Effect of Non-Ideal Kinetics on Hybrid Reactive Distillation Models for Selectivity Engineering

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Abstract

Multi-reaction schemes comprise of highly non-ideal mixtures (such as alcohols, esters, aldehydes, ethers, water, etc.) can be quite often found in fine chemical industries. Our previous work [1-5] has looked at finding the designs for *hybrid reactive distillation* (HRD) columns (simple and complex) targeting to attain the anticipated selectivity in complex reaction schemes having ideal kinetics and in the present work we extend it to cover non-ideal kinetics. In particular, it is found that in case of non-ideal kinetics the single feed HRD models to be used are strongly dependent on the number of components involved in a multireaction scheme, contrary to our earlier work in which for ideal reaction kinetics, HRD model depends on total number of products further subjected to side reactions, and is suitable for any number of components. The developed method is applicable to single reactant as well as multi-reactants single-feed HRD columns, provided all the reactants should be saddle in the residue curve map and is limited to four components.

Keywords: Hybrid Reactive Distillation, Non-ideal kinetics, Conceptual Design, Selectivity

1. Introduction

Reactive Distillation (RD) which is a combination of reaction and distillation in a single functional unit can also be effectively used to attain higher or anticipated selectivities in multi-reaction schemes comprises of highly non-ideal mixtures. Synthesis and design of hybrid reactive distillation columns is very challenging because of the complex interactions between reaction and distillation. Therefore, to reach a suitable HRD model, conceptual design and synthesis methods must be adopted. Although the design of HRD models has been investigated in few studies [6-10], but in all these cases, the analysis is restricted to simple reaction schemes and the emphasis is more on increasing the conversion. Less attention has been paid to the conceptual design of HRD models that can be used in multireaction protocols in order to achieve higher or anticipated selectivity for intermediates. We tried to illustrate this point through a series of papers [1-5]. The present work is in continuation of our earlier work on selectivity engineering with simple and complex HRD models that deals with complex reaction schemes with non-ideal kinetics on which we found that almost no work is available in literature. This work gives the guidelines for the design and selection of type of single feed HRD models depending upon whether the given reaction kinetics is ideal or non-ideal. For this purpose, a van de Vusse type hypothetical reaction scheme having ideal and non-ideal kinetics is used as an illustrative example, with the capability of the new approach demonstrated in terms of its ability to provide promising designs of HRD models to get the anticipated selectivity in multireaction schemes.

2. Design Methodology

The methodology starts with introduction of non-RD column (non-Reactive Distillation Column) and then deal with 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.[11] put forward a geometric interpretation of the CSTR in terms of reaction and mixing as process vectors. To find out whether points in the composition space are achievable, they derive the condition that rate vector at that particular point should be collinear with the mixing vector of the feed stream and the product stream. The component material balance of the CSTR indicates a prerequisite. In the case of CSTR, reaction occurs at product composition but on the other hand, in an arbitrary reactor (R), composition at which reaction occurs may not be identical with product composition, therefore collinearity condition is invalid. The reactive composition at which

reaction occurs is dependent on the type of reactor and can be controlled by separation attributes same as in case of reactive distillation.
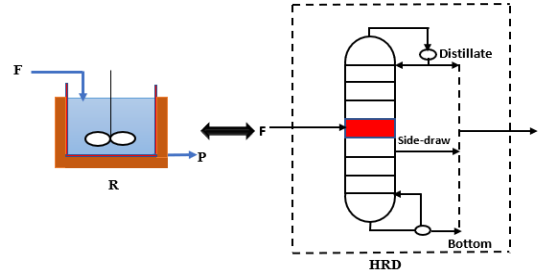

Fig. 1. Correlation between Arbitrary reactor (R) and HRD Column with side draw

Consider HRD side draw column with single reactive stage as shown in Fig. 1. In this column, the reaction does not occur at product stream composition (P), obtained by mixing the top (distillate), bottom and side draw streams. The reactive stage composition also depends on separation attributes such as location of feed, total number of stages, boil-up rate, distillate to feed ratio and side draw to feed ratio. Thus, points of potential reactive stage composition that provides anticipated selectivity in the composition space can be determined with the help of the surface of reactive stage compositions describe in the following section.

2.1. Surface of Reactive Stage Compositions (SRSCs)

Consider an equimolar van de Vusse reaction scheme represented by Eq. (1). In this reaction scheme, except for A to B, all reactions are irreversible with single reactive component A. All reactions are of 1st order except the fourth reaction A to D which is of 2nd order. The reaction kinetic rate constants are represented by $k1, k2, k3, k4$ whose value are taken as 2,1,1,3 respectively. The non-ideal kinetics is given by Eq. (2) and for ideal kinetics (Table 1) the value of activity coefficients of all components is taken as unity.

$$A \underset{undesired\,(k_2)}{\overset{desired\,(k_1)}{\rightleftarrows}} B \xrightarrow{undesired\,(k_3)} C$$
$$A \xrightarrow{undesired\,(k_4)} D$$

(1)

$$\begin{bmatrix} r_A & r_B & r_C & r_D \end{bmatrix} = \begin{bmatrix} -k_1\gamma_A x_A^* - k_4\gamma_A^2 x_A^{*2} + k_2\gamma_B x_B^*, & k_1\gamma_A x_A^* - k_2\gamma_B x_B^* - k_3\gamma_B x_B^*, & k_3\gamma_B x_B^*, & k_4\gamma_A^2 x_A^{*2} \end{bmatrix}$$
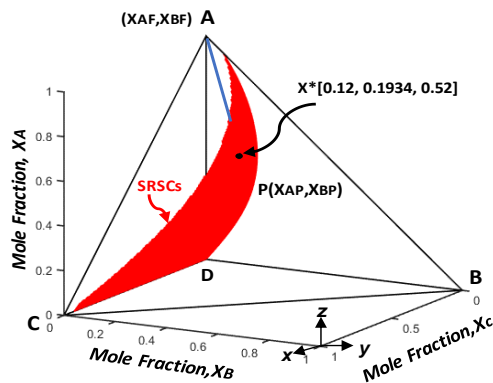
(2)

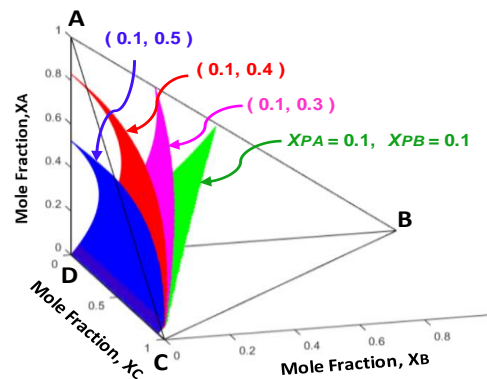Fig. 2. Surface of reactive stage compositions (SRSCs).

Fig. 3. Shifting of SRSCs with variation in desired selectivity

For any arbitrary reactor, material balances for components A and B are given by

$$x_{A,P} - x_{A,0} = \tau . \sum_{k=1}^{nR} r_{k,A}(x^*)$$

(3)

$$x_{B,P} - x_{B,0} = \tau . \sum_{k=1}^{nR} r_{k,B}(x^*) \tag{4}$$

where τ is the residence time and nR represents number of reactions.

Divide (4) by (3) we get,

$$\frac{x_{B,P} - x_{B,0}}{x_{A,P} - x_{A,0}} = \frac{r_B}{r_A} = \frac{k_1 \gamma_A x_A^* - k_2 \gamma_B x_B^* + k_3 \gamma_B x_B^*}{-k_1 \gamma_A x_A^* - k_4 \gamma_A^2 x_A^{*2} + k_2 \gamma_B x_B^*} \tag{5}$$

Where $x_{i,0}$, $x_{i,p}$ are the input and output composition of component i, x^* represents the composition at which reaction is occurring in the reactor. LHS of Eq. (5) represents the slope of straight line connecting point A (x_{A0}, x_{B0}) and point P (x_{AP}, x_{BP}), as shown in Fig.2. One can plot the SRSCs for the quaternary mixture by taking a meshgrid of [x_A^*, x_C^*] and plot x_B^* compositions [by solving a non-linear equation (Eq. 5) at each point of meshgrid; with γ being calculated by *WILSON* model] as shown in Fig. 2. Fig. 3 indicates that with increase in the anticipated selectivity keeping conversion fixed, the feasible reactive stage compositions get reduced.

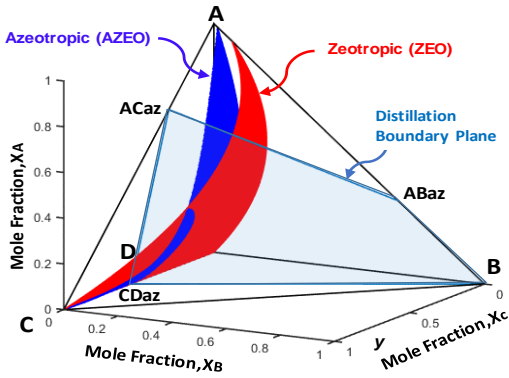## 2.2. Effect of non-ideal kinetics and thermodynamic models on SRSCs

Fig. 4. Effect of non-ideal kinetics on SRSCs for Zeotropic and Azeotropic mixtures.
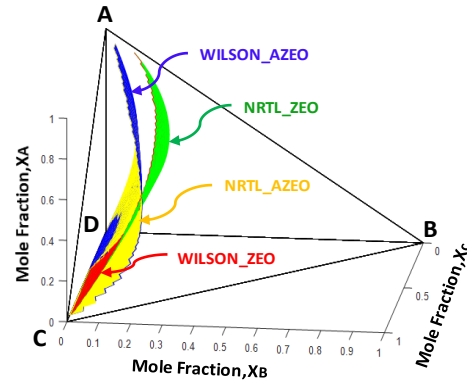

Fig. 5. Effect of thermodynamic models on SRSCs for Zeotropic (ZEO) and Azeotropic (AZEO) mixtures.

Distillation boundaries and non-ideal VLE (vapor-liquid equilibrium) [for multicomponent azeotropic mixture in Fig. 4, see Hasan et al.,[4]; Section 4 (Example 3)] are responsible for the contraction of the feasible reactive stage compositions required for the design of HRD column in case of azeotropic systems. Fig. 4 shows that if non-ideality is present in kinetics as well then, these feasible reactive stage compositions reduces further and thereby increases the design complexity for RD systems. Fig. 5 indicates that there is no effect of thermodynamic models (WILSON & NRTL) on the SRSCs for both zeotropic and azeotropic mixtures.

2.3. Selection of HRD models for ideal and non-ideal kinetics

Hasan et al. [4] developed a design algorithm for complex reaction schemes with ideal kinetics in which the type of HRD models to be used in order to obtain the feasible design of anticipated selectivity is strongly dependent on the nature of reaction schemes i.e. whether in a complex reaction scheme one, two or more products subjected to further side reaction(s). If one product undergoes further side reaction, then simple HRD column (SHRD) is capable to give anticipated selectivity and if two products further subjected to undergo side reactions then HRD side draw column is to be used. In the present example (Eq.1) although only one product further undergoes side reaction, but due to presence of non-ideal kinetics it is found that the anticipated selectivity is achievable by using side draw HRD model. Further we conclude that in case of non-ideal kinetics with three component multi-reaction scheme one has to use SHRD column while for four components multi-reaction scheme with non-ideal kinetics side-draw HRD model is needed. This point will be more clear in following example, the design procedure of which is explained in the next section.

2.4. Design Procedure

Consider a side draw HRD column with single stage of reaction (Fig. 6a) and a reactor followed by separator (Fig. 6b). A systematic approach to a viable design is achieved through HRD column for a given reaction scheme in Eq. (1) using intersection of LFSCs and selected reaction stage composition (*X**). The approach presented here takes

advantage of the fact that division of reaction and distillation attributes of HRD column (Fig. 6a) provide the same performance as the new configuration (Fig. 6b). When the feed stage of the RD column is the reactive stage, the column profiles of the non-RD and RD columns coincide for the same distillation properties. This will be apparent in the example below.

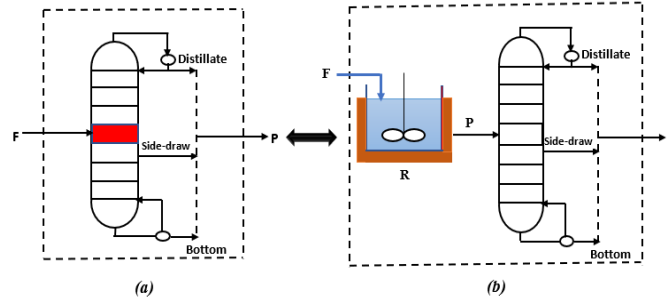(a)   (b)

Fig. 6. (a) HRD column. (b) Reactor separator assembly (Non-RD).

Consider the same reaction scheme represented by Eq. (1) which is chosen as an illustrative example. The reaction takes place in the liquid phase and the assumption of constant molar overflow is valid. Following are the proposed step-by-step design procedure to obtain the anticipated selectivity using HRD column with side draw:

Step 1: First, according to selectivity of intermediate product viz. B, select point P (Fig. 2) in the composition space. This selected point P represents total end composition of HRD side draw column (Fig. 6b), which is regarded as a feed to the Non-RD column (Fig. 6a).

Step 2: Connect point P (0.3, 0.275) and A (1, 0) to get slope of straight-line AP, for plotting SRSCs using Eq. (5) (see Fig. 2).

Step 3: Select any X^* on the curve of SRSCs. For the present case, we have selected $X^* = [x_A^*, x_B^*, x_C^*] = [0.52, 0.1934, 0.12]$.

Step 4: Using the material balances given by Eq. (7-9), compute composition of all components in virtual feed that is to be sent in non-RD column (Fig. 6b). Determine Damkohler number Da, which is the ratio of characteristic liquid residence time to the characteristic reaction time (Eq. 6), by employing material balance to either component A (Eq. 7) or B (Eq. 8) at X^*. Next, find out the composition of C with the help of Eq. 9. Composition of D can be obtained by summation equation.

$$Da = \left(\frac{W_{cat} * k_{ref}}{F} \right) \tag{6}$$

$$x_{A,0} - x_{A,P} + Da\left(\frac{-k_1 \gamma_A x_A^* - k_4 \gamma_A^2 x_A^{*2} + k_2 \gamma_B x_B^*}{k_{ref}} \right) = 0 \tag{7}$$

$$x_{B,0} - x_{B,P} + Da\left(\frac{k_1 \gamma_A x_A^* - k_2 \gamma_B x_B^* + k_3 \gamma_B x_B^*}{k_{ref}} \right) = 0 \tag{8}$$

$$x_{C,0} - x_{C,P} + Da\left(\frac{k_3 \gamma_B x_B^*}{k_{ref}} \right) = 0 \tag{9}$$

Step 5: Specify total number of stages and location of feed (say $N=12$, $Nfl=7^{th}$ stage) with Reboiler as first stage. for present example, location of side draw is underneath the feed location ($Sd= 6^{th}$ stage) because the volatility of component A is greater than the volatility of component C which is the component whose composition is to fix with side draw stream.

Step 6: Next step is to find out parameters so that feed stage of Non-RD column matches with our selected X^*. In order to attain this intersection point, draw family of curves (*FOC*) representing series of LFSCs by first choosing random value of side-draw to feed ratio (say *SD*=0.1) for different values of Boil-up to Feed ratio (V:F) and Distillate to Feed ratio (D:F), as shown in Fig. 7. The range of D:F can be decided on the basis of whether the LFSCs intersects SRSCs of selected X^*. Next in order, the V:F ratio begins at any small value until the performance becomes oblivious

at higher values. Fig. 7a shows three such families of distillate to feed ratio ranges (*0.1 to 0.5*) and boiling to feed ratios (*1 to 10*) at three different *SD* values. As can be seen from Fig. 7, the required selectivity lies near the curve obtained at *SD=0.2*.
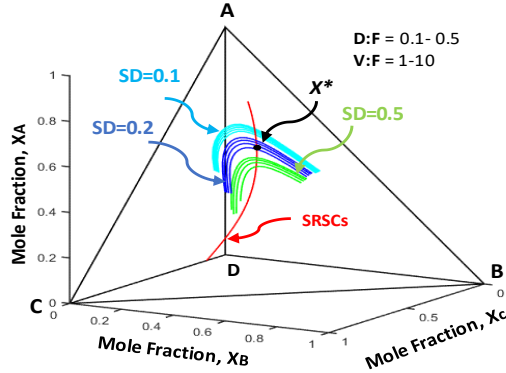

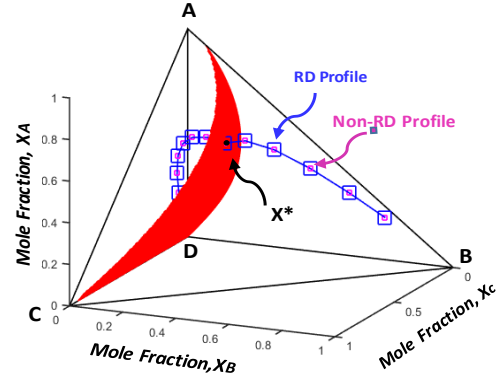Fig. 7. FOC for a range of D:F at different values of V:F and S:F representing LFSCs.

Fig. 8. Identical column profiles in triangular diagram

Step 7: Based on the results shown in Fig. 7, the values of three parameters viz. *SD, D:F, V:F* at which exact match of Non-RD column feed stage with selected *X** are 0.22, 3.225 and 0.321 respectively. Next, the column profile of the Non-RD side draw column (Fig. 4b) is plotted in the 3D composition space (Fig. 8).

Step8: Employing the same parameters used in case of non-RD, a column profile for RD is obtained for feed having single reactant A and feed stage as reactive stage. The profiles match (Fig. 8) indicates that design is executable. Therefore, the anticipated selectivity for given reaction scheme with non-ideal kinetics is attainable through side-draw HRD column with design specifications given in Table 1.

Table 1. Design specifications for HRD Models for ideal and non-ideal reaction kinetics

Kinetics Type	Ideal Kinetics [4]		Nonideal Kinetics [Present work]	
Reaction Scheme	Eq. (1)		Eq. (1)	
Rate Constants	*[k1 k2 k3 k4] = [2 1 1 3]*		*[k1 k2 k3 k4] = [2 1 1 3]*	
RD column configuration	Non-RD SHRD Model	RD SHRD Model	Non-RD Side Draw Model	RD Side Draw Model
Total components, *NC*	4	4	4	4
Components' Volatility Order	B > A > C > D	B > A > C > D	B > A > C > D	B > A > C > D
Total stages, *N*	12	12	12	12
Location of feed, *Nfl*	6th Stage	6th Stage	7th Stage	7th Stage
Flow rate of feed, F	1	1	1	1
Location of Side draw, *Sdl*	-	-	6th Stage	6th Stage
Composition of feed, *Xf*	(0.30, 0.275, 0.0701, 0.3549)	(1, 0, 0, 0)	(0.3, 0.275, 0.0816, 0.3434)	(1, 0, 0, 0)
Total reactive stages, *Nr*	-	1	-	1
Reactive stage Location, *Nrl*	-	6th Stage	-	7th Stage
Damkohler Number, *Da*	-	0.3641	-	0.4741
Distillate to feed ratio, *D:F*	0.3775	0.3775	0.321	0.321
Vapor to feed ratio, *V:F*	2.315	2.315	3.225	3.225
Side draw to feed ratio, *S:F*	-	-	0.22	0.22
End Compositions after virtually mixing the streams	(0.3, 0.275, 0.0701, 0.3549)	(0.30, 0.275, 0.0701, 0.3549)	(0.3, 0.275, 0.0816, 0.3434)	(0.3, 0.275, 0.0816, 0.3434)

3. Conclusions

A combined graphical-simulation algorithm for the design and selection of type of HRD models is developed for complex reaction scheme with non-ideal kinetics. For the same reaction scheme, volatility order, and number of components it is found that for ideal kinetics simple HRD model is sufficient to give the anticipated selectivity while for non-ideal kinetics one has to use HRD side draw model. It is concluded here that to obtain the anticipated selectivity

of any intermediate product in a given complex reaction scheme having non-ideal kinetics the type of HRD model used is strongly dependent on the number of components. For three component reaction schemes with non-ideal kinetics SHRD model is used and for four component reaction schemes with non-ideal kinetics side draw HRD model should be used. The algorithm presented in this work can be easily automated and typically generate multiple designs of anticipated selectivity and is useful where the reactant is of intermediate volatility. The conceptual design algorithm developed here gives good initialization for optimization and rigorous simulations. The next step of the algorithm is to extend its applicability for mixtures (including multiazeotropic) containing more than four components.

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