Dynamics and Control of Reactive Distillation Configurations for Acetic Acid Esterification

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Abstract: Three different flowsheets have been proposed for acetic acid esterification of acetic acid with alcohols ranging from C_1 to C_5 according to the ranking of normal boiling points and immiscibility. This work explores the similarities and differences in the dynamics and control of these three types of flowsheets. The degree of process nonlinearity can be computed quantitatively based on the fraction of "sign reversal" for all tray temperatures or based on Allgower's nonlinearity measure. These measures provide useful information to the potential problems in closed-loop control. Next, a systematic design procedure is proposed to devise control structures for all three types of flowsheets for these five esterification systems. The simulation results reveal that reasonable control can be achieved for all five systems with different degrees of asymmetry in closed-loop responses as predicted by the nonlinearity measures. Simulation results clearly show that the simple decentralized control provides a workable solution for highly nonlinear reactive distillation columns under various flowsheet configurations.

Keywords: reactive distillation, esterification, process control, temperature control, nonlinearity.

1. Introduction

Reactive distillation combines reaction and separation in a single unit which provides substantial economic incentives for some chemical processes. The literature and patents in reactive distillation have grown rapidly in recent years as surveyed by Malone and (Doherty, 2000). The books by (Doherty and Malone, 2001) and (Sundmacher and Kienle, 2003) give updated summaries in the field. The review paper of (Taylor and Krishna, 2000) describes potential advantages, modeling, simulation, and hardware configurations of reactive distillation. However, the multifunctional nature of the reactive distillation complicates already very nonlinear dynamics of either reactors or separators. Thus, the dynamics and control of reactive distillation are less obvious as compared to its single unit counterparts. Last decade has seen a steady growth in the number of papers that deal with control of reactive distillation column, from mere a handful to over a dozen. (Roat et al., 1986), among the first, propose a two-temperature control structure for an industrial column in which two fresh feeds are manipulated by two tray temperatures. This is a rather "unconventional" control structure as far as the distillation control is concerned. The reaction considered is the methyl acetate production with a reversible reaction with two reactants and two products (i.e., $A + B \leftrightarrow C + D$). Moreover, the esterification is carried out in a "neat", i.e., no excess reactant flowsheet as opposed to an "excess-reactant"

flowsheet as defined by (Luyben and co-workers, 2000~2005). The "excess-reactant" flowsheet requires two columns to achieve high purity product and is, therefore, more expensive. The "neat" flowsheet has a greater economical potential because only one column is needed. However, it is more difficult to control because two reactants must be fed in the "exact" amount to satisfy the stoichiometry down to the last molecule. Luyben is, among the first, to recognize this fact and, therefore, not so conventional control structures results. Luyben and co-workers propose eight control structures for the "neat" reactive distillation (CS1- CS6 in (Al-Arfaj, 2000) and (Luyben, 2002) ; CS6-CS7 in (Al-Arfaj and Luyben, 2002) ; CS7-CS8 in (Kaymak and Luyben, 2005)). Typically, a generic distillation column with a second order reversible reaction is investigated. In addition to the control of continuous reactive distillation for $A + B \leftrightarrow C + D$ systems, control of reactive distillations for fuel ether (MTBE, ETBE,TAME) has been studied by (Sneesby et al, 1999). This corresponds to a reactive kinetics of two reactants and one product, i.e., $A + B \leftrightarrow C$. Linear and nonlinear control of semi-batch reactive distillation for ethyl acetate production has been explored by (Engell and Fernholz, 2003). Nonlinear estimation and control of a two-stage reaction has been studied by (Grüner et al, 2003). Because of the difference in the mode of operation (batch versus continuous) and in the reaction kinetics ($A + B \leftrightarrow C + D$ versus $A + B \leftrightarrow C$), the potential problems of the "neat" flowsheet have not been emphasized. This

work continues the earlier effort to explore the control of acetic acid esterification with different alcohols (ranging from C1 to C5; (Tang et al., 2005)). The esterifications lead to three different types of flowsheets (category I ~ III) with different economical potentials (Tang et al., 2005). The esterification processes explored share a common characteristic, "neat" flowsheet, while maintaining their own process configuration and the object of this work is to devise control structures for these three different categories of reactive distillation. A systematic procedure is proposed for the control structure design which is applicable to all three process configurations. Temperature as well as composition controls are explored and interaction between design and control is discussed.

2. Process Characteristics

2.1 Process Studies

As pointed out by (Tang et al., 2005), the esterification of acetic acid with different types of alcohols (ranging from C1 to C5) can be classified into three flowsheets, type I, type II, and type III, as shown in figure 1. Steady-state analysis indicates that the type I and type III systems are more economical than the type II system. Here we would like to explore the dynamical controllability of these three flowsheets. More importantly, we would like to devise a systematic approach to the control of these three types of reactive distillations.
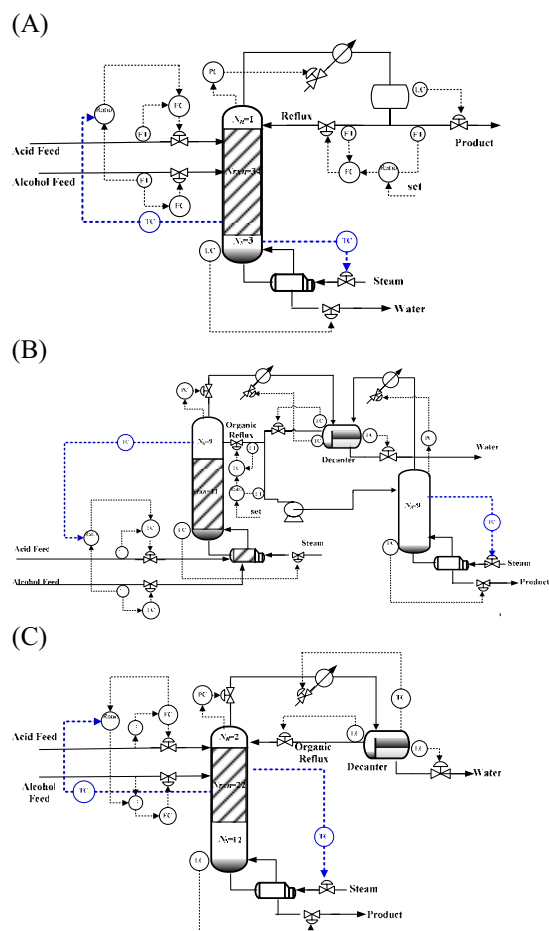
(A)

(B)

(C)

Figure 1. Process flowsheets for temperature control configurations for type I (A), II (B), and III (C) systems

2.2 Quantitative Analysis

Before getting into detailed quantitative analysis, we need to identify manipulated variables for these three different types of processes. As pointed out by (Luyben,) it is important to maintain the stoichiometric balance for the "neat" reactive distillation. (Al-Arfaj and Luyben, 2002) choose to use one of the feed rate and, here, the feed ratio (FR) is used as the manipulated variable. In addition to hold the stoichiometric balance, in theory, we need to control two product compositions using two manipulated variables. However, for reactions such as A + B ↔ C + D, if the conversion is properly maintained and the product flow rate are equally distributed, one-end composition control will do a fairly good job. For type I flowsheet of MeAc production, following Al-Arfaj and Luyben, we choose to control the bottoms composition using vapor boilup while fixing the reflux ratio. For type II flowsheet, the product composition of water from the first column (RD column) is determined by liquid-liquid equilibrium, so no composition control is necessary. However, the reflux ratio of the RD column is fixed. The acetate production is withdrawn from the stripper and the composition is controlled by manipulating the vapor boilup as shown in Figure 1. Similar to the type II flowsheet, a decanter is used for type III flowsheets to separate the water from column overhead and, therefore, composition control is not necessary and the origin phase is totally refluxed back to the column. This is similar to the configuration studied by (Huang et al, 2004). and (Chiang et al., 2003) . The bottoms acetate composition is, however, controlled by changing the reboiler duty. In summary, the manipulated variables are:

Type I: feed ratio, and reboiler duty (fixing reflux ratio)

Type II: feed ratio and reboiler duty in the stripper (fixed organic reflux ratio in RD)

Type III: feed ratio and reboiler duty (organic phase totally refluxed)

3. Nonlinearity

Once the manipulated variables are determined, we could like to evaluate process nonlinearity for these 3 different types of flowsheets. The tray temperatures are treated as the state variables. The manipulated variables are the heat input Q_R and feed ratio FR, respectively. First, the upper and lower bounds of the steady-state gains between the tray temperatures and the manipulated variables (Q_R and FR) are obtained for a range of input variations. In this work, -5% to +5% changes in the heat input (Q_R) and -1% to +1% changes in the feed ratio are made. Note that, for a truly linear system, the upper and lower bounds should coincide with each other. Figure 2 clearly shows that the reactive distillation columns exhibit

strong nonlinearity for all 5 systems studied, despite showing different degrees of severity. Moreover, the "sign reversal" is also observed for all 5 systems under either Q_R or FR change. The results presented here are rather unconventional, because chemical processes are known to be quite nonlinear, but not to this degree in such a consistent manner. Two measures are used to differentiate the degree of nonlinearity for these three types of reactive distillation. One obvious choice is the faction of sign reversal for all tray temperatures. In this aspect, the AmAc system (Figure 2) indicates that more than half of the trays show sign reversal followed by the MeAc system (category I) in which almost half of the tray temperatures exhibit the "sign reversal". The category II system (EtAc and IPAc) show that almost 1/3 of the tray temperatures exhibit the "sign reversal" and the BuAc system is the system with the least sign changes in the tray temperatures. Table 1
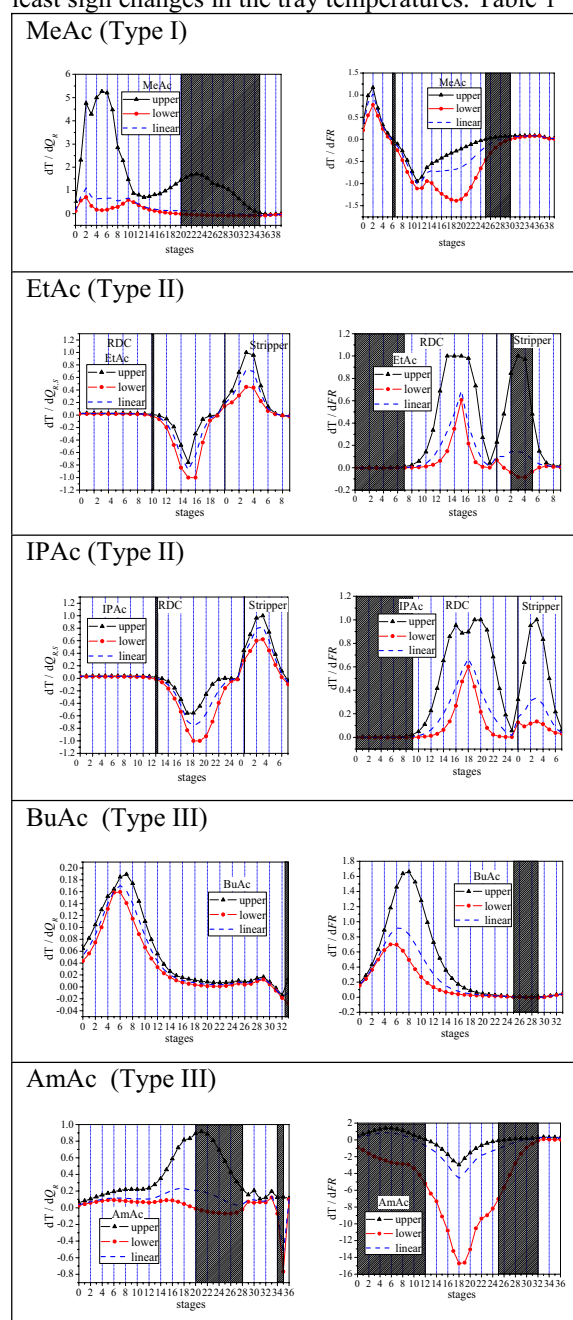
MeAc (Type I)

EtAc (Type II)

IPAc (Type II)

BuAc (Type III)

AmAc (Type III)

summarizes the fraction of a sign changes for all five systems. The second nonlinearity indicator is ϕ^N which is first proposed by (Allgower, 1997) for general dynamic systems and further studied by (Hernjak and Doyle, 2003) for systems under feedback. (Schweickhardt and Allgower, 2004) give an updated summary on the nonlinearity measure. Here, we only consider the steady-state aspect (e.g., can be viewed as the nonlinearity measure for a static function) and the approach of (Schweickhardt and Allgower, 2004) is taken here. In this work, the 2-norm is used to compute ϕ^N and each manipulated variable is considered separately. The measure is defined as:

$$\phi^N = \inf_{G \in \mathbb{G}} \sup_{u \in \mathbb{U}} \frac{\|G(u) - N(u)\|_2}{\|N(u)\|_2} \tag{1}$$

Where G is a linear operator, N is a nonlinear static function, $\mathbb{U}$ is the input set, $\mathbb{G}$ is a set of all linear operators. Physically, this can be viewed as the relative deviation of a linear (static) transfer function to the nonlinear function in a normalized sense. The measure ϕ^N ranges form 0 to 1 and $\phi^N = 0$ indicates a linear system and ϕ^N increases toward 1 as the nonlinearity becomes more severe. For static functions with the upper and lower bounds available, the solution to the optimization problem is simply:

$$\frac{\|\overline{G} - G_+\|_2}{\|G_+\|_2} = \frac{\|\overline{G} - G_-\|_2}{\|G_-\|_2} \tag{2}$$

Where G_+ is the upper bound of $N(u)/u$, G_- is the lower bound of $N(u)/u$, and the nonlinear measure can be computed as:

$$\phi^N = \frac{\|\overline{G} - G_+\|_2}{\|G_+\|_2} = \frac{\|\overline{G} - G_-\|_2}{\|G_-\|_2} \tag{3}$$

Because we treat two manipulated inputs separately, two ϕ^N's are available for a given system. Table 1 gives the nonlinearity measures for all 5 systems with two different inputs. Qualitatively, the results of ϕ^N are consistent with the fractions of sign reversal as shown in Table 1. The 2-norm is employed for overall nonlinearity assessment based on ϕ^N and the results are consistent with the previous "sign reversal" analysis. The ranking of the processes from linear to nonlinear becomes: BuAc (Type III) → IPAc (Type II) → EtAc (Type II) → MeAc (Type I) → AmAc (Type III).

Flow sheet Type	System	Fraction of sign reversal			Nonlinearity measure (Schweickhardt and Allgower)			Overall Assessment ***
		Q_R	FR	Overall*	Q_R	FR	Overall**	
I	MeAc	0.40	0.18	0.43	0.84	0.44	0.67	H
II	EtAc	0.03	0.40	0.43	0.34	0.70	0.55	M
	IPAc	0.03	0.29	0.32	0.32	0.60	0.48	M
III	BuAc	0.03	0.15	0.18	0.16	0.46	0.34	L
	AmAc	0.30	0.57	0.76	0.78	0.79	0.79	H

Table 1 Fractions of sign reversal and nonlinearity measures for all five esterification systems.
* delete overlapping (from each input) trays
** taking as 2-norm of two inputs divided by two
***High (if the averaged value exceeds 0.5), Medium (if the averaged value exceeds 0.3), and Low (if the averaged value less than 0.3),

3. Control Structure Design

In this section, a systematic approach is proposed to the control structure design for these three types of reactive distillation flowsheets. In this work, the feed ratio (*FR*) is adjusted to prevent accumulation of unreacted reactants, stoichiometric imbalance. The next issue is: how many product compositions or inferred product purities should be controlled? For the esterification reactions with A + B $\leftrightarrow$ C + D under the "neat" flowsheet, controlling one-end product purity implied a similar purity level on the other end, provided with equally distributed product flow rates. So, a single-end composition (or temperature control) is preferred. This leads to 2×2 multivariable control, as opposed to a 3×3 multiple input- multiple- output (MIMO) system. The next problem is more of the robustness consideration. Because of input multiplicities and potential sign reversals, the decentralized control is preferred over the inverse-based control. The reason is quite obvious: we are not even sure of the sign in some entries of a process transfer function. The decentralized control is more likely to work than an inversed-based multivariable controller. In summary, the following principles are recommended:
(1) Maintain the stoichiometric balance using the feed ratio.
(2) Prefer to control only one-end composition (or temperature).
(3) Use decentralized control to maintain robust stability.
This leads to the following design procedure for temperature control of reactive distillation systems.
(1) Select an additional manipulated variable. Typically, the other manipulated input is the heat input or the reflux ratio.
(2) Use the non-square relative gain (NRG; Chang and Yu[23]) to select temperature control trays. The larger row sums of the NRG indicate potential temperature control tray. Note that the

temperatures with the "sign reversal" (Figure 2) cannot be used as controlled variable.
(3) Use the relative gain array (RGA) for variable pairing, once the inputs and outputs are determined.
(4) Performance sequential relay feedback test (Shen and Yu) to find the ultimate gain (K_u) and ultimate period (P_u).
Use the Tyreus-Luyben tuning to set the tuning constant for the PI controllers. A simple version is:

$$K_c = K_u/3 \text{ and } \tau_I = 2 P_u .$$

3.1 Selection of Temperature Control Trays

The non-square relative gain (NRG) of Chang and (Yu) is used to find the temperature control trays.
The NRG (Λ^N) is defined as:

$$\Lambda^N = K_p \otimes (K_p^+)^T \tag{3}$$

where K_p is the steady-state gain matrix, $\otimes$ denotes the element-by-element multiplication, the superscript + is the pseudo-inverse, and the superscript *T* means the transpose. The largest row sum of the NRG is selected as the temperature control trays. The controlled variables are:
MeAc : T_2 and T_{11}
EtAc : $T_{RDC,15}$ and $T_{STR,3}$
IPAc : $T_{RDC,18}$ and $T_{STR,3}$
BuAc : T_6 and T_{29}
AmAc : T_{11} and T_{33}
The "sign reversal" areas of Figure 2 are used to check potential sign changes in the selected tray temperatures. For these five systems, the temperature control trays do not exhibit sign reversal in the ranges (±5% for heat input and ±1% for *FR*) of manipulated variable variations. Note that if the NRG selected temperature falls within the "sign reversal" area, alternative temperature should be sought.

	Controlled Variables	Manipulated Variables	Steady State Gain	RGA	Tuning Parameter
MeAc	T_2 T_{11}	F_{Acid}/F_{MeOH} Q_R	$\begin{bmatrix} T_{11} \\ T_2 \end{bmatrix} = \begin{bmatrix} 1.839 & -1.522 \\ 4.802 & 3.659 \end{bmatrix} \begin{bmatrix} Q_R \\ F_{Acid}/F_{MeOH} \end{bmatrix}$	$\Lambda = \begin{bmatrix} 0.479 & 0.520 \\ 0.520 & 0.479 \end{bmatrix} \begin{matrix} T_{11} \\ T_2 \end{matrix}$ $\begin{matrix} Q_R & F_{Acid}/F_{MeOH} \end{matrix}$	Q_R - T_2 : $Kc = 0.464$ $\tau_I = 0.333$(hr) F_{Acid}/F_{MeOH} - T_{11} : $Kc = 1.237$ $\tau_I = 1.98$(hr)
EtAc	$T_{STR,3}$ $T_{RDC,15}$	F_{Acid}/F_{EtOH} $Q_{R,S}$	$\begin{bmatrix} T_{STR,3} \\ T_{RDC,15} \end{bmatrix} = \begin{bmatrix} 0.087 & 1.967 \\ -4.26 & 102.57 \end{bmatrix} \begin{bmatrix} Q_{R,S} \\ F_{Acid}/F_{EtOH} \end{bmatrix}$	$\Lambda = \begin{bmatrix} 0.517 & 0.482 \\ 0.482 & 0.517 \end{bmatrix} \begin{matrix} T_{STR,3} \\ T_{RDC,15} \end{matrix}$ $\begin{matrix} Q_{R,S} & F_{Acid}/F_{EtOH} \end{matrix}$	$Q_{R,S}$ - $T_{STR,3}$: $Kc = 22.65$ $\tau_I = 0.018$(hr) F_{Acid}/F_{EtOH} - $T_{RDC,15}$: $Kc = 0.755$ $\tau_I = 2.069$(hr)
IPAc	$T_{STR,3}$ $T_{RDC,18}$	F_{Acid}/F_{IPOH} $Q_{R,S}$	$\begin{bmatrix} T_{STR,3} \\ T_{RDC,18} \end{bmatrix} = \begin{bmatrix} 0.227 & 1.574 \\ -2.336 & 70.439 \end{bmatrix} \begin{bmatrix} Q_{R,S} \\ F_{Acid}/F_{IPOH} \end{bmatrix}$	$\Lambda = \begin{bmatrix} 0.812 & 0.187 \\ 0.187 & 0.812 \end{bmatrix} \begin{matrix} T_{STR,3} \\ T_{RDC,18} \end{matrix}$ $\begin{matrix} Q_{R,S} & F_{Acid}/F_{IPOH} \end{matrix}$	$Q_{R,S}$ - $T_{STR,3}$: $Kc = 25.5$ $\tau_I = 0.08$(hr) F_{Acid}/F_{IPOH} - $T_{RDC,18}$: $Kc = 3.92$ $\tau_I = 2.66$(hr)
BuAc	T_{29} T_6	F_{BuOH}/F_{Acid} Q_R	$\begin{bmatrix} T_{29} \\ T_6 \end{bmatrix} = \begin{bmatrix} 0.026 & -0.007 \\ 0.299 & -2.127 \end{bmatrix} \begin{bmatrix} Q_R \\ F_{BuOH}/F_{Acid} \end{bmatrix}$	$\Lambda = \begin{bmatrix} 1.041 & -0.041 \\ -0.041 & 1.041 \end{bmatrix} \begin{matrix} T_{29} \\ T_6 \end{matrix}$ $\begin{matrix} Q_R & F_{BuOH}/F_{Acid} \end{matrix}$	Q_R - T_{29} : $Kc = 38.86$ $\tau_I = 0.06$(hr) F_{BuOH}/F_{Acid} - T_6 : $Kc = 5.16$ $\tau_I = 0.9$(hr)
AmAc	T_{33} T_{16}	F_{AmOH}/F_{Acid} Q_R	$\begin{bmatrix} T_{33} \\ T_{16} \end{bmatrix} = \begin{bmatrix} 0.29 & -0.059 \\ 0.31 & 15.995 \end{bmatrix} \begin{bmatrix} Q_R \\ F_{AmOH}/F_{Acid} \end{bmatrix}$	$\Lambda = \begin{bmatrix} 0.961 & 0.038 \\ 0.038 & 0.961 \end{bmatrix} \begin{matrix} T_{33} \\ T_{16} \end{matrix}$ $\begin{matrix} Q_R & F_{AmOH}/F_{Acid} \end{matrix}$	Q_R - T_{33} : $Kc = 29.72$ $\tau_I = 0.08$(hr) F_{AmOH}/F_{Acid} - T_{16} : $Kc = 9.1$ $\tau_I = 1.2$(hr)

Table 2. Controlled variables , manipulated variables, process gain matrices, relative gain array, and tuning parameters for these five esterification systems under temperature control.

4. Perormance

Feed flow and feed ratio disturbances are used to evaluate the control performance of the temperature control for these five esterification systems. Recall

that these reactive distillation systems are highly nonlinear (Figure 2) with significant "sign reversal" and input multiplicity. Figure 3 shows that the simple PI temperature control actually works quite well for all 5 systems.

For the MeAc system, the product composition, $X_{D,acetate}$ in particular, does not settle down 15 hours after the 20% feed flow rate change is introduced. Asymmetrical responses are observed for most of the process variable and steady-state offsets (~ 0.02 m.f.) exist (Figure 3A). For the type II flowsheets, faster responses and much symmetrical responses can be obtained as shown in Figure 3B and 3C. The product composition settles in the less than 10 hours and much smaller offsets in the acetate composition can be achieved (~0.002 m.f. for EtAc and nil for IPAc). For the type III flowsheets, two different dynamics are observed which can be foreseen from nonlinear analysis (Table 1). For the BuAc system, the product composition dynamics settles in less than 5 hours (the fastest response) and symmetrical responses can also been seen for most of the process variables except the trace acid concentration (Figure 3D). Steady-state offsets are also observed, but error is around 0.02 m.f. for ±20% feed flow changes. For the AmAc system, again, fast dynamics is attainable, but the responses are asymmetrical especially for the product compositions ($X_{B,acetate}$ and X_{D,H_2O}). Large steady-state offset (~0.02 m.f.) is also observed for the acetate composition.

Despite the strong nonlinearity, workable temperature control of esterification reactive distillation systems can be obtained using a systematic design procedure with rather simple control structure. It should be emphasized that the selections of controlled and manipulated variables (control structure design) play a crucial role for these highly nonlinear processes and the decentralized control provides a better structure to cope with steady-state gain variations. As expected, MeAc system (type I flowsheet) exhibits relatively poor control performance as can be seen early from quantitative nonlinearity measures. The closed-loop behavior of the EtAc and IPAc (type II flowsheet) is not as quite nonlinear as the steady-state measures predict. Relatively fast and symmetrical dynamics can be obtained as shown in Figures 3B, 3C. One reason for this is that the type II flowsheet has a two-column configuration (Figure 1) and they are separated by a decanter with typically a 20 minutes holdup. In other words, a large surge tank is placed between these two units and they are somewhat decoupled dynamically. As predicted, the BuAc system should be an easy one to control and the closed-loop responses confirmed that (Figure 3D). the other type III flowsheet, the AmAc system, on the other hand, gives significantly different closed-loop performance. Less symmetrical responses are observed as predicted by the nonlinearity measures and a large composition offset results for feed flow rate changes (Figure 3E). However, similar to the BuAc system, the type III flowsheet generally gives fast closed-loop dynamics.
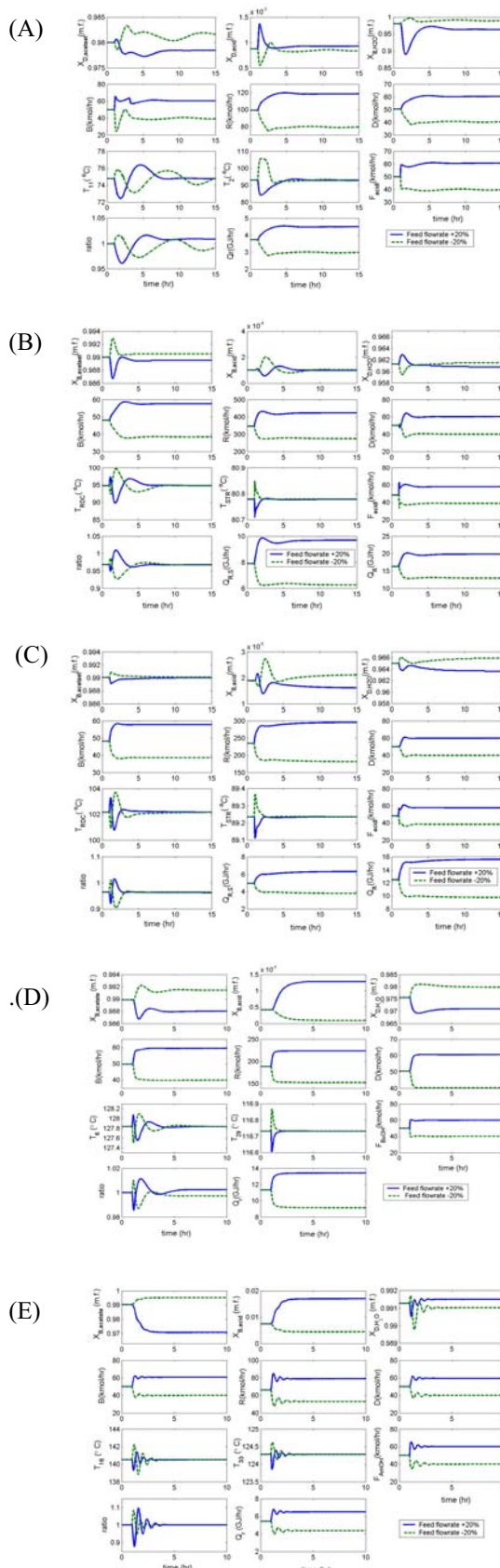
(A)

(B)

(C)

.(D)

(E)

Figure 3. Temperature control responses for ±20% production rate changes for MeAc (A), EtAc (B), IPAc (C), BuAc(D), and AmAc (E) systems.

5. Conclusion

The dynamics and control for three different types of reactive distillation flowsheets (type I, II, and III) are

explored. This covers acetic acid esterification with different alcohols ranging from C_1 (MeOH) to C_5 (AmOH). Simultaneous reaction and separation leads to strongly nonlinearity to all five systems studied. However, the degree of nonlinearity can be analyzed qualitatively or computed quantitatively. A systematic design procedure is proposed to devise the control structures for all three types of flowsheets. The simulation results reveal that workable temperature control can be obtained for these highly nonlinear processes with simple control. Moreover, the closed-loop systems do behave as the preliminary nonlinear analyses predict and inherent strong nonlinearity does lead to asymmetrical responses, especially for the MeAc and AmAc systems. As far as the flowsheet is concerned, the type II flowsheet (EtAc and IPAc) is divided into two units separated by a large decanter. This somewhat damps out the disturbance between the RDC and the stripper which subsequently leads to a more controllable process. The flowsheet (BuAc and AmAc) where a decanter is used to provide a natural one-end composition control via liquid-liquid equilibrium. Interaction between top and bottom composition control can, thus, be alleviated. Finally, the type I flowsheet cannot escape from either the inherent nonlinearity or the dynamic interactions. The nonlinearity and strong interactions lead to a very difficult process to control.

Acknowledgement

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