Towards sustainable separation of the ternary azeotropic mixture based on the intensified reactive-extractive distillation configurations and multi-objective particle swarm optimization

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Abstract: The separation of ternary azeotropic systems has received significant interest as it enables the recovery of value-added organic solvents, subsequently contribute towards environmental protection. In this work, we propose a novel approach that involves the conceptual design, multi-objective optimization, and process evaluations for developing two different processes, i.e., double-column reactive-extractive distillation (DCRED) and reactive-extractive dividing wall column (REDWC), for the separation of ethanol/*tert*-butanol/water ternary azeotropic mixture. The conceptual design of the proposed processes was conducted using kinetic and thermodynamic analysis while optimal operating conditions of the established processes were obtained *via* multi-objective particle swarm optimization algorithm. Then, both developed processes were evaluated based on the total annual cost (TAC), CO_2 emissions, and thermodynamic efficiency. From the steady-state simulation, DCRED and REDWC provides a TAC of $1.056×10^6$ US\$ and $1.117×10^6$ US\$, respectively. Likewise, it provides CO_2 emissions of 731.27 kg/h and 733.42 kg/h, respectively. The energy efficiency of the DCRED and REDWC were found to be 1.285% and 1.055%, respectively. Relative to the conventional extractive distillation process, the TAC and CO_2 emission for the proposed DCRED reduced significantly by 55.4% and 61.8%, respectively. Similar reduction was also observed for the REDWC which provides 52.8% and 61.7% lower TAC and CO_2 with respect to the conventional process. In addition, the thermodynamic efficiency of the developed DCRED and REDWC processes are improved by 40.4% and 15.3% in comparison to the conventional extractive distillation scheme.

Keywords: Energy efficiency; process intensification; ternary azeotropic mixture; multi-objective optimization; sustainability

Nomenclature

DCRED   double-column reactive-extractive distillation

ED   extractive distillation

EG   ethylene glycol

EO   ethylene oxide

ERC   entrainer recovery column

EtOH   ethanol

Ex_{loss} lost work kJ/h

MOPSO   multi-objective particle swarm optimization

MINLP   mixed integer nonlinear programming

NHV   the net heating, kJ/kg

RD   reactive distillation

REDC   reactive-extractive distillation column

TAC   total annual cost, 10^6\$

TBA   *tert*-butanol

TCC   total capital cost, 10^6\$

TCED   triple-column extractive distillation

THF   tetrahydrofuran

TOC   total operating cost, 10^6\$

$T_{F/S/0}$ flame, stack, and ambient temperatures, K

W_{min} minimum separation work, kJ/h

h enthalpy of inlet and output stream, kJ/kmol

η thermodynamics efficiency

s entropy of inlet and output stream, kJ/kmol-K

1. Introduction

As an alternative gasoline additive, *tert*-butanol (TBA) has been widely investigated in the both industrial and academia (Lei et al., 2009). Ethanol (EtOH), on the other hand, is used as a sustainable biomass energy source and organic solvent for various chemical industries (Farrell et al., 2006). The ternary system TBA/EtOH/water is always produced in the pharmaceutical and chemical industries (Shi et al., 2020). However, the presence of multiple azeotropes and distillation boundaries has resulted in the mixture cannot be effectively separated by means of ordinary distillation (Wang et al., 2021b). Therefore, it is necessary to investigate some other separation techniques so that these valuable component (i.e., TBA and EtOH) can be recovered from the ternary mixture of TBA/EtOH/water for sustainable development and environmental protection.

Some of these alternative techniques includes extractive distillation (ED) (Sun et al., 2019), pressure-swing distillation (PSD) (Liang et al., 2017b), and azeotropic distillation (AD) (Tsai et al., 2021). Among these different techniques, the PSD requires massive amount of energy (or steam) and is only applicable to the separation of pressure-sensitive mixture (Wang et al., 2020) while the AD often has several steady-state configurations during its initial design stage, due to the different feed composition combination (Li et al., 2015). The ED, on the other hand, has the advantages of low energy consumption and flexible selection of possible extractants and is more commonly employed for the separation of azeotropic mixtures in the chemical and pharmaceutical industries (Graczová et al., 2018). Zhang et al. (2021b), for

example, investigated the separation of acetone and n-heptane azeotropic mixture using the ED process. Li et al. (2021b) and Zhang et al. (2020) studied ED process for the separation of azeotropic mixtures iso-butanol/ethanol/water and acetonitrile/water, respectively. Yang et al. (2019b; 2021) investigated a triple-column ED scheme for purifying ethyl acetate, EtOH and tetrahydrofuran (THF) from the industrial effluent. Wang et al. (2021b) explored the separation of ternary azeotropic mixture containing methyl acetate/ethyl acetate/methanol by using ED process. Despite featuring the advantage of better separation efficiency, the energy efficiency of the conventional ED however is relatively low. To overcome this limitation, it is necessary to investigate an energy-intensified process so that the energy efficiency can be further improved, further translate to the reduction in the total annual cost (TAC).

One common energy-intensified process is the thermally coupled technique which rely on the application of dividing wall column (DWC) (Petlyuk et al., 1965). Although it was reported that the DWC provides significant reduction in both energy consumption and capital cost, it does not necessarily translate to a reduction in the TAC since the energy cost in the case of DWC may increase due to a higher steam grade quality used, as reported in the work of Wu et al. (2013). Today, the application of DWC has been widely extended to the ED (Li et al., 2021a), AD (Li et al., 2016) and reactive distillation (RD) (Shen et al., 2021).

Another alternative technique that provides significant potential reduction in energy-consumption is the RD, which integrate both the reaction and separation process in one single unit operation (Li et al., 2017a). Tavan et al. (2013) studied a novel RD column to purify ethyl acetate and showed that it provides significant advantage in energy saving. In addition, the RD is further extended to the separation of EtOH/water (Tavan and Hosseini, 2013) and THF/water

mixture (Tavan, 2014). Zheng et al. (2015) studied the reactive-extractive distillation configuration for the recovery of by-product methyl acetate in the synthesis of PVA. Moreover, Kaymak (2019) proposed a RD scheme to purify bioethanol through introducing a third component (ethylene oxide, EO) and showed that the TAC could be reduced by 13.19%. Inspired from the above studies, an energy-saving dimethyl carbonate synthesis process by using dehydration RD with CO_2 and methanol as feedstock is developed by Wu and Chien (2019) and they proved that the energy consumption could be significantly reduced *via* the established scheme. Gao and Geng (2021) developed a green and sustainable method for azeotrope separation *via* the reversible-reaction-assisted distillation process and some case studies are used to illustrate the capability and feasibility of proposed approach. Recently, Yang et al. (2020a) and Li et al. (2021c) developed three columns reactive-pressure swing distillation process for the separation of ternary azeotropic mixtures THF/EtOH/water and acetonitrile/isopropanol/water, respectively. An intensified hybrid triple-column reactive-extractive distillation process is proposed to separate ternary azeotropic mixture THF/EtOH/water (Su et al., 2020b), ethyl acetate/EtOH/water (Wang et al., 2021a), acetonitrile/isopropanol/water (Li et al., 2021d) and TBA/EtOH/water (Zhang et al., 2021c), and the results illustrated that the developed scheme can decrease energy consumption, dioxide carbon emissions, and improve the energy efficiency.

Process optimization plays an important role in the design of distillation process as significant amount of energy could be further reduce by means of optimization. The optimization of the distillation process is commonly expressed in the form of mixed-integer nonlinear programming (MINLP) problem as it contains massive amount of integer and

continuous decision variables (e.g., feed locations and reflux ratio). Stochastic optimization algorithms such as mesh adaptive direct search algorithm, genetic algorithm and particle swarm optimization algorithm could be used to handle the MINLP problem in the distillation process. For example, Li et al. (2020) investigated the optimization of intensified ED process *via* the mesh adaptive direct search algorithm and the results indicated that the cost could be further reduced. The optimization of methanol synthesis, extractive PSD and quasi-continuous pressure-swing batch distillation processes was conducted by Su et al. (2020a) and Zhao et al. (2021), respectively, and both works has indicated that the energy consumption and TAC could be further reduced through optimization. Ehyaei et al. (2020) explored the optimization of organic Rankine cycle and absorption chiller system using the particle swarm optimization algorithm. In summary, the process performances can be further improved *via* the stochastic algorithm-based optimization.

From the above literature summary, the intensified hybrid reactive distillation processes provide significant performance improvement in terms of energy-saving. Nevertheless, the reaction and subsequent separation process are not taking place within the same unit operation for the separation of ternary azeotropic mixture, which resulted in the by-product cannot be directly utilized in the developed schemes. Therefore, the objective of this work is to develop an energy-efficient and sustainable process that integrates both reactive and extractive distillation in a single unit of operation for separating the ternary azeotropic mixtures TBA/EtOH/water, the novelty is further explained as follow,

(1) two intensified hybrid reactive-extractive distillation schemes (i.e., double-column reactive-extractive distillation (DCRED) and reactive-extractive dividing wall column

(REDWC)) are determined *via* the conceptual design;

(2) the multi-objective particle swarm optimization (MOPSO) algorithm combined Aspen Plus is adopted to solve nonlinear optimization of the established processes;

(3) the sustainable process with best economic, environmental and thermodynamic performances is obtained *via* the comparison of TAC, $CO_2/SO_2/NO_X$ emissions and second-law efficiency.
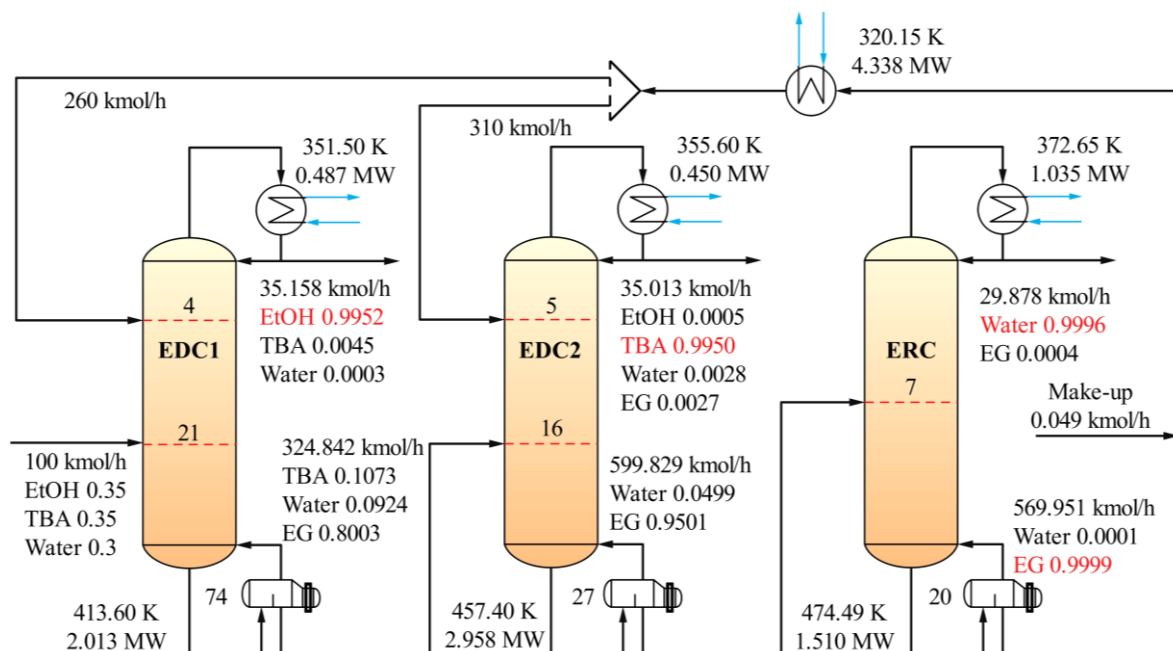
2. The existing triple-column extractive distillation process

Figure 1. The existing optimal triple-column extractive distillation process for the separation of TBA/EtOH/water (Reproduced from Shi et al., 2020)

Figure 1 shows the reproduced existing optimal triple-column extractive distillation (TCED) process with detailed operating parameters for the purification of TBA/EtOH/water from the industrial effluent (Shi et al., 2020). The entrainer and azeotropic mixture are fed into the 4th stage and 21st stage of the first extractive distillation column (EDC1). The bottom mixture separated from the EDC 1 is directed to the second extractive distillation column (EDC 2) and enters the column *via* 16th stage while the entrainer enters from the stage 5th. Water and

EG mixtures are subsequently separated *via* the entrainer recovery column (ERC). Reflux ratios

of three columns (i.e., EDC1, EDC2 and ERC) are 0.27, 0.17 and 2.00, respectively. Finally,

the EtOH, TBA and water of 99.52 mol%, 99.50 mol% and 99.96 mol% are obtained from the

top of EDC1, EDC2 and ERC, respectively. The high purity of EG is cooled, and then is

recycled to the EDC1 and EDC2. The reproduced results in Figure 1 are very similar to those

in Shi et al. (2020), and the process will be used as the base case for subsequent comparison

against the proposed process in this work.

3. Methodology
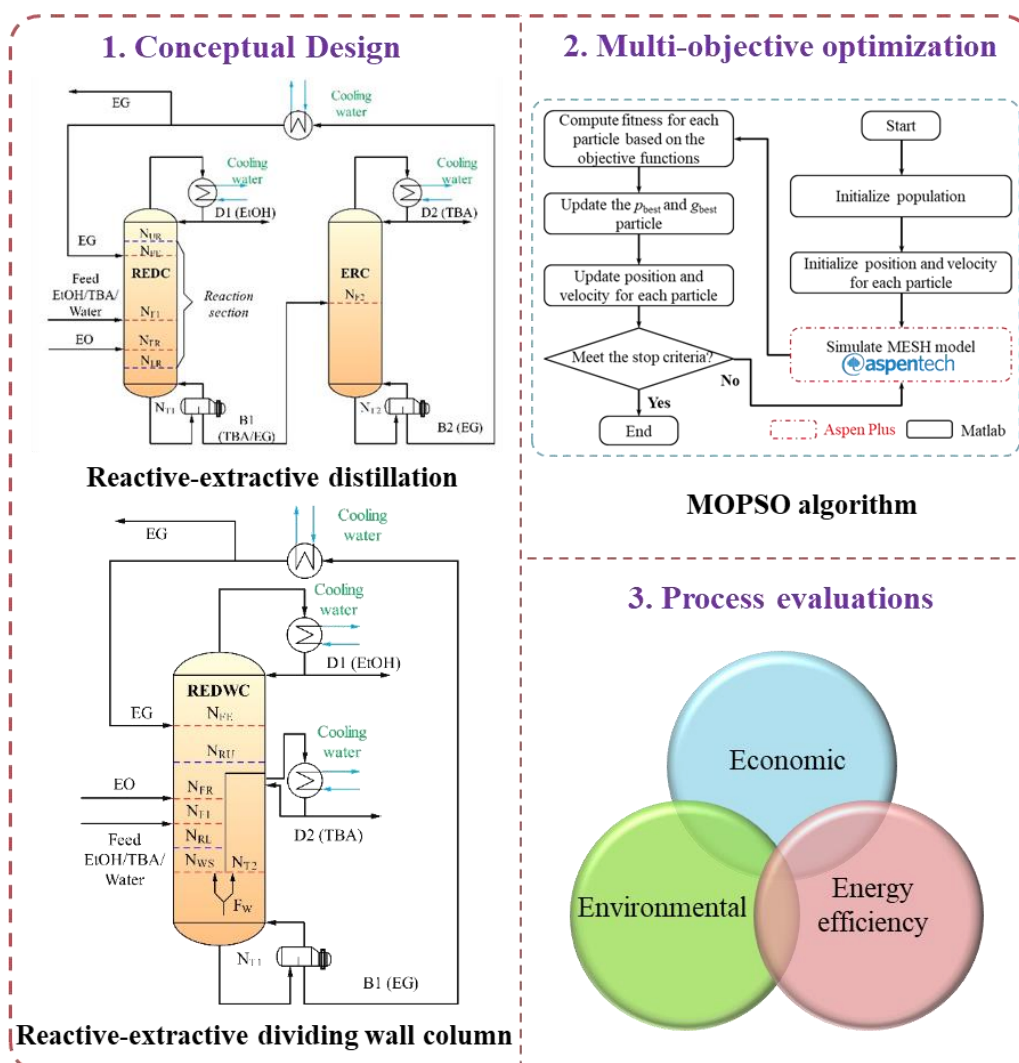
Figure 2. A systematic approach for separating the ternary azeotropic mixture
TBA/EtOH/water by using the novel DCRED and REDWC processes

In this work, a systematic approach for the separation of the ternary azeotropic mixture is proposed by using the novel DCRED and REDWC configurations as shown in Figure 2. In step 1, the conceptual design of the proposed DCRED and REDWC processes are obtained *via* the kinetic and thermodynamic analysis. Then, the MOPSO algorithm is used to found the optimal established process *via* the combination of Matlab and Aspen Plus in step 2. The last step involved the calculations of TAC, $CO_2/SO_2/NO_X$ emissions, and second-law efficiency for assessing the economic, environmental (i.e., greenhouse and acid rain) indices, and thermodynamic efficiency of the DCRED and REDWC processes.

3.1 Conceptual design

The component water can be removed through introducing a third reactant EO. Reaction and kinetic equations are obtained from the work of Lichtenstein and Twigg (1947) and Ciric and Gu (1994).

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

$$r(kmol/m^3/s) = 3.15 \times 10^{12} \exp[-9547/T] x_{EO} x_{Water} \tag{2}$$

where x_{EO} and x_{Water} represent the mole fraction of EO and water. The molar ratio of the EO-to-water is determined as 1.0 (Tavan and Hosseini, 2013), which could completely remove moisture and facilitate subsequent azeotropic separation. Notably, the EO is thermally hydrolyzed to EG without a catalyst (Prihatin et al., 2013).

The UNIQUAC model is used to predict the vapor-liquid equilibrium (Shi et al., 2020). Some missing binary interaction parameters (EtOH-EO, TBA-EO, TBA-EG and EO-EG) are estimated *via* the UNIFAC-DMD method. The built-in and estimated binary parameters used in this work are made available in the supporting information (Table S5). The entrainer EG

shows best performance in the separation of EtOH/TBA, which has been verified *via* the *x-y* diagram (Shi et al., 2020). In addition, the by-product is EG and reaction of EO and water is irreversible. Therefore, it is potential to integrate both the reactive and extractive distillation processes in one single column, i.e., reactive-extractive distillation column (REDC), for the azeotrope separation. Two alternatives processes DCRED and REDWC are developed to separate ternary azeotropic mixture. In the proposed DCRED process, one product is removed from the top of REDC while the entrainer could be recycled *via* the entrainer recovery column (ERC). Two products are obtained at the left and right rectifying sections of the REDWC scheme, and the entrainer EG is obtained at the bottom of the REDWC. For the purpose of fair comparison, the feed composition of the TBA/EtOH/water ternary azeotrope used in this work is the same as those of Shi et al. (2020).

3.2 Optimization

There are various discrete variables (i.e., total number of stages, feed locations, and withdraw stage) and continuous decision variables (i.e., distillate, reflux ratio, and flowrate of entrainer) in the optimization of distillation process (Kruber et al., 2019). Therefore, the optimization of distillation process is a MINLP problem, which can be expressed as follow,

$$
\begin{aligned}
&\min_{(x \text{ and } y) \in R} \left[f_1(x, y), f_2(x, y) \right] \\
&R = \{ x \in X \ \& \ y \in Y \} \\
&\text{subject to} \{ x_i \geq x^{\text{desired}}, i = 1, 2, \cdots n \}
\end{aligned}
\tag{3}
$$

where $f_1(x)$ and $f_2(x)$ are the objective functions total capital cost (TCC) and total operating cost (TOC); x^{desired} represents the constraint variable (i.e., the desired product purity); x and y indicate the discrete and continuous variables, respectively.
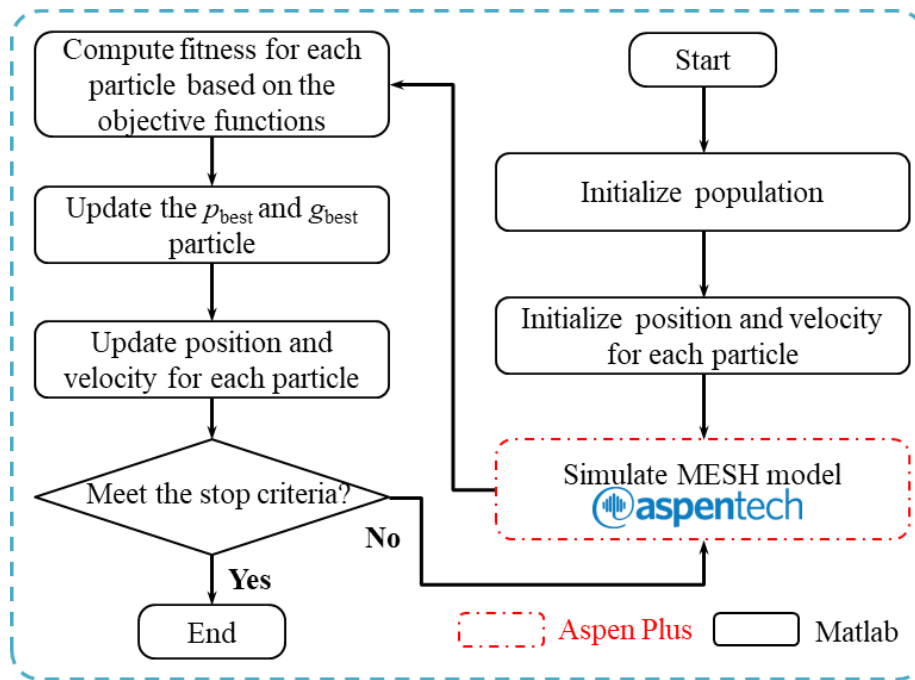
Figure 3. The MINLP optimization scheme by combining Matlab and Aspen Plus (MESH: equation of material balance-M, phase equilibrium-E, mole fraction summations-S, heat balance-H)

Figure 3 illustrates the MOPSO scheme by combining Matlab and Aspen Plus for the optimization of developed distillation processes. Firstly, the initial particles X_i is generated with random real numbers in the specified decision variable range. Non-dominated sorting in the multi-objective optimization process is mainly used to sort the solutions in population based on the Pareto dominance principle. Subsequently, the g_{best} is randomly obtained from the external repository considering a niche count and a crowding distance. There are two situations for updating the p_{best}, i.e., the first one is when the objective function of current particle dominates that of historical particle while the other is when the one-half probability of the individual did not dominates each other. The position and velocity for each particle will be updated. As suggested by Alcocer-García et al. (2019), the optimization could be stopped when the vector of decision variables did not produce any meaningful improvement.

The MOPSO algorithm is validated using the standard methodology currently adopted in

the evolutionary multi-objective optimization community (Coello et al., 2004). The results revealed that the MOPSO is a viable alternative since it demonstrated similar performance with respect to some of the other well-known multi-objective algorithms to date, with some indicator albeit to a slightly better extent. The advantages of MOPSO algorithm can be summarized as the following,

(1) MOPSO was the only algorithm from those adopted in our study that was able to cover the full Pareto front of all the functions used;

(2) the exceptionally low computational times required by the MOPSO make it a very promising approach to problems in which the computational cost is a vital issue (e.g., engineering optimization).

In this work, the code of MOPSO in Matlab is obtained from the Yarpiz's group (Mostapha Kalami Heris, 2015). In the optimization process, objective function, constraints and variables in the Aspen Plus could be accessed *via* the ActiveX technique in Matlab (Zhang et al., 2021a) and the corresponding code is listed in Table S1.

3.3 Process evaluations

3.3.1   Economic index

Douglas (1988) proposed an economic index, i.e., TAC, that includes the TCC and TOC as illustrated in Eq. 4 to evaluate the economics of the existing and the intensified processes.

$$TAC = \frac{TCC}{payback\ period} + TOC \tag{4}$$

The TCC involves the investment of column, condenser, reboiler and heat exchanger. The TOC refers to the cost of cooling water and steam. Additionally, the payback period is assumed as three years (Wang et al., 2022). The detailed formulations of the calculation TAC are

summarized in the Supporting Information (Yang et al., 2019a).

3.3.2 Environmental index

CO$_2$, SO$_2$ and NO$_X$ emissions act as an important environmental index for evaluating the sustainable development of the proposed processes from greenhouse effect and acid rain (Wang et al., 2021c). The coal is determined as the fuel for producing the steam. Thereby, the gas emissions (G_E) can be calculated from the equations 5-6:

$$G_E = \alpha \cdot M_{coal} + \beta \cdot E_C \tag{5}$$

$$M_{coal} = \frac{TEC \cdot t}{Q_S} \tag{6}$$

where M_{coal} in kg represents the coal consumption for the total energy consumption (TEC) of all reboilers; E_C (kW) is the electric consumption. α and β are the factor for different gas emissions, which is summarized in Table S2. t is the operating time, which is assumed as 8000h (Li et al., 2021d). The calorific value of standard coal is denoted as Q_S (Q_S = 29307.6 kJ/kg).

3.3.3 Thermodynamic index

In this work, the second-law thermodynamic efficiency (η) is employed to assess the energy efficiency, which is displayed in Eq. (7) (Hou et al., 2021).

$$\eta = \frac{W_{min}}{W_{min} + Ex_{loss}} \tag{7}$$

where W_{min} and Ex_{loss} in kJ/h are the minimum separation and lost work, which could be calculated *via* the Eqs. (8)-(9) as follows,

$$W_{min} = \sum_{Out}(h - T_0 s) - \sum_{In}(h - T_0 s) \tag{8}$$

$$Ex_{loss} = \left(\sum_{In} Q_R \left(1 - \frac{T_0}{T_S} \right) - \sum_{Out} Q_C \left(1 - \frac{T_0}{T_{CW}} \right) \right) - W_{min} \tag{9}$$

where h in kJ/kmol and s in kJ/kmol-K are the enthalpy and entropy of inlet and output stream;

Q_R and Q_C in kJ/h are denoted as the reboiler and condenser duty, respectively; T_0, T_S, and T_{CW} [K] are the temperatures of ambient, steam, and cooling water.

4. Results
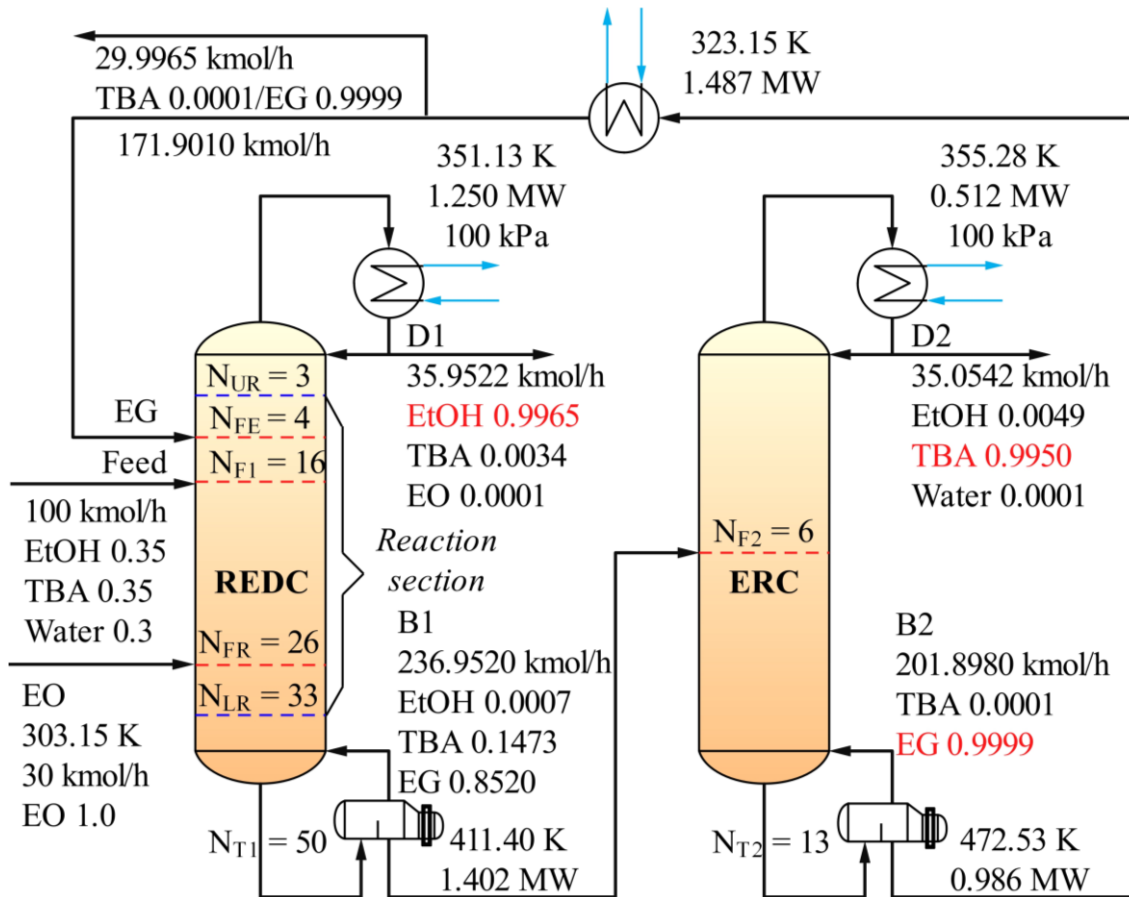
4.1 Conceptual design

Figure 4. Flowsheet of the proposed DCRED process with optimal operation conditions

The flowsheet of the proposed DCRED process is shown in Figure 4. The azeotropic mixture EtOH/TBA/water, reactant EO and entrainer EG are fed into the REDC. EO and water react between the upper and lower reaction stage (i.e., N_{UR} and N_{LR}). Of note is that, the extraction process is occurring between extraction distillation section (i.e., N_{F1} and N_{FE}). The high purity EtOH can be obtained at the top of REDC and the mixture of TBA/EG is sent to the middle section of ERC. TBA and EG with high purities are obtained at the top and bottom
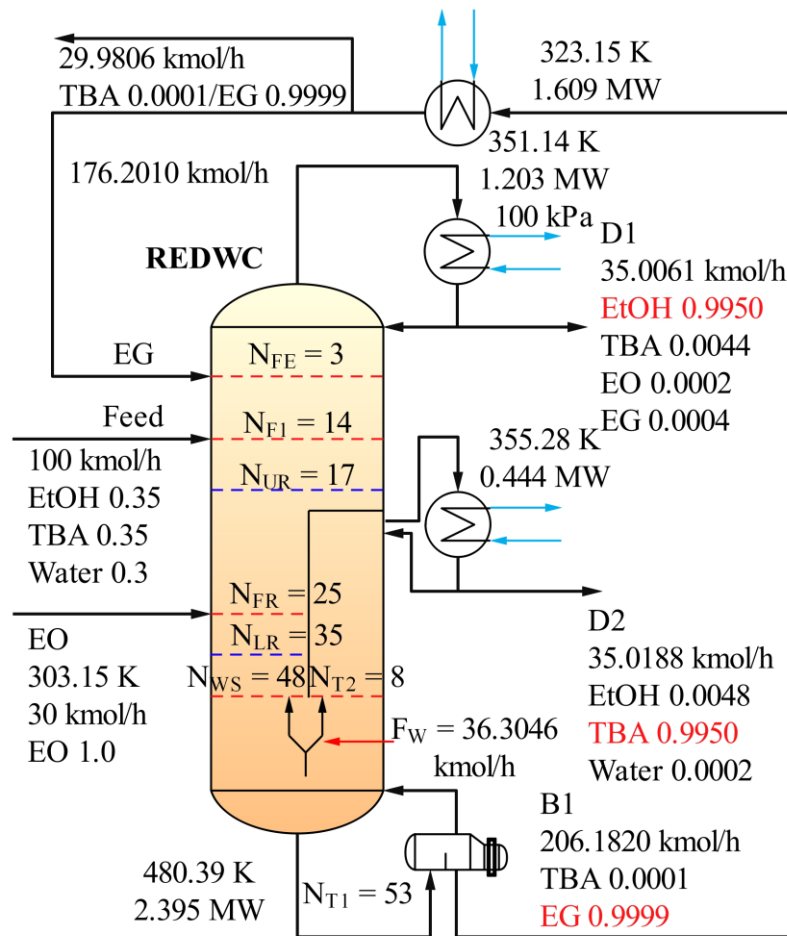
of ERC.

Figure 5. Flowsheet of the proposed REDWC process with optimal operation conditions

Figure 5 displays the flowsheet of the proposed REDWC process for separating the azeotropic mixture EtOH/TBA/water (Feed). In the proposed process, the REDC and ERC are combined into a single unit, also called as REDWC, reducing the capital and land costs. Of note is that, the REDWC involves one reboiler and two condensers. In this work, the operating pressures of all columns are assumed as a constant 101.3 kPa which is consistent with Shi et al. (2020). In addition, the pressure drops of 0.68 kPa is used to all columns.

4.2 Result of optimization

In this work, the simulation and optimization process are carried out on a notebook with Intel® Core™ i7-6700HQ CPU @ 2.60 GHz and 16G memory. As suggestion of Alcocer-

García et al. (2019), the optimization could be stopped when the vector of decision variables did not produce any meaningful improvement. Lower and upper bounds of decision variables in the developed processes are adjusted and obtained *via* the executing algorithm with 20 times for 5 generations which could discard the Pareto front limited by a given variable range (Santaella et al., 2017). Final ranges of optimization variables for the DCRED process are listed in Table S3. The whole optimization of the proposed process takes about 26.23 h. Figure 6 displays the variation trend of Pareto front solution and Pareto front solution of 300th generation for the DCRED scheme.
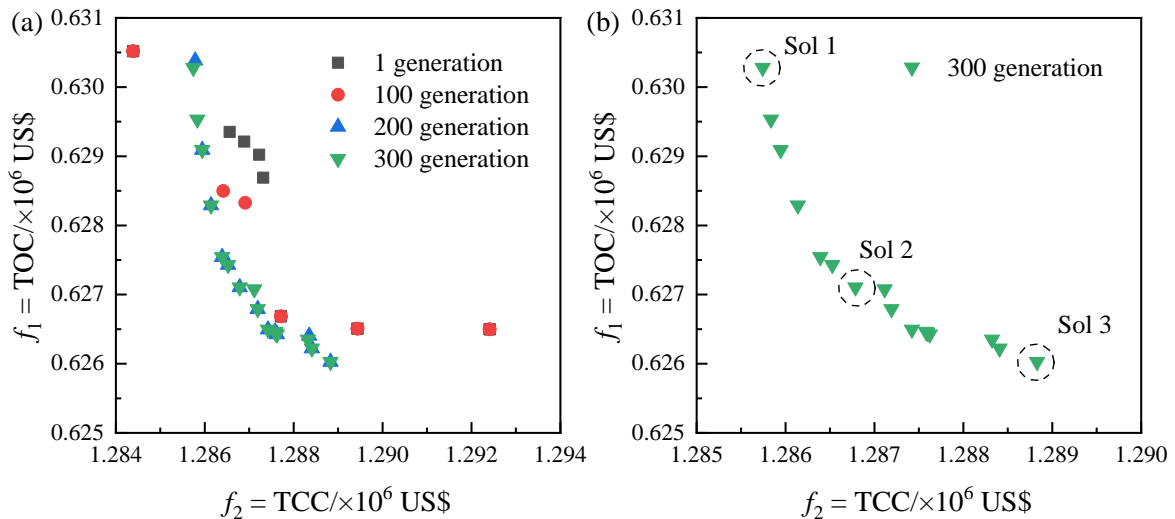

Figure 6. (a) The variation trend of Pareto front solution and (b) Pareto front solution of 300th generation for the DCRED scheme

Sol 1 and Sol 3 are the largest objectives for TOC and TCC. Sol 2 that provides a balance between both objectives is selected as the optimal solution. The DCRED process with optimal operation conditions for separating the ternary azeotropic mixture EtOH/TBA/water is demonstrated in Figure 4. The entrainer EG, azeotropic mixture, and reactant EO are fed into 4th, 16th and 26th stages, respectively. The reaction section is located between 3rd and 33th trays. To completely remove the component water, 0.446 m^3 and 2.282 are needed for the

volume of liquid holdup and reflux ratio. The total number of stage and feed location of ERC are 13 and 6. Reflux ratio of 0.343 is required to obtain the high purity of TBA. Of note is that, the energy for the reboiler of REDC and ERC is provided by the low-pressure steam (7.78 US$/GJ, 433.15K, 5.0 barg) and high-pressure steam (9.88 US$/GJ, 527.15 K, 41 barg), respectively. Figure 7 illustrates the liquid composition and temperature profiles of the optimal DCRED process.
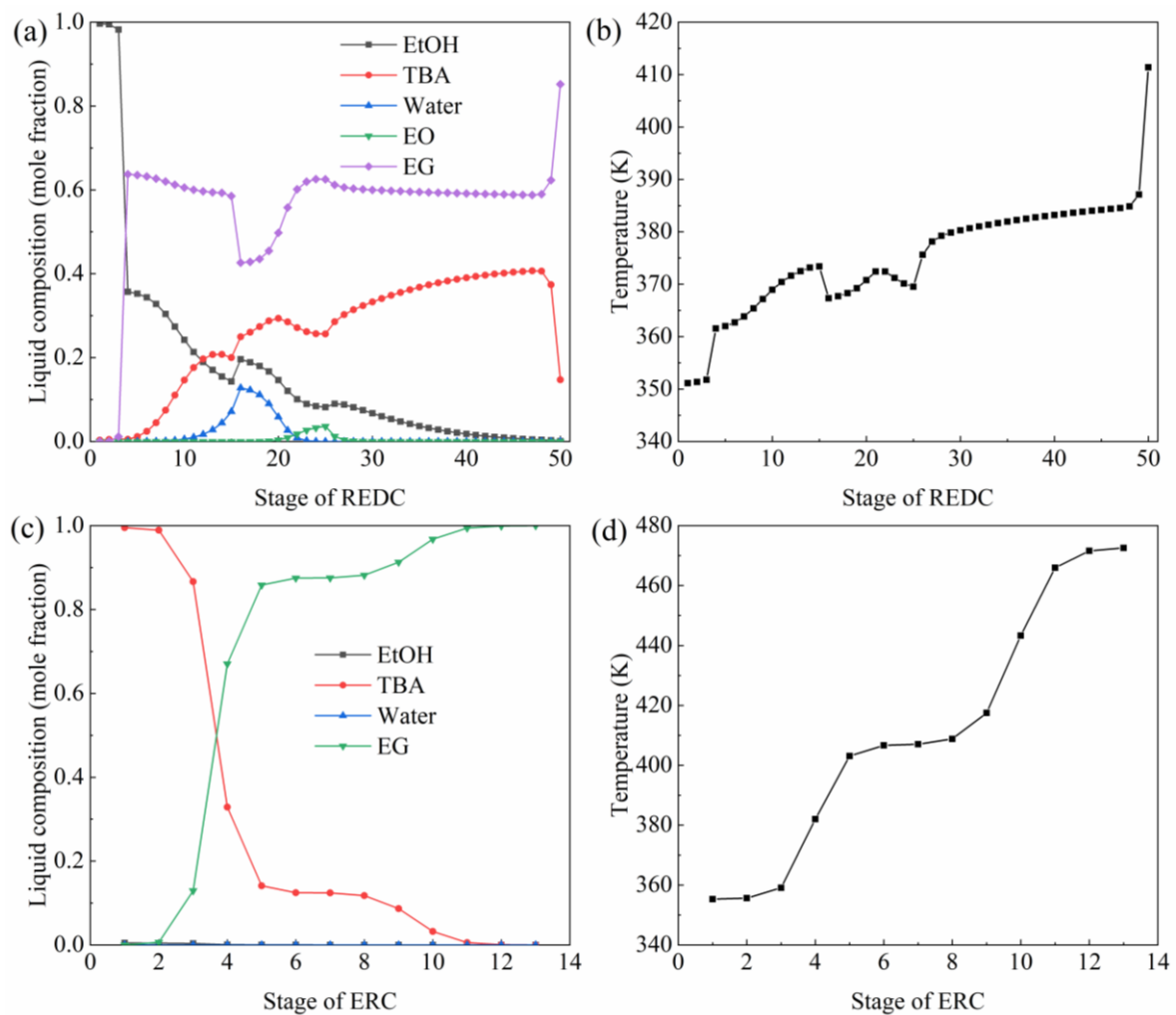

Figure 7. The liquid composition and temperature profiles of the optimal DCRED process
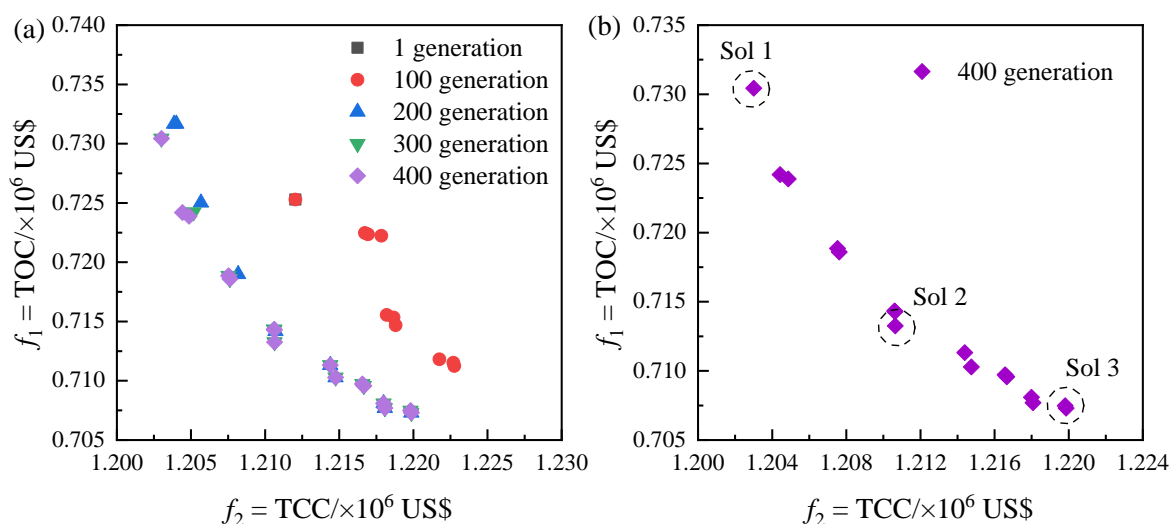
Figure 8. (a) The variation trend of Pareto front solution and (b) Pareto front solution of 400th generation for the REDWC scheme

Table S4 lists the lower and upper bounds of decisions variables for the REDWC process. The effect of optimization iterations on TAC of the REDWC process is shown in Figure 8. The optimization is stopped at 400th generation because the vector of decision variables did not produce any meaningful improvement, as illustrated in Figure 8a. The whole optimization of the proposed process takes about 34.78 h. Figure 8b gives the Pareto front solution of 400th generation for the REDWC scheme. Of note is that, decision variables of the REDWC scheme are have more strong coupling than the DCRED process, resulting in more iterations for the REDWC process.

Figure 5 gives the optimal REDWC process (i.e., Sol 2) for separating the ternary azeotropic mixture EtOH/TBA/water. The entrainer EG, mixture EtOH/TBA/water, and reactant EO are fed into 3rd, 14th and 25th stages, respectively. The reaction of EO and water occurs between 17th and 35th trays. A vapor stream is withdrawn from 49th stage with 36.346 kmol/h, which is split into two streams sending to left and right section of the REDWC. The optimal liquid holdup and reflux ratio are 0.877 m^3 and 2.151, respectively. The liquid

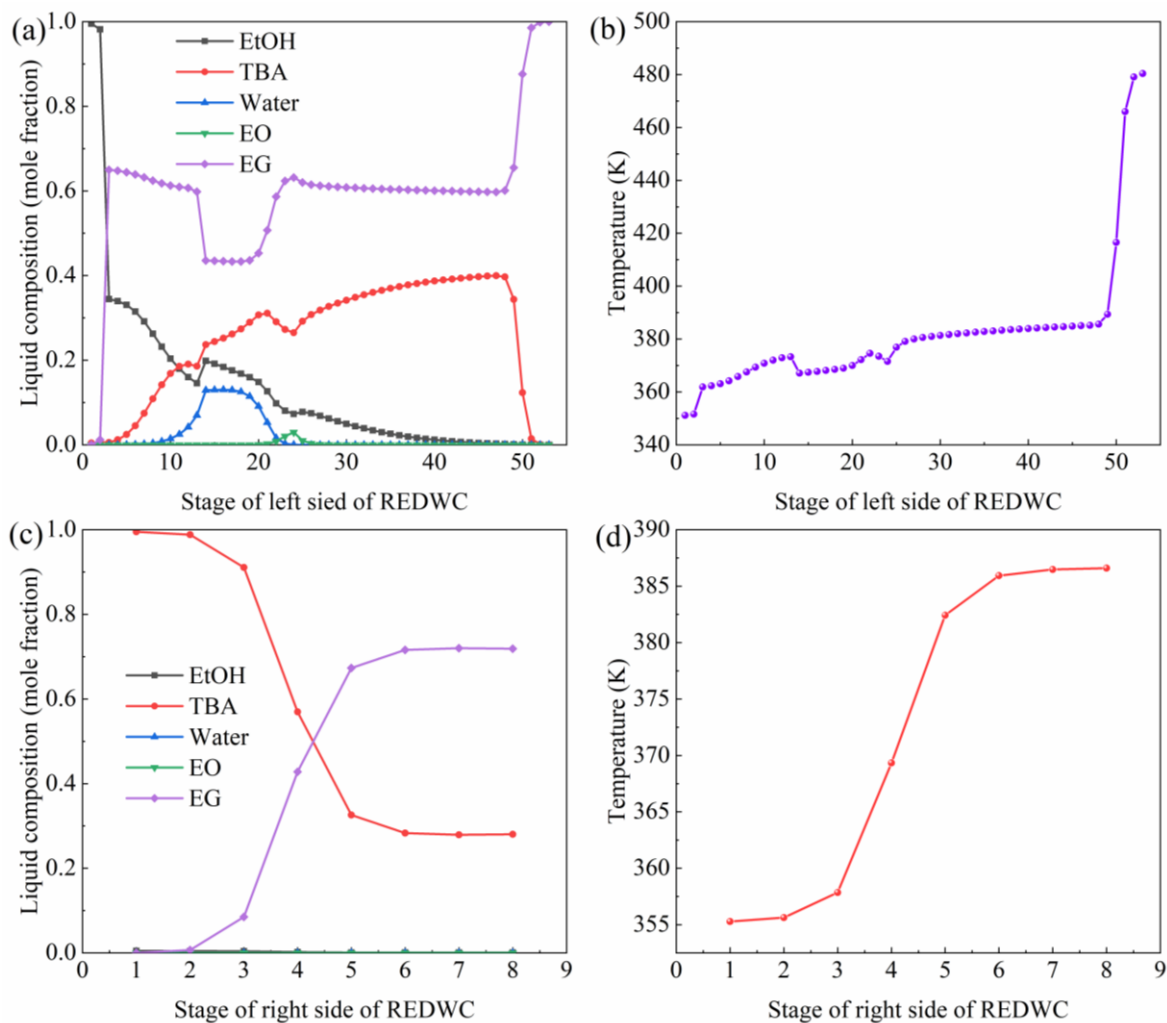composition and temperature of the optimal REDWC process is shown in Figure 9.

Figure 9. The liquid composition and temperature profiles of the optimal REDWC process

4.3 Process evaluations
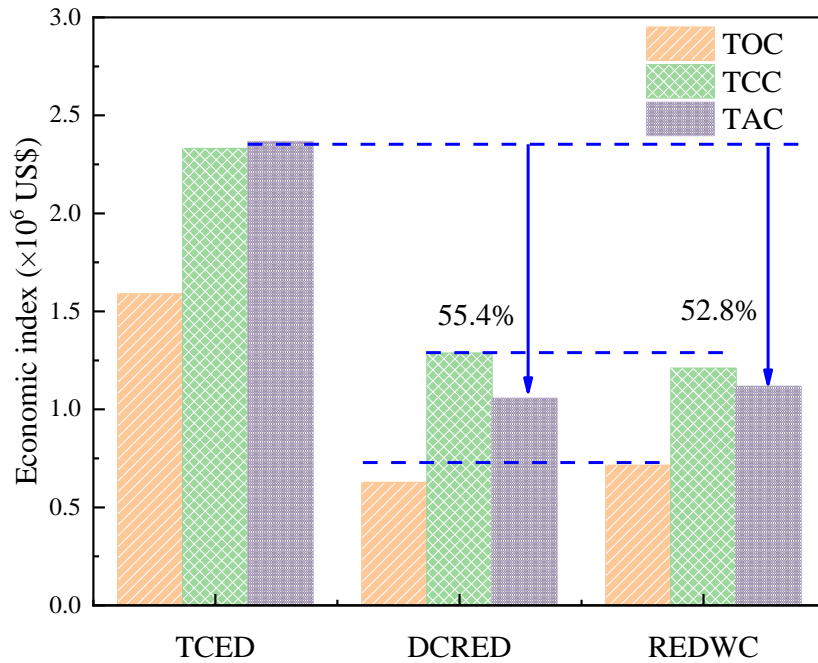
4.3.1 Economic evaluation

Figure 10. The comparison of TCC, TOC and TAC for the existing and proposed processes

The economic comparison of the existing and proposed processes is illustrated in Figure 10. TOC of TCED, DCRED and REDWC is 1.589×10^6 US\$, 0.627×10^6 US\$ and 0.714×10^6 US\$, respectively. 2.331×10^6 US\$, 1.287×10^6 US\$ and 1.210×10^6 US\$ are required for the TCC of three processes. As shown in Figure 10, the TOC of REDWC is higher than that of the DCRED due to the requirement of higher quality steam for REDWC. The TCC of REDWC is lower than that of the DCRED because two columns integrate into a single operating unit for the REDWC process. Compared with the existing TCED process, the TAC of the proposed DCRED and REDWC processes are reduced by 55.4% and 52.8%, respectively.
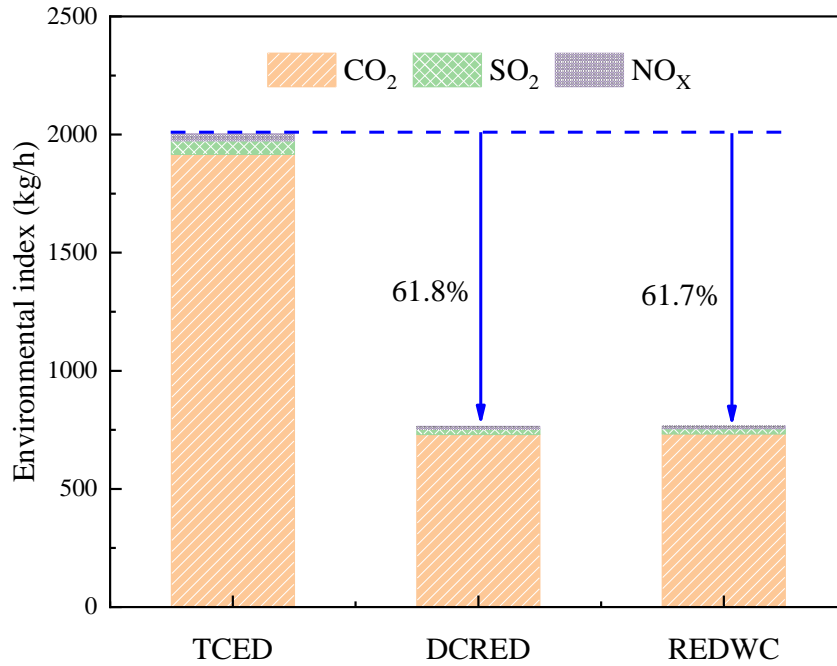
4.3.2 Environmental evaluation

Figure 11. The comparison of environmental performances for the existing and proposed processes

As illustrated in Figure 11, the CO_2 emissions of three processes are 1916.37 kg/h, 731.27 kg/h and 733.42 kg/h. The second environmental indicator also called as SO_2 emissions are 57.65 kg/h, 22.00 kg/h and 22.06 kg/h for the existing and developed processes. NO_X emissions for TCED, DCRED and REDWC are 28.83 kg/h, 11.00 kg/h and 11.03 kg/h, respectively. In summary, environmental performances such as global warning potential and acid rain effect of the DCRED and REDWC schemes could be reduced by 61.8% and 61.7%, respectively, comparing with the existing TCED process.
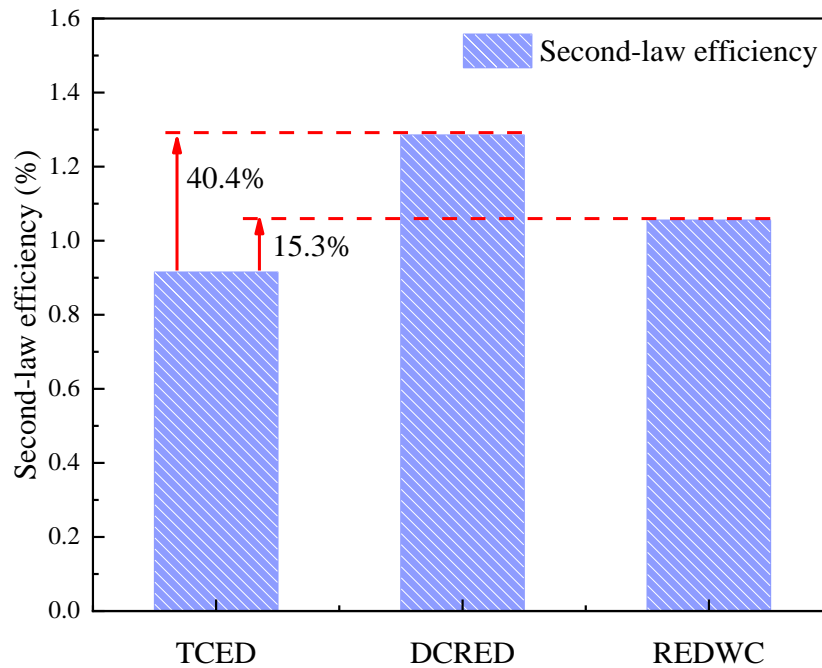
4.3.3 Thermodynamic evaluation

Figure 12. The comparison of energy efficiency for the existing and proposed processes

Figure 12 displayed the energy efficiency comparison for the existing TCED and proposed DCRED/REDWC processes. Compared with the existing TCED process, the second-law efficiency of the DCRED and REDWC processes improved from 0.915% to 1.285% and 1.055%, respectively. In comparison to the existing TCED process, the second-law efficiency of the proposed DCRED and REDWC processes improved by 40.4 and 15.3%, respectively. As a whole, the improvement of energy efficiency for the proposed processes is mainly contributed by the reaction heat could be used to the distillation process.

The energy consumptions and thermodynamic efficiency of the proposed schemes are significantly reduced and improved, respectively, because the partial duty of the distillation process could be provided by the reaction duty. Furthermore, the proposed DCRED show the better performances in term of economic, environmental, and thermodynamic efficiency than the REDWC process due to the required higher steam quality for the REDWC process.

5. Conclusion

In this work, a systematic method has been developed for the recovery of organic solvent from the industrial effluent by using the novel double-column reactive-extractive distillation (DCRED) and reactive-extractive dividing wall column (REDWC) processes. In the established process, the reactant ethylene oxide is used to remove water and by-product ethylene glycol is employed to separate the remaining azeotropic mixture. Of note is that, the reaction and extraction occur in a single operation unit (i.e., reactive-extractive distillation column). Subsequently, the multi-objective particle swarm optimization algorithm is adopted to obtain the optimal processes by minimizing the total operating and capital costs (i.e., TOC and TCC). TOC of TCED, DCRED and REDWC is 1.589×10^6 US\$, 0.627×10^6 US\$ and 0.714×10^6 US\$, respectively. 2.331×10^6 US\$, 1.287×10^6 US\$ and 1.210×10^6 US\$ are required for the TCC of three processes. The calculation demonstrated that total annual cost of the proposed DCRED and REDWC processes have been significantly reduced by 55.4% and 52.8% compared with the existing process. Gas emissions involving CO_2, SO_2 and NO_X of TCED, DCRED and REDWC are 2002.85 kg/h, 764.27 kg/h and 766.51 kg/h. Compared with the TCED process, the gas emissions of DCRED and REDWC processes can be reduced by 61.8% and 61.7%. In addition, the second-law efficiency of the proposed DCRED and REDWC processes are improved by 40.4 and 15.3%, respectively. The DCRED process has the best advantage in term of economy, environment and thermodynamic efficiency. In summary, the economic, environmental, and thermodynamic efficiency of the proposed schemes are significantly improved because the reaction duty in the reaction section could be used to heat the liquid in the tray.

It is worth noting that the proposed approach is limited to the separation of water-containing ternary azeotropic mixtures such as methanol/water/tetrahydrofuran and ethanol/water/tetrahydrofuran, and the by-product (i.e., ethylene glycol) must have a good extraction performance in the remaining azeotropic mixture. The developed processes could not be used when the relative volatility of remaining azeotropic mixture could not be increased *via* the by-product ethylene glycol and the water has low volatility (comparing with other separated components) and content. Therefore, more suitable reactants should be screened *via* the developed computer-aided molecular design to develop a more sustainable and wider scope of application hybrid reactive-extractive distillation process. In summary, the CO_2, SO_2 and NO_X emissions could be significantly reduced by 60% *via* the developed hybrid reactive-extractive distillation processes, which could be extended to other industrial effluent to recover valuable resources and pursue cleaner production processes (i.e., reduction emissions).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

Ao Yang: Conceptualization, Investigation, Methodology, Roles/Writing - original draft; Yang Su: Methodology, Software; Mengna Bai: Writing - review & editing; Shirui Sun: Software, Writing - review & editing; Weifeng Shen: Writing - review & editing, Project administration, Supervision; Jingzheng Ren: Writing - review & editing, Project administration, Supervision.

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