

Simulation and Analysis on Multiple Steady States of an Industrial Acetic Acid Dehydration System*

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Abstract In this work, an industrial acetic acid dehydration system *via* heterogeneous azeotropic distillation is simulated by Aspen Plus software. Residue curves are used to analyze the distilling behavior, and appropriate operating region of the system is determined. Based on steady states simulation, a sensitivity analysis is carried out to detect the output multiple steady states in the system. Different solution branches are observed when the flow rates of the feed stream and the organic reflux stream are selected as manipulated variables. The performance of the column under different steady states is different. A method is proposed to achieve the desired steady state.

Keywords acetic acid dehydration, heterogeneous azeotropic distillation, residue curve, multiple steady states

1 INTRODUCTION

Acetic acid (HAc) dehydration is an important operation in the production of aromatic acids, such as pure terephthalic acid (PTA). Although acetic acid and water do not form an azeotrope at atmospheric pressure, using conventional distillation to separate these two components will require more investment and operating costs. Because the system has a tangent pinch on the pure-water end, it is customary to use an entrainer *via* a heterogeneous azeotropic distillation column for the separation.

However, it is difficult to understand and operate heterogeneous azeotropic distillations [1–3]. The phenomenon of multiple steady states (MSS) is one of the features of heterogeneous azeotropic distillation, and its existence has been demonstrated experimentally [4–7]. Bekiaris *et al.* have presented a thorough review on multiple steady states in distillation and given the definition of output multiple steady states [8]. By multiple steady states in a distillation column we refer to output multiplicities, that is, different product compositions are obtained at steady state for the same operating parameters [7].

Most of the studies about MSS focused on the prediction or simulation of MSS, such as homogeneous azeotropic distillation [7, 9], heterogeneous azeotropic distillation [3, 5, 6, 10, 11], and reactive distillation [12–15]. Little attention was paid to how to achieve the desired steady state. Benz *et al.* [16] studied the attainment of desired or undesired products by applying different start-up strategies when operated with benzene-heptane-acetone mixture. Different steady states were reached with different start-up configurations or policies. Chien *et al.* [11] mentioned that, in practical situation, the desired steady state should be achieved by starting up the column normally with conservatively high reflux and heat duty and then de-

creasing reflux and heat duty slowly, but no explanation was presented. We intend, in this paper, to explain this behavior through the simulation and analysis of the MSS and the method to approach the desired steady state in process simulation will be discussed.

2 DESCRIPTION AND ANALYSIS OF INDUSTRIAL PROCESS

2.1 Industrial process unit

In this study, an industrial process for HAc dehydration *via* heterogeneous azeotropic distillation, which is an important operation in the production of pure terephthalic acid (PTA), is investigated. The process designed according to Mitsui technology is sketched in Fig. 1. It consists of a heterogeneous azeotropic distillation column (T501), a cooler (HX501) and a common decanter (FLS1). The feed (stream 1) comes from the oxidation reactor unit. Its composition includes HAc, H₂O and small amounts of methyl acetate (MA) and *p*-xylene (PX). The desired product, HAc, is collected at the bottom of the T501

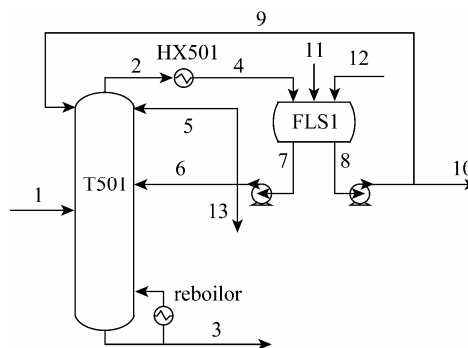


Figure 1 Flowchart of azeotropic distillation system

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column (stream 3), whereas the minimum temperature of water-normal butyl acetate (NBA) heterogeneous azeotrope exits at the top of T501. The top vapor of the heterogeneous distillation column, after condensation to a temperature of 40 °C, enters the decanter and is separated into two liquid phases. The organic phase containing mostly NBA is split into two parts (stream 6 and stream 7), which are recycled to the first and 27th stage of the column as refluxes. The aqueous-phase liquid is mostly drawn off as the distillate (stream 10) and is fed into regenerating column to recover the NBA and MA. Only a small quantity of aqueous phase (stream 9) refluxes back to the dehydration column at the first stage to meet the purity specifications of acetic acid in the distillation products. In the regenerating column, high-purity water is collected at the bottom and the solvent (NBA) is back to the decanter (stream 11). A small amount of pure NBA (stream 12) is also added into the decanter to balance the small loss of NBA through the bottom stream of azeotropic distillation column.

2.2 Analysis of the azeotropic distillation column

In the production process of pure terephthalic acid, tiny amounts of impurities PX and MA may also enter the acetic acid dehydration distillation column, along with acetic acid and water. In order to study the influence of PX and MA on the distillation, a system including impurities (system 1) and a system without impurities (system 2) will be simulated separately. In system 1, three components can form only one minimum boiling binary azeotrope. Fig. 2 illustrates the residue curve map with the binodal curve of LLE for the NBA-H₂O-HAc ternary mixture. The binary azeotrope NBA-H₂O (Z , boiling temperature 90.94 °C at 101.325 kPa) is between H₂O (100 °C) and NBA (126.11 °C). The azeotrope is an unstable node, the H₂O and HAc (117.9 °C) pure component corners are saddles, and the NBA corner is a stable node. The

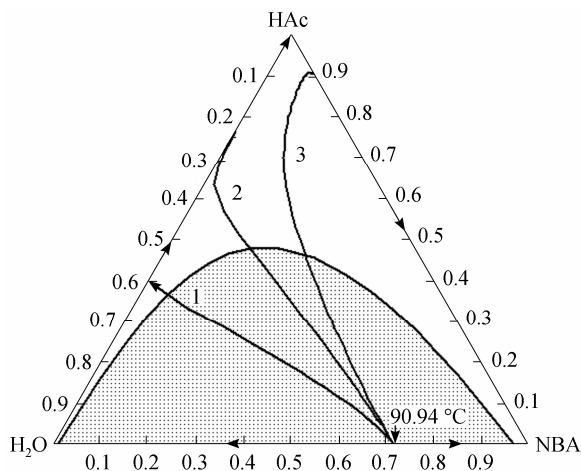


Figure 2 Residue curve map for the system NBA-H₂O-HAc

whole triangle phase map forms a single distillation region. All residue curves start from the azeotrope and end at NBA corner.

In system 2, according to the computation of Aspen Split, five azeotropes including two homogeneous azeotropes, HAc-PX (115.23 °C) and MA-H₂O (56.64 °C), and three heterogeneous azeotropes, PX-H₂O (92.32 °C), NBA-H₂O (90.94 °C) and NBA-PX-H₂O (90.88 °C), are obtained. In the system, PX has the maximum boiling temperature and PX-NBA-H₂O has the minimum azeotropic boiling temperature. Fig. 3 shows the appropriate operating region of the column (not considering MA). In order to ensure that the residual curve does not end at NBA corner (N , in Fig. 3) or PX corner (P , in Fig. 3), the operating region should be located at the left of region of plane Z_1 - Z_2 - Z_3 - H . According to previous study [17], with the accumulation of PX in the column, the reboiler duty will be increased gradually to ensure the purity specifications of the top and bottom products. Moreover, the maximum mass fraction of PX appears at the reflux drum when the mass fraction of PX in reflux is less than 0.15. The operating region should also be located under the plane A - C - B , so that the mass fraction of PX in organic reflux is less than 0.15 and the column runs at a low reboiler duty. Therefore, the operating region of the column is W - Z_1 - H - B - A - Z_4 .

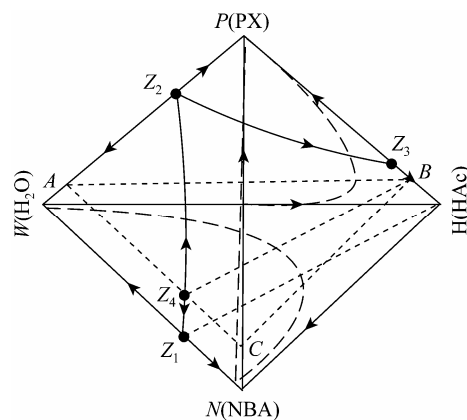


Figure 3 Operating region of impurity system
---- added boundary; — envelope; → boundary

3 PROCESS SIMULATIONS

System 1 and system 2 are simulated by using Aspen plus [18]. All of the setting data (number of trays, pressure, feed flow rate, temperature and product specifications) refer to a practical industrial process. The dehydration column has 61 stages (including a partial reboiler, numbering from the top of the column to the bottom), and its top pressure is 106.341 kPa. The column pressure drop is 25 kPa and the temperature of decanter is 40 °C. During normal operations, the PX component will not leave the column through either a top decanter aqueous outlet stream or a bottom stream. A small draining stream (stream 13,

Fig. 1) is supposed to be added to the decanter to drain some organic phase, so that PX in the column can be balanced. In system 2, the PX concentration in reflux is set at 10% (mass). The flow rate of stream 13 will be set at $3.2 \text{ kg}\cdot\text{h}^{-1}$ in system 2 and at zero in system 1. In rigorous simulation, the concentration of acetic acid in the aqueous phase product is set at $10 \text{ }\mu\text{L}\cdot\text{L}^{-1}$, the bottom HAc mass fraction is set at 0.925, and the NBA content in the bottom product should be less than $1 \text{ }\mu\text{L}\cdot\text{L}^{-1}$. The extended universal quasichemical (UNIQUAC) activity coefficient model is selected to describe the phase equilibrium and the second virial coefficients of Hayden and O'Connell are selected to account for the vapor-phase association of acetic acid due to dimerization and trimerization. The Aspen Plus built-in association parameters are employed to compute fugacity coefficients.

Figure 4 shows a comparison of temperature profiles of the distillation column between plant field and simulation, with small differences. At the top of the column, the temperature of system 1 ($92.25 \text{ }^{\circ}\text{C}$) is

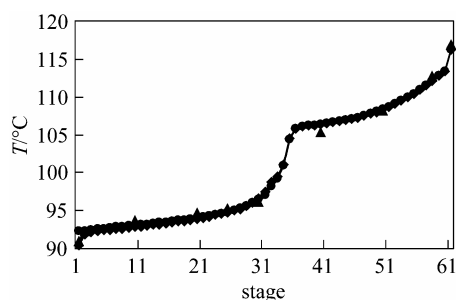


Figure 4 Temperature profiles for the azeotropic distillation column

◆ system 2; ● system 1; ▲ field data

close to the boiling temperature of NBA- H_2O azeotrope ($92.24 \text{ }^{\circ}\text{C}$), while the temperatures of plant field ($90.6 \text{ }^{\circ}\text{C}$) and system 2 ($90.5 \text{ }^{\circ}\text{C}$) are lower, due to the impurity MA accumulated in the column, which has the lowest boiling temperature and is easily vaporized.

The detailed simulation results are given in Table 1. Both of the systems have the same bottom product composition, which can meet the product specification. The concentration of PX in organic reflux system 2 is 10% (mass) which the maximum mass fraction of PX appears at the top of the column, so the system is run in the appropriate operation region (as shown in Fig. 3).

4 ANALYSIS ON MULTIPLE STEADY STATES

Multiplicity usually occurs only for certain sets of specification and only over restricted ranges of certain parameters. Often, sets of multiple solutions contain both stable and unstable solutions. One of the stable solutions is clearly superior for practical application [19]. There are some changes in the process flow-sheet in order to simulate the MSS, that is, the organic reflux (stream 5 in Fig. 1) is disconnected with the column and replaced by an organic reflux stream (also marked as stream 5). In MSS simulation, the flow rate of organic reflux stream 6 and aqueous reflux stream 9 are fixed at 3220 and $200 \text{ kg}\cdot\text{h}^{-1}$, respectively. The bottom flow rate is fixed at $5943 \text{ kg}\cdot\text{h}^{-1}$ for system 1 and $5887.7 \text{ kg}\cdot\text{h}^{-1}$ for system 2. Other input settings are consistent with the values in Table 1. Based on the simulated steady state in Section 3, sensitivity analysis is carried out by varying the flow rate of stream 1 (marked as F_1) and stream 5 (marked as F_5) separately. The change of mass fraction of HAc in bottom is observed at the same time. The current results are used

Table 1 Base-case condition of the purity and impurity system

	System 1	System 2
feed stage	35th stage	35th stage
feed flow rate	$15710 \text{ kg}\cdot\text{h}^{-1}$	$15710 \text{ kg}\cdot\text{h}^{-1}$
feed composition	(0.35, 0.65, 0)	(0.3467, 0.65, 0, 2.05×10^{-5} , 3.28×10^{-3})
top temperature (stage 1)	$92.25 \text{ }^{\circ}\text{C}$	$90.49 \text{ }^{\circ}\text{C}$
bottom temperature (stage 61)	$116.35 \text{ }^{\circ}\text{C}$	$116.34 \text{ }^{\circ}\text{C}$
organic reflux stage	stages 1 and 27	stages 1 and 27
organic reflux flow rate	$24110.1 \text{ kg}\cdot\text{h}^{-1}$ (stream 5) $3220 \text{ kg}\cdot\text{h}^{-1}$ (stream 6)	$27740.7 \text{ kg}\cdot\text{h}^{-1}$ (stream 5) $3220 \text{ kg}\cdot\text{h}^{-1}$ (stream 6)
organic composition	(0, 0.029, 0.971)	(0, 0.026, 0.759, 0.10, 0.115)
aqueous outlet flow rate	$9883.23 \text{ kg}\cdot\text{h}^{-1}$	$10303.28 \text{ kg}\cdot\text{h}^{-1}$
aqueous composition	(1.8×10^{-5} , 0.993, 6.95×10^{-3})	(8.27×10^{-5} , 0.984, 5.75×10^{-3} , 0, 0.01)
aqueous reflux rate	$200 \text{ kg}\cdot\text{h}^{-1}$	$200 \text{ kg}\cdot\text{h}^{-1}$
makeup flow rate and composition	$116 \text{ kg}\cdot\text{h}^{-1}$ (0, 0.592, 0.408)	$482 \text{ kg}\cdot\text{h}^{-1}$ (0, 0.765, 0.128, 0, 0.107)
bottom flow rate and composition	$5943 \text{ kg}\cdot\text{h}^{-1}$ (0.925, 0.075, 0)	$5887.7 \text{ kg}\cdot\text{h}^{-1}$ (0.9249, 0.0751, 0, 0, 0)
reboiler duty	10488 kW	11015 kW
organic draw flow rate (stream 13)	$0 \text{ kg}\cdot\text{h}^{-1}$	$3.2 \text{ kg}\cdot\text{h}^{-1}$

Note: Mass fraction composition (HAc, H_2O , NBA) for system 1 and (HAc, H_2O , NBA, PX, MA) for system 2. If the value is below 10^{-6} , it will be marked as zero.

as initial estimates for the next step.

4.1 Results

The sensitivity analysis results of the two systems are shown in Figs. 5 and 6. In Fig. 5, F_1 is selected as manipulated variable and F_5 is fixed at 27740 kg·h⁻¹. In system 1, based on the steady state simulation in Section 3 [O, Fig. 5 (a)], F_1 is gradually increased from 15710 kg·h⁻¹ to 15800 kg·h⁻¹ and decreased from 15710 kg·h⁻¹ to 14300 kg·h⁻¹ to trace the

solution branch. The increment in each step is 10 kg·h⁻¹. Note that the solution branch jumps from high branch (H_1) to low branch (L) at flow rates of 14510 and 15730 kg·h⁻¹. The region of multiplicity is thus identified to exist between 14510 and 15730 kg·h⁻¹. The situation in system 2 is different from that in system 1. Based on the steady state simulation in Section 3 [O_1 , Fig. 5 (b)], the solution branch jumps from H_1 to another high branch (H_2) at 14620 kg·h⁻¹ when F_1 decreases from 15710 kg·h⁻¹ by an increment of 10 kg·h⁻¹. The second series of sensitivity steps start from 15710 kg·h⁻¹. The solution branch will first jump from

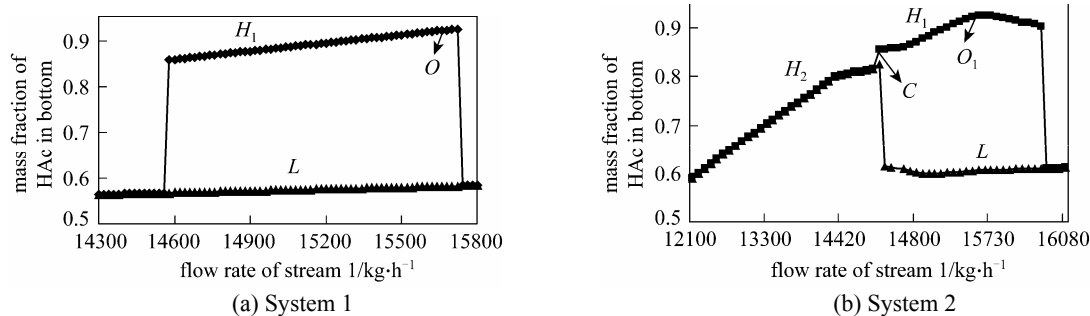


Figure 5 Sensitivity analysis with F_1 as manipulated variable and F_5 fixed at 27740.7 kg·h⁻¹

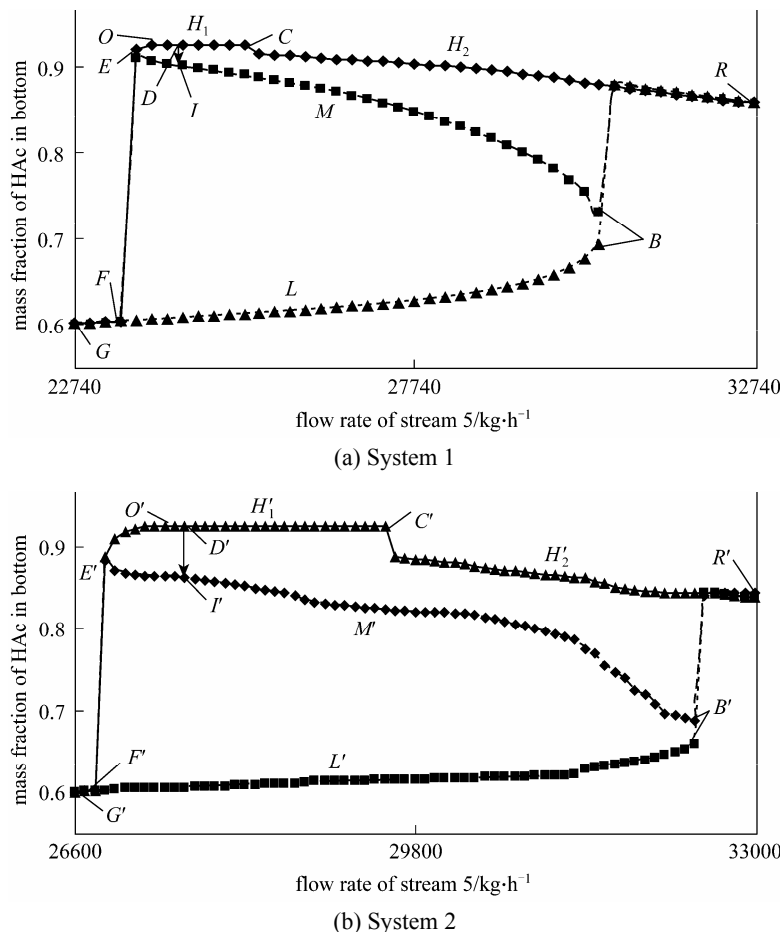


Figure 6 Sensitivity analysis with F_5 as manipulated variable and F_1 fixed at 15710 kg·h⁻¹

Table 2 Detailed information of sensitivity analysis for the two system

Step	Operating routes	Increments/kg·h ⁻¹	Solution branches
1	$O \rightarrow C \rightarrow R$ ($O' \rightarrow C' \rightarrow R'$)	+10 (+10)	$H_1 \rightarrow H_2$ ($H_1' \rightarrow H_2'$)
2	$R \rightarrow C \rightarrow O$ ($R' \rightarrow C' \rightarrow O'$)	-10 or -1 (-10 or -1)	$H_2 \rightarrow H_1$ ($H_2' \rightarrow H_1'$)
3	$O \rightarrow E \rightarrow F \rightarrow G$ ($O' \rightarrow E' \rightarrow F' \rightarrow G'$)	-10 (-10)	$H_1 \rightarrow L$ ($H_1' \rightarrow L'$)
4	$G \rightarrow F \rightarrow B \rightarrow R$ ($G' \rightarrow F' \rightarrow B' \rightarrow R'$)	+10 (+10)	$L \rightarrow H_2$ ($L' \rightarrow H_2'$)
5	$O \rightarrow D \rightarrow I \rightarrow B \rightarrow R$ ($O' \rightarrow D' \rightarrow I' \rightarrow B' \rightarrow R'$)	+5 (+2)	$H_1 \rightarrow M \rightarrow H_2$ ($H_1' \rightarrow M' \rightarrow H_2'$)
4	$I \rightarrow E \rightarrow F \rightarrow G$ ($I' \rightarrow E' \rightarrow F' \rightarrow G'$)	-5 (-2)	$M \rightarrow L$ ($M' \rightarrow L'$)

Note: The content of parentheses denotes the information of system 2.

H_1 to L at $15960 \text{ kg} \cdot \text{h}^{-1}$ when F_1 increases $10 \text{ kg} \cdot \text{h}^{-1}$ in each step, and then jump from L to H_2 at $14620 \text{ kg} \cdot \text{h}^{-1}$ when F_1 decreases from $16080 \text{ kg} \cdot \text{h}^{-1}$ to $12100 \text{ kg} \cdot \text{h}^{-1}$. The region of multiplicity in system 2 is identified to exist between $14620 \text{ kg} \cdot \text{h}^{-1}$ and $15960 \text{ kg} \cdot \text{h}^{-1}$.

When F_5 is selected as manipulated variable and F_1 is fixed at $15710 \text{ kg} \cdot \text{h}^{-1}$, the MSS information is shown in Fig. 6. The adjusting steps of sensitivity analysis for the two systems are listed in Table 2. In system 1, three solution branches are observed within an operating region between E and B (with the flow rates of stream 5 listed in Table 3), as shown in Fig. 6 (a). Three solution branches of system 2 are observed within an operating region between E' and B' , as shown in Fig. 6 (b). The two MSS curves are similar. And we illustrate the searching process of MSS by system 1. The MSS curves can be obtained by starting from the steady state simulation in Section 3 (O in Fig. 6). The sensitivity solution follows the high branch (H_1 and H_2) when F_5 increases. When F_5 exceeds point R , decrease the flow rate of stream 5. The sensitivity solution follows the high branch from point R to point E more than to point F and G in the low branch. And when increase the flow rate of stream 5, the solution follows the low branch and changes to the high one (H_2) until F_5 exceeds point B . However, if F_5 increases with a small step size from point O , the solution branch will change from H_1 to intermediate branch M at point D . Then the solution branch M can follow $I \rightarrow E \rightarrow F \rightarrow G$ or $I \rightarrow B \rightarrow R$ when the flow rate of stream 5 decreases or increases separately.

It is pointed out [19] that the sensitivity study in Aspen Plus is not likely to produce a smooth continuous or bifurcating curve that includes turning points and all multiple solutions, and additional steady state solutions are sometimes found by providing special initial guesses. In the two systems, when F_5 changes from O to R , the solution branch will follow the higher branch H_1 and H_2 . On the contrary, when F_5 changes from R to O , the solution perhaps jumps to the branch L at point C (or C' in system 2). Although divergence occurs at point C , H_1 can also be achieved by reducing the step size. Note that this provides a method for achieving desired steady states in process simulation, and it will be discussed later. The sensitivity result of system 2, as shown in Fig. 6 (b), is similar to system 1.

Table 3 The flow rate of stream 5 in MSS curve

Point	Flow rate of stream 5 in system 1/kg·h ⁻¹	Point	Flow rate of stream 5 in system 2/kg·h ⁻¹
B	30080	B'	32390
C	25320	C'	29660
D	24380	D'	27830
E	23840	E'	26820
F	23820	F'	26800
G	22740	G'	26600
O	24100	O'	27740
R	32740	R'	33000

4.2 Discussion

It is interesting to find a phenomenon that the solution branch along the high branch jumps from H_1 to H_2 at point C (C'). Fig. 7 shows the changes of bottom composition along the high branch. At point C , the mass fraction of H_2O decreases to zero and only HAc and NBA are left. It means that distillation path ends at the boundary of HAc and NBA, and some amount of NBA will loss through the bottom stream.

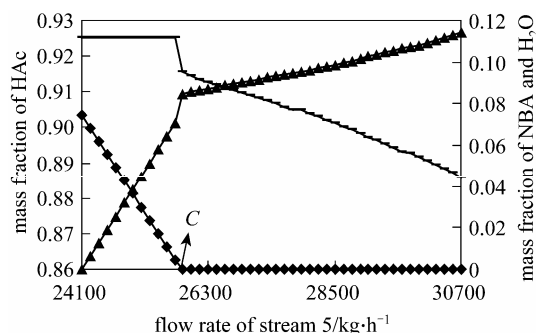


Figure 7 Bottom composition changes along high branch
— HAc; ◆ H_2O ; ▲ NBA

Figures 8 and 9 show the temperature and vapor composition profiles along the column under different steady states for system 1, and $F_5 = 24110 \text{ kg} \cdot \text{h}^{-1}$ for branch H_1 , M and L , $F_5 = 25900 \text{ kg} \cdot \text{h}^{-1}$ for branch H_2 .

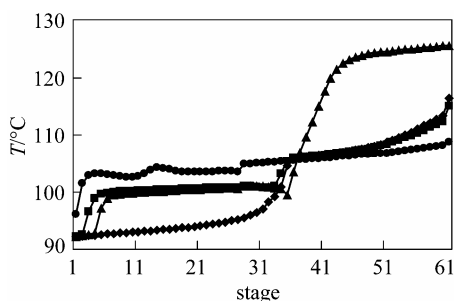


Figure 8 Temperature profiles for different steady states
 ◆ H_1 ; ■ M ; ▲ H_2 ; ● L

At the top of the column, steady H_1 , M and H_2 have the same temperature and composition, which is close to the boiling temperature and composition of NBA-H₂O azeotrope (A in Fig. 9). At the bottom of the column, however, the temperature of H_2 is far different from that of H_1 and M , and its composition is located at C (Fig. 9) while the composition of H_1 and M is located at D and E . The temperature profile and vapor composition profile of steady state L are different from the others. The temperature difference between the top and bottom of the column is small, and there are much water in the bottom (F) and much HAc in the top (B). Therefore, the HAc and H₂O cannot be separated when the system works under steady state L .

4.3 Proposed method for process simulation

In the simulation of an industrial heterogeneous distillation column, two problems may be encountered. The first one is how to ensure sufficient solvent circulating in the system and the other is how to achieve the required steady states. For example, in the acetic acid dehydration system studied, NBA is not con-

tained in the feed stream into the column, so it needs to feed NBA into the column in the initial moment to ensure that enough NBA circulates in the distillation system. There is more than one steady state in the system. Although a reasonable reflux is given in the simulation, the system often works at the low steady state L , and the required steady state H_1 is not easy to achieve. Luyben [20] suggested selecting organic reflux as "tear stream" to obtain high-purity bottom product, but no further operating instructions were proposed. Here, combined with the MSS results obtained, a method is proposed to adjust organic reflux to achieve the desired steady state in process simulation.

Most of the studied MSS phenomena in heterogeneous azeotropic distillation are similar to the simulated results in this paper (Fig. 6). Three steady states usually exist in the system: the low, intermediate and high steady state. From Fig. 6 (b), when the flow rate of organic stream is greater than a certain value, there is only one steady state in the system (H_2). It is worth noting that both steady state H_2 and H_1 locate at the same solution branch, so if the system is at steady state H_2 and with the flow rate of organic reflux stream decreasing, the desired steady state H_1 can be achieved. Thus it is proposed to increase the flow rate of organic reflux stream to a high value first to achieve the steady state H_2 , and then decrease the flow rate slowly, so that the steady state of the system will transform from H_2 to H_1 . Finally, the desirable high-purity bottom products can be obtained.

Although the two steady states H_1 and H_2 locate at the same solution branch, the divergence will occur at the key point C where steady states H_1 and H_2 exchange to each other. Then the step size should be reduced and adjusted repeatedly. Besides, because the heterogeneous distillation system is parametric sensitivity, the step size should not be too big or the simulation will jump from high steady state to low steady state.

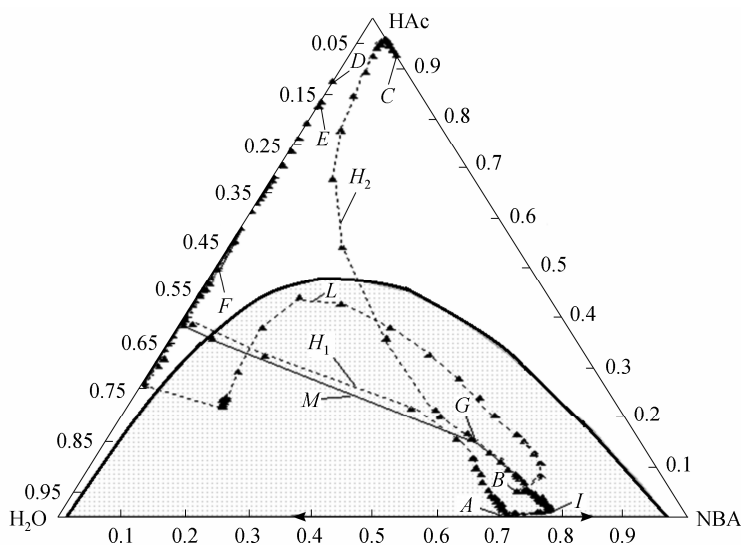


Figure 9 Vapor composition profile of the column

5 CONCLUSIONS

By using the process simulation software Aspen plus, a study of MSS for acetic acid dehydration *via* heterogeneous azeotropic distillation is presented. Some conclusions are obtained as follows.

(1) The appropriate operating region of system 2 should be located at the region in which the residual curve will not end at NBA corner or PX corner and the mass fraction of PX in reflux is smaller than 0.15.

(2) Through the sensitivity analysis, different solution branches are observed. The performance of the column under different steady states is very different. The normal operating point is located at the high steady state (H_1) and it is not easy to be achieved during the process simulation.

(3) The desired steady state can be achieved by starting the simulation with high organic reflux flow rate, and then decrease the organic reflux slowly and adjust the step size repeatedly to the desired steady state. This method is useful for simulating heterogeneous azeotropic distillation process.

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