Impact of disturbance magnitudes and directions on the dynamic behavior of a generic reactive distillation

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Abstract

The dynamic behavior for a high-purity/high-conversion reactive distillation is investigated. The impact of disturbance magnitudes and directions on both open loop and closed loop stability of the system is studied. Excess of less volatile reactant in two-reactant-two-product generic reactive distillation is found to enhance open loop stability, but decreases the products purity. However, excess of more volatile reactant trigger the system to another steady-state. Open loop changes in the manipulated variables (i.e. vapor boilup from the reboiler and reflux rate from the condenser) in certain directions are found to be intolerable due to their effect on both the reaction kinetics and the fractionation capacity of the column. The performance of the open loop system is improved significantly with the inclusion of internal inventory control of one of the reactants but this has been found to be insufficient when there is a change in some inputs in certain directions. Steady-state rating analysis on the system suggests that the limitations on certain inputs could be resolved by including a single-end controller, which will act to maintain the separation capacity of the column and thus stabilizes the system.
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1. Introduction

Because of environmental and economic considerations, researchers in both industry and academia have put tremendous efforts in process intensification. Reactive distillation is one of such promising operations where by reaction and distillation takes place in a single distillation column. Reactive distillation can, in some systems, provide an alternative to conventional multiunit flowsheets, which typically include a reactor followed by a separation section with recycles back to the reaction section. Some of reactive distillation advantages can be summarized as follows:

- Product selectivity can be improved due to a fast removal of reactants or products from the reaction zone.
- Reactive distillation could lead to capital savings as two process steps can be carried out in the same vessel.

- If reactive distillation is applied to exothermic reaction, the reaction heat can be used for vaporization of liquid, thus leads to savings of energy costs.
- Reactive distillation conditions could allow azeotropes to be reacted away.

Although reactive distillation might be an attractive alternative to the conventional multiunit processes, it can be effective for only a fairly small class of chemical systems because of some inherent limitations. Reactive distillation is particularly possible when reactants and products have suitable volatility to maintain high concentrations of reactants and low concentrations of products in the reaction zone. The reaction rates must be comparable to those in the reactor at temperature suitable for distillation.

The potential advantages of reactive distillation could be negated by improper choice of reactant to be run in excess in the reactive zone whenever it is needed to avoid substoichiometry balance. Thus, it is possible to decrease conversion by increasing the amount of catalyst under

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certain circumstances [1]. Increased separation capability could decrease process performance [2].

Numerous studies have been conducted on understanding the fundamental thermodynamics and kinetics in the operation of the columns [3–6]. Steady-state model analysis as well as steady-state multiplicities has been considered in detail by many researchers. Taylor and Krishna [7] presented a detailed review on the modeling of various reactive distillation processes. Recently, several papers have emerged in literature on closed loop performance of reactive distillation system [8–11].

However, successful commercialization of reactive distillation technology requires careful attention to the modeling aspects, including column dynamics, even at the conceptual design stage [12]. The design and operation issues for reactive distillation systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The introduction of an in situ separation function within the reaction zone leads to complex interactions between thermodynamic vapor–liquid equilibrium, intra-catalyst dilution (for heterogeneously catalyzed processes) and chemical kinetics.

Another area of concern in the study of reactive distillation system is the impact of disturbance magnitudes and directions in dynamic behavior of both open loop and closed loop model of reactive distillation. In a typical reactive distillation column, the regions of intense mass transfer are in the middle of the column where the reactive zone is usually located, while the ends of column are essentially used for purification. These regions are more sensitive to disturbance directions as compared to the ends of columns.

The aim of this paper is to investigate the dynamic behavior of high-purity/high-conversion generic reactive distillation system. The effect of disturbance magnitudes and directions on the stability of both open loop and closed loop system of reactive distillation is quantitatively explored. The open loop performance of the system is explored with and without the inclusion of internal composition inventory controller. The impact of certain inventory control loops on the dynamic stability of the system is studied. This investigation is essential to gain a better understanding of this generic class of reactive distillation. In addition, the study will facilitate a better understanding of a similar system and will help in the application of an advanced process control.

For an effective control of a reactive distillation system, the process control engineer needs to understand the impact of disturbance magnitudes and directions on the dynamic behavior of the system. This is because the effectiveness of disturbance suppression in a multivariable control system depends strongly on the direction of disturbance [13]. This study will also provide valuable information on the importance of maintaining a correct stoichiometric balance between the feeds in both open and closed loop multi-feed reactive distillation column.

2. Process description

Among several chemical systems, two-reactant-two-product reactions have received wide application in reactive distillation technology [14]. In this work, we consider an ideal two-reactant-two-product reactive distillation column. The reactive column is shown in Fig. 1. It consists of a reactive section in the middle with nonreactive rectifying and stripping sections at the top and bottoms, respectively. The
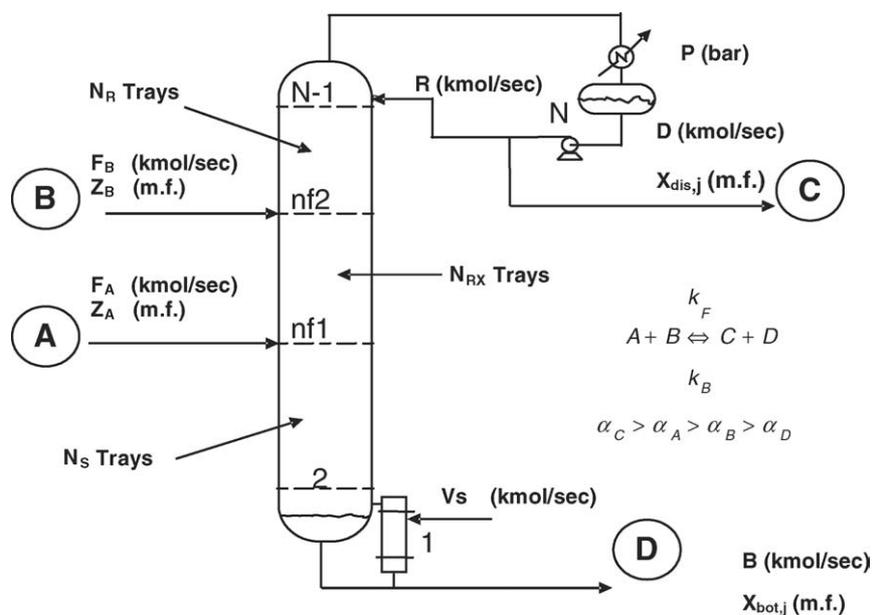

Fig. 1. Distillation column.

elementary reversible reaction occurring in the reactive zone is:

$$A + B \Leftrightarrow C + D$$

The task of the rectifying section is to recover reactant B from the product stream C. In the stripping section, the reactant A is stripped from the product stream D. In the reactive section, the products are separated in situ, driving the equilibrium to the right and preventing any undesired side reactions between the reactants A (or B) with the product C (or D). The reactive sections contain N_{RX} trays. The rectifying section contains N_R trays, and the stripping section below the reactive section contains N_s trays. The column is numbered from the reboiler to the condenser.

The physical properties and kinetic data are provided in the work of Luyben [15]. The process dynamic model for this process is given in Al-Arfaj and Luyben [8]. The base-case conditions for this study are summarized in Table 1. The model assumptions are:

- Ideal vapor–liquid equilibrium.
- Equimolar overflow except in the reaction zone where the vapor boilup changes due to heat of reaction, which vaporizes some liquid on each tray.
- Constant relative volatilities. The volatilities of the components are such that $\alpha_D < \alpha_B < \alpha_A < \alpha_C$.
- Fixed heat of reaction and vaporization.
- Saturated liquid feed and reflux.

We have considered a simplified process model in the present work in order not to cloud the picture with the specific complexities that are typical of many real chemical systems. The simplified process model used in this work is developed to capture the essential dynamics and qualitative properties of a typical reactive distillation column. This will help gaining a better understanding of the generic behavior of this complex

Table 1
Base steady-state conditions

	Variables	Steady-state conditions
Column specifications	Pressure (bar)	9
	Stripping section	7
	Reactive section	6
	Rectifying section	7
Flowrates	Vs (kmol/s)	0.0285
	R (kmol/s)	0.0331
	D (kmol/s)	0.0126
	B (kmol/s)	0.0126
X_{dis}	A	0.0467
	B	0.0033
	C	0.9501
	D	0.0000
X_{bot}	A	0.0009
	B	0.0445
	C	0.0000
	D	0.9545

system, which in return will improve our understanding and analyses on the behavior of the real chemical systems.

3. Dynamic scenarios

The effect of disturbances is studied in order to investigate the dynamic performance of the system. The dynamics of the system under these changes were studied for three scenarios:

1. *Open loop (OL)*: Only the level control loops are closed while F_A, F_B, Z_A and Z_B, Vs and R could be sources of disturbance.
2. *Open loop with internal composition control (OL + IC)*: In addition to level control loops, the internal composition is controlled by feed flowrate. This reduces the number of disturbance by assigning one of the feed flowrates to control the composition.
3. *Single-end control (CL)*: In addition to OL + IC loops, a composition loop is closed by manipulating either Vs or R to control one of the product compositions, which in turn, reduces the disturbance variables by one more.

The main process variables that are considered as sources of disturbances are:

1. Feed flowrates (F_A (kmol/s), F_B (kmol/s))
2. Vapor boilup (Vs (kmol/s))

The effect of feed compositions (Z_A and Z_B) disturbance and reflux flowrate (R, kmol/s) disturbance were studied and will be discussed briefly as they are somewhat similar to those of flowrates and vapor boilup disturbances.

This study considers the model configuration where vapor boilup and reflux flowrate could be the manipulated variables if the system is operated in closed loop mode. In order to investigate the dynamic behavior of the system, three magnitudes (2, 5 and 10%) in both positive and negative directions are studied for each of the process disturbance variables.

4. Open loop model (OL)

4.1. Feed flowrates

Fig. 2 shows the responses of the system to different step changes in both magnitudes and directions of feed flowrate of reactant B (F_B). In this case, the reflux rate, vapor boilup, feed flowrate of reactant A and feed compositions are kept constant at their steady-state values. Fig. 2a shows the impact of this disturbance in the kinetic region of reactive distillation. Excess of reactant B, the heavier reactant, in the reactive zones slightly increases the rate of product formation. This is primarily due to fact that reactant B will concentrate more in the liquid phase and will react with the available reactant A whenever it is available in excess.

On the other hand, reducing F_B (see Fig. 2) has a severe impact on the dynamic behavior of the system, and
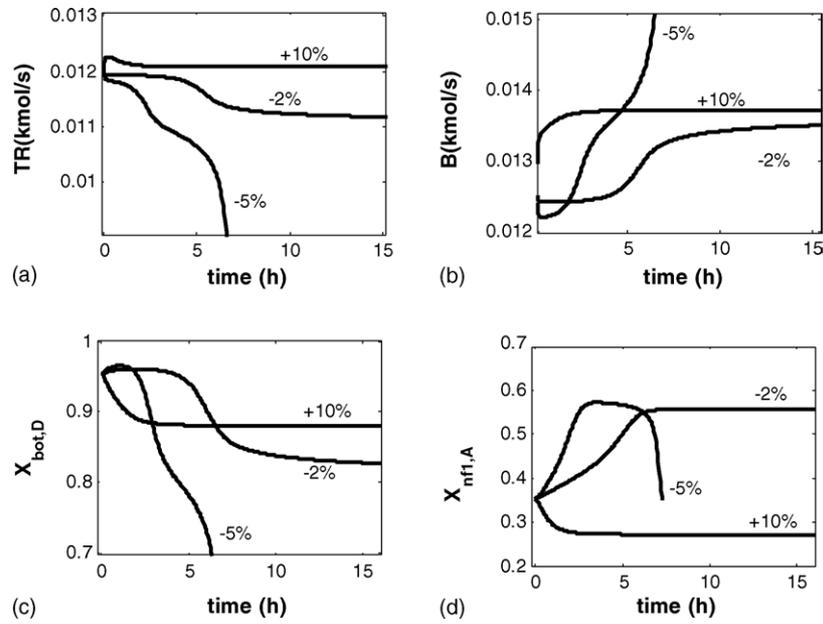
Fig. 2. Dynamic responses of the system to different magnitude changes in feed F_B: (a) total reaction rate; (b) bottoms flowrate; (c) composition of product D in the bottoms; (d) internal composition of reactant A in tray nf1.

consequently its stability. Reducing F_B by 2% causes the total product formation rate to drift to another steady-state. Further decrease in feed flowrate F_B will result in an unstable operation as the bottoms flowrate will increase unbounded (Fig. 2b) and consequently the distillate flowrate drops to zero. The impact of excess of reactant B concentration in the column is reflected by an increase in bottoms rate in similar proportions to the magnitude of disturbance as shown in Fig. 2b.

Increasing F_B has the advantage of increasing the conversion and enhancing the system stability, yet it decreases products purity as shown in Figs. 2c as well as reducing reactant A concentration in the reactive zone as shown in Fig. 2d.

Fig. 3 shows the responses of the system when reactant A flowrate (F_A) is changed. Fig. 3a shows a sharp drop in total product formation rate when F_A is increased. Increasing the flowrate of reactant A in the column seems to have
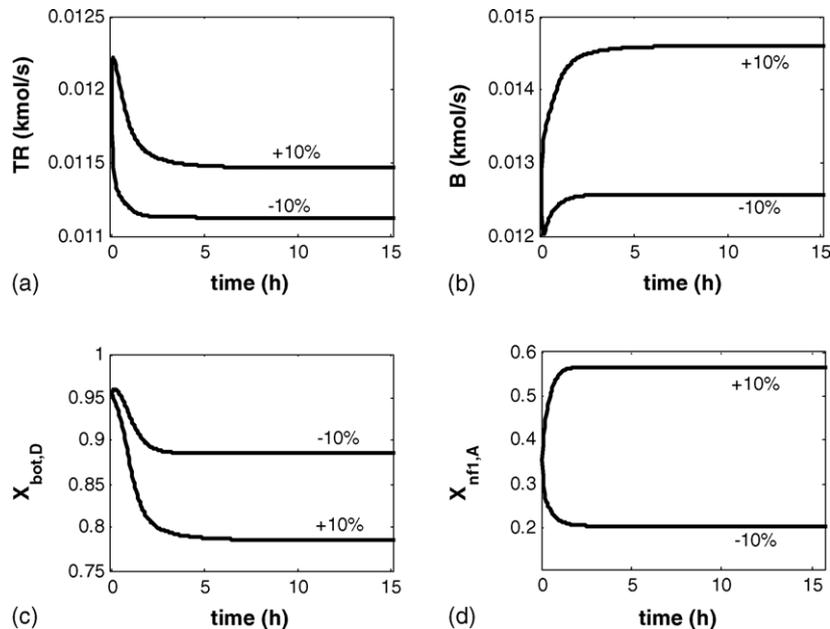

Fig. 3. Dynamic responses of the system to different magnitude changes in feed F_A: (a) total reaction rate; (b) bottoms flowrate; (c) composition of product D in the bottoms; (d) internal composition of reactant A in tray nf1.

the same effect as decreasing the flowrate of the reactant B (F_B), i.e. drift to new steady-state. The rapid buildup of reactant A concentration in the reactive zone decreases the system stability because an excess of a more volatile reactant A will demand an increase in heat duty of the system (which is fixed in this scenario) in order to strip out any unreacted A from product D. On the other hand, decreasing the feed flowrate of reactant A decreases the total product formation rate in reactive zone without drifting or destabilizing the system.

Drifting the system either to another state or to completely unstable conditions when F_A is increased or when F_B is decreased is closely associated to the resulted substoichiometric balance in the reactive zone. This is further studied by investigating the reaction kinetics on reactive trays by ±2% change in F_A and F_B as disturbances. Fig. 4 shows the effect of disturbances on reaction rate in some selected reactive trays. The trays in reactive zone are numbered from bottoms to the top. Both decreasing the feed F_B and increasing the feed F_A in the column results in insufficient concentration of reactant B, and consequently decreases the rate of products formation in the reactive zone. The effect becomes most significant in the first reactive tray (nf1) where the product formation rate is the highest at the base steady-state before introducing any disturbances. The highest steady-state reaction rate is in tray nf1 of reactive zone, which is reasonable as that is where we have the highest concentration of reactant A, the limiting reactant in liquid phase. The effect of reactant B deficiency is the rapid accumulation of concentration of reactant A in the stripping section, which will require more heat to vaporize it. Since in this scenario (OL) the separation capacity is fixed by keeping both the reflux rate and vapor boilup constant, decreasing the feed F_B or increasing the feed F_A will result in flooding the stripping section with an unreacted excess A, which in turn destabilizes the system or shift it to another state.

In general, increase in F_B has similar effects as decrease in F_A. One would expect the other way around is true, i.e. decrease in F_B or increase the feed F_A, would have the same effect, but it is not. Reducing the feed flowrate of reactant B more than 2% is intolerable as it makes the system unstable, while increasing F_A up to 10% merely drifts the system to another stable steady-state. The reason behind that is as follows: when F_A is increased at fixed vapor boilup, more reactant A will leave the bottoms of the column as excess reactant. On the other hand, when F_B is reduced, less than the required amount of reactant B will be available, which upsets the reaction kinetics and thus destabilizes the system.

4.2. Feed compositions

In the steady-state design, the feed composition of reactant A feed is 100% A and similarly 100% B for reactant B feed. In order to study the effect of feed composition, two cases are studied in which feed composition is changed
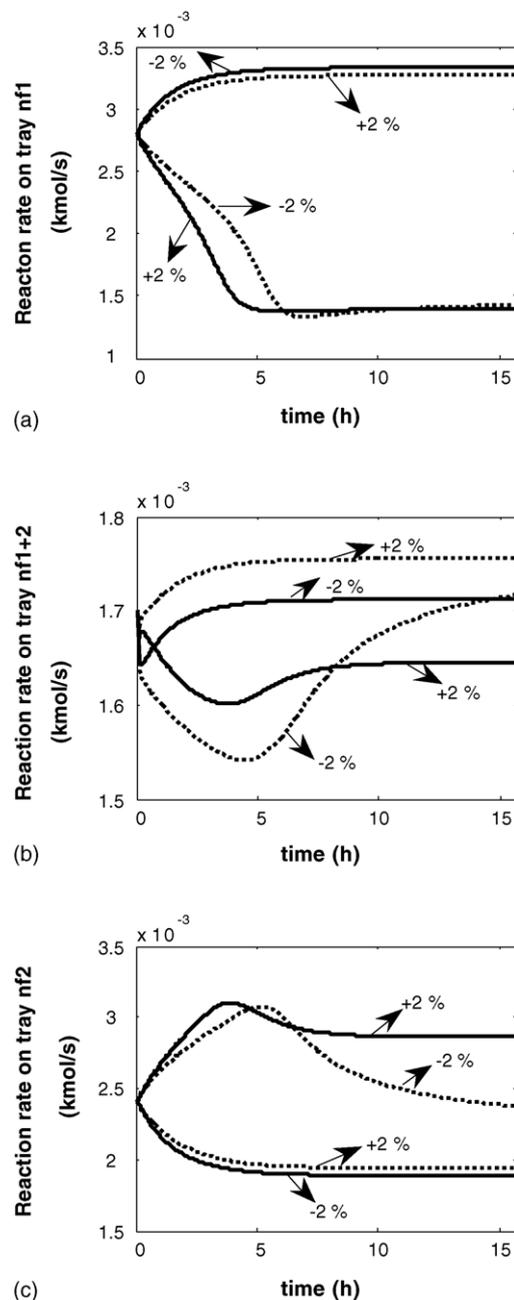

Fig. 4. Responses of the reaction rate in reactive trays to step changes in F_B (- - -) and F_A (—): (a) reactive tray nf1; (b) reactive tray nf1 + 2; (c) reactive tray nf2.

by introducing some impurities from the other reactant, i.e. impurity of reactant A in reactant B feed and impurity of reactant B in reactant A feed.

In general, introducing reactant B in reactant A feed is found to be tolerable similar to increasing F_B since both of these changes will result in more of reactant B in the system, but as they differ in the point where this increase is introduced, the dynamic behavior is different. The reaction rate decreases because of the reduction of reactant A in the reaction zone as a result of decrease in the amount of fresh reactant A entering the column.
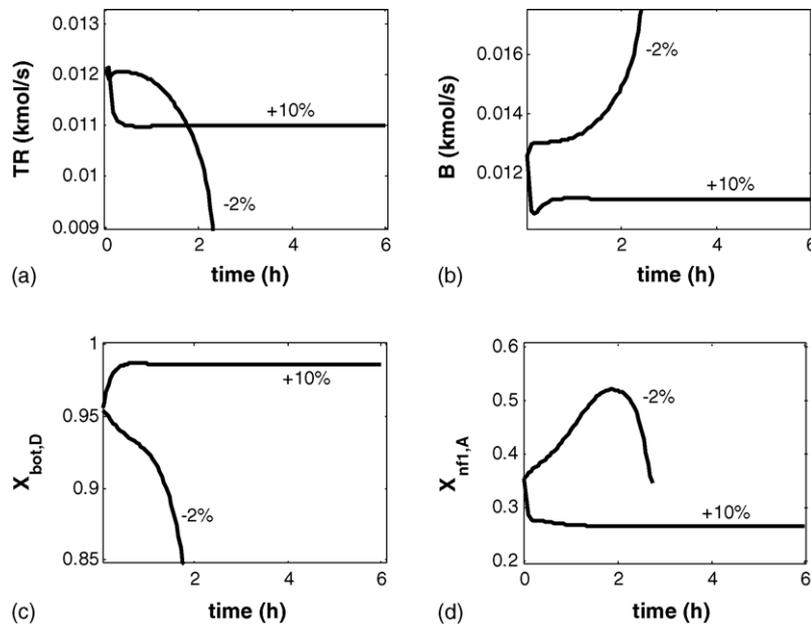
Fig. 5. Dynamic responses of the system to different magnitude changes in vapor boilup: (a) total reaction rate; (b) bottoms flowrate; (c) composition of product D in the bottoms; (d) internal composition of reactant A in tray nf1.

On the other hand, introducing reactant A in feed reactant B feed is intolerable because of the same reason that makes a decrease in F_B intolerable, namely the excess of reactant A in the column while fixing separation capacity. The disturbance in feed compositions affects the system dynamics and increases its nonlinearity more than disturbance in feed flowrates.

4.3. Vapor boilup

Fig. 5 shows the dynamic responses of total product formation rate, bottoms flowrate and some compositions to different magnitude of changes in the vapor boilup from the reboiler. A small decrease in vapor boilup from its base steady-state value makes the system unstable. This might be largely due to the interference effect of fractionation on the system's reaction kinetics. Reducing the heat duty of the reboiler, while the reflux rate and the feed inputs remain constant, adversely affect the separation capacity of the column. Thus, less heat is available to vaporize unreacted A to the vapor phase. This in turn decreases the concentration of reactant A in the reflux rate and causes substoichiometric balance of the two reactants in reactive zone.

Increase in the amount of vapor flowrate at fixed reflux rate will increase the distillate flowrate and slightly decrease the bottoms product. In addition, the total reaction rate slightly decreases because the column fractionation capacity is affected, and more heat is available to enrich volatile components in vapor phase. This invariably increases bottoms product purity and leads to a gradual depletion of reactant A in the reactive zone as more of light reactant is being stripped out from the reactive zone. Thus, more of reactant A is lost

in the overhead and the liquid concentration of reactant A is reduced. This suggests that increased separation capacity could decrease process performance (i.e. conversion and product purity).

It is observed that decreasing the vapor boilup has the same effect on the open loop dynamics of the system as increasing the reflux flowrate at constant feed conditions. Increasing the reflux rate with constant vapor boilup forces the bottoms flowrate to grow unbounded because it returns more volatile reactant A back into the reactive zone than needed. This will necessitate increase in energy consumption of the system.

5. Open loop model with internal controller (OL + IC)

In a typical distillation column where the feed streams are considered to be set by upstream unit, and operating pressure is assumed fixed by heat removal from the condenser, the inventories that must be controlled are essentially the liquid level in the reflux drum and the base of the column. The investigation on the open loop dynamics in the previous section has revealed the impact of stoichiometric imbalance of the reactants entering the column. Thus, the inclusion of internal composition inventory control is necessary to improve the system dynamics.

In this study, the concentration of reactant A on the first tray of reactive section is controlled by manipulating the fresh feed of component A using a Proportional-only controller. The P-only composition controller is used not necessarily to keep the internal composition of reactant A at constant value but to manipulate the fresh feed flowrate of reactant A to
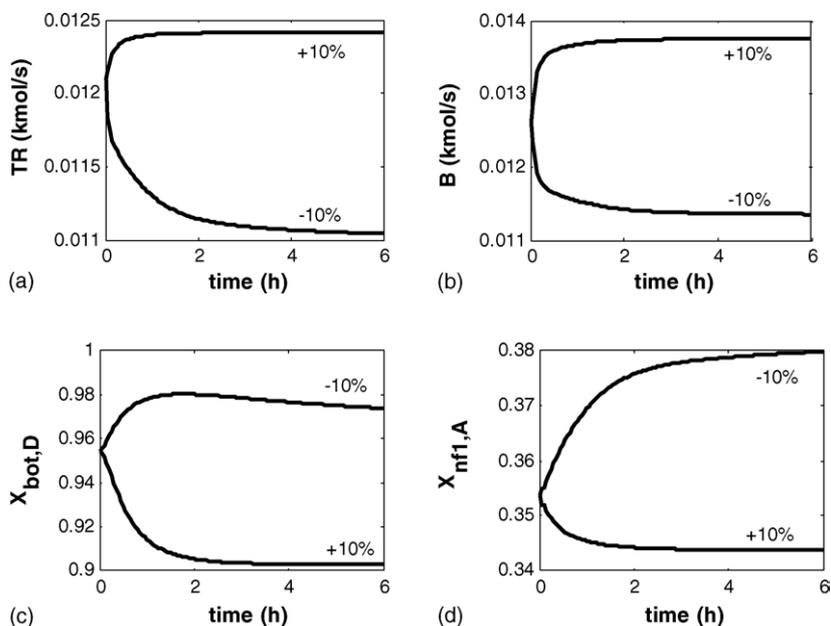
Fig. 6. Responses of the system in presence of an internal composition controller to ±10% change in feed F_B: (a) total reaction rate; (b) bottoms flowrate; (c) composition of product D in the bottoms; (d) internal composition of reactant A in tray nf1.

balance the reaction stoichiometry. The effect of disturbance in feed flowrate of reactant B, feed composition, vapor boilup and reflux rate has been investigated in this section but only the results for changes in feed flowrate of reactant B and vapor boilup are shown.

5.1. Feed flowrates

The responses of the system to different magnitudes of disturbances in feed F_B are shown in Fig. 6. The system is found to be open loop stable when the flowrate of reactant B is increased or decreased. By comparing Fig. 6 to Fig. 2, the clear improvement in the system dynamics is the result of including the internal composition controller, which enforces the stoichiometric balance in the reactive zone. Similar results are obtained when disturbance in feed composition is introduced. As more of B is fed into the column, the internal composition of the reactant A is decreased and the controller responds appropriately by increasing F_A to balance the increase in F_B. The same argument is valid when F_B is reduced as well. Note that the system responses take a longer time to reach steady-state when F_B is reduced as compare to when it is increased with equal magnitude. This indicates how the performance of any control structure on reactive distillation is dependent on the magnitude and direction of the disturbance. Similar observation was pointed out in conventional distillation system by [13].

5.2. Vapor boilup

Fig. 7 shows the responses of the bottoms flowrate when the vapor boilup is increased up to 10% and when decreased

by 2%. Similar to OL scenario, the results show that the inclusion of internal composition inventory is insufficient to handle the decrease in vapor boilup below its optimum condition. The inclusion of internal composition controller does not address the problem of disturbing the separation capacity of the column when either the vapor boilup or reflux rate is changed. Therefore, it is expected that this scenario would be similar to the OL scenario for this class of disturbances.

In general, comparing the open loop model with and without internal composition controller shows that disturbances in feed streams are better handled in presence of internal composition inventory controller because the controller acts to maintain the reaction stoichiometry. In addition, the settling time is generally far shorter when internal composition controller is included as compared to that without it.
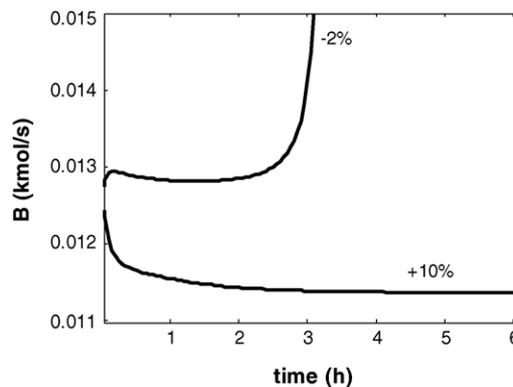

Fig. 7. Response bottoms flowrate to different magnitudes change in vapor boilup (Vs) in presence of an internal composition controller.
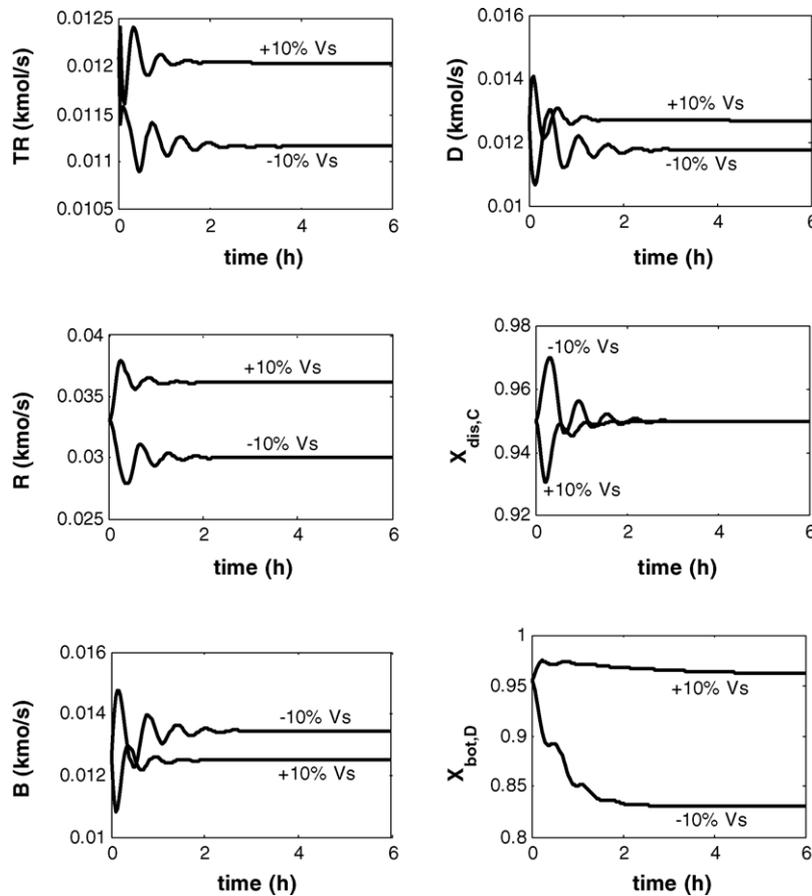
Fig. 8. The response of the system with single-end composition controller.

6. Single-end control (CL)

The introduction of internal composition inventory controller improves the performance of open loop reactive distillation system under disturbances in feed flowrate and composition in both directions. However, controlling the internal composition alone is shown in the earlier section to be inadequate to sustain the system stability whenever there is decrease in vapor boilup or increase in reflux rate. Steady-state rating analysis [16] suggests that a simple single-end control structure could be used since the reflux ratio of the system is fairly constant at 2.6. The composition of C in the distillate is controlled at 95% by manipulating the reflux rate. With the inclusion of this control loop, we are able to increase or decrease the vapor boilup to study its impact on both system stability and dynamic behavior.

Fig. 8 shows the responses of the system when the vapor boilup is changed by ±10%. In this scenario, the system dynamics is improved to tolerate changes in vapor boilup, as the overhead controller will adjust the reflux rate to maintain the required separation capacity. Changing the vapor boilup in either direction changes both the reflux and distillate flowrate in order to maintain the required separation capacity

(i.e. maintaining the same reflux ratio). It is interesting to note that the total reaction rate does not change significantly from its base steady values of 0.01210 kmol/s when the vapor boilup is increased by 10% (i.e. from 0.01210 to 0.01211 kmol/s, which is about 0.08% increase in total reaction rate). On the other hand, decreasing the vapor boilup by the same magnitude of 10%, leads to a significant reduction in total reaction rate from 0.0121 to 0.0112 kmol/s (i.e. 7.5% decrease in total reaction rate). This clearly demonstrates that a negative change in vapor boilup has more impact on the system behavior and influences the performance of the controller more than a positive change in vapor boilup. Examining closely the response of the product compositions, it can be easily noticed that the controller response is slower and has a longer settling time with a negative change than a positive change in vapor boilup. The impurity in the bottoms product is very significant with a negative change in vapor boilup due to the presence of more unreacted component B.

In general, the presence of single-end controller makes the system generally stable, but the effect of the disturbance magnitudes and directions as demonstrated in this work has a significant influence on the performance of the controller. Therefore, this factor must be recognized and be considered

Table 2
Effect of disturbances on the system stability

Input	Direction	OL	OL + IC	CL
F_A	+	Trigger the system sharply to another steady-state	N/A	N/A
	−	Stable		
F_B	+	Stable	Stable	Stable
	−	Trigger the system to another state with small disturbance and unstable with high disturbance	Stable	Stable
Vs	+	Stable	Stable	Stable
	−	Unstable	Unstable	Stable
R	+	Unstable	Unstable	Stable
	−	Stable	Stable	
Change in Z_B		Trigger the system sharply to another steady-state and unstable at high disturbance	Stable	Stable
Change in Z_A		Stable	Stable	Stable

Note: OL, open loop; OL + IC, open loop with internal controller; CL, closed loop; N/A, not a disturbance variable in this scenario.

in the designs and implementation of closed loop reactive distillation system.

7. Conclusion

The effects of disturbance magnitudes and directions on the dynamic behavior of a high-purity/high-conversion reactive distillation have been investigated. Table 2 summarizes the dynamic responses of the system under the three scenarios and for the various disturbances that are investigated. Excess of less volatile reactant in two-reactant-two-product generic reactive distillation has been found to enhance open loop stability, but decreases the products purity. On the other hand, excess of more volatile reactant triggers the system to another steady-state. Change in the manipulated variables (i.e. vapor boilup and reflux rate) in some directions in open loop system is intolerable due to their effect on both the reaction kinetics and fractionation capacity of the column.

The performance of the open loop system is improved significantly with the inclusion of the internal composition inventory control to balance the reactants stoichiometry. However, this has been shown to be insufficient when there is a change in either vapor boilup or reflux flowrate in certain directions due to the disturbance this makes to the separation capacity of the system. A single-end control along with internal composition controller is found to be the minimum required to ensure the systems stability.

Appendix A. Nomenclature

A	reactant component
B	reactant component
B	bottoms flowrate (kmol/s)
C	product component
D	product component
D	distillate flowrate (kmol/s)
F_A	fresh feed flowrate of reactant A (kmol/s)
F_B	fresh feed flowrate of reactant B (kmol/s)
N	total number of stages including reboiler and reflux drum
nf1	first tray of reactive tray (entrance of feed F_A)
nf2	last tray of reactive tray (entrance of feed F_B)
R	reflux rate (kmol/s)
T_i	temperature in tray i (K)
TR	total reaction rate in reactive zone (kmol/s)
Vs	vapor boilup from reboiler (kmol/s)
$X_{dis,C}$	composition of C in the distillate
$X_{bot,D}$	composition of D in the bottoms
$X_{nf1,A}$	composition of A in tray nf1
x_{ij}	liquid mole fraction component j in tray i
Z_A	composition of fresh feed of reactant A
Z_B	composition of fresh feed of reactant B

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