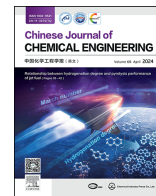




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Full Length Article

Energy-saving design and optimization of pressure-swing-assisted ternary heterogeneous azeotropic distillations

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ABSTRACT

A huge amount of energy is always consumed to separate the ternary azeotropic mixtures by distillations. The heterogeneous azeotropic distillation and the pressure-swing distillation are two kinds of effective technologies to separate heterogeneous azeotropes without entrainer addition. To give better play to the synergistic energy-saving effect of these two processes, a novel pressure-swing-assisted ternary heterogeneous azeotropic distillation (THAD) process is proposed firstly. In this process, the ternary heterogeneous azeotrope is decanted into two liquid phases before being refluxed into the azeotropic distillation column to avoid the aqueous phase remixing, and three columns' pressures are modified to decrease the flowrates of the recycle streams. Then the dividing wall column and heat integration technologies are introduced to further reduce its energy consumption, and the pressure-swing-assisted ternary heterogeneous azeotropic dividing-wall column and its heat integration structure are achieved. A genetic algorithm procedure is used to optimize the proposed processes. The design results show that the proposed processes have higher energy efficiencies and lower CO₂ emissions than the published THAD process.

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1. Introduction

Distillation is the most commonly used separation technology to split a mixture into its pure components in the chemical industry [1], but the frequent presences of multi-azeotropic mixtures limit the regular distillation column usages seriously. The residue curve maps (RCMs) of the most complex ternary azeotropic mixtures contain three binary azeotropes, one ternary heterogeneous azeotrope, and three distillation regions. Some high-value organic components can be recovered from the wastewater by separating these kinds of mixtures. Since such complex mixtures cannot be separated by the regular distillation, therefore, the research on the effective distillation processes to separate these mixtures is of great importance for the high-quality and green development of the chemical industry.

In recent years, more and more studies focused on the separation of the ternary azeotropic mixtures by some novel distillation

processes. Shen, Wang, Ye and Luyben *et al.* [2–5] studied the ternary pressure-swing distillation (TPSD) to separate the ternary mixtures with pressure-sensitive azeotropic compositions. Shen, Wang, and Chien *et al.* [6–14] studied the design, control, and agent-choice problems for the ternary extractive distillation.

The ternary heterogeneous azeotropic distillation (THAD) can separate the ternary azeotropic mixtures by taking advantage of the liquid–liquid equilibrium in a decanter, and no entrainer needed to be used. The first THAD process was probably proposed by Qiu *et al.* [15] in 2017, which was used to separate ethanol/toluene/water mixture with the toluene as the self-entrainer. Similar process is proposed by Guang *et al.* [16] to separate the isopropanol (IPA)/diisopropyl ether (DIPE)/water mixture in 2019. This kind of process contains one heterogeneous azeotropic distillation column and two self-entrainer recovery columns. A large amount of recycled entrainers leads to high energy consumption.

To reduce its energy consumption, Chien *et al.* [17, 18] proposed the energy-efficient THAD with pressure-swing distillation processes; the design results showed that significant energy-saving was achieved due to utilizing natural liquid–liquid separation together with varying operating pressure. In Chien's THAD process,

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all of columns' operation pressures are changed to expand three distillation boundaries, while the first column is operated by the negative pressure. Although a large amount of energy is saved by this process, the operation difficulty is increased significantly compared to the normal pressure column. At the same time, the dividing-wall column (DWC) cannot be applied into Chien's THAD process. In 2020, Guang *et al.* [19] proposed another THAD with pressure-swing process to separate the IPA/DIPE/water mixture with high water composition, in which the former two columns had the same pressure and could be combined into a special DWC, but up to now, it is still lacking to research on the THAD with pressure-swing distillation processes.

Owing to the presents of two recycle streams and large number of design variables, the single-variable optimization procedure (sequential iterative optimization) is hardly used for the THAD process. On the one hand, this kind of optimization procedure will lead to high calculation duties with the optimized variables increasing. On the other hand, the global optimization results are difficult to be achieved for the complex interactions between the variables. For this kind of multi-variable optimization problem, the heuristic optimization algorithms such as the simulated annealing algorithm (SA) and genetic algorithm (GA) and are more suitable [20,21].

In order to make full use the energy-saving advantages of the THAD and the TPSD to separate the pressure-sensitive ternary heterogeneous azeotropic mixtures, a novel pressure-swing-assisted THAD process (PS-THAD) is firstly proposed in this paper. Then the pressure-swing-assisted ternary heterogeneous azeotropic DWC (PS-THADWC) and its heat integration process (heat-integrated pressure-swing heterogeneous azeotropic dividing-wall column [HI-PS-THADWC]) are achieved. The GA, as a dependable heuristic optimization procedure, is chosen for these processes. Finally, some conclusions are summarized.

2. Development of the Proposed Processes

2.1. Analysis of THAD process

The published Guang's THAD process is shown in Fig. 1. A total of $520 \text{ kmol} \cdot \text{h}^{-1}$ mixture containing 0.658 IPA, 0.281 DIPE, and 0.061 water (mole fraction) is fed into the azeotropic distillation column; the ternary heterogeneous azeotrope is withdrawn from the overhead and forms two liquid phases in the decanter. Then the organic and aqueous phases are fed into the self-entrainer recovery columns; three products are achieved from the three columns' bottom. Their mole purities are 0.998, 0.9999, and 0.998, sequentially.

To achieve energy-efficient PS-THAD process for separating pressure-sensitive ternary heterogeneous azeotropic mixture, we compare the Guang's THAD process with the conventional binary heterogeneous azeotropic distillation (BHAD) process [22], as shown in Fig. 2(a) and (b), and find that the sequence of reflux and liquid–liquid separation for the azeotropic column is different. In Guang's THAD process, the condensed liquid is first refluxed partly and then is decanted into two liquid phases [16]. On the contrary, the condensed liquid is first decanted into two liquid phases, and only the organic phase is refluxed into the column in the BHAD process. It is worth investigating to change the sequence of the refluxing and decanting of Guang's THAD process according to the BHAD process.

2.2. PS-THAD process

The PS-THAD process is achieved by two-step modifications based on Guang's THAD configuration. Firstly, the sequence of the refluxing and decanting of the overhead condensed liquid of the first column (Col-1) is changed as the conventional binary HAD

process. In other words, the condensed liquid stream is first decanted, and then part organic phase is refluxed into the azeotropic column; the aqueous phase and other part of the organic phase are purified in other columns (Col-2 and Col-3). Secondly, the operation pressure of the third column is modified as high pressure and the other columns' operation pressures are kept same as normal pressure. After two-steps' modifications, the conceptual PS-THAD process is achieved, as shown in Fig. 2(c).

2.3. PS-THADWC process

Observing the PS-THAD process, as shown in Fig. 2(c), we found that the DWC can be applied into this PS-THAD configuration. On the one hand, Col-1 and Col-2 have the same low pressure. On the other hand, the distillate liquid of Col-2 is back to Col-1. Therefore, these two columns can be arranged into one shell to form a DWC, and the PS-THADWC process is shown in Fig. 3.

3. Design and Optimization Methodologies

3.1. Basic design data

IPA/DIPE/water mixture is chosen as the separation objective for the PS-THAD process design. The feed conditions and products' requirements are the same as those in Guang's THAD processes [16]. Three RadFrac models and a decanter model are used to simulate three columns and the decanter of the PS-THAD process, respectively, in Aspen Plus V8.8 software. The overhead condensed liquid of the first column is firstly split into two liquid phases, and then the organic phase is partly refluxed into the column. The pressures of the Col-1 and Col-2 are set to be at 0.1 MPa, and the pressure of Col-3 is set to be at 0.56 MPa to expand the distillation design and make sure that the low-pressure steam can be used in the reboiler of this column [17]. The universal quasichemical (UNIQUAC) model is used to describe the phase equilibrium behaviors of this mixture [23]. Detailed parameters of the UNIQUAC model are listed in Table 1, and the specific azeotrope properties calculated are listed in Table 2.

3.2. Process optimization

For the PS-THAD process, the optimized variables include the total column-stage numbers of three columns, four feed-stage positions, the split ratio of organic phase of the decanter, the reflux ratios of the second and third columns, and three reboiler duties. The initial values of these variables are adopted from Guang's paper. In these variables, three reboiler duties are chosen as the operation variables to meet three bottom products' purities, and the others should be optimized.

For the PS-THADWC process, the optimized variables include the stage numbers of the DWC, the stage number of the second column, the feed stages of all columns, the coupled liquid location and flowrate, the distillate organic-phase fraction, and the reflux ratio of Col-2.

The GA procedure is introduced to optimize the aforementioned processes. As the objective function, the total annual cost (TAC) consists of annual energy cost (EC) and capital cost (CC) as shown in Eq. (1); the payback period and annual operating time are assumed as 3 years and $8000 \text{ h} \cdot \text{a}^{-1}$, respectively. The EC mainly includes the costs of the low-pressure steam and cooling water. The CC mainly includes the cost of column shells, internals, condenser, and reboiler, whereas the costs of pipes, pumps, and valves are neglected. The calculations of equipment sizing and economic estimation can be found in Guang's papers [16].

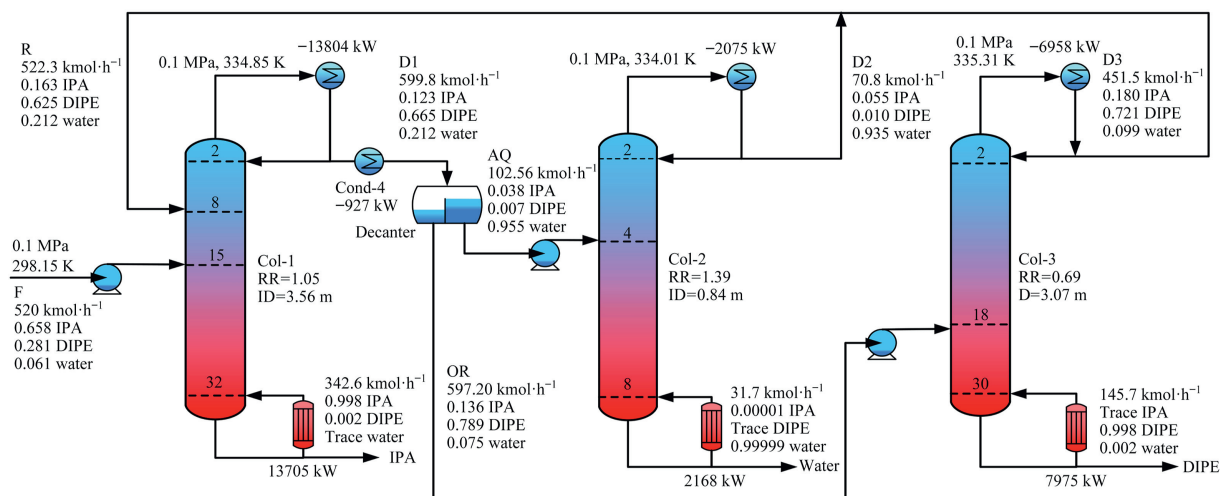


Fig. 1. Published Guang's THAD process [16].

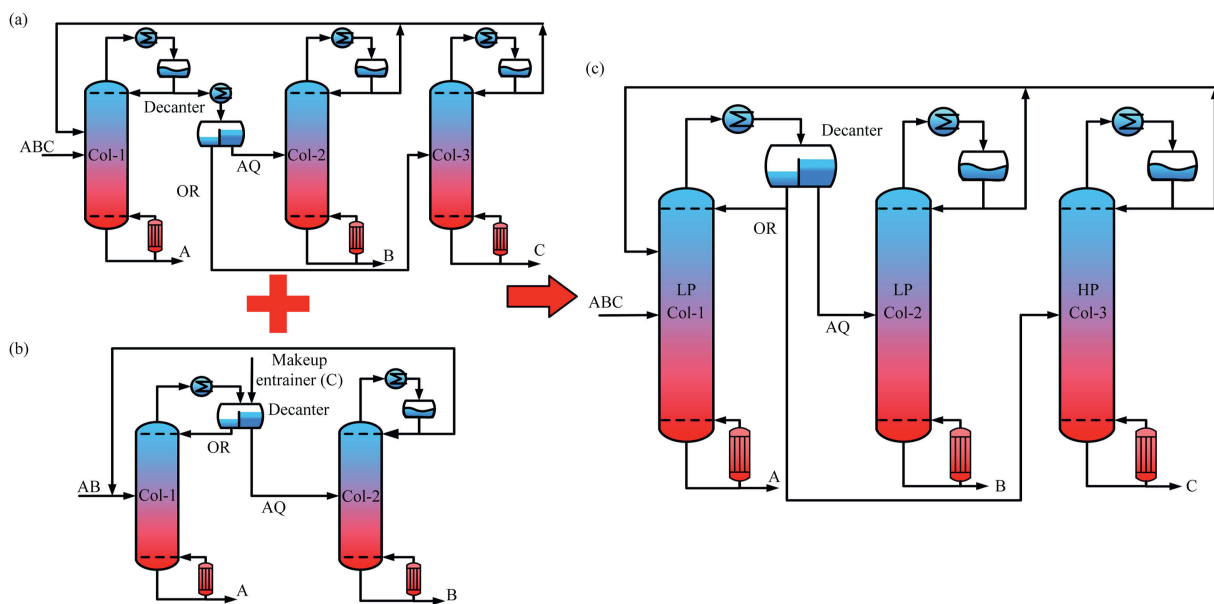


Fig. 2. (a) Guang's THAD process, (b) BHAD process, and (c) PS-THAD process.

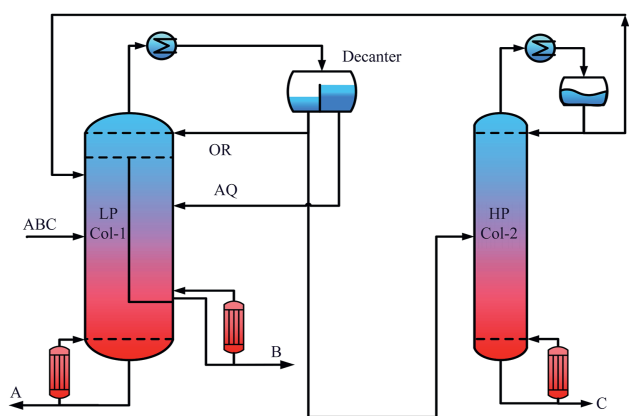


Fig. 3. PS-THADWC process.

$$TAC = \frac{CC}{\text{Payback period}} + EC \quad (1)$$

The GA procedure is carried out by coupling MATLAB 2018a and Aspen Plus V8.8. The data transfer between them is realized by Component Object Model technology. The initial population is generated by GA and is simulated in Aspen Plus software [24]. Then

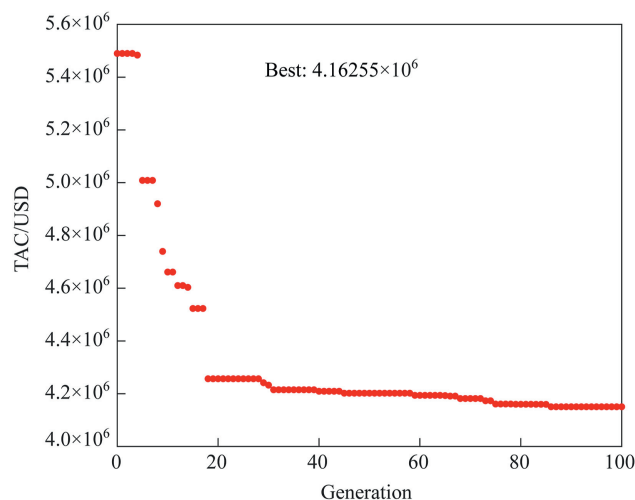
Table 1
UNIQUAC model parameters of the studied system

Comp.i/j	IPA/DIPE	Water/IPA	DIPE/water	DIPE/water
Source	APV88 VLE-IG	APV88 VLE-IG	APV88 VLE-IG	APV88 LLE-ASPEN
a_{ij}	0	2.923	0	-0.322
a_{ji}	0	-3.313	0	-1.049
$b_{ij}(K)$	129.099	-1111.670	-774.712	-497.159
$b_{ji}(K)$	-353.648	1045.580	-202.937	202.937

Table 2

Predicted properties of azeotropes in IPA/DIPE/water at 0.1 MPa

Component	Type	Molar composition	Temperature/K
IPA/water/DIPE	Heterogeneous	0.087/0.208/0.705	334.80
IPA/water	Homogeneous	0.647/0.353	352.72
Water/DIPE	Heterogeneous	0.217/0.783	335.34
IPA/DIPE	Homogeneous	0.227/0.773	339.06

**Fig. 4.** GA optimization procession for PS-THAD.

new generation is formed by selection, crossover, and mutation. When the stopping criterion is reached to the requirement (the generation number is up to be 100), the optimization results are obtained.

3.3. Environmental assessment

To assess the environmental performance of the proposed processes, CO₂ emissions (EM) are calculated. The calculation formula is as follows in Eq. (2):

$$EM_{\text{gas}} = A_{\text{gas}} M_{\text{coal}} \quad (2)$$

where M_{coal} is the mass of standard coal and A_{gas} for CO₂ is 0.2493 [25]. The M_{coal} can be expressed as Eq. (3):

$$M_{\text{coal}} = \frac{Q_R t}{Q_{\text{standard}}} \quad (3)$$

where Q_R is the total duty of reboilers and the t is the annual operating time. The Q_{standard} is the calorific value of the standard coal (29307.6 kJ·kg⁻¹).

4. Design Results and Discussion

4.1. Design results of PS-THAD process

For the PS-THAD process, the optimal values of each generation in GA procedure are listed in Fig. 4. We can see that the TAC of the PS-THAD process is decreased significantly with the increase in generation number.

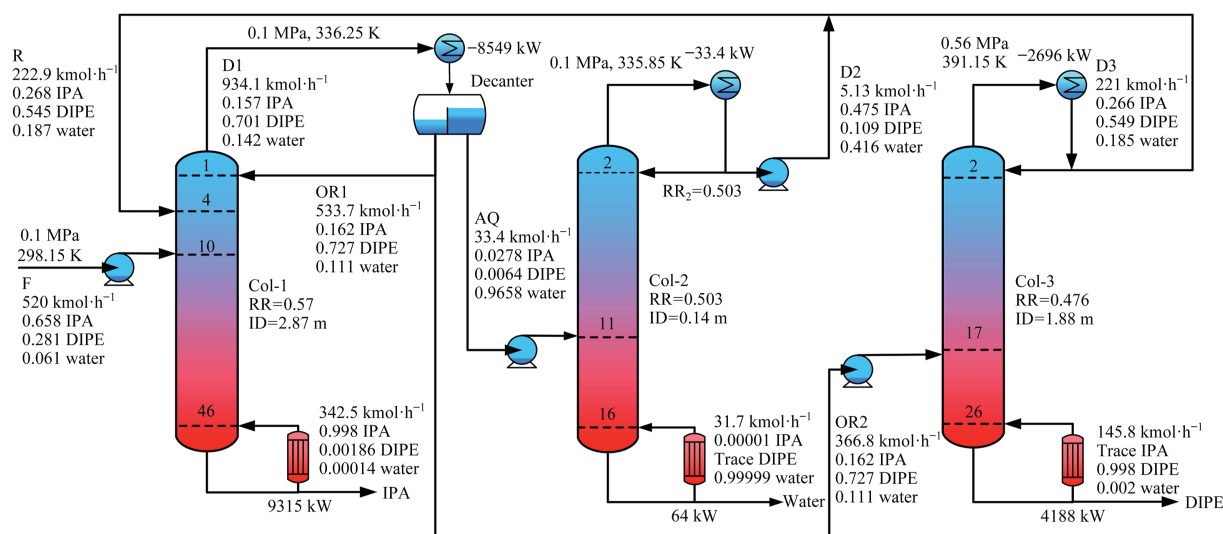
The design result of PS-THAD process is shown in Fig. 5. Compared with Guang's THAD process, the flowrate of total recycle stream (R) is reduced from 522.3 to 222.9 kmol·h⁻¹, which leads to the separation duties of all columns decreased significantly.

The RCMs of the Guang' THAD and the PS-THAD processes are compared in Fig. 6. For Guang' THAD, the material balance lines of D2-AQ and D3-OR are so short that the flowrates of D2, D3, and R are very high. In the PS-THAD process, the lengths of D2-AQ and D3-OR are increased significantly as shown in Fig. 7(b). Therefore, the flowrates of D2, D3, and R as well as the total energy consumption of the PS-THAD are deceased significantly compared to the Guang' THAD.

4.2. Design results of PS-THADWC process

For the PS-THADWC process, the GA procession result is shown in Fig. 7, which indicates that the TAC has come to the minimum value when the calculation is finished within 100 generations.

The design result of PS-THADWC process is shown in Fig. 8. Compared to the PS-THAD process, the flowrate of total recycle stream is decreased from 222.9 to 159.1 kmol·h⁻¹. Accordingly, the total duties of all condensers are reduced from 11278 kW to

**Fig. 5.** Design result of PS-THAD process.

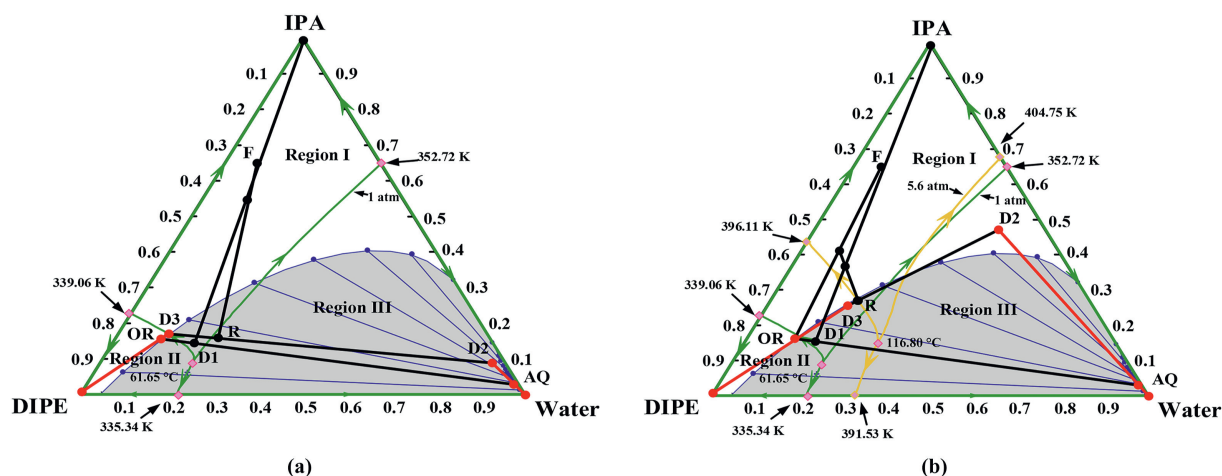


Fig. 6. Residue curve maps with material balance lines for (a) Guang' THAD and (b) PS-THAD. (1 atm = 101.325 kPa).

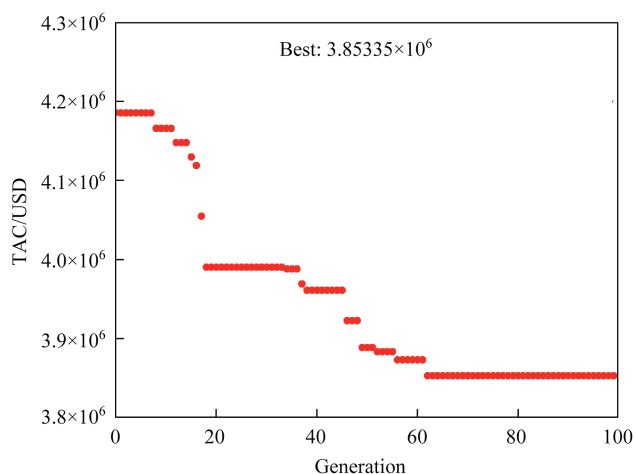


Fig. 7. GA optimization procession for PS-THADWC.

10209 kW, and the total duties of all reboilers are reduced from 13567 kW to 12558 kW.

4.3. Heat integration of PS-THADWC process

In the PS-THADWC process, the operation pressure of Col-2 is as high as 0.56 MPa, and its overhead temperature (390.88 K) is much higher than the bottom temperature (363.05 K) of Col-1. It means that the overhead vapor of Col-2 can be used to vaporize the bottom liquid of Col-1. Then, the HI-PS-THADWC process is shown in Fig. 9. In this process, the reboiler duty of Col-1 and condenser duty of Col-2 can be saved by 1426 kW simultaneously.

4.4. Process evaluation

The economic evaluation results of Guang's THAD and three proposed processes are shown in Table 3. Compared to Guang's THAD, the TACs of the PS-THAD, PS-THADWC, and HI-PS-THADWC are decreased by 40.14%, 44.60%, and 49.26%, respectively. Compared to Guang's THAD, CO₂ emissions of the PS-THAD, PS-

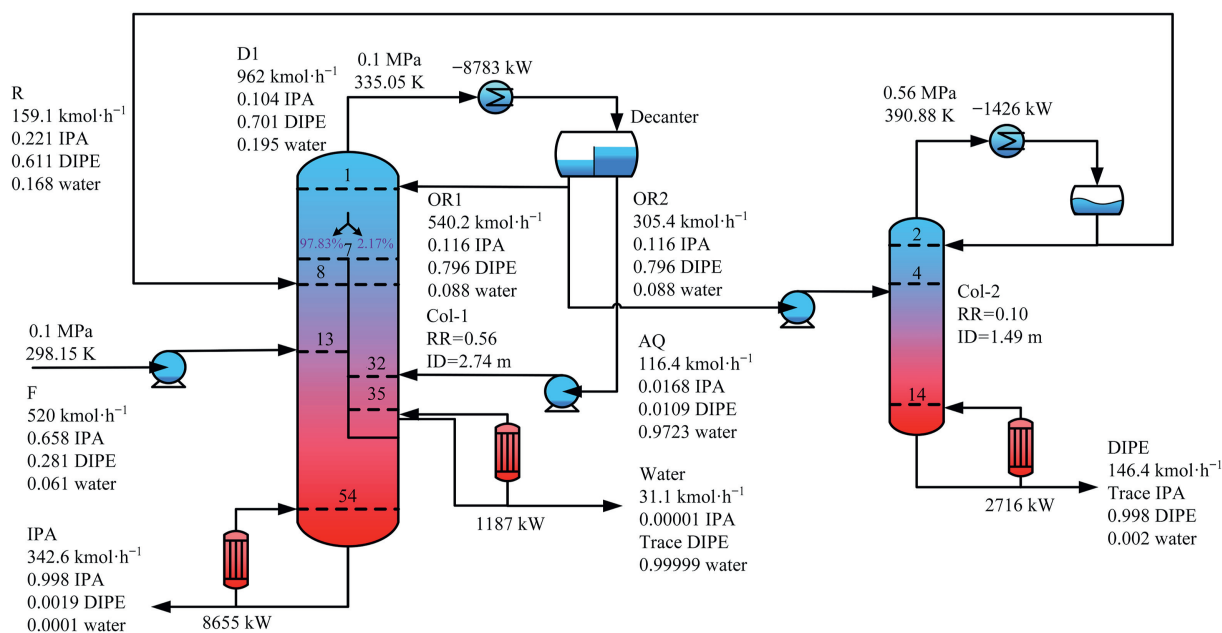


Fig. 8. Design result of PS-THADWC process.

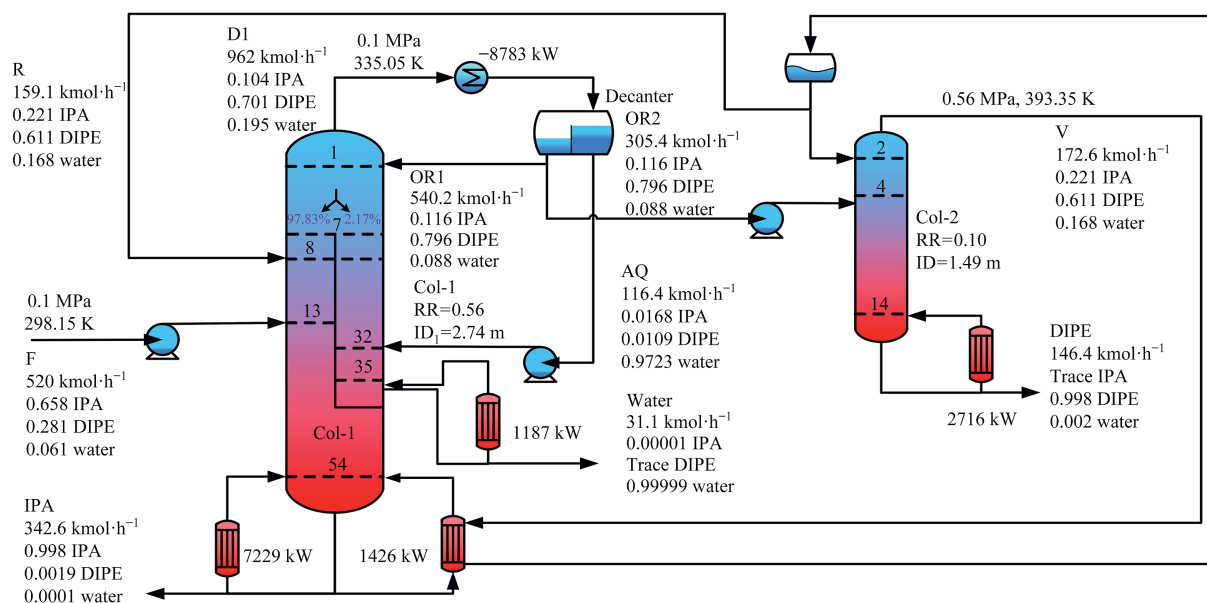


Fig. 9. Design result of HI-PS-THADWC process.

Table 3

The economic comparison of the proposed processes

Performance	THAD [16]	PS-THAD	PS-THADWC	HI-PS-THADWC
Column costs/ 10^5 USD				
Column vessels	21.34	17.15	15.49	15.49
Heat exchangers	20.02	13.07	12.57	12.86
Total capital cost/ 10^5 USD	41.36	30.22	28.06	28.35
Energy costs/ 10^5 USD				
Cooling water	2.33	1.15	1.04	0.90
LP steam	53.43	30.40	28.14	24.94
Annual energy cost/ 10^5 USD $\cdot$ a $^{-1}$	55.76	31.55	29.18	25.84
Energy cost saving/%	0.00	43.42	47.67	53.66
TAC/ 10^5 USD $\cdot$ a $^{-1}$	69.55	41.63	38.53	35.29
TAC saving/%	0.00	40.14	44.60	49.26
CO $_2$ emission/ 10^5 kg $\cdot$ a $^{-1}$	58.43	33.24	30.77	27.27

THADWC, and HI-PS-HADWC are reduced by 43.1%, 47.3%, and 53.3%, respectively.

5. Conclusions

The design and optimization of novel PS-THAD processes are discussed in this paper. The PS-THAD process is achieved by modifying the sequence of refluxing and decanting and the column pressures of the published THAD process. Then the DWC and heat integration technologies are used to further reduce the energy consumption of the PS-THAD process. The design results shown that the TACs of the PS-THAD, PS-THADWC, and HI-PS-THADWC processes can be reduced by 40.14%, 44.60%, and 49.26%, respectively, compared to the published THAD process. At the same time, CO $_2$ emissions produced in the proposed processes are reduced significantly. The energy efficiencies of the proposed processes to separate other complex ternary azeotropic systems with high water content should be investigated in the future study.

Declaration of 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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