



XXII CONGRESSO
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23 a 26 de Setembro de 2018
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XVII ENCONTRO BRASILEIRO
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MULTIPLICITY OF STEADY STATES IN A NON-EQUILIBRIUM SIMPLE BATCH DISTILLATION PROCESS

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RESUMO – *In this work, an analysis was made of the changes in compositional trajectories for the mixture of methanol/isopropanol/water close to distillation boundaries, when the non-equilibrium approach was applied to a simple batch distillation process. Numerically different values of binary azeotropes were observed for different values of the interfacial area in the process of mass transfer between the liquid phase and the vapor phase, and for the different molar flow rates in distillation. It was also observed that when a distiller has a large interfacial area or a small molar flow value for vapor removal, the residue curves and the distillation boundaries (separatrices) of the irreversible model resemble the curves simulated by the model of equilibrium. In the construction of residue curves near the separatrices, a change in stability was observed, which, depending on the design of the equipment (interfacial area) or the operational condition (molar flow of vapor), could result in a steady state with the heavy component or an intermediate component as the bottom product. A bifurcation analysis was carried out, using MATCONT software, to map the steady states of the process, through the construction of bifurcation diagrams (in co-dimension 1) using the interfacial area and the molar flow rate as the parameters of continuation. With this, it was possible to determine the critical value of the parameters of continuation where a change in stability could be observed.*

1. INTRODUCTION

In general, the study of dynamical systems is made using computer simulations. This method, however, is not adequate when the process is very complex and an optimum yield point is desired. A more thorough evaluation is possible using nonlinear dynamic analysis, through the construction of bifurcation diagrams associated with systems (Berezowski, 2000; Pavlou *et al.*, 1999). The first studies of the dynamic distillation column were reported in Magnussen *et al.* (1979); Widagdo *et al.* (1989) and Jacobsen and Skogestad (1991). For a distillation column operating in non-equilibrium, Kienle and Marquardt (Kienle and Marquardt, 1991) were the first to study the multiple steady states for this process.

The non-equilibrium stages has been developed by Silva *et al.* (2003), a more compact model that takes into account mass transfer for a simple batch distillation process. In this model, the total



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effect of mass transfer is incorporated in a factor of irreversibility (α), where the balance becomes a local property, according to the principle of microscopic reversibility (Kuiken, 1994).

In this work, the researchers obtained several interesting results with the "dynamic azeotrope" for non-ideal mixtures and a multiplicity of steady states. The authors used an irreversibility model developed by Silva *et al.* (2003) and concluded that the residue curves and separatrices had to be calculated using the same model. Therefore, the main purpose here is to demonstrate that, according to project and operational variables, differences in compositional trajectories may be observed in a simple batch distillation in non-equilibrium.

It was observed that near the separatrices of the distillation process, different binary dynamic azeotropes can occur, due to the displacement of separatrix (distillation boundary), which is strongly dependent on the mass transfer, which is connected to the design and operation of the equipment.

2. METHODOLOGY

A MATLAB program was developed to calculate residue curve maps employing an irreversible model (Silva *et al.*, 2003) and using the MATCONT software for the construction of bifurcation diagrams. The program calculates the residue compositions and the pressure within the steam. The γ - ϕ approach was used to calculate boiling points, the activity coefficients and the vapor pressure were calculated using the NRTL model and the Antoine equation, respectively. The NRTL model for the pairs of blends was used.

The pressure in vapor phase as well as the mole fractions were calculated using the expressions developed by Silva *et al.* (2003). Therefore, the following system of equations is obtained:

$$y_i = \alpha_i y_i^* = \left(\frac{A k_{gi} P^*}{RT_q + A k_{gi} P} \right) y_i^* \quad (i = 1, 2, \dots, c-1) \quad (1)$$

$$\sum_{i=1}^c y_i = 1 \quad (2)$$

$$y_i^* = \left(\frac{\gamma_i \phi_i^{sat} \exp \left[\frac{V_i^L (P - P_i^{sat})}{RT} \right]}{\widehat{\phi}_i^V P} \right) x_i \quad (i = 1, 2, \dots, c-1) \quad (3)$$

This system of nonlinear algebraic equations was solved using fsolve subroutine, available in the toolbox OPTIM for Matlab®. When y_i^* and P are set, it is possible to calculate α_i , and therefore integrate the differential equation systems below (Teixeira *et al.*, 2009) to get new x_i values.

$$\frac{dx_i}{d\varepsilon} = x_i - \alpha_i y_i^* (\bar{x}), \quad i = 1, 2, \dots, c-1. \quad (4)$$

4. RESULTS AND DISCUSSION

It can be observed that the difference between the pressure in the interface and pressure in the bulk of vapor phase will decrease with time. Analyzing the behavior of trajectories of residue curves can be seen that, as the interface area increases, the trajectory of the residue curve approximates the trajectory of the residue curve calculated by the equilibrium model. This fact shows as the interface area increases, the residue curves calculated by the irreversible model tend towards calculated by the equilibrium model.

Figure 1 demonstrates the stability change when there is a change in the interfacial area and are two stable steady states (pure isopropanol and pure water), characteristic of a saddle point. A bifurcation diagram was constructed to map this behavior using MATCONT software, taking the interfacial area as the parameter of continuity. This type of bifurcation diagram presents a topology similar to bifurcations of the transcritical. Stability change also occurs when a value of the interfacial area, called the critical point, A_c , equals 243 m^2 .

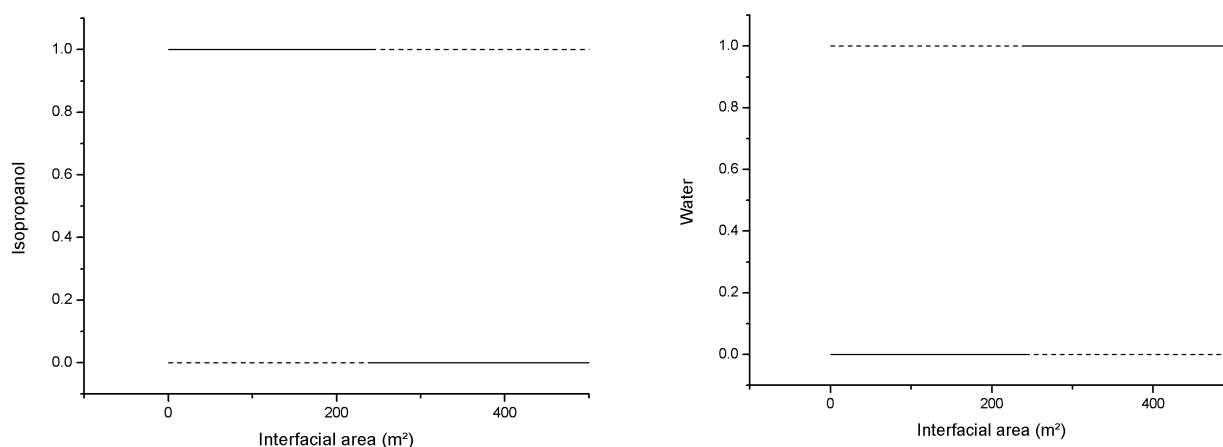


Figure 1 – (a) Region of bifurcation behavior, (b) and (c) Bifurcation diagram of a simple batch distillation process operating irreversibly, where the interfacial area is the parameter of continuity.

Continuing the study of dynamics of simple batch distillers in non-equilibrium, computational experiments were carried out to analyze the influences the residue curves and of the separatrices with respect to different values of molar flow (q) of steam withdrawal.

It was observed the phenomenon called dynamic azeotrope, that occurs due to the physical limitations of the equipment (interface area) it will not be possible to maintain this flow value, then the process is stopped before it reaches the azeotrope value predicted by thermodynamics.

As shown earlier, there are two stable steady states for the water-isopropanol-methanol system, characterized by pure water and by pure isopropanol. Therefore, at the end of the distillation process, depending on the operating condition, it is possible to obtain in the distiller pure isopropanol or pure water, thus characterizing a change of stability. This same behavior was obtained when the continuity parameter, i.e., bifurcation, was the interface area. With the objective of investigating this behavior, Figure 2 shows the bifurcation diagram of the process when the molar flow is the continuity parameter.



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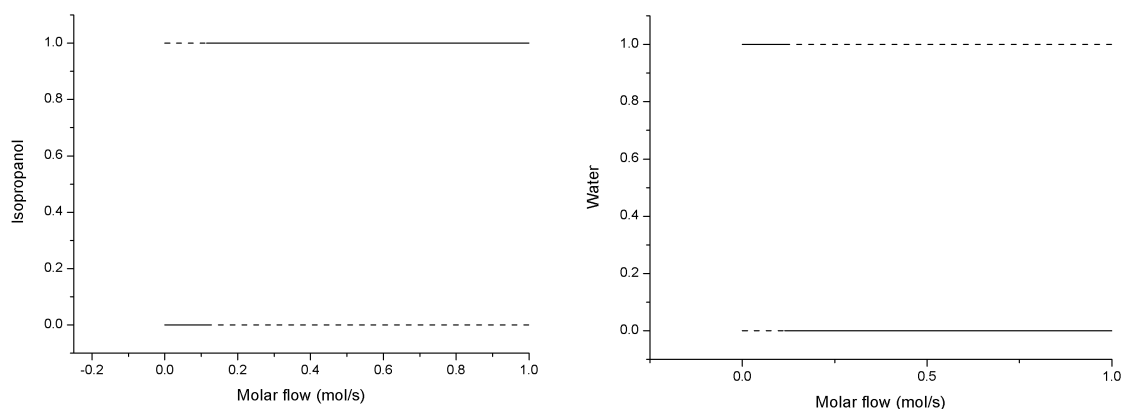


Figure 2 – (a) Region with the behavior of the bifurcation; (b) and (c) Bifurcation diagram of simple batch distillation process operating irreversibly, where is the molar flow is the continuity parameter.

As can be seen in Figure 2 above, when the molar flow is used as the as continuity parameter, in flow simulations where the value is less than 0.1 mol/s, the stable steady state is pure water and the unstable one is isopropanol. This is the flow critical value, i.e., $q_c = 0,1$ mol/s, where the exchange of system stability occurs with the group of parameters in question. Moreover, it was also observed that the residue curves did not intersect their respective separatrices, as can be found in Teixeira *et al.* (2009).

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