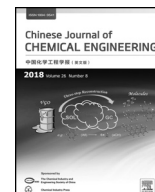




ELSEVIER

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Article

Process optimization of an industrial acetic acid dehydration progress via heterogeneous azeotropic distillation[☆]Xiuhui Huang^{1,*}, Zeqiu Li¹, Ying Tian^{2,*}¹ School of Energy and Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China² School of Optical-Electrical and Computer Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

ARTICLE INFO

Article history:

Received 28 August 2017

Accepted 12 October 2017

Available online 7 December 2017

Keywords:

Acetic acid dehydration

Azeotropic distillation

Process simulation

Operation optimization

ABSTRACT

The simulated process model of the HAC dehydration process under actual overloaded condition was conducted by amending the model of standard condition in our previous work using the process data collected from actual production. Based on the actual process model, the operation optimization analysis of each plant (HAC dehydration column, decanter and NPA recycle column) was conducted using Residue Curve Maps (RCMs), sensitivity analysis and software optimization module. Based on the optimized parameters, the influence of feed impurity MA and the temperature of decanter on the separating effect and energy consumption of the whole process were analyzed. Then the whole process operation optimizing strategy was proposed with the objective that the total reboiler duty Q_{total} of C-1 and C-3 reaches the minimum value, keeping C-1 and C-3 at their optimized separation parameters obtained above, connecting all the broken recycle and connection streams, and using the temperature of D-1 as operation variable. The optimization result shows that the total reboiler duty Q_{total} of the whole process can reach the minimum value of $128.32 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$ when the temperature of decanter is 352.35 K, and it can save $5.94 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$, about $2.56 \text{ t} \cdot \text{h}^{-1}$ low-pressure saturated vapor. © 2017 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

In the production of pure terephthalic acid (PTA), acetic acid (HAC) dehydration system is one of the most important operations. When the *p*-xylene (PX) is oxidized to form PTA, HAC is used as the solvent, and Water is generated in the reaction process, meanwhile, there are unreacted reactant PX and by-product methyl acetate (MA) mixing in the HAC solvent besides Water. To save material consumptions, the solvent mixture should be separated and concentrated for recycle. The binary system of HAC-water has a tangent pinch on the pure-water end and its relative volatility is close to 1, so azeotropic distillation (AD) is commonly adopted to make the separation easier, and an entrainer is often introduced into the system. Previous research works in azeotropic distillation were comprehensively reviewed by Widagdo and Seider [1]. It showed that the most generally used entrainers are acetic esters, such as *n*-propyl acetate (NPA), *n*-butyl acetate (NBA), *i*-butyl acetate (IBA), and ethyl acetate (EA).

In recent years, most of the research about the HAC dehydration system was dedicated to the issues of process synthesis, design and

control. Wasylikiewicz *et al.* [2] proposed using a geometric method for the optimum design of a HAC dehydrating column with NBA as the entrainer. Chien *et al.* [3,4] discussed the design and control of HAC dedhydration system via heterogeneous AD using three candidate entrainers (EA, IBA, and NBA), and also investigated the influence of feed impurity on the dehydration column in which IBA was used as the entrainer. Huang *et al.* [5] and Lee *et al.* [6] also discussed the influence of feed impurity on the design and operation of an industrial HAC addressed the design and control of HAC dehydration column with *p*-xylene (PX) or *m*-xylene (MX) feed impurity in which IBA was used as the entrainer. Wang San Jang *et al.* [7] investigated the energy-saving plant-wide design and plant-wide control of an acetic acid dehydration system via HAD and divided wall distillation with the feed containing MA and PX using IBA as entrainer. Li [8] analyzed reboiler duties at different concentrations of PX in the reflux in the system using NBA as an entrainer, and suggested the optimal operation conditions that the concentration of PX is decreased by draining some organic reflux when the mass fraction of PX accumulation exceeds 0.15. Recently, Wang San Jang *et al.* [9] investigated the use of PX as the entrainer for the separation of HAC and water, and also demonstrate that it is possible to dynamically transform the HAD column with IBA as the entrainer into the HAD column with PX as the entrainer. Qianlong Li *et al.* [10] conducted the dynamic simulation and proposed a control strategy of the acetic acid solvent dehydration system using NPA as entrainer.

[☆] Supported by Shanghai University Youth Teacher Training Program (ZZsl15002) and Shanghai Sailing Program (17YF1413100 and 17YF1428300).

* Corresponding authors.

E-mail addresses: hxxh@usst.edu.cn (X. Huang), tianying009@sina.com (Y. Tian).

Most research of the system focus on the HAC dehydration system using NBA and IBA as entrainers. A few works focused on the influence and control of impurities in the distillation column considering only quaternary components containing unreacted reactant PX in the feed, and the physical parameters were either collected from Aspen Plus build-in or from the literature. There are very few researches for an industrial HAC dehydration system of PTA plant using NPA as entrainer, especially the system considering the influence of feed impurity MA. The research of this paper is aimed at an actual industrial HAC dehydration system of PTA plant using NPA as entrainer under overloaded condition. The quantity of MA in the system is much more than PX, and most other parameters are also changed comparing to the standard designed condition, so it has important practical significance to explore the influence of MA on the separation effect and energy consumption of the whole dehydration process and conduct the whole process operation optimization. Considering PX and MA as feed impurities, there are five components (HAC-Water-NPA-PX-MA) in the system. The research of phase equilibrium, the binary parameters of the quinary system, the thermodynamic analysis and the process simulation of the HAC dehydration system under standard designed condition were all conducted in our previous work [11,12].

In this paper, based on our previous work, the simulated process model of the HAC dehydration process under actual overloaded condition was conducted by amending the model of standard condition using the process data collected from actual production. Based on the model, the operation optimization analysis of each plant (HAC dehydration column, decanter and NPA recycle column) was conducted. And then based on the optimized conditions, the influence of feed impurity MA and the temperature of decanter on the separating effect and energy consumption of the whole process was analyzed, and the whole process operation optimizing strategy were proposed with the objective that the total reboiler duty reaches the minimum value.

2. Actual Industrial Process Simulation

2.1. Industrial process description

The process flow diagram of the studied industrial HAC dehydration process can be seen in Fig. 1. There are four feeds (F1–F4) coming from the upstream process into the dehydration column C-1. The four feeds are separated in C-1 using NPA as entrainer via heterogeneous

azeotropic distillation to make the bottoms containing HAC with high concentration. The overhead of C-1 is cooled in the condenser, then the condensate and vapor goes to the decanter. The NPA make-up and NPA recycle is also feed to the decanter. The mixture in the decanter gets VLL phase equilibrium and phase separation, and then the organic phase returns to C-1 as reflux (there are top reflux and middle reflux in the practical industrial HAC dehydration column), the aqueous phase and vapor phase are sent to the NPA recovered column C-3 to recover NPA and MA. A side-draw is sent to a PX pure column C-2 to remove the accumulated PX in C-1, and the overheads of C-2 returns to C-1. The bottoms of C-2 returns to C-3.

2.2. Physical property and mechanism model

The HAC dehydration system contains five components: HAC + Water + NPA + PX + MA, which is multistage and multicomponent continuous three-phase distillation. For the rectifying tower in this paper, a VLL three-phase mechanism model based upon a rigorous equilibrium stage model for solving the MESH equations [13] (mass balance (M), phase equilibrium (E), summation (S) and energy balance (H)) is adopted. The results of phase composition, stage temperature, and the flow rate of vapor and liquid phase can be got by solving simultaneously the MESH equation, condenser and reboiler equations and corresponding physical equation of each stage. The most commonly used Murphree efficiency is adopted to correct the departure from equilibrium in the industrial column to get the accurate results matching the actual stage.

The quinary system (HAC + Water + NPA + PX + MA) has strong nonideality of vapor–liquid equilibrium (VLE) caused by the association of HAC due to dimerization and trimerization, so it's particularly important to select proper thermodynamic model and parameters to give an accurate description of the system. In this paper, according to our previous work, the UNIQUAC-HOC model [14–16] and the binary parameters in our previous work [11] are adopted.

2.3. Data correction and simulation results

A domestic solvent dehydration process of the PTA plant was imported a whole set of patents from overseas with a design load of $70 \text{ t PTA} \cdot \text{h}^{-1}$. So far, based on continuous improvement of the plant, the operation load under the actual working condition is around 117%

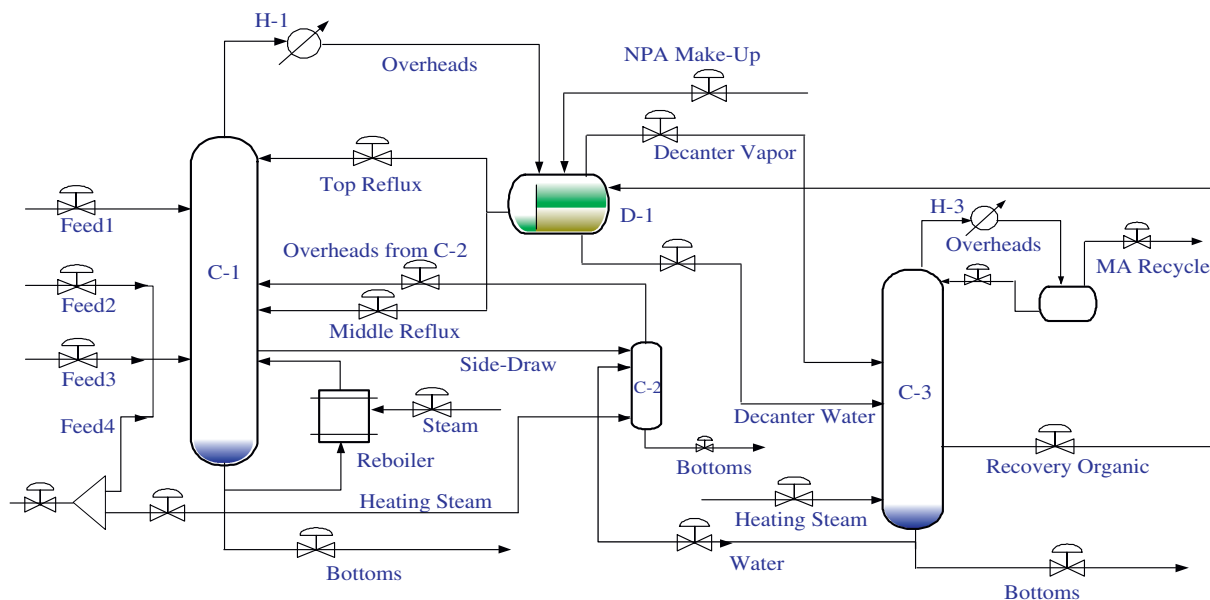


Fig. 1. Process flow diagram of an industrial HAC dehydration process.

(82 t PTA·h⁻¹) compared to that under the design working condition. Many differences are caused by the following factors including load variation, actual raw material (feed) diversity, the modification of some individual equipment, the market demand change for the products, an additional reflux in middle zone, etc., the parameters of the technological process can't be only magnified equivalently according to the load. So, the data is collected, analyzed and preprocessed under the actual working condition. The average values with the deduction of abnormal ones collected from the plant operation under a stable actual working condition during a period of some two months are used in the simulation calculation, and the feed composition is according to the sampling testing and analyzing results during the same time. To decrease data errors, we moderately modify part of the data based on the parameters under the design working condition, as well as the material balance standard. Since a few of the practical plant are not equipped with the flowmeters or the thief hatches in their streams, those data are defined to 117% of that under the design working condition, meanwhile the other stream data which can't be proceeded by the composition analysis is adjusted and defined according to composition parameters under the design working condition based on the material balance standard. In the end, all the parameters added or revised are shown in Tables 1–3.

Table 1
Collection temperature data of each plant in actual overloaded condition

C-1		C-2		C-3	
Location	Temperature/K	Location	Temperature/K	Location	Temperature/K
Top	358.85	2	364.33	Rectifying	329.07
Middle	367.53	7	366.29	section	329.57
zone	370.40	9	368.30		330.50
	375.77	17	372.29		333.43
	379.50	19	373.51		345.42
	382.21	21	374.19	Stripping	334.11
	382.79	23	375.07	section	
Nether	388.66	24	376.14	(Top)	
zone					
Bottom	391.10	Bottom	381.82	Bottom	375.36

Table 2
The flow information in actual overloaded condition

Stream	T/K	P/MPa	Flow rate/kg·h ⁻¹	Composition (mass fraction)
F1	351.15	1.54	75600	0.632 HAc, 0.315 Water, 0.001 PX, 0.052 MA
F2	402.15	1.17	28600	0.799 HAc, 0.186 Water, 0.015 MA
F3	392.15	0.14	38500	0.845 HAc, 0.149 Water, 0.006 MA
F4	431.35	0.43	37200	0.837 HAc, 0.15 Water, 0.013 MA
Fw	313.15	1.43	1200	Pure water
Fs2	431.35	0.43	2700	0.837 HAc, 0.15 Water, 0.013 MA
Fs3	421.15	0.45	5280	Pure water
R1	351.45	0.3	209850	0.854 NPA, 0.117 MA, 0.028 Water, 0.001 PX
Rm	351.45	0.3	8770	0.854 NPA, 0.117 MA, 0.028 Water, 0.001 PX

Table 3
Operating parameters of each plant in actual overloaded condition

Unit	Parameter	Value
C-1	Middle Reflux, stage #	45
	Bottom Stream/kg·h ⁻¹	140520
	Side-draw/kg·h ⁻¹	3800
D-1	Temperature/K	350.75
	Pressure/MPa	0.105
	NPA make-up/kg·h ⁻¹	56
C-3	Top distillate/kg·h ⁻¹	4800
	Side-draw/kg·h ⁻¹	20000

Under the actual overload working condition, compared to the design working condition [12], the unreacted reactant PX entering the dehydration process reduces significantly (from 0.2% to 0.1%), and its impact to C-1 separation effect decreases dramatically, meanwhile the by-product MA content rate increases largely (from 3.4% to 5.2%), and it should be the key factor for the analysis. So, for the space-saving and convenience to study the overall MA impact, the side-draw of C-1 and PX recovery tower C-2 are ignored in this paper. To facilitate the proceed of the optimization analysis and calculation, the HAc dehydration process model in this article is simplified by the following conditions: C-2 is deleted, condenser and decanter are combined and replaced by a three-phase flash vessel D-1, and low-pressure saturated vapor feed in C-3 is removed, meanwhile bottom reboiler duty is replaced as the operation parameter for the column.

Afterwards, based on the proven model under the design working condition and the same model adjusting method in our previous work [12], with keeping the same values of all stages in all columns, and remaining the same feed location, and column pressure drop, as well as adding an additional stream, all the parameters under the design working condition are modified to those under the actual working condition correspondently referring to the values shown in Tables 1–3.

The final process simulation results are shown in Fig. 2. Figs. 3 and 4 show the simulated results of temperature, vapor composition and liquid composition profile in C-1 and C-3. Table 4 is the comparison of the data collected during the solvent dehydration process under the actual working condition and that under the simulation calculation. In terms of the simulation results (Table 4), it fits the current working condition of plant operation although the error is enlarged to some extent compared to that of the calculation result under the design working condition, and its overall relative errors are still less than $\pm 8\%$. Therefore, within the allowable error rang, it can be used for the further research in sensitivity analysis, operation optimization, dynamic simulation and the control of solvent dehydration column under the actual working condition.

3. Operation Optimization

3.1. Problem description

The vapor consumption of the actual PTA plant is around 56 to 58 t·h⁻¹, about $0.7 \text{ t} \cdot (\text{t PTA})^{-1}$. Compared to the design working condition, the energy consumption decreases. But the actual operation normally is abided by the parameters provided by the licensor or to just simply increase or decrease the parameters on a multiple basis according to the increase or decrease of load correspondently, which results in poor separation effect, comparatively higher energy consumption, and big space for the optimization. With the fixed production equipment and production load, the main operation cost generates from the energy consumption of the reboiler of the distillation column. So, the main purpose of the following research is to find the optimal operation condition for each equipment unit and the whole process with the minimal reboiler duty as objective based on the process model in previous content.

In the HAc dehydration process, the three equipment units C-1, D-1, and C-3 affect and restrict each other crossover, so during the operation optimization, we firstly disconnect the recycle stream and connection stream of the equipment units, and work on the optimal analysis of each plant, then based on the analysis results, we connect the whole operation process and find the optimal operation condition.

3.2. Optimization of Unit Operation

3.2.1. Operation optimization analysis of C-1

For C-1 of the HAc dehydration process, from the sensitivity analysis result in our previous work [12], it can be learned that the separation

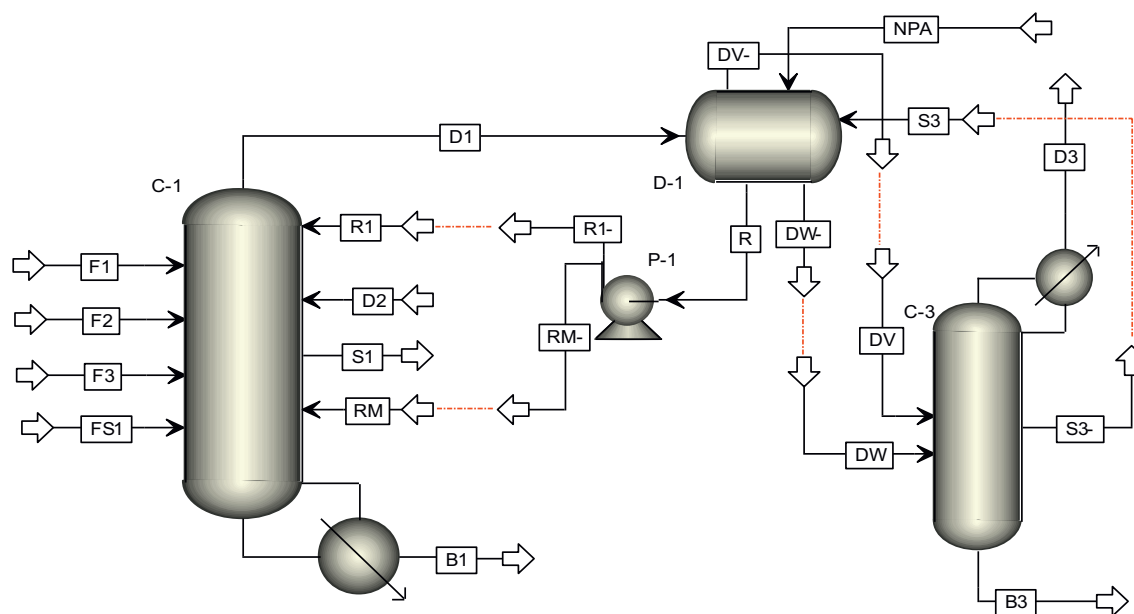


Fig. 2. Process simulation of actual HAC dehydration system for operation optimization.

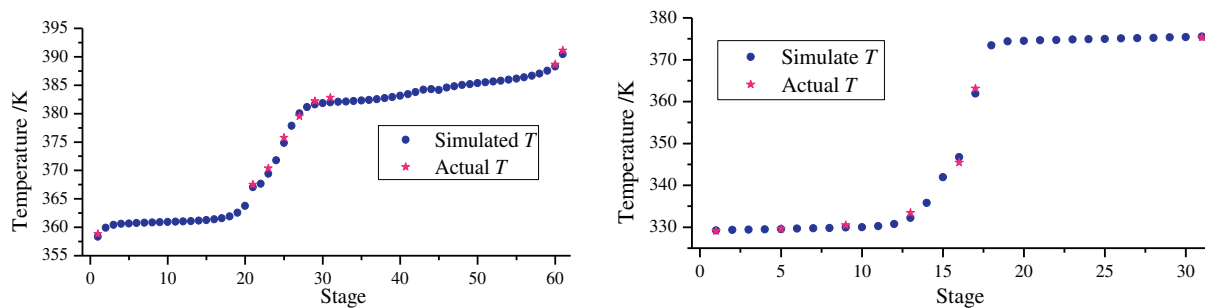


Fig. 3. Temperature Profile in C-1 and C-3 of actual overloaded condition.

effect and energy consumption are influenced by heat feed F_{S1} and side-draw $S1$ of this column in a small scale; besides, the feed is usually fixed and the PX content rate is quite small under the actual working condition, therefore, the influence caused by F_{S1} and $S1$ is not included in this article. The two figures (Figs. 12 and 15) in the ref [12] indicate top reflux is the first and major factor to impact the energy consumption of the column, and the water content rate in the separation column is the secondary influential factor. Moreover, as the main operation variable under the actual working condition, the reflux also makes visible impact to the separation effect in terms of its content, temperature and impurity rate. As a result, the operation optimization in this article sets the top reflux (including reflux flow reflux temperature and the main impurity content MA) and bottom water content rate as the operation variables.

The reflux influences the reboiler duty quite obviously and it's also the key parameter affecting the separation effect, and how to ensure the needed separation effect with the minimal reflux is the key to save the energy consumption. In actual operation, the adjustment of the separation effect is mostly by the control of top reflux. Consequently, under current C-1 working condition, and based on Design Spec/Vary module, in this article the water content rate of dehydration column is added as an equality constraint, and its value under the current working condition is set as 0.63, with the top reflux as a variable, then based on the model calculation, the minimal reflux can be determined, therefore after this calculation, the minimal reflux is $207.15 \text{ t} \cdot \text{h}^{-1}$, and

correspondently, the bottom reboiler duty is $120.97 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$. However Table 2 indicates that under the actual working condition, the top reflux feed flow is $209.85 \text{ t} \cdot \text{h}^{-1}$, the control range of reflux is $208\text{--}230 \text{ t} \cdot \text{h}^{-1}$, and the correspondent bottom reboiler duty is $121.89 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$, then it can be concluded that the overall reflux in practical plant is comparatively high, and in this article it suggests that the control range of reflux can be narrowed in the actual operation.

About bottom water content rate, the sensitivity analysis shows by raising its target control value as high as possible within the HAC concentration range permitted by technology it reduces the heat energy consumption of this column dramatically without obviously extra entrainer consumption in bottom water under the actual working condition. Based on the comparison between the values under the design working condition and the actual working condition, the target control value of the bottom water content rate is raised 1.3%, from 5% under the design working condition to 6.3% under the actual working condition. Meanwhile the vapor consumption of each unit reduces from $0.8 \text{ t} \cdot (\text{t PTA})^{-1}$ to current $0.7 \text{ t} \cdot (\text{t PTA})^{-1}$, which is mainly benefited by raising the target control value of the bottom water content rate. According to technological procedure, the maximum water content rate of solvent HAC within PX oxidation reactors is 6.5% during PTA production, besides the fresh high-concentration HAC is added to feed constantly during the production process, thus there exists the over-separation phenomenon, the target control value of the water content rate can be raised 0.2% to reach 6.5%. After the bottom HAC product

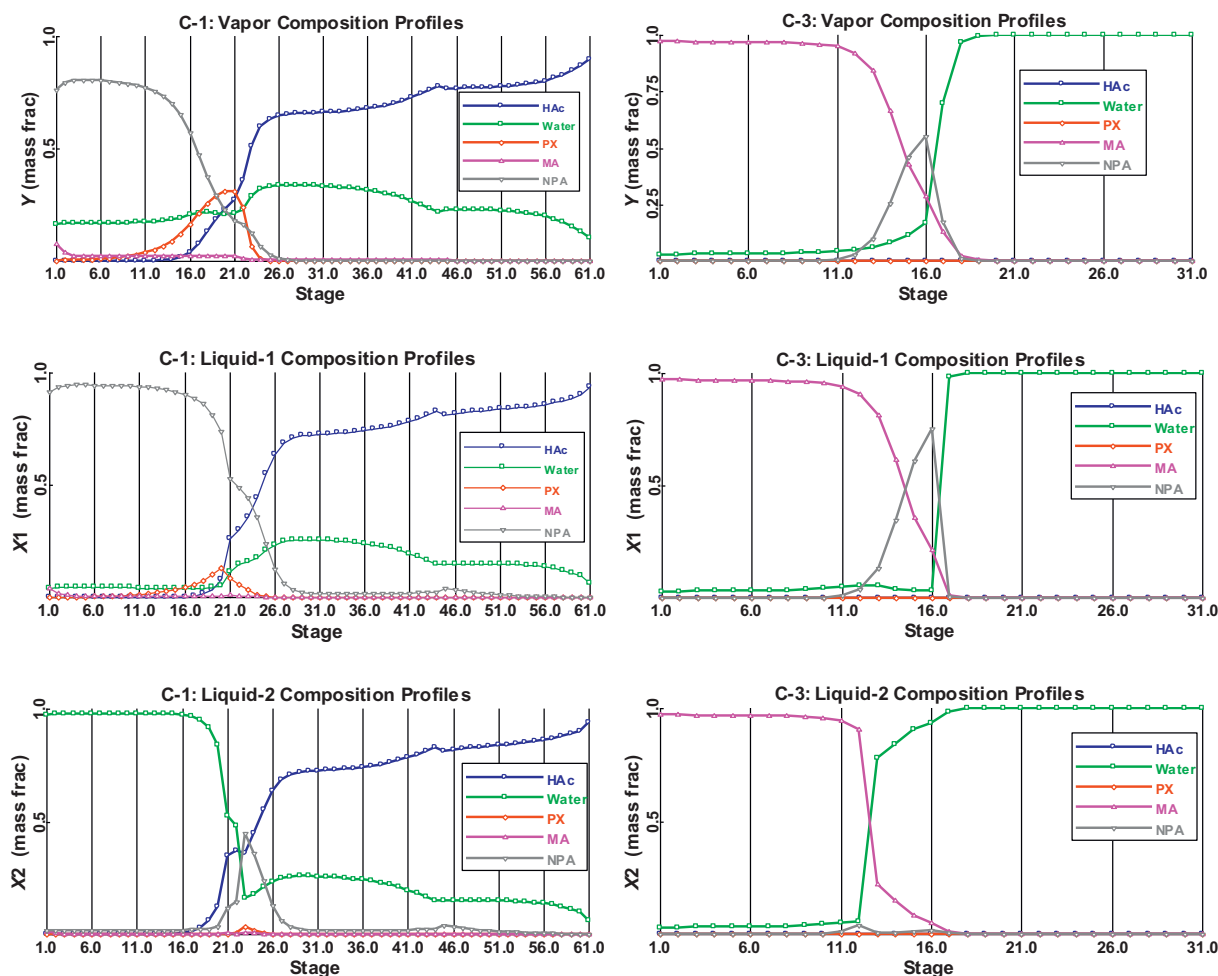


Fig. 4. Vapor, liquid-1 and liquid-2 composition profile in C-1 and C-3 of actual overloaded condition.

Table 4

Data comparison between simulation result and collection data of actual overloaded condition

Unit	Item	Process data	Simulated result	Relative error/%
C-1	Top temperature/K	358.85	358.35	−0.14
	Bottom temperature/K	391.1	390.45	−0.17
	Side-draw temperature/K	367.53	367.05	−0.13
	Top distillate/kg·h ^{−1}	—	252050	—
	Bottom stream/kg·h ^{−1}	—	140520	—
	Side-draw/kg·h ^{−1}	3800	3800	0
	Top HAc content/wt%	<0.1	<0.01	—
	Bottom water content/wt%	6.3	6.2	−1.61
	Side-draw PX content/wt%	—	7.8	—
	Reboiler duty ×10 ^{−12} /kJ·h ^{−1}	—	121.89	—
D-1	Vapor steam/kg·h ^{−1}	20230	21850	7.41
	Aqueous stream/kg·h ^{−1}	34720	33538	−3.52
	Organic stream/kg·h ^{−1}	217770	215217	−1.19
C-3	Top temperature/K	329.07	329.25	0.05
	Bottom temperature/K	375.36	375.45	0.02
	Side-draw temperature/K	345.42	346.65	0.35
	Top distillate/kg·h ^{−1}	4480	4800	6.67
	Bottom stream/kg·h ^{−1}	34720	34320	−1.17
	Side-draw/kg·h ^{−1}	20500	20000	−2.50
	Top MA content/wt%	96.9	97.1	0.21
	Bottom water content/wt%	99.9	100	0.10
	Side-draw NPA content/wt%	—	61.5	—
	Heating steam/kg·h ^{−1}	5270	5280	0.19

is mixed with fresh high-concentration HAc, the water content rate must be below 6.5% to meet the criterion of solvent concentration needed by reactors. Hence in this article, it modifies the value of Design Spec mentioned above in Design Spec/Vary module to 0.65, and change the relevant value of the bottom withdraw stream based on the material balance principle, then with the calculation, the minimal reflux needed by the bottom water content rate to reach the value 0.65 is 204.56 t·h^{−1}, correspondently the needed reboiler duty is 119.05 × 10⁶ kJ·h^{−1}.

Table 5 indicates the comparison of energy consumption about reflux and the bottom water content rate before and after the optimization. It shows the reboiler duty under the working condition after twice optimization reduces 2.84 × 10⁶ J·h^{−1}, and the saturated vapor content rate is 1.22 t·h^{−1}. This optimization strategy is deployed in the actual production process and achieves significant energy-saving effect.

Table 5

Operating condition of C-1 before/after optimization

Parameter	Value before optimization	Optimization condition 1	Optimization condition 2
Bottom water/wt%	6.3	6.3	6.5
Reflux/t·h ^{−1}	209.85	207.15	204.56
Reboiler duty ×10 ^{−6} /kJ·h ^{−1}	121.89	120.97	119.05

Table 5 also indicates that the energy consumption is in direct proportion to reflux, and the energy consumption reduction is in essence the reduction of needed reflux, and the effective composition containing water in reflux is entrainer NPA actually, the rest of composition only can be treated as reflux impurities. The feed PX is in a small amount, and it's even less in reflux, which can be basically ignored. Thus, the main composition of reflux impurities is MA. As the amount of MA in reflux increases, the effective NPA decreases, therefore the MA content rate in reflux is also a possible influential factor to C-1 reboiler heat control. Meanwhile, it can be learned that the MA content rate (the MA content of D-1 outfeed in organic phase) in reflux under the actual working condition is as high as 11.6% based on the data collected in actual operation and simulation.

Fig. 5 shows the variation of reboiler duty and minimum reflux flow with MA content of reflux in C-1, while remaining the same NPA content rate in reflux and the same optimization of Design Spec/Vary mentioned above. It also shows when the MA content rate in reflux rises achieving the same separation effect, the minimal reflux rises dramatically, and the same happens to bottom heat load, which illustrates that the more MA content is in reflux, the less beneficial it is to the dehydration column.

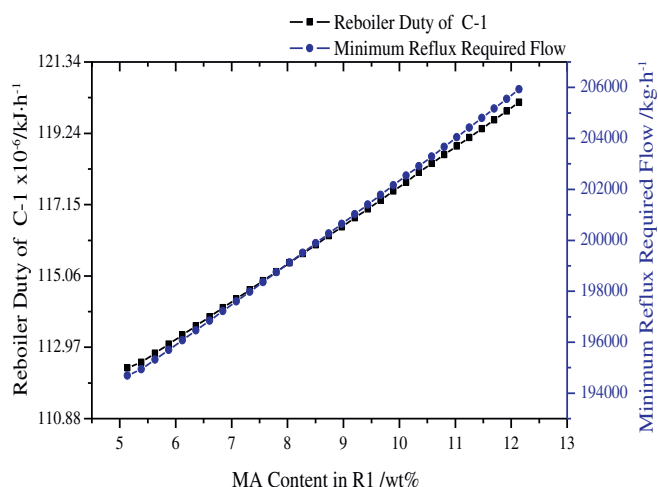


Fig. 5. The variation of reboiler duty and minimum reflux flow with MA content of reflux in C-1.

Based on technological process and simulation results, it can be concluded that MA entering solvent dehydration column mainly reacts with water to form a minimum azeotrope which is distilled from the top of solvent dehydration. Under the normal pressure, the azeotrope temperature of MA-Water formed by MA and water is 329.1 K, that is below than 356.31 K, the temperature of binary azeotrope formed by entrainer NPA and water, consequently it's distilled from the top of column with NPA-Water, theoretically speaking, it can function as an entrainer. Nevertheless, the MA vaporization heat is $409.73 \text{ kJ} \cdot \text{kg}^{-1}$ which is higher than $355.69 \text{ kJ} \cdot \text{kg}^{-1}$ of NPA, meanwhile the binary azeotrope formed with water only contains 2.28% water, lower than the water content rate of 16.64% in NPA-Water azeotrope. By calculation with Formula (1), to distill 1 kg of water needs 33.72 kg MA or 5 kg NPA. And by calculation with Formula (2), the energy consumption of MA is 13,816 kJ, and that of NPA is 1779 kJ. It indicates that the water distillation capability of MA is far less than that of NPA, meanwhile for the same amount of water, the energy consumption of MA is far higher than that of NPA, it also explains why the increase of MA content causes the reflux and bottom heat rise dramatically and simultaneously.

$$m_{\text{MA/NPA}} = m_{\text{water}} / \text{wt}_{\text{water}}\% \times \text{wt}_{\text{MA/NPA}}\% \quad (1)$$

$$H_{\text{MA/NPA}} = m_{\text{MA/NPA}} \times C_{p_{\text{MA/NPA}}} \quad (2)$$

Therefore, reducing the MA content rate in reflux is also an effective solution to decrease reboiler heat. It shows in Fig. 5 that if the MA content rate in reflux reduces 1%, the needed reflux reduces around $1.5 \text{ t} \cdot \text{h}^{-1}$, and reboiler heat reduces about $1 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$, in short, the energy-saving effect is quite magnificent.

However, the MA content rate in reflux is directly connected to D-1, and determined by the feed and operation temperature of D-1 while the operation temperature of D-1 determines the temperature of reflux. Fig. 6 is a variation diagram that shows the minimal reflux flow and bottom heat vary along with reflux temperature based on that reflux composition is fixed and maintained the same rules of Design Spec/Vary as mentioned above which means the same bottom water content of 6.5%. It also shows in the graph that the needed minimal reflux appears an uptrend as the temperature increases with the same separation effect, but the rising is quite small which is only limited to 101 orders of magnitude. Compared to original flow of 106 order of magnitude, its compact can be ignored.

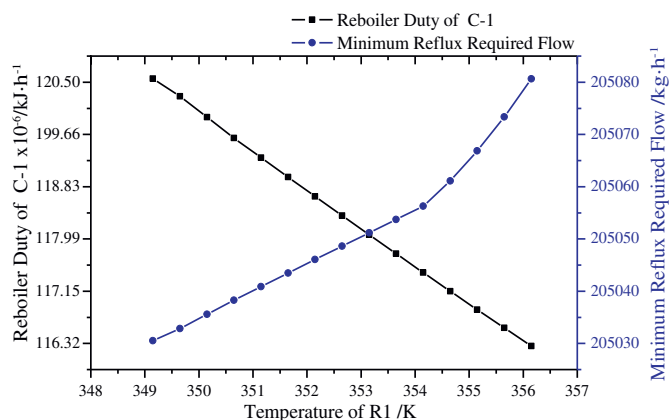


Fig. 6. The variation of reboiler duty and minimum reflux flow with reflux temperature in C-1.

Meanwhile, bottom heat shows an apparent downtrend, as the reflux temperature rises 1 K, which can reduce about $0.627 \times 10^6 \text{ kJ}$ reboiler heat. Thus, it indicates that the entrainer consumption basically remains the same, but bottom heat drops apparently within a certain range (lower than D-1 working pressure 0.105 with azeotrope point 357.15 K of NPA-Water). The main reason is that the azeotrope consumption needed to distill the same amount of water in bottom column remains the same basically, but the higher the reflux temperature is, the more the heat it is to be brought into the solvent dehydration column.

In summary, in order to reduce C-1 energy consumption, the effective solutions include the following: the reflux temperature is increased, and the MA content rate in reflux is decreased by all means; the reflux is reduced and the control range of separation column is widened. However, according to the technological process, it can be known that the temperature of reflux and the MA content rate can't be individual operation variables, which are both directly determined by D-1 feed and temperature, so it should be analyzed with D-1.

3.2.2. Operation optimization analysis of D-1

The sources of decanter D-1 feed include the stream on top of C-1 column which is the majority part, the side-draw in middle zone and a few fresh NPA feed. The three feed streams condensate and composite in D-1, the main compositions include NPA, Water, MA, the amount of PX and HAC which are quite small, it's usually below 0.1%. As a result, about D-1 in this article, only the NPA-Water-MA triad is covered.

Fig. 7 is the NPA-Water-MA triad at a normal temperature and pressure, it shows that NPA and MA are mutually soluble, NPA and Water are soluble partly, so do MA and Water, which form a two-phase region and two mono phase fields. After condensing, the stream in the top of the column appears liquid–liquid lamination, and presents three phases which are water phase and organic phase in majority, and gas phase. The tie line in Fig. 7 shows that the distribution of MA in the two liquid phases is not equivalent. If D-1 feed is located at point F1, then it's divided into water phase W1 and organic phase R1. When the tie line leans to the right, which means that more MA is dissolved in organic phase, and less in water phase, then the relevant gas composition is V1, meanwhile MA in V1 is much more than that in the other two phases. If the feed composition is located in point F2, then it's divided into water phase W2 and organic phase R2, and the relevant gas phase is V2. When the tie line leans to right with a slop more than W1R1, with the consideration of other several tie lines, it can be concluded that the MA content rates both in organic and water phases rise correspondently as the MA content rate in feed increases along with the increase of the tie line slop. Meanwhile, it indicates that when the MA content rate increases in feed, the rising speed of the MA rate in organic phase is faster than that in water phase.

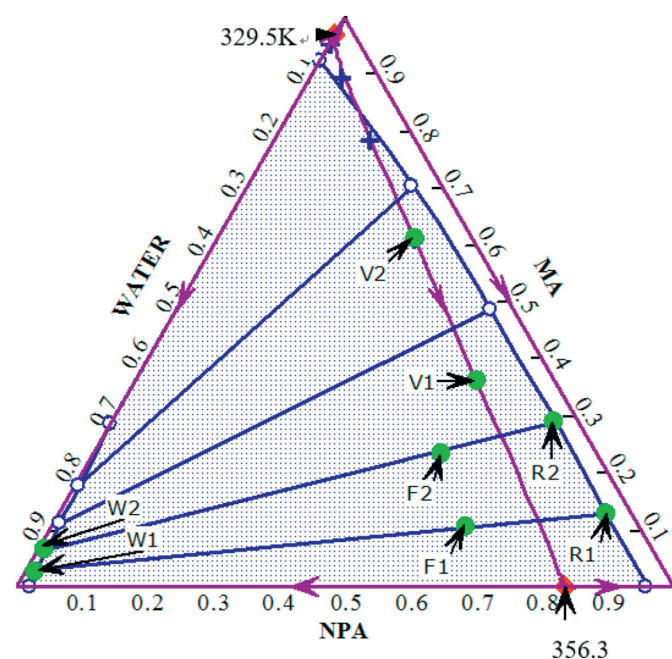


Fig. 7. Ternary VLE map of NPA-Water-MA at normal pressure and temperature. — Distillation Boundary, - - - Tie lines, ■ Envelope, ■ Azeotropes.

In this investigation, D-1 temperature during the dehydration process is 350.75 K, and its pressure is 0.105 MPa. Fig. 8 is a vapor–liquid phase equilibrium diagram. It shows that if D-1 feed starts at the NPA-Water azeotropic point with maintaining the NPA and Water content rates remains the same, the MA content rate gradually increases (namely, feed point moves from A to B along a straight line), the result is that the MA content rates in two phases increase as well. When the point reaches F, gas phase appears, and the compositions of organic phase, water phase and gas phase are shown as the three points R, L, V in the graph. Fig. 9 is a sensitivity analysis diagram for all stream components of D-1 as MA content variation in feed. It shows when the MA content rate is comparatively small (less than 10.8%), all the stream variation tendencies remain the same as that of triphase diagram in Fig. 8, which means that the MA content rates in two liquid phases increase as the NPA content rate decreases, meanwhile

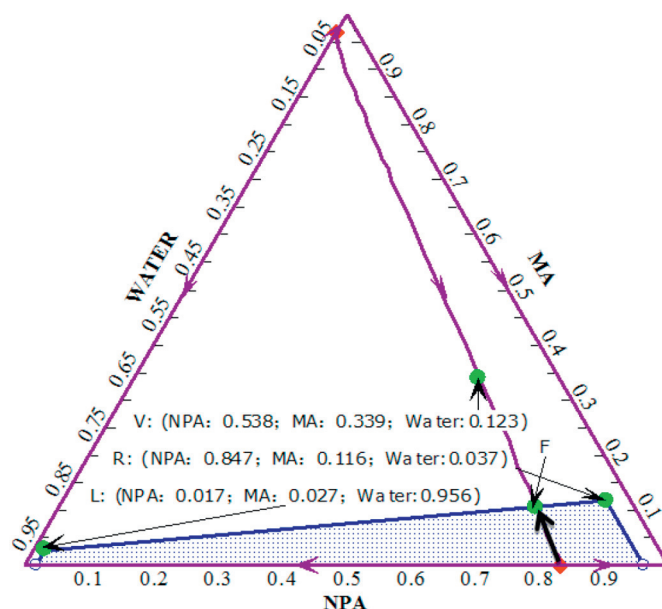


Fig. 8. Ternary VLE map of NPA-Water-MA at 0.105 MPa, 350.75 K. — Distillation Boundary, - - - Tie lines, ■ Envelope, ■ Azeotropes.

the organic phase stream rises as the water phase stream remains the same basically. It indicates that the additional MA in feed is normally accumulated and transferred into the organic phase. When the MA content is more than 10.8%, it starts to present gas phase, and as the MA content rate keeps rising, the compositions of three phases remain the same, respectively corresponding to the three points R, L, and V in Fig. 8. And the triphase streams appear obvious change accordingly, meanwhile two liquid phases reduce as the gas stream increases apparently. It indicates as following: when the MA content rate equals to 10.8%, the feed composition corresponds to point F in Fig. 8. And when the MA content rate in D-1 feed is accumulated to point F (the bubble point under the operation pressure temperature), the content rates in D-1 triphase reach the maximum value (the three points R, L and V in Fig. 8) and remain the same, and the continuous increase of the MA content rate only leads to the triphase stream change, especially the dramatic increase of gas phase flow.

It can be learned that under the stable working condition, the ultimate MA content rate in the organic phase reflux is only related to the D-1 temperature and pressure, as the operation pressure in actual operation normally is fixed. Fig. 10 is a sensitivity analysis diagram which shows how the D-1 triphase composition extremums change along with the D-1 temperature variation when the pressure is set to be 0.105 MPa. The figure also shows the MA content rate maximum in organic phase reflux decreases when the D-1 temperature increases.

Therefore, by raising the D-1 temperature, the MA content rate in organic phase reflux can be reduced. When the D-1 temperature rises, that of the organic phase reflux discharge rises as well. Based on the Figs. 5 and 6 above, it can be learned when the reflux temperature rises or the MA content rate in reflux decreases, both factors are beneficial to the reduction of C-1 reboiler heat for the dehydration column. Hence, the temperature rising is very favorable for the C-1 energy consumption reduction of.

However, Fig. 10 shows when the temperature rises, the MA content rate in the organic phase reflux reduces as the two liquid streams reduce correspondently and the gas phase stream increases significantly, which causes the MA and NPA content rates entering C-3 increase dramatically. Consequently, it should be considered as the impact to C-3 separation characteristics brought by the D-1 temperature

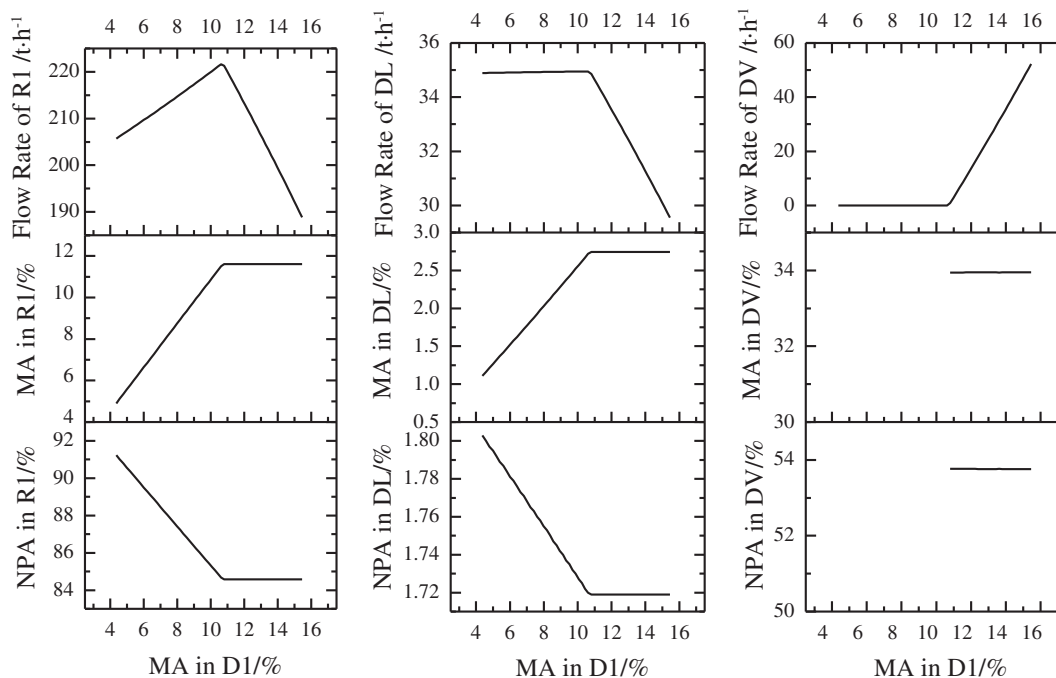


Fig. 9. The variation of composition and flow rate of D-1 products with the MA content in D1.

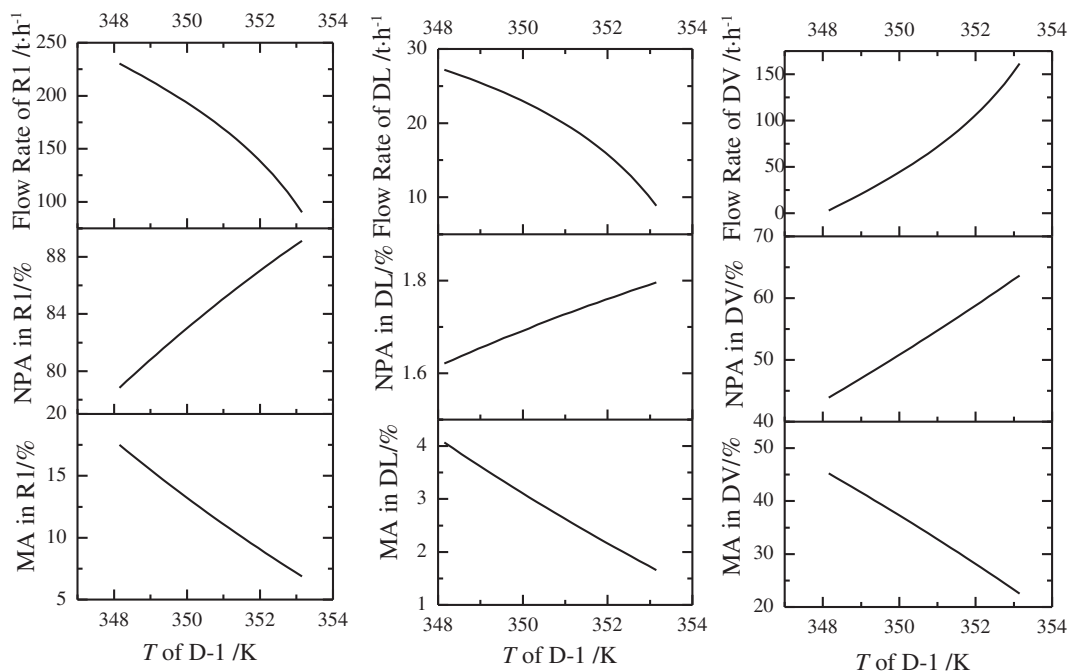


Fig. 10. The variation of final composition of D-1 products with the temperature of D-1.

rising, meanwhile all the NPA recovery by side-draw should be ensured it doesn't cause any extra entrainer consumption. From the sensitivity analysis of bottom saturated vapor and side-draw stream in our previous work [12], it can be learned that the more NPA and MA content are needed to recover, the more correspondent heat is needed. Besides the variation of C-3 stream in middle zone as D-1 feed causes the variation of all D-1 feed streams inevitably. As a result, the D-1 temperature variation should take the consideration of C-3 separation characteristics and the needed energy consumption variations.

3.2.3. Operation optimization of C-3

The separation objectives in entrainer recovery column is to recover NPA and MA in the water and gas phases, and the optimal separation effect includes all NPA in side-draw is recovered, and the most of MA is distilled in top during the gas phase. Compared to C-1, C3 bottom reboiler duty reduces greatly, the saturated vapor feed is $5.28 \text{ t} \cdot \text{h}^{-1}$, which is about $12.25 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$, all those make it as a low energy consumption column. Therefore, in this article, the separation effect is considered as the preferential objective during the operation optimization for this column. Fig. 11 is triad RCM of NPA-Water-MA in this column,

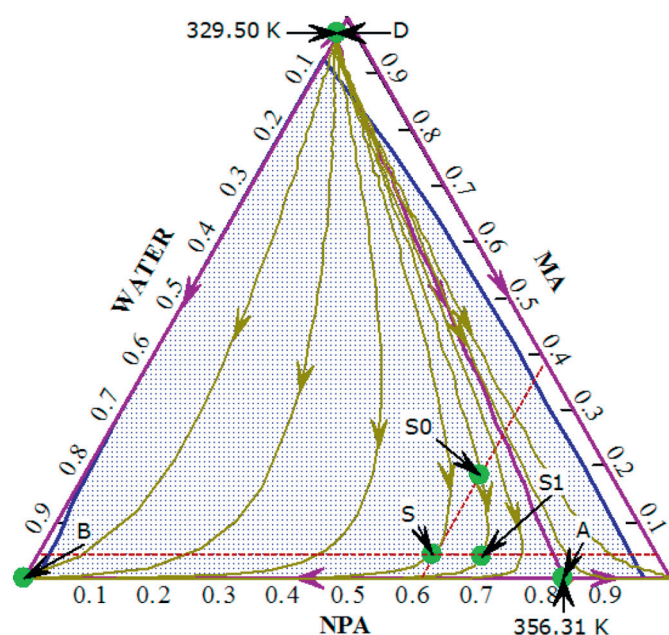


Fig. 11. RCM of NPA-Water-MA in C-3. — Distillation Boundary, - - - Residue curves, ... Envelope.

which shows it's divided by the distillation separatrix into two zones, the left is the high-water content zone, and the right is the low water content zone. If we want to recover all NPA from side-draw, then we must ensure the C-3 feed composition in the high-water content zone to make those NPA gathered in the middle zone of C-3, and the bottom contains the pure water accordingly (as B point in the figure), and the top contains MA-Water azeotrope, meanwhile the optimal side-draw point in middle zone should be the highest point of the NPA content rate. The figure shows the highest point showing the NPA content rate moves to the point of NPA-Water azeotrope (Point A in the figure) gradually. In order to recover all NPA and MA, theoretically, the side-draw stream in middle zone shouldn't contain MA, and the minimal side-draw rate is the result that the amount of total NPA content feed is divided by the amount of NPA in NPA-Water azeotrope. And since the top distillation can't bring NPA out, the maximum amount of the MA content during the top distillation is the result that the total amount of MA feed is divided by the amount of MA content in MA-Water azeotrope. However, in the actual process, due to the following elements such as vapor-gas phase equilibrium, feed composition and operation condition and so on, usually the optimal separation effect can't be achieved.

The top distillation rate is $4800 \text{ kg} \cdot \text{h}^{-1}$ under the actual working condition, and it's pure MA-Water azeotrope whose composition is point D in Fig. 11 (97.1% MA, 2.9% Water), the side-draw rate is $20000 \text{ kg} \cdot \text{h}^{-1}$, which means all NPA is recovered into the recovery column and its composition is Point S0 in Fig. 11 (61.5% NPA, 18.2% MA, 20.3% Water), in which $3634 \text{ kg} \cdot \text{h}^{-1}$ of MA is recycled to D-1, the MA distillation rate is less than 60%, and S3 in side-draw from the recovery column is one of D-1 feed. It can be learned from the analysis result in Figs. 8 and 9 above that after D-1 feed composition reaches the extreme point F, by reducing the MA content rate in feed, the stream in gas phase into C-3 reduces dramatically, which means the separation and recovery load of MA and NPA in C-3 reduce dramatically as well. During C-3 operation optimization in this article, we try to reduce the MA content rate in side-draw as possible as we could with the condition that all NPA is recovered.

The residue curve crossing point S0 in Fig. 11 shows the MA content rate is comparatively high at this point for the side-draw and it isn't the highest point for the NPA content rate in residue curves, which isn't

beneficial to the NPA recovery, therefore the optimal point for the side-draw should be S1 (68% NPA, 4% MA, 28% Water). The sensitivity analysis in our previous work [12] shows the separation effect of NPA and MA can be controlled by the amount of bottom heat for saturated vapor, the side-draw rate in middle zone, and top distillate rate. In this research of operation optimization, for the convenience to study the variation tendency of reboiler duty along with the all parameter variation, the saturated vapor by bottom heat, Fs3 is replaced by the reboiler duty, and by the calculation based on the model, we can get the result of the minimal reboiler duty adding the operation parameter of reflux rate. Under the actual working condition, the point of side-draw in middle zone is fixed, the composition of the side-draw in middle zone is adjusted by the adjustment of the side-draw rate, the top distillate rate in gas phase and the reflux rate. And caused by the fact that the side-draw is recycled to decanter column, its composition in the stream causes the variation of all outfeed in the stream, and the variation of NPA feed in recovery column as well. Then we also adopt the method that we disconnect the reflux and connected streams, and set the proper initial values based on the experience and theory analysis, and proceed on the repeated reiterative calculation. When the calculation result of the model is close to the needed separation goal, with the assistance of the function module in Design Spec/Vary, we can set the NPA rates in bottom stream B3 as zero, the MA content rate and NPA content rate in side-draw S3 as 4% and 68%, and the MA content rate in top distillation as 97.1%, which are 4 targeted equality constraints, meanwhile, we add three operation variables, namely, the S3 stream rate in side-draw, D3 reflux rate in top distillation, and reflux ratio RR, in the end, with the assistance of the initial value reiterate when disconnecting the streams, we get the result based on the model which constrains to achieve the targeted separation effect, and the needed reboiler duty. The optimized operation parameters under the current working condition include the following: the reflux ratio is 4.49, the needed minimal reboiler duty is $12.87 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$, the MA content rate in top distillation is $5094 \text{ kg} \cdot \text{h}^{-1}$, the MA content rate in the side-draw stream is $474 \text{ kg} \cdot \text{h}^{-1}$, and the MA distillation rate is over 90%. Although the increase of the MA content rate in top distillation causes the small increase of the reboiler duty compared to that under the original working condition, the benefits are that the MA distillation rate increases significantly, the influence of MA to D-1 during the side-draw reflux is minimized, and the NPA rate of the side-draw in the column is moved to the highest point.

Under the optimized working condition, the amount of side-draw is $11700 \text{ kg} \cdot \text{h}^{-1}$, 50% less than the value, $20000 \text{ kg} \cdot \text{h}^{-1}$ under the original working condition, and the amount of draw on column top is $5250 \text{ kg} \cdot \text{h}^{-1}$ slightly more than the value $4800 \text{ kg} \cdot \text{h}^{-1}$ in the relations between the all separation indexes and the rate of C-3 side-draw and top distillate. The figure shows the bottom NPA lost when the side-draw S3 is below a certain value, so the minimal out-draw ensures all NPA recovery. When it's below the minimal value, the amount of side-draw increases and NPA content rate in S3 remain almost the same, meanwhile bottom NPA content rate drops to zero directly and the bottom reboiler duty increases largely. On the other hand, when it's above the minimal value, the amount of side-draw increases and the NPA content rate in S3 drops gradually, meanwhile the bottom NPA rate remains zero. So, it shows that the amount of additional side-draw is mainly from water, and the bottom reboiler duty decreases as the amount of side-draw increases. As a result, when achieving the optimal separation effect, we can increase the amount of side-draw, which means that the NPA content rate decreases in side-draw. The variation that all parameters of the separation effect change along with the change of the top distillate rate in Fig. 12 shows the MA content rate in S3 from the side-draw decreases along with the increase of the top distillate rate, when the top distillate rate is below $5400 \text{ kg} \cdot \text{h}^{-1}$, the top distillation hardly contains NPA, and the bottom reboiler duty increases gradually, then when the top distillate rate is above $5400 \text{ kg} \cdot \text{h}^{-1}$, the NPA content rate in top distillation increases largely,

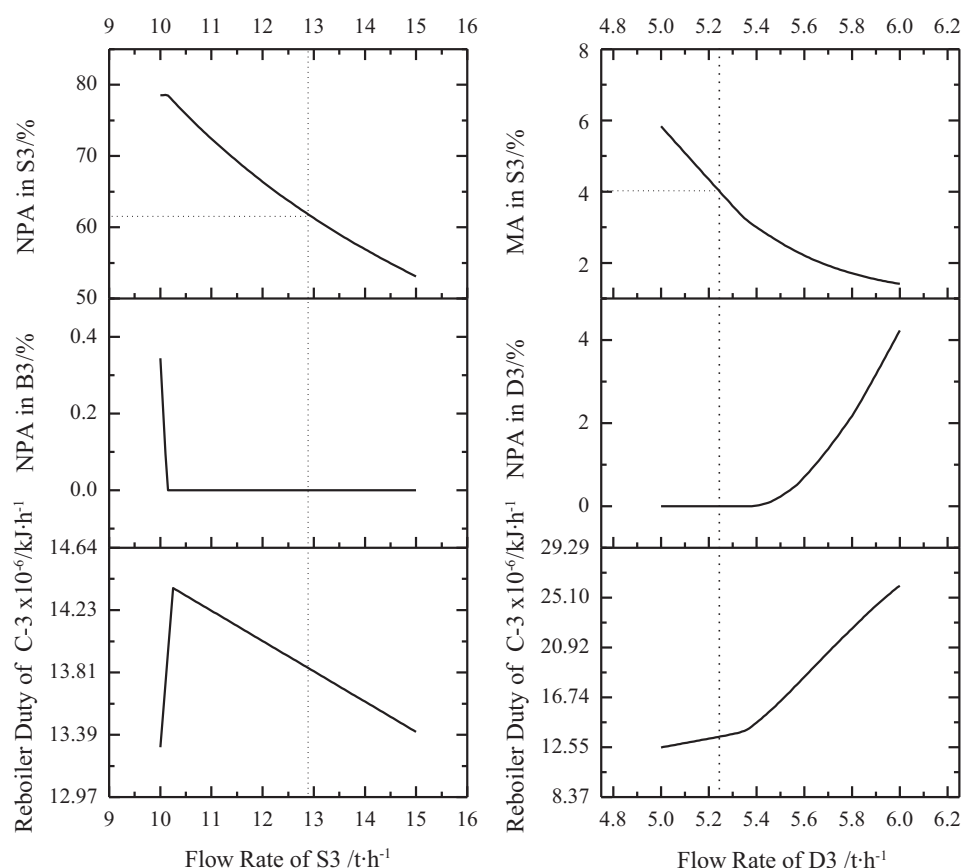


Fig. 12. The variation of separation parameters with flow rate of S3 and D3 in C-3.

and the bottom reboiler duty increases significantly as well. Therefore, under such feed condition, the optimal top distillate rate should be lower than $5400 \text{ kg} \cdot \text{h}^{-1}$. Considering the balance of MA top distillate rate as higher as possible and the comparatively low bottom reboiler duty, we select a moderate value 4% as the MA content rate in side-draw.

Consequently, according to the result of this analysis, it shows in Fig. 12 that if we move forward the original point S1 of optimization parallelly to the direction which shows NPA content reduces along the straight line indicating MA content rate is 4%, and to reach the point S (61.5% NPA, 4% MA, 34.5% Water) which intersects with the straight line which indicates that the NPA content rate is 61.5% under the original working condition, this point is located near to the highest point of the NPA content rate indicated by residue curves, which meets the following requirements, the MA content rate is as low as possible, the amount of side-draw increases and the location of NPA draw is optimal. Then we reset the module of Design Spec/Vary, and the result of simulation calculation is the new optimal point S which is the location used for the draw in middle zone, and the calculation also shows that the minimal reboiler duty needed for this separation effect is $12.16 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$. Table 6 is the comparison of all operation parameters with that under the original working condition. Then it

can be concluded that compared to the original working condition, the separation effect is improved dramatically while the needed reboiler duty decreases in a small scale under the optimized working condition.

3.3. Operation optimization of the overall HAC dehydration process

3.3.1. Problem description

Referring to the optimization result for all unit equipment described above, MA has a significant impact to the separation effect of all unit equipment. Fig. 13 is the main distribution diagram of MA during this Dehydration process. In this process, MA appears as the ternary mixture NPA-Water-MA recycling among C-1, D-1 and C-3. It shows that this process includes two stream recycles with D-1 as the center. And under certain working condition, namely, C-1 feed is stable, and the MA content remains the same, MA enters the dehydration column first, then it is transferred into D-1 in vapor phase from the top of the C-1, and at last in D-1, the ternary mixture NPA-Water-MA reaches VLL phase equilibrium. As D1 stream mainly is in the organic phase, according to the ternary map of NPA-Water-MA in Figs. 7 and 8, most of MA within it refluxes to the dehydration column in the organic phase, the rest of it being a small part enters C-3 along with the gas and water phase of D-1.

If MA from those recycling to the dehydration column and from feed are both distilled from the column top, the MA content rate in vapor at the top of column, and D-1 feed in the organic phase all increases respectively, which recycles back to C-1 in the end. As the recycle keeps running, even if the amount of MA is quite small in feed, the MA content surely is continuously accumulated in a large scale of amount as recycling between the dehydration column and D-1 after a period of operation. From Fig. 5, the result of analysis shows that this kind of accumulation certainly causes a great amount of unnecessary reboiler energy consumption. In this research, when the MA stream in

Table 6
Separation parameters of C-3 before/after optimization

Parameter	Value before optimization	Optimization condition 1	Optimization condition 2
Top distillation/ $\text{t} \cdot \text{h}^{-1}$	4.8	5.25	5.2
Side-draw/ $\text{t} \cdot \text{h}^{-1}$	20	11.7	12.8
Side-draw MA content/wt%	18.2	4	4
MA recovery ratio/wt%	56.2	91.5	90.7
Reboiler duty/ $\times 10^6 \text{ kJ} \cdot \text{h}^{-1}$	12.25	12.87	12.16

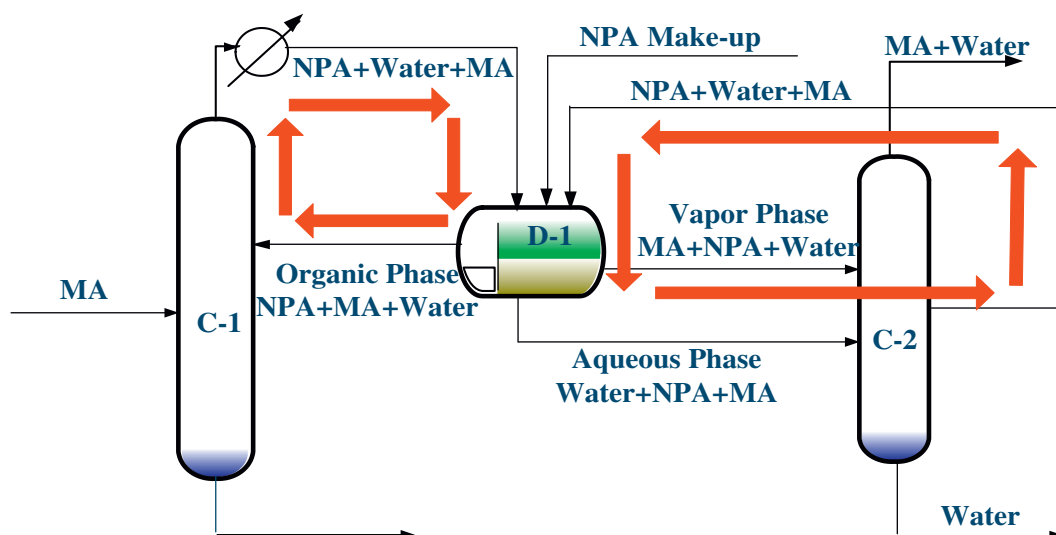


Fig. 13. Distribution map of MA.

feed under the actual working condition is about $3930 \text{ kg} \cdot \text{h}^{-1}$, the MA content rate in the reflux (on top and in middle zone) is about 11.6%, the stream is about $25430 \text{ kg} \cdot \text{h}^{-1}$, which means that the final amount of MA accumulated in the dehydration column is as 6 times as that in feed.

The result of operation analysis and optimization for D-1 shows that the final MA content rate in recovery during the organic phase is only related to D-1 temperature, then by raising D-1 temperature, the amount of MA cycling between the dehydration column and D-1 can be reduced. However, as the temperature of D-1 rises, the stream in gas phase increases significantly as well. By reviewing Fig. 13 of combination tendency, it can be learned that it brings a great amount of MA and NPA into C-3 along with the stream. In this condition, when achieving the same separation effect, the energy consumption increases due to the load increase of C-3, meanwhile, the stream composition of side-draw S3 recycling to D-1 changes accordingly, furthermore, it influences the distribution of three phases in D-1. Hence the two recycle streams formed by two feed streams and three outfeed streams affect and interact among each other. Thus, the determination of the optimal operation temperature must be based on the following consideration, namely, the separation effect of C-1 and C-3 located

before and after D-1 must be optimal, and the overall energy consumption of the HAC dehydration must be optimal.

Therefore, about overall operation optimization of the HAC dehydration process, with the objective that the sum of reboiler duty Q_{Total} reaches the minimum value, the following conditions are the formula is $F(X) = \min Q_{\text{Total}}, Q_{\text{Total}} = Q_{\text{C-1}} + Q_{\text{C-3}}$, the temperature of D-1 is the operation variable, the overall model of the dehydration process under the overload working condition described in our previous work is its basic equality constraints, and the individual column separation effect of C-1 and C-3 is the constrain based on the optimized result of the HAC column and azeotropic recovery column.

3.3.2. Overall process optimization of HAC dehydration process

Based on the results of operation optimization analysis for all unit equipment above, this article illustrates the observation of MA distribution variation during the whole procedure as D-1 temperature changes, and the reboiler duty variation of C-1 and C-3 in the two columns respectively and comprehensively with the following 3 conditions, namely, C-1 bottom water content rate keeps at 6.5%, respective C-3 side-draw distillation composition rate meets S point

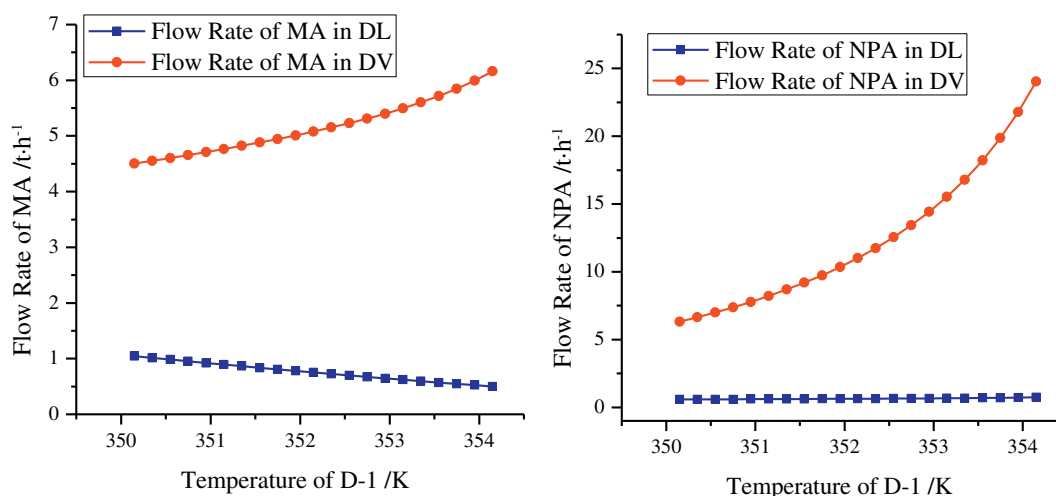


Fig. 14. The variation of MA and NPA content of the feeds in C-3 with the temperature of D-1.

shown in Fig. 11 (61.5% NPA, 4% MA, 34.5% Water), and all recycle stream and connection stream are operated in iterations.

The original working condition temperature is 350.75 K, and according to the analysis result, D-1 temperature increase not only causes the decrease of the MA content rate in reflux, but also the temperature rising of reflux, which are both beneficial to the decrease of C-1 reboiler duty. However, the temperature of D-1 can't rise unlimitedly. In order to recover the compositions in different phases, the operation temperature must be controlled under the azeotropic point (356.31 K) of NPA-Water entrainer for composition under the operation pressure. As a result, this article mainly focuses on the separation and energy consumption performance under the respective working conditions with the temperatures divided every 0.2 K from 350 K to 355 K.

Fig. 14 shows the variation of MA and NPA content rate in D-1 outfeed during the gas phase and water phase along with the D-1 temperature change. It shows that the MA content decreases and the NPA content increases slightly in water phase along with the D-1 temperature rising, since the amount is quite small, it can be ignored almost, and the MA content increases in gas phase gradually with a total amount of around only $1.5 \text{ t} \cdot \text{h}^{-1}$ as the NPA content increases largely which reaches nearly additional $20 \text{ t} \cdot \text{h}^{-1}$. Therefore it can be concluded that the increase of feed load is mainly caused by the increase of NPA content rate in stream feed during the gas phase. This simulation is accordance to the variation tendency in the results of temperature sensitivity analysis shown in Fig. 10 above, however the overall MA content rate and its increasing speed both have obviously decreased, which mainly benefits by the MA content rate optimization in the stream coming from C-3 side-draw and recycling to D-1.

Fig. 15 shows the variation of bottom reboiler duty of C-1 and C-3 in the overall process along with the change of D-1 temperature. It shows that C-1 reboiler reflux decreases dramatically as D-1 temperature rises. Based on Figs. 5 and 6 above, the result of analysis is the same, that is the energy-saving effect is mainly caused by MA content rate decrease and reflux temperature rising. And when C-3 reboiler duty increases slightly before D-1 temperature 352 K and increases significantly after D-1 temperature 352 K. Refer to the variation tendency of feed load, it can be learned that the reason is in the beginning temperature range, NPA content increases comparatively slightly, however the decrease of MA content rate in water phase favors the decrease of reboiler duty quite a bit, which offsets part of reboiler duty increase caused by the feed in gas phase.

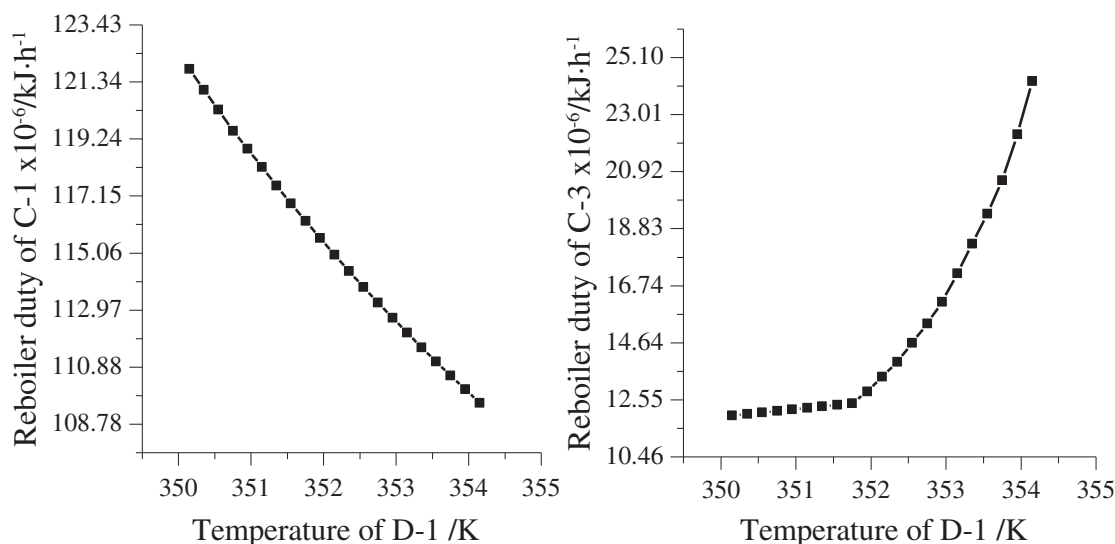


Fig. 15. The variation of reboiler duty of C-1 and C-3 with the temperature of D-1.

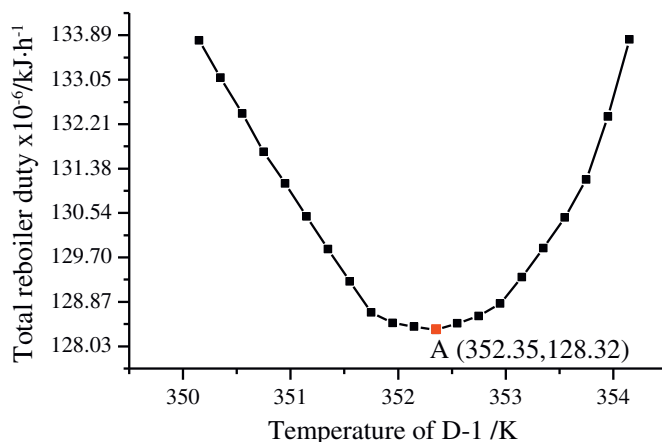


Fig. 16. The variation of total reboiler duty with the temperature of D-1.

From this result, as D-1 temperature rises, the reboiler duty of C-1 drops and that of C-3 rises accordingly, and there must be an optimal temperature point which makes the sum of reboiler duty from the two columns achieves the minimum value. Fig. 16 is the variation tendency of the sum of reboiler duty from the two columns along with the change of D-1 temperature. The figure obviously shows when the temperature is 352.35 K, the sum of reboiler duty reaches the minimum value which is $128.320 \times 10^6 \text{ kJ} \cdot \text{h}^{-1}$, namely point A in this figure. Then the optimal operation temperature of D-1 is 352.35 K.

3.3.3. Analysis of the results

Table 7 is a comparison diagram of all key separation parameters and operation parameters during the HAc process between after all the processes are optimized and under original working condition.

4. Conclusions

It can be concluded that the key separation indexes of the two distillation columns (the composition and temperature on top and bottom) are both in accordance to those under the original working condition, which fully meet the separation requirements. Based on the original working condition, the key operation parameters changed include the following: the control line of the bottom water content rate which rises from 6.3% to 6.5%, D-1 temperature which rises from 350.75 K

Table 7

Comparison of the operation parameters of each plant before/after optimization

Unit	Parameter	Value before optimization	Optimization condition 1
C-1	Top temperature/K	358.35	359
	Bottom temperature/K	390.45	390.3
	Side-draw temperature/K	367.05	366.55
	Top HAc content/wt%	<0.01	<0.1
	Bottom water content/wt%	6.3	6.5
	Top distillate/kg·h ⁻¹	252,050	242,577
	Bottom stream/kg·h ⁻¹	140,520	140,920
	Side-draw/kg·h ⁻¹	3800	3800
	Reflux/kg·h ⁻¹	208,800	198,927
	Reflux MA content/wt%	11.6	8.4
	Reflux temperature/K	350.75	352.35
	Reboiler duty×10 ⁻⁶ /kJ·h ⁻¹	121.89	114.28
D-1	Decanter temperature/K	350.75	352.35
	Vapor steam/kg·h ⁻¹	21,850	19,483
	Aqueous stream/kg·h ⁻¹	33,538	36,126
	Organic stream/kg·h ⁻¹	215,217	207,144
C-3	Top temperature/K	329.25	329.25
	Bottom temperature/K	375.45	375.45
	Top MA content/wt%	97.1	97.1
	Bottom water content/wt%	100	100
	Top distillate/kg·h ⁻¹	4800	5220
	Bottom stream/kg·h ⁻¹	34,320	36,240
	Side-draw/kg·h ⁻¹	20,000	20,120
	Side-draw temperature/K	346.65	354.05
	Side-draw MA content/wt%	18.2	4
	Side-draw NPA content/wt%	61.5	61.5
	Reboiler duty×10 ⁻⁶ /kJ·h ⁻¹	12.25	13.92

to 352.35 K, C-3 top distillation rate which rises from 4800 kg·h⁻¹ to 5220 kg·h⁻¹, and MA content rate of side-draw in middle zone which decreases from 18.2% to 4%, and the modification for the rest of operation parameters are based on material balance principle and the calculation results of respective equipment unite accordingly.

With ensuring the separation effect during the optimization, the needed top reflux flow of C-1 reduces 10 t·h⁻¹, and the needed reboiler duty reduces 7.61 × 10⁶ kJ·h⁻¹ which is around 3.27 t·h⁻¹ low-pressure saturated vapor. Although C-3 reboiler duty increases 1.67 × 10⁶ kJ·h⁻¹ slightly, but the overall reboiler duty still appears a significant decrease from the original value, 134.14 × 10⁶ kJ·h⁻¹ to the current value, 128.2 × 10⁶ kJ·h⁻¹, which saves 5.93 × 10⁶ kJ·h⁻¹, about 2.56 t·h⁻¹ low-pressure saturated

vapor. With the assumption that the operation runs 24 h in 300 days of a year and the price of low-pressure vapor (0.45 MPa, 148 °C) per ton is 150 CNY, the cost saving of per column on a year basis is around 3.35 million CNY, and that of the whole process is around 2.76 million CNY yearly.

References

- [1] S. Widagdo, W.D. Seider, Journal review. Azeotropic distillation, *AIChE J.* 42 (1) (1996) 96–130.
- [2] S.K. Wasylkiewicz, L.C. Kobylka, et al., Optimal design of complex azeotropic distillation columns, *Chem. Eng. J.* 79 (3) (2000) 219–227.
- [3] I.L. Chien, K.-L. Zeng, et al., Design and control of acetic acid dehydration system via heterogeneous azeotropic distillation, *Chem. Eng. Sci.* 59 (21) (2004) 4547–4567.
- [4] I.L. Chien, H.-P. Huang, et al., Influence of feed impurity on the design and operation of an industrial acetic acid dehydration column, *Ind. Eng. Chem. Res.* 44 (10) (2005) 3510–3521.
- [5] H.-P. Huang, H.-Y. Lee, et al., Design and control of acetic acid dehydration column with *p*-xylene or *m*-xylene feed impurity. 1. Importance of feed tray location on the process design, *Ind. Eng. Chem. Res.* 46 (2) (2006) 505–517.
- [6] H.-Y. Lee, H.-P. Huang, et al., Design and control of an acetic acid dehydration column with *p*-xylene or *m*-xylene feed impurity. 2. Bifurcation analysis and control, *Ind. Eng. Chem. Res.* 47 (9) (2008) 3046–3059.
- [7] S.-J. Wang, C.-J. Lee, et al., Plant-wide design and control of acetic acid dehydration system via heterogeneous azeotropic distillation and divided wall distillation, *J. Process Control* 18 (1) (2008) 45–60.
- [8] S.J. Li, Influence of *p*-xylene (PX) accumulation on the operation of pure terephthalic acid (PTA) solvent dehydratic distillation column, *Ind. Eng. Chem. Res.* 48 (13) (2009) 6358–6362.
- [9] S.-J. Wang, D.S.H. Wong, Online switching of entrainers for acetic acid dehydration by heterogeneous azeotropic distillation, *J. Process Control* 23 (1) (2013) 78–88.
- [10] Qianlong Li, Wei Guan, Lei Wang, Hui Wan, Guofeng Guan, Dynamic simulation and control of a complete industrial acetic acid solvent dehydration system in purified terephthalic acid production, *Ind. Eng. Chem. Res.* 54 (45) (2015) 11330–11343.
- [11] X. Huang, W. Zhong, et al., Isobaric vapor-liquid equilibrium of binary systems: *p*-xylene + (acetic acid, methyl acetate and *n*-propyl acetate) and methyl acetate + *n*-propyl acetate in an acetic acid dehydration process, *Chin. J. Chem. Eng.* 21 (2) (2013) 171–176.
- [12] X. Huang, W. Zhong, et al., Thermodynamic analysis and process simulation of an industrial acetic acid dehydration system via heterogeneous azeotropic distillation, *Ind. Eng. Chem. Res.* 52 (8) (2013) 2944–2957.
- [13] U. Block, B. Hegner, Development and application of a simulation model for three-phase distillation, *AIChE J.* 22 (3) (1976) 582–589.
- [14] J.G. Hayden, J.P. O'Connell, A generalized method for predicting second virial coefficients, *Ind. Eng. Chem. Process. Des. Dev.* 14 (3) (1975) 209–216.
- [15] D. Abrams, J. Prausnitz, Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems, *AIChE J.* 21 (1) (1975) 116–128.
- [16] J. Simonetty, D. Yee, et al., Prediction and correlation of liquid-liquid equilibria, *Ind. Eng. Chem. Process. Des. Dev.* 21 (1) (1982) 174–180.