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Simulation of Pressure-swing Distillation for Separation of Ethyl Acetate-Ethanol-Water

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Abstract. In the light of the azeotrope of ethyl acetate-ethanol-water, a process of pressure-swing distillation is proposed. The separation process is simulated by Aspen Plus, and the effects of theoretical stage number, reflux ratio and feed stage about the pressure-swing distillation are optimized. Some better process parameters are as follows: for ethyl acetate refining tower, the pressure is 500.0 kPa, theoretical stage number is 16, reflux ratio is 0.6, feed stage is 5; for crude ethanol tower, the pressure is 101.3 kPa, theoretical stage number is 15, reflux ratio is 0.3, feed stage is 4; for ethanol tower, the pressure is 101.3 kPa, theoretical stage number is 25, reflux ratio is 1.2, feed stage is 10. The mass fraction of ethyl acetate in the bottom of the ethyl acetate refining tower reaches 0.9990, the mass fraction of ethanol in the top of the ethanol tower tower reaches 0.9017, the mass fraction of water in the bottom of the ethanol tower tower reaches 0.9622, and there is also no ethyl acetate in the bottom of the ethanol tower. With laboratory tests, experimental results are in good agreement with the simulation results, which indicates that the separation of ethyl acetate ethanol water can be realized by the pressure-swing distillation separation process. Moreover, it has certain practical significance to industrial practice.

1. Introduction

Ethyl acetate with excellent solubility is an important chemical solvent and commonly used in coatings, paints, synthetic fibers and other production processes [1, 2]. At present, acetic acid and ethanol are used as raw materials to produce ethyl acetate by reactive distillation [3]. However, due to the azeotrope of ethyl acetate-ethanol-water, high purity ethyl acetate cannot be obtained if reactive distillation is the only alternative. Therefore, in view of the azeotrope, whether an efficient separation process can be established is a challenging task. Some special distillation processes, such as azeotropic distillation [4, 5]. extractive distillation [6-8]. and pressure-swing distillation [9, 10]. have been used to solve such problem.

For extractive distillation containing extractive tower and solvent recovery tower, a new component is added to alter relative volatilities of components that need to be separated. For example, Zhang et al. [11]. explored extractive distillation for separating ethyl acetate and ethanol and compared five hydrophilic ionic liquids, which showed that the hydrophilic ILs [Amim]Cl had the highest extraction efficiency and the purity of ethyl acetate could reach 99.27 wt %. However, the addition and recovery of extractants that are essential for extractive distillation will undoubtedly increase the

cost of extractive distillation. Hosgor et al. [12]. compared the two processes (extractive distillation and pressure-swing distillation) for separating methanol-chloroform and explored the controllability of pressure-swing distillation on the basis of economic advantages. Unlike extractive distillation, press-swing distillation that does not need to add any new component can be applied to separating these three compounds more conveniently and economically.

In this paper, a press-swing distillation process is proposed as case studies for separation of ethyl acetate, ethanol and water. Process Optimization is completed in Aspen Plus and laboratory test is used to verify the simulation results.

2. Separation scheme

2.1. Feed and separation requirements

This paper aims at separating the azeotrope including ethyl acetate, ethanol and water, the azeotropic composition of ethyl acetate-ethanol-water under atmospheric pressure (ω (ethyl acetate) =0.7769, thus ω (ethanol)=0.1404, ω (water)=0.0827) is selected as the feed composition and the ethyl acetate mass fraction in the ethyl acetate product and other products is not less than 0.9990 and not more than 0.0005 respectively.

2.2. Ethyl acetate–ethanol-water thermodynamic model

NRTL is the chosen thermodynamic model, and the related binary interaction parameters are shown in Table 1.

Table 1. NRTL binary interaction parameters.

Component 1	Component 2	a_{12}	a_{21}	b_{12}	b_{21}	c_{12}
Ethyl acetate	Ethanol	-0.24	-1.15	282.96	524.42	0.30
Ethyl acetate	Water	-3.72	9.46	1286.14	-1705.68	0.20
Ethanol	Water	-0.80	3.46	246.18	-586.08	0.30

2.3. Feasibility analysis

Table 2 illustrates the azeotropic composition of ethyl acetate-ethanol-water predicted by NRTL under the pressure of 101.3 kPa and 500.0 kPa. The azeotropic composition at 101.3 kPa is ω (ethyl acetate) =0.7769, ω(ethanol)=0.1404 and ω(water)=0.0827, while the azeotropic composition at 500.0 kPa is ω (ethyl acetate) =0.5854, ω(ethanol)=0.4137, ω(water)=0.0008. The results show that the azeotropic composition of ethyl acetate, ethanol and water varies prominently with pressure and Ethyl acetate products with higher purity can be obtained by pressure-swing distillation as well as ethanol and water containing less ethyl acetate. Therefore, the separation of ethyl acetate-ethanol-water azeotropic system by pressure-swing distillation is feasible.

Table 2. Azeotropic composition of ethyl acetate-ethanol-water at 101.3 and 500.0 kPa.

Pressure/kPa	Mass Fraction/%		
	Ethyl acetate	Ethanol	Water
101.3	77.69	14.04	8.27
500.0	58.54	41.37	0.09

2.4. Process flow

Fig. 1 shows the separation process of pressure-swing distillation for ethyl acetate-ethanol-water. Stream F is the feed stream of the azeotrope, and it enters the ethyl acetate refining tower (B1 pressurized tower) after mixing with stream S6. Stream S2 is the high-pressure light liquid phase that the main composition is ethyl acetate, which enters the crude ethanol tower (B2 atmospheric tower) under the action of the pressure difference, and stream S3 is the product of ethyl acetate. Stream S4 is

atmospheric pressure light liquid phase, which is pressurized by a booster pump and mixed with the feed stream to feed the B1 pressurized tower. Stream S5 is mainly a mixture of ethanol and water and further separated after entering B3 ethanol tower. Stream S7 is ethanol product, and stream S8 is water. B1 pressurized tower, B2 atmospheric tower and B3 ethanol tower all select RadFrac model; the mixer uses the Mixer model; booster pump selects Pump model.

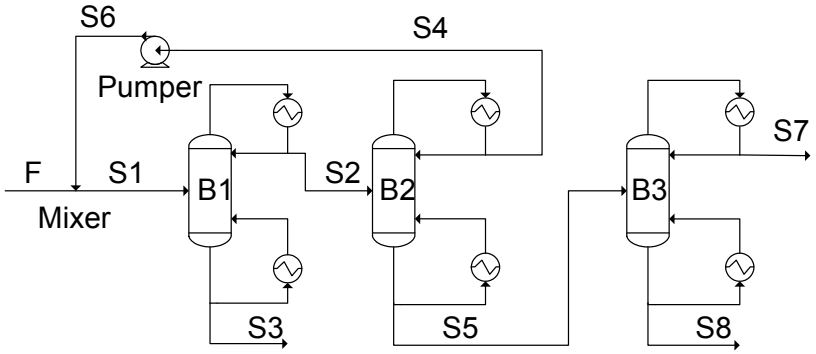

Figure 1. Separation process of pressure-swing distillation for ethyl acetate-ethanol-water.

3. Process simulation and optimization

The main parameters affecting the distillation process include theoretical stage number, reflux ratio and feed position, thus these three parameters are mainly been optimized. At the initial stage of investigation, it stipulates that B1 pressurized tower theoretical stage number is 14, reflux ratio is 1.3, feed stage is 4; B2 tower theoretical stage number is 14, reflux ratio is 0.5, feed stage is 4; B3 ethanol tower theoretical stage number is 25, reflux ratio is 1.2, feed stage is 10.

3.1. Process simulation and optimization of B1 pressurized tower and B2 atmospheric tower

B1 pressurized tower and B2 atmospheric tower functions in the sufficient separation of ethyl acetate. In order to optimize the theoretical stage number, reflux ratio and feed position conveniently, the molar ratios of top to feed (D/F) in the two towers are automatically adjusted through the Design Specs/Vary function, which controls the mass fraction of ethyl acetate at the bottom of B1 pressurized tower and B2 atmospheric tower is 0.9990 and 0.0001 respectively.

3.1.1. Optimization of theoretical stage number of B1 pressurized tower and B2 atmospheric tower, Increasing the theoretical stage number will prolong the vapor-liquid mass transfer time in the distillation tower. Therefore, under the premise of ensuring the degree of separation, increasing the theoretical stage in a certain range will reduce the energy consumption of the distillation tower. Fig. 2 shows the effect of theoretical stage number on the total heat duty of reboilers in B1 and B2 tower. The results show that the total heat duty of the reboilers reduces significantly in the pre-period, and then the trend tends to decrease gradually. Increasing the number of theoretical stages will increase the equipment input of the distillation tower, so the number of theoretical stages of B1 pressurized tower is selected 16, and the number of theoretical stages of B2 atmospheric tower is selected 15.

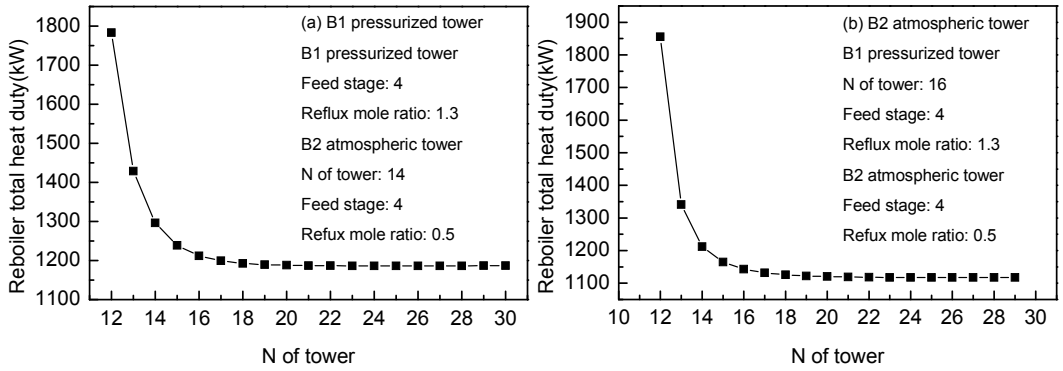

Figure 2. The effect of the theoretical stage number on the reboiler total heat duty of B1 and B2 tower.

3.1.2. Optimization of reflux ratio of B1 pressurized tower and B2 atmospheric tower, Fig. 2 shows the effect of reflux ratio on the total heat duty of the reboilers in the B1 pressurized tower and the B2 atmospheric tower.

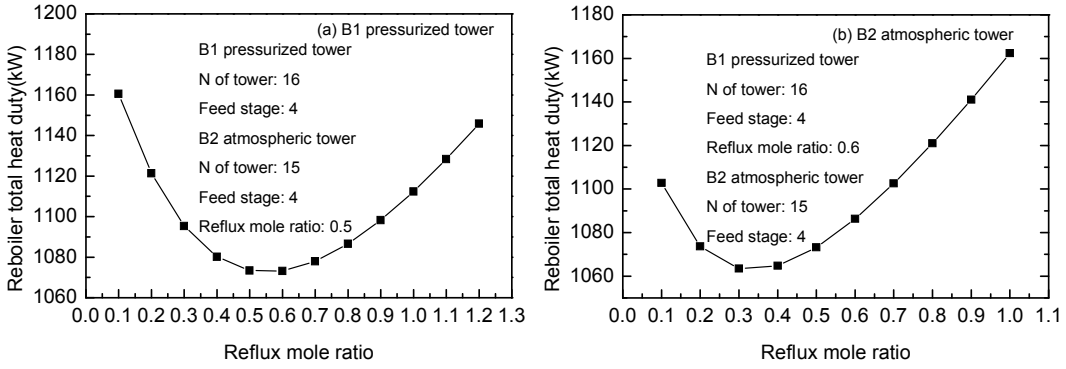

Figure3. The effect of the reflux ratio on the total heat duty of the reboilers in B1 and B2 tower.

The results of Fig. 5(a) show that with the increase of reflux ratio of B1 pressurized tower, the total heat duty decreases at first and then increases, thus the minimum energy consumption appears. This is because, as the reflux ratio of the B1 pressure tower increases, the liquid phase load in the pressurized tower increases gradually, while the liquid phase load in the atmospheric tower decreases gradually. Therefore, the reflux ratio of the B1 pressurized tower is chosen 0.6. Similarly, the results of Fig. 5 (b) show that with the increase of reflux ratio of B2 atmospheric tower, the total heat duty of reboilers in B1 pressurized tower and B2 atmospheric tower also appears lowest, so the reflux ratio of B2 atmospheric tower is chosen 0.3.

3.1.3. Optimization of feed position of B1 pressurized tower and B2 atmospheric tower, In the case of meeting the separation requirements, the high or low feed position will lead to an increase in energy consumption of the distillation tower, so there is the best feed position. Fig. 4 shows the feed positions of B1 pressurized tower and B2 atmospheric tower influence the reboiler heat duty, and the results show that when the feed position of the B1 and B2 tower is 5 and 4 respectively, the total reboiler heat duty of the two distillation towers are the lowest, so the feed stage of B1 pressurized tower is selected 5, and the feed stage of B2 atmospheric tower is chosen 4.

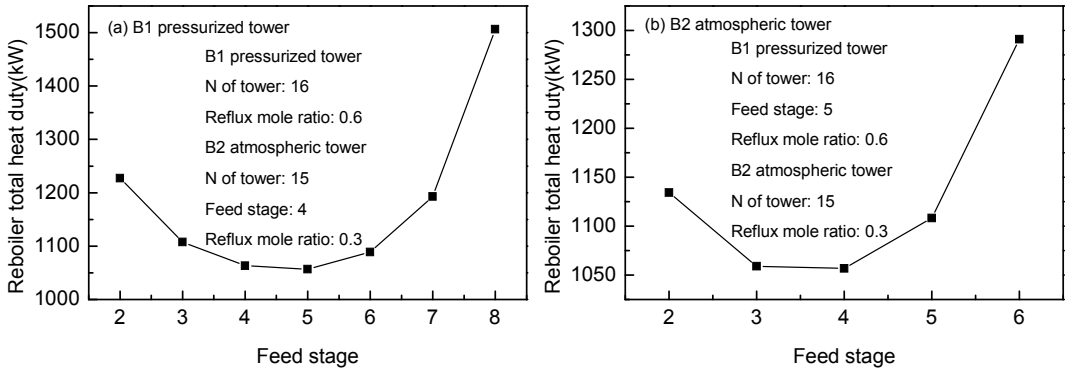

Figure 4. The effect of the feed stage on the reboiler total heat duty of B1 and B2 tower.

3.2. Process simulation and optimization of B3 ethanol tower

The purification of ethyl acetate can be obtained through the B1 pressurized tower, crude ethanol aqueous solution without ethyl acetate can be obtained through B2 atmospheric tower, the role of B3 ethanol tower is to further separate ethanol and water in the crude ethanol aqueous solution. Combined with DSTWU and RadFrac modules in Aspen Plus software to optimize the parameters of B3 ethanol tower, the operating pressure is 101.3kPa, the number of theoretical stages is 25, reflux ratio is 1.2, the feed stage is 10 and the molar ratio of top to feed in B3 ethanol tower is 0.50, the mass fraction of ethanol is 0.9017 in the top, and there is also no ethyl acetate in the bottom.

3.3. Simulation results

The process of pressure-swing distillation for separation of ethyl acetate-ethanol-water is simulated and optimized by Aspen Plus.

Table 3. Optimal parameters of the pressure-swing distillation for ethyl acetate-ethanol-water.

Tower	Stage number	Feed stage	Reflux mole ratio	D/F	Pressure(kPa)
B1	16	5	0.6	0.82	500.0
B2	15	4	0.3	0.82	101.3
B3	25	10	1.2	0.50	101.3

The better process parameters are obtained, and the result is shown in table 3. Table 4 shows the information of the major streams, which is obtained by calculations.

Table 4. Simulation results of the pressure-swing distillation for ethyl acetate-ethanol-water.

Items	F	S3	S5	S7	S8
Temperature(°C)	35.0	136.1	82.9	78.3	100.2
Pressure(kPa)	520.0	510.5	111.1	101.3	118.1
Mass flow(kg/h)	1000	778	222	152	70
Mass fraction					
Ethyl acetate	0.7769	0.9990	0.0001	0.0001	0.0000
Ethanol	0.1404	0.0007	0.6289	0.9017	0.0378
Water	0.0827	0.0003	0.3710	0.0982	0.9622

4. Laboratory experiments

The optimum parameters obtained by simulation are tested in the laboratory, and the experimental data is compared with the simulation data. Table 5 is the comparison of the experimental and simulated data of purity of ethyl acetate at different reflux ratios in B1 pressurized tower without changing other parameter conditions.

Table 5. The comparison of experimental data and the simulation data.

	Reflux mole ratio		
	0.3	0.6	0.9
Experimental value	0.9953	0.9990	0.9989
Simulation value	0.9800	0.9908	0.9890
relative error (%)	1.54	0.82	0.99

5. Conclusion

A pressure-swing distillation process is designed to separate the azeotrope of ethyl acetate-ethanol-water.

(1) Aspen Plus simulation software is used to predict the azeotropic composition of ethyl acetate, ethanol and water under different pressures, which shows that it is feasible to separate this azeotrope by pressure-swing distillation.

(2) Optimizing the main parameters of ethyl acetate refined tower (B1 pressurized tower), crude ethanol tower (B2 tower) and ethanol tower (B3 tower) respectively: for ethyl acetate refined tower theoretical stage number is 16, reflux ratio is 0.6, feeding stage is 5; for crude ethanol tower theoretical stage number is 15, reflux ratio is 0.3, feed stage is 4; for ethanol tower theoretical stage number is 25, reflux ratio is1.2, feed stage is 10.

(3) The simulation results are compared with the laboratory test and the data is in good agreement. Thus, the pressure-swing distillation process can realize the purification and separation of ethyl acetate, ethanol and water, and the established process model has a certain practical significance role to industrial.

Acknowledgments

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