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Separation process of butanol-butyl acetate-methyl isobutyl ketone system by the analysis to residual curve and the double effect pressure-swing distillation☆

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ABSTRACT

The separation of ternary mixture of butanol, butyl acetate, and methyl isobutyl ketone (MIBK) was initially analyzed by the residual curve. In this process, MIBK was chosen as the azeotropic agent during the first step of separation. The optimum mass ratio of extra MIBK was 1.6 in the modified feed stream according to the residual curve. Thus on this condition the top product was butanol-MIBK azeotrope while the bottom product was butyl acetate in the preliminary separation of the mixture. Then the butanol and MIBK azeotrope was separated by the double effect pressure-swing distillation with the low pressure column performing at 30 kPa and the atmospheric pressure column at 101 kPa. The optimal operating conditions were then obtained by using Aspen Plus to simulate and optimize the process. The results showed that the mass purities of butanol, butyl acetate, and MIBK were all more than 99% and reached the design requirements. Additionally, compared with the traditional distillation with outside heating, the double effect pressure swing distillation saved the reboiler duty by 48.6% and the condenser duty by 44.6%.

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1. Introduction

As important industrial raw materials, butyl acetate, butanol, and methyl isobutyl ketone (MIBK) are widely used in many chemical processes. For instance, in a pharmaceutical factory there is an urgent need to deal with the waste liquid which includes 34wt% of butanol, 38wt% of butyl acetate and 28wt% of MIBK. Since the binary azeotropy of butyl acetate and butanol or MIBK can form under atmospheric pressure, the separation becomes greatly difficult. Generally azeotropic distillation or extractive distillation is often used in this circumstance [1], and in some special occasions, the pressure-swing distillation(PSD) is used too [2].

Extractive distillation is a special rectifying method in which the relative volatility of the original components can be changed by adding the third material [3–5]. Although extractive distillation has advantages of low energy consumption, less pollution, and easy recycling of the extractant, it is inevitable to bring impurities to the system. In azeotropic distillation, a third component is usually put in the system to form a new azeotrope, in which way the raw materials can be separated by ordinary distillation method [6,7].

This paper puts forward a method to separate ternary mixtures by azeotropic distillation through the analysis of the residual curve in the triangle phase diagram. Considering that the addition of a third

component could increase the difficulty of separation, it is reasonable to choose one of the raw components as the azeotropic agent. Therefore MIBK is chosen as the entrainer in this work according to the residual curve, and butyl acetate is isolated from the system firstly.

Analyzing azeotropes through residual curve provides a theoretical basis for the separation of azeotropes and deepen the understanding of the process, so the preliminary separation method can be identified. For the separation of the ternary system, such as adding extraction agent or other entrainer, and then the separation will become quaternary system, complexing the process and increasing investment cost. On the contrary making the component in the raw material as entrainer can greatly simplify the process and reduce the difficulty of the separation, at the same time reduce the introduction of contaminants, so it is good for the subsequent separation. And then based on the phenomenon that the azeotropic temperature and composition of butanol–MIBK change with pressures, the azeotrope is separated through double effect PSD. Typically in double effect PSD, the azeotropic composition changes due to the different pressures between two columns [8–11], and the bottom material of one column could be heated by the latent heat of the vapor at the top of the other column, so it can save energy effectively [12–14]. The other advantage of PSD is that it does not need to introduce any impurities during the whole process [15–18]. Thus PSD is suitable for the system that the azeotropic composition is sensitive to pressure, such as methanol–acetone [19], ethanol–tetrahydrofuran [20], and ethylenediamine–water [21].

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2. Determination of Separation Process

2.1. Analysis to residual curve

The residual curve diagram of butanol, butyl acetate, and MIBK is obtained through Aspen Plus as shown in Fig. 1.

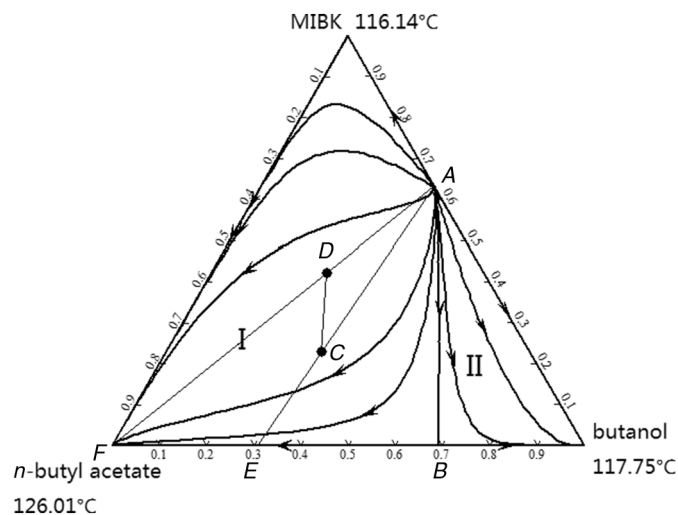


Fig. 1. Residue curve for butanol-butyl acetate-MIBK.

In Fig. 1, A is the azeotropic point formed by butanol and MIBK at 113.36 °C with 37.1wt% of butanol and 62.9wt% of MIBK. B is the azeotropic point at 116.97 °C with 69.2% of butanol and 30.8% of butyl acetate. The line connecting A and B is used as the distillation boundary which divides the diagram into two areas of I and II.

The original feed composition is in C as located in area I in Fig. 1 with 34wt% of butanol, 38wt% of butyl acetate, and 28wt% of MIBK. In a traditional way, butanol and MIBK azeotrope (point A in Fig. 1) is usually obtained from the top of the rectifying column while the mixture of butyl acetate–butanol (point E in Fig. 1) is obtained from the bottom. Then the product in point E goes to another column where the azeotrope of butanol–butyl acetate (point B in Fig. 1) is obtained from the top and pure butyl acetate can be produced from the bottom. After that, the two groups of azeotropes, represented by points A and B, need to be separated subsequently, so the operating and equipment costs are high.

In our process, MIBK is added into the system to change the original composition. When proper amount of MIBK is introduced, the mixture composition gets to point D, from where the azeotrope of butanol–MIBK can be obtained from the top of the column, while butyl acetate can be produced from the bottom according to the residual curve. In this way only one azeotrope of butanol–MIBK needs to be further separated, which can greatly simplify the separation process. Specifically the best dosage of MIBK as the azeotropic agent is to bring all of butanol into the distillate product. It is worth noting that every point in the straight line CD has the same composition ratio of butanol to butyl acetate as point C. Thus, point D should be composed by the original feed and extra MIBK, which becomes the modified feed composition, with 26.9wt% of butanol, 30.06wt% of butyl acetate and 43.04wt% of MIBK as shown in Fig. 1. Each point in the line AF can separate the ternary mixtures into binary mixture of butanol–MIBK and butyl acetate, but if the point of the feed composition is in the other position except for D, at least two components need to be joined in mixture, increasing the complexity. So point D is the optimum modified feed composition. In this paper, the azeotropic agent ratio is defined as the mass ratio of MIBK to butanol in the modified feed stream, which is correspondingly 1.6 based on the calculation with Fig. 1.

2.2. Separation of MIBK–butanol azeotrope

Azeotropic composition usually changes apparently with pressure, so to separate azeotrope by changing pressure is feasible in theory. The azeotropic temperature and composition data of butanol–MIBK binary mixture under different pressures are displayed in Fig. 2.

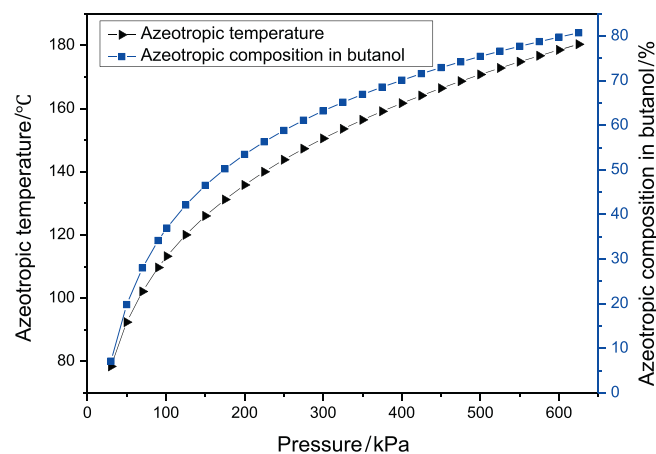


Fig. 2. *p*-*x*-*t* graph of the butanol–MIBK azeotropes.

Fig. 2 shows that the composition of butanol in azeotrope and the azeotropic temperature both rise with the increase of pressure. Therefore a PSD should be suitable for the system. In the process of PSD, pressure is a crucial factor to affect the separating efficiency, so choosing the appropriate pressure is the first priority. When the pressure is 30 kPa, the azeotropic temperature is 78.42 °C with 7.03wt% of butanol and 92.97wt% of MIBK, which is beneficial for butanol to condense easily, so 30 kPa is selected as the low operating pressure. When the condition is at atmospheric pressure, the azeotropic temperature is 116.97 °C with 69.2wt% of butanol and 30.8wt% of MIBK as illustrated in Fig. 2, which can achieve good separation for MIBK and butanol as well. Although continuing to increase the pressure is favorable for the separation, it can increase the operating difficulty and cost, so 101 kPa is selected as the high pressure in this article.

2.3. Separation process

Through the above analysis to the residual curve, the appropriate azeotropic agent ratio is obtained, which can separate the ternary mixture into a binary azeotrope and a pure component. Then the double effect PSD is used to separate the azeotrope into two products, in which the purities of butanol and MIBK are both high. The specific process is shown in Fig. 3. T1 is the preliminary separating column, and its main

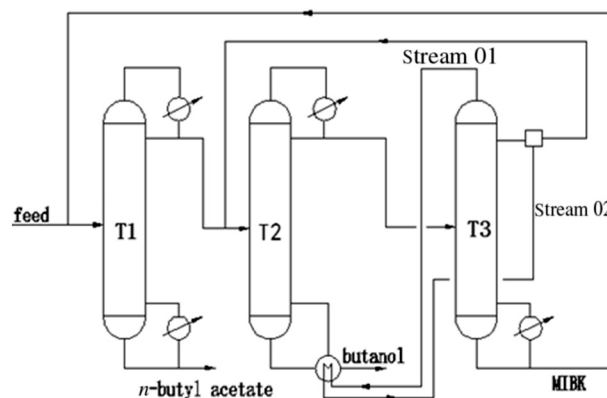


Fig. 3. Separation process of butanol–butyl acetate–MIBK.

purpose is to divide the ternary mixture into butanol–MIBK azeotrope and butyl acetate. The azeotrope with 37.1wt% of butanol and 62.9wt% of MIBK is then treated in the low-pressure (LP) column T2, where the LP azeotrope with a small amount of butanol (7.03%) is got from the top and a large amount of butanol is produced from the bottom of the column. Then the mixture from the top of the LP column goes to the atmospheric pressure column T3, where the atmospheric pressure azeotrope is obtained from the top and MIBK in high purity is attained from the bottom. In order to save energy during the separation process, the azeotrope vapor material (O1) from the top of T3 is transferred with heat to the bottom of T2.

3. Simulation Results and Discussion

3.1. Simulation of column T1

The feed rate was $790 \text{ kg} \cdot \text{h}^{-1}$, and the feed composition was 34wt% of butanol, 38wt% of butyl acetate and 28wt% of MIBK. The feed rate of azeotropic agent was $210 \text{ kg} \cdot \text{h}^{-1}$. The column was operating under the pressure of 0.1 MPa, with 30 theoretical stages, the feed stage of 20 and reflux ratio of 6.

3.1.1. Effects of the theoretical stages

On the basis of fixing the other conditions, the effect of the theoretical stages on the composition of butyl acetate in the distillate and the bottom product is investigated, and the results are shown in Fig. 4.

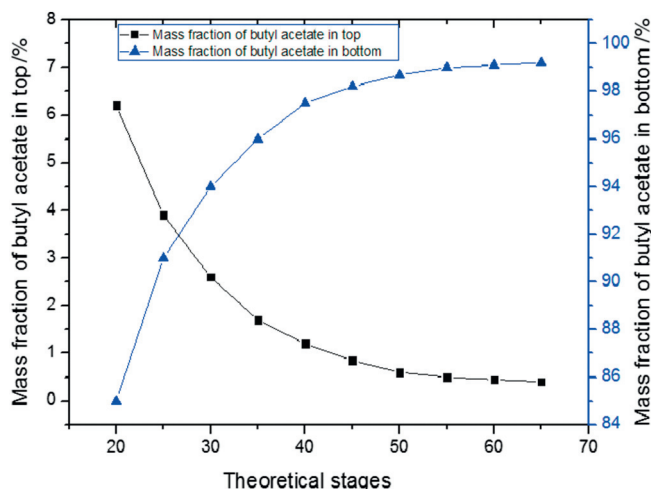


Fig. 4. Effect of theoretical stages on the mass fraction of butyl acetate.

From the simulating results in Fig. 4, it can be seen that the mass fraction of butyl acetate in top decreases gradually with the increase of theoretical stages, while that in bottom increased accordingly. It also worth noting that the mass fractions of butyl acetate in top and bottom both change slowly when the theoretical stages is more than 55, where the composition of butyl acetate reaches 0.39wt% in the top and 99.1wt% in the bottom. When theoretical stages are more than 55, the separation effect can be improved, but it can greatly increase the equipment cost and energy consumption, so the optimal theoretical stages are set as 55.

3.1.2. Effect of the feed stage

The influence of different feed stages on the mass fraction of butyl acetate in top and bottom is shown in Fig. 5. As the feed stage moves from the top to the bottom, the mass fraction of butyl acetate in the top product reduces first and then increases, while the opposite trend appears in bottom. When the feed stage is 32, the content of butyl

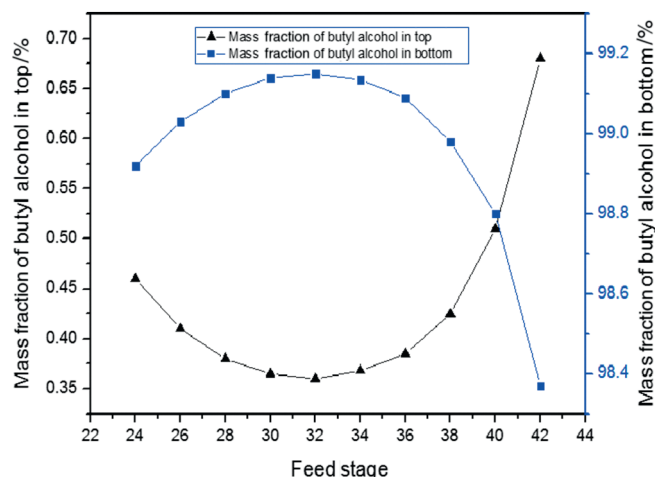


Fig. 5. Effect of the feed stage on the mass fraction of butyl acetate.

acetate in top is the lowest while that in bottom is the highest as illustrated in Fig. 5, so the optimal feed stage is 32.

3.1.3. Effect of azeotropic agent ratio

In order to verify whether the azeotropic agent ratio obtained by residual curve is optimal, the mass fractions of butyl acetate in top and bottom at different azeotropic agent ratios were analyzed, and the results are shown in Fig. 6.

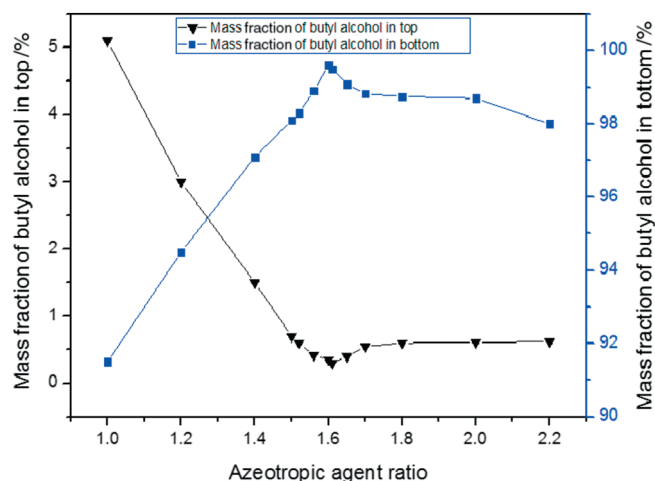


Fig. 6. Effect of azeotropic agent ratio on the mass fraction of butyl acetate.

As can be seen from Fig. 6, the mass fraction of butyl acetate at the top of the column decreases rapidly while that at the bottom increases quickly with the increase of the azeotropic agent ratio. When the azeotropic agent ratio is greater than 1.6, the composition of butyl acetate at the top and the bottom are both stable. So the optimal azeotropic agent ratio is 1.6, which is consistent with that obtained through the analysis to the residual curve.

3.1.4. Effect of reflux ratio

The content of butyl acetate decreases rapidly in top and increases quickly in bottom with the reflux ratio increasing from 2 to 4 as shown in Fig. 7. When the reflux ratio is greater than 5, the butyl acetate content in top and bottom is stable. Since the operating costs increase with increasing reflux ratio, the optimal reflux ratio is 5.

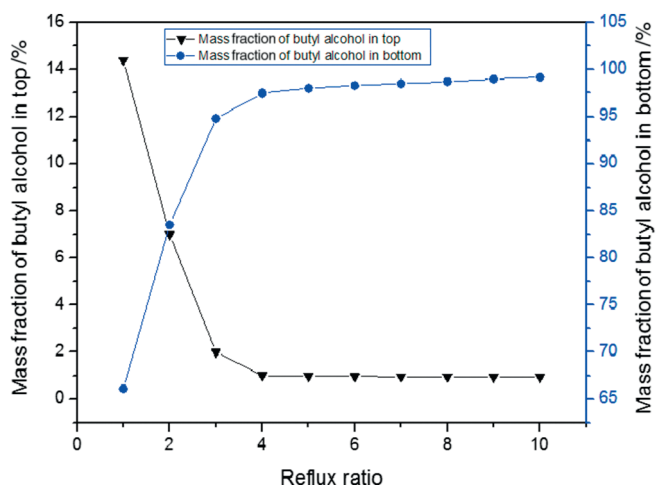


Fig. 7. Effect of reflux ratio on the mass fraction of butyl acetate.

3.2. Double effect PSD simulation of butanol-MIBK azeotrope

In the process of double effect PSD, the steam at the top of T3 is 117 °C and the material at the bottom of T2 is 87 °C, leaving the temperature difference of 30 °C. Thus it is beneficial to use the steam latent heat out of T3 to replenish the reboiler of T2 for saving energy. Specifically the flow rate of stream 01 in Fig. 3 is determined by the heat equilibrium calculation ensuring that the reboiler of T2 can perform efficiently. In this way, the efficient heat integration is carried out by PSD. Finally, T2 and T3 are optimized by sensitivity analysis, and the method is similar to that used in the preliminary separating column. And the results are as the following: the theoretical stages are 40, the feed stage is 25 and reflux ratio is 4 for T1 while the theoretical stages is 50, the feed stage is 25 and reflux ratio is 5 for T2.

3.3. Results in optimum parameters

The simulation results are shown in Table 1 according to the above optimum parameters.

Table 1
Simulating results under optimum parameters

Column	Component	Mass fraction in top/%	Mass fraction in bottom/%	Reboiler duty/kW	Condenser duty/kW
T1	Butanol	38.43	0.01	617	−556
	Butyl acetate	0.52	99.27		
	MIBK	61.05	0.72		
T2	Butanol	14.83	99.12	0	−804
	Butyl acetate	0.41	0.46		
	MIBK	84.74	0.42		
T3	Butanol	49.42	0.01	685	0
	Butyl acetate	0.0015	0.51		
	MIBK	50.57	99.48		

The simulation results indicate that the product mass fraction are all more than 99% with the optimum operating parameters, which can reach the separation requirements in industry.

3.4. Analysis of energy saving effects

In order to analyze the energy saving effect of double effect PSD, the process was simulated without considering the thermal coupling of stream 01 to the bottom of T2. The energy consumption of heat exchangers in the two cases is shown in Table 2. It is clear that the reboiler duty reduced by 48.6%, and the condenser duty reduced by 44.6% in the process of double effect PSD.

Table 2
The heat duty of heat exchanger

Distillation form	Heat exchanger	Heat duty/kW
Double effect PSD	Reboiler	685
	Condenser	−804
Conventional distillation	Reboiler	1333
	Condenser	−1452

4. Conclusions

The paper proposed a separation method for the industrial waste liquid composed by butanol, butyl acetate, and MIBK. Firstly, through the analysis to the residual curve the feasible separating region was found and the azeotropic agent was designated as MIBK to avoid extra separation and also get butyl acetate directly, at the same time, the optimum mass ratio of extra MIBK of 1.6 was determined. Then the binary azeotrope of butanol and MIBK was separated by double effect PSD. Aspen Plus was used to simulate and optimize the whole process, and the optimal process parameters were determined. Under the optimal condition, the results showed that the mass fraction of butanol, butyl acetate, and MIBK were all more than 99%, meeting the designing requirements. Meanwhile compared with conventional distillation, double effect PSD could save reboiler duty by 48.6% and condenser duty by 44.6%. Thus the azeotropic distillation based on the analysis to the residual curve combined with double effect PSD is successfully applied in the separation of the ternary waste liquid illustrated in this paper, and it should have a certain guiding significance for other industrial ternary mixtures.

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