Control Study of Ethyl *tert*-Butyl Ether Reactive Distillation

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Control structures for ethyl *tert*-butyl ether (ETBE) reactive distillation columns are studied. Two process configurations are explored: a design with two fresh reactant feed streams and a design with a single mixed reactant feed. An optimum design for the double-feed case is presented. A design given in the literature is used for the single-feed case. Several control structures are investigated, and their effectiveness in the ETBE case is compared with that in previously studied chemical systems. Results show that the double-feed system requires internal composition control to balance the stoichiometry, along with temperature control to maintain product purity. The single-feed case, which operates with an excess of ethanol, is effectively controlled with only a temperature controller provided disturbances are not too large.

1. Introduction

The use of reactive distillation has grown in recent years because it results in less expensive and more efficient processes for some chemical systems. There is increasing interest in the use of ethyl *tert*-butyl ether (ETBE) for gasoline blending as a replacement for methyl *tert*-butyl ether (MTBE) because of the latter's environmental problems.

The basic reaction combines ethanol and isobutene to form ETBE.

$$iC_4^{=} + \text{ethanol} \rightleftharpoons \text{ETBE}$$

The $C_4^{=}$ feed stream contains both isobutene and normal butene, and the latter does not participate in the reaction. The chemically inert normal butene is much lighter than ETBE, so the distillate is mostly n$C_4^{=}$ and the bottoms is mostly ETBE. Any unreacted isobutene leaves mostly in the distillate. If an excess of ethanol is fed to the column (not "neat" operation), this ethanol will typically leave in the bottoms and be blended with ETBE in the gasoline pool. Even for neat operation, if the conversion is low, the unconverted ethanol would be taken out in the bottoms.

Sneesby et al.[1−5] discuss different designs for the ETBE process using reactive distillation. They also look at some control aspects of this process. In their control work, they studied a reactive column with only nine trays and a small production rate. Their work is limited to the single-feed design, and reaction equilibrium is assumed on all reactive trays.

The purpose of this paper is to extend this work to explore more control structure alternatives and to study both the design and the control of the double-feed system. We also compare the control of the ETBE system with that of other reactive distillation systems that we have studied in previous papers.[6−8] Fewer than a dozen papers dealing with the control of reactive distillation have appeared in the literature,[6] so this area is only beginning to be explored.

Four control structures for the double-feed case and two for the single-feed case are explored in this paper.

2. Reaction Kinetics

ETBE is produced via reactive distillation by either feeding a single partially reacted mixture to the column or by feeding two fresh reactant streams directly to the column at different feed-tray locations. The hydrocarbon feed is obtained from an upstream unit in the refinery (fluidized catalytic cracker, steam cracker, isobutene dehydrogenation unit, etc.). In any of these units the butene product contains isobutene, normal butene, and other light hydrocarbons. Therefore, the butene feed to the column contains large amounts of inerts, which go out the top of the column because they are much lighter than the product ETBE. The ethanol fresh feed is usually essentially pure to minimize side reactions.

ETBE is produced from the reversible reaction of isobutene and ethanol over an acid catalyst, such as the acidic ion-exchanger resin Amberlyst 15.

$$(CH_3)_2C{=}CH_2 + C_2H_5OH \rightleftharpoons (CH_3)_3COC_2H_5$$

The reaction is equilibrium limited in the industrially significant range of temperatures, so that the equilibrium conversion from a stoichiometric mixture of reactants at 70 °C is only 84.7%.[1] Zhang et al.[9] have recently published a paper that studies the chemical equilibrium and the kinetics of the ETBE reaction. They provide expressions for the equilibrium constants and develop the reaction kinetics for the liquid-phase synthesis of ETBE based on the Langmuir−Hinshelwood−Hougen−Watson (LHHW) model. Based on Zhang's results, the following expressions are used in our simulation.

Reaction equilibrium constant

$$K_{ETBE} = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.0191544T + 5.28586 \times 10^{-5}T^2 - 5.32977 \times 10^{-8}T^3$$

Adsorption equilibrium constant

$$\ln K_A = -1.0707 + \frac{1323.1}{T}$$

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Reaction rate constant (mol/h/g of catalyst)

$$k_{\text{rate}} = 7.418 \times 10^{12} \exp\left(\frac{-60.4 \times 10^3}{RT}\right)$$

Generalized rate equation (mol/h)

$$r_{\text{ETBE}} = \frac{M_{\text{cat}}\, k_{\text{rate}}\, a_{\text{EtOH}}{}^2 \left(a_{\text{iBut}} - \dfrac{a_{\text{ETBE}}}{K_{\text{ETBE}}}\right)}{(1 + K_{\text{A}} a_{\text{EtOH}})^3}$$

$$a_i = \gamma_i x_i$$

where a_i is the activity, γ_i is the liquid activity coefficient, x_i is the liquid mole fraction, R is the gas constant (J/mol·K), M_{cat} is the mass of the catalyst (g), and T is the temperature (K).

The ETBE reaction system can also include a side reaction: the dimerization of isobutene to produce diisobutene:

$$(CH_3)_2C{=}CH_2 + (CH_3)_2C{=}CH_2 \rightleftharpoons [(CH_3)_2C{=}CH_2]_2$$

However, this side reaction is essentially eliminated when ethanol is in excess over the isobutene. In addition, the kinetics of this reaction are not readily available. Therefore, the dimerization reaction is ignored in our studies.

We consider two cases. The first has a structure that is similar to the reactive distillation systems studied with other chemical systems in previous papers[6,7] (a hypothetical ideal system and the methyl acetate system). There are two fresh feed streams (pure ethanol and a mixed butene). The control system must be able to perfectly balance the reaction stoichiometry. The second case, which is similar to that reported by Sneesby et al.,[3] has a single mixed feed with an excess of ethanol. This second case would apply when a prereactor is used.

The UNIFAC model and Peng−Robinson equation of state are used in the vapor−liquid equilibrium (VLE) and physical property calculations. Details are given in work by Al-Arfaj.[10] Our basic model assumes VLE on each stage of the column, but it does not assume chemical equilibrium because we want to be able to deal with a variety of reaction systems. A total condenser and a partial reboiler are used. The steady-state equations are solved rigorously using a distillation homotopy continuation method. The set of steady-state algebraic equations are solved for an easy starting problem and then reach the actual problem by moving through a continuation parameter. The details of this method as well as the mathematical modeling of the system are found in work by Al-Arfaj.[10] The dynamic simulation uses a rigorous nonlinear model that utilizes the Francis weir hydraulic formula and assumes negligible energy dynamics.

3. Double-Feed Case

3.1. Steady-State Design. Papers presenting the steady-state economic optimization of the ETBE reactive distillation system have not been published. To provide a reasonable base case for our dynamic studies, we developed an optimum design based on minimizing the total annual cost (energy, raw materials, and annual capital cost).

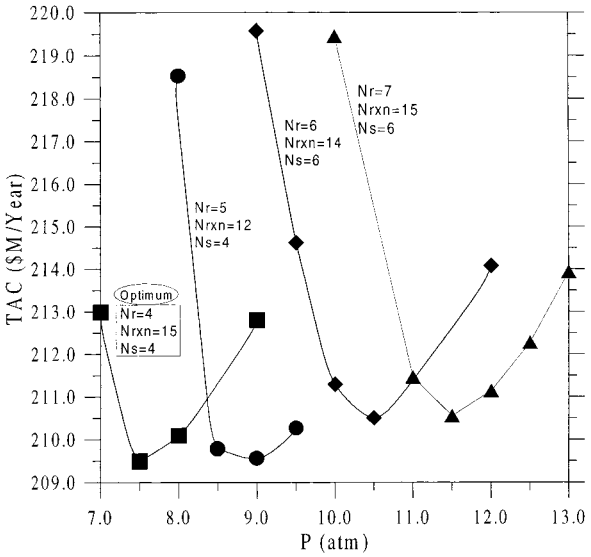

Figure 1. TAC for the double-feed design.

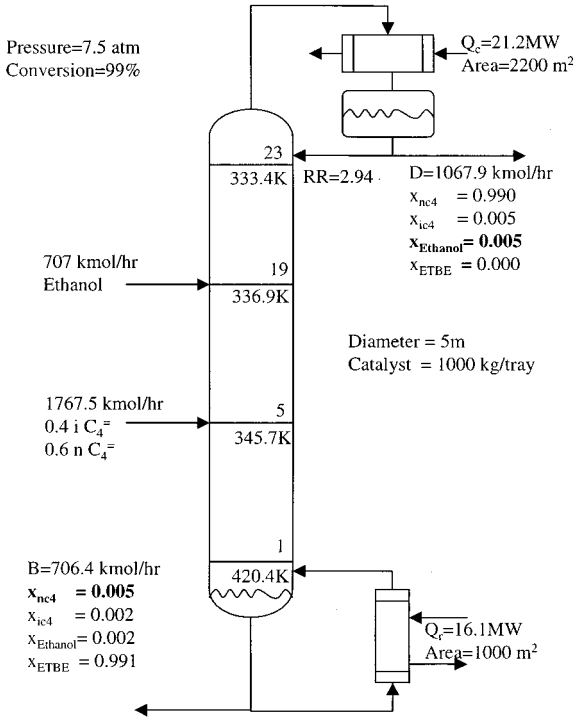

Figure 2. Optimum design for double feed.

$$\text{TAC} = \text{steam} + \text{catalyst} + \text{raw materials} + \frac{\text{cost of column, trays, heat exchangers}}{3}$$

The production rate is fixed at 700 kmol/h. In this optimization, the equipment capital costs (column, trays, reboiler, and condenser) are taken from Douglas.[11] The details of the economic calculations are given in work by Al-Arfaj.[10] The following prices are assumed:

1. Energy: $5/10^6$ Btu.
2. Ethanol: $15/kmol.
3. Butenes (iso + normal): $8.25/kmol.
4. Catalyst (Amberlyst 15): $7.7/kg ($3.5/lb).
5. ETBE price: $25.3/kmol.

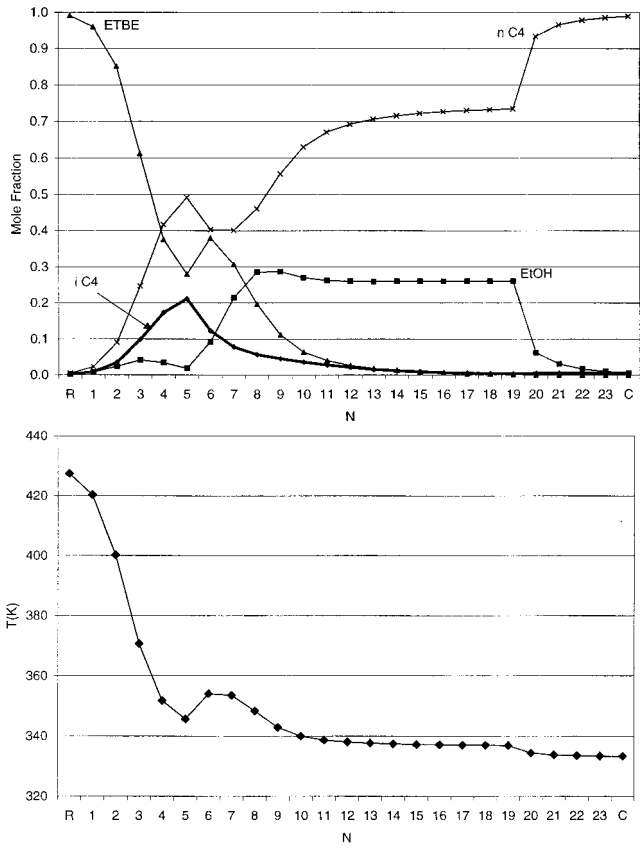

Figure 3. Composition and temperature profile (double feed).

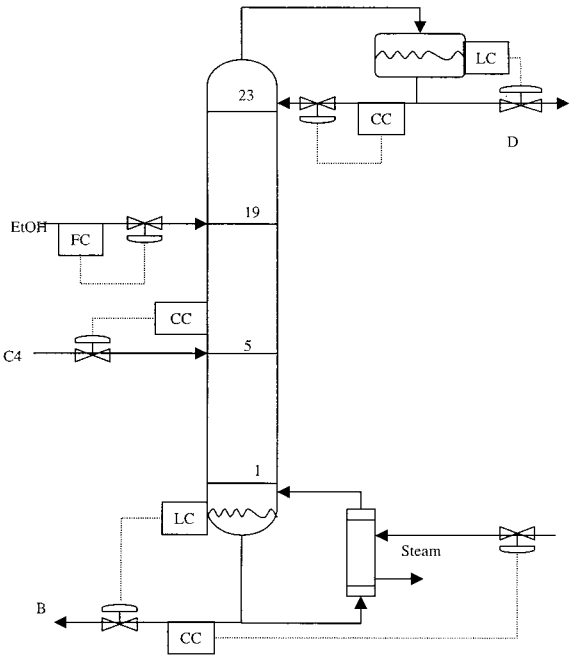

Figure 4. CS1 (double feed).

The column diameter is calculated using an *F* factor of unity (in English engineering units). The catalyst weight on each tray was selected such that the weir height never exceeded 7.5 cm to prevent excessive pressure drop. The final design had 1000 kg of catalyst on each reactive tray. The specifications for the distillate and bottoms products are assumed to be 0.5 mol % $nC_4^=$ in the bottoms and 0.5 mol % ethanol in the distillate product. This corresponds to a 99% conversion.

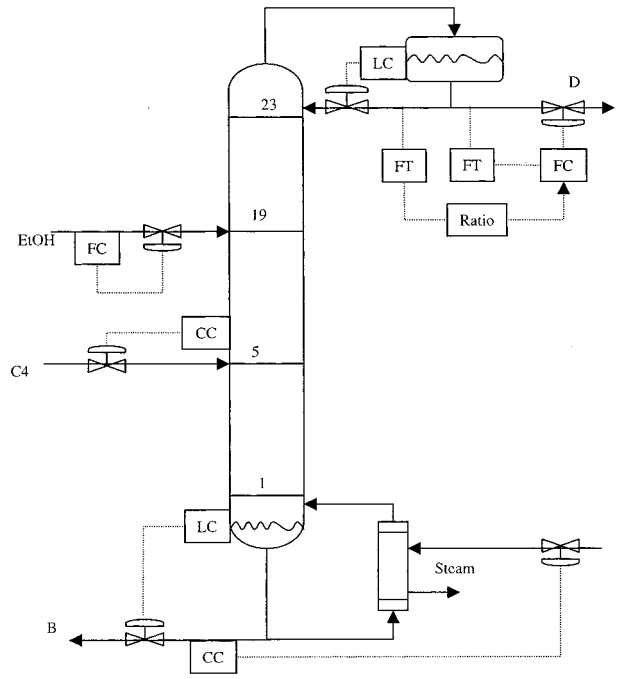

Figure 5. CS1−RR (double feed).

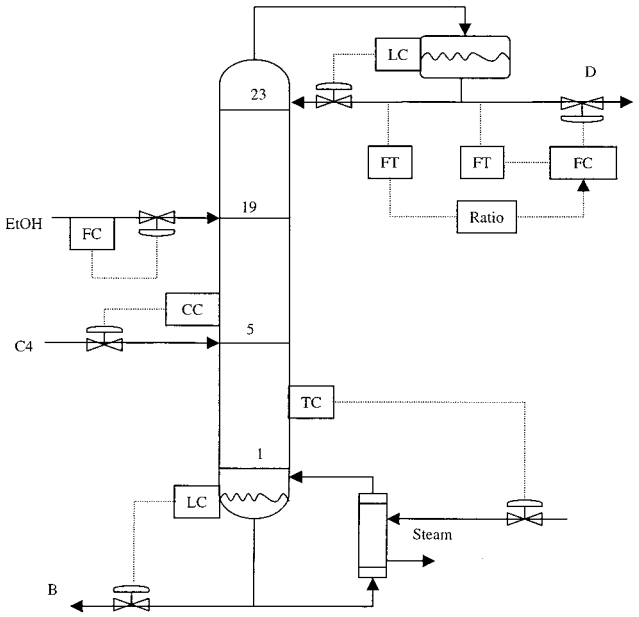

Figure 6. CS5−$iC_4^=$ (double feed).

The design optimization variables are the operating pressure, the number of trays in the stripping section, the number of reactive trays, and the number of trays in the rectifying section. The total amount of catalyst is optimized as a result of optimizing the number of reactive trays. Figure 1 shows how sensitive the optimization is to pressure. Pressure has more effect than the selection of the trays. Pressure is a critical parameter in reactive distillation because of its influence on both the VLE and the reaction kinetics. Phase equilibrium usually favors low pressures and low temperatures. Reaction kinetic rate constants may be too small at low temperatures. However, for exothermic reactions, reaction equilibrium constants may be too small at high temperatures. Therefore, pressure optimization is vitally important in reactive distillation.

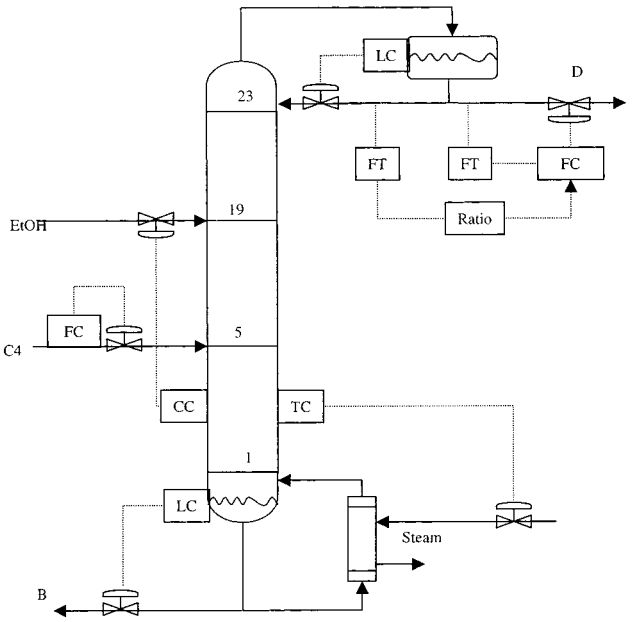

Figure 7. CS5−EtOH (double feed).

A four-dimensional search method yields the optimum steady-state design shown in Figure 2. The column has a total of 23 trays, with 4 stripping trays, 15 reactive trays, and 4 rectifying trays. The optimum column pressure is 7.5 atm. The column diameter is 5 m, catalyst holdup is 1000 kg/tray, reflux ratio is 2.94, and reboiler heat input is 16.0 MW. The reflux drum temperature is 333 K so cooling water can be used in the condenser. Temperatures in the reactive zone vary from 337 to 346 K. The temperature in the reboiler is 427 K. Figure 3 gives the steady-state temperature and composition profiles.

3.2. Control Structures. The four control structures explored for the double-feed system are given in Figures 4−7. All of the structures are single-input single-output structures with proportional−integral (PI) controllers (P only on levels). The controllers are tuned using the Tyreus−Luyben tuning method. The relay-feedback method[12] is used to obtain the ultimate gain and ultimate period. The valves are designed to be half open at steady state. Two measurement lags of 30 s each are used in all composition or temperature loops. Similar labeling of control structures is used in this paper so that a comparison with previous work can be easily made. All of these control schemes use an internal composition controller to balance the stoichiometry by adjusting the flow rate of one of the fresh feeds. The column pressure is assumed to be constant, which is achieved by manipulating the condenser heat duty.

3.2.1. CS1 (Dual Composition). Figure 4 shows the control scheme in which the ETBE purity is controlled in the bottoms by manipulating the reboiler heat input and the ethanol impurity in the top is controlled by manipulating the reflux flow rate. An internal composition is controlled in the reactive zone. There are two alternative cases that depend on which of the two fresh feed streams is flow-controlled to set the production rate and which is manipulated to control the internal column composition. We use the notation CS1−$iC_4^=$ to indicate a structure in which the butene feed stream is manipulated to control an internal isobutene composition. The other case is labeled CS1−EtOH to denote a scheme in which the ethanol fresh feed stream is manipulated to control an internal ethanol composition. The latter case

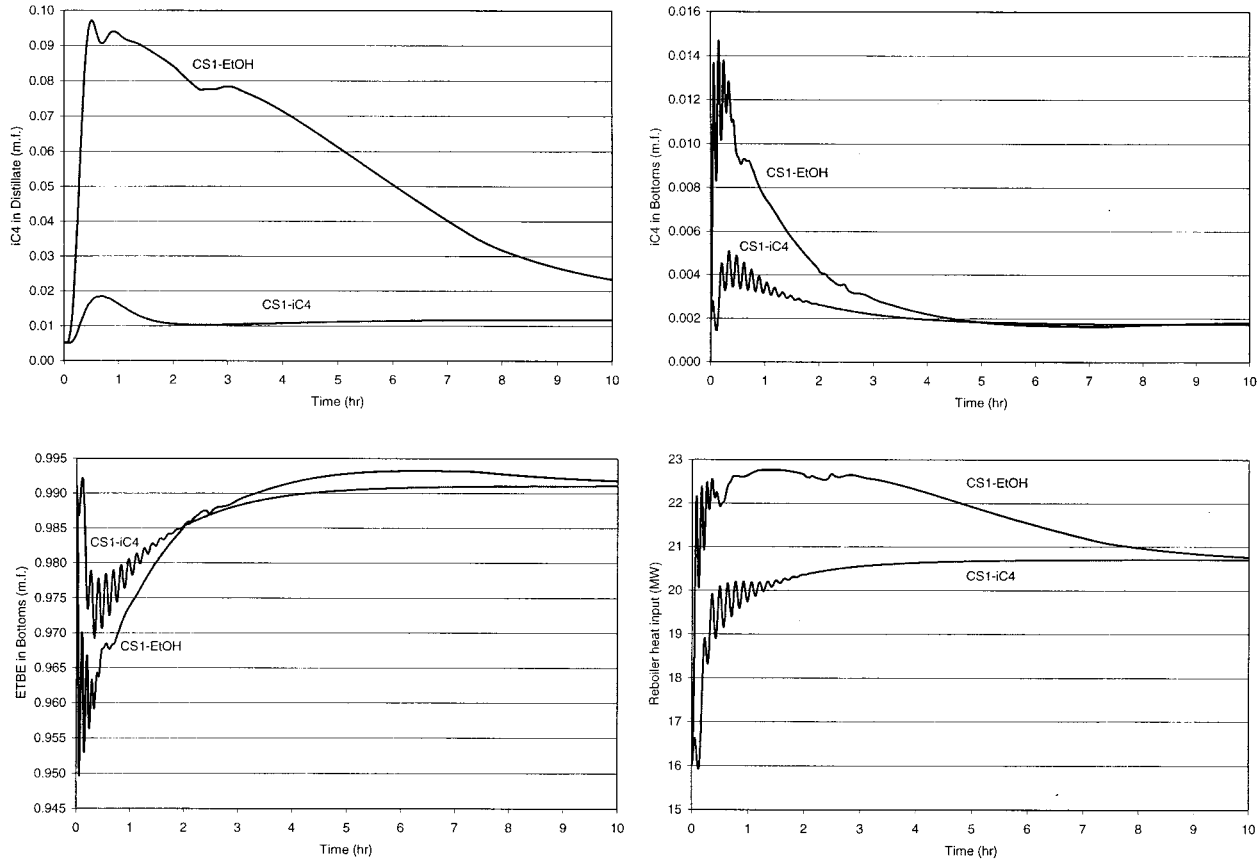

Figure 8. CS1−EtOH versus CS1−$iC_4^=$ (double feed).

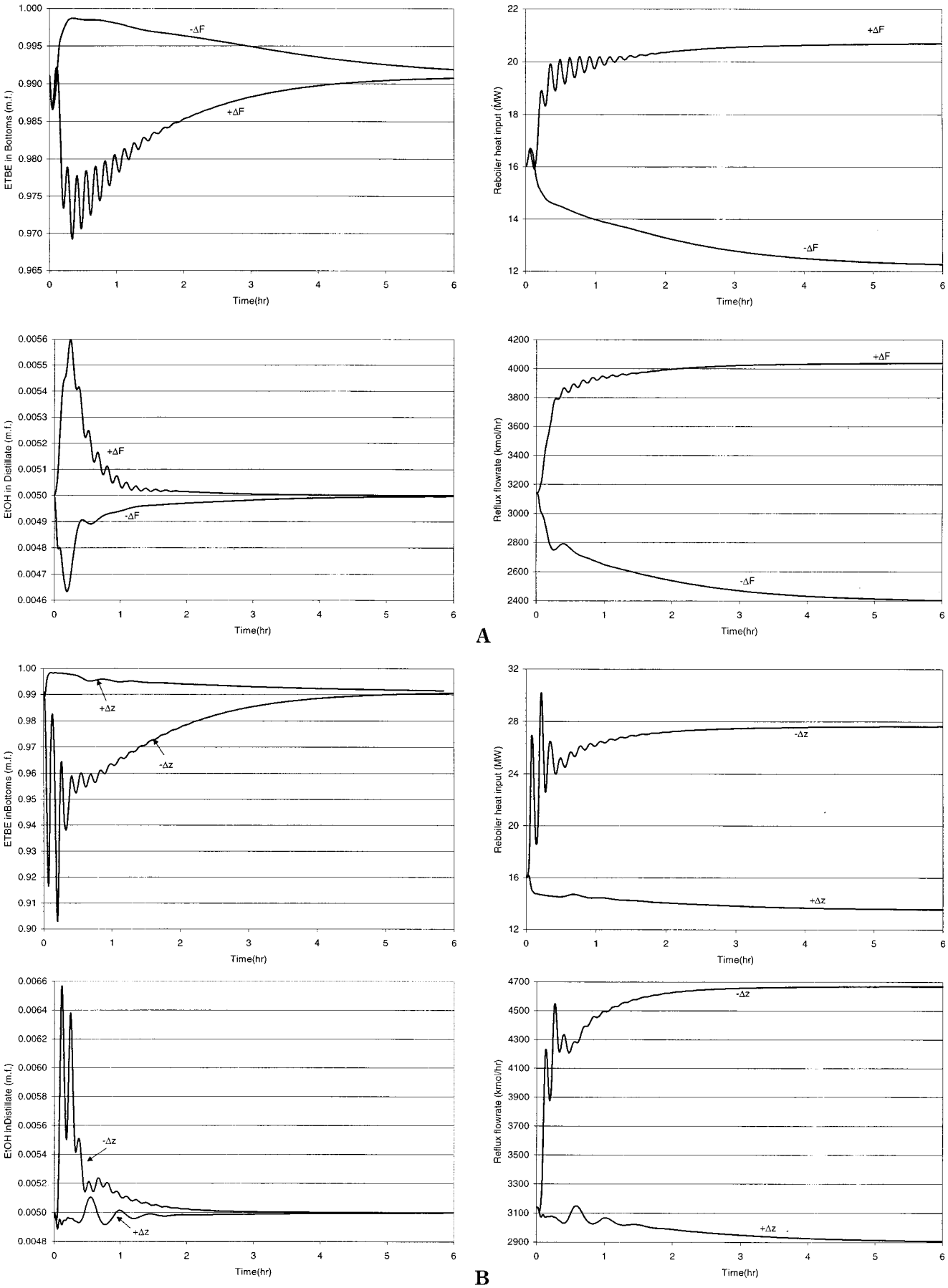

Figure 9. (A) Response of CS1 (double feed): feed-rate disturbances. (B) Response of CS1 (double feed): feed composition disturbances.

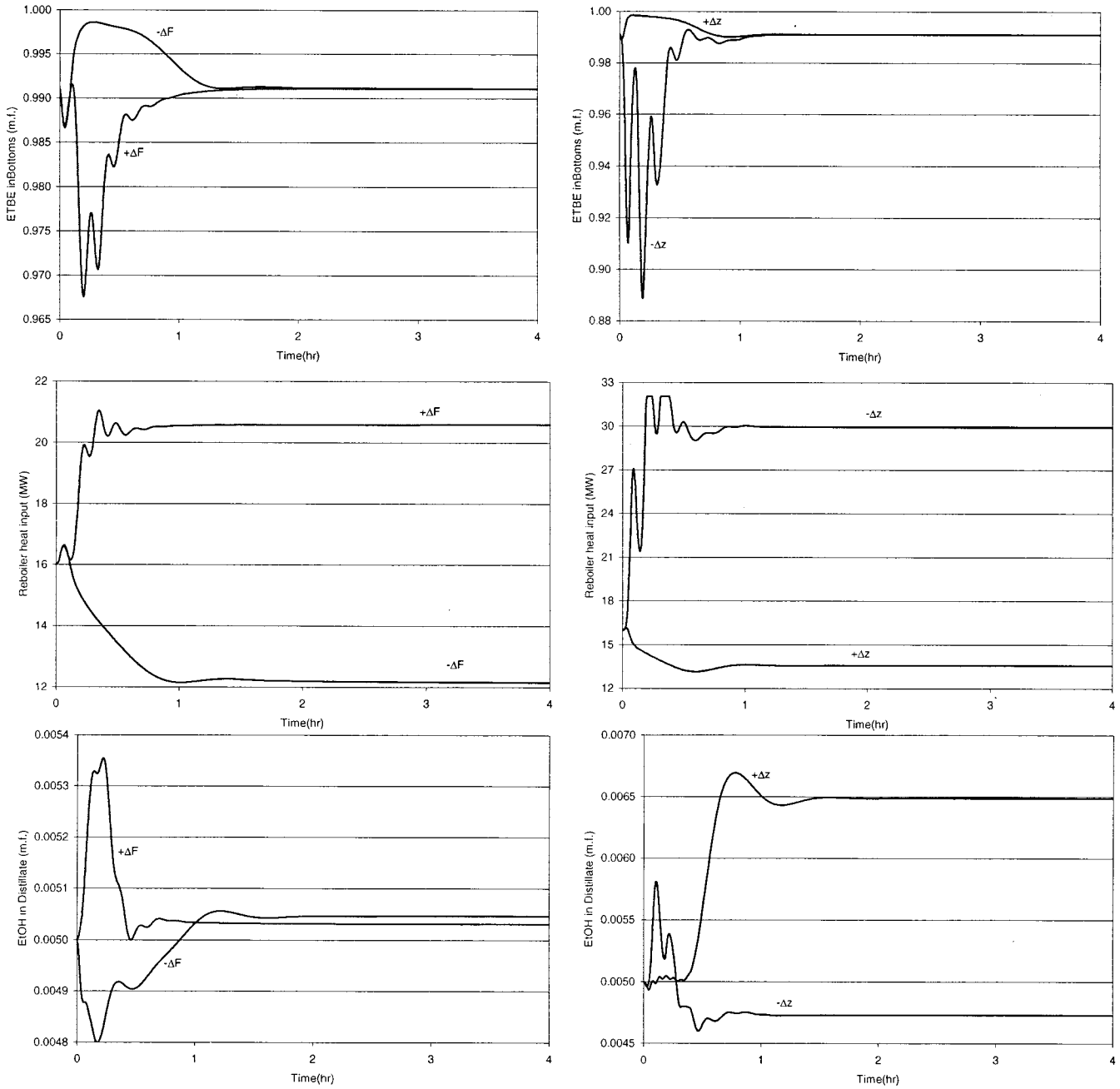

Figure 10. Response of CS1−RR (double feed).

may be more frequently encountered if all of the butene from the upstream unit is fed to the reactive column. The performance of these two alternatives is somewhat different.

3.2.2. CS1−RR−$iC_4^=$ (Single-End Composition). Figure 5 shows that only the ETBE purity in the bottoms is controlled in this structure. The distillate composition is not controlled, and the reflux ratio is held constant.

3.2.3. CS5−RR−$iC_4^=$ (Single-End Temperature). Figure 6 gives this structure in which a stripping tray temperature is used instead of a bottoms composition analyzer. The reflux ratio is held constant. The isobutene concentration is controlled on tray 5 at the bottom of the reactive zone by manipulating the butene fresh feed.

3.2.4. CS5−RR−EtOH (Single-End Temperature). This structure is the same as the previous one except the ethanol fresh feed is manipulated to control an internal ethanol composition (see Figure 7). The interesting feature of this structure is the location of the internal composition (tray 3), which is below the reactive zone. This location is recommended by SVD analysis, looking at the steady-state gain matrix between the ethanol fresh feed and the internal tray *compositions*.

3.3. Disturbances. A number of disturbances were studied, but the results from only feed rate and feed composition changes are reported. These disturbances are probably larger than typical in a plant environment, but they provide a good indication of the robustness of each structure.

1. Step changes of ±25% in the flow-controlled fresh feed ($\pm\Delta F$).

2. Step changes of ±10 mol % in isobutene composition of the feed. The composition of $iC_4^=$ is changed from 40 mol % to either 50 mol % or 30 mol % ($\pm\Delta z$).

3.4. Simulation Results. 3.4.1. CS1−$iC_4^=$ (Dual Composition). Figure 8 compares the responses of the

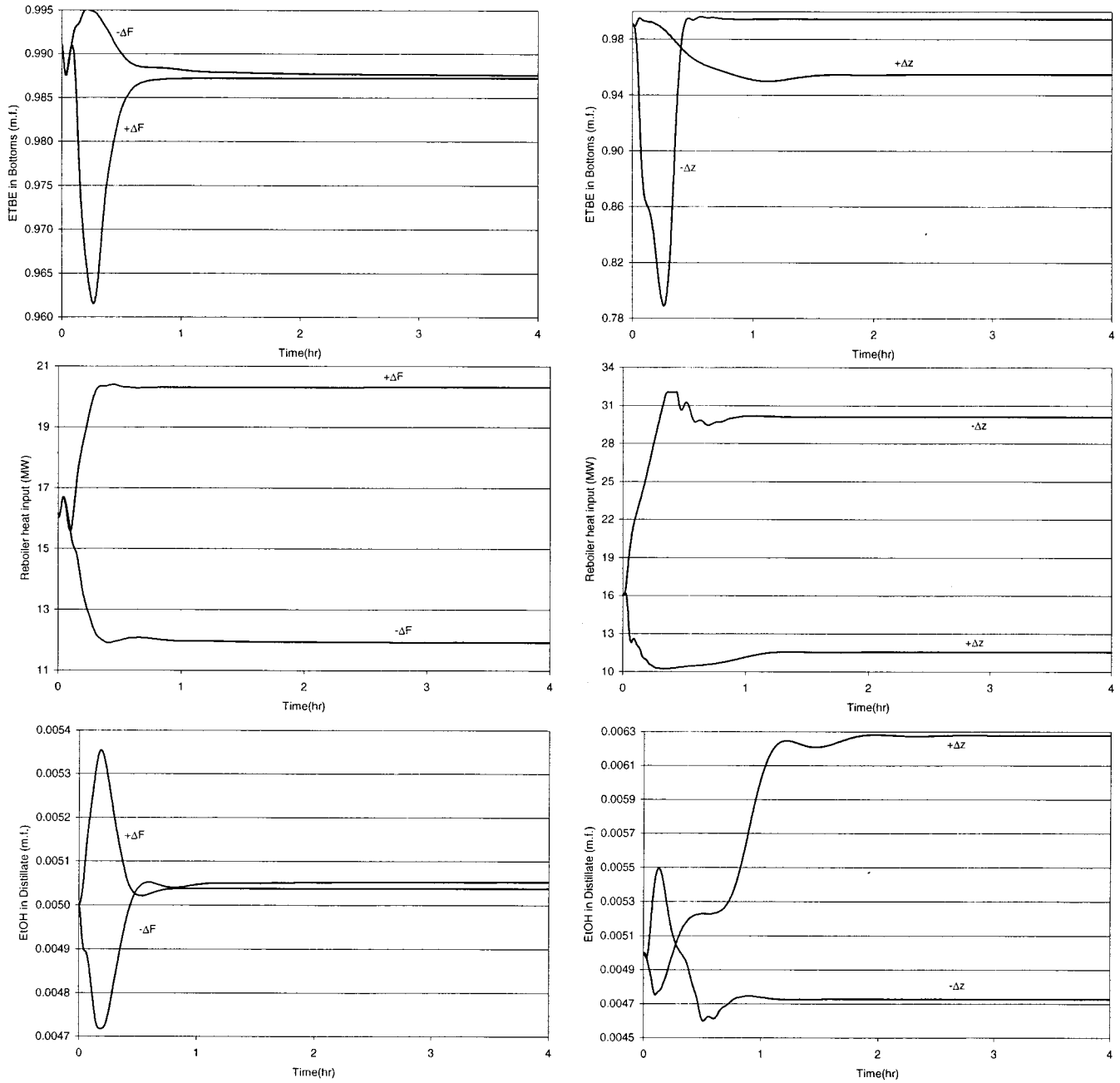

Figure 11. Response of CS5−$iC_4^=$ (double feed).

two alternatives (manipulate ethanol or manipulate the butene fresh feed to control an internal ethanol or $iC_4^=$ concentration) for a 25% increase in the feed flow rate of the flow-controlled feed. These results show that controlling an internal $iC_4^=$ composition by the butene feed provides more effective control from a dynamic point of view. However, there may be a conflict with steady-state objectives. Manipulating the ethanol feed to control an internal ethanol composition may be desirable if the butene feed coming from the upstream units is not free to be adjusted. Thus, it may not be possible to use the control structure that is better dynamically.

The system responses to feed rate and feed composition disturbances are shown in Figure 9 for the structure in which an internal $iC_4^=$ composition is controlled. This structure is able to maintain the ETBE purity within reasonable bounds and prevent excessive losses of both ethanol and $iC_4^=$ in the distillate.

3.4.2. CS1−RR−$iC_4^=$ (Single-End Composition). This structure has the advantage of removing one composition analyzer but could lead to losing a valuable amount of ethanol out the top of the column. The system responses to the disturbances are shown in Figure 10. In this structure, the ETBE purity is maintained but there are losses of ethanol and $iC_4^=$ when the concentration of $iC_4^=$ in the feed is increased. Note that tighter control is obtained in the single-end control structure, as would be expected. Dual composition control has more interaction among control loops, which results in less tightly tuned controllers and slower dynamics.

3.4.3. CS5−RR−$iC_4^=$ (Single-End Temperature). In this structure a temperature in the stripping zone is controlled by the heat input and the internal $iC_4^=$ by the butene feed. The tray temperature was found using the singular value decomposition (SVD) method.[13] Tray 3 was found to be most sensitive. Figure 11 show the responses to the disturbances. In this structure, ETBE

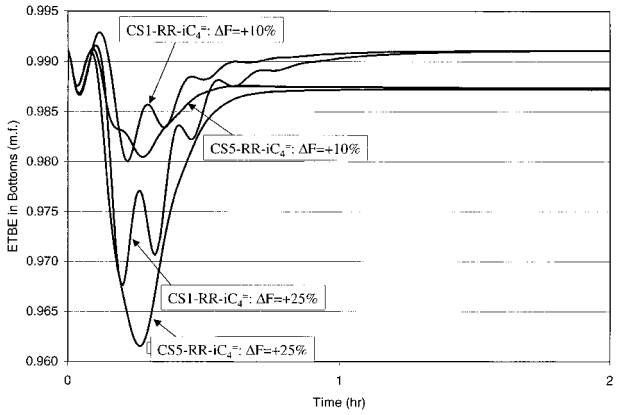

Figure 12. CS1−RR versus CS5−$iC_4^=$ (double feed).

is not controlled directly. The ETBE purity is held reasonably close to the desired level for feed flow-rate disturbances. However, feed composition disturbances affect the ETBE purity. For decreases in the concentration of $iC_4^=$ in the feed, there is a dynamic dip in the ETBE purity. For increases in the concentration of $iC_4^=$ in the feed, the dynamic response is fine, but there is a significant steady-state shift in the ETBE purity.

A decrease in the iC_4 fresh feed concentration produces a higher ETBE bottoms purity, which is somewhat counterintuitive. The control scheme holds a stripping tray temperature constant. The less iC_4 in the feed, the more nC_4 there is to separate in the column. This tends to decrease the control tray temperature, which increases vapor boilup and reflux flow. This increases the fractionation in the column and leads to higher ETBE bottoms purity.

It is interesting to compare the structure with composition control (CS1−RR−$iC_4^=$) with the structure with temperature control (CS5−RR−$iC_4^=$). Both structures

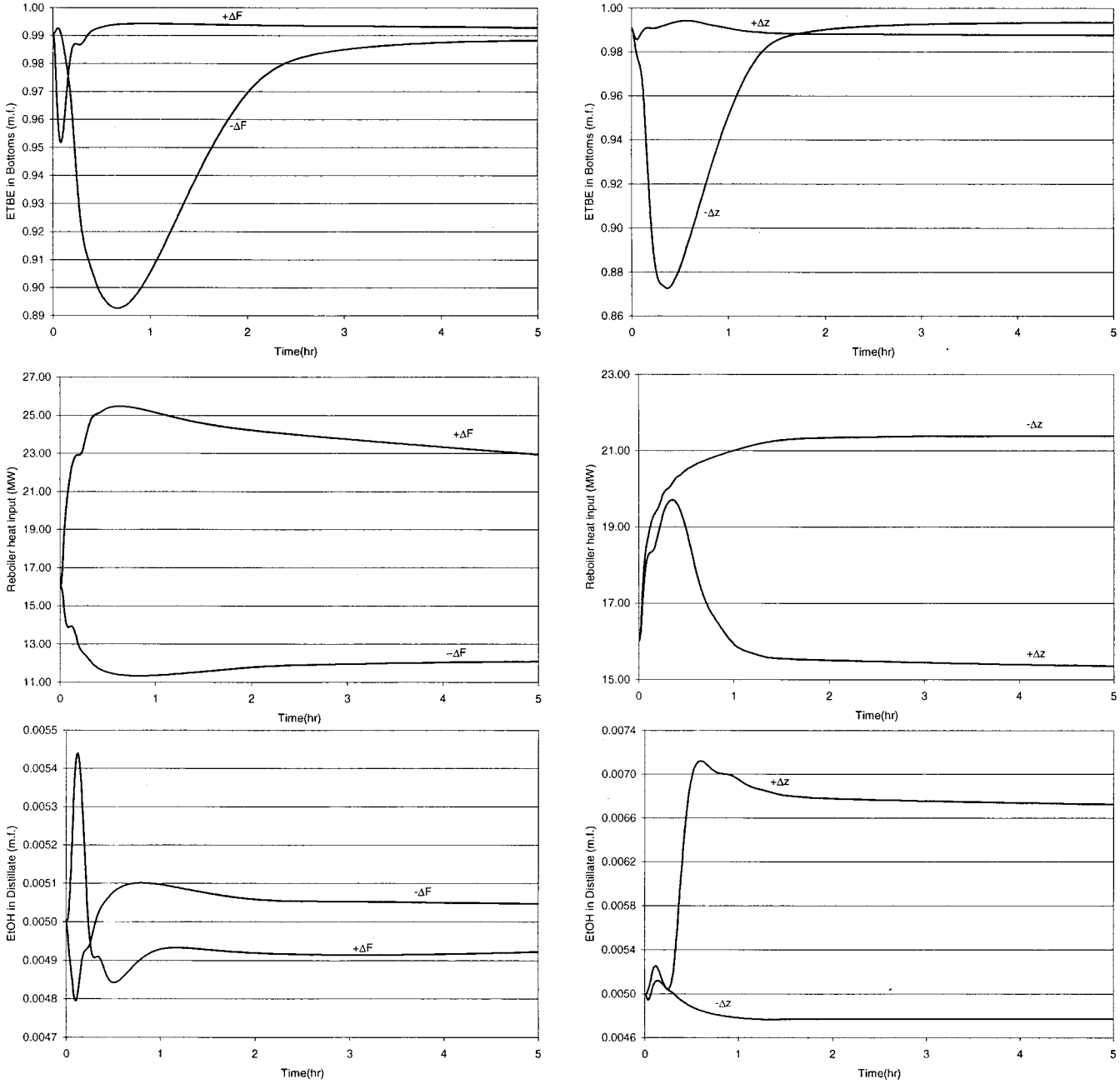

Figure 13. Response of CS5−EtOH (double feed).

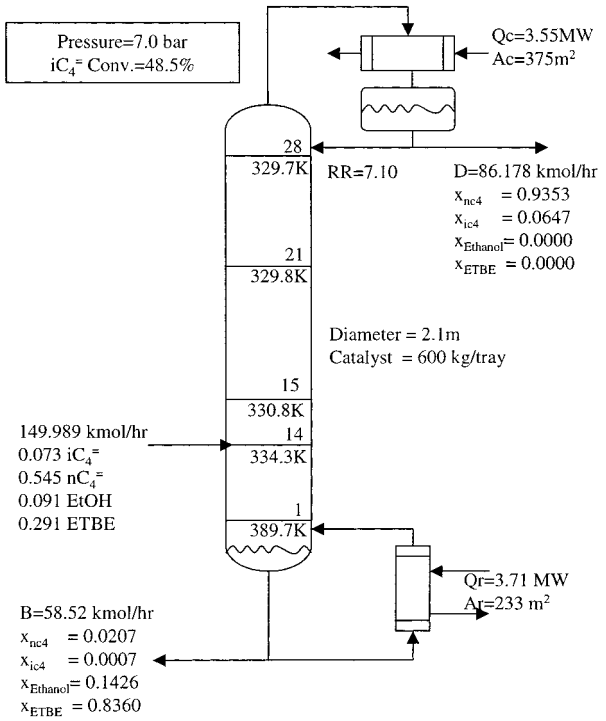

Figure 14. Single-feed design.

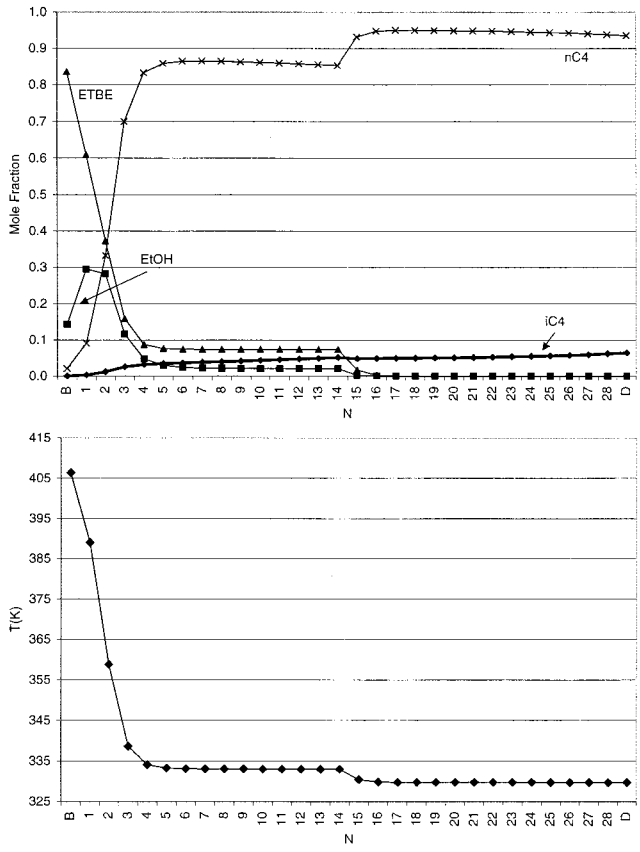

Figure 15. Composition and temperature profile (single feed).

use an internal $iC_4^=$ composition controller with a fixed reflux ratio. Figure 12 shows that for the 25% feed rate disturbance the direct composition control is better. Of course, if larger composition lags are used, the performance would not be as good. For smaller (probably more reasonable) disturbances, temperature control provides adequate control of the product purity.

3.4.4. CS5−RR−EtOH (Single-End Temperature). We demonstrated previously with direct product composition control that manipulating the butene feed gives better control than manipulating the ethanol feed for feed flow-rate disturbances. Figure 13 shows that this is also true when temperature control is used. The bottoms purity is severely affected by the large change in the feed flow rate. The recovery time is very long (4 h).

However, for feed composition changes, this structure provides better dynamic control (compare Figure 11 where the ETBE purity dips to 80% with Figure 13 where it only drops to 87%).

3.4.5. Summary. Direct product composition control handles disturbances best but requires additional online analyzers. Temperature control is easier and less expensive, and it provides adequate control as long as disturbances are not too large. Of course, the use of feedforward control with temperature control would produce a structure that works well even for large disturbances.

Manipulating the butene feed to control an internal butene composition has a better dynamic response than the alternative of manipulating the ethanol feed. This is probably because changes in the flow rate of the light C_4 feed tend to propagate up the column instead of moving down the column and affecting the bottoms ETBE composition.

3.5. Comparison with Other Reactive Distillation Systems. In previous papers, we have studied an ideal reactive distillation system and the methyl acetate reactive distillation system. In these studies the same control structures as were used in this paper (and several others) were investigated. Some interesting similarities and differences have been found.

Both the ideal and the methyl acetate systems produce two products, which leave at the two ends of the column. They both have two fresh feed streams of the two reactants. The ETBE system has only one product, which leaves in the bottoms from the column. This fundamental chemical difference has a profound effect on which control structures work and which do not.

One of the interesting schemes that provided effective control in the ideal and methyl acetate systems was CS7 in which two temperatures in different sections of the column manipulated the two fresh feeds. The big advantage of this scheme is the elimination of the internal composition analyzer.

However, this control structure does not work in the ETBE system, and internal composition control of one of the reactants is necessary in the two-feed "neat" operation to perfectly balance the stoichiometry. The reason the two-temperature structure does not work when there is only one product is the different shape of the temperature profile (see Figure 3). There is only one place in the column where temperatures change from tray to tray, and this change is only due to the change in the ETBE concentration. In the two-product systems, the temperature profiles show changes in two regions that are influenced by the fresh feed flow rates. This is not the case in the one-product system.

A recent paper[14] reports a study of a reactive distillation column in which a single reactant produces two products (one lighter and one heavier than the reactant), which leave out the two ends of the column. The chemical system is the metathesis of 2-pentene to

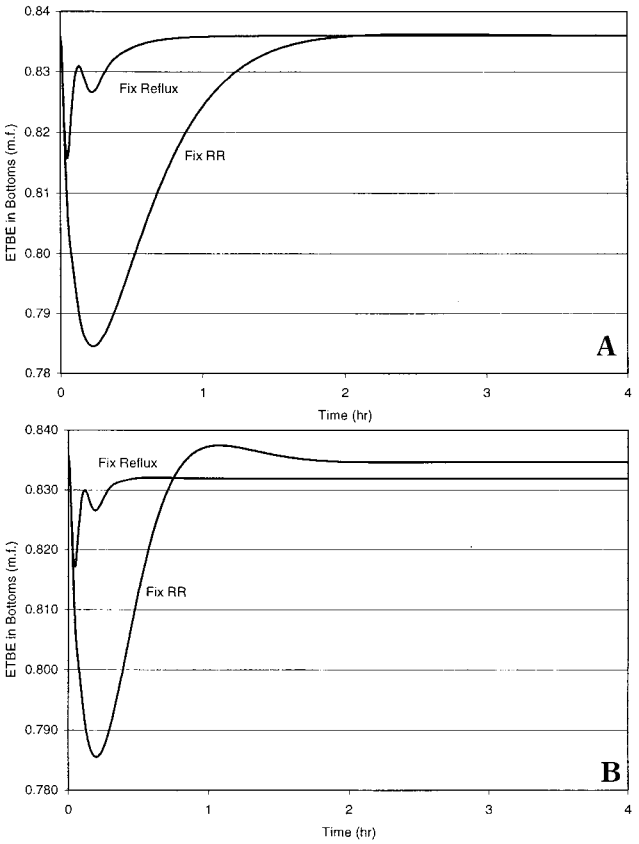

Figure 16. (A) CS1−RR versus CS1−R (single feed). (B) CS5−RR versus CS5−R (single feed).

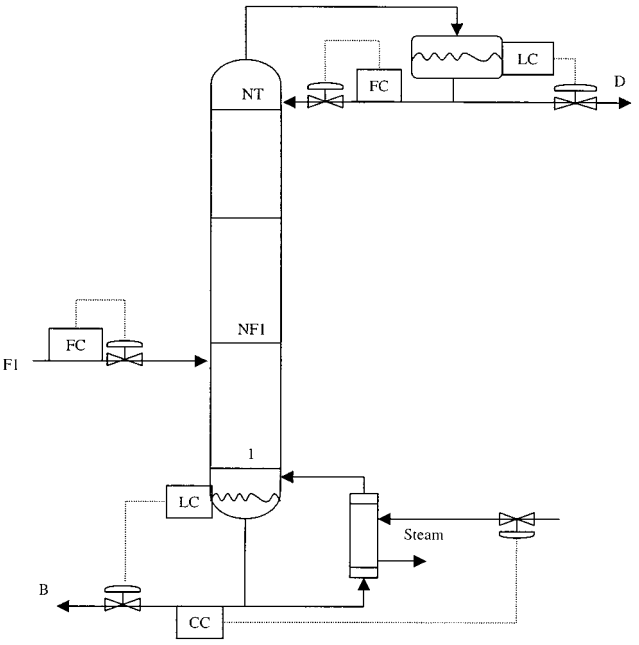

Figure 17. CS1−R (single feed).

form 2-butene and 3-hexene. We have found in this system that two temperatures can be effectively used to control both product purities. Thus, it appears that a generic property of reactive distillation systems may be that there must be two products produced in order to be able to use two temperatures (for either manipulation of the fresh feeds or for dual composition control).

Another difference between the two-product and one-product systems is the effect of interaction when direct composition of two ends of the column is used (CS1).

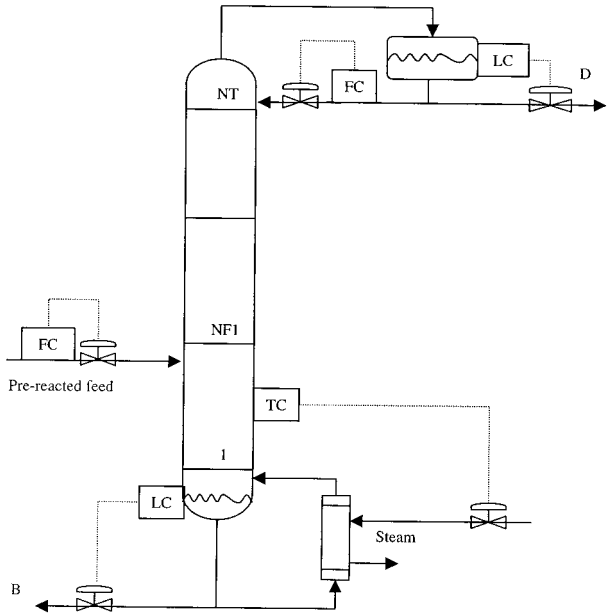

Figure 18. CS5−R (single feed).

Interaction in the high-conversion (high product purity) methyl acetate system caused some problems. These were not found in the ETBE case, even for high conversions.

4. Single-Feed Case

4.1. Steady-State Design. In this case we used a design that was proposed by Sneesby et al.[3] This system uses a single feed that comes from an upstream reactor, so it is a mixture of product and reactants. An excess of ethanol is used. The ETBE production rate and purity in the bottoms are 5000 kg/h and 91.3 wt % ETBE, respectively. Unlike Sneesby's design, chemical equilibrium in the reactive zone is not assumed. A catalyst holdup of 600 kg/tray is used because this gives reasonable values for the liquid height on the tray (about 10 cm). The column has 14 stripping trays, 7 reactive trays, and 7 rectifying trays. The operating pressure is 7 bar, and the column conversion is 48.5%. The overall process (prereactor/column) conversion is 89.7%. The design is shown in Figure 14. Figure 15 shows the composition and temperature profiles.

4.2. Control Structures. Two basic structures are studied. The first uses direct composition control of the bottoms ETBE purity (CS1). The second uses temperature control of a tray in the stripping section (CS5). In both cases, there are two alternatives: constant reflux ratio or constant reflux flow rate. Figure 16 compares these two alternatives when an increase of 25% is made in the feed rate. Fixing the reflux flow is dynamically better in both cases. Figures 17 and 18 show the control structures for both CS1−R and CS5−R.

4.3. Disturbances. In this case, we subject the system to the following disturbances:

1. Step changes of ±25% in the flow-controlled fresh feed ($\pm\Delta F$).

2. Step changes in feed composition. The composition is changed from $iC_4^= = 0.073$, $nC_4^= = 0.545$, EtOH = 0.091, and ETBE = 0.291 to $iC_4^= = 0.07$, $nC_4^= = 0.60$, EtOH = 0.10, and ETBE = 0.23. Thus, the feed contains more inert normal butene and less ETBE.

4.4. Simulation Results. CS1−R (single-end composition control) can hold the ETBE purity to the desired

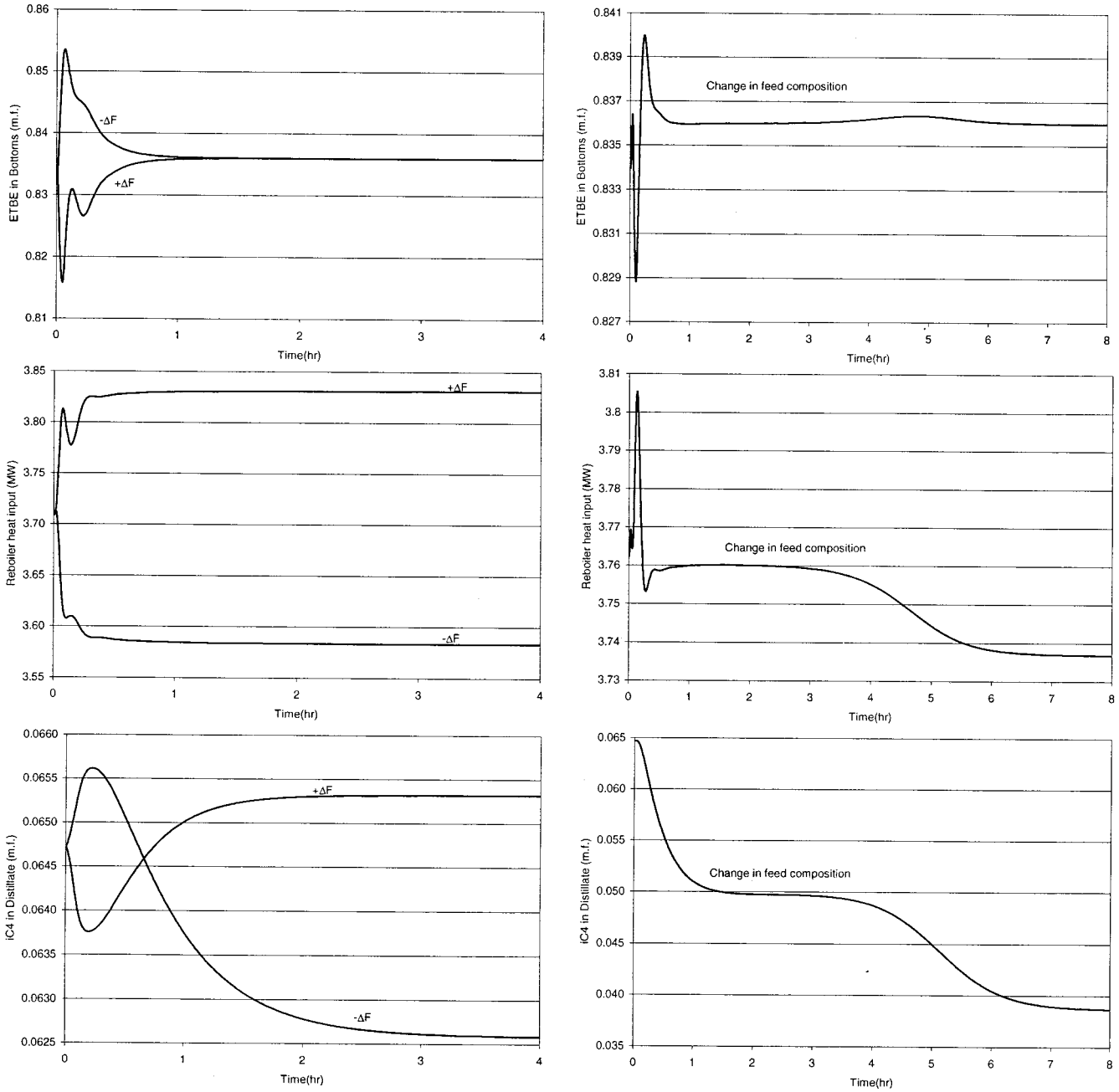

Figure 19. Response of CS1−R (single feed).

level for both types of disturbances as shown in Figure 19. The isobutene in the distillate is not controlled, but the losses when the flow-rate disturbances are made are small. When a feed composition disturbance is made, the system takes a long time to settle.

Figure 20 shows responses of CS5−R (single-end temperature control) to the two disturbances. In this structure, the tray 2 temperature is controlled. Similar responses for feed rate changes are observed in this structure as well: the ETBE purity in the bottom does not change much, and the losses of isobutene in the overhead are small. For the feed composition change, the ETBE purity is reduced about 5% but takes much less time to settle down than that of CS1−R.

In this single-feed column, the tray temperature sees the flow-rate disturbance sooner than the bottoms composition sensor sees it. Therefore, temperature control gives a somewhat better response to this disturbance. Note that, in the single-feed case, the feed rate change produces changes in the flows of both reactants. However, in the double-feed column, composition control was found to be somewhat better than temperature control, as discussed in section 4.4. In the double-feed system, a change in the ethanol feed does not immediately change the C_4 feed. The dynamics of the internal composition control loop and the temperature loop may interact in a way that degrades the control. We speculate that the bottoms composition control may be less affected by this interaction because of the delay in seeing bottoms composition changes.

5. Conclusion

The control of ETBE reactive distillation is investigated using two different designs. A double-feed design is optimized and used in the control study, and a single-

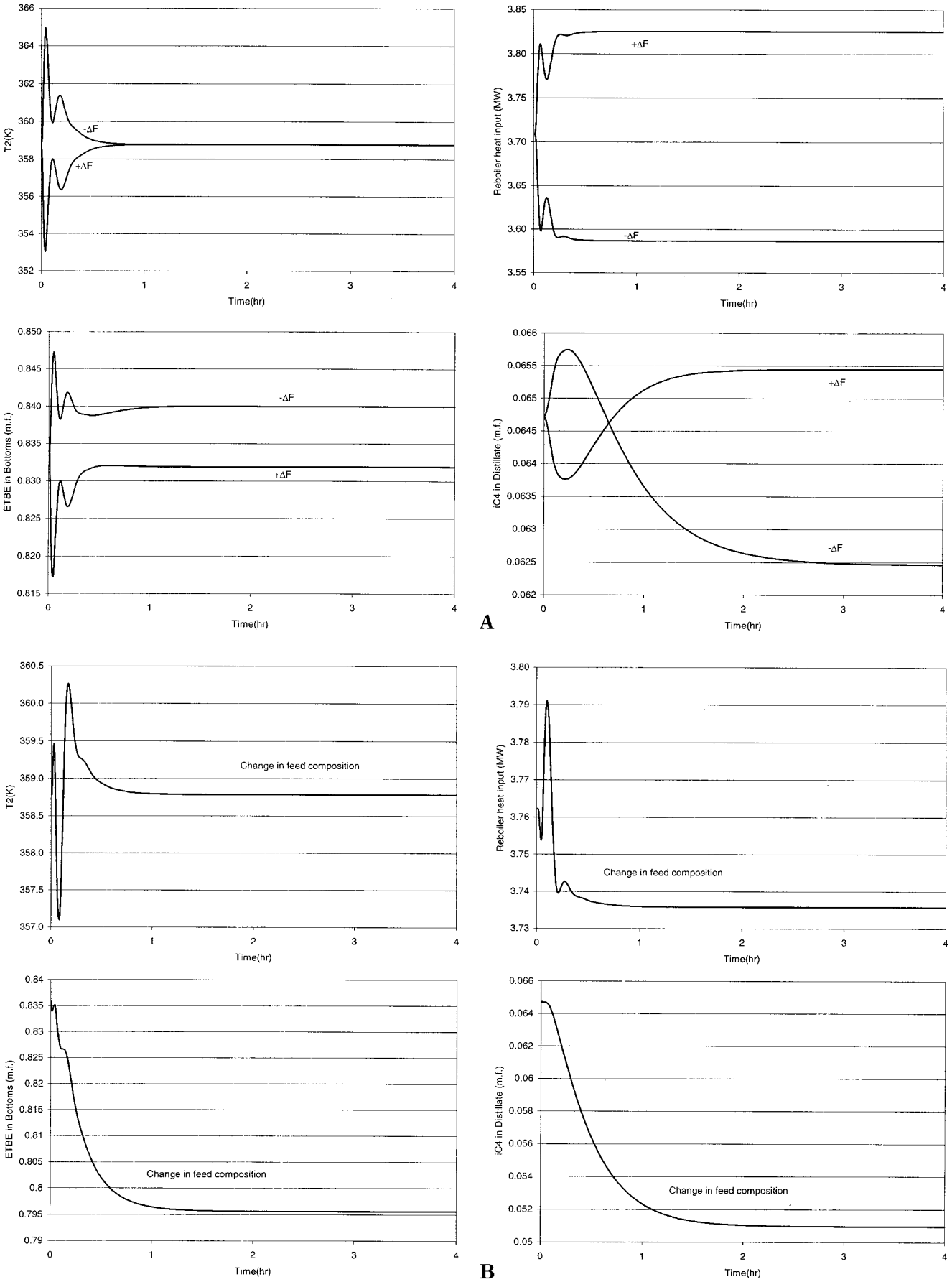

Figure 20. (A) Response of CS5−R (single feed): feed-rate disturbance. (B) Response of CS5−R (single feed): feed composition disturbance.

feed design is used from the literature with some modifications. In the double-feed design, an excess of ethanol is not used, so the manipulation of one of the fresh feed streams is required to perfectly balance the

stoichiometry of the reaction. The use of an internal reactant composition measurement is required. Unlike the two-product methyl acetate reactive distillation, the use of two temperatures cannot be substituted for this internal composition measurement.

Three basic control structures are studied. The first one uses direct composition control of two product purities. The second structure fixes the reflux ratio and controls one end product. The third structure used temperature to infer product composition with a fixed reflux ratio. Temperature control provides fairly effective control provided disturbances are not too large.

Nomenclature

B = bottoms flow rate (kmol/h)
D = distillate flow rate (kmol/h)
k = reaction constant (kmol/h/g)
K_{eq} = reaction equilibrium constant
Nr = rectifying trays
Nrxn = reactive trays
Ns = stripping trays
Qr = reboiler duty (MW)
R = reflux flow rate (kmol/h)
RR = reflux ratio
TAC = total annual cost

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