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Process of separating acetonitrile and water using LTTMs as entrainer

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New extractive distillation configurations, which use low transition temperature mixtures (LTTMs) as entrainers, have attracted widespread attention among scholars due to their green processes. Furthermore, the design and comparison of different processes can promote the application of new solvents in the future. In this study, two extractive distillation processes, the extractive distillation column (ED) and the extraction dividing wall column (EDW), were selected from previous work. The separation process of acetonitrile (ACN)-water ternary mixtures was studied, and GC3:1(choline chloride/glycolic acid mixture (molar mass 1:3)) and EC2:1((choline chloride/ethylene glycol 1:2 molar mass) were used as entrainers. Minimum consumption energy and the purity of ACN and water were set as the goals, and our sensitivity analysis and economic evaluation results showed that both ED and EDW were effective. As a result, LTTMs can be used in extractive distillation for azeotrope separation.

Keywords: LTTMs, ACN, Simulation, Extraction distillation, Sensitivity analysis.

INTRODUCTION

Acetonitrile (ACN) is a commonly used critical organic solvent and chemical material, and it is used for applications such as fine chemicals[1], pharmaceutical[2], spices[3], electronics[4], and organic and inorganic synthesis[5]. Mixtures of ACN and water are continuously formed during production[6], always forming azeotropic mixtures at 76.3°C (1 atm). This adds to the difficulty in separating mixtures of acetonitrile and water mixtures. Pressure swing distillation has been used to separate acetonitrile and water, but the energy and equipment cost has remained high. Instead, an extractive distillation[7] method is normally used to separate ACN and water.

Extractive distillation is widely used for the separation of azeotrope or close-boiling mixtures in the chemical industry[8]. In this process, the entrainer is the most important solvent, and it is added to improve the relative volatility of the azeotrope or close-boiling mixtures to separate the azeotrope[9]. The key to extractive distillation is using a suitable solvent solution to improve efficiency[10–11]. However, the traditional organic solvents used in extractive distillation have some disadvantages, such as environmental pollution, which limits their use[12]. Therefore, new eco-friendly entrainers that are easily recycled are urgently needed.

Low transition temperature mixtures (LTTMs) are a new type of green solvent, compared to traditional solvents. In 2003, Abbott et al.[13] created deep eutectic solvents (DES), which are a type of solvent formed by mixing urea with choline chloride. While LTTMs are known as DES, the name does not completely cover all classes of solvents. This is because many mixtures do not exhibit a (eutectic) melting point and have a glass transition temperature instead. Consequently, LTTMs are consistent with the definition, and studies have focused on LTTMs for material preparation[14], catalytic reactions[15], and biomass deconstruction[16].

In our work, the separation of the ACN and water mixture was investigated by using ethylene glycol (EG) and LTTMs as entrainers using Aspen Plus 10.0. The EC2:1 mixture consisted of choline chloride and ethylene glycol (choline chloride/ethylene glycol 1:2 molar mass), while GC3:1 represented the choline chloride/glycolic acid mixture (molar mass 1:3). The EC2:1 and GC3:1 mixtures were chosen for the vapor-liquid equilibrium (VLE) data, which were investigated experimentally. For further analysis, a sensitivity analysis simulation and total annual cost (TAC) analysis were used to synthesize the simulation process and explore its applications.

Thermodynamic model

For extractive distillation, a non-random two-liquid (NRTL) model was chosen as the thermodynamic model to describe the nonideality of the liquid phase, and the vapor was assumed to be ideal. RK equation is used to correct the non-ideal property of the vapor phase. Zhang et al.[17] conducted an experiment using VLE data for the pseudobinary mixtures of ACN+EC2:1 and water+EC2:1, which were used to estimate the interaction parameters of LTTM-water and LTTM-isopropyl. The NRTL binary parameters for choline chloride-ethylene glycol-acetonitrile-water were estimated using the estimation module in Aspen Plus, and the vapor-liquid equilibrium was input into Aspen Plus to simulate the lack of data. Sharma[18] studied the vapor-liquid equilibrium data for the pseudobinary mixtures of ACN+GC3:1 and water+GC3:1 at atmospheric pressure (101.32 kPa) and obtained the NRTL binary parameters, which were used to simulate the separation process in Aspen Plus. The results are shown in Tables 1 and 2. A few of the properties and estimated normal boiling points of GC3:1 were predicted and these are shown in Table 3. The critical data of EC2:1 was also calculated according to the literature[19].

The Joback method was used to estimate the CPIG parameters(Ideal gas heat capacity) and PLXAN parameters(Saturated vapor pressure), and the results are presented in Tables 4 and 5. The saturated vapor pressure parameters of GC3:1 were estimated according to the Riedel model, which used the critical property parameters to extend the Antoine equation.

The feasibility of extractive distillation

To verify whether EC2:1 and GC3:1 can be used as entrainers to break the azeotropic point of ACN-water

Table 1. The NRTL binary parameters for acetonitrile-water-EC2:1

Component *i*	Component *j*	Binary parameters				
		A_{ij}	B_{ij}	A_{ji}	B_{ji}	C_{ij}
Water	ChCl	0	–1927.68	0	–1079.14	0.3
EG	ACN	0	48.5004	0	452.525	0.3
EG	ChCl	0	–1079.32	0	–900.118	0.3
Water	ACN	0	665.119	0	183.592	0.2858
Water	EG	0	–493.54	0	684.469	0.3
ChCl	ACN	0	1692.68	0	–734.365	0.3

The abbreviation for choline chloride is ChCl.

Table 2. The NRTL binary parameters for acetonitrile-water-GC3:1

Component *i*	Component *j*	Binary parameters				
		A_{ij}	B_{ij}	A_{ji}	B_{ji}	C_{ij}
GC3:1	ACN	0	887.91	0	–390.62	0.3
Water	GC3:1	0	–1119.97	0	100.48	0.3
ACN	Water	0	322.121	0	535.337	0.3

Table 3. Critical property parameters for GC3:1

MW/g/mol	T_b (K)	P_C/bar	Vc/cm^3/mol	Tc/K	Zc	ω
91.64	1353.96	19.72	1002.06	1785.91	0.13121	0.736467

Table 4. Capacity parameters of CPIG of GC3:1/(cal/(mol. K)) used in Aspen Plus

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
59.08	0.1588	–8.23E-5	6.71E-9	0	0	6.85	826.85	8.61	0.011	1.5

Table 5. PLXAN parameters of GC3:1/(N/m^2) used in Aspen Plus

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
112.676	–31220.9	0	0	–10.84	1.50E-20	6	1353.96	1785.91

and obtain a high purity ACN, the VLE curve for ACN--water was obtained using Aspen Plus, using the different entrainers from Fig. 1 and EC2:1 with 0.1–0.5 when the molar ratios as shown in Fig. 2. As also shown in Figs. 1 and 2, the relative volatility of ACN to water varied with the molar fraction of EC2:1/GC3:1.

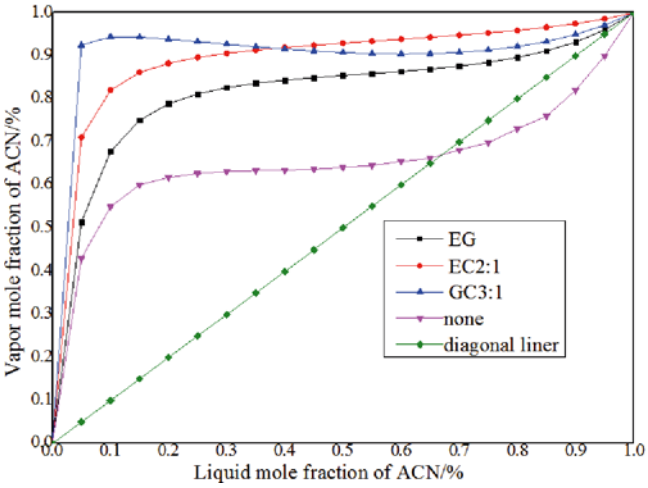


Figure 1. VLE of processes of extraction distillation column using different entrainers

In summary, EC2:1 and GC3:1 showed better performance as the entrainers, which can be used to separate ACN and water. Thus, NRTL can be used to simulate the extraction process when LTTMs are used as entrainers.

PROCESS SIMULATION AND IMPROVEMENT

To further compare the traditional solvent with the LTTMs, the simulation was conducted using EG and EC2:1 and GC3:1 as the entrainers. Fig. 3 shows the extractive distillation processes flow diagram using Aspen Plus 10.0 for ACN-water. The fresh feed flow rate was

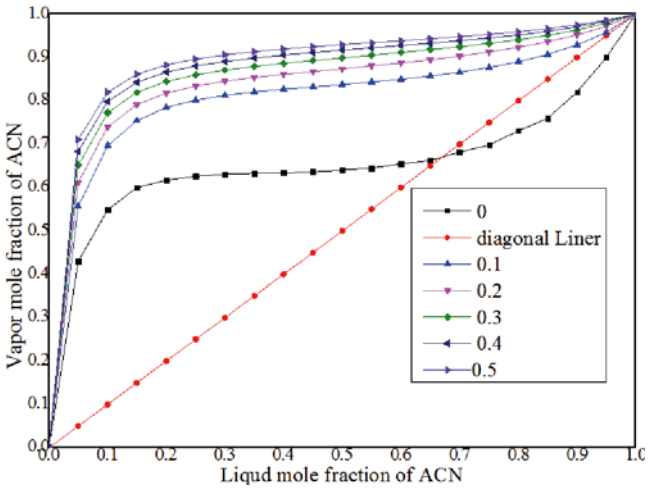


Figure 2. The VLE of processes of extraction distillation column using EC2:1 of different E/F

1000 kg/h, the temperature was set to 25°C, and the feed composition was ACN 70 wt% and water 30 wt%. The purities of ACN and water were both 99.9 wt%.

Steady-state design of the extractive distillation column (ED)

Extractive distillation column process using EC2:1

As shown in Fig. 3, EC2:1 was added to the extractive distillation column (EDC), which changed the volatility between ACN and water, in order to improve the purity of the ACN produced at the top of the column. The entrainer recovery column (ERC) separated the ACN and water, and the purity of EC2:1 was 99.9 wt%, which was used for recycling, while the purity of the water was 99.9 wt%.

Fig. 4a and 4b showed the temperature profile of the EDC and the ERC with theoretical stages. Fig. 4a sho-

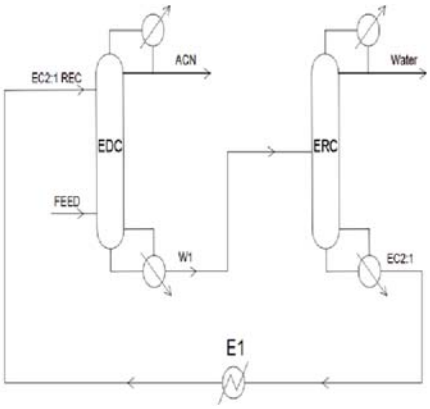


Figure 3. Extractive distillation process flow sheet for ACN--water

wed that the rectifying section temperature remained the same and was close to the boiling point of ACN. Thus, a high-purity ACN could be obtained from the top of the EDC. The extraction section temperature was near the azeotrope temperature, and the stripping section temperature decreased at the beginning, indicating that the entrainer of EC2:1 could extract the ACN from water.

Fig. 4c and Fig. 4d showed that the temperature varied with the number of stages, and EC2:1 was a valuable solvent compared with traditional solvents. Fig. 4c indicated that during rectification, the ACN was divided by EC2:1, while the ACN could be obtained at the top. Fig. 4d also showed that the water could be divided from EC2:1, and water could also be obtained from the top. The purity of water reached 99.9 wt% at the top of the column as shown in Fig. 4d.

Sensitivity analysis of ED using EC2:1

To find an optimal design, it was necessary to establish the operating conditions of the ED. Based on the minimum heat duty and the purity of the ACN-water, a sensitivity analysis was used to determine the main design variables. For example, the number of stages (NSTAGE), reflux ratio (RR), feed stage, entrainer feed stage, and entrainer mass flow, were considered.

Figs. 5–10 showed the optimization process for conventional extractive distillation using EC2:1 as an entrainer. Fig. 5 depicted the effects of a number of stages on the purity of ACN and the reboiler duty of EDC, showing that the reboiler duty decreased with the NSTAGE while the purity of ACN increased with NSTAGE. Thus, when the NSTAGE was set to 16, the reboiler duty was at a minimum, and the purity met the requirements. However, condenser duty analysis is always not considered in the literature.

The effects of the feed stage on reboiler duty and the purity of ACN from the EDC were shown in Fig. 6. According to the results, the reboiler had the lowest energy consumption, and the purity of ACN reached 99.9 wt% when the feed stage was set to 11. It can also be ascertained from Fig. 7 that when the RR changed,

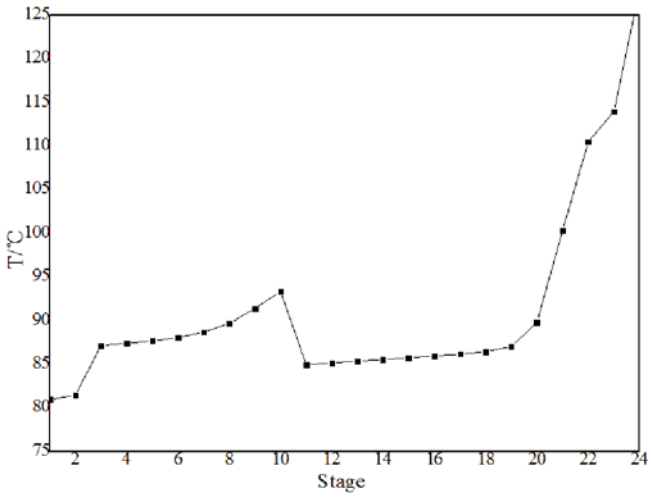


Figure 4a. Temperature profile of EDC

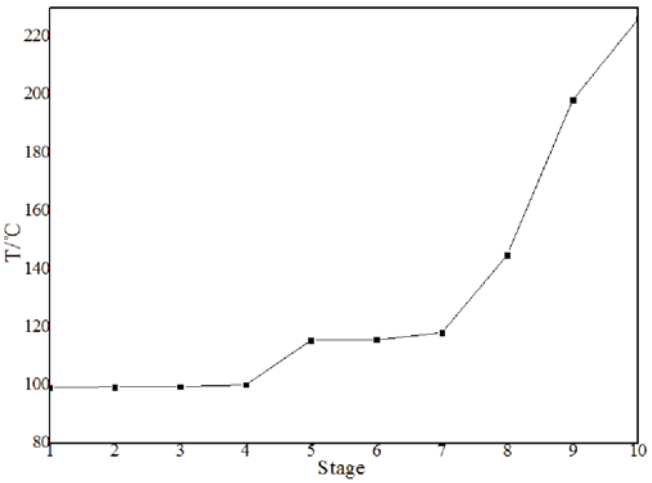


Figure 4b. Temperature profile of ERC

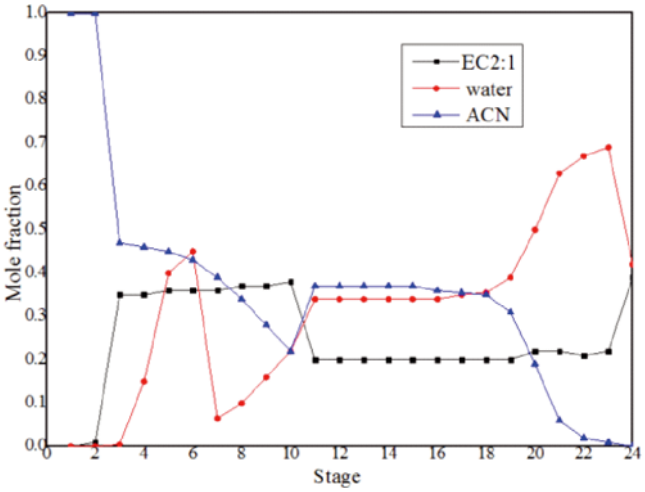


Figure 4c. Composition profile of EDC

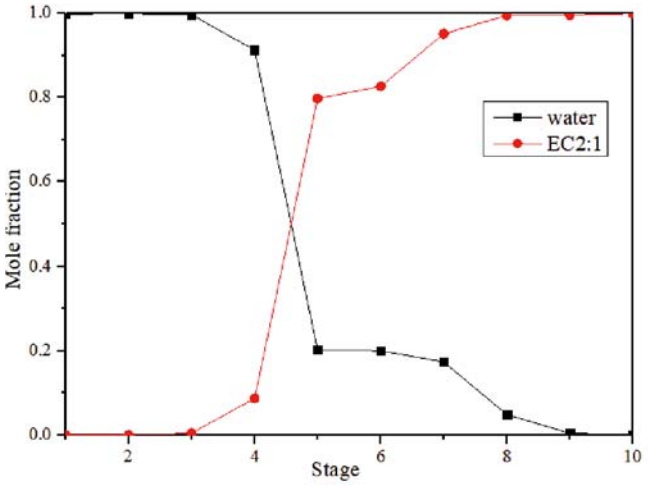


Figure 4d. Composition profile of ERC

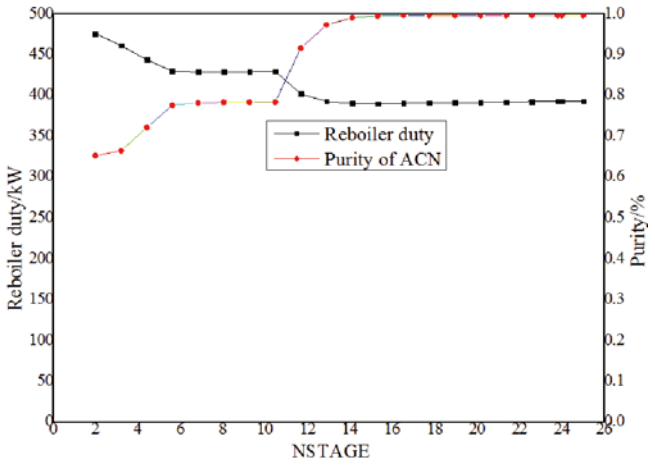


Figure 5. The effect of NSTAGE on the purity of ACN and reboiler duty

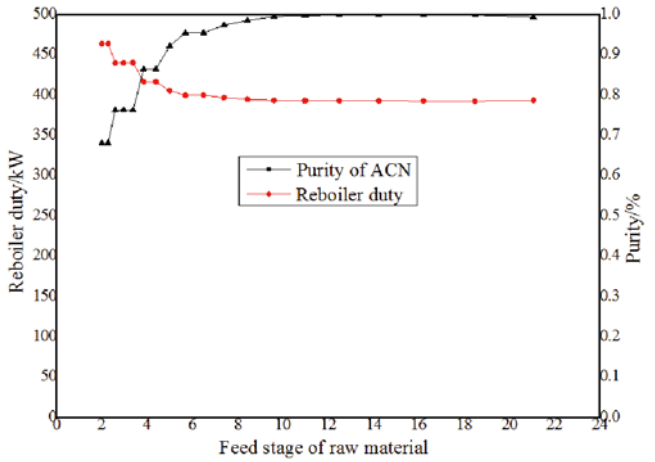


Figure 6. The effect of feed stage of raw material on the purity of ACN and reboiler duty

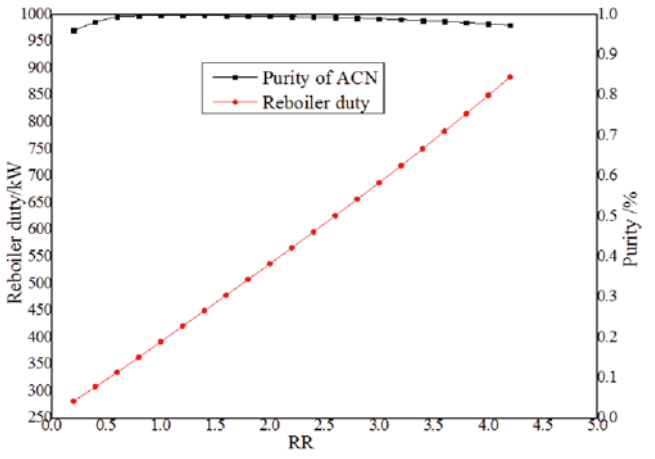


Figure 7. The effect of RR on the purity of the ACN and reboiler duty

the purity of the ACN and reboiler duty changed along with the RR. Thus, the optimal parameter of RR was 1.0, for which the results were ideal. Fig. 8 confirmed the influence of the entrainer mass flow on the purity of ACN and reboiler duty, and the optimal parameter was 2000 kg/h. The entrainer and feed mass flow ratio were set, therefore Fig. 8 did not show the relation between reboiler duty, entrainer, and feed mass flow ratio. It can also be observed from Fig. 9 that when the optimal value of the entrainer feed stage was set to 3, the ED process had a minimum reboiler duty and an ideal ACN

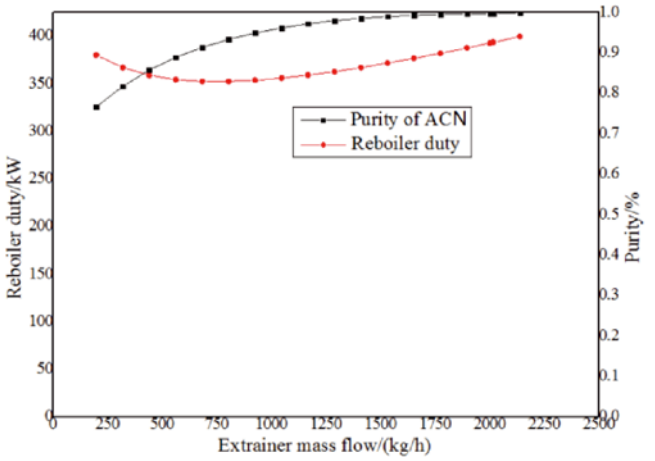


Figure 8. The effect of the entrainer mass flow on the purity of the ACN and reboiler duty

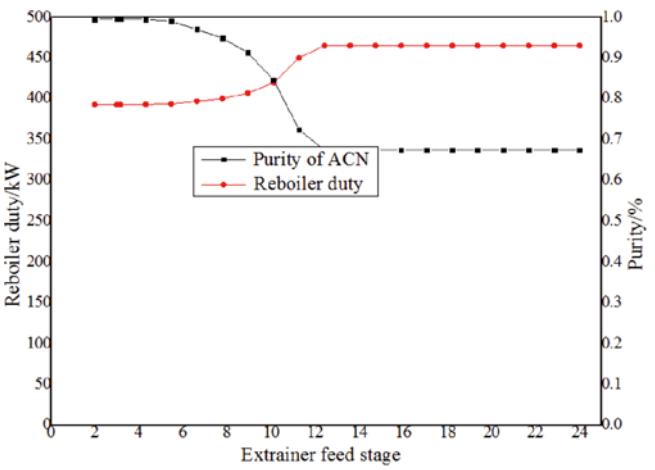


Figure 9. The effect of entrainer feed stage on the purity of the ACN and reboiler duty

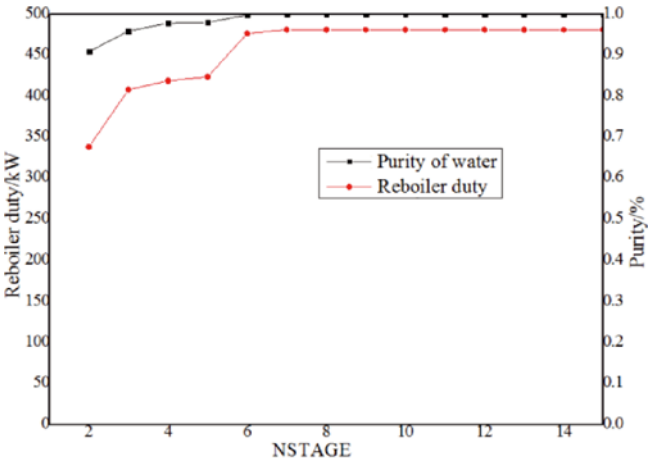


Figure 10. The effect of NSTAGE on the purity of water and reboiler duty

purity(99.9 wt%). The entrainer feed stage was closer to the top, the purity of ACN was lower according to the distillation principle. Thus, as shown in Fig. 10, the raw materials feed stage influenced the reboiler duty and water purity when the optimal value was set to 6.

The simulation process of distillation using GC3:1

As illustrated in Fig.11, the simulation of GC3:1 was similar to EC2:1, and the ERC was used instead of a flash to achieve the high boiling point of GC3:1, in order to decrease operating cost.

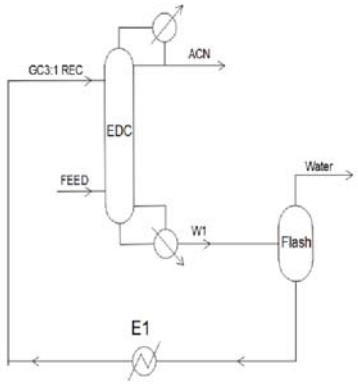


Figure 11. Extractive distillation column process flow sheet for ACN-water using GC3:1 as an entrainer

Sensitivity analysis using GC3:1

The sensitivity analysis of GC3:1 was similar to the EC2:1, and the parameters of the different extraction column processes using EC2:1, GC3:1, and EG are illustrated in Table 6.

The results presented in Table 6 indicated that ACN and water were successfully separated by the EG, EC2:1, and GC3:1 entrainers, the simulation process parameters were different, and the reboiler duty of GC3:1 was lower than the other processes. To find the optimal simulation process, an extraction dividing wall column was used for analysis.

Simulation of Extraction dividing wall column

The extraction dividing wall column (EDW) has been widely studied in recent years to conserve energy conservation[20–21]. Zhang[22] completed a design and control of the EDW process, separating a propylene oxide-methanol-water mixture using water as the entrainer. Kiss[23] also conducted the separation of ethanol dehydration using extractive distillation and azeotropic distillation, using ethylene glycol and *n*-pentane as solvents and strengthened the process via dividing-wall columns. Furthermore, Zhao[24] studied the process of separating ternary azeotropic mixtures of tetrahydrofuran/ethanol/water using EDW. In all of the aforementioned studies, the sequential iterative method was used to determine the best process conditions for lower energy consumption.

In this work, the separation of ACN and water was completed using EC2:1 as the entrainer. When GC3:1 was used as the entrainer, flash was applied to separate the water and GC3:1, replacing the ERC. Therefore, the EDW was unable to separate the ACN and water using the GC3:1 as the entrainer. The separation process for EDWC using EC2:1 is illustrated in Fig. 12.

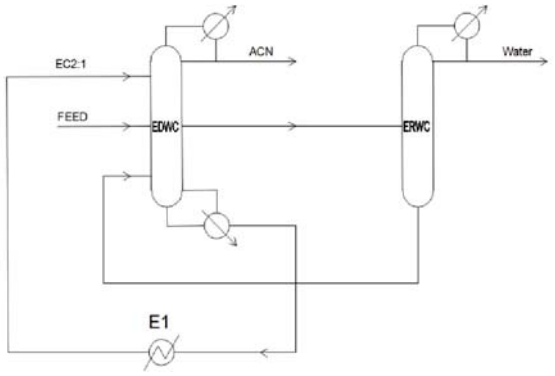


Figure 12. Extractive distillation wall column process flow sheet for ACN-water using EC2:1

The Extractive dividing wall column was usually depicted by the model of two Radfracs in Aspen Plus. In this study, EDWC and ERWC were on behalf of the model of Radfrac.

Fig. 13a and 13b showed the temperature profile trends for the EDWC and the entrainer recovery column with theoretical stages, respectively. In Fig. 13a, the temperature of the rectifying section remained constant, which was close to the boiling temperature of ACN. Therefore, high purity ACN could be collected from the top of the EDWC. The extraction section temperature was near the azeotrope temperature, and the stripping section temperature decreased at the beginning, indicating that the EC2:1 entrainer could extract ACN from water. Fig. 13c and 13d reflected that the temperature varied with the number of stages, and Fig. 13c showed that the ACN was separated by EC2:1 in the rectification section. Thus, the ACN could be obtained at the top. Fig. 13d also showed that the water could be separated from EC2:1, and could also be obtained at the top.

To achieve minimum reboiler heat duty and ACN purity, a sensitivity analysis was used to explore the main design variables of the EDW, such as RR, feed stage, entrainer feed stage, and entrainer mass flow. Figs. 14–19 showed the optimization process of the EDW using EC2:1 as the entrainer. Fig. 14 depicted the effects of a number of stages on the purity of ACN and

Table 6. Parameters for the different extraction column using EC2:1, GC3:1 and EG

Parameter	EGEDC	EGERC	EC2:1EDC	EC2:1ERC	GC3:1EDC	GC3:1Flash
NSTAGE	20	11	16	10	13	–
Feed stage	15	5	11	6	8	–
Entrainer feed stage	4	–	3	–	3	–
Mole RR	0.75	1	1	1	0.6	–
Entrainer mass flow/(kg/h)	2000	–	2000	–	950	–
Mole composition at the top	–	–	–	–	–	–
ACN	0.999	0.001	0.999	0.001	0.999	0.000
Water	0.001	0.999	0.0008	0.999	0.000	0.999
EG/EC2:1/GC3:1	0.0002	0.000	0.0002	0.000	0.001	0.001
Mole composition in bottom/%	–	–	–	–	–	–
CAN	0.0001	0	0.000	0.0002	0.001	0.000
Water	0.130	0.0001	0.130	0.000	0.239	0.038
EG/EC2:1/GC3:1	0.869	0.9998	0.869	0.9995	0.760	0.961
Condenser duty/kW	254.495	337.996	287.17	347.45	238.429	0
Reboiler duty/kW	376.857	434.544	339.16	480.97	286.291	199.84
Temperature at the bottom (°C)	131.97	196.45	127.93	226.32	121.53	150.00
Temperature of top (°C)	80.91	99.52	81.02	99.56	81.14	150.00

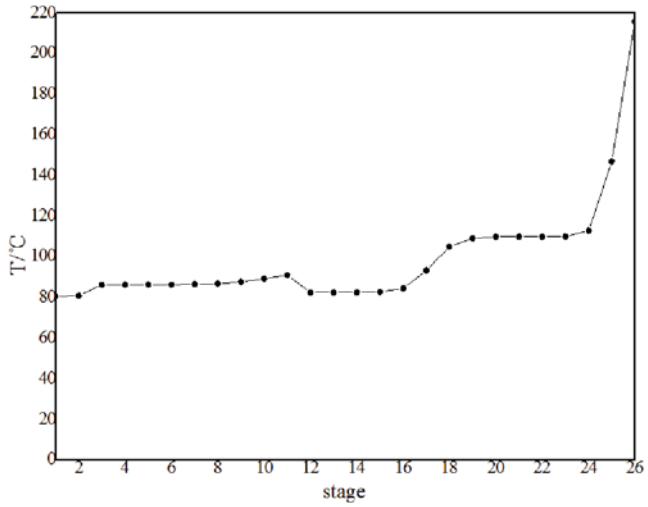


Figure 13a. Temperature profile of EDWC

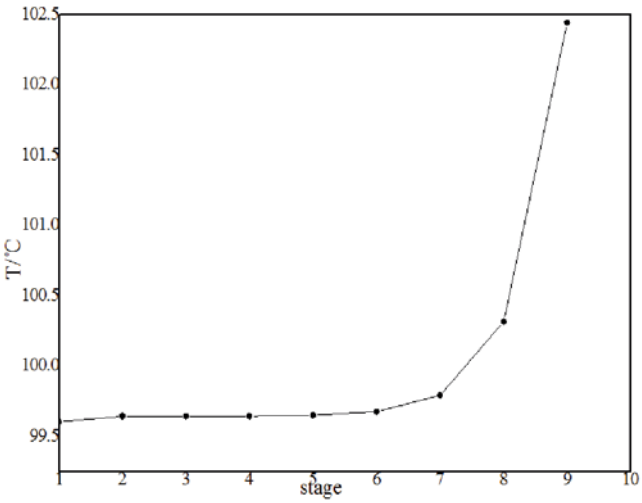


Figure 13b. Temperature profile of ERWC

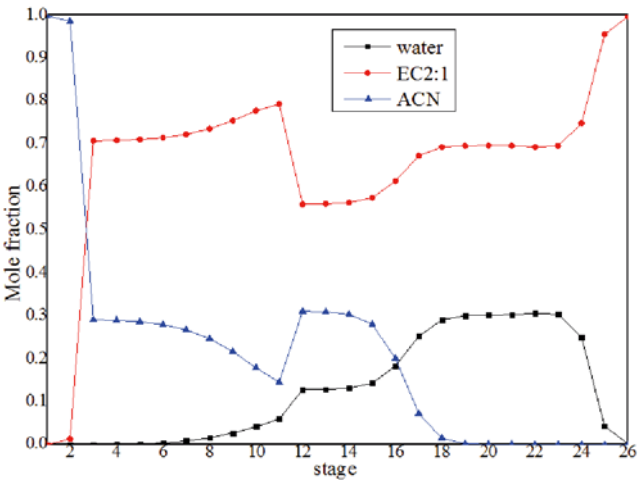


Figure 13c. Composition profile of EDWC

the reboiler duty of EDW. The results showed that the reboiler duty decreased with NSTAGE while the purity of ACN increased with NSTAGE. When the NSTAGE was set to 16, the reboiler duty was at a minimum, and the purity requirement was met. The effect of the feed stage on the reboiler duty of EDW and purity of ACN was also shown in Fig. 15. The reboiler had the lowest energy consumption and the purity of ACN reached 99.9 wt% when the feed stage was set to 12. Fig. 16 also shows that the optimal parameter of RR was 1, which had an ideal result. As shown in Fig. 17, the influence of

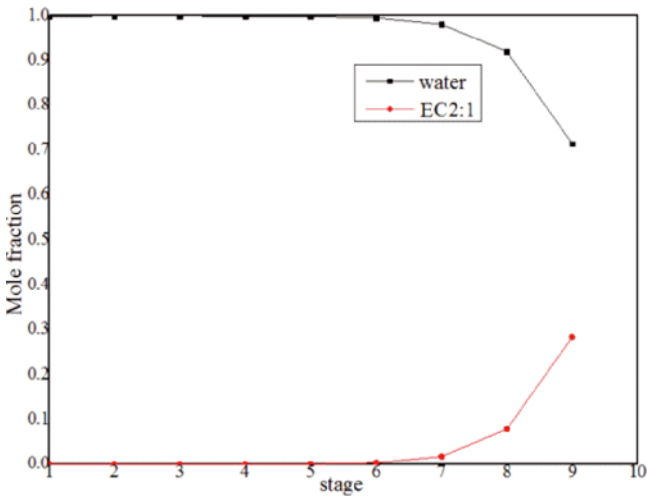


Figure 13d. Composition profile of ERWC

entrainer mass flow on the purity of ACN and reboiler duty was confirmed, and the optimal parameter was1800 kg/h. It can also be observed in Fig. 18 that the EDW process had a minimum reboiler duty and ideal purity for ACN when the optimal value of the entrainer feed stage was set to 3. As Fig. 19 showed, the inside stripper stage influenced the purity of ACN and reboiler duty, and its optimal value was 15. The column parameters are provided in Table 7.

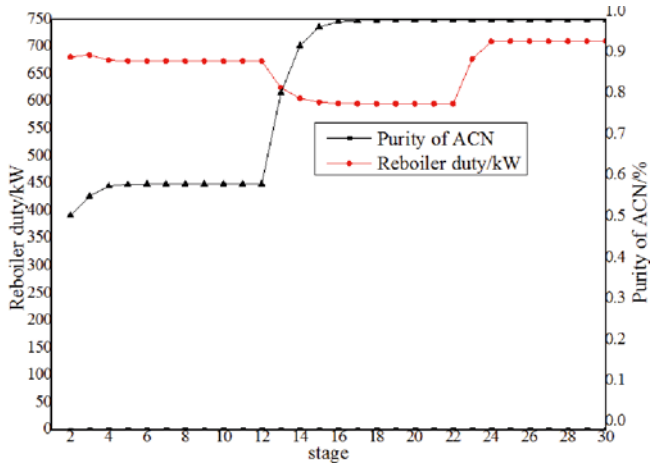


Figure 14. The effects of NSTAGE on ACN purity and reboiler duty

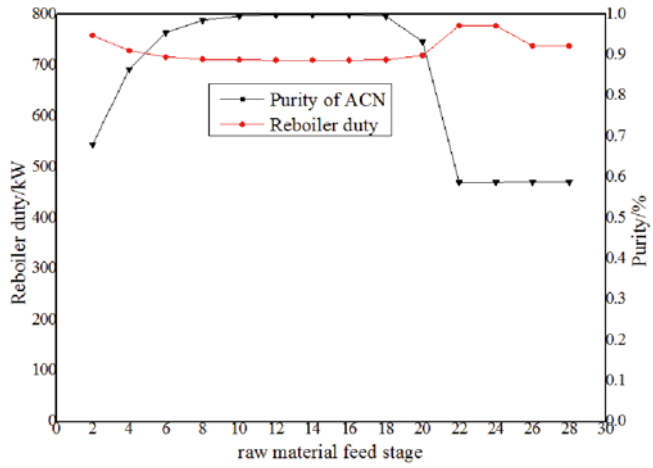


Figure 15. The effects of raw material feed stage on ACN purity and reboiler duty

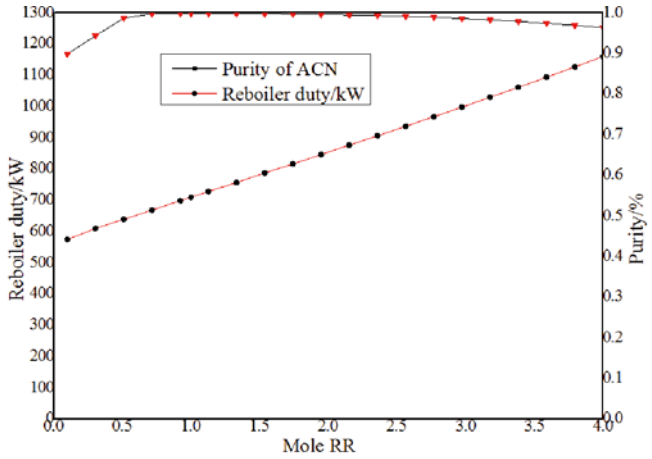


Figure 16. The effects of RR on ACN purity and reboiler duty

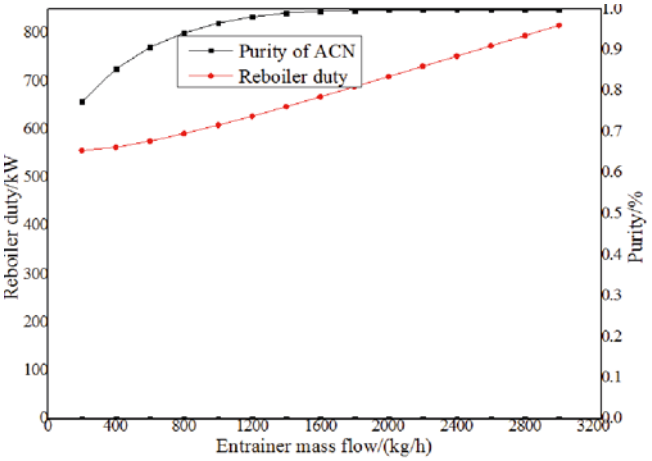


Figure 17. The effects of entrainer mass flow on ACN purity and reboiler duty

Economic evaluation

Total annual cost (TAC)[25–26] was selected as the objective function to evaluate the optimal simulation, as this is an important index for the economic evaluation of different extractive distillation processes. In this study, to analyze the economics of different extractive distillation processes, a Turtonde model[27–28] was used as the basis of calculation. The equations are listed in Table 8, and the operating costs, including the steam cost, cooling water cost, and chilling cost, are shown in Table 9. TAC includes capital cost per year and operating costs and is computed from the following formula:

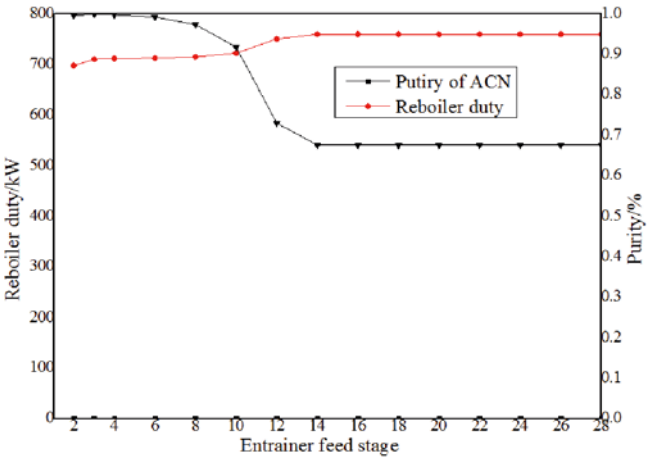


Figure 18. The effects of entrainer feed stage on ACN purity and reboiler duty

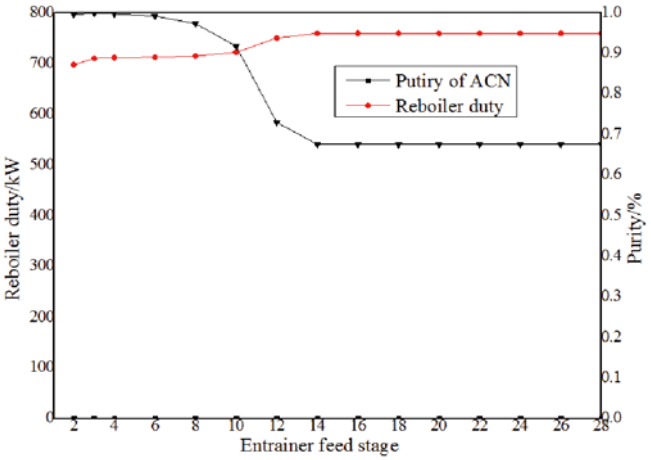


Figure 19. The effects of side stripper stage on ACN purity and reboiler duty

$$TAC = \frac{capital\ \cos t}{payback\ \text{period}} + operating\ \cos t$$

As shown in Table 8, the TAC for different extractive distillations was different. The process that used GC3:1 as the entrainer was the most optimal simulation process, while the TAC of the EDW process using EC2:1 was the least optimal. Compared with the process using EG, LTTMs were more advantageous in terms of energy consumption and economic cost.

Table 7. Parameters of different extraction wall columns (EDW)

Parameter	EGEDWC	EGEDRC	EC2:1 EDWC	GC2:1ERWC
Number of stages	16	10	22	9
Feed stage	14	11	12	10
Extraction feed stage	4	–	3	–
Mole RR	1.2	–	1.0	–
Side stripper stage	19	–	15	–
Extraction mass flow (kg/h)	2300	–	1800	–
Mole composition at the top	–	–	–	–
ACN	0.999	0.001	0.999	trace
Water	0.001	0.999	0.0003	1
EG/GC2:1	0.000	0.000	0.000	0.000
Mole composition at the bottom	–	–	–	–
ACN	0.000	0.000	0.000	0.000
Water	0.999	0.215	0.002	0.715
EG/GC2:1	0.001	0.785	0.998	0.285
Condenser duty/kW	315.98	208.64	286.75	199.84
Reboiler duty /kW	774.277	0	710.89	0
Temperature at the bottom (°C)	195.58	120.68	260.10	99.60
Temperature at the top (°C)	80.89	99.39	81.02	102.44

Table 8. TAC of different extractive distillations for separation of ACN-water

Capital cost
Column ($/y)
Column diameter (m): D = Aspen Tray sizing
Column height (m): H = 1.2*0.6* (N_T-2)
Column sell cost = 17640 $(D)^{1.066*} (H)^{0.802}$
Condenser ($/y)
Heat transfer coefficient (K_C) = 0.852kW/(K*m^2)
Area (m^2) $A_C = Q_C/ (K_C*\triangle T_C)$
Capital cost = 7296 $(A_C)^{0.65}$
Reboiler ($/y)
Heat transfer coefficient (K_R) = 0.658kW/ (K*m^2)
Area (m^2) $A_R= Q_R/(K_R*\triangle T_R)$
Capital cost = 7296 $(A_R)^{0.65}$
Cooler ($/y)
Heat transfer coefficient (K_{CO}) = 0.852kW/(K*m^2)
Area (m^2) $A_{CO} = Q_{CO}/ (K_{CO}*\triangle T_{CO})$
Capital cost = 7296 $(A_{CO})^{0.65}$
Operating cost ($/y)
Cooling water (278K) = $4.43/GJ
LP stream (433K) = $7.88/GJ
MP stream (457K) = $8.22/GJ
HP stream (523k) = $9.88/GJ
TAC
TAC=Capital costs/Payback period+operating costs ($/y) Payback period = 3 years

Table 9. TAC comparison of different extraction processes

Costs/($/y)	EG	EGEDWC	EC2:1 EDC	EC2:1EDWC	GC3:1 EDC
Column	131300.6	150234.2	141556.2	131114.2	69402.6
Condenser	239467.1	225084	251292.6	214327.9	112673.6
Reboiler	81071.9	59352.9	98025.0	76211.3	41844.6
Cooler	20683.5	22605.8	19922.33	19603.8	12840.8
Capital cost	472523.2	457277.5	510796.7	441257.1	336761.6
Water cost	7989.2	7611.6	8597.7	6978.72	3128.6
Vapor cost	230879.3	220316.7	248299.4	201839.3	200993.2
Operating cost	238868.5	227928.3	256897.1	208818.0	204121.8
TAC	396376.3	380354.2	427162.7	355903.7	283042.3

CONCLUSIONS

In this work, different extractive distillation processes using EC2:1 and GC3:1 as entrainers for separating ACN-water mixtures were discussed. The TAC and sensitivity analysis of the extractive section were introduced to evaluate the performance of the extractive distillation process.

A simulation process considered the minimum energy consumption and purity as the goals. Furthermore, a sensitivity analysis that considered the effects of the number of theoretical stages, reflux molar ratio, feed stage, and the entrainer on the ethanol purity or reboiler energy duty was performed. According to the results, the EDW was optimized, and the energy consumption and TAC were reduced compared with the traditional EG solvent. Thus, in this study, we showed that EC2:1 could be used as an entrainer for the separation of ACN-water azeotrope when the process simulation was considered, offering broader applications compared with traditional extraction agents.

AUTHORS CONTRIBUTIONS

All authors contributed equally to this work.

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DATA AVAILABILITY

The sensitivity analysis data that support the findings of this study are available from the corresponding author upon reasonable request. The thermodynamic data that support this study are available within the article [34] and from Aspen Plus. The sensitivity analysis data that support the findings are also available from Aspen Plus.

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