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Multi-objective optimization of organic Rankine cycle system for the waste heat recovery in the heat pump assisted reactive dividing wall column

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Abstract: The application of heat pump (HP) technique to reactive dividing wall column (RDWC) achieving energy-saving has received more and more attention, however, massive low-temperature (<100 °C) waste heat would be hereby produced. Therefore, in this work, the organic Rankine cycle (ORC) is adopted to effectively convert the produced waste heat of the compressed stream to clean energy (i.e., electricity). The HP assisted RDWC (HP-RDWC) of diethyl carbonate process is taken as an example, the ORC system with five working fluids candidates are explored. The operating parameters of the ORC system (e.g., flow rate of working fluid and inlet pressure of evaporator) are optimized based upon the maximum net revenue and ORC thermal efficiency through the improved multi-objective genetic algorithm. The optimal ORC system is determined by considering the economic (i.e., net revenue) and thermodynamic efficiency (i.e., ORC efficiency) performances. The results illustrated that the net revenue of the ORC system with R123 and R600a could achieve 175,807.2 US$ and 133,665.5 US$ with ORC efficiency of 15.57 and 16.19%. In addition, total annual cost of

the HP-RDWC integrated ORC processes with working fluids R123 and R600a could be reduced by 11.78% and 10.30%, respectively.

Keywords: Energy conversion; Waste heat recovery; Clean energy; Organic Rankine cycle; Multi-objective optimization

1. Introduction

Environmental protection and sustainable development could be achieved via the effective utilization of the energy sources [1, 2]. A thermally-coupled technique, dividing wall column (DWC), as a consequence is reported to reduce the fixed investment and utility consumption by integrating two conventional columns into a single separation unit as proved by Petlyuk et al. [3]. DWC is divided into four sections (a shared rectifying and stripping sections, a pre-separation section, and a side draw section) via a divided-wall as shown in Figure A1. The first commercialization of the DWC technology is implemented by BASF [4]. Subsequently, Benyounes et al. [5] explored the application of the DWC to separate non-azeotropic mixtures. Seihoub et al. [6] studied the DWC for the liquefied petroleum gas process. Long et al. [7] investigated a systematic optimization approach for separating ternary mixtures benzene/toluene/*o*-xylene via the DWC configuration. The energy-saving of DWC is further proved through retrofitting six industrial processes [8]. Following that, Kiss et al. [9] proposed an energy-saving process to synthesize fatty acid methyl esters by combining reaction with DWC (denoted as RDWC) and they illustrated that 25% savings of energy consumption could be achieved. Yang et al. [10] reported a RDWC configuration to produce gasoline additive tert-amyl methyl ether and they proved that the proposed RDWC process can save 43.58% of total annual cost (TAC). At the same time, the synthesis of diethyl carbonate is explored via the RDWC sequence and they demonstrated that the utility consumption and TAC of the RDWC scheme could save 18.7% and 13.9% compared with the conventional reactive distillation scheme [11]. The hydrolysis of methyl acetate through the RDWC configuration is studied by Li et al. [12] and they displayed that 20.1% energy savings can be achieved by the RDWC scheme. In summary, energy consumption and TAC could be significantly reduced via the application of the DWC configuration, which is applicable to ideal, azeotropic or reaction systems.

The RDWC configuration has a huge potential in decreasing both energy consumption and TAC. Unfortunately, the latent heat of vaporization of the condensed vapor stream in the condenser has not been fully used, as such, the heat pump (denoted as HP) technique is used [13, 14]. For example, Feng et al. [15] explored a HP assisted RDWC (HP-RDWC) for the synthesis of isopropyl acetate and the computational illustrated that the utility consumption and TAC save 49.9% and 13.8%. An energy-efficient scheme for diethyl carbonate process via the RDWC with different pressure thermally-coupled is investigated by Yang et al. [16] and the result indicated that the significant reduction of TAC is achieved by 20.5%. HP-RDWC configuration for production of *n*-amyl alcohol and *n*-hexanol is explored [17] and the simulation displayed that the steam investment of the HP-RDWC could be reduced to 62.5% compared with the existing RDWC process. Feng et al. [18] proposed an energy-saving HP-RDWC separation scheme for producing *n*-propyl acetate and the calculation demonstrated that the TAC could be significantly reduced. In addition, the HP-RDWC configuration for different process has been extensively studied by other researchers [19, 20].

The utility consumption and TAC could be further reduced via the HP technique. However, the major defects of the HP system are producing a massive low-temperature (<100 ºC) waste heat, that is to say, energy of the compressed stream has not been effectively utilized. To solve this issue, the organic Rankine cycle (ORC) technology is used to utilize the waste heat [21]. ORC system is applied to the HP assisted distillation for separating mixture benzene and toluene as reported by Gao et al. [22] and they illustrated that the TAC can further decrease 6.47% compared with the HP scheme. Following that, the comparison between conventional ORC and a preheater for evaporator ORC are studied [23] and they proved that the electrical energy of the HP process can be reduced by 21.29%. Baccioli et al. [24] investigated the waste heat recovery for the multi-effect distillation process via the ORC system and they presented that the thermodynamic efficiency could be effectively improved. Waste heat recovery of the liquefied natural gas is studied via a triple ORC scheme [25]. Hipólito-Valencia et al. [26] proposed an novel approach for waste heat recovery by combining ORCs and heat exchanger network based on the proposed superstructure. Massive waste heat of the bioethanol purification process is converted to produce clean energy via ORC system and the results displayed that the application of ORC scheme yields significant economic benefits [27]. Additionally, the waste heat in the other industries could be recovered by using the ORC system [28-38]. A dual-loop ORC scheme is used to recover waste heat for engine system [39]. Waste heat recovery of compact heat exchangers is reported via the ORC system [40]. Li et al. [41] proposed a novel extractive distillation process by combining economizer and ORC to effectively use the heat duty of condenser. According to the above listed studies, the low-temperature waste heat could be effectively recovered via the ORC system.

To the best of our knowledge, valuable insights on conceptual design and multi-objective optimization by combining the ORC system to HP-RDWC system have not yet been reported. In this contribution, we report a new diethyl carbonate (DEC) process combining ORC to the HP-RDWC process. In this process, massive waste heat produced by HP is effectively utilized to produce clean energy via ORC system. To obtain the best performances of ORC system, five alternative dry working fluids involving R113, R123, R245fa, R600a, and R601a are selected based on the temperature-entropy (T-S) diagram and thermo-physical properties. An improved multi-objective genetic algorithm is adopted to optimize the ORC system, which can reduce the repeated solutions and increase evolution rate by adding a tournament & select best individuals step. In the optimization process, two conflict objectives including net revenue and ORC thermal efficiency are determined. Finally, two ORC systems are evaluated by considering the economic (i.e., net revenue) and thermodynamic efficiency (ORC efficiency) performances.

2. Methodology

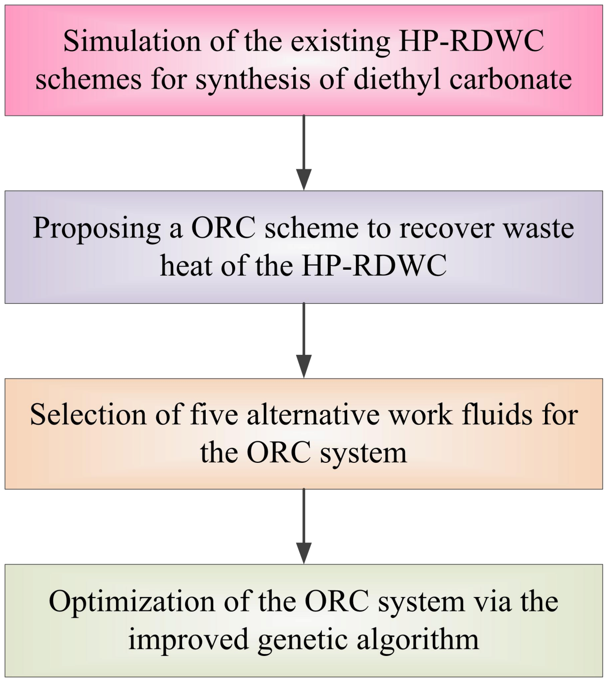

Figure 1. Proposed procedure for the waste heat recovery of the HP-RDWC process via the ORC system (HP-RDWC: heat pump assisted reactive dividing wall column; ORC: organic Rankine cycle)

A systematic approach for the waste heat recovery of the HP-RDWC process via the ORC system is displayed in Figure 1. In this work, the proposed approach is conducted in three steps:

(1) The existing HP-RDWC process for the diethyl carbonate (DEC) process is simulated as the base case.

(2) An alternative configuration for the DEC production is proposed to recover waste heat via the ORC system.

(3) Five alternative working fluids are selected for the ORC system.

(4) The improved genetic algorithm is adopted to optimize the ORC system by using multiple objectives of net revenue and ORC efficiency.

In this section, simulation of the existing HP-RDWC in the first step is necessary. Temperature and heat duty of the heat source could be obtained, which could be used to determine the proposed ORC assisted HP-RDWC configuration in step 2 and to select working fluid in step 3. Optimal design parameters of ORC system in step 4 are obtained via the improved genetic algorithm based on the results in steps 2 and 3.

2.1 Existing heat pump assisted reactive dividing wall column process

According to our previous study [16], the DEC production could be produced by the liquid catalytic reactions in the reactive section of the left side in the RDWC involving dimethyl carbonate (DMC), ethyl-methyl carbonate (EMC), ethanol (EtOH), and methanol (MeOH) as follows,

$$\text{DMC+EtOH} \Leftrightarrow \text{EMC+MeOH} \tag{1}$$

$$\text{EMC+EtOH} \Leftrightarrow \text{DEC+MeOH} \tag{2}$$

An experimental study on the chemical equilibrium and reaction kinetics of the DEC reaction system in a reactive distillation column is investigated by Keller et al. [42]. An improved investigated is studied to produce the DEC production via the catalyst sodium ethoxide as demonstrated in Eqs. 3-4.

$$r_1 = x_{\text{cat}} \times (k_{\text{f1}} e^{\text{-E}_{\text{f1}}/\text{RT}} \alpha_{\text{DMC}} \alpha_{\text{EtOH}} - k_{\text{b1}} e^{\text{-E}_{\text{b1}}/\text{RT}} \alpha_{\text{EMC}} \alpha_{\text{MeOH}}) \tag{3}$$

$$r_2 = x_{\text{cat}} \times (k_{\text{f2}} e^{\text{-E}_{\text{f2}}/\text{RT}} \alpha_{\text{EMC}} \alpha_{\text{EtOH}} - k_{\text{b2}} e^{\text{-E}_{\text{b2}}/\text{RT}} \alpha_{\text{DEC}} \alpha_{\text{MeOH}}) \tag{4}$$

where r_1 and r_2 are the reaction rate of Eqs. 1-2; the x_{cat} is the molar fraction of the catalyst. The temperature in K and the ideal gas constant in J/mol/K demonstrate as T and R, respectively. The liquid activity of component x is expressed as α_x. The values of above mentioned parameters in Eqs. 3-4 are listed in the Table A1. In this work, the thermodynamic model UNIQUAC is selected to predict the vapor-liquid equilibrium. To establish the validity of the thermodynamic model used for this system, corresponding values of the coefficient of determination (R^2) for all binary parameters are introduced. In addition, the built-in, regressing interaction parameters, and value of R^2 are displayed in Table A2.

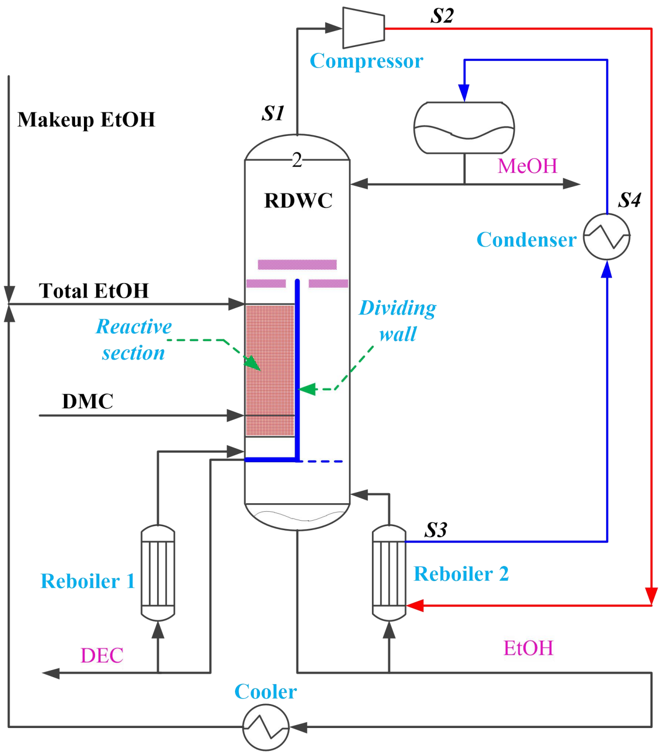

Figure 2. Existing HP-RDWC scheme for producing DEC

Zheng et al. [11] explored the synthesis of DEC via the reactive distillation and RDWC processes. Then, an energy-saving HP-RDWC process for the synthesis of DEC is reported by Yang et al. [16] as displayed in Figure 2. Feed flowrate, product purity, and feed composition of the existing HP-RDWC and the proposed process are consistent with the study of Zheng et al. [11]. The top vapor stream of the RDWC is compressed to heat the right reboiler 2 and it is then cooled via the condenser.

2.2 Conceptual design of the proposed alternative configurations

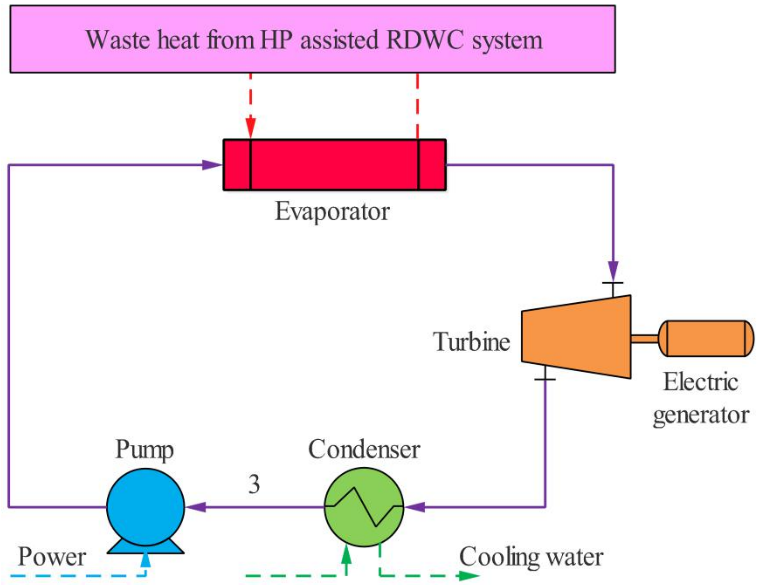

Figure 3. Scheme of waste heat recovery for HP-RDWC via the ORC system

Large amount of low-temperature (<100 ºC) waste heat is produced because the HP technique is used in the RDWC process. Hence, the ORC approach is used to effectively recover the low-temperature waste heat. The conceptual design of the proposed process is displayed in Figure 3.

2.3 Selection of working fluids

To obtain an ORC with best performance, the selection of the working fluids is a crucial step [43, 44]. Dry working fluids should be firstly determined based on the slope of saturation vapor line in the T-S diagram with positive because it has a higher thermodynamic efficiency [45]. Then, the critical temperature of the working fluid should be higher than that of heat source. If the critical temperature is closer to the heat source temperature, the thermodynamic efficiency is higher [43]. It is noteworthy that it is impossible to judge the economic performance directly from a single thermo-physical property. Other important thermo-physical properties (e.g., vaporization heat and environmental impacts) also should be considered in the selecting of working fluids [46]. Finally, the economic performance of different working fluids should be obtained via the process optimization.

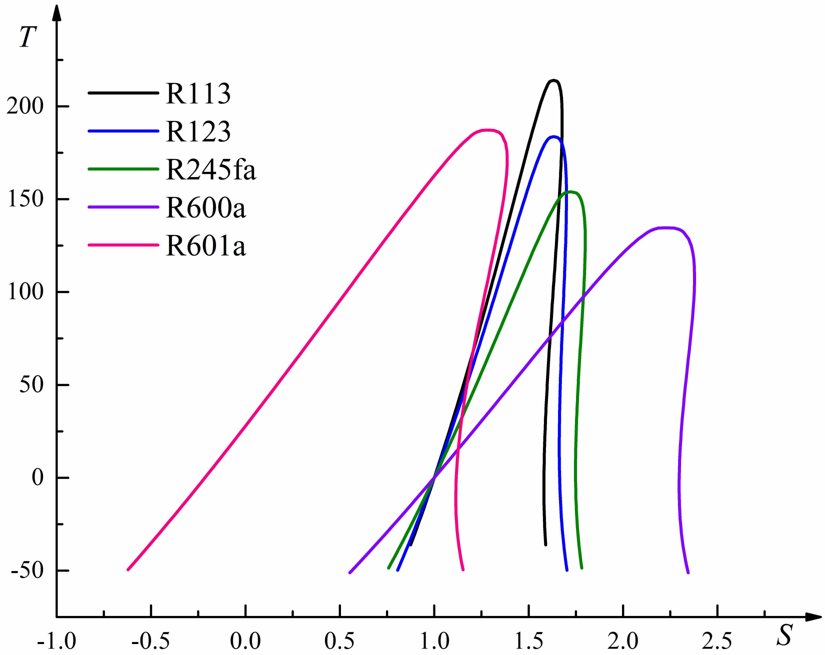

Figure 4. T-S diagram of five working fluids

Table 1. Properties of five organic working fluids studied in this work

Working fluid	R113	R123	R245fa	R600a	R601a
Chemical formula	CCl_2FCClF_2	CF_3CHCl_2	$CF_3CH_2CHF_2$	C_4H_{10}	C_5H_{12}
CAS No.	76-13-1	306-83-2	460-73-1	75-28-5	78-78-4
Boiling point/°C	47.60	27.80	17.10	-11.70	27.80
Critical temperature/°C	214.10	183.70	154.00	134.70	187.80
Critical pressure/atm	33.65	36.12	36.02	36.02	32.86
Vaporization heat/$kJ \cdot kg^{-1}$	143.11	169.90	195.66	364.29	341.36
ODP	[a]0.85	[a]0.01	[a]0.00	[b]0.00	[b]0.00
GWP (100 y)	[a]6,130	[a]77.00	[a]1,050	[b]20.00	[b]20.00

Note: [a]reference [47] and [b]references [33, 48, 49].

Five working fluids candidates including R113, R123, R245fa, R600a, and R601a are chosen to the ORC system. In addition, chemical formula, CAS No., boiling point, critical temperature, critical pressure, vaporization heat, ozone destruction potential (ODP), and global warming potential (GWP) are illustrated in Table 1 [22]. T-S diagram of five working fluids is displayed in Figure 4.

2.4 Multi-objective optimization

In the optimization process, the improved genetic algorithm is adopted to optimize the ORC system by using net revenue and ORC efficiency as objectives (see Eqs. 5 and 6).

$$\max f_1 = \text{Net revenue} \quad (5)$$

$$\max f_2 = \text{ORC thermal efficiency} \quad (6)$$

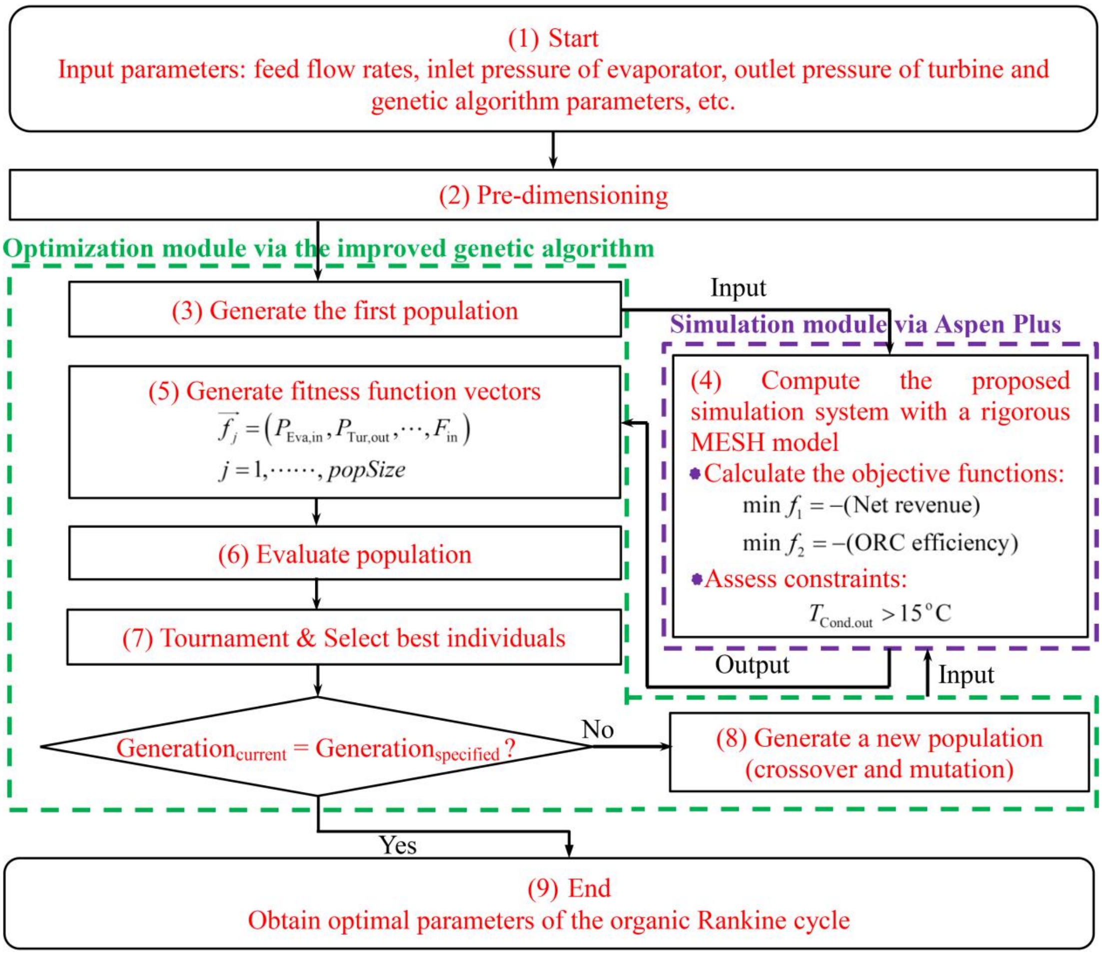

Figure 5. Scheme of the improved genetic algorithm for the organic Rankine cycle

The optimization approach combining the genetic algorithm and Aspen Plus is illustrated in Figure 5. In the optimization, the input parameters (e.g., feed flow rate) in step 1 and pre-dimensioning in step 2 are firstly determined to import the optimization module. The first population generated by the improved genetic algorithm in step 3 as input is sent to step 4 (Simulation module via Aspen Plus). Fitness function vectors are then generated in step 5 via the calculation of objective functions and constraints in step 4. Evaluation of population is realized in step 6. To reduce the repeated solutions and increase evolution rate, the step 7 involving tournament & select best individuals is added. Is the current generation equal to the specified generation? If yes, the optimal parameters of the ORC are obtained in step 9. Otherwise, a new population is returned to step 4 via the crossover and mutation in step 8.

Initial population, evaluation population, tournament & select best individuals, and generation of new population are carried out in the improved genetic algorithm software while the corresponding parameters are listed in Table 2. A rigorous MESH (Mass balance equations, Equilibrium equations, Summation of mole fraction equations, and Heat or enthalpy balance equations) model of the proposed ORC scheme, calculation of objective functions, and evaluation of constraints are carried out in the Aspen Plus. The two conflicting objectives net revenue and ORC efficiency are used to optimize the ORC system (see step 4 in Figure 5). Of note is that, improved genetic algorithm with a step 7 (i.e., tournament & select best individuals) is proposed to reduce the repeated solutions and increase evolution rate.

Table 2. Parameters of the multi-objective genetic algorithm used in the optimization process

Operator	Method	Parameter
Population size	-	*popSize* = 100
Restriction handle method	Dominance based method	*Niching* = yes
Selection method	Binary toumament	Tournament size = 2
Stopping criteria	Maximum number of generations	MaxGen
Crossover operator	SBX	-
Crossover probability	-	0.95
Mutation operator	Polynominal	-
Mutation probability	-	0.1

2.4.1 Net revenue

In this work, total capital cost involves the fixed investment of two heat exchangers and a turbine while the total energy investment includes the cost of electricity and cooling water.

Heat transfer area (A in m^2), capital cost of heat exchanger and turbine, energy cost of cooling water are illustrated in Eqs. 7-10 [22].

$$\mathrm{A} = \frac{Q}{u \times \Delta \mathrm{T}} \tag{7}$$

$$\text{Capital cost of heat exchanger} = (\frac{\mathrm{M\&S}}{280}) \times (101.3 \times \mathrm{A}^{0.65}) \times (2.29 + \mathrm{F_C}) = 9367.8\mathrm{A}^{0.65} \tag{8}$$

$$\text{Capital cost of turbine} = 1.5 \times (225 + 170 \times \mathrm{V_{outlet}}) \tag{9}$$

$$\text{Energy cost of cooling water} = 8000 \times \mathrm{PCW} \times \mathrm{CCW} \tag{10}$$

where 1,468.6 of Marshall and Swift cost index (M&S) is suggested by Shahandeh et al. [50]; correction factor of the heat exchanger (F_C) is determined as 15.3 [51, 52]; V_{outlet} (m^3/s) is the outlet volumetric flow rate of the turbine; heat transfer coefficient, u, is 0.865 kW/K/m^2 for condenser while u is 0.568 kW/K/m^2 for reboiler [53, 54]; price of cooling water is denoted as PCW (PCW = 0.03 US$/t) [55-57]; consumption of cooling water is represented as CCW. It is noted that the cost of pump is neglected.

The total expenditure, earnings of electricity, and net revenue for the ORC system are given in Eqs. 11-13, respectively [14].

$$\begin{aligned}\text{Total expenditure} = (&\text{capital cost of heat exchanger} + \text{capital cost of turbine} \\ &+ \text{energy cost of cooling water})/\text{payback period}\end{aligned} \tag{11}$$

$$\text{Earnings of electricity} = 8000 \times \mathrm{PE} \times \mathrm{GC} \tag{12}$$

$$\text{Net revenue} = \text{earnings of electric} - \text{total expenditure} \tag{13}$$

where PE is the price of electricity (PE = 0.1 US$/kW·h) [22]. The deference between electricity of turbine and pump is denoted as generation capacity (denoted as GC in kW/h).

2.4.2 ORC thermal efficiency

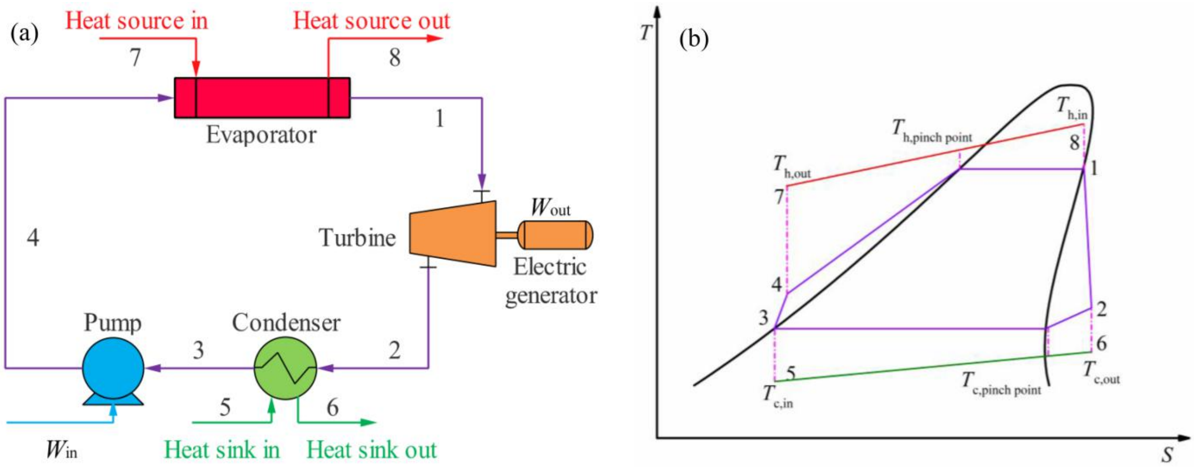

Figure 6. (a) Organic Rankine cycle system and (b) T-S diagram of the ORC system

Figure 6 illustrate the ORC and temperature-entropy (T-S) chart of the ORC system, respectively. As illustrated in Figure 6, four thermodynamic processes, isobaric heating (4→1) in the evaporator, isentropic expansion (1→2) in the turbine, isobaric cooling (2→3) in the condenser and isentropic compression (3→4) in the pump comprise the overall ORC system.

The ORC thermal efficiency is another important index, which could be calculated through the Eq. 14 [22, 23].

$$\text{ORC efficiency} = \frac{H_1 - H_2 - (H_3 - H_4)}{H_4 - H_1} \tag{14}$$

where H_3 and H_4 in kJ/kg are the enthalpy of working fluid at the inlet and outlet of pump; H_1 and H_2 in kJ/kg are the enthalpy of working fluid at the inlet and outlet of turbine.

2.4.3 Constraint

Following the study of Gao et al. [22], the outlet temperature of condenser ($T_{\text{Cond,out}}$) should be greater than 15 °C (see Eq. 15) to ensure that the working fluid at the condenser can be cooled by the cooling water.

$$T_{\text{Cond,out}} > 15\,^{\circ}\text{C} \tag{15}$$

2.4.4 Variables bounds

For the ORC system, four continuous variables as shown in Eqs. 16-19 involving flow rate of working fluid (F_{WF}), output pressure of the turbine (P_{turbine}), outlet pressure of the pump (P_{pump}), and the output temperature of the waste heat ($T_{\mathrm{WH,out}}$) should be optimized.

$$F_{\mathrm{WF}}^{\min} \le F_{\mathrm{WF}} \le F_{\mathrm{WF}}^{\max} \tag{16}$$

$$P_{\mathrm{turbine}}^{\min} \le P_{\mathrm{turbine}} \le P_{\mathrm{turbine}}^{\max} \tag{17}$$

$$P_{\mathrm{pump}}^{\min} \le P_{\mathrm{pump}} \le P_{\mathrm{pump}}^{\max} \tag{18}$$

$$T_{\mathrm{WH,out}}^{\min} \le T_{\mathrm{WH,out}} \le T_{\mathrm{WH,out}}^{\max} \tag{19}$$

3. Computational results and discussion

3.1 Simulation results of the existing HP-RDWC process

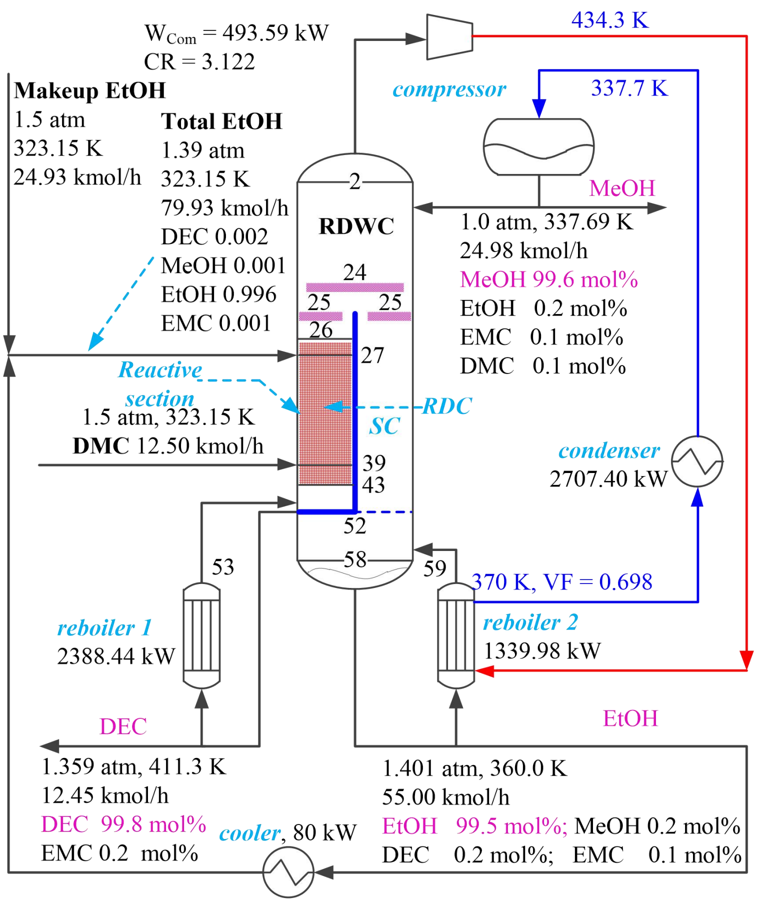

Figure 7. Simulation results of the existing HP-RDWC scheme

The reproduction of the existing HP-RDWC process for synthesis DEC is carried out in

Aspen Plus via two rigorous RadFrac models (see Figure A2). Figure 7 displays the simulation results of the existing HP-RDWC scheme. Product purities of DEC, EtOH, and MeOH are 99.8 mol%, 99.5 mol%, and 99.6 mol%, respectively. The vapour stream of the RDWC is compressed by the compressor to 3.14 atm with temperature increases to 434.3 K. In this process, the power of 493.59 kW is required to the compressor. The duty of the reboiler 2 is provided by the compressed stream. After that, the compressed stream with 370 K is cooled to 337.7 K by using cooling water.

3.2 Optimization results

All design variables of ORC system are obtained via the improved genetic algorithm with net revenue and ORC efficiency as objective functions. The optimization is completed on the personal computer with Intel Core i7-7700 CPU@3.60GHZ, 8 GB memory. Lower and upper bounds of all design parameters and computational time are listed in Table A4.

3.2.1 ORC system with working fluid R113

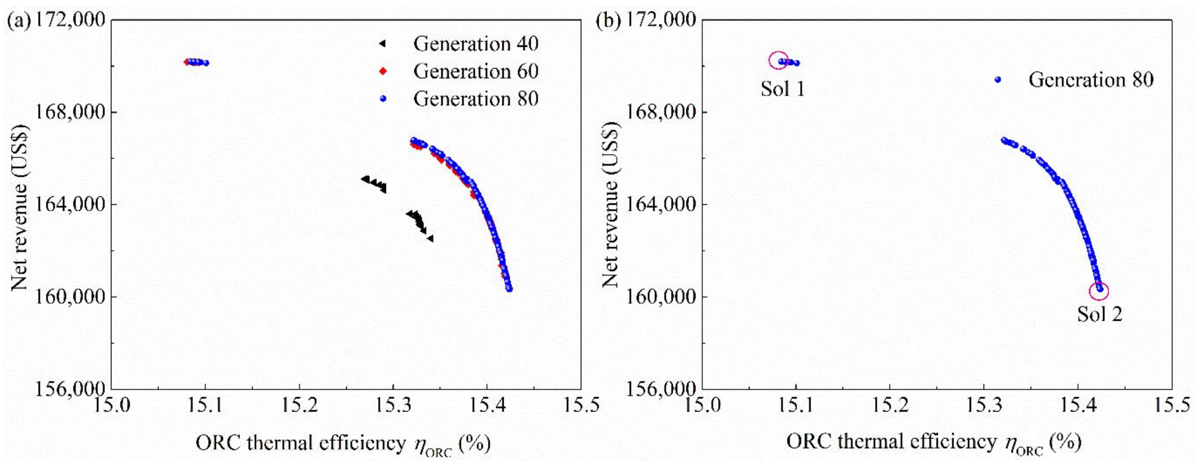

Figure 8. Multi-objective optimization (a) with different generations and (b) Pareto front solutions by using working fluid R113

An initial population of 100, crossover probability of 0.95, and mutation probability of 0.1 are used for the ORC system with working fluid R113. The optimization is terminated after 80 generations by observing the vector of decision variables and it does not produce any meaningful improvement as illustrated in Figure 8a. The Pareto fronts between net revenue and ORC efficiency of 80 generations are shown in Figure 8b. There have two interesting solutions with highest net revenue solution (Sol 1) and highest ORC efficiency solution (Sol 2).

3.2.2 ORC system with working fluid R123

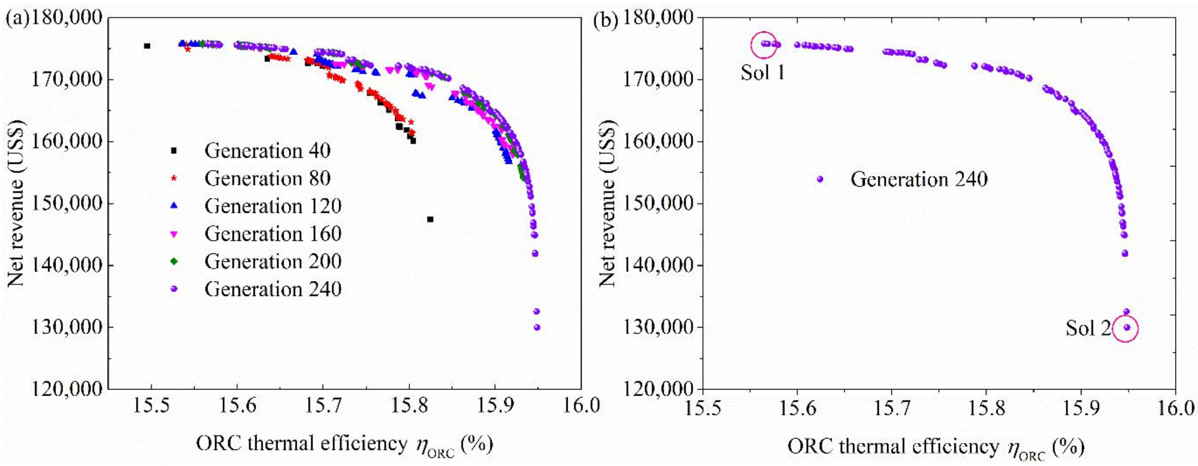

Figure 9. Multi-objective optimization (a) with different generations and (b) Pareto front solutions by using working fluid R123

The same settings (e.g., population and crossover strength) are used for the ORC system with working fluid R123. As illustrated in Figure 9a, very limited improvement in decision variables (i.e., net revenue and ORC thermal efficiency) can be seen from 200th to 240th generations indicating that the optimization procedure could be terminated after 240 generations. Pareto fronts between net revenue and ORC efficiency of 240 generations are shown in Figure 9b. Two alternative solutions Sol 1 and Sol 2 (i.e., best economic and thermodynamic efficiency) are displayed in Figure 9b.

3.2.3 ORC system with working fluid R245fa

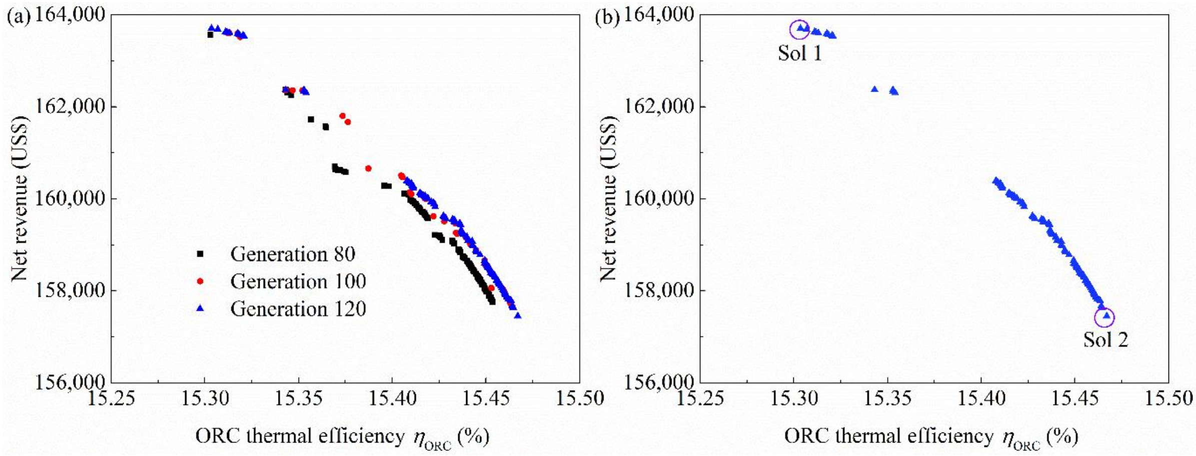

Figure 10. Multi-objective optimization (a) with different generations and (b) Pareto front solutions by using working fluid R245fa

Figure 10 displays the optimization results of the ORC system with working fluid R245fa. The trend of different generation and the optimal Pareto fronts between net revenue and ORC efficiency of 120 generations are shown in Figure 10a-b.

3.2.4 ORC system with working fluid R600a

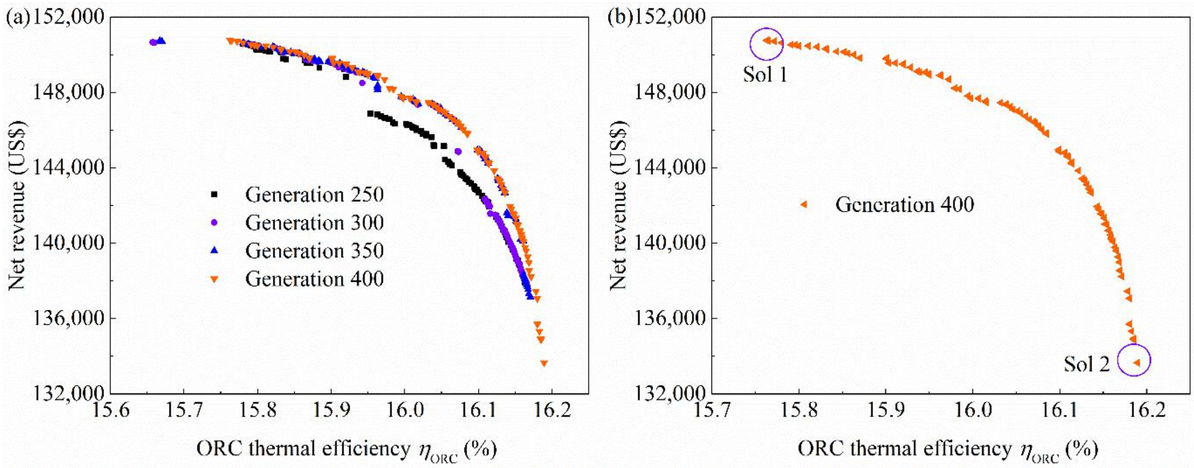

Figure 11. Multi-objective optimization (a) with different generations and (b) Pareto front solutions by using working fluid R600a

From the observation of multi-objective optimization with different generations as shown in Figure 11a, the optimization is terminated at 400 generations. The Pareto chart of ORC system with working fluid R600a is illustrated in Figure 11b, the values of the net revenue for this working fluid range from US$ 132,000 to 152,000, whereas the ORC thermal efficiency values obtained were in the range from 15.7% to 16.2%. Best net revenue design Sol 1 and best ORC thermal efficiency design Sol 2 are displayed in Figure 11b.

3.2.5 ORC system with working fluid R601a

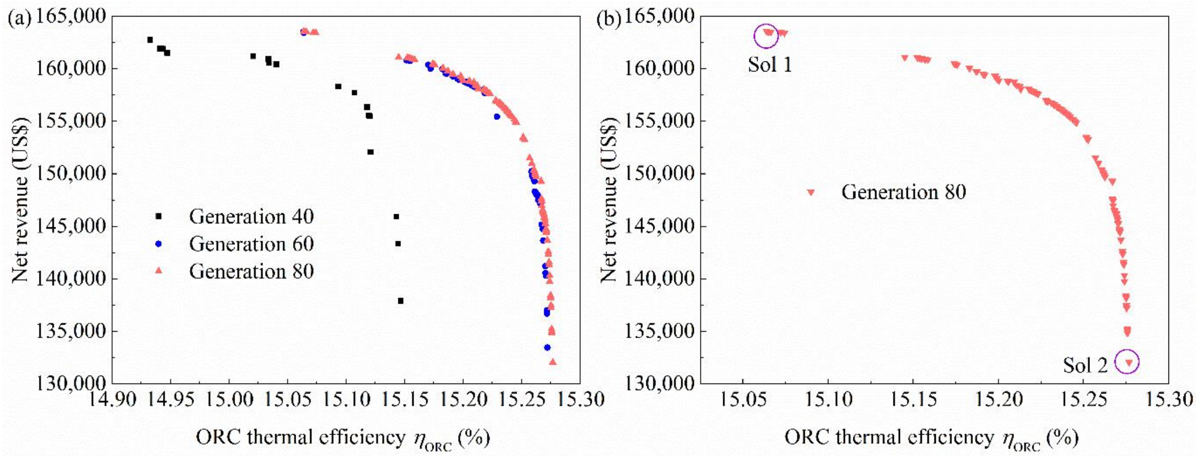

Figure 12. Multi-objective optimization (a) with different generations and (b) Pareto front solutions by using working fluid R601a

The settings of initial population, crossover probability, and mutation probability for the optimization of the ORC system with working fluid R601a are consistent with the settings of the working fluid R113. The multi-objective optimization of 40, 60, and 80 generations and the Pareto front of 80 generations are displayed in Figure 12a-b, respectively. In the same way, two representative optimized points are selected, Sol1 and Sol 2, the design variables of these designs are demonstrated in Figure 12b.

3.3 Discussion and comparison

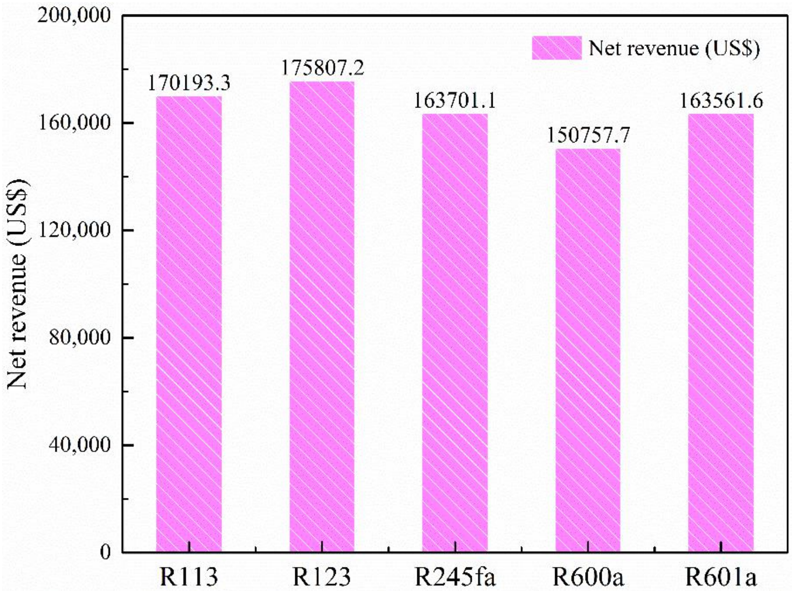

Figure 13. Net revenue comparison of the ORC scheme by using five working fluids

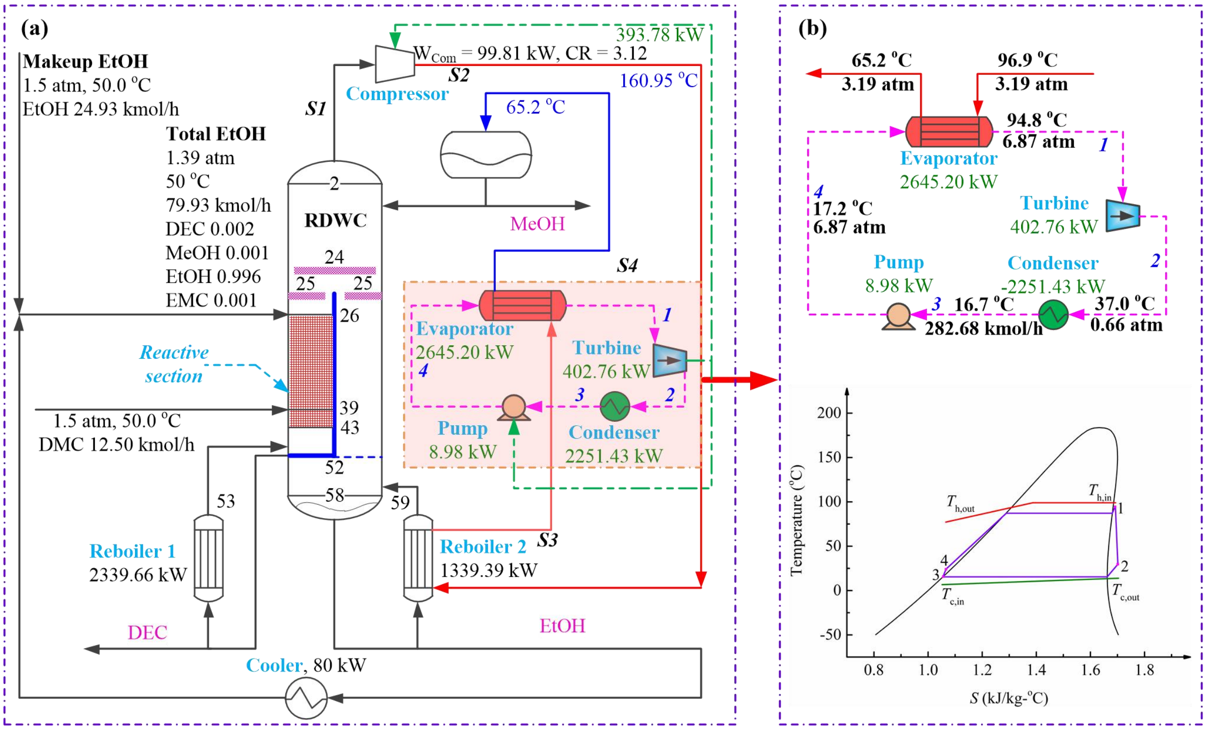

Figure 14. The optimal ORC coupled with HP-RDWC scheme by using working fluid R123

Figure 13 gives the net revenue comparison of the proposed ORC scheme by using five working fluids. The ORC system with working fluid R123 shows the best performance in the net revenue. The corresponding optimal ORC coupled with HP-RDWC scheme by using working fluid R123 is shown in Figure 14. The auxiliary power of compressor is 99.81 kW and the 393.78 kW is provided by the ORC system. In summary, the per year net revenue (removing equipment costs of the ORC system) 175,807.2 US$/y of the HP-RDWC process can be improved by using the ORC system.

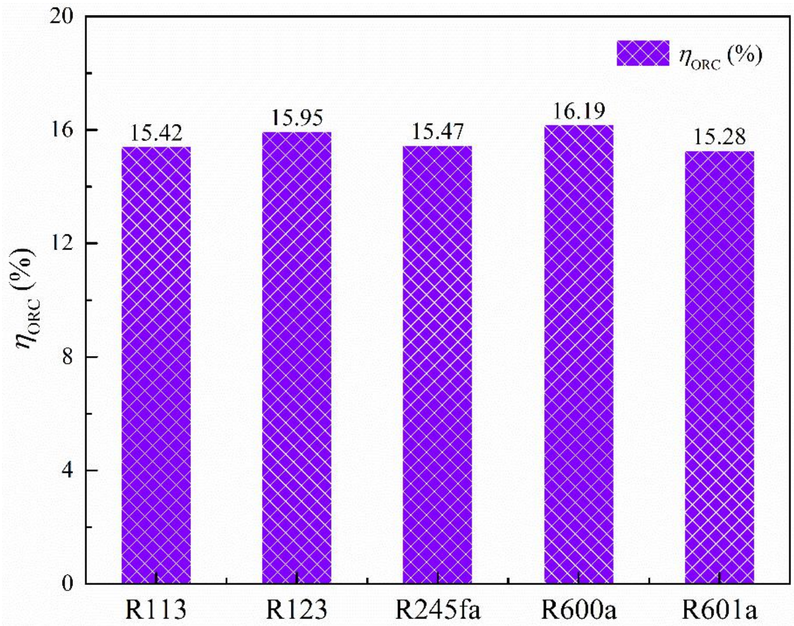

Figure 15. ORC efficiency comparison of the ORC scheme by using five working fluids

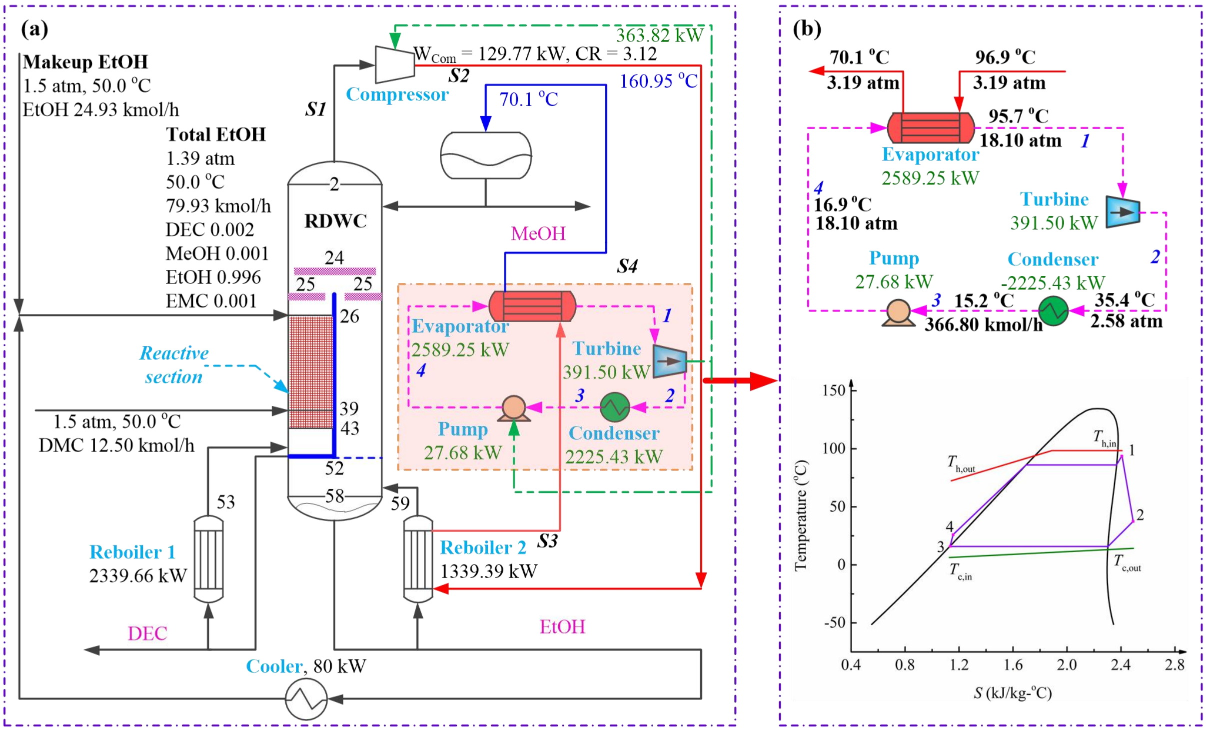

Figure 16. The optimal ORC coupled with HP-RDWC scheme by using working fluid R600a

The ORC thermal efficiency comparisons of five alternative working fluids are displayed in Figure 15. The ORC system with working fluid R600a has the best performance in the ORC thermal efficiency (η_{ORC} = 16.19%). The HP-RDWC process combined with ORC system with detailed operating condition information is demonstrated in Figure 16. The amount power of 363.82 kW for the compressor could be provided by the ORC system while the auxiliary power of compressor is 129.77 kW. In summary, the per year net revenue (removing equipment costs of the ORC system) of the HP-RDWC process applying the ORC system can be improved by 133,664.5 US$/y.

It can be seen from Figure 13, the working fluid R123 shows the best performance in economy while the ODP and GWP are slightly larger than the working fluid R600a. The results of Figure 15 demonstrated that the working fluid R600a has the highest thermodynamic efficiency, which is consistent with the description in Section 2.3. In addition, the working fluid R600a has the best performances in the environmentally friendly category because it has a lowest ODP and GEP.

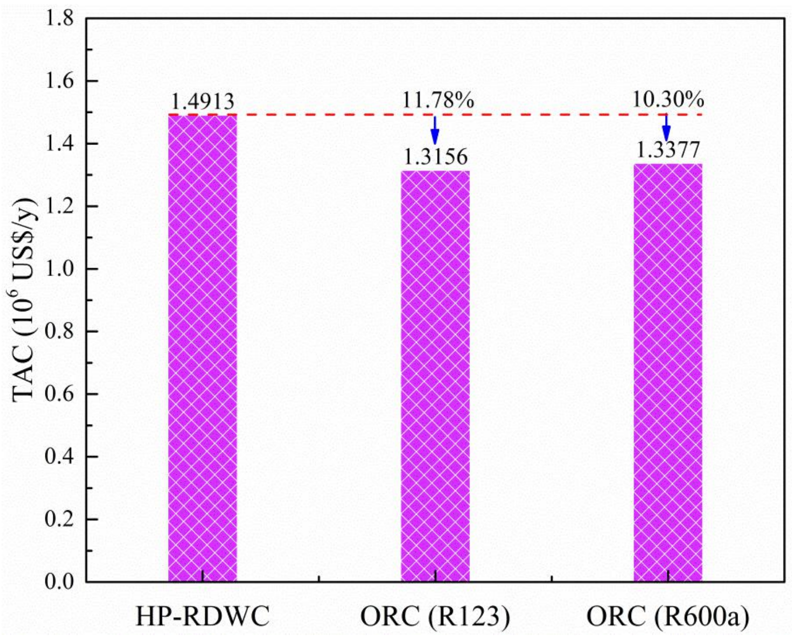

Figure 17. Economic comparisons of the existing and proposed processes

The detailed economic performances involving capital and energy costs of three designs and each unit are displayed in Figure 17 and Table A5, respectively. TAC of the ORC assisted HP-RDWC schemes with working fluids R123 and R600a are respectively reduced by 11.78% and 10.30%. In summary, economic benefit of the heat pump process could be significantly improved via the ORC system.

4. Conclusion

A sustainable process of heat pump assisted reactive dividing wall column (HP-RDWC) combined with organic Rankine cycle (ORC) is proposed for the synthesis of diethyl carbonate. A great deal of low-temperature (<100 ºC) waste heat of the HP-RDWC process has been demonstrated to be converted to the clean energy via the proposed ORC system. Five safer, greener, and dry working fluids are determined to the ORC system. The ORC system with the best performance is optimized using the improved genetic algorithm while taking both net revenue and ORC thermal efficiency as objectives. The optimizations illustrated that the net output power of 393.78 kW, the net revenue of 175,807.2 US$/y, and ORC efficiency of 15.57% could be produced via adding the ORC system with working fluid R123. Net output power of 363.82 kW, net revenue of 133,665.5 US$/y, and ORC efficiency of 16.19% could be achieved via adding the ORC assisted HP-RDWC with working fluid R600a. Compared with the existing HP-RDWC process, HP-RDWC integrated ORC scheme with working fluids R123 and R600a can save 11.78% and 10.30% of total annual cost, respectively. It is noted that the proposed approach could be extended to other heat pump or overall plant systems to produce clean energy.

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Nomenclature

DWC	dividing wall column
HP	heat pump
ORC	organic Rankine cycle
TAC	total annual cost
RDWC	reactive dividing wall column
η_{ORC}	ORC thermal efficiency
HP-RDWC	heat pump-reactive dividing wall column
DEC	diethyl carbonate
EMC	ethyl-methyl carbonate
DMC	dimethyl carbonate
ethanol	EtOH
methanol	MeOH
r_i	reaction rate of the reaction *i*
k_{fi}	forward pre-exponential factors of the reaction *i*
k_{bi}	backward pre-exponential factors of the reaction *i*
E_{fi}	forward activation energies of the reaction *i*, kJ/kmol

E_{bi} backward activation energies of the reaction i, kJ/kmol

H enthalpy, kW

S entropy, kJ/(kg·K)

GWP global warning potential

ODP ozone destruction potential

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