquid phase (global) at a certain stage of the column ($x_{H_N}^{H_2O}$): 2500 ppm of H_2O (approximately the saturation value of EDC with H_2O, at 45 °C). If the formation of two liquid phases throughout the column wasn't desired, the constraint was imposed on the 1st stage (counted from top to bottom) of the column due to the finding that the formation of two liquid phases begins at this stage. For operations with two liquid phases, the stage was chosen according to the purpose. Mathematically, the problem was formulated as follows:

$$\min J = Q_r \tag{1}$$

$$\text{subject to}$$

$$x_{H_N}^{H_2O} \leq 0.0025 \tag{2}$$

The optimization procedure considered the distillate flow of the column as manipulated variable (stream OCSUM1 in Figure 1). The objective function was inserted using the tool *Model Analysis / Optimization* from Aspen Plus™, which uses the Sequential Quadratic Programming (SQP) method to search for the optimum. The constraints were inserted using the tool *Model Analysis / Constraint*.

Table 1: Comparison between the real and simulation data (Guedes et al,2007)

Variable	Real	Simulation
Reboiler heat duty (kcal/h)	1.52×10^6	1.53×10^6
Temperature at top (°C)	79.0	79.4
Temperature at stage 6 (°C)	85.0	87.0
Temperature at bottom (°C)	93.0	93.4

The result provided by steady state simulation was used as initial value for the dynamic simulations, which were performed with the aid of the simulator Aspen Dynamics™. To make the model represent the real

plant more accurately, the *Pressure Driven™* dynamic simulation was used, which considers the influence of the pressure of the connected equipments (Luyben, 2002). Figure 1 shows the complete flowchart used in dynamic simulations. When exporting from Aspen Plus ™ to Aspen Dynamics ™ platform, some level and pressure controllers were automatically added. The flowchart in Figure 1 shows the temperature controller ate the bottom of the column (only used in closed loop simulations) and a level controller for the 2nd liquid phase in the decanter, which was added at the Aspen Dynamics™ platform.
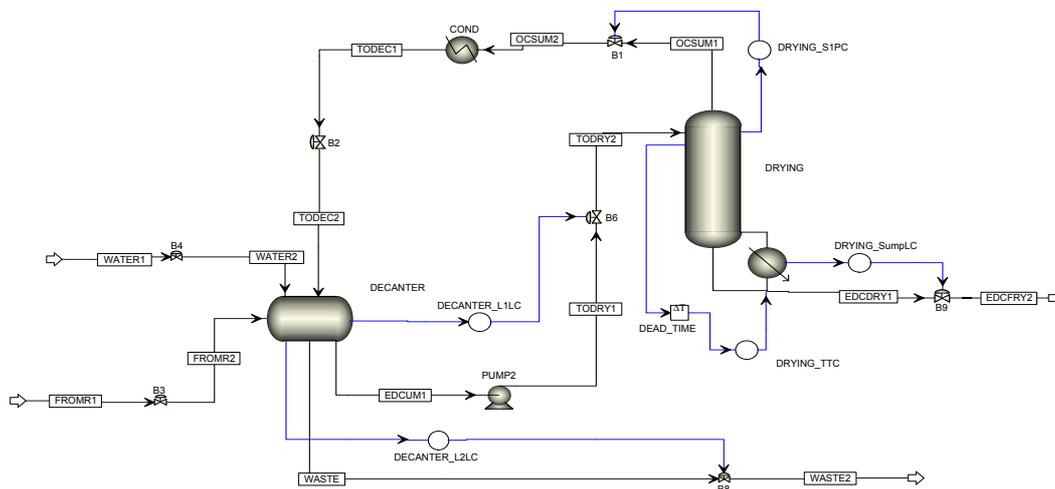
Figure 1: EDC dehydration process flowchart used to perform the dynamic state simulations.

4. Steady-state Results

Table 2 presents the results for all three operating conditions: i) historical ii) current iii) and optimized. With the formation of two liquid phases (Case II), the reduction of energy consumption compared with the situation with a single liquid phase (case I) was 19.4%, a result caused by the decrease of distillate flow rate. In both cases, the production of "dry" EDC (stream EDCDRY2) was almost the same.

On Figure 2 it's possible to see a great difference between the temperature profiles for the two situations. For Case I, a significant variation occurs between the 1st and 5th stage, then it increases almost linearly until the base. On the other hand, for Case II, the variation between the 1st and 16th stage is almost linear, then it increase significantly until the base. This significant change in the temperature profile occurs because of the formation of a 2nd liquid phase (aqueous) on the stages of the column. The good agreement between azeotropic data (Azeotropic Data, 1973) and solubility data (Dechema, 1990) found in the literature for the system H_2O-EDC and those predicted by the simulations, are the mainstays of this conclusion.
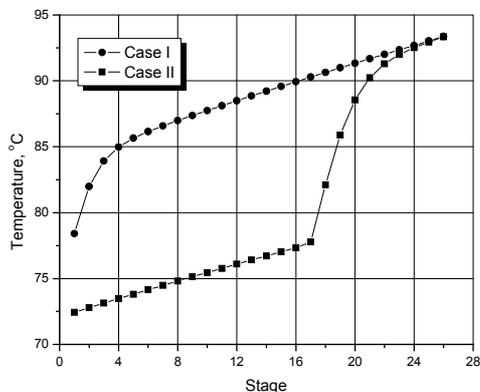
Figure 2: Temperature profile for the two optimizing.
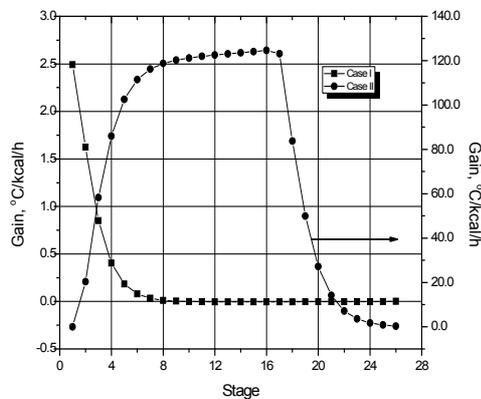
Figure 3: SVD analysis for the two optimizing.

Considering a manipulated variable (heat duty of the reboiler) and controlled variable (temperature), the SVD analysis provided only one MSV (Minimum Singular Value) for each situation: 0.000013083 for Case I and 0.0019 for Case II. According to these results and the theoretical point of view, Case II exhibits better control properties than Case I. The singular value calculation was performed using Matlab® application. To implement the control system, a stage-to-stage gain analysis was performed, which indicates the best stage to control the temperature (most easily measured variable). More specifically, this analysis recommends that the control be carried out at the stage that presents higher gain, which is calculated from changes in the manipulated variable (Luyben, 2005).

Figure 3 shows the gains (^{o}C/kcal/hr) for each stage of the column, which were obtained after applying a positive disturbance of 2% to the heat duty of the reboiler. For Case I, stage 1 must have its temperature controlled, while for Case II, stage 16; these results were used in the closed-loop simulations.

Table 2: Main results of the optimizations.

	History	Actual	Optimized	
			Case I	Case II
Distillate flowrate (kg/h)	4850.0	4849.0	4616.9	1465.3
Reboiler heat duty (kcal/h)	1.52×10^6	1.52×10^6	1.4985×10^6	1.2079×10^6

5. Dynamic Results

The transition between one situation and another was analyzed, more specifically, considering the conditions in Table 3, it was evaluated when the 2nd liquid phase appears and/or disappears, as well as the stage(s) where this occurs. Figure 4 shows the transition from operation with one liquid phase to the operation with two liquid phases (organic and aqueous) and vice versa. For both situations, the disturbance in the heat duty of the reboiler was performed for a time equal to 2 hours. Starting from Case I, the heat duty of the reboiler was reduced (in order to bring up the 2nd phase liquid) from 1.4985 kcal/h to 1.1800 kcal/h, while starting from Case II, a increase (designed to take away the 2nd liquid phase) from 1.2079 kcal/h to 1.1400 kcal/h was performed. The reduction in the heat duty of the reboiler implies lower flowrate at the top (OCUM1) and consequently less removal of H_2O by this stream. Since the column feed stream (TODRY2), which at any condition is saturated with H_2O, is carried out at stage 1, this is the first stage to provide H_2O concentration above saturation, causing the appearance of the 2nd liquid phase, which occurs a few instants after the disturbance, as can be seen in Figure 4a. Figure 4b shows that the disappearance of the 2nd liquid phase, in stages where this 2nd phase is present, starts at the lower section of the column, where the effect of the disturbance occurs first (increase in the heat duty of the reboiler); which is the removal of H_2O. However, at all stages, the disappearance of the 2nd liquid phase occurs abruptly, due to the ease in which H_2O is removed, since H_2O forms azeotrope with all the organic compounds here considered; a result that indicates that the VLLE has greater instability than the VLE.

Figure 4a also shows that, on the 11th stage, the 2nd liquid phase only appears nearly 3 hours after the disturbance and that the 20th stage showed no formation of the 2nd liquid phase. This is an interesting result if analyzed together with Figure 5a, where there is a large variation in temperature values of these stages, however only the 1st and 11th stages showed the formation of a 2nd liquid phase; ie, the temperature of these stages can be an indicator of the formation of a 2nd liquid phase, but the temperature of the 20th stage can't. The same can be concluded from the analysis of Figure 5b: the temperature of the 20th stage varies without changes in the number of liquid phases.

The closed-loop results for temperature are shown in Figures 6 and 7. In Case I, the opening of the process feed stream valve (FROMR1) was increased by 10% (in order to favor the appearance of a 2nd liquid phase); in Case II, it was reduced by 10%. Interestingly, an increase in the feed flow rate of the process has a similar effect as a decrease in the heat duty of the reboiler. Table 3 presents the parameters of the controllers; except the temperature controller, which was tuned using the Tyreus-Luyben method (Luyben, 2006), all the other parameters were (proportional gain, k_C, and integral time, τ_i) Aspen standard. As shown in Figure 6a, in both situations the control system, after a small over-shoot, get to keep the temperature (in the 1st stage for Case I and in the 16th stage for Case II) at set-point; however, the controlling for Case II presents faster performance. Figure 6b shows the composition of H_2O at the the bottom stream of the column; for Case I, the change was irrelevant and remained near to zero.

For Case II, the composition of H_2O at the bottom stream showed a considerable off-set, and even that the off-set had been in order to maintain the bottom product within specification, the question of what would happen to a disturbance in the opposite direction (10% increase in opening of the process feed stream

valve) was raised. The results of this evaluation are shown in Figure 7, which shows that the temperature was maintained at set point and its variation was even smaller. However, the bottom product was totally out of specification; an offset of about 1,400 ppm.

Considering that the stage 16 is the penultimate to present two liquid phases, then the next stage that presents a single liquid phase had its temperature controlled (stage 18). The result is represented by the dotted line in Figure 11, where it can be observed, once again, that the temperature is satisfactorily controlled and the H_2O mass fraction off-set in the bottom stream was lower than 2 ppm.
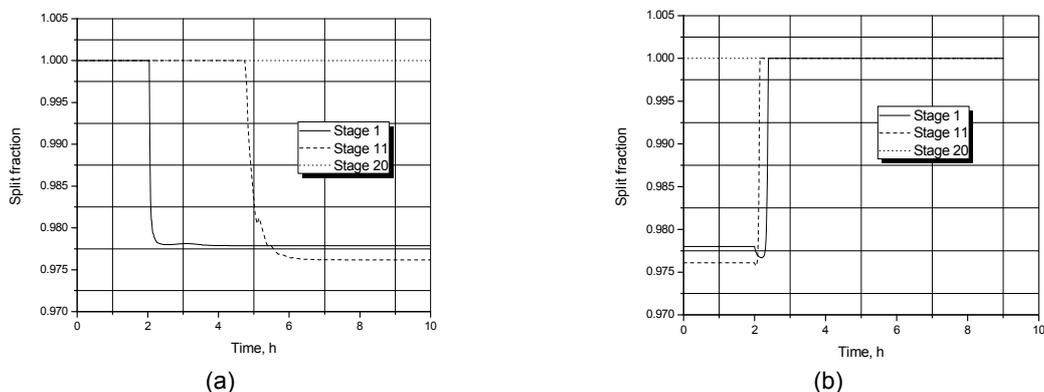
Figure 4: Transition between the existence of one and two liquid phases to changes in the heat duty of the reboiler: (a) from Case I to Case II; (b) from Case II to Case I.
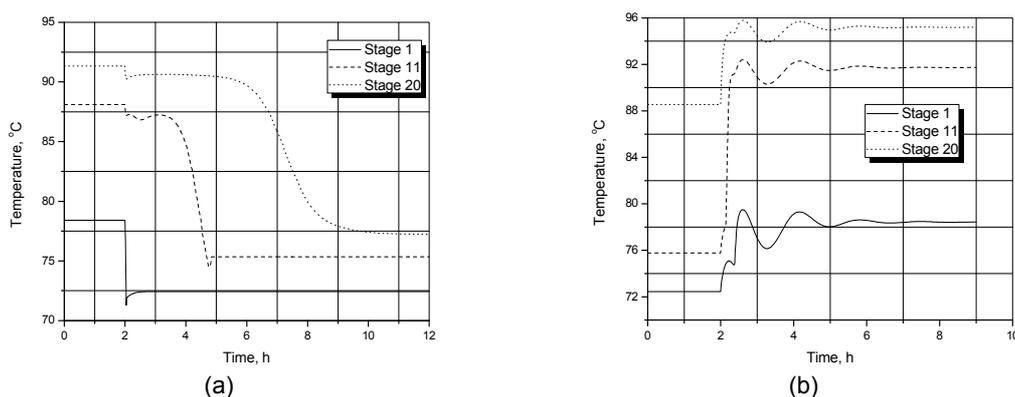
Figure 5: Transient behavior of the temperature for a change in the heat duty of the reboiler: (a) from Case I to Case II; (b) from Case II to Case I.
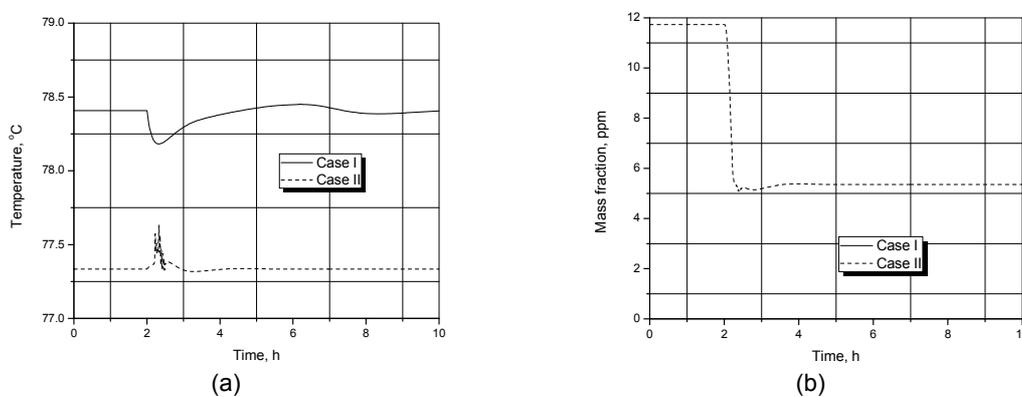
Figure 6: Closed loop transient behavior of the temperature (a) and mass fraction of H2O in the bottom stream (b) to changes in the process feed flowrate.

Table 3: Parameters of the controllers.

	DECANTER_L1LC	DECANTER_L2LC	DRYING_SumpLC	DRYING_S1PC	DRYING_TTC
Case I					
k_C	1	1	10	20	3.87
τ_i, min	20	10	60	12	5.28
Deadtime, min					0.5
Case II					
k_C	1	1	10	20	14.69
τ_i, min	20	10	60	12	3.96
Deadtime, min					0.5

(a)

(b)
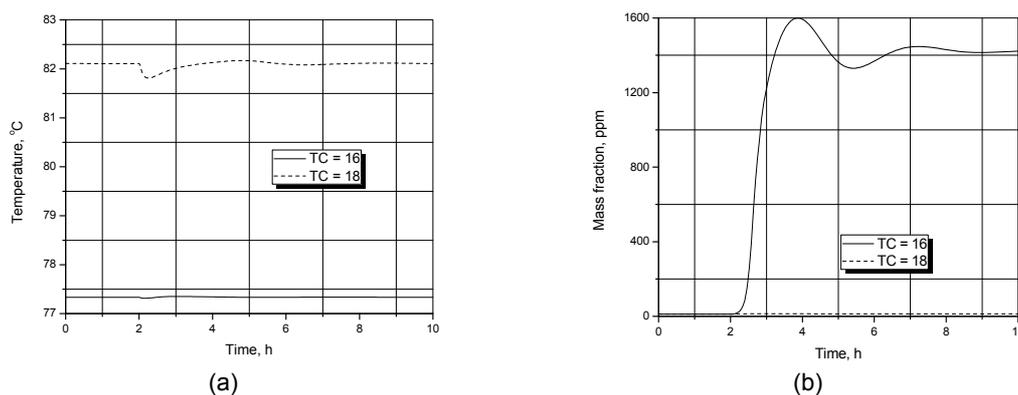
Figure 7: Closed loop transient behavior of the temperature (a) and mass fraction of H_2O in the bottom stream (b) to changes in the process feed flowrate; case II: 10% increase in valve opening.

6. Conclusions

The operation of the column with two liquid phases over some stages satisfies the bottom product specification (mass fraction of H_2O) and consumes less energy. The formation of two liquid phases occurs even with a reduced amount of H_2O in the feed stream.

For each evaluated situation, the SVD analysis recommends controlling the temperature at opposite regions of the column: for Case I, the upper region and for Case II, the lower region. From a theoretical viewpoint, Case II exhibits better control property than Case I.

The transition from Case II to Case I presents much faster dynamics than the opposite, demonstrating the greater instability of the VLLE.

For some stages, the temperature can be used as an indicator of the appearance or disappearance of a 2nd liquid phase. For both situations, the control system maintains the controlled variable (temperature) near the set point. However, the use of temperature as inference to the mass fraction of H_2O at the bottom stream and as indicated by SVD analysis should be performed carefully. In fact, the results indicate that controlling the temperature of stages with two liquid phases should be avoided.

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