Attainable regions of reactive distillation. Part II: Single reactant azeotropic systems

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Abstract

In reactive distillation (RD) one can conveniently manipulate the concentration profiles on the reactive stages by exploiting the difference in volatility of the various components. This property of RD can be advantageously used to improve the selectivity toward the desired product in case of series or series parallel reactions, and obtain a performance superior to the network of conventional reactors. In the previous work [Agarwal, V., et al., 2008. Attainable regions of reactive distillation—Part I. Single reactant non-azeotropic systems. Chemical Engineering Science, submitted for publication], we introduced representative unit models of RD to obtain the attainable regions of RD for non-azeotropic systems. In this work, we extend the approach to a system involving single binary azeotrope. Design guidelines have been formulated based on the residue curve maps, to obtain the improved attainable region with the help of these representative RD models either alone or in the form of their network.

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

1. Introduction

Reactive distillation (RD) can be effectively used to improve the selectivity of a reaction especially when an intermediate product is desired in the series or combination of series and parallel reactions. It can be seen as a promising multifunctional reactor, which with an appropriate design can be used to obtain considerably high yields of the desired product. It is necessary to formulate a systematic method to determine maximum potential of RD for a given reacting system. The use of geometric concepts through the construction of attainable regions in concentration space or on conversion vs. selectivity plot for the ideal conventional reactor network synthesis has been well established (Biegler et al., 2002). Attainable region approach first introduced by Horn (1964) has been extensively studied and developed by Hildebrandt and co-workers (Glasser et al., 1987; Hildebrandt and Glasser, 1990; Hildebrandt et al., 1990; Feinberg and Hildebrandt, 1997). Further extension to this approach for the systems with reaction and separation was presented by Nisoli et al. (1997), Gadewar et al. (2002), and Chadda et al. (2001).

In our previous work (Agarwal et al., 2008) we introduced a new approach to determine the attainable regions of RD and its potential for increasing the selectivity in a given reaction system. We introduced two new models, namely the reactive condenser (RC) and reactive re-boiler (RR) (Figs. 1a and b), to extend the attainable region approach to RD. These units may be treated as batch reactors and the relevant model equations may be solved to obtain the conversion vs. selectivity (or yield) plot for the corresponding unit. These models help one to decide the location of the reactive zone in the distillation column. In RC model reaction takes place only in the condenser and the re-boiler is a total re-boiler. In RR model the reaction takes place in the re-boiler and the condenser is a total condenser. If RC model expands the feasible region of conversion vs. selectivity then one can place reactive zone in the rectifying section of the column and if RR model expands the feasible region then reactive zone may be placed in the stripping section of the column. These models can be modified further to obtain a set of two additional models namely reactive rectification and...
reactive stripping (see Figs. 1c and d). These are the multistage surrogates of the RC and RR models and have the ability to expand the feasible region at sufficiently large number of stages. The potential of these models was shown for the non-azeotropic reaction systems wherein the feasible region obtained was able to surpass the attainable region of any of the conventional reactors or their combinations. With the help of these models a selectivity of almost 100% may be realized for the entire range of conversion (see Fig. 1e) in a system with series as well as a combination of series and parallel reactions irrespective of the order of volatilities. This was possible because there were no constraints imposed by VLE and separation and a sharp split rejecting the component of interest was made possible using the above models. Due to this, there exist certain zones in the RD column wherein, a pure reactant is present thereby creating extremely favorable conditions for the desired reaction to offer attainable selectivity. For example, in the reactive rectification unit one can manipulate the design and operating parameters such that only the volatile reactant A exists in very large proportion on the reactive stages thereby boosting the selectivity toward B. However, for the azeotropic systems, the presence of azeotrope brings in constraints on separation and may limit the selectivity of the desired product. In the present work, an extensive study of the azeotropic systems is performed and design guidelines have been formulated to obtain an improved attainable region using these models alone, or with the help of their network. Azeotropic systems are best represented by residue curve maps (RCMs) and hence RCMs form a basis for the analysis presented here.

The article is organized as follows: First we define the reaction system considered as an illustrative example and briefly review the model equations. The limitations imposed by the
presence of azeotrope are then discussed by considering several representative examples. Further we show how the feasible region can be improved by the combination of the unit models and their network. General design guidelines are provided based on the RCMs. A single binary azeotrope, depending on its nature (i.e. minimum boiling or maximum boiling) and relative volatility, generates several possible RCMs representing qualitatively different systems in a thermodynamic sense. Here, we restrict ourselves to only the systems with single binary azeotrope; however, the analysis can be easily extended to the systems with multiple azeotropes.

2. Reaction system

A typical series parallel reaction system with single parent reactant has been considered for the analysis. Following is the reaction scheme:

\[ 2A \xrightarrow{k_1} B, \quad r_1 = k_1 x_A^2, \]
\[ A + B \xrightarrow{k_2} C, \quad r_2 = k_2 x_A x_B. \]  \hspace{1cm} (1)

The reactant, A undergoes dimerization or condensation to give the product B, which further reacts with A to form the side-product C. Both the reactions are irreversible and as is well known, among CSTR and PFR, one would opt for PFR to obtain better selectivity with respect to B if both the reactions are of positive order with respect to the reactants (Levenspiel, 1999). The reaction is assumed to be taking place only in the liquid phase. Since B is the desired product, the conversion of the first reaction needs to be maximized. The order of volatility is assumed to be A > B > C unless otherwise specified. Simple mole fraction based kinetic equations are assumed with reactions considered as elementary. The rate constants for both the reactions are assumed to be equal. In this reaction two moles of A react to give one mole of B. The yield, which is defined as the amount of product B formed divided by the amount of A reacted, cannot exceed half the conversion value. In the analysis performed here, we consider this reaction system as a base example.

3. Model equations

Figs. 1a and b show the RC and RR units. Assumptions and the model equations for these units can be found in Agarwal et al. (2008). Reactive rectification and reactive stripping models are shown in Figs. 1c and d, respectively. The model equations for reactive rectification and reactive stripping models can be found in Agarwal et al. (2008).

4. Single binary azeotropic systems

In this section, we present some representative examples wherein, there is a formation of single binary azeotrope. We prove that the direct extension of the previously developed approach for non-azeotropic systems, which is based only on the volatilities of the pure components, can sometimes lead to incorrect results for the azeotropic systems of interest. In such case the RCM of the system of interest can be used to get an insight into the behavior of the system and devise configurations that improve the performance and expand the feasible region.

4.1. Example 1: azeotrope between A and C

First, we consider the case wherein C, the undesired product, is involved in the formation of azeotrope. The RCM with minimum boiling azeotrope between A and C, as an unstable node, is shown in Fig. 2a and the yield vs. conversion plots for such a system in PFR and reactive rectification are shown in Fig. 2b. The performance is similar to the non-azeotropic case and almost 100% selectivities can be realized for the entire range of conversion in the reactive rectification model when A is lighter than the desired product. Instead of pure A one would realize the azeotropic composition everywhere in the column as it is an unstable node. The reaction rates of both the reactions are independent of concentration of C and the presence of C in the form of either minimum or maximum boiling azeotrope on the reactive stages does not limit the attainable region.

For other azeotropic cases, wherein reactant A is the lightest and C is the heaviest, almost 100% selectivities are realized using reactive rectification and the trends are similar to that shown in Fig. 2b. The cases with B–C azeotrope need to be analyzed with caution and are explained later.

4.2. Example 2: azeotrope between A and B as unstable node and A as saddle

The RCM for the minimum boiling azeotrope between A and B, as an unstable node, is shown in the Fig. 3a. A is more volatile than B and C and if one ignores the presence of azeotrope then reactive rectification becomes the obvious choice (Agarwal et al., 2008). However, the performance obtained using a reactive rectification model with large number of stages, as shown in Fig. 3b, is exactly opposite and is even worse than PFR especially at higher conversions. This is expected as the liquid phase composition on the reactive stages would be close to the minimum boiling azeotrope (A–B) and not pure A. It should be noted here that this behavior is realized because the azeotrope is an unstable node. The presence of B in the form of azeotrope on the reactive stages aggravates the side reaction and with an increase in the number of stages the performance decreases further. Hence, instead of reactive rectification, the reactive stripping may be a better option to start with. This aspect is discussed in detail in the section on design guidelines.

4.3. Example 3: azeotrope between A and B as saddle

The RCM for the maximum boiling azeotrope between A and B, as a saddle, is shown in Fig. 4a and the yield vs. conversion plot for such a system is shown in Fig. 4b. It can be seen that the RCM is divided into two zones with a distillation boundary. A and B are the unstable nodes in the respective zones. A being more volatile than B one would opt for reactive
Fig. 2. (a) RCM for minimum boiling azeotrope between A and C and (b) yield vs. conversion plot for minimum boiling azeotrope between A–C. N is the number of stages required in the reactive rectification unit, reaction system $2A \rightarrow B$, $A + B \rightarrow C$, $k_1 = k_2$.

Fig. 3. (a) RCM for minimum boiling azeotrope between A and B; A: saddle order of volatility: $A > B > C$ and (b) yield vs. conversion plot for minimum boiling azeotrope between A–B. N is the number of stages required in the reactive rectification unit, reaction system $2A \rightarrow B$, $A + B \rightarrow C$, $k_1 = k_2$.

rectification. For such a system in the region where A is the lightest, reactive rectification with sufficiently large number of stages gives 100% selectivities up to a certain conversion level till the product (i.e. re-boiler) composition corresponds to the azeotropic composition. This is because with sufficiently large number of stages, one can maintain the concentration close to the unstable node in the reactive rectifying section. However, once the azeotropic composition is reached in the re-boiler i.e.,
at relatively large conversion, B would also be present on the stages in the form of azeotrope, which reduces the selectivity sharply. For a large number of stages the reactive rectification model is not able to cross the boundary. On the contrary, it can be seen that at large number of stages the attainable region at high conversion is inferior to that obtained at relatively lower number of stages. It means it is not advisable to continue with the reactive rectification if the composition of reboiler exceeds the azeotropic composition at higher conversion levels.

5. Selectivity lines and RCMs

Before we proceed further to formulate the network of RD units that would offer improved feasible region, it is necessary to first understand the selectivity behavior of the system with the help of the triangular diagrams used for RCMs. For the reaction of interest, the selectivity is higher at higher $r_1/r_2$ ratio as both the reactions take place on the same amount of catalyst.

We introduce a term, selectivity parameters as

$$ S = \frac{k_1x_2^2}{k_2x_Ax_B} = \frac{r_1}{r_2}, \quad (2) $$

$$ x_B = \left( \frac{k_1}{k_2S} \right) x_A. \quad (3) $$

Eq. (3) is the equation of a straight line on the triangular diagram in the rectangular coordinates. Fig. 5 shows the selectivity lines at different values of ‘$S$’ and also indicates the direction in which selectivity increases with a change in the position of the liquid phase composition. It means, when reaction is performed at concentrations in different zones, then the order of selectivity is

Selectivity (I) > Selectivity (II) > Selectivity (III) > ... \quad (4) $$

5.1. Selectivity in PFR

PFR is the preferred reactor over CSTR for series and series–parallel reacting systems (Levenspiel, 1999). The PFR concentration profile on the triangular diagrams may be plotted as below. The composition changes of components A and B along the length/volume are given by Eqs. (6)–(7)

$$ r_A = \frac{dx_A}{d\tau} = -2k_1x_A^2 - k_2x_Ax_B, \quad (5) $$

$$ r_B = \frac{dx_B}{d\tau} = k_1x_B^2 - k_2x_Ax_B, \quad (6) $$

$$ \frac{r_B}{r_A} = \frac{dx_B}{dx_1} = \frac{k_1x_A^2 - k_2x_Ax_B}{-2k_1x_A^2 - k_2x_Ax_B} = \frac{k_2x_B - k_1x_A}{2k_1x_A + k_2x_B}. \quad (7) $$

Eq. (7) can be solved to get the relationship between $x_1$ and $x_2$ along the PFR coordinate. The PFR profiles are plotted in Fig. 6 by solving Eq. (7) numerically starting with the different feed compositions lying on the binary edge A–B.

The relative positions of PFR profiles starting from the binary edge and together with the selectivity lines provide some important inputs to design the network of RD and PFR that can
improve the feasible region. For example, a reactor operating at a constant composition corresponding to point $P$ (see Fig. 6) gives much better selectivity than a PFR that receives the feed of the corresponding composition. This is because all the PFR compositions lie in the region of the composition space giving less selectivity than that obtained by operating at constant composition corresponding to point $P$. The following section makes use of this observation to obtain an improved feasible region by a clever combination of different RD model units.

6. Networking of different units to improve the performance

In the previous section it was found that a limit to the achievable selectivity is realized with reactive rectification model when $A$ is lighter than $B$ and azeotrope is present between $A$ and $B$. In all the other cases for the entire range of conversion, 100% selectivities can be obtained. In this section, we show, how one can expand the region of feasibility by the combination of representative RD units or combination with the conventional reactors. Examples 2 and 3 wherein, an upper limit to selectivity is realized, are further analyzed here as illustrative examples.

6.1. Azeotrope between $A$ and $B$ as unstable node; $A$: saddle

Here, we explore a possibility of obtaining an improved feasible region for example 2 with RCM given by Fig. 3a (order of volatility $A > B > C$). It has been shown in the previous section that if we use reactive rectification with sufficiently large number of stages then the column composition, instead of $A$, will be close to the minimum boiling azeotrope due to which the selectivity is adversely affected. Composition close to pure $A$ in the reactive zone can be obtained only by reactive stripping. Hence, if we use reactive stripping till the conversion corresponding to the azeotropic composition in the condenser then 100% selectivity is realized. However, in this case beyond the azeotropic composition, there is a decrease in performance. This is because reactive zone is then enriched with respect to product $B$ leading to an increased formation of $C$, thus lowering the selectivity. Till the conversion corresponding to the azeotropic composition one can use reactive stripping to obtain 100% selectivity. For higher conversion, instead of continuing with reactive stripping, we investigate the possibility of using other units such as PFR or reactive rectification, to be used in series with reactive stripping. Hence, the outlet of reactive stripping corresponding to the azeotropic composition can be fed to either PFR or reactive rectification.
Fig. 7 shows the non-reactive RCM of the system of interest. The dotted line represents the PFR trajectory starting from point N that corresponds to the azeotropic point. If point N (see Fig. 7) is an unstable node or stable node in the RCM then we can use reactive rectification or reactive stripping to conveniently manipulate the composition in the entire reactive zone close to point N (see Fig. 8) and obtain selectivity higher than a PFR. Based on the earlier discussion, the PFR trajectory lies in the composition region that gives poorer selectivity compared to a reactor operating at constant composition corresponding to point N. This observation can be used to determine an appropriate network/sequence that gives an improved feasible region. Since in this case, point N is an unstable node, one can use reactive rectification such that a composition near to azeotrope (or point N) is obtained in the entire reactive zone as shown in Fig. 8. The profiles in Fig. 8 are plotted at a conversion 81% at which re-boiler composition of B is higher than the azeotropic composition. Hence, when it comes to the choice of the unit that would follow reactive stripping, reactive rectification scores over a conventional PFR. The attainable regions of PFR and reactive stripping are shown in Fig. 9a, whereas the improved attainable region obtained by a combination of reactive stripping and reactive rectification is as shown in Fig. 9b. The attainable selectivities reported in Fig. 9b have been confirmed by independent simulations. It can be easily proved that the boundary of the attainable region, after the azeotropic point, is linear with the slope \((k_1 x_A, az/(k_1 x_A, az + k_2 x_B, az)))\), which is 0.286 in the present case. \(x_A\) and \(x_B\) represent the azeotropic composition corresponding to the unstable node.

The same logic may be applied to the RCMs wherein, the \(A-B\) azeotrope is maximum boiling and a stable point in the RCM. In this case the proposed network is reactive rectification followed by reactive stripping for which the attainable region may be determined in the same manner as described before. In both the cases mentioned above, up to the azeotropic point (stable or unstable node) the attainable region is given by the 100% selectivity line and thereafter it depends on the azeotropic composition and the reaction kinetics.

6.2. Example: 2 azeotrope between A and B as saddle

In this case, as shown in Fig. 4a, the azeotrope is the saddle node whereas A and B act as unstable nodes. We get close to 100% selectivity in reactive rectification till the conversion corresponding to the azeotropic composition in the re-boiler or the product stream is obtained. At the conversions higher than this conversion, there is a drastic fall in the selectivity, which can be attributed to the presence of B on the reactive stage, leading to formation of C. As discussed before, till the azeotropic composition we can use reactive rectification, which may be followed by a PFR or reactive stripping. Though we found that one may opt for a PFR in series with reactive rectification and expand the feasible region as shown in Fig. 10a, the region can be expanded further with the use of more complex configurations such as the one with multiple product streams (Fig. 10b) as discussed below.

6.3. Multiproduct configurations

It has been shown in the previous work (Agarwal et al., 2008) that multiproduct configurations (Figs. 11a and b) can be effectively used for the cases wherein the reactant is a saddle point. The units with multiple product streams, i.e. the continuous versions (Figs. 11c and d) of semi-batch reactive rectification (SRR) and semi-batch reactive stripping (SRS) have
Fig. 10. Feasible region plot for maximum boiling azeotrope between $A$ and $B$: reaction system $2A \xrightarrow{k_1} B$, $A + B \xrightarrow{k_1} C$, $k_1 = k_2$. (a) Comparison reactive rectification followed by PFR and reactive rectification followed by multiproduct configuration and (b) reactive rectification followed by multiproduct configuration.

Fig. 11. (a) Semi-batch reactive rectification (SRR) unit, (b) semi-batch reactive stripping unit (SRS), (c) multiproduct continuous version of SRR and (d) multiproduct continuous version of SRS.

been described in detail for non-azeotropic systems, wherein the composition corresponding to saddle (i.e. pure reactant) was maintained on reactive stages. A similar situation is encountered here in the azeotropic systems. In this case, the RCM is divided into two distillation regions. At the higher conversion the working space is the upper region of the RCM (Fig. 4a) with $B$ as unstable node. The saddle in this region is the $A\sim B$ azeotrope and a multiproduct configuration that can maintain
the azeotropic composition in the reactive zone would be preferred in this case. The $A$–$B$ azeotrope from the first unit is fed to the re-boiler of the continuous version of SRR. The non-reactive stages are placed above the reactive zone and pure $B$ is obtained continuously from top, maintaining the azeotropic composition on the reactive stages. The bottom stream contains all the three components: $B$, $C$ and unreacted $A$. The selectivity obtained in this case is always less than 100% as some amount of $B$ is always present on reactive stages. Thus by using very large number of stages, the separation effect is made dominant and the selectivity is improved. The distillate is the desired product ($B$) and hence the reflux ratio should be kept as low as possible. The combination of reactive rectification and the multiproduct hybrid reactive rectification expands the attainable region as shown Fig. 10b. The 100% selectivity is obtained till azeotropic composition. For the second unit, the slope of attainable region boundary is dependent on kinetic parameters and the azeotropic composition and is given by $\frac{k_1 x_A, az}{k_1 x_A, az + k_2 x_B, az}$.

6.4. Azeotrope between $B$ and $C$ as stable or unstable nodes

The RCMs of the system shown in Fig. 12 have $B$–$C$ azeotrope either as stable node or unstable node. Since the parent reactant $A$ is not involved in the azeotrope, either reactive rectification or reactive stripping, depending on volatility difference between $A$ and $B$, may be used to obtain 100% selectivities for the entire range of conversion and the system behaves as a binary system. However, it should be noted that even a slightest presence of $C$ in this case will force the liquid composition on the reactive stages toward the azeotrope $B$–$C$. The presence of $B$ will further increase the formation of $C$ and a decline in the selectivity is expected. This may result in a performance inferior to even PFR and it will not be advisable to select the RD configuration suggested above. In reality we cannot eliminate the presence of $C$ in the feed or its formation during the process. Thus for all practical purposes, it is always advisable to use a configuration equivalent to the SRR and SRS options for the cases in Figs. 12a and b. The continuous version of which is the multiproduct hybrid configurations as discussed in the previous section.

6.5. Effect of non-reactive section

It has been proved in the analysis of non-azeotropic systems that the hybrid column containing non-reactive sections increase the efficiency of separation and one must consider introducing these section in the RD columns to improve the economics and reduce the capital cost. The same guideline is applicable to azeotropic systems. It should be noted that the attainable region in the single product configuration is unaffected by the introduction of non-reactive zone. In the case of multi-product configurations, however, the presence of non-reactive section is mandatory to attain the saddle composition in the reactive zone.

7. Guidelines for selecting the best configuration

By far it has been confirmed that the non-reactive distillation behavior of a system through RCM can be conveniently used to evaluate the possible impact of distillation on selectivity and explore the use of proper RD configuration to expand the feasible (attainable) region. Hence, for azeotropic systems RCMs form a base to evaluate the configuration for maximum selectivity. In this section some guidelines are presented which can be used to obtain the best possible configuration when a system with single non-ideal azeotrope is encountered.

- If there is no azeotrope between $A$ and $B$, irrespective of whether $C$ forms azeotrope with either $A$ or $B$, 100% selectivity is attainable with reactive rectification if $A$ is more volatile than $B$ and reactive stripping if $A$ is less volatile than $B$. If $A$ is saddle and $B$ is involved in the azeotrope formation then a hybrid column configuration is recommended.
Table 1
Guidelines for selecting best configuration for reaction systems: (a) \( A \xrightarrow{k_1} B \xrightarrow{k_2} C \) and (b) \( 2A \xrightarrow{k_1} B, A + B \xrightarrow{k_2} C \)

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<td>$C &gt; A &gt; B$</td>
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100% selectivity can be achieved at any conversion level using reactive rectification model.

| 5     | $C > B > A$        | ![Diagram](image2)            |

100% selectivity can be achieved at any conversion level using reactive stripping model.
for all practical purposes. The relevant cases are given in Table 1.

- If A and B form a minimum boiling azeotrope which is saddle, a series combination of single product reactive stripping and a multiproduct reactive stripping provides the maximum selectivity and hence the attainable region. On the other hand, if A and B form a maximum boiling azeotrope which is saddle then single product reactive rectification followed by multiproduct reactive rectification gives the attainable region. The relevant cases are given in Table 2.

- If the maximum or minimum boiling azeotrope between A and B are either unstable or stable nodes and A is a saddle node, then combination of reactive rectification and reactive stripping gives the attainable region. If the azeotrope is unstable then reactive rectification should follow reactive

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<td>A typical system wherein ideally one can achieve entire concentration space using reactive stripping, however, presence of slightest of C in the re-boiler will force the maximum boiling azeotropic composition on the reactive stages giving lesser performance than even PFR</td>
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Table 2
Guidelines for selecting best configuration when azeotrope between A and B as saddle for reaction systems: (a) $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ and (b) $2A \xrightarrow{k_1} B, A+B \xrightarrow{k_2} C$

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stripping and if it is stable the sequence is reverse. The relevant cases are given in Table 3.

- If the maximum boiling azeotrope $A-B$ is a stable node and $A$ is an unstable node, then only reactive rectification may be used to get attainable region. If azeotrope $A-B$ is an unstable node, and $A$ is stable node then only reactive stripping offers maximum selectivity. In these cases one can obtain close to 100% selectivities. The relevant cases are given in Table 4.

8. Attainable region with pore diffusion effects

In heterogeneous porous catalyst, pore diffusion and external mass transfer resistances play important roles in determining the product distribution under certain conditions. In our previous paper (Agarwal et al., 2008), we explained the effect of Thiele modulus on concentration profile of $A$ and $B$ inside the particle. For the large values of Thiele modulus (i.e. high pore
Table 3
Guidelines for selecting best configuration when azeotrope between A and B is unstable node for reaction systems: (a) $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ and (b) $2A \xrightarrow{k_1} B$, $A + B \xrightarrow{k_2} C$

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<th>Order of volatility</th>
<th>RCM</th>
<th>Configuration and comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$B &gt; A &gt; C$</td>
<td></td>
<td>Limit to selectivity. 100% selectivity can only be achieved up to Azeotropic composition</td>
</tr>
<tr>
<td>2</td>
<td>$A &gt; C &gt; B$</td>
<td></td>
<td>Limit to selectivity, the configuration shown will give best performance, however, the point to shift from one model to another can only be determined through vector analysis</td>
</tr>
<tr>
<td>3</td>
<td>$B &gt; C &gt; A$</td>
<td></td>
<td>Limit to selectivity, the configuration shown will give best performance; however, the point to shift from one model to another can only be determined through vector analysis</td>
</tr>
<tr>
<td>4</td>
<td>$C &gt; B &gt; A$</td>
<td></td>
<td>Limit to selectivity. 100% selectivity can only be achieved up to Azeotropic composition</td>
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</table>
Table 3 (Contd.)

<table>
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<th>S. no.</th>
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<th>RCM Configuration and comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>C &gt; A &gt; B</td>
<td>Limit to selectivity, 100% selectivity can only be achieved up to Azeotropic composition</td>
</tr>
</tbody>
</table>

Table 4

Guidelines for selecting best configuration when azeotrope between A and B is stable node for reaction systems: (a) $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ and (b) $2A \xrightarrow{k_3} B, A + B \xrightarrow{k_4} C$

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<tr>
<td>1</td>
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<td>100% selectivity can be achieved at any conversion level using reactive rectification model</td>
</tr>
<tr>
<td>2</td>
<td>B &gt; C &gt; A</td>
<td>100% selectivity can be achieved at any conversion level using reactive stripping model</td>
</tr>
</tbody>
</table>
Fig. 13. Effect of Thiele modulus on (a) composition profile of A inside the particle and (b) composition profile of B inside the particle.

Fig. 14. Effect of Thiele modulus and \( k_2/k_1 \) ratio on selectivity of B for \( D_{Ae}/D_{Be} = 1 \).

diffusion resistance), the concentration of B inside the particle is high, which leads to a decrease in the selectivity for the desired product B. As the value of Thiele modulus increases, the selectivity of B decreases for ideal systems. Similar results are obtained for the non-ideal systems. Figs. 13a and b show the concentration profiles of species A and B at different values of Thiele modulus inside the catalyst for a non-ideal system with the concentrations \( x_1 = 0.8 \) and \( x_2 = 0.2 \) (i.e. \( \beta_A = 1, \beta_B = 0.25 \) and \( \theta = 1 \)) at the external surface of the catalyst. Fig. 14 shows the effect of Thiele modulus and \( k_2/k_1 \) ratio on the selectivity of B for a given \( D_{Ae}/D_{Be} \) ratio and for 100% conversion. 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 ratios, rate constant ratios 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 ratio and rate constant ratio can be assumed to be reasonably constant. If we can maintain the external surface concentration uniform throughout the reactive zone then Thiele modulus and hence selectivity can be easily determined. In all the recommended configuration in the foregoing discussion the concentration of the reactive zone is nearly constant and is kept at either the unstable node, stable node or the saddle. Hence, it can be concluded that, for the constant values of \( D_{Ae}/D_{Be}, k_2/k_1, \frac{C_{BS}}{C_{As}} \) and \( \Phi \), we get a constant selectivity for the entire range of conversion.

As discussed in the previous section, in case of azeotropic systems, depending on the relative volatility of A–B azeotrope with respect to the desired product B we can choose one of the options from the four different models viz. reactive rectification, reactive stripping, SRR and SRS to obtain pure A–B azeotrope on the reactive stages. Thus for a constant concentration of A–B azeotrope throughout the reactive zone we get a selectivity of 59.6% as shown in Fig. 15, for \( D_{Ae}/D_{Be} = 1, k_2/k_1 = 1, \frac{C_{BS}}{C_{As}} = 0.25 \) and \( \Phi = 2 \). The attainable region thus obtained with pore diffusion is plotted in Fig. 15 against the attainable region without pore diffusion. For the case with pore diffusion effects the selectivity of 84% is realized up to the conversion corresponding to the azeotropic point. This is the case when catalyst is surrounded by the pure reactant. The procedure of calculating the selectivity is discussed by Agarwal et al. (2008). For the higher conversion case the external surface concentration corresponds to the azeotropic composition and hence the selectivity of 59.6% is realized for the parameters given above.
9. Conclusions

Based on the analysis presented here it can be concluded that for series or series–parallel reactions when no azeotrope is present in between reactant and desired intermediate product 100% selectivities can be obtained for the entire range of conversion using RD. However, when an azeotrope is present between reactant and the desired product there exists an upper to selectivity, and the design guidelines, based on the RCMs, have been presented to obtain the improved attainable region. The configurations considered are combination of RD, reactive stripping and their multiproduct versions. The analysis presented here can be further extended to multireactant, multiazeotropic systems and systems with complex kinetics. The presence of intraparticle diffusion limitation causes attainable region to further shrink and give lower selectivity.

Notation

Alphabetic

\( a \) activity
\( F_o \) feed flow rate, mol/s
\( H \) hold up
\( H_{cat} \) 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

Greek letters

\( \alpha \) relative volatility
\( \xi \) warped time

Subscripts

\( a \) re-boiler unit
\( b \) condenser unit
\( cat \) catalyst
\( i \) \( i \)th component
\( i, az \) azeotropic composition of component \( i \)
\( j \) \( j \)th stage
\( l \) liquid side
\( NC \) total number of components
\( 0 \) initial
\( ref \) reference component

Superscripts

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

Abbreviations

AR attainable region
\( Da \) Damköhler Number
RC reactive condenser
RD reactive distillation
RR reactive re-boiler

Graphical symbols

- reactive condenser unit
- reactive re-boiler
- reactive rectification unit
- reactive stripping unit
- semi-batch reactive rectification (SRR) unit
- semi-batch reactive stripping (SRS) unit
- plug flow reactor
- CSTR
- two phase CSTR

References


