Attainable regions of reactive distillation—Part I. Single reactant non-azeotropic systems

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Abstract

Reactive distillation (RD), a promising multifunctional reactor, can be used to improve the selectivity of the desired product by manipulating the concentration profiles in the reactive zone of the column. In this work, a new approach has been proposed to obtain the feasible regions of RD for the reactive systems involving single reactants, e.g. dimerization, aldol condensation, etc. Two new models namely the reactive condenser and the reactive re-boiler have been proposed. These models indicate the best location of the reactive zone in a column. Multistage versions of these models namely, reactive rectification and reactive stripping further expand the feasible region and are capable of representing the performance offered by a conventional RD unit. Several hypothetical non-azeotropic ideal systems have been extensively studied using these models and it has been shown that selectivity close to 100% is attainable over the entire range of conversion for a series as well as a combination of series and parallel reactions with positive reaction orders. Two industrially important cases of aldol condensation of acetone and dimerization of isobutylene have also been addressed using this approach. For porous catalysts, the presence of intra-particle diffusion resistance may limit the feasible region and even in the case of ideal non-azeotropic systems it may not be possible to obtain 100% selectivity. A methodology to incorporate pore diffusion effects is also illustrated.

Keywords: Chemical reactors; Conceptual design; Design; Kinetics; Reactive distillation; Selectivity

1. Introduction

Reactive distillation (RD) as the name suggests is the integration of reaction and separation in a single piece of equipment. Such integration can be effectively used to improve the selectivity of a series or combination of series and parallel reactions especially when the intermediate product is the desired one. RD, when designed judiciously, can offer significantly high yields compared to the conventional reactor systems in such case. One can conveniently manipulate the concentration profiles of various species in the reactor, which involves in situ separation, to obtain better selectivity for the desired product. The multiple reactions involved in the system may be irreversible or a combination of reversible and irreversible reactions.

Attainable region (AR) approach, first introduced by Horn (1964), is used to assess the reactor network feasibility. It has been extensively studied and investigated by Hildebrandt, Glasser and their co-workers. Glasser et al. (1987) defined AR, essentially a plot of yield vs conversion, as the region in concentration space which can be obtained by any combination of conventional reactors and mixing. This AR is sometimes called the “kinetically attainable region” to distinguish it from the “thermodynamically attainable region,” which is determined by equilibrium constraints (Shinnar and Feng, 1985). To identify a region as AR, Glasser et al. (1987) defined a reaction vector. Simple steady state models for the isothermal CSTR (Eq. (1)) and PFR (Eq. (2)) with constant volume were applied to construct the AR in concentration space:

\[ c - c_0 = \tau r(c), \]

\[ \frac{dc}{d\tau} = r(c), \quad c(t = 0) = c_0, \]
where \( r \) is the reaction vector. The direction of reaction vector indicates the direction of change of concentration in the concentration space.

For ideal reactors certain geometric properties were identified:

- The reaction vector is tangent to every point on the PFR performance locus.
- The reaction vector is collinear with the vector obtained from the difference of feed concentration and exit concentration at each point on the CSTR performance locus.
- The feed to the PFR section in recycle reactor lies on the line joining the feed and exit streams of the system representing mixing of two concentration vectors.

The necessary conditions derived by Glasser et al. (1987) to identify region as attainable, are:

- The region is convex.
- No reaction vector on the region points outwards.
- In the complement of the AR no reaction vector when extrapolated intersects the AR.

AR approach is not an optimization technique. It can, however, provide insights for devising a superstructure in an optimization problem. Lakshamanan and Biegler (1996) used the AR properties to formulate a reaction network and Pahor et al. (2000) suggested an iterative procedure using AR analysis to update the superstructure in MINLP formulation. AR approach only identifies the feasible region for the production of a desired product. It serves an important purpose of generating process alternatives at the conceptual design stage. The approach has been successfully applied to assess reactor network synthesis.

Nisoli et al. (1997) combined the concept of AR for reaction-mixing system with the geometric methods used for the feasibility of separations. A systematic approach was developed to identify compositions that can be achieved by combining reaction, mixing and separation in co-current devices. The reaction-separation devices considered were: CSTR with vapor removal and PFR with vapor removal. They modified the reaction vector for systems with simultaneous reaction and separation to give a reaction-separation vector. This reaction-separation vector was also shown to follow the same geometric properties as that defined by Glasser et al. (1987). The steady state equations of CSTR with vapor removal and PFR with vapor removal are given by

\[
\begin{align*}
  x - x_0 &= DaR(x, y), \\
  \frac{dx}{dt} &= R(x, y), \quad x(t = 0) = x_0,
\end{align*}
\]

where \( R \) is the reaction-separation vector which is a combination of reaction and separation effects. It was further modified by Gadewar et al. (2002) for the cascade of two phase CSTRs. The countercurrent cascade model of two phase CSTRs was considered as the surrogate for stripping and rectifying sections by Gadewar et al. (2002). For the consecutive series reaction they showed that the suggested model offers enhanced selectivity when the reactant is heavier than the desired product. We extend this work further to encompass other reacting systems and propose a new approach to construct AR of RD on a conversion vs selectivity plot.

The work emphasizes on a single reactant system involving multiple reactions with intermediate product as the desired one. Such systems are relatively simple to analyze and hence considered as case studies to begin with. However, we believe, the approach can be extended to other cases as well. Several simplified model reactor–separator units have been proposed that are capable of surpassing the performance of the conventional flow reactors depending on the kinetics and vapor–liquid equilibrium of a given reacting system. With this method it is expected that one can avoid use of rigorous optimization techniques, at least at a conceptual level, as RD with its complex behavior and large number of design and operating parameters is still a challenging problem for current optimization routines (Gangadwala et al., 2006). These simplified models not only help in knowing the AR but also indicate the location of reactive zone in the RD column before going for a rigorous design and simulation exercise. The model systems are also simple enough so that direct laboratory experiments can be conveniently performed in such units, in the absence of kinetic and thermodynamic data, to obtain the desired representative results.

2. Model development

Each segment or a stage of RD column can be viewed as a combination of a reactor and separator units, which repeats along the length of the column as shown in Figs. 1 and 2. This reactor–separator combination traveling along the length of the column (Figs. 1a and 2a) is in a sense analogous to the batch reactor separator units shown in Figs. 1b and 2b progressing along the time co-ordinate. The units shown are a combination of two stages, namely re-boiler and condenser, of which one

Fig. 1. (a) Rectifying section of RD column and (b) reactive condenser unit.
Fig. 2. (a) Stripping section of RD column and (b) reactive re-boiler unit.

is considered reactive, and the other as non-reactive. This results in two separate units which can be considered as special cases of batch reactors of which the composition and conversion change with respect to time. The reactive condenser (RC) model represents a reactive rectification section as shown in Fig. 1 whereas reactive re-boiler (RR) model represents reactive stripping section as shown in Fig. 2. For example, in a single reactant system, if the reactant is a more volatile component then as we move upward in the rectifying section the liquid is enriched in the reactant and depleted with the product hence it is advantageous to perform reaction in the rectifying section. Similar effect is realized in RC in which reaction is performed with the liquid enriched in terms of the more volatile component, i.e. reactant. It must be noted that the analogy that is being discussed here is only qualitative and these simple models help one to only arrive at some important decisions like placement of catalyst in the column.

3. Model equations

Following assumptions are made while formulating equations for these models:

(a) In the RC model, condenser is considered as a total condenser and re-boiler as a non-reactive equilibrium stage. On the other hand, in the RR model, re-boiler is a total re-boiler and the condenser as a non-reactive equilibrium stage.

(b) The molar hold up of a stage on which reaction takes place (e.g. condenser in RC model) is assumed to be negligible. This assumption enables us to conveniently calculate the conversion and selectivity based on the hold up on the non-reactive stage (e.g. re-boiler in the RC model).

(c) The extent of the reaction on the reactive stage is dependent on Damköhler number ($Da$) which is based on the catalyst weight and not on the volume or molar hold up. The reaction takes place in liquid phase only.

(d) The heat duty is adjusted such that the vapor flow rate with respect to time is constant for the RC model. This allows us to club the vapor flow rate in $Da$. Similarly the liquid flow rate is assumed to be constant for the RR model.

(e) Energy balances on both reactive and non-reactive stages are ignored. The liquid flow rate in RC and vapor flow rate in RR, however, may change with respect to time in the case of a non-equi-molar reaction.

4. Reactive condenser

(a) Overall and component material balances around the re-boiler are given as

$$\frac{d(H_{ta})}{dt} + \frac{d(H_{ta,x})}{dt} = -V + L,$$

$$\frac{d(H_{ta,y})}{dt} + \frac{d(H_{ta,x})}{dt} = -V_{y} + L_{x}$$

for $i = 1, 2, \ldots, NC - 1$ (5)

Now, assuming $H_{ta} \gg H_{va}$ and rearranging, we get

$$H_{ta} \frac{d(x_{ia})}{d\xi} = V(x_{ia} - y_{ia}) + L(x_{ib} - x_{ia})$$

for $i = 1, 2, \ldots, NC - 1$. (7)

Dividing by $V$ we get,

$$\frac{d(x_{ia})}{d\xi} = (x_{ia} - y_{ia}) + \frac{L}{V}(x_{ib} - x_{ia})$$

for $i = 1, 2, \ldots, NC - 1$. (8)

where $d\xi = V/H_{ta} dt$, also known as dimensionless time.

(b) Overall and component material balances around the condenser are given as

$$\frac{d(H_{ib})}{dt} + \frac{d(H_{ib,y})}{dt} = -L + V + \sum_{k=1}^{R} v_{T,k} r_{k}(x_{ib}) H_{cat},$$

$$\frac{d(H_{ib,y})}{dt} + \frac{d(H_{ib,x})}{dt} = -L_{xib} + V_{y} + \sum_{k=1}^{R} v_{i,k} r_{k}(x_{ib}) H_{cat} \quad \text{for } i = 1, 2, \ldots, NC - 1.$$ (9)

Assuming hold ups in the condenser to be negligible,

$$-L + V + \sum_{k=1}^{R} v_{T,k} r_{k}(x_{ib}) H_{cat} = 0,$$

$$-L_{xib} + V_{y} + \sum_{k=1}^{R} v_{i,k} r_{k}(x_{ib}) H_{cat} = 0 \quad \text{for } i = 1, 2, \ldots, NC - 1.$$ (10)
Dividing by $V$, which is assumed to be constant, we get

$$\frac{-L}{V} + 1 + Da \sum_{k=1}^{R} v_{T,k} r'_k(x_a) = 0,$$

(13)

$$\frac{-L}{V} y_{ia} + y_{ia} + Da \sum_{k=1}^{R} v_{i,k} r'_k(x_b) = 0$$

for $i = 1, 2, \ldots, NC - 1,$

(14)

where, $Da = k_{cat} H_{cat}/V$.

(c) VLE equation: The vapor leaving the re-boiler is assumed to be in equilibrium with the re-boiler liquid and the VLE relationship may be given by

$$y_{ia} = f(x_{ia}) \quad \text{for } i = 1, 2, \ldots, NC - 1$$

(15)

5. Reactive re-boiler

(a) Overall and component material balances around the re-boiler are given below:

$$\frac{d(H_{ta})}{dt} + \frac{d(H_{ta})}{dt} = -V + L + \sum_{k=1}^{R} v_{T,k} r_k(x_a) H_{cat},$$

(16)

$$\frac{d(H_{ta,y_{ia}})}{dt} + \frac{d(H_{ta,x_{ia}})}{dt} = -V y_{ia} + L x_{ib} + \sum_{k=1}^{R} v_{i,k} r_k(x_a) H_{cat}$$

for $i = 1, 2, \ldots, NC - 1$

(17)

Assuming hold ups in the re-boiler to be negligible,

$$-V + L + \sum_{k=1}^{R} v_{T,k} r_k(x_a) H_{cat} = 0,$$

(18)

$$-V y_{ia} + L x_{ib} + \sum_{k=1}^{R} v_{i,k} r_k(x_a) H_{cat} = 0$$

for $i = 1, 2, \ldots, NC - 1.$

(19)

Dividing by $L$, which is assumed to be constant, we get

$$\frac{-V}{L} + 1 + Da \sum_{k=1}^{R} v_{T,k} r'_k(x_a) = 0,$$

(20)

$$\frac{-V}{L} y_{ia} + x_{ib} + Da \sum_{k=1}^{R} v_{i,k} r'_k(x_a) = 0$$

for $i = 1, 2, \ldots, NC - 1,$

(21)

where, $Da = k_{cat} H_{cat}/L$.

Also, $y_{ia} = x_{ia}$ since it is a total re-boiler

(b) Overall and component material balances around the condenser are given below:

$$\frac{d(H_{cb})}{dt} + \frac{d(H_{ib})}{dt} = -L + V,$$

(22)

$$\frac{d(H_{cb,y_{ib}})}{dt} + \frac{d(H_{ib,x_{ib}})}{dt} = -L x_{ib} + V y_{ia}$$

for $i = 1, 2, \ldots, NC - 1.$

(23)

Assuming $H_{cb} \gg H_{ib}$ and rearranging, we get

$$H_{cb} \frac{d(y_{ib})}{dt} = L(y_{ib} - x_{ib}) + V(y_{ia} - y_{ib})$$

for $i = 1, 2, \ldots, NC - 1.$

(24)

Dividing by $L$ which is assumed to be constant, we get

$$\frac{d(y_{ib})}{dt} = (y_{ib} - x_{ib}) + \frac{V}{L}(y_{ia} - y_{ib})$$

for $i = 1, 2, \ldots, NC - 1,$

(25)

where, $d\zeta = \frac{L}{H_{cb}} dt$.

(c) VLE equation: The liquid leaving the condenser is assumed to be in equilibrium with the vapor in the condenser and the VLE relationship may be given by

$$y_{ib} = f(x_{ib}) \quad \text{for } i = 1, 2, \ldots, NC - 1.$$  

(26)

6. Reaction system

Following two reaction systems are considered for the theoretical analysis in this work:

(a)

$$A \rightarrow B \rightarrow C,$$

(27)

(b)

$$2A \rightarrow B, \quad A + B \rightarrow C.$$  

(28)

The first reaction system is a combination of consecutive series reactions and the second one is a combination of series and parallel reactions. The reactions are considered to be elementary and the rate equation is given by simple mole fraction based kinetics as: (a) $r_1 = k_1 x_A$, $r_2 = k_2 x_B$; (b) $r_1 = k_1 x_A^2$, $r_2 = k_2 x_A x_B$. The reactions in both the cases are irreversible. It is known that if both the reactions are of positive order then between CSTR and PFR, one would opt for PFR to obtain better selectivity with respect to B (Levenspiel, 1999). B is the desired product and thus the conversion of the first reaction needs to be enhanced and the second reaction needs to be suppressed in order to achieve high yields. Here, yield is defined as moles of product (B) per moles of reactant fed (A) and conversion is defined as moles of reactant (A) consumed per mole of reactant fed. The yield and conversion are calculated based on the extents of reactions taking place. Extent of reaction in turn can be determined based on the difference in the initial amount of reactant and that remains unreacted at a given time. Selectivity
is defined as the yield divided by conversion. In case of the second reaction system (b), two moles of A react to give one mole of B (Eq. (28)). Hence, as per the above definition, the yield cannot exceed half the conversion value.

7. Effect of Damköhler number

Feasible regions on the yield vs conversion plot obtained by solving the set of differential-algebraic equations (DAE) in the RC model at different values of $Da$ are shown in Fig. 3a. The set of equations was solved using DAE solver of MATLAB such as ODE15s. One can decrease the value of $Da$ either by reducing the catalyst loading or increasing the vapor/liquid flow rate. The yield and conversion increase with time and integration of the model equations over a sufficiently long time covers the entire conversion range. As $Da$ decreases the region expands and the performance is improved. However, there is a critical $Da$ value ($Da_c$) below which no further improvement in the performance is possible. Similar results are obtained for the RR model and are shown in Fig. 3b. The region given by the $Da_c$ may be considered as an AR of the RC or RR. The above said effect may be explained based on the interplay between reaction and distillation. At relatively large values of $Da$, reaction dominates over distillation and the selectivity is relatively poor. At lower values of $Da$ distillation is more effective to achieve product separation giving rise to enhanced performance.

8. Comparison of RC and RR with conventional reactors

Fig. 4 compares ARs of all the reactors. It can be seen that the performance of RC model is superior to all. This is because the reactant (A) is more volatile than the intermediate product (B) and in RC model, the reaction takes place in the condenser which is relatively rich in A. Hence, the side reaction is suppressed more as compared to that in the conventional reactors. Also as seen, the performance of RR model is inferior to that of PFR because of the reaction taking place in the re-boiler which is enriched in B due to separation taking place in the partial condenser.

Thus this exercise helps us to explain the improvement in selectivity with RD compared to conventional reactors and also guides us on where to place the reactive zone in a normal RD column. “If RC model expands the feasible region as compared to the conventional reactor system, one can place reactive zone in rectifying section and if RR model expands the feasible region, reactive zone may be placed in the stripping section”.

Fig. 3. Effect of Damköhler number for (a) reactive condenser model and (b) reactive re-boiler model: reaction system $2A \xrightarrow{k_1} B$, $A + B \xrightarrow{k_2} C$, $k_1 = k_2$ and $x_A = 4.5$, $x_B = 1.5$, $x_C = 1$.

Fig. 4. Comparison of yield vs conversion of PFR and CSTR with reactive condenser and reactive re-boiler: reaction system $2A \xrightarrow{k_1} B$, $A + B \xrightarrow{k_2} C$, $k_1 = k_2$ and $x_A = 4.5$, $x_B = 1.5$, $x_C = 1$. 
the relative volatilities of A (reactant) and B (desired product) are close to each other then the performances of both RC and RR models converge to the performance of PFR.

From the foregoing discussion, we conclude that the AR of conventional reactor network given by Glasser et al. (1987) can be improved by in situ separation. However, the new yield vs conversion plot, obtained by one of the proposed models, that expands this region, need not necessarily represent a region that cannot be surpassed by the conventional continuous RD column which has more parameters, such as reflux ratio and number of stages, to play with. Our independent simulation exercise indicated that the region defined by RC for the present case can be easily surpassed by a continuous RD with judicious choice of operating and design parameters. Thus in the following section we modify the RC and RR models further so as to encompass all the possible regions obtained by the simulations of a continuous RD.

9. Reactive rectification and reactive stripping

The composition of the product in the re-boiler of RC or in the condenser of RR builds up as conversion increases with time. As the time proceeds, more and more product would appear in the stream going to the RC. As a result, the concentration of B on the reactive stage would increase with time, thereby adversely affecting the selectivity of B. One can use more number of stages to purify the stream going to the reactive stages to enhance the overall yield, or in other words, minimize the concentration of B in the reactive zone of the system. Hence, though simple RC and RR models help in making the important decision of placement of the reactive zone, as mentioned before, they need to be modified further by introducing multiple reactive stages. This analysis gives birth to two more models, i.e. reactive rectification, an extension of the RC model and reactive stripping, an extension of the RR model.

10. Reactive rectification

The unit is termed as reactive rectification as the configuration is similar to the batch rectification unit and is shown in Fig. 5. The reaction takes place on all the stages in the rectification column and the re-boiler is non-reactive. The assumptions made while developing the RC and RR models apply here as well.

(a) Overall and component material balances on the re-boiler (stage 1):
\[
\frac{1}{H_1} \frac{d(H_1)}{d\xi} = -1 + \frac{L_2}{V_1},
\]
\[
\frac{d(x_{i,1})}{d\xi} = (x_{i,1} - y_{i,1}) + \frac{L_2}{V_1} (x_{i,2} - x_{i,1})
\text{ for } i = 1, 2, \ldots, NC - 1,
\]
where \(d\xi = V_1/H_1\) dr.

(b) Overall and component material balances on the \(j\)th stage (for \(j = 2\) to \(N-1\)):
\[
L_{j+1} - L_j + V_{j-1} - V_j + \sum_{k=1}^{R} v_{k} r_k(x_j) H_{cat}^j = 0, \tag{31}
\]
\[
L_{j+1} x_{i,j+1} - L_j x_{i,j} + V_{j-1} y_{i,j-1} - V_j y_{i,j} + \sum_{k=1}^{R} v_{i,k} r_k(x_j) H_{cat}^j = 0 \text{ for } i = 1, 2, \ldots, NC - 1.
\]
Assuming \(V_{j-1} = V_j = V\), we get
\[
-L_j + L_{j+1} + \sum_{k=1}^{R} v_{k} r_k(x_j) H_{cat}^j = 0, \tag{33}
\]
\[
L_{j+1} x_{i,j+1} - L_j x_{i,j} + V (y_{i,j-1} - y_{i,j}) + \sum_{k=1}^{R} v_{i,k} r_k(x_j) H_{cat}^j = 0 \text{ for } i = 1, 2, \ldots, NC - 1.
\]
Assuming catalyst loading on each stage to be same, we get
\[
H_{cat}^2 = H_{cat}^3 = \cdots = H_{cat}^i = \cdots = H_{cat}^N = H_{cat} = \frac{H_{cat}^T}{N-1}. \tag{35}
\]
Dividing by \(V\), we get
\[
-l_j + l_{j+1} + \frac{Da}{N-1} \sum_{k=1}^{R} v_{k} r_k'(x_j) = 0, \tag{36}
\]
\[
l_{j+1} x_{i,j+1} - l_j x_{i,j} + y_{i,j-1} - y_{i,j} + \frac{Da}{N-1} \times \sum_{k=1}^{R} v_{i,k} r_k'(x_j) = 0 \text{ for } i = 1, 2, \ldots, NC - 1, \tag{37}
\]
where \(l_j = L_j/V\) and \(Da = k_{cat} H_{cat}^T / V\).
(c) Overall and component material balance on the \( N \)th stage (condenser):

\[
-l_N + 1 + \frac{D}{N-1} \sum_{k=1}^{k=R} v_{T,k}r_k'(x_N) = 0, \tag{38}
\]

\[
-l_N x_{i,1} + y_{i,2} + \frac{D}{N-1} \sum_{k=1}^{k=R} v_{i,k}r_k'(x_N) = 0
\]

for \( i = 1, 2, \ldots, NC - 1 \). \tag{39}

Along with these equations, the VLE equations are also valid for each stage except condenser which is a total condenser.

Reactive stripping can be modeled in the same way as the reactive rectification except that the feed is in the vapor form and is introduced into the non-reactive condenser (Fig. 6) and the model equations are given in the supplementary data. The results presented here are independently confirmed with the help of a steady state simulator in AspenPlus (Aspen Technology Inc., 2001).

11. Yield vs conversion plots for reactive rectification/stripping

The critical value of \( Da \) (\( Da_c \)), obtained for the RC/RR model, below which there was no improvement in the selectivity (Fig. 3) was distributed equally over the \( N - 1 \) stages equally and the calculation was performed at several values of \( N \). The yield vs conversion plot is shown in Fig. 7. As the number of stages is increased, i.e. as the \( Da \) per stage is decreased with the overall \( Da \) being constant, the performance improves and for the system of interest almost 100% selectivity is realized for 100% conversion (i.e. virtually no formation of \( C \)). The case \( N = 2 \) corresponds to the reactive condenser model. As expected, the region expands beyond the one predicted by RC model, especially at higher conversions. Similar results were obtained for the reactive stripping model in the case wherein, reactant is less volatile than the desired intermediate product. In other words, for a single reactant with elementary kinetics and ideal VLE behavior, one can claim with confidence that the selectivity close to 100% may be realized in RD with sufficiently large number of stages and there are no bounds to the AR imposed by the kinetics and thermodynamics (VLE) of the system. The exceptionally high yield can be explained based on the composition profiles of the reactive rectification unit. Fig. 8 shows the profiles of A and B plotted at 90% conversion. One can conclude from the profiles that negligible concentration of B on the reactive stages is responsible for suppressing the formation of C. We observed the similar behavior of reactive stripping model in the case when the reactant is heavier than the desired product. The above result may
be interpreted as follows. In RD, reaction and distillation compete with each other. In a conventional reactor (e.g. PFR) there is no separation and hence reaction effects dominate. Kinetics clearly shows that minimum concentration of the intermediate product in the reactive zone is certainly beneficial. At lower number of stages, reaction kinetics may still dominate the distillation effects and one may get lower selectivity. Whereas, increase in \( N \) helps achieve efficient separation of B resulting in an enhanced selectivity. The composition profile indicating a negligible concentration of B in the reactive zone is shown in Fig. 8. The on the other hand for the given number of stages, reaction effect can be suppressed by reducing the value of \( Da \) per stage, which can be achieved by increasing the vapor flow rate or boil up (see e.g. Eq. (37)). However, there is a limit on attainable yield at a given number of stages beyond which there is no further increase even if value of \( Da \) per stage is reduced further. These feasible regions meet the maximum attainable yield at sufficiently large number of stages as shown in Fig. 7.

12. Effect of non-reactive stages

The introduction of non-reactive stages in a fully reactive rectification unit at proper position may give better performance by strengthening the “distillation effect” by effectively separating B from the reactive zone. Such columns with both reactive and non-reactive sections are called as hybrid columns. It is observed that, even in the absence of non-reactive section one can still obtain the desired yield by manipulating \( Da \) and number of stages. However, since economics is the criterion while designing a real column, the decrease in total number of stages in hybrid column certainly indicates the need for a non-reactive section in practice. For example, we found that the performance of a fully reactive rectification with 10 reactive stages is inferior to that of a hybrid reactive rectification with five reactive and five non-reactive stages. A hybrid reactive rectification unit of two reactive and two non-reactive stages offered the same performance as that of fully reactive 10 stage reactive rectification unit, indicating considerable reduction in the capital cost. The total \( Da \) was same in both the cases as shown in Fig. 9. This

![Fig. 9. Effect of non-reactive stages on the reactive rectification unit: reaction system \( 2A \rightarrow B \), \( A + B \rightarrow C \), \( k_1 = k_2 \) and \( \xi_A = 4.5, \xi_B = 1.5, \xi_C = 1 \).](image_url)

![Fig. 10. Effect of non-reactive stages on the reactive rectification unit (a) without non-reactive section and (b) with non-reactive section: reaction system \( 2A \rightarrow B \), \( A + B \rightarrow C \), \( k_1 = k_2 \) and \( \xi_A = 4.5, \xi_B = 1.5, \xi_C = 1 \).](image_url)
can be explained with the help of Fig. 10. The shaded region in Fig. 10b represents the non-reactive section. As can be seen from Fig. 10a and b, the presence of non-reactive stages results in further reduction of B on the reactive stages, resulting in a still higher selectivity under otherwise similar conditions. Thus a non-reactive section may be introduced to enhance the separation and minimize the concentration of the desired intermediate product in the reactive zone. This indicates that in the case of reactant being lighter than the desired product the non-reactive section should be placed below the reactive section and in the case of reactant being heavier than the desired product non-reactive section should be placed above the reactive section to achieve better separation.

It must be noted here that though the maximum possible yield is attainable with the newly defined models of non-hybrid systems (reactive stripping and rectification), it may not be practically possible to use them in practice as the design requirement such as column height or vapor flow rate in the continuous RD unit may be exorbitant, expensive and sometimes unrealistic. Thus, we reiterate that the AR plot alone does not suggest an economical design, neither it is meant for this purpose. The aim is to indicate bounds, if any, on the AR imposed by kinetic and/or thermodynamic (VLE) constraints. In the actual design one should always explore the possibility of employing non-reactive section to make the design economically attractive.

13. Continuous models

In this section, we show the relation between the batch models defined earlier and a continuous conventional RD column. The continuous version of the reactive rectification model is shown in Fig. 11a. Number of reactive rectification/reactive stripping units are arranged in series with a continuous feed and continuous output.

One can see from Fig. 11a that the feed to the subsequent units is relatively concentrated in terms of the intermediate desired component B, and thus with each succeeding unit a better separation will be desired to avoid the presence of B on the reactive rectifying stages. However, if, the units, instead of arranging them in series, are stacked on the top of each other as shown in Fig. 11b and the vapor flow is increased, we can observe similar or even better performance. This is because the feed to the subsequent units in Fig. 11b is purer in reactant as compared to that in Fig. 11a. A configuration thus obtained by this arrangement, as shown in Fig. 11c, is continuous reactive rectification. Similarly one can use continuous reactive stripping if desired. Hence, we conclude that if batch reactive rectification (or stripping) offers selectivity of 100%, then a continuous RD can also match this performance and the ARs for both these units are same. Again it should be noted that this system is bound to have practical limitations in reality and it will sometimes lead to unrealistic design (e.g. very large number of stages). As mentioned before, we are interested here in obtaining the bounds imposed by unrealistic design. The model equations for continuous reactive rectification are given below:

\[
\begin{align*}
F_0 / V - l_1 + l_2 - 1 &= 0, \\
F_0 x_{i,f} / V - l_1 x_{i,1} + l_2 x_{i,2} - y_{i,2} &= 0 \quad \text{for } i = 1, 2, \ldots, NC - 1,
\end{align*}
\]

where \( l_j = L_j / V \).

(b) Overall and component material balances on \( j \)th stage (for \( j = 2 \) to \( N - 1 \)):

\[
\begin{align*}
l_{j+1} - l_j + \frac{Da}{N - 1} \sum_{k=1}^{R} \nu_{r,k} r_k'(x_j) &= 0, \\
R \sum_{k=1}^{R} v_{r,k} r_k'(x_j) &= 0 \quad \text{for } i = 1, 2, \ldots, NC - 1. \tag{43}
\end{align*}
\]
Fig. 12. Yield vs conversion plot for continuous reactive rectification unit: reaction system $2A \overset{k_1}{\rightarrow} B, A + B \overset{k_2}{\rightarrow} C, k_1 = k_2$ and $x_A = 4.5, x_B = 1.5, x_C = 1$.

(c) Overall and component material balance on $N$th stage (condenser):

$$1 - l_N + \frac{Da}{N - 1} \sum_{k=1}^{R} v_{T,k} r'_k(x_N) = 0,$$  \hspace{1cm} (44)

$$y_{i,N-1} - l_N x_{i,N} + \frac{Da}{N - 1} \sum_{k=1}^{R} v_{i,k} r'_k(x_N) = 0$$  

for $i = 1, 2, \ldots, NC - 1$. \hspace{1cm} (45)

Similar to continuous reactive rectification, continuous reactive stripping can also be modeled. It will consist of number of reactive stages and a non-reactive condenser. Fig. 12 shows the profiles obtained in a continuous reactive rectification unit with different number of stages. These plots have been obtained by decreasing the $F_0/V$ ratio to cover the entire range of conversion. In these plots overall $Da$ for the system is same and by increasing the number of stages the $Da$ gets divided among the stages equally. One can see that with an increase in number of stages close to 100% selectivity can be obtained for 100% conversion in case of a non-azeotropic system, surpassing all the limits of conventional continuous flow reactors.

14. Examples of non-azeotropic systems

The results presented above are confirmed here by considering reaction systems $(A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C, A \overset{k_3}{\rightarrow} B \overset{k_4}{\rightarrow} C, A \overset{k_5}{\rightarrow} B \overset{k_6}{\rightarrow} C)$ involving single reactant with different VLE and kinetic parameters. In the following section the theory developed is applied to the industrially important reactions.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
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<tr>
<td>$k_{1,0}$</td>
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<tr>
<td>$k_{2,0}$</td>
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<tr>
<td>$k_{3,0}$</td>
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<td>$E_{3,0}$</td>
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### Table 2

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<th>DIB</th>
<th>TRIB</th>
<th>TEIB</th>
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<td>DIB</td>
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<td>52.339</td>
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<tr>
<td>TEIB</td>
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<td>-58.194</td>
<td>-60.173</td>
<td>0</td>
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</tbody>
</table>

14.1. Case 1: Reaction system $2A \rightarrow B, A + B \rightarrow C, A + C \rightarrow D$, dimerization of Isobutylene (IB)

Dimerization of IB produces diisobutlenes [DIB; 2,4,4-trimethyl-1-pentene (TMP-1) and 2,4,4-trimethyl-2-pentene (TMP-2)]. Side reactions include the formation of trisobutlenes (TRIBs) and higher oligomers such as tetraisobutlenes (TEIBs). The reaction scheme can be represented as follows:

$$IB + IB \overset{k_1}{\rightarrow} DIB,$$

$$IB + DIB \overset{k_2}{\rightarrow} TRIB,$$

$$IB + TRIB \overset{k_3}{\rightarrow} TEIB.$$

The kinetic model is taken from Talwalkar et al. (2006). For simplicity, the presence of water and the side product tert-butyl alcohol (TBA) is neglected. The kinetic model after simplification becomes:

$$r_{DIB} = k_1 a_{IB}^2,$$  \hspace{1cm} (47)

$$r_{TRIB} = k_2 a_{IB} a_{DIB},$$  \hspace{1cm} (48)

$$r_{TEIB} = k_3 a_{IB} a_{TRIB}.$$  \hspace{1cm} (49)

Activity coefficients are calculated using UNIQUAC equation with binary interaction parameters estimated by UNIFAC model from ASPEN PROPERTY PLUS. The VLE and kinetic parameters are given in the Tables 1 and 2. It is a non-azeotropic system with order of volatility as IB > DIB > TRIB > TEIB. Analysis was performed at 15 atm column pressure and the results are plotted in Fig. 13 and are found to be in agreement with the theory developed.
14.2. Case 2: reaction system $2A \rightleftharpoons B$, $A + B \rightarrow C$

Diacetone Alcohol (DAA) or 1-methyl-4-hydroxy-2-pentanone is an industrially important solvent which can be produced by aldol condensation of acetone. Further, the dehydration of DAA produces 4-methyl-3-penten-2-one, commonly known as mesityl oxide (MO). Aldol condensation of mesityl oxide with acetone produces heavier products, such as isophorone.

$$Acetone \xrightarrow{k_1} \text{Diacetone alcohol (DAA)},$$

$$\text{Diacetone alcohol (DAA)} \xrightarrow{K_3} \text{Mesityl oxide (MO) + water},$$

$$\text{Acetone} + \text{Mesityl oxide (MO)} \xrightarrow{K_4} \text{Heavier products}. \quad (50)$$

For simplicity the side reaction to the heavier products is neglected. Activity coefficients are calculated using UNIQUAC equation with binary interaction parameters estimated by UNIFAC model from ASPEN PROPERTY PLUS. The order of volatility is acetone > water > MO > DAA. Kinetic model (Eqs. (51) and (52)) based on a modified Langmuir–Hinselwood mechanism (Thotla et al., 2007) has been used for the simulations. The VLE and kinetic parameters are given in the Tables 3 and 4.

$$r_{Ac} = k_1 a_{Ac}^2 - k_2 a_{DAA}, \quad (51)$$

$$r_{DAA} = -r_{Ac} + \frac{k_3 a_{DAA}}{(1 + k_w a_w)^2}. \quad (52)$$

As acetone being the lightest component it is expected that reactive rectification will give the best performance in terms of selectivity of DAA. It is a peculiar reaction system wherein, the first reaction is intrinsically very slow in comparison with the second undesired reaction. The simulation results are shown in Fig. 13 and are found to be in good agreement with the theory developed. The plot shows that it is possible to get 100% selectivity; however, the number of stages required is exceptionally high (> 5000). This is because the second undesired reaction is much faster than the desired reaction. This number of stages may be reduced by using a hybrid system (Thotla et al., 2007).

14.3. Other cases

In the analysis performed here, we use moderate values of relative volatility and rate constants. However, there may be cases where extreme conditions exist like very large or very small differences in volatilities. Moreover, there may be cases wherein the first reaction is very fast as compared to the second
or vice versa. The analysis for these cases was also carried out and it was found that in all the cases mentioned above, it is possible to obtain close to 100% selectivities for the entire range of conversion; however, the minimum number of stages required to achieve this may vary from case to case.

15. A case with reactant (A) as saddle

In this section we present a peculiar case when the reactant A has intermediate volatility and the typical residue curve map for the ternary system is given by either Fig. 15a or b. As mentioned before, since it is a non-azeotropic system ideally it is possible to obtain 100% selectivity at all the conversion levels using reactive rectification if A is more volatile than B (Fig. 15a) and reactive stripping if A is less volatile than B (Fig. 15b). However, practically it is difficult to avoid formation of C and slightest formation of C or the presence of C in the feed would result in complexities leading to limited conversion or reduced selectivities. This is because in the presence of C, A being a saddle cannot exist in a pure form either in the rectifying section or in the stripping section when operated under total reflux or total reboil conditions, respectively. In such case, it is necessary to withdraw one of the products from either top or bottom, depending on the volatility, to establish a zone in the column wherein, A exists in a pure form. This is an alternate configuration that helps achieve 100% selectivity at all the conversion levels. In this case, we need a hybrid column configuration with reactive and non-reactive stages placed at the appropriate locations to avoid the side reactions. Hence for such cases, we propose two additional basic RD units, viz., semi-batch reactive rectification (SRR) and semi-batch reactive stripping (SRS) which maintain pure reactant on the reactive stages by removing desired product from either from top or from bottom depending on its volatility (see Figs. 16a and b). The continuous versions of these models would be multiproduct units with feed introduced continuously in the re-boiler of SRR or condenser of SRS. The two product streams, e.g. in the case of SRR are, pure B as an overhead product and unreacted A, if any, from the bottom. The AR of the continuous units is same as that of the corresponding semi-batch units. In the following section, we present the detailed analysis of the performance of these unit models.

15.1. Semi-batch reactive rectification (SRR)

SRR (Fig. 16a) is similar to the reactive rectification unit described earlier except that SRR has non-reactive stages below condenser, and the desired product, preferably in pure form, is removed continuously as distillate. The re-boiler is non-reactive and the reaction takes place only in the reactive zone placed between the reboiler and the non-reactive zone. The assumptions made while developing the RC and RR models apply here as well. As against reactive rectification and stripping, two additional parameters viz., the number of non-reactive stages and the reflux/re-boil ratio appear in the model.

(a) Overall and component material balances on the re-boiler (stage 1) and the reactive $j$th stage (for $j = 2$ to $N - 1$) are same as that of RR model and given by Eqs. (29)–(37).

(b) Overall and component material balances on non-reactive stages ($k = N$ to $M - 1$):

\[
L_{k+1} = L_k \quad \text{for} \quad i = 1, 2, \ldots, NC - 1.
\]

\[
l_k(x_{i,k+1} - x_{i,k}) + (y_{i,k-1} - y_{i,k}) = 0 \quad \text{for} \quad i = 1, 2, \ldots, NC - 1.
\]

Fig. 15. (a) RCM for volatility order $B < A < C$ and (b) RCM for volatility order $B > A > C$. Fig. 16. (a) Semi-batch reactive rectification unit and (b) semi-batch reactive stripping unit.
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(c) Overall and component material balances on the $M$th stage (total condenser):

$$1 = I_m + D/V,$$

$$y_{i,m} = I_m x_{i,m} + D x_{i,D}/V_m. \tag{55}$$

As condenser is total condenser

$$y_{i,m} = x_{i,m} = x_{i,D}. \tag{57}$$

Along with these equations, the VLE equations are also valid for each stage except the total condenser.

15.2. Semi-batch reactive stripping (SRS)

SRS is similar to the reactive stripping and the only difference is that the desired product is removed from the bottom continuously as shown in Fig. 16b. The re-boiler is non-reactive and the reaction takes place on the stages below the condenser. Condenser is non-reactive and a non-reactive section is placed in between reactive zone and the re-boiler. The model equations and the assumptions are similar to that of SRR, except that the unsteady state balance in SRS is written for the condenser instead of the reboiler.

16. Effect of various parameters on yield vs conversion

From the above model equations, we have four parameters, which influence the selectivity of the desired product, i.e., the location of the non-reactive zone, reflux ratio, $Da$ per stage and the number of non-reactive stages. We study the effect of these parameters for the reaction system $2A \rightarrow B, A + B \rightarrow C$ with order of volatility as $B > A > C$ represented by the RCM given in Fig. 15a.

16.1. Location of non-reactive zone

As mentioned before, for a ternary system shown in Fig. 15a, B being the most volatile component (unstable node) can be continuously removed as an overhead product of the column to maintain high concentration of A in the reactive zone thereby increasing the selectivity. Fig. 17a and b show the column profiles of B with non-reactive section placed below and above the reactive section, respectively. In the latter case, B in the reactive zone is much less resulting in an improvement in the selectivity under otherwise similar conditions. The removal of B is efficient if a non-reactive zone is placed above the reactive zone. Similarly in the case represented by RCM in Fig. 15b, the non-reactive section may be placed below the reactive zone in the SRS model. It should be noted here that the non-reactive section is essential, in both the cases, to avoid exposure of B to the catalyst.

16.2. Number of reactive stage or $Da$ per stage

As explained before, the number of reactive stages and the value $Da$ per stage have an influence on whether the reaction kinetics or distillation would dominate the column performance. For an effective separation required to minimize the side products formation one needs to use a very large number of stages or small values of $Da$ per stage. $Da$ per stage can be reduced either by increasing the re-boiler duty for the same catalyst loading per stage or by increasing the number of reactive stages for the given total catalyst loading and the re-boiler duty. Fig. 18 shows that as the catalyst loading per stage is reduced the weighted average concentration of B in contact with the catalyst reduces to suppress the side reaction. This average concentration is proportional to the area under the curve in Fig. 18. As expected, the feasible region expands with a decrease in the value of $Da$ per stage. However, the upper limit on selectivity is decided by the efficacy of removal of B as the overhead product from the top, which in turn is also influenced by the number of non-reactive stages and reflux ratio used. These two parameters can be
Fig. 19. Effect of location of non-reactive stages on composition profile of B for \( k_1/k_2 = 1 \) Da per stage = 0.1 and \( R = 10 \).

manipulated such that the distillate is pure B, i.e., the unstable node.

### 16.3. Effect of number of non-reactive stages and reflux ratio

The non-reactive section serves the purpose of enrichment of the desired product B in the distillate. More importantly, an increase in the number of non-reactive stages, under otherwise similar conditions, would result in a favorable change in the profiles of A and B in the column. As shown in Fig. 19, the concentration of B in the reactive zone decreases with increase in number of non-reactive stages which helps to suppress the side reaction. Hence, for a sufficiently large number of reactive stages and non-reactive stages the column tends to give 100% selectivity.

It would be interesting to know the role of reflux in this case. For a large number of stages, when the top composition corresponds to the unstable node (i.e. B), an increase in reflux ratio would result in an increase in the concentration of B in the reactive zone, which adversely affects the selectivity. Fig. 20 shows the effect of reflux ratio and number of non-reactive stages on the yield at a given conversion (50%). Hence, for the sufficiently tall column the reflux ratio should be as low as possible and a lower limit will be decided by the desired conversion and the practical considerations such as column hydrodynamics and wetting of packing, etc. For insufficient number of stages, very low value of reflux ratio would result into a loss of reactant A from the overhead stream thereby imposing a limit on the possible conversion. Hence, in such case an optimum combination of number of non-reactive stages and reflux ratio that offers desired conversion, close to 100% selectivity and minimum cost should be worked out for a given problem.

From the foregoing discussion, it is clear that the feasible region can be stretched to its maximum limit of 100% selectivity at any given conversion, either by increasing number of reactive and non-reactive stages or by decreasing the per stage Da value. The reflux ratio can be increased only up to a particular limit beyond which one encounters drop in selectivity under otherwise similar conditions. Fig. 21a and b show a case
wherein, for the suitable design and operating parameters, the desirable 100% selectivity is achieved by following these guidelines. Similarly the case given by the RCM in Fig. 15b can be treated by using SRS to obtain the desired AR. To sum up, for a system with a reactant of intermediate volatility (saddle) one can suitably design a multiproduct hybrid RD column such that the reactive zone consists of pure A, and obtain close to 100% selectivity at any conversion level.

17. Vector analysis

In this section we define a set of two new vectors for the representative RD models. The two-stage continuous reactive rectification and stripping units are chosen for this purpose. The analysis would provide a basis to include reactive distillation in the existing theory of ARs applicable to network of ideal reactors.

(a) Overall and component material balances for the 1st stage, i.e., re-boiler:

\[ F_0 - L_1 + L_2 - V = 0, \]  
\[ F_0 x_{i,f} - L_1 x_{i,1} + L_2 x_{i,2} - V y_{i,2} = 0 \quad \text{for} \quad i = 1, 2, \ldots, NC - 1, \]  

where, \( L_j = L_j/V \) and \( x_{i,f} \) is the concentration of the feed to the reboiler. \( x_{i,1} \) and \( x_{i,2} \) represent the liquid compositions of component \( i \) in the re-boiler and the condenser, respectively.

(b) Overall and component material balances for the 2nd stage, i.e., RC:

\[ V - L_2 + \sum_{k=1}^{R} v_{T,k} r_k(x_2) \Delta H_{\text{cat}} = 0, \]  
\[ V y_{i,1} - L_2 x_{i,2} + \sum_{k=1}^{R} v_{i,k} r_k(x_2) \Delta H_{\text{cat}} = 0 \quad \text{for} \quad i = 1, 2, \ldots, NC - 1. \]

Eliminating \( y_i, L, V \) from the Eqs. (58)–(61), we get

\[ x_{i,1} - x_{i,f} = \frac{1}{F_0} \sum_{k=1}^{R} (v_{i,k} - v_{T,k} x_{i,1}) r_k(x_2) \Delta H_{\text{cat}} \]  
\[ \text{for} \quad i = 1, 2, \ldots, NC - 1. \]  

Now for any general \( j \)th unit in the series of \( n \) such two-stage reactive rectification units (Fig. 11a), one can write

\[ x_{i,1}^{j} - x_{i,1}^{j-1} = \frac{1}{L_{j-1}} \sum_{k=1}^{R} (v_{i,k} - v_{T,k} x_{i,1}^{j-1}) r_k(x_2^j) \Delta H_{\text{cat}}^{j} \]  
\[ \text{for} \quad i = 1, 2, \ldots, NC - 1, \]  
\[ \frac{x_{i,1}^{j} - x_{i,1}^{j-1}}{k_{f,\text{ref}} \Delta H_{\text{cat}}^{j}/L_{j-1}} = \sum_{k=1}^{R} (v_{i,k} - v_{T,k} x_{i,1}^{j-1}) r_k'(x_2^j) \]  
\[ \text{for} \quad i = 1, 2, \ldots, NC - 1. \]
For the given reaction system, plot the AR for the conventional reactor network as described by Glasser et al. (1987).

At every point, check the RC and RR vectors defined in Eqs. (65) and (66) and if anyone of them points outwards, the multistage models of corresponding unit can be used to obtain the enhanced performance.

This procedure can be followed for the subsequent points to obtain the entire AR till all the vectors are either tangent or point inward.

18. Attainable region with pore diffusion limitations

In heterogeneous porous catalyst, pore diffusion and external mass transfer resistances play important roles in determining the product distribution under certain conditions. It is a well-known fact that the presence of intra-particle diffusion can alter the concentration profiles inside the pores of the porous catalyst, reducing the overall rate since the concentration of reactant near the surface in this case is higher than that at the interior of the catalyst pore. In the case of multiple reaction systems the presence of intra-particle diffusion can considerably alter the selectivity of the desired product. In the previous sections we have shown that for ideal systems wherein no mass transfer limitations are present, one can attain almost 100% selectivities in RD for the entire range of conversion for the reaction system of interest. However, when intra-particle diffusion is present there may be a limit to the AR obtained by RD. In this section we illustrate how one can incorporate the intra-particle diffusion effects in our analysis. The external mass transfer limitations are neglected. The effect of intra-particle diffusion on selectivity in multiple reactions is summarized in Aris (1975). Approximate analytical solutions for parallel consecutive series reactions can be found in Gottinfredi et al. (1994).

Following assumptions are made while developing equations for these models:

(1) The catalyst is of spherical geometry with radius $R$.
(2) Uniform catalyst activity is assumed throughout the catalyst surface.
(3) Steady state conditions with outside surface concentration of catalyst as constant.

Reaction system considered for analysis is $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. Performing a steady state mole balance on species which is entering, leaving and reacting in a spherical shell of inner radius $r$ and outer radius $r + \Delta r$ of the pellet (Fogler, 2004), we get

For species $A$

$$\frac{d(-D_{Ae}(dC_A/dr)r^2)}{dr} - r^2 \rho c r_A = 0,$$

where $D_{Ae}$ is the effective diffusivity of $A$ which can be calculated as given in Fogler (2004), $r_A$ is the rate of formation of $A$ ($r_A = -k_1 C_A$), $\rho_c$ is the density of catalyst and $C_A$ is the concentration in the shell.

The boundary conditions are:

(i) $C_A$ is finite at $r = 0$, \hspace{1cm} (68)
(ii) $C_A = C_{AS}$ at $r = R$, \hspace{1cm} (69)

where $C_{AS}$ is the surface concentration of $A$ at the entrance of the porous catalyst.
Fig. 23. Concentration profiles inside catalyst particle: reaction system $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. $k_1 = k_2$, $D_{Ae} = D_{Be}$, $C_{BS} = 0$.

(b) For species B

$$d(-D_{Be}(dC_B/dr)r^2) \over dr - r^2 \rho_c r_B = 0$$

(70)

where $D_{Be}$ is the effective diffusivity of B which can be calculated as given in Fogler (2004), $r_B$ is the rate of formation of B ($r_B = -k_2 C_B + k_1 C_A$), $\rho_c$ is the density of catalyst and $C_B$ is the concentration in the shell.

The boundary conditions are:

(i) $C_B$ is finite at $r = 0$,

(71)

(ii) $C_B = C_{BS}$ at $r = R$,

(72)

where $C_{BS}$ is the surface concentration of B at the entrance of the porous catalyst.

(c) In dimensionless form Eqs. (67) and (70) become

$$\frac{d^2 \beta_A}{d \theta^2} + \frac{2 d \beta_A}{d \theta} - \phi^2 \beta_A = 0, \quad \phi_1 = 0$$

(73)

$$\frac{d^2 \beta_B}{d \theta^2} + \frac{2 d \beta_B}{d \theta} - \frac{D_{Ae}}{D_{Be}} \phi^2 \left( \frac{k_2}{k_1} \beta_B - \beta_A \right) = 0, \quad \phi = \phi_1$$

(74)

where

$$\beta_A = \frac{C_A}{C_{AS}}, \quad \beta_B = \frac{C_B}{C_{AS}}, \quad \theta = \frac{r}{R}, \quad \phi = \frac{R^2 k_1 \rho_c}{D_{Ae}}$$

$\phi$ is known as the Thiele modulus.

The non-dimensional boundary conditions become:

(i) $\beta_A$ is finite at $\theta = 0$,

(75)

(ii) $\beta_A = 1$ at $\theta = 1$,

(76)

(iii) $\beta_B$ is finite at $\theta = 0$,

(77)

(iv) $\beta_B = C_{BS}/C_{AS}$ at $\theta = 1$.

(78)

Eqs. (73) and (74) are solved using shooting method with boundary conditions given by Eqs. (75)-(78). The iterative procedure of solution can be found in Kim and Lee (2004).

Fig. 23a and b show the concentration profiles of species A and B at different values of Thiele modulus inside the catalyst. From Fig. 23a and b it is clear that at large values of Thiele modulus (i.e. high pore diffusion resistance), high concentration of B is present in the intra-particle region facilitating the second reaction, thus decreasing selectivity. The effect on selectivity of Thiele modulus is shown in Fig. 24 which shows that with an increase in Thiele modulus the selectivity of B decreases. Fig. 24 also shows the effect of $k_2/k_1$ ratio by keeping $D_{Ae}/D_{Be}$ constant. Similar effect is observed by varying $D_{Ae}/D_{Be}$ ratio and by keeping $k_2/k_1$ constant. Thus selectivity of the desired product depends on the Thiele modulus, diffusivity.

Fig. 24. Selectivity vs thiele modulus plot: reaction system, A $\xrightarrow{k_1} B \xrightarrow{k_2} C$. $D_{Ae} = D_{Be}$, $C_{BS} = 0$. 

Eqs. (73) and (74) are solved using shooting method with boundary conditions given by Eqs. (75)-(78). The iterative procedure of solution can be found in Kim and Lee (2004).
ratio, rate constant ratio and the external surface concentration of the various species. For constant values of these parameters one would realize constant selectivity. For a particular system, diffusivity ratios and rate constant ratios can be assumed to be reasonably constant. As mentioned before, in RD, it is possible to maintain the external surface concentration of the reactant constant. As a result the Thiele modulus and selectivity remain unchanged.

For a non-azeotropic system, depending on the relative volatility of A and B we can use reactive rectification or reactive stripping to maintain pure A on the reactive stages, through in situ separation of B. From the above discussion we can conclude that one can achieve constant selectivity for the entire range of conversion. Thus for $D_{AC}/D_{BE} = 1, k_2/k_1 = 1, C_{BS} = 0$ and $\phi = 2.5$ we get a selectivity of 80%. The AR thus obtained with pore diffusion is plotted in Fig. 25a which can be compared to the AR without pore diffusion plotted in Fig. 25b. The shaded region represents the AR. Fig. 25b shows that it is not possible to surpass the 80% selectivity line for the given values of parameters.

19. Conclusions

Attainable region concept plays an important role in the conceptual design of reactive distillation (RD) system for selectivity engineering. The aim of the work was to identify the boundaries, imposed by thermodynamics and kinetics, if any, in the yield vs conversion plots of RD. In all the simple case studies in the present work, we have found that a properly designed RD system can surpass all the boundaries imposed by conventional reactors and can virtually avoid side reactions. Various simplified model units that qualitatively represent a real continuous RD column under extreme conditions have been developed to prove the above mentioned findings. Following are some important outcomes of the analysis performed in this work:

- The best possible location of catalyst is decided by whether RC expands the feasible region or the RR expands the feasible region in comparison to the conventional flow reactors.
- For the best possible selectivity the column should be divided in as many numbers of reactive stages ($N$) as possible and with as low value of $Da/N$ as possible. This facilitates better separation that helps in obtaining enhanced selectivity.
- Hybrid columns help in modifying the composition profile in the reactive section to obtain better selectivity for the given $Da$. It is always a recommended choice against the fully reactive column as it may result in economical benefit in terms of equipment and energy cost savings.
- For non-azeotropic systems reactive rectification model gives the best selectivity when reactant is lighter than the desired product and reactive stripping gives the best attainable selectivity ($\sim 100\%$) when reactant is heavier than the desired product.
- For a system in which the reactant (A) is saddle, a hybrid column with two product streams can also be used to obtain close to 100% selectivity by manipulating reflux ratio and number of reactive/non-reactive stages. This option may prove more reliable and economical than the single product configurations based on reactive rectification or stripping.
- The theory can be extended easily to systems in which pore diffusion limitations are present. There is limit to selectivity in such cases and the limit on selectivity is determined by the parameters such as Thiele modulus, diffusivity ratios, rate
constant ratios and external surface concentration of reactants and products.

This analysis presented here may be further extended to azeotropic systems and multi-reactant systems. The effect of external mass transfer and complex kinetics may also be incorporated.

**Notation**

- \( a \) activity
- \( C \) concentration
- \( D_e \) effective diffusivity
- \( F_0 \) feed flow rate, mol/s
- \( H \) hold up
- \( H_{\text{cat}} \) catalyst hold up, kg
- \( k \) rate constant
- \( l \) \( L/V \) ratio
- \( L, V \) liquid, vapor flow rate, respectively, mol/s
- \( P \) pressure
- \( r_k \) rate for \( k \)th reaction, moles/s gm catalyst loading
- \( v \) \( V/L \) ratio
- \( x, y \) liquid, vapor composition, respectively

**Greeks letters**

- \( \alpha \) relative volatility
- \( \zeta \) warped time
- \( \nu \) molar coefficient in reaction equation

**Subscripts**

- \( a \) reboiler unit
- \( b \) condenser unit
- \( \text{cat} \) catalyst
- \( i \) \( i \)th component
- \( j \) \( j \)th stage
- \( l \) liquid side
- \( \text{NC} \) total number of components
- \( 0 \) initial
- \( \text{ref} \) reference component

**Superscript**

- \( j \) \( j \)th stage

**Abbreviations**

- \( \text{Ac} \) acetone
- \( \text{AR} \) attainable region
- \( \text{Da} \) Damköhler number
- \( \text{DAA} \) diacetone alcohol
- \( \text{DIB} \) diisobutylene
- \( \text{IB} \) isobutylene
- \( \text{MO} \) mesityl oxide
- \( \text{RC} \) reactive condenser
- \( \text{RD} \) reactive distillation
- \( \text{RR} \) reactive re-boiler
- \( \text{TEIB} \) tetra-isobutylene
- \( \text{TRIB} \) tri-isobutylene

**Graphical symbols**

- Reactive condenser unit
- Reactive re-boiler
- Reactive rectification unit
- Reactive stripping unit
- Plug flow reactor
- CSTR
- Two phase CSTR

**Appendix A. Supplementary data**

Supplementary data associated with this article can be found in the online version at 10.1016/j.ces.2008.02.006.

**References**


