

CHAPTER 9

REACTIVE DISTILLATION

9.1 INTRODUCTION

Reactive distillation columns incorporate both phase separation and chemical reaction. They have economic advantages in some systems over conventional reactor, separation, and/or recycle flowsheets, particularly for reversible reactions in which chemical equilibrium constraints limit conversion in a conventional reactor. Because both reaction and separation occur in a single vessel operating at some pressure, the temperatures of reaction and separation are not independent. Therefore, reactive distillation is limited to systems in which the temperatures conducive to reaction are compatible with temperatures conducive for vapor-liquid separation.

Pressure in conventional distillation design is usually set by a minimum temperature in the reflux drum (so that cooling water can be used) or a maximum temperature in the reboiler (to prevent fouling or thermal decomposition). Establishing the optimum pressure in a reactive distillation column is more complex because of the interplay between reaction and phase separation. Most VLE relationships show an increase in volatility with decreasing temperature. On the other hand, reaction rates decrease with decreasing temperature. If the reaction is exothermic, the chemical equilibrium constant increases with decreasing temperature. So low operating pressure or temperature, which facilitates the phase separation, may require lots of catalyst or liquid tray holdup to compensate for the low reaction rates.

In conventional distillation design, tray holdup has no effect on steady-state composition. In reactive distillation, tray holdup (or amount of catalyst) has a profound effect on conversion, product composition, and column composition profiles. So, in addition to the normal design parameters of reflux ratio, number of trays, feed tray location, and

pressure, reactive distillation columns have the additional design parameter of tray holdup. If there are two reactant feedstreams, an additional design parameter is the location of the second feed.

Reactive distillation is usually applied to systems in which the relative volatilities of the reactants and products are such that the products can be fairly easily removed from the reaction mixture while keeping the reactants inside the column. For example, consider the classical reactive distillation system with reactants A and B reacting to form products C and D in a reversible reaction.



For reactive distillation to be effective, the volatilities of the products C and D should be greater or less than the volatilities of the reactants A and B. Suppose the volatilities are

$$\alpha_C > \alpha_A > \alpha_B > \alpha_D$$

Reactant A would be fed into the lower section of a reactive column and rise upward. Reactant B would be fed into the upper section and flow downward. As the components react, product C would be distilled out the top of the column, and product D would be withdrawn out the bottom. The reactants can be retained inside the column by vapor boilup and reflux while the products are removed. Figure 9.1 illustrates this ideal case.

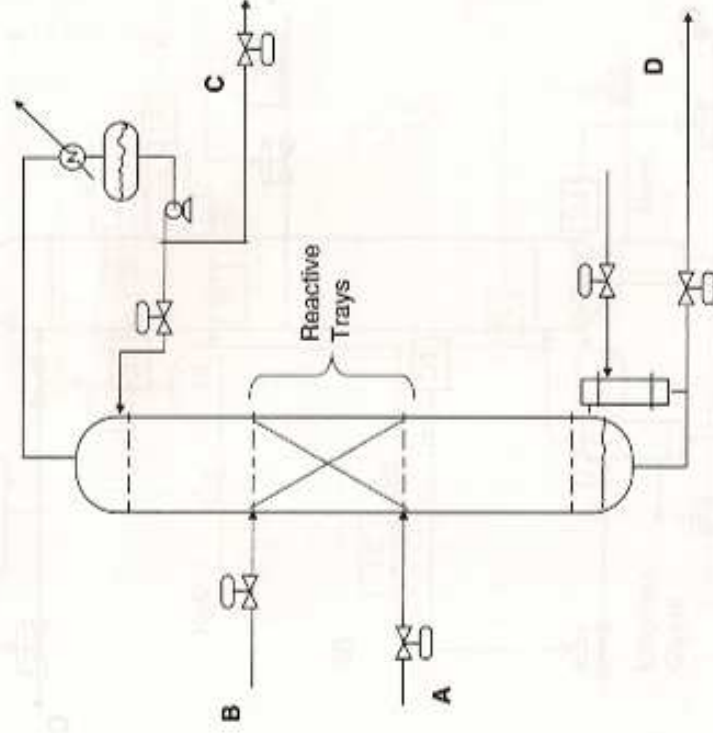


Figure 9.1 Ideal reactive distillation.

9.2 TYPES OF REACTIVE DISTILLATION SYSTEMS

There are many types of reactive distillation systems because several types of reactions are carried out in reactive columns. There are also several types of process structures that are used, some with recycle of an excess reactant and others without any reactant recycle.

9.2.1 Single-Feed Reactions

Reactions with a single reactant producing two products are easy to design and control because there is no need to balance the stoichiometry:



Only one reactant is fed to the column. The two products are removed out the two ends of the column. Olefin metathesis is an example of this type of reactive distillation column. Figure 9.2 illustrates this system and gives an effective control scheme. A C_5 olefin reacts to form a light C_4 olefin, which is removed in the distillate, and a heavy C_6 olefin, which is removed in the bottoms. The two temperature controllers are used to maintain conversion and product quality. The production rate is set by a feed flow controller.

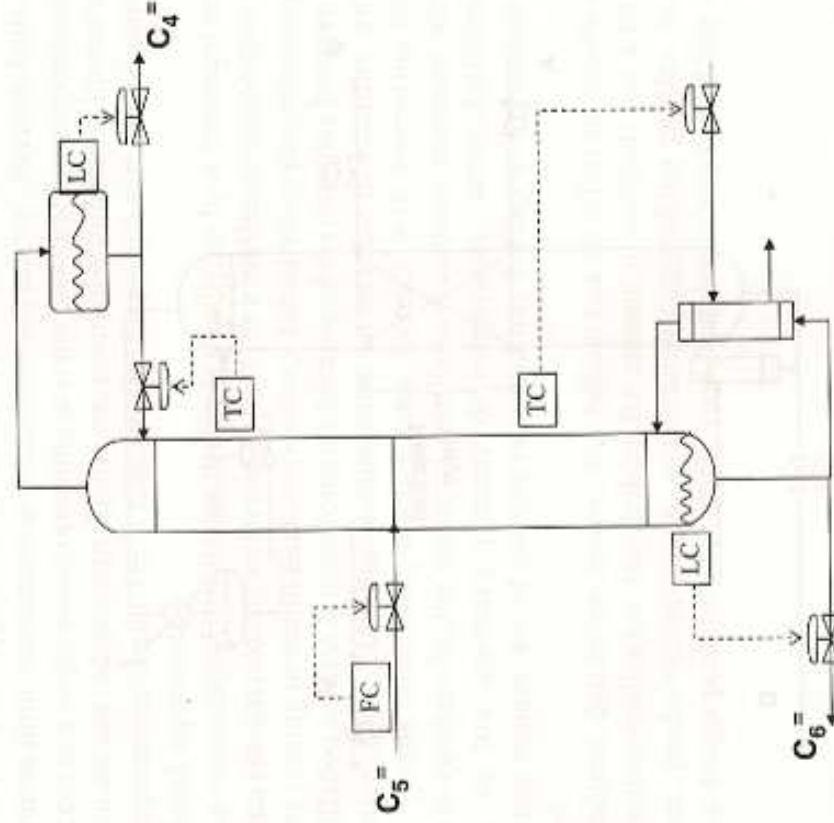


Figure 9.2 Olefin metathesis.

9.2.2 Irreversible Reaction with Heavy Product

The ethylene glycol reactive distillation system is an example of a reactive distillation system with two reactants that are consumed in a fast and irreversible reaction.

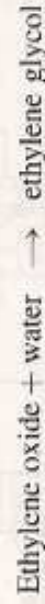


Figure 9.3 shows the system and an effective control structure. Ethylene oxide is very volatile, and ethylene glycol is very heavy, so the product is removed from the bottom of the column. The ethylene oxide concentrates in the top of the column. No distillate product is removed. The water feed is introduced to hold the liquid level in the reflux drum. This level loop achieves the necessary balancing of the reaction stoichiometry by adjusting the makeup water flowrate to exactly match the water consumption by reaction with ethylene oxide. Production rate is set by flow-controlling the ethylene oxide.

9.2.3 Neat Operation versus Use of Excess Reactant

If the reaction involves two reactant feedstreams, two basic flowsheets that are used. Consider the reaction $A + B \rightleftharpoons C + D$. One way to design the process is to feed an excess of one of the reactants into the reactive distillation column along with the other reactant. Figure 9.4 shows a system in which an excess of reactant B is fed. In most cases this excess must be recovered. A second distillation column is used in Figure 9.4 to achieve this recovery. The fresh feed of reactant B is mixed with the recycle of B coming from the recovery column.

The control of this system is fairly easy. The total flow of B to the reactive column is controlled by manipulating the fresh feed of reactant B. The fresh feed of reactant A sets

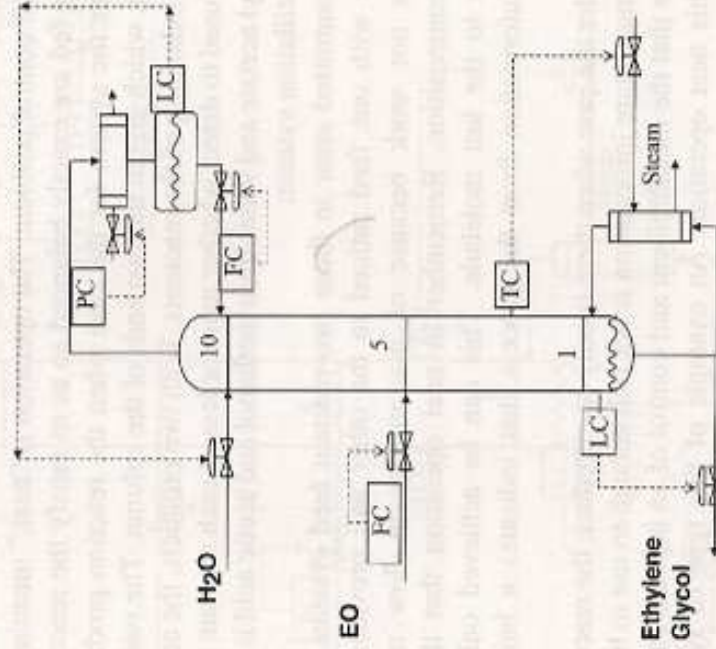


Figure 9.3 Ethylene glycol.

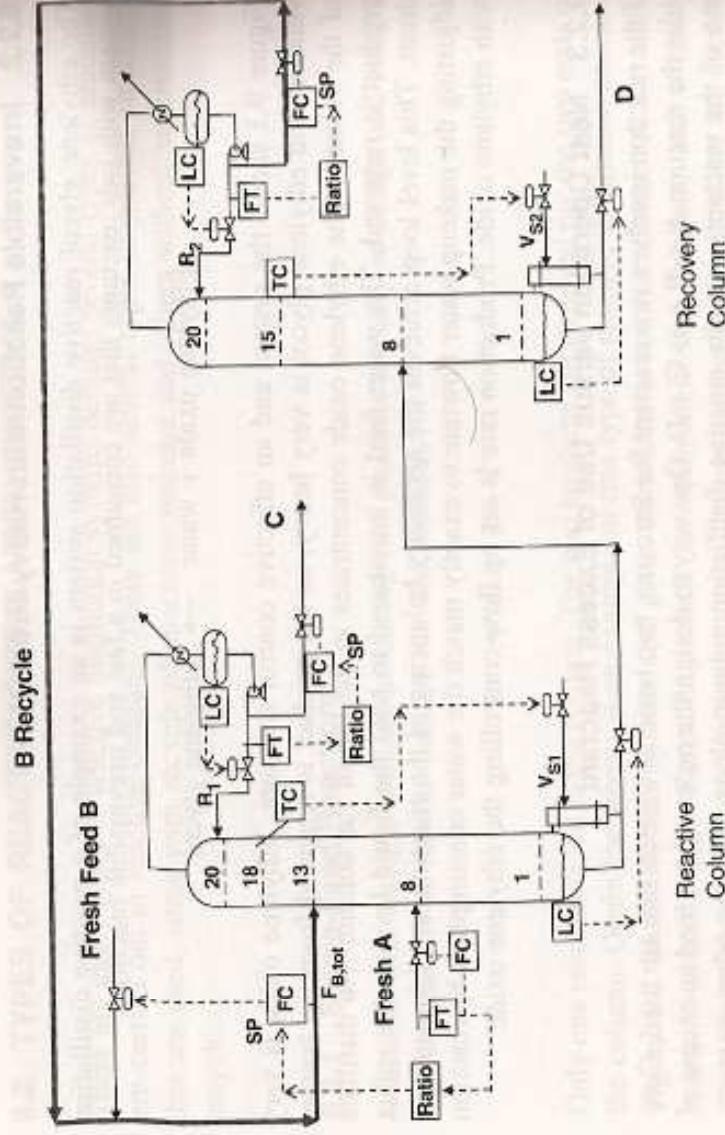


Figure 9.4 Excess of reactant B.

the production rate, and the setpoint of the total B flow controller is ratioed to the flowrate of A. The control scheme features reflux ratio control and temperature controllers in both columns.

The alternative flowsheet used just one column and is more economical, but it presents a much more difficult control problem. The operation is "neat," meaning that the amounts of the two reactants fed are exactly balanced so as to satisfy the reaction stoichiometry. Figure 9.5 illustrates the system for the case when the reaction produces two products ($A + B \rightleftharpoons C + D$), which go out the two ends of the column. The two temperature controllers achieve the balancing of the reactants. With two products, the column temperature information can be used to detect whether more or less of each reactant should be fed. The production of methyl acetate and water from methanol and acetic acid is an example of this type of reactive distillation system.

A commonly committed error in these two-reactant feed systems is to assume that a control structure with one feed ratioed to the other will provide effective control. This scheme does not work because of inaccuracies in flow measurements and changes in feed composition. Remember in neat operation that the reactants must be balanced down to the last molecule. This can be achieved only by using some sort of feedback information from the process that indicates a buildup or depletion of reactant.

However, consider the case when there is only one product: the reaction $A + B \rightleftharpoons C$. Now the column temperature information is not rich enough to use to balance the stoichiometry. This means that the measurement and control of an internal column composition must be used in this neat operation. An example of this type of system is shown in Figure 9.6. The production of ETBE from ethanol and isobutene produces a heavy product, which goes out the bottom of the column. The C_4 feedstream contains inert

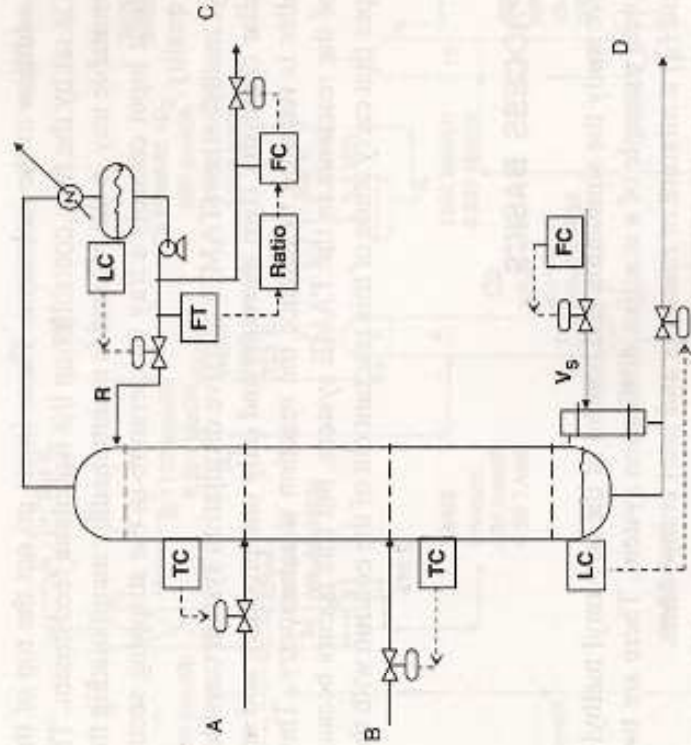


Figure 9.5 Neat operation (two products).

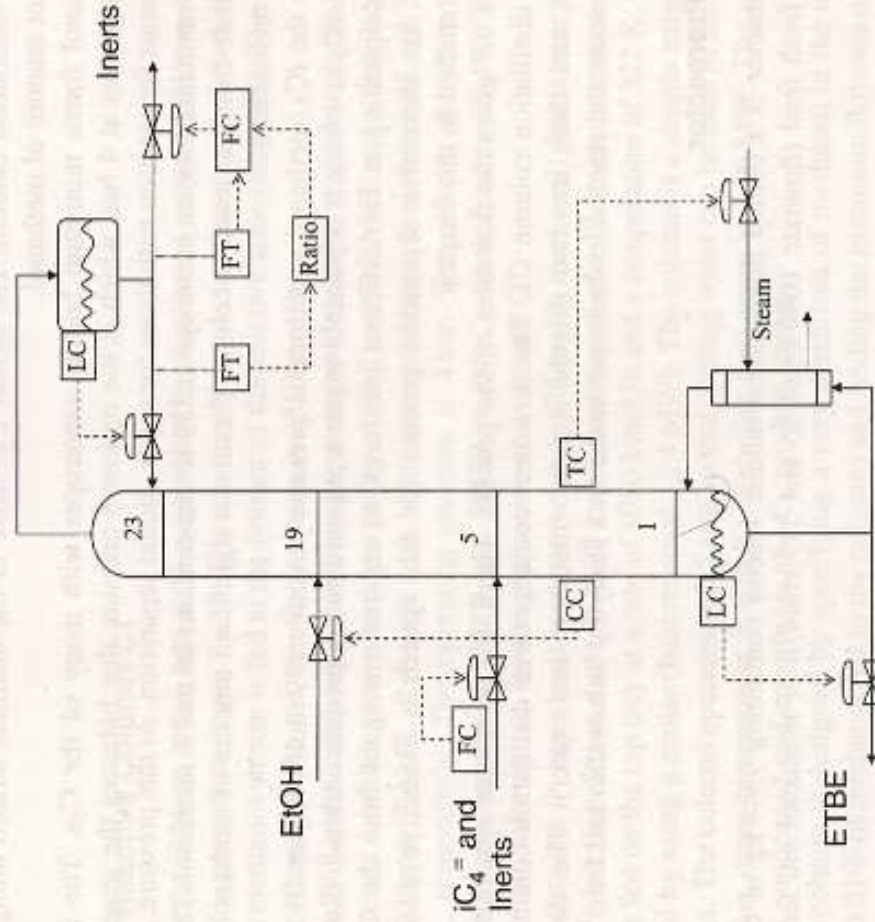


Figure 9.6 ETBE reactive distillation.

components in addition to the isobutene. These inerts go out the top of the column. The production rate is set by the flow controller on the isobutene feedstream. The ethanol concentration on a suitable tray in the column is maintained by manipulating the ethanol fresh feed. Reboiler heat input controls a tray temperature in the stripping section to maintain ETBE product quality.

The *tert*-amyl methyl ether (TAME) reactive distillation system considered in the next section has similar chemistry (two reactants and only one product), and an internal composition controller is required to balance the reaction stoichiometry. There is a recycle stream of one of the reactants in the TAME system, but this occurs because of the existence of azeotropes that carry some of this reactant out of the column with the inerts present in the feed.

9.3 TAME PROCESS BASICS

In this section we study the simulation and control of the *tert*-amyl methyl ether (TAME) process as a typical example of a reactive distillation system. There are two feedstreams: (1) methanol and (2) a mixture of reactants and inert components.

The C_5 feedstream to the TAME process contains about 24 mol% reactive isoamylenes: 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B). The remaining components are pentanes and pentenes (largely isopentane, iC_5), which are inert in the TAME reaction. TAME is the highest-boiling component, so it leaves in the bottoms stream from the reactive distillation column. The lighter C_5 s leave in the distillate stream along with a significant amount of methanol.

Methanol forms minimum boiling azeotropes with many of the C_5 s. The reactive column operates at 4 bar, which is the optimum pressure that balances the temperature requirements for reaction with those for vapor-liquid separation. At this pressure, isopentane and methanol form an azeotrope at 339 K that contains 26 mol% methanol. Therefore the distillate from the reactive column contains a significant amount of methanol, which must be recovered.

Since the iC_5 /methanol azeotrope is pressure-sensitive (79 mol% iC_5 at 10 bar and 67 mol% iC_5 at 4 bar), it is possible to use a pressure-swing process with two distillation columns, operating at two different pressures, to separate methanol from the C_5 components. An alternative separation process for this system is extractive distillation, which is studied in this chapter.

Figure 9.7 gives the flowsheet of the process. There is a prereactor upstream of the reactive distillation column C1. The flowsheet contains three distillation columns (one reactive), and there are two recycle streams (methanol and water). The design of the prereactor and reactive column are based on a study by Subawalla and Fair.¹

9.3.1 Prereactor

The prereactor is a cooled liquid-phase tubular reactor containing 9544 kg of catalyst. The C_5 fresh feed (flowrate 1040 kmol/h) and 313 kmol/h of methanol are fed to the reactor.

¹H. Subawalla and J. R. Fair, Design guidelines for solid-catalyzed reactive distillation systems, *Ind. Eng. Chem. Research* **38**, 3693 (1999).

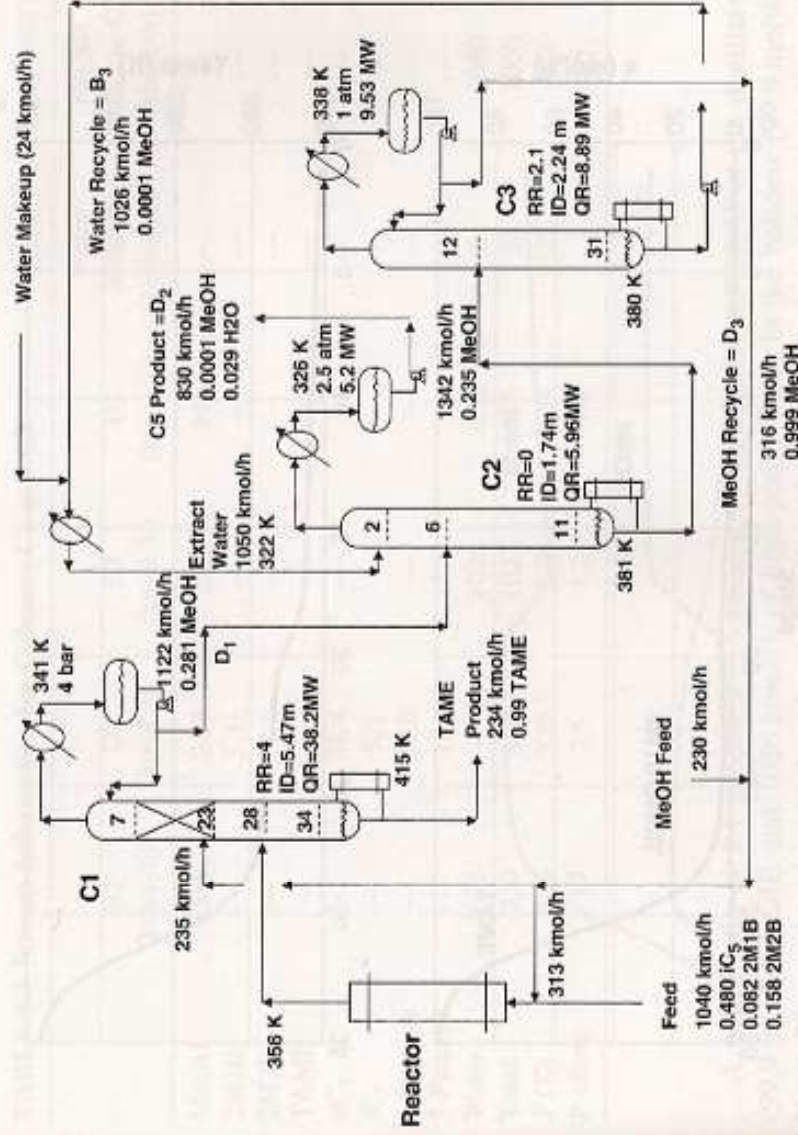


Figure 9.7 TAME process with extractive distillation methanol recovery.

9.3.2 Reactive Column C1

The reactor effluent is fed into a 35-stage reactive distillation column (C1) on stage 28. Catalyst is present on stages 7–23. The reactor effluent is fed five trays below the reactive zone. A methanol stream is fed at the bottom of the reactive zone (stage 23). The flowrate of the methanol fed to the reactive column is 235 kmol/h.

Figure 9.8 gives composition and temperature profiles in the reactive column C1. The reflux ratio is 4, which gives a bottoms purity of 99.2 mol% TAME and a distillate impurity of 0.1 ppm TAME. Reboiler heat input and condenser heat removal are 38.2 and 39 MW, respectively. The operating pressure is 4 bar. The column diameter is 5.5 m. The overall conversion of 2M1B and 2M2B in the C_5 fresh feed is 92.4%. Table 9.1 gives stream information for the pre reactor and column C1.

The distillate D_1 has a methanol composition (28 mol% methanol) that is near the azeotrope at 4 bar. It is fed at a rate of 1122 kmol/h to stage 6 of a 12-stage extraction column. Water is fed on the top tray at a rate of 1050 kmol/h and a temperature of 322 K, which is achieved by using a cooler (heat removal 1.24 MW). The column is a simple stripper with no reflux. The column operates at 2.5 atm so that cooling water can be used in the condenser (reflux drum temperature is 326 K). Reboiler heat input is 5.96 MW. The overhead vapor is condensed and constitutes the C_5 product stream.

This column is designed by specifying a very small loss of methanol in the overhead vapor (0.01% of methanol fed to the column) and finding the minimum flowrate of extraction water that achieves this specification. Using more than 10 trays or using reflux did not affect the recovery of methanol.

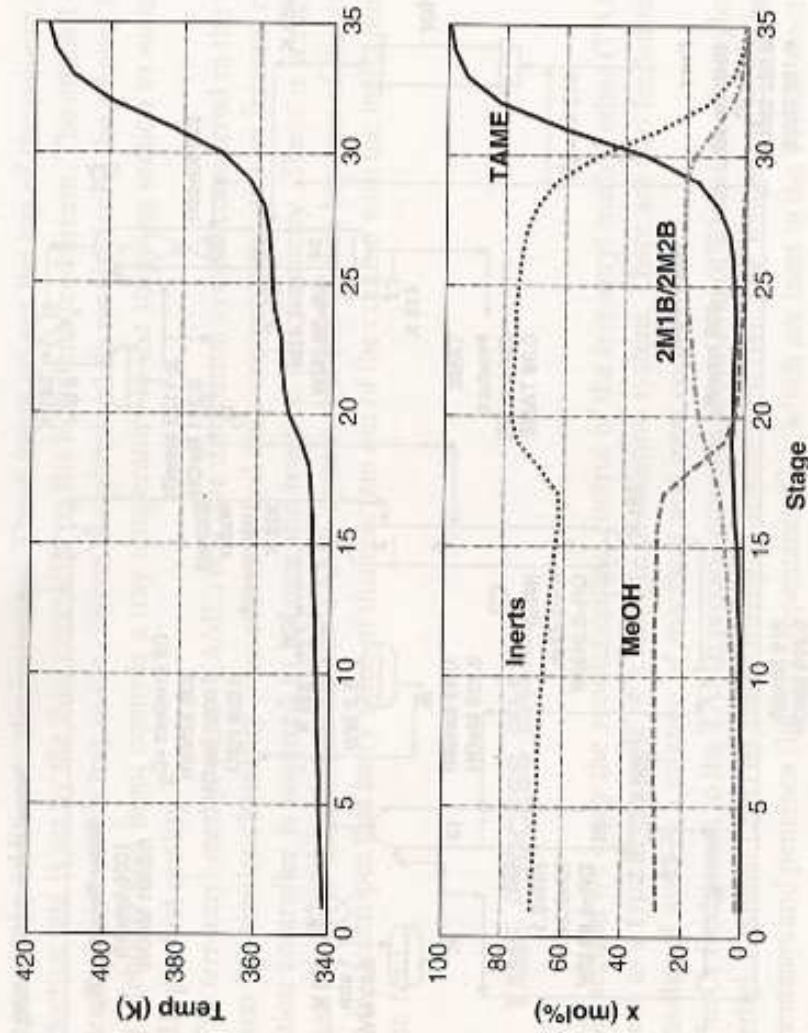


Figure 9.8 C1 temperature and composition profiles.

The bottoms is essentially a binary methanol/water mixture (23.5 mol% methanol), which is fed to a 32-stage column operating at atmospheric pressure. The number of trays in the second column is optimized by determining the total annual cost of the column over a range of tray numbers. Reboiler heat input and condenser heat removal are 8.89 and 9.53 MW, respectively. The column diameter is 2.24 m.

TABLE 9.1 Stream Information for Prereactor and Column C1

	Fresh Methanol (kmol/h)	Feed (kmol/h)	MeOH Reactor (kmol/h)	Reactor Effluent (kmol/h)	MeOH C1 (kmol/h)	B1 (kmol/h)	D1 (kmol/h)
MeOH	230	—	313	188	235	—	316
2M1B	—	85.6	—	13.7	—	0.01	3.31
2M2B	—	165	—	112	—	0.60	14.1
TAME	—	—	—	125	—	232	—
<i>n</i> C ₅	—	88.4	—	88.4	—	0.22	88.2
<i>i</i> C ₅	—	501	—	501	—	0.17	501
1-Pentene	—	38.1	—	38.1	—	0.18	37.9
2-Pentene	—	162	—	162	—	0.76	161
Total	230	1040	313	1228	235	234	1122
<i>T</i> (K)	325	343	351	355	351	415	341
<i>P</i> (atm)	17	10	7	6	4	4.29	3.95

TABLE 9.2 Stream Information for Columns C2 and C3

	B2 (kmol/h)	D2 (kmol/h)	B3 (kmol/h)	D3 (kmol/h)	Water Makeup (kmol/h)	Extract Water to C2 (kmol/h)
MeOH	316	0.03	1.03	315	—	—
2M1B	—	3.31	—	—	—	—
2M2B	—	14.1	—	—	—	—
TAME	—	—	—	—	—	—
<i>n</i> C ₅	—	88.4	—	—	—	—
<i>i</i> C ₅	—	501	—	—	—	—
1-Pentene	—	38.0	—	—	—	—
2-Pentene	—	161	—	—	—	—
Water	1025	—	1026	0.32	24	1050
Total	230	830	1027	315	24	1050
<i>T</i> (K)	325	326	379	338	325	322
<i>P</i> (atm)	17	2.5	1.2	1.0	7	2.5

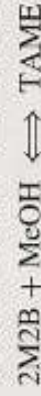
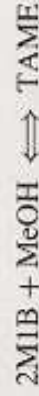
A reflux ratio of 2.1 produces 316 kmol/h of high-purity methanol in the distillate (99.9 mol% MeOH) and 1026 kmol/h of high-purity water in the bottoms (99.9 mol% H₂O). The methanol is combined with 230 kmol/h of fresh methanol feed, and the total is split between the methanol feed streams to the prereactor and to the reactive column. The water is combined with a small water makeup stream, cooled, and recycled back to the extractive column C2.

Some makeup water is needed because a small amount of water goes overhead in the vapor from column C2 (2.9 mol% water). The solubility of water in pentanes is quite small, so the reflux drum of column C2 would form two liquid phases (not shown in Fig. 9.1). The aqueous phase would be 19.9 kmol/h with 99.9 mol% water. The organic phase would be 809 kmol/h with 0.5 mol% water. Table 9.2 gives stream information around columns C2 and C3.

The convergence of the steady-state flowsheet was unsuccessful, so it was converged in the dynamic simulation, using the methods discussed in Chapter 8.

9.4 TAME REACTION KINETICS AND VLE

The liquid-phase reversible reactions considered are



The kinetics for the forward and reverse reactions are given in Table 9.3. These reaction rates are given in units of $\text{kmol s}^{-1} \text{kg}_{\text{cat}}^{-1}$ and are converted to the Aspen-required units of $\text{kmol s}^{-1} \text{m}^{-3}$ by using a catalyst bulk density of 900 kg/m^3 . The concentration units in the reaction rates are in mole fractions. The reactive stages in the column each contain

TABLE 9.3 Reaction Kinetics

Reaction	A_F ($\text{kmol s}^{-1} \text{kg}^{-1}$)	E_F (kJ/mol)	A_K ($\text{kmol s}^{-1} \text{kg}^{-1}$)	E_R (kJ/mol)	ΔH_{ex} (kJ/mol)
R1	1.3263×10^8	76.103737	2.3535×10^{11}	110.540899	-34.44
R2	1.3718×10^{11}	98.2302176	1.5414×10^{14}	124.993965	-26.76
R3	2.7187×10^{10}	96.5226384	4.2933×10^{10}	104.196053	-7.67

1100 kg of catalyst. This corresponds to 1.22 m^3 on each tray, which gives a weir height of 0.055 m for a reactive column with a diameter of 5.5 m.

The reactions and all the kinetic parameters must be set up in Aspen Plus. In the *Exploring* window, click on *Reactions* and then the second *Reactions*. Right-click and select *New*. This opens the window shown in Figure 9.9a, in which the type of reaction is selected

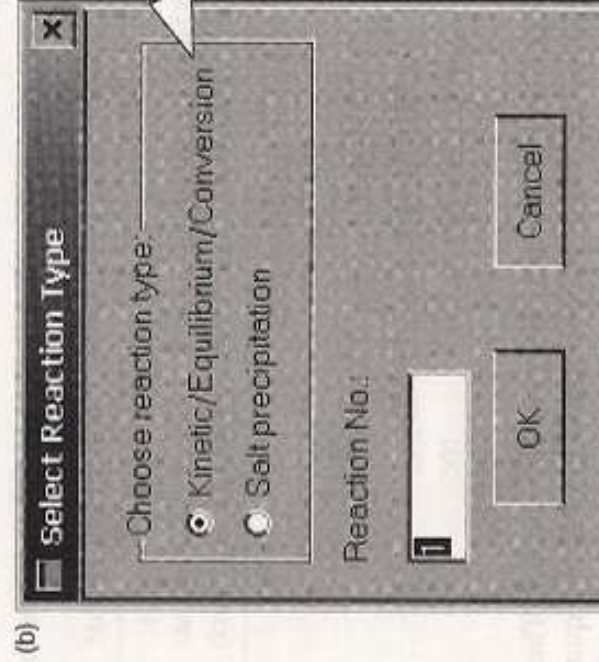
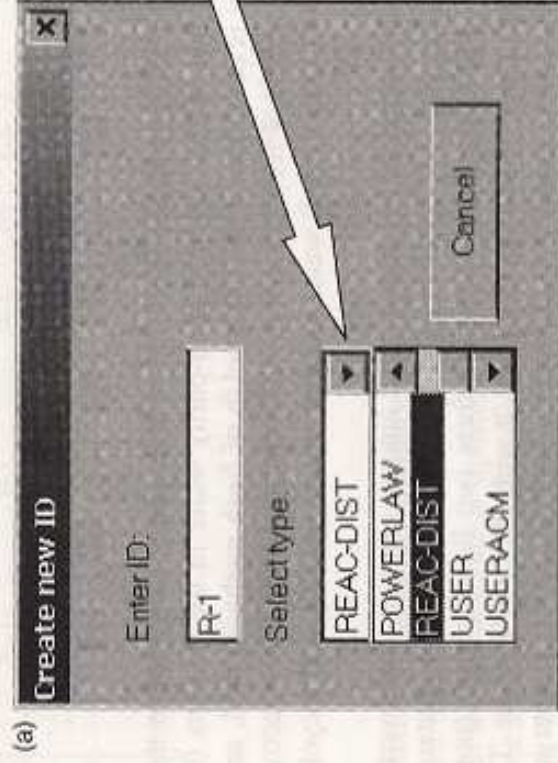


Figure 9.9 (a) Create new reaction; (b) select reaction type; (c) input reactants and products.

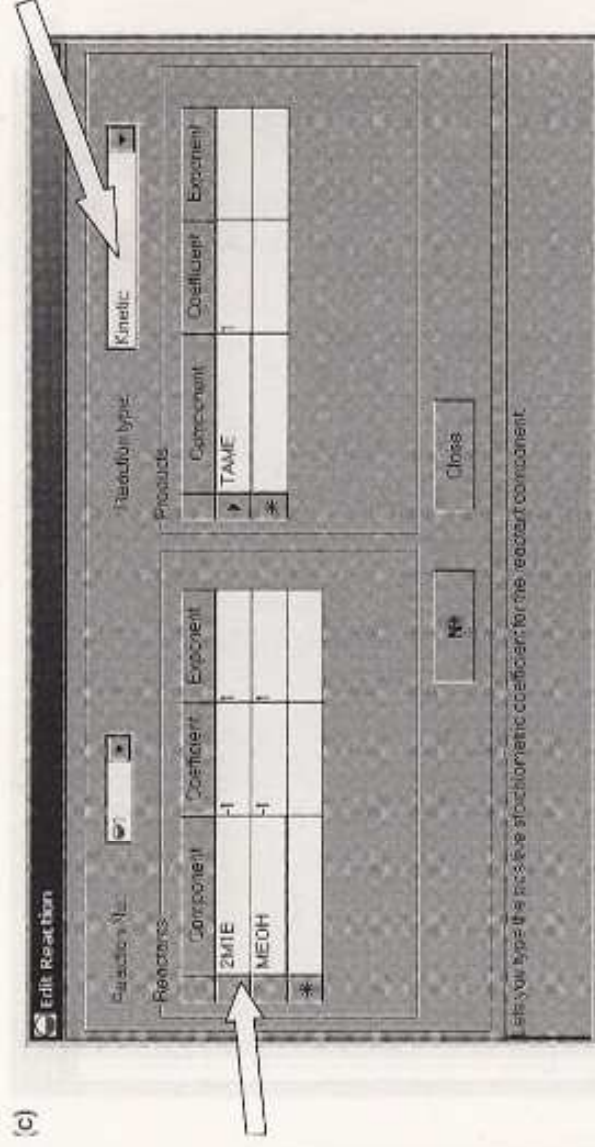


Figure 9.9 Continued.

to be *REAC-DIST*. Then click on the new reaction *R-1*, which opens the window shown in Figure 9.9b, on which *Kinetic* is selected.

Clicking *OK* opens the window shown in Figure 9.9c, on which reactant and product components are selected. The reactant coefficients are negative, and the product coefficients are positive. The *Exponent* is the power-law exponent used in the reaction rate expression. Make sure to select *Kinetic* in the upper right corner.

The procedure is repeated for the three forward reactions and for the three reverse reactions. These are shown in Figure 9.10. All of this input is done on the *Stoichiometry* page tab. Clicking the *Kinetic* page tab and selecting one of the six reactions opens the window shown in Figure 9.11a, on which all the kinetic parameters are entered for that reaction. Remember to select *Liquid* for reacting phase and *mole fraction* for the concentration basis (see Fig. 9.11b).

It is important to point out that for reactive distillation Aspen Plus does not list *activities* as a standard option for the concentration basis. This is a distinct limitation because many of the reactions that occur in reactive distillation systems use activities. Special-purpose programs can be written, but these are beyond the scope of this book. Later versions of Aspen Plus should remove this limitation.

Now the reactions have been set up. Go to the C1 block and click *Reactions*. Enter the starting and ending stages on which reaction occurs on the *Specifications* page tab in Figure 9.12a and select the reaction *R-1*. Note that *R-1* is a set of six reactions.

Clicking the *Holdups* page tab opens the window shown in Figure 9.12b, in which the molar or volumetric holdups on each of the reactive trays are entered. The reactive liquid volume on each tray is set at 1.22 m^3 , which corresponds to a liquid height of 0.055 m for a reactive column with a diameter of 5.5 m.

It is important to note that the diameter of the column is not known initially because this depends on vapor velocities that are unknown until the column is converged to the desired specifications. So column sizing in a reactive distillation column is an iterative procedure. A diameter is estimated, tray holdups calculated, and the column is converged. Then the

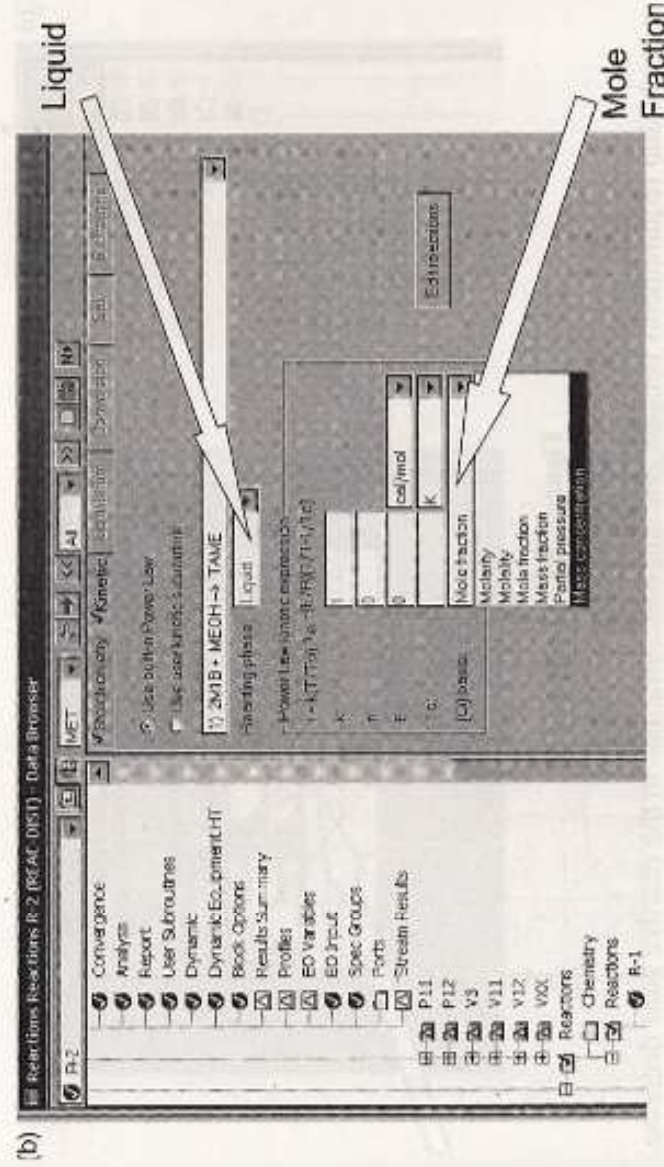


Figure 9.11 Continued.

diameter calculated in *Tray Sizing* is compared with the estimated diameter and the calculations repeated.

The other important issue is the height of liquid on a tray. Hydraulic limitations prevent excessive liquid depth because this would cause large pressure drops. Liquid depths are limited to about 0.1 m. If more liquid holdup is needed, the column diameter can be increased beyond the minimum calculated from sizing calculations. Of course, more reactive trays could also be added to the column. However, reactive distillation columns have the interesting feature that there is an optimum number of reactive stages. Having too few reactive stages results in high energy consumption because the reactant concentrations in the reactive zone must be large, and this requires large vapor rates to keep the reactants from leaving in the bottoms or the distillate. Adding more reactive stages reduces the

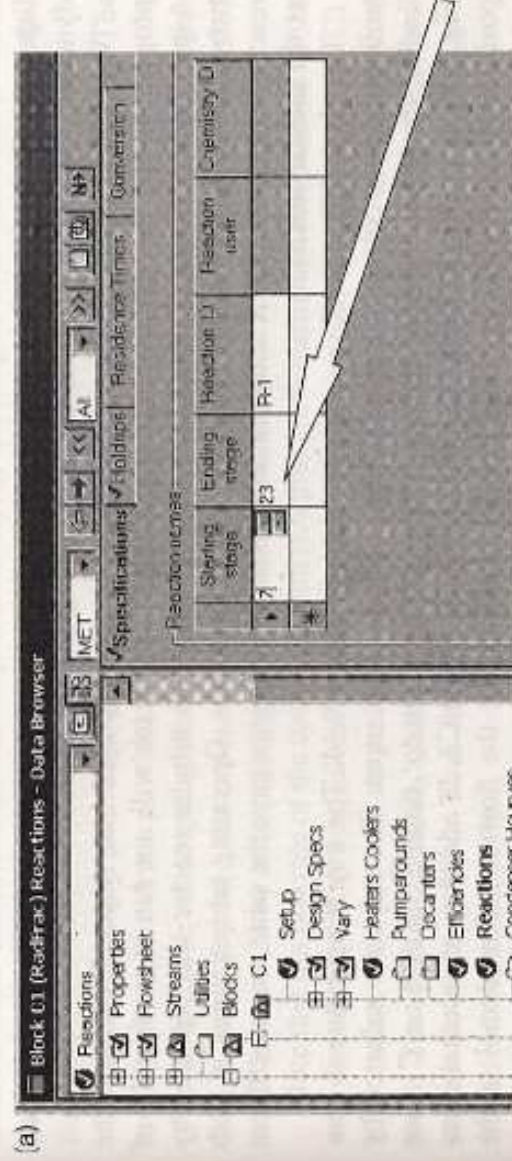


Figure 9.12 (a) Specifying reactive trays and holdups; (b) tray holdups.

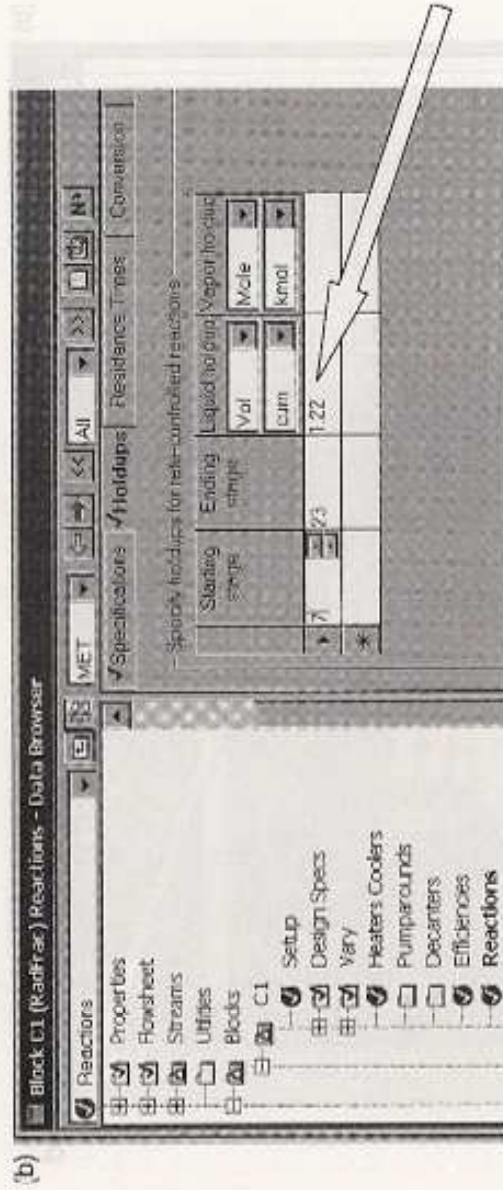


Figure 9.12 Continued.

vapor boilup requirements because reactant concentrations in the reactive zone decrease. However, beyond some point, adding more reactive stages begins to increase energy consumption because the reactant concentrations in the reactive zone start to increase due to a larger contribution from the reverse reactions.

Figure 9.13 gives a ternary diagram for the isopentane/methanol/TAME system at 4 bar. The phase equilibrium of this system is complex because of the existence of azeotropes. The Unifac physical property package in Aspen Plus is used to model the vapor-liquid equilibrium in all units except the methanol/water column, where the van Laar equations are used because of their ability to accurately match experimental data.

9.5 PLANTWIDE CONTROL STRUCTURE

In preparation for exporting the steady-state flowsheet into Aspen Dynamics, all equipment is sized. Column diameters are calculated by Aspen tray sizing. Reflux drums and column bases are sized to provide 5 min of holdup when 50% full, based on the total liquid entering the surge capacity. Pumps and control valves are specified to give adequate dynamic rangeability. Typical valve pressure drops are 2 atm.

When the flowsheet with a tubular reactor was exported into Aspen Dynamics, the program would not run. A liquid-filled plug-flow reactor will not run in version 12 of Aspen Dynamics. To work around this limitation, the tubular reactor was replaced by two continuous stirred tank reactors (CSTRs) in series. Operating temperatures in both reactors were set at 355 K and volume at 10 m^3 . This design gave the same reactor effluent as the tubular reactor.

The plantwide control structure is shown in Figure 9.14. The tray temperature is controlled in each column by manipulating reboiler heat input. The trays are selected by finding the location where the temperature profile is steep: stage 31 in column C1 (see Fig. 9.8), stage 7 in column C2, and stage 7 in column C3. In addition, an internal composition in column C1 is controlled by manipulating the flowrate of methanol to the column. Stage 18 is selected (see Fig. 9.8). The flowrate of methanol to the reactor is ratioed to the feed flowrate.

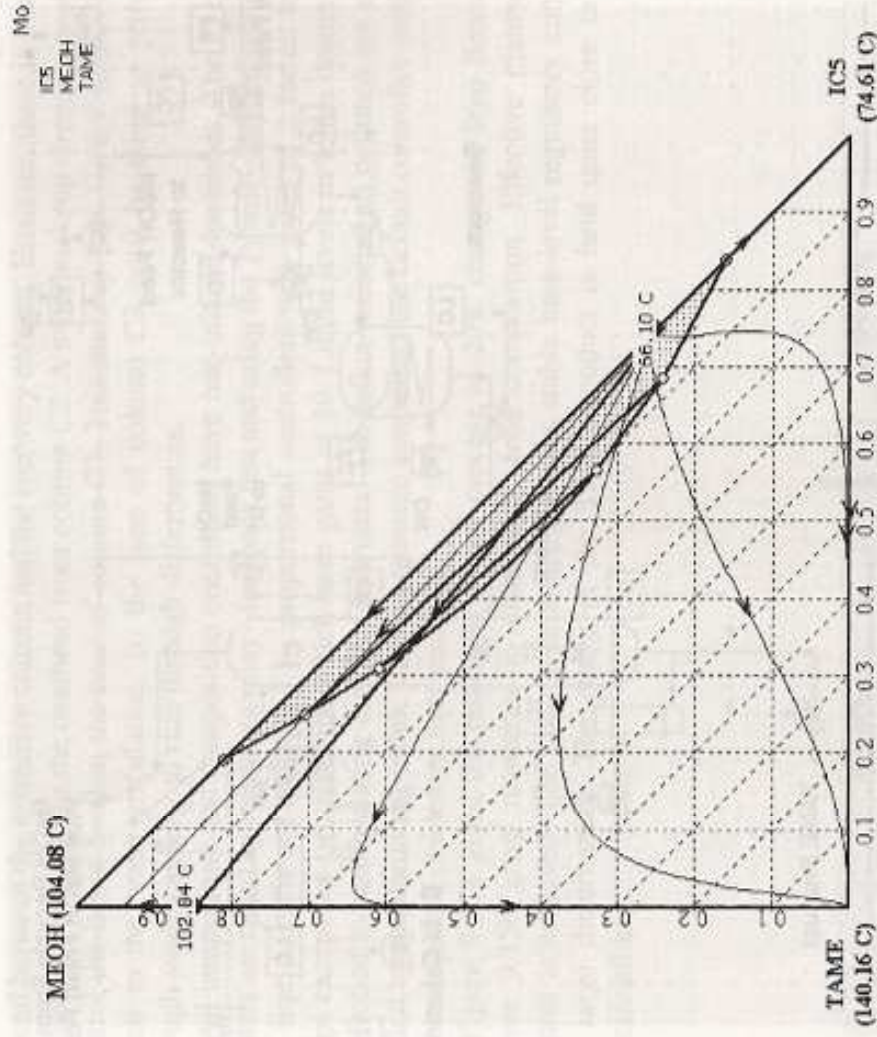


Figure 9.13 iC5/MeOH/TAME at 4 bar.

The flowrate of extraction water fed to the top of column C2 is ratioed to the feed to the feed to this column D_1 by using a multiplier and a remotely set flow controller. The temperature of the extraction water is controlled by manipulating cooling water to the cooler. Base level is controlled by manipulating bottoms, and reflux drum level is controlled by manipulating distillate. The binary methanol/water mixture from the bottom of column C2 is fed to column C3. A constant reflux ratio is maintained in this column by adjusting reflux flowrate.

There are two key plantwide material balance loops associated with column C3. The level in the reflux drum provides a good indication of the inventory of methanol in the system. If this level is going down, more methanol is being consumed in the reaction than is being fed into the process. Therefore the control structure maintains the reflux drum level in C3 by manipulating the methanol fresh feed.

Note that the flowrate of the total methanol (D_3 plus fresh methanol feed) is fixed by the two downstream flow controllers setting the flowrates to the reactor and to column C1. This means that there is an immediate effect of fresh feed flowrate on reflux drum level. The distillate flow D_3 changes inversely with fresh feed flow because the downstream flowrate is fixed. Thus the reflux drum level sees the change in the methanol fresh feed instantaneously.

At the other end of the column, the base level provides a good indication of the inventory of water in the system. Ideally there should be no loss of water since it just circulates

around between the extractive column and the recovery column. However, there is a small amount of water lost in the overhead from column C2. A water makeup stream is used to control the liquid level in the base of column C3. This makeup flow is very small compared to the water circulation, so the base of column C3 must be sized to provide enough surge capacity to ride through disturbances.

All temperature and composition controllers have one-minute deadtimes. The PI controllers are tuned by running a relay-feedback test and using the Tyreus-Luyben settings. All liquid levels are controlled by proportional controllers with gains of 2 for all level loops except the two reactors, which have gains of 10. Liquid levels in reflux drums are controlled by manipulating distillate flowrates. The reflux ratios in all columns are controlled by manipulating reflux. Column pressure controllers use default controller settings and manipulate condenser heat removal.

Figure 9.15a gives the responses of the process to 20% changes in feed flowrate. Figure 9.15b gives responses to changes in feed composition. Effective plantwide control is achieved. The control structure provides stable base-level regulatory control for large disturbances. The purity of the TAME product is held quite close to its specification.

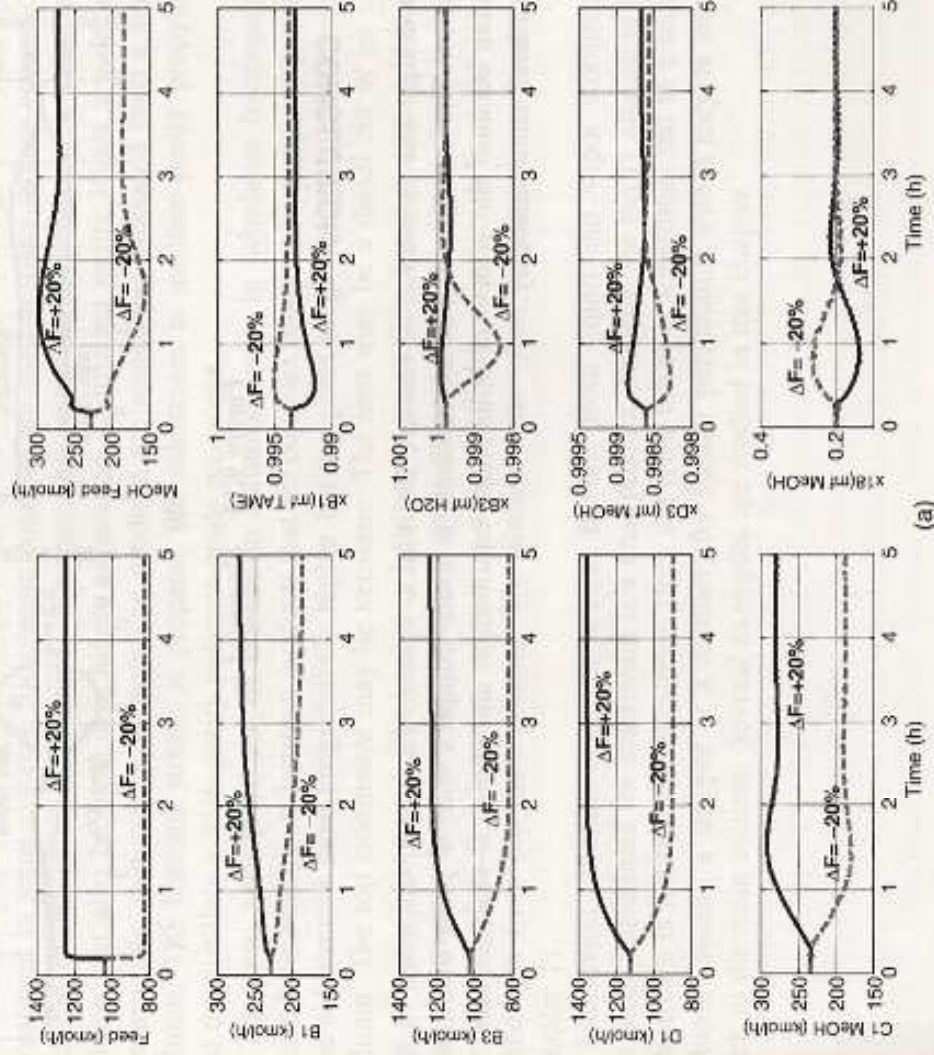


Figure 9.15 (a) Feed rate disturbances; (b) feed composition disturbances.

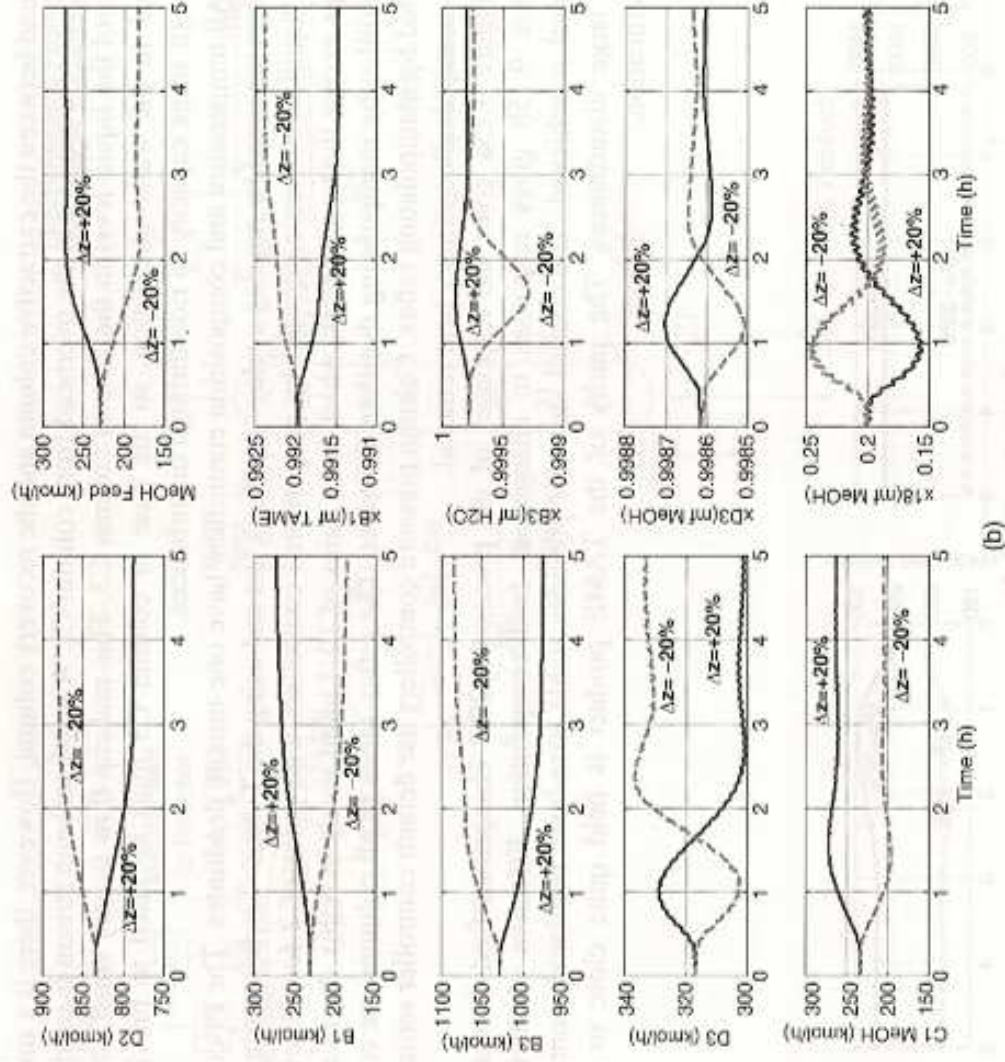


Figure 9.15 Continued.

9.6 CONCLUSION

The design and simulation of reactive distillation systems have been discussed in this chapter. The reactive distillation column is more complex than a plain distillation column because the effects of both phase equilibrium and chemical reaction must be considered simultaneously.