

Operating Parameters and Selectivity in Batch Reactive Distillation

Wei Qi and Michael F. Malone*

Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States

This Article provides new predictions for selectivity in batch reactive distillation, identifying the reflux or reboil ratio and a Damköhler number (Da) as the key operating parameters. The dimensionless Da incorporates the influence of liquid holdup, vapor rate, and rate of reaction. Example results for a system of serial isomerization reactions and for the synthesis of ethylene glycol are provided. The results show that selectivity improvements in BRD are limited for high values of Da or for high values of the reflux or reboil ratio and that selectivity is enhanced as Da or reflux or reboil ratio is decreased. However, decreasing Da can cause conversion loss, which can be mitigated by increasing the reflux (or reboil) ratio at the expense of selectivity. Consequently, there is an optimum value of reflux or reboil ratio that gives a maximum yield for systems operated at low or moderate Da . For the isomerization in a BRD, the heat released by reaction can improve selectivity at the expense of conversion. For ethylene glycol synthesis at a low reboil ratio, BRD has a negative impact on both conversion and selectivity by causing separation of the reactants. We also show that decreasing the reboil ratio near the end of the BRD can increase the removal rate of EG and thereby improve selectivity. This operating strategy is different from a common operating strategy in distillation of increasing reboil ratio near the end of a batch or cut. We also find that an operation with a constant volumetric liquid flow rate provides lower selectivity than a constant molar liquid flow rate.

Introduction

Batch processes have been widely used for the production of specialty, life science, and consumer chemicals, that is, low-volume, short-term production of high-margin products. By integrating the batch process with reactive distillation, the flexibility of batch process and advantages of reactive distillation may be combined in batch reactive distillation (BRD). One of these advantages can be in selectivity improvement, which can lower raw material consumption and waste production.

For example, Talwalkar et al.¹ studied the dimerization of C_4 olefins and showed that BRD can significantly improve selectivity to C_8 dimers, eliminating the need to use additional polar components as selectivity enhancers. Thotla et al.² reported experimental and simulation results for BRD in the aldol condensation of acetone. They demonstrated remarkable selectivity improvement over a batch reactor: at a conversion of 40%, BRD achieved a 60% selectivity as compared to 2% selectivity to diacetone alcohol in a conventional batch reactor.

However, as shown by Mahajan et al.,³ BRD does not always improve selectivity. They studied the self-condensation of cyclohexanone and showed that the byproduct water, which also acts as a selectivity enhancer, is removed by BRD, causing the side reaction to be more significant than in a conventional batch reactor.

BRD is also used for catalyst screening to develop reactive distillation processes. Lange and Otten^{4,5} utilized BRD, to identify promising catalysts for the dehydration of phenyl ethanol to styrene under reactive distillation conditions, where selectivity can be a crucial issue. Medium-pore zeolites were found to be very active and selective in BRD, and the formation of heavy byproducts was found inside the zeolite pores, prior to styrene desorption. Chiu et al.⁶ used BRD in semibatch mode to screen catalysts for the dehydration of glycerol to acetol and

found that high acetol selectivity can be achieved under mild conditions using a copper-chromite catalyst.

Agarwal et al.⁷ investigated some single-reactant, nonazeotropic systems using an attainable region approach and gave some guidelines on BRD design, for example, reaction location and number of reactive stages. Agarwal et al.⁸ extended this approach to the hypothetical single-reactant systems with one binary azeotrope. Some design guidelines based on residue curve map structure to improve selectivity by choosing column configuration were provided.

Operating parameters play an important role in selectivity of BRD, as shown by Bollyn and Wright⁹ in their case study of scaling up a laboratory BRD process for the synthesis of ethyl ester of pentenoic acid, where selectivity was increased from 49% to 83% by decreasing the reflux ratio from 8 to 1. For the methyl acetate/dimethyl ether system, Venimadhavan¹⁰ predicted the maximum yield, as well as the corresponding selectivity and conversion as a function of the normalized Damköhler number, and showed the trade-off between selectivity and maximum yield by choosing different values of the Damköhler number. Gadewar et al.¹¹ described a simplified method to estimate the potential selectivity advantage of BRD over a conventional reactor. That method can also determine the effect of operating parameters on yield and selectivity. For an idealized case of serial reactions, they showed that the selectivity advantage in BRD is more significant for systems with fast side reactions. Often these BRD studies are done under a simplified operation condition, for example, assuming the specified product composition is always achievable, or operating in a simple reactive distillation¹² without reflux, which provides limited information on the operating parameters.

This Article investigates the effects of BRD operating parameters on selectivity for more realistic operating conditions. Understanding these effects allows us to identify and exploit trade-offs in BRD and to avoid unfavorable impacts on selectivity caused by inappropriate operations. In this Article, we consider systems with ideal VLE and simple reaction kinetics. By wiping away complexities in VLE and reaction

* To whom correspondence should be addressed. Tel.: (413) 545-5270. Fax: (413) 577-0007. E-mail: mmalone@umass.edu. Present address: Vice Chancellor for Research & Engagement, 354 Whitmore Administration Building, 181 Presidents Dr., Amherst, MA 01003-9313.

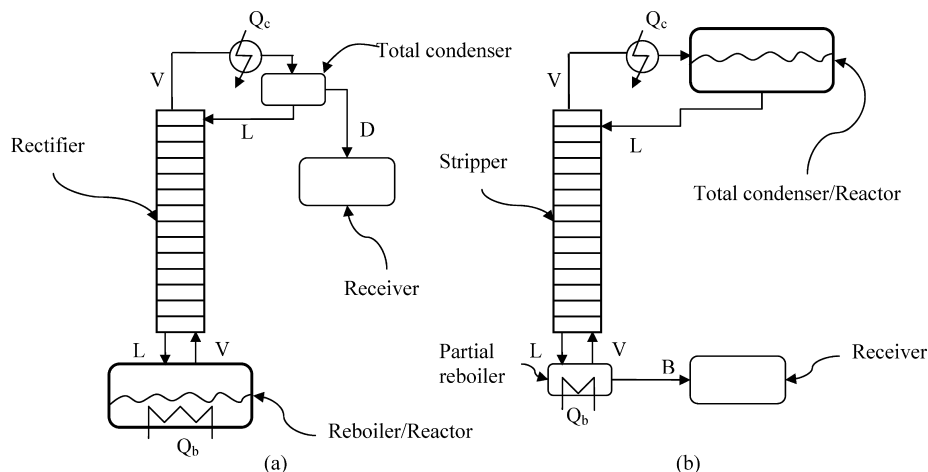


Figure 1. Schematics of two BRD devices: (a) batch reactor-rectifier, and (b) batch reactor-stripper.

kinetics, we can better understand the common picture clouded behind specific cases.

Model Development for BRD

Figure 1 shows the schematics of two BRD systems: (a) is a batch reactor-rectifier, in which reactions occur in a reboiler/reactor and products are collected as distillates from a rectifying section; and (b) is a batch reactor-stripper, where reactions occur in condenser/reactor, and products are withdrawn as bottoms from a stripping section.

The following assumptions are made in the model development:

(a) Reactions take place only in the liquid phase of the reaction vessel, that is, in the reboiler for the batch reactor-rectifier, or the condenser for the batch reactor-stripper. For example, the catalyst is present only in the reboiler or condenser, respectively.

(b) A total condenser produces a saturated liquid overhead.

(c) As compared to the liquid holdup in the reaction vessel, the liquid holdups on the stages and in the condenser (for the batch reactor-rectifier) or in the reboiler (for the batch reactor-stripper) are negligible.

(d) Vapor and liquid molar flow rates are constant from stage-to-stage (constant molar overflows (CMO)) at any given time. However, they do vary with time; that is, they are in a quasi-steady state.

(e) A constant reflux ratio for the batch reactor-rectifier and a constant reboil ratio for the batch reactor-stripper are used.

A mass balance model for the batch reactor-rectifier is developed as follows.

i. Reboiler/Reactor.

$$\frac{dH_r}{dt} = L - V + \sum_{k=1}^R \nu_{k,T} r_k H_r \quad (1)$$

$$\frac{dH_r x_{r,i}}{dt} = L x_{N,i} - V y_{r,i} + \sum_{k=1}^R \nu_{k,i} r_k H_r \quad i = 1, \dots, m-1 \quad (2)$$

where H_r is the molar liquid holdup at time t , L is the liquid flow rate, V is the vapor flow rate, $\nu_{k,T}$ is the sum of the stoichiometric coefficients in reaction k (i.e., $\nu_{k,T} = \sum_{i=1}^m \nu_{k,i}$), r_k is the rate of reaction k with units of inverse time, $x_{r,i}$ is the liquid phase mole fraction of component i in the reaction vessel, $x_{N,i}$ is the liquid phase mole fraction of component i on stage N , $y_{r,i}$ is the vapor phase mole fraction of component i leaving

the reaction vessel, and $\nu_{k,i}$ is the stoichiometric coefficient of component i in reaction k .

ii. Stages.

$$\frac{dH_j}{dt} = 0 \quad j = 1, \dots, N \quad (3)$$

$$\frac{dH_j x_{j,i}}{dt} = L(x_{j-1,i} - x_{j,i}) + V(y_{j+1,i} - y_{j,i}) \quad j = 1, \dots, N; \quad i = 1, \dots, m-1 \quad (4)$$

where subscript j is the stage number (increasing from top to bottom), stage 0 represents the condenser, and stage $N+1$ represents the reaction vessel (reboiler).

iii. Condenser.

$$\frac{dH_c}{dt} = V - L - D = 0 \quad (5)$$

$$\frac{dH_c x_{c,i}}{dt} = V y_{1,i} - L x_{c,i} - D x_{c,i} \quad i = 1, \dots, m-1 \quad (6)$$

where c represents the condenser, and D is the distillate flow rate, given by

$$D = \frac{L}{r} = \frac{V}{r+1} \quad (7)$$

where r is the reflux ratio.

iv. Receiver.

$$\frac{dH_{\text{recv}}}{dt} = D \quad (8)$$

$$\frac{dH_{\text{recv}} x_{\text{recv},i}}{dt} = D x_{c,i} \quad i = 1, \dots, m-1 \quad (9)$$

where the subscript recv represents the receiver.

It is useful to introduce a Damköhler number (Da), which represents the ratio of a characteristic process time to reaction time:

$$Da = \frac{H_r/V}{1/k_{\text{main,ref}}} \quad (10)$$

where $k_{\text{main,ref}}$ is the reaction rate constant of the main reaction at a reference temperature.

By using a dimensionless time defined as

$$\tau = tk_{\text{main,ref}} \quad (11)$$

together with eqs 7 and 10, eqs 1 and 2 can be rewritten as

$$Da \frac{dH_r}{d\tau} = \left(\frac{r}{r+1} - 1 \right) H_r + Da \sum_{k=1}^R v_{k,T} \kappa_k H_r \quad (12)$$

$$Da \frac{dx_{r,i}}{d\tau} = \frac{r}{r+1} (x_{N,i} - x_{r,i}) + (x_{r,i} - y_{r,i}) + Da \left(\sum_{k=1}^R v_{k,i} \kappa_k - x_{r,i} \sum_{k=1}^R v_{k,T} \kappa_k \right) \quad i = 1, \dots, m-1 \quad (13)$$

in which κ is a dimensionless reaction rate, defined by

$$\kappa_k = \frac{r_k}{k_{\text{main,ref}}} \quad (14)$$

On the right-hand side of eqs 12 and 13, the last term represents the impact of the reaction, while the first term in eq 12 and the first two terms in eq 13 represent the impact of distillation. The impact of distillation weakens with increasing Da . In fact, for large Da , the distillation term(s) are negligible as compared to the reaction term, and distillation has little impact on the holdup and concentration profiles of the reaction vessel. In the limiting case of $Da \rightarrow \infty$, eqs 12 and 13 can be rewritten as

$$\frac{dH_r}{d\tau} = \sum_{k=1}^R v_{k,T} \kappa_k H_r \quad (15)$$

$$\frac{dx_{r,i}}{d\tau} = \left(\sum_{k=1}^R v_{k,i} \kappa_k - x_{r,i} \sum_{k=1}^R v_{k,T} \kappa_k \right) \quad i = 1, \dots, m-1 \quad (16)$$

which have the same forms as a conventional batch reactor.

For another limiting case, $r \rightarrow \infty$, eq 12 again can be simplified to eq 15, while eq 13 can be simplified to

$$Da \frac{dx_{r,i}}{d\tau} = (x_{N,i} - y_{r,i}) + Da \left(\sum_{k=1}^R v_{k,i} \kappa_k - x_{r,i} \sum_{k=1}^R v_{k,T} \kappa_k \right) \quad i = 1, \dots, m-1 \quad (17)$$

If the stages are in a quasi steady-state (QSS), we have

$$(x_{N,i} - y_{r,i}) = 0 \quad i = 1, \dots, m-1 \quad (18)$$

Equation 13 can be further simplified as

$$\frac{dx_{r,i}}{d\tau} = \left(\sum_{k=1}^R v_{k,i} \kappa_k - x_{r,i} \sum_{k=1}^R v_{k,T} \kappa_k \right) \quad i = 1, \dots, m-1 \quad (19)$$

which also has the same form as a conventional batch reactor.

The mass balance for a batch reactor-stripper can be developed in a similar manner.

i. Condenser/Reactor.

$$\frac{dH_r}{dt} = V - L + \sum_{k=1}^R v_{k,T} r_k H_r \quad (20)$$

$$\frac{dH_r x_{r,i}}{dt} = Vy_{1,i} - Lx_{r,i} + \sum_{k=1}^R v_{k,i} r_k H_r \quad i = 1, \dots, m-1 \quad (21)$$

where $y_{1,i}$ is the vapor phase mole fraction of component i entering the reaction vessel from stage 1.

ii. Stages.

$$\frac{dH_j}{dt} = 0 \quad j = 1, \dots, N \quad (22)$$

$$\frac{dH_j x_{j,i}}{dt} = L(x_{j-1,i} - x_{j,i}) + V(y_{j+1,i} - y_{j,i}) \quad j = 1, \dots, N; \quad i = 1, \dots, m-1 \quad (23)$$

where the subscript j is the stage number (increasing from top to bottom), stage 0 represents the reaction vessel (condenser), and stage $N+1$ represents the reboiler.

iii. Reboiler.

$$\frac{dH_{rb}}{dt} = L - V - B = 0 \quad (24)$$

$$\frac{dH_{rb} x_{rb,i}}{dt} = Lx_{N,i} - Vy_{rb,i} - Bx_{rb,i} \quad i = 1, \dots, m-1 \quad (25)$$

where subscript rb represents the reboiler, and B is the bottom flow rate, given by

$$B = \frac{V}{s} = \frac{L}{s+1} \quad (26)$$

where s is the reboil ratio.

iv. Receiver.

$$\frac{dH_{\text{recv}}}{dt} = B \quad (27)$$

$$\frac{dH_{\text{recv}} x_{\text{recv},i}}{dt} = Bx_{rb,i} \quad i = 1, \dots, m-1 \quad (28)$$

As in the batch reactor-rectifier model, we introduce a Damkohler number as

$$Da = \frac{H_r J L}{1/k_{\text{main,ref}}} \quad (29)$$

With eqs 11, 26, and 29, we can rewrite eqs 20 and 21 as

$$Da \frac{dH_r}{d\tau} = \left(\frac{s}{s+1} - 1 \right) H_r + Da \sum_{k=1}^R v_{k,T} \kappa_k H_r \quad (30)$$

$$Da \frac{dx_{r,i}}{d\tau} = \frac{s}{s+1} (y_{1,i} - x_{r,i}) + Da \left(\sum_{k=1}^R v_{k,i} \kappa_k - x_{r,i} \sum_{k=1}^R v_{k,T} \kappa_k \right) \quad i = 1, \dots, m-1 \quad (31)$$

As might be expected, this model is structurally similar to the batch reactor-rectifier model. The impact of distillation also weakens with increasing Da and for large Da distillation has little impact on holdup and concentration profiles of the reaction

vessel. For the limiting cases $Da \rightarrow \infty$, or $s \rightarrow \infty$ (with a QSS assumption for stages), eqs 30 and 31 can be simplified to

$$\frac{dH_r}{d\tau} = \sum_{k=1}^R \nu_{k,T} \kappa_k H_r \quad (32)$$

$$\frac{dx_{r,i}}{d\tau} = \left(\sum_{k=1}^R \nu_{k,i} \kappa_k - x_{r,i} \sum_{k=1}^R \nu_{k,T} \kappa_k \right) \quad i = 1, \dots, m-1 \quad (33)$$

which also have forms identical to those of a conventional batch reactor.

Note that in addition to the explicit impacts from distillation terms in eqs 12 and 13, and eqs 30 and 31, distillation also has an implicit impact on the reaction terms. This is because integrating distillation with reaction restricts the operating temperature to lie on the boiling surface of the mixture at the given pressure. Consequently, for a liquid phase reaction, the operating temperature of a BRD is higher than a conventional batch reactor at the same pressure and cannot be constant. The variation of temperature and its impact depends on the phase equilibrium characteristics of the mixture, and on the temperature dependence of the reaction equilibria and the rate constants.

Example I: A Simple Case of Serial Reactions

Consider a liquid-phase reaction system in an ideal solution,



where A (boiling point 100 °C) is the reactant, B (65 °C) is the desired product, and C (80 °C) is an undesired byproduct. The VLE is described with Raoult's law. The reaction rates are

$$r_1 = k_1 x_A \quad (35)$$

and

$$r_2 = k_2 x_B \quad (36)$$

We assume that k_1 and k_2 have the same pre-exponential factor and temperature dependence (a more realistic case is considered in the next example).

Because A has the highest boiling point and B the lowest, we use a batch reactor-rectifier, Figure 1a. The reboiler serves as the reactor, while products are collected in a receiver from the distillate.

For this case, the conversion, selectivity, and yield are defined as

$$\text{conversion} = \frac{\text{initial A in reboiler} - (\text{A in reboiler} + \text{A in receiver})}{\text{initial A in reboiler}} \quad (37)$$

$$\text{selectivity} = \frac{\text{B in reboiler} + \text{B in receiver}}{\text{initial A in reboiler} - (\text{A in reboiler} + \text{A in receiver})} \quad (38)$$

$$\text{yield} = \text{conversion} \times \text{selectivity} = \frac{\text{B in reboiler} + \text{B in receiver}}{\text{initial A in reboiler}} \quad (39)$$

Using eqs 35 and 36, we can rewrite eq 12 as

$$Da \frac{dH_r}{d\tau} = \left(\frac{r}{r+1} - 1 \right) H_r \quad (40)$$

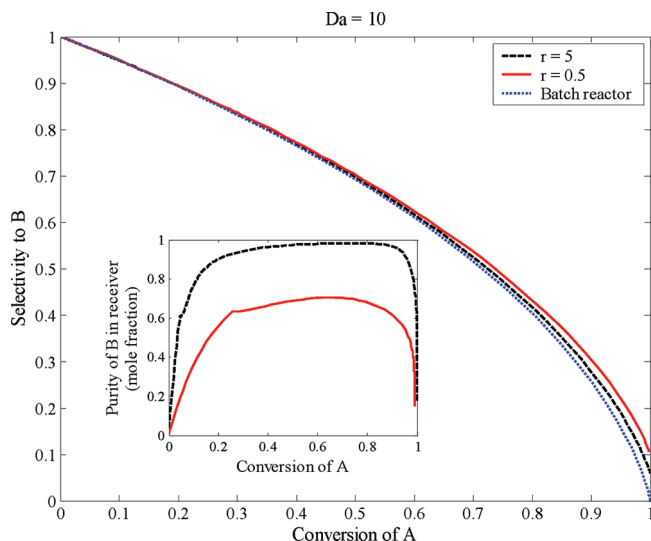


Figure 2. Impact of large Da on selectivity in BRD for example I.

and eq 13 as

$$Da \frac{dx_{r,A}}{d\tau} = \frac{r}{r+1} (x_{N,A} - x_{r,A}) + (x_{r,A} - y_{r,A}) - Da \kappa_1 \quad (41)$$

$$Da \frac{dx_{r,B}}{d\tau} = \frac{r}{r+1} (x_{N,B} - x_{r,B}) + (x_{r,B} - y_{r,B}) + Da(\kappa_1 - \kappa_2) \quad (42)$$

where

$$\begin{aligned} \kappa_1 &= \frac{r_1}{k_{1,\text{ref}}} \\ \kappa_2 &= \frac{r_2}{k_{1,\text{ref}}} \end{aligned} \quad (43)$$

The reference temperature for this system is chosen as 82.5 °C, the average of the highest and the lowest boiling points. We assume that the reactions are catalyzed and that the rate constants are proportional to the catalyst concentration W as

$$\frac{k}{k_0} = \frac{W}{W_0} \quad (44)$$

where

$$W = \frac{M_{\text{cat}}}{H_r} \quad (45)$$

M_{cat} is the number of moles of catalyst in the reaction vessel. The holdup of the reaction vessel H_r decreases as a function of time, but the amount of catalyst is unchanged provided that the catalyst is nonvolatile and that there is no deactivation of the catalyst on the time scale of the process. From eqs 44 and 45 we have

$$\frac{k_0}{k} = \frac{H_r}{H_{r,0}} \quad (46)$$

In this example, eq 46 together with a constant vapor rate V gives us a constant Da value.

Figure 2 shows that for a large Da , for example, 10 or higher, the BRD performs essentially the same as a conventional batch reactor with respect to selectivity and conversion. As shown in

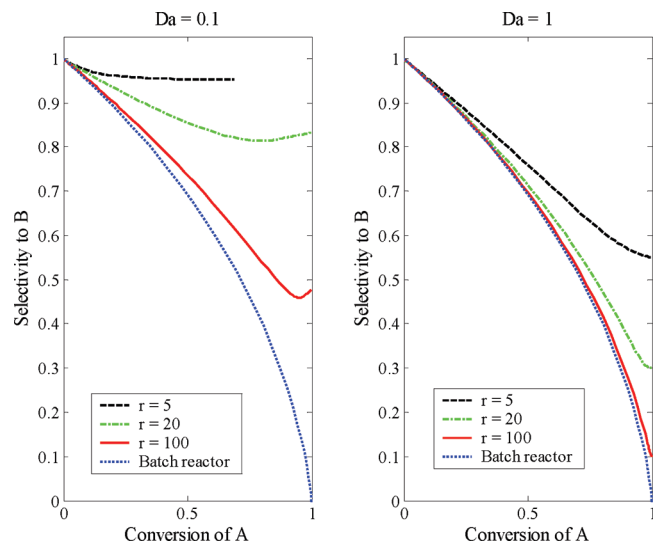


Figure 3. Selectivity in BRD for example I at (a) low and (b) moderate Da . For $Da = 0.1$ and $r = 5$, the reboiler/reactor dries up before achieving full conversion of A.

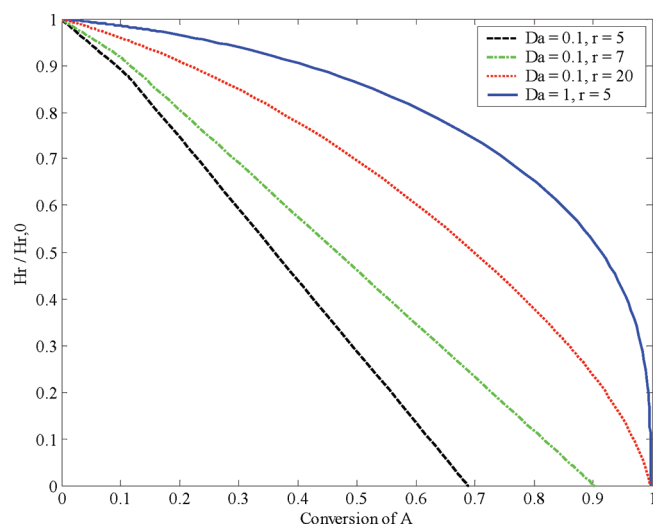


Figure 4. Holdup versus conversion for example I at low to moderate Da . The inset, a high purity product cut can be obtained by adjusting the reflux ratio, but the BRD provides little or no improvement of selectivity.

For low to moderate Da values, Figure 3 shows that BRD can substantially improve selectivity over a conventional batch reactor. For the same reflux ratio, BRD with low Da provides more significant improvement than BRD with high Da . However, as the product B is removed, it is also possible to lose reactant A from the top. Low Da exacerbates the loss of reactant A, because distillation dominates the competition between reaction and distillation at low Da . In Figure 4, as compared to moderate Da , low Da ($Da = 0.1$) leads to a dry reactor at less than complete conversion, which results in a lower conversion. Figure 4 shows that loss of conversion can be mitigated by increasing the reflux ratio. However, for a large reflux ratio (as expected from the limiting cases described above in the section on model development), the selectivity in BRD approaches that of a conventional batch reactor.

Figure 5 shows some limits for conversion and the coupling between reflux ratio and Da . The upper edge of the square represents total reflux operation, where complete conversion of reactant A is always achievable regardless of the Da value. For high values of Da , on the right-hand side, the reaction dominates

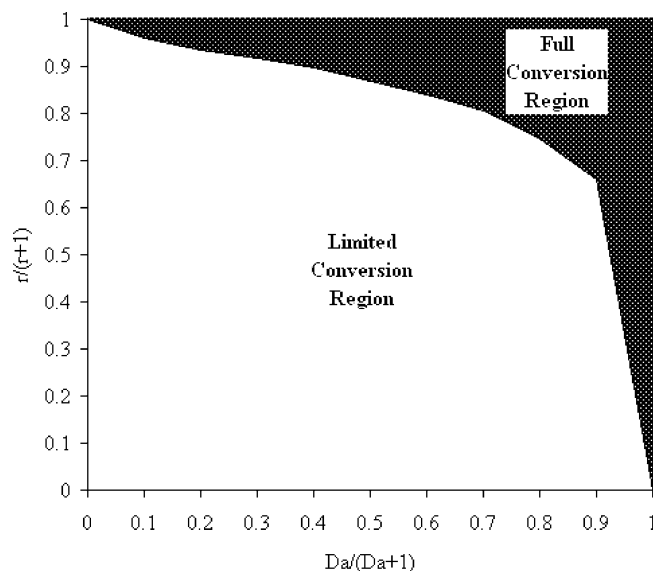


Figure 5. Area of operating parameters for a system of reactions in series $A \rightarrow B \rightarrow C$, in which full conversion can be achieved.

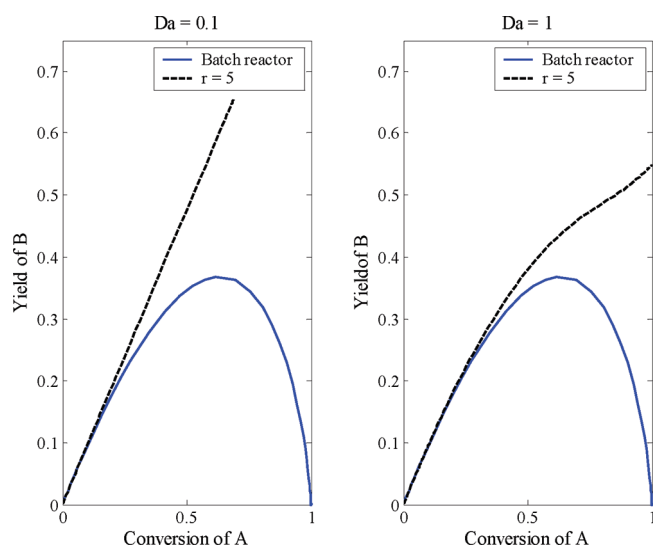


Figure 6. Yield plots for example I at low and moderate Da . For the case of $Da = 0.1$ and $r = 5$, the reboiler/reactor dries up before achieving a full conversion of A.

the competition between reaction and distillation, and complete conversion can be achieved at a low reflux ratio (r). However, for high values of Da , the selectivity improvement is quite limited. For low values of Da , distillation dominates, and complete conversion requires a high reflux ratio. As shown in Figure 3, a high reflux ratio (r) will decrease the selectivity improvement.

For processes without recycle, yield is often a more important issue than selectivity. As shown in Figure 6, there is little or no yield improvement in BRD for low conversions. However, at intermediate or high conversions, BRD provides a very significant improvement in the maximum yield over a conventional batch reactor. As shown in Figure 7, the most significant improvement in the maximum yield occurs at lower values of Da . For an extremely large reflux ratio (the right edge), regardless of Da value, there is very limited improvement in the maximum yield for BRD. If both Da and reflux ratio are low, the maximum yield in BRD is actually lower than a conventional batch reactor. The reflux ratio has a greater impact on the maximum yield for BRD with lower Da values. Thus,

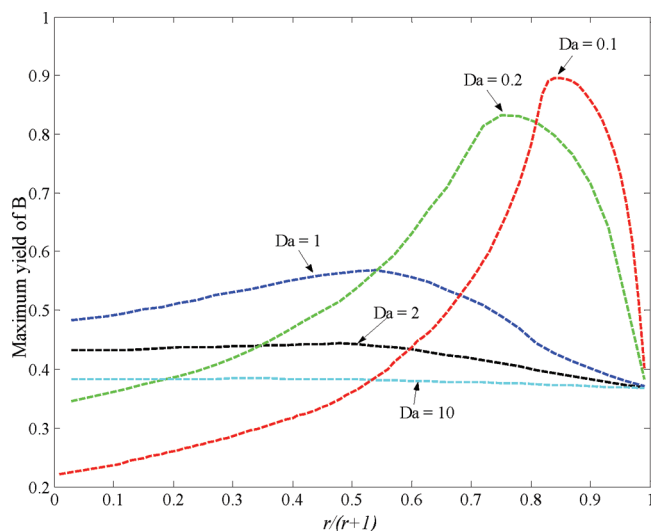


Figure 7. Impact of Da and reflux ratio (r) on the maximum yield in BRD for a system of reactions in series $A \rightarrow B \rightarrow C$.

for BRD with low to moderate Da values, there is an optimum reflux ratio that corresponds to the maximum yield (see Figure 7).

The vapor rate is an important factor in determining Da . So far, as we discuss Da , we have assumed a constant vapor flow rate (V) in this example. Next, we will consider an operation strategy with a constant external heating rate (Q), taking into account the heat of reaction ($-\Delta H_R$). We assume that the heat of vaporization (λ) of this ternary mixture is approximately constant. We also assume that, as compared to the main reaction, the $-\Delta H_R$ of the side reaction is negligible. The total heat applied in the system is

$$Q_T = Q + (-\Delta H_R)k_1 H_r x_A \quad (47)$$

The vapor flow rate (V) can be written as

$$V = \frac{Q}{\lambda} + \frac{(-\Delta H_R)k_1 H_r x_A}{\lambda} \quad (48)$$

On the right side of eq 48, the first term represents the vapor flow caused by the external heat input (Q), and the second term represents the vapor flow caused by the heat released by reaction.

With eq 48, Da can be written as

$$Da = \frac{H_r k_1}{V} = \frac{H_r k_1}{\frac{Q}{\lambda} + \frac{(-\Delta H_R)k_1 H_r x_A}{\lambda}} \quad (49)$$

Also, it is useful to introduce Da_Q

$$Da_Q = \frac{H_r k_1}{Q/\lambda} \quad (50)$$

which has a physical meaning of the portion of Damköhler number (Da) resulting from external heat input (Q). With eq 50, eq 49 can be rewritten as

$$\frac{1}{Da} = \frac{1}{Da_Q} + \frac{(-\Delta H_R)}{\lambda} x_A \quad (51)$$

where $-\Delta H_R/\lambda$ is the “heat utilization factor”.¹³

For $(-\Delta H_R)k_1 H_r x_A \gg Q$, eq 51 can be simplified to

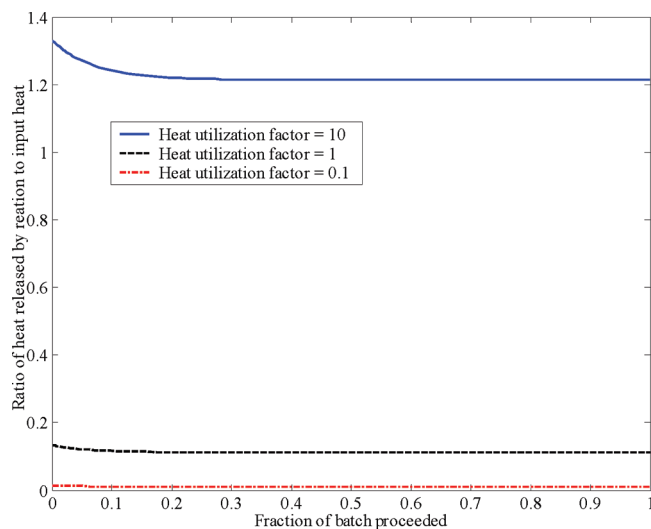


Figure 8. Heat released by reaction of different heat utilization factors for a system of reactions in series $A \rightarrow B \rightarrow C$ under a constant heating operation with $r = 5$, at low Da_Q .

$$Da \approx \frac{\lambda}{(-\Delta H_R)x_A} \quad (52)$$

For $(-\Delta H_R)k_1 H_r x_A \ll Q$, eq 51 can be simplified to

$$Da \approx Da_Q = \frac{H_r k_1}{Q/\lambda} \quad (53)$$

Equation 52 shows that if the heat released by reaction is significantly larger than the external heat input, the vapor flow is mostly generated by the reaction, which has a great impact on the Da , so that in the limit, the Da value is approximately independent of Da_Q . In contrast, eq 53 shows that if the external heat input is significantly larger than the heat released by reaction, the vapor flow caused by the heat of reaction is negligible, so that heat of reaction has little impact on the Da value and is approximately Da_Q .

In Figure 8, at low $Da_Q (= 0.1)$ and a low heat utilization factor, the heat released by reaction is negligible as compared to the external heat input. As the heat utilization factor increases, the heat of reaction becomes more significant. For a high heat utilization factor, the heat released by reaction is greater than the external heat input.

In Figure 9 ($Da_Q = 0.1$), for the case of $(-\Delta H_R)/\lambda = 0$, we have $Da = Da_Q = 1$, which means that without the reaction heat, a constant heating rate results in a constant vapor rate. The plot for $(-\Delta H_R)/\lambda = 0$ is indistinguishable from the plot for $Da = 0.1$, $r = 5$ in Figure 3. For the case of $(-\Delta H_R)/\lambda = 0.1$ (the plot is not shown because it is overlapping with the plot of $(-\Delta H_R)/\lambda = 0$), we have $Da \approx Da_Q = 0.1$, which implies that the vapor flow is mostly generated by external heat input, and the heat of reaction has little impact on selectivity. As $(-\Delta H_R)/\lambda$ increases, the vapor flow generated by the heat of reaction increases, and the impact of the heat of reaction increases. Although Da_Q stays at a value of 0.1, the value of Da decreases with the increased $(-\Delta H_R)/\lambda$. Therefore, as $(-\Delta H_R)/\lambda$ increases, BRD with a constant external heat input shows improvement on selectivity at expense of conversion, which is consistent with the results shown for Da decreasing.

The simulation results show that the same conclusion also can be drawn for the moderate values of Da_Q (Figure 10b, $Da_Q = 1$) and high values of Da_Q (Figure 10c, $Da_Q = 10$). That is,

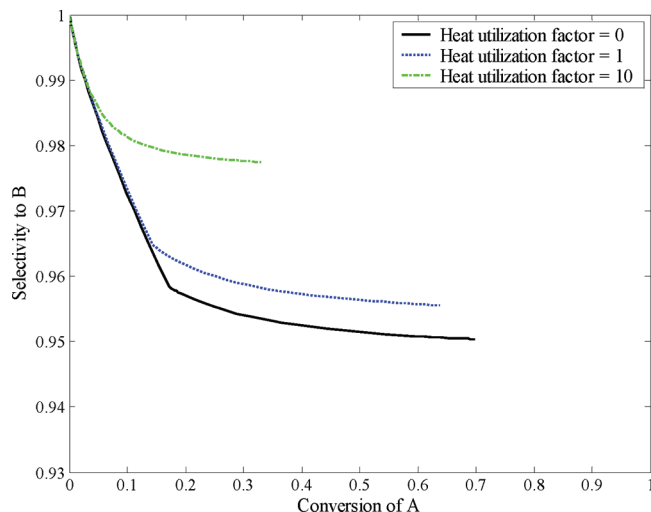
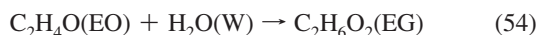


Figure 9. Impact of the heat utilization factor on selectivity for a system of reactions in series $A \rightarrow B \rightarrow C$ under a constant heating operation with $r = 5$, at low Da_Q . For all three cases, the reboiler/reactor dries up before achieving a full conversion of A.

as $(-\Delta H_R)/\lambda$ increases, the value of Da decreases. Consequently, for BRD with a constant heating rate, as $(-\Delta H_R)/\lambda$ increases, the selectivity improves at the expense of conversion. As compared to the low values of Da_Q (Figure 10a, $Da_Q = 0.1$), $(-\Delta H_R)/\lambda$ has more significant impact for moderate or large values of Da_Q .

Example II: Ethylene Glycol

The production of ethylene glycol (EG) from ethylene oxide (EO) and water (W) is a nonequimolar, irreversible reaction and can be represented as



The reaction rate can be described by

$$r_1 = 1.9214 \times 10^{11} \exp(-9359.8/T) x_{EO} x_W \text{ (h}^{-1}\text{)} \quad (55)$$

This reaction rate at pH = 10 is adapted from Okasinski and Doherty¹⁴ and considers the mixture to be an ideal solution.

One representative side reaction is the formation of diethylene glycol (DEG)



This reaction has the same activation energy¹⁵ as the main reaction and a rate given by Chen et al.¹⁶

$$r_2 = 3.8428 \times 10^{11} \exp(-9359.8/T) x_{EO} x_{EG} \text{ (h}^{-1}\text{)} \quad (57)$$

The vapor liquid equilibrium^{17,18} is modeled by Raoult's Law (Table 1).

Because the desired product (EG) has a higher boiling point than both reactants, we choose a batch reactor-stripper, Figure 1b; this is to contain EO while recovering EG. The reflux drum acts as the condenser as well as the reactor, while the products are withdrawn from the reboiler.

The conversion, selectivity, and yield are defined as

$$\text{conversion} = \frac{\text{initial EO in condenser} - (\text{EO in condenser} + \text{EO in receiver})}{\text{initial EO in condenser}} \quad (58)$$

$$\text{selectivity} = \frac{\text{EG in condenser} + \text{EG in receiver}}{\text{initial EO in condenser} - (\text{EO in condenser} + \text{EO in receiver})} \quad (59)$$

$$\text{yield} = \text{conversion} \times \text{selectivity} = \frac{\text{EG in condenser} + \text{EG in receiver}}{\text{initial EO in condenser}} \quad (60)$$

Equation 30 can be rewritten as

$$Da \frac{dH_r}{d\tau} = \left(\frac{s}{s+1} - 1 \right) H_r - Da(\kappa_1 H_r + \kappa_2 H_r) \quad (61)$$

and eq 31 as

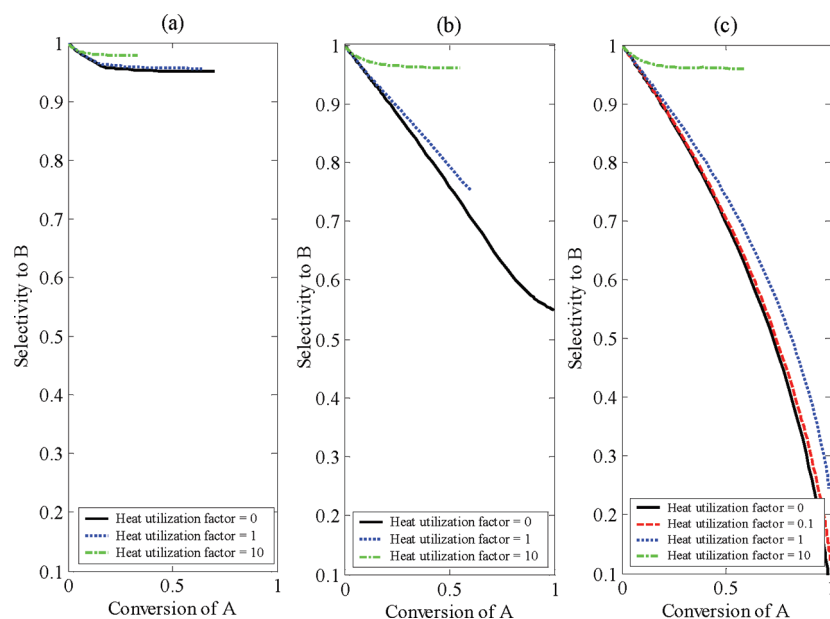


Figure 10. Impact of heat utilization factor on selectivity for a system of reactions in series $A \rightarrow B \rightarrow C$ under a constant heating operation with $r = 5$, at different values of Da_Q . The plots of $(-\Delta H_R)/\lambda = 0.1$ are not shown in subplots (a) and (b), because they are overlapping with the plots of $(-\Delta H_R)/\lambda = 0$; subplot (a) is a rescaling of Figure 9. The end points of the curves correspond to a dry reboiler/reactor.

$$Da \frac{dx_{r,EO}}{d\tau} = \frac{s}{s+1}(y_{1,EO} - x_{r,EO}) + Da(x_{r,EO} - 1)(\kappa_1 + \kappa_2) \quad (62)$$

$$Da \frac{dx_{r,W}}{d\tau} = \frac{s}{s+1}(y_{1,W} - x_{r,W}) + Da[(x_{r,W} - 1)\kappa_1 + x_{r,W}\kappa_2] \quad (63)$$

$$Da \frac{dx_{r,EG}}{d\tau} = \frac{s}{s+1}(y_{1,EG} - x_{r,EG}) + Da[(x_{r,EG} + 1)\kappa_1 + (x_{r,EG} - 1)\kappa_2] \quad (64)$$

where

$$\kappa_1 = \frac{r_1}{k_{1,ref}} \quad (65)$$

$$\kappa_2 = \frac{r_2}{k_{1,ref}}$$

The reference temperature for this system is set as 55.4 °C, which is the average of the boiling points of the two reactants.

Because the difference of boiling points of two reactants is large, low Da may provide a condition where separation of two reactants is significant. Consequently, low Da will either cause very low conversion or require a very large reboil ratio in BRD. For large Da , BRD performs like a conventional batch reactor in agreement with the limiting case discussed earlier in the model development. Next, we focus on BRD with moderate Da .

In example I, we considered a constant vapor rate V . The analogous choice in the current example is a constant liquid rate L , which, together with eq 46, gives a constant instantaneous Da value.

In Figure 11, at a relatively low reboil ratio, $s = 2$, BRD shows a lower selectivity to EG, as well as a lower conversion of EO than a conventional batch reactor. As we increase the reboil ratio ($s = 30$), both selectivity and conversion are improved significantly. However, as we further increase the reboil ratio ($s = 50$), the selectivity performance of BRD approaches a conventional batch reactor.

Figure 12 shows that the decrease of selectivity at low reboil ratio occurs because distillation causes the separation of two reactants, which leads to low conversion of EO. In this low conversion region, because the composition of EG is very low, distillation does not impact the composition of EG significantly. However, as the composition of water in the reactor decreases and the composition of EO in the reactor increases, the main reaction is suppressed while the side reaction is exacerbated, which leads to a lower selectivity than that of a conventional batch reactor (Figure 11).

Figure 13, for $s = 30$, shows that if the two reactants, EO and water, are kept in the reactor, this leads to essentially complete conversion of EO. Distillation removes EG so the composition of EG in the reactor is low for most of the process (in the range of conversion less than 0.85), which leads to a higher selectivity than that of a conventional batch reactor (Figure 11).

At a conversion of approximately 0.86, we decrease the reboil ratio from 30 to 25 during the operation, as shown in Figure 11. This leads to a better selectivity over the remaining batch time. Figure 14 shows that as we decrease the reboil ratio, the composition of EG in the condenser/reactor decreases, which suppresses the side reaction; at the same time, the composition of water increases, which improves the main reaction. Unlike “squeezing the batch”¹⁹ for nonreactive batch distillation near

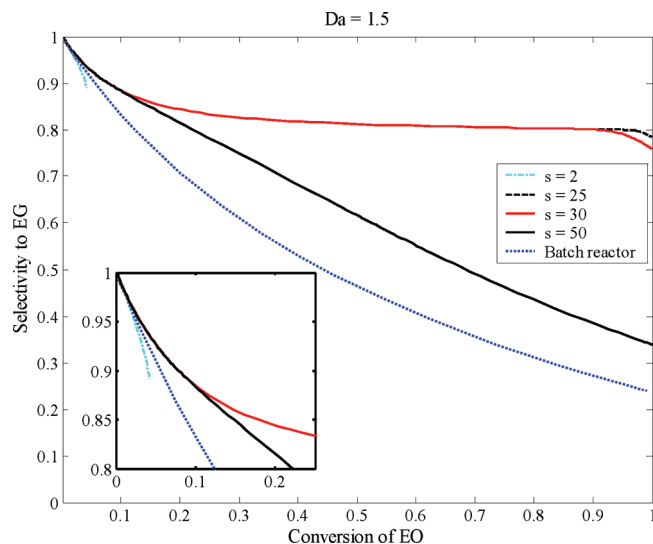


Figure 11. Effect of reflux ratio on selectivity in BRD at $Da = 1.5$ for the EG system.

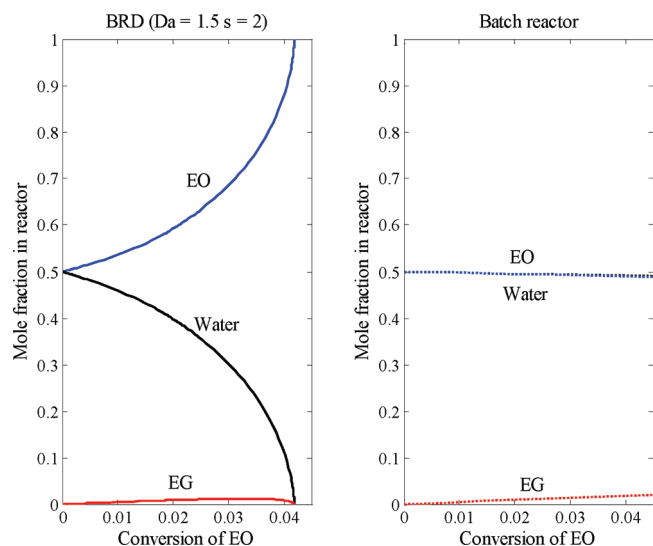


Figure 12. Comparison of compositions in reactor between BRD ($s = 2$) and a conventional batch reactor for the EG system.

the end of operation, to improve selectivity to EG, we need to decrease the reboil ratio of BRD near the end of process.

In this example, we have so far assumed a constant liquid molar flow rate (L). It is easier in experiments to conduct BRD using a constant liquid volume flow (L_v) instead of a constant liquid molar flow (L). For a constant L_v , we have

$$L_v = \frac{L_0}{\rho_0} = \frac{L}{\rho} = \text{constant} \quad (66)$$

where ρ is molar density of the reaction mixture, given by

$$\rho = \frac{1}{\sum_i x_i \rho_i} \quad (67)$$

where x_i is the liquid mole fraction of component i in reaction mixture, and ρ_i is the molar density of component i . Also, Da can be written as

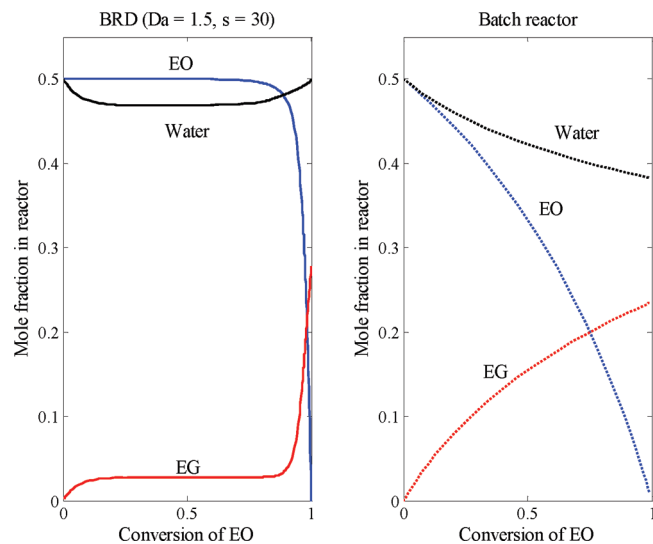


Figure 13. Comparison of compositions in reactor between BRD ($s = 30$) and a conventional batch reactor for the EG system.

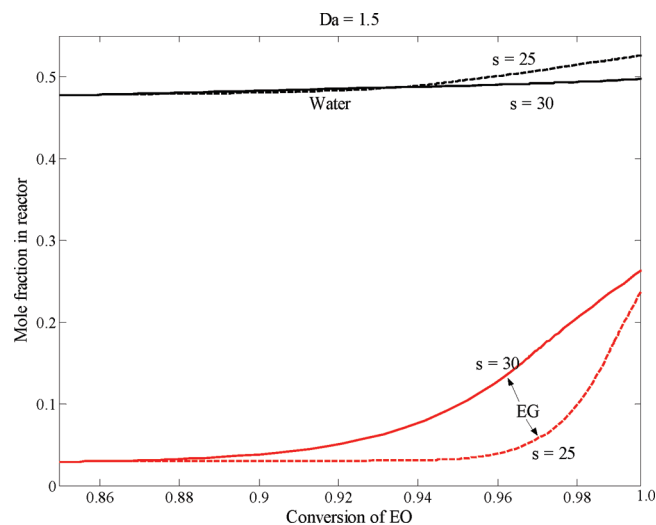


Figure 14. Comparison of compositions in the reactor between $s = 30$ and $s = 25$ for the EG system.

$$Da = \frac{H_r/(\rho L_v)}{1/k_{\text{main,ref}}} \quad (68)$$

In the ethylene glycol system, ρ decreases as reaction decreases the number of moles. Therefore, as we operate with a constant volume rate (L_v), the molar rate (L) is decreasing, which means that Da increases with time. In Figure 15, with the same initial value of Da ($Da_0 = 1.5$), there is little difference between the operation with a constant L_v and the operation with a constant L in the low conversion region. However, as the conversion increases, operation with a constant L_v shows a noticeably lower selectivity than the operation with a constant L . As shown in Figure 15, with conversion increasing, the selectivity of the constant L_v operation with $Da_0 = 1.5$ approaches the selectivity of the constant L operation with higher initial value of Da ($Da = Da_0 = 1.6$).

Conclusions

We have described the impact of operation on selectivity in terms of two key dimensionless groups, the Damköhler number (Da) and the reflux/reboil ratio. The models and examples show

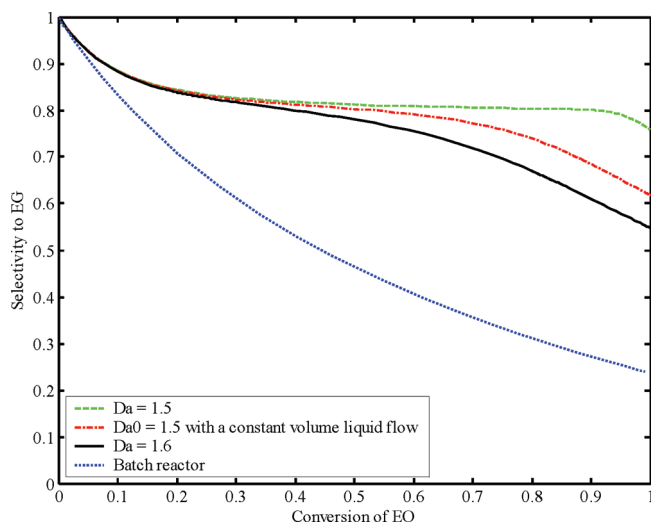


Figure 15. Comparison between an operation with a constant liquid molar flow rate and an operation with a constant liquid volume flow rate under the same reboil ratio ($s = 30$).

Table 1. Antoine Coefficients¹⁸ for Ethylene Glycol System^a

components	normal boiling point (°C)	a	b	c
ethylene oxide	10.7	21.3066	-2428.2	-35.388
water	100.0	23.2256	-3835.18	-45.34
ethylene glycol	197.3	25.1431	-6022.18	-28.25
diethylene glycol	244.5	23.8578	-6085.25	-26.15

^a Antoine equation: $\ln P^{\text{sat}} = a + (b)/(T + c)$, P^{sat} in Pa, T in K.

that the selectivity improvement in BRD is limited for large Da or for large reflux/reboil ratios, where it approaches that of a conventional batch reactor.

For a series isomerization, the selectivity in BRD is enhanced as Da is decreased and the reflux ratio is held constant. Decreasing Da may cause conversion loss, which can be mitigated by increasing the reflux ratio at expense of selectivity. This leads to an optimum reflux ratio corresponding to maximum yield for BRD, which is found for low to moderate Da values. If both Da and reflux ratio are low, the maximum yield in BRD is worse than in a conventional batch reactor. In this example, we also showed that for an operation with a constant external heat input, as the heat of reaction increases, Da decreases. Consequently, the selectivity can be improved at the expense of conversion. The heat of reaction has more significant impacts for moderate or high values of Da_0 than for low values Da_0 .

For a two-reactant system in EG synthesis, at a low reboil ratio, BRD can have a negative impact on both selectivity and conversion by separating the two reactants. A common operating strategy in batch distillation without reaction is to increase the reboil ratio at the end of a batch. However, to improve selectivity in this BRD, we need to decrease the reboil ratio near the end of a batch to increase the removal rate of EG. For an operation with a constant liquid volume flow, selectivity is lower than a constant liquid molar flow operation with the same initial value of Da in moderate or high conversion region.

Acknowledgment

Part of this work was presented in Paper 84a, Distillation Topical Conference, AIChE Tampa National Meeting, April, 2009. We are grateful to the sponsors of the Process Design and Control Center at the University of Massachusetts Amherst.

Nomenclature

a, b, c = Antoine equation parameters
 B = bottom product molar flow rate (mol/time)
 D = distillate molar flow rate (mol/time)
 Da = Damköhler number (dimensionless)
 Da_Q = portion of Damköhler number (Da) caused by input heating (dimensionless)
 EG = ethylene glycol
 EO = ethylene oxide
 H = liquid molar holdup (mol)
 k = reaction rate constant (1/time)
 L = liquid molar flow rate (mol/time)
 L_v = liquid volume flow rate (volume/time)
 M = amount of catalyst (mol)
 m = number of components in system
 N = total number of stages
 P = pressure (Pa)
 Q = input heating (j/time)
 Q_T = the total heat applied in the system (j/time)
 R = total number of reactions in system
 r = molar reflux ratio (dimensionless)
 r_k = reaction rate of k th reaction (1/time)
 r_1 = reaction rate of reaction 1 (1/time)
 r_2 = reaction rate of reaction 2 (1/time)
 s = molar reboil ratio (dimensionless)
 T = temperature (K)
 t = clock time
 V = vapor molar flow rate (mol/time)
 W = catalyst concentration (mol catalyst/mol mixture)
 x = mole fraction in liquid phase
 y = mole fraction in vapor phase
 y_1 = mole fraction in vapor phase of stage 1
 $-\Delta H_R$ = reaction heat (j/mol)

Greek Letters

λ = heat of vaporization (j/mol)
 κ = dimensionless reaction rate
 $\nu_{k,i}$ = stoichiometric coefficient of component i in the k th reaction
 $\nu_{k,T}$ = algebraic sum of the stoichiometric coefficient of the components in the k th reaction
 ρ = molar density (mol/volume)
 τ = "warped" time defined in eq 11

Subscripts

A = component A
 B = component B
 c = condenser
 cat = catalyst
 EG = ethylene glycol
 EO = ethylene oxide
 i = component i
 j = j th stage
 k = k th reaction
 $main$ = main reaction
 N = N th stage
 r = reactor
 rb = reboiler
 $recv$ = receiver

ref = at reference temperature

W = water

0 = initial status

1 = reaction 1

2 = reaction 2

Superscript

sat = saturation

Literature Cited

- (1) Talwalkar, S.; Mankar, S.; Katariya, A.; Aghalayam, P.; Ivanova, M.; Sundmacher, K.; Mahajani, S. Selectivity Engineering with Reactive Distillation for Dimerization of C4 Olefins: Experimental and Theoretical Studies. *Ind. Eng. Chem. Res.* **2007**, *46*, 3024–3034.
- (2) Thotla, S.; Agarwal, V.; Mahajani, S. M. Simultaneous Production of Diacetone Alcohol and Mesityl Oxide from Acetone Using Reactive Distillation. *Chem. Eng. Sci.* **2007**, *62*, 5567–5574.
- (3) Mahajan, Y. S.; Kamath, R. S.; Kumbhar, P. S.; Mahajani, S. M. Self-Condensation of Cyclohexanone over Ion Exchange Resin Catalysts: Kinetics and Selectivity Aspects. *Ind. Eng. Chem. Res.* **2008**, *47*, 25–33.
- (4) Lange, J. P.; Otten, V. J. Dehydration of Phenyl-Ethanol to Styrene: Zeolite Catalysis Under Reactive Distillation. *J. Catal.* **2006**, *238*, 6–12.
- (5) Lange, J. P.; Otten, V. J. Dehydration of Phenyl Ethanol to Styrene Under Reactive Distillation Conditions: Understanding the Catalyst Deactivation. *Ind. Eng. Chem. Res.* **2007**, *46*, 6899–6903.
- (6) Chiu, C. W.; Dasari, M. A.; Suppes, G. J.; Sutterlin, W. R. Dehydration of Glycerol to Acetol via Catalytic Reactive Distillation. *AIChE J.* **2006**, *52*, 3543–3548.
- (7) Agarwal, V.; Theta, S.; Mahajani, S. M. Attainable Regions of Reactive Distillation - Part I. Single Reactant Non-Azeotropic Systems. *Chem. Eng. Sci.* **2008**, *63*, 2946–2965.
- (8) Agarwal, V.; Theta, S.; Mahajani, S. M. Attainable Regions of Reactive Distillation. Part II: Single Reactant Azeotropic Systems. *Chem. Eng. Sci.* **2008**, *63*, 2928–2945.
- (9) Bollyn, M. P.; Wright, A. R. Development of a Process Model for a Batch Reactive Distillation—A Case Study. *Comput. Chem. Eng.* **1998**, *22*, S87–S94, Suppl.
- (10) Venimadhavan, G. Effects of Kinetics on Reactive Distillation, Chapter 4, Ph.D. Thesis, University of Massachusetts, Amherst, 1998.
- (11) Gadewar, S. B.; Malone, M. F.; Doherty, M. F. Selectivity Targets for Batch Reactive Distillation. *Ind. Eng. Chem. Res.* **2000**, *39*, 1565–1575.
- (12) Barbosa, D.; Doherty, M. F. The Simple Distillation of Homogeneous Reactive Mixtures. *Chem. Eng. Sci.* **1988**, *43*, 541–550.
- (13) Sundmacher, K.; Rihko, L. K.; Hoffmann, U. Classification of Reactive Distillation Processes by Dimensionless Numbers. *Chem. Eng. Commun.* **1994**, *127*, 151–167.
- (14) Okasinski, M. J.; Doherty, M. F. Design Method for Kinetically Controlled, Staged Reactive Distillation Columns. *Ind. Eng. Chem. Res.* **1998**, *37*, 2821–2834.
- (15) Ciric, A. R.; Gu, D. Synthesis of Nonequilibrium Reactive Distillation Processes by MINLP Optimization. *AIChE J.* **1994**, *40*, 1479–1487.
- (16) Chen, F.; Huss, R. S.; Malone, M. F.; Doherty, M. F. Simulation of Kinetic Effects in Reactive Distillation. *Comput. Chem. Eng.* **2000**, *24*, 2457–2472.
- (17) Kumar, A.; Daoutidis, P. Modeling, Analysis and Control of Ethylene Glycol Reactive Distillation Column. *AIChE J.* **1999**, *45*, 51–68.
- (18) Rodríguez, I. E.; Zheng, A.; Malone, M. F. Parametric Dependence of Solution Multiplicity in Reactive Flashes. *Chem. Eng. Sci.* **2004**, *59*, 1589–1600.
- (19) Doherty, M. F.; Malone, M. F. *Conceptual Design of Distillation Systems*; McGraw-Hill: New York, NY, 2001; Chapter 9.5.

Received for review July 2, 2010

Accepted September 14, 2010

IE101417M