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Nonlinear Dynamics of Homogeneous Azeotropic Distillations

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Abstract

In spite of significant nonlinearities even in the simplest model, some types of steady-state and dynamic behavior common for nonlinear systems have never been associated with distillation columns. In recent years, multiplicity of steady states has been a subject of much research and is now widely accepted. Subsequently, stability of steady states has been explored. Another phenomenon that, although widely observed in chemical reactors, has not been associated with models of distillation columns is the existence of periodic oscillations.

In this article we study the steady-state and dynamic behavior of the azeotropic distillation of the ternary homogeneous system methanol-methyl butyrate-toluene. Our simulations reveal nonlinear behavior not reported in earlier studies. Under certain conditions, the open-loop distillation system shows a sustained oscillation associated with branching to periodic solutions. The limit cycles are accompanied by traveling waves inside the column. Significant underdamped oscillations are also observed over a wide range of product rates.

1. INTRODUCTION

Azeotropic distillation is one of the most widely used and important separation processes in the chemical and the specialty chemical industries. Since their understanding is a necessary prerequisite for proper column design and operation, the steady state and dynamic behavior of azeotropic distillation has been studied extensively over the past decades. Laroche *et al.* (1992) have shown that azeotropic distillation columns can exhibit unusual features not observed in non-azeotropic distillation. In particular, multiplicity of steady states has been a subject of much recent research interest. An overview of steady state multiplicity in distillation is given by Guttinger *et al.* (1997)

By multiple steady states in a distillation column we mean the general notion of multiplicities, i.e., that a system with as many system parameters specified as there are degrees of freedom exhibits different solutions at steady state condition. In this article, the term "multiple steady states" (MSS) refers to the output multiplicities only. Furthermore, throughout this work, only multi-

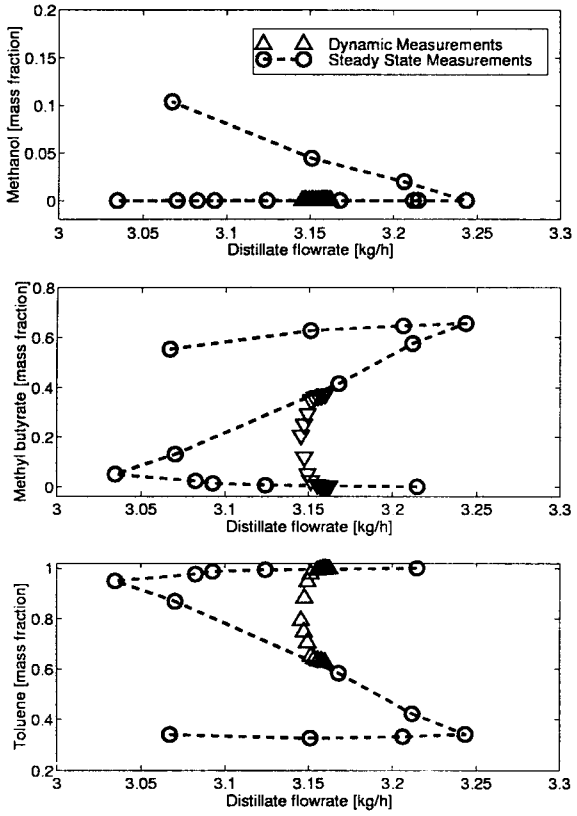

Fig. 1. Measured steady-state bottoms compositions together with the measured bottoms compositions during the transient (Dorn *et al.*, 1998).

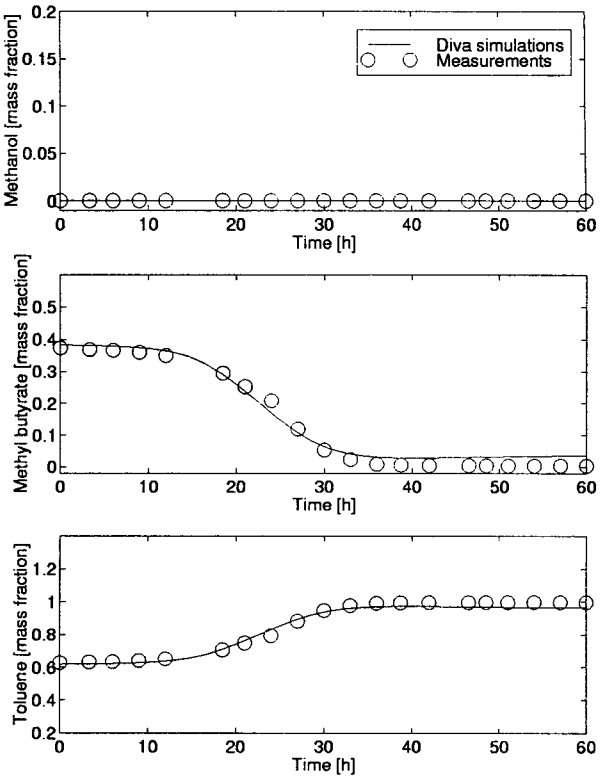

Fig. 2. Measured and simulated composition of the bottoms during the transient from an unstable to a stable steady state on the high branch (Dorn *et al.*, 1998).

plicities of type II according to the classification by Güttinger *et al.* (1997) which are caused by the vapor-liquid equilibrium (VLE) will be considered. This type of multiplicities can be predicted from minimal data with the ∞/∞ analysis (Bekiaris *et al.*, 1993) (first conjectured by Petlyuk and Avet'yan (1971)). This type of multiplicities has been verified experimentally (Güttinger *et al.*, 1997; Müller and Marquardt, 1997) and is now widely accepted.

A directly related dynamic phenomenon is the instability of steady states. It has been studied both in simulation and experiment (Dorn *et al.*, 1998). Figures 1 and 2 show a measured transient of a column separating the mixture methanol–methyl butyrate–toluene. After steady-state operation at an open-loop unstable steady state was achieved, the stabilizing controller was switched off. Clearly, the plant diverges from the unstable to a stable steady state on the high branch.

In addition to multiple steady states, another well known phenomenon which nonlinear systems can exhibit is branching to periodic solutions which accompany sustained oscillations (limit cycles). However, in spite of significant nonlinearities in the distillation models, all the solutions discovered so far are stationary. Until now, no periodic solution has been associated with any clas of open-loop column models while it has been well recognized in the chemical reactor literature for several decades. In this context, *"Open-loop"* means that only the pressure and level control loops are closed under perfect control. The evidence of other behavior such as underdamped oscillation has also been rare whereas it commonly occurs in other nonlinear systems.

Recently, some oscillatory behavior has been observed in experiments. Sundmacher and Hoffmann (1995) reported sustained oscillations in a packed column for MTBE production as well as for nonreactive distillation of methanol and isobutene. Wang *et al.* (1997) observed oscillatory behavior in a pilot-scale column for the azeotropic distillation of cyclohexane– isopropyl alcohol–water. However, the accompanying dynamic simulations did not reproduce the oscillations. Thus it is unclear whether the oscillations observed were caused by system nonlinearities in the vapor-liquid equilibrium or just by unmeasured control actions and peculiarities in the experimental setup. Simulations by Jacobsen and Skogestad (1994) demonstrated Hopf bifurcations and limit cycles in the distillation of methanol and propanol. However, those were caused by interactions of the level controllers and the column.

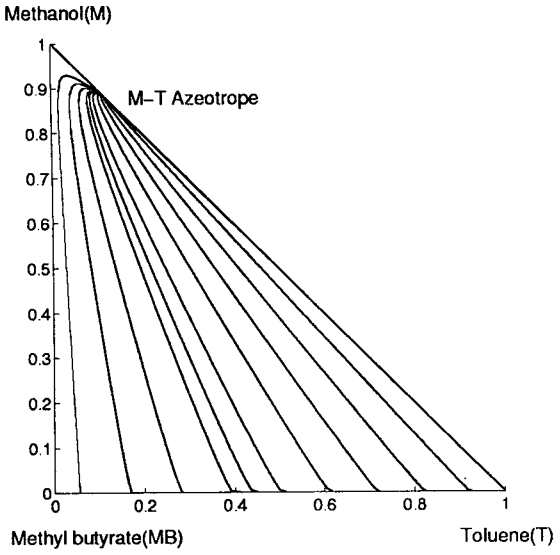

Fig. 3. Residue curve diagram (mole fractions) of the ternary mixture methanol(M)–methyl butyrate(MB)–toluene(T) at $p = 1$atm.

In light of these discussions, it is natural to ask whether open-loop distillation is able to exhibit periodic solutions (Hopf-bifurcation).

In this paper, the presence of periodic solutions in an open-loop distillation model is demonstrated through the simulation of the azeotropic distillation of methanol–methyl butyrate–toluene. In the next section, we describe the dynamic model used in the simulations. Finally, we present results of the nonlinear dynamic simulations and the bifurcation analysis of the column.

2. SIMULATION SETUP

2.1 *Mixture*

The ternary homogeneous mixture methanol(M)–methyl butyrate(MB)–toluene(T) used in the experimental study by Güttinger *et al.* (1997) is chosen here. The mixture belongs to the clas 001 according to Matsuyama and Nishimura (1977). The residue curve diagram for the mixture is given in Figure 3. The binary M–T azeotrope is located at 88 mole % methanol.

2.2 *CMO Model*

In order to focus on the nonlinear behavior caused by the vapor–liquid equilibrium, a constant molar overflow (CMO) model is used. Several assumptions are made in the model including: (1) constant molar overflow (neglect energy balances); (2) constant molar liquid hold-up on the trays, the condenser and reboiler; (3) negligible vapor hold-up; (4) total condenser without subcooling; (5) saturated feed; (6) constant column pressure and no pressure drop between trays; (7) tray efficiency of 1.

The vapor phase is assumed to be ideal and the vapor pressures are calculated with the Antoine equation. The liquid activity coefficients are computed using the Wilson model. The thermodynamic parameters are taken from Güttinger *et al.* (1997).

For the dynamic simulations, the CMO model is integrated using DDASSL (Stewart *et al.*, 1995). AUTO (Doedel and Wang, 1994) is used for a steady-state bifurcation analysis of the CMO model. To investigate the local dynamic behavior and stability, the eigenvalues are calculated with LAPACK (Anderson *et al.*, 1995) by linearizing the nonlinear CMO model at every steady state. Because of the delicate nature of the dynamic problem under study, special attention was paid to numerical computation; all the routines used were in double precision with sufficiently tight tolerances.

In all simulations, compositions and flow rates are specified on a *"molar"* basis so that any effect due to the nonlinear relationship between the mass and molar flow rates (Jacobsen and Skogestad, 1991) is excluded.

3. SIMULATION RESULTS

3.1 ∞/∞ *Prediction and Steady State Simulation*

First, the ∞/∞ analysis was applied for a quick preliminary bifurcation analysis. From the ∞/∞ analysis, it is conjectured that for the given system class the maximum product flow rate range for multiplicity is achieved as the feed composition tends to the binary M–T azeotrope. Thus, the feed composition was chosen such that a large multiplicity range would exist.

The bifurcation diagrams predicted by the ∞/∞ analysis are shown in Figures 4 and 5 (solid lines). The distillate flow rate was used as the bifurcation variable. In the same Figures, the steady state solution branches calculated with the CMO model are given. Since the column is operated at finite reflux and has a finite number of trays, there are some quantitative differences between the ∞/∞ predictions and the simulations with the CMO model (specifically, close to one turning point). However, the results are in good qualitative agreement.

3.2 *Bifurcation Analysis and Dynamic Simulations*

Figure 6 shows the bifurcation diagram based on the computations from AUTO and eigenvalue

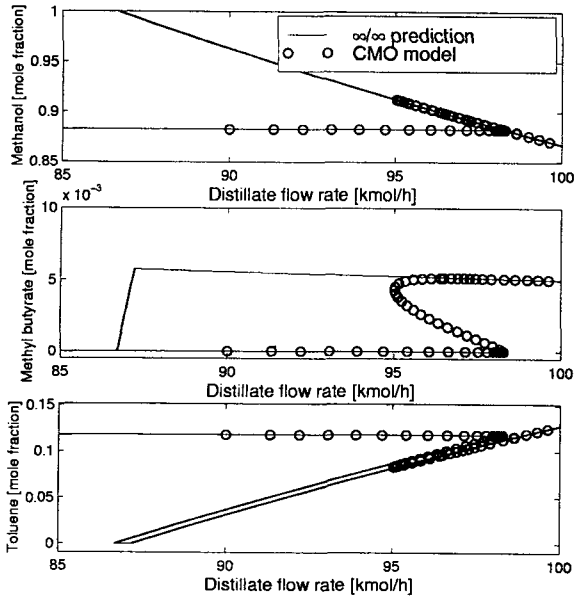

Fig. 4. Steady-state bifurcation diagram showing the distillate compositions as a function of the distillate flow rate.

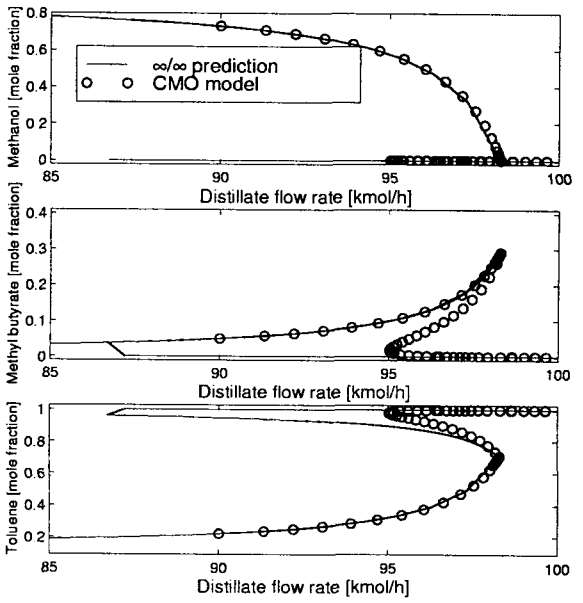

Fig. 5. Steady-state bifurcation diagram showing the bottom compositions as a function of the distillate flow rate.

calculations. For the bifurcation diagram, the weighted average temperature of all trays, the reboiler, and the condenser is chosen as a scalar index for the state variables of the column:

$$T^{\text{avg}}(t) = \frac{\sum_{j=1}^{N} T^j(t) M^j}{\sum_{j=1}^{N} M^j},$$

In Figure 6 one can see two turning points (L_1 and L_2) which accompany multiple solutions. This type of bifurcation is well recognized in distillation. An interesting new type of bifurcation

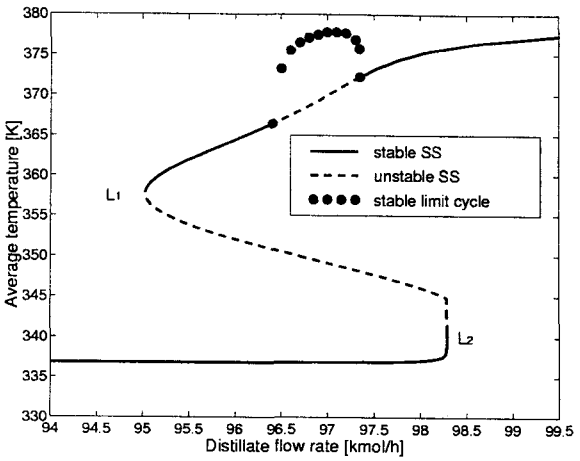

Fig. 6. Steady state bifurcation (CMO model) showing the average temperature in the column.

observed here is the Hopf bifurcation. The upper branch bifurcates to limit cycles for $D/F \in (0.9641, 0.9735)$. The limit cycles are plotted as solid dots in Figure 6. The distance of the dots from the steady state branch depicts half of the difference between the maximum and minimum average temperatures during the sustained oscillation and thus indicates the amplitude of the limit cycle.

Let us now proceed to a detailed discussion of the dynamic behavior as D/F is varied from 0 to 1. The qualitatively different kinds of dynamic behaviors caused by the existence of one or three steady states which can be stable or unstable nodes, saddles, foci etc. are illustrated with dynamic simulations. For selected values of the bifurcation parameter, nonlinear dynamic simulations were carried out starting from different unsteady initial conditions. The average liquid composition in the column

$$x_c^{\text{avg}}(t) = \frac{\sum_{j=1}^{N} x_c^j(t) M^j}{\sum_{j=1}^{N} M^j},$$

is plotted in the composition space in Figures 7.a-e. The average liquid composition x_c^{avg} is a normalized measure of the column inventory of component c.

D/F<0.9502: One steady state

For values of D/F to the left of the turning point L_1, only a single stable steady state exists. Figure 7.a shows selected phase plane trajectories for $D/F = 0.945$. The column has a single stable node (no oscillation) in this particular case.

0.9502<D/F<0.9641: Three steady states (Oscillation)

In this part of the region of multiplicity, the

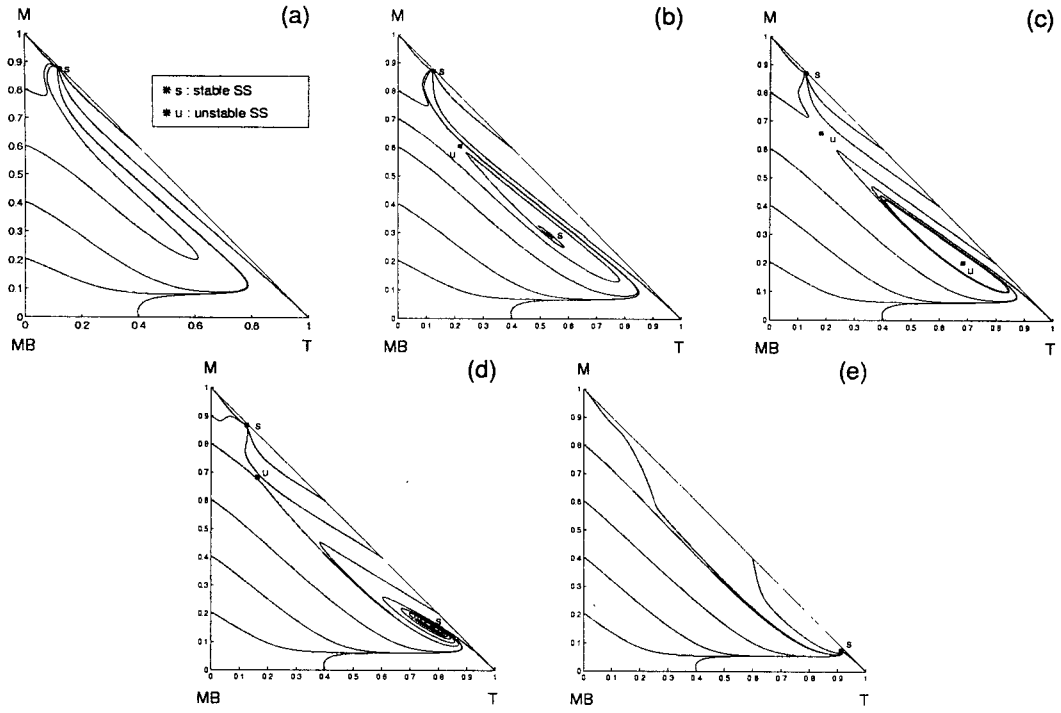

Fig. 7. Phase diagrams of the average liquid composition in the column (corresponding to different regions in Fig. 6). (a) $D/F = 0.945$, (b) $D/F = 0.962$, (c) $D/F = 0.97$, (d) $D/F = 0.974$, (e) $D/F = 0.99$.

steady states on the low and high branch are stable and those on the intermediate branch are unstable. As illustrated in Figure 7.b for $D/F = 0.9620$, the trajectories converge to either the stable node or the stable focus. The stable node corresponds to the steady state on the low branch. An interesting observation is the appearance of the focus corresponding to the stable steady state on the high branch which has been rarely observed in open-loop distillation.

0.9641<D/F<0.9735: Three steady states (Limit Cycle)

For values of the bifurcation parameter in this region, branching to periodic solutions occurs, the steady state on the upper branch becomes unstable and a limit cycle grows around it. Therefore, two types of attractors exist for values of D/F in this region: a stable node and a limit cycle. Figure 7.c illustrates a phase plot corresponding to this case. A pronounced stable limit cycle surrounds the unstable steady state on the high branch. The bifurcation is supercritical in this case as the resulting limit cycle is stable.

Figure 8 shows the time domain responses of the average liquid composition in the column to a small perturbation in D starting from the unstable steady state on the high branch for $D/F = 0.9700$. The period of oscillation is $\approx$ 110h. The instability and limit cycle related to the Hopf bifurcation also appear in each state variable of the column with various nonlinear patterns. Figure 9 illustrates the phase plane response of the actual

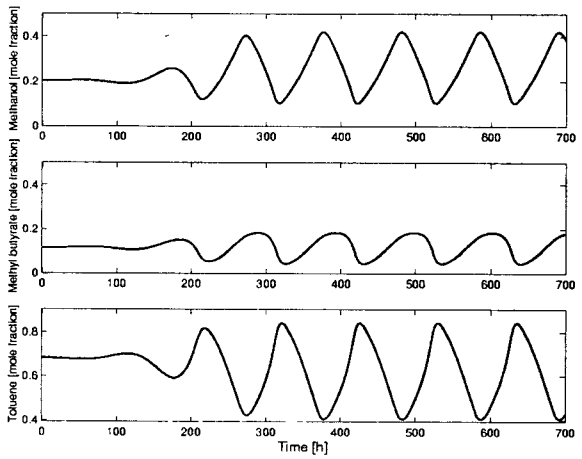

Fig. 8. Response of average liquid composition in the column starting at an unstable steady state on the high branch for $D/F = 0.97$ (see also Fig. 7.c).

liquid composition on tray 12. The variables eventually reach a limit cycle with asymmetric shape. Figure 10 shows the corresponding time domain responses of temperature and liquid composition on tray 12. The response of the methyl butyrate fraction shows a periodicity with double peak as expected from the sickle shape of the limit cycle in Figure 9. During each period of the oscillation, the composition varies significantly, e.g. the methanol mole fraction between 0.002 and 0.9606. In Figure 11, the movement of the temperature front inside the column during the oscillation is given at intervals of $\Delta t = 10$h. Note that the velocity and shape of the front moving up and down is different.

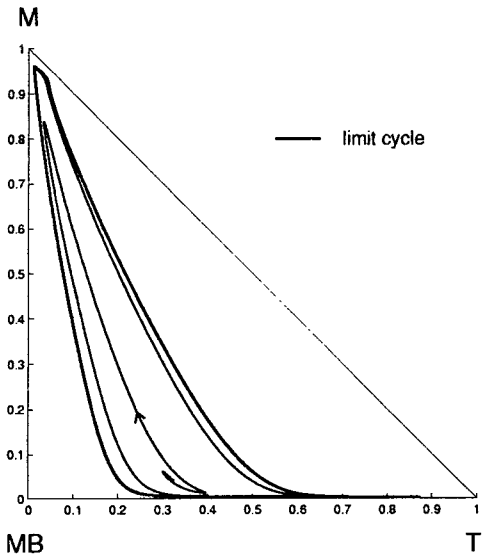

Fig. 9. Phase plot of liquid composition on tray 12 starting at an unstable steady state on the high branch for $D/F = 0.97$ (see also Fig. 7.c).

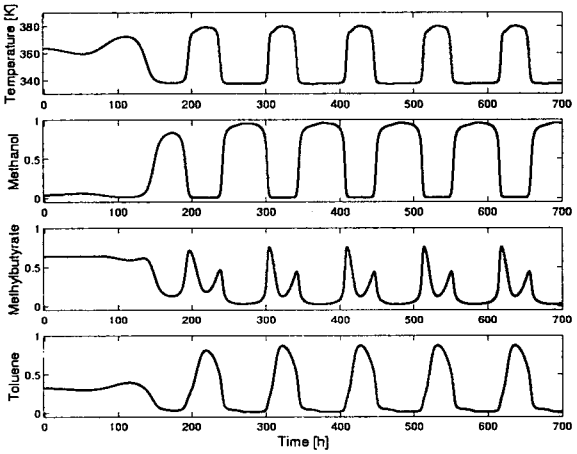

Fig. 10. Responses of temperature and liquid mole fractions on tray 12 starting at an unstable steady state on the high branch for $D/F = 0.97$ (see also Fig. 7.c).

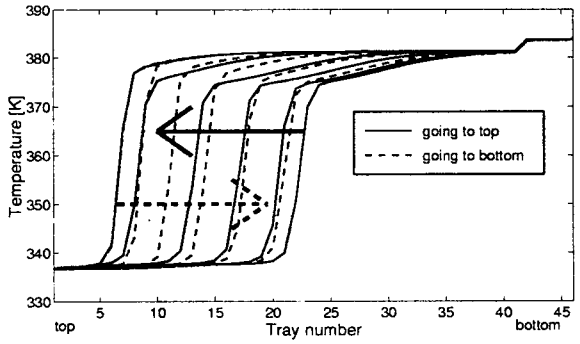

Fig. 11. Temperature profiles ($\Delta t = 10$h) during the sustained oscillation.

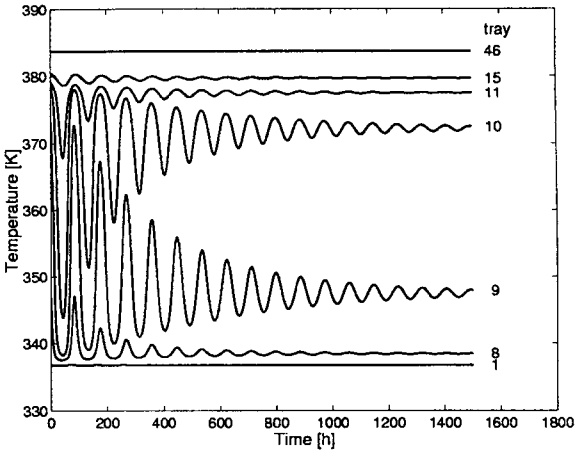

Fig. 12. Responses of the tray temperatures to the step decrease in D from $D/F = 0.976$ to $D/F = 0.974$.

0.9735<D/F<0.9828: Three steady states (Oscillation)

In this region, the limit cycle disappears and the steady state on the high branch is stable again. Phase plane trajectories for this case are shown in Figure 7.d. Three steady states exist: one stable node, one saddle, and one stable focus. The phase pattern is qualitatively the same as that in Figure 7.b, but in this case the column shows more severe oscillatory behavior with a larger region of attraction around the stable focus.

Figure 12 shows the time responses of selected tray temperatures when the distillate flow rate is decreased from steady-state operation at $D/F = 0.9760$kmol/h to $D/F = 0.9740$kmol/h at $t = 0$. The oscillation also appears in the temperature profiles: The temperature front of the column approaches the steady state position in an oscillatory manner (not illustrated).

0.9828<D/F: One steady state

For values of D/F to the right of the turning point L_2, only one stable steady state exists on the high branch. It is observed that the underdamped oscillatory phenomena continue somewhat after the bifurcation parameter is increased to values outside the region of multiplicity and finally disappear. Figure 7.e illustrates the phase trajectories when $D/F = 0.9900$. Only one steady state exists in the form of a stable node.

4. CONCLUSIONS

In this paper, we study the dynamic behavior of a ternary homogeneous azeotropic distillation column with the CMO model. Our computations reveal several interesting nonlinear phenomena not reported in previous studies of distillation: a Hopf bifurcation is found. Thus, the column ex-

hibits periodic oscillations over the corresponding region. The sustained oscillations result in periodic movements of the profiles inside the column. The column also shows significant underdamped responses over a wide range of conditions.

5. NOTATION

F	Molar feed flow rate
D	Molar distillate flow rate
L	Molar reflux flow rate
x_c^j	Molar liquid fraction of component c on tray j
T^j	Temperature on tray j
M^j	Molar liquid holdup on tray j
N	Number of trays

ACKNOWLEDGMENT

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