# Enhancing Mass and Energy Integration by External Recycle in Reactive Distillation Columns

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*The synthesis and design of reactive distillation columns separating reacting mixtures with the most unfavorable relative volatilities (i.e., the reactants are the heaviest and lightest components with the products being the intermediate ones) are described. The unfavorable thermodynamics poses great difficulties in combining the reaction operation and the separation operation involved and limits severely the potential of reactive distillation columns in the reduction of capital investment (CI) and operating cost. To remove the limitation, we propose two strategies for facilitating the synthesis and design of this kind of reactive distillation columns in this article. One is to arrange prudentially the reactive section so as to strengthen internal energy integration between the reaction operation and the separation operation involved; that is, while the reactive section should be placed at the bottom of the reactive distillation columns separating exothermic reactions, it should be at the top of the reactive distillation columns separating endothermic reactions. The other is to introduce an external recycle flow between the two ends of the reactive distillation columns to reinforce internal mass integration and internal energy integration between the reaction operation and the separation operation involved; that is, whereas the external recycle flow should be directed from the top to bottom of the reactive distillation columns separating exothermic reactions, it should be from the bottom to top of the reactive distillation columns separating endothermic reactions. Separation of four hypothetical ideal (i.e., two quaternary and two ternary systems, respectively) and two real nonideal (i.e., two quaternary systems) reacting mixtures is chosen to evaluate the proposed strategies. The results show that they can considerably lower energy requirement besides a further reduction in CI.* © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 2015–2032, 2013

*Keywords: process intensification, reactive distillation column, internal mass integration, internal energy integration, process design*

## Introduction

In terms of the relative volatilities of the reacting mixtures separated, it is reasonable to divide reactive distillation columns into six broad categories and these comprise of the following circumstances: (1) reactants are the light and heavy components, and products are the lightest and heaviest ones; (2) reactants are the light and heaviest components, and products are the heavy and lightest ones; (3) reactants are the lightest and heavy components, and products are the light and heaviest components; (4) reactants are the light and lightest components, and products are the heavy and heaviest ones; (5) reactants are the heavy and heaviest components, and products are the light and lightest ones; and (6) reactants are the lightest and heaviest components, and products are the light and heavy ones.[1] Although reactive distillation columns appear to be a very promising technology that renders an effective way to accommodate a reaction operation and its follow-up separation operation, their steady-state performance in separating these kinds of reacting mixtures is actually sharply different from each other due to the great difference in the ranking of relative volatilities. For the first category of reactive distillation columns, they are usually called a kind of systems separating reacting mixtures with the most favorable relative volatilities because the smallest utility consumption is required among all of the categories of reactive distillation columns mentioned above. For the last category of reactive distillation columns, on the other hand, they are usually referred to as a sort of systems separating reacting mixtures with the most unfavorable relative volatilities because the greatest utility consumption is required among all of the categories of reactive distillation columns mentioned above. The rest categories of reactive distillation columns are generally termed a class of systems separating reacting mixtures with somewhat unfavorable relative volatilities.[1] Up to now, a great number of studies, including both theoretical researches and industrial applications, have been conducted on the reactive distillation columns separating reacting mixtures with the most favorable and somewhat unfavorable relative volatilities.[2–5] Regarding the reactive distillation columns separating reacting mixtures with the most unfavorable relative volatilities

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(RDC-MURV), however, relatively scarce attention has been given so far.

The economical advantages of reactive distillation columns originate essentially from the intensified internal mass integration and internal energy integration between the reaction operation and the separation operation involved (i.e., the so-called process intensification). [6–11] A number of methods have already been proposed for the reinforcement of internal mass integration and internal energy integration within a reactive distillation column, and these included the superimposition of reactive section onto the rectifying section and/or stripping section, the relocation of feed stages and multiple feed arrangement, and the redistribution of catalyst in the reactive section.[12–19] Apart from these structural design strategies, the detailed operating conditions of a reactive distillation column, for example, the thermal conditions of reactant feed flows and operating pressure, may also affect the combination between the reaction operation and the separation operation involved and should be considered carefully during process synthesis and design. [20,21] These philosophies are, in fact, very effective to guide the synthesis and design of reactive distillation columns separating reacting mixtures with the most favorable and somewhat unfavorable relative volatilities. For the RDC-MURV, however, only a marginal reduction in capital investment (CI) and operating cost (OC) can be secured with these philosophies and the reason is mainly due to the deficiency of process configurations in coping with the most unfavorable ranking of relative volatilities. To overcome this drawback, one must, therefore, devise specific strategies for facilitating the synthesis and design of this kind of reactive distillation columns.

In this work, two effective strategies are proposed for facilitating the synthesis and design of the RDC-MURV. One is the arrangement of reactive section according to the thermodynamic characteristics of the reaction operation involved. More specifically, if the reaction operation involved is exothermic, then the reactive section should be placed at the bottom of the RDC-MURV. On the other hand, if the reaction operation involved is endothermic, then the reactive section should be placed at the top of the RDC-MURV. The other is to add an external recycle flow between the two ends of the RDC-MURV to reinforce internal mass integration and internal heat integration between the reaction operation and the separation operation involved. More specifically, if the reaction operation involved is exothermic, then the external recycle flow should be directed from the top to bottom of the RDC-MURV. Conversely, if the reaction operation involved is endothermic, then the reverse direction should be adopted. Four hypothetical ideal (i.e., two quaternary and two ternary reacting systems, respectively) and two real nonideal (i.e., two quaternary reacting systems) reactive distillation systems are then thoroughly studied. Through intensive comparison with the currently available design methods, the effectiveness of the proposed strategies is highlighted for the synthesis and design of the RDC-MURV.

## Overview of the Currently Available Design Methods for the RDC-MURV

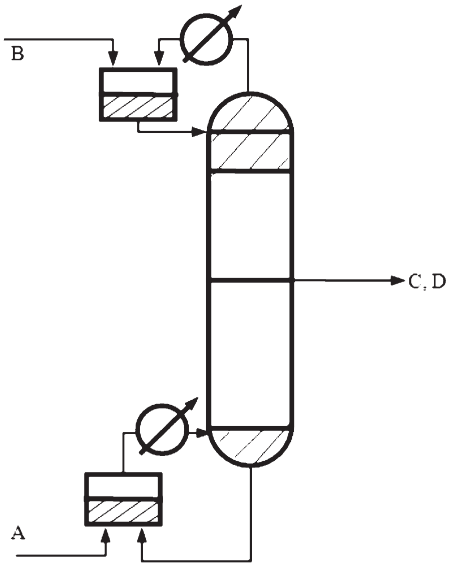
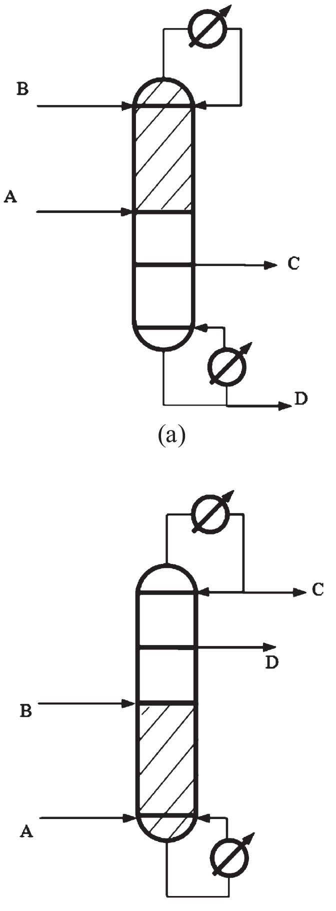


**Figure 1. A reactive distillation column with two reactive sections at the opposite ends.**

In terms of the separation of a hypothetical reaction, $A + B \leftrightarrow C + D$, with an ideal vapor–liquid equilibrium relationship, Tung and Yu[1] once studied systematically the impact of the ranking of relative volatilities on the synthesis and design of reactive distillation columns. As shown in Figure 1, they devised a unique process configuration with two reactive sections placed at the opposite ends of the RDC-MURV. Note that the top condenser and bottom reboiler were also compiled with catalyst and the reactants B and A were directly introduced into them. The desired product (i.e., a mixture containing mainly components C and D in this case) was taken out as a side withdrawal and an additional distillation column was needed to produce the high-purity C and D. Although the arrangement of multiple reactive sections appeared to be a novel idea and helped to increase conversion rate to a certain extent, the potential of internal mass integration and internal energy integration between the reaction operation and the separation operation involved was certainly not fully exploited. Internal mass integration requires that reactive section should be located to favor the reaction operation and the separation operation involved. In case of conflicts occurring between these two operations, a careful compromise should be made during process synthesis and design.[14,19] For the RDC-MURV with two reactive sections at its top and bottom, respectively, although the reaction operation could be strengthened with the introduction of the lightest reactant A and the heaviest reactant B onto the reboiler and condenser, respectively, a detrimental effect was aroused actually to the separation operation. Closely dependent on the detailed physical state of the side product withdrawn (i.e., in vapor or liquid phase), either the lightest reactant A or the heaviest reactant B was inclined to present with the components C and D, thus posing additional difficulties to reach the desired product specification. Internal energy integration requires that reactive section should be located according to the thermodynamic characteristics of the reaction operation involved.[14,20,21] If the reaction operation involved is exothermic, then reactive section should be superimposed onto the stripping section and the thermal effect of the reaction operation can serve as a means of utility to heat the stripping section. Conversely, if the reaction operation involved is endothermic, then reactive section should be superimposed onto the rectifying section and the released heat from the latter can work as a means of utility to heat the former. For the RDC-MURV



(a)

(b)

**Figure 2. Reactive distillation columns with one reactive section at either of its ends.**

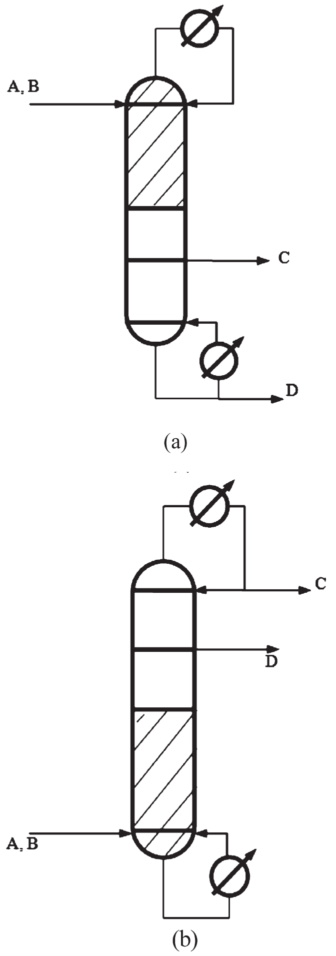
**(a) For endothermic reaction; (b) for exothermic reaction.**

with two reactive sections at its top and bottom, respectively, while the thermal heat released from the upper reactive section leads to adverse internal energy integration in case of exothermic reactions, the reaction operation occurring in the lower reactive section cannot make use of the heat released from the rectifying section in case of endothermic reactions. These are apparently the inherent drawbacks of the process configuration and inevitably result in a great degradation in system performance.

In 2009, Thotla and Mahajani[22] devised a new scheme of the RDC-MURV. Instead of using multiple reactive sections, they advocated placing only one reactive section at the top of the RDC-MURV and Figure 2a sketches the process configuration in terms of the separation of the hypothetical ideal reaction, A + B $\leftrightarrow$ C + D. Both simulation studies and experimental work were conducted with reference to the separation of three reaction systems, that is, the esterification of lactic acid with methanol, the aldol condensation of acetone, and the esterification of fatty acid with methanol, and the obtained results confirmed the enhancement in reaction conversion. They, however, overlooked the issue of internal energy integration and did not show the process configuration for separating exothermic reactions (as shown in Figure 2b). Although adverse internal energy integration could be avoided in these two schemes, internal mass integration was not adequately considered because the lightest/heaviest reactants were quite possible to accumulate in the top/bottom of the reactive distillation columns.

Recently, Gao et al.[23] proposed a novel process flow sheet involving one reactive distillation column and one conventional distillation column (CDC) column for the hydrolysis of MeOAc by modifying an existing plant with one reactive distillation column and two CDCs. With reference to the separation of the hypothetical ideal reaction, A + B $\leftrightarrow$ C + D, the reactive distillation column is reproduced in Figure 3a. It was clarified that a substantial enhancement in reaction conversion could be achieved in addition to a further reduction of utility consumption. Again, they neglected the issue of internal energy integration and did not present the process configuration for separating exothermic reactions (as shown in Figure 3b). In the aspect of internal mass integration, no measure was taken either to deal with the high presence of the lightest/heaviest reactants at the top/bottom of the reactive distillation column. Despite the difference in the arrangement of two reactant feed flows, the two schemes shared actually the same mechanism as those shown in Figure 2.

Based on the above overview, one can readily understand that the synthesis and design of the RDC-MURV represents a challenging issue in process intensification. Novel strategies therefore need to be devised.



(a)

(b)

**Figure 3. Reactive distillation columns with one reactive section at either of its ends.**

**(a) for endothermic reaction; (b) for exothermic reaction.**

## Two Strategies for the Synthesis and Design of the RDC-MURV

To strengthen internal mass integration and internal energy integration between the reaction operation and the separation operation involved, we propose therefore two strategies for the synthesis and design of the RDC-MURV. The first strategy is to locate prudentially the reactive section along the height of the RDC-MURV. More specifically, while the reactive section should be placed at the bottom (frequently including the bottom reboiler as well) of the RDC-MURV in case of exothermic reactions, it should be at the top (frequently including the top condenser as well) of the RDC-MURV in case of endothermic reactions. The way of distributing the reactive section serves to strengthen internal energy integration between the reaction operation and the separation operation involved. The second strategy is to introduce an external recycle flow between the two ends of the RDC-MURV. Although the external recycle flow should be directed from the top to bottom in case of exothermic reactions, it should be from the bottom to top in case of endothermic reactions. Because the lightest/heaviest reactants are quite likely to accumulate at the top/bottom of the RDC-MURV, the addition of an external linking between the top and bottom helps to reinforce internal mass integration and internal energy integration between the reaction operation and the separation operation involved and this should certainly contribute to the improvement in system performance.

With the application of the two strategies proposed, two novel schemes can easily be generated for the RDC-MURV and are shown in Figure 4. As can be noted, the reactive section is arranged either at the top or at the bottom of the RDC-MURV, which is solely dependent on the thermodynamic characteristics of the reacting operation separated. In case that an exothermic reaction operation ($\Delta H_r < 0$) is involved, the reactive section should be placed at the bottom (frequently including the bottom reboiler as well) of the RDC-MURV so that the thermal effect of the reaction can be used to heat the stripping section and bottom reboiler (c.f., Figure 4a).[24] Despite the fact that the RDC-MURV is now operated in a totally refluxed operation mode, the lightest Component A is still quite likely to accumulate at the top of the process and a certain amount of it could easily be withdrawn in the side product, limiting the degree of reaction conversion achieved. The inclusion of an external recycle flow from the top to bottom can certainly benefit the reaction operation and help to strengthen internal mass integration and internal energy integration between the reaction operation and the separation operation involved. In this situation, a total condenser and a total reboiler should be adopted in the RDC-MURV. In case that an endothermic reaction operation ($\Delta H_r > 0$) is involved, the reactive section should be arranged at the top (frequently including the top condenser as well) of the RDC-MURV (c.f., Figure 4b) so that the thermal heat released from the rectifying section and top condenser can be supplied to the reaction operation involved.[24] In spite of the fact that the RDC-MURV is now operated in a totally reboiled operation mode, the heaviest Component B is still likely to accumulate at the bottom of the process and a certain amount of it could easily be withdrawn in the side product, limiting again the degree of the reaction conversion achieved. The addition of an external recycle flow from the bottom to top of the reactive distillation column can certainly benefit the reaction operation involved and serve to strengthen internal mass integration and internal energy integration between the reaction operation and the separation operation involved. In this situation, a total condenser and a partial reboiler should be used in the RDC-MURV.

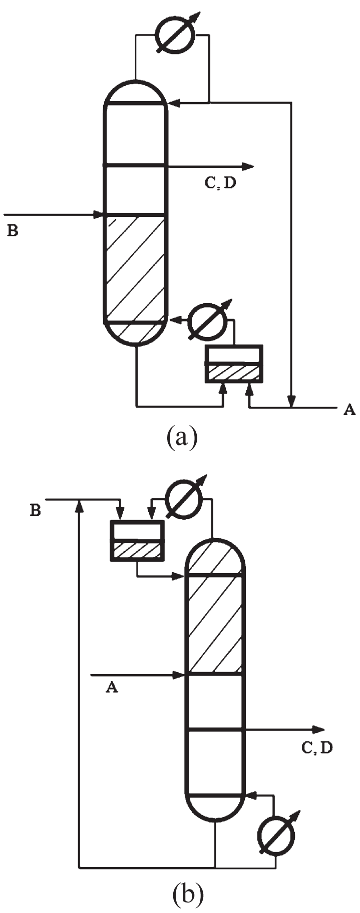


**Figure 4. Reactive distillation columns devised with the application of the two strategies proposed.**

**(a) For exothermic reaction; (b) for endothermic reaction.**

The intricate mechanism of adding an external recycle flow to the RDC-MURV can also be analyzed with the aid of the steady-state models. According to the two envelops illustrated in Figures 5a, b, respectively, (note that an exothermic reaction operation has been involved in this situation. In the case of an endothermic reaction, the analysis can be conducted in the same fashion), the overall mass balance equations and component balance equations of the lightest Component A can be written as follows.

Overall mass balance equations

$$L_{k-1} - V_k + \sum_{j=k}^{n} F_j \delta_{j,m} = 0 \tag{1a}$$

$$L^*_{k-1} - V^*_k + \sum_{j=k}^{\mathrm{n}} F^*_j \delta_{j,m} + \mathrm{RF} = 0 \tag{1b}$$

Component balance equations for the lightest Component A

$$L_{k-1} x_{A,k-1} - V_k y_{A,k} + \sum_{j=k}^{n} F_j z_{A,j} \delta_{j,m} + \sum_{j=k}^{n} \mathrm{rate}_{A,j} = 0 \tag{2a}$$

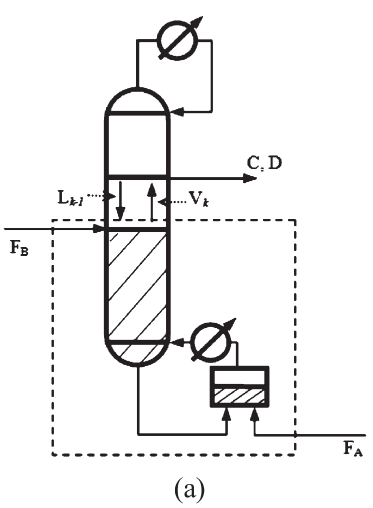


**Figure 5. Envelopes for overall mass balance equations and component balance equations of the lightest Component A.**

**(a) Reactive distillation column without an external recycle flow; (b) reactive distillation column with an external recycle flow.**

$$L^*_{k-1}x^*_{A,k-1} - V^*_k y^*_{A,k} + \sum_{j=k}^{n} F^*_j z^*_{A,j}\delta_{j,m} + \sum_{j=k}^{n} \mathrm{rate}^*_{A,j} + \mathrm{RF}x^*_{A,1} = 0 \tag{2b}$$

where the asterisk * indicates the variables belonged to the reactive distillation column with an external recycle flow between its top and bottom (RDC-ERTB), $k$ is the number assigned for the top stage in the envelop, $L_{k-1}$ is the liquid flow rate from the $k-1$-th stage, $V_k$ is the vapor flow rate from the k-th stage, and RF is the external recycle flow rate from the top to bottom of the RDC-MURV.

With the same design specifications for the two processes shown in Figures 5a, b (i.e., $\sum_{j=k}^{n} F^*_j = \sum_{j=k}^{n} F_j$ and $\sum_{j=k}^{n} rate^*_{A,j} = \sum_{j=k}^{n} rate_{A,j}$), the following equations can be derived by subtracting Eqs. 1a and 2a from 1b and 2b, respectively

$$\left(L^*_{k-1} - L_{k-1}\right) - \left(V^*_k - V_k\right) + \mathrm{RF} = 0 \tag{3a}$$

$$\left(L^*_{k-1}x^*_{A,k-1} - L_{k-1}x_{A,k-1}\right) - \left(V^*_k y^*_{A,k} - V_k y_{A,k}\right) + \mathrm{RF}x^*_{A,1} = 0 \tag{3b}$$

Combining Eqs. 3a and 3b yields

$$V^*_k - V_k = \frac{V_k\left(y_{A,k} - y^*_{A,k}\right) - L_{k-1}\left(x_{A,k-1} - x^*_{A,k-1}\right) + \mathrm{RF}\left(x^*_{A,1} - x^*_{A,k-1}\right)}{\left(y^*_{A,k} - x^*_{A,k-1}\right)} \tag{4}$$

When RF is relatively small [note the fact that RF($x^*_{A,1} - x^*_{A,k-1}$) is also small in this situation], because Reactant A is the lightest component and has the greatest relative volatility (i.e., $y^*_{A,k} - x^*_{A,k-1} > 0$), the addition of an external recycle flow to the RDC-MURV leads to increases in $x^*_{A,k-1}$ and $y^*_{A,k}$, and this results in a relatively greater reduction in the first term than in the second term in the numerator of Eq. 4. Thus, $V^*_k - V_k$ becomes minus and this signifies the reduction in reboiler duty by the reinforcement of internal mass integration and internal energy integration between the reaction operation and the separation operation involved. When RF is relatively large [note the fact that RF($x^*_{A,1} - x^*_{A,k-1}$) is also large in this situation], because more of the heaviest Reactant B is driven to the top of the reactive section, the addition of an external recycle flow to the RDC-MURV leads to decreases in $x^*_{A,k-1}$ and $y^*_{A,k}$. Because Reactant A is the lightest component and has the greatest relative volatility, the increase in the first term is greater than in the second term in the numerator of Eq. 4. Thus, $V^*_k - V_k$ turns to be plus and this signifies the enlargement in reboiler duty by the excessive reinforcement of internal mass integration and internal energy integration between the reaction operation and the separation operation involved. In terms of the above qualitative analysis, one can readily understand that the heat duty of reboiler holds a somewhat parabolic relationship with the external recycle flow rate RF. More specifically, while a relatively small recycle flow rate can favor the performance of the RDC-MURV, a relatively large one can do the opposite.

For the two schemes shown in Figure 4, the feed flows of reactants are usually placed onto the edges of the reactive section. It is certain that their locations can be adjusted to reinforce internal mass integration and internal energy integration between the reaction operation and the separation operation involved. However, for the sake of examining clearly the effect of the two strategies proposed, we do not consider these structural design options here. The external recycle flow rate (or its composition) is a key factor that influences the behaviors of the reactive distillation columns and should be carefully determined in process synthesis and design. Because the reaction products are the intermediate boiling components, they are usually withdrawn as a number of products and these can be achieved with the same principle as shown in Figures 2 and 3. In the current work, the schemes with one side draw are studied exclusively.

In what follows, the separation of four hypothetical ideal (including two quaternary and two ternary systems, respectively) and two real nonideal (including two quaternary systems) reacting mixtures is chosen to evaluate the proposed strategies for the synthesis and design of the RDC-MURV. Thorough comparison is also made with the currently available design methods mentioned in the preceding section.

## Example I: Synthesis and Design of an Ideal Reactive Distillation Column Separating a Hypothetical Exothermic Reaction A + B ↔ C + D

### *Problem Description*

Separation of a quaternary reversible liquid-phase reaction is considered in this example.[25]

$$\mathrm{A} + \mathrm{B} \leftrightarrow \mathrm{C} + \mathrm{D} \qquad \Delta H_r = -20,920\ \mathrm{kJ/kmol} \tag{5}$$

where the double-headed arrow indicates that the reaction is a kinetically controlled one.

Ideal vapor and liquid-phase behaviors are assumed for the reaction system and the vapor–liquid equilibrium relationship can be expressed as

$$P_j = x_{A,j}\, P_A^S + x_{B,j}\, P_B^S + x_{C,j}\, P_C^S + x_{D,j}\, P_D^S \tag{6}$$

$$y_{i,j} = x_{i,j}\, / P_j\, P_i^S \tag{7}$$

The vapor saturation pressure is calculated as

$$\mathrm{Ln}\, P_i^S = A_{vp,i} - B_{vp,i}/T_j \tag{8}$$

The reaction rate of component *i* on stage *j* can be expressed in terms of mole fractions $x_{i,j}$ and the kinetic holdups $RHoldup_j$.

$$\mathrm{rate}_{i,j} = v_i RHoldup_j (k_{F,j} x_{A,j} x_{B,j} - k_{B,j} x_{C,j} x_{D,j}) \tag{9}$$

where $k_{F,j}$ and $k_{B,j}$ are the forward and backward specific reaction rates, respectively, which are given by

$$k_{F,j} = a_F e^{-E_F/RT_j} \tag{10a}$$

$$k_{B,j} = a_B e^{-E_B/RT_j} \tag{10b}$$

Owing to the thermal heat of the reaction involved, the liquid and vapor flow rates change from stage to stage in the reactive section and can be calculated as

$$V_j = V_{j+1} - \mathrm{rate}_{C,j} \times \Delta H_\mathrm{r}/\Delta H_\mathrm{v} \tag{11a}$$

$$L_j = L_{j-1} + \mathrm{rate}_{C,j} \times \Delta H_\mathrm{r}/H_\mathrm{v} \tag{11b}$$

The liquid and vapor flow rates are kept constant in the nonreactive section

$$V_j = V_{j+1} \tag{12a}$$

$$L_j = L_{j-1} \tag{12b}$$

The hypothetical ideal reactive distillation column can be simulated with the steady-state model described in Appendix A. Similar first-principle models can also be found elsewhere.[25,26]

### *Comparative evaluation of the proposed process design*

In Table 1, the physicochemical properties and operating conditions are tabulated for the reactive distillation columns to be developed. It is noted that the relative volatilities of the hypothetical reacting mixture are such that the Reactants A and B are the lightest and heaviest components, respectively, and the Products C and D are the intermediate boiling components between the two reactants. Therefore, the reactive distillation columns belong to the category of systems separating reacting mixtures with the most unfavorable relative volatilities.

Tung and Yu[1] once designed a novel reactive distillation column as shown in Figure 6a. It included totally 32 stages and had a structure with two reactive sections. Although the upper one was superimposed onto the reflux-drum and the top three stages, the lower one was placed onto the bottom stage and reboiler. They further stipulated that the kinetic holdups should not exceed 20 times of the stage's reactive holdup in case that the reaction was allowed to occur in the condenser and/or reboiler. The reactants of A and B, each with a flow rate of 1.26 × $10^{-2}$ kmol/s, are fed, respectively, to the reboiler and reflux-drum. The product is a mixture of Components C and D and withdrawn at the 14-th stage from the top of the reactive distillation column.

**Table 1. Physicochemical Properties and Operating Conditions of Example I**

| Parameter | Value |
|---|---|
| Product specification (mol %) | |
| C | 47.5 |
| D | 47.5 |
| Activation energy (kJ/kmol) | |
| Forward | 50,208 |
| Backward | 71,128 |
| Specific reaction rate at 366K (kmol/s/kmol) | |
| Forward | 0.008 |
| Backward | 0.004 |
| Relative volatility A:B:C:D | 8:1:4:2 |
| Heat of reaction (kJ/kmol) | −20,920 |
| Latent heat of vaporization (kJ/kmol) | 29,053.7 |
| Vapor pressure constants | |
| A ($A_{vp}/B_{vp}$) | 17.65/3862 |
| B ($A_{vp}/B_{vp}$) | 15.57/3862 |
| C ($A_{vp}/B_{vp}$) | 16.95/3862 |
| D ($A_{vp}/B_{vp}$) | 16.26/3862 |

In terms of the same separation specification, a reactive distillation column with one reactive section is then designed and shown in Figure 6b. Because the reaction involved is an exothermic one, the reactive section is now placed at the bottom and the reboiler is also filled with catalyst. It should be noted here that the total reactive holdups are kept the same as those of the reactive distillation column having two reactive sections at its top and bottom, respectively (i.e., Figure 6a). At the given operating condition, the scheme cannot reach the desired conversion rate and this fact reveals that it is inferior to the one shown in Figure 6a. To meet the required design specification, one must therefore elevate its operating pressure from 1200 kPa to a value as high as 6500 kPa, and this gives rise to an extremely large reflux flow rate and reboiler heat duty as indicated in Figure 6b.

In the light of the same separation specification, the synthesis and design of a reactive distillation column with an external recycle flow is attempted and the resultant scheme is shown in Figure 6c. Again, the total reactive holdups are kept the same as those in the reactive distillation columns with two or one reactive sections shown in Figures 6a, b, respectively. Because the reaction involved is an exothermic one, the reactive section should be distributed at the bottom, and the external recycle flow be directed from the top to bottom. Figure 7 shows the relationship between the external recycle flow rate and heat duty of reboiler. It can readily be noted that the addition of an external recycle flow can considerably influence the performance of the RDC-MURV and the optimum value of the external recycle flow rate should be 8.6 × $10^{-3}$ kmol/s in this case.

In Figure 8, the comparison of net reaction rates and liquid composition profiles is exercised between the three process designs outlined above. Throughout this article, it is stipulated that the dotted line represents the behavior of a reactive distillation column with two reactive sections at its top and bottom,

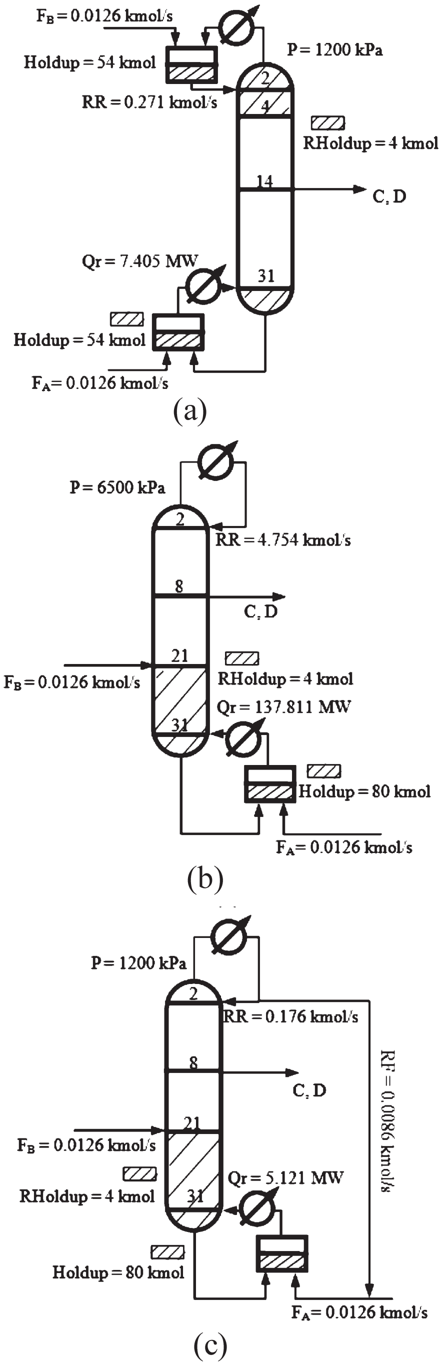


**Figure 6. Results of process synthesis and design for Example I.**

**(a) Scheme with two reactive sections at the opposite ends; (b) scheme with one reactive section at its bottom; (c) the proposed scheme.**

respectively. The dashed line stands for the behavior of a reactive distillation column with one reactive section at either its top or bottom, and the solid line the behavior of a RDC-ERTB. As shown in Figure 8a, while the reaction occurs mainly at the top and bottom of the reactive distillation column with two reactive sections, it occurs primarily at the bottoms of the schemes with one reactive section or an external recycle flow, respectively. As for the profiles of liquid compositions (c.f., Figure 8b), sharp differences are found between them. The Components C and D form two higher and wider plateaus in the reactive distillation column with two reactive sections at its top and bottom, respectively, than in the schemes with one reactive section or an external recycle flow. These phenomena are definitely caused by the different arrangements of the reactive sections and the different locations for withdrawing the side product. As can readily be noted, the addition of an external recycle flow leads to relatively lower compositions of the lightest Component A at the top and the heaviest Component B at the bottom in the reactive distillation column with an external recycle flow than in the scheme with one reactive section. This should certainly be aroused by the reinforcement of internal mass integration and internal energy integration between the reaction operation and the separation operation involved, which consequently allows the former to operate at an operating pressure of 1200 kPa. As far as the comparison of performance

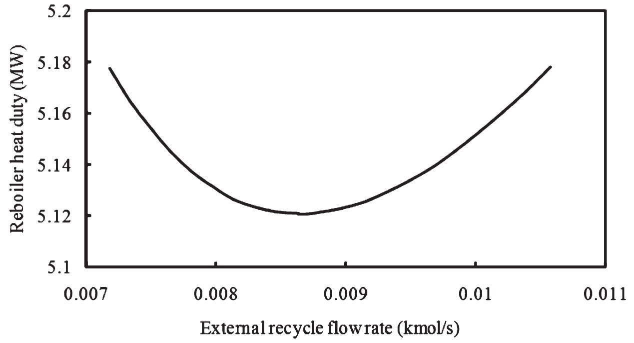


**Figure 7. Reboiler heat duty vs. external recycle flow rate of the proposed scheme for Example I.**

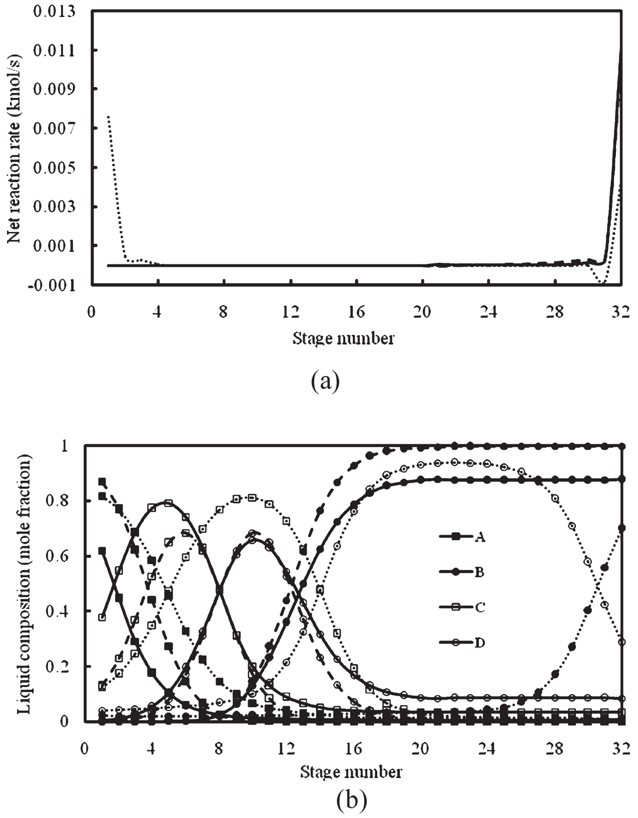


**Figure 8. Profiles of net reaction rates and liquid compositions for Example I.**

**(a) Net reaction rates; (b) liquid composition. Dotted line: scheme with two reactive sections; dashed line: scheme with one bottom reactive section; and solid line: scheme with an external recycle flow from its top to bottom.**

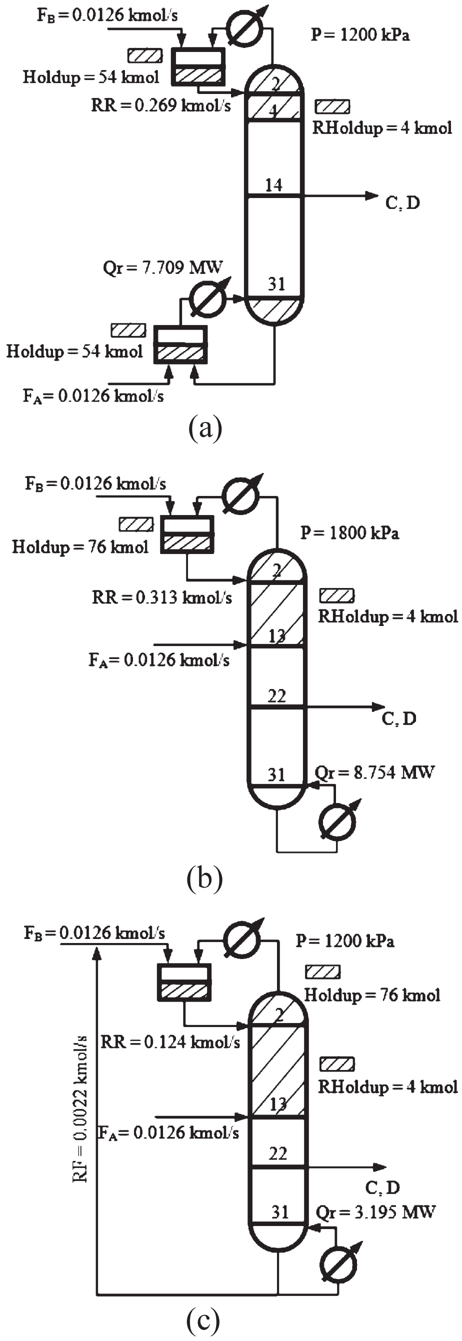


**Figure 9. Results of process synthesis and design for Example II.**

**(a) Scheme with two reactive sections at the opposite ends; (b) scheme with one reactive section at its top; (c) the proposed scheme.**

between the three process designs is concerned, the reactive distillation column with an external recycle flow from its top to bottom reduces the heat duty of reboiler by 30.84 and 96.29 %, respectively, as compared to the schemes having two or one reactive sections (c.f., Figure 6).

## Example II: Synthesis and Design of an Ideal Reactive Distillation Column Separating a Hypothetical Endothermic Reaction A + B ↔ C + D

### *Problem Description*

The problem has been adapted from Example I with the following modifications:

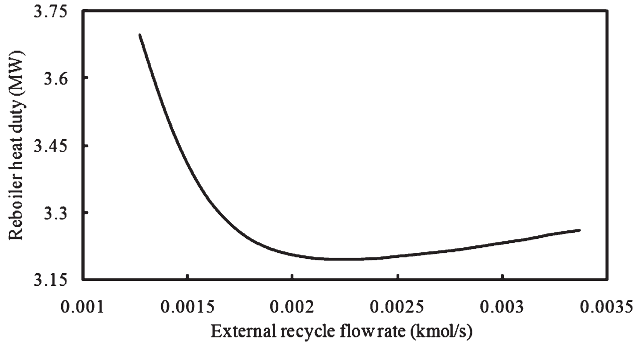


**Figure 10. Reboiler heat duty vs. external recycle flow rate of the proposed scheme for Example II.**

The reaction is assumed to be an endothermic one with a heat of reaction

$$\Delta H_r = 20,920 \text{ kJ/kmol} \tag{13}$$

The forward and backward activation energies have been exchanged with each other, namely

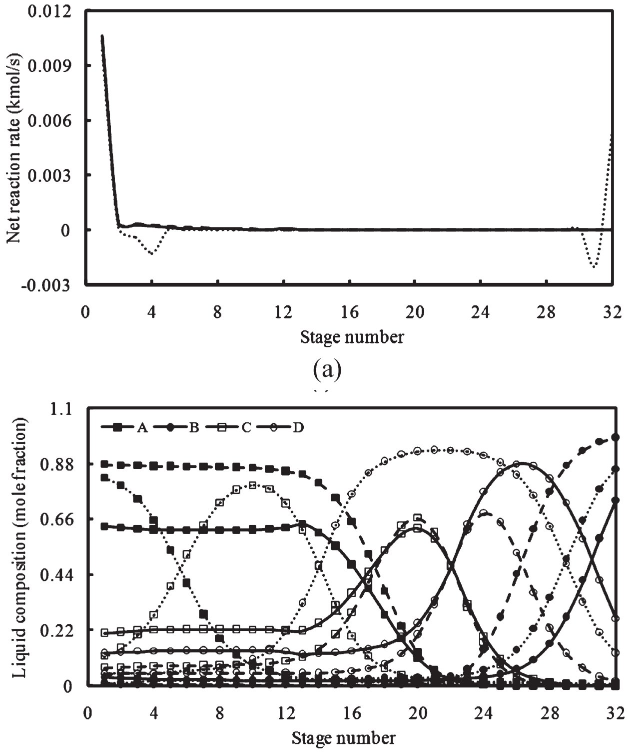
$$E_F = 71,128 \text{ kJ/kmol} \tag{14a}$$

$$E_B = 50,208 \text{ kJ/kmol} \tag{14b}$$

### *Comparative evaluation of the proposed process design*

Figure 9 shows the resultant process designs, which include a reactive distillation column with two reactive sections at its top and bottom, respectively (Figure 9a), a reactive distillation column with one reactive section (Figure 9b), and a reactive distillation column with an external recycle flow from its bottom to top (Figure 9c). Because the reaction operation involved is now endothermic, the reactive section should be placed at the tops of the schemes with one reactive section or an external recycle flow. Figure 10 shows the relationship between the external recycle flow rate and heat duty of reboiler for the scheme with an external recycle flow from its bottom to top. Again, the addition of an external recycle flow is found to affect considerably the performance of the RDC-MURV and the optimum value of the external recycle flow rate lies at $2.2 \times 10^{-3}$ kmol/s in this circumstance.

In Figure 11, the comparison of net reaction rates and liquid composition profiles is made between the three process designs outlined above. Again, the reaction occurs mainly at the top and bottom of the reactive distillation column with two reactive sections (c.f., Figure 11a). For the schemes with one reactive section or an external recycle flow, it occurs primarily at their tops. Sharp differences are still found in the widths and heights of the plateaus of Components C and D between the reactive distillation column with two reactive sections at its top and bottom, respectively, and the schemes with one reactive section or an external recycle flow (c.f., Figure 11b). The addition of an external recycle flow leads again to relatively lower presences of the lightest Component A at the top and the heaviest Component B at the bottom in the reactive distillation column with an external recycle flow than in the scheme with one reactive section. The former is allowed to operate at 1200 kPa, much lower than 1800 kPa of the latter. It turns out that the reactive distillation column



(a)

(b)

**Figure 11. Profiles of net reaction rates and liquid compositions for Example II.**

**(a) Net reaction rates; (b) Liquid composition. Dotted line: scheme with two reactive sections; dashed line: scheme with one top reactive section; and solid line: scheme with an external recycle flow from its bottom to top.**

with an external recycle flow cuts the heat duty of reboiler by 58.56 and 63.50 %, respectively, as compared with the schemes having two or one reactive sections (c.f., Figure 9).

## Example III: Synthesis and Design of an Ideal Reactive Distillation Column Separating a Hypothetical Exothermic Reaction A + B ↔ 2C

### *Problem Description*

Separation of a ternary reversible liquid-phase reaction is considered in this example

$$A + B \leftrightarrow 2C \qquad \Delta H_r = -20,920\ \text{kJ/kmol} \tag{15}$$

where the double-headed arrow indicates that the reaction is a kinetically controlled one.

The reaction rate of component *i* on stage *j*, as well as the forward and backward specific reaction rates are expressed as follows

$$\text{rate}_{i,j} = v_i RHoldup_j(k_{F,j}x_{A,j}x_{B,j} - k_{B,j}x^2{}_{C,j}) \tag{16}$$

$$k_{F,j} = a_F e^{-E_F/\text{RT}j} \tag{17a}$$

$$k_{B,j} = a_B e^{-E_B/\text{RT}j} \tag{17b}$$

Ideal vapor and liquid-phase behaviors are assumed for the reaction system and the vapor-liquid equilibrium relationship can be expressed as

$$P_j = x_{A,j}\,P_A^S + x_{B,j}\,P_B^S + x_{C,j}\,P_C^S \tag{18}$$

**Table 2. Physicochemical Properties and Operating Conditions of Example III**

| Parameter | Value |
|---|---|
| Product specification (mol %) | |
| C | 95 |
| Activation energy (kJ/kmol) | |
| Forward | 50,208 |
| Backward | 71,128 |
| Specific reaction rate at 366K (kmol/s/kmol) | |
| Forward | 0.008 |
| Backward | 0.0004 |
| Relative volatility A:B:C | 4:1:2 |
| Heat of reaction (kJ/kmol) | −20,920 |
| Latent heat of vaporization (kJ/kmol) | 29,053.7 |
| Vapor pressure constants | |
| A ($A_{vp}/B_{vp}$) | 16.95/3862 |
| B ($A_{vp}/B_{vp}$) | 15.57/3862 |
| C ($A_{vp}/B_{vp}$) | 16.26/3862 |

$$y_{i,j} = x_{i,j}\,/P_j\,P_i^S \tag{19}$$

The vapor saturation pressure is calculated as

$$\text{Ln}\,P_i^S = A_{vp,i} - B_{vp,i}/T_j \tag{20}$$

The liquid and vapor flow rates in the reactive section are calculated as

$$V_j = V_{j+1} - (\text{rate}_{C,j}/2) \times \Delta H_r/\Delta H_v \tag{21a}$$

$$L_j = L_{j-1} + (\text{rate}_{C,j}/2) \times \Delta H_r/\Delta H\text{v} \tag{21b}$$

The liquid and vapor flow rates in the nonreactive section are calculated as

$$V_j = V_{j+1} \tag{22a}$$

$$L_j = L_{j-1} \tag{22b}$$

The hypothetical ideal reactive distillation column can still be simulated with the steady-state model described in Appendix A.

### *Comparative evaluation of the proposed process design*

The physicochemical properties and operating conditions are given in Table 2 for the reactive distillation columns to be designed. Because the Reactants A and B are the lightest and heaviest components, respectively, with the Product C in-between, the reactive distillation columns should be categorized into the systems separating reacting mixtures with the most unfavorable relative volatilities.

With reference to the detailed physicochemical properties and normal operating conditions shown in Table 2, three process designs are performed and shown in Figure 12, which comprise of a reactive distillation column with two reactive sections at its top and bottom, respectively (Figure 12a), a reactive distillation column with one reactive section at its bottom (Figure 12b), and a reactive distillation column with an external recycle flow from its top to bottom (Figure 12c). Figure 13 shows the relationship between the external recycle flow rate and heat duty of reboiler for the scheme with an external recycle flow. The addition of an external recycle flow presents apparently a strong impact to the RDC-MURV, and the optimum value of the recycle flow rate is found to be 4.2 $\times$ $10^{-3}$ kmol/s in this case. In Figure 14, the comparison of net reaction rates and liquid composition profiles is depicted between the three process designs outlined above. Again, the reaction occurs mainly at the top and bottom of the reactive

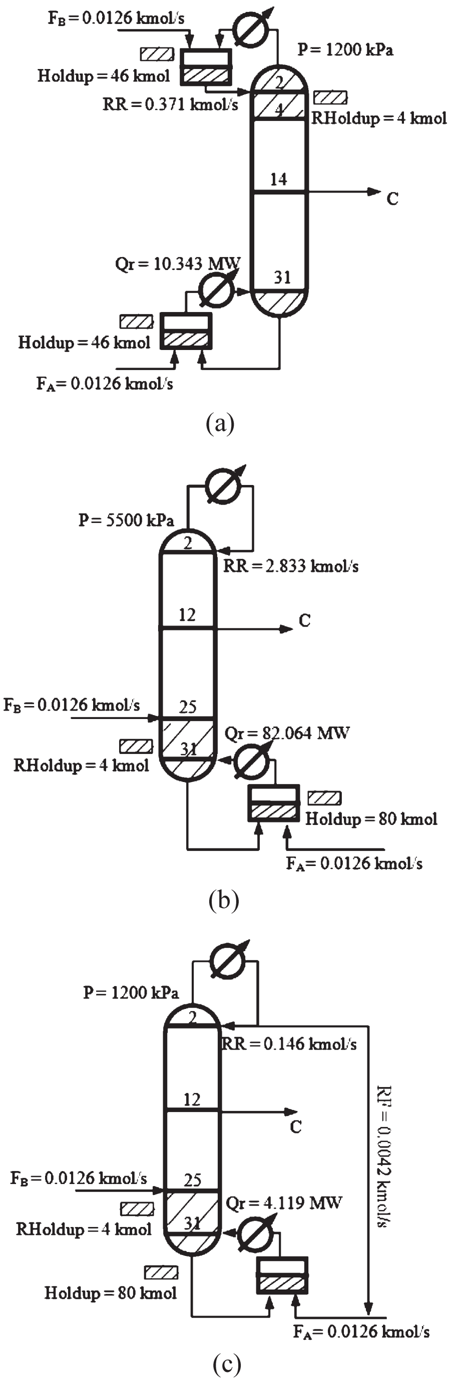


**Figure 12. Results of process synthesis and design for Example III.**

**(a) Scheme with two reactive sections at the opposite ends; (b) scheme with one reactive section at its bottom; (c) the proposed scheme.**

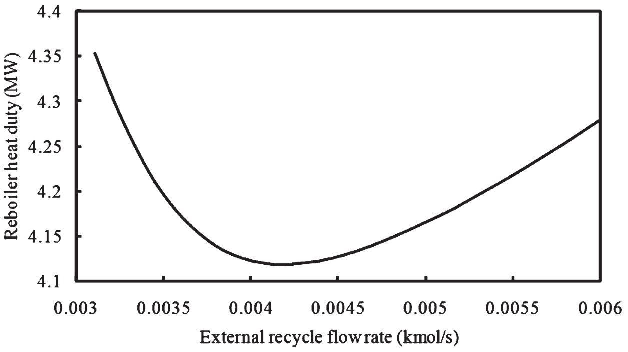


**Figure 13. Reboiler heat duty vs. external recycle flow rate of the proposed scheme for Example III.**

distillation column with two reactive sections (c.f., Figure 14a). For the schemes with one reactive section or an external recycle flow, it occurs primarily at their bottoms. The plateau of Component C in the reactive distillation column with two reactive sections at its top and bottom, respectively, differs considerably in shape with those in the reactive distillation columns with one reactive section or an external recycle flow (c.f., Figure 14b). In terms of the comparison between the reactive distillation columns having one reactive section and an external recycle flow, one can readily find that the incorporation of an external recycle flow lowers the compositions of the lightest Component A at the top and the heaviest Component B at the bottom. The latter can be operated at 1200 kPa, a pressure much lower than 5500 kPa of the former. The reactive distillation column with an external recycle flow from its top to bottom reduces the heat duty of reboiler by 60.18 and 94.98 %, respectively, as compared to the schemes having two or one reactive sections (c.f., Figure 12).

## Example IV: Synthesis and Design of an Ideal Reactive Distillation Column Separating a Hypothetical Endothermic Reaction A + B ↔ 2C

### *Problem Description*

The problem has been adapted from Example III with the following modifications:

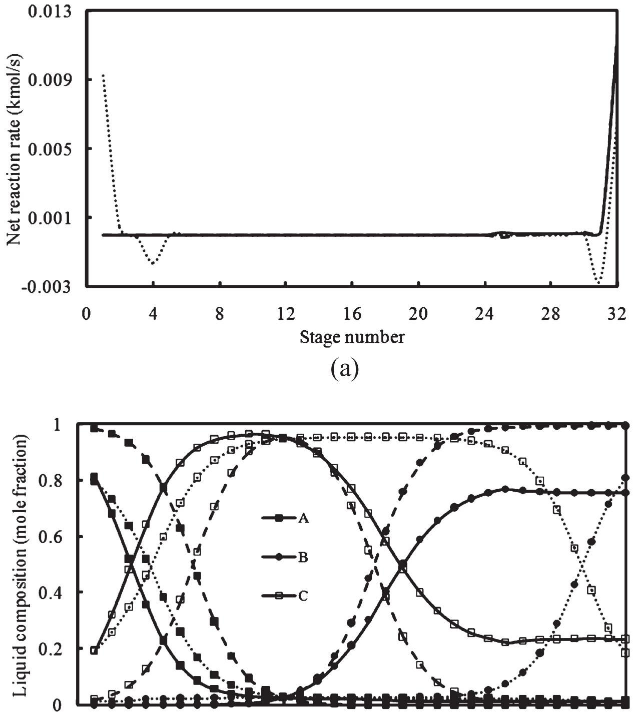


**Figure 14. Profiles of net reaction rates and liquid compositions for Example III.**

**(a) Net reaction rates; (b) liquid composition. Dotted line: scheme with two reactive sections; dashed line: scheme with one bottom reactive section; and solid line: scheme with an external recycle flow from its top to bottom.**

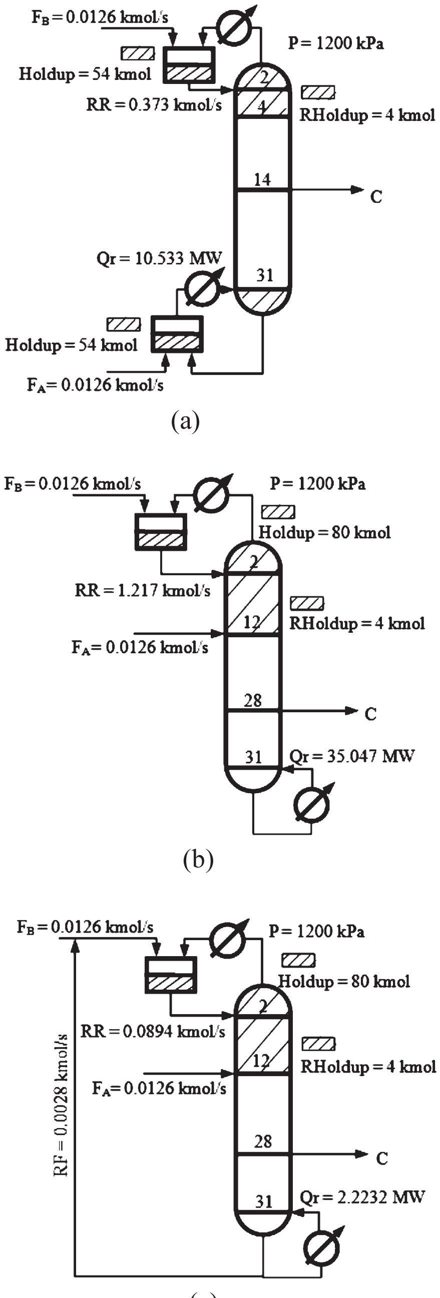


**Figure 15. Results of process synthesis and design for Example IV.**

**(a) Scheme with two reactive sections at the opposite ends; (b) scheme with one reactive section at its top; (c) the proposed scheme.**

The reaction is assumed to be an endothermic one with a heat of reaction

$$\Delta H_r = 20,920\ \text{kJ/kmol} \tag{23}$$

The forward and backward activation energies have been exchanged with each other, namely

$$E_F = 71,128\ \text{kJ/kmol} \tag{24a}$$

$$E_B = 50,208\ \text{kJ/kmol} \tag{24b}$$

### *Comparative evaluation of the proposed process design*

Three reactive distillation columns with the configurations mentioned above are designed and shown in Figure 15. Figure 16 shows the relationship between the external recycle flow rate and heat duty of reboiler for the scheme with an external recycle flow from its bottom to top. Again, the addition of an external recycle flow is found to exhibit a great effect on the RDC-MURV, and the optimum value of the external recycle flow rate is located at $2.8 \times 10^{-3}$ kmol/s in this situation. In Figure 17, the comparison of net reaction rates and liquid composition profiles is displayed between the three process designs. Again, the reaction occurs mainly at the top and bottom of the reactive distillation column with two reactive sections (c.f., Figure 17a). For the schemes with one reactive section or an external recycle flow, it occurs primarily at their tops. Although a wide plateau of Component C occurs in the reactive distillation column with two reactive sections at its top and bottom,

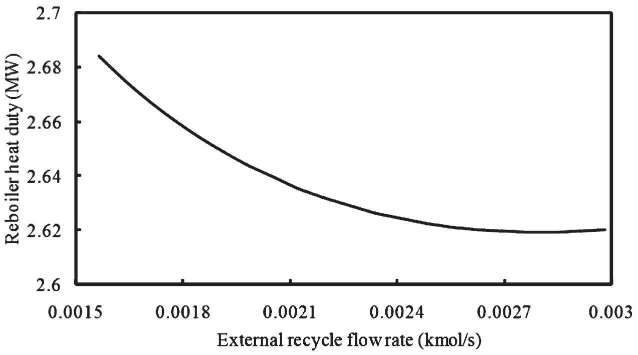


**Figure 16. Reboiler heat duty vs. external recycle flow rate of the proposed scheme for Example IV.**

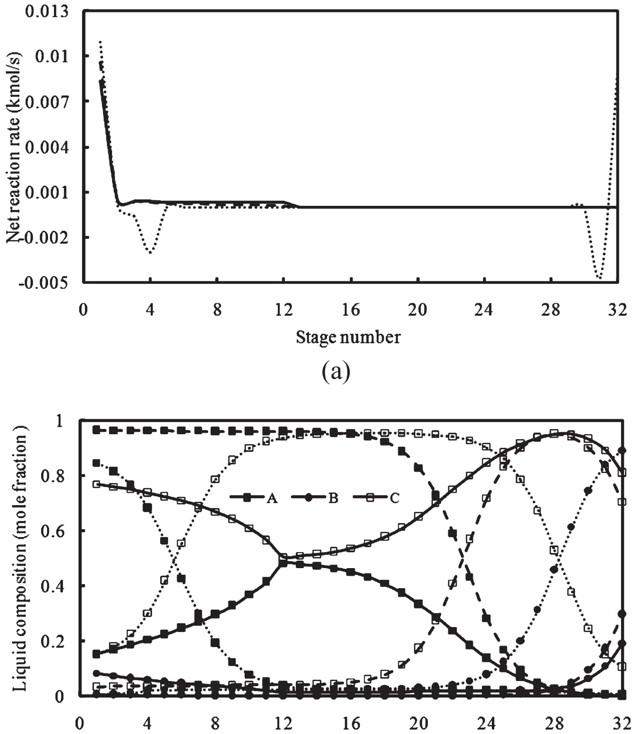


**Figure 17. Profiles of net reaction rates and liquid compositions for Example IV.**

**(a) Net reaction rates; (b) liquid composition. Dotted line: scheme with two reactive sections; dashed line: scheme with one top reactive section; and solid line: scheme with an external recycle flow from its bottom to top.**

**Table 3. Physicochemical Properties and Operating Conditions of Example V**

| Parameter | Value |
|---|---|
| Pressure (kPa) | 100 |
| Product specification (mol %) | 49.7 (MLA) |
| Boiling point (K) | 337.85 (MeOH)<br>373.15 (W)<br>417.95 (MLA)<br>490 (LA) |

respectively, a relatively narrow one appears in the schemes with one reactive section or an external recycle flow (c.f., Figure 17b). As compared to the reactive distillation column having one reactive section at its top, the incorporation of an external recycle flow reduces again the compositions of the lightest Component A at the top and the heaviest Component B at the bottom of the reactive distillation column with an external recycle flow. The reactive distillation column with an external recycle flow from its bottom to top cuts the heat duty of reboiler by 78.89 and 93.66 %, respectively, in comparison with the schemes containing two or one reactive sections (c.f., Figure 15).

## Example V: Synthesis and Design of a Reactive Distillation Column for the Esterification of Lactic Acid with Methanol

### *Problem Description*

Separation of a real exothermic reaction, esterification of lactic acid with methanol, is studied in this example.[22]

$$\begin{aligned} &\text{Methanol (MeOH)} + \text{Lactic Acid (LA)} \\ &\quad \leftrightarrow \text{Methyl lactate (MLA)} + \text{Water (W)} \\ &\quad \Delta H_r \text{ (298 K)} = -7230.91 \text{ kJ/kmol} \end{aligned} \tag{25}$$

where the double-headed arrow indicates that the reaction is a kinetically controlled one.

The normal boiling points of the reacting components, which are found from the database of the commercial software Aspen Plus V7.1, are tabulated in Table 3. It is noted that the lightest and the heaviest components are the reactants methanol and lactic acid, respectively, and the products methyl lactate and water, are the intermediate boiling components. Therefore, the lactic acid reactive distillation column belongs to the category of systems separating reacting mixtures with the most unfavorable relative volatilities.

As described in Appendix B, the lactic acid reactive distillation column is simulated using the commercial software Aspen Plus and the UNIQUAC property method is used to calculate the activity coefficients.[27] A pseudohomogeneous activity-based kinetic model is used to calculate the reaction rate (c.f., Eq. 26). The relevant binary interaction parameters and the values of kinetic parameters are denoted in Tables 4 and 5, respectively.

**Table 4. Binary Interaction Parameters of UNIQUAC Model for Example V**

| | LA | MeOH | MLA | W |
|---|---|---|---|---|
| LA | 0 | 452.35 | −288.41 | 357.47 |
| MeOH | −1040.75 | 0 | −7.37 | 165.26 |
| MLA | 208.41 | −41.42 | 0 | −394.57 |
| W | −499.38 | −351.0861 | 219.62 | 0 |

**Table 5. Kinetic Parameters for Example V**

| Parameter | Value |
|---|---|
| $E_F \times 10^3$ (kJ/kmol) | 53.1 |
| $E_B \times 10^3$ (kJ/kmol) | 40.1 |
| Log $k_F$ (kmol/kg/s) | 18.84 |
| Log $k_B$ (kmol/kg/s) | 13.45 |

$$\begin{aligned} \text{rate}_{i,j} = {} & k_F exp(-E_F/RT_j)(\alpha_{LA,j}\alpha_{MeOH,j}) \\ & - k_B exp(-E_B/RTj)(\alpha_{MLA,j}\alpha_{W,j}) \end{aligned} \tag{26}$$

### *Comparative evaluation of the proposed process design*

Three reactive distillation columns, containing the scheme with two reactive sections at its top and bottom, respectively, the scheme with one reactive section at its bottom, and the scheme with an external recycle flow from its top to bottom, are designed and shown in Figure 18. Figure 19 shows the relationship between the external recycle flow rate and heat duty of reboiler for the scheme with an external recycle flow from its top to bottom. The addition of an external recycle flow is still found to give great influences to the RDC-MURV and the optimum value of the external recycle flow rate is 3.3 $\times$ $10^{-3}$ kmol/s in this case. In Figure 20, the comparison of net reaction rates and liquid composition profiles is illustrated between the three process designs outlined above. The reaction occurs mainly at the bottoms of the reactive distillation columns with two or one reactive sections (c.f., Figure 20a), leaving a high presence of the heaviest reactant lactic acid there (c.f., Figure 20b). For the scheme with an external recycle flow, the reaction takes place primarily at the top of the reactive section and this leads to a much low presence of the heaviest reactant lactic acid at the bottom, signifying the favorable effect of the external recycle flow. Although two plateaus of methyl lactate and water are observed in the reactive distillation columns with one or two reactive sections, three ones (i.e., two for methyl lactate and one for water) are found in the reactive distillation column with an external recycle flow (c.f., Figure 20b). Despite the nonideal physicochemical properties of the reacting mixture separated, the compositions of the lightest component methanol at the top and the heaviest component lactic acid at the bottom are still lowered with the addition of an external recycle flow as compared with those of the reactive distillation columns with two or one reactive sections. The reactive distillation column with an external recycle flow from its top to bottom lowers the heat duty of reboiler by 33.81 and 37.41%, respectively, as compared to those containing two or one reactive sections (c.f., Figure 18).

## Example VI: Synthesis and Design of a Reactive Distillation Column for the Esterification of Palmitic Acid with Isopropanol

### *Problem Description*

Separation of a real endothermic reaction, esterification of palmitic acid with isopropanol, is studied in this example.

$$\begin{aligned} &\text{Isopropanol (IP)} + \text{Palmitic acid (PA)} \\ &\quad \leftrightarrow \text{Isopropyl palmitate (IPP)} + \text{Water (W)} \\ &\quad \Delta H_r \text{ (298 K)} = 18,900.01 \text{ kJ/kmol} \end{aligned} \tag{27}$$

where the double-headed arrow indicates that the reaction is a kinetically controlled one.

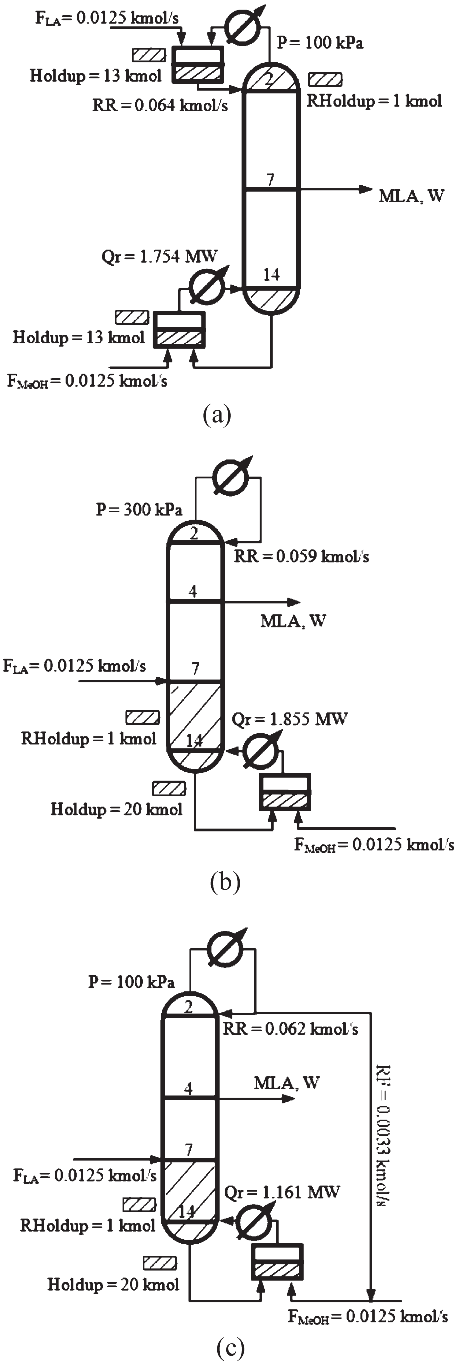


**Figure 18. Results of process synthesis and design for Example V.**

**(a) Scheme with two reactive sections at the opposite ends; (b) scheme with one reactive section at its bottom; (c) the proposed scheme.**

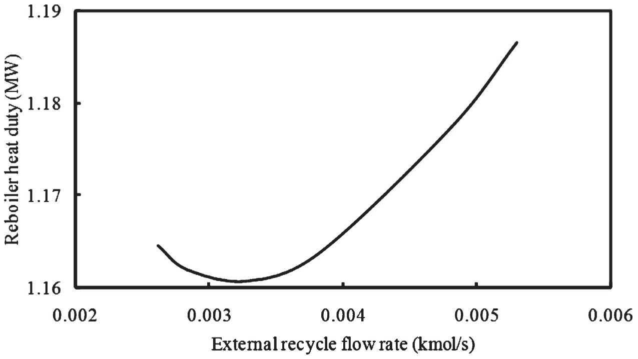


**Figure 19. Reboiler heat duty vs. external recycle flow rate of the proposed scheme for Example V.**

The normal boiling points of the reacting mixture are found from the Bhatia's work and reproduced in Table 6 for easy reference.[28] Although water and isopropanol forms a minimum-boiling azeotrope, its influences can be neglected because of the high conversion rate specified in the current work. It is thus still reasonable to treat the reactants isopropanol and palmitic acid, as the lightest and the heaviest components, respectively, and the products isopropyl palmitate and water, as the intermediate boiling components. Therefore, the isopropyl palmitate reactive distillation column can be approximately regarded as the systems separating reacting mixtures with the most unfavorable relative volatilities.

As described in Appendix B, the isopropyl palmitate reactive distillation column is still simulated with the commercial software Aspen Plus and the UNIQUAC property method is applied to calculate the activity coefficients. The reaction rate can be represented with the LHHW model that is described by Eqs. 28 and 29. The UNIQUAC binary interaction parameters are listed in Table 7 and the adsorption equilibrium constants as well as the kinetic parameters are given in Table 8.[29]

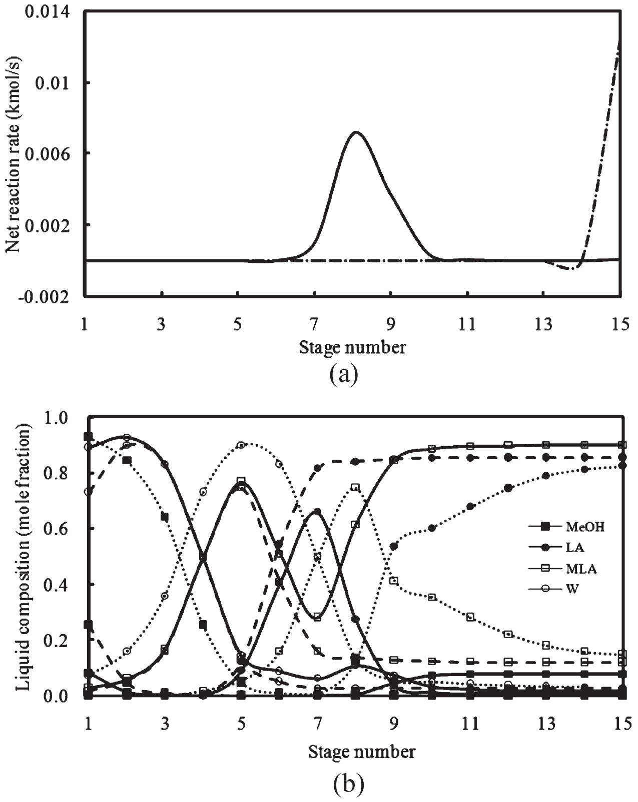


**Figure 20. Profiles of net reaction rates and liquid compositions for Example V.**

**(a) Net reaction rates, (b) liquid composition. Dotted line: scheme with two reactive sections; dashed line: scheme with one bottom reactive section; and solid line: scheme with an external recycle flow from its top to bottom.**

**Table 6. Physicochemical Properties and Operating Conditions of Example VI**

| Parameter | Value |
|---|---|
| Pressure (kPa) | 100 |
| Product specification (mol %) | 49.7 (IPP) |
| Boiling point (K) | 353.46 (IP/W)<br>355.4 (IP)<br>373.15 (W)<br>599.9 (IPP)<br>624.15 (PA) |

$$\text{rate}_{i,j}=k_F\exp\left(-\frac{E_0}{RT_j}\right)\frac{\left(\alpha_{PA,j}\alpha_{IP,j}-\alpha_{IPP,j}\alpha_{W,j}/K_{a,eq}\right)}{\left(1+K_{PA}\alpha_{PA,j}+K_{IP}\alpha_{IP,j}+K_W\alpha_{W,j}\right)^n} \tag{28}$$

$$K_{a,\text{eq}}=1256e^{-1505/T_j} \tag{29}$$

### *Comparative evaluation of the proposed process design*

Three reactive distillation columns, including the scheme with two reactive sections at its top and bottom, respectively, the scheme with a reactive section at its top, and the scheme with an external recycle flow from its bottom to top, are designed and shown in Figure 21. Figure 22 shows the relationship between the external recycle flow rate and heat duty of reboiler for the scheme with an external recycle flow from its bottom to top. The inclusion of an external recycle flow is still found to considerably affect the performance of the RDC-MURV and the optimum value of the external recycle flow rate locates at $4.9 \times 10^{-3}$ kmol/s in this circumstance. In Figure 23, the comparison of net reaction rates and liquid composition profiles is illustrated between the three process designs outlined above. Again, the reaction occurs mainly at the top and bottom of the reactive distillation column with two reactive sections (c.f., Figure 23a). For those with one reactive section or an external recycle flow, it occurs primarily at their tops. The plateaus of isopropyl palmitate and water in the reactive distillation column with two reactive sections at its top and bottom, respectively, differs considerably in shape and locations with those in the reactive distillation columns having one reactive section or an external recycle flow (c.f., Figure 23b). In spite of the highly nonideal physicochemical properties of the reacting mixture separated, the compositions of the lightest component isopropanol at the top and the heaviest component palmitic acid at the bottom are still lessened with the addition of an external recycle flow to the reactive distillation column with one reactive section. The reactive distillation column with an external recycle flow from its bottom to top reduces the heat duty of reboiler by 13.83 and 18.46%, respectively, as compared with those containing two or one reactive sections (c.f., Figure 21).

## Discussion

The outcomes of all the example systems studied in this work demonstrate that the two strategies proposed can

**Table 7. Binary Interaction Parameters of UNIQUAC Model for Example VI**

| | PA | IP | IPP | W |
|---|---|---|---|---|
| PA | 0 | 300.239 | −137.681 | 783.613 |
| IP | −94.050 | 0 | −150.672 | 59.713 |
| IPP | 165.381 | 605.248 | 0 | 1490.770 |
| W | 418.407 | 383.050 | 417.930 | 0 |

**Table 8. Reaction Parameters of LHHW Models for Example VI**

| Parameter | Value |
|---|---|
| $E_0$ (kJ/kmol) | 35,000 |
| $k_F$ (kmol/kg/s) | 5999.98 |
| $K_{PA}$ | 0.0049 |
| $K_{IP}$ | 0.0966 |
| $K_W$ | 0.6483 |
| $N$ | 2 |

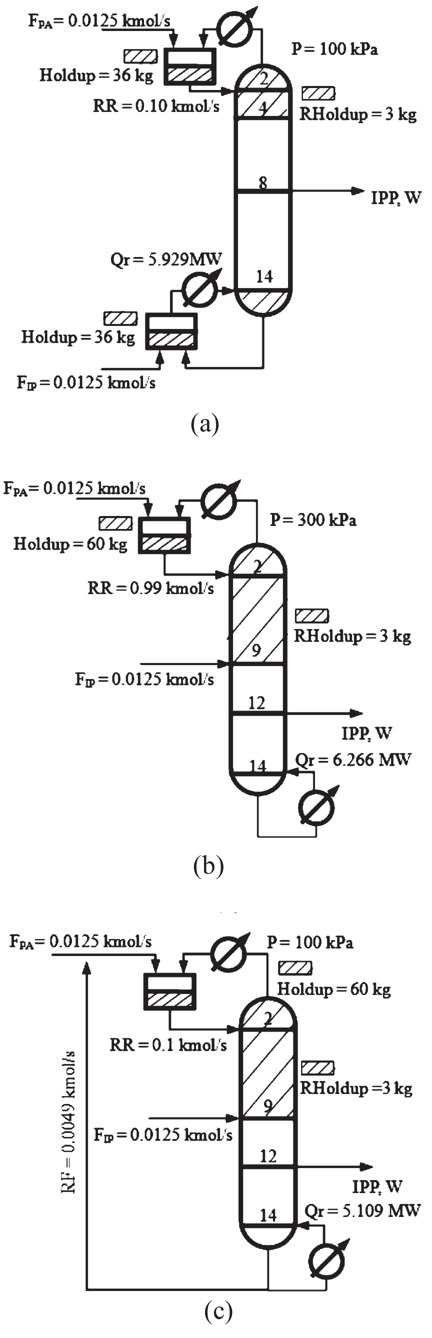


**Figure 21. Results of process synthesis and design for Example VI.**

**(a) Scheme with two reactive sections at the opposite ends, (b) scheme with one reactive section at its top, (c) the proposed scheme.**

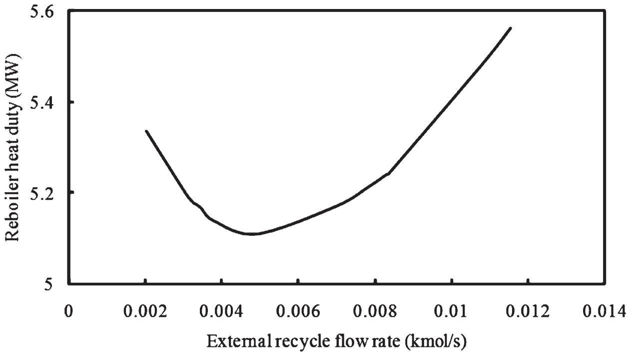


**Figure 22. Reboiler heat duty vs. external recycle flow rate of the proposed scheme for Example VI.**

enhance considerably the performance of the RDC-MURV. The reason is no doubt due to the reinforcement of internal mass integration and internal energy integration between the reaction operation and the separation operation involved. With the proper location of the reactive section along the height of a reactive distillation column, although internal energy integration can be strengthened between the reaction operation and the separation operation involved, internal mass integration can generally not well be considered because of the most unfavorable relative volatilities of the reacting mixture separated, leading inevitably to a much high presence of the most volatile and least volatile reactants at the top and bottom of the RDC-MURV, respectively (c.f., Figures 8b, 11b, 14b, 17b, 20b, and 23b). Note also that too high an operating pressure has been exclusively needed to effect the desired separation for the scheme with one reactive section at either its top or bottom. These deficiencies make it even inferior to the scheme with two reactive sections at its top and bottom, respectively, in spite of the fact that the latter must suffer from adverse internal heat integration in one of its reactive sections. With the inclusion of an external recycle flow between the top and bottom of the RDC-MURV, internal mass integration and internal energy integration are greatly intensified and this can readily be confirmed from the relatively low presence of the most volatile and least volatile reactants at the top and bottom of the scheme, respectively. The variations signify a certain enhancement of the conversion rate of the reactants and help to ease the difficulties in reaching the desired product specification. Therefore, a substantial improvement can be secured in system performance as compared with those reactive distillation columns having two or one reactive sections at both or either of their ends. This explanation points out why the RDC-ERTB can be much superior to those with two or one reactive sections for the entire example systems studied in this work.

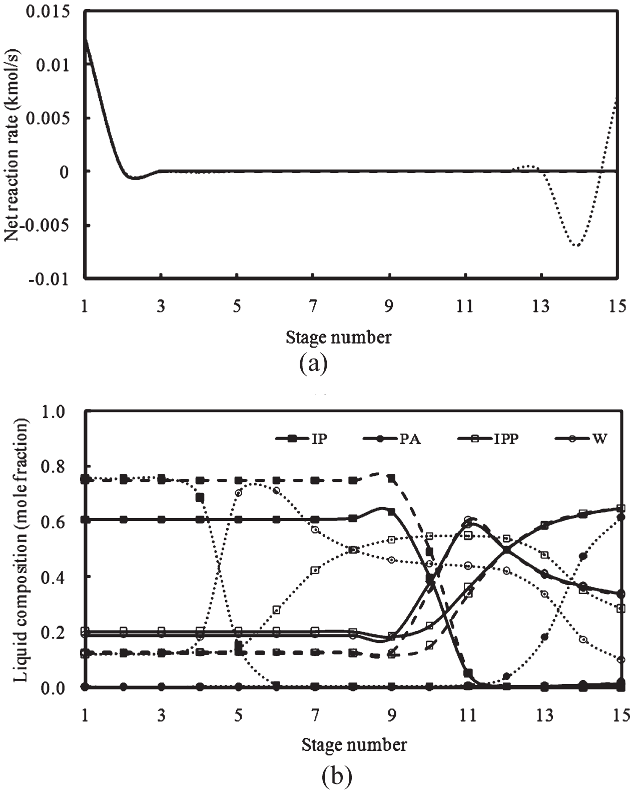


**Figure 23. Profiles of net reaction rates and liquid compositions for Example VI.**

**(a) Net reaction rates, (b) liquid composition. Dotted line: scheme with two reactive sections; dashed line: scheme with one top reactive section; and solid line: scheme with an external recycle flow from its bottom to top.**

It is interesting to evaluate further the performance of the novel reactive distillation column proposed in this work in terms of strict comparison with a conventional scheme. Here, the conventional scheme is chosen to be a continuous stirred-tank reactor plus a CDC (CSTR-DC) separating the most volatile and least volatile reactants from the intermediate products and recycling them back to the reactor. The CSTR-DC is assumed to have the same amount of catalyst and the same total number of stages as in the reactive distillation columns studied in the current work (i.e., the scheme with two reactive sections, the scheme with one reactive section, and the scheme with an external recycle flow). The compositions of the top and bottom products of the CDC are adjusted to deliver the best performance of the CSTR-DC. Here, total annual cost (TAC) is used as a performance index. The TAC is the sum of OC and annual CI, which is the CI divided by a payback period of three years. The costs of equipment and utilities are estimated with the formulas by Luyben and his coworker.[30] Two specific cases are considered here. One is to add a constraint that the amount of reactive holdups in reflux-drum or reboiler should not be greater than 20 times of the stage's holdup and it is actually the situation that has been considered in the current work. The other is to pose no constraints at all on the amount of reactive holdups in reflux-drum or reboiler. The obtained results are summarized in Tables 9 and 10, respectively, for the two cases. Closely dependent on the specific operating conditions chosen and the physicochemical properties of the reacting mixtures processed, the RDC-ERTB is found to be competitive with the CSTR-DC in some circumstances. The former can exhibit not only a smaller TAC but also a lower OC than the latter (e.g., Example V in cases I and II). These outcomes imply that the RDC-ERTB should be considered as an alternative option for the separation of reacting mixtures with the most unfavorable relative volatilities.

It should be pointed out here that additional care should be taken in distributing the reactive section in terms of the thermal effect of reaction operation involved because other thermodynamic characteristics might also exhibit dominant effects in this issue. Agrawal and Fidkowski[31] once indicated

Table 9. CSTR-DC vs. RDC-ERTB for All the Examples Studied (Case I)

| Example | CI × $10^6$ ($) |  | OC × $10^6$ ($) |  | TAC × $10^6$ ($) |  |
|---|---|---|---|---|---|---|
|  | CSTR-DC | RDC-ERTB | CSTR-DC | RDC-ERTB | CSTR-DC | RDC-ERTB |
| Example I | 0.325 | 0.331 | 0.424 | 0.759 | 0.748 | 1.090 |
| Example II | 0.256 | 0.228 | 0.232 | 0.445 | 0.488 | 0.673 |
| Example III | 0.332 | 0.295 | 0.442 | 0.611 | 0.774 | 0.906 |
| Example IV | 0.258 | 0.195 | 0.271 | 0.330 | 0.529 | 0.525 |
| Example V | 0.315 | 0.141 | 2.708 | 0.720 | 3.024 | 0.862 |
| Example VI | 0.313 | 0.378 | 3.417 | 3.680 | 3.729 | 4.057 |

that it was favorable to introduce intermediate reboilers to the rectifying section and intermediate condensers to the stripping section of the CDCs separating mixtures with highly nonideal vapor-liquid equilibrium relationships. In the case of reactive distillation columns separating reacting mixtures with highly nonideal vapor–liquid equilibrium relationships, similar circumstances are quite likely to occur. Namely, it might be reasonable to place the reactive section in the rectifying section in case of exothermic reactions and in the stripping section in case of endothermic reactions. If the reactions separated involve negligible thermal effect, the reactive section might even be arranged in both the rectifying section and stripping section. Moreover, in the case of the reactions separated involving imbalanced reaction stoichiometry (e.g., $A + B \leftrightarrow C$ or $A \leftrightarrow B + C$), it might also be reasonable to place the reactive section in the rectifying section in case of exothermic reactions and in the stripping section in case of endothermic reactions because the imbalance of reaction stoichiometry may coincide with the reversible operation principle of distillation columns. With regard to the direction of the external recycle flow between the top and bottom of the RDC-MURV, exceptional cases might also occur. For the reactions with highly thermal effect, it should certainly be from the top to bottom in case of exothermic reactions and from the bottom to top in case of endothermic reactions. However, for the aforementioned scheme with the reactive section in both the rectifying section and stripping section, the direction of the external recycle flow might be difficult to predict and must be determined through detailed optimization studies. For those reactive distillation columns separating reactions with imbalanced reaction stoichiometry (e.g., $A + B \leftrightarrow C$), the arrangement of the external recycle flow is actually quite different, which should be directed from either the top or the bottom of the processes to a certain place in the reactive section.

The great improvement in system performance by the addition of an external recycle flow between the top and bottom of the RDC-MURV reminds us of the inherent limitations in process configuration for the separation of reacting mixtures with the most unfavorable relative volatilities. Even for the separation of reacting mixtures with somewhat unfavorable relative volatilities (i.e., the categories ii to v mentioned in the introduction section), the limitations in process configuration might also exist. To remove the limitations, one can also rely on the addition of an external recycle flow. However, its arrangement can be sharply different from the philosophy proposed for the RDC-MURV. Therefore, further systematic studies are worth conducting in the near future.

## Conclusions

In this article, two effective strategies have been proposed for the synthesis and design of the RDC-MURV. The first one is to locate prudentially the reactive section to strengthen internal energy integration between the reaction operation and the separation operation involved. Although the reactive section should be placed at the bottom of the reactive distillation columns separating exothermic reactions, it should be at the top of the reactive distillation columns separating endothermic reactions. The second strategy is to introduce an external recycle flow between the two ends of the reactive distillation columns to reinforce internal mass integration and internal energy integration between the reaction operation and the separation operation involved. Although the external recycle flow should be directed from the top to bottom in case of exothermic reactions, it should be from the bottom to top in case of endothermic reactions. The external recycle flow rate (or its composition) is actually an extremely important variable that can considerably affect the performance of the RDC-MURV. Exceptional cases have also been pointed out in the arrangement of the reactive section and external recycle flow because of the highly nonideal vapor–liquid equilibrium relationship and complicated reaction kinetics. Therefore, special caution should be taken in these two issues.

In terms of the separation of two ideal quaternary reaction systems, two ideal ternary reaction systems, and two real nonideal reaction systems, the two strategies proposed have been evaluated via thorough comparison with the currently available design methods, that is, the arrangement of two or one reactive sections in the RDC-MURV. It has been demonstrated that sharp improvement in

Table 10. CSTR-DC vs. RDC-ERTB for All the Examples Studied (Case II)

| Example | CI × $10^6$ ($) |  | OC × $10^6$ ($) |  | TAC × $10^6$ ($) |  |
|---|---|---|---|---|---|---|
|  | CSTR-DC | RDC-ERTB | CSTR-DC | RDC-ERTB | CSTR-DC | RDC-ERTB |
| Example I | 0.325 | 0.266 | 0.424 | 0.528 | 0.748 | 0.795 |
| Example II | 0.256 | 0.228 | 0.232 | 0.445 | 0.488 | 0.673 |
| Example III | 0.332 | 0.268 | 0.442 | 0.528 | 0.774 | 0.796 |
| Example IV | 0.258 | 0.167 | 0.271 | 0.250 | 0.529 | 0.417 |
| Example V | 0.315 | 0.141 | 2.708 | 0.720 | 3.024 | 0.862 |
| Example VI | 0.313 | 0.371 | 3.417 | 3.572 | 3.729 | 3.943 |

system performance can be achieved with the two strategies proposed.

Future work will be centered on the dynamics and control of the reactive distillation columns with an external recycle flow in the separation of reacting mixtures with the most unfavorable relative volatilities. Special attention should be given to the impact of the external recycle flow on process dynamics and controllability. Moreover, the feasibility of using the reactive distillation columns with an external recycle flow to separate reacting mixtures with somewhat unfavorable relative volatilities needs also to be studied in the near future.

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## Notation

$a$ = pre-exponential factor
$A$ = hypothetical component
$A_{\mathrm{vp}}$ = vapor pressure constant, kPa
$B$ = hypothetical component
$B_{\mathrm{vp}}$ = vapor pressure constant, kPa K
$C$ = hypothetical component
$D$ = hypothetical component
$E$ = activation energy, kJ/kmol
Holdup = kinetic holdup in condenser or reboiler, kmol
$K_{\mathrm{a,\ eq}}$ = equilibrium constant
$L$ = liquid flow rate, kmol/s
$P$ = pressure, kPa
$Qr$ = heat duty of reboiler
$R$ = ideal gas law constant, kJ/(kmol K)
rate = reaction rate, kmol/s
$RR$ = reflux flow rate, kmol/s
$RHoldup$ = kinetic holdup on the reactive stage, kmol
$T$ = temperature, K
$V$ = vapor flow rate, kmol/s
$x$ = liquid composition
$y$ = vapor composition
$z$ = feed composition
$\Delta H_{\mathrm{r}}$ = heat of a reaction, kJ/kmol
$\Delta H_{\mathrm{v}}$ = heat of vaporization, kJ/kmol

### *Greek letters*

$\alpha$ = activity
$\delta$ = kronecker function
$\varepsilon$ = error tolerance
$\nu$ = stoichiometric coefficient

### *Superscripts*

$s$ = saturated
$sp$ = product specification

### *Subscripts*

$B$ = backward
$bot$ = bottom effluent
$F$ = forward
$IP$ = isopropanol
$IPP$ = isopropyl palmitate
$LA$ = lactic acid
$m$ = feed stage
$MeOH$ = methanol
$MLA$ = methyl lactate
$PA$ = palmitic acid
$sd$ = side draw
$top$ = top effluent
$W$ = water

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## Appendix A: Steady-State Models of the Hypothetical Ideal Reactive Distillation Columns and CSTR-DC Studied

In the case of the hypothetical ideal reaction systems, the steady-state simulation of the reactive distillation columns and CSTR-DC studied is conducted using the commercial software Mathematica. In terms of the principle of mass and energy balance in conjunction with the given vapor–liquid equilibrium relationship and reaction kinetics, their steady-state models can readily be derived. In the current work, the following assumptions have been made to simplify the resultant nonlinear equations:

1. Theoretical stages with perfect mixing and no pressure drop are assumed;
2. Sensible heat is neglected and the latent heat of all components is equal;
3. Vapor holdups can be neglected and liquid holdups are constant;
4. Relative volatilities are constant.

For the CSTR-DC, the liquid composition on each stage, the heat duty of condenser (or reboiler), and the flow rates of top and bottom recycles are chosen as decision variables. For the reactive distillation column with a side draw, the liquid composition on each stage and the heat duty of condenser (or reboiler) are chosen as the decision variables. For the reactive distillation column with an external recycle flow, besides the liquid composition on each stage and the heat duty of condenser (or reboiler), the external recycle flow rate must also be chosen as the decision variable. Once the decision variables have been determined, other process variables can be calculated in a sequential manner. For instance, after the temperature distribution has been searched to match the given operating pressure, the profile of vapor compositions can be calculated, and the mass balance and energy balance equations can be solved to yield the vapor and liquid flow rates. The decision variables are then updated using the Broyden's (quasi-Newton) method, and the satisfaction of component mass balance equations, that is, Eq. A1 (for the scheme where the external recycle flow is directed from the top to bottom in case of exothermic reactions) or Eq. A2 (For the scheme where the external recycle flow is directed from the bottom to top in case of endothermic reactions), and product specification (i.e., Eq. A3), are taken as the convergence criterion. For the CSTR-DC, the attainment of composition specifications in the top and bottom effluents of the CDC (i.e., Eqs. A4 and A5) should also be included as the convergence criterion. The steady-state models appear to be quite robust and can approach the desired steady state fairly quickly for the various hypothetical ideal reactive distillation columns and CSTR-DC

$$\begin{aligned}|L_{j-1}x_{i,\,j-1} + V_{j+1}y_{i,\,j+1} - L_jx_{i,\,j} - V_jy_{i,\,j} + F_jz_i, \delta_j + \mathrm{rate}_{i,\,j}\\ + RF_j * x_{i,\,1}| < \varepsilon\end{aligned} \tag{A1}$$

$$\begin{aligned}|L_{j-1}x_{i,\,j-1} + V_{j+1}y_{i,\,j+1} - L_jx_{i,\,j} - V_jy_{i,\,j} + F_jz_i, \delta_j + \mathrm{rate}_{i,\,j}\\ + RF_j * x_{i,\,nt}| < \varepsilon\end{aligned} \tag{A2}$$

$$|x_{\mathrm{sd}} - x_{\mathrm{sd}}{}^{sp}| < \varepsilon \tag{A3}$$

$$|x_{\mathrm{top}} - x_{\mathrm{top}}{}^{sp}| < \varepsilon \tag{A4}$$

$$|x_{\mathrm{bot}} - x_{\mathrm{bot}}{}^{sp}| < \varepsilon \tag{A5}$$

## Appendix B: Steady-State Models of the Real Reactive Distillation Columns and CSTR-DC Studied

In the case of real reaction systems, the steady-state simulation of the reactive distillation columns and CSTR-DC studied is conducted using the commercial software Aspen Plus. While the RadFrac column module is used in the former, the RCSTR and RadFrac column modules are adopted in the latter. An external Fortran subroutine is programmed to model the kinetics of the reaction operation involved. For the description of the totally refluxed operation mode, a trace of the overhead product is deliberately withdrawn and then recycled to the top of the process because the RadFrac column module requires the specification of an overhead product flow rate. The steady-state models thus developed can accurately represent the behavior of the totally refluxed reactive distillation columns for no overhead product is essentially distillated out. With regard to the external recycle flows contained in the proposed reactive distillation columns and CSTR-DC, their flow rates and/or compositions must be chosen as tear variables. The Broyden's convergence method is used to solve the resultant nonlinear equations and the steady-state models can approach the desired steady state fairly quickly for the various real reactive distillation columns and CSTR-DC.

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