Comparative control study of ideal and methyl acetate reactive distillation

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Abstract

The control of an ideal reactive distillation column is compared with that of a similar, but somewhat different, real chemical system, the production of methyl acetate. Similarities and differences are observed. Three control structures are evaluated for both systems. A control structure with one internal composition controller and one temperature controller provides effective control of both systems for both high and moderate conversion designs. A two-temperature control structure is effective when the system is overdesigned in terms of number of reactive trays, holdup and/or catalyst load. Direct control of product purity for the high-conversion/high-purity design is difficult because of system nonlinearity and interaction. Tray temperature control avoids the nonlinearity problem.
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1. Introduction

Reactive distillation combines both separation and reaction in one unit. It has been used in a small number of industrial applications for many years, but the last decade has shown an increase in both research and applications. It can offer significant economic advantages in some systems, particularly for reversible reactions. The literature up to 1992 was reviewed by Doherty and Buzad (1992). Many papers have discussed steady-state design. Some have dealt with openloop dynamics, which in some systems feature multiplicity.

Only a small number of papers discuss the closedloop control of reactive distillation columns or the interaction between design and control. The control papers up to 1999 were discussed by Al-Arfaj and Luyben (2000). Several new papers have appeared. Sneesby, Tade and Smith (2000) studied three control structures for a single-feed ETBE reactive distillation column. Monroy-Loperens, Perez-Cisneros and Alverz-Ramirez (2000) studied the control of ethylene glycol reactive distillation using nonlinear control. Luyben (2000) studied the economic and control effects of using excess reactant.

In our previous paper (Al-Arfaj & Luyben, 2000) we presented a comparison of several control structures for an ideal two-product reactive distillation system. Simple vapor–liquid equilibrium, reaction kinetics and physical properties were used so that the inherent control features of reactive distillation could be explored without clouding the picture with the complexities that can occur in some real chemical systems. All of the workable control structures used a measurement of a reactant composition in the reactive section of the column so that operation with exactly stoichiometric feeds could be achieved ("neat" operation).

We studied several other chemical systems. In the ETBE system (Al-Arfaj & Luyben, 2002a), there are two reactants, one product and one inert. We studied single-feed and double-feed designs and several control schemes were examined. The ethylene glycol system (Al-Arfaj & Luyben, 2002b) has two feeds but only one product. A control scheme where a temperature in the stripping section is controlled by the heat input was found to be effective. Olefin metathesis (Al-Arfaj & Luyben, 2002c) has only one reactant and two products. A temperature in the stripping section is controlled by the heat input and another temperature in the rectifying section is controlled by the reflux rate. This scheme was found to be effective. A plantwide flowsheet that contains reactive distillation column was developed for the production of TAME

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(Al-Arfaj & Luyben, submitted). The flowsheet consists of one reactor, one reactive column, two conventional columns and two recycles. The importance of plantwide control and the role of reactive distillation were discussed.

The present work will study the control of a new reactive distillation system (methyl acetate). Methyl acetate reactive distillation is an important system since it is being used in the industry. In addition, a comparison between this chemical system and the ideal system we studied before will be given. The compatibility and effectiveness of control structures for the two superficially similar systems are discussed.

The production of methyl acetate (MeOAc) via reactive distillation system involves the reaction

$$\text{Methanol} + \text{Acetic acid} \rightleftharpoons \text{Methyl acetate} + \text{Water}.$$
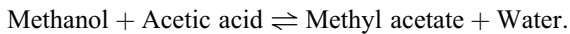
In this system, the heavy reactant is heavier than the heavy product (acidic acid is less volatile than water). The impact of this on both steady-state design and dynamic control is explored in this paper. Three control structures are presented in this work. The interaction between design and control is studied by changing the conversion level inside the reactive column.

2. Steady-state analysis

2.1. Reaction kinetics

The production of methyl acetate is a good candidate for reactive distillation. The conventional method using a reactor and separation section is very complex due to reaction equilibrium limitations and the formation of methyl acetate–methanol and methyl acetate–water minimum-boiling azeotropes. A complex multi-unit separation/reaction/recycle system is required. Reactive distillation provides a much more economical process (Agreda & Partin, 1984; Agreda, Partin, & Heise, 1990). The continuous removal of products drives the reaction to high conversions.

Methyl acetate (MeOAc) can be made by the liquid-phase reaction of acetic acid (HOAc) and methanol (MeOH), catalyzed by sulfuric acid or an ion-exchange resin in the temperature range of 310–325 K and at a pressure of 1 atm. Since the high polarity of water and methanol compared to methyl acetate leads to strongly nonideal solution behavior, the rate expression is given in terms of activities. A new activity-based model, utilizing the Langmuir–Hinshelwood/Hougen–Watson isotherm, was developed by Song, Venimadhavan, Manning, Malone and Doherty (1998).

$$k_1 = 6.942 \times 10^9 \exp\left(\frac{-6287.7}{T}\right)$$

$$K_{\text{eq}} = 2.32 \exp\left(\frac{782.98}{T}\right)$$

$$K_{\text{HOAc}} = 3.18$$

$$K_{\text{MeOH}} = 4.95$$

$$K_{\text{MeOAc}} = 0.82$$

$$K_{\text{H}_2\text{O}} = 10.5$$

$$a_i = \gamma_i x_i$$

where a_i is the activity, γ_i is the liquid activity coefficient, x_i is the liquid mole fraction, k_1 is the reaction rate constant (mol/(g cat h)), M_{cat} is the mass of the catalyst (g), and T is the temperature (K). One of the side reactions in the methyl acetate system is the dehydration of methanol to dimethyl ether (DME) and water.

$$2\text{MeOH} \rightleftharpoons \text{DME} + \text{H}_2\text{O}.$$

It appears that most studies ignore this side reaction, so we have not considered it.

An increase in pressure leads to an increase in the boiling points of the components and hence the operating temperature of the reactive distillation column. This leads to higher rates of reaction and smaller equipment, which reduces investment costs. On the other hand, an increase in temperature leads to a decrease in the equilibrium constant (and hence the equilibrium conversion) and could potentially trigger unwanted side reactions such as the methanol dehydration reaction.

Accurate prediction of the VLE of the methyl acetate system is vital to the simulation and design of the process. To correlate the VLE in mixtures containing a vapor-phase associating substance such as acetic acid, Mark's method (Mark, 1955) in combination with a liquid activity coefficient model is usually used. The Wilson equation is recommended in the DECHEMA Vapor Liquid Equilibrium Data Collection. Therefore, the Wilson model and Mark's method are used to predict the VLE in our research.

The industrial specifications on this process are 99% conversion and 95% MeOAc purity. We use this as the high-conversion design and also develop a low-conversion case. Both are shown in Fig. 1. We modified the Eastman design (Agreda et al., 1990) in two ways. Since it is easier to deal with theoretical trays, we assumed a tray efficiency of 50% and reduced the number of trays to 35 trays. Lee and Dudukovic (1998) found that the tray efficiency for a similar system, ethyl acetate, is about 60%. The Eastman design uses homogeneous kinetics, but these are not available in

$$R_{\text{MeOAc}} = \frac{M_{\text{cat}} k_1 \left(a_{\text{HOAc}} a_{\text{MeOH}} - \dfrac{a_{\text{MeOAc}} a_{\text{H}_2\text{O}}}{K_{\text{eq}}} \right)}{(1 + K_{\text{HOAc}} a_{\text{HOAc}} + K_{\text{MeOH}} a_{\text{MeOH}} + K_{\text{MeOAc}} a_{\text{MeOAc}} + K_{\text{H}_2\text{O}} a_{\text{H}_2\text{O}})^2}$$
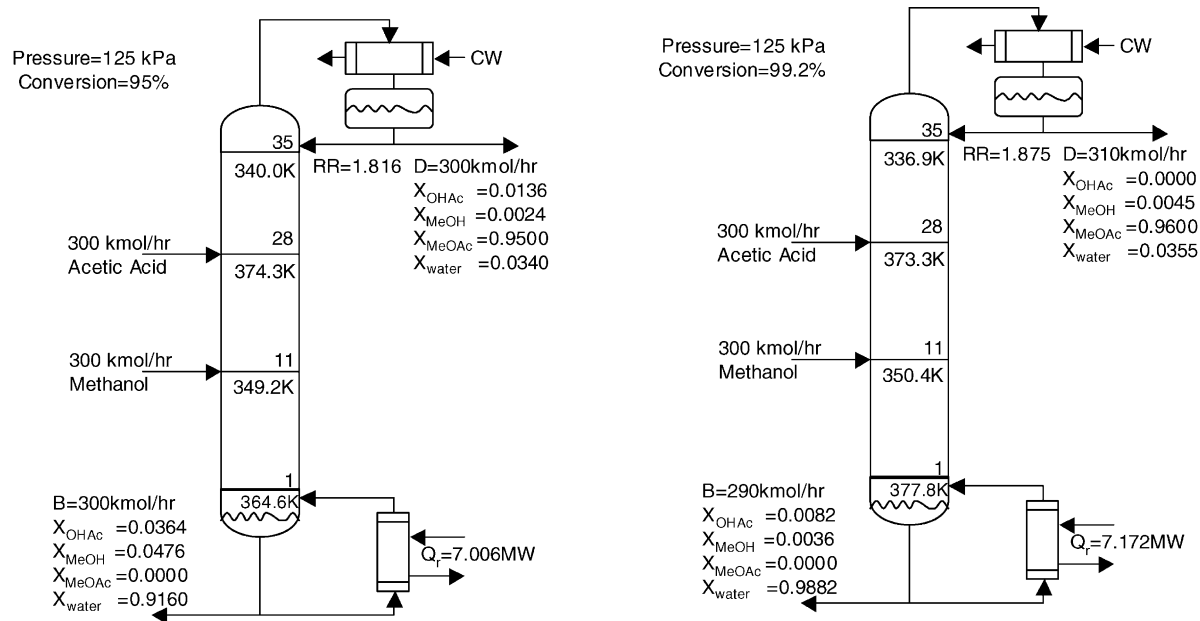
Fig. 1. High- and low-conversion methyl acetate system designs.

the literature. We used the heterogeneous kinetic model reported by Song et al. (1998), modified to fit the Eastman design specifications by multiplying the rate constant by a factor of 2.5 to account for the use of theoretical trays and heterogeneous reaction. The details of the model used are available in Al-Arfaj (1999). Fig. 1 gives two designs: (1) the base high-conversion design and (2) a low-conversion design. These two designs will be used in the steady-state and dynamic analysis.

2.2. Steady-state multiplicities

Reactive distillation columns are highly nonlinear, and multiple steady-state solutions have been reported by many researchers, e.g. Guttinger and Morari (1999a, b). The impact of such phenomena on the design and control of the two reactive distillation systems is discussed in this paper. The control of unstable systems is more difficult than controlling stable systems.

Three multiplicity analyses are investigated: output multiplicity Class 1, output multiplicity Class 2 and input multiplicity.

2.2.1. Output multiplicity (Class 1)

This type of multiplicity is the case when fixed inputs give more than one set of outputs. In our system the inputs are the two feed streams, the reflux flowrate (R) and the heat input (Q_R). The outputs are the flowrates of the product streams (D and B), the compositions of the distillate and bottoms (x_{Dj} and x_{Bj}) and all tray vapor and liquid streams. The column configuration is fixed: the numbers of rectifying, reactive and stripping trays are constant.

A homotopy continuation method is used in which the distillate flowrate is varied with a fixed reflux flowrate. Plots of distillate flowrate D versus reboiler heat-input Q_R reveal the existence of multiple steady states in the methyl acetate system. Fig. 2 shows that at the same heat input and reflux flowrate there are multiple values of the distillate flowrate. This type of multiplicity is present in both high and low-conversion columns. However, Fig. 2 shows that unlike the high-conversion design the low-conversion design is stable. This suggests that the low-conversion design would easier to control than the high-conversion design. This multiplicity was verified dynamically as well. A pulse change was made in one of the feed flowrates while the other feed, heat input and reflux flow are fixed. The reflux drum level was controlled by the distillate, and the base level was controlled by the bottoms flowrate. Depending on the direction of the pulse change, the distillate flowrate moved to one of the two stable points. The desired operating point of the high-conversion design is openloop unstable, which indicates a more difficult control situation.

2.2.2. Output multiplicity (Class 2)

In the previous case the physical inputs to the process are fixed: reflux and heat input. Now we wish to fix inputs that are sometimes used in control structures. The *reflux ratio* (RR) is fixed instead of the *reflux flowrate*. This means that reflux flowrate is not fixed, but varies with the distillate flowrate. Fig. 3 shows that for a given RR and heat input, the column can have more than one distillate flowrate. Neither the high-conversion nor the low-conversion methyl acetate designs fall in the multiplicity region, indicating that the fixed RR control structure is openloop stable under these
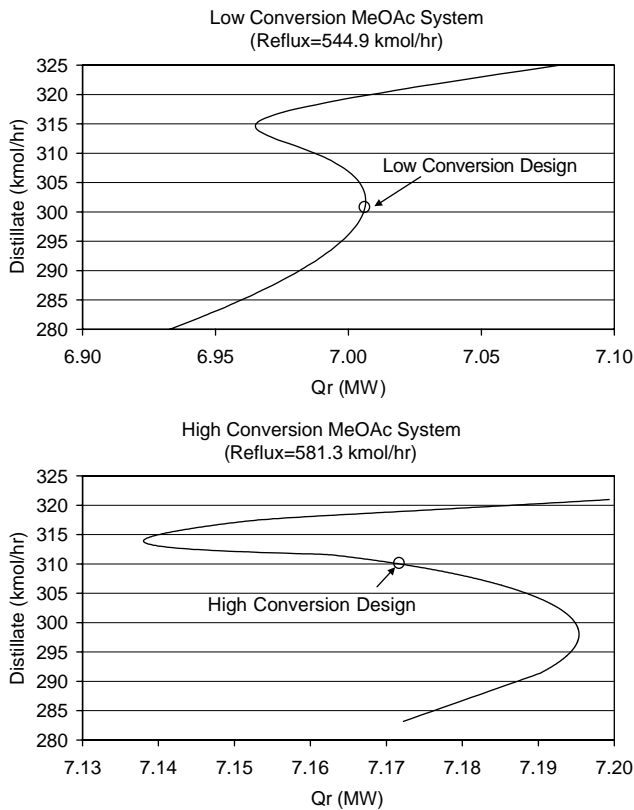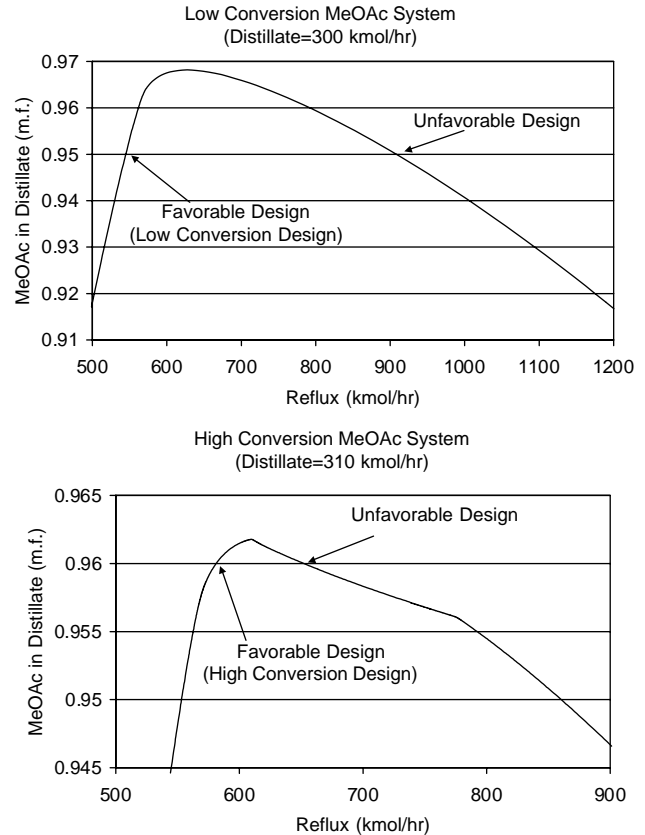
Low Conversion MeOAc System
(Reflux=544.9 kmol/hr)

Low Conversion MeOAc System
(Distillate=300 kmol/hr)

High Conversion MeOAc System
(Reflux=581.3 kmol/hr)

High Conversion MeOAc System
(Distillate=310 kmol/hr)

Fig. 2. Output multiplicity (Class 1).

Fig. 4. Input multiplicity.

Low Conversion MeOAc System
(Reflux Ratio=1.816)

High Conversion MeOAc System
(Reflux Ratio=1.875)
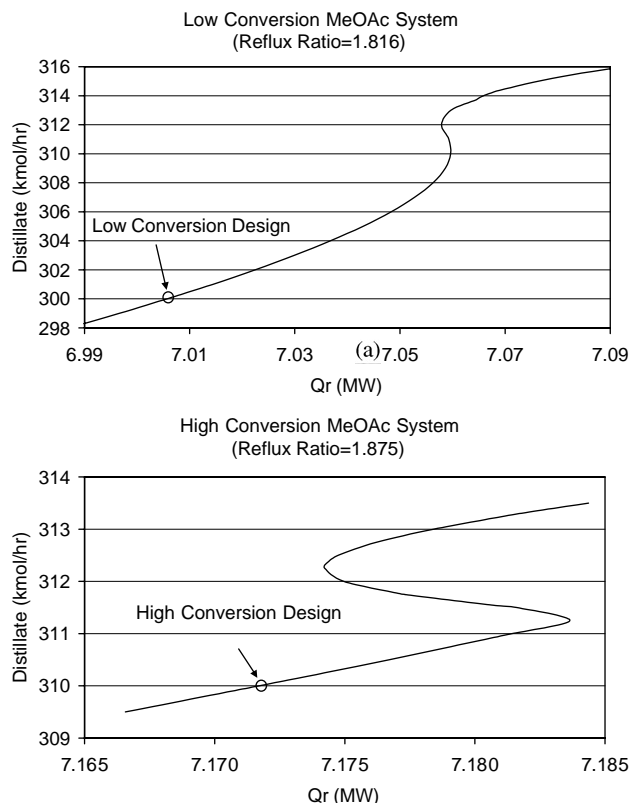
Fig. 3. Output multiplicity (Class 2).

operating conditions. This was verified dynamically. The pulse test described above was done on the column with fixed feeds, heat input and RR. Reflux drum level was controlled by reflux flow, and base level was controlled by the bottoms flow rate. The column was openloop stable and returned to the original operating conditions regardless of the direction of the pulse change.

2.2.3. Input multiplicity

The existence of output multiplicities indicates the possibility of input multiplicities. In this type the column has more than one set of inputs that give the same outputs. The fixed outputs are the distillate flowrate and the distillate composition. Two feed inputs are also fixed. The inputs that can vary are the reflux flowrate and the heat input.

The lightest component (MeOAc) always goes overhead in the distillate, so specifying the light-product purity in the distillate and the distillate flowrate fixes both conversion and the production rate of the desired product. Therefore, if we can obtain the same product purity while fixing the distillate flowrate and varying the reflux flowrate we have input multiplicity.

Fig. 4 shows that there are two reflux flowrates (and corresponding reboiler heat inputs) that give the same distillate flowrate and composition in the methyl acetate system. Of course the more economical design is the one with the lower reflux flowrate (lower energy consumption).
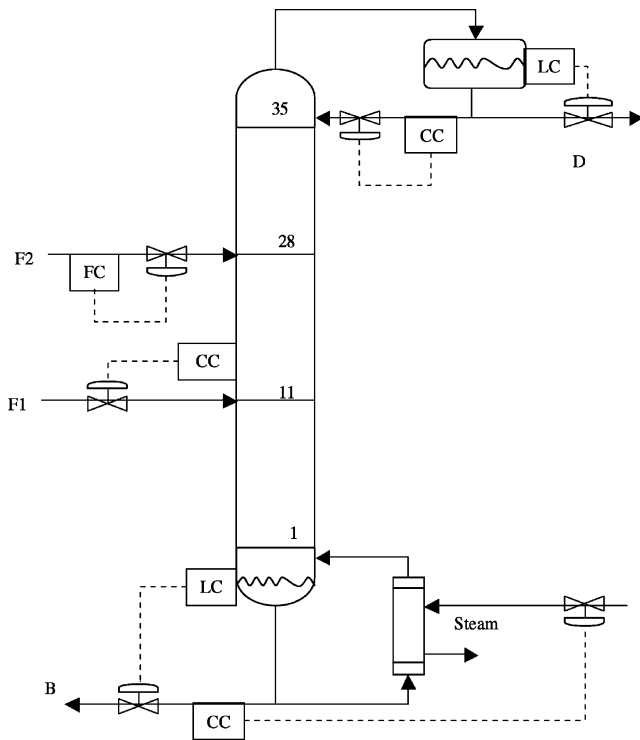
Fig. 5. Control structure 1.

Fig. 6. Control structure 5.

3. Control study

In this paper we explore three control structures applied to both the methyl acetate and the ideal systems. All the structures are SISO structures with PI controllers (P only on levels). The controllers are tuned using the Tyreus–Luyben turning method (Tyreus & Luyben, 1992). The relay-feedback method (Yu, 1999) is used to obtain the ultimate gain and ultimate period. All valves are designed to be half open at steady state. Two first-order measurement lags with a time constant of 30 s each are used in all composition or temperature loops.

For easy comparison with previous work (Al-Arfaj & Luyben, 2000), which explored six alternative structures, the same labelling of control structures is used. Two of the previous control structures are used in this paper (CS1 and CS5) and a new structure is studied (CS7).

3.1. Control structure 1

Fig. 5 gives CS1 in which three compositions are measured and controlled. The purities of the distillate and bottoms are controlled by manipulating reflux and reboiler heat-input, respectively. A composition inside the reactive zone of the column is measured and controlled by manipulating one of the fresh feeds. This loop permits the "neat" operation of the column (no excess of one of the reactants is used). Exact stoichiometric amounts of the two reactants must be fed, and this can only be achieved by some type
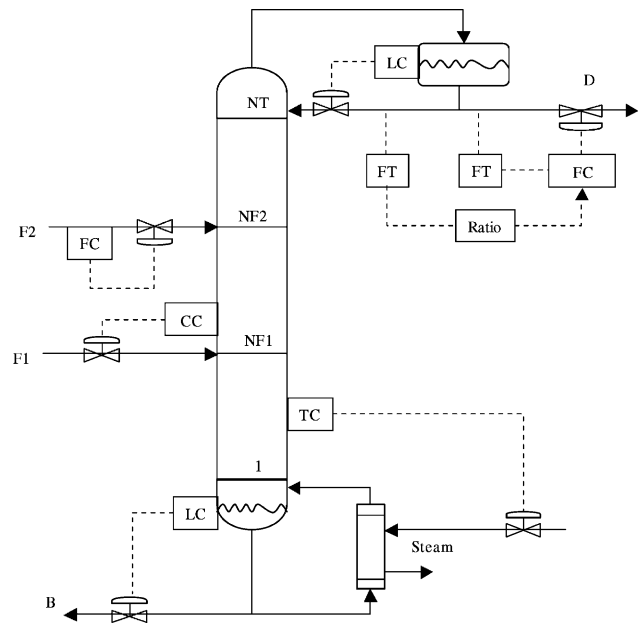
of feedback of composition information about the amounts of the reactant components in the system. Any imbalance in the inflow of the two reactants will result in a gradual buildup of the reactant that is in excess. This will lead to an unavoidable drop in product purity when one or more of the manipulated variables hits a constraint.

In practical applications, it is impossible to simply ratio the two feed streams, as has been proposed in some of the literature papers. Flow measurement inaccuracies and feed composition changes doom to failure any ratio structure that does not somehow incorporate information about compositions inside the system and feed this information back to adjust fresh feed.

In the previous paper (Al-Arfaj & Luyben, 2000), this internal composition control loop appeared in all six configurations. In this paper one of the control structure studied uses temperature measurements instead of a composition measurement to achieve the required balancing of the stoichiometry.

3.2. Control structure 5

Fig. 6 shows CS5 in which only one composition is controlled (the column internal composition) and a temperature is controlled in the stripping section. This temperature controller maintains bottoms purity at or above its specified value by keeping light components from dropping out the bottom with the heavy product component (HOAc). The setpoint of the temperature controller must set high enough to make sure the bottoms purity is at or above its specification value under worst-case conditions. A RR control scheme is used, with the RR set high enough to guarantee the distillate purity under worst-case conditions.
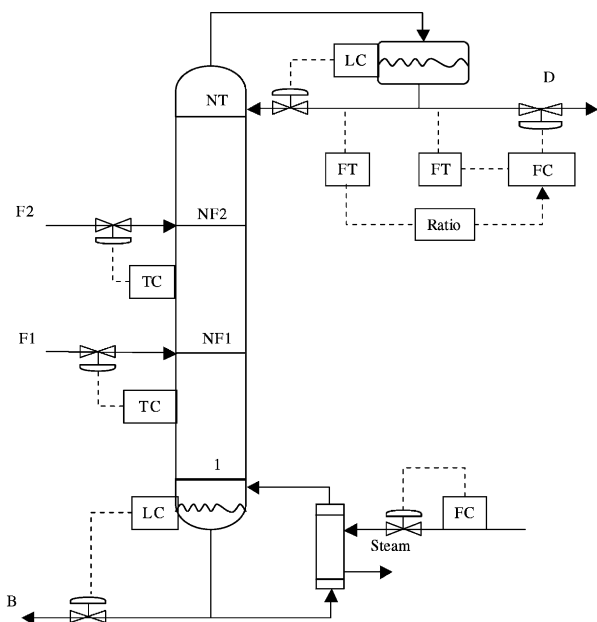
Fig. 7. Control structure 7.

Fig. 8. CS1 for high-conversion MeOAc.

The CS5 control structure is a more practical approach since it does not require three composition analyzers. In both CS1 and CS5 there is a direct production-rate handle, the flowrate of one of the fresh feeds.

3.3. Control structure 7

A new structure, which was not studied in the previous work, features the use of two temperatures that manipulate the two fresh feeds. Fig. 7 shows the scheme. Reboiler heat-input is flow controlled and serves as the production rate handle. RR is controlled. This structure was proposed by Roat, Downs, Vogel and Doss (1986) but no quantitative control studies were presented.

The selection of the tray temperatures to control is a central issue in this structure. The singular-value-decomposition method proposed by Moore (1992, Chap. 8) is used. The gain matrix between the inputs (the two fresh feed flowrates) and the outputs (the temperatures on all trays) is calculated numerically.

4. Results

4.1. Control structure 1

The composition of methyl acetate in the distillate is controlled by the reflux flowrate. The composition of the water in the bottoms is controlled by the heat input to the reboiler. The acetic acid flowrate is flow controlled. The levels in the reflux drum and the base of the column are controlled by the distillate flowrate and the bottoms flowrate, respectively. The concentration of methanol on the tray it is being fed to
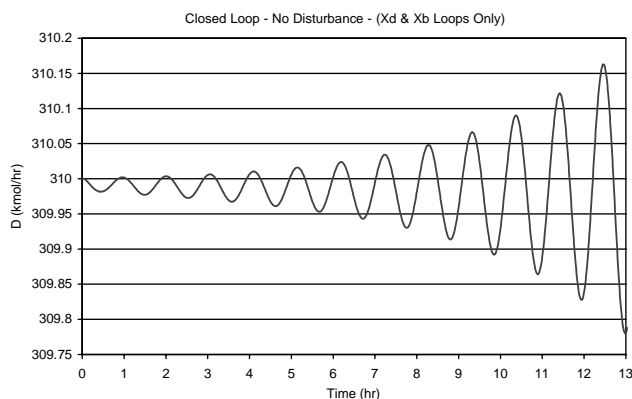
(Tray 11) at the bottom of the reactive zone is measured and controlled by manipulating the fresh methanol feed flowrate.

The steady-state multiplicity analysis predicts that the system is openloop unstable. It will drift to either a higher-conversion state or a lower-conversion state if no feedback control is used. This structure controls purities at both ends of the column, and for the high-conversion case, these purities are high. High product purities produce columns that are highly nonlinear in their dynamic behavior and present difficult control problems.

In order to study the basics of this structure, we turn off the composition controller in the reactive zone. We are left with only the two composition controllers in the top and bottom of the column. The Niederlinski index (Niederlinski, 1971) is negative for this system at the high conversion level. This means the system will exhibit integral instability as Fig. 8 demonstrates. The distillate and bottoms composition loops are on automatic, and the system is not subjected to any kind of disturbance. It should be noted that this control structure was shown in the previous paper (Al-Arfaj & Luyben, 2000) to work well for the low-conversion *ideal* system. It is also interesting to note that the system is closedloop *stable* when the third composition controller is put on automatic. It appears that this controller acts to reduce interaction. However, the performance of this structure is poor in the face of load disturbances and changes in setpoints.

Fig. 9 shows a control scheme that is a slight modification of CS1. Instead of having the distillate composition control change reflux flowrate, it changes the RR. This seemingly minor change produces a system with a positive Niederlinski index, which is openloop stable. Fig. 10 shows the response of this structure when the two product composition controllers are on automatic and a small pulse in one of the fresh feed flowrates is introduced. The ratio strategy reduces the interaction between the distillate purity and bottoms purity loops.

However, with the high product purities, the problems with nonlinearity still exist. Therefore, even though this
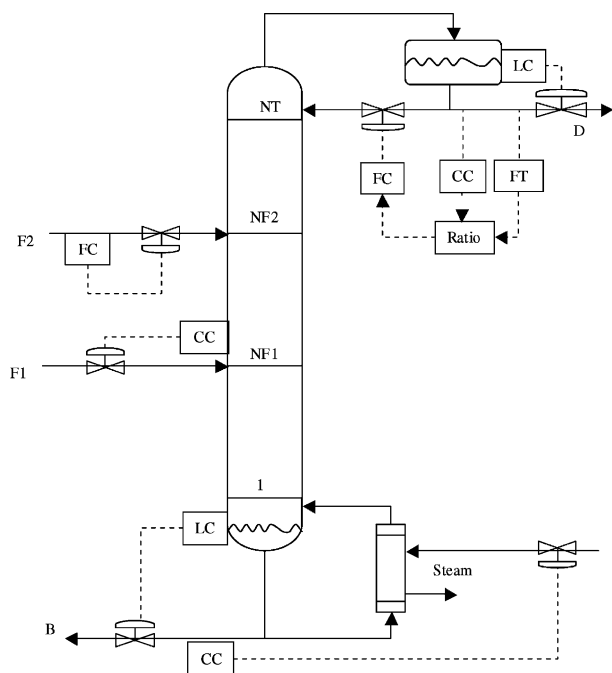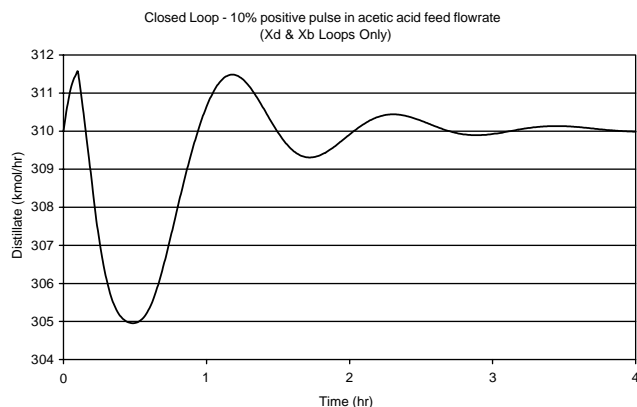
Fig. 9. Control structure 1-RR.

Fig. 10. CS1-RR for high-conversion MeOAc.

structure is better than the previous one, simulations show that neither structure can handle a 10% increase in the acetic acid feed flowrate.

The level of conversion and purity set the degree of system's nonlinearity. This is an important design variable that affects the controllability of the column directly. This nonlinearity makes dual composition very difficult even in conventional distillation columns. The interaction of this design variable on the controllability of the column is examined by changing the conversion and purity levels. Cases were studied over a range of conversions and product purities. Only one case is presented here in which the design conversion level is 95% and the design methyl acetate purity is 95 mol%. This 95/95 design should be compared with the

high-conversion case with 99.2% conversion and 96 mol% methyl acetate purity. The 95/95 design was analyzed for input and output multiplicity as discussed before. Results predicted the system should be openloop stable for the control structure CS1. The Niederlinski index is positive. Simulation studies verified openloop stability.

For the low-conversion/low-purity design, control structure CS1 gives effective control for moderate load disturbances and setpoint changes. The structure is able to handle changes in acetic acid feed flowrate up to 20% as shown in Fig. 11. Purities of both ends are approaching their setpoint. The methyl acetate composition controller needs to be retuned to reduce the settling time. Other than that the structure seems to be stable and effective. It also is able to reject methanol feed composition disturbances in which the feed composition is changed from 100% methanol to 90% methanol and 10% water. The structure is able to move the methyl acetate product purity setpoint from 95% to 97%.

These results show how important it is to do the design and control simultaneously. If CS1 must be used to control this system, designing the column to a high conversion would make control very difficult. On the other hand, if the high-conversion design is required, the system can be easily controlled if a different control structure is used as discussed below.

4.2. Control structure 5

The temperature on the third tray and the composition of methanol in Tray 11 are controlled (Fig. 6). RR is held constant. Even for the high-conversion/high-purity case, this control structure handles disturbances in the acetic acid feed flowrate. Fig. 12 gives results for a 20% step increase in the acetic acid flowrate. The system settles in around 4 h. Although methyl acetate and water purities are not controlled directly, this structure is able to indirectly maintain them very close to their desired levels. Temperature setpoint changes of ±2 K were tested. Even with these setpoint changes this structure is able to hold the methyl acetate and water purities close to their desired levels. For these temperature setpoint changes, methyl acetate ranges between 95.98% and 96.03% while water ranges between 98.55% and 99.00%.

These tests indicate that the CS5 control structure provides effective control even at high purity and conversion levels. Controlling an internal composition and one temperature reduces loop interaction. Controlling an intermediate tray temperature instead of a product purity significantly reduces the nonlinearity, even for high-purity levels. The temperature loop sees much more linear dynamics than does a composition loop. It should be kept in mind that there is no direct control of product compositions, so the temperature controller setpoint and the reflux ratio must be set to handle worst-case conditions. The low-conversion design is easier
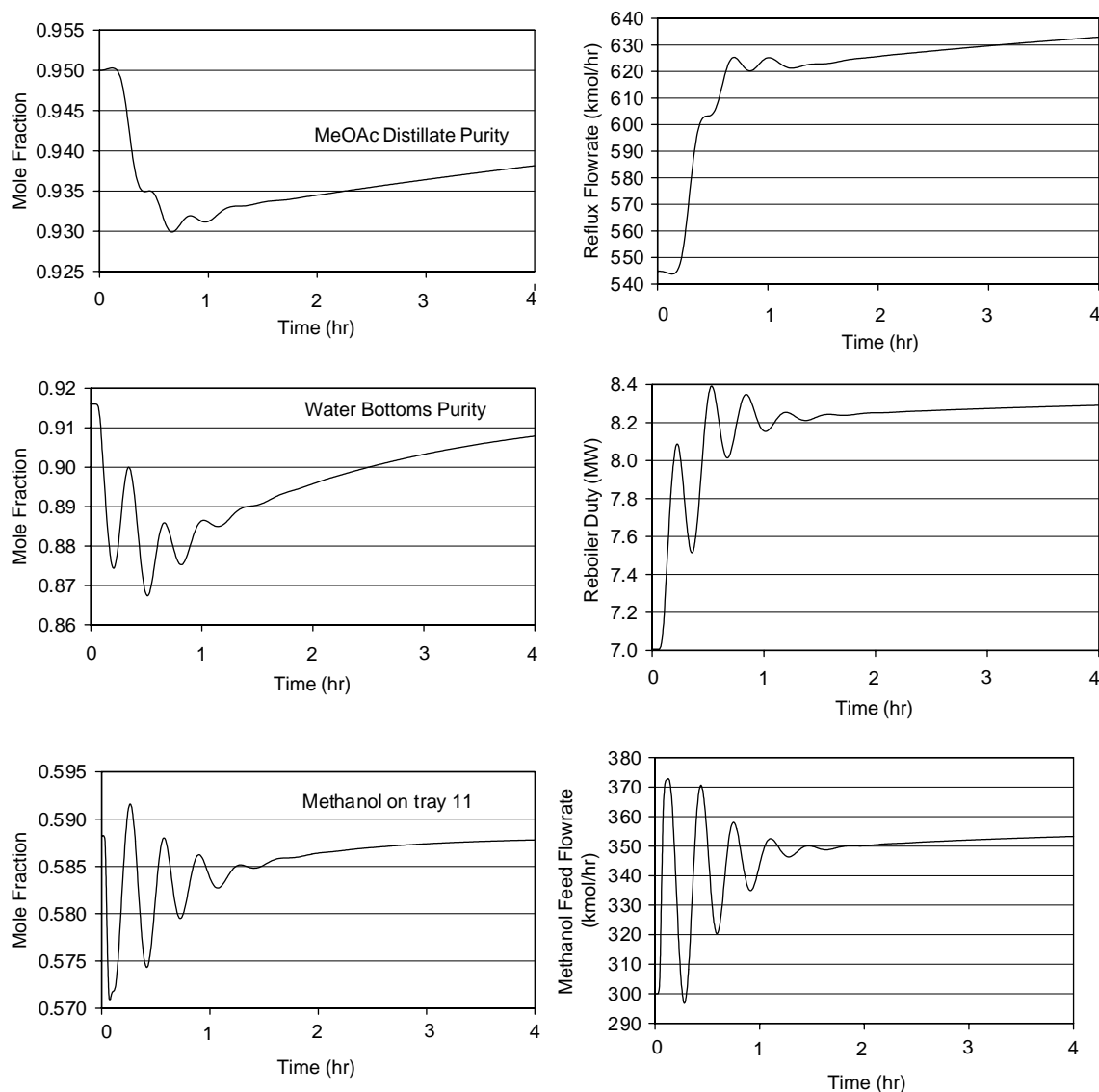
Fig. 11. CS1 for low-conversion MeOAc with +20% increase in HOAc feed.

to control than the high-conversion design as discussed above. CS5 is effective on the high-conversion design and would be expected to perform as well in the low-conversion design.

4.3. Control structure 7

This inferential control was first suggested by Roat et al. (1986). Temperature controllers on two trays in the column manipulate the two fresh feed flowrates. The reflux drum level is controlled by the reflux flow rate, and the base level by the bottoms flowrate (Fig. 7). The distillate flowrate is adjusted to give a constant RR. The heat input is fixed. This control structure has the very significant advantage of not requiring any composition measurement.

Singular value decomposition is used to select the most sensitive trays to be controlled, which are Tray 3 and 15. The Niederlinski index for this system is 0.94. Closed-loop response tests show that this control structure handles load disturbance very effectively, even for the high purity/conversion case. As shown in Fig. 13, a 20% increase in the reboiler heat input (the production handle) is handled by this structure very well. The temperature controllers increase both feeds flowrates by the same magnitude which balances the increase in the reboiler heat input. The methyl acetate and water purities at both ends are maintained close to the desired levels. Setpoint changes of ± 2 K in the temperature controllers were tested. The results of these changes show that the structure is not sensitive to inaccuracies in temperature sensors. Under these temperature setpoint changes, methyl acetate ranges
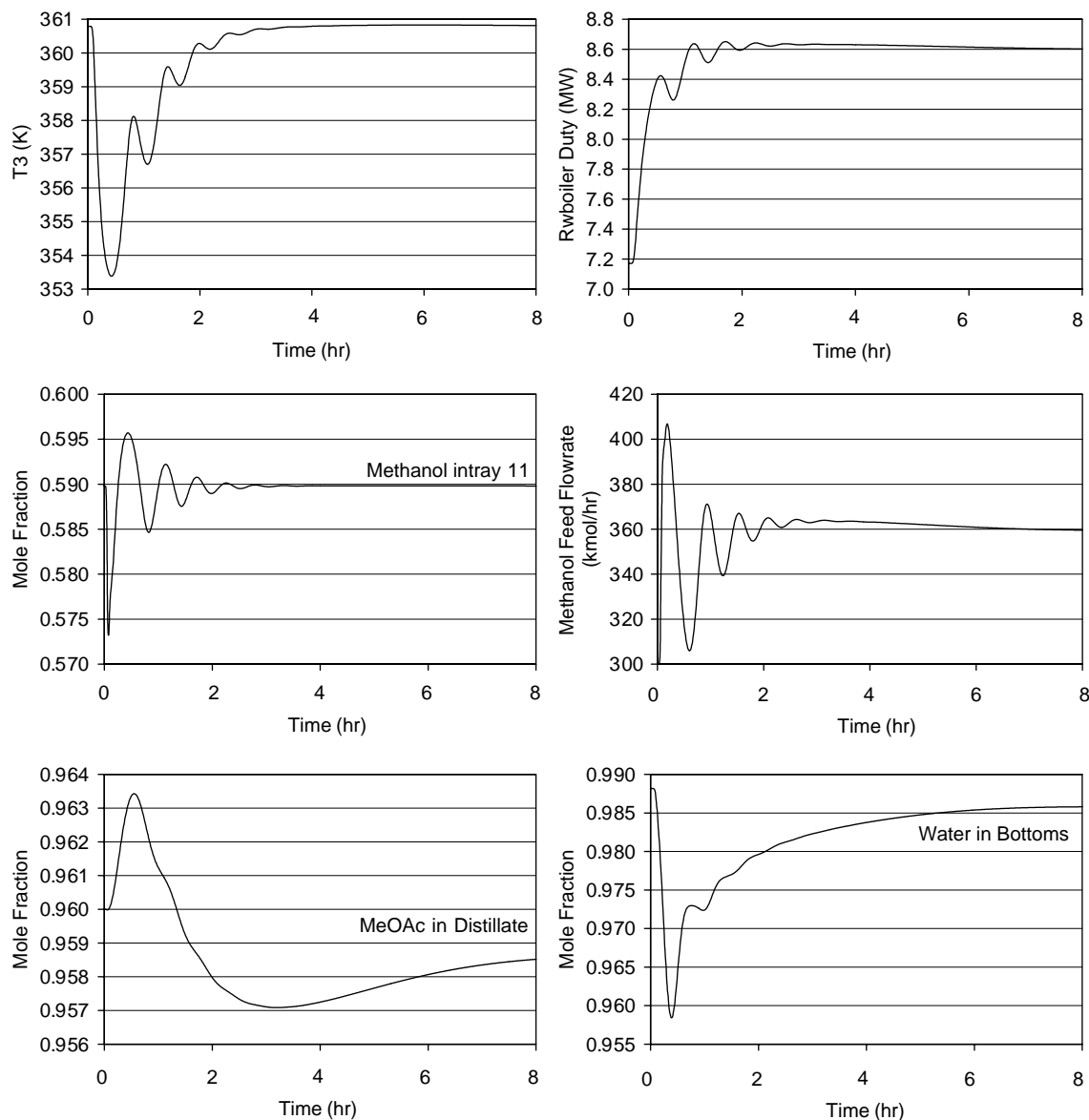
Fig. 12. CS5 for high-conversion MeOAc with +20% increase in HOAc feed.

between 95.9% and 96.1% while water ranges between 98.2% and 99.2%.

Unlike CS1, this structure is effective for the high-conversion design. To explore the effect of the conversion level on the controllability of this system, we tested the CS7 structure on the low-conversion design. Since this structure works well for the high-conversion design, which presents a more difficult control problem, one would expect it to perform well at low-conversion levels, and simulation results confirmed this. Since this structure does not control product purities directly, large disturbances can drive products off-spec unless the system is designed for purities that are higher than specifications. More reactive trays, higher tray holdups or catalyst loading are required to handle the worst-case conditions.

5. Comparison with ideal system

5.1. Steady-state design

The ideal system consists of two reactants and two products. The chemical reaction is

$$A + B \rightleftharpoons C + D.$$
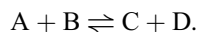
The volatilities are such that the products C and D are the lightest and heaviest, respectively, in the system. The volatilities are as follows: $\alpha_C > \alpha_A > \alpha_B > \alpha_D$. The reactants A and B are intermediate boiling between the products. Therefore the fresh feed stream containing reactant A is fed at the bottom of the reactive zone, and the fresh feed stream containing reactant B is fed at the top of the reactive zone.
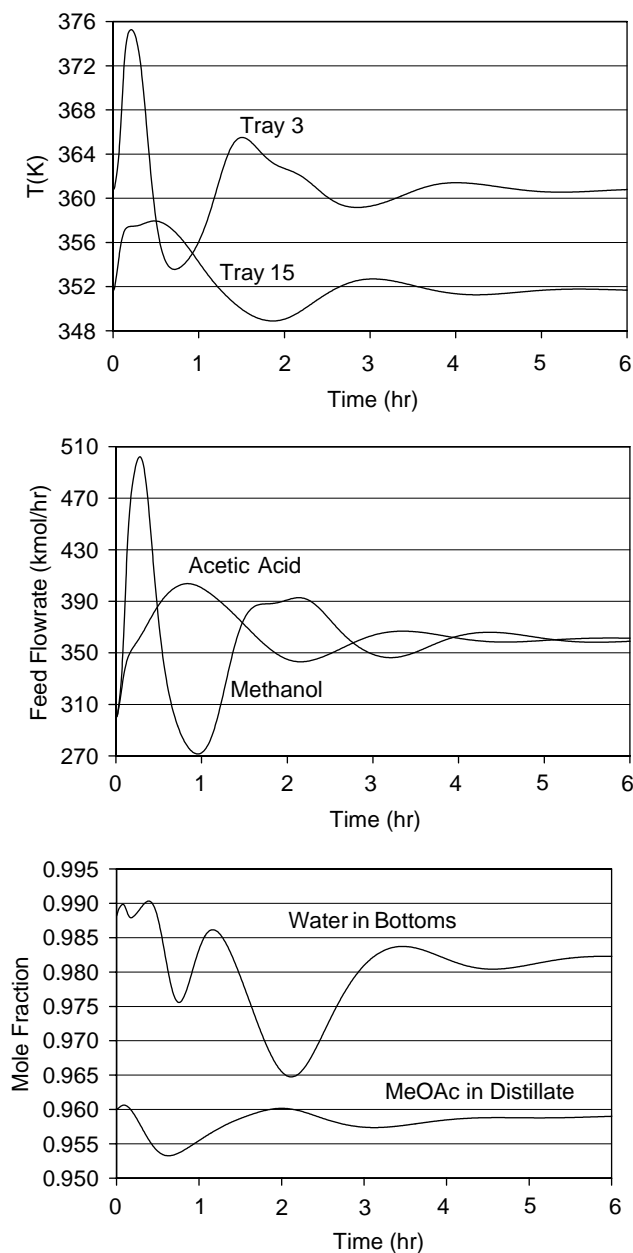
Fig. 13. CS7 for high-conversion MeOAc with +20% in Q_R.

Ideal VLE and constant equimolal overflow are assumed in this system.

Details of the ideal system are presented in the previous paper (Al-Arfaj & Luyben, 2000). The conversion and product purity for the base design in the paper was 95% conversion and 95% product purities. That design is considered as a low-conversion design in this work. A high-conversion design is developed. A higher RR must be used to obtain the higher conversion when the same holdup is used. A reactive tray holdup of 2 kmol (the low-conversion design uses only 1 kmol/tray) is used in the high-conversion design to insure adequate reaction capacity. The RR for the high-conversion design is less than the low-conversion design because the holdup is twice that of the low-conversion design. These two designs are used to study the impact of conversion level on the controllability of ideal systems.

5.2. Physical properties and chemical kinetics

On the surface, these two systems seem quite similar. Both systems have two reactants and produce two products, which are produced at the top and the bottom of the column. However, a more detailed look reveals some very significant differences. In addition to the obvious differences between ideal and nonideal vapor–liquid equilibrium and equimolal overflow versus nonequimolal overflow, the two systems differ in rates of reaction and reaction equilibrium constants.

The ideal system has smaller specific reactions rates and a smaller equilibrium constant. Table 1 summarizes some of these differences. The ideal reaction constant is smaller than the methyl acetate, and the methyl acetate reaction equilibrium constant is larger than the ideal at typical reaction temperatures. Since the heat of reaction of the ideal system is larger than that of the methyl acetate system, the rate of change of the ideal reaction equilibrium constant with respect to temperature is larger than that of the methyl acetate reaction. All these factors make the methyl acetate reaction more favorable than the ideal reaction.

Another significant difference is the product/reactant volatilities for the heavy reactant and product. In the ideal system, product D is less volatile than reactant B, so it is easy to keep B from being lost out the bottom of the column.

Table 1
General comparison

	Ideal system		Methyl acetate system	
Relative volatility	C > A > B > D		MeOAc > MeOH > H_2O > OHAc	
Activity coefficient	1		Wilson	
Equal molar overflow	Yes		No	
Equation of state	No		Peng Robinson	
Reaction rate	Simple power law		Activity based complex law	
Heat of reaction	−41.8 kJ/mol (constant)		−14.3 kJ/mol (function of T)	
T (K)	$K_{forward}$ (kmol/h/tray) Holdup = 1 kmol/tray	K_{eq}	$K_{forward}$ (kmol/h/tray) Catalyst load = 1000 kg/tray	K_{eq}
350	4381	3.75	274,000	21.73
390	363,202	0.86	1,728,000	17.27
430	13,236,800	0.26	7,743,000	14.33

In the methyl acetate system, product H_2O is somewhat *more* volatile than reactant HOAc. Therefore any acetic acid that is not reacted in the reactive zone will drop out the bottom of the stripping section. This means that the reactive section must have plenty of catalyst (or holdup) to guarantee a high conversion of the acetic acid that is fed to the top of the reactive zone. Fortunately the favorable kinetics and equilibrium constant aid in achieving a higher conversion of HOAc.

5.3. Control system

5.3.1. Control structure 1 and 5

In our previous paper, we examined the CS1 and CS5 structures for the low-conversion design and found they are effective. To explore their effectiveness for high-conversion designs, simulation studies were conducted. The CS5 was found to work well for a high-conversion design.

Somewhat surprisingly, the CS1 structure was also found to work well for the high-conversion design. Remember that in the methyl acetate case the CS1 structure is not effective for the high-conversion design. This difference appears to be due to the higher degree of nonlinearity in the methyl acetate system than in the ideal. In the ideal system, the reaction kinetics are nonlinear and the VLE are only mildly nonlinear. In the methyl acetate system, both the kinetics and the VLE are highly nonlinear due to significant activity coefficients.

5.3.2. Control structure 7

This structure was not examined in the previous paper. Similar to the methyl acetate case, the tray selection was done using the SVD method. The two trays selected for temperature control are Trays 5 and 15 for the high-conversion design. This structure was tested on both the high-conversion and low-conversion designs.

Fig. 14 gives results when the system is subjected to a 20% increase in the reboiler duty. The control structure is able to maintain the bottoms purity very close to its desired level. The distillate purity dropped about 1.5%. If this drop is not tolerable, the temperature controller setpoint would have to be adjusted such that the overhead purity would not drop below 99%. Another approach to overcome this problem is to design the column for higher product purities so that they remain above specification even in worst-case conditions.

5.3.3. Discussion

These results show an important finding. Even though there are some differences between the ideal and methyl acetate systems, extending effective control structures from one to the other is possible. Due to some physical or chemical restrictions this applicability of effective control structures between similar systems could be limited. For example, CS1 is more sensitive to the nonlinearity of the system. Therefore, we could expect that highly nonlinear
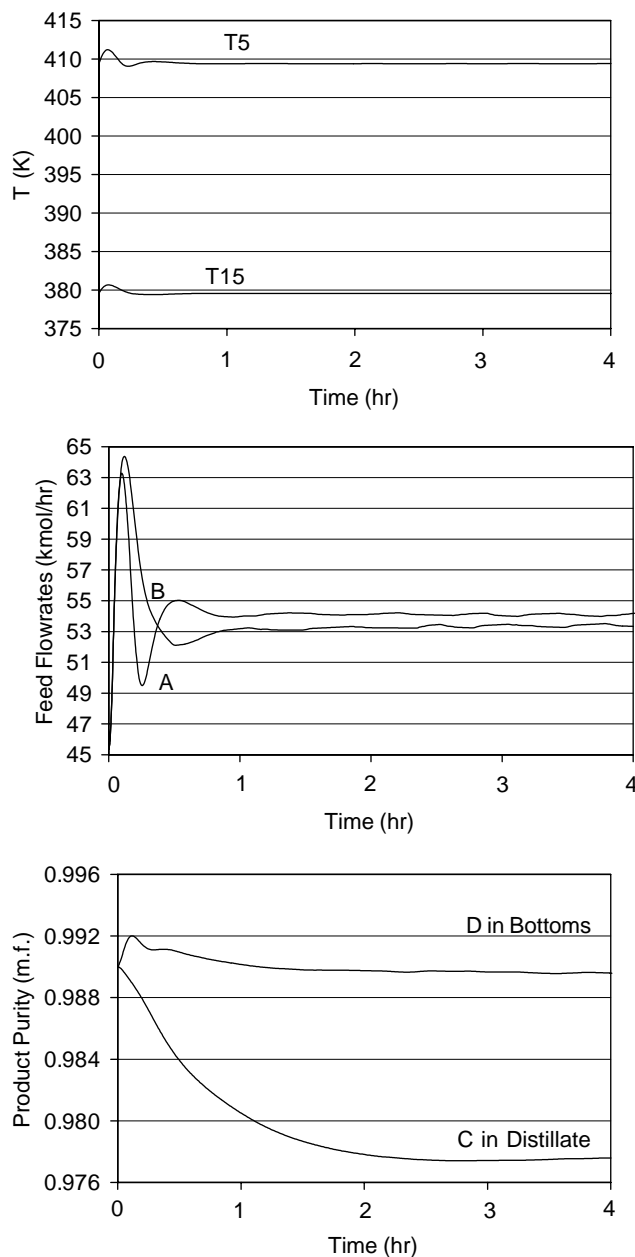

Fig. 14. CS7 for high-conversion ideal with +20% in Q_R.

system will not be effectively controlled by this structure. This is why CS1 works on the ideal system and not on the high-conversion methyl acetate column. On the other hand, CS5 and CS7 are not sensitive to this point of difference between the two systems (the nonlinearity due to high conversion), and they could be extended from one system to the other.

6. Conclusion

The design and control of a methyl acetate reactive distillation column have been studied. Several steady-state

multiplicities are found. The impact of these multiplicities on the openloop stabilities is discussed. The systems that are openloop unstable are harder to control than openloop stable systems. Several control structures have been studied. The CS1 control structure is effective provided loop interaction and system nonlinearity are not severe. However, this structure requires three composition analyzers, so is less practical than the CS5 control structure, which uses only one composition measurement.

The interaction between the design and control is examined by changing the conversion level. Low-conversion designs are less nonlinear and are easier to control. It is important to consider both design and control together in the design stage. The control of the methyl acetate reactive column process is very difficult if a CS1 structure is implemented on the high-conversion design.

The CS7 control structure uses only temperature measurements and provides effective control, provided the disturbances are not too large and the column has been designed for higher-than-required purity levels.

The methyl acetate system is compared to an ideal system with similar chemistry. The two systems have some differences and similarities. It is found that some control structures can be used on both systems.

Notation

A	component A in ideal system
B	component B in ideal system
B	bottoms flowrate, kmol/h
C	component C in ideal system
D	component D in ideal system
D	distillate flowrate, kmol/h
HOAc	acetic acid
K	reaction constant, kmol/h/g or kmol/h/kmol
K_{eq}	reaction equilibrium constant
MeOAC	methyl acetate
MeOH	methanol
Q_R	reboiler duty, MW
R	reflux flowrate, kmol/h
RR	reflux ratio
m.f.	mol fraction
α	relative volatility

References

Agreda, V., & Partin, L. (1984). *Reactive distillation process for the production of methyl acetate*. U.S. Patent 4,435,595, 6 March.

Agreda, V. H., Partin, L. R., & Heise, W. H. (1990). High-purity methyl acetate via reactive distillation. *Chemical Engineering Progress*, *86*, 40–46.

Al-Arfaj, M. A. (1999). *Quantitative heuristic design of reactive distillation*. Master's thesis, Lehigh University, Bethlehem, PA.

Al-Arfaj, M. A., & Luyben, W. L. (2000). Comparison of alternative control structures for an ideal two-product reactive distillation column. *Industrial and Engineering Chemistry Research*, *39*, 3298–3307.

Al-Arfaj, M. A., & Luyben, W. L. (2002a). Control study of ETBE reactive distillation. *Industrial and Engineering Chemistry Research*, *41*, 3784–3796.

Al-Arfaj, M. A., & Luyben, W. L. (2002b). Control of ethylene glycol reactive distillation column. *A.I.Ch.E. Journal*, *48*(4), 905.

Al-Arfaj, M. A., & Luyben, W. L. (2002c). Design and control of an olefin metathesis reactive distillation column. *Chemical Engineering Science*, *57*, 715–733.

Al-Arfaj, M. A., & Luyben, W. L. Plantwide control for TAME production using reactive distillation. *Chemical Engineering Science*, submitted for publication.

Doherty, M. F., & Buzad, M. G. (1992). Reactive distillation by design. *Transactions of the Institution of Chemical Engineers, Part A*, *70*, 448–458.

Guttinger, T., & Morari, M. (1999a). Predicting multiple steady states in equilibrium reactive distillation. 1. Analysis of nonhybrid systems. *Industrial and Engineering Chemistry Research*, *38*, 1633–1648.

Guttinger, T., & Morari, M. (1999b). Predicting multiple steady states in equilibrium reactive distillation. 2. Analysis of hybrid systems. *Industrial and Engineering Chemistry Research*, *38*, 1649–1665.

Lee, J., & Dudukovic, M. (1998). Comparison of the equilibrium and nonequilibrium models for a multicomponent reactive distillation column. *Computers in Chemical Engineering*, *23*, 159–172.

Luyben, W. L. (2000). Economic and dynamic impact of the use of excess reactant in reactive distillation systems. *Industrial and Engineering Chemistry Research*, *39*, 2935–2946.

Mark, J. (1955). Vapor–liquid equilibrium in mixtures containing an associating substance. II binary mixtures of acetic acid at atmospheric pressure. *Collection of Czechoslovak Chemical Communication*, *20*, 1490.

Monroy-Loperens, R., Perez-Cisneros, E., & Alverz-Ramirez, J. (2000). A robust PI control configuration for a high-purity ethylene glycol reactive distillation column. *Chemical Engineering Science*, *55*, 4925–4937.

Moore, C. (1992). Selection of controlled and manipulated variables. In W. Luyben (Ed.), *Practical distillation control*. New York: Van Nostrand Reinhold.

Niederlinski, A. (1971). A heuristic approach to the design of linear multivariable interacting control systems. *Automatica*, *7*, 691.

Roat, S., Downs, J., Vogel, E., & Doss, J. (1986). Integration of rigorous dynamic modeling and control system synthesis for distillation columns. In *Chemical process control-CPC III*. Amsterdam: Elsevier.

Sneesby, M. G., Tade, M. O., & Smith, T. N. (2000). A multi-objective control scheme for an ETBE reactive distillation column. *Transactions of the Institution of Chemical Engineers, Part A*, *78*, 283–292.

Song, W., Venimadhavan, C., Manning, J., Malone, M., & Doherty, M. (1998). Measurement of residue curve maps and heterogeneous kinetics in methyl acetate synthesis. *Industrial and Engineering Chemistry Research*, *37*, 1917–1928.

Tyreus, B. D., & Luyben, W. L. (1992). Tuning PI controllers for integrator/dead time processes. *Industrial and Engineering Chemistry Research*, *31*, 2625–2628.

Yu, C.-C. (1999). *Autotuning of PID controllers*. London: Springer.