

Towards sustainable separation and recovery of dichloromethane and methanol azeotropic mixture through process design, control, and intensification

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Abstract

Background: Here we analysed the possibility of improving the sustainability performance for the recovery of dichloromethane and methanol from a binary azeotropic mixture using different energy-intensified extractive distillation-based processes: side-stream extractive distillation (SSED), thermally coupled extractive distillation (TCED), and extractive dividing wall column (EDWC). The sustainability performance of the different processes was analysed based on three main factors: total annual cost (TAC), CO₂ emissions, and condition number.

Results: The EDWC was found to give the best improvement in terms of TAC and CO₂ emissions by about 18% and 21%, relative to conventional extractive distillation (CED). These however were traded-off by the increase in conditional number (CN) by 186 times, signifying a complex dynamic characteristic for the EDWC. Thus, the SSED was suggested as an alternative sustainable option as it also provides significant improvement in TAC and CO₂ emissions by about 11%, and 18% with respect to the CED, whilst providing the least reduction in operational controllability, as evidenced by the marginal increase in the CN of about 1.5 times. We also investigated the dynamic performance of the SSED and found that the SSED provides identical dynamic performance in handling both $\pm 10\%$ throughput and $\pm 5\%$ feed composition disturbances as those of the CED.

Conclusion: Among the different processes, SSED is the best sustainable alternative that provides compromised steady-state (i.e. TAC and CO₂ emissions) and dynamic (i.e. control) performance for the recovery of dichloromethane and methanol.

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Keywords: resource recovery; extractive distillation; binary azeotropic separation; energy-intensified techniques; design and control

INTRODUCTION

The COVID-19 pandemic wrought varying levels of devastation worldwide, forcing people to adjust their lifestyles to adapt to the crisis and new realities. The pandemic also affected various industries globally, benefiting some while disrupting, or even relegating, others in different ways. Among the different industries, the pharmaceutical sector across the globe is growing with the increase in self-awareness in human healthcare. For example, antibiotics production in the U.S.A. and Canada is expected to grow at a compound annual growth rate (CAGR) of 4.7%. Such a rate is projected to be triple in Asia than in the U.S.A. and Canada.¹ However, these surges in the pharmaceutical production capacity globally translate to a higher volume of effluent discharge. One such waste effluent is the binary mixture of dichloromethane and methanol that are commonly discharged from the manufacturing of prednisolone,^{2,3} which present potential threats to human health and environment.⁴⁻⁶ Therefore, proper separation is required to facilitate resource recovery and environmental protection. Extensive research efforts indeed have been directed towards recovering various components from waste effluents in the past few

decades, for sustainable operation and to comply with increasingly stringent environmental regulations.⁷⁻¹¹

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The binary mixture of dichloromethane and methanol contains a minimum boiling azeotrope when the dichloromethane purity is 86.13 mol% at atmospheric pressure, which means that the separation cannot be carried out efficiently using an ordinary distillation technique. Thus, special types of distillation techniques are needed to ensure efficient recovery of the two components, such as pressure swing distillation (PSD), azeotropic distillation (AD), and conventional extractive distillation (CED). To date, our literature survey has indicated that although there are myriad studies for the separation of different azeotropic mixtures using various special distillation techniques (the details of which have been made available in our review paper¹²), there are only two existing studies in the literature which worked on the separation process for the binary mixture containing dichloromethane and methanol. The first study³ relied on the pressure swing batch distillation (PSBD) with heat-integration for the separation of binary mixture whereas the second study¹ focused on the continuous distillation-based processes that includes PSD, AD, and CED, in an attempt to improve the separation efficiency of the PSBD from the first work.³ Analysing the results from both studies,^{1,3} it was revealed that the CED is the best process as it provides the lowest energy consumption and total annual cost (TAC) in comparison to the heat-integrated PSBD by about 5% and 27.62%, respectively. Likewise, the energy consumption and TAC for the CED is lower by about 55.8% and 35.86% relative to the conventional PSBD without heat integration. Moreover, the CED provides 52% and 31% lower energy consumption and TAC, respectively, relative to the AD whereas it is also 58% and 80% lower with respect to the HI-PSD. Other than the economic benefits, the CED also demonstrated superior dynamic performance, as evident by its capability for handling $\pm 10\%$ throughput and $\pm 5\%$ feed composition disturbances as reported in the previous work.¹

In order to further promote a sustainable (i.e. economical, environmentally friendly, and stable) purification and resource recovery processes, various recent studies have relied on the application of different energy-intensified configurations such as thermally coupled (TC) and dividing wall column (DWC). For example, Sánchez-Ramírez *et al.* evaluated the sustainability of TC and DWC configurations for the purification of methyl-ethyl ketone based on economic, environmental, safe, and controlled performance.¹³ The same indicators also were employed by Amezcua-Ortiz *et al.* for assessing the energy-intensified TC and Petlyuk configurations for the purification of acetone.¹⁴ González-Navarrete *et al.* investigated on the application of process intensification such as TC, DWC, and Petlyuk, applied to the reactive distillation (RD) for sustainable purification of lactic acid, focusing on the economic viability, environmental impact, and inherent safety as the three main sustainability indicators.¹⁵ Bravo-García *et al.* compared the sustainability of energy-intensified TC and DWC for the recovery of valuable components from nylon industry effluents based on similar green metrics such as economics, environmental emissions, safety, and dynamic controllability.¹⁶ From these studies, it is clear that the economics, environmental impact, controllability, and process safety are important metrics that can reflect the characteristics of a sustainable process, which is consistent with several review papers in the existing literature.^{17–21} Associating these important metrics with the separation and recovery of azeotropic mixtures is of interest in this work, we realized that no existing studies have explicitly assessed the possibility of refining the sustainability of the extractive distillation (ED) process through the application of different energy-intensified configurations. To this end, we explore the

possibility of improving the CED for the separation and recovery of dichloromethane and methanol from a sustainable perspective.

The paper is arranged as follows. Section 2 provides a brief description on all the energy-intensified processes studied in this work, to provide our readers with a clearer understanding of the process flow diagram. Section 3 elucidates the methodology for steady-state and dynamic simulation employed in this work, and elaborates on the indicators used to evaluate the sustainability performance of the different proposed processes. The results of the steady-state and dynamic simulations are discussed in Section 4, whereas Section 5 wraps up this work by summarising the main findings and providing recommendations for future work.

PROCESS DESCRIPTION

The process flow diagram for the CED reproduced from a previous work is given in Figure 1.¹ The feed containing the binary azeotropic mixture of dichloromethane and methanol enters the extractive distillation column (EDC) together with the dimethylformamide (DMF), which acts as a solvent that alters the relative volatility of binary components in the mixture. The high-purity dichloromethane is obtained from distillate (D1) of the EDC whereas the remaining components, which include methanol and DMF are directed to the solvent recovery column (SRC) for subsequent separation. In the SRC, high-purity methanol is obtained from the distillate (D2) whereas the regenerated DMF is obtained at the bottom of SRC (B2) and subsequently is cooled before it is recycled back to the EDC. Some of the solvent that is lost during the distillation processes in the EDC and SRC are compensated via a make-up flowrate.

METHODOLOGY

Figure 2 graphically illustrates a general overview of the methodology employed in this work. Step 1 simulates three different energy-intensified processes: side-stream extractive distillation (SSED), thermally coupled extractive distillation (TCED), and extractive dividing wall column (EDWC). In Step 2, the sustainability of all the three processes are compared against the CED from previous work¹ based on economic, environmental, and theoretical control perspectives. The most sustainable (i.e. best) process that provides the most compromised improvement on all three sustainable indicators is selected for subsequent dynamic simulation in Step 3, to further warrant the absence of trade-off between the proposed and the conventional processes.

Steady-state design

Solvent selection

Before the steady-state simulation, we first explored the performance of using different solvents in CED for the separation and recovery of dichloromethane and methanol. Although it has been demonstrated in previous work¹ that using DMF provides decent separation performance, it is not clear if there are other solvent which could provide better separation performance for the same separation mixture. Here, we compare the performance of DMF with some other common solvents used for ED, such as *N*-methyl-2-pyrrolidone (NMP),²² ethylene glycol (EG),²³ and dimethyl sulfoxide (DMSO).²³

Process simulation

The steady-state simulation for all of the energy-intensified processes proposed in this work was carried out using ASPEN PLUS v11. The RADFRAC module is used to represent the distillation

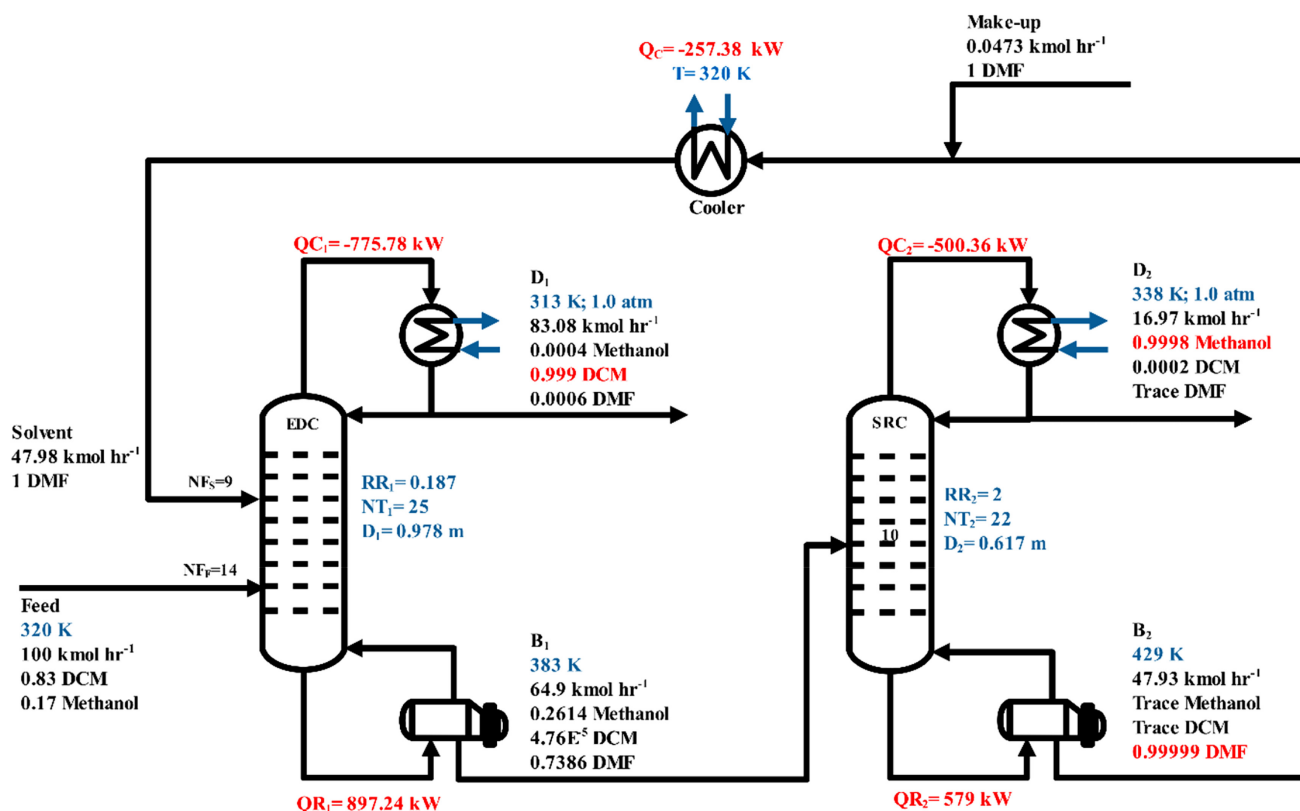


Figure 1. CED reproduced from previous work.¹

unit in ASPEN PLUS with the default sieve tray as the internal packing. The design variables such as the solvent-to-feed flowrate, total number of trays, feed tray locations, and the solvent feed temperature were considered in the previous work for the CED through DSTWU analysis and sensitivity based economic optimisation. In this work, the CED is reproduced from the previous work, and it is assumed that the reproduced CED is retrofitted to become a SSED and TCED. For the simulation of EDWC, the original EDC that contains 25 stages (Fig. 1) is combined with the SRC as upper part of the EDWC and thus, the number of stages for the SRC increases from 22 to 29 stages [as shown in Fig. 7(c)]. Such an integration methodology is analogous to previous work.²⁴ All of the simulation parameters such as feed flowrate, feed composition, column parameters, and thermodynamic package are the same as those in the previous study for the sake of fair economic comparison.¹ Any saving from the energy consumption can be directly reflected on the TAC. Note that such retrofitting-based simulation methodology was employed by the existing study.²⁴ The fresh feed flowrate is 100 kmol hr⁻¹ with 83 mol% dichloromethane and 17 mol% methanol, which is close to their azeotropic point. Here, we assume that the waste effluent contains only dichloromethane and methanol, which are of interest in this work, because this is only a preliminary study. Such an assumption has been used in many other similar publications in this area.²⁵⁻²⁷ The purity specification for the dichloromethane and methanol obtained from the distillate of EDC and SRC are 99.9 mol%. The thermodynamic properties package used in this work is NRTL (Table 1), which is identical to the previous work.¹ Note however that the NRTL parameters in this work are slightly different compared to previous work,¹ owing to the different versions of ASPEN PLUS used in both studies. It should be highlighted that the

accuracy of the thermodynamic properties is not discussed in this work, because this already had been verified in the previous study.¹

Sustainability evaluation

The sustainability of the different energy-intensified processes investigated in this work were evaluated based on economic, environmental, and theoretical control perspectives, which are represented by the TAC, CO₂ emissions, and conditional number (CN). Here, we limit ourselves to just these three indicators which will preliminarily represent the characteristic of a sustainable process, analogous to most of the existing studies that we reviewed in Section 1. A second (i.e. future) study may be conducted to include additional sustainability indicators such as social, safety, and thermodynamic efficiency, if any of the proposed configurations in the present work prove sustainable.

Economic parameters

In this work, the economics of the different proposed processes is assessed using the TAC, which is calculated using Eqn (1):

$$\text{TAC} = \frac{\text{TCC}}{\text{PP}} + \text{TOC} \quad (1)$$

The TCC and TOC are the total capital cost and the total operating cost, respectively, whereas PP refers to the payback period of 3 years. The TCC includes the cost of all main equipment in the plant such as the distillation column, reboiler, condenser, and cooler. The TOC involves the different pressurized steam and cooling water costs. The price for high-pressure steam (527 K), medium-pressure steam (457 K), and low-pressure steam are US

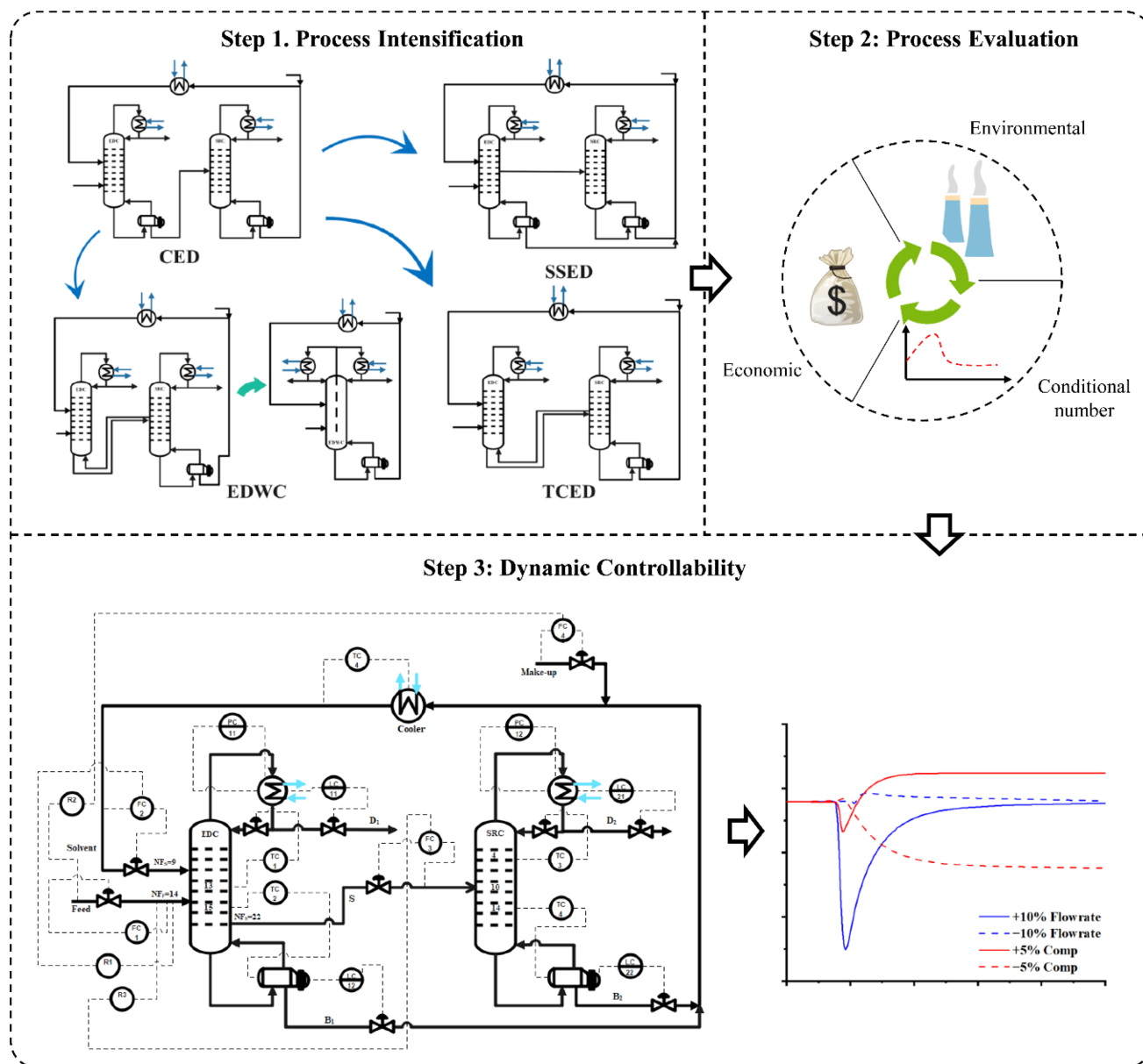


Figure 2. Overview of the methodology employed in this work.

Table 1. NRTL model parameters for separation of dichloromethane and methanol using DMF

Component <i>i</i>	Component <i>j</i>	A_{ij}	A_{ji}	B_{ij}	B_{ji}	Temp unit
Dichloromethane	Methanol	0	0	812.783	-102.531	°C
Dichloromethane	DMF	-2.74351	-9.44897	1401.15	3263.88	
Methanol	DMF	-0.501	-0.8325	712.266	-208.209	

\$9.88, 8.22 and 7.78 per GJ, respectively, whereas the price for cooling water is \$0.354 per GJ, analogous to previous works.^{23,28} The number of operating hours for all processes is 8000 h, identical to previous works.^{29,30} Figure 3 graphically summarised the formula for the TAC calculation used in this work, whereas more details on the calculations can be found in Douglas' book.³¹

Environmental parameters

The environmental impact of the different energy-intensified processes considered are analysed based on their CO₂ emissions, given by Eqn (2). Such an evaluation method has been used widely by existing studies in the same field on azeotropic separation using ED.³²⁻³⁴

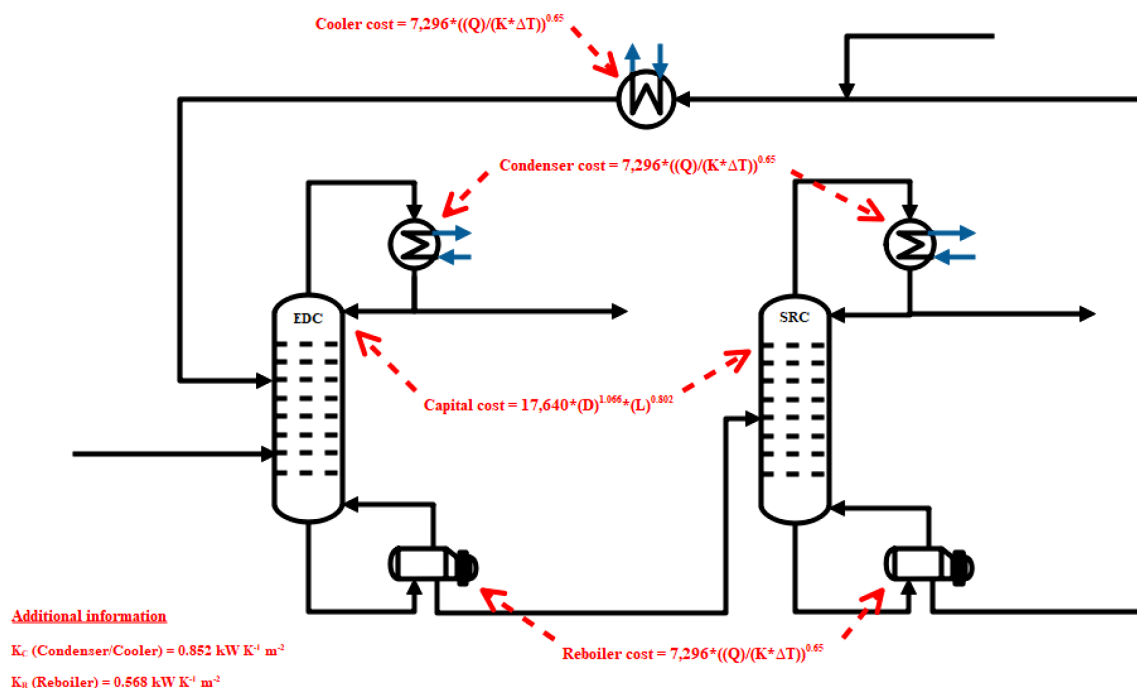


Figure 3. Economic basis for TAC calculations employed in this work.

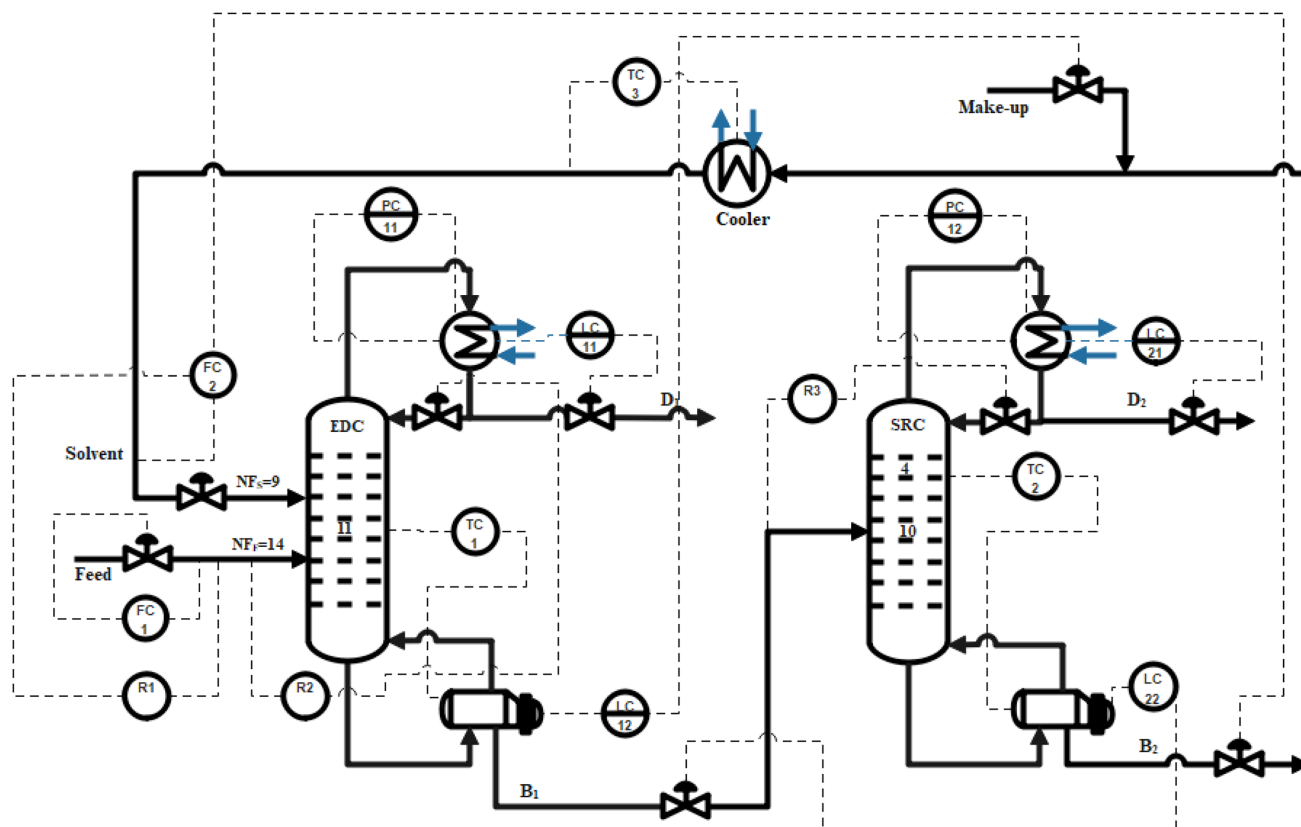


Figure 4. Inventory control loop employed in this work for the SSSED.

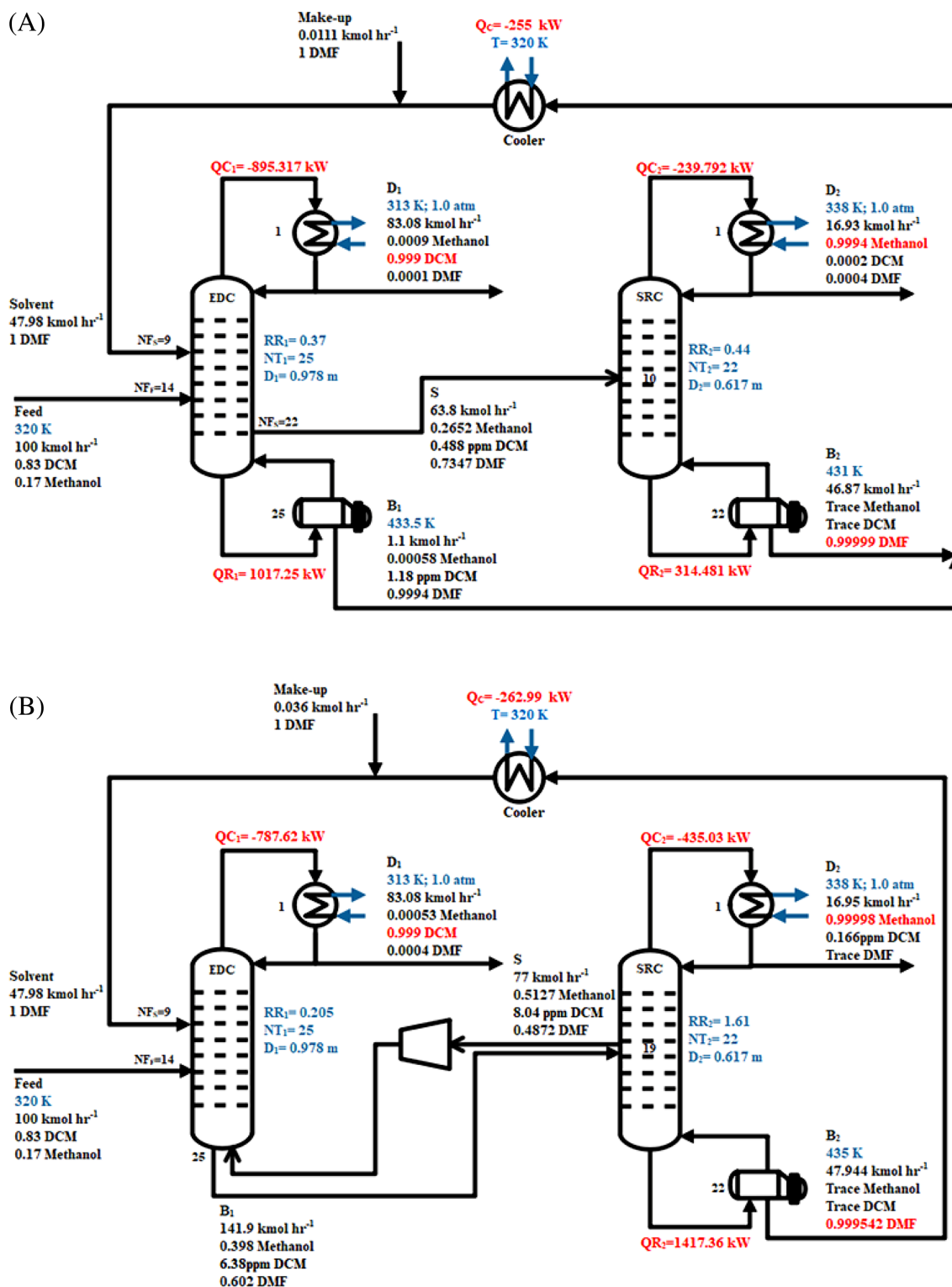


Figure 5. Control structure for CED (extracted from previous work¹).

$$\text{CO}_2 \text{ emissions} = \frac{Q_F}{\alpha} \times \frac{\omega}{100} \times \varphi$$

$$Q_F = \frac{Q_T}{\lambda_{\text{steam}}} \times (h_{\text{steam}} - 419) \times \left(\frac{T_{\text{flame}} - T_{\text{ambient}}}{T_{\text{flame}} - T_{\text{stack}}} \right) \quad (2)$$

Here, Q_F is the energy consumption of heavy oil fuel in kJ, Q_T represents the energy consumption of the reboiler duty in (kJ), α is the net heating value ($39\,881 \text{ kJ kg}^{-1}$), ω is the carbon content of the heavy oil fuel (86.5 kg kg^{-1}), λ_{steam} ($2083.47 \text{ kJ kg}^{-1}$), and h_{steam} ($2683.64 \text{ kJ kg}^{-1}$) are the latent heat and enthalpy of the steam, respectively; T_{flame}

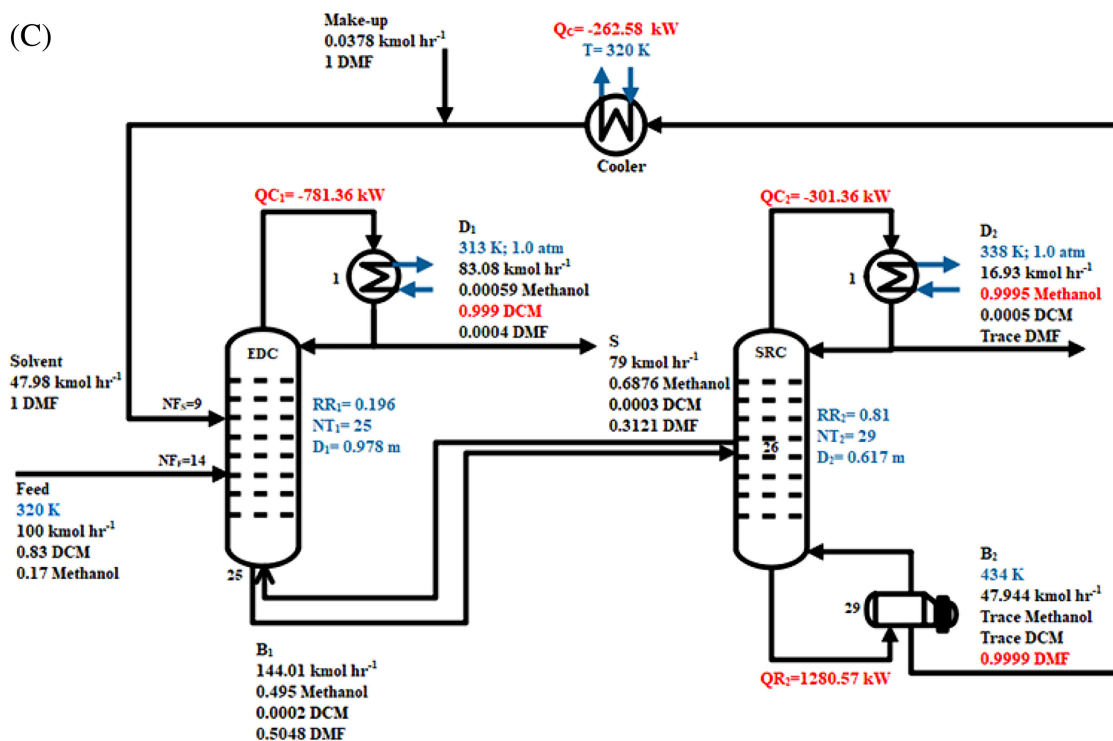


Figure 5 (Continued)

(2073.15 K), T_{ambient} (298.15 K), and T_{stack} (433.15 K) are the flame temperature, ambient temperature, and stack temperature, respectively. These parameters are identical to those presented in previous work.³²

Control properties

The controllability of the three different energy-intensified processes are preliminary evaluated using the CN. The CN provides preliminary insights on the sensitivity of the system under

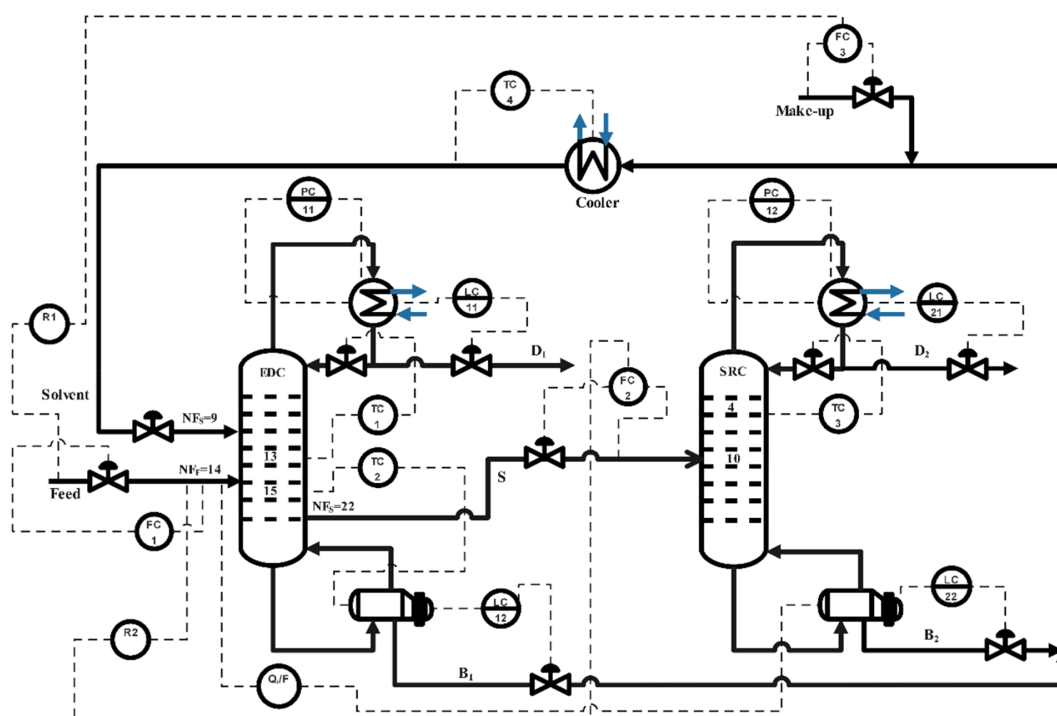


Figure 6. Effect of different entrainers on VLE of dichloromethane and methanol.

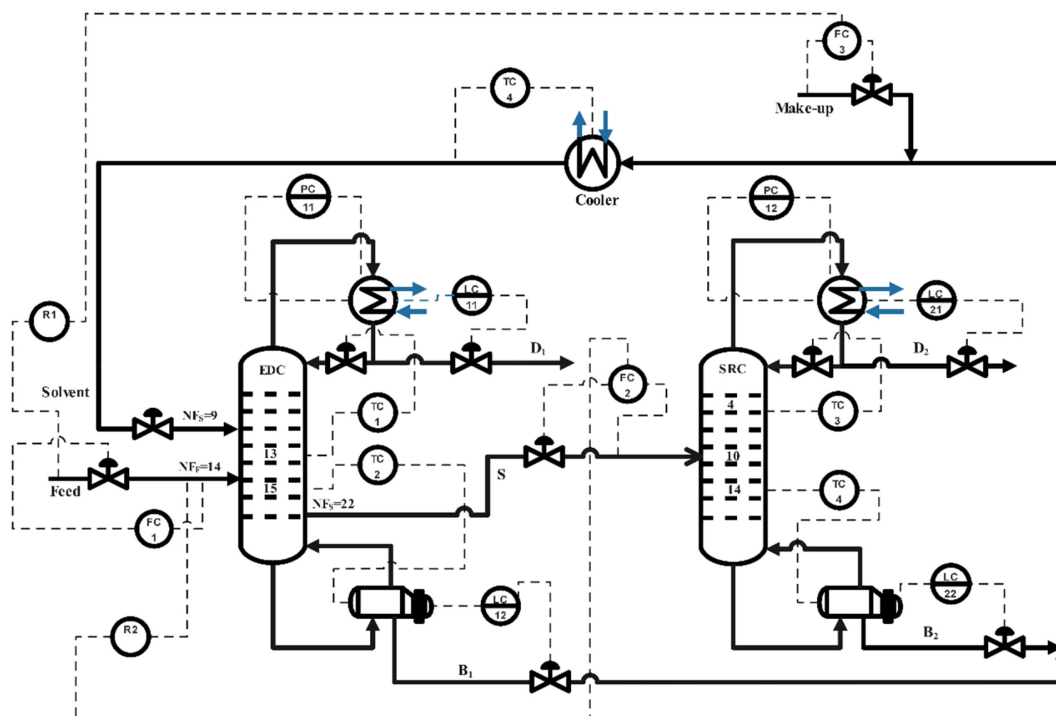


Figure 7. The proposed (A) SSED, (B) TCED, and (C) EDWC using DMF.

different uncertainties (e.g. throughput disturbances) and lay out the qualitative analysis on the theoretical control properties for the different energy-intensified processes considered. The CN (γ) is the ratio between the maximum ($\sigma^{\max}$) and minimum ($\sigma_{\min}$) singular values, given by Eqn (3).

$$\gamma = \frac{\sigma^{\max}}{\sigma_{\min}} \quad (3)$$

Note that the $\sigma^{\max}$ and $\sigma_{\min}$ can be obtained from the singular value decomposition (SVD) analysis, which is regarded as an important tool for modern numerical analysis, given by Eqn (4).

$$K = U\sigma V^H \quad (4)$$

In Eqn (4), K is the matrix target for SVD analysis, U and V are matrices, which comprise the left-singular vector of K and the composed left-singular vector of K , respectively. σ is a diagonal

matrix, which comprises of the singular values of K . To date, several existing studies have employed the usage of CN for evaluating the dynamic characteristic and operational flexibility of the different chemical processes.^{35–37} The process with a lower conditional number (or a higher minimum singular values) [Eqn (3)] generally signifies better dynamic characteristics under disturbance.^{13,38} In this work, $\sigma^{\max}$ and $\sigma_{\min}$ are calculated with the MATLAB program using the temperature difference obtained from the sensitivity analysis (see Section 3.3).

Dynamic simulation

Following sustainable evaluation for different processes, we investigated the control performance of the proposed SSED and compared them against the CED from previous work.¹ As indicated in Section 3.2, only the energy-intensified process that provides the least depreciation in operational controllability (i.e. lowest increase in CN) is considered for further dynamic simulation.

Table 2. Sustainable evaluation of the different energy-intensified processes against the CED from previous work¹

Indicators	CED	SSED	TCED	EDWC
Total reboiler energy (MW)	1.63	1.33 (−18%)	1.43 (−13%)	1.28 (−21%)
Total steam cost (US\$ million)	3.70616	3.15349 (−15%)	3.37484 (−9%)	3.303157 (−18%)
TAC (US\$ million)	0.674846	0.59782 (−11%)	0.61044 (−10%)	0.55079 (−18%)
CO₂ emissions (kg yr^{−1})	551.03	450.31 (−18%)	481.91 (−13%)	432.90 (−21%)
Conditional number (CN)	30.33	45.61 (50%)	107.12 (253%)	5656.87 (18551%)

Before developing a robust control structure, the size of all the equipment in the process must be determined accordingly. The tray diameter and pressure drop for both columns were calculated automatically using ASPEN PLUS. The tray spacing and weir height for both columns used in this work are 0.6096 and 0.1016 m, respectively. The volume of column base and reflux drum has a holdup time of 10 min with a 50% liquid level. Then, the inventory control loops are installed, which includes the level controller, pressure controller, and flow controller. Figure 4 depicts all of the inventory control loops used in this work, which is based on the SSED configuration (see Section 4.1) that

provides the best operational controllability among the three different processes considered, as evident from the lowest increase in CN.

Comparing the inventory control used in this work (Fig. 4) against the CED from previous work¹ (Fig. 5), two interesting differences were observed as outlined below:

- (a) In the CED, the bottom level of the SRC is controlled by manipulating the bottom flowrate of EDC (i.e. feed flowrate to the SRC column) whereas the bottom level of the EDC is controlled by manipulating the solvent make-up flowrate. In this

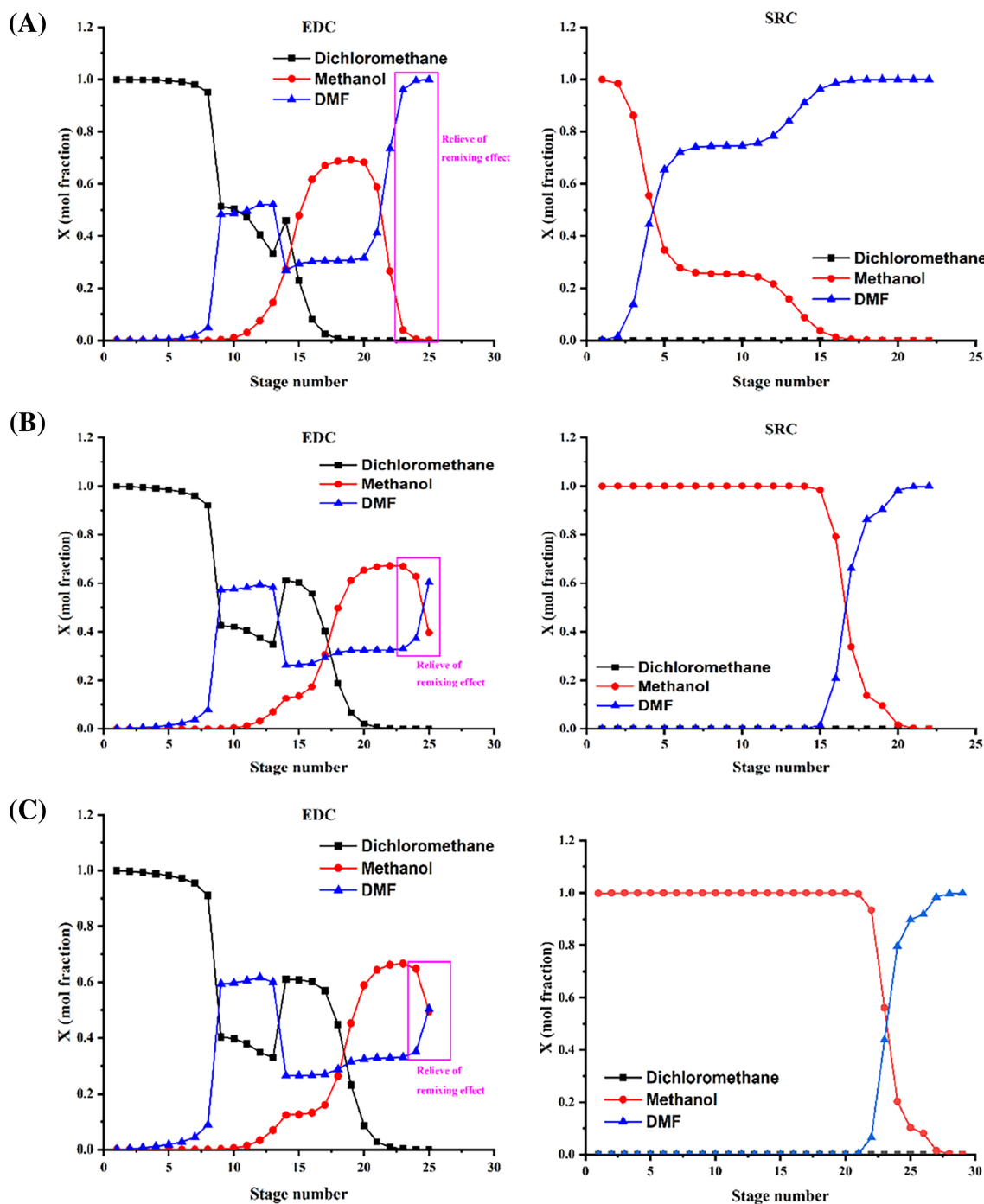


Figure 8. Composition profile for the proposed (A) SSED, (B) TCED, and (C) EDWC.

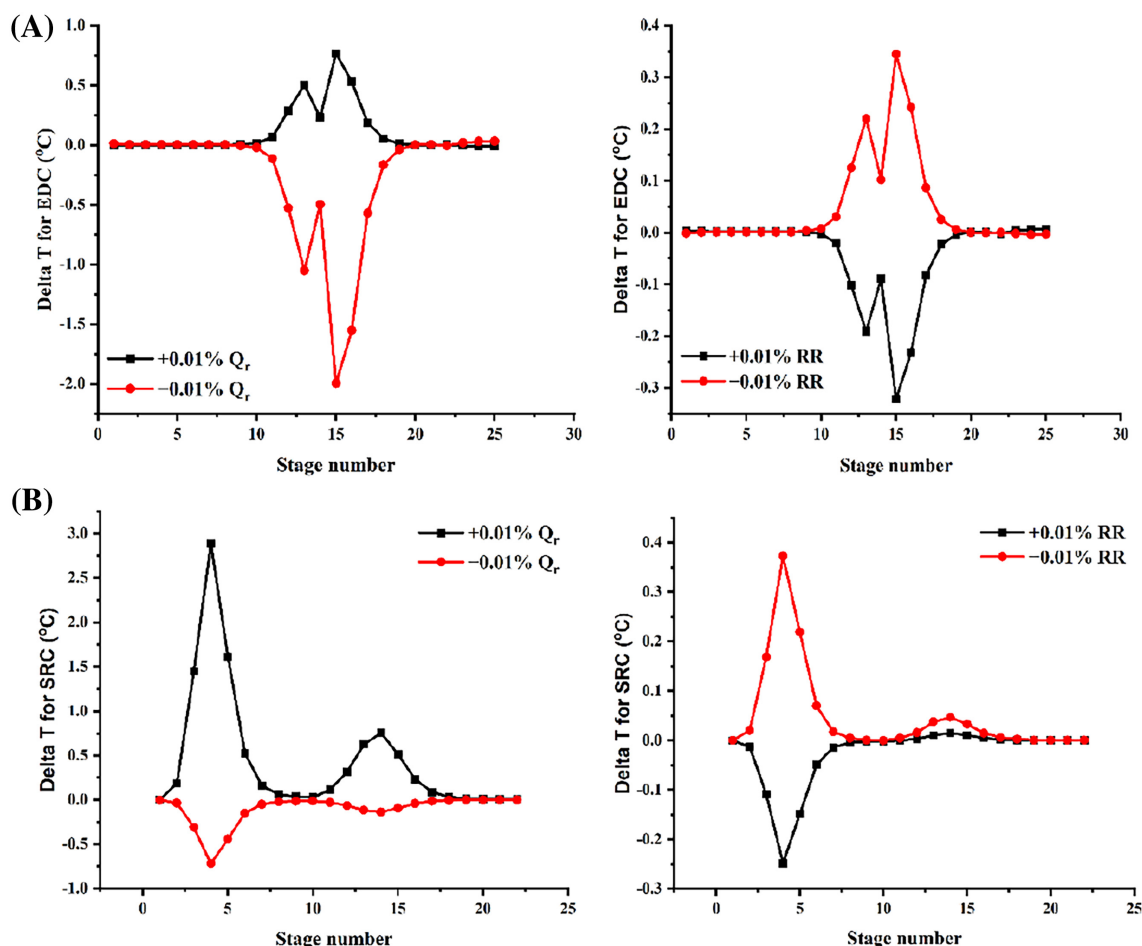


Figure 9. Results for open-loop sensitivity analyses $\pm 0.01\%$ change in reboiler duty and $\pm 0.01\%$ change in reflux ratio for the (A) EDC and (B) SRC in SSed.

work, the bottom levels of both columns are controlled by manipulating the corresponding bottom flowrate.

- (b) In the CED, the solvent flowrate is flow-controlled by manipulating the bottom flowrate of SRC and is ratioed to the fresh feed flowrate. In SSed, the solvent flowrate, however, is flow-controlled by manipulating the solvent make-up flowrate that is ratioed to the fresh feed flowrate.

Once the inventory control has been installed, we install next the quality control loops. In this work, we refrain from using costly composition controllers that are usually hard to maintain,³⁹ and instead employ only temperature control to maintain the product qualities. The temperature-sensitive tray (i.e. location) is determined through open-loop sensitivity analysis by providing a marginal change ($\pm 0.01\%$) to the manipulating variables such as reboiler duty or reflux ratio in both columns, and the tray(s) with the highest fluctuation in temperature is selected as the temperature-sensitive tray. Note that some other methods also are available for determining the temperature-sensitive tray such as the slope criterion⁴⁰ or SVD analysis,⁴¹ each method having its own characteristic and benefits. The detailed methodology of the open-loop sensitivity analysis is covered in Luyben's textbook.⁴² If the column contains multiple temperature-sensitive tray(s), relative gain array (RGA) analysis is employed to determine the best control pairing.

Table 3. RGA analysis for EDC

	Q_r	RR
Stage 13	-0.5484	1.5484
Stage 15	1.5484	-0.5484

RESULTS AND DISCUSSION

Steady-state design

Figure 6 shows the effect of different solvents on the VLE of dichloromethane and methanol at solvent to feed ratio of 0.47. From Fig. 6, all of the solvents enhanced the relative volatility of dichloromethane and methanol, albeit to slightly different extents. DMF, in particular, provided the greatest enhancement in comparison with other solvents, which signifies that DMF is a good solvent for CED, in agreement with previous study.¹

Figure 7 displays the flowsheets for the proposed SSed, TCED, and EDWC using DMF. Altogether, it was revealed that all of the energy-intensified processes proposed in this work provide lower energy consumption relative to the CED from previous work,¹ which further translates to the reduction in the TAC. Among the three different energy-intensified processes, the EDWC consumed the lowest energy and provided the lowest TAC by 21% and 18%,

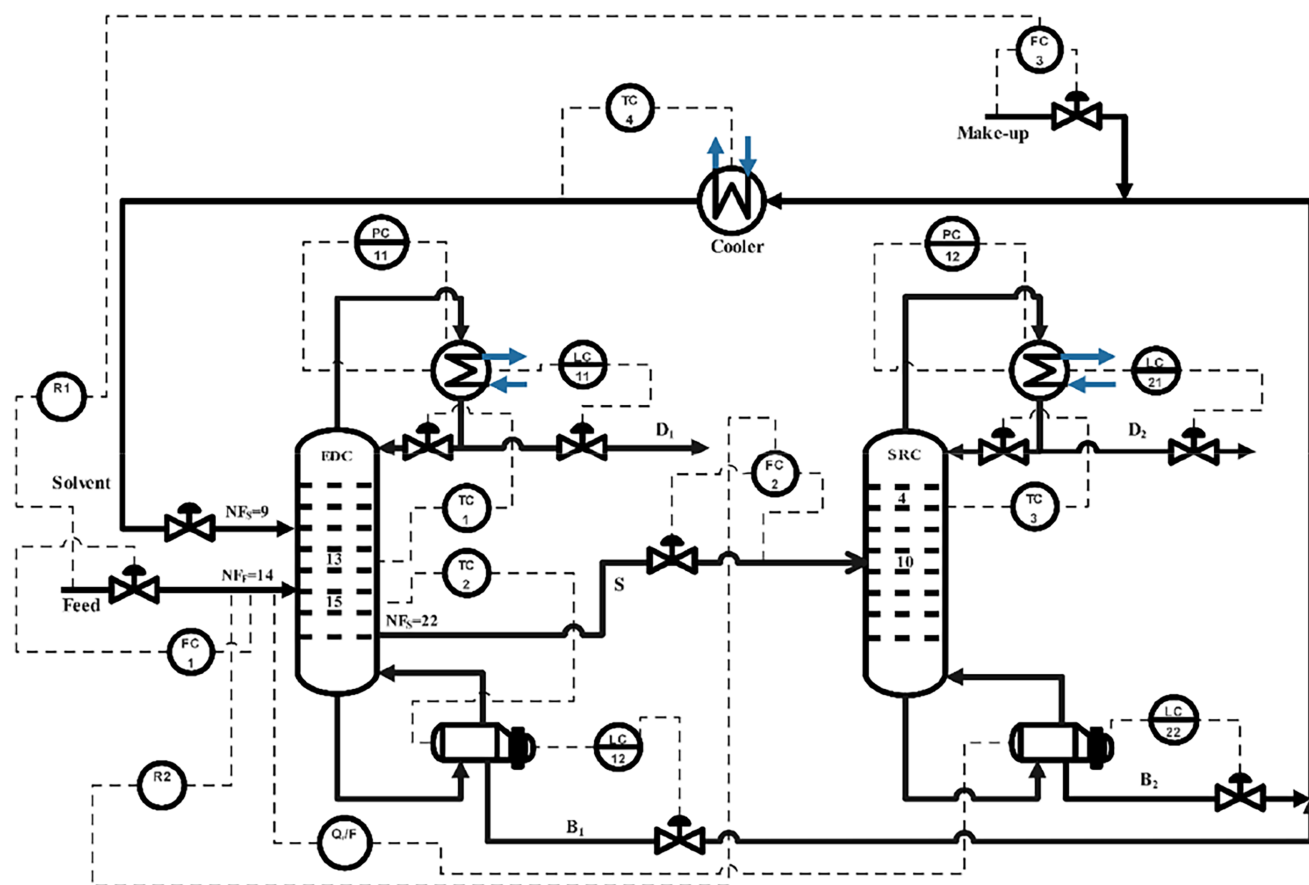


Figure 10. Proposed CS 1.

Table 4. Tuning parameters for CS 1

Controllers	Gain (K_c)	Integral time (τ_{min})
Temperature control 1 (TC 1)	0.789343% % ⁻¹	14.52 min
Temperature control 2 (TC 2)	0.216392% % ⁻¹	25.08 min
Temperature control 3 (TC 3)	2.147094% % ⁻¹	10.56 min
Temperature control 4 (TC 4)	0.149684% % ⁻¹	3.96 min

respectively, with respect to those of the CED¹ (Table 2). This was followed by the SSED, which provided 18% and 12% improvement in the energy consumption and TAC, respectively, relative to the CED.¹ The TCED, however, provided the smallest improvement to the energy consumption and TAC by 13% and 9%, respectively, in comparison to the CED.¹ These improvements were attributed to the relieve or elimination in the remixing effect in all of the energy-intensified processes, as reflected by their corresponding composition profile as given by Fig. 8.

In terms of CO₂ emissions (Table 2), the EDWC also provided the greatest reduction by 21% relative to the CED.¹ Likewise, the SSED and TCED provided 18% and 13% improvement, respectively,

with respect to the CED.¹ Such improvement can be correlated to the decrease in the energy consumption by these energy-intensified processes, as the CO₂ emissions are proportional to the energy consumption as indicated by Eqn (2).

Nonetheless, the improvement of the energy consumption, TAC, and CO₂ emissions brought by these different energy-intensified processes, were traded-off at the expense of an increase in the CN, which generally signifies the increase in complexity in operational controllability. Here all of the energy-intensified processes demonstrated a higher CN relative to the CED. The CN of the EDWC, in particular, provided the largest increase of about 186 times relative to the CED, followed by the TCED that provided an increase in CN by about 3.5 times. The SSED, however, provided the smallest increase in CN by about 1.5 times with respect to the CED, which indicates its potential flexibility in handling different disturbances. These observations can be explained by the fact that the EDWC and TCED loses one important control degree of freedom as a result of the integration between the two reboilers as one, which eventually hinders the dynamic performance of the overall TCED or EDWC. As reported by the existing studies, the TCED and EDWC generally require more complicated control structures for handling disturbances, such as controlling tray temperature using the vapour split ratio (i.e. the ratio of vapour side-stream withdrawal flowrate to the total vapour flowrate)⁴³ or even using the slow-yet-expensive composition controllers.⁴⁴ The SSED, however, possessed better dynamic characteristic relative to TCED and EDWC, as the side-

stream flowrate from the EDC to the SRC can be flow-controlled, typically by ratio to the fresh feed flowrate.⁴⁵ Another possible reason for the increase in the CN in all energy-intensified processes can be attributed to the fact that these energy-intensified processes have not been optimised to achieve their minimum energy consumption,^{35–37} and our assumption that these energy-intensified processes were retrofitted from their corresponding CED, thus having identical column parameters and operating conditions as those of CED (Section 3.1.2).

Overall, the EDWC provided the best improvement in terms of energy consumption and TAC, which was achieved at an expense of complex dynamic characteristic, as reflected by the CN. Relative to the EDWC, however, the SSSED provided considerable improvement, albeit to a slightly lesser extent (4%) for both energy consumption and TAC, but the dynamic characteristic was 124 times better. Therefore, it appears that the SSSED provides the most compromised solution that balances all sustainable indicators (i.e. economic, environmental, and control). To this end, we

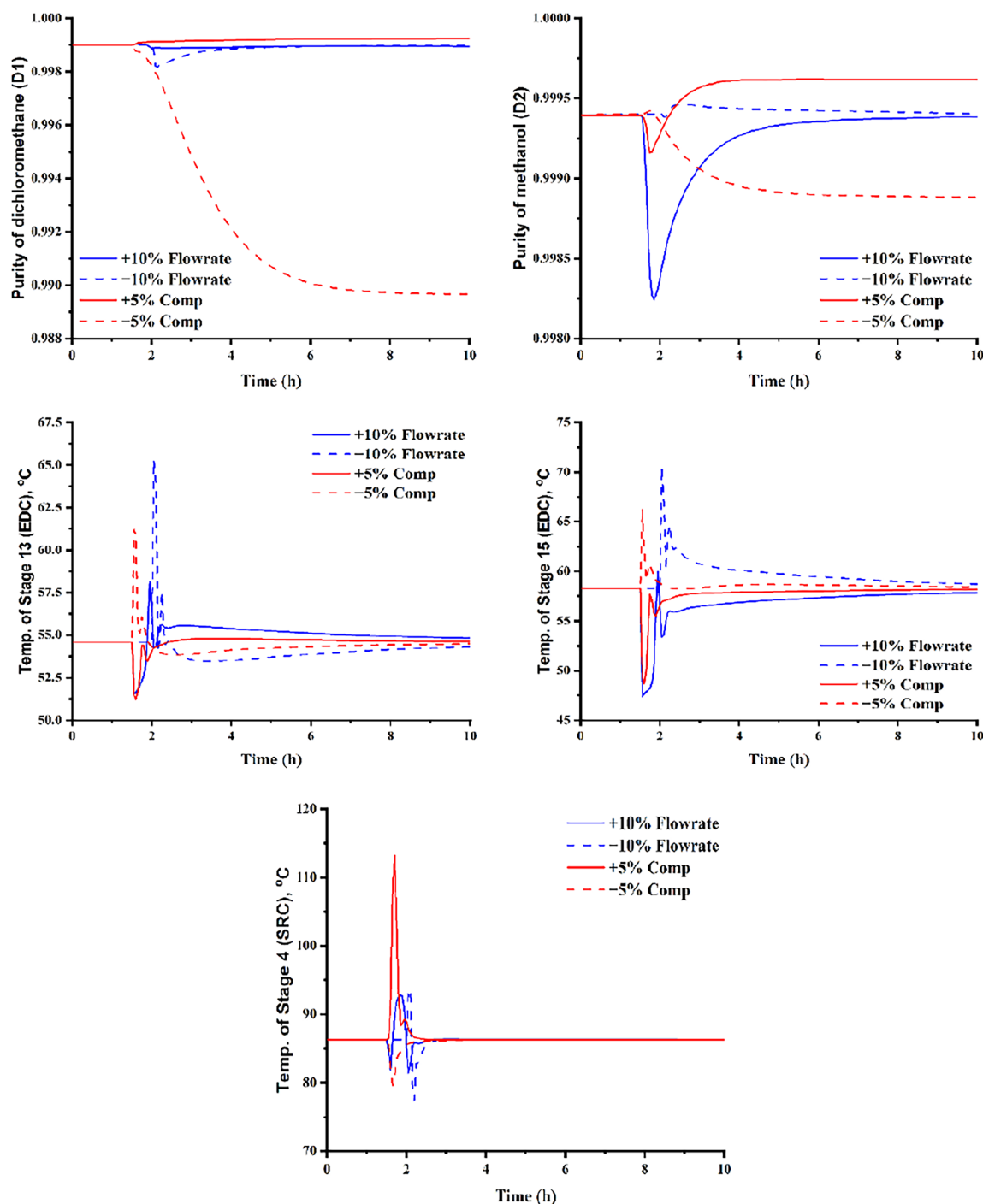


Figure 11. The dynamic performance of CS 1 under $\pm 10\%$ throughput disturbance and $\pm 5\%$ feed composition disturbances.

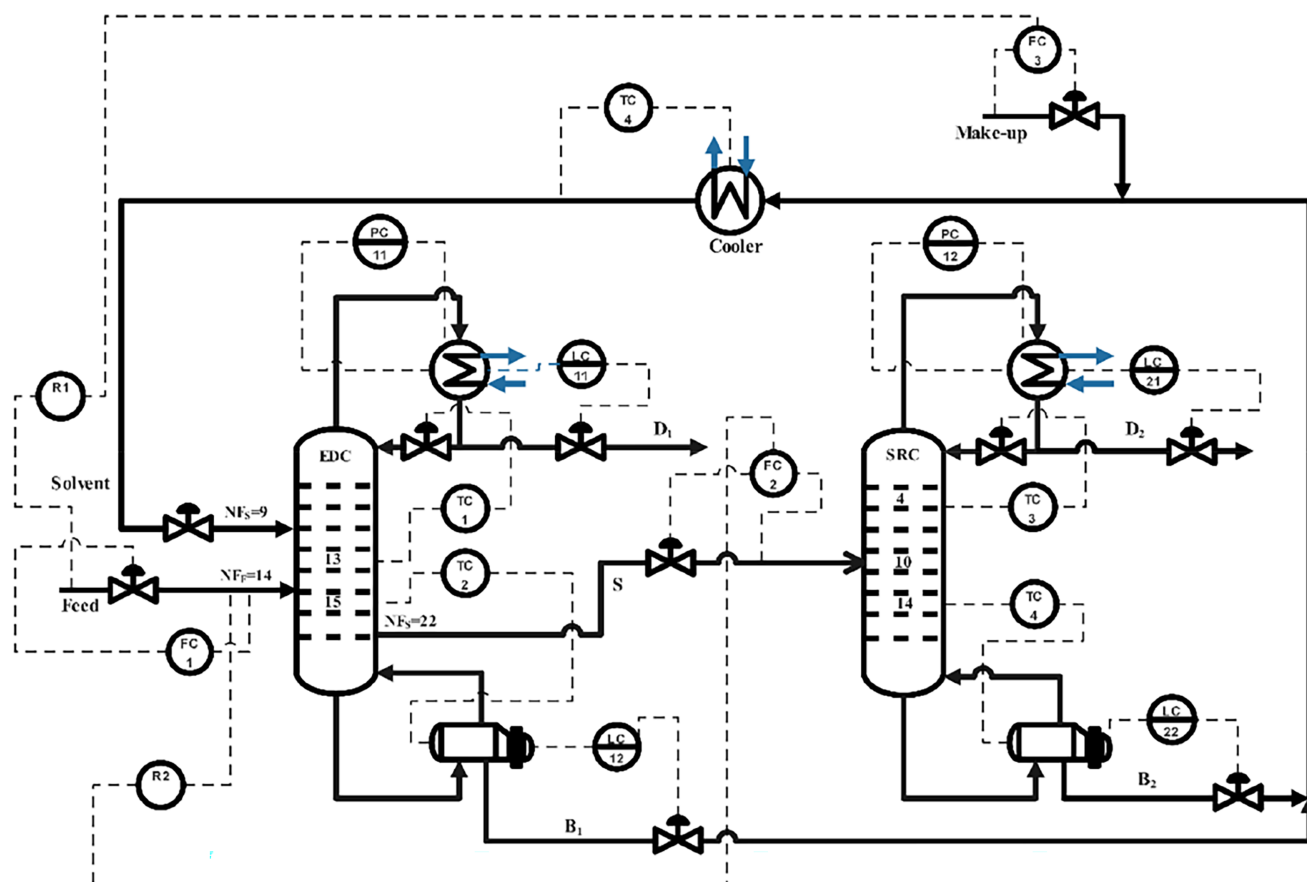


Figure 12. Improved CS 2.

Table 5. Tuning parameters for CS 2

Controllers	Gain (K_c)	Integral time (τ_{min})
Temperature control 1 (TC 1)	0.606618% % ⁻¹	19.8 min
Temperature control 2 (TC 2)	0.270365% % ⁻¹	26.4 min
Temperature control 3 (TC 3)	1.740642% % ⁻¹	19.8 min
Temperature control 4 (TC 4)	0.45189% % ⁻¹	26.4 min
Temperature control 5 (TC 5)	0.149684% % ⁻¹	3.96 min

explore next a suitable control structure for the SSED using ASPEN PLUS DYNAMICS, to ensure that the proposed SSED can be subjected to various disturbances.

Dynamic simulation

Open-loop sensitivity analysis

Before setting up the control structure for the SSED, the location of the temperature-sensitive tray is first identified via open-loop sensitivity analysis using $\pm 0.01\%$ change in reboiler duty and reflux ratio, as depicted in Fig. 9. From Fig. 9, two temperature-sensitive locations were identified, stages 13 and 15, to both the reboiler duty and

reflux ratio. Following this, we performed RGA to identify the best control pairing, the result of which is summarised in Table 3. From Table 3, it was revealed that Stage 13 should be paired with reflux ratio, whereas Stage 15 should be controlled by using the reboiler duty. For the SRC, the open-loop sensitivity analysis suggested that Stage 4 is sensitive to both reflux ratio and reboiler duty, whereas Stage 14 is sensitive to reboiler duty only (Fig. 9).

Control structure 1 (CS1)

As suggested by the open-loop sensitivity analysis in Section 4.2.1, the EDC requires a dual temperature control strategy where two temperature controllers are installed to control the temperature of stages 13 and 15 by using the reflux ratio and reboiler duty, respectively. For the SRC, the open-loop sensitivity analysis in Section 4.2.1 suggested that three different control strategies are possible: control Stage 4 by using reflux ratio, control Stage 4 by using reboiler duty, or to control Stage 4 using reflux ratio and Stage 14 using reboiler duty (i.e. dual temperature control strategy). Here, we decided to first explore the dynamic performance by controlling Stage 4 using reflux ratio, as Stage 4 is located near the top of the column, whereas the reboiler duty of the SRC is maintained using the reboiler duty to feed ratio. The resultant control structure is defined as control structure 1 (CS 1), which is shown in Fig. 10. Here, another interesting difference between the proposed control structure for SSED and the CED from previous work is that the reflux for both columns in this work are used to control the temperature-sensitive tray, whereas in the case of CED, both reflux ratios are upheld by ratioed to the

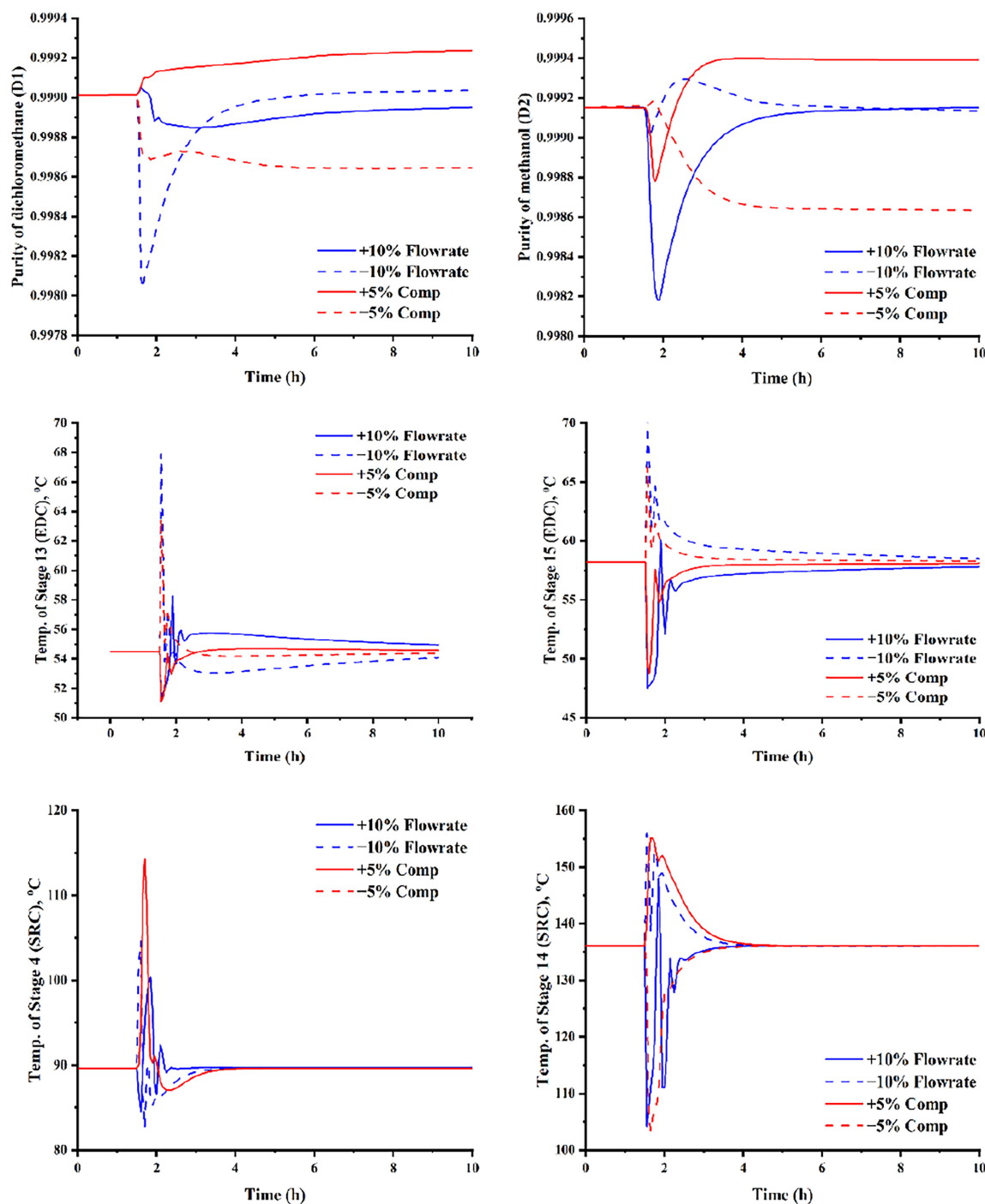


Figure 13. The dynamic performance of CS 2 under $\pm 10\%$ throughput and $\pm 5\%$ feed composition disturbances.

distillate flowrate (Fig. 5). The tuning parameters for all controllers are given in Table 4. The performance of CS 1 is tested using $\pm 10\%$ throughput and $\pm 5\%$ feed composition disturbances and the dynamic performance is depicted in Fig. 11. These disturbances are identical to the previous work¹ for the sake of fair comparison.

From Fig. 11, it appears that all of the tray temperature returned to their setpoint under 3 h. The purity of the methanol in D2 also reached steady-state under 3 h. Although the purity of methanol dropped marginally during the -5% feed composition disturbance, it was still within the accepted purity limit of 99.9 mol%. The purity of dichloromethane, however, deviated

from its steady-state value and fell to about 99 mol% when subjected to -5% feed composition disturbance. To further improve the dynamic performance, we propose to install an additional temperature controller to control the Stage 14 of the SRC by using the reboiler duty, because it is located near to the bottom of the column. This will result in both columns having a dual temperature control configuration [control structure 2 (CS 2)], which will be explored in Section 4.2.3. Here, note that the CED from the previous work only requires a single tray temperature control in each column, which results in a simpler control structure (Fig. 5). This possibly may explain

why the CN for the CED is slightly lower than the SSED proposed in this work.

Control structure 2 (CS 2)

Figure 12 shows the flowsheet for CS 2 and the tuning parameters for all controllers are given in Table 5. The performance of CS 2 was tested using $\pm 10\%$ throughput and $\pm 5\%$ feed composition, identical to CS 1. The resulting dynamic performance is given in Fig. 13.

From Fig. 13, it appears that both product purities were held close to their steady-state values during the throughput and feed composition disturbances. Although the dichloromethane product purity deviated slightly from its desired setpoint to 99.86 mol% when the system was subjected to -5% feed composition disturbance, it shows significant improvement in comparison to the previous CS 1, where the purity of dichloromethane dropped significantly to 99 mol%. For the temperature-sensitive trays, all of the temperatures returned to their setpoint values in less than 3 h, identical to the performance observed in CS 1. These results indicate the dynamic superiority of SSED and warrant the operational controllability of SSED, in addition to a lower energy consumption requirement and TAC.

In comparison to the dynamic performance of the CED from previous work¹ (not shown in this manuscript), the SSED proposed in this work demonstrates identical dynamic performance where it can hold both product purities close to their desired specifications when the system is subjected to $\pm 10\%$ throughput disturbance. In terms of feed composition disturbance, the purities for both dichloromethane and methanol dropped by ≈ 0.04 mol% from their steady-state values when the system was subjected to -5% feed composition disturbance. One interesting observation here is that the purity of dichloromethane dropped by 0.05 mol% when the CED was subjected to $+5\%$ feed composition disturbance instead of -5% feed composition disturbance, as in the case of the present SSED, whereas the purity of methanol dropped by 0.06 mol% when subjected to -5% throughput disturbance. Because the differences in deviation are quite marginal, it can be deduced that both the CED and SSED exhibit analogous control performance.

CONCLUSION

For the purpose of separating dichloromethane and methanol from their binary azeotropic mixture, we used energy consumption, TAC, CO₂ emissions, and CN as sustainability indicators to evaluate the performances of three different energy-intensified extractive distillation processes – SSED, TCED, and EDWC. Although these three intensified processes all gave lowered energy consumption, TAC, and CO₂ emissions relative to the CED configuration, the EDWC provided the greatest reduction in energy consumption, TAC, and CO₂ emissions by about 21%, 18%, and 21%, respectively. The CNs of all three intensified processes, however, were increased with respect to that of the conventional configuration, which indicates poorer controllability. EDWC in particular exhibited the worst controllability among the three intensified processes.

Upon weighing the improvement in energy, economic, and environmental metrics against the reduction in controllability, we recommended SSED as the system giving the best balance in terms of significant improvement in the energy consumption, TAC, and CO₂ emissions (by about 18%, 11%, and 18% with

respect to the CED, respectively) and the lowest reduction in the operational controllability (an increase in CN by about 1.5 times relative to the CED). To ensure that the SSED configuration can handle the disturbances in actual operation, we then subjected SSED to dynamic simulation incorporating $\pm 10\%$ throughput and $\pm 5\%$ feed composition disturbances. SSED was capable of holding both product purities close to its desired specification in the presence of these disturbances.

Three future directions can be recommended in light of the results from this work:

- (i) Although the CN of the EDWC process was significantly higher than those of CED and SSED, it is not clear what type of control structure is required and how the EDWC will respond to same disturbances. Future work thus can consider developing a robust control structure for the EDWC and comparing the dynamic performance with the SSED developed in this work.
- (ii) None of the energy-intensified processes featured in this work were optimised to their minimum energy consumption. A more in-depth study can be carried out to explore the benefits and drawbacks of optimising all of the energy-intensified processes.
- (iii) Future study also can consider the presence of additional substance in the waste effluent, as this work assumed that the waste effluent discharged from the production of prednisolone contains only dichloromethane and methanol, which is analogous to all of the existing studies in this area.

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NOMENCLATURE

AD	Azeotropic distillation
CED	Conventional extractive distillation
CAGR	Compound annual growth rate
CN	Conditional number
DMF	Dimethylformamide
DWC	Dividing wall column
DMSO	Dimethyl sulfoxide
EDC	Extractive distillation column
EDWC	Extractive-dividing wall column
EG	Ethylene glycol
IMC	Internal model control
NMP	<i>N</i> -methyl-2-pyrrolidone
PSD	Pressure swing distillation
PSBD	Pressure swing batch distillation
PP	Payback period
RGA	Relative gain array
RD	Reactive distillation
SVD	Singular value decomposition
SSED	Side-stream extractive distillation
SRC	Solvent recovery column
TAC	Total annual cost
TCED	Thermally coupled extractive distillation
TCC	Total capital cost
TOC	Total operating cost
TC	Thermally coupled

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