Energy-efficient recovery of tetrahydrofuran and ethyl acetate by triple-column extractive distillation: Entrainer design and process optimization

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Abstract An energy-efficient triple-column extractive distillation process is developed for recovering tetrahydrofuran and ethyl acetate from industrial effluent. The process development follows a rigorous hierarchical design procedure that involves entrainer design, thermodynamic analysis, process design and optimization, and heat integration. The computer-aided molecular design method is firstly used to find promising entrainer candidates and the best one is determined via rigorous thermodynamic analysis. Subsequently, the direct and indirect triple-column extractive distillation processes are proposed in the conceptual design step. These two triple-column extractive distillation processes are then optimized by employing an improved genetic algorithm. Finally, heat integration is performed to further reduce the process energy consumption. The results indicate that the indirect triple-column extractive distillation process with heat integration shows the highest performance in terms of the process economics.

Keywords extractive distillation, solvent selection, conceptual design, process optimization, heat integration

1 Introduction

Tetrahydrofuran (THF) and ethyl acetate (EtAC) are regularly used as organic solvents and biofuels as well as sustainable biomass energy sources for the internal combustion engines [1-2]. According to the report from He et al. [3], wastewater mixtures containing THF and EtAC are generally produced in the chemical and pharmaceutical industries. However, the separation of such mixtures is difficult via the conventional distillation process because the distillation boundary and multiple azeotropes exist in this system. Thereby, the explorations of efficient processes for separating such mixtures are significant in realizing the recovery of available resources and reducing the environmental pollution [4-5].

Extractive distillation (ED) [6-7], pressure-swing distillation [8-9] and azeotropic distillation [10-11] are employed as effective approaches to separate azeotropic mixtures. Pressure-swing distillation is limited to

pressure-sensitive systems [12] and multiple steady-states can exist in the azeotropic distillation process [13]. Therefore, the ED process becomes one of the most popular separation techniques for handling azeotropic or close-boiling systems in the chemical and petroleum industries due to its advantage in the operational and control aspects [14-15]. For example, Yang et al. [16] reported an ED process to separate the binary azeotropic mixture dimethyl carbonate and ethanol by varying the operating pressures. Shi et al. [17] explored the separation of the ternary mixture isopropyl alcohol/isopropyl acetate/water with multiple azeotropes via two-alternative ED schemes. The separation of azeotropic systems has also been investigated by other researchers [18-20] using ED.

The selection of entrainer plays a key role in designing the energy-saving ED processes [21-22]. Cui et al. [23] studied the separation performance of two different entrainers via phase diagram analysis and they found that ethylene glycol is more suitable for the separation of benzene/isopropanol/water by ED. Zhu et al. [24] developed a heuristic method employing the relative volatility to determine the optimal solvent with the best economic performance. Shen et al. [25] proposed a solvent selection approach employing five properties (i.e., relative volatility, solubility power, molecular weight, melting point and boiling point) as objectives to screen the best entrainer. Blahušiak et al. [26] developed another quick calculation procedure for the preselection of solvents by considering the minimum energy consumption and solvent-to-feed ratio. The efficiency and reliability of this method were successfully verified via several industrial application cases. Unfortunately, these previous works all considered a limited, pre-specified solvents and tried to find the best candidate from these solvents. In comparison with the previous solvent screening methods, the computer-aided molecular design (CAMD) method developed by Gani and Brignole [27] attempts to rationally design the most suitable solvents [28-33] from a list of molecular building groups. Recently, Zhou et al. [34] proposed a multi-objective CAMD approach to design solvents for the separation of binary azeotropic mixture *n*-hexane/methanol. In the present work, we use this method to find potential entrainers for the ternary azeotropic system THF/EtAC/water. Subsequently, thermodynamic insights are employed to further determine the best entrainer for the ED process.

In addition to the optimal selection of solvent, energy saving could be further achieved by the process optimization technique [35]. Waltermann et al. [36] formulated extractive and heteroazeotropic distillation process design tasks into mixed-integer nonlinear programming (MINLP) problems and solved them as a series of successively relaxed nonlinear programming problems. Krone et al. [37] proposed a superstructure-based modeling environment to facilitate the MINLP optimization of complex distillation processes where rigorous thermodynamic models are used. It should be noted that conventional gradient-based optimization algorithms are not efficient for handling complex MINLP problems in distillation processes with massive coupled discrete and continuous decision variables [38]. By contrast, stochastic or hybrid optimization algorithms can be very powerful for solving these problems [39]. For example, Kruber et al. [40] optimized ED processes using a hybrid evolutionary-deterministic optimization approach. Yang et al. [41] optimized a thermally coupled ED process via the genetic algorithm (GA). You et al. [42] discussed the optimization of the ED process by using the SQP and GA approaches and they proved that the process economic performance can be further improved via the GA-based optimization.

In this work, we develop an efficient extractive distillation process to recover THF and EtAC from industrial wastewater. A rigorous hierarchical design procedure involving entrainer design, thermodynamic analysis, process design and optimization, and heat integration (HI) is followed in the process development. Specifically, candidate entrainers for the separation of THF/EtAC/water are first screened via the CAMD method. The iso- and uni- volatility lines between the azeotropic mixture and the entrainer are compared to obtain the most efficient entrainer for the separation task. Subsequently, volatility orders and distillation sequences (i.e., direct and indirect separation flowsheets) are determined in the conceptual design step. An improved GA is then employed to optimize the direct and indirect ED processes. Finally, HI is performed to further reduce the energy consumption of the processes.

2 Methodology

A systematic approach (as illustrated in Fig. 1) involving the selection of entrainer via CAMD and thermodynamic analysis, conceptual design, process optimization, and HI is proposed to find an energy-efficient ED process for the separation of the ternary azeotropic mixture THF/EtAC/water. In Step 1, candidate entrainers are first designed via the CAMD method and then the most suitable entrainer is determined via the comparison

of iso- and uni- volatility lines of the ternary phase diagrams. In Step 2, the conceptual design of the ED process considering the direct and indirect separation sequences is performed via the rigorous thermodynamic analysis. In Step 3, an improved GA is used to optimize the operating variables (e.g., total number of stages and reflux ratios) for both direct and indirect separation processes. Finally, in Step 4, HI is performed for the optimized processes to further reduce the energy consumptions.

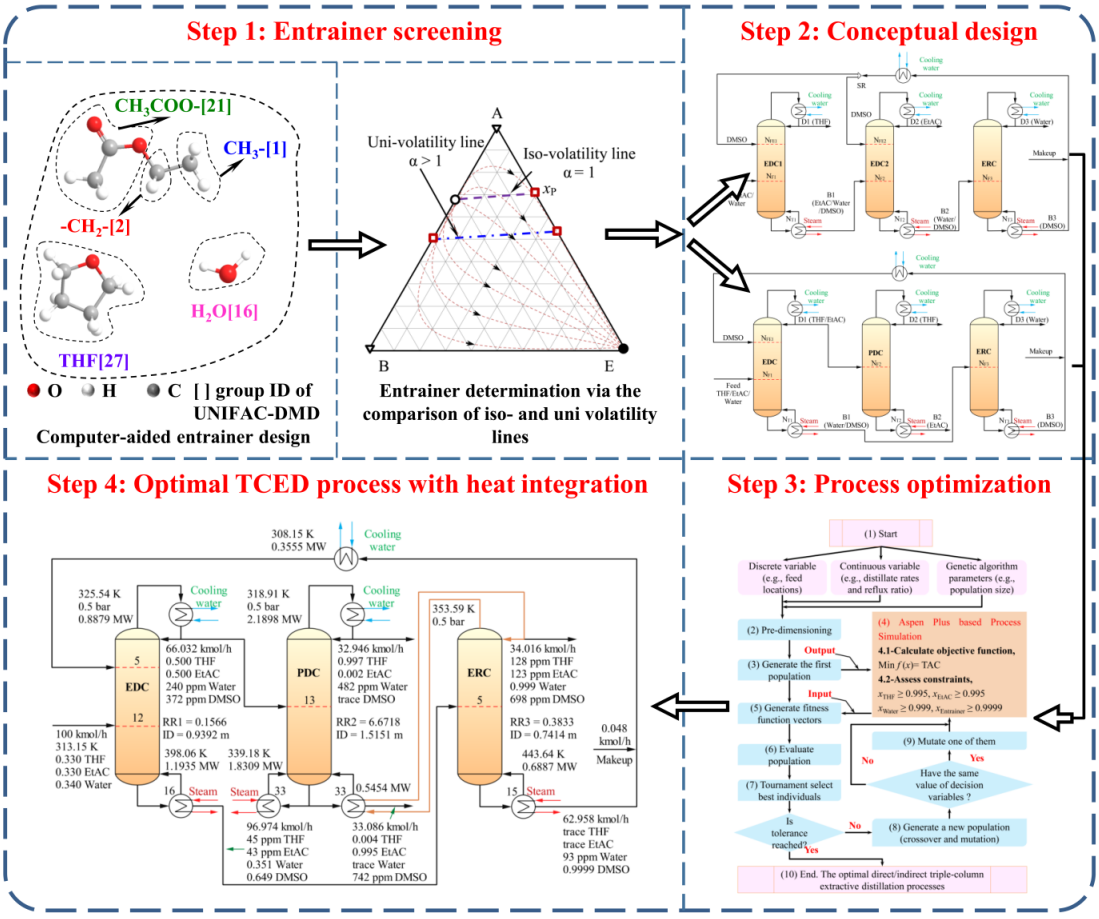

Fig. 1 Systematic approach for conceptual design and optimization of the THF/EtAC/water separation process

2.1 Screening of entrainer

2.1.1 Computer-aided entrainer design

The entrainer plays a significant role in the ED process [43]. In this work, the CAMD approach is employed to obtain the potential candidate entrainers. In total, 22 UNIFAC-Dortmund (UNIFAC-DMD) groups for building the entrainer molecules are considered in this work. Their UNIFAC-DMD group IDs, valences, and maximum occurrences are listed in Table 1. The van der Waals volume R_j and surface area Q_j are summarized in Table S1.

Table 1 Functional groups and single-group molecules with their IDs, valences, and maximum numbers

Group ID	Group *j*	Valence *v*(*j*)	Group classification
1	CH_3	1	Mg[a)]
2	CH_2	2	Mg[a)]
3	CH	3	Mg[a)]
4	C	4	Mg[a)]
14	OH(P)	1	Ceg[b)]

Group ID	Group *j*	Valence *v*(*j*)	Group classification
15	CH_3OH	0	Sg[c)]
16	H_2O	0	Sg[c)]
18	CH_3CO	1	Ceg[b)]
19	CH_2CO	2	Nceg[d)]
20	CHO	1	Ceg[b)]
21	CH_3COO	1	Ceg[b)]
22	CH_2COO	2	Nceg[d)]
23	HCOO	1	Ceg[b)]
24	CH_3-O	1	Ceg[b)]
25	CH_2-O	2	Nceg[d)]
26	CH-O	3	Nceg[d)]
27	THF	0	Sg[c)]
61	Furfural	0	Sg[c)]
67	DMSO	0	Sg[c)]
72	DMF	0	Sg[c)]
81	OH(S)	1	Ceg[b)]
82	OH(T)	1	Ceg[b)]

a) Mg: main groups; b) Ceg: chain-ending function groups; c) Sg: single-group molecules; d) Nceg: non chain-ending function groups.

Following the study of Zhou et al. [34], the solvent infinite dilution selectivity (S_{AB}^{∞}) and infinite dilution capacity toward B (C_{B}^{∞}) as shown in Eqs. 1-2 can be used in the CAMD program to find promising entrainers for the separation of B from A using ED. Herein, due to the trade-off between these two selection criteria, we introduced a weighted function, displayed in Eq. 3, as our final objective function.

$$S_{\mathrm{AB}}^{\infty} = \frac{\gamma_{\mathrm{A}}^{\infty}}{\gamma_{\mathrm{B}}^{\infty}} \tag{1}$$

$$C_{\mathrm{B}}^{\infty} = \frac{1}{\gamma_{\mathrm{B}}^{\infty}} \tag{2}$$

$$\textit{Objective function} = \max\left(\omega_1 S_{AB}^{\infty} + \left(1-\omega_1\right) C_{\mathrm{B}}^{\infty}\right) \tag{3}$$

where ω_1 and $\left(1-\omega_1\right)$ represent the weight coefficients of S_{AB}^{∞} and C_{B}^{∞} , respectively. In the CAMD approach, ω_1 is a variable from 0.0 to 1.0 with a step size of 0.1. $\gamma_{\mathrm{A}}^{\infty}$ and $\gamma_{\mathrm{B}}^{\infty}$ are the infinite dilution activity coefficients of A and B in the entrainer, respectively. They can be calculated using the UNIFAC-DMD model at the infinite dilution condition. In this work, the ternary mixture being separated has two azeotropes, THF/water and EtAC/water. Thereby, A and B indicate the THF (or EtAC) and water, respectively.

The molecular structure should be constrained in the CAMD to ensure that the generated molecule is structurally feasible and uncomplicated. The structural feasibility and complexity rules are taken directly from Zhou et al. [34]. The upper limit of the number of groups in the solvent molecule is set to 6. Melting and boiling points are used as the property constraints. The melting point as shown in Eq. 4 is used to ensure that the designed

molecules are liquid at room temperature. In the ED process, the entrainer is recovered via distillation. Thereby, lower and upper bounds (Eq. 5) are employed to constrain the normal boiling point of the entrainer.

$$\sum_{j=1}^{N} n_j t_{m,j} \leq \exp\left(\frac{T_m^{\text{upper}}}{T_{m0}}\right) \tag{4}$$

$$\exp\left(\frac{T_b^{\text{lower}}}{T_{b0}}\right) \leq \sum_{j=1}^{N} n_j t_{b,j} \leq \exp\left(\frac{T_b^{\text{upper}}}{T_{b0}}\right) \tag{5}$$

where n_j is the number of group j present in the entrainer molecule and N denotes the total number of groups considered in this work ($N = 22$, see Table 1). The upper temperature of the melting point (T_m^{upper}) is 315 K; the lower and upper bounds of the boiling point (T_b^{lower} and T_b^{upper}) are 393.15 K and 493.15 K; T_{m0} and T_{b0} are 147.45 K and 222.54 K, respectively. Group contributions $t_{m,j}$ and $t_{b,j}$ can be found from Marrero and Gani [44]. The detailed formulation of the CAMD problem can be found in Zhou et al. [34]. The resulting mixed-integer optimization problem is coded and solved in Python.

2.1.2 Solvent determination via the thermodynamic analysis

The suitable entrainer of the ED process could be further determined via the thermodynamic feasibility analysis. Fig. 2 illustrates the residue curve maps (RCMs) of the EtAC/THF/water, EtAC/water/E and THF/water/E systems where E indicates an arbitrary effective entrainer. As shown in Fig. 2a, there are two azeotropes (one between THF and water and the other between EtAC and water). Their azeotropic temperatures are 335.74 K and 344.61 K and the corresponding azeotropic compositions are 78.72 mol% and 61.32 mol%, respectively. The black dot, hollow triangle and hollow circle represent the stable node, saddle and unstable node, respectively. In Fig. 2a, the ternary diagram is divided into two regions via the distillation boundary between azeotropes of EtAC/water and THF/water. In Regions 1 and 2, all residue curves are directed from an unstable node to a stable node. Due to the existence of distillation boundary, it is impossible to separate the components by simple distillation. Fig. 2b and 2c show the RCMs with an effective entrainer. In Fig. 2b, the intersection of the iso-volatility line and the EtAC-E edge is denoted as x_P. The position of x_P can be adopted to preliminarily evaluate the separation performance of the entrainer E. When a heaviest entrainer has a much stronger interaction with water (making EtAC the lightest component), the x_P point will be closer to the EtAC vertex, leading to a higher separation performance [45]. Additionally, the performance of the entrainer can be further verified via the intersection of the uni-volatility line and the EtAC-E edge. Water-EtAC-E indicates that water as a heavier component (in comparison with EtAC) can be distilled out from the top of the ED column (EDC) when the total feed composition locates above the iso-volatility line. On the other hand, when the total feed composition is below the iso-volatility line, EtAC can be first distilled out. The analysis of the THF/water/E system in Fig. 2c is very similar to that of the EtAC/water/E system.

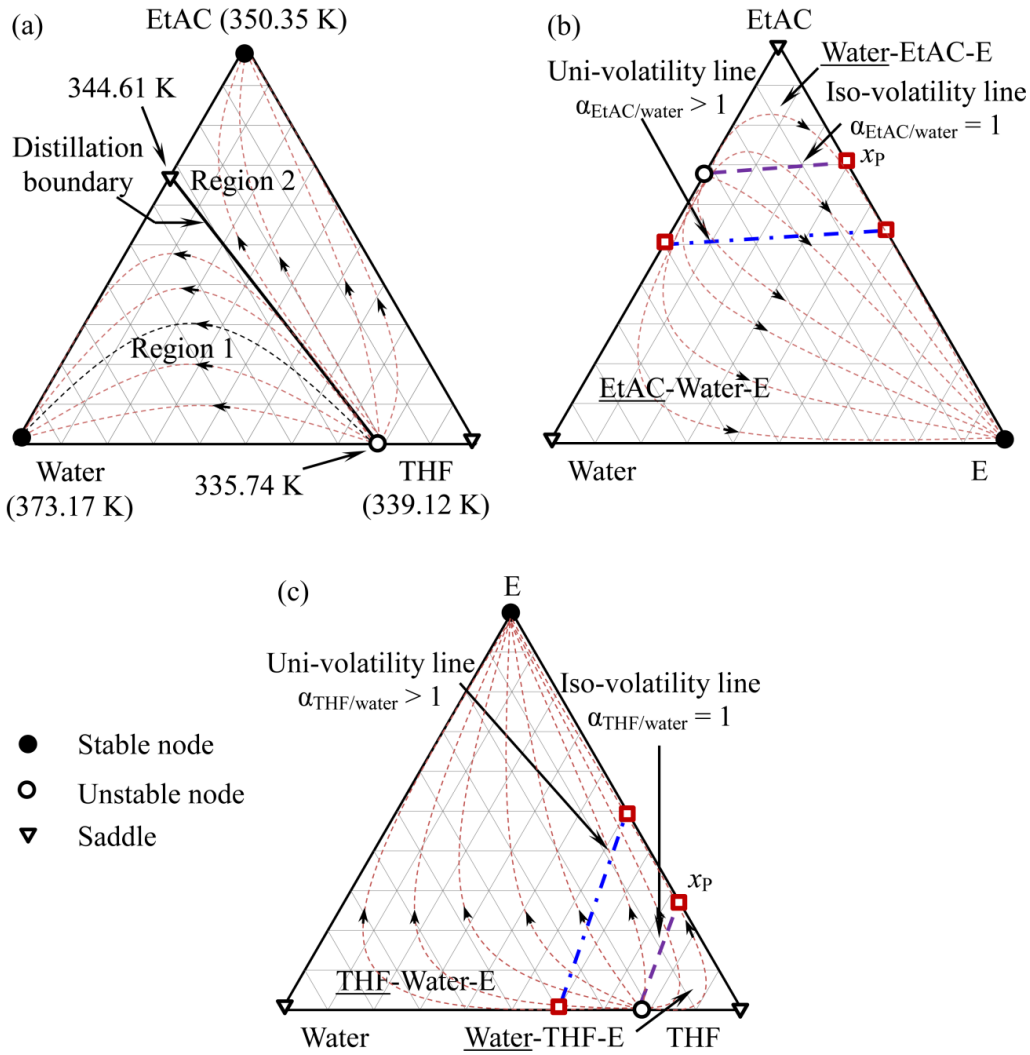

Fig. 2 RCMs of the (a) studied EtAC/THF/water system, (b) mixture of EtAC-water together with an entrainer E, and (c) THF-water with an entrainer E

2.2 Conceptual design via RCMs

The ED process flowsheets can be designed via the analysis of the RCMs after the entrainer is determined. Normally, we can obtain two different process flowsheets with one following the direct separation sequence and the other following the indirect separation sequence.

2.3 Process optimization

The optimization of the ED process is carried out via the combination of the improved GA and Aspen Plus-based process simulation. Fig. S1 demonstrates the scheme of the optimization process. Firstly, the discrete variables (e.g., feed locations), continuous variables (e.g., distillate rates and reflux ratios), and GA parameters (e.g., population size) are imported into an improved GA based software developed in our group. The first population is generated and sent to Aspen Plus to calculate the objective function and assess the constraints. In addition, the results are fed back to generate fitness function vectors, evaluate population and select the best individuals. The process optimization is terminated when the tolerance (difference between adjacent objective function values) satisfies the stop criteria. Otherwise, a new generation is created. The created generation is directly fed to Aspen Plus when there is no same individual in this generation; if not, mutation is imposed on one of them.

2.3.1 Objective function

In this work, the total annual cost (TAC) as illustrated in Eq. 6 is used to assess the economic performance of the proposed processes, which involves two parts: total capital cost (TCC) and annual operating cost (AOC) [46]. The AOC is made up of the steam and cooling water costs while the TCC includes the heat exchanger and distillation column costs. The payback period is assumed to be three years [47]. The detailed calculation of TCC and AOC could be found in the *Supporting Information*.

$$TAC = \frac{TCC}{Payback\ period} + AOC \tag{6}$$

2.3.2 Constraints

In this work, three product purities and the entrainer purity in Eq. 7 are specified as constraints for the GA-based optimization.

$$\begin{aligned} x_{\mathrm{THF}} &\geq 99.50\ \text{mol\%} \\ x_{\mathrm{EtAC}} &\geq 99.50\ \text{mol\%} \\ x_{\mathrm{Water}} &\geq 99.90\ \text{mol\%} \\ x_{\mathrm{Entrainer}} &\geq 99.99\ \text{mol\%} \end{aligned} \tag{7}$$

2.3.3 Upper and lower bounds of decision variables

In the optimization process, upper and lower bounds of the discrete and continuous decision variables for the direct and indirect triple-column ED (TCED) processes are summarized in Table S2. There are eight integer decision variables including the total number of stages of the three columns (N_{T1}, N_{T2} and N_{T3}), feed locations of entrainers (N_{FE1} and N_{FE2}) and feed locations of the three columns (N_{F1}, N_{F2} and N_{F3}). Continuous decision variables include molar reflux ratios (RR_1, RR_2 and RR_3), flow rate of entrainer (F_E), split ratio of entrainer (SR), and distillate rates (D_1, D_2 and D_3).

2.4 HI

The HI technique could be employed to reduce the process energy consumption when a sufficient temperature difference exists between the condenser and the reboiler [48].

3 Results and discussion

3.1 The entrainer screening

3.1.1 Results of CAMD

There are two binary azeotropes EtAC/water and THF/water in the ternary mixture EtAC/THF/water. In the UNIFAC-DMD model, EtAC is divided into three groups, CH_3, CH_2, and CH_3COO, and THF and water are single-group molecules. After the CAMD computation, dimethyl sulfoxide (DMSO), furfural and N,N-dimethylformamide (DMF) are identified as the most promising entrainers for all the different w_1 values (see Table S3). According to the vapor-liquid equilibrium in Yang et al. [49], N-methyl-2-pyrrolidone (NMP) is an efficient solvent for separating the ternary mixture. Therefore, together with DMSO, DMF and furfural, NMP is considered as the fourth candidate entrainer to further verify the performance of the entrainers obtained from the CAMD.

3.1.2 Final determination of entrainer

The thermodynamic analyses such as iso- and uni- volatility lines are adopted to further determine the most powerful entrainer for the separation of the ternary azeotropic mixture EtAC/THF/water. The selection of thermodynamic model is important to accurately describe the vapor-liquid equilibrium of the system at different

temperatures. Herein, the activity coefficient model UNIQUAC is employed and the corresponding binary interaction parameters are summarized in Table S4 (*Supporting Information*). Among the four entrainers, furfural is first excluded because it can form an extra azeotrope with water, leading to two separate distillation regions and thus making it incapable to separate THF/EtAC/water. For the other three entrainers, we performed a rigorous thermodynamic analysis, as discussed below.

Fig. 3 displays the iso- and uni- volatility lines for azeotropes EtAC-water and THF-water using DMSO, NMP and DMF as the entrainers. These plots are generated via the separation module 'Flash2' in Aspen Plus. As demonstrated, the entrainer DMSO shows a higher performance for the separation of EtAC/water and THF/water because its x_P point is closer to the components EtAC and THF, compared to the cases where NMP and DMF are used. Therefore, DMSO is finally selected as our entrainer for further process design and evaluation.

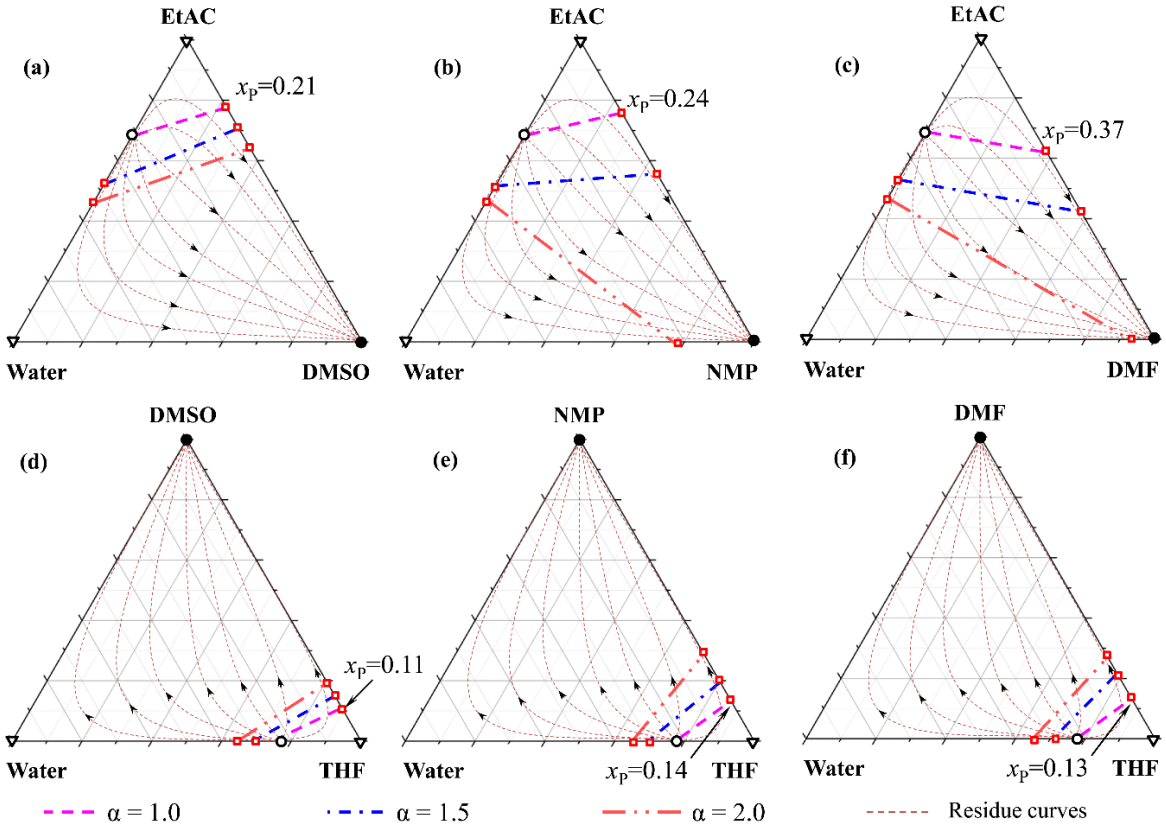

Fig. 3 The iso- and uni- volatility lines for (a-c) EtAC-water and (d-f) THF-water azeotropic mixtures by using the entrainers DMSO, NMP and DMF

3.2 Conceptual design of the ED process

As seen in Fig. 3a and 3c, the point of x_P locates on the edges of EtAC-DMSO and THF-DMSO indicating that EtAC and THF are more volatile than water when using DMSO as the entrainer. Thereby, the component THF with the lowest boiling point can be firstly distilled out in an EDC when applying the direct separation sequence. Subsequently, EtAC can be obtained in another EDC and finally, water and DMSO can be separated in a conventional distillation column. In the indirect ED process, the mixture of THF and EtAC can be firstly obtained in an EDC and then separated in another distillation column. In summary, the separation of the ternary mixture THF/EtAC/water with two azeotropes can be achieved using DMSO as the entrainer via both the direct and indirect separation schemes.

3.2.1 Direct separation sequence

Fig. 4 shows the direct TCED process for separating the ternary mixture THF/EtAC/water with two azeotropes. The process includes two EDCs (EDC1 and EDC2) and one entrainer recovery column (ERC). The entrainer DMSO is split into two substreams. One substream and the ternary mixture THF/EtAC/water are fed into EDC1 where THF and the mixture of EtAC/water/DMSO are distilled at the top and bottom, respectively. The mixture of EtAC/water/DMSO and the other entrainer substream are sent to EDC2 where EtAC and water/DMSO are obtained at the top and bottom, respectively. Finally, water and DMSO are separated in the ERC. SR denotes the ratio of the molar flow rate of the entrainer sent to EDC2 to the molar flow rate of the entire DMSO stream.

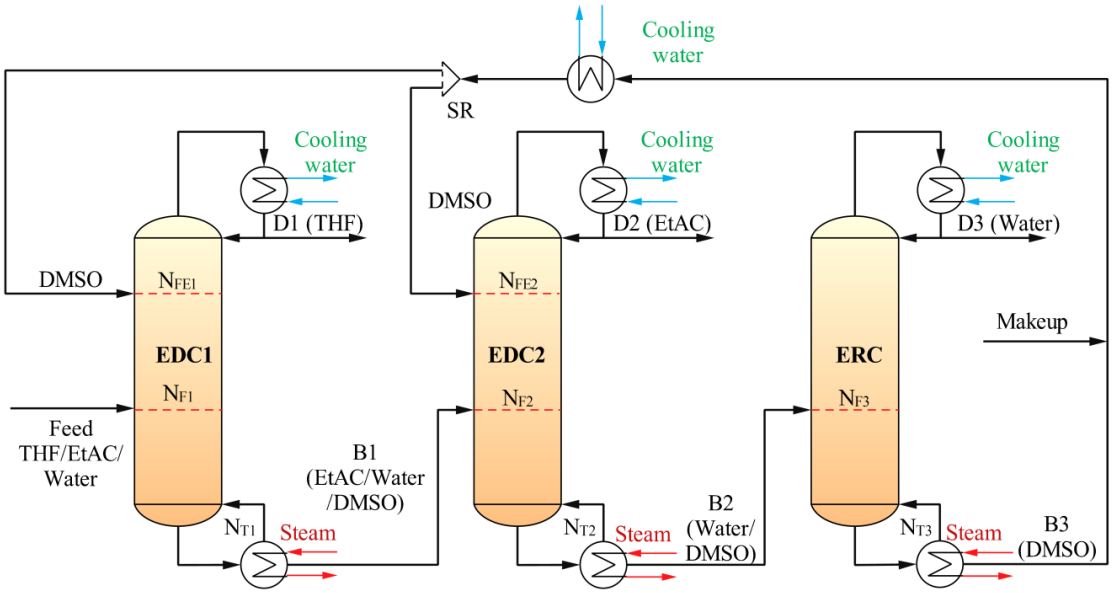

Fig. 4 The scheme of the direct TCED process for separating THF/EtAC/water

3.2.2 Indirect separation sequence

The indirect TCED process includes one EDC, one product distillation column (PDC) and one ERC (see Fig. 5). DMSO and the THF/EtAC/water mixture are fed into the EDC and then the mixtures of THF/EtAC and water/DMSO are obtained at the top and bottom of the EDC, respectively. The mixture of THF/EtAC enters the PDC and high purities of THF and EtAC are obtained at the top and bottom of PDC, respectively. The entrainer DMSO is finally separated from water in ERC and recycled back to EDC.

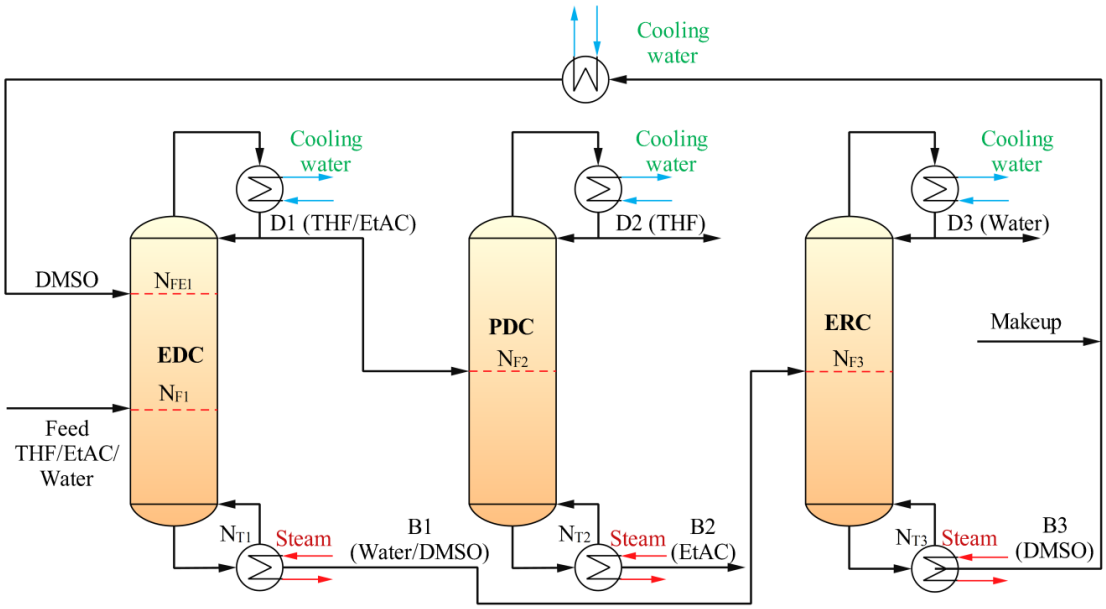

Fig. 5 The scheme of the indirect TCED process for separating THF/EtAC/water

In the indirect process, it is necessary to separate the THF-EtAC mixture. Figure S2 gives T-xy diagram for THF-EtAC under 1.0 and 0.5 bar. As illustrated in Fig. S2a, the high purity of THF could not be obtained at 1.0 bar because the vapor and liquid lines are extremely close to each other (see the blue circle). The corresponding T-xy diagram of this binary system under 0.5 bar is shown in Fig. S2b. As indicated, to use such a reduced pressure makes this binary separation possible [50]. For the EDCs in both direct and indirect processes, we chose to operate them at 0.5 bar as well because this can increase the relative volatility of both EtAC-water and THF-water systems (see the uni-volatility lines at 1.0 bar and 0.5 bar in Figure S3). To use an even lower pressure will dramatically increase the cost for vacuuming thus is not considered here. For the ERC in both direct and indirect processes, the task is to separate water and DMSO. We plot the *x-y* diagram for this binary system in Figure S4. As demonstrated, this binary mixture is easy to separate regardless of the operating pressure. Herein, 0.5 bar is selected again because keeping the same pressure level as the previous columns can save pumping cost. Moreover, a reduced operating pressure in the ERC is also beneficial for decreasing the reboiler temperature, which helps save the cost for high-pressure steam. In summary, all the distillation columns are operated at 0.5 bar.

3.3 Process optimization results

The optimization of the two proposed processes is implemented in the desktop computer with Intel® Core™ i7-7700 CPU@3.60 GHZ and 8G RAM. Table S5 summarizes the setup parameters of the improved GA used in the optimization process as suggested by our previous work [41].

3.3.1 Direct TCED process

Fig. 6 illustrates the dependence of the TAC of the direct TCED process on the number of generations. The optimization is stopped at 400 generations because the tolerance is lower than 10^{-5}. The whole process takes 1108 minutes. The optimal direct TCED process for separating the ternary azeotropic mixture THF/EtAC/water is demonstrated in Fig. 7 where all the stream information and column specifications are provided.

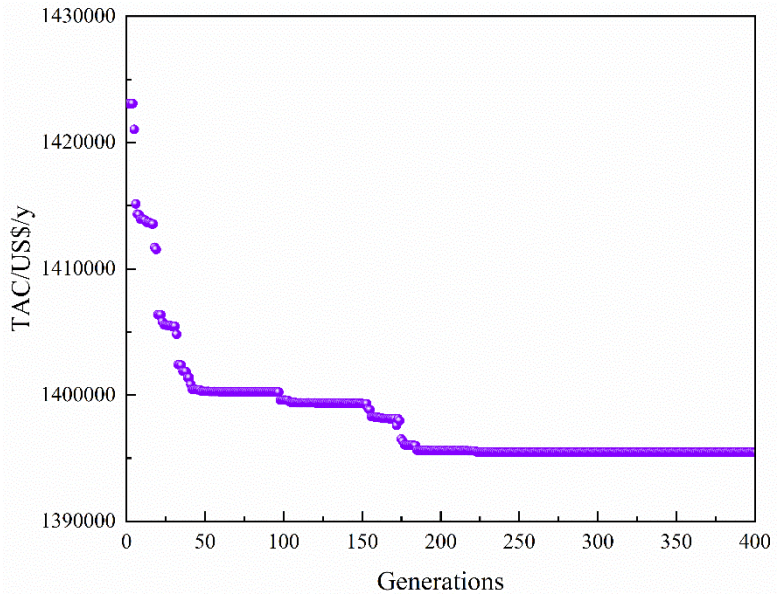

Fig. 6 The optimization result of the direct TCED process

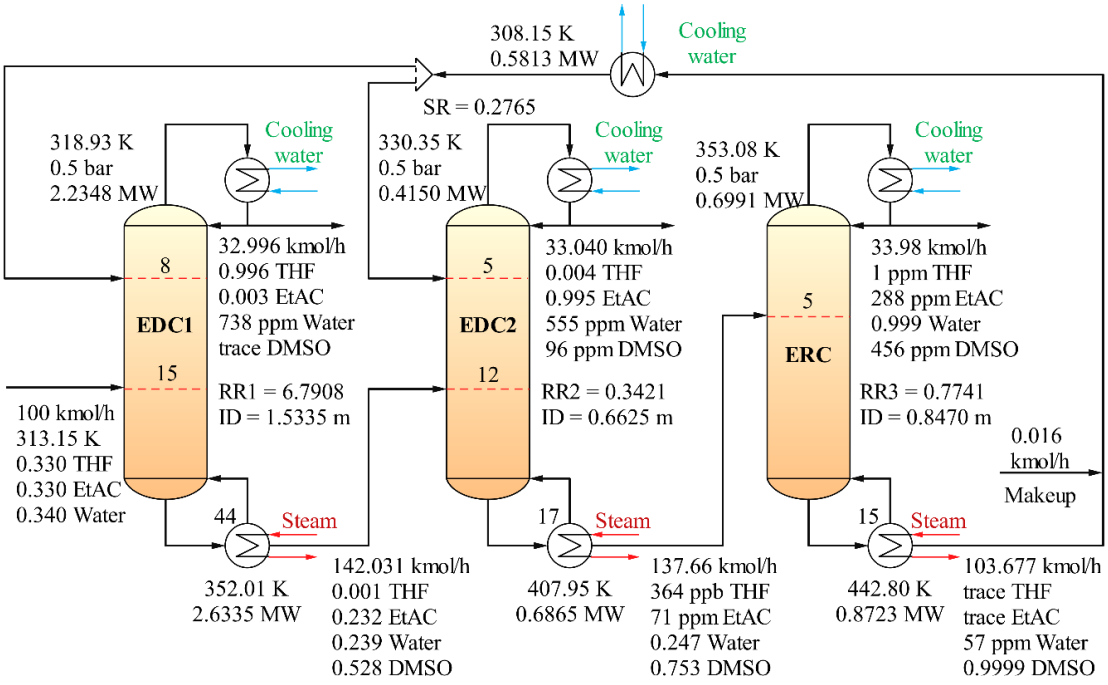

Fig. 7 The optimal direct TCED process for separating THF/EtAC/water using DMSO as the entrainer

Fig. S5 shows the liquid composition and temperature profiles of the optimal direct separation process. As demonstrated, THF, EtAC and water with high-purities are respectively distilled at the top of EDC1, EDC2 and ERC (Stage 1 of Fig. S5 a, c, and e). The DMSO with 99.99 mol% is obtained at the bottom of ERC. Moreover, temperature transitions can be observed near (or at) the feed locations, as shown in Fig. S5 b, d, and f.

3.3.2 Indirect TCED process

The reduction of TAC with number of generations for the indirect TCED process is given in Fig. 8. As shown, the optimization is terminated at 180 generations when the tolerance is lower than 10^{-5}. The whole calculation takes about 602 minutes.

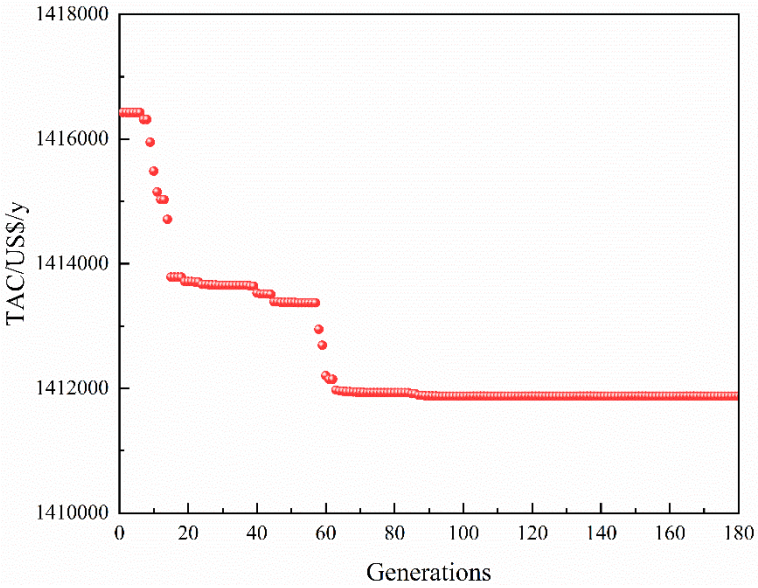

Fig. 8 The optimization results of the indirect TCED process

Fig. 9 illustrates the optimal indirect TCED process for separating the ternary azeotropic mixture THF/EtAC/water. The total number of stages of EDC, PDC and ERC are 16, 33 and 15, respectively. The entrainer DMSO and the ternary mixture are fed into the 5th and 12th trays of EDC while the feed locations of PDC and ERC are the 13th and 5th stages, respectively. To achieve the separation of THF/EtAC and water, 63.006 kmol/h of DMSO and 0.1566 of reflux ratio are required in the EDC. High purities of THF and EtAC (*i.e.*, 99.7 mol% and 99.5 mol%) are obtained at the top and bottom of PDC. Water and DMSO are finally separated in the ERC column with 0.3833 of reflux ratio. The condenser duties of the three columns are 0.8879 MW, 2.1898MW, and 0.5454 MW while the corresponding reboiler duties are 1.1935 MW, 2.3763 MW, and 0.6887 MW, respectively.

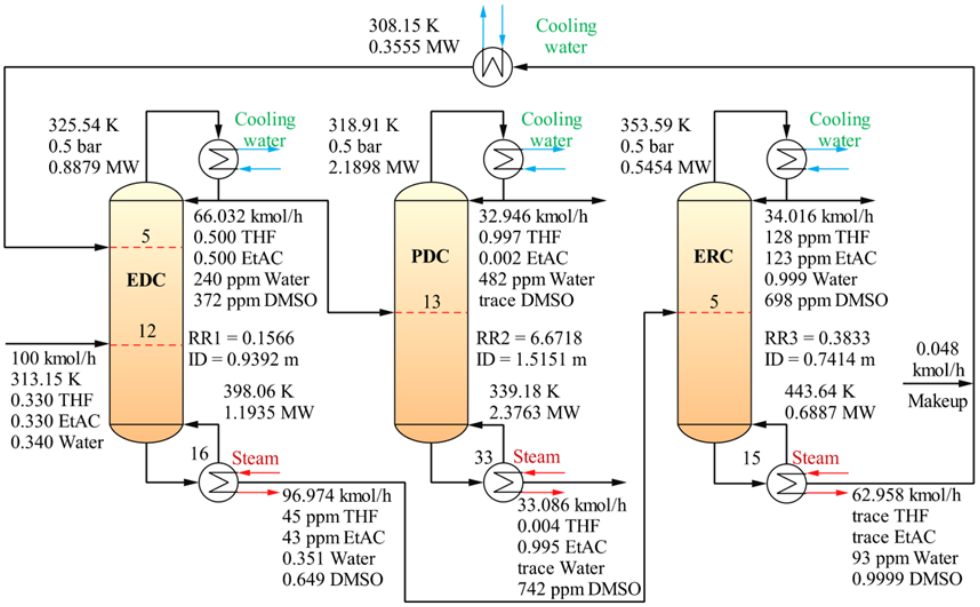

Fig. 9 The optimal indirect TCED process for separating THF/EtAC/water using DMSO as the entrainer

The liquid composition and temperature profiles of the indirect TCED process are displayed in Fig. S6. As indicated, THF/EtAC and water are separated at the extractive section (from 5th to 12th tray) while the concentrations of THF and EtAC get accumulated towards the top of the ED column. Notably, remixing occurs

in the stripping section, resulting in more heat input. The composition and temperature profiles in PDC and ERC are easy to interpret because both of the columns separate binary mixtures.

3.4 HI results

As illustrated in Fig. 7, the HI technology could not be employed for the direct TCED process because the difference between the temperature in the condenser (353.08 K) and the temperature in the reboiler (352.01 K) is too small. However, HI can be adopted to further reduce the energy consumption of the indirect TCED process because the temperature difference between the top of ERC and the bottom of PDC is higher than 14 K, as illustrated in Fig. 9.

Fig. 10 depicts the optimal indirect TCED process where HI is applied. As shown, the reboiler duty of the PDC can be divided into two parts with 0.5454 MW supplied by the top vapor stream of the ERC and 1.8309 MW provided by external steam. In other words, we can save 0.5454 MW heating and cooling duties by employing HI.

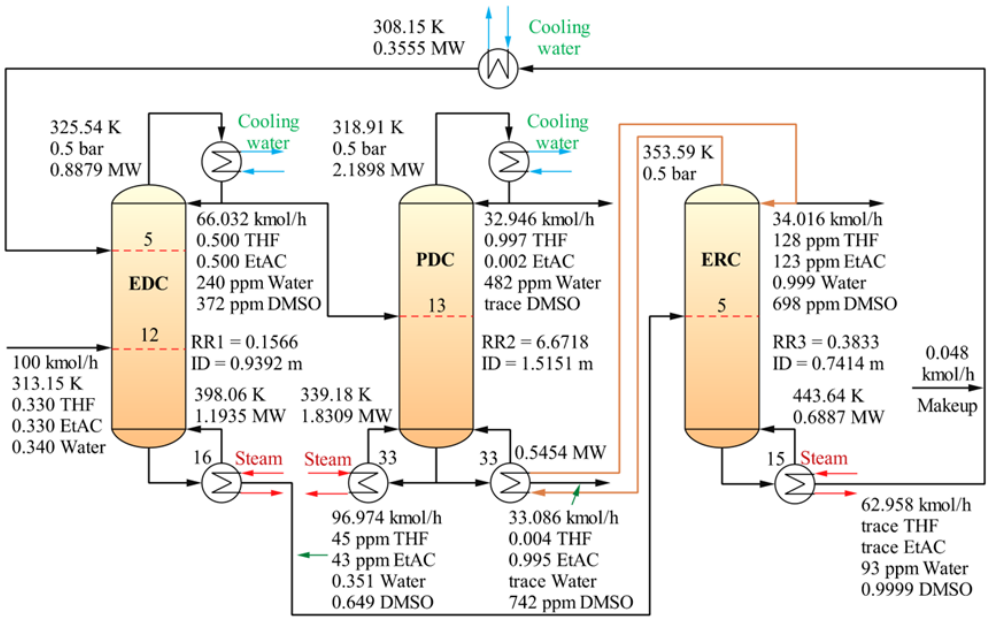

Fig. 10 The optimal indirect TCED process with HI scheme for separating THF/EtAC/water using DMSO as the entrainer

3.5 Comparison and discussions

The economic performance for the direct and indirect processes without and with HI is summarized in Table 2. The TAC of the three processes are 1,397,320.33 US$/y, 1,413,626.41 US$/y and 1,373,366.41 US$/y, respectively. As indicated, the proposed direct process with 99.6 mol% THF purity shows a higher performance than the indirect one because it can avoid the repeat heating of components. Of note is that, a relatively higher THF purity (99.7 mol%) and economic performance could be achieved via the indirect TCED process after HI is employed.

Table 2. Economic performance of the direct and indirect processes with and without HI

	Direct process	Indirect process without HI	Indirect process with HI
TCC (US$)	1,219,334.38	1,229,563.80	1,141,299.66
AOC (US$/y)	990,875.54	1,003,771.81	992,933.19

	Direct process	Indirect process without HI	Indirect process with HI
TAC (US$/y)	1,397,320.33	1,413,626.41	1,373,366.41

4 Conclusion

In this contribution, an energy-efficient TCED process is developed for recovering THF and EtAC from industrial wastewater. A rigorous hierarchical design procedure involving entrainer design, thermodynamic analysis, process design and optimization, and HI is followed in the process development. First, candidate entrainers are screened via the CAMD method, and then the most efficient entrainer DMSO is determined via the comparison of the iso- and uni- volatility lines. Later, two alternatives of direct and indirect TCED processes are proposed. An improved GA is employed to optimize the proposed two processes. HI is finally performed for the optimized processes. The TAC of the direct TCED process, indirect process without and with HI are 1,397,320.33 US$/y, 1,413,626.41 US$/y, and 1,373,366.41 US$/y, respectively, which proves that the indirect separation process with HI is the best process alternative for separating THF/EtAC/water.

In order to reduce the remixing effects of the direct and indirect processes, intensified configurations such as dividing wall column and side-stream ED will be explored in the future work. In addition, innovative solvents such as ionic liquids will be considered in the entrainer design to find a potentially better ED process. Finally, life cycle environmental assessment can be included in the optimal process design.

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