

# Selectivity Engineering with Hybrid Reactive Distillation Column: Mixtures Containing Inerts and Multi-Azeotropes

Deepshikha Singh, Antaram Dutta, Ankur Gaur, Shabih UI Hasan\*

Department of Chemical Engineering, Motilal Nehru National Institute of Technology, Allahabad-211004  
[shasan@mnnit.ac.in](mailto:shasan@mnnit.ac.in)

Reactive Distillation (RD) which combines reaction and distillation can be effectively used to get desired selectivities in multi-reaction systems. In case of azeotropic systems, nonideal vapor-liquid equilibrium and distillation boundaries are responsible for the contraction of the feasible reactive stage composition region required for the design of hybrid RD column. In the present study, we show that if the mixture contains inert as well then this feasible reactive stage composition region reduced further and thereby decreases the feasible design options of desired selectivity in multireaction systems. Therefore, an attempt is made here, to developed a conceptual design algorithm which is based on combined graphical-simulation approach and attainable region concepts. The developed methodology successfully finds at least one feasible design of hybrid RD column to give desired selectivity. Method gives excellent starting values for rigorous simulations suited to industrial applications.

## 1. Introduction

Reactive distillation (RD) which integrates reaction and distillation is a promising multi-functional reactor which has a potential of giving desired selectivities when designed astutely. The present work is the continuation of our series of work on selectivity engineering with reactive distillation columns [Agarwal et al., 2008a, b; Amte et al. 2011; Amte et al. 2012; Hasan et al., 2013a, b; Hasan et al., 2014; Hasan et al., 2015]. If the reactant is unstable or stable node in the corresponding residue curve map, then the fully reactive configurations such as reactive rectification or reactive stripping can be used. However, for the cases wherein reactant is saddle, hybrid RD configurations are to be employed to achieve the desired performance. For such mixtures, Hasan et al., (2013a, 2013b, 2014, 2015), proposed a design algorithm for simple and complex hybrid RD columns to achieve a desired selectivity in case of single reactant multi-reaction schemes. The type of configuration used strongly depends on the volatility of reactants and on the number of products that undergo further side reactions in a given multi- reaction scheme. For example, if only one product is involved in further side reaction then one can use simple hybrid RD column to obtain the desired selectivity in a multireaction system. Here, we extend the applicability of the developed algorithm for the mixtures containing inert and multiazeotropes. The main underlying principle of designing the RD column of desired selectivity is to maintain a composition on the reactive stage at which reaction occurs. The presence of inert component does not affect the reaction but influences the composition profiles and hence the reactive stage compositions in a RD column. Presence of inerts and multiazeotropes makes the design of RD Column of desired selectivity a very challenging task. As a result, an algorithm is developed, which is a combination of geometric and simulation methods. The developed methodology successfully finds one of the feasible design of hybrid RD column for the desired selectivity.

## 2. Design Methodology

The methodology starts with non-reactive distillation column (non-RD) and then introduces the reaction related attributes. For non-RD, we use the concept of visualization of the locus of feed stage compositions (LFSCs) in 3D composition space. For reaction related attributes we view the column as a reactor and relate it to the conventional reactors for which geometric interpretation is well studied through the attainable region approach.

Glasser et al. (1987) presented geometrical interpretation of CSTR in terms of process vectors viz. reaction and mixing. In order to know whether a point in the composition space is attainable or not, they derived a condition that the rate vector at that point is collinear with the mixing vector of feed and product stream. The component material balance of CSTR gives the required condition. It must be noted that the reaction takes place at the product composition in the case of CSTR. On the other hand, in an arbitrary reactor (R), if the composition at which reaction takes place is different than the product composition, then the collinearity condition is no longer valid. The composition at which reaction takes place is dependent on the type of reactor. One can control this composition by introducing separation attributes as is done the case of reactive distillation.

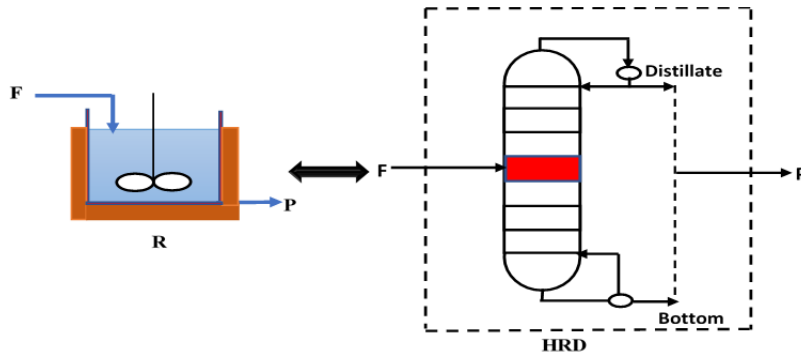


Figure 1. Analogy between arbitrary reactor (R) and hybrid RD Column (HRD)

Now, as shown in Figure 1, let us consider a simple hybrid column with single reactive stage. It may be noted that the reaction in the column does not take place at a composition corresponding to that of the product (P). The overall product composition is the one obtained by virtually mixing the distillate and bottom streams. The composition of the reactive stage depends on the distillation attributes such as reflux ratio, feed location, number of stages, etc. Therefore, the next exercise is to know –which are the points in the composition space that can be the potential reactive stage composition(s) giving the desired selectivity corresponding to the point of desired product composition. The following section determines the surface of such feasible reactive stage compositions.

## 2.1 Surface of Reactive Stage Compositions (SRSCs)

Consider an equimolar simple series reaction scheme (Eq. 1) with only one reacting component A. All the reactions are irreversible with 1st order. The feed is pure reactant A along with 25% inert and the kinetic rate constants are given by  $[k_1 \ k_2] = [1 \ 1]$ .



The material balances for components A and B on any arbitrary reactor, yield the following relation

$$x_A - x_{A0} = \tau \cdot \sum_{k=1}^{nR} r_{k,A}(x^*) \quad (2)$$

$$x_B - x_{B0} = \tau \cdot \sum_{k=1}^{nR} r_{k,B}(x^*) \quad (3)$$

Divide (3) by (2) we get

$$\frac{x_{B,P} - x_{B,0}}{x_{A,P} - x_{A,0}} = \frac{r_B}{r_A} = \frac{k_1 x_A^* - k_2 x_B^*}{-k_1 x_A^*} \quad (4)$$

where  $x_{i,p}$  is the product composition of component i,  $x_{i,0}$  is the inlet composition of component i and  $x^*$  denotes the compositions at which the reaction takes place in the reactor. The LHS of Eq. (4) is the slope of line joining points A ( $x_{A0}$ ,  $x_{B0}$ ) and P ( $x_{AP}$ ,  $x_{BP}$ ) as shown in Figure 2. It should be noted that point P is on ABI

plane in Figure 3 and since Eq. (4) is independent of  $x_{CP}$ , its value is not required for plotting the SRSCs. Hence, for any desired point P in the composition space, Eq. (4) gives a relation between  $x_A^*$  and  $x_B^*$ . One can plot the SRSCs for the quaternary mixture by taking a meshgrid of  $[x_A^*, x_C^*]$  and plot  $x_B^*$  compositions as shown in Figure 3.

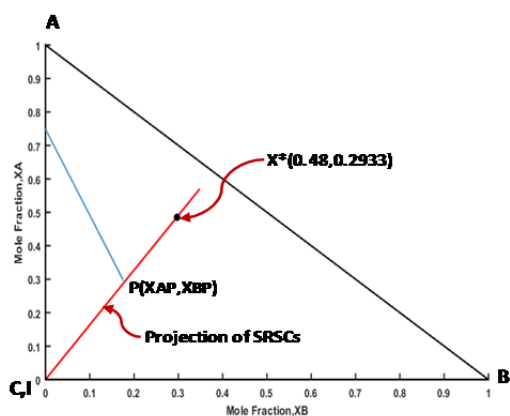


Figure 2. Selected reactive stage composition,  $X^*$  on the projection of SRSCs(2-D).

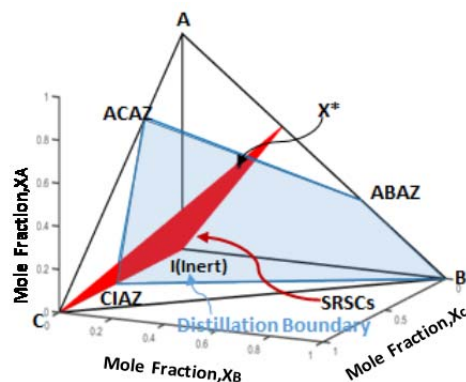


Figure 3. Selected reactive stage composition,  $X^*$  and distillation boundary(3-D)

Moreover, it should be kept in mind that once we choose point P in the composition space it implies fixed selectivity, which we call as the desired selectivity and hence if the reaction occurs at any of the compositions on the SRSCs then the desired selectivity is ensured.

## 2.2 Effect of percentage of Inert and desired selectivity on SRSCs

In case of azeotropic systems, nonideal vapor-liquid equilibrium and distillation boundaries are responsible for the contraction of the feasible reactive stage compositions required for the design of hybrid RD column.

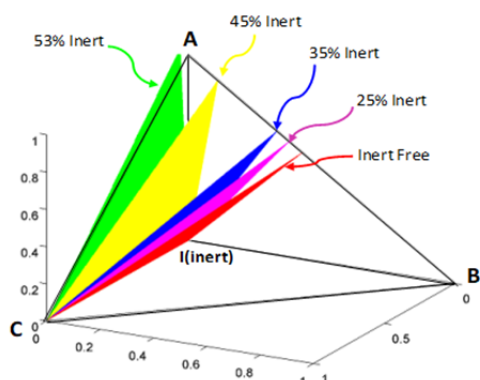


Figure 4. Shifting of SRSCs with variation in inert percentage in feed.

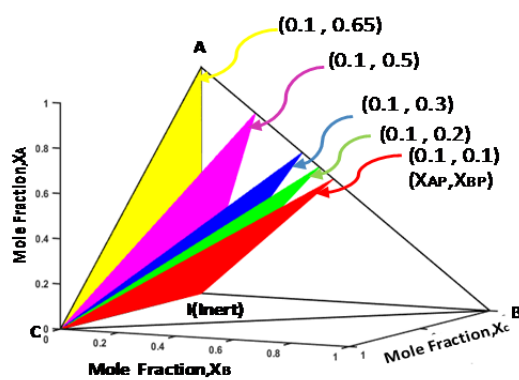


Figure 5. Shifting of SRSCs with variation in desired selectivity.

Figure 4 shows that if the mixture contains inert as well then these feasible reactive stage compositions reduces further with increase in the percentage of inert (e.g. no design of fixed selectivity is possible for 53% inert). Figure 5 indicates that with increase in the desired selectivity with fixed conversion, the feasible reactive stage compositions get reduced.

## 2.3 Design procedure

Consider a simple hybrid RD column with one reactive stage (Figure 6a) and a reactor-separator system (Figure 6b). A systematic methodology that uses intersection of LFSCs with the selected reactive stage composition,  $X^*$  to obtain feasible designs of desired selectivity using hybrid RD column for the reaction scheme given by Eq. (1) is described. The approach presented here exploits the fact that if we split the reaction and distillation attributes of the hybrid RD column (Figure 6a), then the new configuration (Figure 6b) gives the same performance as that of a hybrid RD column. If the feed stage in the RD column is the reactive

stage, then the column profiles of non-RD and RD column coincide for the same distillation attributes. This would be made clear by considering the following example.

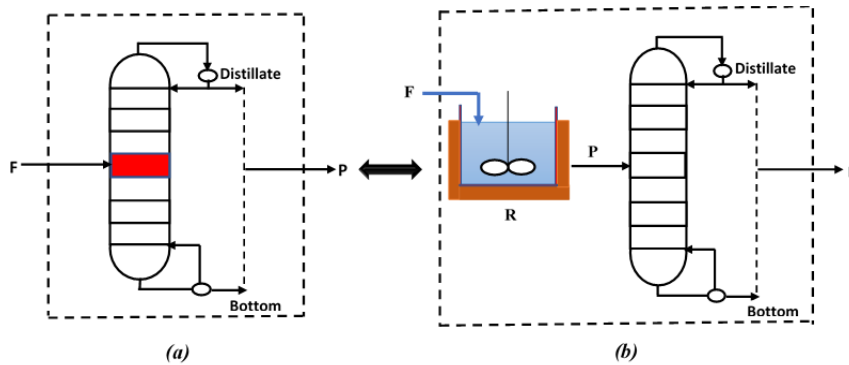


Figure 6 (a) Hybrid (RD) column. (b) Reactor separator system (Non-RD).

A simplified equimolar series reaction scheme (Eq. 1) with rate constants,  $[k_1 \ k_2] = [1 \ 1]$  and volatilities as  $[\alpha_A \ \alpha_B \ \alpha_C \ \alpha_I] = [2 \ 5 \ 3 \ 1]$ , is chosen as an illustrative example. Inert (I) is the least volatile component. Assume constant molar overflow and the reaction takes place in the liquid phase. Following are the proposed step-by-step design procedure:

**Step-1:** Select any point P (Figure 2) according to the desired selectivity of intermediate product, B in the composition space. This point represents the overall output composition of hybrid RD column (Figure 4a), obtained by virtually mixing distillate (D) and bottoms (B) streams. Hence, it can be considered as the feed to Non-RD column in Figure 4b.

**Step-2:** Join point P (0.3, 0.175) with A (0.75, 0) to calculate the slope of line AP, and hence obtain the surface of reactive stage compositions (SRSCs) using Eq. (2) as shown in Figure 2.

**Step-3:** Select any reactive stage composition,  $X^*$  on the SRSCs as shown in Figure 2. For the present example let  $X^* = [X_A^* \ X_B^*] = [0.48, 0.2933]$ . Also only those compositions are plotted which lie within the 3D composition space as shown in Figure 3. The multicomponent azeotropic mixture (Rooks et al., 1998) consists of three minimum boiling binary azeotropes. The distillation boundary shown by the shaded surface in Figure 3, divides the space into two distillation regions.

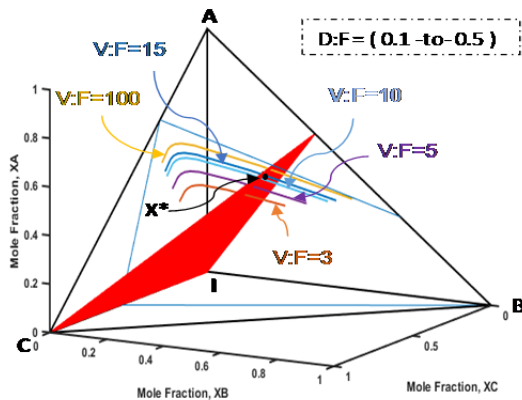


Figure 7. Curves for a range of D:F at different values of V:F representing LFSCs.

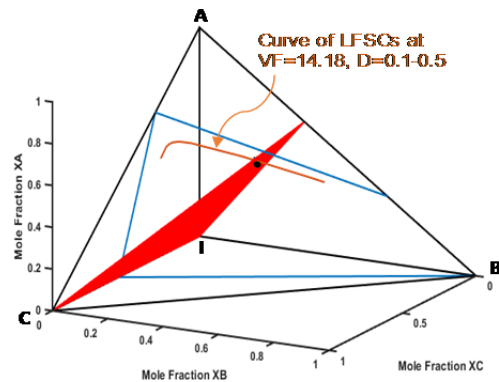


Figure 8. Feasible condition that satisfies our requirements

**Step-4:** Find the composition of all the components in the feed that is sent to the distillation column as we visualize RD as a combination of reactor followed by distillation column (Figure 6b). We need to know the composition of all the components including C and I(Inert) in the feed that is sent to the distillation column.

$$Da = \left( \frac{W_{cat} * k_{ref}}{F} \right) \tag{5}$$

The composition of C is related to the extent to which individual reactions take place, which in turn depends on the Damkohler number ( $Da$ ) number i.e. the ratio of characteristic liquid residence time to the characteristic reaction time (Eq. 5). We determine  $Da$  by applying material balance for either component A (Eq. 6) or component B (Eq. 7) for any arbitrary reactor in which reaction takes place at the selected composition,  $X^*$ . Further, by using material balance for component C (Eq. 6), one can find the composition of C in the feed to the distillation column. Composition of I can be obtained by summation equation.

$$x_{A,0} - x_{A,P} + Da \left( \frac{-k_1 x_A^*}{k_{ref}} \right) = 0 \quad (6)$$

$$x_{B,0} - x_{B,P} + Da \left( \frac{k_1 x_A^* - k_2 x_B^*}{k_{ref}} \right) = 0 \quad (7)$$

$$x_{C,0} - x_{C,P} + Da \left( \frac{k_2 x_B^*}{k_{ref}} \right) = 0 \quad (8)$$

**Step-5:** For the simulation of Non-RD column, along with the feed composition, we also have to specify the number of stages, feed location and operating parameters. Number of stages can be chosen on the basis of cost considerations (e.g  $N=12$ , *reboiler* = 1<sup>st</sup> stage). Since the reactant A in our case is of intermediate volatility one can choose the feed location anywhere near the middle of the column ( $N_{fl}=6$ th stage).

**Step-6:** Find the operating parameters such that the feed stage of Non-RD column coincides with the selected reactive stage composition,  $X^*$ . To obtain this intersection draw the family of curves representing LFSCs obtained for a range of Distillate to Feed ratio (D:F) and boil-up to Feed ratio (V:F) as shown in Figure 7. Range of D:F can be decided based on whether or not one of the LFSCs crosses the curve of SRSCs containing selected reactive stage composition,  $X^*$ , while the V:F ratio can start from any small value till the performance becomes insensitive at higher values. It can be clearly seen in Figure 7 that the reactive composition,  $X^*$  of interest lies in the vicinity of curves obtained for V:F=15.

**Step-7:** The exact intersection of feed stage of Non-RD column with the selected reactive stage composition,  $X^*$  is shown in Figure 8. The values of two operating parameters viz. V/F and D:F at this intersection are found to be 14.18 and 0.2389 respectively.

**Step-8:** Obtain the column profile for RD, with the feed as A (75% pure A, 25% inert) and the feed stage as the reactive stage, using the same design and operating parameters as used for the Non-RD case. As discussed in our earlier work (Appendix A in Hasan et al., 2013a), it is necessary that the feed stage should be the reactive stage to avoid the feed effect on column profile. The column profiles coincide (Figure 9) to indicate that the design is feasible. Hence, the desired selectivity for the given series reaction scheme is attainable through hybrid RD column, the design specifications of which are given in Table 1.

Table 1: Design specifications for hybrid RD column with 25% Inert in Feed

Column configuration	Non-RDC	RDC
Number of components, $NC$	4	4
Volatility Order, $B > A > C > I$	Non-ideal VLE	Non-ideal VLE
Number of stages, $N$	12	12
Feed location, $N_{fl}$	6 <sup>th</sup> Stage	6 <sup>th</sup> Stage
Feed flow rate, $F$	1	1
Feed composition, $X_f$	(0.3, 0.175, 0.275, 0.25)	(0.75,0,0,0,0.25)
Feed stage composition, $X^*$	(0.48, 0.2933, 0.1708, 0.0559)	(0.48, 0.2933, 0.1708, 0.0559)
Number of reactive stages, $N_r$	-	1
Location of Reactive stage, $N_{rl}$	-	6 <sup>th</sup> Stage
Damkohler Number, $Da$	-	0.9375
Distillate to feed ratio, $D:F$	0.2389	0.2389
Vapor to feed ratio, $V:F$	14.18	14.18
End Compositions after mixing the distillate and bottom streams	(0.3, 0.175, 0.275, 0.25)	(0.3, 0.175, 0.275, 0.25)

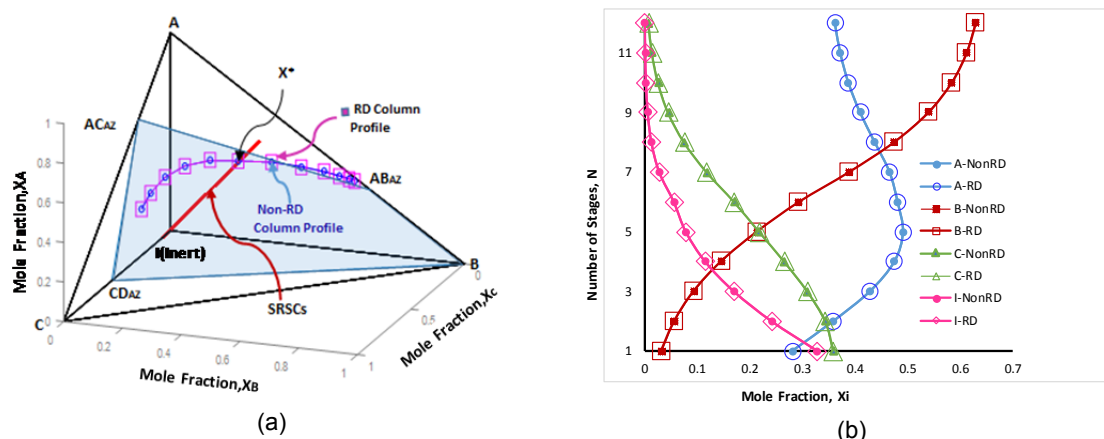


Figure 9. (a) Identical column profiles in triangular diagram. (b) Column profile along the length of the column. The close overlap indicates that the design is feasible.

### 3. Conclusions

A combined graphical-simulation algorithm for the design of hybrid RD columns, is developed using the concepts of attainable region. The design methodology utilizes the concept of visualization of the LFSCs of non-RD column and its intersection with that composition in space at which reaction takes place in RD column. The developed methodology successfully finds promising designs of hybrid RD column, to give desired selectivity in case of single reactant multi-reaction systems. Depending on the specification of number of stages, feed location the developed algorithm generates multiple feasible designs which can be evaluated and compared in terms of capital cost, energy requirement and catalyst loading to determine a good/optimal design for the given set of design goals. In the present work we restrict ourselves to series reaction schemes containing inerts and multi-azeotropes. The next step is to extend the applicability of the developed algorithm to complex reaction schemes and to investigate the effect of inert on the developed algorithm for reactive systems having activity coefficient based kinetics with multi-azeotropes. The method developed here gives excellent starting values for rigorous simulations and for further optimizing the designs in order to obtain maximum selectivity.

### References

- Agarwal, V., Thotla, S. and Mahajani, S. M., 2008a, Attainable regions of reactive distillation. Part I. Single reactant non-azeotropic systems, *Chem. Eng. Sci.* 63 (11), 2946-2965.
- Agarwal, V., Thotla, S. and Mahajani, S. M., 2008b, Attainable regions of reactive distillation. Part II. Single reactant azeotropic systems, *Chem. Eng. Sci.* 63 (11), 2928-2945.
- Amte, V., Sriharsha, N., Malik, R.K., Mahajani, S., 2011, Attainable regions of reactive distillation—Part III. Complex reaction scheme: van de Vusse reaction, *Chem. Eng. Sci.* 66 (11), 2285–2297.
- Amte, V., Gaikwad, R., Malik, R.K., Mahajani, S., 2012, Attainable regions of reactive distillation—Part IV. Inclusion of multistage units for complex reaction schemes, *Chem. Eng. Sci.* 68, 166–183.
- Gadewar, S.B., Malone, M. F., Doherty, M. F., 2002, Feasible Region for a Countercurrent Cascade of Vapor-Liquid CSTRs, *AIChE J.* 48, 800–814.
- Glasser, D., Hildebrandt, D., Crowe, C., 1987, A geometric approach to steady flow reactors: the attainable region and optimization in concentration space, *Ind. Eng. Chem. Res.* 26, 1803-1810.
- Hasan, S.U., Malik, R.K., & Mahajani, S., 2013a, Selectivity engineering with single-feed hybrid reactive distillation columns, *Chemical Engineering Science* 99, 324–334.
- Hasan, S.U., Mahajani, S., & Malik, R.K., 2013b, A conceptual design algorithm for single-feed hybrid reactive distillation column involving azeotropic systems, *Computer Aided Chemical Engineering* 32, 313–318.
- Hasan, S.U., Mahajani, S., & Malik, R.K., 2014a, Selectivity Engineering with Simple and Complex Hybrid Reactive Distillation Columns, *Industrial and Engineering Chemistry Research* 53, 18526–18538.
- Hasan, S.U., Mahajani, S., & Malik, R.K., 2015, Selectivity Engineering with Single Feed Multi-Side Draw Hybrid Reactive Distillation Columns, *Chemical Engineering Journal* 278, 479-491.
- Rooks, R. E., Julka, V., Doherty, M. F., Malone, M. F., 1998, Structure of distillation regions for multicomponent azeotropic mixtures, *AIChE J.* 44(6), 1382-1391.