STEADY STATE ANALYSIS FOR THE SYNTHESIS OF REACTIVE DISTILLATION COLUMN CONTROL STRUCTURES

Nitin Kaistha [*], Bhanu P. Singh, M.V. Pavan Kumar, and Ram Singh
Department of Chemical Engineering
Indian Institute of Technology, Kanpur 208016

Abstract
The synthesis of effective control structures for reactive distillation (RD) columns through a systematic analysis of the steady state relationship between potential manipulated variables (inputs) and potential controlled variables (outputs) is demonstrated. The industrially important double feed RD columns for MTBE and methyl acetate production are used as examples. In order to regulate product purity and reaction conversion, two control loops are required. The first is to balance the fresh feeds as per the reaction stoichiometry and the second is to adjust the column internal flows for the desired separation. The input-output pairings for the two control loops are chosen so that they are sensitive and avoid steady state multiplicities as well as instability problems due to loop interaction. The proposed MTBE control structure uses the reboiler duty to maintain a stripping tray temperature and adjusts the fresh butene feed to maintain a reactive tray composition. The proposed control structures for the methyl acetate column use the fresh acetic acid feed to maintain a reactive tray temperature / composition and the reboiler duty to regulate a stripping tray temperature. Alternatively, the fresh methanol flow may be used to regulate a stripping tray temperature. Results show that the proposed control structures maintain the steady state purity and conversion for production rate and feed composition changes near the design values for both the example columns.

Keywords: Reactive distillation, control structure synthesis, control structure screening

[*] Corresponding author. Email: nkaistha@iitk.ac.in; Phone: +91-512-2597136; Fax: +91-512-2590104.

Introduction

In the past two decades, reactive distillation has emerged as a very promising technology replacing conventional "reactor followed by separator" processes at a fractional cost whenever the VLE and reaction kinetics favor high reaction rates on the trays. Commercial examples include RD processes for producing methyl acetate (Agreda and Partin, 1984) and octane enhancing alkyl ethers (Smith, 1981; and Hickey and Adams, 1994). The combination of reaction and separation in a single column causes high non-linearity so that multiple steady states are quite common (Jacobs and Krishna, 1994; Ciric and Miao, 1994; and Chen et al, 2002). When we also consider the non-monotonic temperature profiles, unlike in ordinary distillation, and the fewer available valves vis-à-vis conventional processes, for regulating both the separation and conversion, it is not surprising that the control of RD columns can be quite a challenging task. The RD control literature has thus naturally witnessed a spate of publications in recent years (Al-Arfaj and Luyben, 2000; Vora and Daoutidis, 2001; and Al-Arfaj and Luyben, 2002a-d).

An RD column requires a robust control system that maintains the product purity and reaction conversion at the design values in the face of disturbances such as production rate changes and feed composition changes. The choice of the control structure is the most crucial decision in devising such a control system. The RD control literature recognizes this fact (Al-Arfaj and Luyben, 2002a-d). However, little guidance is available on what constitutes a "good" control structure and why is it so. Most reports rely on ranking the different possible control structures in terms of their ability to handle anticipated disturbances through dynamic simulations. This may aptly be termed as the control structure screening approach. It would be most desirable to move towards a control structure synthesis approach. This is the primary motivation behind this work.

In order to synthesize an effective control structure, the choice of the controlled and manipulated variables must be made carefully. A sensitive controlled variable is desired so that the occurrence of even a small disturbance is detected and compensated for through appropriate feedback action. The manipulated variable should be chosen such that it affects the controlled variable in a substantial and easily predictable way. In other words, the steady state input-output relationship should be simple and avoid any multiplicities. Also, in case multiple control loops are to be used, the input-output pairings should be such that instability does not occur due to interaction between the loops. Finally, since sensor measurements are never exact, the column performance should be relatively insensitive to typical measurement biases or errors in the input set-point. Clearly, a systematic study of the steady state response of the column outputs (tray temperatures / compositions etc), as the column inputs (fresh feed rate, reboil ratio etc) are varied about their base case design values would reveal potential input-output pairings. Pairings where the input significantly affects the output ensuring adequate "muscle" for control and that avoid multiplicities should be preferred. Two types of multiplicities are noted, namely, input multiplicity and output multiplicity. The former refers to multiple inputs giving the same output while the latter refers to the same input giving multiple outputs.

In this work we demonstrate the systematic analysis of steady state input-output relationships for the synthesis of effective control structures for an RD column. A case study approach is taken. The industrially important MTBE and methyl acetate RD columns are used for illustrating the synthesis of robust control structures.

RD Columns Studied

A schematic of the MTBE and methyl acetate RD columns used in this work is shown in Figure 1. The important column design parameters and base case operating conditions are shown in the Figure. The double feed configuration is used for both the columns. The fresh feed to the MTBE column contains a slight excess of methanol while the fresh feeds to the methyl acetate column are in perfect stoichiometric balance. For the MTBE column, the bottoms stream is the product stream with 99.98 mol % MTBE purity. The reaction conversion achieved is 92 %. The unreacted isobutene, methanol and inert n-butane leave primarily in the distillate stream. The reaction kinetics is taken from Seader and Henley, 1998. The component mole fraction terms in the kinetic expression are replaced by the component activities in this work. For the methyl acetate column, the distillate stream is 95 % pure methyl acetate while the bottoms stream is 98% pure water. The reaction conversion achieved is 98 %. The reaction kinetic expression is taken from Al-Arfaj and Luyben, 2002b.

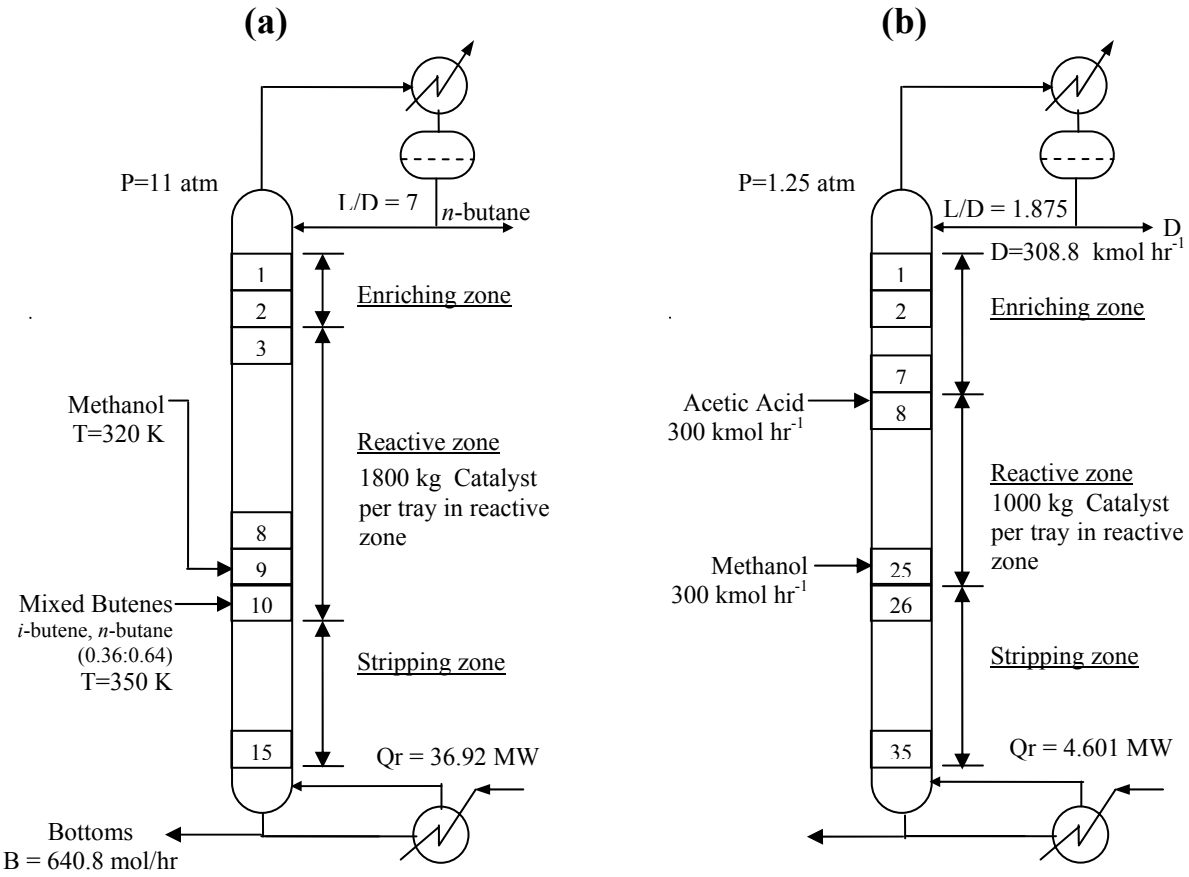

Figure 1. Schematic of reactive distillation columns studied
(a) MTBE column
(b) Methyl Acetate column

The VLE calculations assume ideal vapor phase. The extended Antoine equation is used to obtain the saturation vapor pressure. The liquid phase activity coefficients are modeled using the Wilson equation. The Wilson parameters are obtained from the DECHEMA series for the methyl acetate system and from Chen et al, 2002, for the MTBE system. For the methyl acetate system, the effect of acetic acid dimerization in the vapor phase on the VLE is modeled using Marek's method (Marek, 1955). The vapor phase enthalpies are obtained using the DIPPR equation. The liquid phase enthalpy is obtained by subtracting the heat of vaporization from vapor enthalpy and correcting for non-idealities by adding the excess enthalpy term. The heat of vaporization is obtained using the DIPPR method. Details of the reaction kinetic parameters, VLE parameters and enthalpy parameters can be found in Singh, 2004.

Manipulated Variables

The fresh feed rates, reflux rate / ratio and reboil rate / ratio are the available manipulated variables for column regulation. For simplicity, we assume a fixed reflux rate or reflux ratio operating policy. RD columns typically have large tray hold ups so that changes in the reflux flow take a long time to propagate throughout the column. In contrast, changing the reboil rate causes an immediate change in the vapor flow throughout the column.

Reflux Ratio vs Reflux Rate

In order to decide between the fixed reflux rate and the fixed reflux ratio policy, Figure 2 plots the variation in the product purity and conversion as the reboiler duty is varied about the base case value at fixed reflux and at fixed reflux ratio, for the two example columns.

In the MTBE system, output multiplicity is observed for both fixed reflux rate and fixed reflux ratio. In the former, the base case operating condition lies in the zone of multiplicity so that the column may drift from a high conversion steady state to a low conversion steady state even though there is no apparent change in the column input. This is a most undesirable situation. In contrast, for the fixed reflux ratio policy, the base case operating condition is away from the zone of output multiplicity. Also the reboiler duty range with no output multiplicity is larger. In the methyl acetate column, output multiplicity is observed at fixed reflux rate. On the other hand, no multiplicity is seen if the reflux ratio is fixed. It is thus clear that the fixed reflux ratio policy should be used for both the columns.

Sensitivity Analysis

Output variables that are sensitive to changes in manipulated variables are generally also sensitive to the occurrence of disturbances. A sensitive measurement thus detects the occurrence of small disturbances as deviations from the set-point. These deviations can easily be compensated for by appropriate feedback control action since the measurement is highly responsive to changes in the manipulated variable. Thus sensitive controlled variables are the key to good column regulation.

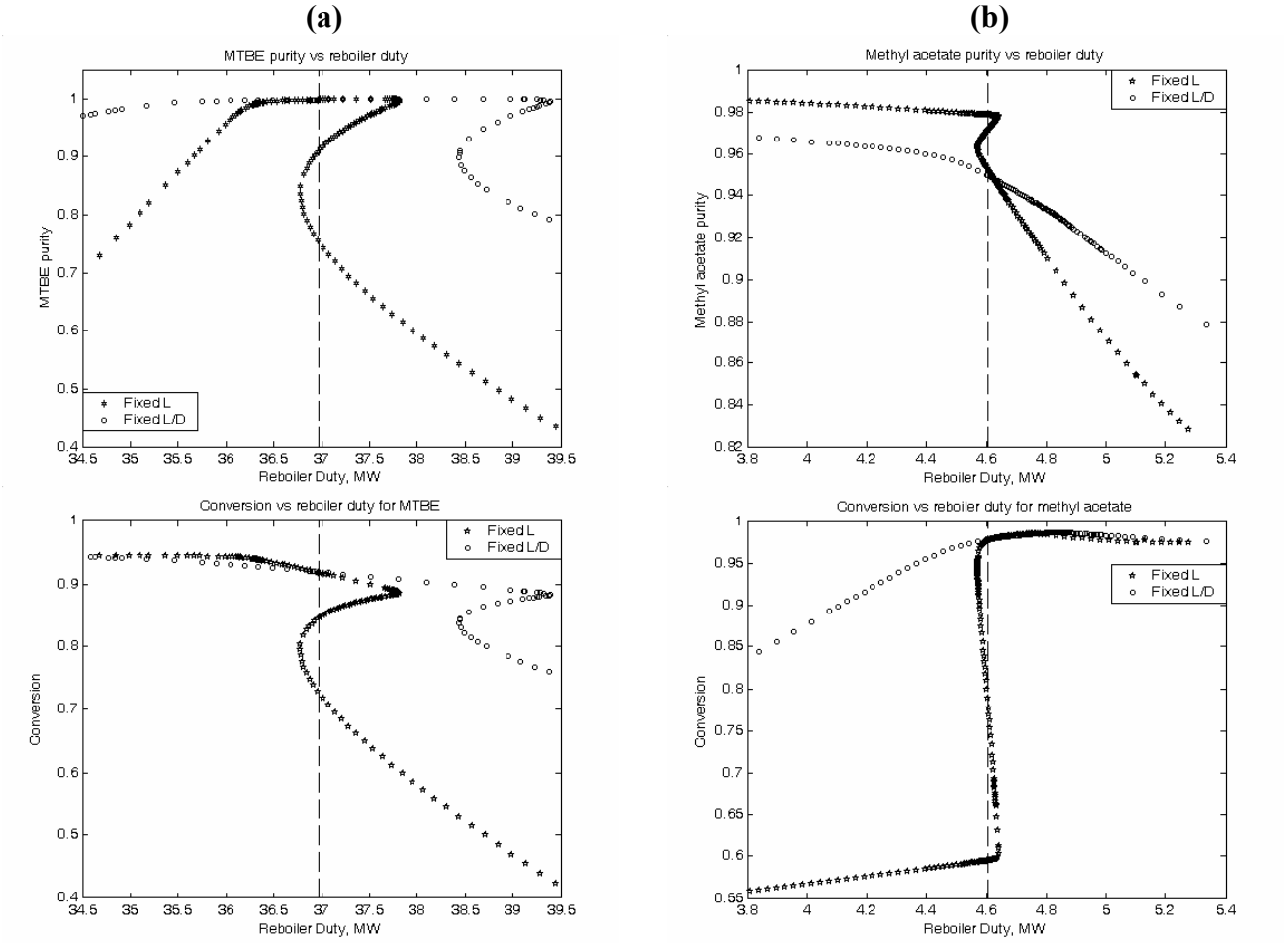

Figure 2. Variation in product purity and reaction conversion with reboiler duty
(a) MTBE column
(b) Methyl acetate column

The sensitivity of an output variable (y) to changes in an input (x) is defined as $\partial y/\partial x$. For an RD column, tray temperatures and compositions are obvious candidate controlled variables. Temperature measurements are certainly preferred because of their reliability and fast response. In contrast, an analytical composition measurement may be inaccurate and can take anywhere from 15 minutes to a day.

Figure 3 plots the tray temperature and composition sensitivity with respect to the reboiler duty, and the two fresh feed flow rates for the example columns. For the MTBE column, Tray 12 temperature is most sensitive to changes in all the column inputs. The tray composition sensitivities indicate that Tray 8 isobutene composition in the reactive section is comparatively more sensitive to changes in the fresh methanol feed. Tray 11 isobutene composition is sensitive to the fresh isobutene feed. The sensitivity of the other tray compositions is generally lower.

The methyl acetate column sensitivities indicate that the temperature / composition of Tray 35 in the stripping section and Tray 20 in the reactive section are sensitive to the reboiler duty and the fresh acetic acid feed. With respect to the fresh methanol feed, only

Tray 35 in the stripping section is sensitive. The input-output relationships of these trays should be studied further.

Control Tasks

A control system in an RD column must accomplish two tasks for proper column regulation. The first is to adjust the column internal flow for handling the separation load as in ordinary distillation and the second is to maintain the stoichiometric balance of the fresh feeds into the column. The latter is crucial since any unreacted excess reactant must necessarily leave in one of the product streams so that for a large enough excess, overall material balance constraints would preclude the possibility of maintaining the product purity. Two feedback loops are therefore necessary for adjusting the column internal flow and the fresh feed balance.

(a) **(b)**

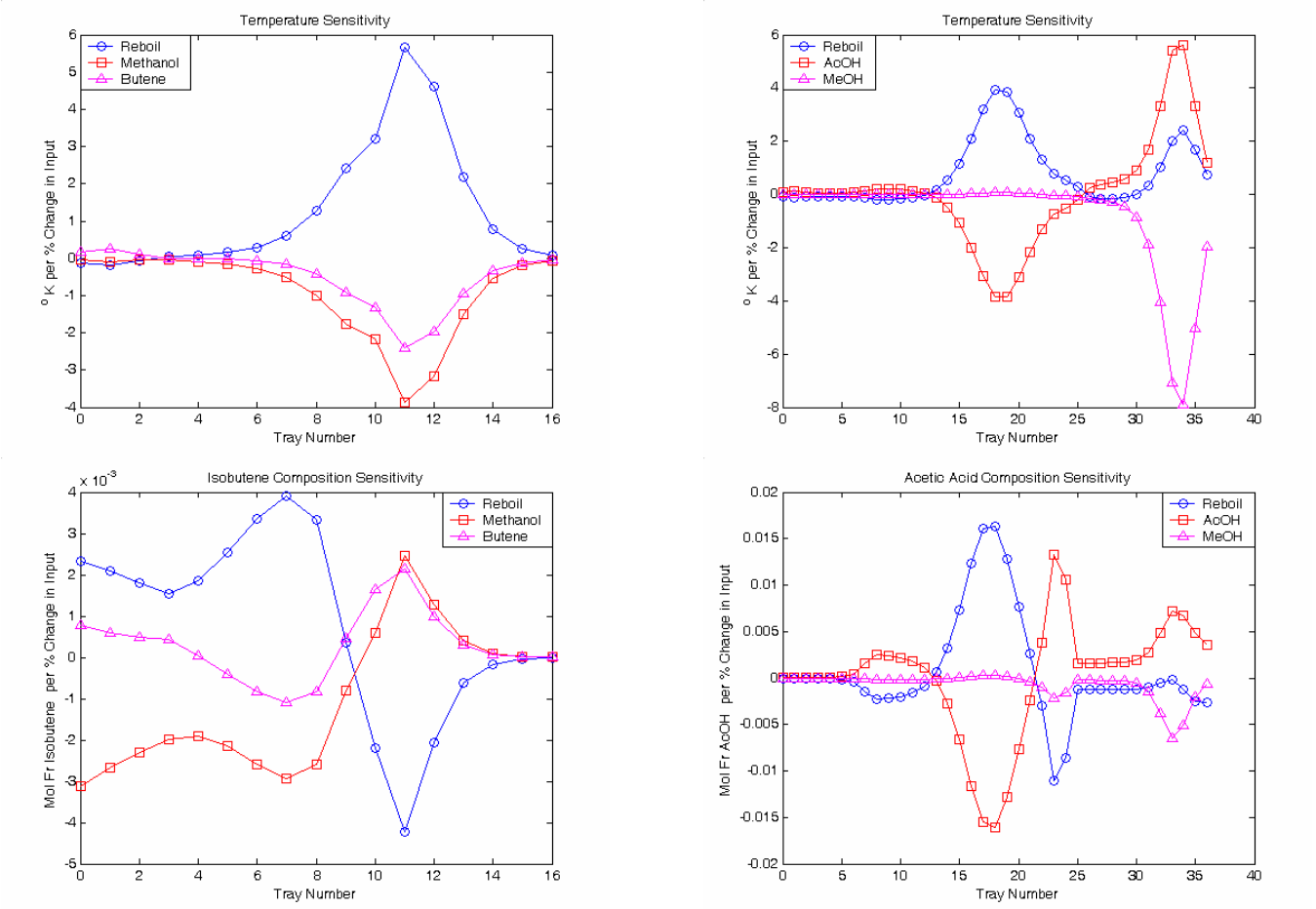

Figure 3. Temperature and composition sensitivities
(a) MTBE column
(b) Methyl acetate column

The column control system should maintain the product purity and conversion for different production rates. There are two ways in which production rate changes can be handled. The first is to change the fresh feed flow and then adjust the column internal flow for the desired separation. In this case, one of the fresh feeds acts as the production rate handle. The second feed is used to maintain a sensitive reactive tray temperature / composition at its base case value for ensuring stoichiometric feed balance. The reboiler duty (or reflux) is adjusted to maintain a tray temperature / composition at its base case value for regulating the separation. Such structures are referred to as direct control structures.

The second way of handling production rate changes is to first alter the achievable separation by changing the column internal flow and then adjust the fresh feeds so that purity is maintained. In this case, the reboiler duty (or reflux) acts as the production rate handle. A change in the reboiler duty affects a sensitive non-reactive tray temperature (or composition). One of the fresh feeds is adjusted so that this tray temperature is maintained. The other fresh feed is used to maintain a reactive tray temperature (or composition) for stoichiometric feed balance. This is referred to as an indirect control structure.

Input-Output Relationships

For the two example columns, the steady state input-output relationships for tray temperatures and compositions need to be studied in order to decide on the most appropriate pairings. The variation in representative tray temperatures with respect to reboiler duty and fresh feed rates is plotted in Figure 4 for the two columns. In both the columns, the stripping tray temperatures are quite sensitive to changes in the reboiler duty about the base case conditions. Also no output multiplicity is seen near the base case reboiler duty. Thus the reboiler duty can be used to control a stripping section tray temperature. The sensitivity of Tray 11 and Tray 34 temperatures in the stripping section of the MTBE and methyl acetate columns respectively, is evident.

In the plot, input multiplicity in the reactive tray temperatures with respect to the fresh feed flows is seen for both the columns. For the MTBE column, the fresh butenes feed should not be used to control any temperature due to the lower sensitivity. Also for the reactive trays, the difference between the extremum temperature and the base case temperature is only about 2 °K. Since typical temperature sensor biases are of that order, an infeasible tray temperature set-point can easily result if we try to maintain a reactive tray temperature using the fresh isobutene feed. This is not the case with the fresh methanol feed where the difference of the extremum point from the base case operating point is about 5 °K. Thus the methanol fresh feed may be used to control a tray temperature in the reactive section.

For the methyl acetate column on the other hand, even though the sensitive Tray 19 temperature in the reactive section shows input multiplicity with respect to the fresh acetic acid feed rate, the base case operating condition is about 5 °K away from the extremum temperature so that the problem of infeasible set points due to sensor biases does not occur. The fresh acetic acid feed can therefore be used for maintaining the Tray

19 temperature in the reactive section. On similar arguments, we can also use the fresh methanol feed to regulate Tray 34 temperature in the stripping section. The indirect control structure where fresh acetic acid and methanol maintain Tray 19 and Tray 34 temperatures respectively, is therefore a distinct possibility for this system. The direct control structure where the reboiler duty maintains Tray 34 temperature and fresh acetic acid maintains Tray 19 temperature, is of course another possibility.

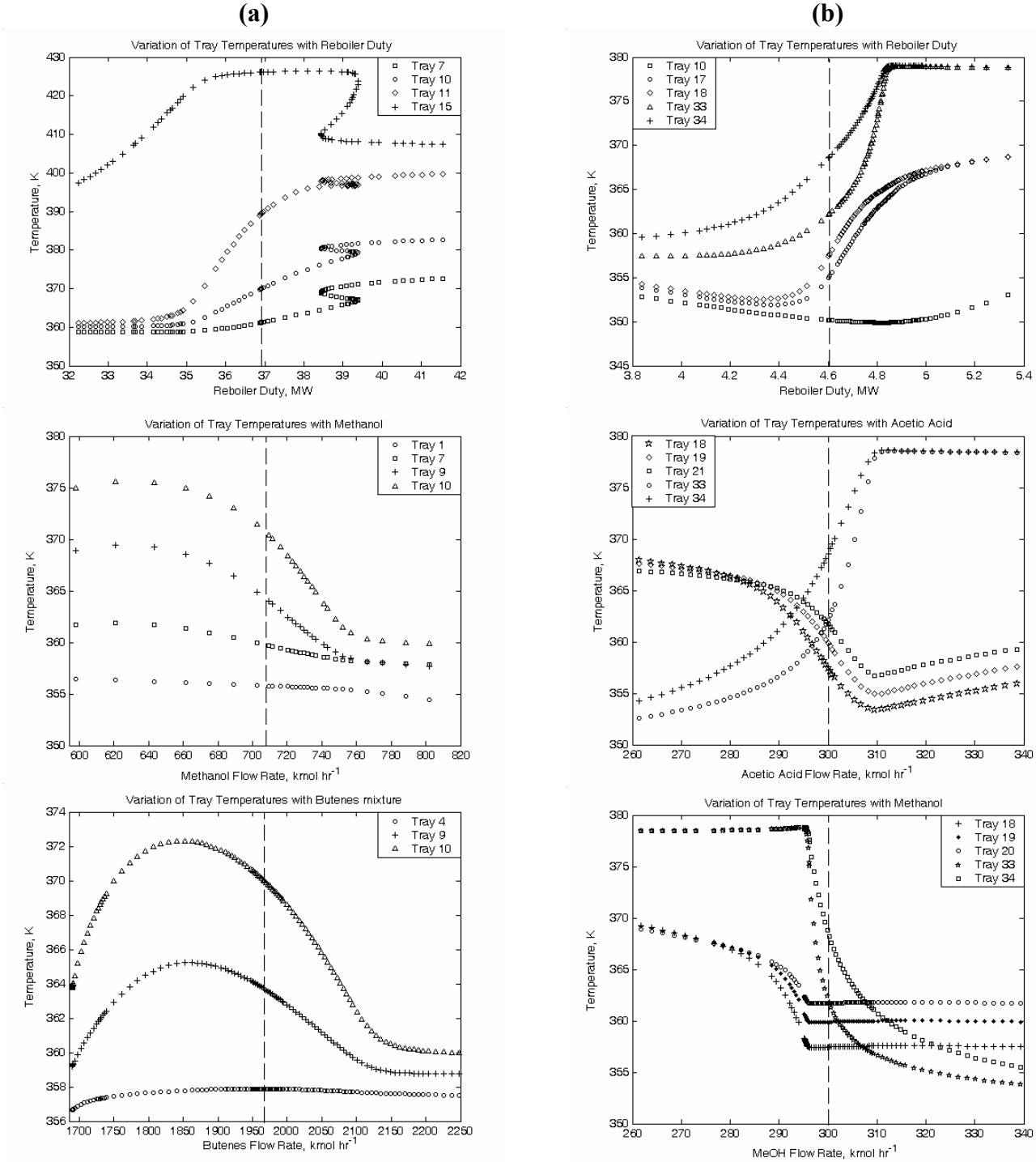

Figure 4. Variation of tray temperatures with reboiler duty and fresh feed flows
(a) MTBE column
(b) Methyl acetate column

Control Structures

The two control loops for regulating the separation and balancing the fresh feeds must avoid instability due to interaction between the loops. For the MTBE system, the direct control structure where the reboiler duty maintains Tray 11 temperature and the fresh methanol maintains Tray 10 temperature gives a near zero Niederlinski Index (NI) indicating ill-conditioning problems (the trays are adjacent so that their temperatures are not independent). In fact the NI is nearly zero for all the reactive tray temperatures. A negative NI for all the reactive tray temperatures is obtained if the fresh butene feed is used as the manipulation handle. Feed balancing using temperature measurements is thus not possible. A tray composition in the reactive section is therefore sought for the purpose.

Figure 5 plots the isobutene composition variation of representative reactive trays with the fresh methanol and the fresh butene feed. As seen earlier, Tray 7 composition appears sensitive with respect to the former while Tray 10 appears sensitive with respect to the latter. Input multiplicity in the tray compositions with respect to the methanol flow is noted. However, the extremum point is reasonably away from the base case operating conditions. If used in a control loop for balancing the fresh feeds into the column along with the temperature loop controlling Tray 11 temperature using the reboiler duty, the Niederlinski Index is 0.18, which is positive but small. This control structure is therefore accepted with reservations.

Alternatively, the fresh butenes feed may be used to control the composition of Tray 10. It is seen from Figure 5 that the input multiplicity for this input-output pairing is quite mild. The Niederlinski Index, assuming Tray 12 temperature is controlled by the reboiler duty, is a healthy 0.71. This structure is therefore a candidate control structure for the MTBE column.

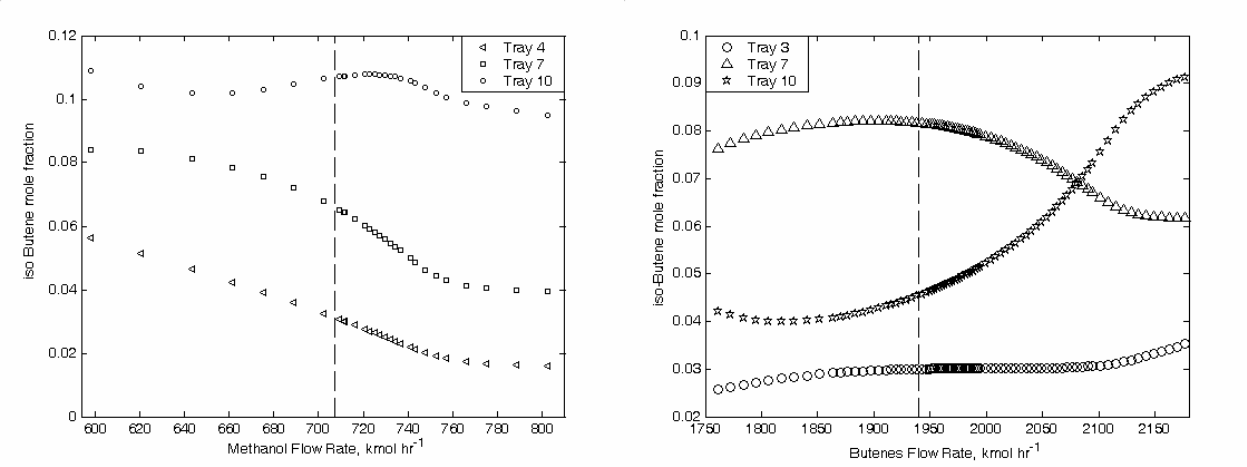

Figure 5. Variation of iso-Butene mole fraction with fresh methanol and isobutene feeds

For the methyl acetate column, the indirect control structure using the acetic acid and methanol fresh feeds to control the Tray 19 (reactive section) and Tray 34 (stripping section) temperatures respectively, gives a positive Niederlinski Index of 0.98 indicating negligible interaction between the control loops. The control structure should provide good column regulation in the face of disturbances. In fact, this is the control structure implemented by Eastman for their industrial scale column. For the direct control structure using fresh acetic acid to maintain Tray 19 temperature and reboiler duty to maintain Tray 34 temperature, a positive Niederlinski index of 3.34 indicates another candidate control structure.

For the sake of completeness, the variation in the composition of representative reactive trays with fresh acetic acid is plotted in Figure 6. Input multiplicity is seen. However, as with the tray temperatures, since the base case composition is reasonably away from the extremum points, fresh acetic acid may be used for balancing the fresh feeds. The Niederlinksi Index is again positive at 3.34. This indirect control structure is thus another candidate control structure for the column. Note that we have not studied the option of using the fresh methanol for composition control due to its low sensitivity in the reactive trays.

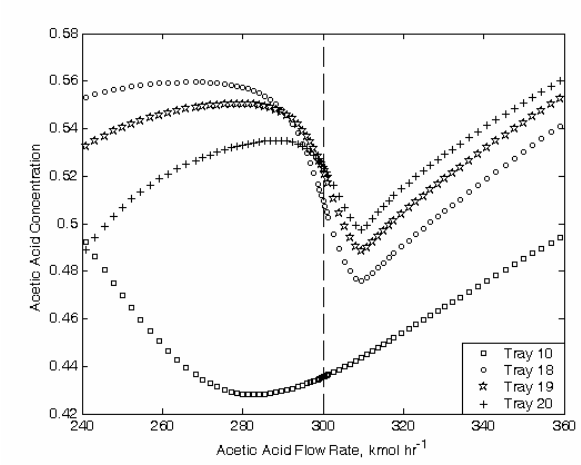

Figure 6. Variation of acetic acid concentration with fresh acetic acid

The control structures synthesized for the two example RD columns are shown in Figure 7. Note that these candidate control structures are obtained only through a systematic analysis of the governing steady state input-output relationships. In the proposed direct control structures, the fresh feeds are kept in ratio so that feedforward compensation occurs for production rate changes. The ratio set-point is adjusted in a cascade feedback arrangement to ensure stoichiometric feed balance.

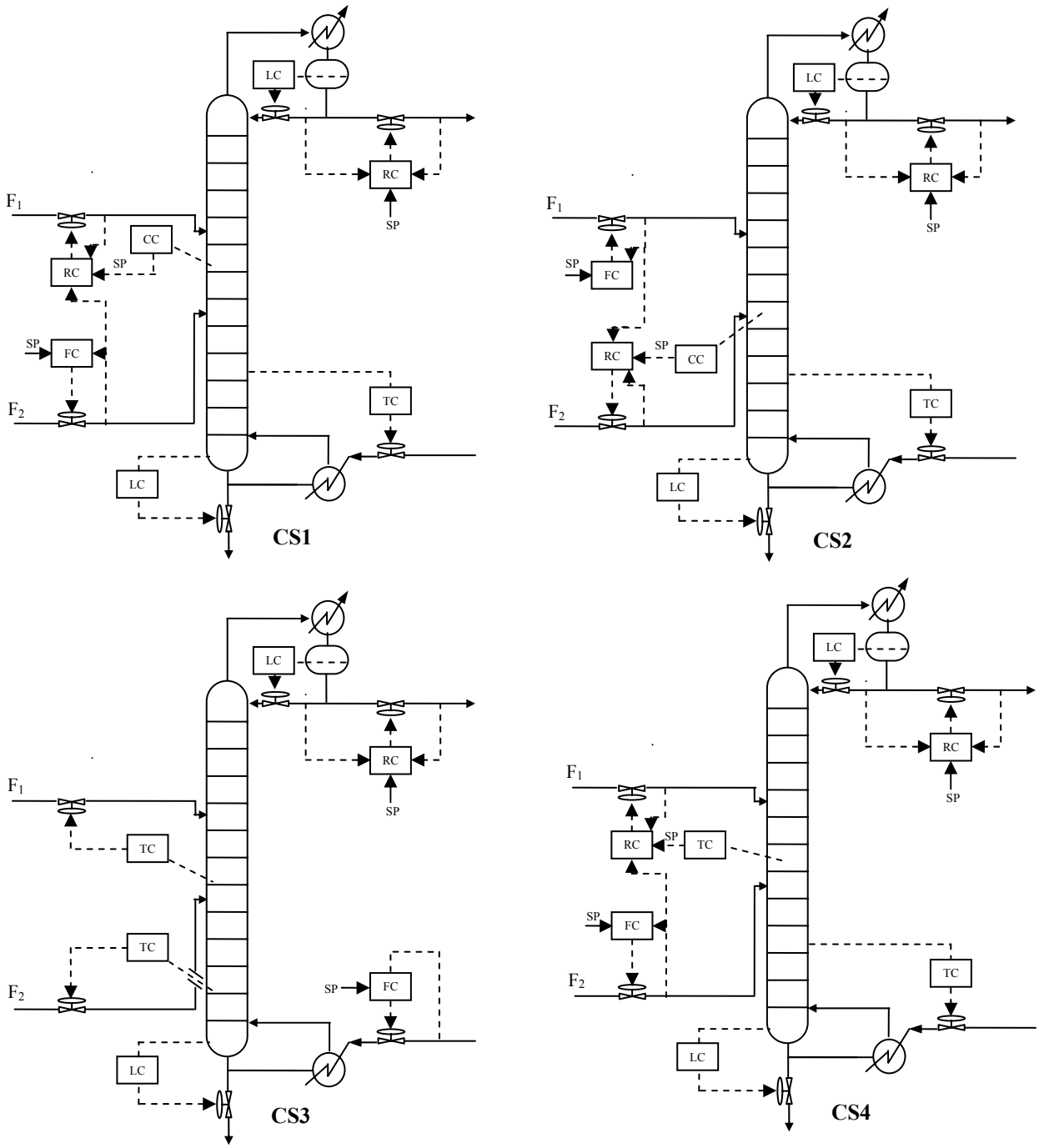

Figure 7. Proposed control structures proposed
MTBE – CS1 and CS2
Methyl acetate– CS1, CS3 and CS4

Disturbance Rejection

The proposed control structures should maintain the product purity and conversion near their design values for production rate changes and changes in one of the fresh feed compositions. The purity and conversion for these anticipated disturbances are noted in Table 1 for the MTBE and methyl acetate columns. The data clearly shows that the proposed control structures maintain the column close to the design purity and conversion for large production rate changes, changes in the feed composition and in the presence of sensor bias. Note that similar values for the conversion and purity are obtained in case of bias in the sensor measurements.

For the MTBE column, if Tray 7 composition is maintained using the fresh methanol feed (CS1), large production rate changes cannot be handled due to the problem of infeasible set-points. This is illustrated in Figure 7, which plots the variation in Tray 7 composition as the methanol feed flow is varied for different production rates (fresh isobutene feed) with Tray 11 temperature being maintained at its set point (the TQ controller is on). If a composition set-point corresponding to the base case design tray composition is used, a feasible solution does not exist for the Tray 7 composition for a 10% increase in the production rate. The choice of the tray location for the composition measurement and the chosen manipulated variable is thus crucial for effective column regulation (Moore, 1992).

Table 1: Product purity and conversion for production rate and feed composition changes. Bracketed values are for negative changes.

(a) MTBE System

Control Structure	± 20% production rate		± 5% IB composition change	
	Conversion	Purity	Conversion	Purity
CS1	ISP (96.8)	ISP (99.9)	ISP (96.06)	ISP (99.87)
CS2	93.3 (91.2)	99.9 (99.9)	92.9(91.8)	99.8 (99.8)

(b) Methyl Acetate System

Control Structure	± 20% production rate		5% water in Methanol feed	
	Conversion	Purity	Conversion	Purity
CS2	97.67 (98.31)	95.01 (94.93)	97.65	94.99
CS3	97.66 (98.32)	95.03 (94.91)	97.7	95.00
CS4	97.62 (98.31)	95.01 (94.93)	97.55	95.01

Dynamic simulations are necessary to assess the effectiveness of the proposed control structures in accomplishing smooth production rate changes and adjusting for feed composition changes. For the MTBE system, Wang et al, 2003 have shown that a control structure similar to our proposed structure can easily handle ±20% changes in the production rate. Similarly, Al-Arfaj and Luyben, 2002b, have shown the effectiveness of the Eastman control structure and the conventional direct control structure through dynamic simulations. Our work shows that these control structures can be synthesized for RD columns using purely steady state analyses.

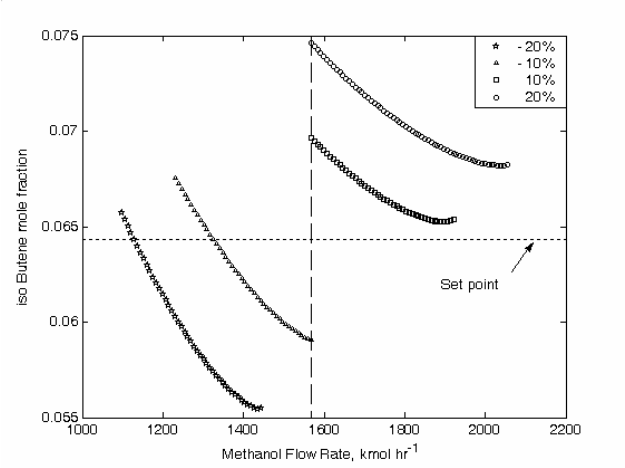

Figure 7. Infeasible composition set point for CS1 in the MTBE column

Conclusions

This article has demonstrated the systematic study of steady state input-output relationships for synthesizing effective control structures for RD columns. In an RD column, these input output relationships can be quite complex with both input and output multiplicity. For control structure synthesis, we prefer output variables that are sensitive to changes in the input variables, avoid steady state multiplicities and do not cause stability problems due to interaction with other control loops. For the MTBE example RD column, the synthesized control structure maintains a tray temperature in the stripping section with the reboiler duty and a reactive tray composition with the fresh butene feed. The fresh methanol feed flow acts as the production rate handle. The reflux ratio is kept fixed. For the methyl acetate column, the synthesized control structure maintains a reactive tray temperature with the fresh acetic acid feed and a stripping section tray temperature with the fresh methanol feed. The reboiler duty acts as the production rate handle. Other control structures where the fresh methanol feed acts as the production rate handle, a reactive tray temperature / composition is maintained by manipulating the fresh acetic acid feed and a stripping section tray temperature is maintained using the reboiler duty also give satisfactory column regulation for production rate changes and changes in the feed composition. The work also shows that it is necessary to maintain the stoichiometric balance of the fresh feeds into the RD column for maintaining the product purity.

Acknowledgements

The financial assistance from the IIT Kanpur Initiation Grant Scheme is gratefully acknowledged.

References

Agreda, V. H.; and Partin, L. R (1984). "Reactive distillation process for the production of methyl acetate", *U.S. Patent* 4435595.

Al-Arfaj, M.A., and 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.; and Luyben, W.L. (2002a). "Control of ethylene glycol reactive distillation column", *AIChE Journal,* **48(4)***,* 905-908

Al-Arfaj, M.A.; and Luyben, W. L. (2002b). "Comparative control study of ideal and methyl acetate reactive distillation", *Chemical Engineering Science,* **57**, 5039-5050.

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

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

Chen, F.; Huss, R. S.; Doherty, M.F.; and Malone, M.F. (2002). "Multiple steady states in reactive distillation: kinetic effects", *Computers and Chemical Engineering,* **26(1)**, 81-93.

Ciric, A. R.; and Miao, P. (1994). "Steady state multiplicities in an ethylene glycol reactive distillation column", *Industrial and Engineering Chemistry Research,* **33**, 2738-2748.

Garrison, A.A.; Moore, C.F.; Roberts, J.J. and Hall, P.D. (1992). "Distillation Process Control Using Fourier Transform Raman Spectroscopy," *Process Control and Quality*, **3**, 57-63.

Hickey, T.P. and Adams, J.R., 1994, U.S.Patent 5,321,163 to Chemical Research and Licensing Company.

Jacobs, R.; and Krishna, R. (1993). "Multiple solutions in reactive distillation for methyl-tert- butyl ether synthesis", *Industrial and Engineering Chemistry Research,* **32**, 1706-1709.

Marek, J. (1955). "Vapor liquid equilibria in mixtures containing an associating substance. II binary mixtures of acetic acid at atmospheric pressure", *Collection of Czechoslovak Chemical Communications,* **20**, 1490-1496.

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

Seader, J. D.; and Henley, E. J. (1998). Chapter 10 in *Separation Process Principles*. John Wiley and Sons.

Singh, B.P. (2004). *Steady State Analysis of Reactive Distillation Systems Using Homotopy Continuation*. M Tech Thesis, Indian Institute of Technology, Kanpur, India.

Smith L.A., 1981, U.S.Patent 4,307,254 to Chemical Research & Licensing Company.

Vora, N.; and Daoutidis, P. (2001). “Dynamics and control of an ethyl acetate reactive distillation coloumn”, *Industrial and Engineering Chemistry Research,* **40,** 833-849

Wang, S.J; Wang, D.S.H.; and Lee, E.K. (2003). “Effect of interaction multiplicity on control system design for a MTBE reactive distillation column”, *Journal of Process Control,* **13**, 503-515.