

Design of novel side-stream hybrid reactive-extractive distillation for sustainable ternary separation of THF/ethanol/water using mixed entrainer

Zong Yang Kong^a, Gabriel Contreras Zarazúa^{b,c}, Hao-Yeh Lee^d, Justin Chua^a,
Juan Gabriel Segovia-Hernández^{c,*}, Jaka Sunarso^{a,*}

^a Research Centre for Sustainable Technologies, Faculty of Engineering, Computing and Science, Swinburne University of Technology, Jalan Simpan Tiga, Kuching, Sarawak 93350, Malaysia

^b CONACyT, CIATEC A.C. Center for Applied Innovation in Competitive Technologies, León, GTO 37545, Mexico

^c Universidad de Guanajuato, Campus Guanajuato, División de Ciencias Naturales y Exactas, Departamento de Ingeniería Química, Noria Alta s/n, Guanajuato, GTO 36050, Mexico

^d Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

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ABSTRACT

This work explored the possibility of using mixed entrainer in a hybrid reactive-extractive distillation to improve the sustainability of the recovery process for the ternary azeotropic mixture containing THF/ethanol/water. A double column reactive-extractive distillation (DCRED) using mixed entrainer (i.e. dimethyl sulfoxide (DMSO) + ethylene glycol (EG)) is initially proposed and intensified to a side-stream DCRED (SS-DCRED). Both the initial DCRED and SS-DCRED designs are optimised using particle swarm optimisation (PSO) to obtain optimum column configurations. The sustainability of the proposed processes using mixed entrainer are compared against pure EG as entrainer based on five different indicators, i.e. economic, environmental, safety, operational controllability, and thermodynamic efficiency. Generally, it was demonstrated that using mixed entrainer provides significant improvement in all sustainability indicators. Although there may be some trade-offs in the controllability and economic, such drawbacks are consistent with previous publications where the improvement in sustainability are always achieved at an expense of an increase in the economics. Overall, it was revealed that the optimised SS-DCRED using mixed entrainer provides the best improvement to the economic, controllability, safety, environmental, and thermodynamic efficiency by 21 %, 97 %, 19 %, 29 %, and 100 %, with respect to using pure entrainer, which reflects the sustainability of the proposed process.

1. Introduction

Tetrahydrofuran (THF) and ethanol are common organic solvents used in the chemical and pharmaceutical industries. These two components can additionally be used as sustainable biomass energy source for internal combustion engines (Luis et al., 2014; Wang et al., 2015a). Therefore, the recovery of these two components from the wastewater is

beneficial for the environmental protection and resource conservation. The common source for obtaining these two components is from the waste effluent discharged from the synthesis of liquid crystal monomer (Wang et al., 2015a) or from the production process of norgestrel (Zhao et al., 2017a). However, the existence of the multiple azeotropes and distillation boundaries in the ternary azeotropic mixtures of THF/ethanol/water provides complex separation issues between the individual components, making the azeotropic mixture cannot be completely

Abbreviation: BLEVE, Boiling liquid expanding vapor explosion; CED, Conventional extractive distillation; DCRED, Double-column reactive—extractive distillation; DMSO, Dimethyl sulfoxide; EO, Ethylene oxide; EG, Ethylene glycol; EDWC, Extractive dividing wall column; HAZOP, Hazard and operability study; MINLP, Mixed integer nonlinear programming; NSGA, Non-dominated sorting genetic algorithm; PSD, Pressure swing distillation; PSO, Particle swarm optimisation; QRA, Quantitative risk analysis; RD, Reactive distillation; REDC, Reactive-extractive distillation column; SS-DCRED, Side-stream double-column reactive—extractive distillation; SQP, Sequential quadratic programming; TCED, Thermally coupled extractive distillation; TCRED, Triple-column reactive—extractive distillation; TAC, Total annual cost; THF, Tetrahydrofuran; UVCE, Unconfined vapor cloud explosion; UFL, Upper flammability limit.

* Corresponding authors.

E-mail addresses: zkong@swinburne.edu.my, skzyang@outlook.com (Z.Y. Kong), gago_9014@hotmail.com (G.C. Zarazúa), haoyehlee@mail.ntust.edu.tw (H.-Y. Lee), justinchua.98@hotmail.com (J. Chua), gsegovia@ugto.mx (J.G. Segovia-Hernández), barryjakasunarso@yahoo.com, jsunarso@swinburne.edu.my (J. Sunarso).

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Nomenclature

Variables

$\alpha_{b,k}$	The damage caused in category k per unit of chemical b emitted to the environment.	G	The matrix target for SVD analysis.
β_b	The total amount of chemical b released per unit of reference flow due to direct emissions.	h	Enthalpy (kJ kmol^{-1}).
λ_{steam}	Latent heat of steam (kJ kg^{-1}).	h_{steam}	Enthalpy of steam (kJ kg^{-1}).
Σ	The diagonal matrix which comprises of the singular values of G .	LW	Lost work (kJ hr^{-1}).
ω_d	The weighting for the damage in category d .	NHV	Net heating value kJ kg^{-1} .
δ_d	Normalisation for the damage in category d .	n	Molar flowrate (kmol hr^{-1}).
σ^*	Minimum singular value.	$P_{x,y}$	The probability of injury or decease caused by the incident i .
σ^*	Maximum singular value.	Q_{fuel}	Energy consumption of the heavy oil fuel (kJ).
γ	The ratio between the maximum and minimum singular value.	Q_{total}	Energy consumption of the reboiler (kJ).
$C\%$	Carbon content of the heavy oil fuel (kg kg^{-1}).	s	Entropy ($\text{kJ kmol}^{-1} \text{K}^{-1}$).
f_i	The occurrence frequency of injury or decease caused by the incident i .	T_{ambient}	Ambient temperature.
		T_{flame}	Flame temperature.
		T_{stack}	Stack temperature.
		T_{steam}	Temperature of steam (K).
		V	The matrix which comprises the left-singular vector of G .
		W	The matrix composed by the left-singular vectors of G .
		W_{min}	Minimum required work (kJ hr^{-1}).
		W_s	Shaft work for crossing the boundary of the system (kJ).

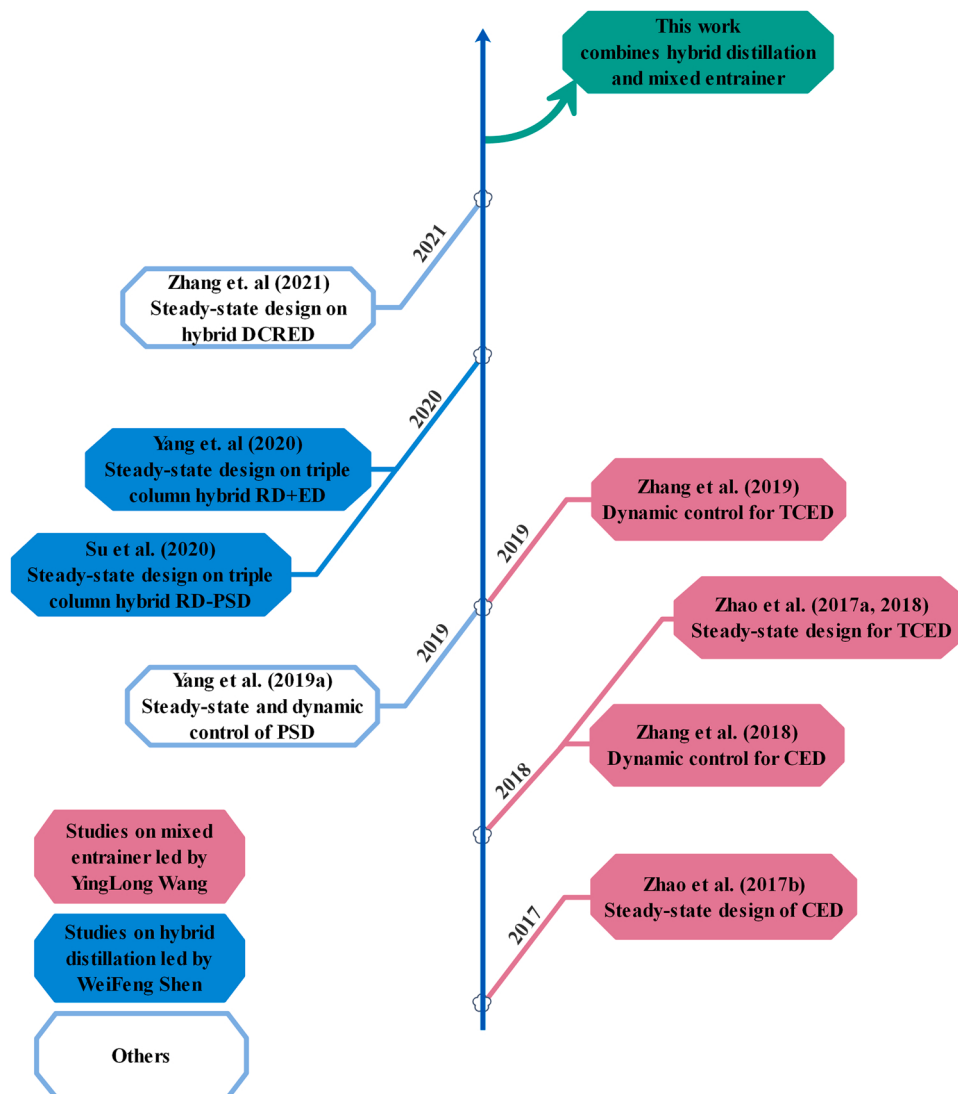


Fig. 1. Summary of existing studies in chronological order for ternary azeotropic separation of THF/ethanol/water.

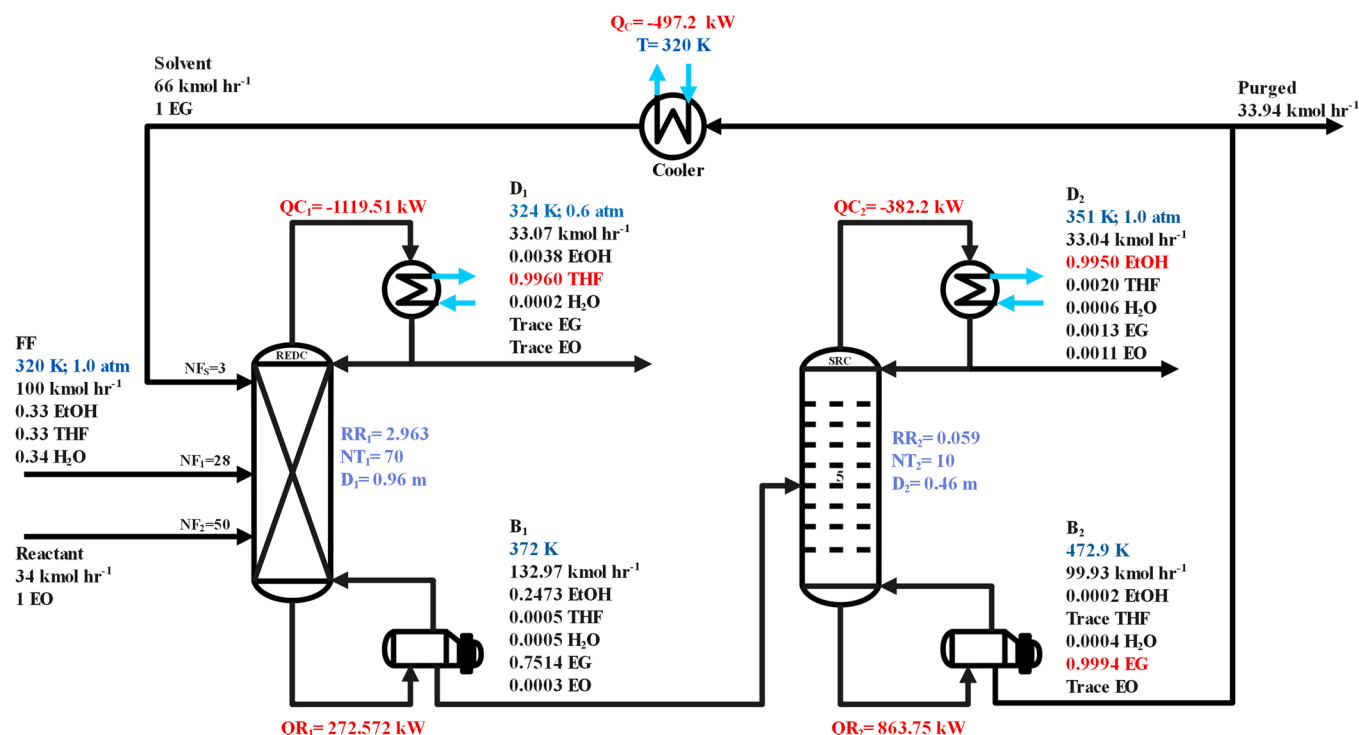


Fig. 2. DCRED using pure EG as entrainer.
Reproduced from the work of Zhang et al. (2021).

separated using traditional distillation techniques. To overcome this, special distillation techniques are required for this ternary component separation such as pressure-swing distillation (PSD) (Yang et al., 2019c; Yin et al., 2022), conventional extractive distillation (CED) (Yang et al., 2022b), and reactive distillation (RD) (Tang et al., 2005).

Based on our literature survey, the process design and control related studies, which feature the separation and recovery of THF and ethanol from wastewater have gained its popularity since 2015. Today, there is a large number of publications for the separation of THF/ethanol/water, the details of which are summarised in our review paper for the interested readers (Kong et al., 2022). Fig. 1 graphically summarises these studies in chronological order. Note that these studies are limited to the design and control studies using the distillation-based processes. Other than the ternary azeotropic separation of THF/ethanol/water, there are also a handful number of studies that present the binary separation of THF and ethanol (Wang et al., 2015b), the details of which are made available in a review paper by Alcántara Avila et al. (2021).

The first design and control related studies were pioneered by the research group of YingLong Wang in 2017 where they analysed the benefits of using mixed entrainer in CED process for the ternary azeotropic separation (Zhao et al., 2017b). An interesting conclusion derived from their study was that a mixture of 60 mol. % dimethyl sulfoxide (DMSO) and 40 mol.% ethylene glycol (EG) (i.e. mixed entrainer) provides the lowest total annual cost (TAC) for the ternary separation relative to the pure DMSO or the pure EG as entrainer. In addition, the CED using mixed entrainer also provides better dynamic performance relative to pure entrainer, as shown by Zhang et al. (2018) in the subsequent year. Then, the same research group also extended the usage of mixed entrainer to the thermally coupled extractive distillation (TCED) for energy consumption reduction (Zhao et al., 2018, 2017a) and showed that the TCED using mixed entrainer provides a lower TAC, CO₂ emission, and a higher thermodynamic efficiency in comparison to the CED. The dynamic performance of the TCED using mixed entrainer was later investigated by Zhang et al. (2019a) in which they confirm that there is no trade-off between the economics and controllability between the CED and TCED.

Another research group that has been intensively pursuing the design and control studies for the ternary separation of THF/ethanol/water is the group of WeiFeng Shen. Instead of using CED, they focused on the steady-state design and dynamic simulation of PSD for the ternary separation mixture (Yang et al., 2019a). Other than the PSD, they also proposed two novel separation processes that involve three distillation columns, i.e. the first process combines the RD and ED in series (Su et al., 2020c) while the second process integrates both RD and PSD in series (Yang et al., 2020). In both processes, the water is first removed in the first column (i.e. RD column) by reacting it with ethylene oxide (EO) as a reactant to form EG, which is removed from the bottom of the RD. The remaining components, i.e. THF and ethanol, leave the RD from the distillate and are directed to the subsequent ED using DMSO as pure entrainer or PSD for subsequent separation. Inspired by these processes, Zhang et al. (2021) explored the possibility of reducing the number of distillation columns for the ternary azeotropic separation from three to two columns, by integrating the RD and ED as one column. Their simulation results demonstrated that the hybrid double-column reactive-extractive distillation (DCRED) reduces the energy consumption by about 49 %, which translates to a further reduction in TAC by approximately 39 % in comparison to the triple column reactive-extractive distillation (TCRED) process using pure DMSO as entrainer.

Analysing together all the existing design and control studies that have been performed for the ternary separation of THF/ethanol/water (Su et al., 2020c; Yang et al., 2020, 2019a; Zhang et al., 2019, 2018; Zhang et al., 2021; Zhao et al., 2018, 2017a), three important features and characteristics were observed, which can be summarised based on the entrainer usage (1), process configuration (2), and process intensification (3) aspects:

- (1) The usage of mixed entrainer (e.g. DMSO + EG) in CED as proposed by the research group of YingLong Wang provides a better separation performance (i.e. lower TAC) relative to pure entrainer.
- (2) The hybrid reactive-extractive distillation configurations using pure entrainer (e.g. EG or DMSO) as proposed by the research

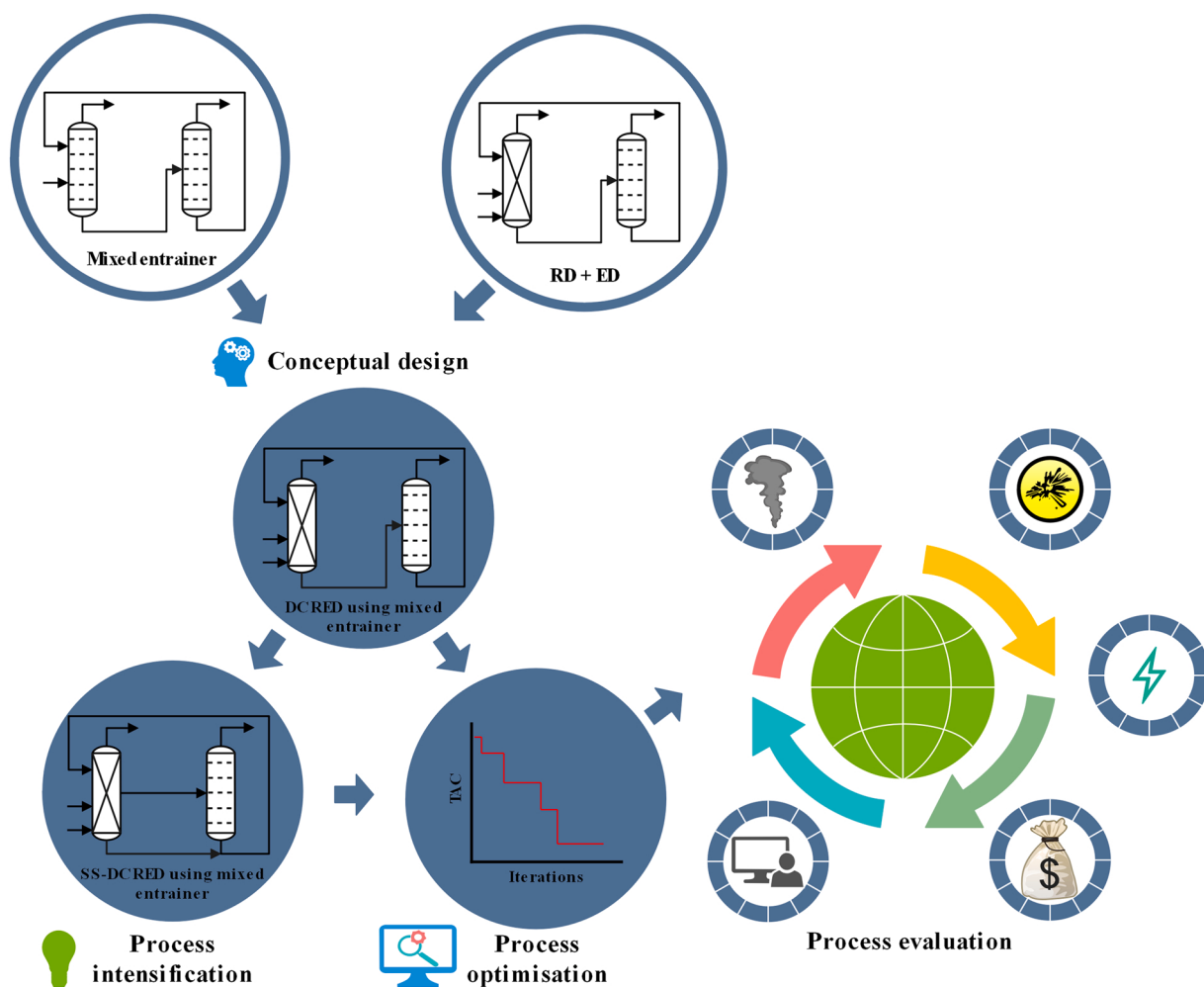


Fig. 3. The methodology framework employed in this work.

group of WeiFeng Shen also provide significant improvement on the same separation process (i.e. lower energy consumption and TAC) relative to only CED.

- (3) As evident by the existing studies in Fig. 1, the design and control studies to date are moving towards sustainable separation by means of reducing the energy, environmental, and economic impacts through different process intensification techniques such as hybrid distillation or TCED. For instance, most of the recent studies (i.e. 2020 or 2021) always demonstrate lower energy consumption, TAC, and CO₂ emission relative to the earlier processes (i.e. the work back in 2017 or 2018).

In this context, we realised that no existing studies have explored the possibility of replacing the pure entrainer (i.e. DMSO or EG) in the DCRED, with a mixed entrainer, to improve the sustainability of recovery process for THF/ethanol/water. To this end, we intend to investigate the possibility of using mixed entrainer in the DCRED configuration in this work. The performance of the proposed process using mixed entrainer is compared against the identical configuration (i.e. DCRED) using pure EG as entrainer from the work of Zhang et al. (2021), which is referred as the base case hereafter. The performance assessment is evaluated from a sustainable process perspective that includes environmental, social, and economic metrics, as these are some of the important characteristics that a sustainable process must possess according to several review papers (Constable et al., 2002; Curzons et al., 2001; Jiménez-González et al., 2012). Other than the three aforementioned metrics, three other important metrics are also

considered, i.e. controllability, safety, and thermodynamic efficiency, to achieve stable, safe, and efficient processes. These metrics are further elaborated in Section 3.4. Traditionally, all the existing design and control studies for the separation of THF/ethanol/water (Fig. 1) were assessed by prioritising the economic factor with only a handful number of studies accounted for the environmental and thermodynamic efficiency aspects. As a result, there is no overview of the role played by the other green indicators such as the inherent safety. In fact, another contribution of this paper is that no existing studies have evaluated the sustainability of special distillation-based processes (i.e. ED or RD) using these green metrics, for the separation of ternary azeotropic mixture.

The rest of the paper is arranged as follows. Section 2 describes the process flow diagram of the default DCRED process using pure entrainer to allow our readers to have a complete understanding of the process. Section 3 outline the methodology employed in this work that includes the conceptual design of the newly proposed DCRED using mixed entrainer, possibility of process intensification to a side-stream DCRED (SS-DCRED), process optimisation, and the different green indices used to evaluate the performance of the proposed processes. The results are discussed in Section 4 while Section 5 concludes this work and provides several recommendations for future work.

2. DCRED using pure entrainer

Fig. 2 shows the process flow diagram for the default DCRED using pure entrainer. Here, the RD and ED take place simultaneously in the reactive-extractive distillation column (REDC) where water and EO

react together to form EG, which is subsequently used as entrainer to facilitate the ED separation between the remaining components, i.e. THF and ethanol, within the same column (i.e. REDC). Then, the THF is removed as distillate from the REDC while the remaining mixture containing EG and ethanol is directed to the SRC where the ethanol is removed as distillate. The high purity (i.e. regenerated) EG entrainer is subsequently cooled before it is recycled back to the REDC. Here, excessive amount of EG is purged out of the system.

3. Methodology

Fig. 3 provides a general overview of the methodology employed in this work. Firstly, the DCRED that employs a mixture of EG + DMSO as entrainer is conceptually designed through retrofitting the existing DCRED using pure EG as entrainer (Fig. 2). Then, we investigate next the possibility of reducing the energy consumption of the initial DCRED design through retrofitting to an energy-intensified side-stream configuration (SS-DCRED). Both the initial DCRED and SS-DCRED design are preliminary analysed based on five different metrics, i.e. economic, safety, environmental, controllability, and thermodynamic efficiency, to verify the effectiveness of using mixed entrainer in DCRED. Lastly, both the initial DCRED and SS-DCRED design are further optimised to obtain the optimum column configuration. The performance of the optimised configurations is also evaluated using the same indicators and compared against the initial design and the DCRED using pure entrainer.

3.1. Conceptual design

In this section, the configuration of DCRED using mixed entrainer is conceptually developed and analysed in a preliminary way to examine the feasibility of combining the beneficial features of using mixed entrainer and reactive-extractive distillation. The configuration of the proposed DCRED using mixed entrainer is similar to those using pure EG as entrainer as described in Section 2 (Fig. 2). Here, the DCRED using pure EG as entrainer from the work of Zhang et al. (2021) is reproduced (Fig. 2) and employed as the base case since it is the latest (i.e. most up-to-date) publication that works on the ternary azeotropic separation of THF/ethanol/water. Further, the DCRED model reported by Zhang et al. (2021) is also an improvised version of the TCRED from their base case (Su et al., 2020c). To ensure a fair economic comparison against the base case, the column parameters of the conceptual design for the DCRED using mixed entrainer in this work are kept identical to those of the base case scenario (Zhang et al., 2021) so that any saving can be directly reflected on the TAC. Here, the percentage difference between the reproduced flowsheet (Fig. 2) and the base case is less than 10 %, which highlights the accuracy and reliability of our reproduced flowsheet.

The simulations were carried out using Aspen Plus V11 and thermodynamic package employed in this work is NRTL, identical to those of Zhang et al. (2021). The fresh feed flowrate is 100 kmol hr⁻¹ with 33 mol. % of ethanol, 33 mol. % of THF, and 34 mol. % of water. Such feed condition is also identical to several other existing studies that work on the ternary azeotropic separation of THF/ethanol/water (Su et al., 2020c; Yang et al., 2020, 2019a). The purity specification for the THF and ethanol obtained from the distillates of REDC and SRC are both held at minimum of 99.5 mol %.

3.2. Process intensification

Several recent studies have shown that the application of process intensification facilitates significant improvement to the sustainability of a process (Amezquita-Ortiz et al., 2022; Bravo-García et al., 2021; González-Navarrete et al., 2022). Therefore, we investigate next the possibility of intensifying the initial DCRED design to a SS-DCRED. The side-stream configuration is among one of the promising energy-intensified techniques for reducing the remixing effect and

energy consumption, as reported by many existing studies for CED (Cui et al., 2020; Yang et al., 2019b). In addition, the side-stream configuration (i.e. SS-DCRED) can also be easily retrofitting at an industrial scale. Here, it is therefore assumed that the initial DCRED design using mixed entrainer undergoes a retrofit to become a SS-DCRED and thus, all the column specification (i.e. total number of stages, fresh feed location, and entrainer feed location) remains identical to those of the proposed DCRED. As a result, any saving from the energy consumption can be directly reflected on the TAC. The side draw location and flowrate for the SS-DCRED are varied until a minimum value of TAC is reached where both products specifications can be met. Such retrofitting method is analogous to that employed by Wu et al. (2013) to retrofit an existing CED to an extractive dividing wall column (EDWC).

3.3. Process optimisation

As mentioned in Section 3.1 and Section 3.2, the initial DCRED and SS-DCRED was designed based on retrofitting and it is possible that the performance of the proposed process deteriorate as a result of the process is not at their optimal configuration (as shown in the later section). In addition, the objective of previous sections (i.e. Section 3.1 and Section 3.2) was only to verify the feasibility of using mixed entrainer in reactive-extractive distillation. As it will be demonstrated later in Section 4.1, it is feasible to employed the mixed entrainer in the DCRED but the developed process has several limitations. To overcome this, we further explore the possibility of improving the process performance through process optimisation, which can effectively reduce the energy consumption and lower the environmental emission, as evident by a handful number of recent studies for reactive or extractive-based distillation (Alcántara Avila et al., 2021; Cui et al., 2020; Yang et al., 2022c; Yang and Ward, 2018; Zhao et al., 2017b). The proposed process in this work contains of various types of decision variables, such as discrete or continuous, which forms a mixed integer nonlinear programming (MINLP) problem that cannot be effectively handled using sequential quadratic programming (SQP) optimisation method or the traditional sequential iterative approach. Several strategies have been devised to overcome this problem, which can be classified as deterministic or stochastic optimisation. The deterministic optimisation involved explicit mathematical model equations which required high mathematical efforts and the formulation of such design models is difficult and very time consuming (Segovia-Hernández et al., 2015). The stochastic optimisation, on the other hand, is suitable for tackling the design and optimisation of complex separation systems with reasonable computational effort. Moreover, stochastic optimisation is capable of solving unknown structure problems (i.e. black box models such as Aspen Plus), which require the calculations of the objective function that cannot be effectively implemented using deterministic optimisation. Today, various stochastic optimisation algorithms such as non-dominated sorting genetic algorithm (NSGA) (Su et al., 2020a; Sun et al., 2020), mesh adaptive direct search (MADS) algorithm (Li et al., 2020), and particle swarm optimisation (PSO) (Yang et al., 2022a) have been applied for optimising the distillation-based processes. Among the different aforementioned algorithms, PSO has the advantage of exceptionally low computational times and have been applied to optimise the traditional distillation-based processes (Qian et al., 2020). Nonetheless, no study has yet to apply the PSO for optimising a hybrid RED. In this work, we employed the PSO for optimising the proposed process, which is expressed in the form of MINLP problem, given by Eq. 1:

$$\min_{x \in R} f(x) = \text{TAC} \quad (1)$$

$$R = \{y \& z\}$$

Subject to

$$\{p_i \geq p_i^{\text{desired}}, i = 1, 2, \dots, n\}$$

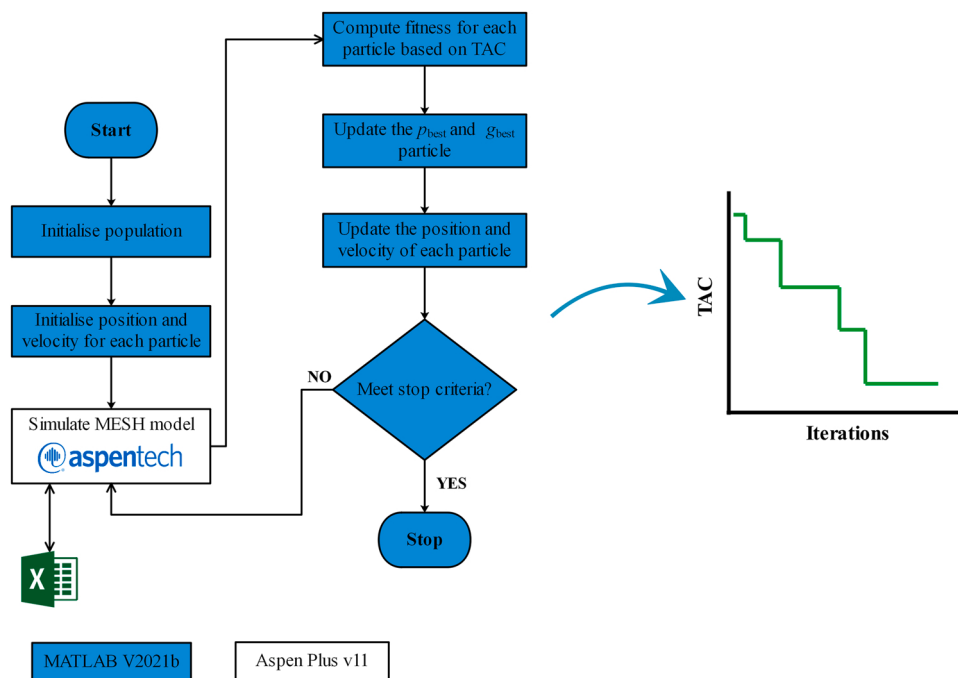


Fig. 4. The PSO optimisation algorithm employed in this work.

Here, the objective function ($f(x)$) is to minimise the TAC, and the MINLP is bounded by the product purities (p_i^{desired}) as indicated in Section 3.1. The y and z in Eq. 1 are the discrete and continuous decision variables, respectively, which includes the total number of stages in each column, fresh feed and entrainer feed tray locations, reboiler duty, distillate rate, reaction zone, side-stream location, side-stream flowrate, and entrainer composition. These design variables are analogous to previous studies (Yang et al., 2022c). Altogether, the objective function, bounds, design variables, and initial values in Aspen Plus are integrated with the PSO in MATLAB via the ActiveX technology (You et al., 2018), and the overall optimisation procedure is graphically illustrated in Fig. 4.

The PSO algorithm employed in this work was modified from Heris (2015) group. First, the initial particle (x_i) is generated randomly using real numbers that is within the specified bound (i.e. initialise population and initialise their position and particle velocity) and the fitness of each particle is computed based on the TAC as the objective function. The best individual (p_{best}) and group (g_{best}) solution is updated based on two scenarios: (1) the objective function of the current particle dominates that of the historical particle (i.e. the TAC is lower than the previous), and (2) when less than half (i.e. 50 %) of the individual solution did not dominate each other. Finally, the optimisation can stop once the requirement is met, while on the other hand, the position and velocity for each particle will be updated.

3.4. Process evaluation

In this work, all the proposed processes are evaluated based on the “green indices” concept as reported by Jiménez-González et al. (2012) and Jiménez-González and Constable (2014) to facilitate a wider goal of environmental sustainability, that includes the aspects of economic, safety, environmental, and operational controllability. The thermodynamic efficiency of the proposed processes is additionally evaluated for the purpose of achieving sustainable and efficient design.

3.4.1. Economic index

The TAC is employed as the economic index in this work, which can be calculated using Eq. (2).

$$\text{TAC} = \frac{\text{Total capital cost}}{\text{Payback period}} + \text{Operational cost} \quad (2)$$

The total capital cost is the sum of all major equipment cost in the plant, which includes the column vessel, reboiler, condenser, and cooler. The height of the distillation column is 1.2 times (i.e. 20 %) larger than the height required for the trays and the column diameter is extracted from Aspen Plus. The pump cost is not included in the calculation given its marginal contribution compared to the column cost. The operational cost, on the other hand, includes the different pressurised steam and the cooling water costs. The plant is set to operate for 8500 h per year and the payback period is 3 years. Table S1 summarises the economic basis for the TAC calculation which are extracted from Douglas (1988).

3.4.2. Inherent safety index

In this work, the individual risk (IR) index is employed to measure the safety aspect of the proposed process. The IR is quantified by the probability of affection (i.e. a result of a specific hazard that occurs within a particular frequency), as indicated by Eq. (3), and it is not affected by the number of people exposed to the hazard (CCPS - Center for Chemical Process Safety, CCPS, 1990).

$$\text{IR} = \sum f_i P_{x,y} \quad (3)$$

where f_i and $P_{x,y}$ are the occurrence frequency and probability of injury or death caused by the incident i , respectively. An irreparable injury (i.e. death) is employed in this work where more data are recorded. The IR can be calculated through identifying the hazards, accidents, and their corresponding consequences, commonly known as the quantitative risk analysis (QRA) method. Such methodology begins with the hazard and operability study (HAZOP) to identify all potential circumstances, such as the continuous and instantaneous releases for the case of distillation column. A continuous release is defined as the leak caused by pipeline rupture or partial rupture on a unit operation. On the other hand, the instantaneous release is represented by the total loss of the unit-operation (i.e. process equipment) matter initiated by a catastrophic rupture. The incident hazards employed in this study includes the boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud explosion (UVCE), flash fire, and toxic release for the

instantaneous release incidents whereas the continuous release incidents are jet fire, flash fire, and toxic release. The occurrence frequency for each incident (f_i) can be extracted from the existing values published by the [CCPS - Center for Chemical Process Safety](#). [CCPS \(1990\)](#), with the aid of an event tree diagrams obtained with all probabilities of instantaneous and continuous incident hazards, along with their respective frequencies. After all the potential incidents have been identified, a consequence assessment can be conducted to estimate the probability $P_{x,y}$, which involves determining the physical variables such as the thermal radiation, the overpressure, and the concentration of the leak initiated by incidents hazard and their corresponding damages. The calculations of these physical variables were also performed using the equations reported by [CCPS - Center for Chemical Process Safety](#). [CCPS \(1990\)](#). More details of the IR calculations are made available in the [Supporting Information](#).

3.4.3. Environmental index

The environmental index in this work is quantified based on the Eco-Indicator 99 (EI99) to measure the sustainability of the proposed process and evaluate the environmental impact caused by the activities carried out in the process. Such indicator was first proposed by [Goedkoop and Spruiensma \(2000\)](#) based on the life cycle analysis and has become an established method to measure the overall environmental performance related to chemical-based processes. Today, such indicator has been used by many different researchers to facilitate a more sustainable design ([Sánchez-Ramírez et al., 2022, 2021](#)). The EI99 accounts for 11 impact categories, which account for three major damages categories, i.e. human health, ecosystem quality, and resource depletion. The EI99 is calculated as follows:

$$EI99 = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (4)$$

where β_b indicates the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ represents the damage caused in category k per unit of chemical b emitted to the environment, ω_d and δ_d are the weighting and normalisation for the damage in category d , respectively. The basis for the EI99 is measured in a fashion where 1 point represent one per thousand of the annual environmental load of one average European resident. Three important factors are considered in the impact calculations in this work, i.e. the steam utility used to heat up the reboiler, the electricity used for pumping, and the steel material used to build the unit operation, the values of which are made available in [Table S3](#). In this work, the weighting factor employed is analogous to that of EI99, separating the impact categories as damages to the human health, ecosystem quality, and resources. Here, hierarchical perspective is considered in the calculation where the damage to the human health and ecosystem quality are considered to be equally important (40 % each) while the damage to the resources is considered to be about half as important (20 %).

Other than the EI-99, we also assessed the CO₂ emissions of the individual proposed process, as it also contributes towards the environmental impact. The CO₂ emissions can be estimated using [Eq. \(5\)](#) and [Eq. \(6\)](#).

$$CO_2 \text{ emissions} = \frac{Q_{\text{fuel}}}{NHV} \times \frac{C\%}{100} \times \varphi \quad (5)$$

$$Q_{\text{fuel}} = \frac{Q_{\text{total}}}{\lambda_{\text{steam}}} \times (h_{\text{steam}} - 419) \times \left(\frac{T_{\text{flame}} - T_{\text{ambient}}}{T_{\text{flame}} - T_{\text{stack}}} \right) \quad (6)$$

where Q_{fuel} and Q_{total} represents the energy consumption of the heavy oil fuel and reboiler (kJ), respectively. NHV is the net heating value of 39,771 kJ kg⁻¹. The C% is the carbon content of the heavy oil fuel (86.5 kg kg⁻¹) while the value of φ is 3.67. The λ_{steam} and h_{steam} represent the latent heat and enthalpy of the steam given in kJ kg⁻¹, respectively. Lastly, the T_{ambient} , T_{flame} , and T_{stack} are the ambient

temperature, flame temperature, and stack temperature, respectively.

3.4.4. Control properties index

In addition to the economic, safety, and environmental aspects, it is also important to analyse the operational controllability of the proposed process, which is evaluated using the singular value decomposition (SVD), represented by [Eq. \(7\)](#).

$$G = V \Sigma W^H \quad (7)$$

where G is the matrix target for SVD analysis, V is a matrix, which comprises the left-singular vector of G , Σ is a diagonal matrix, which comprises of the singular values of G , and W is the matrix composed by the left-singular vectors of G . The details of the mathematical derivation and fundamental of SVD can be found in [Klema and Laub \(1980\)](#) for interested readers.

The SVD analysis is regarded as an important tool of modern numerical analysis, which can be used to investigate the theoretical control properties of a chemical process. Here, two parameters are of interest, i.e. the minimum singular value (σ^*) and the maximum singular value (σ^*), the values of which are calculated using MATLAB by inputting the changes in column temperature profile obtained through open-loop sensitivity analysis (i.e. applying a small change (± 0.01 %) to the manipulated variables such as reboiler duty and reflux ratios). The ratio between the maximum and minimum singular value is the condition number, given by [Eq. \(8\)](#).

$$CN = \frac{\sigma^*}{\sigma_*} \quad (8)$$

The condition number reflects the sensitivity of the system under different uncertainties in process parameters and modelling errors. These parameters provide a qualitative indicator to evaluate the theoretical control properties of the alternative proposed designs. From [Eq. \(8\)](#), the systems with a lower condition number (or a higher minimum singular values) are expected to show the better dynamic characteristic under feedback control ([Klema and Laub, 1980](#); [Luyben and Floudas, 1994](#)). Several existing studies have recently employed the condition number as an index for assessing the dynamic characteristic or as an objective function for simultaneous optimisation of steady-state design and control for different chemical processes ([Amezquita-Ortiz et al., 2022](#); [Ramírez-Márquez et al., 2021](#)).

3.4.5. Thermodynamic efficiency

Apart from evaluating the proposed processes based on the “green indices” concept as reported by [Jiménez-González et al. \(2012\)](#), we additionally evaluate the thermodynamic efficiency of the proposed process, based on the second-law of thermodynamic ([Eq. \(9\)](#) to [Eq. \(11\)](#)). Such evaluation has been widely applied by many different researchers in the same field for assessing the thermodynamic efficiency of ED ([Feng et al., 2020](#); [Ma et al., 2019](#); [Yang et al., 2022a, 2022c](#)).

$$\eta = \frac{LW}{W_{\min} + LW} \quad (9)$$

$$W_{\min} = \sum_{\text{out}} n(h - T_{\text{ambient}}s) - \sum_{\text{in}} n(h - T_{\text{ambient}}s) \quad (10)$$

$$LW = W_{\min} + \left\{ \sum_{\text{in}} \left[Q \left(1 - \frac{T_{\text{ambient}}}{T_{\text{steam}}} \right) + W_s \right] - \sum_{\text{out}} \left[Q \left(1 - \frac{T_{\text{ambient}}}{T_{\text{steam}}} \right) + W_s \right] \right\} \quad (11)$$

where LW and $W_{\min}$ are the lost work and minimum required work given in kJ hr⁻¹, n represent the molar flow rate in kmol hr⁻¹, h and s represent the enthalpy and entropy for the input and output streams given in kJ kmol⁻¹ and kJ kmol⁻¹ K⁻¹, T_{steam} is the temperature of steam given in K, W_s is the shaft work for crossing the boundary of the system given in kJ.

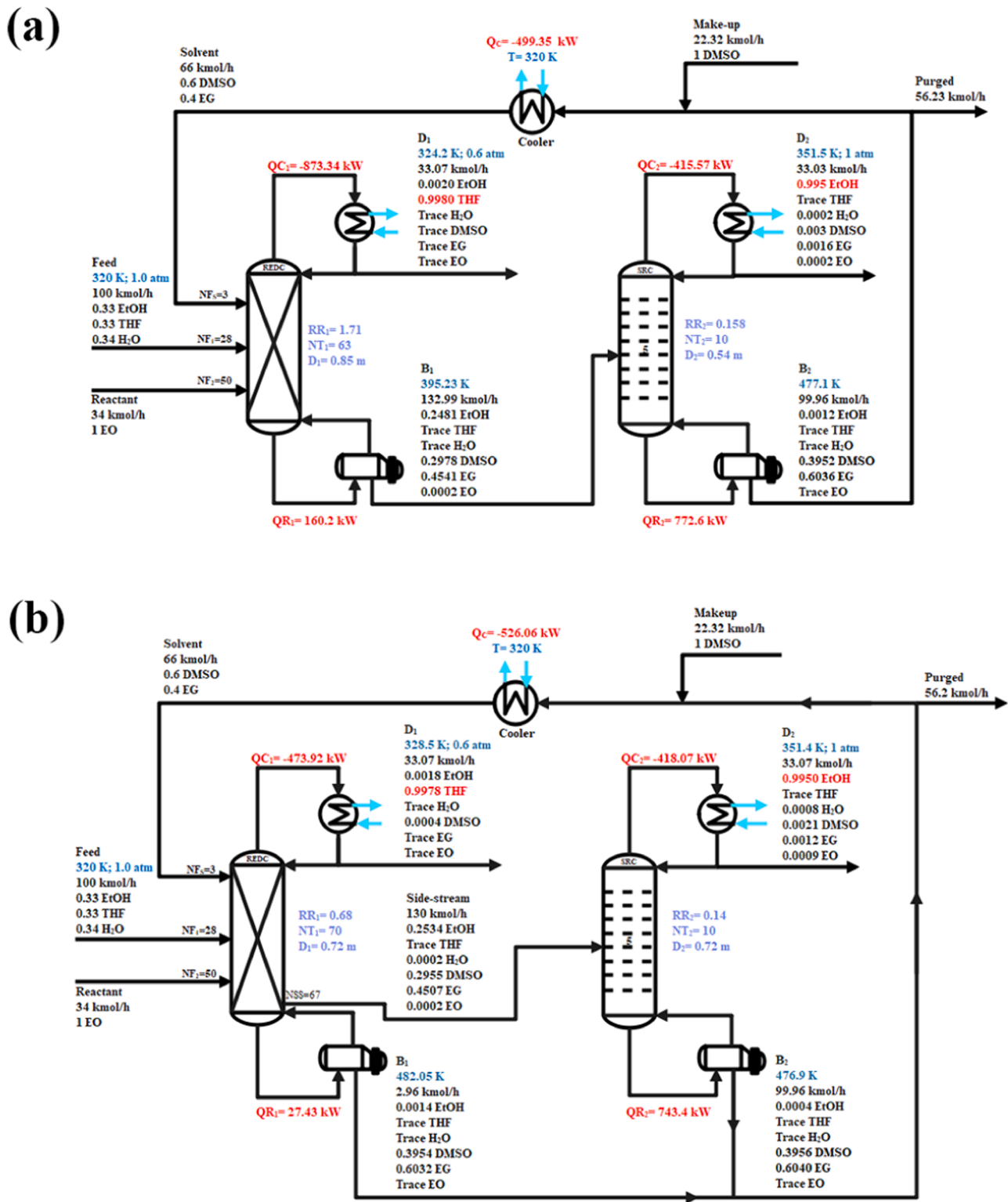


Fig. 5. Conceptual design for (a) DCRED and (b) SS-DCRED using mixed entrainer.

4. Results and discussion

4.1. Initial design for DCRED and SS-DCRED

The process flow diagrams for the initial DCRED and SS-DCRED design using mixed entrainer are depicted in Fig. 5. Relative to the pure entrainer case (Fig. 2), the DCRED using mixed entrainer (Fig. 5 (a)) provides 18 % reduction in the reboiler energy, which translates to a

reduction in TAC by about 12 %, as indicated in [Table 1](#). Such reduction was mainly attributed to the decrease in reboiler energy in the REDC. Other than that, the reboiler temperatures of both processes (i.e. DCRED using pure entrainer from literature ([Fig. 2](#)) and initial DCRED design using mixed entrainer ([Fig. 5\(a\)](#))) are analogous, which requires the same steam grade as heating utility and thus, there are no significant differences contributed to the operation cost caused by the difference in steam grade between both processes. The SS-DCRED ([Fig. 5\(b\)](#)) further

Table 1

Result summary between the initial design using mixed entrainer against using pure EG as entrainer from the work of Zhang et al. (2021).

Entrainers	Literature	This work	
	EG	60 % DMSO + 40 % EG	
Type	DCRED	DCRED	SS-DCRED
Total reboiler energy (kW)	1136.3	932.8 (−18 %)	770.8 (−32 %)
Total steam cost (\$10 ³ yr ^{−1})	306.39	255.46 (−17 %)	219.334 (−28 %)
TAC (\$10 ³ yr ^{−1})	581.95	511.56 (−12 %)	422.86 (−27 %)
Conditional Number (CN)	5979	50456 (+744 %)	8350 (+40 %)
Inherent Safety (10 ^{−5})	9.67	9.15 (−5 %)	7.98 (−17 %)
El-99 (Million)	0.340	0.237 (−30 %)	0.230 (−32 %)
CO ₂ emissions (kg yr ^{−1})	384.13	315.33 (−18 %)	263.32 (−31 %)
Thermodynamic efficiency (%)	10.48	18.76 (+79 %)	34.04 (+225 %)

reduces the energy consumption and TAC, both by about 17 %. Such reduction can be attributed to the decrease in remixing effect as observed in the composition profile given in Fig. 6. In the SS-DCRED, a side-stream is employed to transfer maximum amount of ethanol from REDC to SRC to eliminate the remixing effect, and the location of side-stream must be below stage 50 or otherwise the side-stream would contain some of the unreacted water. In the initial design of the SS-DCRED, stage 67 of REDC was selected since the purity of ethanol is the highest in REDC whilst the purity drops marginally when it is at the bottom of the REDC. Such finding aligned with the previous study (Lyu

et al., 2021). Altogether, the initial SS-DCRED design using mixed entrainer (Fig. 5(b)) provides a lower energy consumption and TAC by about 32 % and 27 %, respectively, with respect to the DCRED using pure entrainer (Fig. 2).

Then, it is worth noting that Zhang et al. (2021) had explored the possibility of reducing the energy consumption of the DCRED using pure entrainer by implementing a feed-effluent heat-exchanger, instead of using the energy-intensified side-stream configuration. Their simulation results reveal that the implementation of two feed-effluent heat-exchanger provides significant reduction to the energy consumption. Although the implementation of two additional heat-exchanger units has resulted in an increase in the total capital cost, the overall TAC for the heat-integrated DCRED is much lower than that without heat-integration. A direct comparison was made between the initial SS-DCRED design using mixed entrainer against the heat-integrated DCRED using pure entrainer from the work of Zhang et al. (2021). It was demonstrated that our initial SS-DCRED design provides a slightly lower TAC by about 2 %, even without the implementation of the feed-effluent heat-exchanger. In fact, the feed-effluent heat-exchanger can also be implemented to the proposed process in this work to facilitate greater energy savings. Here, it is not our intention to declare that our proposed process is superior to the heat-integrated DCRED from the work of Zhang et al. (2021), but our intention here is to present an alternative configuration for designer's consideration.

Other than economic indicator, the environmental impact also shows considerable improvement where the initial DCRED design using mixed entrainer provides 30 % lower environmental impact as reflected by the

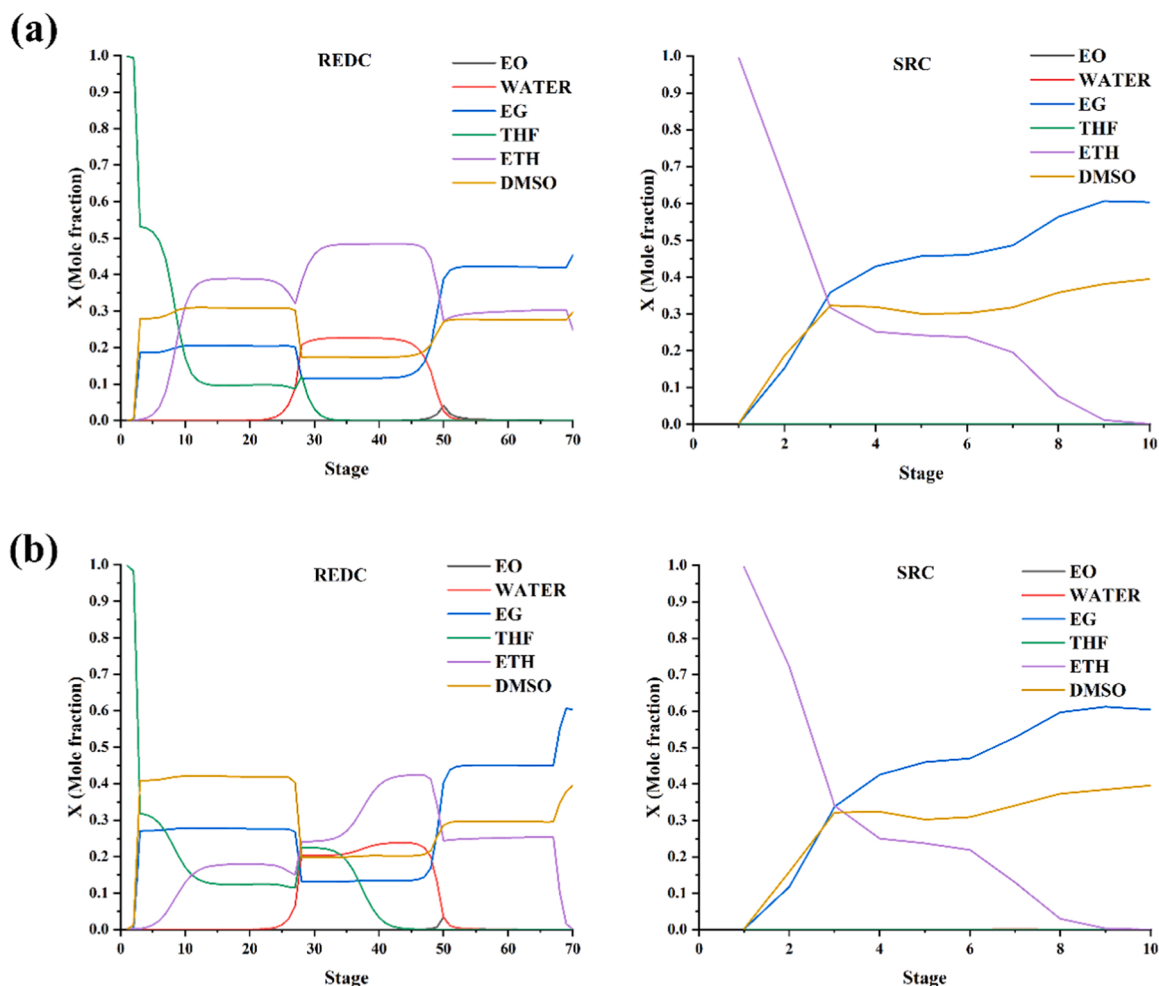


Fig. 6. Composition profile for REDC and SRC for the initial design of (a) DCRED using mixed entrainer and (b) SS-DCRED using mixed-entrainer.

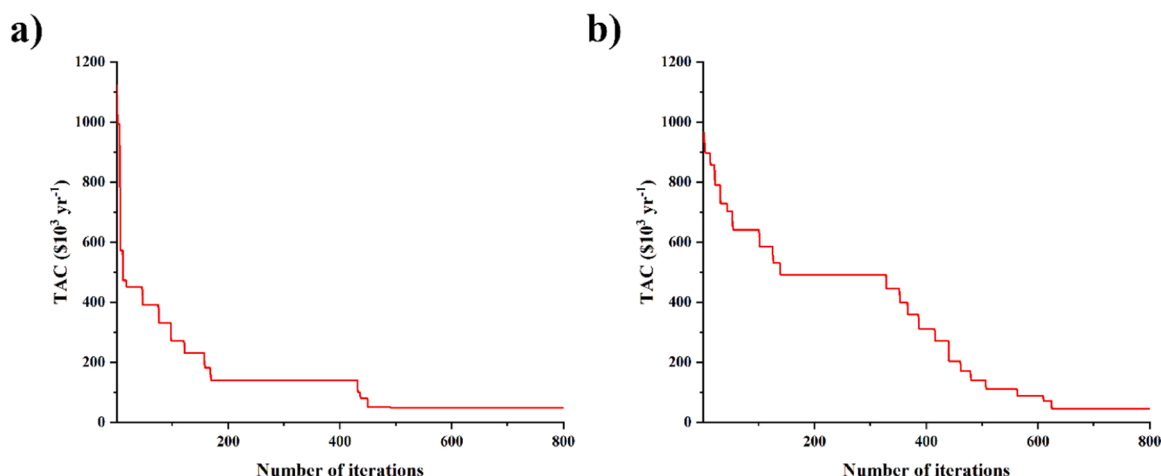


Fig. 7. Optimisation results of the (a) DCRED and (b) SS-DCRED using the PSO algorithm.

lower EI-99 value. Such improvement, upon meticulous analysis, was mainly attributed to the decrease in the total steam usage and the reduction in the overall energy consumption in the case of using mixed entrainer relative to the pure entrainer. Subsequently, the initial SS-DCRED design using mixed entrainer provides further improvement on the environmental impact by about 3 %, as it further lowers the energy consumption and steam utility consumption. Overall, the environmental impact of the initial SS-DCRED design using mixed entrainer provides 32 % improvement in comparison to the DCRED using pure entrainer, contributed by the beneficial combination between the decrease in reboiler energy by 32 % and the steam cost by about 28 %. In addition to the EI-99, the CO₂ emissions when using mixed entrainer decreases by about 18 % in comparison to using pure entrainer (Table 1). Further application of side-stream configuration provides additional 16 % reduction in CO₂ emissions and altogether, the CO₂ emissions for the initial SS-DCRED design using mixed entrainer decreases by 31 % relative to the pure entrainer. Such improvement again can be mainly attributed to the decrease in the energy consumption by about 32 %, as the CO₂ emissions is interlinked to the energy consumption as indicated by Eq. (5) and Eq. (6).

The safety index of the initial DCRED design using mixed entrainer is similar to that of the pure entrainer, albeit to a slightly lower extent by about 5 % (Table 1). Upon careful analysis on the safety index, it was observed that the marginal improvement is mainly due to the decrease in the toxic release incident. Other than the toxic release, the BLEVE and UVCE also contributed to the safety index improvement. The inherent risk caused by the flash fire for the proposed case remains analogous to that of the pure entrainer as the concentration was found to be outside the lower flammability limit (LFL) and upper flammability limit (UFL) and thus, there are no probability of affectation. Next, the initial SS-DCRED design provides further reduction to the safety impact by about 13 % (Table 1). Altogether, the safety impact of the initial SS-DCRED design using mixed entrainer (Fig. 5(b)) provides 17 % improvement relative to the DCRED using pure entrainer (Fig. 2). This can be mainly attributed to the decreasing risk of toxic release, which is strongly correlated to the total mass of instantaneous release (Equation (S6)). The total mass of instantaneous release, on the other hand, is strongly associated to the mass of reboiler (i.e. reboiler flowrate) (Equation (S11)) and because most of the product (i.e. ethanol) and entrainer are transferred via side-stream in the case of SS-DCRED using mixed entrainer (Fig. 5(b)), instead of from the bottom of the column as in the case of DCRED using pure entrainer (Fig. 2), the flowrate of the reboiler in the case of SS-DCRED reduced significantly. To further improve the inherent safety, we recommend future study to explore on the potential application of integrating the REDC and SRC as one to become a dividing-wall configuration, as previous study have reported

that reducing the number of equipment pieces generally translate to a lower probability of catastrophic event, subsequently decreases the inherent safety of the proposed process (Sánchez-Ramírez et al., 2022).

In terms of theoretical control, the condition number of the initial DCRED design using mixed entrainer is higher than that of the pure entrainer, which generally signifies a more complicated dynamic characteristic (i.e. complex operational controllability) (Table 1). This is consistent with previous publication by Luyben (2008) that conjectured the changes in thermodynamic properties (e.g. VLE) between different entrainers (i.e. in this case the changes between the pure and mixed entrainer) affect the dynamic controllability of the system. Another possible explanation is that the initial design using mixed entrainer (i.e. DCRED or SS-DCRED) are retrofitted from that of pure entrainer and therefore, the column specifications (e.g. total number of stages) for all the three configurations are identical. In essence, although retrofitting the conventional system may increase the energy efficiency and TAC, the control properties of the intensified system may be worsened or remain similar. This is since the column properties such as total number of stages, feed and entrainer stage locations, and column diameter are associated with a specific composition mixture that impact the dynamic controllability of a process. Thus, by keeping the same configurations while changing the feed flow or composition, one cannot guarantee that the control properties remain identical since the system is no longer at its optimum design. Note that most of the previous studies that show improvement in control properties are those that had undergone optimisation rather than retrofitting (Cabrera-Ruiz et al., 2017; Santaella et al., 2017; Vázquez-Castillo et al., 2015). Therefore, it appears that keeping the same column configuration (i.e. retrofit) while changing the feed (i.e. entrainer) composition degrades the operational controllability.

In terms of thermodynamic efficiency, the initial DCRED design using mixed-entrainer provides improvement by about 79 % relative to the pure entrainer. Such improvement can also be attributed to the decrease in the reboiler energy, which decreases the minimum required work (Eq. (9) to Eq. (11)). For the same reason, the application of energy-intensified side-stream configuration (i.e. initial SS-DCRED design) provides extra improvement of 81 % in thermodynamic efficiency.

Altogether, both the initial DCRED and SS-DCRED design using mixed entrainer provides significant enhancement in most of the sustainability indicators with respect to using pure entrainer, which generally signifies the feasibility of using mixed entrainer in the reactive-extractive distillation. In comparison to the initial DCRED design using mixed entrainer, the initial SS-DCRED design using mixed entrainer provides better economic, environmental, safety, and thermodynamic efficiency performances in comparison to the DCRED using

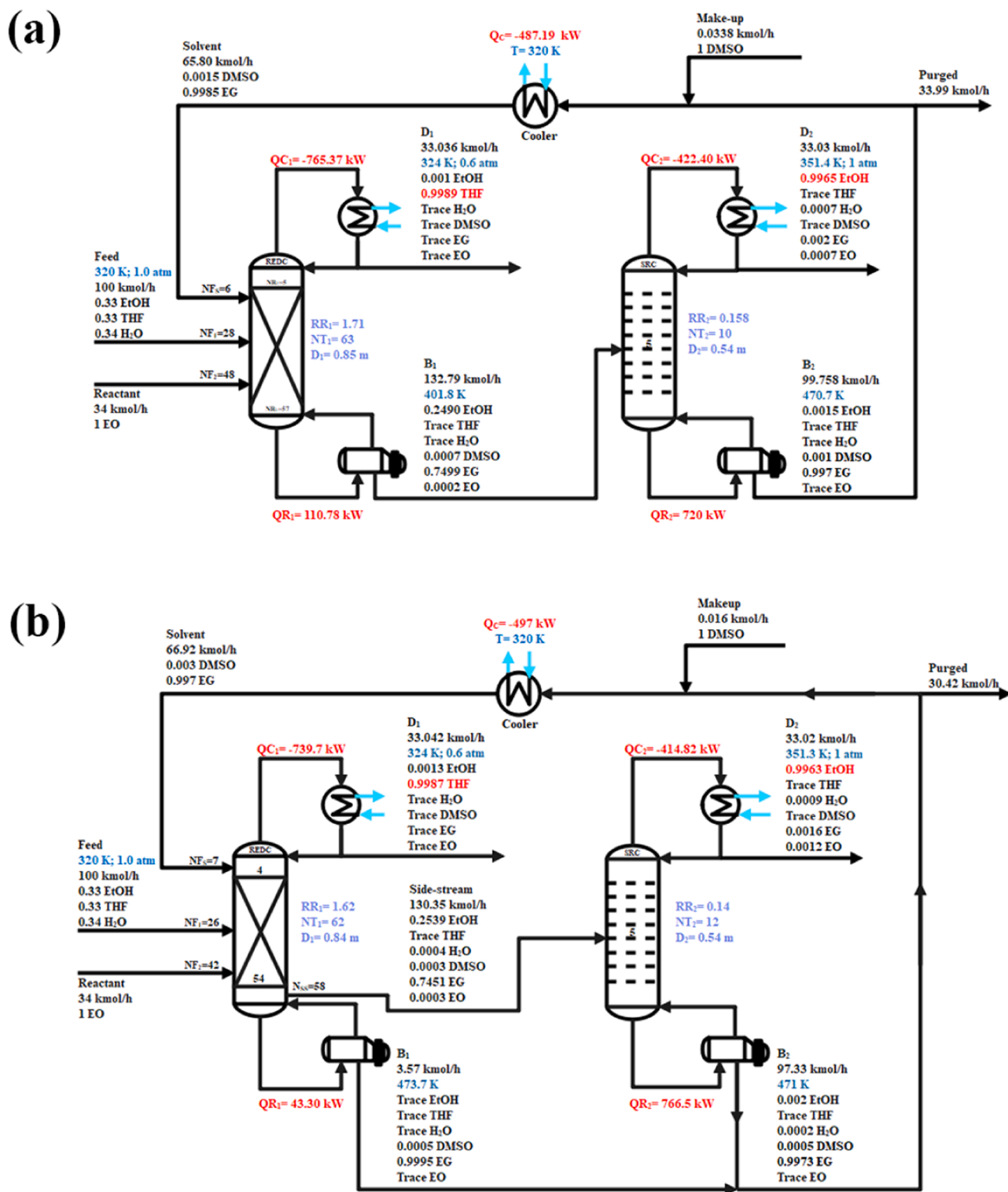


Fig. 8. Optimised (a) DCRED and (b) SS-DCRED using mixed entrainer.

pure entrainer by about 27 %, 32 %, 17 %, and 225 %, respectively. Such benefits however were traded-off by an increase in the dynamic controllability by about 40 % relative to the DCRED using pure entrainer. These results are similar to those observed in several existing studies where the energy-intensified configurations provide considerable improvement to all the sustainability indicators but was achieved at an expense of an increase in the condition number, which translates to an undesirable impact to the operational controllability of the process

(Sánchez-Ramírez et al., 2022, 2021). Another limitation of the initial design lies in the fact that some of the DMSO entrainer was unintentionally purged out of the system due to the nature of the configuration (Fig. 5), subsequently leading to a higher DMSO make-up rate required by the system. Note however that the DMSO make-up cost is not considered in the initial design stage in this section (Table 1, Section 4.1). Accounting for the DMSO make-up cost, the TAC of the initial DCRED and SS-DCRED using mixed entrainer will increase

Table 2

Result summary between the optimised design using mixed entrainer against using pure EG as entrainer from the work of Zhang et al. (2021).

	Literature	This work (After optimisation)	
Entrainer	EG	0.15 % DMSO + 99.85 % EG	0.3 % DMSO + 99.7 % EG
Type	DCRED	DCRED	SS-DCRED
Total reboiler energy (kW)	1136.3	830.77 (–27 %)	809.8 (–29 %)
Total steam cost (\$10 ³ yr ^{–1})	306.39	229.5 (–25 %)	230.4 (–25 %)
Total entrainer cost (\$10 ³ yr ^{–1})	n/a	46.44	21.85
TAC (\$ Million yr ^{–1})	581.95	490.86 (–16 %)	462.3 (–21 %)
Conditional Number (CN)	5979	5601.93 (–6 %)	199.58 (–97 %)
Inherent Safety (10 ^{–5})	9.67	7.93 (–18 %)	7.84 (–19 %)
EI-99 (Million)	0.340	0.248 (–27 %)	0.241 (–29 %)
CO ₂ emissions (kg yr ^{–1})	384.13	280.85 (–27 %)	273.76 (–29 %)
Thermodynamic efficiency (%)	10.48	21.2 (+102 %)	20.99 (+100 %)

tremendously by 6000 % and 7259 %, respectively, owing to the unreasonably high amount of mixed entrainer make-up cost. This is since the entrainer ratio used in the initial design in this section was merely extracted directly from previous work (Zhao et al., 2017b) as our intention here was to preliminary analyse the feasibility of using mixed entrainer in the reactive-extractive distillation system to improve the sustainability performance of the THF/ethanol/water recovery process. The proposed process deemed feasible will be subjected to process optimisation in the subsequent section (Section 4.2) to obtain the optimum entrainer ratio that provides the minimum TAC.

4.2. Optimised design for DCRED and SS-DCRED

In this section, the initial DCRED and SS-DCRED design from Section 4.1 is further optimised using the PSO algorithm, and the result is given in Fig. 7, with the optimised column parameters depicted in Fig. 8.

In comparison to the initial DCRED design, the optimised DCRED using mixed entrainer provides further improvement in all sustainability aspects where the energy-consumption, TAC, conditional number, inherent safety, EI-99, and CO₂ emissions reduces by 11 %, 4 %, 89 %, 13 %, 5 %, and 11 %, respectively. The thermodynamic efficiency additionally increases by about 13 %. Here, one important highlight is that the new entrainer ratio for the optimised DCRED is 99.85 mol. % EG + 0.15 mol. % DMSO, which minimises the amount of DMSO entrainer purge rate out of the system and subsequently, reduces the DMSO top-up rate required by the system. This further leads to a lower entrainer make-up cost in comparison to the initial design, which leads to the overall reduction in TAC by about 4 % (Table 2) even after accounting for cost of DMSO make-up. Although the amount of DMSO required appears to be marginal, which may not improve the separation performance significantly, it is important to note that the relative volatility using DMSO is much larger than using EG for separation of THF/ethanol azeotrope, as reported by many existing studies (Zhao et al., 2018, 2017b). Therefore, introducing the DMSO into the separation system further enhances the separation between THF and ethanol that takes place in the REDC. Other than that, it was observed that the total number of stages in the REDC reduces from 70 stages to 63 stages after optimisation, which translates to the reduction in total capital cost.

From Table 2, it was also observed that the optimised DCRED provides considerable improvement on the environmental performance where the EI-99 and CO₂ emissions are further reduced by additional 5 % and 11 %, respectively, relative to the initial design. This was mainly due to the decrease in total steam usage and overall energy consumption in both columns. In terms of inherent safety, the optimised DCRED provides significant improvement by about 13 % relative to the initial

design and this is mainly attributed to the decrease in the toxic release incident since the instantaneous mass release for the optimised DCRED is lower than that in the initial design. For the theoretical control, the condition number of the optimised design is 89 % better than the initial design, owing to the fact that the column configuration is now at their optimum design. Such finding aligned with previous studies, which reveals that optimising the process instead of retrofitting generally provides significant improvement to the control properties (Cabrera-Ruiz et al., 2017; Santaella et al., 2017; Vázquez-Castillo et al., 2015). Lastly, the optimised DCRED also provides 13 % improvement in the thermodynamic efficiency with respect to the initial design and such improvement again was attributed to the decrease in the reboiler energy, which decreases the minimum required work (Eq. (9) to Eq. (11)).

Table 2 also shows the performance of the optimised SS-DCRED where the energy-consumption, TAC, conditional number, inherent safety, EI-99, and CO₂ emissions are further reduced by 3 %, 6 %, 96 %, 1 %, 3 %, and 3 %, respectively, which reflect its outstanding sustainability characteristic. The entrainer ratio for the optimised SS-DCRED (Fig. 8(b)) was found to be 99.7 mol. % of EG + 0.3 mol. % DMSO, in which the amount of DMSO entrainer purge rate out of the system is minimised. Identical to the case of optimised DCRED, this low DMSO entrainer purge rate translates to a lower DMSO top-up rate required by the system, leading to a lower entrainer make-up cost in comparison to the initial design. Then, the optimised SS-DCRED (Fig. 8(b)) also provides a lower total number of stages in the REDC, which translates to reduction in total capital cost, analogous to the case of optimised DCRED (Fig. 8(a)).

Relative to the optimised DCRED (Fig. 8(a)), the optimised SS-DCRED (Fig. 8(b)) reduces the EI-99 and CO₂ emissions further by 3 % and 1 % and these improvements were mainly contributed by the decrease in reboiler energy, as the environmental impact is closely associated to the energy consumption, given by Eq. (4) and Eq. (5). The inherent safety of the optimised SS-DCRED provides marginal improvement by about 1 % relative to the optimised DCRED. Similar to the optimised DCRED, this again was mainly due to the decrease in the toxic release incident as a result of the decrease in the instantaneous mass release for the optimised SS-DCRED. Moreover, the total mass of instantaneous release is also strongly correlated to the mass of reboiler (i.e. reboiler flowrate) (Eq. (S11)). Since most of the product (i.e. ethanol) and entrainer are transferred via side-stream in the case of SS-DCRED (Fig. 8(b)) instead of from the bottom of the column as in the case of DCRED (Fig. 8(a)), the flowrate of the reboiler in the case of SS-DCRED decreases tremendously. The conditional number of the optimised SS-DCRED is improved further by 96 % with respect to the DCRED, which represent better operational controllability for the proposed process. This again was attributed to the fact that the column configuration has now been optimised and it is at their optimum configuration. Lastly, it should be noted that all the benefits obtained by using the optimised SS-DCRED are traded-off by the marginal decrease in thermodynamic efficiency of about 1 %. Such finding aligned with previous study, which reported that the thermodynamic efficiency of the energy-intensified reactive-extractive distillation (e.g. dividing wall) is lower, because the reboiler of both the REDC and SRC now requires high-pressure steam as heating utility instead of the low or medium-pressure steam as in the case of conventional reactive-extractive distillation (Liu et al., 2022; Yang et al., 2022c).

Overall, the optimised SS-DCRED design using mixed entrainer provides better sustainability performance in terms of economic, environmental, safety, and control aspects in comparison to the optimised DCRED but these benefits are traded-off by the marginal decrease in the thermodynamic efficiency. Here, it is also important to note that the both the DCRED and SS-DCRED required a lower DMSO entrainer rate of 0.15 % and 0.3 %, respectively, in comparison to the initial design (Section 4.1) that has high DMSO purge rate, which leads to a higher DMSO make-up rate and a higher make-up cost required by the system. Nonetheless, it is important to reiterate that the entrainer ratio used in

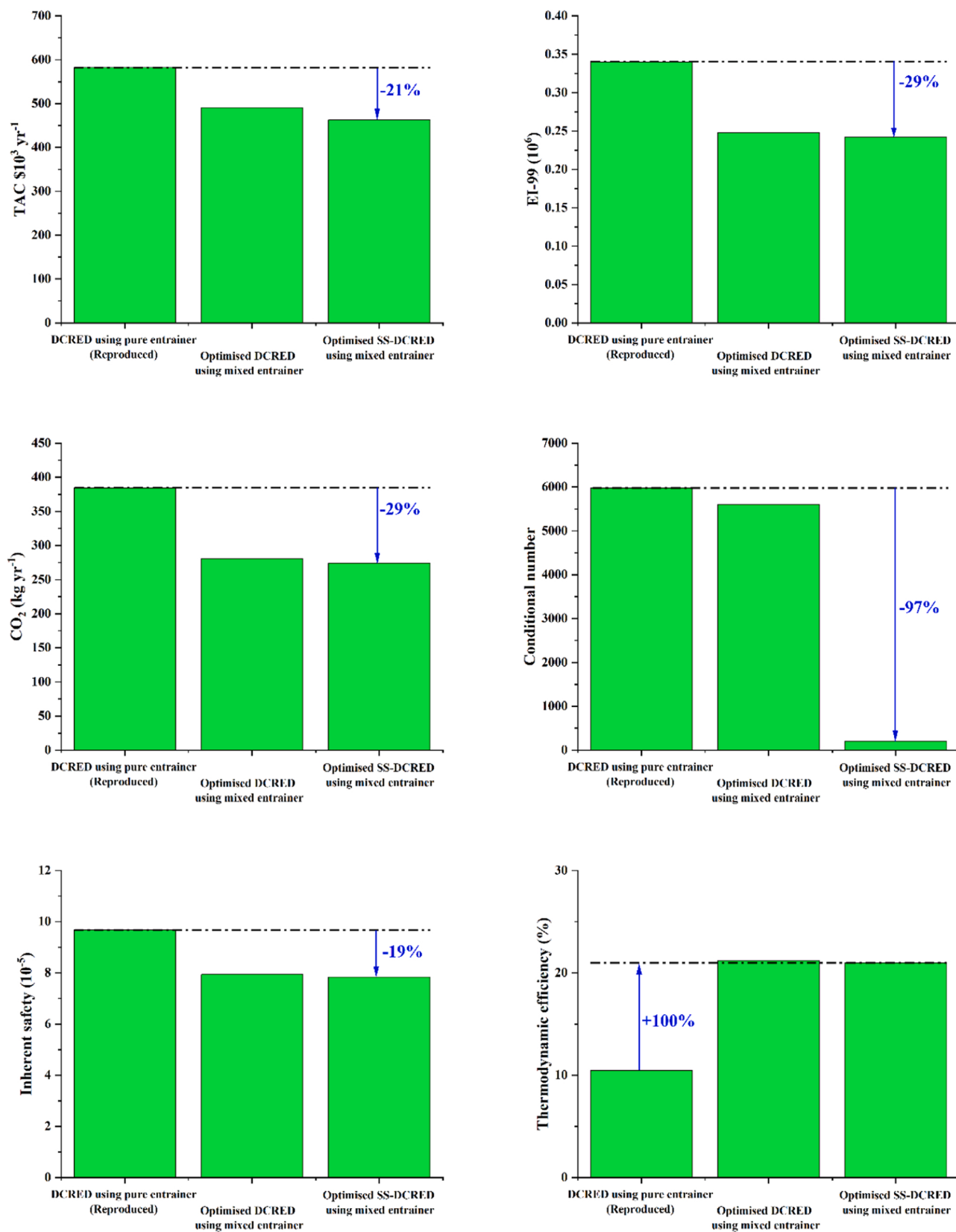


Fig. 9. Result comparison between the different processes proposed in this work against previous work.

the initial design (Section 4.1) was obtained directly from previous work (Zhao et al., 2017b) for the sake of preliminary analysing the feasibility of using mixed entrainer in the reactive-extractive distillation system for improving the sustainability performance of the THF/ethanol/water recovery process.

4.3. Result summary

In summary, both the optimised DCRED and SS-DCRED using mixed entrainer provides better sustainability performance relative to using pure entrainer as in previous work. Fig. 9 summarised the result comparison between the optimised DCRED and SS-DCRED processes using mixed entrainer against the DCRED using pure entrainer from previous work (Zhang et al., 2021). Overall, the optimised SS-DCRED is the most sustainable process where the TAC reduces by 21 %. In addition, the optimised SS-DCRED also provides better environmental aspect, as evident by the reduction in EI-99 and CO₂ emission, both by about 29 % relative to the DCRED using pure entrainer. Other than that, the inherent safety and the conditional number of the of the optimised SS-DCRED are 19 % and 97 % lower than the DCRED using pure entrainer, respectively, which reflects the operational safety reliability and dynamic flexibility (i.e. good operational control) of the proposed process. Lastly, the thermodynamic efficiency of the optimised SS-DCRED improved by about 100 % relative to the DCRED using pure entrainer.

5. Conclusion

In conclusion, we explored the possibility of integrating the beneficial features from the existing studies, i.e. the usage of mixed entrainer and the hybrid reactive-extractive distillation for improving the sustainability of the ternary azeotropic separation containing THF/ethanol/water. The conceptual design of the DCRED using mixed entrainer was initially designed followed by retrofitting to an energy-intensified SS-DCRED. The two processes were initially compared against the DCRED using pure entrainer from previous work based on five different sustainability metrics, i.e. economic (TAC), environmental (EI-99), safety (inherent safety index), operational controllability (condition number), and thermodynamic efficiency. Although both the initial designs were found to provide significant improvement in economic, environmental, safety, and thermodynamic efficiency, the dynamic controllability for both designs deteriorate due to the increase in condition number. Another major limitation is that the initial design requires unreasonably high amount of DMSO make-up rate, which resulted in both initial designs not economically attractive. This was mainly attributed to the fact that the entrainer ratio was obtained directly from previous work for the sake of preliminary analysis. These limitations however are consistent with previous publication, where the improvement in sustainability are normally achieved at an expense of an increase in the economics. Therefore, both the initial design was further optimised using PSO and it was revealed that the optimised SS-DCRED using mixed entrainer provides the best sustainability performance where the economic, dynamic controllability, safety, environmental, and thermodynamic efficiency are enhanced by 21 %, 97 %, 19 %, 29 %, and 100 %, respectively, in comparison to the pure entrainer. For future work, the concept of using mixed entrainer can be extended to separation and recovery of other mixtures or to explore on the reactive-extractive dividing wall column using mixed entrainer that may potentially reduce the overall installation space (i.e. land) required by the process plant, which in turn generates significant savings in the capital cost that leads to a lower TAC. In addition, future work can also consider multi-optimising all the green indicators so they can be evaluated simultaneously to ensure all the indicators are at their optimum point.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.psep.2022.08.056.

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