

SELECTIVITY ENGINEERING WITH REACTIVE DISTILLATION: DETERMINATION OF ATTAINABLE REGION

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Reactive distillation (*RD*), a combination of reaction and separation, holds the potential of giving selectivity/yield much above that offered by the conventional reactors or combination of them. It can be effectively used to improve selectivity of a reaction especially when an intermediate product is desired in series or parallel reactions. In this work, some representative model systems are introduced to obtain attainable region. A series as well as a combination of series parallel reactions (irreversible and mixture of reversible and irreversible reaction systems) were studied with the proposed models and it was found that for the single reactant ideal systems one can obtain almost 100% selectivity for a near quantitative conversion, which is much greater than that obtained in the conventional reactors like PFR and CSTR. These models were also studied for the non-ideal azeotropic systems and it was found that there is a limit to feasible region. The results obtained in the theoretical analysis are supported by experiments on aldol condensation of acetone.

KEYWORDS: reactive distillation, conceptual design, attainable regions, acetone, aldol condensation

INTRODUCTION

Reactive distillation (*RD*) as the name suggests is the integration of reaction and separation in a single piece of equipment. Such an integration can be effectively used to manipulate the concentration profiles of various species to obtain better selectivity for the desired product in the case of a reacting system involving multiple reactions with irreversible or a combination of reversible and irreversible reactions. Most of the work in *RD* has been performed keeping the product purity in mind i.e. treating it more as a distillation column. In our opinion, *RD* can also be viewed as “multifunctional reactor” having the potential of giving desired selectivities.

Attainable Region (*AR*) approach was first introduced by Horn (1964). The concept of *AR* was introduced and developed as a way of representing all possible states that can be reached by a system, given a number of fundamental processes and parameters that can be controlled. Glasser et al. (1987) have examined the *AR* approach using geometric ideas to generate the region and its boundary. They defined attainable region, 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. They introduced a reaction vector to geometrically define the boundary of the attainable region. The concept of *AR* was

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extended to systems with simultaneous separation by Nisoli et al. (1997) who introduced a reaction-separation vector. Gadewar et al. (2002) further extended the approach to a cascade of reactor-separator units. Attainable Region approach is not an optimization technique. It only identifies the feasible region for the production of a desired product. However, it serves an important purpose of generating process alternatives at the conceptual design stage. The approach has been successfully applied to access reactor network synthesis. However, as mentioned above not much work has been reported in the field of reactive distillation.

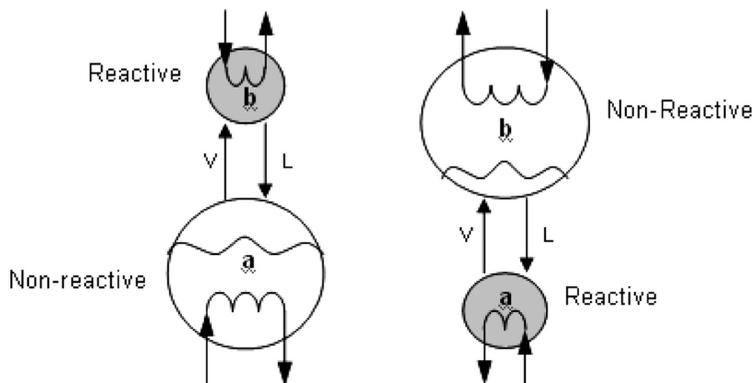
A new approach to construct feasible region for reactive distillation systems has been proposed in this work. A set of simplified model reactor-separator units has been introduced, which are capable of surpassing the performance of the conventional flow reactors, depending on the kinetics and vapor-liquid equilibrium of a given reacting system. The emphasis is on multiple reactions with intermediate product as the desired one. However, the approach can be easily extended to other cases as well. With this method it is expected that one can avoid use of rigorous optimization techniques, at least at a conceptual level, as reactive distillation with its complex behavior and large number of design and operating parameters is still a challenging problem for current optimization routines. These simplified models not only help in knowing the attainable selectivity 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 simplified enough that direct laboratory experiments can be conveniently performed, in the absence of kinetic and thermodynamic data, to obtain the desired representative results. Following two reaction schemes are used for analysis in this work:



Simple kinetic models have been assumed with reactions considered to be elementary and the rate equation given by mole fraction based kinetics. Yield is defined as moles of desired product (B) per mole of reactant fed (A) and conversion is defined as moles of reactant (A) consumed per mole of reactant fed.

MODELS DEVELOPED

Each section or a stage of RD column can be seen as a combination of a reactor and a separator unit. If the reaction takes place on each stage, this reactor separator unit gets repeated along the length of the column. This reactor separator traveling along the length of the column is in a sense analogous to reactor separator units shown in Figure 1 traveling with respect to time (time here refers to the batch time). Both the units can be considered as special cases of batch reactors of which the composition and



Reactive Condenser (RC) Reactive Reboiler (RR)

Figure 1. *Reactive condenser and reactive re-boiler models*

conversion change with respect to time. Study of these models helps us to identify the best possible location of the reactive zone in the column. A conclusion was drawn:

“If reactive condenser (RC) model expands the feasible region in comparison to the conventional flow reactor, one can place reactive zone in rectifying section and if reactive reboiler (RR) model expands the feasible region in comparison to the conventional reactor system with best selectivity curve, reactive zone may be placed in the stripping section.”

Damköhler number (Da) is a dimensionless number characterizing the extent of a reaction and is given by equation 4. The study on the effect of Da by solving the model equations given below revealed that with a decrease in its value there is an increase in performance of RC/RR models up to a certain level after which there is no effect as shown in Figure 2. We also found that instead of using a single reactive stage, if we divided the catalyst in number of stages (i.e. keeping the overall Da as constant) there is an increase in performance when the reactant is lighter for the RC model indicating better separation on the reactive stages. Thus modification of the above two models led us to come up with two more model systems namely the *reactive rectification* and *reactive stripping* as shown in Figure 3. These can be considered as the multistage surrogates of the RC and RR model respectively with reaction taking place on each column stage.

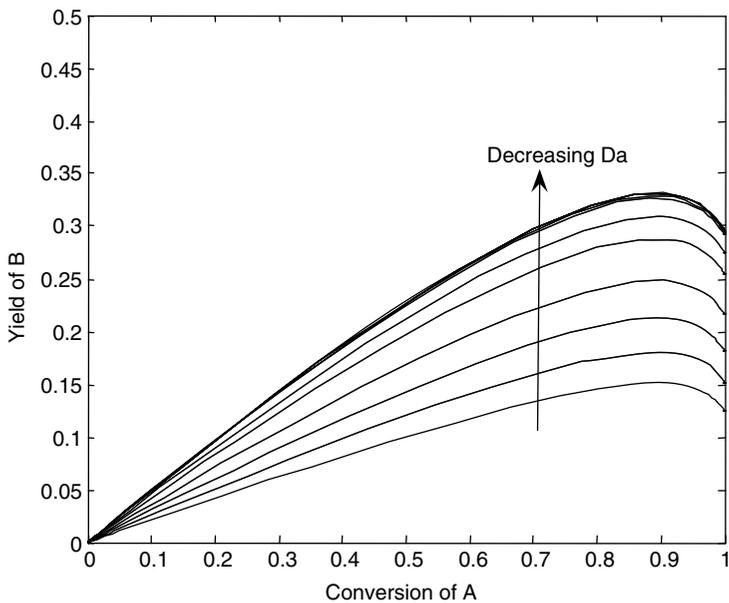


Figure 2. Effect of Damköhler number for *reactive condenser* model

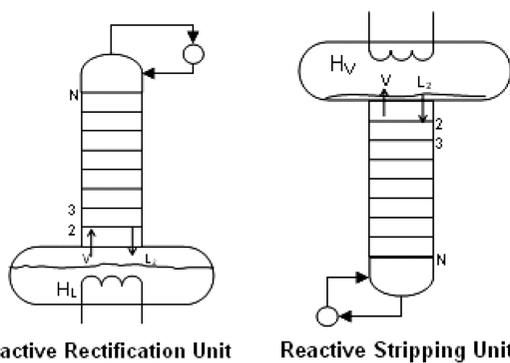


Figure 3. *Reactive rectification and reactive stripping models*

MODEL EQUATIONS

Reactive condenser

- a) Overall and component material balances around the re-boiler:

$$\frac{d(H_{ia})}{d\xi} = H_{ia} \left(-1 + \frac{L}{V} \right); \quad \frac{d(x_{ia})}{d\xi} = (x_{ia} - y_{ia}) + \frac{L}{V} (x_{ib} - x_{ia})$$

for $i = 1, 2, \dots, \text{NC}-1$ (3)

where $d\xi = \frac{V}{H_{ia}} dt$, also known as warped time.

- b) Overall and component material balances around the condenser:

$$-\frac{L}{V} + 1 + \text{Da} \sum_{k=1}^R v_{T,k} r'_k(x_b) = 0; \quad -\frac{L}{V} x_{ib} + y_{ia} + \text{Da} \sum_{k=1}^R v_{i,k} r'_k(x_b) = 0$$

for $i = 1, 2, \dots, \text{NC}-1$ (4)

- c) where $\text{Da} = \frac{k_{\text{ref}} H_{\text{cat}}}{V}$
 VLE equation

The vapor leaving the re-boiler is assumed to be in equilibrium with the liquid in re-boiler

$$y_{ia} = f(x_{ia}) \quad \text{for } i = 1, 2, \dots, \text{NC}-1 \quad (5)$$

Similarly equations were developed for the *reactive re-boiler* model.

Reactive rectification

- a) Overall and component material balance on the re-boiler (stage 1)

$$\frac{1}{H_1} \frac{d(H_1)}{d\xi} = -1 + \frac{L_2}{V_1};$$

$$\frac{d(x_{i,1})}{d\xi} = (x_{i,1} - y_{i,1}) + \frac{L_2}{V_1} (x_{i,2} - x_{i,1}) \quad \text{for } i = 1, 2, \dots, \text{NC}-1 \quad (6)$$

where $d\xi = \frac{V_1}{H_1} dt$.

b) Overall and component material balance on the j th stage (for $j = 2$ to $N-1$)

$$-l_j + l_{j+1} + Da \sum_{k=1}^{k=R} v_{T,k} r'_k(x_j) = 0;$$

$$l_{j+1} x_{i,j+1} - l_j x_{i,j} + y_{i,j-1} - y_{i,j} + Da \sum_{k=1}^{k=R} v_{i,k} r'_k(x_j) = 0$$

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

where $l_j = \frac{L_j}{V}$ and $Da = \frac{k_{ref} H_{cat}}{V}$.

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

$$-l_N + 1 + Da \sum_{k=1}^{k=R} v_{T,k} r'_k(x_N); \quad -l_1 x_{i,1} + y_{i,2} + Da \sum_{k=1}^{k=R} v_{i,k} r'_k(x_N) = 0$$

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

Along with these equations the VLE equations are also valid for each stage except condenser which is a total condenser. Similarly equations were developed for the reactive stripping model.

CONTINUOUS MODELS

The continuous version of *reactive rectification* model is shown in the Figure 4a. Here number of units of *reactive rectification/ reactive stripping* are repeated with a continuous feed and continuous output.

However, if we closely examine the model in Figure 4a, it will be revealed that the feed to the subsequent units has significant amount of the desired intermediate component, B , and thus with each succeeding unit a better separation will be desired thus requiring more effort. If, however the stages are stacked on the top of the unit one and the vapor flow is increased, we can observe the same or even better performance. This is because

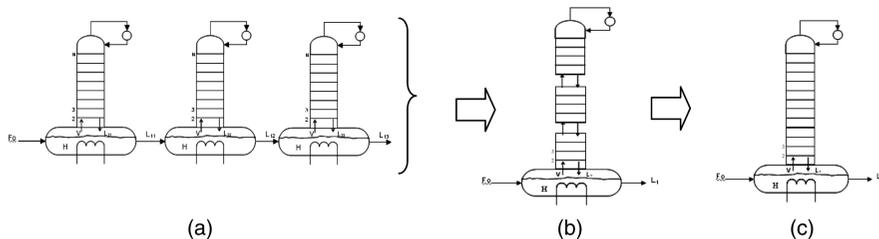


Figure 4. Continuous reactive rectification models

the feed to the subsequent units in Figure 4b is purer in reactant as compared to that in Figure 4a. The unit thus obtained is a typical *continuous reactive rectification* model shown in Figure 4c. Similarly one can have *continuous reactive stripping* if desired. Again it should be noted that this system is bound to have practical limitations in reality and it will lead to unrealistic design (e.g. very large number of stages) but we are here interested in obtaining the bounds imposed by thermodynamics and kinetics on selectivity. Moreover, the theory developed can be effectively applied to the real system with practical constraints to maximize the yield/selectivity of the desired product. The model equations for *continuous reactive rectification* are given below:

- a) Overall and Component Material Balance on 1st Stage of the Figure 4c gives:

$$F_o/V - l_1 + l_2 - 1 = 0; \quad F_o x_{i,f}/V - l_1 x_{i,1} + l_2 x_{i,2} - y_{i,2} = 0$$

for $i = 1, 2, \dots, NC-1$ (9)

where $l_j = \frac{L_j}{V}$.

- b) Overall and Component Material Balance on jth Stage (for $j = 2$ to $N-1$)

$$l_{j+1} - l_j + Da \sum_{k=1}^R v_{T,k} r'_k(x_j) = 0;$$

$$l_{j+1} x_{i,j+1} - l_j x_{i,j} + y_{i,j-1} - y_{i,j} + Da \sum_{k=1}^R v_{i,k} r'_k(x_j) = 0 \quad \text{for } i = 1, 2, \dots, NC-1 \quad (10)$$

- c) Overall and Component Material Balance on Nth Stage (condenser)

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

$$y_{i,N-1} - l_N x_{i,N} + Da \sum_{k=1}^R v_{i,k} r'_k(x_N) = 0 \quad \text{for } i = 1, 2, \dots, NC-1 \quad (11)$$

Similar to *continuous reactive rectification*, *continuous reactive stripping* can be modeled. In such a model there will be number of reactive stages and a non-reactive condenser with a continuous vapor feed and a continuous vapor output.

YIELD VS CONVERSION FOR REACTIVE RECTIFICATION/STRIPPING

The critical value of Da obtained for the RC/RR model below which there was no improvement in performance (Figure 2) was divided among "N" number of stages and the calculation was performed at several values of "N." The yield vs conversion plot is shown in Figure 5. As the number of stages is increased i.e. the Da per stage is decreased

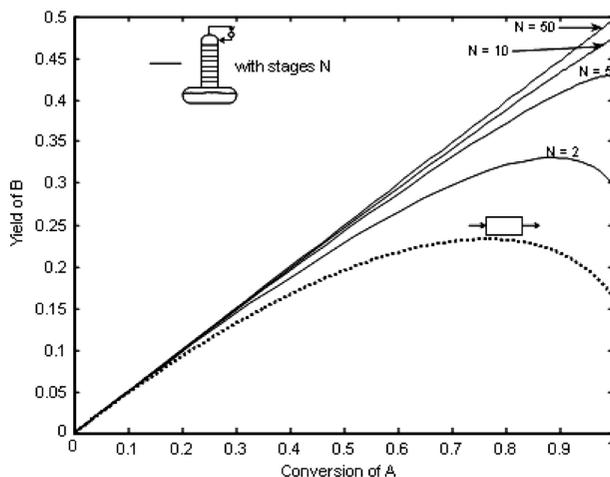
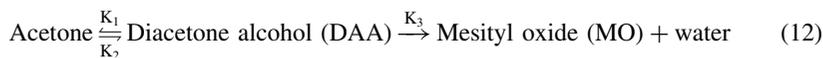


Figure 5. Effect of number of stages (N) on feasible region of *reactive rectification* unit

by keeping overall Da constant, the performance increases and for the system wherein the reactant is the lightest, almost 100% selectivity is observed for 100% conversion (i.e. virtually no formation of the side products). This trend of increasing selectivity with the division of Da on the reactive stages has also been observed through experiments and the results are presented later. As expected, the region expands beyond the one predicted by the RC model, especially at higher conversion. Similar results were obtained with the *reactive stripping* model for the case wherein, the reactant is less volatile than the desired intermediate product. In other words, for a single reactant with simple kinetics and ideal VLE behavior, one can claim with confidence that the selectivity close to 100% may be realized with RD and there are no bounds to the attainable region imposed by the kinetics and thermodynamics (VLE) of the system. The exceptionally high yield can be explained on the basis of the composition profiles of *reactive rectification* unit as shown in Figure 6. The presence of the reactant on the reactive stages and virtual absence of product on the reactive stages lead to such high selectivities.

To validate the theory put forth experimentally, batch reactive distillation (*BRD*) runs were performed on acetone system with a non-reactive reboiler and reaction occurring only on the stages. Dimerization of acetone gives diacetone alcohol (*DAA*) which on further dehydration produces mesityl oxide (*MO*). Aldol condensation of mesityl oxide and acetone also produces heavier products, such as isophorone.



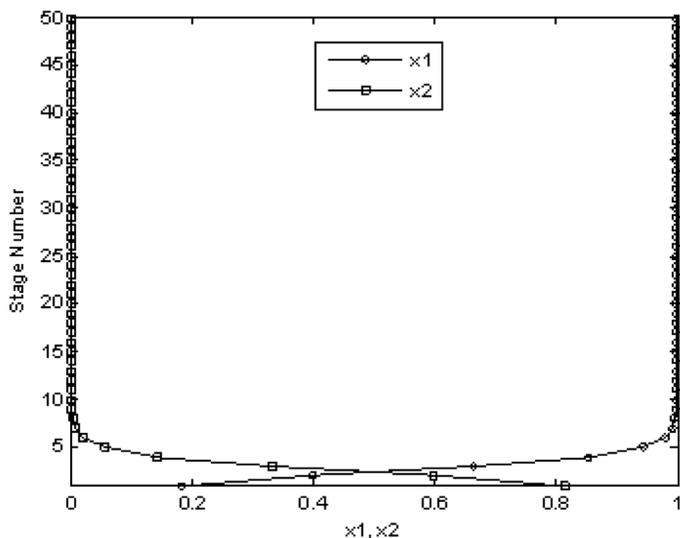


Figure 6. Composition profiles for *reactive rectification* at 90% conversion

The system is a non-azeotropic system with acetone being the lightest and one can expect *reactive rectification* to give best performance. Figure 7 shows experimental results on the acetone system. The figure shows that with the increase in number of stages but keeping the total catalyst loading same (i.e. total Da constant), there is an improvement in selectivity towards DAA as predicted by the theory presented above.

NON-AZEOTROPIC SYSTEMS

For the series and series parallel reaction schemes given in equations 1 and 2, it is well known that 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. Since B is the desired product, the conversion of the first reaction needs to be maximized. The feasible region obtained by *reactive rectification/reactive stripping* model for all the cases considered in Figures 8a and 8b are able to surpass all other reactors. As mentioned before the Da/N value for *reactive rectification/reactive stripping* models is sufficiently small to obtain the best possible yield. Thus for an irreversible series reaction, the region obtained by *reactive rectification/reactive stripping* can be described as the “Attainable Region” and is shown in the Figure 9. For non-azeotropic systems *reactive rectification* model gives the best selectivities when reactant is lighter than the desired product and *reactive stripping* gives the best selectivities when reactant is heavier than the desired product, irrespective of the absolute values of rate constants and relative volatilities.

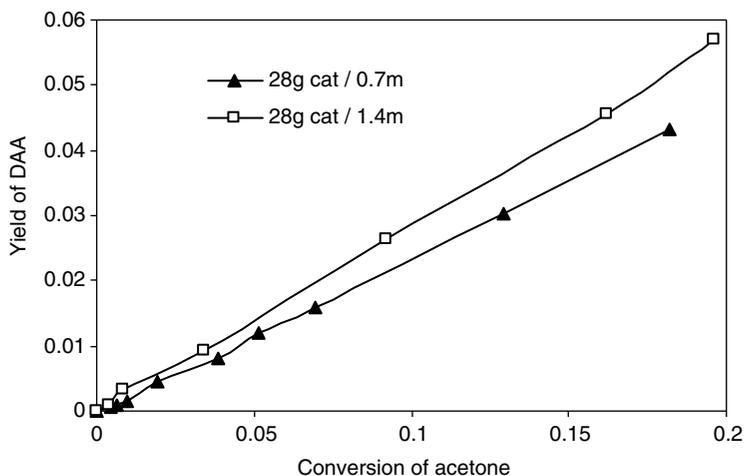


Figure 7. Yield vs conversion at 28g catalyst loading and 0.6KW re-boiler duty

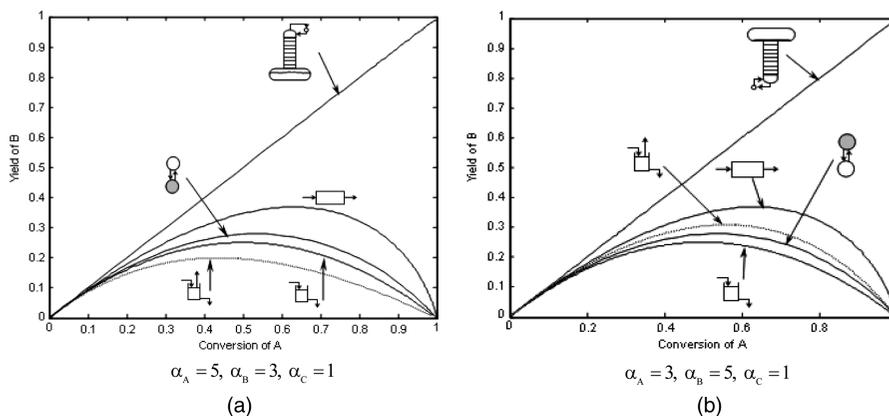


Figure 8. Feasible regions with different relative volatilities for reaction system $A \rightarrow B \rightarrow C$

AZEOTROPIC SYSTEMS

The 100% selectivity in our earlier case was possible because there were no phase equilibrium constraints on the system and a reaction with sharp split was made possible using the above models. However, the presence of azeotrope between the reactant and the desired product limits the selectivity of the desired product and it may not be possible

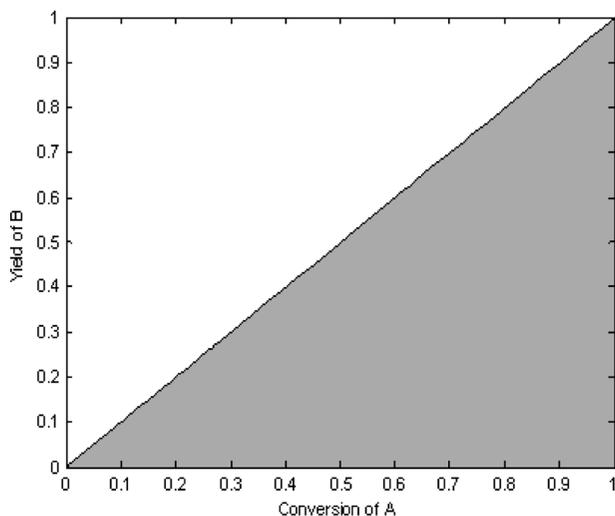


Figure 9. Attainable region for non-azeotropic systems

to surpass a certain performance level with a system where both reaction and separation take place simultaneously. As an example, a case with maximum boiling azeotrope between reactant and desired product is shown in Figure 10. Simple kinetics is assumed with reactions considered to be elementary and the rate equation given by mole fraction based kinetics. The rate constant for both the reactions are assumed to be equal. The yield vs conversion plot for such a system is shown in Figure 11. Clearly, the residue curve map (RCM) is divided into two zones with a distillation boundary. In one zone, *A* is the unstable point and in the other zone *B* is the unstable point. For this kind of system, the region wherein *A* is the lightest, *reactive rectification* gives 100% selectivity up to the certain conversion levels but once the azeotropic composition is reached the performance decreases drastically. The curve actually follows the distillation boundary. Because of the maximum boiling azeotrope there is presence of *B* (shown in Figure 12) on the reactive stages instead of pure *A* and the performance decreases sharply. If we closely analyze the system it is revealed that for a large number of stages the *reactive rectification* is not able to cross the distillation boundary. The use of a PFR in series with *reactive rectification* can expand the region as shown in Figures 13a and 13b.

DISCUSSION

The methodology developed for obtaining the attainable region of RD is quite efficient. The two models i.e. the RC and RR models give the best possible location of the catalyst in the distillation column. For nonazeotropic systems one can obtain 100% selectivities for

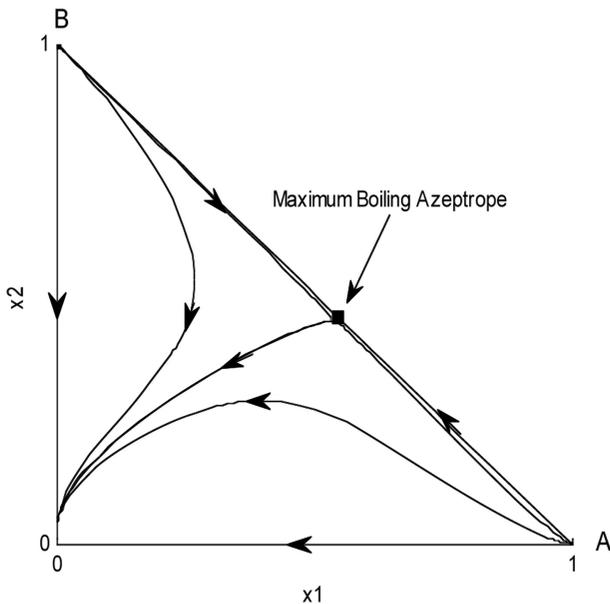


Figure 10. Residue curve map for maximum boiling azeotrope between A-B

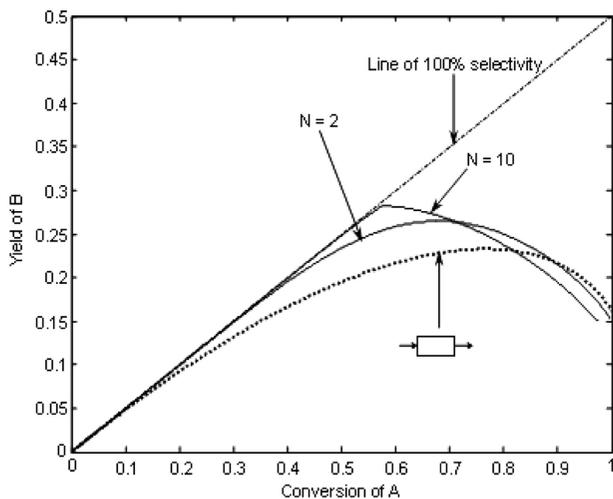


Figure 11. Yield vs conversion plot for maximum boiling azeotrope b/w A-B for reaction system $2A \rightarrow B$, $A + B \rightarrow C$: N is the number of stages required in the *reactive rectification unit*

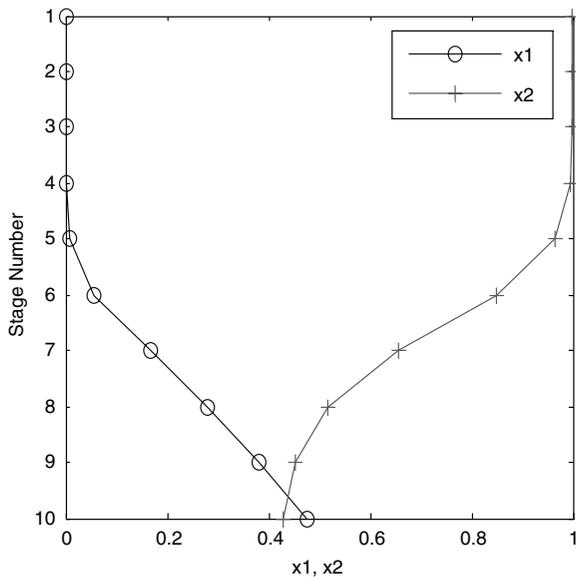


Figure 12. Composition profile at 70% conversion

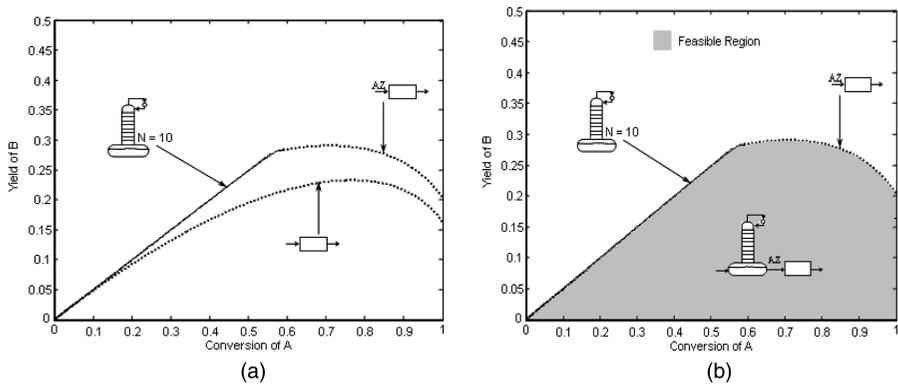


Figure 13. Yield vs conversion plot for maximum boiling azeotrope b/w A-B for reaction system $2A \rightarrow B$, $A + B \rightarrow C$: N is the number of stages required in the *reactive rectification* unit

the entire range of conversion with *reactive rectification* model when the reactant is lighter than the desired product and with *reactive stripping* unit when the reactant is heavier than the desired product. However, for azeotropic systems it was found that when the azeotrope is present between reactant and desired product there is a limit to selectivity. In these cases the design strategy discussed can be followed to obtain the maximum possible region of the concentration space. It must be noted that the present analysis does not consider the mass transfer effects. It is developed for a single reactant system, though it can be extended further to the general multiple reactant system as well.

NOMENCLATURE

ALPHABETIC

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 kth reaction, moles/s-catalyst loading
v	V/L ratio
x, y	Liquid, Vapor composition respectively

GREEKS

α	Relative Volatility
ξ	Warped time
ν	Molar coefficient in reaction equation

SUBSCRIPTS

a	Reboiler unit
b	Condenser unit
i	ith component
j	jth Stage
l	Liquid side
NC	Total number of components
o	Initial
ref	Reference Component

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