https://doi.org/10.1016/j.jclepro.2020.123145

Investigation on ternary system tetrahydrofuran/ethanol/water with three azeotropes separation via the combination of reactive and extractive distillation

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Abstract: In this work, a systematic method for conceptual design and multi-objective optimization of an energy-efficient and sustainable reactive/extractive distillation (RED) process is proposed to separate a ternary wastewater mixture with multi-azeotrope tetrahydrofuran/ethanol/water. Conceptual design of the proposed scheme is carried out by the analysis of thermodynamic feasibility (*e.g.*, residue curve maps and iso-volatility line). In the proposed process, the component of water in the ternary system is firstly removed by adding the reactant in a reactive distillation column and the remaining binary azeotropic mixture is then separated *via* ED. During the ED process, the best entrainer dimethyl sulfoxide could be determined *via* the comparison of iso- and uni- volatility. An improved multi-objective genetic algorithm is employed for optimizing the established process with some key decision variables (*e.g.*, feed locations and distillate rate). The results illustrated that the economic and environmental benefits of the proposed RED process will be greatly improved.

Keywords: Extractive distillation; Reactive distillation; Energy-saving; Multi-objective optimization; CO_2 emissions; Cleaner production

1. Introduction

Ternary azeotropic mixtures such as tetrahydrofuran (THF)/ethanol/water are normally produced in the chemical and pharmaceutical industries (Yang et al., 2019a). THF and ethanol are biofuels as well as the sustainable biomass energy source for internal combustion engines (Farrell et al., 2006; Tran et al., 2015). Significantly, THF and ethanol act as the organic solvents in the chemical industries (He et al., 1995; Jaime et al., 2018). Therefore, it is promising for the purification of azeotropic mixtures of THF/ethanol/water, which could achieve environmental protection and recovery of high value-added solvents. However, multiple azeotropes and distillation boundaries exist in the THF/ethanol/water system (Figure 1) causing the tough separation issues (Kiva et al., 2003).

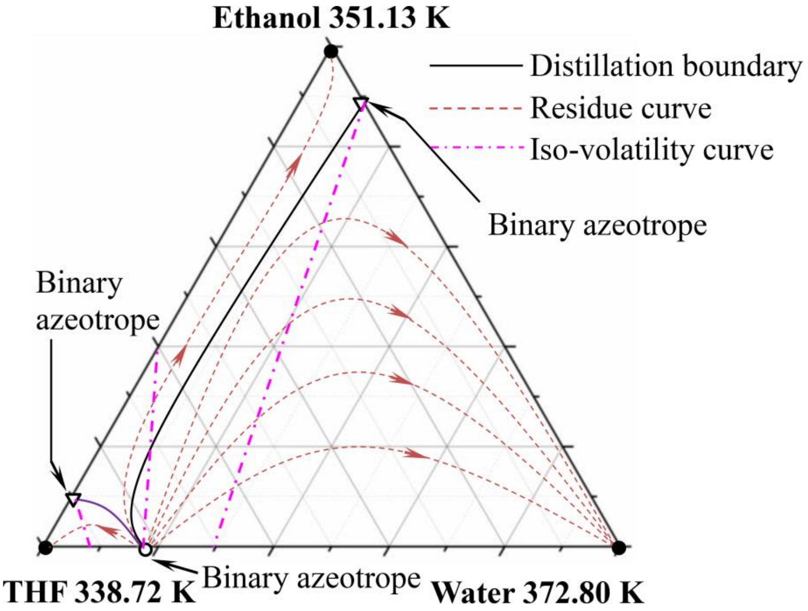

Figure 1. The residue curve maps for the ternary azeotropic mixture of THF/ethanol/water

Pressure-swing distillation, azeotropic distillation, extractive distillation (ED) and reactive distillation could be used to separate azeotropic systems. Pressure-swing distillation can be adopted to separate azeotropic system when the azeotropic point is sensitive to the pressures (Liang et al., 2017). Extractive, azeotropic, and reactive distillations enable separating azeotropic mixture by introducing a third component (Gerbaud et al., 2019; Sun et al., 2019a). However, pressure-swing and azeotropic distillations are energy intensive processes (Wang et al., 2020). Among these advanced distillation processes, extractive and reactive distillations have been extensively used to separate azeotropic system and they are frequently the best option in the industrial applications (Lei et al., 2003). In terms of the ED, Shen et al. (2015) explored ED process for separating the binary azeotropic mixture of acetone/chloroform with different heavy entrainers to provide a systematic approach for screening best entrainer. Yang et al. (2019e) developed an energy-efficient ED process for separating binary minimum azeotropic dimethyl carbonate/ethanol by changing operating pressure via the thermodynamic insights such as volatility lines. Yang et al. (2019f) reported an energy-efficient triple-column ED process for separating ternary azeotropic system of ethyl acetate/ethanol/water via the comparison the extractive performance of two candidate entrainers and the result illustrated that the proposed process with screened entrainer has less energy consumption and total annual cost. In summary, a suitable entrainer could enhance the separation performance for the azeotropic system. For the reactive distillation, the research group of Tavan (Tavan et al., 2013; Tavan and Hosseini, 2013) reported an intensified reactive distillation process for separating the binary azeotropic ethyl acetate/water and ethanol/water and the results shown that the energy saving and emissions reduction could be achieved by using the heat released of reaction. An energy-saving reactive distillation for THF dehydration is investigated by Tavan (2014) and they illsutrated that the reactive equilibrium could be broken via the reactive distillation. The investigation of bioethanol dehydration *via* the azeotropic and reactive distillation processes is explored and compared by Kaymak (2019) and the results displayed that the less energy consumption is required via the reactive distillation. Li et al. (2019) proposed a reactive distillation process for purifying formaldehyde solution to reduce the investment and energy consumption. Following that, the optimization and plant-wide control of the proposed reactive distillation process is explored to explore the separation performance facing the flowrate and composition disturbances (Pan et al., 2019). Recently, a dehydration reactive distillation scheme is explored to the dimethyl carbonate synthesis process and results illustrated that the energy consumption and eco-cost could be significantly reduced (Wu and Chien, 2019).

Of note is that the above mentioned separation technologies are modeled involving mass and energy balances, equations to represent liquid-vapor and reaction equilibriums, turning the model highly non-linear, and potentially non-convex (Alcocer-García et al., 2019). To solve these complex optimization problems, stochastic optimization algorithms such as genetic algorithm (GA) is adopted without explicit equation. For example, the optimization of the reactive distillation scheme for producing diphenyl carbonate *via* the multi-objective GA embedded in Matlab is investigated by Contreras-Zarazúa et al. (2017). Optimization of the triple-column ED process for separating binary azeotropic through the GA in Matlab is reported (You et al., 2018) and the results illustrated that the less energy consumption could be achieved via the GA approach with longer computional time. The optimization of the ED process considering the operating pressures of column by a GA in Matlab is explored by Cui and Sun (2019) and they shown that the mixed integer non-linear programing could be effective handled by the GA approach. Li et al. (2019) explored the optimization of the ternary ED scheme by using GA in Matlab. To effectively reduce the repeated solutions and increase the evolutionary rate, an improved GA with the step of 'Tournament & Select best individuals' is developed, which has been successfully applied in our previous studies. For instance, the application of GA for the optimization of double-thermally coupled ED process is investigated by Yang et al. (2019b) and they proved that the process with optimal operating conditions could be obtained via the GA method. Recently, Yang et al. (2019c) applied the multi-objective GA to optimize the organic Rankine cycle for the waste heat recovery to obtain the optimal process with minimum economic and maximum environmental performances. In summary, the GA optimization model can effective solve the complex mixed non-liner chemical process.

Many investigations are focused on the pressure-swing and ED for separating ternary azeotropic systems. However, massive utilities are required in the pressure-swing (or extractive) distillation process since the multi-distillation boundary (or multi-azeotrope) should be crossed (or broken) by varying pressures (or adding entrainers). Additionally, the exploration of the reactive distillation process is limited to separate binary azoetropic mixtures. According to the above review, the energy-saving reactive/extractive distillation (RED) process for the separation of ternary mixture with multi-azeotrope has not been reported. Consequently, in this work, a systematic approach is proposed involves conceptual design as well as multi-objective optimization of the sustainable RED process for the separation of the ternary azeotropic system THF/ethanol/water with multiple azeotropes. Firstly, the component of water is removed *via* the reactive distillation process and the separation process is determined by the thermodynamic conceptual design. The design parameters of the proposed sustainable process are obtained by using the stochastic optimization algorithm (*i.e.*, improved multi-objective genetic algorithm) with the total capital cost and total operating cost as two conflicting objective functions. Finally, total annual cost (TAC) and CO_2 emissions are introduced to assess the economic and environmental performances of the proposed scheme.

2. The existing triple-column pressure-swing distillation

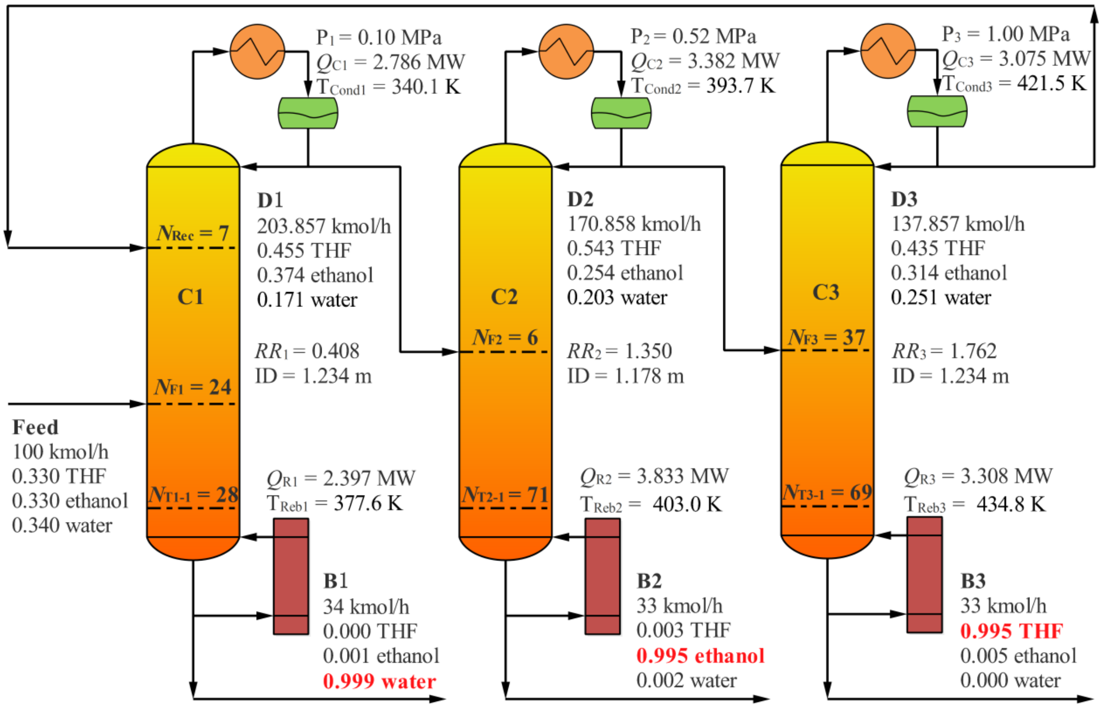

Figure 2. The existing TCPSD process with detailed operating parameters

In our previous study (Yang et al., 2019a), we studied a new TCPSD process with detailed design parameters as is shown in Figure 2. The theoretical stages of the three columns C1, C2, and C3 are 29, 72, and 70 while the corresponding operating pressures are 0.10, 0.52, and 1.00 MPa, respectively. The recycled stream (D3) and the fresh feed stream (Feed) are fed to the 7th and 24th trays of the column C1. To obtain water of 99.9 mol% at the bottom of the column C1, the reflux ratio is 0.408. The ethanol of 99.5 mol% is obtained while the stream D1 feeds at the 6th stage and the reflux ratio is 1.350. The THF of 99.5 mol% can be achieved at the bottom of the column C3 while the feed locations and reflux ratio are 37th stages and 1.762, respectively. TAC of the existing TCPSD process reaches 2,181,000 US$/y.

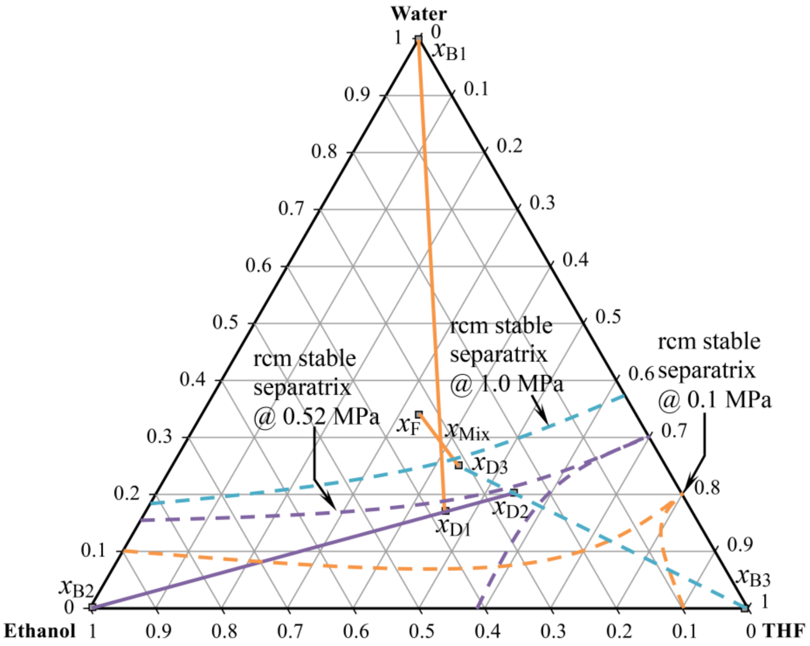

Figure 3. The ternary diagram of the TCPSD process for the separation of THF/ethanol/water

Figure 3 shows the ternary composition diagram of the existing optimal TCPSD process for separating the ternary azeotropic mixture THF/ethanol/water. Solid and dash lines are the component balance lines and distillation boundaries. Orange, purple, and azure lines represent these lines at 0.10, 0.52, and 1.00 MPa for columns C1, C2, and C3, respectively. High purities of three products water, ethanol, and THF could be obtained at the bottom of columns (*i.e.*, vertex of triangle diagram) with 99.9, 99.5, and 99.5 mol%, respectively by varying the operating pressure.

3. Methodology

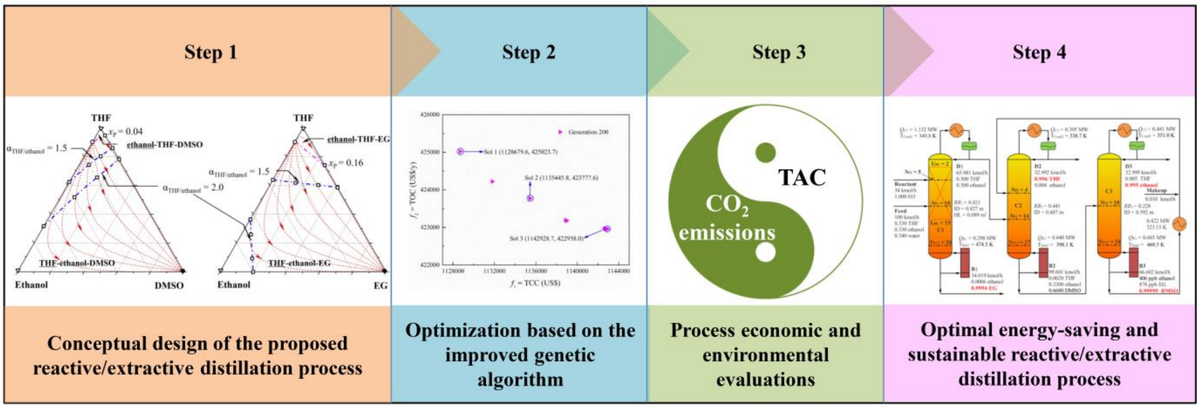

Figure 4. A systematic design procedure for the proposed sustainable RED process

Herein, a systematic approach for conceptual design and process optimization of the sustainable RED process is reported to separate ternary azeotropic mixtures THF/ethanol/water (Figure 4). Firstly, conceptual design of the proposed process is obtained by the thermodynamic feasibility analysis (*e.g.*, residue curve maps). After that, the process optimization is implemented *via* the improved in-house GA model to obtain the optimal design including optimal operating conditions (*e.g.*, feed locations and distillate rate). To assess the economic and environmental benefits of proposed process, TAC and CO_2 emissions are introduced. Finally, the optimal sustainable RED process is obtained.

3.1 Conceptual design

As is well known that the selection of thermodynamic model is a key to provide accurate calculation (Su et al., 2019; Wang et al., 2019). The vapor-liquid equilibrium of studied system could be well predicted by the thermodynamic model NRTL as suggested by Yang et al. (2019a) while the built-in and predicted interaction parameters are listed in Table 1.

Table 1. The binary interaction parameters of NRTL model for the THF/ethanol/water system

Comp i	THF	THF	Ethanol	THF	Ethanol	Water	Water	THF
Comp j	Ethanol	Water	Water	EG	EG	EG	EO	EO
Temp units	^oC	^oC	^oC	^oC	^oC	^oC	^oC	^oC
A_{ij}	2.3225	1.2142	-0.8009	-1.7548	14.8422	0.3479	0.0000	0.0000
A_{ji}	-2.7770	4.7601	3.4578	0.6819	-0.1115	-0.0567	0.0000	0.0000
B_{ij}	-524.9086	157.7809	246.1800	1083.1951	-4664.4058	34.8234	188.6878	-99.3106
B_{ji}	905.7390	-733.4016	-586.0809	32.8620	157.5937	-147.1373	868.9710	272.4629
C_{ij}	0.3000	0.4726	0.3000	0.4000	0.4700	0.3000	0.3000	0.3000

Comp i	ethanol	EO	THF	ethanol	water	EG	EO
Comp j	EO	EG	DMSO	DMSO	DMSO	DMSO	DMSO
Temp units	^oC	^oC	^oC	^oC	^oC	^oC	^oC
A_{ij}	0.0000	0.0000	0.0000	0.0000	-1.2449	0.0000	0.0000
A_{ji}	0.0000	0.0000	0.0000	0.0000	1.7524	0.0000	0.0000
B_{ij}	-275.3563	157.5453	347.5491	116.5373	586.8010	-407.9908	-332.3992
B_{ji}	380.6161	-142.3719	74.9371	-393.3192	-1130.2155	125.2802	426.4235
C_{ij}	0.3000	0.3000	0.3000	0.3000	0.3000	0.3000	0.3000

Note: DMSO represents dimethyl sulfoxide.

An intensified reactive distillation process for the ethanol dehydration is reported by Tavan and Hossein (2013). Subsequently, the exploration of reactive distillation for separating azeotropic mixture THF/water (Tavan, 2014) and ethyl acetate/water (Tavan et al., 2013) are investigated. Recently, the bioethanol dehydration through the reactive distillation from fermentation broth is investigated by Kaymak (2019). Inspired from the above listed studies, a reactant ethylene oxide (EO) is added in the reactive distillation column to remove the component of water in the ternary wastewater system and produce a by-product ethylene glycol (EG) as displayed in Eq. 1. The reaction kinetics as illustrated in Eq. 2 are used according to the suggestion of Tavan and Hossein (2013).

$$\mathrm{EO} + \mathrm{water} \rightarrow \mathrm{EG} \tag{1}$$

$$r(\mathrm{kmol/m^3/s}) = 3.15\times10^{12}\exp[-9547/T]x_{\mathrm{EO}}x_{\mathrm{Water}} \tag{2}$$

On the basis of research from Tavan and Hossein (2013), the molar ratio of the EO in reactant feed and water in the feed mixture is selected as 1.0.

The remaining THF/ethanol mixture from the top of reactive distillation column could be separated *via* an ED process.

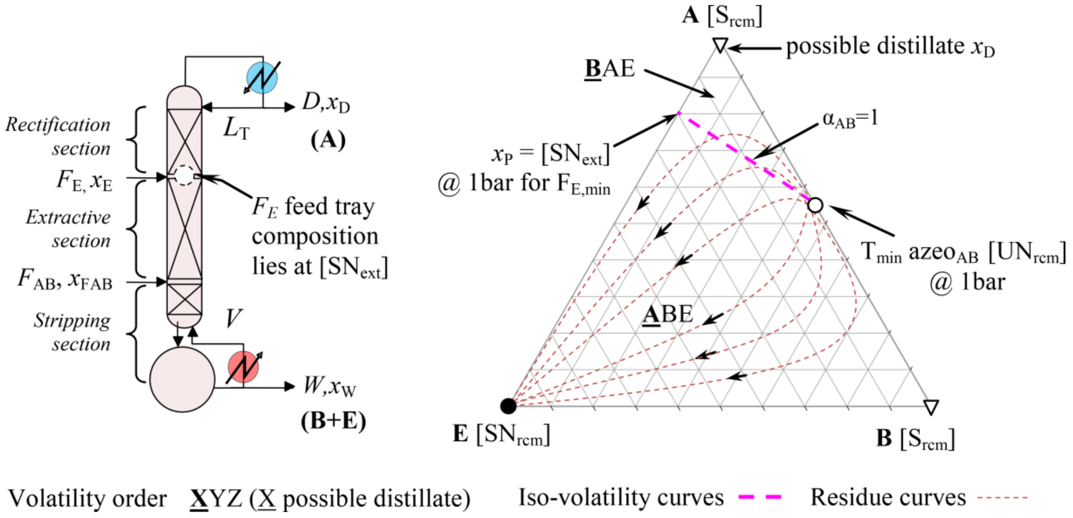

Figure 5. The extractive distillation scheme and thermodynamic features of class 1.0-1a

Figure 5 illustrates the flowchart of the ED scheme and thermodynamic features of class 1.0-1a at 1 atm for separating binary aeotropic mixtures (A-B) by using heavy entrainer (E). The intersection of iso-volatility line and A-E side could be used to model the minimum flowrate of entrainer, which is called as x_P. A and B are saddles; azeotropic point is unstable node; E is stable node. In the ternary diagram of Figure 5, residue curve maps is starting at unstable node and ending at stable node.

The selection of entrainer plays an important role for the ED process. There are several guidelines for entrainer selection: (1) the azeotrope could be broken by adding the entrainer (relative volatility of separated system could be improved); (2) the solvent should also be easily separated from the distillation products; (3) no new azeotrope would be formed by introducing the entrainer.

3.2 Optimization

In the optimization process, total capital cost (TCC) and total operating cost (TOC) are determined as conflicting objective functions, which is demonstrated in Eq. 3.

$$\begin{cases} \min\ f_1(\mathrm{TCC}) = f\left(N_{\mathrm{T1\text{-}3}}, ID_{1-3}, H, A_{\mathrm{R}}, A_{\mathrm{C}}\right) \\ \min\ f_2(\mathrm{TOC}) = f\left(Q_{\mathrm{R1\text{-}3}}, Q_{\mathrm{C1\text{-}3}}, Q_{\mathrm{cooler}}\right) \end{cases} \tag{3}$$

Herein, the equipment cost of the column shell, column tray and heat exchanger constitutes TCC as shown in Eq. 4.

$$\mathrm{TCC} = \text{shell cost} + \text{tray cost} + \text{HX cost} \tag{4}$$

where the tray spacing is assumed to 0.609 m and the diameters (ID) of three columns are calculated using the ‘Tray sizing’ tool in Aspen Plus$^{®}$.

Total length of column (L in m) could be obtained *via* the Eq. 5.

$$L=\left(N_T-1\right)\times 0.609 \tag{5}$$

Detailed formulas of shell, tray, and HX costs and exchanger area are displayed in Eqs. 6-9.

$$\text{Shell cost}=\left(\frac{\text{M\&S}}{280}\right)\times\left(101.9\times D^{1.066}\times L^{0.802}\right)\times\left(2.18+F_C\right)=22522.8D^{1.066}L^{0.802} \tag{6}$$

$$\text{Tray cost}=\left(\frac{\text{M\&S}}{280}\right)\times\left(4.7\times D^{1.55}\times L\times F_C\right)=1423.7D^{1.55}L \tag{7}$$

$$\text{HX cost}=\left(\frac{\text{M\&S}}{280}\right)\times\left(101.3A^{0.65}\right)\times\left(2.29+F_C\right)=9367.8\times\left(A_R^{0.65}+A_C^{0.65}\right) \tag{8}$$

$$A=\frac{Q}{u\times\Delta T} \tag{9}$$

where the capital investment of heat exchanger is denoted as HX, $F_C = F_m \times F_P$, F_m and F_P are the construction material and pressure range, respectively, and the value of Marshall & Swift index (M&S) is assumed as 1518.1. The overall heat transfer coefficient is expressed as u (kW/m^2/K) while $u = 0.852$ for condenser, and 0.568 for the reboiler.

TOC in Eq. 10 consist of two parts: steam cost and cooling water cost.

$$\text{TOC}=\left(Q_R\cdot C_S+Q_C\cdot C_{CW}\right)\times 7200 \tag{10}$$

where Q_R and Q_C represent the reboiler and condenser duty; the investment of cooling water (C_{CW}) is 0.354 US\$/GJ; C_S = 7.78 and 9.88 US\$/GJ represent the investment of low- and high-pressure steams.

Purities of one by-product, two products, and one entrainer should be constrained in the optimization process as displayed in Eq. 11.

$$\begin{cases} x_{\mathrm{EG}} \ge 99.90 \text{ mol\%} \\ x_{\mathrm{THF}} \ge 99.50 \text{ mol\%} \\ x_{\mathrm{ethanol}} \ge 99.50 \text{ mol\%} \\ x_{\mathrm{DMSO}} \ge 99.99 \text{ mol\%} \end{cases} \tag{11}$$

To achieve the process optimization, the flowchart for the combination of the improved multi-objective GA and Aspen Plus® is demonstrated in Figure 6.

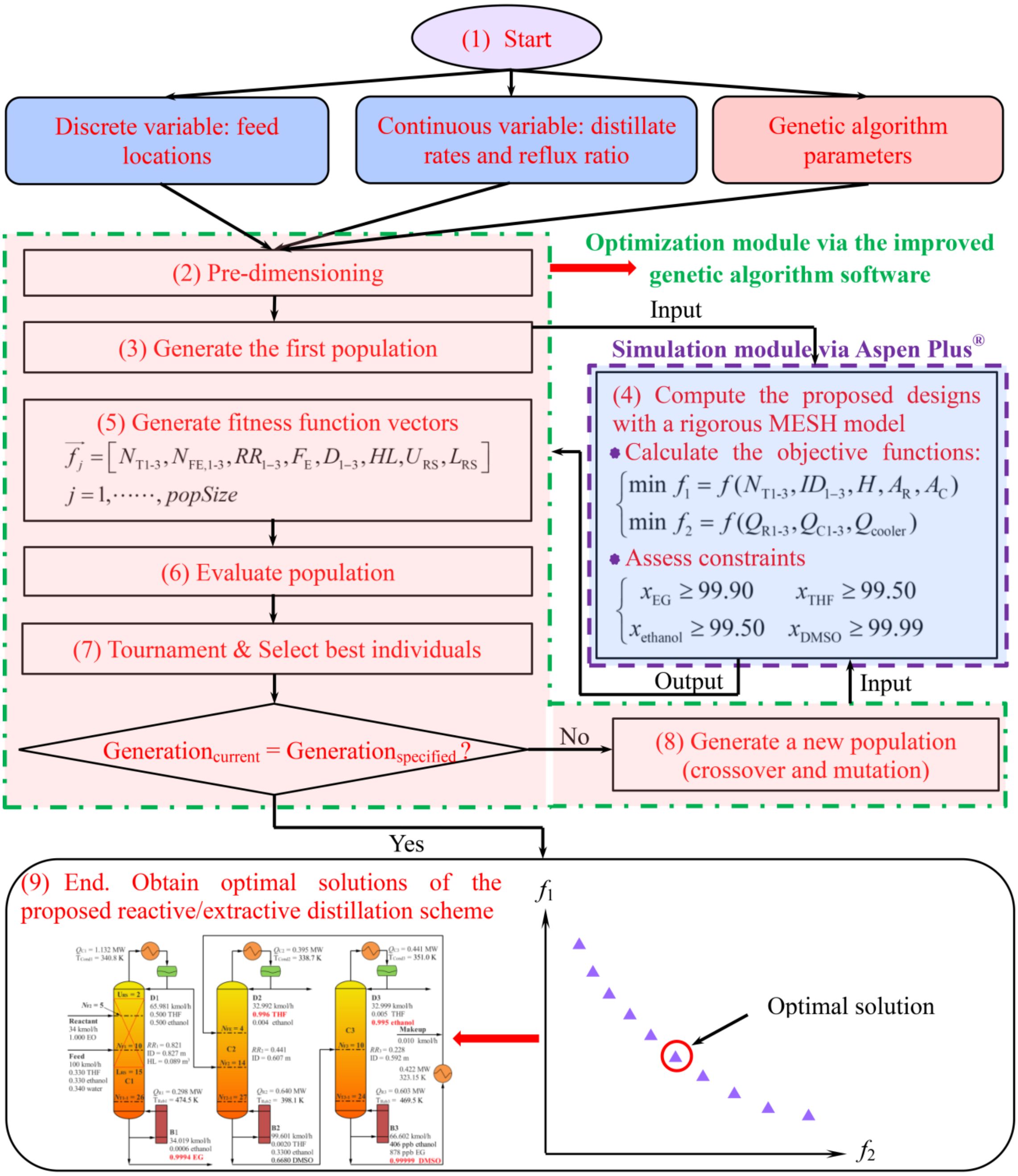

Figure 6. The flowchart of the improved multi-objective genetic algorithm optimization approach

As shown in Figure 6, the input parameters of decision variables (*e.g.*, feed locations, distillate rates, and reflux ratios) and pre-dimensioning are defined in steps 1 and 2. The first random generation data is then produced in step 3 of the GA model. Of note is that the data from GA model is imported to Aspen Plus® (step 4) to calculate two conflicting objective functions f_1 (TCC) and f_2 (TOC) and assess four product purities constraints. The calculations of step 4 export to GA model to generate the fitness function vectors (step 5) and evaluate the population (step 6). To effectively reduce the repeated solutions and increase the evolutionary rate, step 7 (*i.e.*, Tournament & Select best individuals) is added. The optimization process could be terminated when the current generations equals the specified generations. Otherwise, crossover and mutation is occurred in step 8 to generate a new population and repeat implementing steps 4-8.

Table 2. The lower and upper bounds of the decision variables in the optimization process

	Variables	Lower bound	Upper bound	Initial specification
Discrete variable	N_{T1}	28	40	31
	N_{F1}	3	10	6
	N_{FR}	10	25	22
	U_{RS}	2	10	3
	L_{RS}	15	25	18
	N_{T2}	25	40	35
	N_{F2}	10	24	16
	N_{FE}	3	10	4
	N_{T3}	25	40	35
	N_{F3}	5	24	10
Continuous variable	D_1, kmol/h	65.5	66.5	65.98
	RR_1	0.1	10	0.83
	HL, m^3	0.001	1	0.09
	D_2, kmol/h	32.8	33.2	33
	RR_2	0.1	10	0.5
	F_E, kmol/h	1	200	70
	D_3, kmol/h	32.8	33.2	33
	RR_3	0.1	10	0.4

In the optimization process, ten discrete and eight decision continuous variables in Table

2 should be optimized to screen the optimal RED process. Discrete decision variables involve total number of stages for columns C1-C3 (N_{T1}, N_{T2}, and N_{T3}), feed locations (N_{F1}, N_{FR}, N_{F2}, N_{FE}, and N_{F3}), and upper and lower reaction stages (U_{RS} and L_{RS}). Distillate rates (D_1, D_2, and D_3), reflux ratios (RR_1, RR_2, and RR_3), flowrate of entrainer (F_E), and liquid holdup (HL) are the continuous decision variables.

3.3 Process evaluation

Economic and environment benefits (*i.e.*, TAC and CO_2 emissions) should be introduced to evaluate the proposed RED process. TAC proposed by Douglas (1988) involves TCC and TOC as described in Eq. 12. In this research, payback period is assumed as three years.

$$\mathrm{TAC} = \frac{\mathrm{TCC}}{\text{payback period}} + \mathrm{TOC} \tag{12}$$

CO_2 emissions are used to investigate the sustainability of the proposed design (Sun et al., 2019b; Yang et al., 2019d). Smith and Delaby (1991) illustrated that CO_2 emissions for generating the steam in the boilers and furnaces could be modeled by using the energy consumption. Following which, a simple computation model for the CO_2 emissions is developed (Gadalla et al., 2006) as follows,

$$\mathrm{CO_2\ emissions} = \left(\frac{Q_{\mathrm{fuel}}}{\mathrm{NHV}}\right)\times\left(\frac{\mathrm{C\%}}{100}\right)\alpha \tag{13}$$

where α is the ratio of molecular weight between CO_2 and C and the value is 3.67; required heat released by fuel per hour, net heating, and carbon content are denoted as Q_{fuel} (kJ/h), NHV = 39771 kJ/kg, and C% = 86.5, respectively. Q_{fuel} could be attained as follow,

$$Q_{\mathrm{fuel}} = \frac{Q_{\mathrm{seq}}}{\lambda_{\mathrm{seq}}}\times\left(h_{\mathrm{seq}} - 419\right)\times\left(\frac{T_{\mathrm{F}}-T_0}{T_{\mathrm{F}}-T_{\mathrm{S}}}\right) \tag{14}$$

where latent heat of required steam is denoted as λ_{seq} in kJ/kg; enthalpy of the required steam is expressed as h_{seq} in kJ/kg; energy consumption of the process is represented as Q_{seq} in kJ. In addition, flame, stack, and ambient temperatures are abbreviated as T_F (K), T_S (K), and T_0 (K), respectively.

4. Results and Discussions

4.1 Conceptual design

The component of water is firstly removed in the ternary mixture THF/ethanol/water via the reactive distillation column C1 (see Eq. 1 in Section 3.1). The remaining binary azeotropic mixture THF/ethanol is separated in ED. The iso- and uni- volatility lines of DMSO and EG is displayed in Figure 7 to screen the best entrainer.

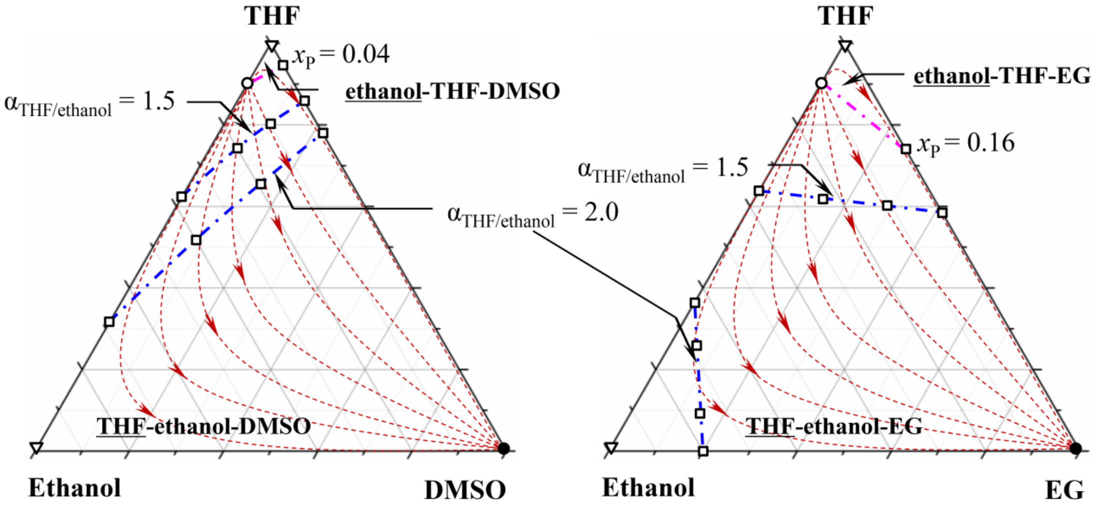

Figure 7. Iso- and uni- volatility lines at 0.1 MPa for (a) DMSO and (b) EG, respectively

As is evident in Figure 7, the value of x_P for DMSO is lower than the EG indicating that the DMSO is better than EG. Additionally, the intersection between one target component and univolatility of DMSO is also smaller than that of EG. Hence, DMSO is chosen as the appropriate entrainer for separating THF/ethanol.

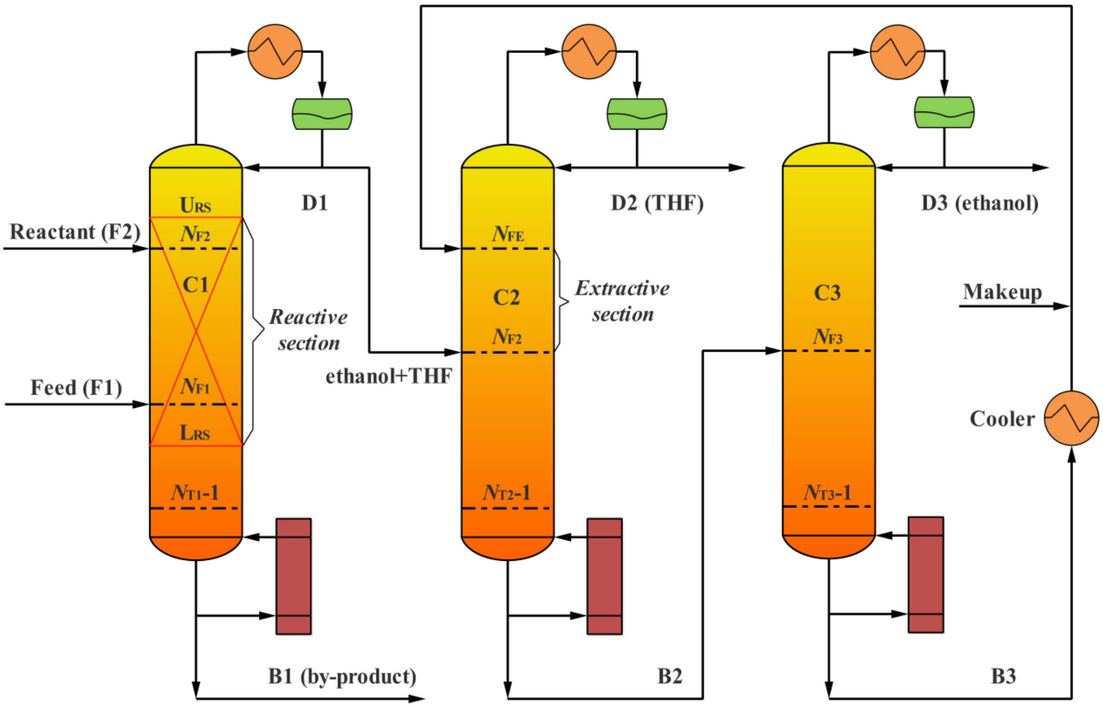

Figure 8. The flowchart of the RED for separating ternary azeotropic mixture THF/ethanol/water

The flowsheet of the proposed RED process for separating THF/ethanol/water is given in Figure 8.

4.2 Process optimization

The optimization of RED process is carried out in the desktop computer with Intel® Core™ i7-7700 CPU @ 3.60 GHz 8G RAM. Ten discrete decision variables (*e.g.*, N_{T1}, N_{F1}, and U_{RS}) and eight continuous decision variables (*e.g.*, D1 and RR1) are optimized in this stage. Additionally, the overall optimization lasts about 88.57 h.

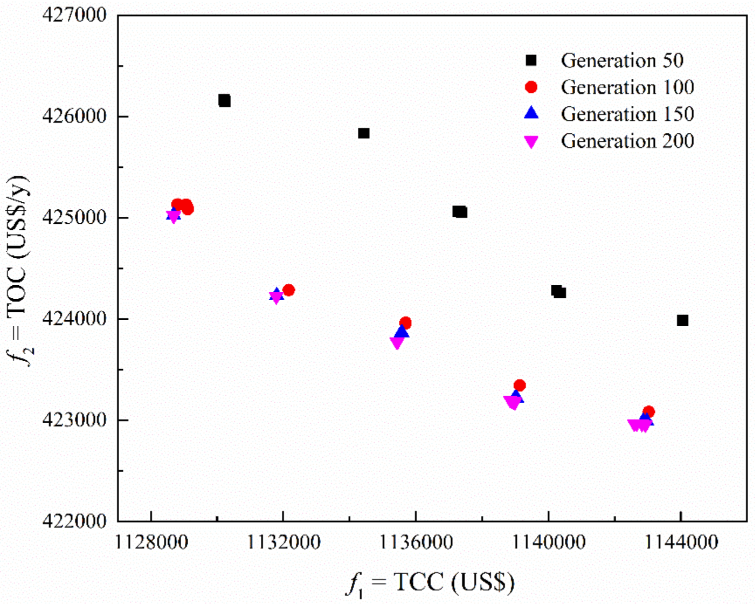

Figure 9. The Pareto-optimal front of the proposed RED for a population of 200 and generation of 200

An initial population of 200, crossover probability of 0.95, and mutation probability of 0.1 are used in the improved GA for the optimization of the proposed RED process. The optimization process is terminated after 200 generations by observing the vector of the objective functions and it does not produce any meaningful improvement as illustrated in Figure 9.

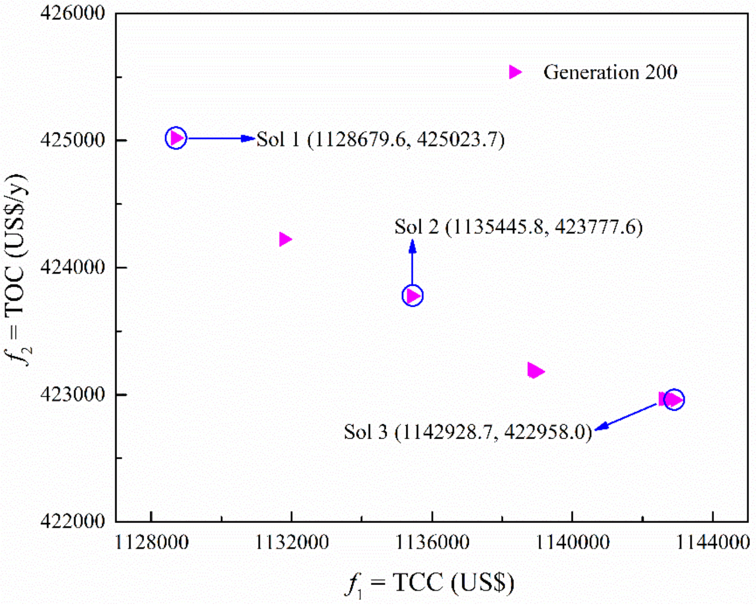

Figure 10. The Pareto front between TOC and TCC for the proposed RED

The Pareto fronts between f_1 (TCC) and f_2 (TOC) of 200 generations are demonstrated in Figure 10. There have three interesting solutions with highest operating cost (Sol 1), the design considered optimal Sol 2 (considered where both objective functions are balanced and find its minimum values) and highest capital cost (Sol 3). Table 3 gives the detailed parameters of three solutions in the Pareto front of generation 200.

Table 3. Design parameters and objective functions for the RED process

	Variable	Sol 1	Sol 2	Sol 3
Column C1	N_{T1}	27	27	27
	N_{F1}	5	5	5
	N_{FR}	10	10	10
	U_{RS}	2	2	2
	L_{RS}	15	15	15
	HL, m^3	0.089	0.089	0.089
	D_1, kmol/h	65.981	65.981	65.981
	RR_1	0.821	0.821	0.821
Column C2	N_{T2}	26	28	30
	N_{F2}	13	14	14
	N_{FE}	4	4	4
	F_E, kmol/h	66.612	66.612	66.612
	D_2, kmol/h	32.991	32.992	32.997
	RR_2	0.459	0.441	0.429
Column C3	N_{T3}	25	25	25
	N_{F3}	8	10	8
	D_3, kmol/h	32.999	32.999	32.997
	RR_3	0.227	0.228	0.227
Product purities	x_{EG}, mol%	99.944	99.944	99.944
	x_{THF}, mol%	99.527	99.556	99.514
	$x_{ethanol}$, mol%	99.500	99.530	99.500
	x_{DMSO}, mol%	99.999	99.999	99.999
Objective functions	f_1 (TCC), US$	1128679.6	1135445.8	1142928.7
	f_2 (TOC) , US$	425023.7	423777.6	422958.0

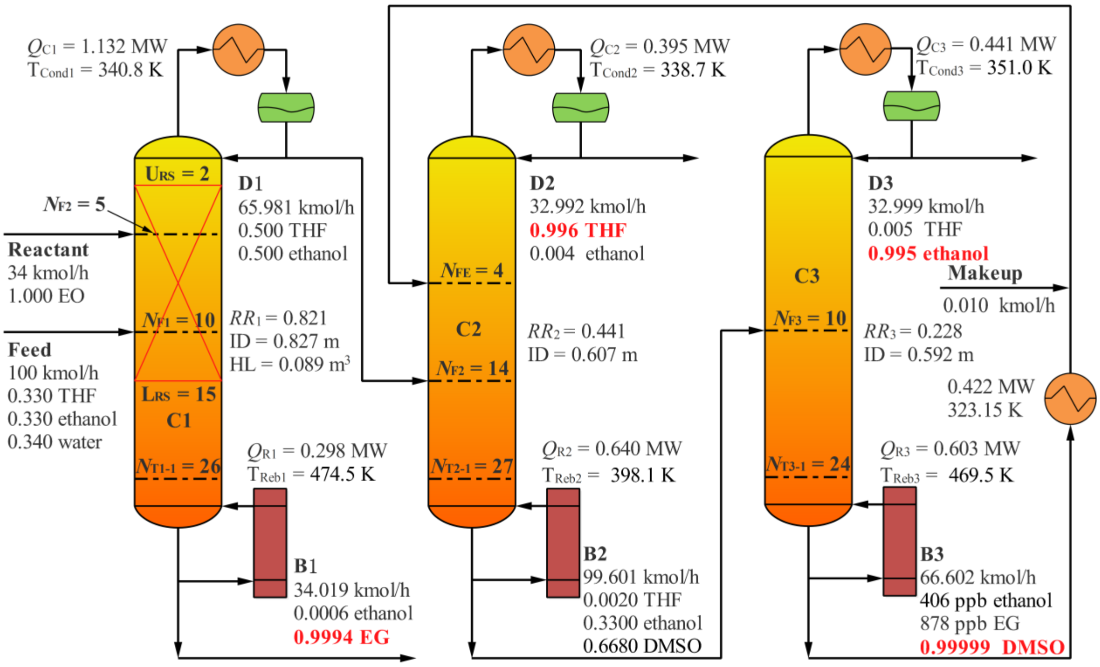

Figure 11. The optimal RED process for separating ternary azeotropic mixture THF/ethanol/water

The optimal energy-saving RED process for the separation of THF/ethanol/water is displayed in Figure 11. In this process, the reaction of EO and water occurs in the reactive distillation column C1 with 27 theoretical stages (including condenser and reboiler). Reflux ratio of 0.821 for column C1 is determined to obtain EG of 99.94 mol% in the bottom stream. Two streams of reactant EO and azeotropic mixture of THF/ethanol/water are fed to 5th and 10th stages, respectively, while the reaction sections are located between 2th and 15th stages with liquid holdup 0.089 m^3 of each tray in the reactive section. ED column C2 and entrainer recovery column C3 have 28 and 25 theoretical stages, respectively with reflux ratios of 0.441 and 0.228. The entrainer stream B3 and THF/ethanol mixture are fed to 4th and 14th trays while the feed locations of column C3 is located at 10th stage. DMSO of 0.010 kmol/h is required to supply the amount of losses in D2 and D3 streams. THF of 99.6 mol% and ethanol of 99.5 mol% are obtained at the top streams of columns C2 and C3.

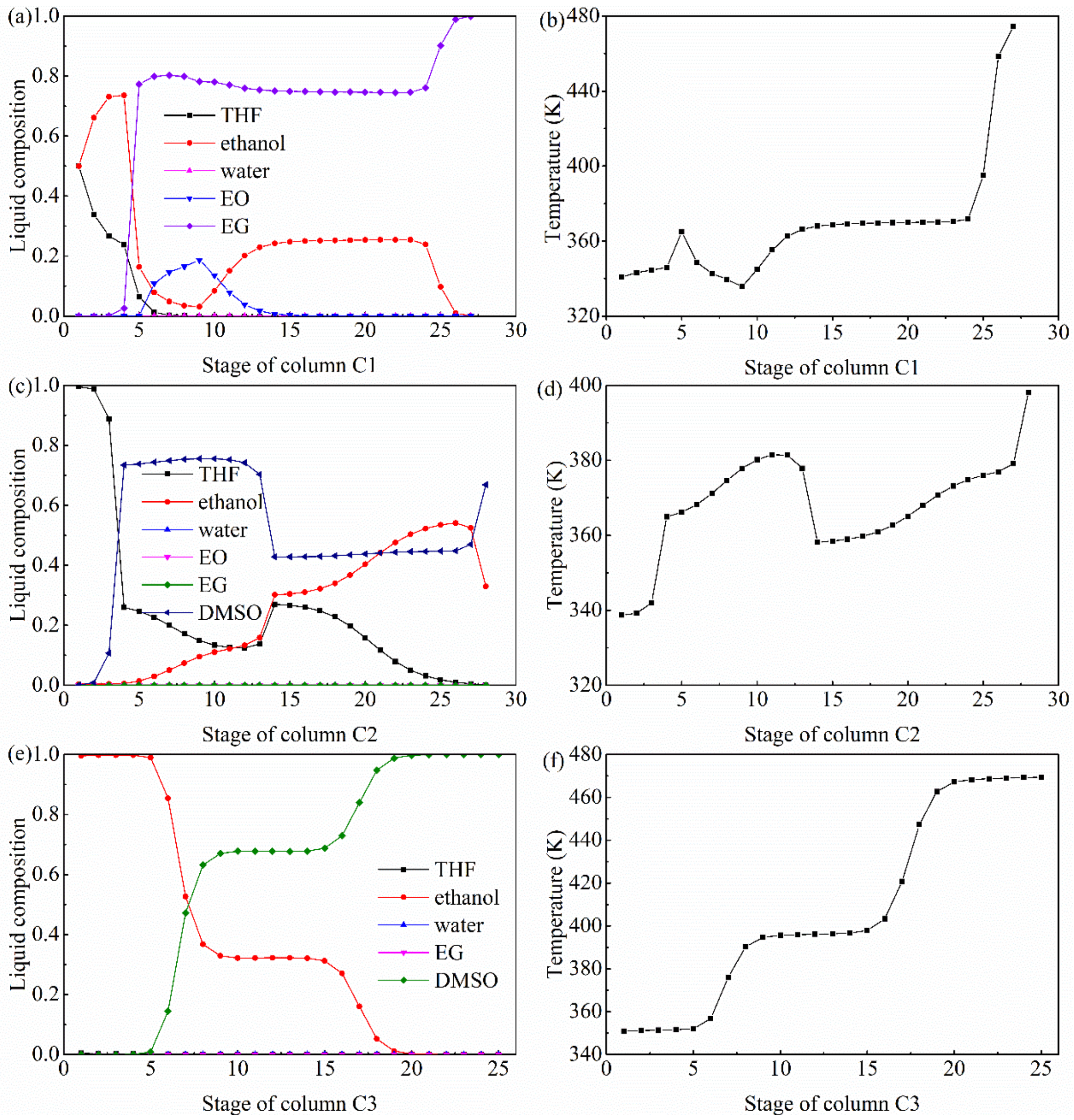

Figure 12. The liquid composition and temperature profiles (a, b) column C1, (c, d) column C2, and (e, f) column C3

Figure 12 illustrates the liquid composition and temperature profiles of the three columns C1-C3. Based on Figure 12a, the EG is produced in the reactive section (from 5th to 10th stages) and then is purified in the stripping section of column C1. High-purity EG of 99.94 mol% is achieved at the bottom stream while the corresponding temperature profile is given in Figure 12b. Similar observation can be made from Figure 12c,d,e,f. In summary, the optimization results of three columns are reasonable since the profiles of three columns are steep.

4.3 Comparison and discussion

Table 4. The comparison of the TAC and CO_2 emissions for the existing TCPSD and the proposed processes

	Variables	Existing TCPSD	Proposed process
C1	N_{T1}	29	27
	ID, m	1.234	0.827
	Q_{C1}, MW	2.786	1.132
	Q_{R1}, MW	2.397	0.298
C2	N_{T2}	72	28
	ID, m	1.178	0.607
	Q_{C2}, MW	3.382	0.395
	Q_{R2}, MW	3.833	0.640
C3	N_{T3}	70	25
	ID, m	1.234	0.592
	Q_{C3}, MW	3.075	0.441
	Q_{R3}, MW	3.308	0.603
Objective functions	f_1 (TCC), US$	3,342,000	1,135,445.8
	f_2 (TOC), US$	1,067,000	423,777.6
Economic index	TAC, US$	2,181,000	802,259.5
	TAC saving, %	0.00	63.22
Environment index	CO_2 emissions, kg/h	3,696.279	597.187
	CO_2 emissions saving, %	0.00	83.84

Table 4 lists the comparison of TAC and CO_2 emissions for the existing TCPSD and the proposed RED processes. Reduction of TAC and CO_2 emissions could be attained at 63.22% and 83.84%, respectively. Overall, the proposed RED process exhibits great advantages in economic and environmental benefits.

5. Conclusion

A systematic approach for design and optimization of the energy-saving and sustainable reactive/extractive distillation (RED) process is proposed for separating the ternary azeotropic mixture THF/ethanol/water. In the proposed process, the reactant ethylene oxide is added to the first reactive distillation column to remove water by producing the by-product ethylene glycol. Next, the binary azeotropic mixture THF/ethanol is separated *via* the extractive distillation with entrainer dimethyl sulfoxide. The improved multi-objective genetic algorithm is used to optimize the proposed RED process by minimizing the process TCC and TOC. The result illustrated that the proposed process herein has a significant reduction of both TAC and CO_2 emissions compared with the existing triple-column pressure-swing distillation process.

It is worth noting that besides the separation system studied in this research, the proposed approach could be extended to separate other complex ternary azeotropic systems with multiple azeotropes such as methanol/water/THF, acetonitrile/methanol/water, and ethyl acetate/ethanol/water to recover valuable resources and pursue cleaner production processes. In addition, the intensified process such as side-stream distillation and extractive dividing wall column scheme will be investigated in the further work to reduce energy consumption and CO_2 emissions (Rashid et al., 2019).

However, the limitation is that this work is focused on the specific mixture THF/ethanol/water by the reactive/extractive distillation, which may restrict the applicability of the proposed approach. In addition, the proposed approach can only be used to separate wastewater system because the selected reactant ethylene oxide can only be used to remove water in ternary systems. Thereby, the investigation can be further extended to the separation of other ternary azeotropic systems via reactive distillation.

Acknowledgments

We acknowledge the financial support provided by the National Natural Science Foundation of China (Nos. 21878028, 21606026 to W. Shen; No. 21808117 to P. Cui); the Fundamental Research Funds for the Central Universities (No. 2019CDQYHG021 to W. Shen).

Nomenclature

A	area, m^2
C_{CW}	cost of cooling water, US$/GJ
C_S	cost of steam, US$/GJ
D_{1-3}	distillate rates of column C1-C3, kmol/h
DMSO	dimethyl sulfoxide
ED	extractive distillation
EO	ethylene oxide
EG	ethylene glycol
F_E	flowrate of entrainer, kmol/h
GA	genetic algorithm
HL	liquid holdup, m^3
M&S	Marshall & Swift index
N_{T1-3}	total number of stages of columns C1-C3
N_{F1-3}	feed locations of columns C1-C3
N_{FE}	feed locations of entrainer
U_{RS}	upper reaction stage
L_{RS}	lower reaction stage
RED	reactive/extractive distillation
RR_{1-3}	reflux ratios of columns C1-C3
ID_{1-3}	diameter of columns C1-C3, m
TAC	total annual cost, US$

TCC	total capital cost, US$
TOC	total operating cost, US$
THF	tetrahydrofuran
r	reaction rate, kmol/m^3/s
u	heat transfer coefficient, kW/m^2/K

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