Composite Extraction Separation of Ethyl acetate-Ethanol-Water

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Abstract: The production technology of ethyl acetate was introduced in this work. Extraction separation results of ethyl acetate-ethanol-water were simulated with wilson equation By triangle-matrix method. Reflux ratio et al. effected on separation efficiency were discussed. Extraction separation apparatus was established. Separation experiment of ethyl acetate-ethanol-water was studied by two extraction solvents, composite extraction method is used for separation of ethyl acetate-ethanol-water, above 99% ethyl acetate can be obtained one time by composite extraction, ethyl acetate recovery rate reached to above 97%, also above 95% ethanol can be obtained, water quantity used is only twice times raw material, this technology is simple and energy consumption is low. Research results were provided a base for farther industry test.

Key words: composite extraction, ethyl acetate, ethanol, water, simulation, experiment

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0 Introduction

Ethyl acetate can be produced by kinds of methods, but final products are composed of ethyl acetate, ethanol, water, paucity ethanol and acetic ether, Ethanol and acetic ether can be easily disrobed in this solution, but in which ethyl acetate-ethanol-water can constitute binary and ternary azeotropic solution, which can not be separated by distillation. Putting watering and azeotropic distillation are adopted[2] in traditional industry, from which 83% ethyl acetate azeotropic solution can be formed, combining more than twice times water with azeotropic solution, then mixed solution is putted into settling vessel, upper layer putted into distillation tower is distillated, above 99% ethyl acetate can be obtained, under layer is returned into azeotropic tower, waste water quantity is 3.45 times than product, reflux ratio of azeotropic distillation is above 5∶1, this technology which is composed of azeotropic distillation, mixing, settling separation and distillation technology is complicate and demands large energy consumption, at present new technology is developed which is composed of putting water extraction and azeotropic distillation[3,4]. 89% Ethyl acetate, 5% water and 6% ethanol were obtained by putting twice times water in raw material, above 99% ethyl acetate can be obtained by farther water washing and azeotropic apparatus, this technology is also complex, using water quantity is four times more than raw material, energy consumption is large. when composite extraction method is used for separation of ethyl acetate-ethanol-water, above 99% ethyl acetate can be obtained one time by composite extraction[5], also above 95% ethanol can be obtained, water quantity used is only twice times raw material, this technology is simple and energy consumption is low.

In this work extractive separation results of ethyl acetate-ethanol-water were simulated with ethylene glycerol and water by triangle matrix method, the parameters of reflux ratio, theory plate, solvent ratio, *et al.* were studied, the separation apparatus was established, the separation experimental results were measured, and compared with the simulation, all results were provided for farther industry research.

1 Extractive simulation calculation

Extractive distillation technology was designed as Fig. 1, after mixture solution of ethyl acetate-ethanol-water was separated, above 99% ethyl acetate was obtained on tower top, mixture solution with extractive agent on tower bed was treated again, extractive agent was circulated into extractive tower under regeneration tower bed, ethanol aqueous solution on the top was transferred

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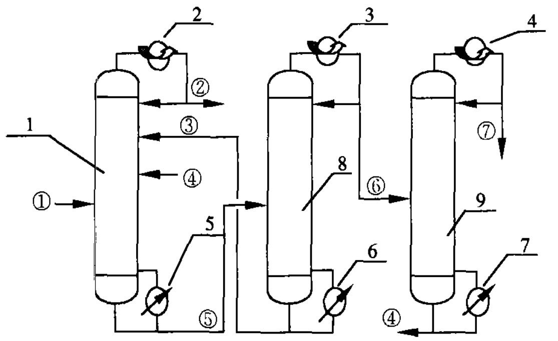
to recovery tower, 95% ethanol was obtained on the recovery tower top, bottom solution was transferred to extractive tower.



1. composite extraction tower; 2、3、4. condensor; 5、6、7. reboiler; 8. regenerative tower; 9. recovery tower

Fig. 1 Technology chart of composite extraction for ethyl acetate-ethanol-water

Gas liquid equilibrium data was provided according to literature[6~8], gas liquid equilibrium data of ethyl acetate-ethanol-diethyl glycerol and ethyl acetate-water-diethyl glycerol were measured in this paper, Wilson model parameters were correlated with VLE data by minimum variance method, model parameters of four compounds were correlated by binary model parameters and VLE data of ternary system, model parameters were arranged in Table 1. Separation results of extraction tower, regenerative tower and recovery tower were simulated by tri-diagonal matrix method, simulating calculation black diagram and calculation conditions were in literature[9], simulating results were arranged in Table 3 under conditions of Table 2.

Table 1 Model parameters of Wilson equation

Temp/ ℃	System											
	Ethanol(2) water(3)		Ethyl acetate(1) ethylene glycol(4)		ethanol(2) ethylene glycol(4)		water (3) ethylene glycol(4)		Ethyl acetate(1) Water(3)		Ethyl acetate(1) ethanol(2)	
75.3~80.3	A23	A32	A14	A41	A24	A42	A34	A43	A13	A31	A12	A21
	0.1262	0.9378	1.1441	0.0477	1.3732	0.0412	2.3007	0.0064	−0.1399	0.6270	0.0732	1.4060

Table 2 Technical references of simulation calculation

Reference	Apparatus		
	Composite extraction tower	Regeneration tower	Recovery tower
Theory plate number/ N	78	15	48
Input place of material/ NF	67	8	20
Input place of solvent/ NS_1	13	—	—
Input place of solvent/ NS_2	31	—	—
Reflux ratio/ R	4	3	5
Temperature of tower top/ ℃	77.1	78.8	79
Temperature of tower bottom/ ℃	97.2	197	101

Table 3 Results of Simulation calculation

Material	flow (kg/ h)	Concentration(mass)			
		ethyl acetate	ethanol	water	ethylene glycol
①	2504	0.2172	0.6814	0.1014	0.0000
②	537	0.9951	0.0027	0.0022	0.0000
③	3000	0.0000	0.0000	0.0000	1.0000
④	5000	0.0000	0.0000	1.0000	0.0000
⑤	9967	0.0010	0.1710	0.5270	0.3010
⑥	6967	0.0013	0.2447	0.7539	0.0000
⑦	1793	0.0053	0.9505	0.0439	0.0000

At $N=78$, $NF=67$, $NS_1=13$, $NS_2=31$, $R=4$ (other conditions were constant), the effect of solvent proportion (S/F) on top concentration (Xd) and bottom concentration (Xw) were shown in Fig. 2, the calculation results indicated that the overhead concentration (Xd) reached above 99.5%, the bottom concentration (Xw) were under 0.10% at $S_1/F=1.2:1$, $S_2/F=2:1$, the recovery rate reached above 97%, the effect of reflux ratio on Xd, Xw was arranged in Fig. 3 at $S_1/F=1.2:1$, $S_2/F=2:1$, the results indicated that reflux ratio ($R=4$) was better condition, the effect of theory plate number was arranged in Fig. 4 at above conditions, the input situation of solvent (s_1, s_2) has no effect on the concentration of tower top and tower bottom at $NS_1=9\sim15$, $NS_2=28\sim37$. The results indicated that above 99.5% ethyl acetate and above 97% recovery rate were obtained on extractive tower top at $N=78$, $R_1=4$, $NS_1=13$, $NS_2=31$.

2 Experiment

The extractive distillation apparatus as Fig. 5 was established. At normal pressure, tower inside diameter was 22 mm, the inside was filled with Φ3 × 30 type stainless steel helices, raw material was measured by standard system, this packed height equivalent to a theoretical plate (HETP) was 27 mm, tower pot was heated by electric jacket, raw material and solvent was measured by glass rotameter, also did tower pot output, the reflux ratio was adjusted by electric magnetism bar, tower material was drived out by vacuum pump, bottom outflow material was transferred to regenerative tower, the

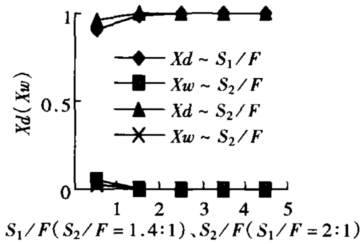


Fig. 2　Effect of solvent ratio on ethyl acetate concentration of tower top and bottom

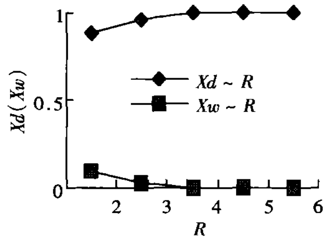


Fig. 3　Reflux ratio effect on ethyl acetate concentration of tower top and bottom

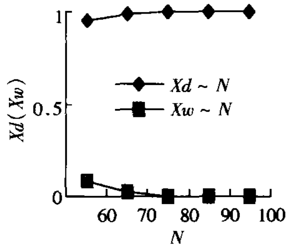
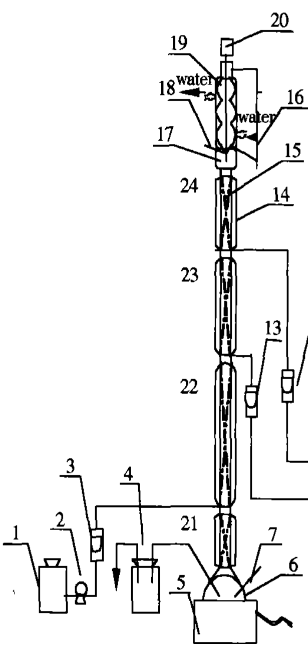


Fig. 4　The effect of theoretical number on ethyl acetate concentration of tower top and bottom

solvent was recirculated by disrobed alcohol and dehydrated, the overhead material was transferred to the recovery tower. Esterification reaction mixture solution was as raw material, composition was analyzed by HP chromatograph, raw material was extracted by binary solvents, conditions of experiment and separation were arranged in Table 4, the results indicated that above 99.2% ethyl acetate was obtained by binary solvents, ethyl acetate recovery rate reached to above 97%, alcohol aqueous was obtained with 0.3% ethyl acetate (solvent S_1 was not in), above 95% ethanol was obtained on recovery tower top, the experiment results were consistent with the simulation results.



1. raw material tank; 2. pump; 3. glass rotameter; 4. tower pot sampling tap; 5. electric hot jacket; 6. tower pot; 7. towerpot thermometer; 8. solvent tank; 9. pump; 10. solvent tank; 11. pump; 12. glass rotameter; 13. glass rotameter; 14. glass cellocotton; 15. filler; 16. tower top sampling tap; 17. refluxmouth; 18. tower top thermometer; 19. condenser; 20. eleetromagnetism bar; 21. recovery section; 22. extraction section; 23. extraetive section; 24. distillation section

Fig. 5　Experiment apparatus of extractive distillation

Table 4　Results of extraction separation experiment

Reference	Apparatus	
	Composite Extraction tower	Regenerative tower
Temp. of top/ ℃	77~ 78	79~ 80
Temp. of bottom/ ℃	99~ 105	199~ 201
Reflux ratio/ R	4	3
Tower high/m	3.10	0.70
Distillation section/ m	0.50	0.35
Extraction first section/m	0.80	-
Extraction second section/m	1.50	-
Top conc. of ethyl acetate	0.9921	0.0043
Top conc. of ethanol	0.0032	0.9502
Top conc. of water	0.0047	0.0055
Bottom conc. of ethyl acetate	0.0032	0.0000
Bottom conc. of ethanol	0.2434	0.0000
Bottom conc. of water	0.7536	1.0000

3　Conclusion

Separation results of ethyl acetate-ethanol-water were simulated with Wilson by triangle matrix method, the calculation results provided conditions for experiment schemes and apparatus designs, ethyl acetate-ethanol-water was extracted by binary solvents, experiment results were consistent with simulation results, ethyl acetate content reached to above 99.2% after extraction separation, the recovery rate reached to above 97%, the results of experiment and simulation provided for farther studies and industrial test.

Symbols

Xd、Xw content of extraction tower top and bottom(mass)

N theory plate number of tower

NS_1、NS_2 input situation of extractive solvents

S_1、S_2 inputting quantity of extractive solvents(kg/h)

R reflux ratio

F inputting raw material quantity(kg/h)

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复合萃取分离乙酸乙酯–乙醇–水

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[摘要]　介绍了乙酸乙酯工艺; 提出了复合萃取法分离乙酸乙酯-乙醇-水, 采用三对角距阵法模拟计算乙酸乙酯-乙醇-水分离结果; 建立萃取分离装置, 采用合适的萃取剂, 考察了不同溶剂比及回流比等因素对产品纯度的影响. 结果表明, 采用复合萃取分离法分离乙酸乙酯-乙醇-水, 在溶剂比 1∶1∶1, $R=4$ 时能一次得到高浓度(99%)乙酸乙酯, 同时得到 95% 的乙醇溶液, 乙酸乙酯得率达到 97%, 分离过程水的用量仅为原料的 2 倍, 能耗低, 为工业试验提供了基础数据。

[关键词]　复合萃取, 乙酸乙酯, 乙醇, 水, 模拟, 实验

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