

CHAPTER 11

DESIGN AND CONTROL OF A METHANOL REACTOR/COLUMN PROCESS

Methanol is one of the prime candidates for providing an alternative to petroleum-based liquid transportation fuels. It can be made from any renewable biomass hydrocarbon source by partial oxidation in an oxygen-blown gasifier to produce synthesis gas, which is then converted into methanol.

The purpose of this chapter is to develop the economically optimal design of a methanol reactor/distillation column system with three gas recycle streams to produce high-purity methanol from synthesis gas. The economics consider capital costs, energy costs, the value of the methanol product, and the heating value of a vent stream that is necessary for purging off inert components entering in the feed. A plantwide control structure is developed that is capable of effectively handling large disturbances in production rate and synthesis gas composition. The unique features of this control scheme are no control of pressure in the reactor/recycle gas loop and a high-pressure override controller to handle stoichiometric imbalances in the composition of the synthesis gas feed.

11.1 INTRODUCTION

Global economic, environmental, and political forces have increased interest in developing sources of liquid transportation fuels that are not petroleum based. Renewable biomass has the potential to provide an alternative energy source that offers many long-term advantages over petroleum. Biomass can be converted into synthesis gas by gasification, and the synthesis gas can be efficiently converted into methanol using existing technology. It is possible that, in the not too distant future, most liquid-consuming transportation vehicles (cars, trucks, trains, and airplanes) may use methanol as their energy source. Olah et al.¹ propose

a “methanol economy” as a more practical approach compared to the widely discussed “hydrogen economy” because existing liquid fuel infrastructure (pipelines and tanks) could be used with little modification and the safety concerns associated with hydrogen could be avoided.

This chapter studies the process used to convert synthesis gas into methanol. A cooled tubular reactor is used to react hydrogen with the carbon monoxide and carbon dioxide in the synthesis gas to produce methanol. Water is a by-product. The gas-phase exothermic reactions are conducted in a packed tubular reactor, which is cooled by generating steam. A large gas recycle stream is required to obtain high overall conversion. A distillation column separates methanol from water.

A fixed amount of synthesis gas is fed into the system, and the effects of the many design optimization variables on the yield of methanol, the energy costs, and the capital costs are evaluated. These variables include reactor pressure, reactor size, concentration of inert components in the recycle gas, and pressure in a flash tank upstream of the column. The purpose of the flash tank is to keep light components that would blanket the condenser from entering the column.

The investigation reveals that the economics are dominated by methanol yield. Energy costs and capital costs are an order of magnitude smaller than the value of the product. The major energy cost is compression of the synthesis gas, so the optimum reactor operating pressure is a trade-off between compression costs and methanol yield. Reactor temperature is set so that high-pressure steam can be produced in the reactor. Reactor size is a trade-off between reactor and catalyst capital investment and recycle compression costs (energy and capital). Inert component concentration in the recycle gas is a trade-off between methanol yield (reactant losses in the vent) and compression costs. Selection of pressure in the flash tank is a trade-off between compressor costs in two compressors that are affected in opposite directions by varying flash tank pressure.

11.2 PROCESS STUDIED

Figure 11.1 shows the flowsheet of the process. The equipment sizes and conditions shown are the economic optimum developed in Section 11.6. The Aspen RK-Aspen physical properties model is used in all units of the process, except in the distillation column in which the van Laar equations are used to calculate liquid activity coefficients.

11.2.1 Compression and Reactor Preheating

Synthesis gas at 51.2 bar is compressed in a two-stage compression system to 110 bar. The fresh feed is mostly hydrogen, carbon dioxide, and carbon monoxide, but it also contains small amounts of methane and nitrogen. The inert components must be purged out of the system. The two feed compressors consume a total of 8.98 MW of electric energy.

Three recycle gas streams are added and the total gas stream enters a feed-effluent heat exchanger (FEHE) at 53 °C. The hot reactor effluent at 266 °C transfers 43.9 MW of heat into the cold stream, which heats it to 144 °C. The required area is 2157 m² using an overall heat-transfer coefficient of 144 kcal h⁻¹ m⁻² K⁻¹. The gas is then heated to 150 °C in a reactor preheater (HX3), which has a duty of 2.99 MW and uses medium-pressure steam (184 °C and 11 bar).



The packed tubular reactor has 8000 tubes with length 12.2 m and diameter 0.03675 m. The reactor is cooled by generating high-pressure steam (254 °C and 42 bar), so the reactor temperatures through the tubes climb to a peak of about 280 °C. The reactor effluent is at 266 °C. The heat transfer rate is 28.3 MW, using an overall heat-transfer coefficient of 244 kcal h⁻¹ m⁻² K⁻¹. The catalyst has a density of 2000 kg/m³ and the reactor void volume is 0.5. The reaction kinetics are discussed in Section 11.3. The reasons for the selections of temperature, pressure, and reactor size are discussed in Section 11.6.

After the reactor effluent is cooled to 174 °C in the FEHE, it is further cooled to 38 °C and partially condensed in a water-cooled heat exchanger with a heat duty of 102 MW. The stream is separated in a tank operating at 106.6 bar and 38 °C. The total pressure drop around the gas loop (heat exchangers and reactor) is 3.4 bar.

Most of the vapor stream is compressed back up to 110 bar and recycled. The recycle compressor work is 1.10 MW. The gas recycle flowrate is 38,465 kmol/h for the 11,450 kmol/h of synthesis gas feed (recycle-to-feed ratio = 3.36). A small fraction (0.022) is vented off at a flowrate of 865 kmol/h. This is where the inert methane and nitrogen in the synthesis gas fresh feed are removed from the system. The concentration of methane and nitrogen in the vent and recycle streams are 28.5 and 4 mol%, respectively. These compositions should be compared with the 2.17 mol% methane and 0.3 mol%

nitrogen in the fresh synthesis gas feed. The inerts are allowed to build up so that the losses of the reactants (hydrogen, carbon monoxide, and carbon dioxide) are kept small.

The hydrogen that is lost in the vent stream is 6.17% of the hydrogen in the synthesis gas feed. The carbon monoxide lost is 1.23% of the carbon dioxide in the synthesis gas feed. The carbon dioxide lost is 8.75%. The yield of methanol from the carbon monoxide and carbon dioxide in the synthesis gas feed is 96%.

11.2.4 Flash and Distillation

The liquid from the separator contains significant amounts of light components because of the high pressure in the separator. The concentration of hydrogen is 0.2 mol%, the concentration of methane is 1.2 mol%, and the concentration of carbon dioxide is 3.9 mol%. **If this stream were fed directly into the distillation column, these inert components would build up in the condenser and blanket the condenser.** Either a high pressure or a low temperature would be needed in the condenser, which may require the use of expensive refrigeration.

Therefore, **a flash tank is used to remove most of the light components before the stream is fed into the column.** The flash tank is operated at 2 bar. The gas (224.8 kmol/h) is compressed to 110 bar and recycled to the reactor. The compressor power is 1.341 MW.

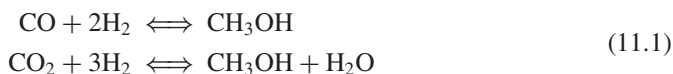
The liquid from the flash tank is pumped into a 42-stage distillation column on stage 27. The column operates at 1 bar, and a reflux-drum temperature of 50 °C is used so that cooling water can be used in the condenser. A small vapor stream from the top of the reflux drum recycles the small amount of inert components entering the column. This small vapor stream (0.0669 kmol/h) is compressed back up to 110 bar (work is 4.9 kW).

There are three specifications in this column. Two specifications set the compositions of the bottoms (0.01 mol% methanol) and the distillate (0.1 mol% water). The third specification sets the reflux-drum temperature at 50 °C, which establishes the amount of vapor that must be removed from the top of the reflux drum for compression and recycle.

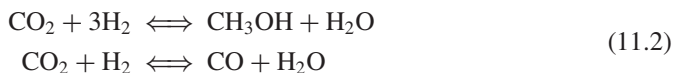
The methanol/water separation is reasonably easy, so the required reflux ratio (RR) is only 0.407. Reboiler energy is 54.8 MW. Low-pressure steam (160 °C and 6 bar) can be used in the reboiler since the base temperature is 110 °C.

11.3 REACTION KINETICS

The chemistry of the methanol process involves the reaction of both carbon dioxide and carbon monoxide with hydrogen.



The kinetics are given by vanden Bussche and Froment² in the following form by using the water-shift reaction.



The reactions are exothermic and use a solid catalyst. The kinetics are described by LHHW-type equations (Langmuir–Hinshelwood–Hougen–Watson). Conversion of the

reaction rate equations and their units given in the original paper into the form required by Aspen Plus is a daunting task. The original data use pressures in bar and reaction rates in $\text{kmol min}^{-1} \text{kg}^{-1}$ catalyst. These must be transformed to Pascals. This transformation was provided by Emmanuel Lejeune (AspenTech), and his invaluable assistance is gratefully acknowledged.

The LHHW kinetic structure has the form

$$\mathfrak{R} = (\text{Kinetic term}) \frac{(\text{Driving-force term})}{(\text{Adsorption term})} \quad (11.3)$$

The reaction rate for the first reaction for the production of methanol from carbon dioxide is given in Eq. (11.4).

$$\mathfrak{R}_1 = (k_4 p_{\text{CO}_2} p_{\text{H}_2}) \frac{\left[1 - \frac{1}{K_{E1}} \left(\frac{p_{\text{CH}_3\text{OH}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}} \right) \right]}{\left[1 + k_3 \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right) + k_1 \sqrt{p_{\text{H}_2}} + k_2 p_{\text{H}_2\text{O}} \right]^3} \quad (11.4)$$

The reaction rate for the water-shift reaction is given in Eq. (11.5).

$$\mathfrak{R}_2 = (k_5 p_{\text{CO}_2}) \frac{\left[1 - \frac{1}{K_{E2}} \left(\frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}} \right) \right]}{\left[1 + k_3 \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right) + k_1 \sqrt{p_{\text{H}_2}} + k_2 p_{\text{H}_2\text{O}} \right]} \quad (11.5)$$

Table 11.1 gives the kinetic and adsorption parameters entered into the Aspen LHHW reaction model to implement these kinetics. Note that the activation energy of the first reaction when put in LHHW form turns out to be negative, which makes no physical sense.

Since the reactions are exothermic, the chemical equilibrium constants decrease with increasing temperature. Therefore, low reactor temperatures should improve conversion, provided they are not so low that the specific reaction rates are too small. For a given reactor size and a desired conversion, recycle flowrate increases as reactor temperatures are lowered, which mean higher compressor work.

The reactor is simulated in Aspen using the RPLUG model with a *constant medium temperature* as the dynamic heat-transfer selection. The reactor is cooled by generating saturated steam, and the temperature of the boiling water on the shell side of the reactor tubes is the same at all axial positions. The selection of the medium temperature inferentially sets the reactor temperature profile.

The medium temperature is set at 264 °C so that high-pressure steam (254 °C and 42 bar) can be generated. Thus, one of the important design optimization variables (reactor temperature) is established a priori so that valuable high-pressure steam can be generated, which can be used to drive compressors.

11.4 OVERALL AND PER-PASS CONVERSION

With the design conditions and equipment sizes shown in Figure 11.1, there are 28,920 kmol/h of hydrogen entering the reactor, 4066 kmol/h of carbon monoxide and 3976 kmol/h of carbon dioxide. The corresponding component flowrates leaving the reactor

TABLE 11.1 Kinetic LHHW Parameters

R1 ($\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$)	
Kinetic factor $k = 1.07 \times 10^{-3}$	
$E = -36,696 \text{ kJ/kmol}$	
<i>Driving-force expressions</i>	
Term 1	
Concentration exponents for reactants: $\text{CO}_2 = 1$; $\text{H}_2 = 1$	
Concentration exponents for products: $\text{CH}_3\text{OH} = 0$; $\text{H}_2\text{O} = 0$	
Coefficients: $A = -23.02581$; $B = C = D = 0$	
Term 2	
Concentration exponents for reactants: $\text{CO}_2 = 0$; $\text{H}_2 = -2$	
Concentration exponents for products: $\text{CH}_3\text{OH} = 1$; $\text{H}_2\text{O} = 1$	
Coefficients: $A = 24.388981$; $B = -7059.7258$; $C = D = 0$	
<i>Adsorption expression</i>	
Adsorption term exponent = 3	
Concentration exponents	
Term 1: $\text{H}_2 = 0$; $\text{H}_2\text{O} = 0$	
Term 2: $\text{H}_2 = -1$; $\text{H}_2\text{O} = 1$	
Adsorption constants	
Term 1: $A = 0$, $B = 0$, $C = 0$, $D = 0$	
Term 2: $A = 8.1471087$, $B = 0$, $C = 0$, $D = 0$	
R2 ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$)	
Kinetic factor $k = 1.22 \times 10^9$	
$E = 94765 \text{ kJ/kmol}$	
<i>Driving-force expressions</i>	
Term 1	
Concentration exponents for reactants: $\text{CO}_2 = 1$; $\text{H}_2 = 0$	
Concentration exponents for products: $\text{CO} = 0$; $\text{H}_2\text{O} = 0$	
Coefficients: $A = -11.512952$; $B = C = D = 0$	
Term 2	
Concentration exponents for reactants: $\text{CO}_2 = 0$; $\text{H}_2 = -1$	
Concentration exponents for products: $\text{CO} = 1$; $\text{H}_2\text{O} = 1$	
Coefficients: $A = -16.184871$; $B = 4773.2589$; $C = D = 0$	
<i>Adsorption expression</i>	
Adsorption term exponent = 1	
Concentration exponents	
Term 1: $\text{H}_2 = 0$; $\text{H}_2\text{O} = 0$	
Term 2: $\text{H}_2 = -1$; $\text{H}_2\text{O} = 1$	
Adsorption constants	
Term 1: $A = 0$, $B = 0$, $C = 0$, $D = 0$	
Term 2: $A = 8.1471087$, $B = 0$, $C = 0$, $D = 0$	

are 21,673, 1468, and 3292 kmol/h, which means that the per-pass conversion of hydrogen is 25%, the per-pass conversion of carbon monoxide is 64%, and the per-pass conversion of carbon dioxide is 17%.

The overall conversion of the carbon monoxide and carbon dioxide in the fresh synthesis gas feed to methanol is 96%. There are 2630 kmol/h of carbon dioxide and 785 kmol/h of carbon monoxide in the synthesis gas, totaling 3415 kmol/h. The methanol in the distillate product is 3278 kmol/h.

There are 2 mol of hydrogen needed to react with the carbon monoxide, and 3 mol of hydrogen needed to react with the carbon dioxide. If there were complete conversion of all the carbon dioxide and carbon monoxide in the synthesis gas feed, the hydrogen consumed in the reactions would be $2630 \times 2 + 786 \times 3 = 7616$ kmol/h of hydrogen. The hydrogen supplied in the fresh synthesis gas feed is 7724 kmol/h. So there is a small excess. The overall conversion of hydrogen to produce methanol is quite high (98.6%).

These high conversions of reactants indicate that the design has achieved only small losses of the valuable reactants, despite the need to purge out the inert components in the fresh feed (methane and nitrogen). The economics discussed in Section 11.6 demonstrate that energy and capital can be expended to improve yield so that losses of reactants and products are very small. Douglas³ established this principle in his pioneering work on conceptual process design over two decades ago.

It should be noted that an alternative design could be developed if medium or low-pressure steam were generated in the reactor. Low-pressure steam (160 °C and 6 bar) could be generated if the medium temperature were set at 170–180 °C, and this steam could be used in the reboiler of the distillation column. The resulting lower reactor temperatures would result in a smaller reactor and less recycle. This alternative design is not considered in this chapter.

11.5 PHASE EQUILIBRIUM

There are two vapor-liquid flash separations in the process. The Aspen Flash2 model is used in the separator block and the flash block. Most of the light components are removed in the vapor streams leaving these vessels, but small amounts of light components are dissolved in the liquid streams. This is what necessitates the need for the flash tank and the vapor stream from the reflux drum.

The methanol/water separation is nonideal but fairly easy. The van Laar equations are used in the distillation column. Figure 11.2 gives a T_{xy} diagram at 1 bar pressure.

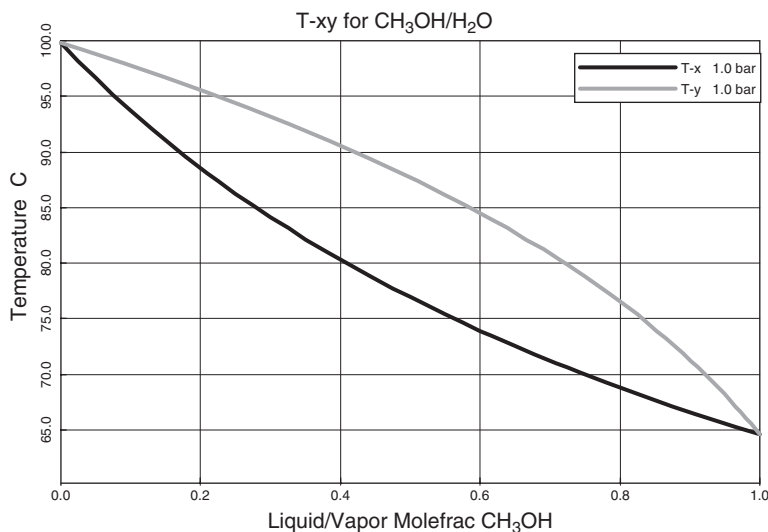


Figure 11.2. T_{xy} diagram for methanol/water at 1 bar.

11.6 EFFECTS OF DESIGN OPTIMIZATION VARIABLES

The methanol process has a number of design optimization variables that impact energy and capital economics in conflicting ways. We explore these effects quantitatively in this section.

11.6.1 Economic Basis

The economics consider both capital investment (compressors, heat exchangers, reactor, catalyst, separator tank, flash tank, and column) and energy costs (compressor work, steam used in the reactor preheater, and reboiler duty in the column). Table 11.2 summarizes the sizing and cost basis used in this analysis. These parameters are taken from Douglas³ and Turton et al.⁴

The compressors use electricity at \$16.8/GJ. The reactor preheater uses medium-pressure steam at \$8.22/GJ. The column reboiler uses low-pressure steam at \$7.78/GJ.

There are two credits in the economics. One is for the steam generated in the reactor. It is at high-pressure but is saturated, not superheated, so \$6/GJ is assumed for its value. The second is the heating value of the vent stream, which contains mostly hydrogen and methane with some carbon monoxide. These components can be burned to recover heat. The amount of air to completely combust each component, the component heats of

TABLE 11.2 Basis of Economics and Equipment Sizing

Column diameter: Aspen tray sizing
Column length: NT trays with 2-ft spacing plus 20% extra length
Column vessel (diameter and length in meters)
Capital cost = $17,640(D)^{1.066}(L)^{0.802}$
<i>Condensers (area in m²)</i>
Heat-transfer coefficient = 0.852 kW/K-m ²
Differential temperature = Reflux-drum temperature – 303 K
Capital cost = $7296(A)^{0.65}$
<i>Reboiler (area in m²)</i>
Heat-transfer coefficient = 0.568 kW/K-m ²
Differential temperature = 34.8 K
Capital cost = $7296(A)^{0.65}$
<i>Reactor and FEHE (area in m²)</i>
Capital cost = $7296(A)^{0.65}$
Heat-transfer coefficient FEHE = 144 kcal h ⁻¹ K ⁻¹ m ⁻²
Heat-transfer coefficient reactor = 244 kcal h ⁻¹ K ⁻¹ m ⁻²
Catalyst cost = \$10/kg
Compressor capital cost = $(1293)(517.3)(3.11)(hp)^{0.82}/280$
<i>Energy cost</i>
LP steam = \$7.78/GJ
MP steam = \$8.22/GJ
HP saturated steam from reactor = \$6.00/GJ
Electricity = \$16.8/GJ
$TAC = \frac{\text{Capital cost}}{\text{Payback period}} + \text{Energy cost}$
Payback period = 3 yr

combustion, and the mean heat capacities of the resulting nitrogen, carbon dioxide, and water gas stream are used to find the heating value of the vent stream (0.331 kJ/kmol). The sensible heat of changing the combustion products from ambient up to a 260 °C stack gas temperature is subtracted from the heat of combustion. A value of \$6/GJ is used for this fuel.

The assessment of economics uses the income derived from the process for a fixed amount of synthesis gas fed. The value of methanol is assumed to be \$2/gallon (\$21/kmol). In all cases the fresh feed of synthesis gas is fixed at 11,450 kmol/h. As design parameters change, the amount of product methanol changes, the amount of venting changes, the amount of reactor steam changes, and the energy consumption changes (compressors, reactor preheater, and column reboiler).

We define income as the sum of the value of the methanol produced plus the value of the vent and reactor steam credits minus the energy costs minus the annual capital cost.

$$\begin{aligned} \text{Income} = & (\text{Flowrate methanol})(\$ \text{ Value}) + (\text{Flowrate vent})(\$ \text{ Value}) \\ & + (\text{Reactor steam})(\$ \text{ Value}) - (\text{Work of 5 compressors})(\$/\text{MW}) \\ & - (\text{Reboiler energy})(\$/\text{MW}) - \left(\frac{\text{Total capital}}{3} \right) \end{aligned} \quad (11.6)$$

Total capital investment includes the cost of the five compressors, the intercooler between the feed compressors, the FEHE, the reactor preheater, the reactor with catalyst, the cooler/condenser, the separator vessel, the flash drum, the distillation column vessel, the condenser, and the reboiler.

We choose to look at income instead of profit because this avoids having to assign a value for the synthesis gas feed. The incremental increase in income when changing a design parameter and the incremental increase in the required capital investment are evaluated to see if the incremental return on investment is sufficient to justify the investment.

As the numbers given in the following sections will reveal, the value of the product is an order of magnitude larger than the cost of energy and capital. Douglas³ pointed out this basic design principle many years ago. Small increases in product yield are worth more than the corresponding required increases in capital and energy to achieve them. This is true up to a point.

In the following sections, the effects of variables on the economics of the process are studied one at a time to present a clear picture of the trends. After each variable is explored, the dominant variables are varied in an iterative procedure to arrive at the optimum values of the design variables.

11.6.2 Effect of Pressure

High pressure in the reactor favors the production of methanol because of the increase in reactant partial pressures. Both reactions are nonequimolar with fewer molecules of products than reactants. So Le Châtelier's principle would indicate that high pressure drives the reactions to the right. At a given recycle flowrate, the higher the pressure, the smaller the reactor can be, which reduces reactor vessel and catalyst capital investment. With a given reactor size, the higher the pressure, the smaller the recycle flowrate can be, which reduces recycle compression energy and recycle compressor capital investment.

However, the higher the pressure, the more compression of the feed synthesis gas is required. The synthesis gas is assumed to be supplied at 51.2 bar from an upstream unit. A two-stage compressor system is used with intermediate cooling. Following the common design heuristic, the compression ratio is specified to be the same in both stages. For a given synthesis gas pressure P_1 and a system pressure P_2 , the compression ratio in each stage of a two-stage compression system is $\sqrt{P_2/P_1}$.

Figure 11.3 and Table 11.3 show the effects of changing pressure on a number of important variables. These results are generated with the other design optimization variables set at reasonable initially guessed values. The number of reactor tubes is 5000, the flash tank pressure is 10 bar, and the vent/recycle split fraction is 0.025. This split affects the composition of the inert components in the recycle gas. The number of stages in the distillation column is set at 42 with feed on stage 20. All of these variables will be optimized later.

The top left graph in Figure 11.3 shows that compressor work in the feed compressors increases as system pressure is increased. The work in the first compressor (K1) is shown, and the work in the second compressor (K2) is essentially the same as K1. The changes in compressor work are quite significant and impact both energy cost (expensive electrical energy at \$16.8/GJ) and compressor capital investment (see Table 11.2).

On the other hand, the top right graph in Figure 11.3 shows that required recycle flowrate decreases as pressure increases. This reduces the cost of compression of the gas recycle in compressor K3 (second graph from the top on the left in Figure 11.3). The net effect is an increase in total capital cost and total energy cost (third graphs from the top in Figure 11.3).

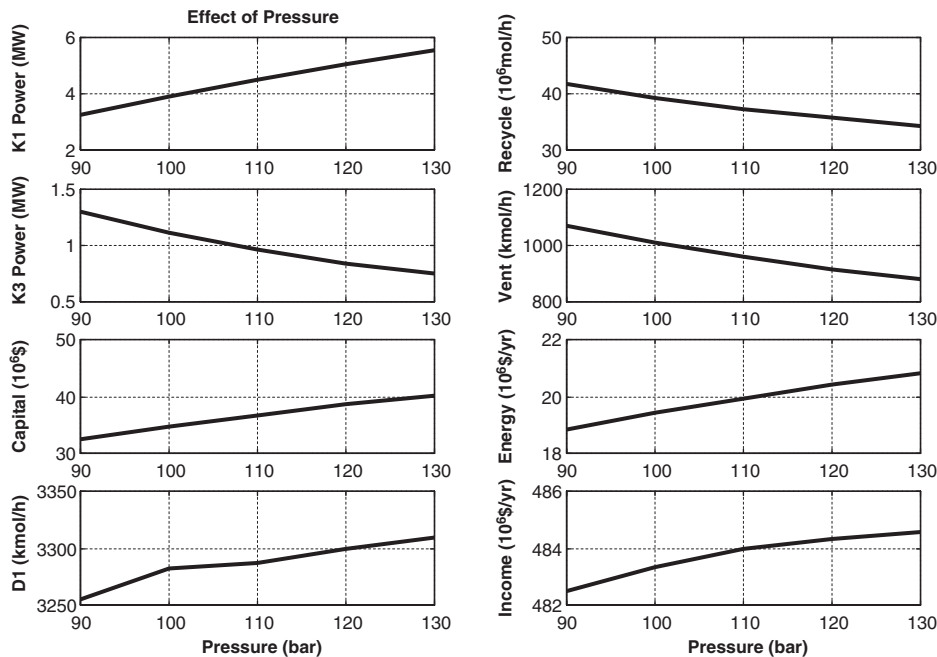


Figure 11.3. Effect of reactor pressure.

TABLE 11.3 Effect of Pressure^a

System Pressure (bar)	90	100	110	120	130
Compressor K1 (MW)	3.254	3.901	4.499	5.053	5.571
Compressor K2 (MW)	3.254	3.899	4.483	5.037	5.559
Compressor K3 (MW)	1.303	1.109	0.958	0.841	0.747
D_1 (kmol/h)	3254.7	3272.7	3287.3	3299.5	3309.7
Vent (kmol/h)	1069.0	1008.8	957.9	915.9	879.0
Recycle (kmol/h)	41,690	39,343	37,358	35,720	34,281
Q_{HX1} (MW)	4.444	5.101	5.709	6.272	6.798
Total capital (\$10 ⁶)	32.55	34.74	36.70	38.53	40.21
Total energy (\$10 ⁶ /yr)	18.83	19.41	19.92	20.42	20.86
Income (\$10 ⁶ /yr)	482.48	483.34	483.96	484.33	484.57
Incremental capital (\$)	—	2,192,000	1,961,100	1,830,000	1,679,000
Incremental income (\$/yr)	—	860,000	618,000	373,000	239,000
Incremental ROI (%)	—	39.2	31.5	20.4	14.2

^a5000 tubes, 10 bar flash, 0.025 split.

The bottom two graphs of Figure 11.3 show that the production rate (D_1) of the methanol product gradually increases as pressure is increased, which produces a gradual rise in income despite the increases in both energy cost and capital cost. Remember that the feed of synthesis gas is fixed. The increase in product is accompanied by a corresponding decrease in the vent rate (second graph on the right in Figure 11.3). Due to the improvement in kinetics, there are smaller losses of reactants in the vent stream as pressure increases.

However, capital investment increases as pressure rises, so we need to see if the incremental investment is justified by the incremental increase in income. The detailed numbers are presented in Table 11.3. Moving from 90 to 100 bar provides a \$860,000 per year increase in income and requires a \$2,192,200 increase in capital investment. The incremental return on investment is a healthy 39%.

Evaluating the move from 100 to 110 bar shows a 31% incremental return on incremental investment. Going from 110 to 120 bar yields a 20% return, and going from 120 to 130 bar yields a 14% return. These results clearly demonstrate that there is a point of diminishing returns for investing capital. A system pressure of 110 bar is selected as the design value.

11.6.3 Effect of Reactor Size

Using a pressure of 110 bar and holding the other design optimization variables constant, the effect of changing the number of tubes in the reactor is explored. Tube diameter is kept constant at the smallest practical value (0.03675 m) to provide the maximum heat-transfer area per unit volume. Tube length is kept constant to provide a reasonable pressure drop through the reactor (1.5 bar).

Increasing reactor size will increase capital investment in both the multi-tube vessel and the catalyst inside the tubes. However, the per-pass conversion should increase, so the required recycle flowrate would decrease. This will decrease compressor work in the recycle compressor K3 and also decrease its capital cost.

Figure 11.4 shows the effect on several important variables of changing the number of reactor tubes. The upper left graph shows that capital investment in the reactor vessel, catalyst, and K3 compressor increases as more tubes are used. All the other units are essentially

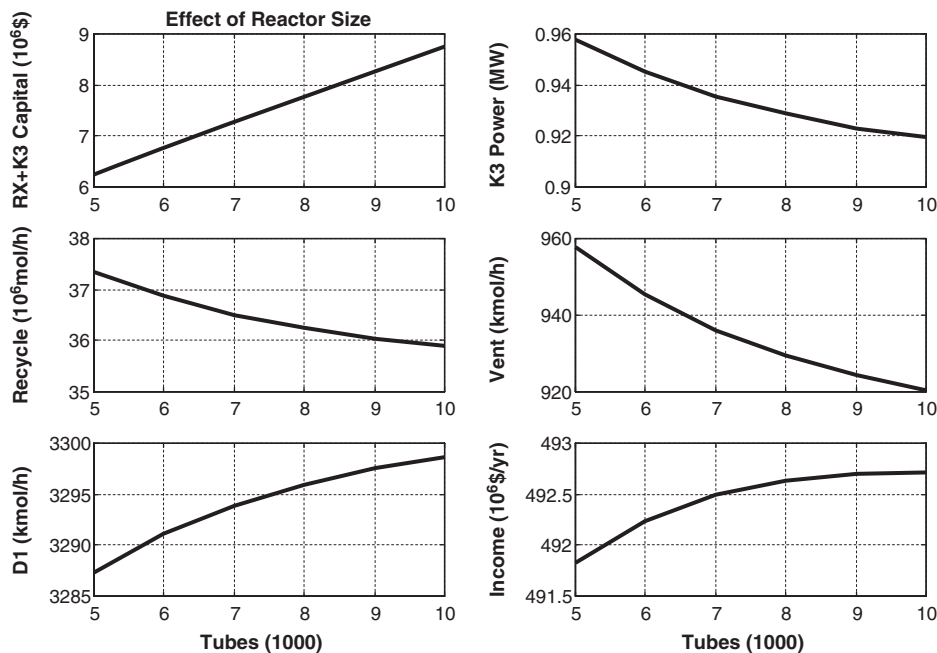


Figure 11.4. Effect of reactor size.

unaffected by changes in reactor size. The middle left graph shows that there is a decrease in recycle, which results in a decrease in work in the recycle compressor K3 (top right graph) and its capital cost. The effect of increases in reactor vessel and catalyst capital is larger than the effect of decreases in compressor capital, so the total capital investment in these two units increases.

The larger reactor improves the yield of methanol, as reflected in the gradual increase in the distillate (D1), which is the methanol product stream (bottom left graph in Figure 11.4). The vent flowrate decreases as the product flowrate increases (middle right graph in Figure 11.4) because the flowrate of synthesis gas is fixed.

Income increases gradually, but the rate of increase slows down as more tubes are added. Table 11.4 gives details of the economics. Return on investment calculations show a gradual decrease in the incremental return on incremental investment. Going from 7000 to 8000 tubes gives a 28% return. Going from 8000 to 9000 gives a small 14% return on investment.

A reactor with 8000 tubes is selected.

11.6.4 Effect of Vent/Recycle Split

All previous designs have used a vent-to-recycle split of 0.025. The resulting inert component compositions in the vent stream are about 26 mol% methane and 3 mol% nitrogen. The remaining components represent losses of the reactants hydrogen, carbon monoxide, and carbon dioxide. Lowering the split ratio (less venting) will increase the composition of the inert components in the vent and reduce reactant losses in the vent, which only has fuel value.

TABLE 11.4 Effect of Reactor Size^a

Tube Number	5000	6000	7000	8000	9000	10,000
Recycle (kmol/h)	37,351	36,869	36,507	36,247	36,044	35,897
D_1 (kmol/h)	3287.34	3291.09	3293.93	3295.96	3297.52	3298.66
Compressor K3 (MW)	0.9580	0.9453	0.9356	0.9289	0.9231	0.9197
Vent (kmol/h)	957.7	945.4	936.1	929.4	924.2	920.4
Reactor + K3 capital (\$10 ⁶)	6.238	6.7592	7.2705	7.7751	8.2705	8.7618
Income (\$10 ⁶ /yr)	491.83	492.23	493.49	492.63	492.70	492.71
Incremental capital (\$)	—	521,200	511,300	504,600	495,400	491,300
Incremental income (\$/yr)	—	400,000	260,000	140,000	70,000	10,000
Incremental ROI (%)	—	77	51	28	14	2

^a110 bar, 10 bar flash, 0.025 split.

On the other hand, having higher inert concentrations in the recycle gas going to the reactor will adversely affect kinetics and require higher recycle flowrates, which will increase recycle compressor costs. So there is a trade-off between vent losses and recycle compressor energy and capital costs.

In order to accurately show the effects of higher recycle gas flowrates around the gas loop, pressure drops through the various units in the loop are varied with recycle flowrate. The base-case pressure drop around the loop is 3 bar: 0.5 bar through both sides of the FEHE, 1.5 bar through the reactor, 0.1 bar through the reactor preheater, and 0.4 bar through the condenser. The base-case recycle flowrate is 36,200 kmol/h. Pressure drops change with the square of the flowrate changes. The discharge pressure of the feed compressors is kept at 110 bar.

Figure 11.5 shows that recycle flowrates increase as the split ratio is *decreased* (second graph from the top on the left), as does the work of the recycle compressor K3 (top right graph). Vent rates decrease, and methanol product rates increase as the split ratio is decreased. But both capital investment and energy costs increase when the split ratio is decreased. A split ratio of 0.022 gives the maximum income.

Moving from a split ratio of 0.023 down to 0.022 gives an incremental increase in income of \$620,000/yr and requires only a \$25,000 increase in capital investment. Moving from 0.022 down to 0.021 produces a *decrease* in income, while at the same time increasing capital investment. Therefore, a split ratio of 0.022 is selected.

11.6.5 Effect of Flash-Tank Pressure

A flash-tank pressure of 10 bar has been used in all the previous designs. This design optimization variable is now explored with all the other variables fixed: 110 bar pressure, 8000 tubes, and a split ratio of 0.022.

The flash tank's job is to keep inert components out of the distillation column. The lower the flash pressure, the fewer inert components entering the column, which reduces the vapor coming off the top of the reflux drum, thus reducing costs of the compressor K4 on this stream. On the other hand, lowering flash pressure results in more vapor leaving the flash tank, which increases energy and capital cost of the compressor (Kflash) that is recycling this stream back to the 110-bar reactor pressure. So there is a trade-off between the cost of the two compressors, which are affected in opposite ways by flash pressure.

Figure 11.6 illustrates all these trends. The top left graph shows that the vapor V1 from the reflux drum of the distillation column decreases as flash pressure is decreased. This

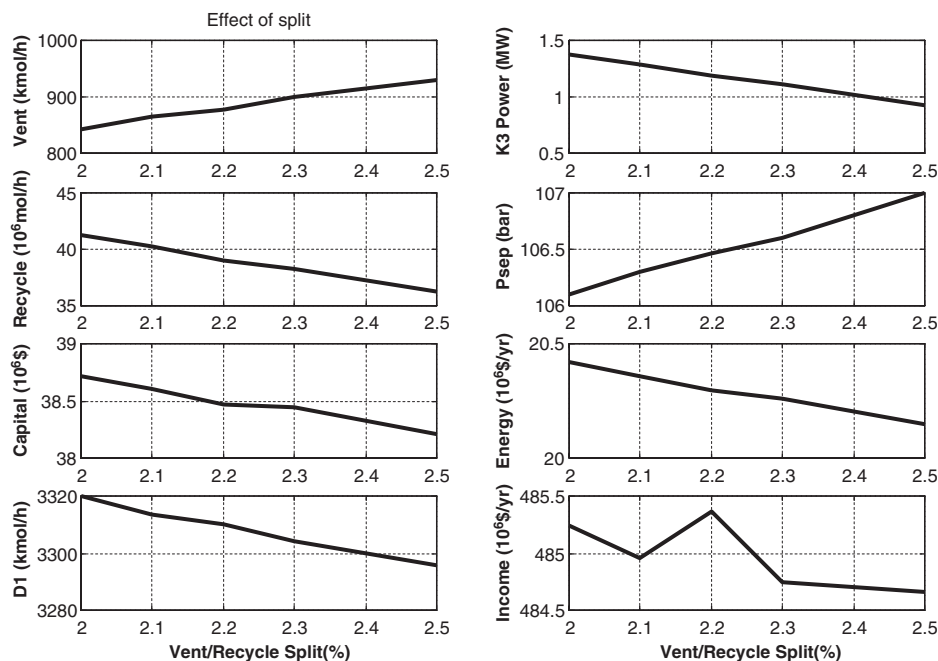


Figure 11.5. Effect of vent/recycle split.

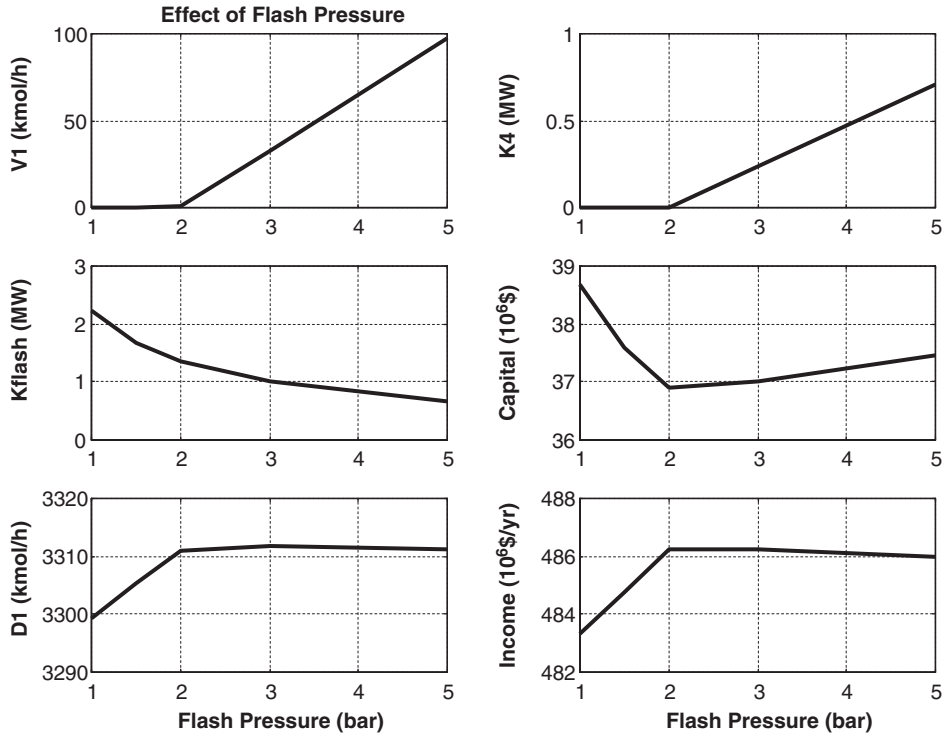
reduces the work in compressor K4. Once flash pressure gets down to 2 bar, there are only very small amounts of inert components entering the column.

However, the flowrate of vapor leaving the flash tank increases as flash pressure is decreased, as shown by the increase in compressor work (middle left graph in Figure 11.6). Going from 2 bar to 1 bar results in a rapid change in Kflash compressor work. A pressure of 2 bar gives the maximum income and at the same time gives the minimum capital investment. So the flash drum pressure is set at 2 bar.

It is interesting to note that there is additional advantage of running a low flash-drum pressure. The reduction in the amount of inert components coming into the reflux drum of the column improves the purity of the methanol product. The specification used is 0.1 mol% water in the distillate, but there is some carbon dioxide present in the liquid product. With a flash-drum pressure of 2 bar, the carbon dioxide composition is 0.9 mol% in the distillate, which gives a methanol purity of 98.9 mol%. With a flash-drum pressure of 1.5 bar, the carbon dioxide composition is 0.7 mol% in the distillate, which gives a methanol purity of 99.2 mol%. With a flash-drum pressure of 1 bar, the carbon dioxide composition is 0.5 mol% in the distillate, which gives a methanol purity of 99.4 mol%. So, if very high purity methanol is desired, a low flash-drum pressure would be required.

11.6.6 Optimum Distillation Column Design

The last design optimization variable explored is the number of stages and the feed-stage location in the distillation column. The values that minimize TAC were determined. The results are shown in Table 11.5. The optimum feed stage is found for each case by determining the feed stage that minimizes reboiler heat input.

**Figure 11.6.** Effect of flash tank pressure.

As the number of total stages is increased, energy costs and heat exchanger capital costs decrease, but the capital cost of the shell increases. Total capital increases with increasing stages. The 42-stage column has the lowest TAC.

Note that the variation of the economic objective function (TAC) with total stages is quite modest, with less than 1% change over the entire range from 32 to 52 stages. Thus, a rigorous determination of precisely the optimum number of stages, narrowing it down to a precision of a single stage, is unnecessary.

TABLE 11.5 Optimum Distillation Column Design

NT	32	42	52
NF _{opt}	19	27	30
ID (m)	5.979	5.806	5.674
Q _R (MW)	59.85	54.27	54.26
Q _C (MW)	48.45	47.83	47.79
Area reboiler (m ²)	2770	2741	2740
Area condenser (m ²)	2838	2802	2800
Capital costs (10 ⁶ \$)			
Shell	1.318	1.623	1.928
Reboiler and condenser	2.542	2.523	2.522
Energy cost (10 ⁶ \$/yr)	13.46	13.32	13.31
TAC (10 ⁶ \$/yr)	14.75	14.70	14.80

Figure 11.7 gives the temperature and composition profiles in the distillation column. These will be used in developing a control structure in the next section.

The flowsheet shown in Figure 11.1 shows the final design. The system pressure is 110 bar, the reactor has 8000 tubes, the vent/recycle split is 0.022, the flash-drum pressure is 2 bar, and the column has 42 stages. An effective plantwide control scheme for the process is developed and tested in the next section.

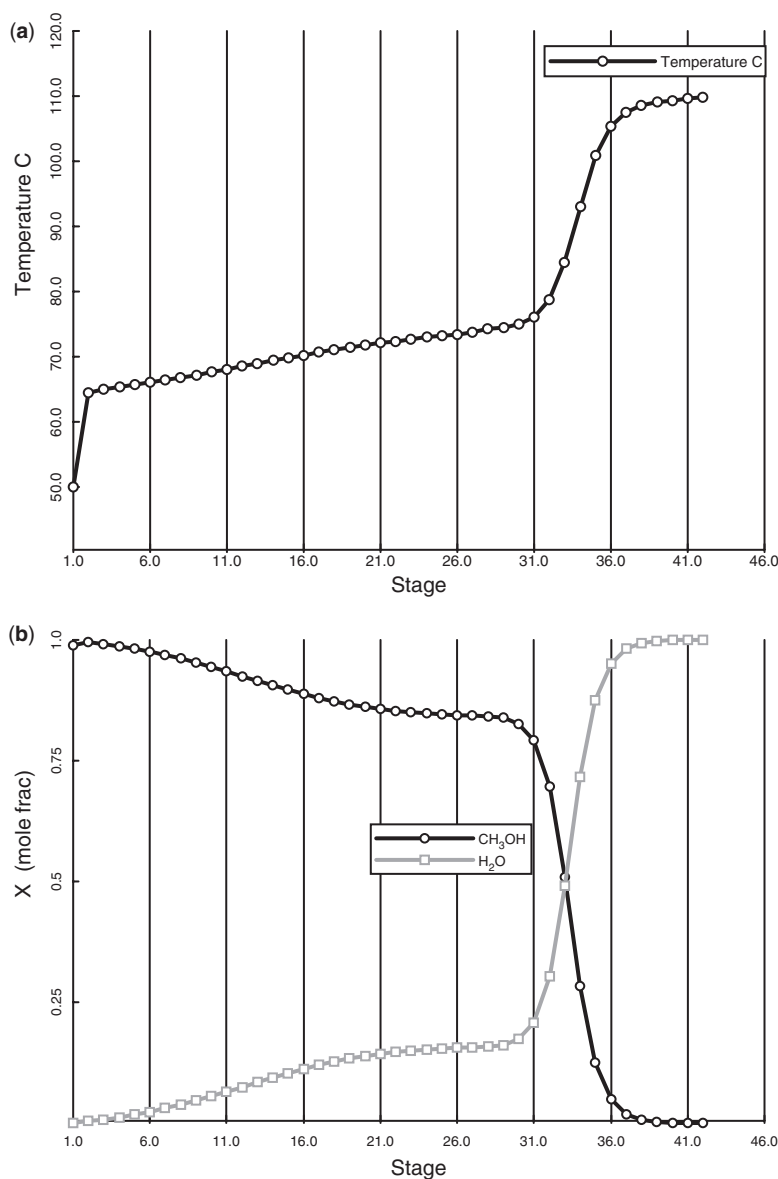


Figure 11.7. (a) Column temperature profile. (b) Column composition profiles.

11.7 PLANTWIDE CONTROL

Before exporting the steady-state Aspen Plus simulation into Aspen Dynamics, the size of the reflux drum and column base in the distillation column are determined to provide 5 min of liquid holdup at 50% level. The size of the reactor and column vessel are known from the steady-state design. The sizes of the separator and flash drum were also determined during steady-state design so that their capital investment costs could be calculated. The size of the separator is set by the maximum superficial vapor velocity, using the gas flowrate and its density. An F factor of 0.5 is used (in English engineering units). The diameter is 6.5 m, since there is a very large gas recycle stream. The size of the flash tank is set by 5 min of liquid holdup (2.8 m in diameter, 5.6 m in length). The compressors and heat exchangers are assumed have negligible dynamic lags.

The development of the plantwide control structure presented below is based on the heuristic procedure proposed a decade ago (see Luyben et al.⁵), which has been successfully applied to many industrial processes.

11.7.1 Control Structure

Figure 11.8 shows the plantwide control structure developed for this process. Conventional PI controllers are used in all loops. All level loops are proportional with $K_C = 2$. Flow controllers that manipulate compressors use a gain of 0.5 and an integral time of 0.5 min. The column tray temperature controller has a 1-min deadtime. The reactor temperature loop has a 2-min deadtime to account for the steam generation dynamics. The composition controller has a 3-min deadtime. These temperature and composition controllers are tuned by using

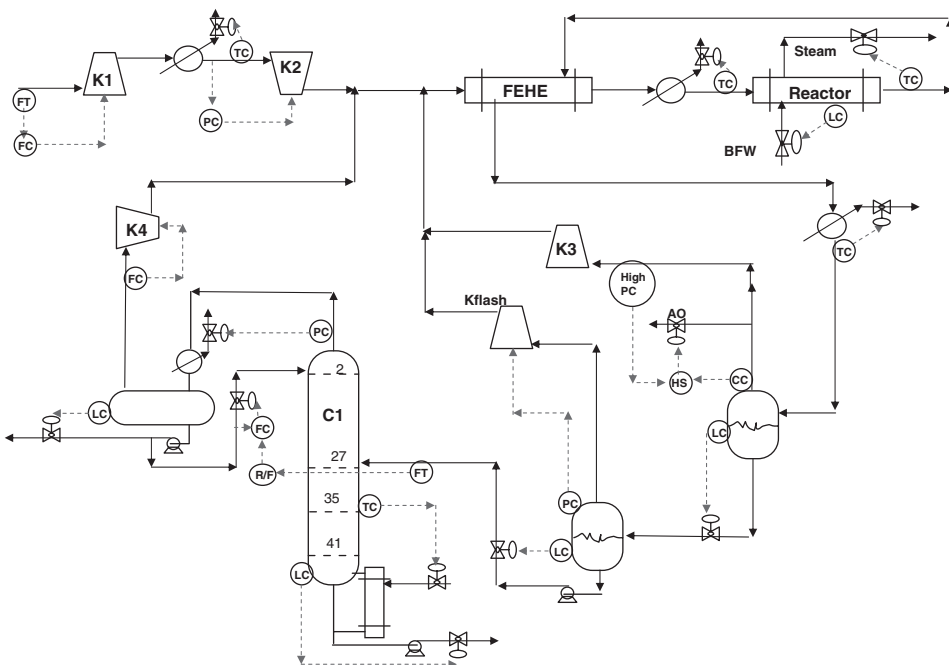


Figure 11.8. Plantwide control structure.

relay-feedback tests to obtain ultimate gains and periods, and then applying Tyreus-Luyben tuning rules.

All of the loops are listed below with their controlled and manipulated variables.

1. The synthesis gas is flow-controlled by manipulating work to compressor K1. If the synthesis gas is being generated in an upstream gasification unit, a pressure controller in that unit typically would change the setpoint of the flow controller.
2. The temperature of the compressed gas leaving the interstage cooler is controlled by manipulating heat removal in the heat exchanger (cooling water).
3. The suction pressure of the second compressor K2 is controlled by manipulating its compressor work.
4. The reactor inlet temperature is controlled by manipulating the heat input to the reactor preheater (medium-pressure steam).
5. Reactor exit temperature is controlled by manipulating the temperature of the cooling medium on the shell side of the reactor in the Aspen plug-flow reactor model. Physically this corresponds to adjusting the setpoint of a steam back-pressure controller and bringing in BFW to hold the liquid level on the shell of the reactor vessel.
6. The temperature of the gas leaving the condenser and going into the separator is controlled by manipulating the heat removal (cooling water) in the condenser.
7. A composition controller manipulates the control valve in the vent stream to maintain the composition of methane in the gas recycle.
8. A high-pressure override controller can also change the position of the control valve in the vent line if the separator pressure exceeds some specified value. A high selector determines which signal will position the vent valve. The setup and the need for this controller are discussed in Section 11.7.3.
9. The liquid level in the separator is controlled by manipulating the liquid flowrate from the separator into the flash tank.
10. The pressure in the flash tank is controlled by manipulating work in the Kflash compressor, which recycles the gas back to the reactor.
11. The liquid level in the flash tank is controlled by manipulating the liquid flowrate from the flash tank into the distillation column.
12. Base liquid level in the column is controlled by manipulating bottoms flowrate. This is the water product stream leaving the process.
13. Reflux-drum level is controlled by manipulating distillate flowrate. This is the methanol product stream leaving the process.
14. The reflux is ratioed to the feed to the column using a multiplier that adjusts the setpoint of a flow controller on the reflux. The feed flowrate is the other input to the multiplier.
15. Column pressure is controlled by manipulating condenser heat removal (cooling water).
16. The temperature on stage 35 is controlled by manipulating reboiler heat input (low-pressure steam).
17. The small vapor stream from the top of the reflux drum is flow-controlled by manipulating work in compressor K4.

Note that the throughput is set by the synthesis gas flowrate into the process, and inventory loops are in the direction of flow. Note also that the pressure in the system is *not*

controlled but floats up and down as throughput and synthesis gas composition change. Further discussions and the rationale for the important loops are given in Section 11.7.3.

11.7.2 Column Control Structure Selection

For reasons of simplicity and low maintenance cost, many industrial distillation columns use some type of single-end temperature control. However, this simple structure may not provide effective control for some columns. Even if a single-end control structure is possible, we have to decide how to select the other control degree of freedom. The most common choices are holding a constant reflux-to-feed (R/F) ratio or holding a constant reflux ratio (RR).

Selecting Reflux Ratio or Reflux-to-Feed Ratio. To explore this question, a series of steady-state runs are made in which the effects of changes in feed composition on the required changes in R/F ratio and RR are determined while holding both products at their specified compositions. Table 11.6 gives results of these calculations.

The required changes in the R/F ratio are only about 3% over the entire range of feed compositions from 86.5 to 76.5 mol% methanol. An appropriate change in the water feed composition is made as the methanol composition is varied. The required changes in the RR are much larger (about 16%). Therefore, from a steady-state standpoint, the R/F control structure should handle feed composition disturbances better than the RR control structure.

Selecting Temperature/Composition Control Tray Location. Another important issue in distillation control is the location of the tray with the temperature that is to be controlled in a single-end structure. There are many methods for making this selection, but a simple and effective approach is to select a tray where there are significant changes in temperature from tray to tray.

Figure 11.7a shows a large change in the temperature profile in the lower part of the column. Stage 35 is selected, which has a temperature of 101 °C. The controller parameters that result from relay-feedback testing are given in Table 11.7.

11.7.3 High-Pressure Override Controller

As the dynamic simulation results presented in the next section will demonstrate, there is no need for an override controller when disturbances in throughput occur. The design values of the composition of the synthesis gas provide the necessary balance between the carbon monoxide and carbon dioxide fed and the hydrogen fed so as to satisfy the stoichiometry of the two reactions. For 1 mol of carbon monoxide, 2 mol of hydrogen are required. For 1 mol of carbon dioxide, 3 mol of hydrogen are required.

TABLE 11.6 Column Control Structure Selection

		Reflux-to- Feed Ratio	Reflux Ratio
Design	0.86517 MeOH 0.12674 H ₂ O	0.3355	0.3771
	0.81517 MeOH 0.17674 H ₂ O	0.3297	0.4071
	0.76517 MeOH 0.22674 H ₂ O	0.3394	0.385

TABLE 11.7 Controller Parameters

	TCRX	TC1	CC Vent	High PC
Controlled variable	Reactor exit temperature	Stage 35 temperature	Recycle gas composition	Separator pressure
Manipulated variable	Steam temperature	Reboiler heat input	Signal to high selector on vent valve position	Signal to high selector on vent valve position
SP	267 °C	101 °C	0.258 mole fraction CH ₄	130 bar
Transmitter range	200–300 °C	50–150 °C	0–0.5 mole fraction CH ₄	120–140 bar
OP	264 °C	45.38 Gcal/h	14.77%	0%
OP range	200–300 °C	0–90.77 Gcal/h	0–100%	0–100%
Deadtime	2 min	1 min	3 min	–
K_C	0.456	1.37	5.0	5
τ_I	9.2 min	9.2 min	56 min	–

There are 2630 kmol/h of carbon monoxide in the synthesis gas that require 5260 kmol/h of hydrogen. There are 785.3 kmol/h of carbon dioxide in the synthesis gas that require 2356 kmol/h of hydrogen. Thus, the total hydrogen required to completely react all the carbon monoxide and carbon dioxide is 7616 kmol/h. The hydrogen in the synthesis gas feed is 7839 kmol/h, so there is a slight excess, which leaves the system in the vent stream along with the unreacted carbon monoxide and carbon dioxide.

If the synthesis gas composition changes such that this delicate stoichiometric balance no longer holds, the component(s) in excess will build up and pressure will increase in the system. Remember that the feed into the system is flow-controlled. Therefore, a strategy to handle this problem is required.

An override controller is a simple way to achieve this objective. The vent valve is air-to-open (fails shut). A high selector chooses between the higher of two signals. The first signal comes from the composition controller. This signal normally sets the vent valve position. The second signal comes from the high-pressure override controller, which has an output signal that only increases and takes over the vent valve when the separator pressure get above 120 bar. The override controller is proportional-only, with a gain of 5 and a normal output signal of 0%. As pressure changes from 120 to 140 bar, its output signal changes from 0 to 100%. At some pressure, this output will exceed the signal coming from the composition controller and begin opening the vent valve.

The synthesis gas composition disturbances discussed below demonstrate the effectiveness of the proposed control structure.

11.7.4 Dynamic Performance Results

Several large disturbances are made to test the ability of the proposed plantwide control structure. These disturbances include synthesis gas feed flowrate and synthesis gas composition (adding more inert methane or changing the relative amounts of the reactants).

Throughput Disturbances. Figure 11.9 gives results for 20% changes in the setpoint of the synthesis gas flow controller. The solid lines are 20% increases; the dashed lines are 20% decreases. The disturbances are made at 0.2 h.

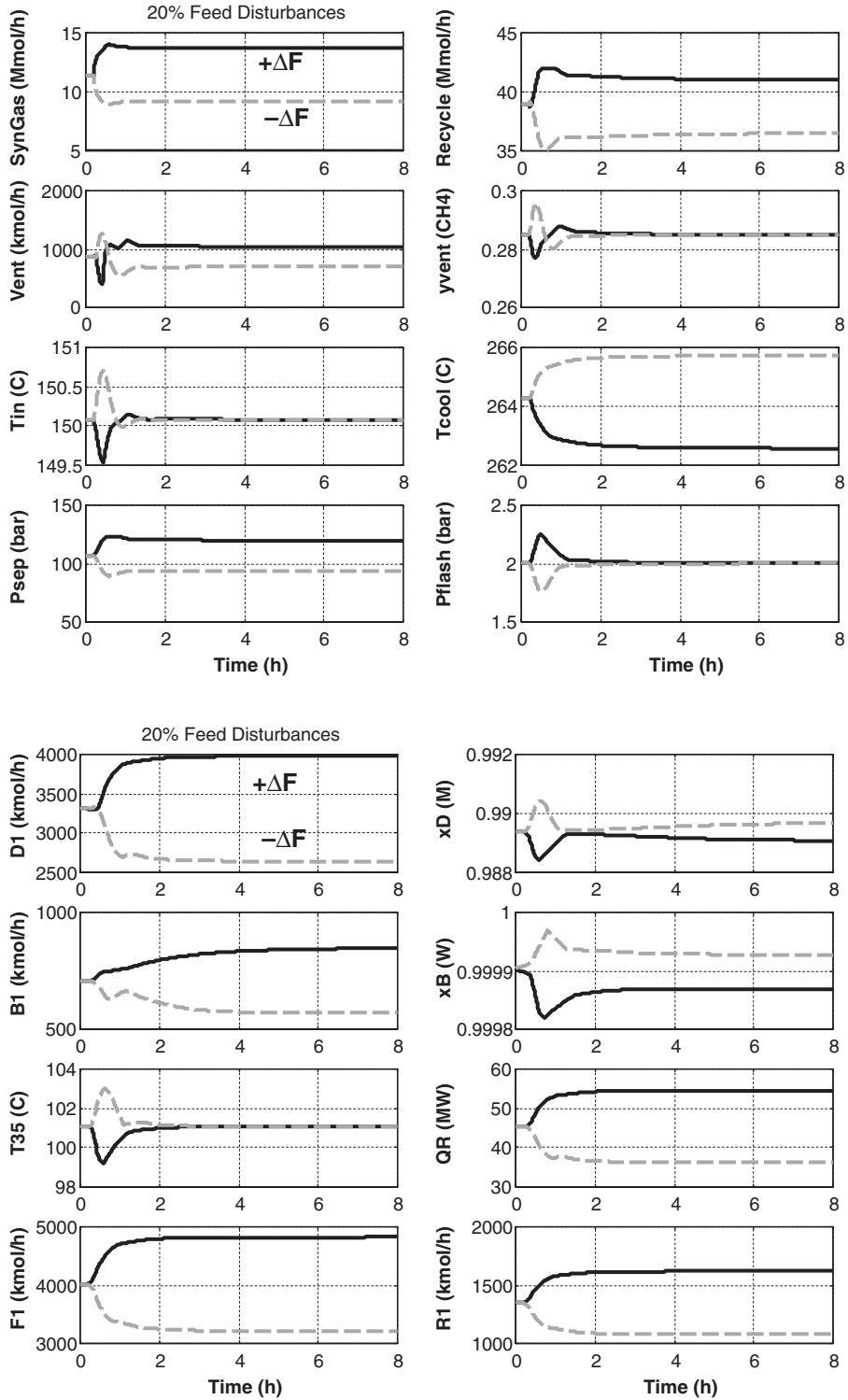


Figure 11.9. 20% feed flowrate disturbances.

Stable regulatory control is achieved. Notice that the pressure in the separator (P_{sep}) rises up to a new steady-state level for increases in throughput and drops to a lower level for decreases in throughput. The pressure in the gas loop (FEHE, preheater, reactor, and separator) is *not* controlled in this plantwide control structure, but varies with conditions in the reactor that affect reaction rates.

Recycle, distillate, and bottoms flowrates increase as throughput increases. The coolant temperature (T_{cool}) in the reactor decreases as throughput increases, so that the increased heat removal can be achieved by providing a larger differential temperature driving force.

Stage 35 temperature is well controlled by manipulating reboiler heat input (T35). The R/F ratio system changes the column reflux R1 as the feed to the column F1 changes.

Of primary importance, the compositions of the two products leaving the process are held quite close to their specified values. The distillate composition $x_{\text{D(M)}}$ and the bottoms water composition $x_{\text{B(W)}}$ remain near their specifications.

Methane Impurity in Synthesis Gas Feed. Figure 11.10 gives results for changes in the methane impurity in the synthesis gas. The design value of this inert impurity is 2.17 mol% methane. The design hydrogen feed composition is 67.46 mol% hydrogen. The solid lines show results for an increase in methane impurity to 3.17 mol% and an appropriate decrease in hydrogen composition to 66.46 mol%. The dashed lines show results for a decrease in methane impurity to 1.17 mol% and an appropriate increase in hydrogen composition to 68.46 mol%.

First, let us consider the effects of increasing the methane impurity in the synthesis gas. There is a substantial increase in the vent flowrate (Vent), which results in higher losses of the reactants. Consequently, less methanol D1 and water B1 are produced. The pressure in the system goes down (P_{sep}). Product purities are held close to their specifications.

Now consider the effects of decreasing the methane impurity in the synthesis gas. More products are made because the vent flowrate decreases, meaning smaller losses of reactants. Product purities are again held close to their specifications.

However, this disturbance shows the need for the high-pressure override controller. Notice that the recycle gas methane composition is *not* held at its setpoint (y_{vent}) but drifts downward. This occurs because the pressure in the gas loop P_{sep} starts to increase. When the pressure gets up to 120 bar, the override controller takes over and opens the vent valve to maintain system pressure.

Reactant Concentrations in Synthesis Gas Feed. Figure 11.11 also demonstrates the need for the override controller. The disturbances are changes in the carbon monoxide, carbon dioxide, and hydrogen compositions in the feed.

Carbon Monoxide to Carbon Dioxide Ratio. The solid line gives results for the case in which the feed contains more carbon dioxide and less carbon monoxide. Carbon dioxide is changed from 6.858 to 8.858 mol%. Carbon monoxide is changed from 22.97 to 20.97 mol%.

As expected, more water is produced (B1 increases), since there is more carbon dioxide. The amount of methanol produced (D1) decreases slightly because the vent rate increases from 872 to 939 kmol/h, so reactant losses increase. There is a slight drop in methanol purity.

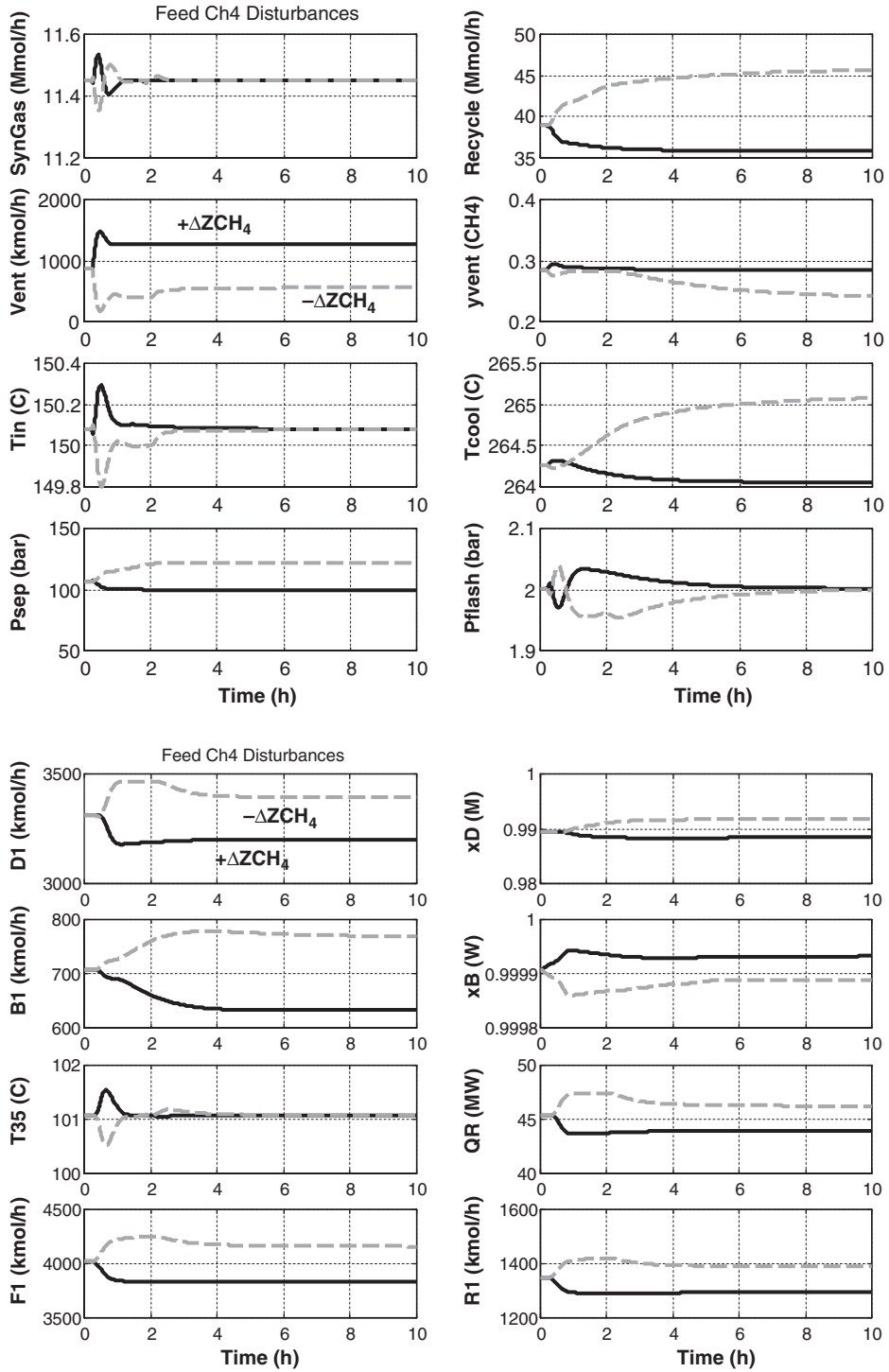


Figure 11.10. Feed methane composition disturbances.

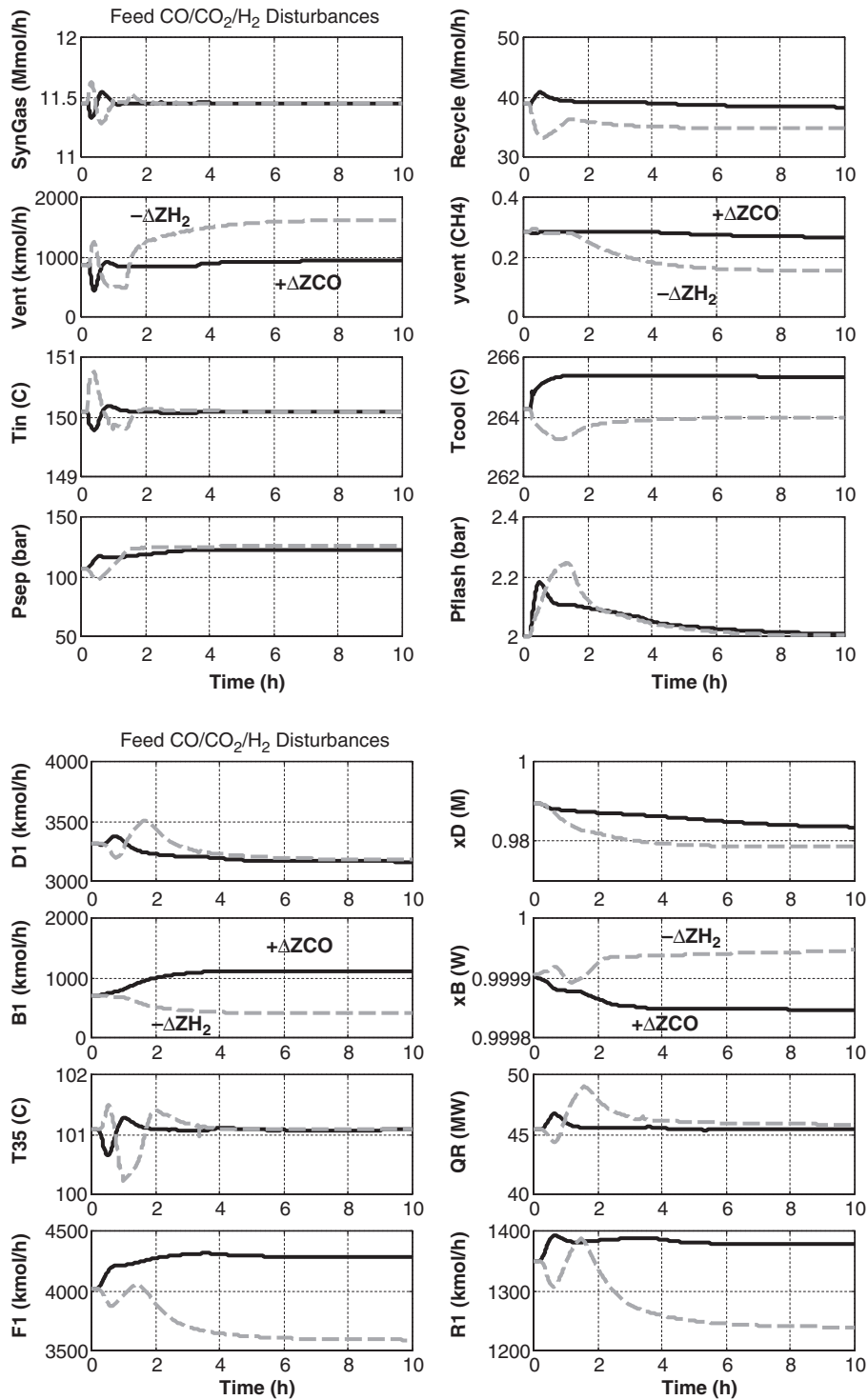


Figure 11.11. Feed hydrogen composition disturbances.

Pressure increases from 110 to 115.9 bar, so the override controller does not come into play for this disturbance. The vent methane composition controller is able to maintain the desired 28.5 mol% methane.

Since carbon dioxide consumes more hydrogen than carbon monoxide, the amount of hydrogen lost in the vent drops from 479 to 207 kmol/h for this disturbance. On the other hand, the amount of carbon dioxide lost increases from 69.8 to 206.9 kmol/h.

Hydrogen to Carbon Ratio. The dashed lines in Figure 11.11 give results when the synthesis gas composition is changed from 67.46 to 61.46 mol% hydrogen, 22.97 to 25.97 mol% carbon monoxide, and 6.86 to 9.86 mol% carbon dioxide. This disturbance increases the demand for hydrogen by feeding in more carbon monoxide and carbon dioxide, but provides less hydrogen.

The result is an initial drop in pressure (P_{sep}), as the hydrogen is consumed at a higher rate. However, it does not take long for the pressure to start increasing because the carbon monoxide and carbon dioxide are not being consumed due to the shortage of hydrogen. When the pressure builds up to 120 bar, the override controller take over the vent valve and removes gas from the system. The vent methane composition is not controlled and drops from 28.5 to 15.4 mol% methane.

The reactor pressure eventually levels out at 131 bar with a very large vent rate (1623 kmol/h). Large losses of reactants in the vent stream occur, so the production of methanol drops from 3311 to 3178 kmol/h. The water produced drops from 707 to 411 kmol/h. The loss of carbon dioxide in the vent climbs from 69.8 kmol/h to a whopping 673 kmol/h. The high reactor pressure requires a huge increase in the work of the Kflash compressor from 1.015 to 8.77 MW.

These results demonstrate the need to provide precise control of the synthesis gas feed by varying conditions in upstream units. For example, if the synthesis gas is being generated from coal in a gasifier, there will be a shortage of hydrogen since coal has a hydrogen-to-carbon ratio of about one. The synthesis gas is typically split into two streams. One is sent directly to the methanol plant. The other stream is sent to a water–gas shift reactor unit to produce more hydrogen and carbon dioxide from water and carbon monoxide. Then the carbon dioxide is removed from the gas, typically using amine scrubbing. The resulting hydrogen-rich stream is combined with the other synthesis gas stream, and the total is fed to the methanol process. The fraction of the synthesis gas fed to the water–gas shift unit must be precisely set, so that the methanol plant feed has the correct amount of hydrogen for reaction with the carbon dioxide and carbon monoxide it contains.

11.8 CONCLUSION

The methanol process presents some interesting design and control features. Design trade-offs exist between reactor pressure and feed compressor energy, between reactor size and recycle flowrate, between venting rate and reactant losses, and between flash pressure and flash compression energy.

The plantwide control structure has the unusual feature of permitting the pressure in the reactor to vary as conditions change. A high-pressure override controller is needed to handle imbalances in the stoichiometry of the reactants in the synthesis gas feed.

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