



# The energy-efficient design based on co-process intensification for the transesterification of hexanol with n-butyl acetate

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**Abstract.** The transesterification of hexanol (HeOH) with n-butyl acetate (BuAc) has a low conversion rate and high energy consumption in reactor-separator system due to its unfavorable reaction kinetics and thermodynamic properties. The conventional reactive distillation column (CRDC) and the reactive single dividing-wall distillation column (R-SDWDC) consider the coupling between the reaction and separation operations, but their inherent structural deficiencies still prevent them from effectively reducing the irreversibility of separation operations. In this work, the recently proposed principle of co-process intensification is adopted for the process synthesis and design. Full consideration is given to process intensification of the remaining separation operations based on the non-sharp separation mode in the reaction column, resulting in a step-by-step derivation of the reactive double dividing-wall distillation column (R-DDWDC). The resultant outcomes indicate that the R-DDWDC is the optimal topological structure for implementing transesterification of HeOH with BuAc. The advantages are certainly attributed to the inclusion of the process intensification between the separation operations and its coordination with the process intensification between the reaction operation and associated separation operations involved. Although the proposed methodology is derived in terms of the transesterification of HeOH with BuAc, it has universal guiding significance for reaction systems with unfavorable kinetics and thermodynamic properties.

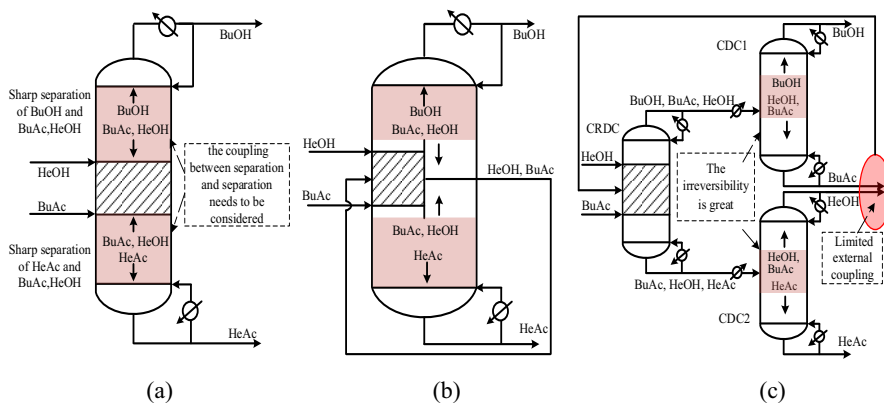
**Keywords:** process intensification; co-process intensification principle; energy-efficient design; reactive double dividing-wall distillation column; process design.

## 1 Introduction

Hexyl acetate (HeAc) with a banana aroma is widely used in desserts, beverages, and baked foods and holds significant economic value. The transesterification of hexanol (HeOH) with n-butyl acetate (BuAc) represents a viable pathway for the synthesis of the HeAc. However, due to unfavorable kinetic and thermodynamic properties, the conversion rate of reactor-separator system is low, and there are disadvantages such as high

energy consumption and prolonged reaction times [1]. Thus, it is necessary to explore the feasibility of using process intensified reactive distillation devices.

As depicted in Fig. 1(a), conventional reactive distillation column (CRDC) integrates reaction and separation operations within a single unit and reduces energy consumption and equipment investment by intensifying the coupling between reaction and separation operations of the HeOH with BuAc transesterification system [2]. The sharp separation of BuOH/HeAc from BuAc and HeOH, respectively, in the rectification/stripping section leads to great irreversibility (exergy losses caused by mass and heat transfer [3]), which lowers the thermodynamic efficiency of CRDC. Therefore, it is necessary to consider the coupling between the rectification section and the stripping section.



**Fig. 1.** Schematic of the CRDC, R-SDWDC and its thermodynamics equivalent.

Fig. 1(b) shows a schematic diagram of the structure of the reactive single dividing-wall distillation column (R-SDWDC). The coupling between the rectification section and the stripping section and the inclusion of circulation stream increases the strength of system integration, inevitably leading to an improvement in the steady-state performance of the R-SDWDC [4–6]. Egger [7,8] developed an enzyme catalyzed R-SDWDC for the transesterification of HeOH with BuAc and yielded promising outcomes. Fig. 1(c) shows a schematic diagram of the thermodynamic equivalent structure of R-SDWDC. Although the R-SDWDC considers the coupling between the rectification section and the stripping section of the CRDC, it only relies on the limited external coupling method of side withdrawal and cannot fully reduce the irreversibility of separation operations. Therefore, the R-SDWDC fails to effectively tap the potential of coupling owing to its internal structural deficiency.

In order to tap fully the potential of process intensification, our research group recently proposed the co-process intensification principle for the design of reactive dividing-wall distillation column, as shown in Fig. 2. It can be found that process intensification is simultaneously performed in the two subsystems: one is between the reaction operation and associated separation operations involved; the other is between the remaining separation operations involved. Further coordination of the two subsystems

will inevitably result in a reactive double dividing-wall distillation column (R-DDWDC). Huang and Zang<sup>[9,10]</sup> fully considered the coupling between the remaining separation operations, and used the dividing-wall column or Kaibel dividing-wall column for the remaining separation operations. By carefully coordinating the relationship between the two coupling subsystems, they proposed the optimal R-DDWDC structure design under the most unfavorable and somewhat unfavorable ranking of relative volatilities respectively.

This article focuses on the energy-efficient structure design for the transesterification of BuAc with HeOH. The topological configurations of the R-DDWDC are derived via co-process intensification principle. Intensive comparison between the CRDC, R-SDWDC, and R-DDWDC is conducted to reveal the advantages of the principle, and some important results are given in the conclusion section.

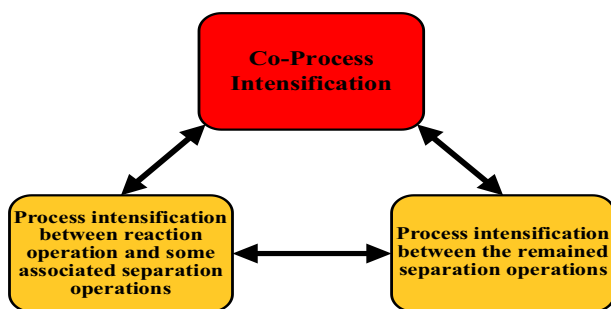


Fig. 2. A novel principle of co-process intensification.

## 2 System dynamics properties and operating conditions

The transesterification of the HeOH with BuAc to produce butanol (BuOH) and HeAc can be represented by equation (1):



Under three atmospheric pressures, the boiling points of BuOH, BuAc, HeOH, and HeAc are 425.82 K, 442.12 K, 470.30 K, and 490.78 K, respectively, making them the most favorable reactant system for relative volatility ranking. The given operating conditions and product specifications are listed in Table 1. The relevant dynamic parameters are all taken from the literature of Fieg<sup>[1]</sup>.

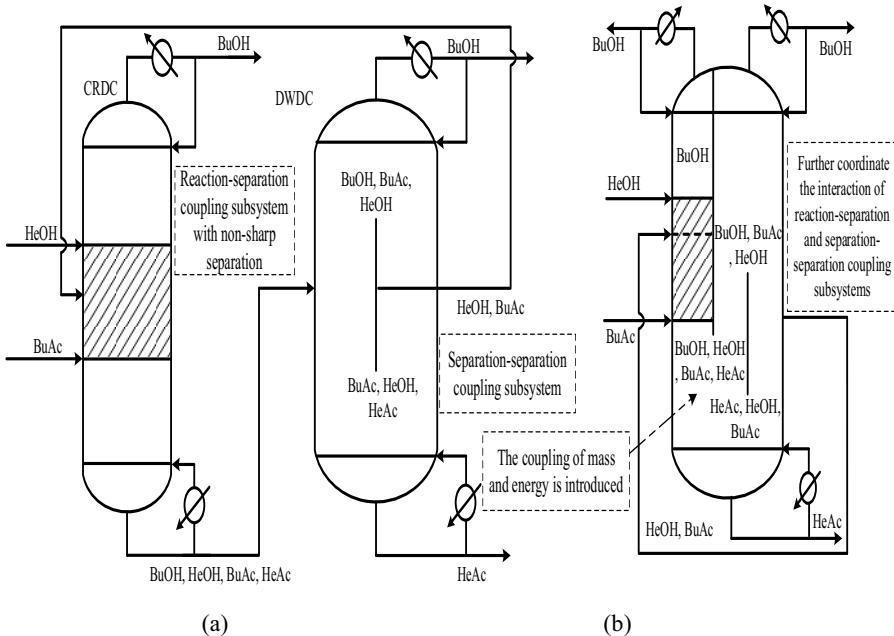
Table 1. Operating conditions and product specifications.

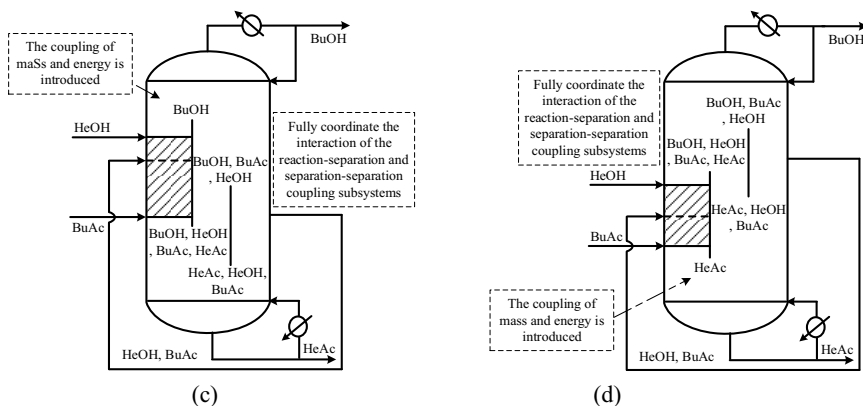
Parameter		Value
Operation pressure (atm)		3
Feed flow rate (kmol/h)	HeOH	50
	BuAc	50
Product specification (mole fraction)	BuOH	0.99
	HeAc	0.99

### 3 Synthesis and design of the HeOH with BuAc transesterification reaction system

#### 3.1 Derivation of the topological structure of the R-DDWDC based on the co-process intensification principle

According to the ranking of relative volatilities, it is recommended to position the reaction section in the middle of the column. For the CRDC to include process intensification between the remaining separation operations involved, the CRDC must be modified to allow non-sharp separations between the unconverted reactant and generated products. It can be inferred that the CRDC only has two more favorable non-sharp separation modes. One mode is to extract the BuOH from the top of the CRDC and extract all four components from the bottom of the CRDC. The corresponding topology, CRDC-DWDC, is shown in the Fig. 3(a), which contains two coupling subsystems of reaction-separation and separation-separation. It can be observed that, compared to the CRDC in Fig. 1(a), this system exhibits relatively soft operating conditions, thereby enhancing the potential exploitation of the separation-separation coupling subsystem. This approach not only simplifies system design, but also improves the steady-state performance of the system. The BuOH and HeAc are extracted from the top and bottom of DWDC, respectively, and the reflux of reactants still allowed them to meet the given product specifications.





**Fig. 3.** Derivation of the R-DDWDC by the principle of co-process intensification: (a) CRDC-DWDC (b) R-DDWDC1 (c) R-DDWDC2 (d) R-DDWDC3.

The incomplete coupling structure termed R-DDWDC1 shown in Fig. 3(b) can be obtained by introducing the coupling of mass and energy between the CRDC and DWDC. The left dividing-wall is positioned at the top, while the right dividing-wall is located in the bottom of the left dividing-wall. The inclusion of mass and energy coupling can mitigate the back-mixing degree of the CRDC and improve the steady-state performance of the whole system. The mass and energy coupling can be further introduced into the R-DDWDC1 to obtain the full coupling structure termed R-DDWDC2 shown in Fig. 3(c). The improvement can be achieved simply by relocating the left dividing-wall, shifting it from the top to the middle position, while maintaining the relative position of the right dividing-wall unchanged. The inclusion of mass and energy coupling realizes the full coupling of the system design, which can further reduce the back-mixing degree of the CRDC and improve the steady-state performance of the system.

Another mode is to extract all four components from the top of the CRDC, while the HeAc is extracted from the bottom of the CRDC. The R-DDWDC3 in Fig. 3(d) can be derived in the same way. The systems shown in Fig. 3(c) and Fig. 3(d) are the final structure of R-DDWDC obtained based on the co-process intensification principle in this article.

### 3.2 System optimization design simulation

For the convenience of comparing and analyzing the steady-state performance of the CRDC, R-SDWDC, and R-DDWDC, it is assumed that all structures have the same number of trays and catalyst amounts. System optimization design takes the heat duty of the reboiler ( $Q_{reb}$ ) as the objective function and uses grid search method to search for operational design variables (including reflux rate and gas/liquid separation ratio  $\alpha_V/\beta_L$ ) and structural design variables (including reaction section and recycle stream

location). The optimal design results are shown in Fig. 4. It is found that the R-DDWDC2 is the optimal energy-efficient configuration.

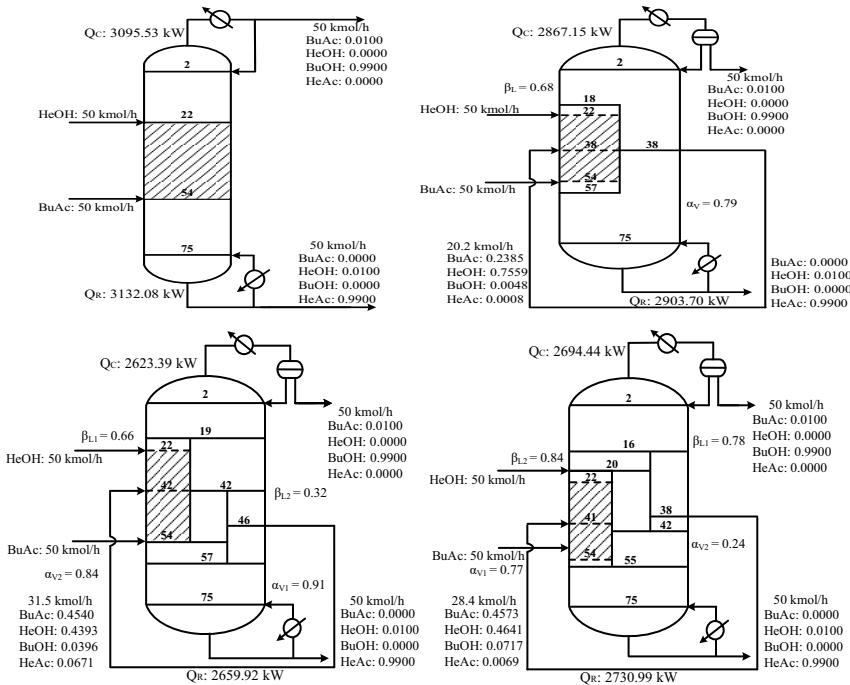


Fig. 4. Designs of the CRDC, R-SDWDC, R-DDWDC2, and R-DDWDC3.

The energy consumption of R-DDWDC2 is reduced by 15.07% and 7.78% compared with the CRDC and R-SDWDC. The comparison between the topological structures is shown in Table 2.

Table 2. Comparisons of the CRDC, R-SDWDC, R-DDWDC2, and R-DDWDC3.

Process design	Reboiler heat duty (KW)	Comparison (%)
CRDC	3132.08	100
R-SDWDC	2903.70	92.71
R-DDWDC2	2659.92	84.93
R-DDWDC3	2730.99	87.20

## 4 Discussion

The results clearly demonstrate the optimality of R-DDWDC, as it not only accounts for the coupling between reaction-separation and separation-separation operations but also effectively coordinates them through the implementation of left and right dividing-walls and a circulation stream, thereby ensuring its superior thermodynamic efficiency. Furthermore, the comprehensive system design with full coupling also induces notable

alterations in the composition profiles of the system, as evidenced by variations in the composition of the external circulation stream. Moreover, the relatively similar peak concentrations of HeOH and BuAc contribute to enhancing the steady-state performance of R-DDWDC.

## 5 Conclusion

For the transesterification of HeOH with BuAc featuring the most favorable relative volatility ranking, the CRDC and R-SDWDC cannot fully tap the potentiality of process intensification. It is necessary to include the coupling between separation operations and fully coordinate its interaction with the coupling subsystem of reaction-separation operations, and this leads inevitably to the R-DDWDC. The intensive comparison between the CRDC, R-SDWDC and R-DDWDC reveals that the R-DDWDC is the energy-efficient topological structure and highlights the feasibility, effectiveness, and optimality of the co-process intensification principle.

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