Synthesis and design of reactive distillation columns with two reactive sections

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Abstract

The synthesis and design of reactive distillation columns with two reactive sections (RDC-TRS) are attempted for the separations of reacting mixtures with somewhat unfavorable ranking of relative volatilities (RM-SURRV, i.e., two reactants are the light and heaviest components and two products the lightest and heavy ones). With the deliberate arrangement of the two reactive sections, the disadvantages by the unfavorable relative volatility can be substantially alleviated, facilitating consequently the reaction operation and separation operation involved. The separations of a hypothetical quaternary reaction, the esterification of acetic acid with methanol, and the transesterification of butyl acetate with ethanol are employed to evaluate the RDC-TRS. The process is found considerably superior to the reactive distillation column with a single reactive section and this demonstrates its feasibility and effectiveness in the separations of RM-SURRV. The RDC-TRS is found to present comparable or even improved performance in comparison with the reactive distillation column with an external recycle from bottom to reactive section and this corroborates it a potentially competitive alternative for the separations of the RM-SURRV. The RDC-TRS is also highlighted for the other kind of RM-SURRV (i.e., two reactants are the lightest and heavy components and two products the light and heaviest ones).

Keywords: Reactive distillation column; Single reactive section; External recycle; Double reactive sections; Process synthesis; Process design.

1. Introduction

The advantages of reactive distillation columns, e.g., the reduction of capital investment and operating cost, originate essentially from their capability of driving equilibrium-limited reactions to completion due to the in-situ separations of products from reactants in the reactive section (Doherty and Buzad, 1992; Malone and Doherty, 2000; Stankiewicz, 2003). In the case of the separations of reacting mixtures with the most favorable ranking of relative volatilities (RM-MFRRV, i.e., two reactants are the light and heavy components and two products the lightest and heaviest ones), such advantages can fully be exploited because of the light and heavy reactants unconverted are readily separated from the lightest and heaviest products (in the rectifying and stripping sections) and recycled back to the reactive section with the manipulations of reflux and reboil flow rates, respectively (Luyben, 2000; Kaymak and Luyben, 2004; Tung and Yu, 2007). This is indicated clearly in Fig. 1a in terms of the separation of a hypothetical quaternary reaction, $A + B \xrightleftharpoons[k_B]{k_F} C + D$ ($\alpha_C > \alpha_A > \alpha_B > \alpha_D$). In the case of the separations of reacting mixtures with somewhat unfavorable ranking of relative volatilities (RM-SURRV, i.e., two reactants are the light and heaviest components and two products the lightest and heavy ones), such advantages can, however, only be partially exploited. Fig. 1b illustrates the detailed reason for the degradation of steady-state performance in terms of the separation of a hypothetical quaternary reaction, $A + B \xrightleftharpoons[k_B]{k_F} C + D$ ($\alpha_C > \alpha_A > \alpha_D > \alpha_B$). Although the light reactant A unconverted can readily be separated from the lightest product C in the rectifying section and recycled back to the reactive section through the manipulation of reflux flow rate, the heaviest reactant B unconverted is extremely difficult to be separated from the heavy product D in the stripping section and recycled back to the reactive section with the manipulation of reboil flow rate (it tends actually to accumulate at bottom). Thus, the unfavorable relative volatility between reactant B and product D accounts for the degradation in steady-state performance of conventional reactive distillation columns (Tung and Yu, 2007; Lin et al., 2008; Wang et al., 2011). Similar reasoning can also be applied to the separations of another kind of the RM-SURRV (i.e., $\alpha_A > \alpha_C > \alpha_B > \alpha_D$). Namely, the unfavorable relative volatility occurs between reactant A and product C. Some specific measures were frequently taken to suppress the drawback and these included, for example, the employment of an extended reactive section and use of excessive light reactant (Luyben, 2000; 2008; Tsai et al., 2008). The expenses were, however, increased capital investment and/or operating cost. Huang et al. (2014) proposed to use external recycle to return the heaviest reactant unconverted from bottom to the reactive section and found effective in improving the steady-state performance of conventional reactive distillation columns (The process is termed the RDC-ERBR, hereinafter, in the current work). So far, conventional reactive

distillation columns with a single reactive section (RDC-SRS) have been used almost exclusively to separate the RM-SURRV and this fact has stimulated us to attempt other kinds of process synthesis and design.

Recently, reactive distillation columns with two reactive sections (RDC-TRS) were proposed to separate reacting mixtures with complicated physicochemical properties (Yu et al., 2014). Tung and Yu (2007) firstly recommended using a RDC-TRS for the separations of quaternary reacting mixtures with the most unfavorable ranking of relative volatilities (i.e., two reactants are the lightest and heaviest components and two products the light and heavy ones). Sundmacher and his coworkers (2008; 2009) mentioned that a reactive distillation column with multiple reactive sections might be favorable to the indirect hydration of cyclohexene to cyclohexanol with formic acid as reactive entrainer. Zhang et al. (2015) suggested adopting feed splitting in the synthesis and design of RDC-TRS and demonstrated great improvement in steady-state performance due to the reinforcement of internal mass integration and internal energy integration between the reaction operation and separation operation involved. Since the RDC-TRS involves more degrees of freedom (e.g., the number of reactive stages in the two reactive sections, the number of stages between the two reactive sections, and feed splitting ratio of the light/heavy reactant) for process synthesis and design than the RDC-SRS, it is quite likely that it holds relatively high potential in the separations of the RM-SURRV. As a result, a substantial improvement is likely to be expected in steady-state performance.

In this work, the synthesis and design of the RDC-TRS are attempted for the separations of the RM-SURRV. The detailed strategies for the arrangement of the two reactive sections are pointed out and three examples, including the separations of the representative hypothetical ideal reaction, $A + B \xrightleftharpoons[k_B]{k_F} C + D$ ($\alpha_C > \alpha_A > \alpha_D > \alpha_B$), the esterification of acetic acid with methanol, and the transesterification of butyl acetate with ethanol, are chosen as illustrative examples to evaluate the steady-state performance of the RDC-TRS. In terms of in-depth comparisons with the RDC-TRS and RDC-ERBR, the feasibility and effectiveness of the RDC-TRS are highlighted for the separations of the RM-SURRV. The potential schemes of the RDC-TRS are also indicated for the separations of the other kind of RM-SURRV (i.e., two reactants are the lightest and heavy components and two products the light and heaviest ones).

2. Principle and Potential Configurations of the RDC-TRS

Since the unconverted heaviest reactant tends to accumulate at bottom and is impossible to be completely recycled back to the reactive section (with the manipulation of reboil flow rate), these constitute the primary reasons that lower the

steady-state performance of the RDC-SRS. To suppress the negative effect, one may use an additional reactive section to convert the unconverted heaviest reactant into the desired products and prevent its accumulation at bottom, thereby alleviating the difficulty in separation operation. The inclusion of an additional reactive section into the RDC-SRS thus gives rise to the RDC-TRS. It is straightforward to understand that the steady-state performance of the RDC-TRS depends heavily on the arrangement of the two reactive sections.

With reference to the separation of the hypothetical quaternary reaction: $A + B \xrightleftharpoons[k_B]{k_F} C + D$ ($\alpha_C > \alpha_A > \alpha_D > \alpha_B$), the potential configurations of the RDC-TRS are sketched in Figs. 2a and 2b. Since the relative volatility between the lightest product C and light reactant A permits to purify the lightest product C through reacting away the light reactant A, a reactive section, termed, hereinafter, the upper reactive section, is thus needed below the rectifying section to accomplish the two tasks simultaneously. As can readily be seen, it takes exactly the same structure with the top part of the RDC-SRS (c.f., Figs. 1a and 1b). Since the relative volatility between the heavy product D and heaviest reactant B does not allow the recycle of the unconverted reactant B to the upper reactive section (through the manipulation of reboil flow rate), a reactive section, termed, hereinafter, the lower reactive section, is thus needed somewhere below the upper reactive section to convert the unconverted reactant B into the products C and D. Fig. 2a sketches such a process configuration with the product D as a bottom effluent. The stages between the upper and lower reactive sections serve mainly to enhance the composition of the heaviest reactant B and aid the reaction operation in the lower reactive section. In the case that the reaction conversion is high in the upper reactive section, the composition of the heaviest reactant B is likely to be small below the upper reactive section. It is then reasonable to drain off the product D as an intermediate effluent, as sketched in Fig. 2b. Note that the lower reactive section is now deliberately arranged at bottom (include frequently the reboiler as well) to eliminate the unconverted heaviest reactant B. In both situations, feed splitting of the light reactant A should be included to facilitate the reaction in the upper and lower reactive sections.

Despite the steady-state performance of the RDC-TRS depends heavily on the arrangement of the upper and lower reactive sections, its synthesis and design are not so complicated in comparison with those of the RDC-SRS and RDC-ERBR. In terms of the commonly used grid-search philosophy, Yu et al. (2014) once presented a systematic procedure for the development of the RDC-TRS. In the current work, the same procedure is to be used for the synthesis and design of the RDC-TRS separating the RM-SURRV.

3. Example I: Separation of an Ideal Exothermic Reaction $A + B \xrightleftharpoons[k_B]{k_F} C + D$ ($\alpha_C > \alpha_A > \alpha_D > \alpha_B$)

3.1. Problem Description. The reaction kinetics is expressed below.

where the symbol $\xrightleftharpoons[k_B]{k_F}$ indicates that the reaction is a kinetically controlled one.

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

$$P_j = x_{A,j} P_A^s + x_{B,j} P_B^s + x_{C,j} P_C^s + x_{D,j} P_D^s \quad (2)$$

$$y_{i,j} = x_{i,j} P_i^s / P_j \quad (3)$$

The vapor saturation pressure is calculated as

$$\ln P_i^s = A_{vp,i} - B_{vp,i} / T_j \quad (4)$$

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

$$Rate_{i,j} = v_i M_j (k_{F,j} x_{A,j} x_{B,j} - k_{B,j} x_{C,j} x_{D,j}) \quad (5)$$

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

$$k_{F,j} = a_F e^{-E_F/RT_j} \quad (6a)$$

$$k_{B,j} = a_B e^{-E_B/RT_j} \quad (6b)$$

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

$$V_j = V_{j+1} - rate_{C,j} \times \Delta H_r / \Delta H_v \quad (7a)$$

$$L_j = L_{j-1} + rate_{C,j} \times \Delta H_r / \Delta H_v \quad (7b)$$

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

$$V_j = V_{j+1} \quad (8a)$$

$$L_j = L_{j-1} \quad (8b)$$

The physicochemical properties and operating conditions are given in Table 1 for the reactive distillation columns to be designed. Since the relative volatilities of the hypothetical reacting components are such that the reactants A and B are the light and heaviest components and the products C and D the lightest and heavy ones, the reactive distillation columns to be designed belong to the category of systems separating the RM-SURRV. The steady-state models of these processes

are described in Appendix A and similar first-principle models can also be found, elsewhere (Huang et al., 2006, 2010; Sun et al., 2009).

3.2. Process Synthesis and Design. For the simplification of process synthesis and design as well as the follow-up comparative assessment, the RDC-SRS, RDC-ERBR, and RDC-TRS are arbitrarily assumed to share the same total number of stages in the current work. In addition, they are also assumed to have the same amount of catalyst though its distribution might be quite different from each other. This allows simply the employment of reboiler heat duty as a metric for the comparison of their steady-state performance. Here the total number of stages is chosen to be 61 (including condenser and reboiler as well) and the total amount of catalyst to be 49 kmol. These two decision variables were actually obtained for the RDC-SRS with a grid-search method in terms of the minimization of total annual cost in our earlier work (Huang et al., 2014). Despite that the RDC-ERBR and RDC-TRS are not the optimum designs with these two decision variables, they lead to a rather conservative comparison with the RDC-SRS and can still reveal clearly their potential advantages in steady-state performance. The relationships between the reboiler heat duty and those relevant decision variables (i.e., the catalyst distribution, feed stages, the stage for withdrawing the intermediate product, and the feed splitting ratio of the light reactant A) are shown in Fig. 3 for the RDC-TRS. The detailed designs of the RDC-SRS, RDC-ERBR, and RDC-TRS are sketched in Figs. 4a, 4b, and 4c, respectively. Unlike the RDC-SRS, the RDC-ERBR and RDC-TRS features an intermediate withdrawal of the product D. Owing to the inclusion of the lower reactive section and external recycle, they need considerably fewer reactive stages than the RDC-SRS.

3.3. Comparative Evaluation of the RDC-TRS. The comparison between the RDC-SRS, RDC-ERBR, and RDC-TRS is included in Table 2. The RDC-TRS is found to be the best process design, followed by the RDC-ERBR, and RDC-SRS. More specifically, in comparison with the RDC-TRS, the RDC-ERBR and RDC-SRS need amplified reboiler heat duty by a factor of 0.46 % and 7.13 %, respectively. This outcome demonstrates the feasibility and effectiveness of employing the RDC-TRS to the separations of the RM-SURRV. Although relatively more amount of catalyst is needed on each reactive stage in the RDC-ERBR and the RDC-TRS than in the RDC-SRS (c.f., Figs 4a, 4b, and 4c), it actually occupies less than half room of the reactive stages and arouses no contradiction with the column diameters determined in terms of the maximal vapor flow rate. In case that the column diameters do confine the arrangement of catalyst on reactive stages, a careful coordination must be made between these two decision variables during process synthesis and design.

Fig. 5 shows the comparison of the profiles of net reaction rates and liquid compositions between the RDC-SRS,

RDC-ERBR, and RDC-TRS. Throughout this article, it is stipulated that the dotted lines represent the steady-state behaviors of the RDC-SRS, the dashed lines the steady-state behaviors of the RDC-ERBR, and the solid lines the steady-state behaviors of the RDC-TRS. The RDC-SRS features rather low net reaction rate (especially between the 26th and 34th stage) and this implies that the employment of one reactive section cannot effectively deal with the unfavorable ranking of relative volatilities (c.f., Fig. 5a). The RDC-TRS shares quite comparable profile of net reaction rate with the RDC-ERBR and this reflects that the inclusion of the lower reactive section to the former functions similarly with the addition of the external recycle to the latter. While the three process designs exhibit quite similar profiles of liquid compositions in the rectifying section, they show dramatic differences in the sections below (c.f., Fig. 5b). The RDC-SRS leads to a rather slow decrease of the heaviest reactant B toward the bottom and this corresponds well to the low net reaction rate mentioned above. With the inclusion of the lower reactive section and external recycle, the RDC-TRS and RDC-ERBR react away quickly the heaviest reactant B and lower its composition almost to zero in the intermediate separating section, thereby allowing the withdrawal of the product D as an intermediate effluent.

4. Example II: Separation of the Esterification of Acetic Acid with Methanol

4.1. Problem Description. The reaction kinetics is described by the following equation (Popken et al., 2000).

where the symbol $\xrightleftharpoons[k_B]{k_F}$ indicates that the reaction is a kinetically controlled one.

The net reaction rate is expressed by the pseudo-homogeneous activity-kinetic model.

$$\text{Rate}_{\text{MeAc},j} = M_j (k_{F,j} a_{\text{HAc}} a_{\text{MeOH}} - k_{B,j} a_{\text{MeAc}} a_{\text{H}_2\text{O}}) \quad (10a)$$

$$k_{F,j} = (2.961 \times 10^4) e^{-49190/(RT_j)} \quad (10b)$$

$$k_{B,j} = (1.348 \times 10^6) e^{-69230/(RT_j)} \quad (10c)$$

With reference to the database of the commercial software Aspen Plus V7.1, the normal boiling-points of the reacting components, MeOH, HAc, MeAc, and H₂O, are found to be 64.53 °C, 118.01 °C, 57.03 °C, and 100.02 °C, respectively. The reactants MeOH and HAc are the light and heaviest components and the products MeAc and H₂O the lightest and heavy components, respectively. Therefore, the processes to be developed belong to the category of systems separating the RM-SURRV.

The physicochemical properties and operating conditions are given in Table 3. The steady-state models are developed with the commercial software Aspen Plus (c.f., Appendix B) and the UNIQUAC property method is employed to calculate the activity coefficients of the reacting components (Popken et al., 2000). The dimerization of HAc is described by the Hayden-O'Connell second Virial coefficient model and the Aspen Plus built-in association parameters are used to compute its fugacity coefficients.

4.2. Process Synthesis and Design. Fig. 6 illustrates the relationships between the reboiler heat duty and those relevant decision variables (i.e., the catalyst distribution, feed stages, and the feed splitting ratio of the light reactant MeOH) for the RDC-TRS. Fig. 7 shows the detailed designs of the RDC-SRS, RDC-ERBR, and RDC-TRS. The RDC-TRS accommodates two reactive sections located, respectively, between the 3rd and 36th stages and between 38th and 39th stages. Similar to the RDC-SRS and RDC-ERBR, the product D is also withdrawn as a bottom effluent.

4.3. Comparative Evaluation of the RDC-TRS. The comparison between the RDC-SRS, RDC-ERBR, and RDC-TRS is also included in Table 2. The RDC-TRS is found again to be the best process design, followed by the RDC-ERBR, and RDC-SRS. As compared with the RDC-TRS, the RDC-ERBR and RDC-SRS lead to increased reboiler heat duty by a factor of 4.92 % and 8.27 %, respectively, and this outcome corroborates again the feasibility and effectiveness of employing the RDC-TRS to the separations of the RM-SURRV.

Fig. 8 shows the comparison of the profiles of net reaction rates and liquid compositions between the RDC-SRS, RDC-ERBR, and RDC-TRS. In comparison with the RDC-SRS, the RDC-ERBR and RDC-TRS make the reaction occur intensively towards the bottom (c.f., Fig. 8a). Since the reaction is exothermic, these modifications favor certainly internal energy integration between the reaction operation and separation operation involved. As can readily be noticed, these modifications reduce also the composition of methanol at bottom and lower consequently the separation difficulties involved (c.f., Fig. 8b).

5. Example III: Separation of the Transesterification of Butyl Acetate with Ethanol

5.1. Problem Description. The reaction kinetics is described with the following equation (Wang et al., 2010).

where the symbol $\xrightleftharpoons[k_B]{k_F}$ indicates that the reaction is a kinetically controlled one.

With reference to the database of the commercial software Aspen Plus V7.1, the normal boiling-points of the reacting components, EtOH, BuAc, EtAc, and BuOH, are found to be 78.29 °C, 126 °C, 77.06 °C, and 117.66 °C, respectively. The reactants EtOH and BuAc are the light and heaviest components, and the products EtAc and BuOH the lightest and heavy components, respectively. Therefore, the processes to be developed belongs to the category of systems separating the RM-SURRV.

The physicochemical properties and operating conditions are given in Table 4. The steady-state models of the processes are developed with the commercial software Aspen Plus (c.f., Appendix B), in which the NRTL physical property method is applied to calculate the activity coefficients of the reacting components. The net reaction rate is represented by a first-order dependence on each of the two reactants and products with concentration in molarity (kmol/m³) (c.f., eqs. 12a, 12b, and 12c).

$$Rate_{BuAc} = k \left(C_{BuAc} C_{EtOH} - \frac{C_{EtAc} C_{BuOH}}{k_{eq}} \right) \quad (12a)$$

$$k = 24.4e^{-50.8/RT} \quad (12b)$$

$$k_{eq} = 0.96 \quad (12c)$$

5.2. Process Synthesis and Design. Fig. 9 shows the relationships between the reboiler heat duty and those relevant decision variables (i.e., the catalyst distribution, feed stages, the stage for withdrawing the intermediate product, and the feed splitting ratio of the light reactant EtOH) for the RDC-TRS. Fig. 10 sketches the detailed designs of the RDC-SRS, RDC-ERBR, and RDC-TRS. The RDC-TRS accommodates two reactive sections located, respectively, between the 5th and 45th stages and within reboiler. Unlike in the RDC-SRS, the product D is withdrawn as an intermediate effluent in the RDC-ERBR and RDC-TRS.

5.3. Comparative Evaluation of the RDC-TRS. The comparison between the RDC-SRS, RDC-ERBR, and RDC-TRS is also included in Table 2. The RDC-TRS is found again to be the best process design, followed by the RDC-ERBR, and RDC-SRS. In comparison with the RDC-TRS, the RDC-ERBR and RDC-SRS result in amplified reboiler heat duty by a factor of 1.25 % and 6.89 %, respectively. This outcome corroborates again the feasibility and effectiveness of employing the RDC-TRS to the separations of the RM-SURRV.

Fig. 11 shows the comparison of the profiles of net reaction rates and liquid compositions between the RDC-SRS, RDC-ERBR, and RDC-TRS. The inclusion of the lower reactive section and external recycle in the RDC-TRS and

RDC-ERBR enable again the reaction to occur intensively toward the bottom and this reinforces internal energy integration between the reaction operation and separation operation involved (c.f., Fig. 11a). With reference to Fig. 11b, these modifications are also found to reduce the composition of ethanol at bottom and help to ease the separation difficulties involved.

6. Discussion

The three examples studied in the current work have demonstrated that the RDC-TRS can lower operating cost and thus capital investment (because low operating cost leads to low capital investment) in comparison with the RDC-SRS in the separations of the RM-SURRV. The substantial improvement in steady-state performance should definitely be attributed to the employment of two reactive sections in the RDC-TRS, which yields some relevant degrees of freedom to cope with the unfavorable relative volatility between the heavy product and heaviest reactant. While the upper reactive section plays a dominant role in the reaction operation, the lower reactive section is instrumental to the enhancement of reaction conversion. The outcomes have confirmed the feasibility and effectiveness of applying the RDC-TRS to the separations of the RM-SURRV. The RDC-TRS has also been found to yield comparable or even better steady-state performance than the RDC-ERBR. The comparison reminds us of the fact that the process should be viewed as a competitive alternative for the separations of the RM-SURRV.

In the case that the unfavorable ranking of relative volatility occurs between the light product and lightest reactant, the strategy proposed in the current work can still be employed straightforwardly to synthesize and design the RDC-TRS. Fig. 12 sketches the potential schemes of the RDC-TRS in terms of the separation of a hypothetical quaternary reaction, $A + B \xrightleftharpoons[k_B]{k_F} C + D$ ($\alpha_A > \alpha_C > \alpha_B > \alpha_D$). Contrary to those schemes shown in Fig. 2, the lower reactive section is now arranged above the stripping section and the upper reactive section below the rectifying section or at top (including frequently condenser as well). While the lower reactive section plays a dominant role in the reaction operation, the upper reactive section is instrumental to the enhancement of reaction conversion under this circumstance.

7. Conclusions

In the current work, the RDC-TRS has been employed to separate the RM-SURRV (i.e., two reactants are the light and heaviest components and two products the lightest and heavy ones). The upper and lower reactive sections must be

deliberately arranged in order to favor the reaction operation and separation operation involved. More specifically, while the upper reactive section is located below the rectifying section, the lower reactive section above the stripping section or at bottom. In terms of the separations of the representative hypothetical quaternary reaction: $A + B \xrightleftharpoons[k_B]{k_F} C + D$ ($\alpha_C > \alpha_A > \alpha_D > \alpha_B$), the esterification of acetic acid with methanol, and the transesterification of butyl acetate with ethanol, the RDC-TRS has been found to yield much better steady-state performance than the RDC-SRS and this demonstrates the feasibility and effectiveness of applying the RDC-TRS to separate the RM-SURRV. The RDC-TRS has also been found to present comparable and even better steady-state performance than the RDC-ERBR. The outcome implies that the RDC-TRS should be considered as a potentially competitive alternative for the separations of the RM-SURRV.

As for the separations of the other kind of RM-SURRV (i.e., two reactants are the lightest and heavy components and two products the light and heaviest ones), the strategy proposed in the current work can still be used and the potential schemes of the RDC-TRS have also been indicated.

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Appendix A. Steady-state models of the RDC-SRS, RDC-ERBR, and RDC-TRS for Example I

The steady-state models of the RDC-SRS, RDC-ERBR, and RDC-TRS have been developed in terms of mass and energy conservation principle in conjunction with the given vapor-liquid equilibrium relationship. They are programmed with the commercial software Mathematica and solved with a modified Newton-Raphson method. The satisfaction of component mass balance equations (i.e., Eq. (A. 1)) and attainment of top, intermediate or bottom product specifications (i.e., Eqs. (A. 2) and (A. 3) or (A. 2) and (A. 4)) are taken as convergence criterion. With the given process configuration and operating conditions, these models can yield a steady-state solution fairly quickly.

$$\left| L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} - L_jx_{i,j} - V_jy_{i,j} + F_jz_{i,j}\delta_{j,m} + r_{1i,j} + r_{2i,j} \right| \leq \varepsilon \quad (\text{A. 1})$$

$$\left| x_d - x_d^{sp} \right| \leq \varepsilon \quad (\text{A. 2})$$

$$\left| x_{sd} - x_{ip}^{sp} \right| \leq \varepsilon \quad (\text{A. 3})$$

$$\left| x_{bot} - x_{bot}^{sp} \right| \leq \varepsilon \quad (\text{A. 4})$$

Appendix B. Steady-state models of the RDC-SRS, RDC-ERBR, and RDC-TRS for Examples II and III

The steady-state models of the RDC-SRS, RDC-ERBR, and RDC-TRS have been developed with the commercial software Aspen Plus. The RadFrac column module is adopted with distillate flow rate and reflux ratio adjusted to keep top, intermediate or bottom product compositions at their given specifications, respectively. The secant method is used to search the desired steady-state and can find the solution fairly quickly.

Notation

a	liquid activity
A	hypothetical component
A_{vp}	vapor pressure constant (kPa)
B	hypothetical component
$BPFR$	bottom product flow rate (mol/s)
B_{vp}	vapor pressure constant (kPa·K)
C	hypothetical component
D	hypothetical component
DFR	distillate flow rate (mol/s)
E	activation energy of the hypothetical ideal reaction (J/mol)
F	feed flow rate (mol/s)
$IPFR$	intermediate product flow rate (mol/s)
k	specific reaction rate (mol/(s·mol))
k_{eq}	reaction equilibrium constant
L	liquid flow rate (mol/s)
M	kinetic holdup on a reactive stage (mol)
M_{REB}	kinetic holdup within reboiler (mol)
P	pressure (kPa)

Q_{reb}	heat duty of reboiler (MW)
R	ideal gas law constant (J/(mol·K))
$Rate$	net reaction rate (mol/s)
RF	external recycle flow rate (mol/s)
RR	reflux flow rate (mol/s)
T	temperature (K)
V	vapor flow rate (mol/s)
x	liquid composition
y	vapor composition
ΔH_R	heat of a reaction (J/mol)

Abbreviations

$BuAc$	butyl acetate
$BuOH$	butanol
$EtAc$	ethyl acetate
$ETOH$	ethanol
HAc	acetic acid
H_2O	water
$MeAc$	methyl acetate
$MEOH$	methanol
$RDC-ERBR$	reactive distillation column with external recycle from bottom to reactive section
$RDC-SRS$	reactive distillation column with a single reactive section
$RDC-TRS$	reactive distillation column with two reactive sections
$RM-MFRRV$	reacting mixtures with the most favorable ranking of relative volatilities
$RM-SURRV$	reacting mixtures with somewhat unfavorable ranking of relative volatilities

Greek Letters

α	relative volatility
β	feed splitting ratio

δ	Kronecker delta function
ε	error tolerance
ν	stoichiometric coefficient of a reaction

Subscripts

A	component index
B	component index
bot	bottom
C	component index
D	component index
d	distillate
i	component index
ip	intermediate product
j	stage index
m	feed stage index

Superscript

s	saturation
sp	product specification

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Figure captions

- Fig. 1. Separations of the RM-MFRRV ($\alpha_C > \alpha_A > \alpha_B > \alpha_D$) and RM-SURRV ($\alpha_C > \alpha_A > \alpha_D > \alpha_B$) with the RDC-SRS: (a) RM-MFRRV, (b) RM-SURRV.
- Fig. 2. Potential schemes of the RDC-TRS in the separations of the RM-SURRV ($\alpha_C > \alpha_A > \alpha_D > \alpha_B$): (a) RDC-TRS with the product D as an intermediate effluent, (b) RDC-TRS with the product D as a bottom effluent.
- Fig. 3. Reboiler heat duty versus design variables of the RDC-TRS for Example I: (a) catalyst distribution, (b) feed stages, (c) stage of withdrawing the intermediate product, (d) feed splitting ratio.
- Fig. 4. Designs of the RDC-SRS, RDC-ERBR, and RDC-TRS for Example I: (a) RDC-SRS, (b) RDC-ERBR, (c) RDC-TRS.
- Fig. 5. Profiles of net reaction rates and liquid compositions for Example I: (a) net reaction rate, (b) liquid composition.
- Fig. 6. Reboiler heat duty versus design variables of the RDC-TRS for Example II: (a) catalyst distribution, (b) feed stages, (c) stage of withdrawing the intermediate product, (d) feed splitting ratio.
- Fig. 7. Designs of the RDC-SRS, RDC-ERBR, and RDC-TRS for Example II: (a) RDC-SRS, (b) RDC-ERBR, (c) RDC-TRS.
- Fig. 8. Profiles of net reaction rates and liquid compositions for Example II: (a) net reaction rate, (b) liquid composition.
- Fig. 9. Reboiler heat duty versus design variables of the RDC-TRS for Example III: (a) catalyst distribution, (b) feed stages, (c) stage of withdrawing the intermediate product, (d) feed splitting ratio.
- Fig. 10. Designs of the RDC-SRS, RDC-ERBR, and RDC-TRS for Example III: (a) RDC-SRS, (b) RDC-ERBR, (c) RDC-TRS.
- Fig. 11. Profiles of net reaction rates and liquid compositions for Example III: (a) net reaction rate, (b) liquid composition.
- Fig. 12. Potential schemes of the RDC-TRS in the separations of the RM-SURRV ($\alpha_A > \alpha_C > \alpha_B > \alpha_D$): (a) RDC-TRS with the product C as an intermediate effluent, (b) RDC-TRS with the product C as a top effluent.

Fig. 1
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 Synthesis and design of reactive distillation columns with two reactive sections

Fig. 2
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Fig. 4

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(a)

(b)

Fig. 5
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Fig. 6
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Fig. 7
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Fig. 8
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(a)

(b)

(c)

(d)

Fig. 9
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Fig. 10

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(a)

(b)

Fig. 11
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Fig. 12
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Table captions

- Table 1. Physicochemical Properties and Operating Conditions of Example I
- Table 2. Comparison between All Process Designs for Examples I, II, and III
- Table 3. Design Specifications and Operating Conditions of Example II
- Table 4. Design Specifications and Operating Conditions of Example III

Table 1. Physicochemical Properties and Operating Conditions of Example I

Parameter		Value
Feed flow rate of reactant A (mol/s)		12.6
Feed flow rate of reactant B (mol/s)		12.6
Product specification (mol %)	C	95.0
	D	95.0
Activation energy (kJ/kmol)	Forward	50, 208
	Backward	71, 128
Specific reaction rate at 366 K (kmol/s/kmol)	Forward	0.008
	Backward	0.004
Relative volatilities A:B:C:D		9:1:27:3
Heat of reaction (kJ/kmol)		−20, 920
Latent heat of vaporization (kJ/kmol)		29, 053.7
Vapor pressure constants	A (A_{vp}/B_{vp})	17.77/3862
	B (A_{vp}/B_{vp})	15.57/3862
	C (A_{vp}/B_{vp})	18.87/3862
	D (A_{vp}/B_{vp})	16.67/3862

Table 2. Comparison between All Process Designs for Examples I, II, and III

Example	Process design	Q_{REB} (MW)	Comparison
Example I	RDC-SRS	0.466	+107.13 %
	RDC-ERBR	0.437	+100.46 %
	RDC-TRS	0.435	100 %
Example II	RDC-SRS	1.034	+108.27 %
	RDC-ERBR	1.002	+104.92 %
	RDC-TRS	0.955	100 %
Example III	RDC-SRS	3.086	+106.89 %
	RDC-ERBR	2.923	+101.25 %
	RDC-TRS	2.887	100 %

Table 3. Design Specifications and Operating Conditions of Example II

Parameter		Value
Feed flow rate of HAc (kmol/h)		50.0
Feed flow rate of MeOH (kmol/h)		50.0
Product specification (mol %)	MeAc	98.0
	H ₂ O	98.0

Table 4. Design Specifications and Operating Conditions of Example III

Parameter		Value
Feed flow rate of BuAc (kmol/h)		100.0
Feed flow rate of EtOH (kmol/h)		100.0
Product specification (mol %)	EtAc	80.0
	BuOH	80.0

Graphical Abstract