CHAPTER 11

Vinyl Acetate Process

11.1 Introduction

The final example to illustrate our plantwide control design procedure comes from Luyben and Tyreus (1998), who present design details of an industrial process for the vapor-phase manufacture of vinyl acetate monomer. This process is uniquely suited for researchers pursuing process simulation, design, and control studies. It has common real chemical components in a realistically large process flowsheet with standard chemical unit operations, gas and liquid recycle streams, and energy integration.

The study was conveyed as if we had been assigned the task of designing the control system for a proposed new vinyl acetate process that is to be built. A particular preliminary design was given that had *not* been optimized. The data provided are what would typically be available or easily obtainable: (1) kinetic reaction parameters and physical property data, (2) a flowsheet structure with stream and equipment information, and (3) the location of control valves included in the preliminary design.

The industrial process for the vapor-phase manufacture of vinyl acetate monomer is quite common (Daniels, 1989) and utilizes widely available raw materials. Vinyl acetate is used chiefly as a monomer to make polyvinyl acetate and other copolymers. Hoechst-Celanese, Union Carbide, and Quantum Chemical are reported U.S. manufacturers. DuPont also currently operates a vinyl acetate process at its plant in LaPorte, Texas. To protect any proprietary DuPont information, all of the physical property and kinetic data, process flowsheet information, and modeling formulation in the published paper come from sources in the open literature. The process flowsheet is based upon the description in Report 15B by SRI International (1994). No relation, either implied or intended, exists between the published study and the DuPont process.

Figure 11.1 shows the eleven basic unit operations in the reaction section of the vinyl acetate process. Three raw materials, ethylene (C_2H_4), oxygen (O_2), and acetic acid (HAc), are converted into the vinyl acetate (VAc) product. Water (H_2O) and carbon dioxide (CO_2) are byproducts. We assume that an inert component, ethane (C_2H_6), enters with the fresh ethylene feed stream. We consider the following two reactions:

$$C_2H_4 + CH_3COOH + \tfrac{1}{2}\,O_2 \rightarrow CH_2 = CHOCOCH_3 + H_2O \quad (11.1)$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad (11.2)$$

The exothermic reactions occur in a reactor containing tubes packed with a precious metal catalyst on a silica support. Heat is removed from the reactor by generating steam on the shell side of the tubes. Water flows to the reactor from a steam drum, to which makeup water (boiler feeder water; BFW) is supplied. The steam leaves the drum as saturated vapor. The reactions are irreversible and the reaction rates have an Arrhenius-type dependence on temperature.

The following rate expressions were derived from the experimental kinetic data in Samanos et al. (1971) for a particular vinyl acetate catalyst.

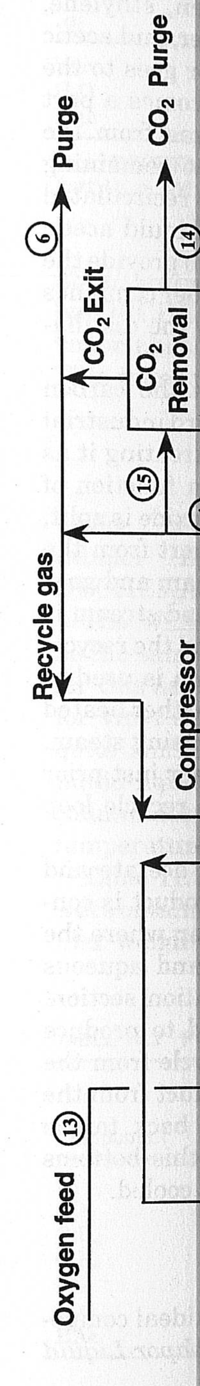
$$r_1 = 0.1036 \exp(-3674/T)\,\frac{p_O\, p_E\, p_A\,(1 + 1.7p_W)}{[1 + 0.583p_O(1 + 1.7p_W)](1 + 6.8p_A)} \quad (11.3)$$

$$r_2 = 1.9365 \times 10^5 \exp(-10{,}116/T)\,\frac{p_O(1 + 0.68p_W)}{1 + 0.76p_O(1 + 0.68p_W)} \quad (11.4)$$

where r_1 has units of moles of vinyl acetate produced per minute per gram of catalyst and r_2 has units of moles of ethylene consumed per minute per gram of catalyst. T is the absolute temperature in kelvin and p_i is the partial pressure of component i (O is oxygen, E is ethylene, A is acetic acid, and W is water) in psia.

The ideal-gas standard state heat of reaction is −42.1 kcal/mol of vinyl acetate for r_1 and −316 kcal/mol of ethylene for r_2. These values are calculated from ideal-gas heats of formation from the DIPPR database. Thus the reactions are quite exothermic, particularly the combustion reaction to carbon dioxide, which also is more sensitive to temperature because of the higher activation energy.

The reactor effluent flows through a process-to-process heat ex-



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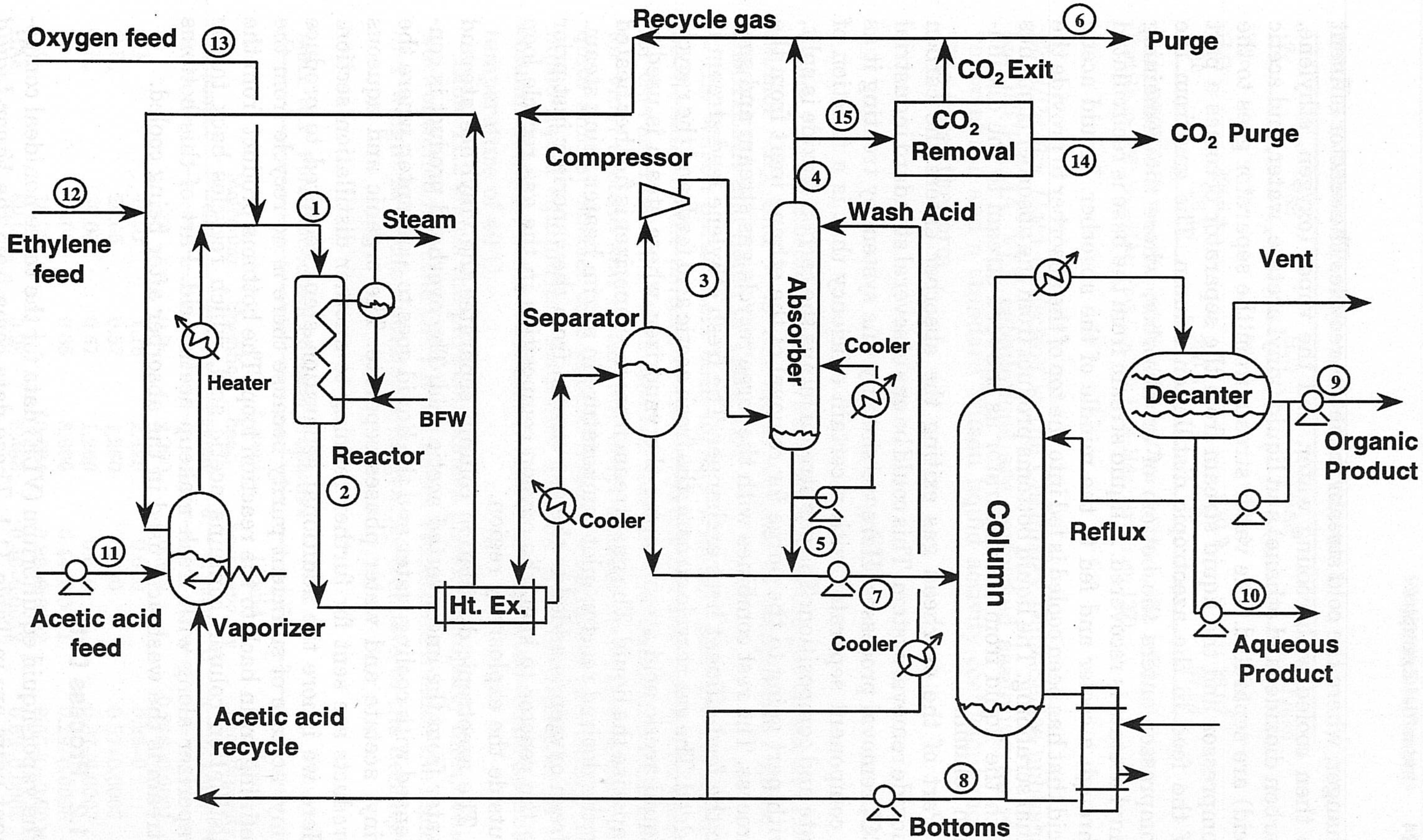

Figure 11.1 Vinyl acetate process flowsheet.

changer, where the cold stream is the gas recycle. The reactor effluent is then cooled with cooling water, and the vapor (oxygen, ethylene, carbon dioxide, and ethane) and liquid (vinyl acetate, water, and acetic acid) are separated. The vapor stream from the separator goes to the compressor and the liquid stream from the separator becomes a part of the feed to the azeotropic distillation column. The gas from the compressor enters the bottom of an absorber, where the remaining vinyl acetate is recovered. A liquid stream from the base is recirculated through a cooler and fed to the middle of the absorber. Liquid acetic acid that has been cooled is fed into the top of the absorber to provide the final scrubbing. The liquid bottoms product from the absorber combines with the liquid from the separator as the feed stream to the distillation column.

Part of the overhead gas exiting the absorber enters the carbon dioxide removal system. This could be one of several standard industrial CO_2 removal processes. Here we simplify this system by treating it as a component separator with a certain efficiency that is a function of rate and composition. The gas stream minus the carbon dioxide is split, with part going to the purge for removal of the ethane inert from the process. The rest combines with the large recycle gas stream and goes to the feed-effluent heat exchanger. The fresh ethylene feed stream is added. The gas recycle stream, the fresh acetic acid feed, and the recycle liquid acetic acid stream enter the vaporizer, where steam is used to vaporize the liquid. The gas stream from the vaporizer is further heated to the desired reactor inlet temperature in a trim heater using steam. Fresh oxygen is added to the gas stream from the vaporizer just prior to the reactor to keep the oxygen composition in the gas recycle loop outside the explosivity region.

The azeotropic distillation column separates the vinyl acetate and water from the unconverted acetic acid. The overhead product is condensed with cooling water and the liquid goes to a decanter, where the vinyl acetate and water phases separate. The organic and aqueous products are sent for further refining to another distillation section. Here we ignore the additional separation steps required to produce vinyl acetate of sufficient purity because there is no recycle from the refining train back to the reaction loop. The bottoms product from the distillation column contains acetic acid, which recycles back to the vaporizer along with fresh makeup acetic acid. Part of this bottoms stream is the wash acid used in the absorber after being cooled.

11.2 Process Data

The vapor-liquid equilibrium (VLE) data for the three nonideal component pairs are in Table 11.1. These data come from the *Vapor-Liquid*

TABLE 11.1 Wilson Parameters a_{ij} and Molar Volumes V_i

a_{ij}	VAc	H_2O	HAc	V_i, mL/mol
VAc	0	1384.6	−136.1	93.1
H_2O	2266.4	0	670.7	18.07
HAc	726.7	230.6	0	57.54

From DECHEMA *Vapor-Liquid Equilibrium Data Collection,* Vol. 1 (VAc–H_2O: Part 1b, p. 236; VAc–HAc: Part 5, p. 90; H_2O–HAc: Part 1, p. 127).

Equilibrium Data Collection in the Chemistry Data Series published by DECHEMA. VLE calculations are performed assuming an ideal vapor phase and a standard Wilson liquid activity coefficient model. This takes the form

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(-a_{ij}/RT\right) \tag{11.5}$$

where T is the absolute temperature in K, R is the gas constant (1.987 cal/mol · K), and V_i is the molar volume of component i given in DECHEMA and listed in Table 11.1.

The Wilson parameters used for the VAc–H_2O pair are assumed to be the same as the parameters for ethyl acetate and water. The reason for this assumption is that no VLE data are presented in DECHEMA for vinyl acetate and water, but ethyl acetate and vinyl acetate are quite similar species and should behave essentially identically. The liquid-liquid equilibrium solubility data for the VAc–H_2O pair in the column decanter come from Smith (1942) extrapolated to the decanter temperature of 40°C.

Table 11.2 shows the pure component physical property data, which were obtained from the DIPPR database. These data include the molecular weight MW, the liquid specific gravity (relative to the density of

TABLE 11.2 Pure Component Physical Properties

Component	Molecular weight	Specific gravity	Latent heat, cal/mol	Liquid heat capacity $a - b$, cal/g · °C	Vapor heat capacity $a - b$, cal/g · °C
O_2	32	0.5	2,300	0.3–0	0.218–0.0001
CO_2	44.01	1.18	2,429	0.6–0	0.23–0
C_2H_4	28.05	0.57	1,260	0.6–0	0.37–0.0007
C_2H_6	30.05	0.57	1,260	0.6–0	0.37–0.0007
VAc	86.09	0.85	8,600	0.44–0.0011	0.29–0.0006
H_2O	18.02	1	10,684	0.99–0.0002	0.56–(−0.0016)
HAc	60.05	0.98	5,486	0.46–0.0012	0.52–0.0007

water), the latent heat of vaporization ΔH_v extrapolated to 0°C (in cal/mol), and the liquid c_p^l and vapor c_p^v heat capacity parameters. The heat capacity expressions have the following temperature dependence:

$$c_p = a + bt \tag{11.6}$$

where c_p is in cal/(g · °C) and t is the temperature in °C.

Component vapor pressures P^s in psia (Table 11.3) are calculated by using the Antoine equation, with the Antoine coefficients based on the DECHEMA volumes:

$$\ln P^s = A + \frac{B}{(t + C)} \tag{11.7}$$

where t is the temperature in °C. For the four gas components, the A parameters of the Antoine equation were estimated on the basis of the vapor pressure at the operating conditions in the absorber. The temperature dependence was removed to facilitate the dynamic simulation. However, in the case of ethylene and ethane, it was found that a small temperature dependence needed to be included for the bubble point calculations to function properly.

The process design assumes a production basis with new catalyst of 785 mol/min VAc and at the given conditions 85 mol/min CO_2 is also produced. For a plant with 90 percent operating utility, this corresponds to an annual production rate of 32 × 10^6 kg/yr, if the VAc rate is sustained over the life of the catalyst. The catalyst lifetime is assumed to be 1 year. Available on the plant are the following utilities: cooling tower water at a supply temperature of 30°C, steam at supply pressures of 50 and 200 psia, refrigeration at −25°C, and electricity and process water. Economic data for raw material and energy costs are listed in Table 11.4. Capital equipment and vessel cost data can be found in Guthrie (1969); these costs should be updated to current prices with the appropriate material of construction factors applied.

TABLE 11.3 Component Vapor Pressure Antoine Coefficients*

Component	A	B	C
O_2	9.2	0	273
CO_2	7.937	0	273
C_2H_4	9.497	−313	273
C_2H_6	9.497	−313	273
VAc	12.6564	−2984.45	226.66
H_2O	14.6394	−3984.92	233.426
HAc	14.5236	−4457.83	258.45

*$\ln P^s = A + B/(t + C)$, where P^s is in psia and t is in °C.

TABLE 11.4 Economic Data for Vinyl Acetate Process

Item	Cost/unit
Acetic acid	\$0.596/kg
Oxygen	\$0.044/kg
Ethylene	\$0.442/kg
Vinyl acetate	\$0.971/kg
200-psia steam	\$11/1000 kg
50-psia steam	\$8.8/1000 kg
Cooling tower water	\$0.02/1000 L
Process water	\$0.15/1000 L
−25°C refrigeration	\$0.12/h · ton
Electricity	\$0.065/kWh

Tables 11.5 to 11.7 contain process stream data. These data come from the TMODS dynamic simulation and not from a commercial steady-state simulation package. The corresponding stream numbers are shown on the flowsheet in Fig. 11.1. Tables 11.8 to 11.10 list the process equipment and vessel data. In the simulation, all gas is removed in a component separator prior to the distillation column. This involves the liquid from the separator and the absorber. The gas is sent back and combines with the vapor product from the separator to form the vapor feed to the absorber. Figure 11.2*a* shows the temperature profile in the azeotropic distillation column.

The reactor is modeled in 10 sections in the axial direction. The reactor temperature profile is shown in Fig. 11.2*b*. The flowsheet design conditions are for a new catalyst with an activity of 1. However, the

TABLE 11.5 Process Stream Data, Part 1

	Reactor in	Reactor out	Absorber vapor in	Absorber vapor out	Absorber liquid out	Purge flow
Stream number	1	2	3	4	5	6
Flow, mol/min	19,250	18,850	16,240	15,790	1210	3
Temperature, °C	148.5	158.9	80	40.4	47.7	40.4
Pressure, psia	128	90*	128	128	128	128
O_2, mole fraction	0.075	0.049	0.057	0.058	0.001	0.059
CO_2	0.007	0.011	0.013	0.014	0.001	68†
C_2H_4	0.583	0.551	0.642	0.658	0.025	0.667
C_2H_6	0.216	0.221	0.256	0.263	0.010	0.266
VAc	0	0.043	0.021	0.002	0.255	0.002
H_2O	0.009	0.055	0.007	0.001	0.129	0.001
HAc	0.110	0.070	0.004	0.004	0.579	0.005

*Pressure drop in gas loop assumed to be in reactor.
†Moles per million.

TABLE 11.6 Process Stream Data, Part 2

	Column feed	Column bottoms	Organic product	Aqueous product	Fresh HAc feed
Stream number	7	8	9	10	11
Flow, mol/min	3820	2160	826	831	785
Temperature, °C	42.5	137.2	40	40	30
Pressure, psia	84	30	18	18	150
VAc, mole fraction	0.206	11*	0.950	0.002	0
H_2O	0.281	0.093	0.050	0.998	0
HAc	0.513	0.907	370*	370*	1

*Moles per million.

TABLE 11.7 Process Stream Data, Part 3

	Fresh C_2H_4 feed	Fresh O_2 feed	CO_2 purge	CO_2 removal in flow
Stream number	12	13	14	15
Flow, mol/min	831	521	85	6411
Temperature, °C	30	30	40.4	40.4
Pressure, psia	150	150	128	128
O_2, mole fraction	0	1	0	Same as stream 4
CO_2	0	0	1	
C_2H_4	0.999	0	0	
C_2H_6	0.001	0	0	

TABLE 11.8 Reactor and Vaporizer Equipment Data

Catalyst weight	2590 kg
Catalyst porosity	0.8
Catalyst bulk density	0.385 kg/L
Catalyst heat capacity	0.23 cal/g · °C
Overall heat transfer coefficient	150 kcal/h · °C · m^2
Number of tubes	622
Tube length	10 m
Tube diameter	3.7 cm
Circumferential heat transfer area	725 m^2
Shell side temperature	133 °C
Reactor heat duty	2.8×10^6 kcal/h
Steam drum volume	2 m^3
BFW to steam drum	79.5 kg/min
Reactor feed heater duty	5.3×10^5 kcal/h
Vaporizer duty	1.3×10^6 kcal/h
Vaporizer total volume	17 m^3
Vaporizer working level volume	4 m^3
Vaporizer temperature	119 °C

TABLE 11.9 FEHE, Separator, and Absorber Equipment Data

FEHE duty	4.4×10^5 kcal/h
FEHE hot outlet temperature	134 °C
FEHE *UA*	6800 kcal/h · °C
Separator:	
Cooler duty	2.7×10^6 kcal/h
Volume	15 m^3
Working level volume	8 m^3
Gas loop volume	170 m^3
Approximate compressor size	350 kW
Absorber:	
Base volume	8 m^3
Bottom section	2 theoretical stages
Top section	6 theoretical stages
Stage efficiency	50 %
Tray holdup	14 kmoles
Liquid recirculation	15 kmol/min
Cooler duty	6.5×10^5 kcal/h
Wash acid feed	756 mol/min
Wash acid cooler duty	1.3×10^5 kcal/h

catalyst does deactivate over the course of operation. This deactivation via sintering is a nonlinear function of operating time (t_{yr}) and temperature, since higher temperatures within the tubes (t_{tube}) promote deactivation. The activity a decays exponentially with time from 1.0 to 0.8 after 1 year according to

$$a = f(t_{tube}) \exp(-t_{yr}/0.621) \tag{11.8}$$

If the tube temperature has not exceeded 180°C, then $f(t_{tube}) = 1$. Above this temperature, then $f(t_{tube}) = \exp[-(t_{tube} - 180)/50]$, where t_{tube} is in °C.

Catalyst selectivity (SEL) determines the fraction of the ethylene consumed that makes the desired vinyl acetate product.

$$\text{SEL} = 100 \frac{\text{mol/min VAc}}{\text{mol/min VAc} + 0.5 \text{ mol/min CO}_2} \tag{11.9}$$

For our new catalyst conditions, the selectivity is 94.84 percent. At a

TABLE 11.10 Column and Decanter Equipment Data

Theoretical stages	20
Feed stage	15 from bottom
Stage efficiency	50 %
Tray holdup	2.3 kmol
Reboiler duty	4.0×10^6 kcal/h
Condenser duty	3.9×10^6 kcal/h
Base working level volume	6 m^3
Decanter working level volume	5 m^3

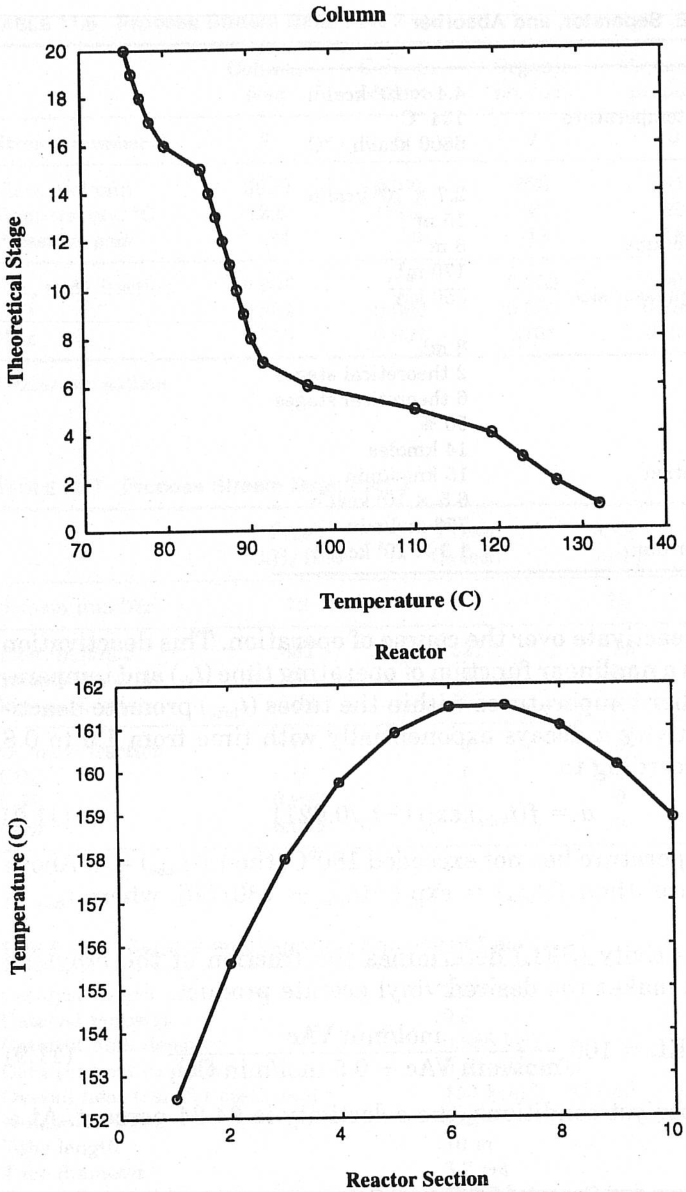

Figure 11.2 Temperature profiles. (*a*) Azeotropic distillation column; (*b*) reactor.

catalyst activity of 0.8, higher reactor temperatures are required to achieve about the same VAc production rate, increasing the production rate of CO_2 to 126 mol/min and reducing the selectivity to 92.4 percent.

The CO_2 removal system is assumed to be a component separator that removes just carbon dioxide at a certain efficiency, which is the fraction in the feed leaving in the CO_2 purge. This efficiency (Eff) is a function of the feed rate (F_{CO_2} in mol/min) and composition (x_{CO_2} in mole fraction). At the design conditions, the efficiency is 0.995 for a feed rate of 6410 mol/min at 0.014 mole fraction CO_2. The maximum allowable feed rate to the CO_2 removal system is 8000 mol/min set by its capacity. The following correlation determines the system efficiency:

$$\text{Eff} = 0.995 - 3.14 \times 10^{-6}(F_{CO_2} - 6410) - 32.5(x_{CO_2} - 0.014) \qquad (11.10)$$

where the efficiency must lie between 0 and 1.

11.3 Plantwide Control Strategy

Step 1. For this process we must be able to set the production rate of vinyl acetate while minimizing yield losses to carbon dioxide. During the lifetime of the catalyst charge, catalyst activity decreases and the control system must operate under these different conditions. To maintain safe operating conditions, the oxygen concentration in the gas loop must remain outside the explosivity region for ethylene. The azeotropic distillation column must produce an overhead product with essentially no acetic acid and a bottoms product with no vinyl acetate. The absorber must recover essentially all of the vinyl acetate, water, and acetic acid from the gas recycle loop to prevent yield losses in the CO_2 removal system and purge.

Step 2. There are 26 control degrees of freedom in this process. They include: three feed valves for oxygen, ethylene, and acetic acid; vaporizer and heater steam valves; reactor steam drum liquid makeup and exit vapor valves; vaporizer overhead valve; two coolers and absorber cooling water valves; separator base and overhead valves; absorber overhead, base, wash acid, and liquid recirculation valves; gas valve to CO_2 removal system; gas purge valve; distillation column steam and cooling water valves; column base, reflux, and vent valves; and decanter organic and aqueous product valves.

Step 3. Energy management is critically important because of the highly exothermic reactions and potential for runaway or catalyst damage at high temperatures. By design, heat is removed from the reactor via transfer from the tubes to the shell, generating steam. Hence reactor temperature is controlled by steam temperature, which is set by controlling the pressure in the steam drum via the steam exit valve. This is a good example of how a degree of freedom needs to be used based upon the process design. If temperature measurements are available along the length of the tubes, then a reactor peak temperature or a profile can be controlled. Otherwise, the controlled variable is reactor exit temperature.

The reactor effluent stream is cooled in a process-to-process heat exchanger with the gas recycle stream. A bypass line and control valve are necessary here only if we want to control one of the exchanger exit temperatures. If this exchanger is designed for only vapor flow, then the hot-side exit temperature must be controlled to a value above the dewpoint temperature by manipulating the bypass valve around the exchanger on the cold side (to avoid a control valve on hot stream side). The bypass line would have to be added if it were not included in the original design or the heat exchanger must be redesigned to handle two-phase flow.

Step 4. Ethylene and oxygen makeup feeds come from headers and the acetic acid feed is drawn from a supply tank. The vinyl acetate and water products go to downstream units. As a result, there are no design constraints that require production rate to be set either on supply or demand. Therefore, we look at reactor conditions to determine how to change production rate. Because the reactor feed contains both excess ethylene and acetic acid, manipulating the partial pressure of either component would not be effective. The partial pressure of oxygen is constrained by the safety limit, and once this is reached no further adjustments could be made. Pressure is limited by the process equipment design maximum. Hence the most direct handle for setting production rate is by changing the reactor exit or peak temperature.

Alternatively we could use the fresh oxygen feed flow to set production rate since it is the limiting component. However, there are two issues with this choice. Since oxygen is not completely consumed, we must worry about its accumulation in the system (component balance), which is constrained here by the safety limit. If oxygen were completely consumed, we must still worry about the reactor inlet oxygen composition because of the safety constraint. In either case, with oxygen feed rate we would have to control oxygen composition with some other variable to change production rate safely.

Step 5. The azeotropic distillation column does not produce the final salable vinyl acetate product. Its primary role is to recover and recycle unreacted acetic acid and to remove from the process all of the vinyl acetate and water produced. So we want little acetic acid in the overhead because this represents a yield loss. Also, the bottoms stream should contain no vinyl acetate since it polymerizes and fouls the heat-exchange equipment at the elevated temperatures of the column base and the vaporizer. Hence we have two control objectives: base vinyl acetate and top acetic acid compositions. And we have two manipulators, steam and organic reflux flows. The temperature profile (Fig. 11.2*a*) has a sharp break representing the change in vinyl acetate composition near the bottom of the column. Column steam (boilup) is the appropriate choice for temperature control because of its fast response compared with reflux. Then the overhead acetic acid composition must be controlled with reflux.

The overriding safety constraint in this process involves oxygen concentration in the gas loop, which must remain below 8 mole % to remain outside the explosivity envelope for ethylene mixtures at process conditions. The most direct manipulated variable to control oxygen composition at the reactor feed is the fresh oxygen feed flow.

If in Step 4 we had chosen to set production rate by flow-controlling the fresh oxygen feed, then we would need an alternative manipulator to control oxygen composition. The only choice would be to use reactor temperature. We now can consider which choice, safety or production rate, is better. Temperature is *not* the most direct handle to control oxygen composition since its effectiveness hinges on incomplete oxygen conversion in the reactor and oxygen recycle. Because of the safety implications, we would choose to use fresh oxygen flow to control reactor inlet oxygen composition, which means production rate is set via reactor temperature.

Step 6. Two pressures must be controlled: in the column and in the gas loop. The most direct handle to control column pressure is by manipulating the vent stream from the decanter. We have three choices to control gas loop pressure: purge flow, flow to the CO_2 removal system, and the fresh ethylene feed flow since fresh oxygen flow has been previously selected. Both the purge flow and the flow to the CO_2 removal system are small relative to the gas recycle flowrate. Any changes in either one would not have a large effect on gas loop pressure. Since ethylene composes a substantial part of the gas recycle stream, pressure is a good indication of the ethylene inventory. So we choose the fresh ethylene feed flow to control gas recycle loop pressure.

Note that there are three vessels (vaporizer, separator, absorber) within the gas loop where apparently pressure can also be controlled. However, these pressures actually cannot be selected arbitrarily once the compressor capacity and gas loop pressure drop are established. In fact, to minimize pressure drop in the gas loop we would open completely or remove the overhead vapor control valves on these units, saving both compressor and valve costs.

Seven liquid levels are in the process: vaporizer, reactor steam drum, separator, absorber, column base, and two decanter layers. Control of the decanter levels is straightforward. The organic product flow controls the organic phase inventory; the aqueous product flow controls the aqueous phase inventory. Reactor steam drum level is maintained with boiler feed water makeup flow.

The most direct way to control the remaining levels would be with the exit valves from the vessels. However, if we do this we see that all of the flows around the liquid recycle loop would be set on the basis of levels, which would lead to undesirable propagation of disturbances. Instead we should control a flow somewhere in this loop. Acetic acid is the main component in the liquid recycle loop. Recycle and fresh acetic acid feed determine the component's composition in the reactor feed. A reasonable choice at this point is to control the total acetic acid feed stream flow into the vaporizer. This means that we can use the fresh acetic acid feed stream to control column base level, since this is an indication of the acetic acid inventory in the process. Vaporizer level is then controlled with the vaporizer steam flow and separator and absorber levels can be controlled with the liquid exit valves from the units.

Step 7. Ethane is an inert component that enters with the ethylene feed. It can be removed from the process only via the gas purge stream, so purge flow is used to control ethane composition. Carbon dioxide is an unwanted by-product that leaves in the CO_2 removal system. As long as the amount of carbon dioxide removed is proportional in some way to the CO_2 removal system feed, we can use this valve to control carbon dioxide composition. Oxygen inventory is accounted for via composition control with fresh oxygen feed. Inventory of ethylene can be controlled to maintain gas loop pressure, since ethylene composes the bulk of the gas recycle.

Acetic acid inventory is regulated by using the fresh acetic acid feed to control base level in the distillation column. The temperature control loop in the distillation column achieves vinyl acetate composition control. Water, however, is an intermediate component with a boiling point between vinyl acetate and acetic acid. The inventory of water in the process will not be automatically accounted for by controlling those other two components. Instead we must use reflux flow to control the water composition in the bottoms stream. Otherwise, there is no regulation of water to ensure it is removed from the process. By using column reflux to control base water, we are forced to give up on using reflux to control acetic acid recovery (Step 5). To ensure that the acetic acid composition in the decanter is acceptable, the column must have a sufficient number of stages. This means we may have to revisit its design.

Table 11.11 summarizes the component balance control strategy.

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TABLE 11.11 Component Material Balance

Component	Input	+Generation	−Output	−Consumption	=Accumulation Inventory controlled by
O_2	Fresh feed	0	0	$V_R(0.5r_1 + 3r_2)$	Composition control of reactor feed
CO_2	0	$2V_Rr_2$	CO_2 removal	0	Composition control of recycle gas loop
C_2H_4	Fresh feed	0	0	$V_R(r_1 + r_2)$	Pressure control of recycle gas loop
C_2H_6	Fresh feed	0	Purge stream	0	Composition control of recycle gas loop
VAc	0	V_Rr_1	Product stream	0	Temperature control in distillation column
H_2O	0	$V_R(r_1 + 2r_2)$	Product stream	0	Column base composition control with reflux
HAc	Fresh feed	0	0	V_Rr_1	Level control in column base

Step 8. Several control valves now remain unassigned. Steam flow to the trim heater controls reactor inlet temperature. Cooling water flow to the trim cooler is used to control the exit process temperature and provide the required condensation in the reactor effluent stream. Liquid recirculation in the absorber is flow-controlled to achieve product recovery, while the cooling water flow to the absorber cooler controls the recirculating liquid temperature. Acetic acid flow to the top of the absorber is flow-controlled to meet recovery specifications on the overhead gas stream. Cooling water flow to the cooler on this acetic acid feed to the absorber is regulated to control the stream temperature. Cooling water flow in the column condenser controls decanter temperature.

Step 9. We have now established the basic regulatory plantwide control strategy (Fig. 11.3). Based upon the heuristic established by Fisher et al. (1988) that recycle gas flows should be maximized to improve reactor yield, we open or remove the separator, vaporizer, and absorber overhead valves and run the compressor full out. To minimize the decanter temperature for improved organic recovery, the column condenser cooling water is set at maximum flow. Optimization of several controller

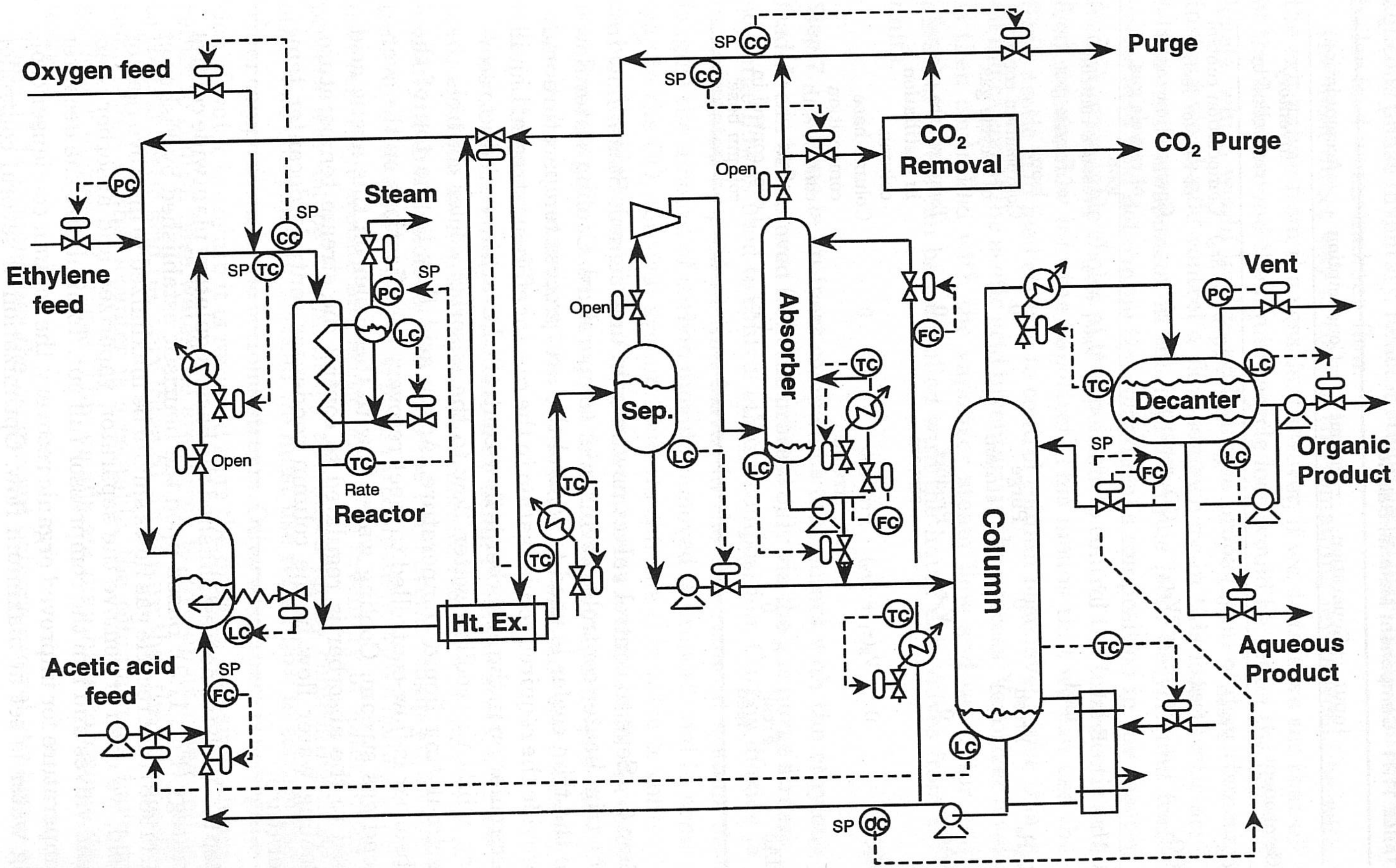

Figure 11.3 Vinyl acetate process control strategy.

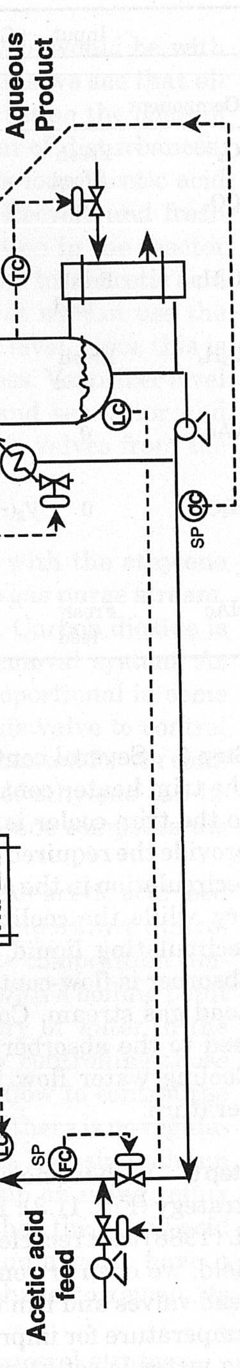

Figure 11.3 Vinyl acetate process control strategy.

setpoints can be based upon economics. We must balance the trade-offs in maximizing vinyl acetate production and recovery with minimizing carbon dioxide production and energy consumption. This involves considering the reactor temperature setpoint, reactor feed temperature setpoint, composition of carbon dioxide and ethane in the gas recycle loop, oxygen composition setpoint (up to the maximum constraint), total flowrate of acetic acid to the vaporizer, and water composition in the recycle acetic acid. Additionally, economic evaluations must account for the effects of catalyst deactivation with time over the duration of the charge. To achieve the same vinyl acetate production rate, we must increase reactor temperature. However, this produces more carbon dioxide representing yield loss. Raw material costs, energy costs, and product price will all affect plant operation.

11.4 Dynamic Simulations

We have constructed a rigorous nonlinear first-principles dynamic model of this process with TMODS. We have used the model to test the control strategy and show that it does provides effective control of the vinyl acetate monomer process.

Figures 11.4 to 11.9 present some results of the rigorous dynamic simulation to various disturbances. Because of the model size, many different variables could be plotted, but we have tried to include the key ones. Some of the dynamic behavior turns out to be not intuitively obvious. But the most important comment to make at the start is these results demonstrate that the control scheme developed with our design procedure works! We have generated a simple, easily understood regulatory control strategy for this complex chemical process that holds the system at the desired operating conditions.

The critical product-quality and safety-constraint loops were tuned by using a relay-feedback test to determine ultimate gains and periods. The Tyreus-Luyben PI controller tuning constants were then implemented. Table 11.12 summarizes transmitter and valve spans and gives controller tuning constants for the important loops. Proportional control was used for all liquid levels and pressure loops.

11.4.1 Changes in reactor temperature

Figure 11.4 shows what happens when the production rate handle (reactor exit temperature) is changed. The starting conditions are the base-case design where reactor exit temperature is 159°C. The reactor temperature controller is tuned at this operating point. Step changes of 8°C at time 5 minutes and 120 minutes are made in the setpoint of the reactor temperature controller (Figure 11.4*a*). Decreasing the

TABLE 11.12 Controller Settings for Certain Loops

	Base case		High-temperature case	
Loop	K_c	τ_I, min	K_c	τ_I, min
$T_R - P_S^{set}$	10	5.5	0.6	11
$P_S - F_S$	20	1	20	1
$x_{B,W} - R$	0.2	60	0.2	60

P_S transmitter span: 40–60 psia
T_R transmitter span: 0–200°C
$x_{B,W}$ transmitter span: 0–10 wt %
R transmitter span: 0–7600 mol/min
T_R is reactor temperature, P_S is steam drum pressure, F_S is steam flowrate
$x_{B,W}$ is column base water composition, R is column reflux flow.

temperature reduces the rate of production of vinyl acetate but increases selectivity, i.e., the fraction of ethylene consumed producing vinyl acetate. The fresh feeds of oxygen and ethylene decrease fairly quickly (30 minutes). The fresh feed of acetic acid changes much more slowly. The changes in the reactor and the gas recycle are fast because the process has a gas-phase reactor. The changes in the column and liquid recycle are much slower because of the large liquid residence times. Note that the reactor production of VAc shown in Fig. 11.4*b* is the instantaneous reaction rate in the reactor, not the flowrate of organic product leaving the decanter. The flowrate of this stream changes quite slowly due to the large holdup in the decanter. Oxygen composition remains within about 0.1 mol % of setpoint. The step increase in reactor temperature is slightly more oscillatory than the decrease, but overall the performance is quite satisfactory for a change of this size.

Figure 11.5 gives results for a step increase in the reactor temperature controller setpoint from 159 to 165°C. It is clear that the loop becomes more oscillatory at the higher temperature. The loop becomes unstable if the setpoint is raised above 170°C. The reason for this change in the closed-loop damping coefficient is the change in reactor dynamics. This reactor is highly nonlinear, so we would not expect a linear controller to be effective over a wide range of operating conditions. If the reactor temperature controller is retuned at a higher 180°C operating point, we find (as shown in Table 11.12) that the controller gain is much smaller (0.6 versus 10 at the lower temperature). This is due to the change in the difference between the reactor exit temperature and the coolant temperature as temperature increases. Section 4.5.3 discusses this change in the reactor process gain with temperature. The higher temperature operating point also requires that the controller reset time be about twice that of the lower temperature operating point (larger ultimate period, slower closed-loop response).

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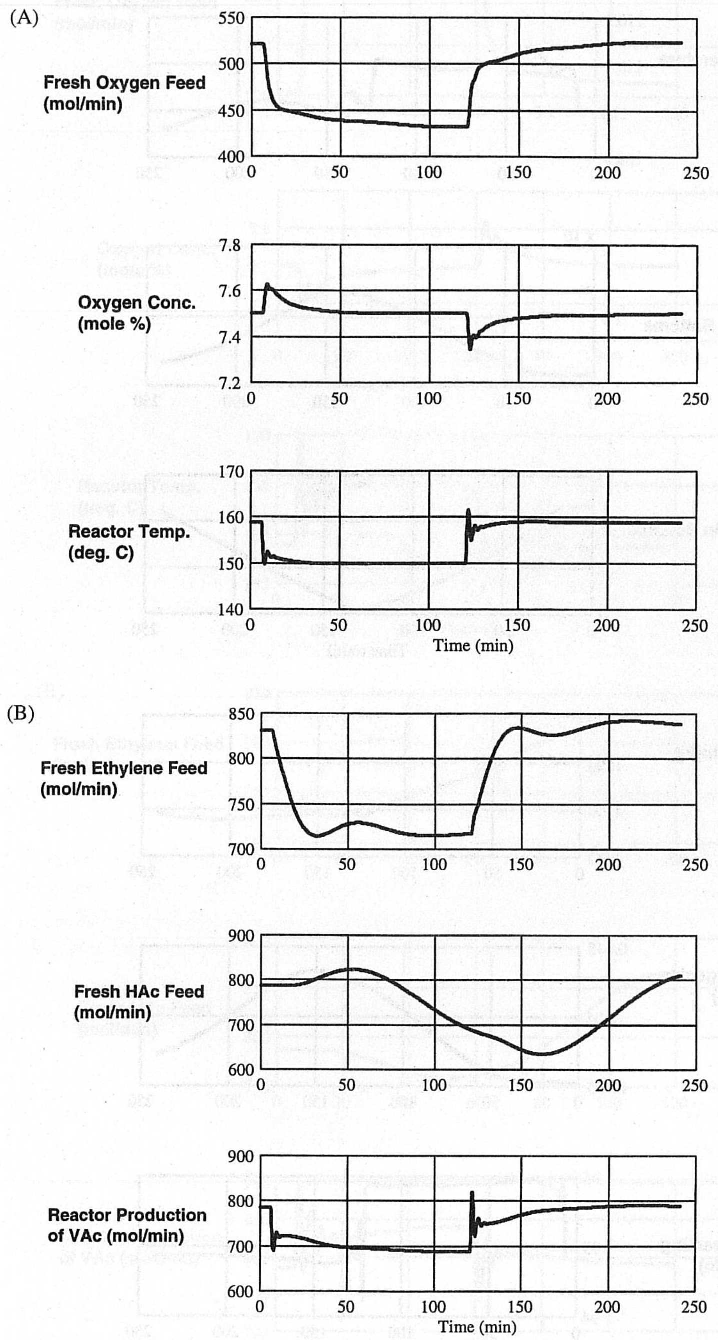


Figure 11.4 Dynamic response of base case to 8°C decrease in reactor temperature.

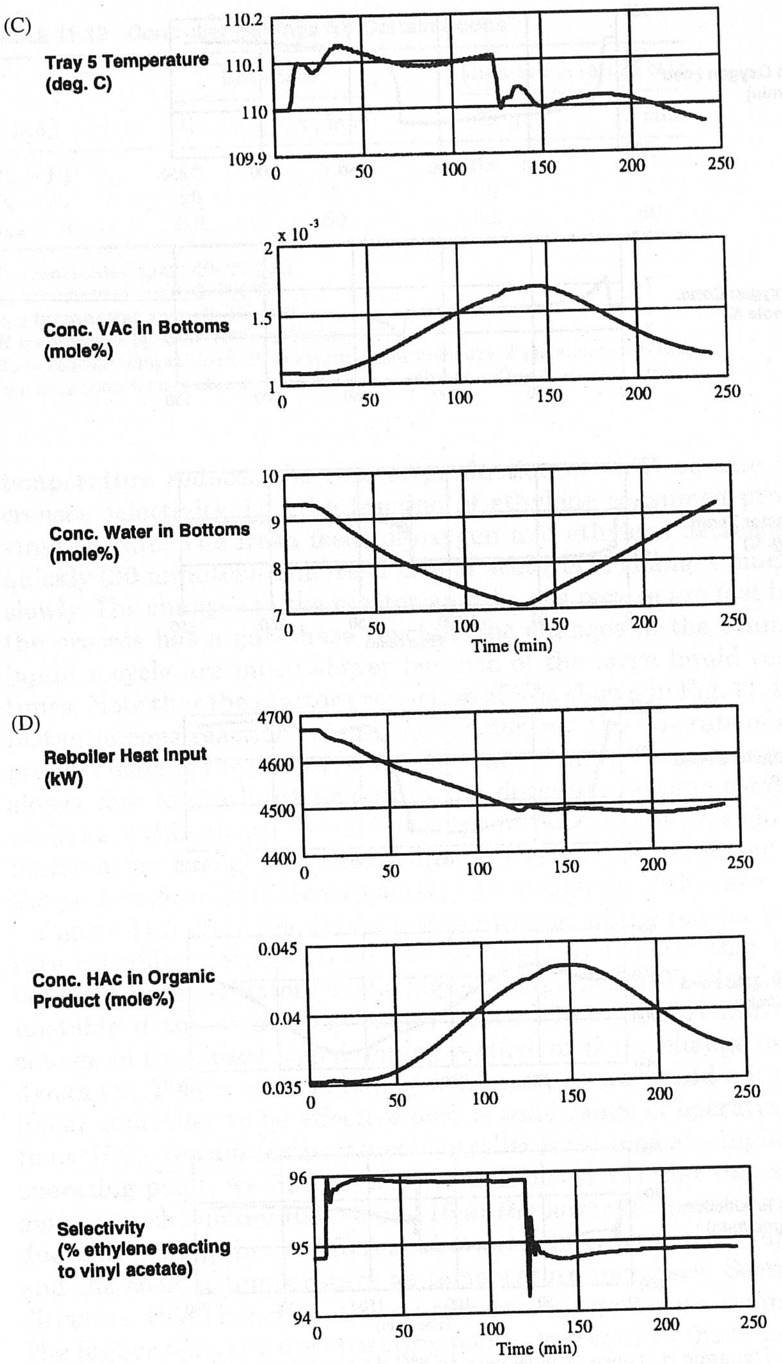
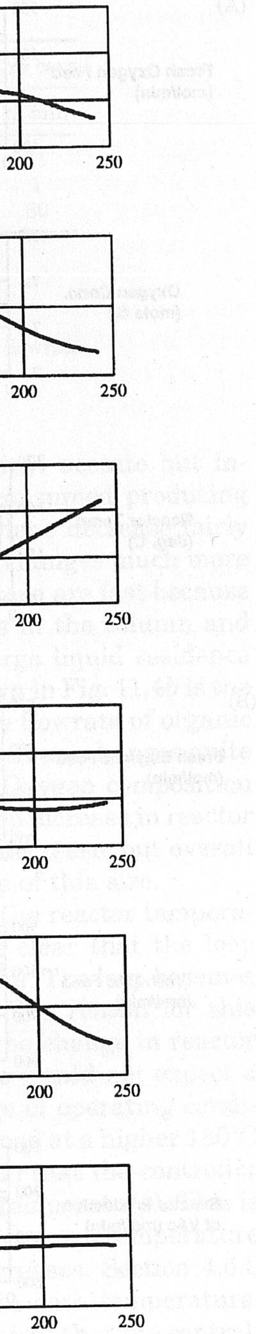


Figure 11.4 *(Continued)*



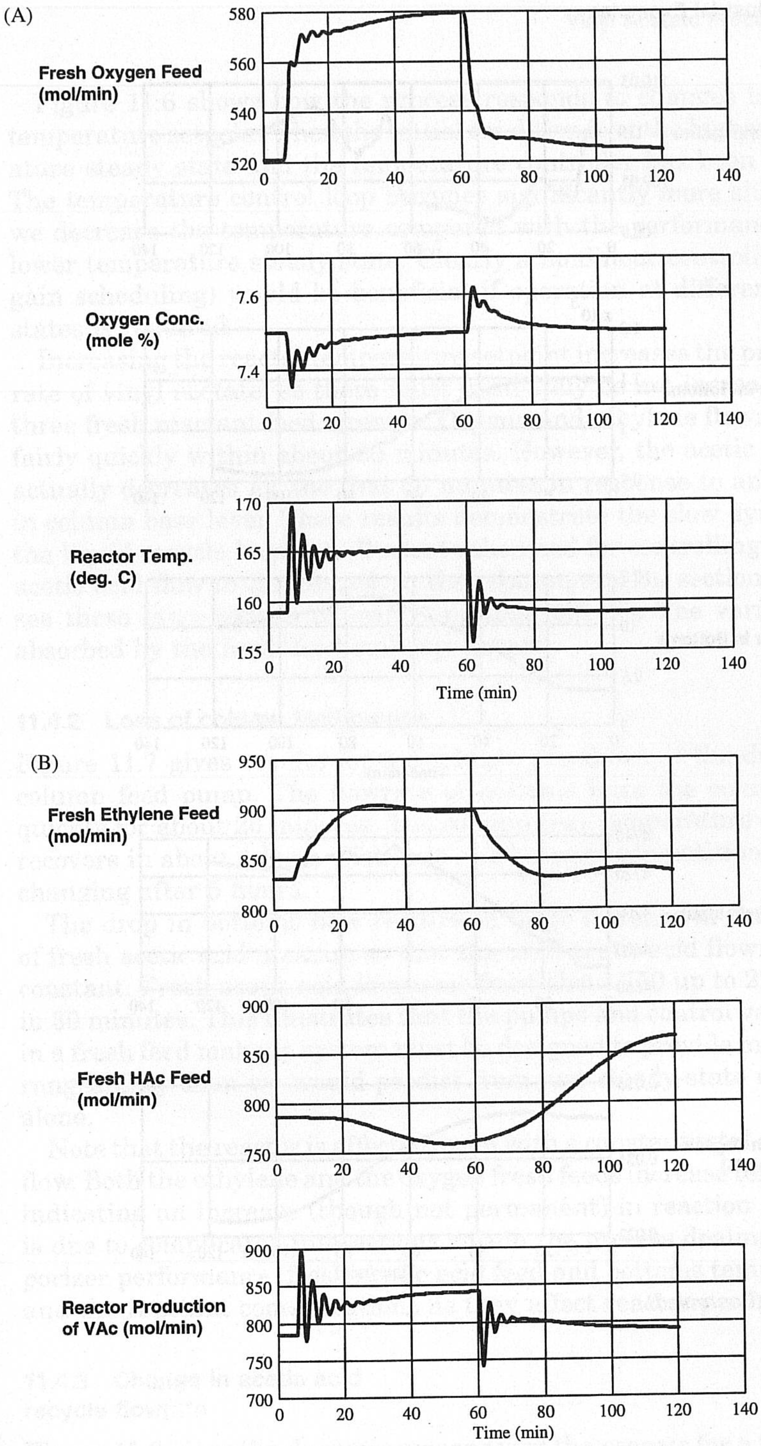


Figure 11.5 Dynamic response of base case to 6°C increase in reactor temperature.

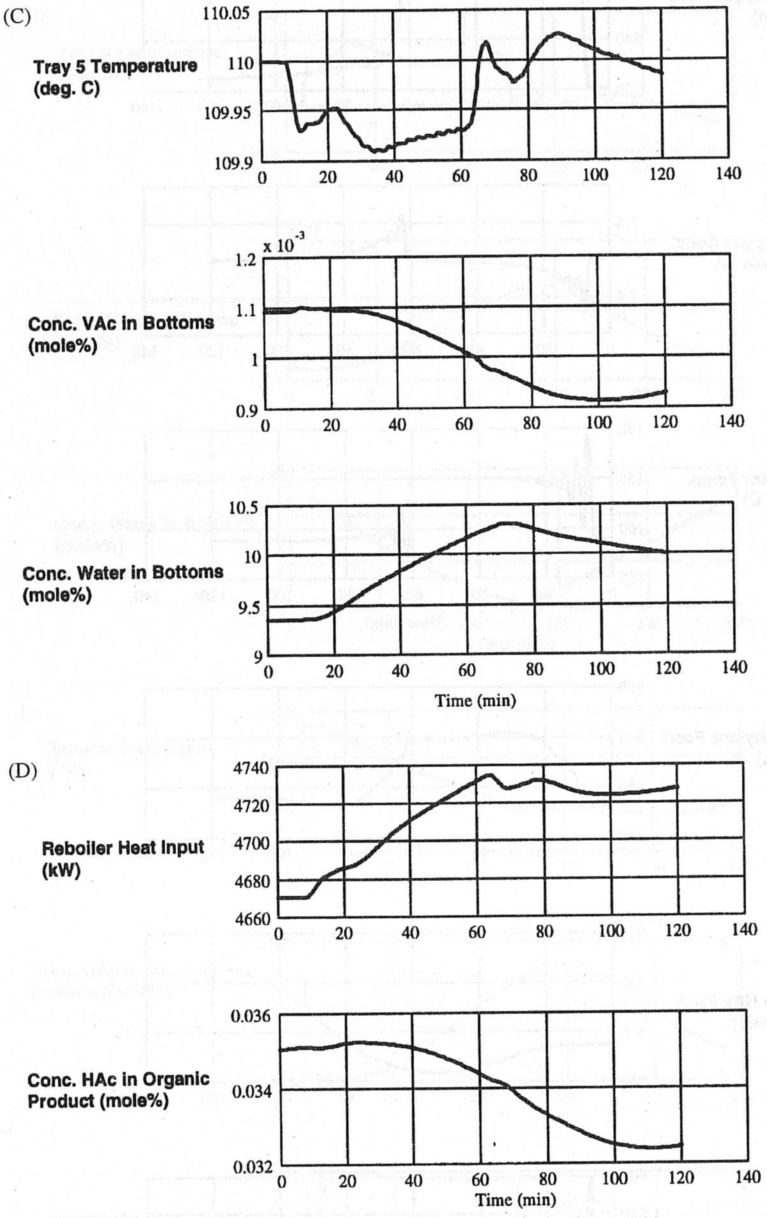


Figure 11.5 *(Continued)*

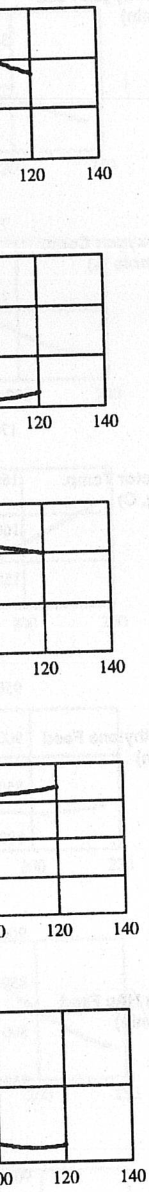


Figure 11.6 shows how the process responds to changes in reactor temperature setpoint when the initial condition is at the higher temperature steady state and the temperature controller has been retuned. The temperature control loop becomes significantly more sluggish as we decrease the temperature compared with the performance at the lower temperature steady state. Clearly a nonlinear controller (using gain scheduling) would be beneficial if operation at different steady states is required.

Increasing the reactor temperature setpoint increases the production rate of vinyl acetate, so there must ultimately be net increases in all three fresh reactant feed streams. Oxygen and ethylene flows respond fairly quickly within about 20 minutes. However, the acetic acid feed actually decreases for the first 60 minutes in response to an increase in column base level. These results demonstrate the slow dynamics of the liquid recycle loop and illustrate the need for controlling the total acetic acid flow to the reactor so that the separation section does not see these large swings in load ("snowball effect"). The variability is absorbed by the fresh feed makeup stream.

11.4.2 Loss of column feed pumps

Figure 11.7 gives results for a 5-minute shutdown of the distillation column feed pump. The flowrate of bottoms from the column drops quickly for about 20 minutes. The column tray temperature controller recovers in about 1 hour. Distillate and bottoms compositions are still changing after 5 hours.

The drop in bottoms flow requires a large increase in the flowrate of fresh acetic acid makeup so that the total acetic acid flowrate stays constant. Fresh acetic acid increases from about 750 up to 2200 mol/h in 30 minutes. This illustrates that the pumps and control valves used in a fresh feed makeup system must be designed to provide much wider rangeability than we would predict from just steady-state conditions alone.

Note that the reactor is affected, even with a constant total acetic acid flow. Both the ethylene and the oxygen fresh feeds increase temporarily, indicating an increase (though not permanent) in reaction rate. This is due to complicated interactions within the process dealing with vaporizer performance, fresh acetic acid feed and bottoms temperatures, and the reactant concentrations as they affect reactor performance.

11.4.3 Change in acetic acid recycle flowrate

Figure 11.8 gives the dynamic responses of the process for a 20 percent increase in the flowrate of total acetic acid to the vaporizer. The flow is

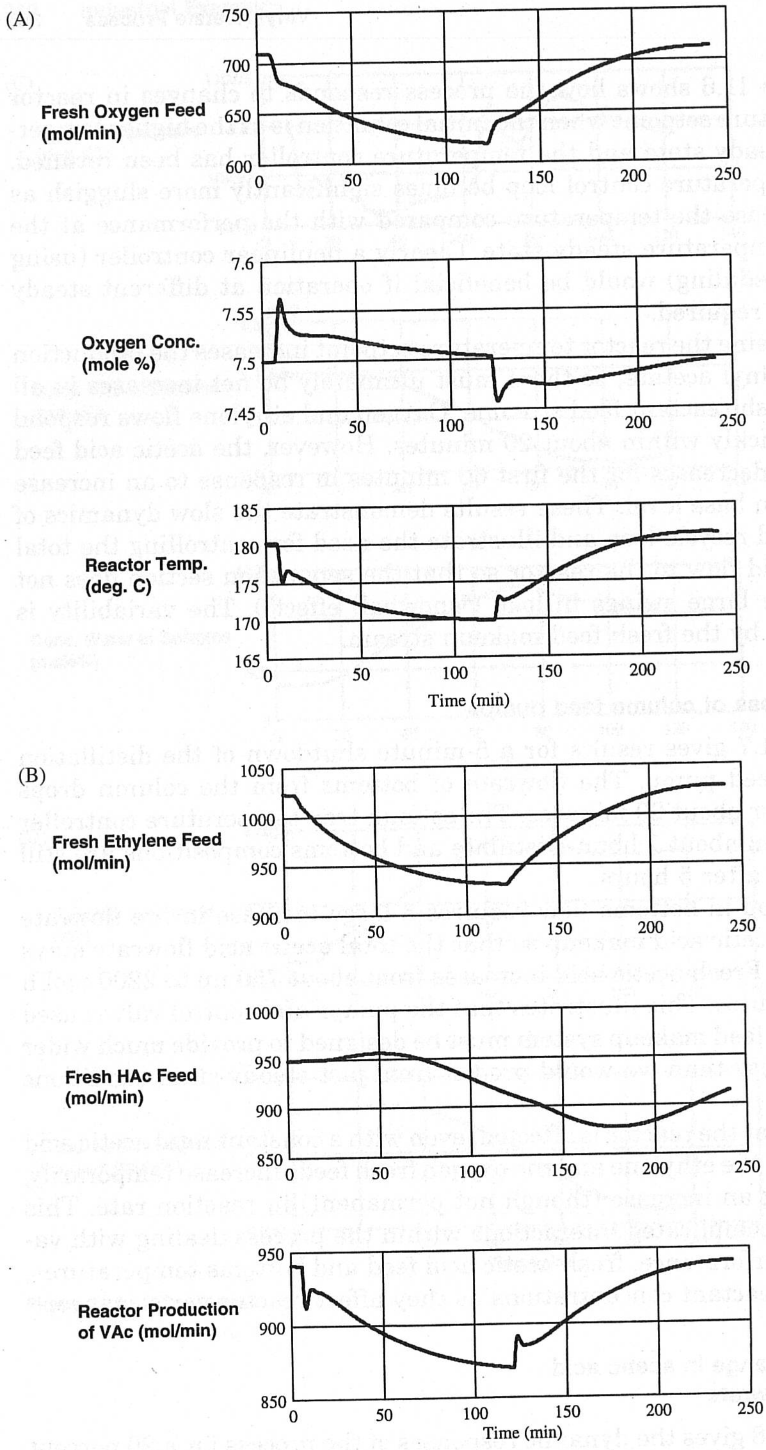
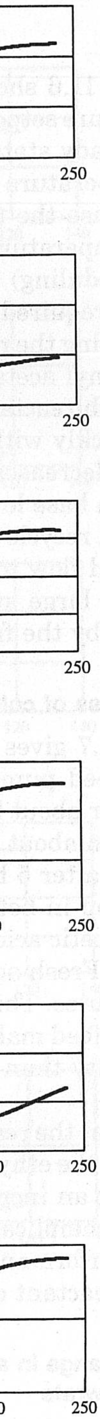


Figure 11.6 Dynamic response of high temperature case to 10°C decrease in reactor temperature.



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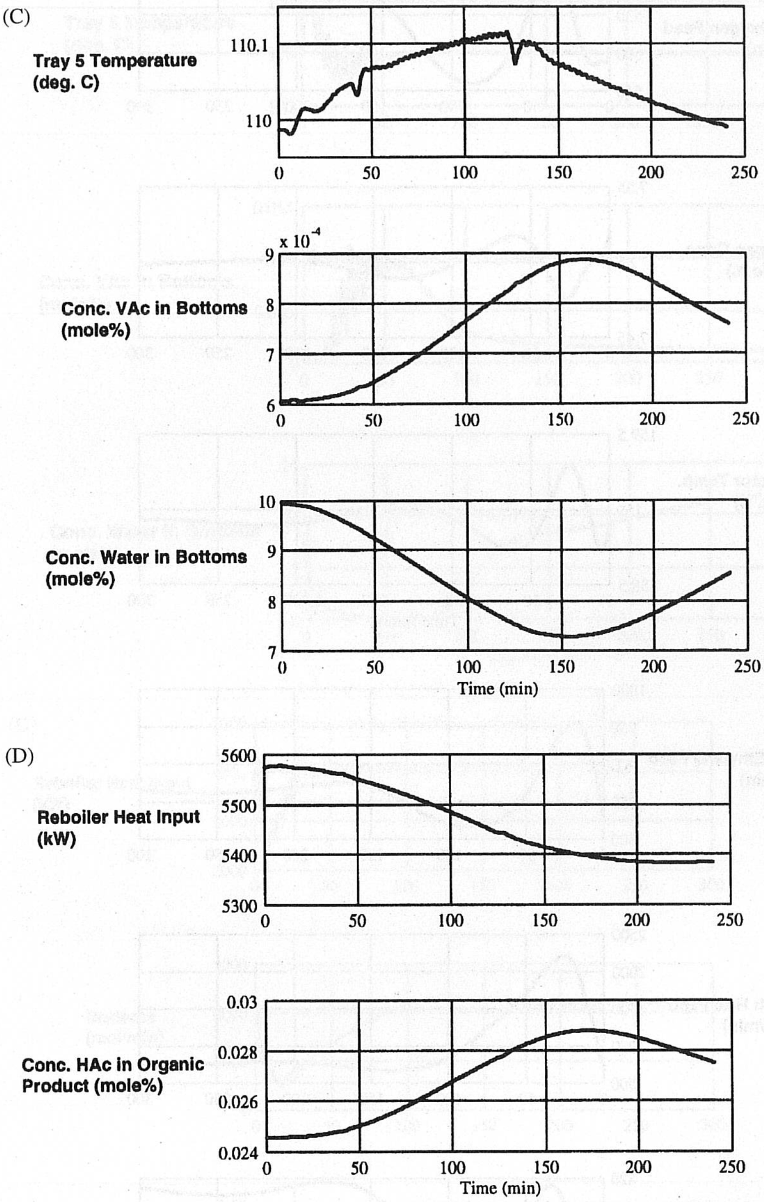


Figure 11.6 *(Continued)*

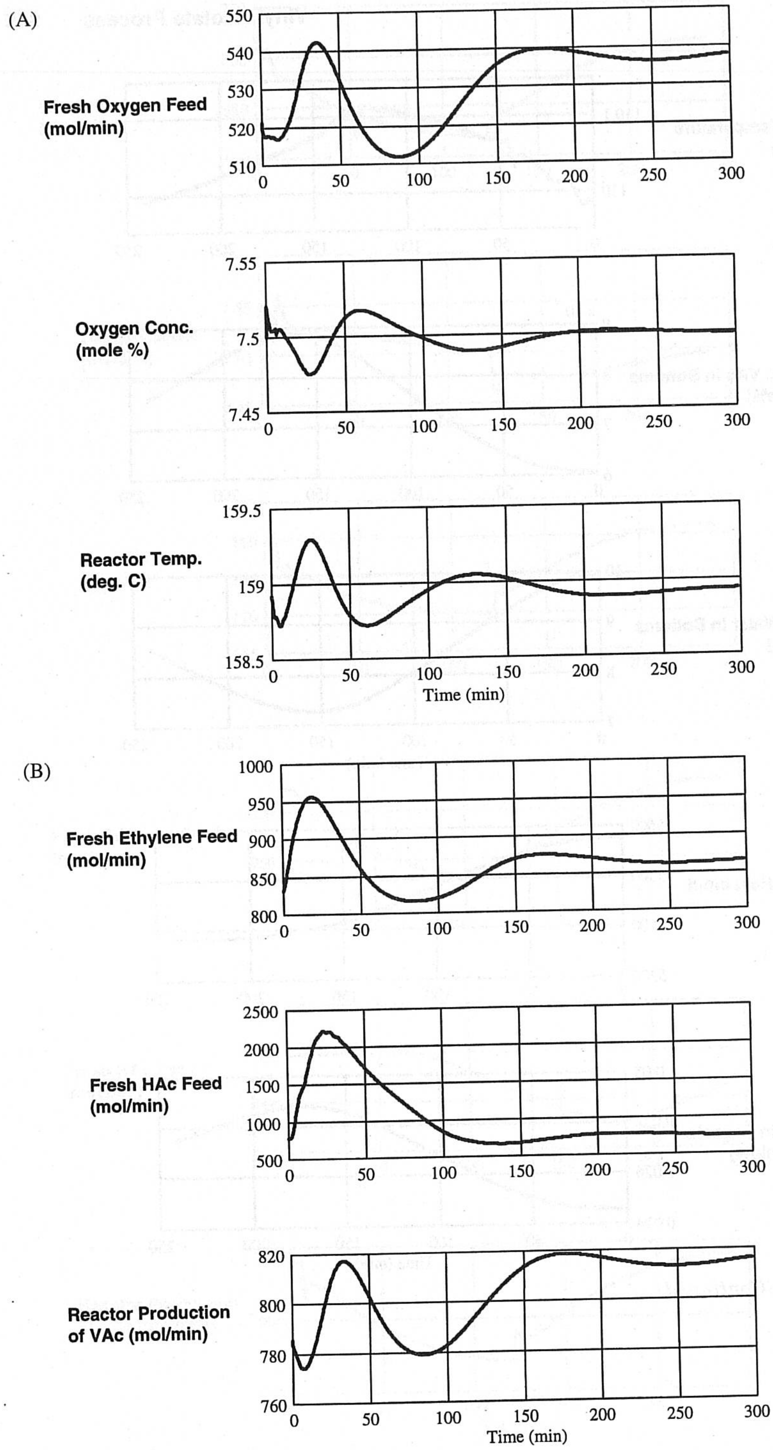
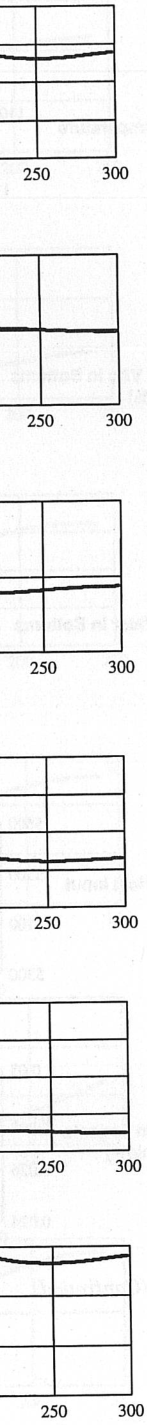


Figure 11.7 Dynamic response of base case to 5-minute shutoff of column feed.



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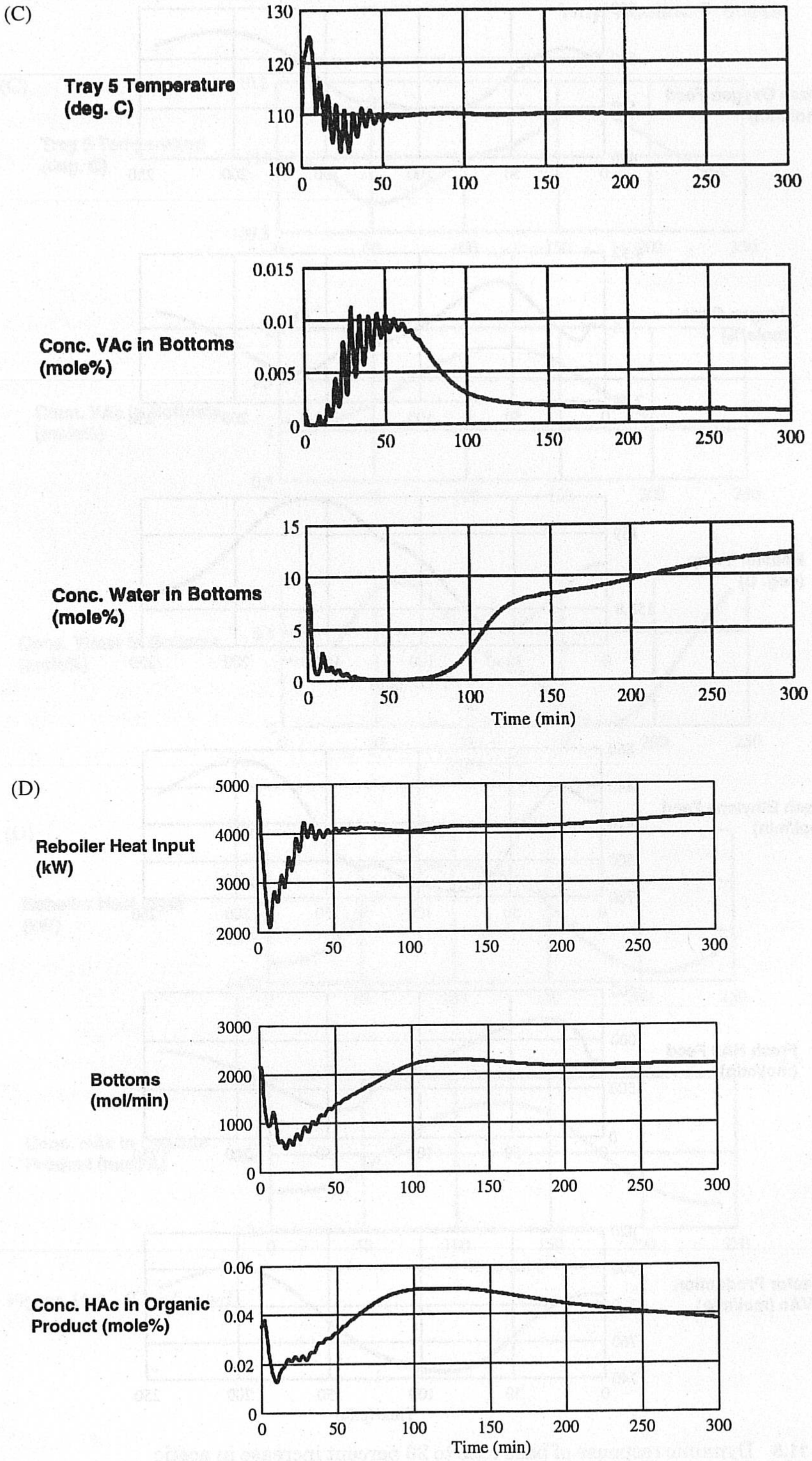

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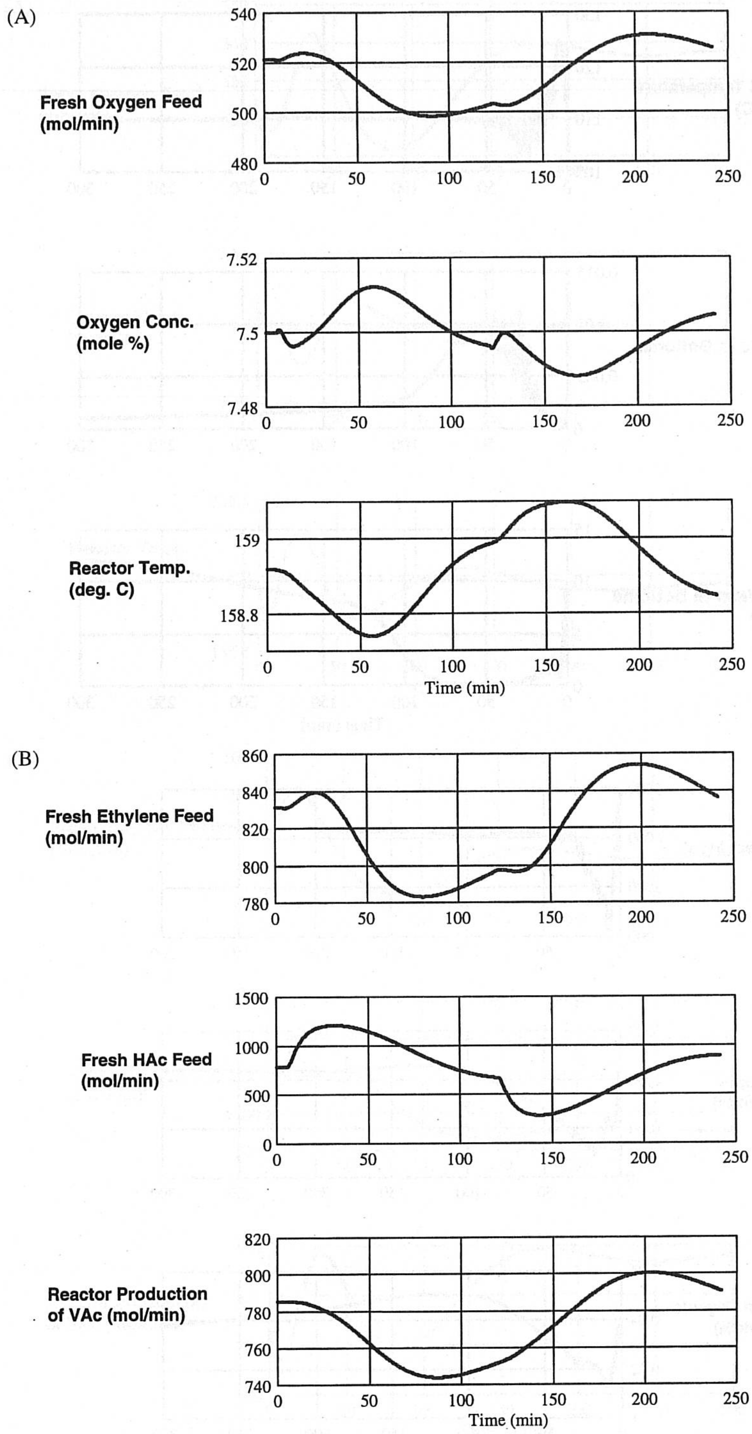
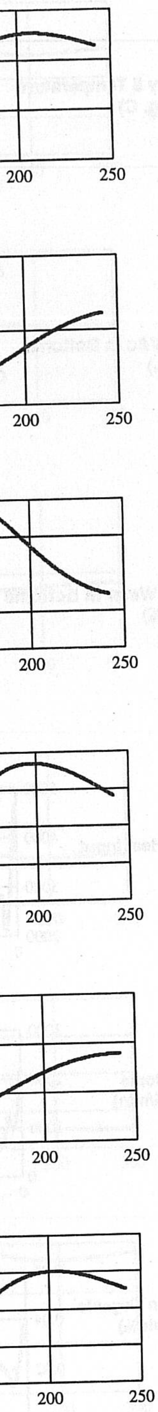


Figure 11.8 Dynamic response of base case to 20 percent increase in acetic acid recycle flow.



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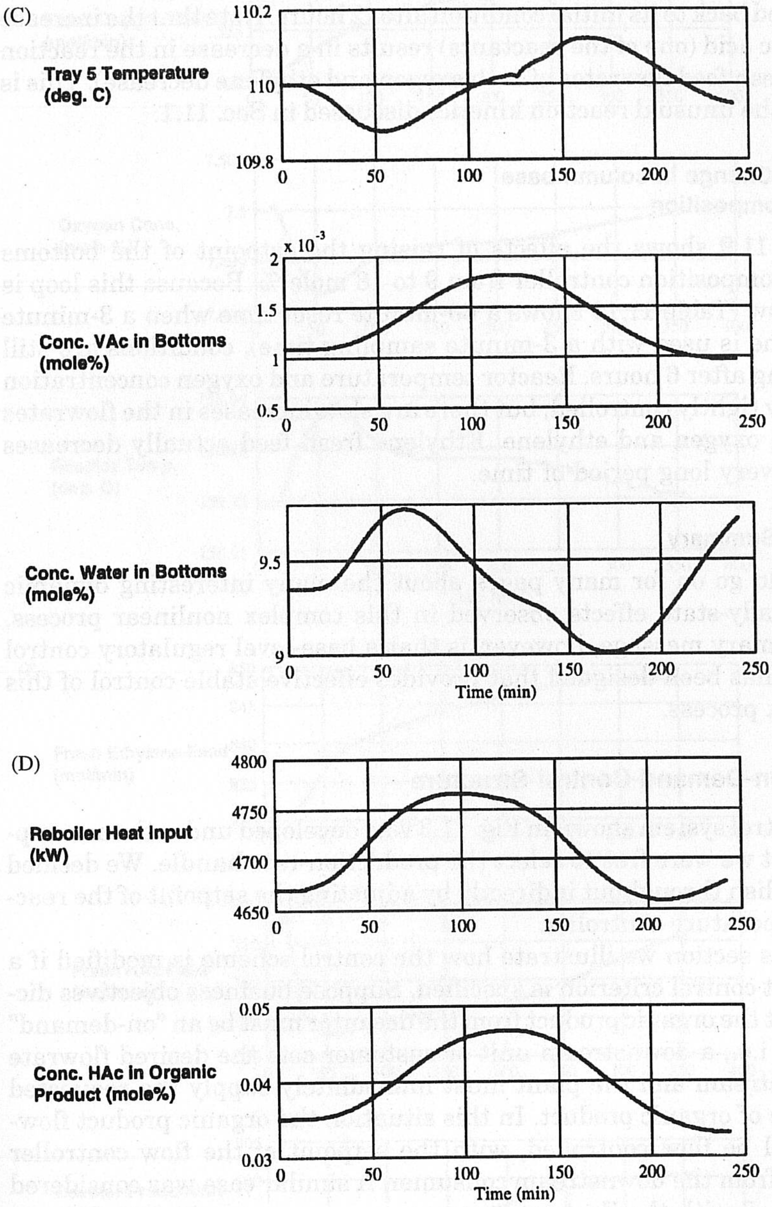

Figure 11.8 *(Continued)*

returned back to its initial condition after 2 hours. Note that the increase in acetic acid (one of the reactants) results in a decrease in the reaction rate (fresh feed flowrates of both oxygen and ethylene decrease). This is due to the unusual reaction kinetics discussed in Sec. 11.1.

11.4.4 Change in column base water composition

Figure 11.9 shows the effects of raising the setpoint of the bottoms water composition controller from 9 to 18 mole %. Because this loop is very slow (Table 11.12 shows a 60-minute reset time when a 3-minute deadtime is used with a 3-minute sampling time), conditions are still changing after 6 hours. Reactor temperature and oxygen concentration are very tightly controlled, but there are slow increases in the flowrates of fresh oxygen and ethylene. Ethylene fresh feed actually decreases for the very long period of time.

11.4.5 Summary

We could go on for many pages about the many interesting dynamic and steady-state effects observed in this complex nonlinear process. The primary message, however, is that a base-level regulatory control system has been designed that provides effective stable control of this complex process.

11.5 On-Demand Control Structure

The control system shown in Fig. 11.3 was developed under the assumption that we were free to select the production-rate handle. We decided to establish throughput indirectly by adjusting the setpoint of the reactor temperature controller.

In this section we illustrate how the control scheme is modified if a different control criterion is specified. Suppose business objectives dictate that the organic product from the decanter must be an "on-demand" stream, i.e., a downstream unit or customer sets the desired flowrate of this stream and the plant must immediately supply the requested flowrate of organic product. In this situation the organic product flowrate will be flow controlled, with the setpoint of the flow controller coming from the downstream consumer. A similar case was considered in Chap. 8 with the Eastman process.

Fig. 11.10 shows a modified control structure that incorporates this new on-demand criterion. It differs from the control scheme shown in Fig. 11.3 in only three loops:

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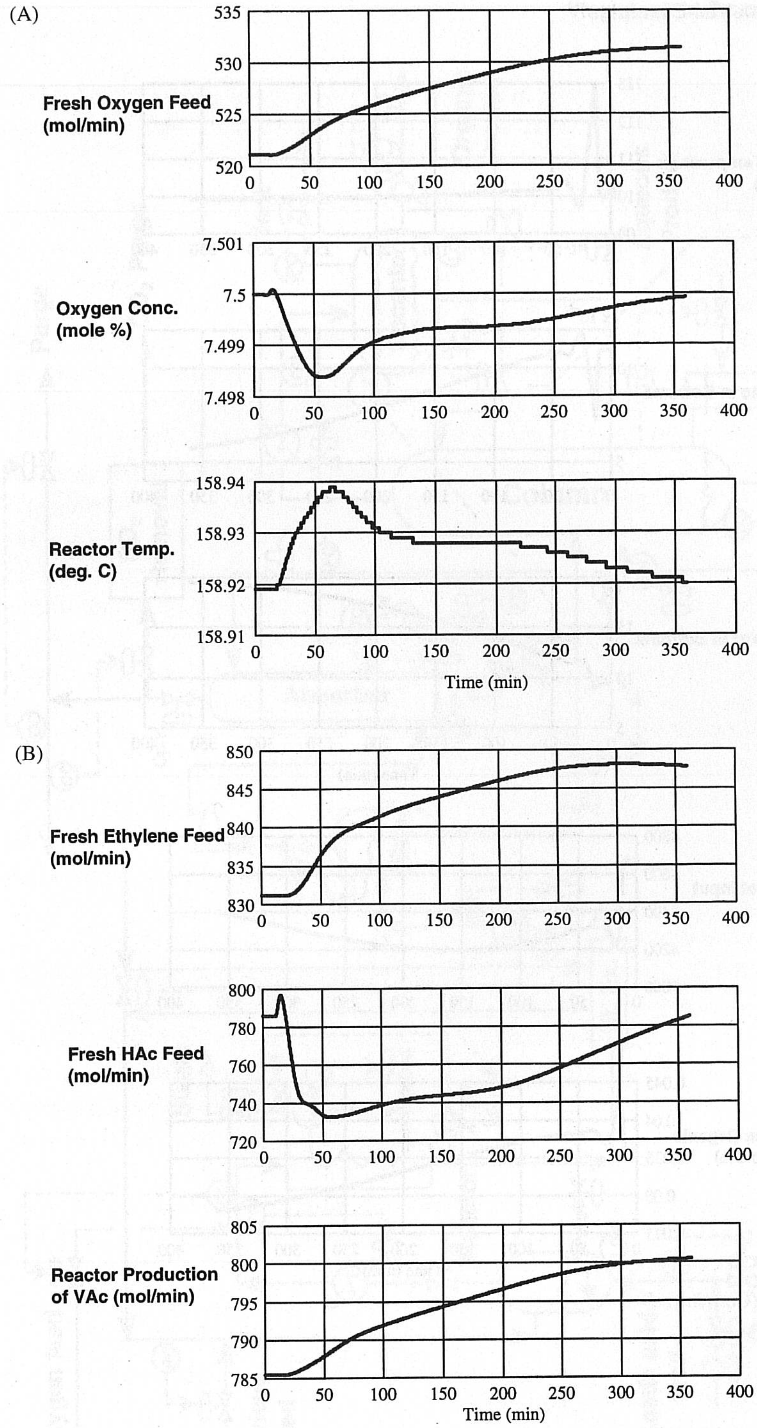


Figure 11.9 Dynamic response of base case to increase in column base water composition from 9 to 18 mol %.

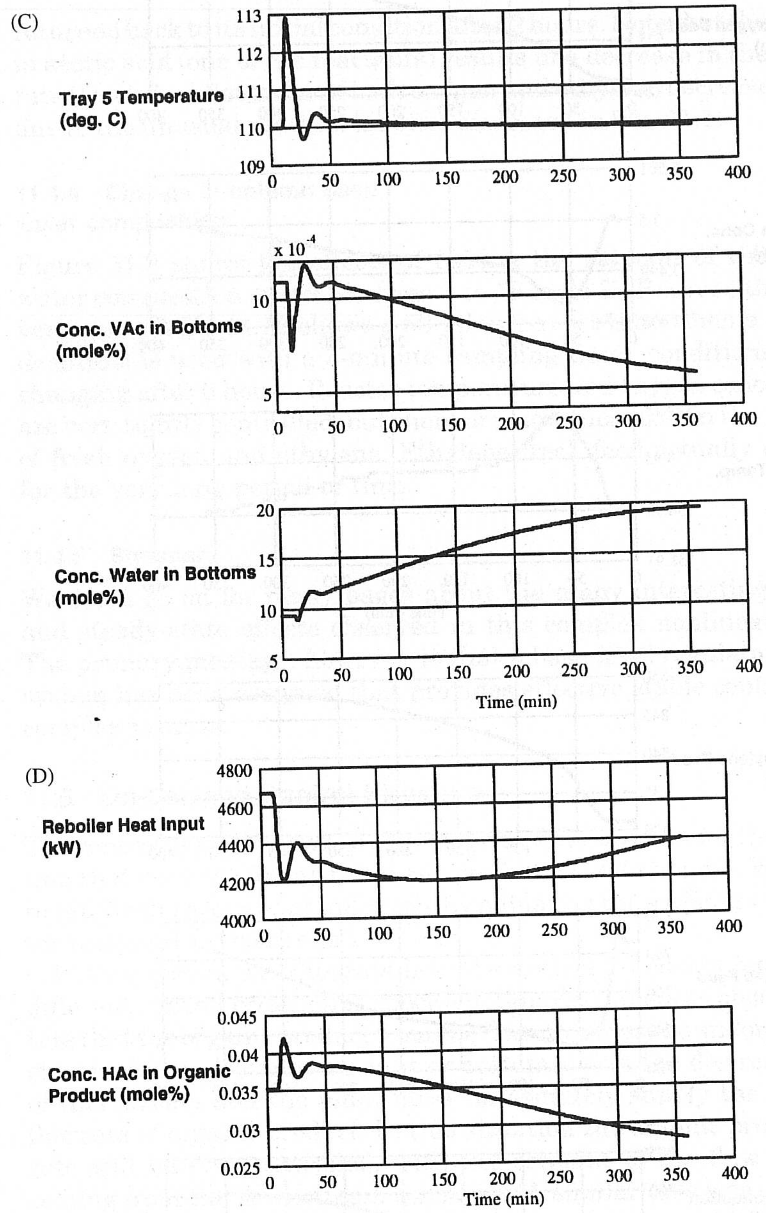
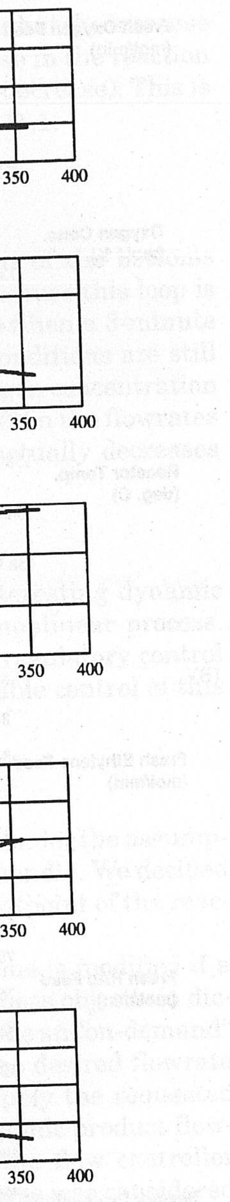


Figure 11.9 *(Continued)*



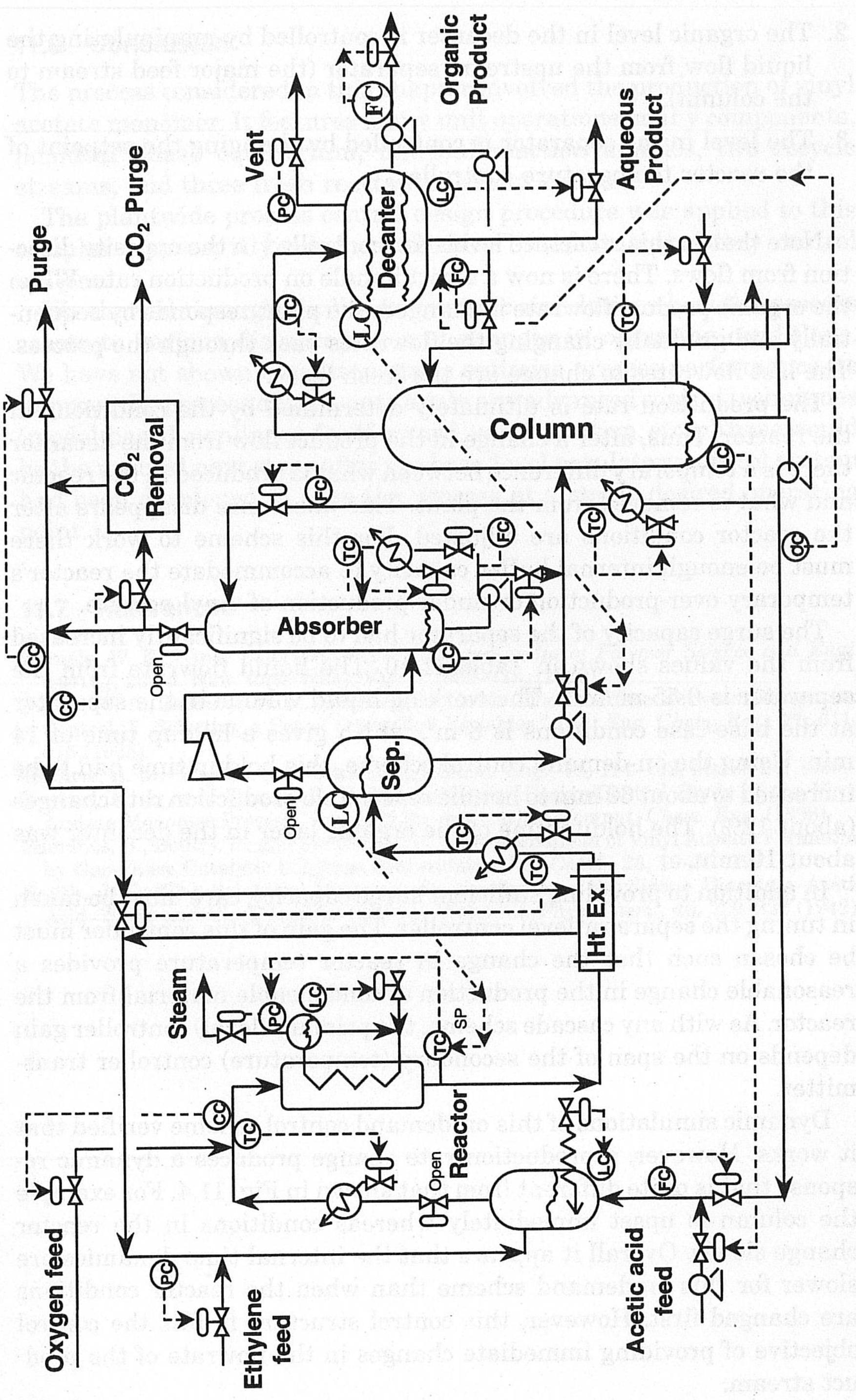


Figure 11.10 Vinyl acetate process control structure for "on-demand" product

2. The organic level in the decanter is controlled by manipulating the liquid flow from the upstream separator (the major feed stream to the column).
3. The level in the separator is controlled by changing the setpoint of the reactor temperature controller.

Note that in this structure levels are controlled in the opposite direction from flows. There is now a direct handle on production rate. When the organic product flowrate is changed, the plant responds by sequentially and gradually changing the flowrates back through the process. The last flowrates to change are the fresh feeds.

The production rate is ultimately determined by the conditions in the reactor. Thus, after a change in the product flow from the decanter there is a temporary difference between what is produced in the reactor and what is removed from the plant. This imbalance disappears after the reactor conditions are adjusted. For this scheme to work there must be enough internal buffer capacity to accommodate the reactor's temporary over-production or under-production of vinyl acetate.

The surge capacity of the separator had to be significantly increased from the values shown in Table 11.10. The liquid flowrate from the separator is 0.55 m^3/min. The working liquid volume in the separator at the base-case conditions is 8 m^3, which gives a holdup time of 14 min. Using the on-demand control scheme, this holdup time had to be increased to about 60 min to handle reasonable production rate changes (about 12%). The holdup time of the organic layer in the decanter was about 10 min.

In addition to providing sufficient surge capacity, care must be taken in tuning the separator level controller. The gain of this controller must be chosen such that the change in reactor temperature provides a reasonable change in the production of condensable material from the reactor. As with any cascade scheme, the primary (level) controller gain depends on the span of the secondary (temperature) controller transmitter.

Dynamic simulations of this on-demand control scheme verified that it works. However, a production rate change produces a dynamic response that is quite different from that shown in Fig. 11.4. For example the column is upset immediately whereas conditions in the reactor change slowly. Overall it appears that the internal time dynamics are slower for this on-demand scheme than when the reactor conditions are changed first. However, this control structure fulfills the control objective of providing immediate changes in the flowrate of the product stream.

11.6 Conclusion

The process considered in this chapter involved the production of vinyl acetate monomer. It features many unit operations, many components, nonideal phase equilibrium, unusual reaction kinetics, two recycle streams, and three fresh reactant makeup streams.

The plantwide process control design procedure was applied to this complex process; it yielded an effective base-level regulatory control system.

We showed through nonlinear dynamic simulations how the process reacts to various disturbances and changes in operating conditions. We have not shown any attempts to optimize process performance, to improve the process design, or to apply any advanced control techniques (model-based, nonlinear, feedforward, valve-position, etc.). These would be the natural next steps after the base-level regulatory control system had been developed to keep the process at a stable desired operating point.

11.7 References

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