Reactive Distillation Design with Considerations of Heats of Reaction

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Although reactive distillation columns allow direct utilization of heat of reaction to separation operation, the effectiveness of internal heat integration appears generally to be unsatisfactory and their thermodynamic efficiency could quite often be improved substantially through seeking further internal heat integration between the reaction and separation operations. Prudent arrangement of reactive section, effective determination of feed location, and deliberate distribution of catalyst constitute the three methods that can complement internal heat integration within a reactive distillation column. The reactive section is suggested to superimpose properly onto the stripping section for exothermic reactions and onto the rectifying section for endothermic reactions. Feed location and distribution of catalyst should be determined so that the effect of internal heat integration can be maximized to its fullest extent. A sequential procedure is proposed to determine an appropriate process configuration for internal heat integration within a reactive distillation column. Five reactive distillation systems, involving not only equilibrium-limited but also kinetically controlled reactions, are used to evaluate the design philosophy proposed. It has been found that a substantial improvement in system performance can be achieved even for some reaction systems with side reactions and/or unfavorable thermodynamic properties. Seeking further internal heat integration has been demonstrated to be an effective method for refining process design of a reactive distillation column involving reactions with highly thermal effect. These conclusions are of great significance and can provide process designers with additional latitude to elaborate their process designs. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2518–2534, 2006

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Introduction

Because of the combination of the reaction and separation operations within one unit, a reactive distillation column is frequently said to allow direct use of the heat of reaction to the separation operation, although this is merely an intuitive observation. The thermodynamic efficiency is often far from satisfactory for a reactive distillation column involving reactions with a highly thermal effect, arising from the neglect of internal heat integration between the reaction and separation operations. In a worst-case scenario, in some process designs published in the open literature, the resultant internal heat

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integration even worked adversely to the separation operation and was actually in sharp contradiction to the second law of thermodynamics.[1] Although reactive distillation columns have received considerable attention over the last 15 years, to date there have been only a few papers that systematically addressed the issues of internal heat integration during the synthesis and design of a reactive distillation column.[2-4]

Eldarsi and Douglas[5] investigated the performance of a reactive distillation column synthesizing methyl tertiary butyl ether (MTBE) from methanol and isobutylene. They found that by installing an intermediate cooler at the bottom of the reactive section the degree of reaction conversion and system performance could be enhanced. Because the stripping section generally takes in heat during operation, it is quite likely to achieve a somewhat similar effect by superimposing a certain part of the reactive section onto the stripping section, thereby creating a new process design with not only low energy consumption but also small capital investment.

Based on the fixed point of material and energy balance equations and their associated eigenvectors, Okasinski and Doherty[6] proposed a design method for staged reactive distillation columns involving kinetically controlled reactions. They recognized the positive effect of positioning an appropriately reactive section within a reactive distillation column involving reactions with highly thermal effect, including, for instance, the reduction of minimum boil-up ratio and number of stages. Subawalla and Fair[7] advocated distributing the reactive section and determining feed location in terms of the relative volatilities of reacting mixtures, but gave no further insight into the effective use of heat of reaction in process synthesis and design. Melles et al.[8] suggested using variable liquid holdups (to express more exactly the amount of catalyst per stage) in the design of reactive distillation columns and indicated that heat of reaction could lead to a reduced reflux/reboil ratio, although at the expense of an increased number of stages. Because internal heat integration decreased the driving forces of mass transfer in the rectifying/stripping section, the number of stages had to be increased accordingly to effect a specified separation. Based on the concept of a difference point, Lee et al.[9,10] devised a graphical method for the interpretation of process design of reactive distillation columns. They systematically demonstrated the advantages of effectively distributing a reactive section within a reactive distillation column, including, for example, the circumvention of azeotropes and use of heat of reaction to aid the separation operation.

Although for binary reaction systems, the graphical method proposed appears extremely effective for elucidating the correct position of the reactive section within a reactive distillation column, it becomes rather complicated in the visualization of process design for multicomponent reaction systems resulting from the increased dimensionality.[11,12] A number of researchers (such as Ciric and Gu,[13] Papalexandri and Pistikopoulos,[14] Cardoso et al.,[15] Ismail et al.,[16] Stichlmair and Frey,[17] and Jackson and Grossmann[18]) addressed the design of reactive distillation columns in terms of a mixed-integer nonlinear programming (MINLP) formulation. They demonstrated that adopting a multiple feed scheme and variable liquid holdups in the reactive section could substantially improve system performance. The potential problems behind this kind of methods are the complexities in problem formulations and difficulties in searching for the global optimum (such as for nonlinear and/or nonconvex models), even though considerable effort has already been expended to simplify the problem.[19] Kaymak and Luyben[20] investigated the influences of feed location on the energy consumption of a hypothetical reactive distillation column. They noticed the pronounced effect of feed location, but presented no further discussion on how to tackle this issue to achieve the maximum reduction of energy consumption in process synthesis and design.

Although distillation is a mature technology for separation operation, it is characterized by a low thermodynamic efficiency. To deal with the deficiency, a considerable amount of research has been undertaken ever since the beginning of the last century and, to date, a number of modified schemes have been proposed. These primarily include: heat pump–assisted distillation processes,[21-24] distillation processes with intermediate heat exchangers,[25-28] and internally heat-integrated distillation processes.[29-33] The common principle behind these processes is to reduce the irreversibility of the separation operation in terms of the thermodynamic interpretation of distillation columns, that is, a rectifying section is usually a potential heat source and the stripping section, a potential heat sink.[34-36] For a reactive distillation column involving reactions with a highly thermal effect, the enhancement of thermodynamic efficiency sometimes still appears possible by seeking further internal heat integration between the reaction and separation operations.

The heat of reactions might be used effectively as either a heat source (in case of exothermic reactions) or a heat sink (in case of endothermic reactions) to drive the separation operation in the stripping section or in the rectifying section, accordingly. Contrary to conventional distillation columns, it seems to require almost no additional capital investment but merely a delicate combination of the reaction and separation operations. The primary objective of the current work is therefore to investigate the feasibility and effectiveness of seeking further internal heat integration between the reaction and separation operations in a reactive distillation system involving reactions with a highly thermal effect. A sequential procedure is developed for the reinforcement of internal heat integration during the synthesis and design of a reactive distillation column. Five reactive distillation systems, involving not only equilibrium-limited but also kinetically controlled reactions, are used to evaluate the proposed design philosophy. The energy-saving potentials of the supplementary internal heat integration between the reaction and separation operations are examined through intensive comparison with conventional design methods. The feasibility of elaborating process design by seeking further internal heat integration is highlighted for reactive distillation columns involving reactions with a highly thermal effect.

Process Design by Seeking Further Internal Heat Integration within a Reactive Distillation Column

To effectively conduct process design for a reactive distillation column involving reactions with a highly thermal effect, it is frequently necessary to consider further internal heat integration between the reaction and separation operations through a careful combination of these two operations. Three methods can be favorable to the reinforcement of internal heat integration within a reactive distillation column:

(1) The first method is to extend the reactive section to either the rectifying section or the stripping section in terms of the detailed reaction system at hand. The common zone where reactive stages are superimposed onto nonreactive ones can serve to supplement internal heat integration between the reaction and separation operations.

(2) The second method is to deliberately choose the feed location of the dominant feed in the reactive section. The change of feed location affects the number of stages in the rectifying section and/or in the stripping section and thus the degree of internal heat integration (that is, superimposition) between the reaction and separation operations.

(3) The third method is to deliberately determine the distribution of catalyst in the reactive section. For instance, the catalyst should quite often be used more carefully in the common zone where reactive stages are superimposed onto nonreactive ones than on the other reactive stages, thereby establishing a distribution of catalyst that can facilitate internal heat integration between the reaction and separation operations.

It should be pointed out here that the distribution of catalyst is, in principle, valid for both kinetically controlled and equilibrium-limited reactions. However, in the case of an equilibrium-limited reaction, if its reaction velocity is so fast that chemical equilibrium can be reached instantaneously on all reactive stages, then the distribution of catalyst has no influence on system performance because the amount of catalyst equally influences both forward and backward reactions and has no net influence on reaction equilibrium. In most cases, the combinatorial use of these three methods could provide higher flexibility and more benefits than each of them, separately, in tapping the potentials of internal heat integration and is therefore highly recommended in this work.

To determine an effective combination of the reaction and separation operations within a reactive distillation column involving reactions with a highly thermal effect, it frequently requires a trial-and-error search by means of the three methods proposed for seeking further internal heat integration. A sequential procedure is outlined in Figure 1, which can easily be combined into any conventional design methods based on an economical criterion, such as minimization of total annual cost. Starting from a process design with a reactive section in between the rectifying section and the stripping section (that is, a basic process design), a process designer can easily develop it into a more efficient one by conducting some simple process simulations. Although the sequential procedure is described here for a reactive distillation column with two feeds at the ends of the reactive section and evenly distributed catalyst, it is not restricted to the process configuration itself and can actually be applied to any complicated column arrangements involving multiple feeds. In the latter case, there usually is only one feed that dominates internal heat integration between the reaction and separation operations. In terms of the dominant feed, the sequential procedure can be applied straightforwardly. Because internal heat integration reduces the driving forces of mass transfer, the number of separating stages must be adjusted accordingly in the rectifying/stripping section to guarantee the resultant process design with sufficient redundancy and high flexibility. Note that this adjustment is also necessary for the maintenance of dynamic controllability of the resultant process design.

It should be stressed here that seeking further internal heat integration can work as an effective way to elaborate process design of a reactive distillation column. The reason lies primarily in the improvement of the synergism between the reaction and separation operations. By seeking further internal heat integration within a reactive distillation column, not only could the conversion rate be enhanced for a reversible reaction, but also the irreversibility associated with separation operation could be reduced, both of which actually contribute to the enhancement of thermodynamic efficiency. For the former case, a lower energy consumption can result from the recycle of fewer reactants unconverted back to the reactive section, and for the latter case, a smaller boil-up/reflux ratio can achieve a specified separation. Furthermore, the improvement in thermodynamic efficiency permits further reduction in capital investment and therefore leads to a more compact process design, which is also one of the main features of process intensification.[37,38]

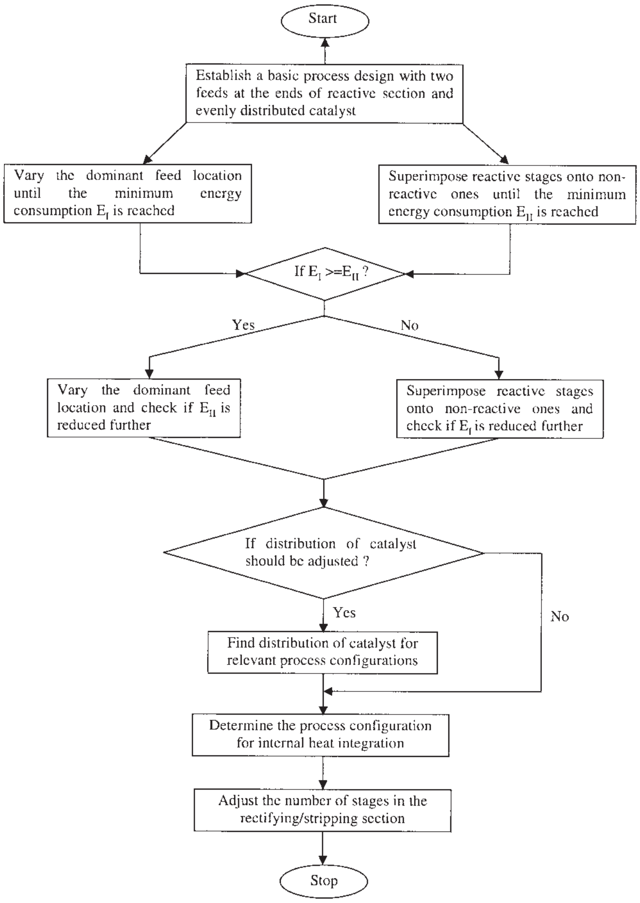

Figure 1. Sequential procedure to determine an appropriate process configuration for internal heat integration within a reactive distillation column.

Considering Further Internal Heat Integration within a Reactive Distillation Column Involving a Highly Exothermic Reaction

Example I: A hypothetical reactive distillation column

Process Description. This reactive distillation system was defined and studied by Luyben and coworkers.[39,40] The process

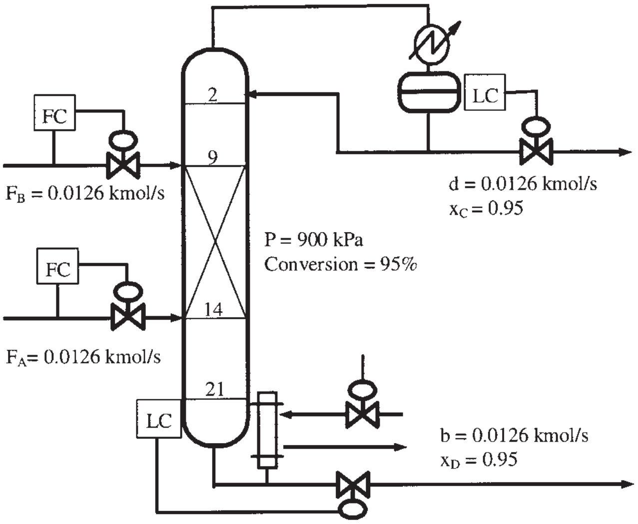

Figure 2. Hypothetical reactive distillation column.

has three zones: a rectifying section, a stripping section, and a reactive section in between (Figure 2). It is equipped with a total condenser at the top and a partial reboiler at the bottom. Two pure reactant fresh feeds, F_A and F_B, are fed into the bottom and the top of the reactive section, respectively. Table 1 summarizes the physical properties and steady-state operating conditions for the reactive distillation system and other relevant information can be found in the corresponding references.

The hypothetical reversible reaction occurring on the reactive stages is

$$\mathrm{A} + \mathrm{B} \leftrightarrow \mathrm{C} + \mathrm{D} \qquad \Delta H_R = -41{,}840 \text{ kJ/kmol} \tag{1}$$

The volatilities are such that the products C and D are the lightest and heaviest, respectively, in the system. The net reaction rate for component *i* on stage *j* in the reactive section is given by

$$r_{i,j} = \nu_i H_j (k_{f,j} x_{A,j} x_{B,j} - k_{b,j} x_{C,j} x_{D,j}) \tag{2}$$

where $k_{f,j}$ and $k_{b,j}$ are the forward and backward specific reaction rates, given by

$$k_{f,j} = \alpha_f e^{-E_f/(RT_j)} \tag{3a}$$

$$k_{b,j} = \alpha_b e^{-E_b/(RT_j)} \tag{3b}$$

Here, the liquid holdup H is an important design parameter that can reflect the amount of catalyst installed on a reactive stage. A large value represents an operating condition that a large amount of catalyst has been installed on a reactive stage, and vice versa.

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

$$P_j = x_{A,j} P_A^s + x_{B,j} P_B^s + x_{C,j} P_C^s + x_{D,j} P_D^s \tag{4a}$$

$$y_{i,j} = x_{i,j} P_i^s / P_j \tag{4b}$$

The vapor saturation pressure is represented as

$$\ln P_i^s = A_{vp,i} - B_{vp,i}/T_j \tag{5}$$

Constant overflow is assumed for the rectifying and the stripping sections of the hypothetical reactive distillation column. In the reactive section, the overflow changes from stage to stage because the heat of reaction vaporizes some liquid on each stage.

$$V_j = V_{j+1} - r_{j,C} \Delta H_R / \Delta H_V \tag{6}$$

$$L_j = L_{j-1} + r_{j,C} \Delta H_R / \Delta H_V \tag{7}$$

The process is simulated with a generalized steady-state model described in the Appendix. It is noted that strict specifications have been imposed on the top and bottom products. They exactly define system performance (such as a constant overall conversion rate in the reactive section) on which the effect of seeking further internal heat integration between the reaction and separation operations will be examined.

The Effect of Seeking Further Internal Heat Integration. Luyben and coworkers performed process design for the hypothetical reactive distillation column, and we regard their resultant process design as the basic one here and investigate the influences of seeking further internal heat integration within

Table 1. Physical Properties and Operating Conditions of Example I

Item		Value
Activation energy (kJ kmol^{-1})	Forward	125,520
	Backward	167,360
Specific reaction rate at 366 K (kmol · s^{-1} · kmol^{-1})	Forward	0.008
	Backward	0.004
Stage holdup (kmol)		1
Thermal condition of F_A		1.0
Thermal condition of F_B		1.0
Relative volatility A:B:C:D		4:2:8:1
Latent heat of vaporization (kJ kmol^{-1})		29053.7
Vapor pressure constants	A (A_{vp}/B_{vp})	12.3463/3862
	B (A_{vp}/B_{vp})	11.6531/3862
	C (A_{vp}/B_{vp})	13.0394/3862
	D (A_{vp}/B_{vp})	10.96/3862

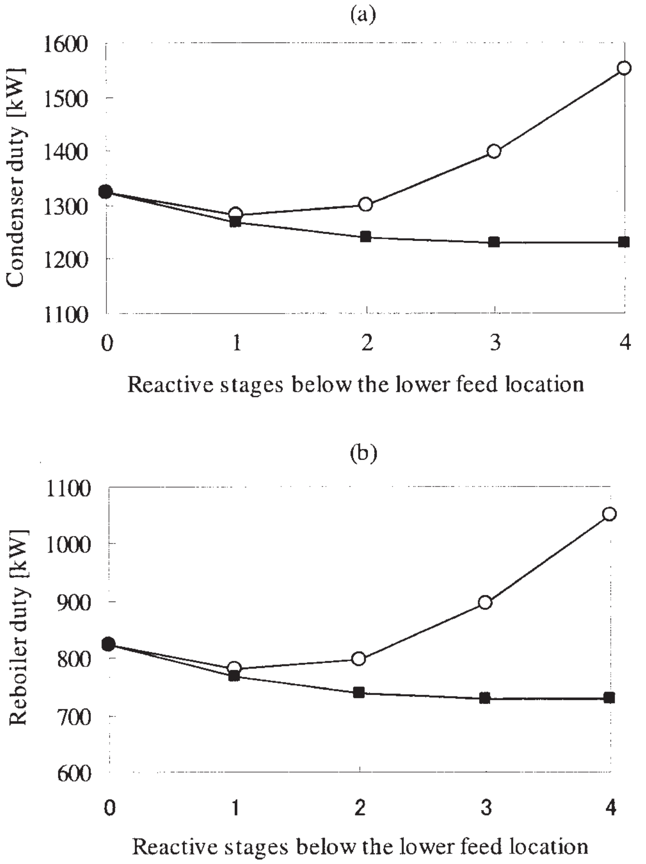

Figure 3. Strengthening internal heat integration for the hypothetical reactive distillation column involving a highly exothermic reaction.

–■–: Superimposition of reactive stages onto stripping section; –○–: ascent of the lower feed location from the bottom of reactive section.

the process. Because the reaction involved is a highly exothermic one, the heat of reaction released should be used effectively at certain positions in the stripping section so that the irreversibility associated with separation operation could be reduced. In Figure 3, the effect of seeking further internal heat integration between the reaction and separation operations is illustrated on the basic process design. The same total amount of catalyst has been maintained here, if without further indication. With the raising of the lower feed location from the bottom of the reactive section, however, the process behaves in an inconsistent manner. When the lower feed location has been raised to stage 13 from stage 14 of the basic process design, the heat duties of condenser and reboiler decrease, simultaneously, indicating the enhancement of system performance. When the lower feed location has been raised further, the heat duties of condenser and reboiler turn to increase, implying, nevertheless, the degradation of system performance.

The initial improvement in system performance has certainly been caused by the reinforcement of internal heat integration between the reactive and stripping sections. However, further raising the lower feed location results in heat of reaction taken in only by stages that are farther away from the bottom reboiler in the stripping section, thereby representing an increasingly ineffective way of internal heat integration between the reactive and stripping sections. Moreover, excessively raising the lower feed location leads to an unfavorable distribution of net reaction rates (see Eq. 2) in the reactive section and imparts a detrimental effect to the separation operation. As demonstrated in Figure 4, the reaction tends to occur intensively at the top of the reactive section with the ascent of the lower feed location (here, N_A denotes the lower feed location for reactant A), certainly resulting in the high presence there of the heaviest component D. For the purpose of simultaneously maintaining a product purity of 95 mol % for components C and D at the top and the bottom (that is, a total conversion rate of 95%), the internal vapor and liquid overflow must be increased accordingly, thereby degrading system performance.

In the case of superimposition of reactive stages onto the stripping section, it is readily apparent that the process shows a substantial improvement in system performance. As more reactive stages have been superimposed below the lower feed location, the heat duties of condenser and reboiler decrease monotonically, positively demonstrating the strong effect of internal heat integration. When three reactive stages have been superimposed onto the stripping section, the heat duties of condenser and reboiler decrease to their minimum values at the same time. Further superimposition of reactive stages onto the stripping section leads to a slight increase in the heat duties of condenser and reboiler because the lightest component C is produced near the bottom and presents extra difficulties to the separation operation. The complicated relationship between system performance and the two methods of internal heat integration signifies the great importance of properly determining the process configuration for the reactive distillation column.

Table 2 shows a detailed comparison between process designs with and without further internal heat integration between the reactive and stripping sections. A unified notation, $N_r(n1)/N_{rea}(n2)/N_s(n3)^*$, is used to represent different process designs with and without further internal heat integration throughout this work. N_r, N_{rea}, and N_s signify the number of stages in the rectifying, reactive, and stripping sections, respectively. The numbers in the parentheses, $n1$ and $n3$, stand for the additional

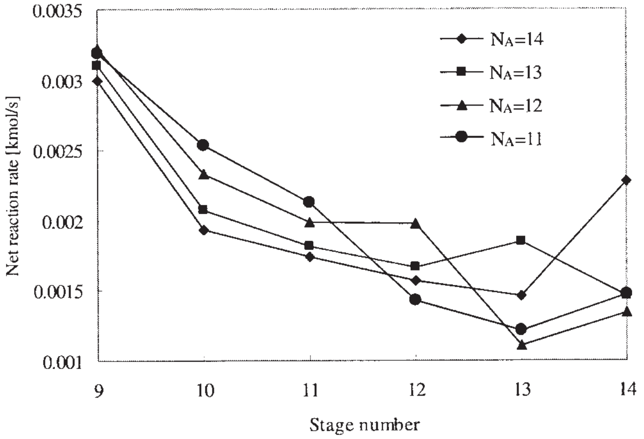

Figure 4. Excessive elevation of the lower feed location leads to an unfavorable distribution of net reaction rates in Example I.

Table 2. Effect of Seeking Further Internal Heat Integration for the Hypothetical Reactive Distillation System Involving a Highly Exothermic Reaction

Example I	Process Configurations	Condenser Duty (kW)	Reboiler Duty (kW)	Evaluations	
				Condenser	Reboiler
Basic process design with holdup to be 1.0 kmol per stage	7/6/7	1323.69	822.86	100%	100%
Raising the lower feed location one stage from the bottom of reactive section with holdup to be 1.0 kmol per stage	7/6(1)/7	1282.28	781.45	96.87%	94.97%
Superimposing three reactive stages onto stripping section with holdup to be 0.67 kmol per stage	7/6/7(3)	1228.59	727.77	92.82%	88.44%
Combinatorial use of the above methods with holdup to be 0.67 kmol per stage	7/6(1)/7(3)	1232.61	731.79	93.12%	88.93%
Redistribution of catalyst	7/6(1)/7(3)*	1215.49	714.66	91.83%	86.85%
Combinatorial use of the above methods with holdup to be 1.0 kmol per stage	7/6(1)/7(3)	1196.77	695.94	90.41%	84.58%

arrangement of reactive stages onto the rectifying and stripping sections, and $n2$ denotes the movement of feed location of the dominant feed in the reactive section. The asterisk (*) indicates a process design finished after redistribution of catalyst in the reactive section. As can be seen, introducing the lower feed at stage 13 reduces the heat duties of condenser and reboiler by 3.13 and 5.03%, whereas superimposing three reactive stages onto the stripping section diminishes them by 7.18 and 11.56%. The combinatorial use of these two methods exhibits no further improvement in system performance with a reduction of energy consumption by 6.88% in the condenser and 11.07% in the reboiler.

It should be indicated here that, although the reaction involved is a reversible one, it has not approached the equilibrium state in all reactive stages. Therefore, distribution of catalyst should be considered for the enhancement of system performance. It is noted that the combinatorial use of these three methods brings about the largest reduction of energy consumption with 8.17% in the condenser and 13.15% in the reboiler. If liquid holdups are permitted to be 1.0 kmol for all reactive stages, the reduction of energy consumption can even hit a high value with 9.59% in the condenser and 15.42% in the reboiler. This reality indicates that distribution of catalyst can be an important design variable for the reinforcement of internal heat integration for a reactive distillation column involving a kinetically controlled reaction. Figure 5 illustrates the evolution of profiles of net reaction rates. It is readily obvious that a certain amount of heat of reaction has been supplied to the stripping section after seeking further internal heat integration between the reactive and stripping sections. It is essentially the main reason why system performance has been substantially improved.

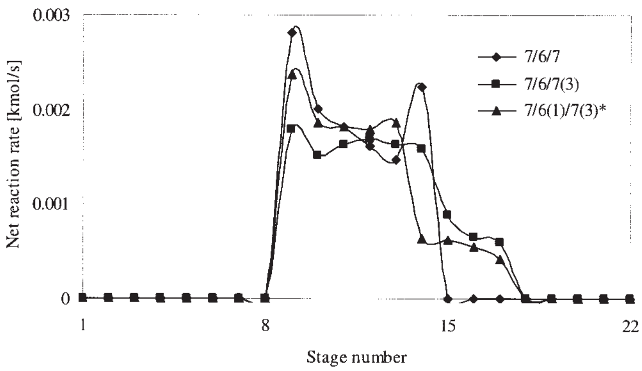

Figure 5. Profiles of net reaction rates for Example I.

Example II: A reactive distillation column for synthesizing MTBE from isobutylene and methanol

Process Description. MTBE is produced by a reversible exothermic reaction of methanol and isobutylene in the presence of a strong acidic ion exchange resin (Eq. 8). The MTBE synthesis reactive distillation column has been extensively studied by many researchers in the aspects of process design, multiple steady states, process dynamics, and process operation.[41-45] A basic process design for the MTBE synthesis reactive distillation column is shown in Figure 6. Again, the process involves a three-sectional configuration: 2/8/5, in addition to a total condenser at the top and a partial reboiler at the bottom. A C4 vapor at 350 K, consisting of 35 mol % isobutylene and 65 mol % inert n-butene, is fed into the bottom of the reactive section, and a pure methanol liquid at 320 K into the top of the reactive section:

$$\begin{aligned}&\mathrm{MEOH(CH_3OH)} + \mathrm{IBUT}(i\text{—}\mathrm{C_4H_8}) \leftrightarrow \\ &\qquad \mathrm{MTBE(C_4H_8O)} \qquad \Delta H_{R,298} = -37.7 \times 10^3 \text{ kJ/kmol} \qquad (8)\end{aligned}$$

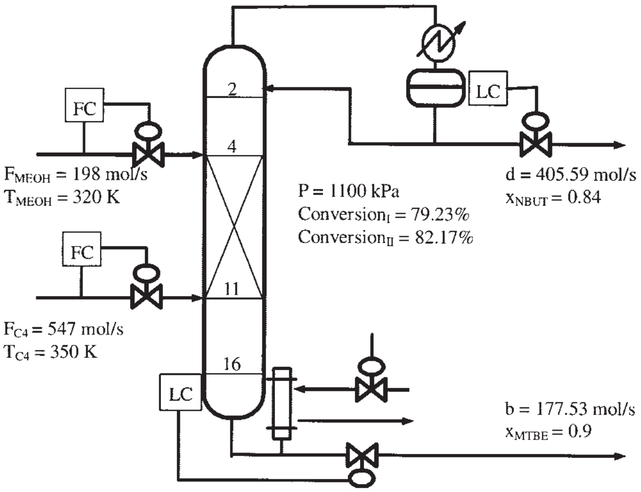

Figure 6. MTBE synthesis reactive distillation column.

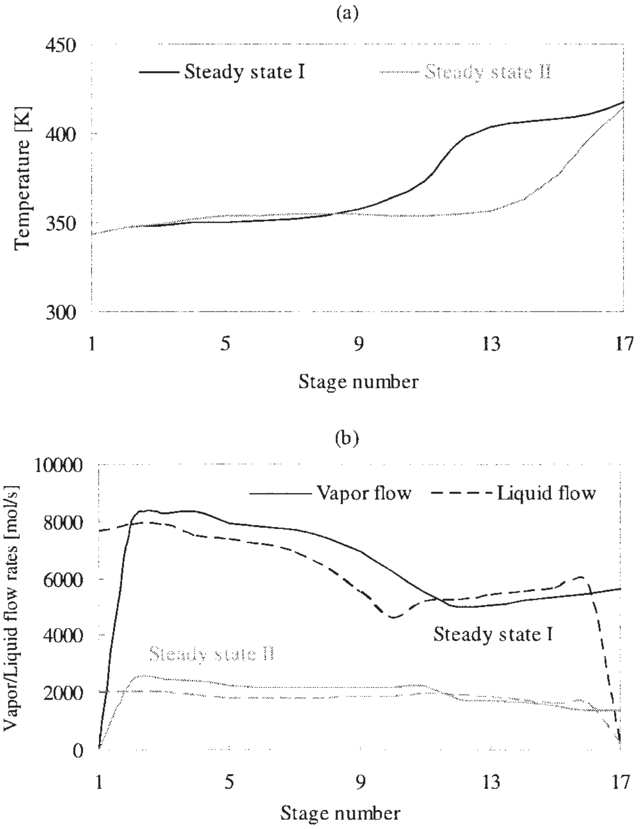

Figure 7. Profiles of temperature, liquid, and vapor flow rates of MTBE synthesis reactive distillation column.

Simulation of the MTBE synthesis reactive distillation column is carried out using the commercial ChemCad software. The liquid-phase activities are calculated using the UNIQUAC model with the binary interaction parameters reported by Rehfinger and Hoffmann.[46] Every reactive stage is assumed to be in chemical equilibrium and the following equation is used to represent the temperature dependency of the reaction equilibrium constant:

$$\ln K_{eq} = -16.33 + 6820/T \tag{9}$$

The top and bottom products are specified to be 84 and 90 mol % for *n*-butene and MTBE, respectively. Because of the existence of an inert component (*n*-butene), it is impossible to maintain a constant conversion rate by the product specifications. Two steady states have been found in this process and Figure 7 illustrates their corresponding temperature, liquid, and vapor flow profiles. As can be seen, sharp difference exists in system performance between the two steady states with an overall isobutylene conversion rate of 79.23% in steady state I and 82.17% in steady state II. A substantial improvement in process design can be expected for both steady states despite the complicated thermodynamic nature of the reacting mixture. The reinforcement of internal heat integration is then performed with respect to each of them in the sequel.

The Effect of Seeking Further Internal Heat Integration for Steady State I. It is found that the overall isobutylene conversion rate undergoes almost no changes with respect to the variations in process configuration. Therefore, its influences on system performance can be neglected. The effect of seeking further internal heat integration between the reaction and separation operations is demonstrated in Figure 8. With the raising of C4 feed location from the bottom of the reactive section, the

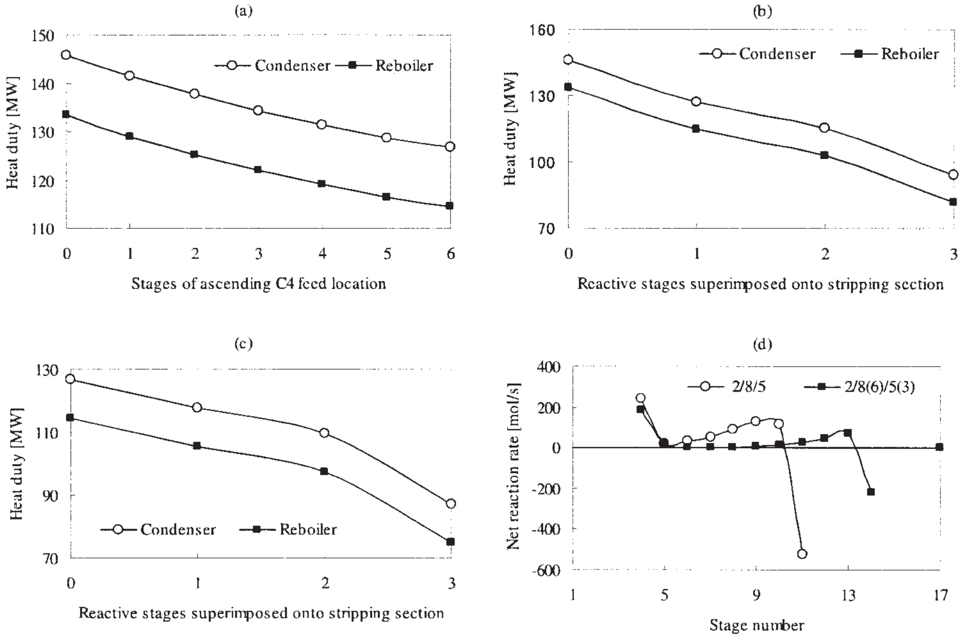

Figure 8. Strengthening internal heat integration for steady state I of MTBE synthesis reactive distillation column.

(a) Ascent of C4 feed location, (b) superimposition of reactive stages onto stripping section for process design, 2/8/5, (c) superimposition of reactive stages onto stripping section for process design, 2/8(6)/5, (d) profiles of net reaction rates.

Table 3. Effect of Seeking Further Internal Heat Integration for Steady State I of the Reactive Distillation System Synthesizing MTBE

Example II	Process Configurations	Condenser Duty (MW)	Reboiler Duty (MW)	Evaluations	
				Condenser	Reboiler
Basic process design	2/8/5	145.70	133.36	100%	100%
Raising C4 feed location six stages from the bottom of reactive section	2/8(6)/5	126.89	114.55	87.09%	85.90%
Combinatorial use of the methods of internal heat integration	2/8(6)/5(3)	87.33	74.92	59.94%	56.18%

heat duties of condenser and reboiler decrease monotonically and it thus appears advantageous to feed the C4 mixture at the top part of reactive section (Figure 8a). In terms of the superimposition of reactive stages onto the stripping section, the heat duties of condenser and reboiler substantially decrease in comparison with the basic process design, 2/8/5 (Figure 8b). For the process design, 2/8(6)/5, the effect of superimposing additional reactive stages onto the stripping section is examined again and the results are shown in Figure 8c. Extremely analogous to the basic process design, 2/8/5, a substantial reduction has still been found in the heat duties of condenser and reboiler. Figure 8d compares the profiles of net reaction rates for process designs 2/8/5 and 2/8(6)/5,(3) and it is readily apparent that seeking further internal heat integration strengthens the synergistic effect between the reaction and separation operations. Table 3 summarizes the effect of seeking further internal heat integration between the reactive and stripping sections. In comparison with the basic process design (2/8/5), introducing C4 feed flow at stage 5 reduces the heat duties of condenser and reboiler by 12.91 and 14.10%, respectively. The combinatorial use of the two methods of internal heat integration [that is, in 2/8(6)/5(3)] cuts down energy consumption by 40.06% in the condenser and 43.82% in the reboiler.

The Effect of Seeking Further Internal Heat Integration for Steady State II. Neither the ascent of C4 feed location from the bottom of the reactive section nor the superimposition of additional reactive stages onto the stripping section appears to be effective for the improvement of system performance. C4 feed flow is then considered not to be the dominant one and MEOH feed flow should be used instead in the reinforcement of internal heat integration between the reaction and separation operations. There is only one design option left in this case: the change of feed location. Figure 9a demonstrates the relationship between MEOH feed location and the heat duties of condenser and reboiler. A steady improvement in system performance is noticed when MEOH feed location has been lowered from stage 4 of the basic process design. To understand this phenomenon more fully, one needs to examine the profile of net reaction rates, and Figure 9b compares the profiles of net reaction rates for two process configurations: 2/8/5 and 2/8(4)/5. As can be seen, the reaction occurs mainly at the top of the reactive section in the basic process design, 2/8/5. In particular, backward reaction occurs on the last three reactive stages, representing a kind of adverse internal heat integration between the reactive and stripping sections.

This unfavorable distribution of net reaction rates is apparently caused by the inappropriate determination of MEOH feed location. More specifically, MEOH feed location has been raised too many plates from the bottom of the reactive section. After adjustment of MEOH feed location, the drawback of the basic process design has been substantially alleviated. The reaction now occurs primarily in the middle and at the bottom of the reactive section and no backward reaction occurs at all in the process design 2/8(4)/5. Although adverse internal heat integration occurs on the reactive stages above MEOH feed location, its negative effect appears to be smaller than the positive one of internal heat integration below the MEOH feed location. Table 4 sums up the effect of seeking further internal heat integration between the reactive and stripping sections. In comparison with the basic process design (2/8/5), introducing MEOH feed flow at stage 8 reduces the heat duties of condenser and reboiler by 42.08 and 58.10%, respectively. It should be indicated here that the overall isobutylene conversion

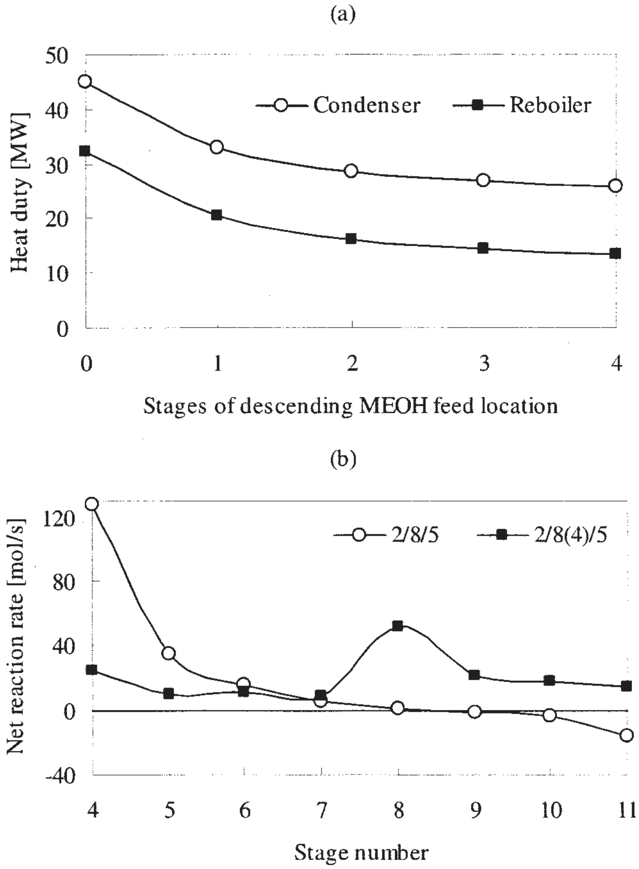

Figure 9. Reinforcement of internal heat integration for steady state II of the MTBE synthesis reactive distillation column.

(a) Descent of MEOH feed location, (b) profiles of net reaction rates.

Table 4. Effect of Seeking Further Internal Heat Integration for Steady State II of the Reactive Distillation System Synthesizing MTBE

Example II	Process Configurations	Condenser Duty (MW)	Reboiler Duty (MW)	Evaluations	
				Condenser	Reboiler
Basic process design	2/8/5	44.87	32.36	100%	100%
Lowering MEOH feed location four stages from the top of reactive section	2/8(4)/5	25.99	13.56	57.92%	41.90%

rate decreases to 80.28% in the process design 2/8(4)/5. Although it really influences system performance, its effect appears to be extremely small compared with the reduction of energy consumption obtained. Therefore, seeking further internal heat integration is no doubt the primary reason for the dramatic improvement in system performance.

Considering Further Internal Heat Integration within a Reactive Distillation Column Involving a Highly Endothermic Reaction

Example III: A hypothetical reactive distillation column

Process Description. The reactive distillation system has been adapted from Example I with the following modifications:

The hypothetical reversible reaction is now assumed to be an endothermic one with a heat of reaction:

$$\Delta H_R = 41{,}840 \text{ kJ/kmol}$$

The forward and backward activation energy has been exchanged with each other. That is,

$$E_f = 167{,}360 \text{ kJ/kmol}$$

$$E_b = 125{,}520 \text{ kJ/kmol}$$

A three-sectional configuration—7/6/7—is still assigned to the reactive distillation column and termed again as the basic process design here. Other operating conditions are assumed to be the same as those of Example I.

The Effect of Seeking Further Internal Heat Integration. Because the reaction involved is now an endothermic one, it is thus reasonable to recover a certain amount of heat at proper positions in the rectifying section and then supply it to the reactive section, thereby reducing the irreversibility associated with the separation operation and lessening the negative factors of reactive distillation to the endothermic reaction—for instance, the relatively large temperature driving forces from the bottom reboiler to the reactive section and the frequent necessity of intermediate heat exchangers.[47,48] Figure 10 presents the effect of seeking further internal heat integration between the reactive and rectifying sections on the reactive distillation column. The same total amount of catalyst has been maintained here, if without further indication. By lowering the upper feed location from the top of the reactive section, the process again shows an irregular tendency. When the upper feed location has been lowered from stage 9 of the basic process design, the heat duties of condenser and reboiler begin to decrease and simultaneously reach their minimum values at stage 11. If the upper feed location is lowered further, they turn to increase, indicating, nevertheless, the degradation of system performance. By superimposing reactive stages onto the rectifying section, the reactive distillation column displays a steady improvement in system performance. With more reactive stages superimposed onto the rectifying section, the heat duties of condenser and reboiler decrease monotonically.

Table 5 details a comparison between the basic process design and those with further internal heat integration between the reaction and separation operations. The heat duties of condenser and reboiler are reduced by 11.84 and 7.20%, respectively, when the upper feed flow for reactant B has been fed onto stage 11. In case four reactive stages have been superimposed onto the rectifying section, they are reduced by 10.52 and 6.39%, respectively. In terms of the combinatorial

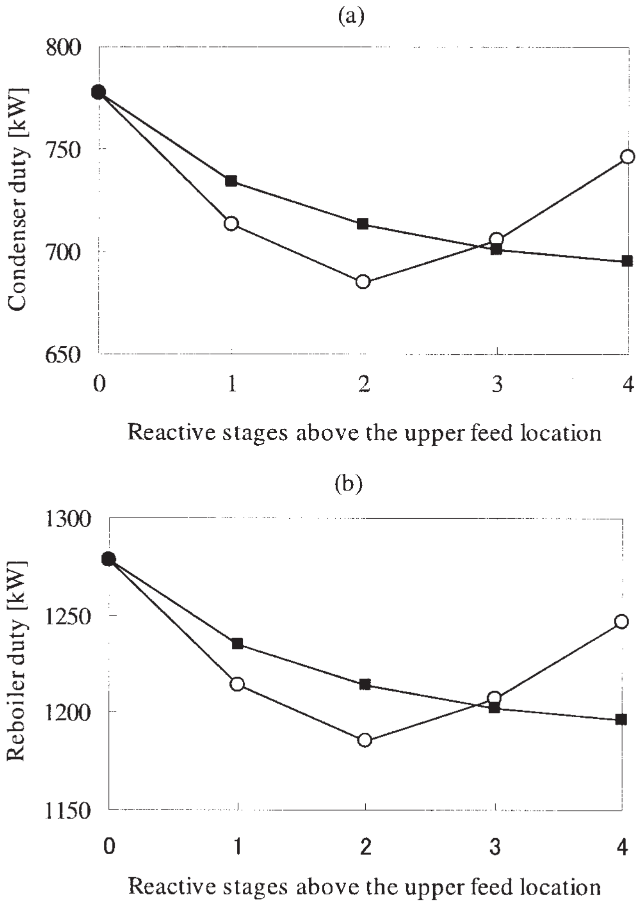

Figure 10. Strengthening internal heat integration for the hypothetical reactive distillation column involving a highly endothermic reaction.

–■–: superimposition of reactive stages onto rectifying section; –○–: descent of the upper feed location from the top of reactive section.

Table 5. Effect of Seeking Further Internal Heat Integration for the Hypothetical Reactive Distillation System Involving a Highly Endothermic Reaction

Example III	Process Configurations	Condenser Duty (kW)	Reboiler Duty (kW)	Evaluations	
				Condenser	Reboiler
Basic process design with holdup to be 1.0 kmol per stage	7/6/7	777.20	1278.03	100%	100%
Lowering the upper feed location two stages from the top of reactive section with holdup to be 1.0 kmol per stage	7/6(2)/7	685.14	1185.97	88.16%	92.80%
Superimposing four reactive stages onto rectifying section with holdup to be 0.6 kmol per stage	7(4)/6/7	695.40	1196.31	89.48%	93.61%
Combinatorial use of the above methods with holdup to be 0.75 kmol per stage	7(2)/6(2)/7	672.38	1173.21	86.51%	91.80%
Redistribution of catalyst	7(2)/6(2)/7*	668.79	1169.63	86.05%	91.52%
Combinatorial use of the above methods with holdup to be 1.0 kmol per stage	7(2)/6(2)/7	649.99	1150.84	83.63%	90.05%

use of these two methods [such as in 7(2)/6(2)/7], a further reduction of energy consumption has been achieved with 13.49% in the condenser and 8.20% in the reboiler. Redistribution of catalyst in the process design 7(2)/6(2)/7* shows the greatest reduction of energy consumption with 13.95% in the condenser and 8.48% in the reboiler. If liquid holdups are set to be 1.0 kmol for all reactive stages, the reduction of energy consumption can even approach a high value with 16.37% in the condenser and 9.95% in the reboiler. In Figure 11, the evolution of profiles of net reaction rates is illustrated. It is easily observable that a certain amount of heat recovered from the rectifying section has been used to drive the reaction operation. Although redistribution of catalyst makes only a slight adjustment of the amount of heat recovered in the process design 7(2)/6(2)/7, it actually facilitates further internal heat integration between the reaction and separation operations.

Example IV: A reactive distillation column for decomposing MTBE into isobutylene and methanol

Process Description. MTBE decomposition (Eq. 10) is becoming the preferred way of producing isobutylene because it can easily be integrated into the refinery and petrochemical sources of isobutylene-containing C4 streams.[49-51] In Figure 12, a basic process design for the MTBE decomposition reactive distillation column is depicted. The process again contains a three-sectional configuration, 5/6/5, besides a total condenser at the top and a partial reboiler at the bottom. The pure MTBE flow is fed into the top of the reactive section because it is the heaviest boiler of the reacting mixture. Simulation of the MTBE decomposition reactive distillation column is carried out using the commercial ChemCad software and the top and bottom products are kept strictly at their specifications, 94 mol % (IBUT) and 94 mol % (MEOH), respectively, in the following heat integration analysis:

$$\mathrm{MTBE}(C_4H_8O) \leftrightarrow \mathrm{MEOH}(CH_3OH) + \mathrm{IBUT}(i\text{—}C_4H_8) \qquad \Delta H_{R,298} = 37.7 \times 10^3\ \mathrm{kJ/kmol} \quad (10)$$

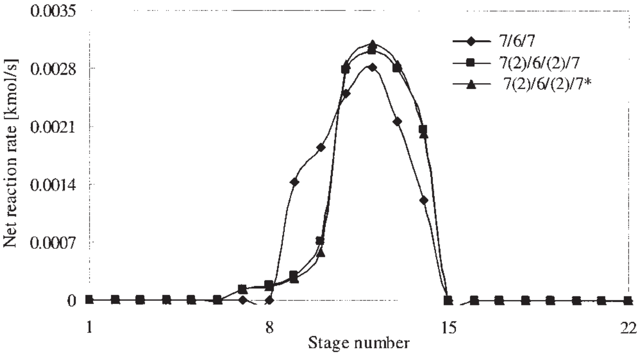

Figure 11. Profiles of net reaction rates for Example III.

The Effect of Seeking Further Internal Heat Integration. The effect of seeking further internal heat integration between the reaction and separation operations is illustrated in Figure 13. With regard to the descent of MTBE feed location from the top of the reactive section, the process again displays an inconsistent variation in system performance and the heat duties of condenser and reboiler simultaneously reach their minimum values at stage 11. For the superimposition of additional reactive stages onto the rectifying section, the heat duties of condenser and reboiler decrease monotonically and it is therefore reasonable to allow the reaction to occur at all stages in the rectifying section. Table 6 tabulates in great detail the effect of seeking further internal heat integration between the reactive and rectifying sections. In comparison with the basic process design 5/6/5, the heat duties of condenser and reboiler have

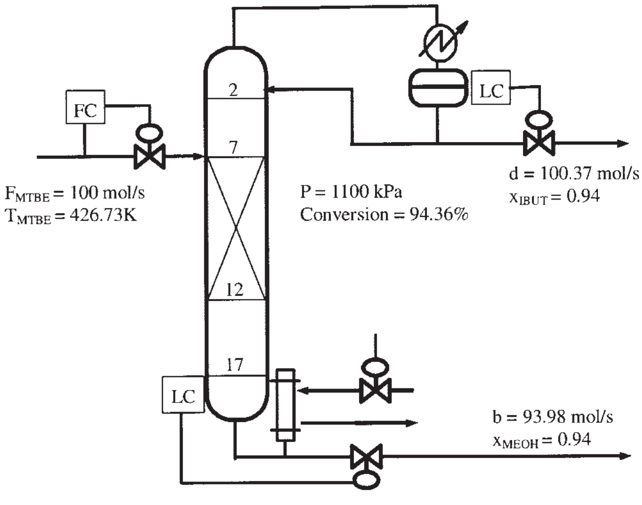

Figure 12. Schematic representation of MTBE decomposition reactive distillation column.

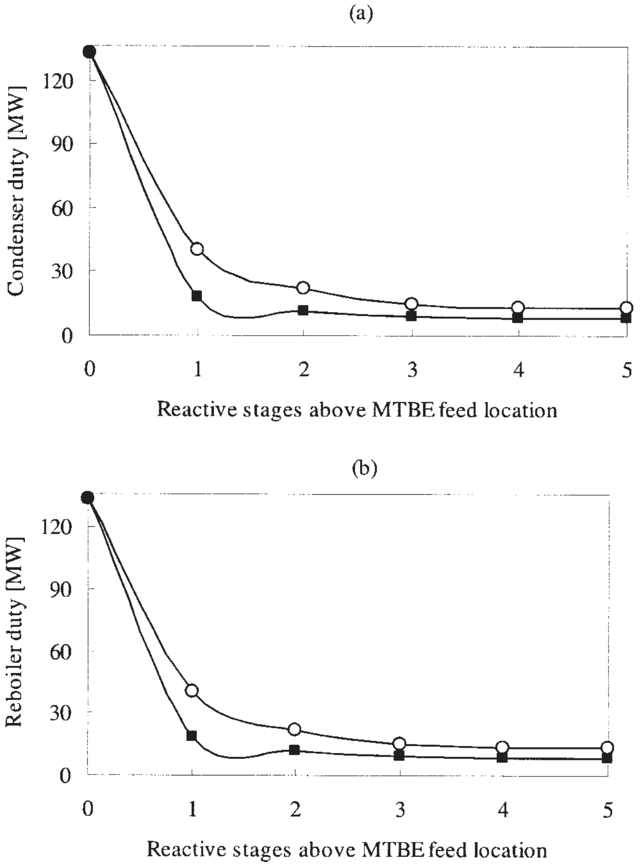

Figure 13. Strengthening internal heat integration for MTBE decomposition reactive distillation column.

–■–: Superimposition of reactive stages onto rectifying section; –○–: descent of MTBE feed location from the top of reactive section.

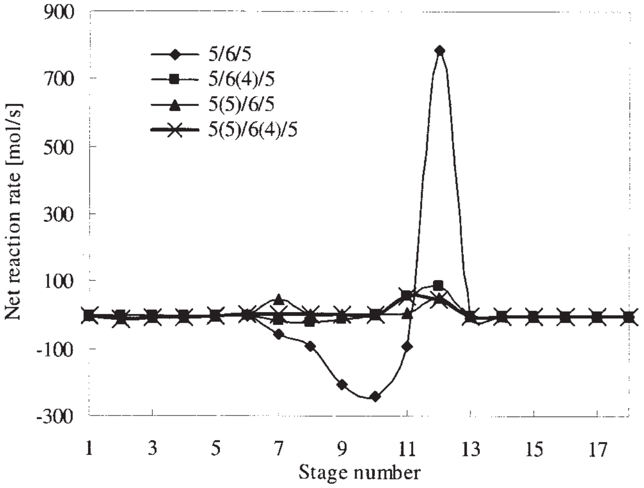

Figure 14. Profiles of net reaction rates in the MTBE decomposition reactive distillation column.

been abated by 90.42 and 90.13%, respectively, after lowering the MTBE feed from stage 7 to stage 11. With the replacement of all stages in the rectifying section by reactive ones, the heat duties of condenser and reboiler have been diminished by 94.01 and 93.81%, respectively. The combinatorial use of these two methods achieves the largest reduction of energy consumption with 94.51% in the condenser and 94.31% in the reboiler.

In Figure 14, the effect of seeking further internal heat integration is illustrated through comparison of the profiles of net reaction rates. In the basic process design 5/6/5, forward reaction occurs excessively on the bottom stage of the reactive section and leads to backward reactions that occur on the remaining reactive stages, apparently representing an ineffective combination of the reaction and separation operations. As can be seen, only after seeking further internal heat integration has the synergism between the reaction and separation operations been substantially enhanced.

Considering Further Internal Heat Integration within a Reactive Distillation Column Involving Multiple Reactions

Example V: A reactive distillation column for synthesizing ethylene glycol

Process Description. Ethylene glycol ($C_2H_6O_2$) is produced from the reaction of ethylene oxide ($C_2H_6O_2$) and water:

$$C_2H_4O(EO) + H_2O \rightarrow C_2H_6O_2(EG) \qquad \Delta H_R = -80.0 \times 10^3 \text{ kJ/kmol} \quad (11a)$$

$$r(\text{mol cm}^{-3}\text{ s}^{-1}) = 3.15 \times 10^9 \exp[-9547/T] x_{EO} x_{H_2O} \quad (11b)$$

Ethylene oxide can react further with ethylene glycol to produce the unwanted by-product diethylene glycol ($C_4H_{10}O_3$):

$$C_2H_4O(EO) + C_2H_6O_2(EG) \rightarrow C_4H_{10}O_3(DEG) \qquad \Delta H_R = -13.1 \times 10^3 \text{ kJ/kmol} \quad (12a)$$

$$r(\text{mol cm}^{-3}\text{ s}^{-1}) = 6.3 \times 10^9 \exp[-9547/T] x_{EO} x_{EG} \quad (12b)$$

Table 6. Effect of Seeking Further Internal Heat Integration for the Reactive Distillation System Decomposing MTBE

Example IV	Process Configurations	Condenser Duty (MW)	Reboiler Duty (MW)	Evaluations	
				Condenser	Reboiler
Basic process design	5/6/5	132.90	133.30	100%	100%
Lowering MTBE feed location four stages from the top of reactive section	5/6(4)/5	12.73	13.15	9.58%	9.87%
Superimposing five reactive stages onto rectifying section	5(5)/6/5	7.96	8.25	5.99%	6.19%
Combinatorial use of the above methods	5(5)/6(4)/5	7.29	7.59	5.49%	5.69%

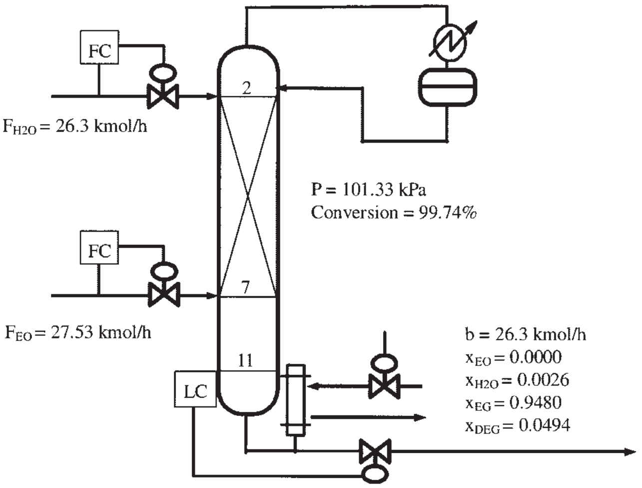

Figure 15. Ethylene glycol reactive distillation column.

Both reactions are highly exothermic and occur at moderate temperatures, allowing production by a reactive distillation column. Figure 15 shows such a basic process design (0/6/4), with a total of 12 stages including a total condenser at the top and a partial reboiler at the bottom. The process has no rectifying section and is operated in a total reflux mode. Water and EO are fed onto the top and bottom of the reactive section, respectively, and liquid holdups are assumed to be 0.1 m^3 for all stages in the reactive section. An ideal vapor–liquid equilibrium relationship is assumed for the reaction system and the detailed physiochemical properties are taken from Ciric and Gu.[13] The process is simulated by means of the generalized steady-state model described in the Appendix.

The Effect of Seeking Further Internal Heat Integration. In this system, there are two severe constraints that make the reinforcement of internal heat integration difficult between the reactive and stripping sections. One is the large relative volatility between the reactants EO and water, which spans a considerable range from 14.16 to 93.73 along the column. EO exists mainly in the vapor phase and its liquid composition is extremely small throughout the column, thereby severely restraining the superimposition of reactive stages onto the stripping section. The other is the existence of a side reaction. Because its reaction rate increases more rapidly with temperature than that of the main reaction, it is anticipated that the arrangement of these reactions occurring in the stripping section will be critically confined as long as a stringent reaction selectivity has been maintained. In Figure 16, the effect of seeking further internal heat integration between the reaction and separation operations is displayed on the basic process design. In all situations the amount of catalyst has been maintained as identical to that in the basic process design here. It is amazing to see that seeking further internal heat integration can still yield a significant improvement in system performance. With the raising of EO feed location from the bottom of the reactive section, the process again shows an inconsistent variation and the heat duties of condenser and reboiler simultaneously reach their minimum values when EO is fed on stage 5. With the superimposition of additional reactive stages onto the stripping section, the heat duties of condenser and reboiler decrease monotonically and it is therefore reasonable to allow the reactions to occur at all stages in the stripping section. Similar arrangements of the reactive section were also reported by Papalexandri and Pistikopoulos[14] and Cardoso et al.[15] in terms of a MINLP optimization formulation.

Table 7 summarizes the effect of seeking further internal heat integration between the reactive and stripping sections. Relocation of EO feed at stage 5 leads to a reduction of the heat duties of condenser and reboiler by 0.75 and 0.81%, respectively. The change of all stages in the stripping section into reactive ones shows a relatively large effect and the heat duties of condenser and reboiler have been reduced by 6.23 and 6.72%, respectively. The combinatorial use of these two methods achieves the second largest reduction of energy consumption with 5.73% in the condenser and 6.18% in the reboiler because the ascent of EO feed location by one stage no longer favors internal heat integration in the process design 0/6/4(4).

Because the reactions involved are kinetically controlled

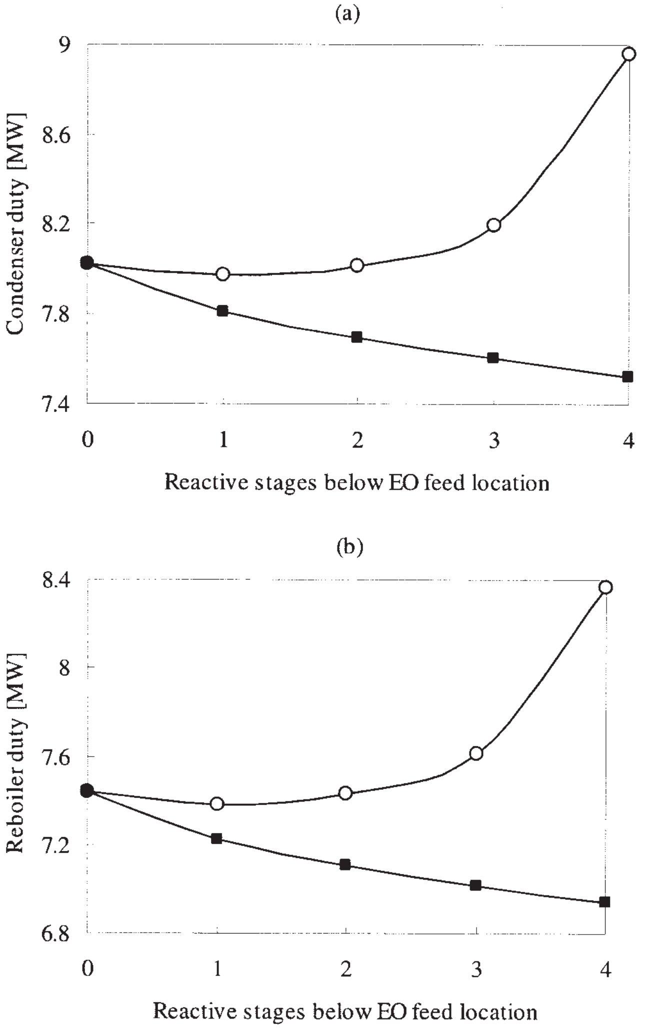

Figure 16. Strengthening internal heat integration for the ethylene glycol reactive distillation column.

–■–: Superimposition of reactive stages onto stripping section; –○–: ascent of EO feed location from the bottom of reactive section.

Table 7. Effect of Seeking Further Internal Heat Integration for the Reactive Distillation System Synthesizing Ethylene Glycol

Example V	Process Configurations	Condenser Duty (MW)	Reboiler Duty (MW)	Evaluations	
				Condenser	Reboiler
Basic process design with holdup to be 0.1 m^3 per stage	0/6/4	8.03	7.44	100%	100%
Raising EO feed location one stage from the bottom of reactive section with holdup to be 0.1 m^3 per stage	0/6(1)/4	7.97	7.38	99.25%	99.19%
Superimposing four reactive stages onto stripping section with holdup to be 0.06 m^3 per stage	0/6/4(4)	7.53	6.94	93.77%	93.28%
Combinatorial use of the above methods with holdup to be 0.06 m^3 per stage	0/6(1)/4(4)	7.57	6.98	94.27%	93.82%
Redistribution of catalyst	0/6/4(4)*	7.23	6.65	90.04%	89.38%

ones, it is therefore necessary to pursue further internal heat integration by exploring an appropriate distribution of catalyst in the reactive section. In Figure 17, the relationship between the distribution of catalyst and the heat duties of condenser and reboiler is illustrated for process design 0/6/4(4). It is obvious that the variation of catalyst distribution can impart a significant influence to system performance. When liquid holdups have been increased in the common zone where the reactive section overlaps the stripping section, the heat duties of condenser and reboiler begin to decrease and reach their minimum values at the same time when the liquid holdups are set to equal 0.1 m^3. When the liquid holdups have been further increased, they in turn decrease. In Table 7, the effectiveness of catalyst distribution is also indicated. As can be seen, the redistribution of catalyst achieves a further reduction of energy consumption in process design 0/6/4(4)*, with 3.73% in the condenser and 3.90% in the reboiler. The improvement of system performance definitely evidences the necessity of seeking further internal heat integration by effective distribution of catalyst in the reactive section. In Figure 18, the evolution of heat load profiles is illustrated. Although only a small proportion of the heat of reactions is released to the stripping section, it actually plays an important role in the improvement of system performance.

Discussion

It has been demonstrated that seeking further internal heat integration can be effective in the refinement of process design of a reactive distillation column involving either equilibrium-limited or kinetically controlled reactions. Even for some complicated reaction systems with side reactions and/or unfavorable thermodynamic properties, it is still possible to achieve a substantial reduction of energy consumption compared with that achieved by conventional design methods. This finding is of practical significance and can encourage process designers to elaborate their process designs by exploring the most effective combination of the reaction and separation operations. It is worth mentioning here that seeking further internal heat integration has led to a simultaneous shrinkage of heat duties in both condenser and reboiler for all the example systems studied. This reality confirms that seeking further internal heat integration helps to intensify the synergistic effect within a reactive distillation column, which is actually an essential design objective for all kinds of process intensifications. A more refined relationship has certainly been developed between the reaction and separation operations in the resultant process designs than in the basic ones.

It is noted that a considerable reduction of energy consumption has been achieved after seeking further internal heat integration between the reaction and separation operations in Examples II and IV. Such a large improvement in system performance is supposed to stem from two aspects. One is, of course, the reinforcement of internal heat integration between the reaction and separation operations. The other is the complicated thermodynamic nature of the reacting mixtures, which might make the processes sensitive to changes in process configurations. Although it is difficult to identify whose effect is dominant for these systems, it is still reasonable to view the reinforcement of internal heat integration as the principal reason because it provides an effec-

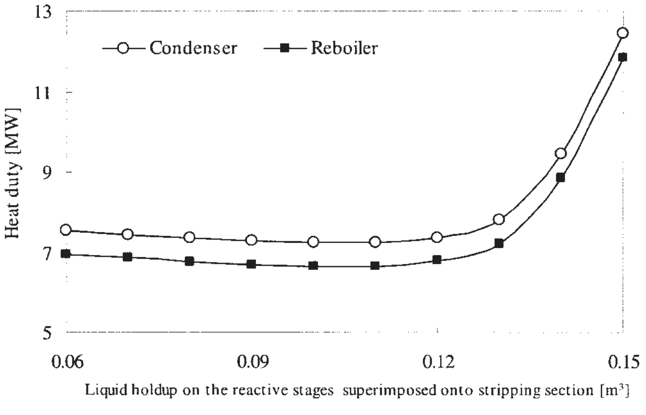

Figure 17. Redistributing catalyst within reactive section of the ethylene glycol reactive distillation column.

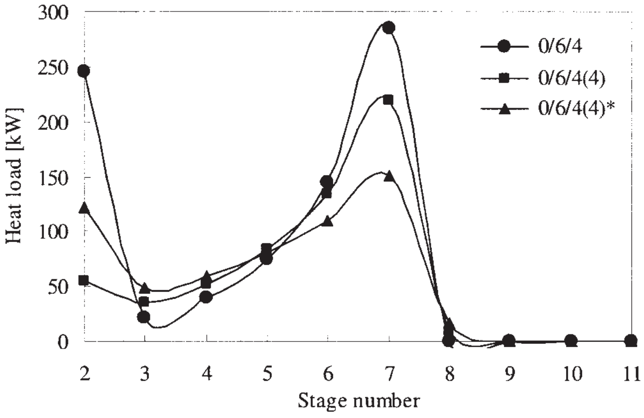

Figure 18. Heat load profiles in the ethylene glycol reactive distillation column.

Table 8. Influences of Product Composition on Internal Heat Integration of Example I

	Example I				
				Net Reduction of Energy Consumption (kW)	
Product Specification (mole fraction)	Process Configurations	Condenser Duty (kW)	Reboiler Duty (kW)	Condenser	Reboiler
$x_C = 0.95$ and $x_D = 0.95$	7/6/7	1323.69	822.86	126.92	126.92
	7/6(1)/7(3)	1196.77	695.94		
$x_C = 0.99$ and $x_D = 0.99$	7/6/7	1813.37	1291.45	37.99	38.99
	7/6/7(3)	1775.38	1253.46		
$x_C = 0.995$ and $x_D = 0.995$	7/6/7	2610.76	2086.21	2.50	2.50
	7/6/7(1)	2608.26	2083.71		

tive guideline for process innovation. Without the aid of this guideline, it would be difficult and time-consuming to yield those process designs obtained in this paper. It should be stressed here that the complicated thermodynamic nature of these reacting mixtures appears to present no limitations on the reinforcement of internal heat integration between the reaction and separation operations. On the contrary, a much greater improvement in system performance has been observed than the ideal reaction systems presented in Examples I, III, and V, probably implying that the consideration of internal heat integration is even more important for nonideal reaction systems than for ideal ones.

One may argue that finding an effective combination of the reaction and separation operations can be tackled for a reactive distillation column by means of a constrained nonlinear optimization formulation. The answer is “yes”—although this never means the immateriality of seeking further internal heat integration between the reaction and separation operations. Although these two methods work in totally different ways, they are considered to approach the same thermodynamically most efficient process design. Therefore, the method proposed in this work may be viewed as a practical alternative to the optimization-based approaches. In particular, when a rule of thumb method is adopted in process design, seeking further internal heat integration between the reaction and separation operations can play an important role in appropriately deciding feed locations, effectively distributing the reactive section within the reactive distillation column, and approximately finding the optimum distribution of catalyst in the reactive section. It certainly provides process designers with additional latitude in process synthesis and design.

It should be pointed out here that the improvement in system performance caused by a multiple feed arrangement and/or variable liquid holdups in the reactive section can also be interpreted with the principle of internal heat integration between the reaction and separation operations. The arrangement of multiple feeds and/or variable liquid holdups actually modifies the inherent thermodynamic characteristics of a reactive distillation column and can thus be favorable to internal heat integration between the reaction and separation operations. Although it is rather difficult to interpret the detailed mechanism of internal heat integration in this kind of process designs as clearly as in the single- or two-feed configurations, they are considered to work by the same principle. A potential problem with this kind of process designs might be the possibility of high sensitivity to changes in operating conditions, such as the deactivation of catalyst and the uncertainty of feed flow rates, which might considerably degrade system performance.

Analogous to the case of conventional distillation columns, the effect of seeking further internal heat integration depends heavily on the thermodynamic properties of reacting mixtures and the detailed operating conditions of reactive distillation columns. It is likely that internal heat integration might not be the primary factor that dominates process development. In process synthesis and design it is therefore necessary to make a careful judgment whether seeking further internal heat integration should be considered as a major design guideline. In Table 8, the influences of product composition are shown on internal heat integration of Example I. As can be seen, the advantage of internal heat integration gradually decreases with the enhancement of product purity. When the composition of top and bottom products increases to be 99.5 mol %, seeking further internal heat integration leads only to a reduction of 2.50 kW in the condenser and reboiler. It actually amounts to about 1.97% of the corresponding value when the composition of top and bottom products is 95 mol %. In terms of the resultant process designs, it is not difficult to understand that the degree of internal heat integration has been substantially restrained by the enhancement of product composition. In Table 9, the influences of product composition are shown on the internal heat integration of Example II. Contrary to the above circumstance, the advantage of internal heat integration increases with the enhancement of product purity. When the composition of top and bottom products increases to be 89.8

Table 9. Influences of Product Composition on Internal Heat Integration of Example II

	Example II				
				Net Reduction of Energy Consumption (MW)	
Product Specification (mole fraction)	Process Configurations	Condenser Duty (MW)	Reboiler Duty (MW)	Condenser	Reboiler
$x_{NBUT} = 0.84$ and $x_{MTBE} = 0.9$	2/8/5	44.87	32.36	18.88	18.88
	2/8(4)/5	25.99	13.48		
$x_{NBUT} = 0.898$ and $x_{MTBE} = 0.992$	2/8/5	865.57	853.09	809.59	809.59
	2/8(6)/5	55.98	43.50		

and 99.2 mol %, seeking further internal heat integration leads to a much larger reduction of 809.59 MW in the condenser and reboiler, representing approximately 42.88 times the corresponding value when the composition of top and bottom products is 84 and 90 mol %. Note again that the process configurations for internal heat integration are significantly affected by the enhancement of product composition. It is probably attributable to the complicated thermodynamic nature of the reaction system that makes possible the substantial improvement in system performance.

Conclusions

By seeking further internal heat integration between the reaction and separation operations, the thermodynamic efficiency can sometimes be substantially improved in addition to a further reduction of capital investment for a reactive distillation column involving reactions with a highly thermal effect. The reason lies mainly in the fact that a more synergistic relationship has been developed between the reaction and separation operations in the resultant process designs than that in the basic ones. Appropriately designating feed location in the reactive section and properly superimposing reactive stages onto either the rectifying section (in case of endothermic reactions) or the stripping section (in case of exothermic reactions) can be effective ways for the reinforcement of internal heat integration within a reactive distillation column. Moreover, achieving an effective distribution of catalyst in the reactive section can also work as a potential method for a reactive distillation column involving kinetically controlled reactions. It is even effective for a reactive distillation column involving equilibrium-limited reactions in the event that chemical equilibrium has not been reached on all reactive stages. The combinatorial use of these three methods could provide more benefits and higher flexibility than each of them, separately, and is highly recommended in this work. A sequential procedure has been devised to determine an appropriate process configuration for internal heat integration within a reactive distillation column. It can guide process designers to work more effectively than efforts based on conventional design philosophy during process synthesis and design.

Five reactive distillation systems, including both equilibrium-limited and kinetically controlled reactions, are studied in this work. Although the effectiveness of seeking further internal heat integration between the reaction and separation operations appears to be closely dependent on the thermodynamic properties of reacting mixtures and the operating conditions of reactive distillation columns, it is still possible to attain a substantial improvement in system performance, even under some extremely severe circumstances, demonstrating the high applicability and effectiveness to the design of reactive distillation columns. This outcome is of practical significance and could present a substantial influence on the design of various reactive distillation processes involving reactions with a highly thermal effect.

Acknowledgments

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Notation

A = reactive component
A_{vp} = vapor pressure constant, Pa
b = bottom product flow rate, kmol s^{-1}
B = reactive component
B_{vp} = vapor pressure constant, Pa·K
C = product component
d = distillate flow rate, kmol s^{-1}
D = product component
E = activation energy of a reaction, kJ kmol^{-1}
E_{I}, E_{II} = energy consumption, kJ s^{-1}
F = feed flow rate of reactants, kmol s^{-1}
H = stage holdup, kmol
ΔH_{V} = heat of vaporization, kJ kmol^{-1}
ΔH_{R} = heat of reaction, kJ kmol^{-1}
k = specific reaction rate, kmol s^{-1} kmol^{-1}
K_{eq} = equilibrium constant
L = liquid flow rate, kmol s^{-1}
N = number of stages
P = pressure, Pa
r = reaction rate, kmol s^{-1}
R = ideal gas law constant, kJ kmol^{-1} K^{-1}
T = temperature, K
V = vapor flow rate, kmol s^{-1}
x = liquid composition
y = vapor composition
z = feed composition

Greek letters

α = preexponential factor
δ = Kronecker function
ε = error tolerance
ν = stoichiometric coefficients of a reaction

Superscripts

s = saturation
sp = specified product composition

Subscripts

A = component index
b = backward reaction
B = component index
bot = bottom product
C = component index
d = distillate
D = component index
f = forward reaction
i = component index
j = stage index
m = feed stage index
r = rectifying section
rea = reactive section
s = stripping section
vp = vapor pressure

Literature Cited

1. Smith JM, Van Hess HC. *Introduction to Chemical Engineering Thermodynamics*. 4th Edition. New York, NY: McGraw-Hill; 1987.
2. Doherty MF, Buzad G. Reactive distillation by design. *Trans IChemE.* 1992;70A:448-458.
3. Malone MF, Doherty MF. Reactive distillation. *Ind Eng Chem Res.* 2000;39:3953-3957.
4. Almeida-Rivera CP, Swinkels PLJ, Grievink J. Designing reactive

distillation processes: Present and future. *Comput Chem Eng.* 2004; 28:1997-2020.

5. Eldarsi HS, Douglas PL. Methyl-tert-butyl-ether catalytic distillation column. Part I: Multiple steady states. *Trans IChemE.* 1998a;76A:509-516.
6. Okasinski MJ, Doherty MF. Design method for kinetically controlled staged reactive distillation columns. *Ind Eng Chem Res.* 1998;37: 2821-2834.
7. Subawalla H, Fair J. Design guidelines for solid-catalyzed reactive distillation systems. *Ind Eng Chem Res.* 1999;38:3696-3709.
8. Melles S, Grievink J, Schrans SM. Optimization of the conceptual design of reactive distillation columns. *Chem Eng Sci.* 2000;55:2089-2097.
9. Lee JW, Hauan S, Westerberg AW. Graphical methods for reaction distribution in a reactive distillation column. *AIChE J.* 2000a;46:1218-1233.
10. Lee JW, Hauan S, Westerberg AW. Extreme condition in binary reactive distillation. *AIChE J.* 2000b;46:2225-2236.
11. Lee JW, Westerberg AW. Visualization of stage calculation in ternary reacting mixtures. *Comput Chem Eng.* 2000;24:639-644.
12. Lee JW, Westerberg AW. Graphical design applied to MTBE and methyl acetate reactive distillation processes. *AIChE J.* 2001;47:1333-1345.
13. Ciric AR, Gu D. Synthesis of non-equilibrium reactive distillation process by MINLP optimization. *AIChE J.* 1994;40:1479-1487.
14. Papalexandri KP, Pistikopoulos EN. Generalized modular representation framework for process synthesis. *AIChE J.* 1996;42:1010-1032.
15. Cardoso MF, Salcedo RL, Azevedo S, Barbosa D. Optimization of reactive distillation processes with simulated annealing. *Chem Eng Sci.* 2000;55:5059-5078.
16. Ismail SR, Proios P, Pistikopoulos EN. Modular synthesis framework for combined separation/reaction systems. *AIChE J.* 2001;47:629-649.
17. Stichlmair J, Frey Th. Mixed integer non-linear programming optimization of reactive distillation processes. *Ind Eng Chem Res.* 2001;40: 5978-5982.
18. Jackson JR, Grossmann IE. A disjunctive approach for the optimal design of reactive distillation columns. *Comput Chem Eng.* 2001;25: 1661-1673.
19. Seferlis P, Grievink J. Optimal design and sensitivity analysis of reactive distillation units using collocation models. *Ind Eng Chem Res.* 2001;40:1673-1685.
20. Kaymak DB, Luyben WL. Effect of chemical equilibrium constant on the design of reactive distillation columns. *Ind Eng Chem Res.* 2003; http://pubs.acs.org:80/cgi-bin/sample.cgi/iecred/asap/pdf/ieo305871.pdf.
21. Freshwater DC. The heat pump in multi-component distillation. *Br Chem Eng.* 1961;6:388-391.
22. Flower JR, Jackson R. Energy requirement in the separation of mixtures by distillation. *Trans IChemE.* 1964;42A:249-258.
23. Null HR. Heat pumps in distillation. *Chem Eng Prog.* 1976;72:58-64.
24. Lynd LR, Grethlein HE. Distillation with intermediate heat pumps and optimal side-stream return. *AIChE J.* 1986;32:1347-1359.
25. Petlyuk FB, Platonov VM, Girsanov LV. The design of optimal rectification cascades. *Int Chem Eng.* 1965;5:309-317.
26. Naka Y, Terashita M, Hayashiguchi S, Takamatsu T. An intermediate heating and cooling method for a distillation column. *J Chem Eng Jpn.* 1980;13:123-129.
27. Agrawal R, Herron DM. Efficient use of an intermediate reboiler or condenser arrangement in a binary distillation. *AIChE J.* 1998a;44: 1303-1315.
28. Agrawal R, Herron DM. Intermediate reboiler and condenser arrangement for binary distillation columns. *AIChE J.* 1998b;44: 1316-1324.
29. Haselden GG. An approach to minimum power consumption in low temperature gas separation. *Trans IChemE.* 1958;36A:123-132.
30. Mah RSH, Nicholas JJ, Wodnik RB. Distillation with secondary reflux and vaporization: a comparative evaluation. *AIChE J.* 1977;23:651-658.
31. Takamatsu T, Lueprasitsakul V, Nakaiwa M. Modeling and design method for internally heat-integrated packed distillation columns. *J Chem Eng Jpn.* 1988;21:595-601.
32. Nakaiwa M, Huang K, Endo A, Ohmori T, Akiya T, Takamatsu T. Internally heat-integrated distillation columns: A review. *Trans IChemE.* 2003;81A:162-177.
33. Olujic Z, Fakhri F, Rijke A, Graauw J, Jansens PJ. Internal heat integration—The key to an energy-conserving distillation column. *J Chem Technol Biotechnol.* 2003;78:241-248.
34. Fonyo Z. Thermodynamic analysis of rectification. I: Reversible model of rectification. *Int Chem Eng.* 1974;14:18-27.
35. Umeda T, Niida K, Shroko K. A thermodynamic approach to heat integration in distillation systems. *AIChE J.* 1979;25:423-429.
36. Dhole VR, Linnhoff B. Distillation column targets. *Comput Chem Eng.* 1993;17:549-560.
37. Stankiewicz A, Moulijn JA. Process intensification. *Ind Eng Chem Res.* 2002;41:1920-1924.
38. Stankiewicz A. Reactive separations for process intensification: An industrial perspective. *Chem Eng Process.* 2003;42:137-144.
39. Luyben WL. Economic and dynamic impact of the use of excess reactant in reactive distillation systems. *Ind Eng Chem Res.* 2000;39: 2935-2946.
40. Al-Arfaj MA, Luyben WL. Comparison of alternative control structures for an ideal two-product reactive distillation column. *Ind Eng Chem Res.* 2000;39:3298-3307.
41. Jacobs R, Krishna R. Multiple solutions in reactive distillation for methyl-tert-butyl-ether synthesis. *Ind Eng Chem Res.* 1993;32:1706-1709.
42. Eldarsi HS, Douglas PL. Methyl-tert-butyl-ether catalytic distillation column. Part II: Optimization. *Trans IChemE.* 1998b;76A:517-524.
43. Sneesby MG, Tade MO, Smith TN. Steady state transitions in the reactive distillation of MTBE. *Comput Chem Eng.* 1998;22:879-892.
44. Baur R, Taylor R, Krishna R. Dynamic behavior of reactive distillation columns described by a non-equilibrium stage model. *Chem Eng Sci.* 2001;56:2085-2102.
45. Wang SJ, Wong DSH, Lee EK. Effect of interaction multiplicity on control system design for a MTBE reactive distillation column. *J Process Control.* 2003;13:503-515.
46. Rehfinger A, Hoffmann U. Kinetics of methyl tertiary butyl ether liquid phase synthesis catalyzed by ion exchange resin—I. Intrinsic rate expression in liquid phase activities. *Chem Eng Sci.* 1990;45: 1605-1617.
47. Bock H, Wozny G, Gutsche B. Design and control of a reaction distillation column including the recovery system. *Chem Eng Process.* 1997;36:101-109.
48. Tuchlenski A, Beckmann A, Reusch D, Dussel R, Weidlich U. Reactive distillation—Industrial applications, process design and scale up. *Chem Eng Sci.* 2001;56:387-394.
49. Clementi A, Oriani G, Ancillotti F, Pecci G. Upgrade C4's with MTBE process. *Hydro Process.* 1979;58:109-113.
50. Stein E, Kienle A, Sundmacher K. Separation using coupled reactive distillation column—A case study. *Chem Eng.* 2000;107:68-72.
51. Beckmann A, Nierlich F, Popken T, Reusch D, Scala C, Tuchlenski A. Industrial experience in the scale-up of reactive distillation with examples from C4-chemistry. *Chem Eng Sci.* 2002;57:1525-1530.

Appendix: Steady-State Simulation of Reactive Distillation Columns

In terms of the principle of mass and energy balance in conjunction with the vapor–liquid equilibrium relationship, a generalized steady-state model has been developed and frequently used in the simulation of some reactive distillation columns studied in this work. The steady-state model is solved using the Newton–Raphson method. As shown in Eqs. A1 and A2, two strict constraints have been imposed on the top and the bottom products within the steady-state model, which can, in most cases, guarantee a fair basis for the comparative studies of system performance between different process designs with and without further internal heat integration between the reaction and separation operations. Satisfaction of the component mass balance equations

(Eq. A3) and attainment of the product specifications (Eqs. A1 and A2) have been taken to constitute the convergence criterion. The steady-state model appears to be quite robust and can approach a solution fairly quickly even for some highly nonideal reaction systems:

$$|x_d - x_d^{sp}| \leq \varepsilon \tag{A1}$$

$$|x_{bot} - x_{bot}^{sp}| \leq \varepsilon \tag{A2}$$

$$|L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} - L_j x_{i,j} - V_j y_{i,j} + F_j z_{i,j}\delta_{j,m} + r_{i,j}| \leq \varepsilon \tag{A3}$$

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