

# Steady State Multiplicity of Novel Reactive Distillation Combined Distillation Column with Side Reactors for the Production of Cyclohexyl Acetate

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Multiple steady states (MSS) of a novel reactive distillation combined distillation column with side reactors for the production of cyclohexyl acetate were theoretically studied. A set of steady-state solution branches for product content in the column bottom with the variation of reboiler heat duty were tracked based on the "Sensitivity" and "Design Specs/Very" functions in ASPEN PLUS. For identical module and feed specifications, three distinctly different composition profiles corresponding to high/medium/low conversion of cyclohexene respectively were obtained. The main variables that affect the steady state behavior are the reboiler heat duty and the number of stripping stages. To explore the physical explanation of the MSS in the integrated process, residual curve analysis was presented in both the actual and ideal ternary systems for comparison. The bottom-product point is not singular and a distillation trajectory can pass through the material balance curve, which explains the existence of MSS.

## 1. Introduction

Reactive distillation (RD) coupling chemical reaction and distillation separation in a single unit operation has attracted much attention. By operating reaction and separation simultaneously, RD has advantages such as improvement of conversion or selectivity (Edreder et al., 2015) and reduction of energy or equipment costs than conventional multistep process (Kiran et al., 2015). However, the design of RD is more complex than its nonreactive counterpart due to the nonlinear behavior of process models and the simultaneous physical and chemical equilibrium, which may cause multiply steady states (MSS) (Yamaki et al., 2012).

To design a RD process, it's important to discover if all MSS within the practical domain of operating variable are desirable and how the column responds to changes in operation variables, which facilitate subsequent studies like optimization and control. Two computational methods, namely oriented-equation models and modular models, have been reported to detect and analyze MSS for chemical processes including RD. While working with equation-based models, it's possible to use continuation algorithms included in packages such as gPROMS (Kang et al., 2016). Although modular simulators don't allow detailed nonlinear analysis, the aim of several works has been to develop procedures for the construction of bifurcation diagrams in modular simulators like ASPEN PLUS (Cárdenas-Guerra et al., 2010).

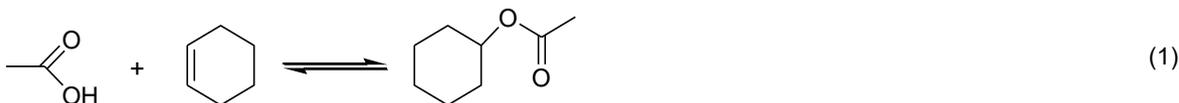
Despite the numerous publications reporting the MSS in RD, little papers discuss the specific causes. Rodríguez et al. (2004) noted that MSS is caused by interaction between reaction and separation in systems with sufficiently large activation energy and boiling temperature versus composition gradient. Katariya et al. (2006) considered feed condition and Damköhler number as important parameters that had influence on the existence of MSS in RD for TAME synthesis. Jaime-Leal et al. (2013) found that the reflux ratio, the reboiler duty and the feed condition affected the presence of MSS in the RD for production of fuel ethers. The cause of MSS for each specific reaction system may be different, and a universal explanation is lacking.

Cyclohexyl acetate (CA) is an alternative intermediate in the indirect hydration route for the cyclohexanol synthesis from cyclohexene via cyclohexyl carboxylate proposed by Imam et al. (2013). In this work, MSS of a novel reactive distillation that combines distillation column with side reactors (DCSR) for the production of CA

were theoretically studied. A procedure for multiplicity analysis in ASPEN PLUS based on bifurcation diagrams is presented. Specifically, residual curve analysis was presented in both the actual and ideal ternary systems for comparison to explore the physical explanation of the MSS in the integrated process.

## 2. Process and simulation

This study is based on the production of CA via DCSR process using the reaction between acetic acid (AA) and cyclohexene (CH). The achievable conversion in this reversible reaction is limited by the chemical equilibrium. The esterification of AA with CH follows the elementary reaction below:



A heterogeneous catalyst, e.g. a strong acidic macro porous ion exchange resin, can be used for the addition esterification of CH and AA. Chen et al. (2015) established a LHHW macrokinetics model to describe the kinetics of CA synthesis catalyzed by sulfonic acid type styrene cation exchange resin (D006) and the rate equation is as follows:

$$r_{CA} = \frac{5.33 \times 10^9 \exp\left(\frac{-93.06}{RT}\right) \left( c_{AA} c_{CH} - \frac{c_{CA}}{\exp\left(\frac{4873}{T} - 13.813\right)} \right)}{(1 + 0.0437c_{AA} + 0.2277c_{CH} + 0.0992c_{CA})^2} \quad (2)$$

Figure 1 shows a schematic diagram of DCSR process for CA production. The lighter CH and AA moves toward the top and the heavier CA move to the bottom as product. Several stages in the reaction section are linked with side reactors. The total liquid stream leaving the special stage is completely rerouted through a side reactor before it is fed back to the stage below. The column contains 6 stages, a reboiler and a total condenser. Both CH and AA are fed to the first side reactor with a stoichiometric ratio. In each reactor 0.5 kg of catalyst is introduced and the reaction rates are calculated with a CSTR model. The vapor-liquid equilibrium was calculated with NRTL model due to the strong non-ideality of the reactive mixture. The design and operating parameters for the base case are shown in Figure 1.

## 3. Multiplicity analysis

### 3.1 Tracking MSS

Cárdenas-Guerra et al. (2010) proposed the approach to detect MSS in RD using the built-in sensitivity tool of ASPEN PLUS. The region of output multiplicity can be detected by the two turning points with increasing and decreasing reboiler duties ( $Q_R$ ). Figure 2a shows that two steady states occur in a range of  $Q_R$ . The low and high solution branch can be obtained when  $Q_R$  is increased from 50 W to 350 W and decreased from 350 W to

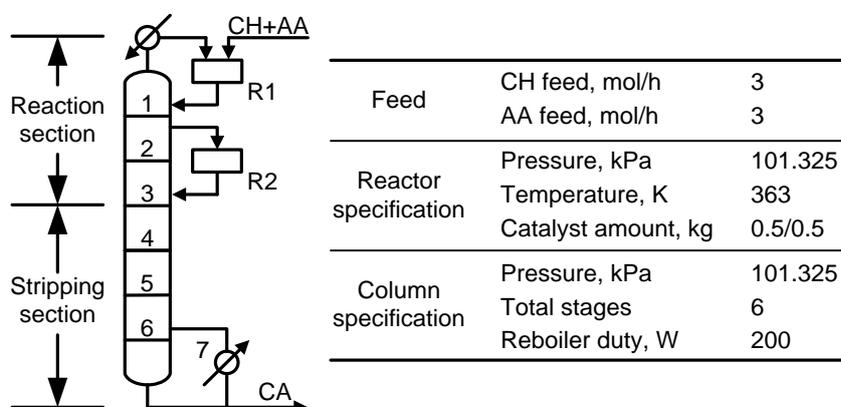


Figure 1: Flowsheet of a DCSR process for the CA production

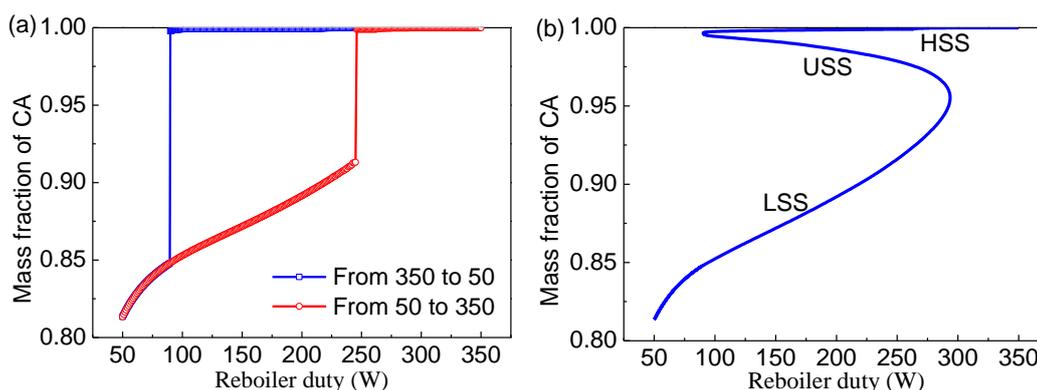


Figure 2: Output multiplicities for a variation of reboiler duty: (a) "Sensitivity"; (b) "Sensitivity" and "Design Specs/Vary"

50 W. However, it's found that even if good initializations are provided for the modules, and sensitivity analysis is performed with small steps, the simulations to find the medium solutions fail to converge. That is to say, sensitivity analysis is not always very effective in tracking the unstable steady-state solution branch.

In this paper, a novel strategy using the "Design Specs/Vary" function is proposed to track the unstable steady-state solutions. The strategy is based on the fact that there is only one input variable for an output variable associated with it in the typical output multiplicity. It lays out as follows: first, one of the process variables such as the mass fraction of CA at the bottom is assigned as the "Design Specs", and the bifurcation parameter  $Q_R$  is adjusted as the "Vary" to meet this specification; then the specified value of the process variable is adjusted continuously with very small steps, and the corresponding  $Q_R$  is obtained as it was done in the first step. In all these cases, the temperature and composition profiles simulated in the last one are supplied to accelerate the convergence of the next. Finally, the unstable steady-state solution can be traced, and the USS branch is plotted using the simulated results. A typical S-shaped bifurcation curve of three steady state solution branches can be obtained based on the "Sensitivity" and "Design Specs/Vary" functions in ASPEN PLUS as shown in Figure 2b. For identical specifications, three different column profiles corresponding to high/medium/low conversion of CH respectively are obtained. The temperature and liquid composition profiles of the distillation column for the three steady states of the case  $Q_R = 200$  W are shown in Figure 3. These steady states differ considerably not only with regard to their product concentration in the bottoms but also with regard to the temperature and compositions profile inside the column. For the LSS branch, with the exception of sharp changes in the reboiler, the temperatures rise slowly from the top to the bottom. The composition of tower top is very close to that of the CH-AA azeotrope. The liquid compositions on the upper stages are almost unchanged while a drastic change is observed near the bottom. For the HSS branch, the temperatures and liquid compositions change significantly in the reactive section. The column shows excellent separation performance, thus CA of high purity (99.7 wt %) is obtained at the bottom. For the USS branch, the column profiles are similar to that of LSS, but the column performs better and the product stream is mainly composed of CA (98.6 wt %).

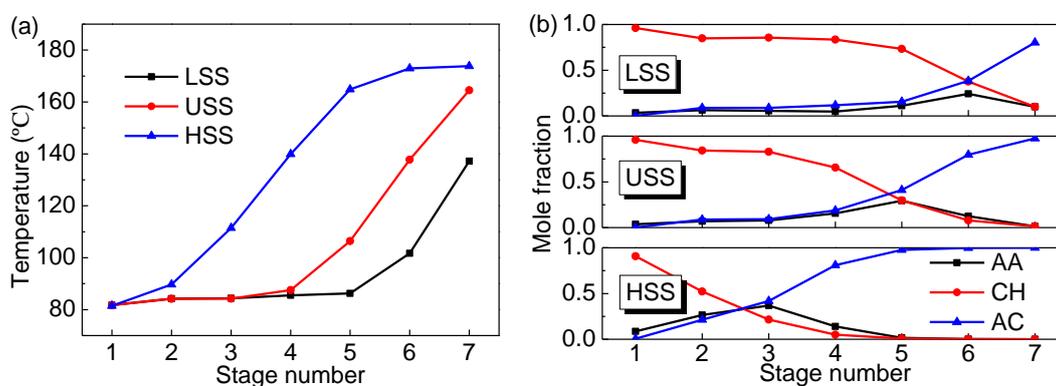


Figure 3: (a) Temperature and (b) liquid composition profiles for three steady states at  $Q_R = 200$  W

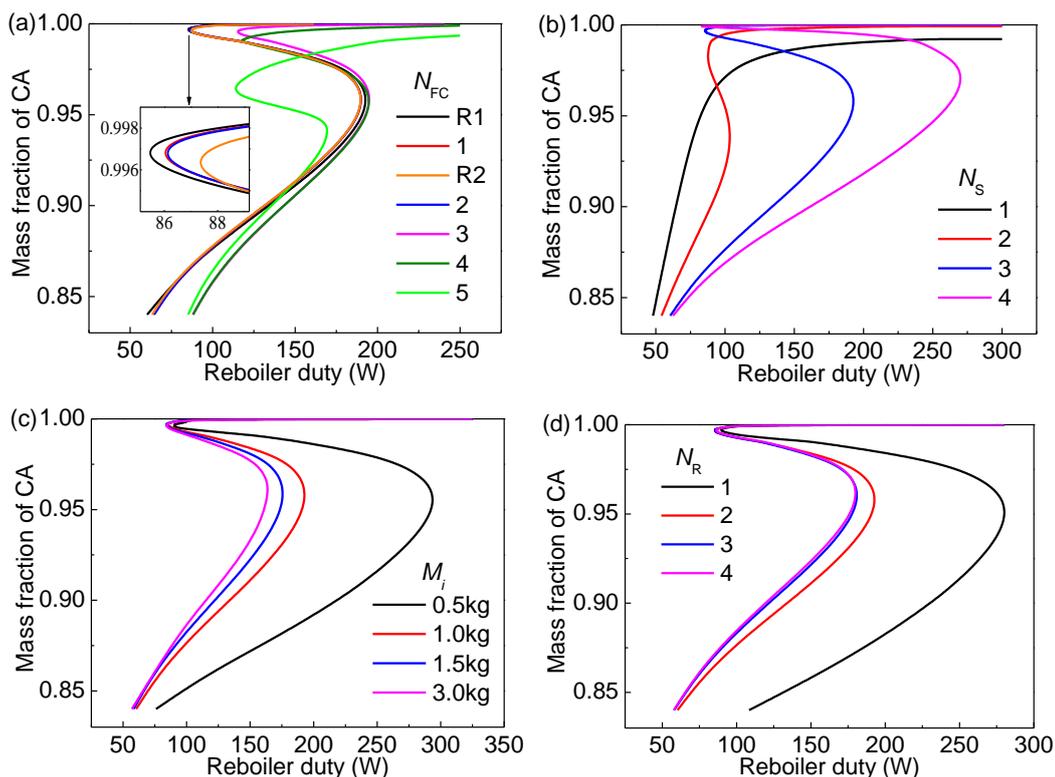


Figure 4: Effect of design parameters on the mass fraction of CA at the bottom with respect to reboiler duty

### 3.2 Parameters analysis

As RD involves the combined effects of reaction and distillation, many design parameters are relevant to MSS. Therefore, it's necessary to study these parameters to know in which operating region a DCSR process is operating, to understand how the column will respond to changes in operating variables. Effects of the feed location of CH ( $N_{FC}$ ), the number of stripping stages in the separation section ( $N_s$ ), the catalyst loading amount in each side reactor ( $M_i$ ) and the number of the side reactors ( $N_R$ ) on the mass fraction of CA in the bottom with respect to  $Q_R$  are investigated as shown in Figure 4.

A judicious choice of the feed location can lead to improved column performance. The feed location of highly volatile CH was moved from the first side reactor to the last stage of the base case. For all cases, MSS is detected in different range of  $Q_R$  as shown in Figure 4a. A less  $Q_R$  corresponding to the lower turning point of the MSS region is needed if CH fed to the top. This is expected, as both CH and AA are fed into the side reactors, so the large reaction capacity and concentration difference contribute to raising conversion.

The separation zone is introduced in the column to separate the desired product CA and keep it away from the reaction zone. The bifurcation diagrams given in Figure 4b are calculated for columns with different  $N_s$ . It is shown that even in a comparatively short column with  $N_s = 2$  steady state multiplicities occur in a larger range of  $Q_R$  with  $N_s$  increasing. Only when the  $N_s$  is further decreased to 1, the solution multiplicity finally reduces to a unique steady state.

The variation of  $M_i$  from low to high values relates to a physically motivated continuation from reaction equilibrium. The effect of  $M_i$  on the bifurcation diagram is shown in Figure 4c. At  $M_i = 0.5$  kg corresponding to the operating point, three steady state are found. While increasing  $M_i$ , multiplicity behavior still exists and shrinks into narrower distribution area.

The effect of  $N_R$  on the system performance is discussed here. Each side reactor loads the same amount of catalyst, namely 0.5 kg. MSS is unavoidable but their distribution areas tend to narrow while increasing  $N_R$  from 1 to 4 as shown in Figure 4d. It can be shown that the process with two reactors can display the most satisfactory system performance.

Given all this, those parameters have great effects on the distribution of MSS with respect to  $Q_R$ . Moreover, parameters related to the separation performance of column such as  $Q_R$  and  $N_s$  influence the number of steady states, which may provide some inspiration for understanding the sources of MSS.

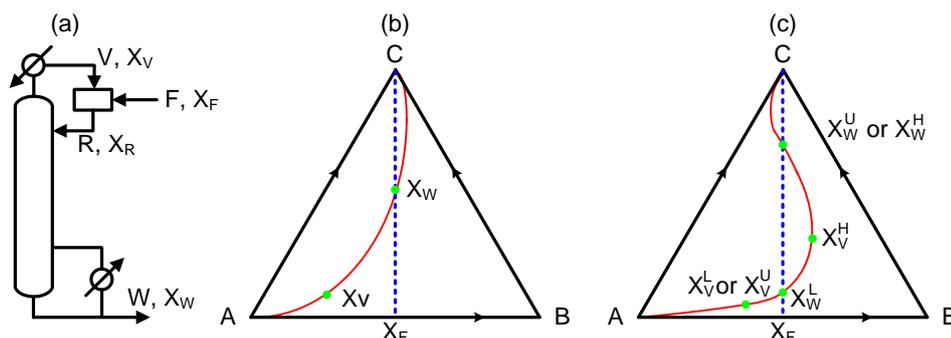


Figure 5: (a) Flowsheet of a DCSR process for the reaction system  $A+B\leftrightarrow C$ ; distillation lines in the concentration triangle: (b) ideal ternary system ( $\alpha_{ij} = \text{const}$ ) and (c) actual ternary system

### 3.3 Cause analysis

To explore the physical cause of the MSS in the DCSR process, residual curve analysis was presented in both the actual and ideal ternary systems for comparison. Firstly, let us consider a simplified system (Figure 5a) involving a distillation column with only one side reactor in which an  $A+B\leftrightarrow C$  reversible reaction occurs. The boiling temperatures increase in the order  $T_A < T_B < T_C$ . For a stoichiometric mixture of the reactants, two variants of the residual curve map are possible, which differ in the number of steady states. The number of steady states depends on the number of intersection of residual curve and material balance line (red solid line and blue dotted line in Figure 5). A single steady state is observed for an ideal ternary system with constant relative volatilities. In this case, the trend of the distillation lines (Figure 5b) is such that moving along a line away from the bottom-product point brings the recycle composition point to the region of high concentrations of A (close to the vertex A of the concentration triangle). If the ternary system is nonideal, the residual curves may be S-shaped (Figure 5c). In this case, there are two intersections between residual curve and material balance line, resulted in two possible bottom-product points in the same condition. The distillation lines may pass through the material balance line or even the recycle point may occur in the region rich in B, thus, three steady states are feasible, of which two are characterized by a higher conversion of the reactants. Overall, the trend of residual curves affects the existence of MSS in the system.

Concerning the CH-AA-CA system, the column composition distributions corresponding to different  $Q_R$  cases are shown in Figure 6. Figure 6a shows the distillation trajectories of an imaginary ideal CH-AA-CA system realized by setting the property method as "IDEAL". The mass fraction of CA in the bottom increases monotonously with increasing  $Q_R$  from 50 W to 250 W. Consistent with the residual curve analysis in Figure 5b, all the composition points of the tower top are distributed in the region of high concentrations of CH. However, MSS and diversified distillation trajectories can be found in the actual CH-AA-CA system as shown in Figure 6b. For the case  $Q_R = 150$  W, three distillation trajectories corresponding to three steady states exhibits great differences. Distillation trajectories 150W-L and 150W-U differ only slightly with regard to their compositions in the tower top but differ considerably with regard to the bottom-product point. Note that distillation trajectory 150W-U passes across the material balance line, which means that there is another possible bottom-product point in the same condition. The existence of this point is further confirmed by the fact that distillation trajectory 150W-H starts from the region rich in AA and ends with high concentration of CA.

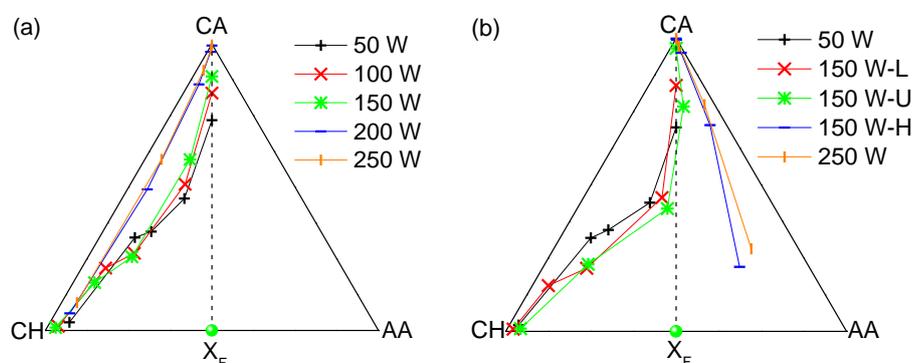


Figure 6: Distillation trajectories of the system  $CH+AA\leftrightarrow CA$ : (a) imaginary ideal system; (b) actual system

It's concluded that MSS occurs because the simultaneous physical and chemical equilibrium of the nonideal ternary system makes it possible for the DCSR process that two available bottom-product points and three different distillation trajectories can be developed in the same configuration and specification. These different distillation trajectories result in different conversions of reactants: HSS correspond to distillation trajectories starting near the region rich in middle component, namely AA in the system; LSS correspond to distillation trajectories starting from CH-AA azeotrope, which is poor in AA; USS correspond to distillation trajectories passes across the material balance line, although their starting points are similar to that of LSS.

#### 4. Conclusions

In this article, MSS of a DCSR process for the production of CA is studied. Three steady-state solution branches for product content in the bottom with the variation of  $Q_R$  were tracked based on the "Sensitivity" and "Design Specs/Very" functions in ASPEN PLUS, which performs better in detecting unable solutions than the conventional method only using "Sensitivity". Three steady states corresponding to high/medium/low mass fraction of CA in the bottom, for example 89.2%, 98.6% or 99.7% respectively, differ by dramatic changes in the temperature and composition profiles within the column in the same condition. Design parameters, such as  $Q_R$ ,  $N_{FC}$ ,  $N_S$ ,  $M_i$  and  $N_R$ , have great effects on the MSS distribution with respect to  $Q_R$ . Moreover,  $Q_R$  and  $N_S$  affect the number of steady state, implying that the existence of MSS is closely related to the distillation operation. In particular, residual curve analysis was presented in both the actual and ideal ternary systems for comparison to explore the physical explanation of MSS in the integrated process. Results suggest that the trend of residual curves affects the existence of MSS in the ternary system. The number of steady states depends on the number of intersection of residual curve and material balance line. MSS in the CH-AA-CA system arises from the nonideal VLE showing an S-shaped residual curve, and two bottom-product points and three distillation trajectories are feasible in the same configuration and specification.

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