

Control of the Heterogeneous Azeotropic *n*-Butanol/Water Distillation System

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The interest in *n*-butanol as a biofuel has increased in recent years because of its superior fuel qualities compared to ethanol: higher octane number, lower heat of vaporization, higher energy density (energy/volume), and lower vapor pressure. However, the concentration of *n*-butanol coming from the fermenter is lower than that achieved in ethanol fermentation. In addition, acetone and ethanol are also produced. Recent studies to improve yield and increase *n*-butanol concentration have explored fed-batch systems with stripping, adsorption, liquid–liquid extraction, distillation, and/or pervaporation to recover products. The production of *n*-butanol involves removing the acetone and ethanol and separating the *n*-butanol from the water. This separation is made difficult by the presence of an azeotrope. Fortunately, unlike the homogeneous azeotrope found in the ethanol/water system, the *n*-butanol/water azeotrope is heterogeneous; thus, two liquid phases occur in the decanter. Therefore, a simple two-column distillation system can be used. This paper studies the control of the *n*-butanol/water azeotropic distillation system and develops a simple effective control structure that is capable of handling very large disturbances in throughput and feed composition. The control system is very robust and is demonstrated to be applicable for systems that are designed for a wide range of feed compositions.

1. Introduction

Industrial production of *n*-butanol from fermentation was developed almost a century ago (the ABE process) and was widely used in Europe and the United States until inexpensive petroleum made its production from petrochemical raw materials a less expensive process. The recent surge in crude-oil prices and issues of energy independence and carbon dioxide emissions have generated new interest in biofuels. Ethanol is now being produced on a fairly large scale for blending into gasoline. Qurishi et al.¹ discuss the advantages of *n*-butanol over ethanol: lower heat of vaporization, lower vapor pressure, higher octane number, and higher energy density (energy/volume). The last characteristic translates into more range for a given volume fuel tank on the vehicle.

However, the concentration of *n*-butanol produced in the batch fermenter is quite low (20 g/L) because of toxicity problems. In addition, acetone and ethanol are also produced, which must be removed from the mixture coming from the fermenter.

There are four isomers of butanol: *n*-butanol, iso-butanol, 2-butanol, and tert-butyl alcohol. The butanol produced in fermentation is *n*-butanol. Water and *n*-butanol form a heterogeneous azeotrope at atmospheric pressure and 364.6 K, with a composition of 76.33 mol % water. At 0.5 atm, the azeotropic composition is 76.45 mol % water, with a temperature of 347.7 K. The composition of the *aqueous* liquid phase is 97 mol % water, and the composition of the *organic* liquid phase is 58 mol % *n*-butanol.

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Table 1. Controller Tuning Parameters

	2 mol % butanol feed	10 mol % butanol feed	40 mol % butanol feed
TC1			
controlled variable	$T_9 = 352.8 \text{ K}$	$T_9 = 353.2 \text{ K}$	$T_9 = 353.2 \text{ K}$
manipulated variable	Q_{R1}	Q_{R1}	Q_{R1}
transmitter range (K)	300–400	300–400	300–400
controller output range (cal/s)	$0–1.52 \times 10^6$	$0–1.5 \times 10^6$	$0–0.6 \times 10^6$
K_c	0.55	1.35	2.28
τ_I (min)	10.6	6.6	10.6
TC2			
controlled variable	$T_8 = 386.7 \text{ K}$	$T_8 = 368.7 \text{ K}$	$T_8 = 368.7 \text{ K}$
manipulated variable	Q_{R2}	Q_{R2}	Q_{R2}
transmitter range (K)	300–400	300–400	300–400
controller output range (cal/s)	$0–1.26 \times 10^6$	$0–0.80 \times 10^6$	$0–3.0 \times 10^6$
K_c	1.60	0.76	1.19
τ_I (min)	9.2	10.6	7.9

Qurishi et al.,¹ Ladisch,² and Phillips and Humphrey³ discuss some of the issues concerning the separation of the fermenter products. Doherty and Malone⁴ indicate that a two-column distillation system in conjunction with a decanter can be used to separate the heterogeneous binary butanol/water azeotrope. Sticklmair and Fair⁵ discuss the separation of the ternary acetone/water/butanol system in a two-column system. Pucci et al.⁶ suggest that the ternary separation can be achieved in a single column, in which a side decanter is used to remove the water. The dynamics and control of these systems have not been considered in any of these references.

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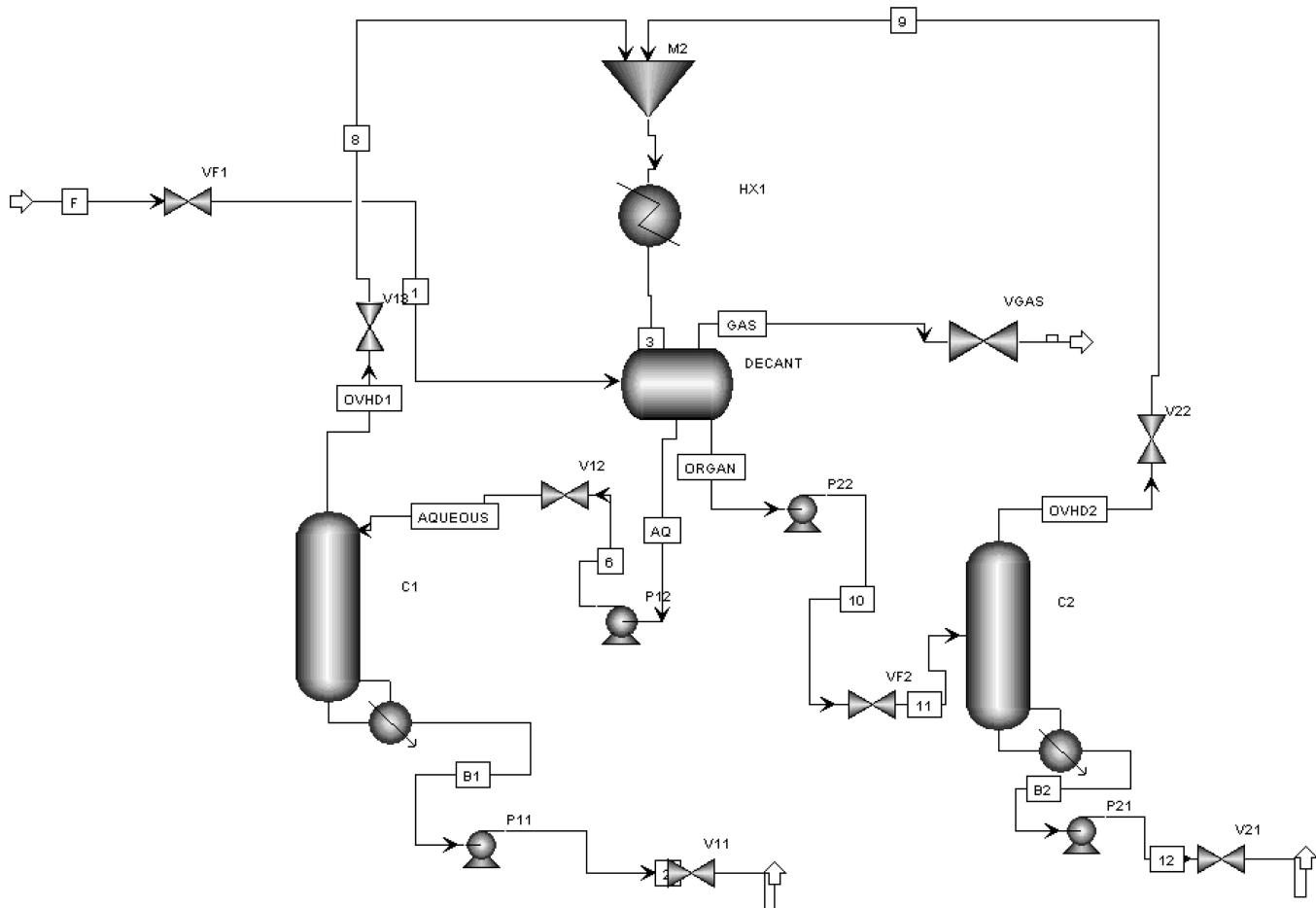


Figure 1. Aspen Plus process diagram.

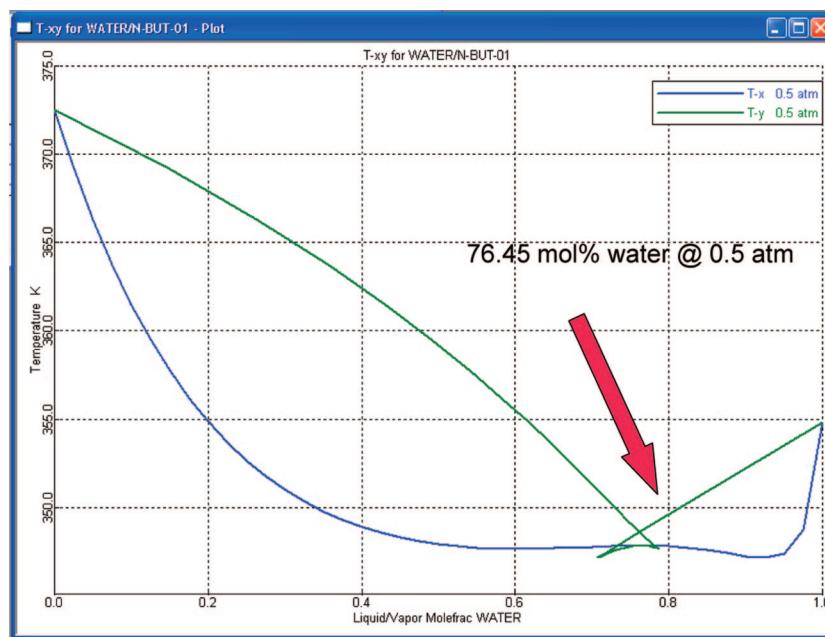


Figure 2. Txy diagram for butanol/water at 0.5 atm.

There are a number of papers that have looked at the control of other azeotropic systems. Pressure swing,^{7–11} light entrainers,^{12–22} and extractive distillation^{11,23–25} have been studied for a variety of chemical systems. The separations of ethane/water and isopropyl alcohol/water have been widely explored because of their industrial importance. However, other systems have also been studied: acetone/methanol, isobutane/methanol,

and acetic acid/water. No papers have been found that deal with the control of the binary heterogeneous *n*-butanol/water system. That is the purpose of this paper.

The two-column/decanter flowsheet suggested by Doherty and Malone⁴ is used. It should be noted that no third component needs to be added as a light entrainer or as a extracting solvent in the *n*-butanol/water binary separation. Several different

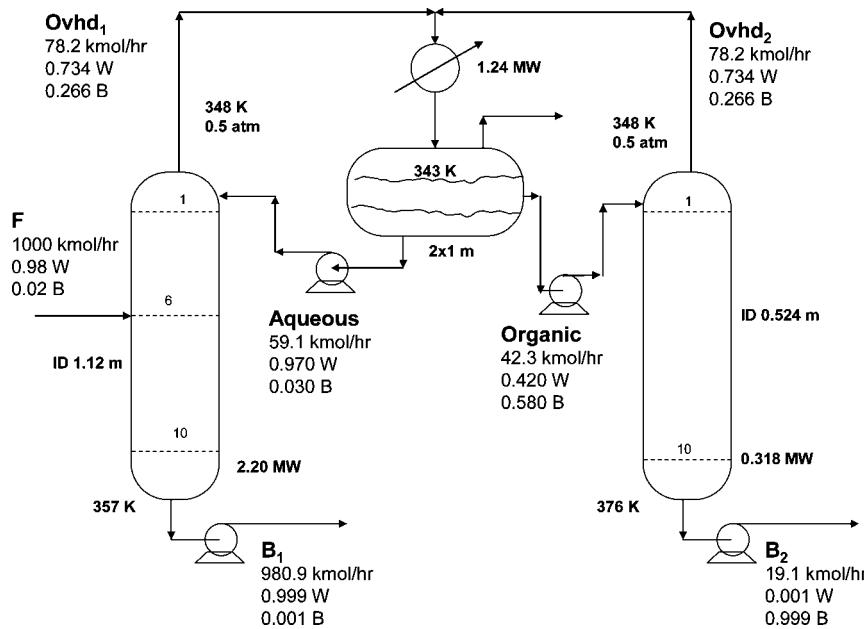


Figure 3. Butanol/water flowsheet for 3 mol % butanol feed.

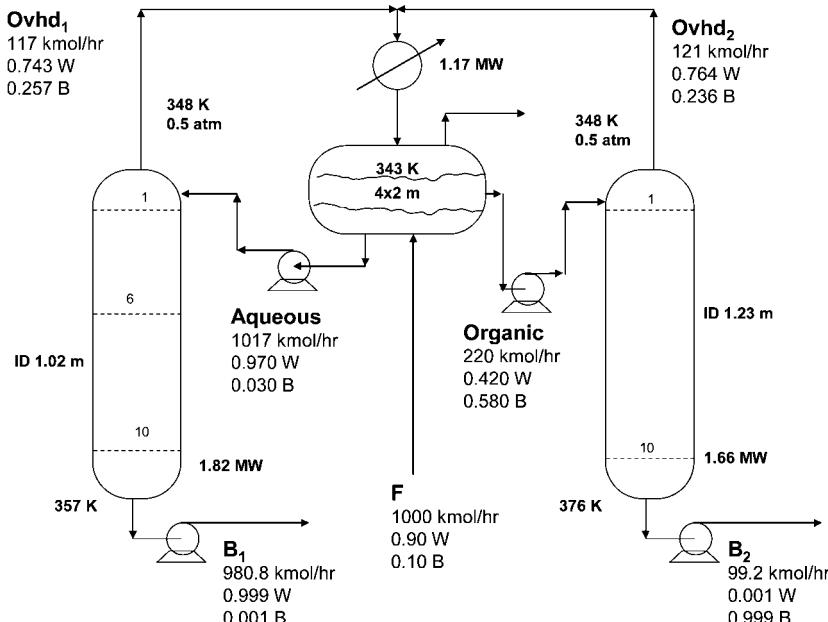


Figure 4. Butanol/water flowsheet for 10 mol % butanol feed.

designs are generated for feed compositions ranging from 2 mol % *n*-butanol to 40 mol % *n*-butanol, and a control structure is developed that provides effective control for all of these designs. Aspen Technology simulation software is used for steady-state and dynamic studies. The UNIQUAC physical property in Aspen Plus is used. The Aspen stage numbering convention is used, in which stages are numbered from the top down (reflux drum is stage 1). The design feed flow rate is 1000 kmol/h. Product purities are 99.9 mol %.

2. Steady-State Design

Figure 1 shows the Aspen Plus process flowsheet of the two-column system. Each column is a stripper with its individual reboiler. The bottom of the first column C1 is 99.9 mol % water. The bottom of the second column C2 is 99.9 mol % *n*-butanol. The overhead vapors from the two strippers are fed to a single condenser HX1. The compositions of the two vapor streams are almost the same, with values that are on opposite sides of the azeotropic composition.

Liquid from the condenser flows to a decanter, in which the aqueous and organic liquid phases separate. The aqueous phase is returned to the top of the first column. The organic phase is fed to the top of the second column.

The point where the feed is introduced depends upon its composition. For low butanol feed compositions (2 mol % *n*-butanol), feed is added on an intermediate tray in the first column. For high butanol feed compositions (10 mol % or greater), the feed is fed directly to the decanter.

The economics were explored by evaluating capital and energy costs. The design optimization variables are the number of trays in each column, pressure, and feed location. As the Txy diagram given in Figure 2 shows, the separation between the saturated liquid and saturated vapor curves are quite similar on both sides of the azeotrope. This means that the difficulty of separation is similar and suggests that the number of trays in both columns should be approximately the same. Making this assumption, the number of trays is varied from 20 down to 10. A 10-tray column is assumed to be a reasonable practical minimum size. The reboiler heat inputs actually decrease slightly as the number of trays is reduced, which

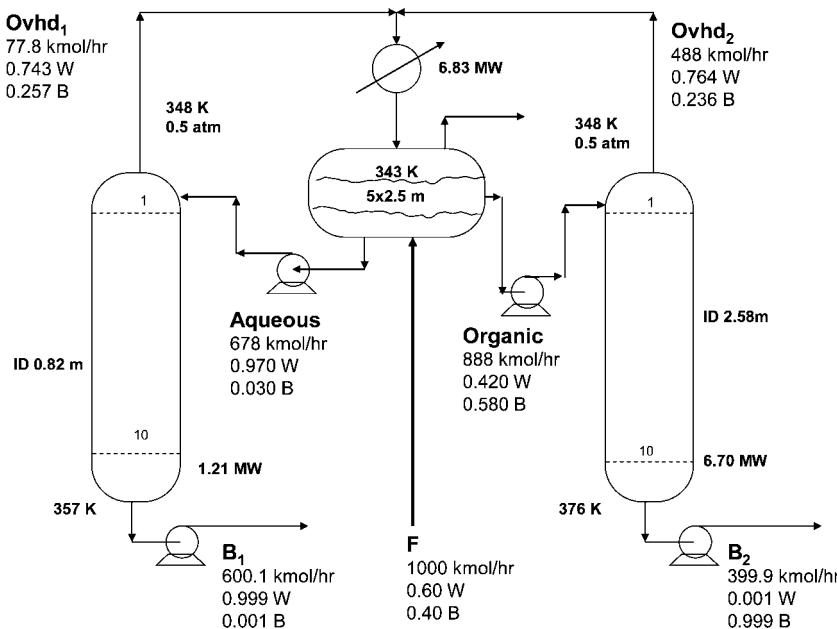


Figure 5. Butanol/water flowsheet for 40 mol % butanol feed.

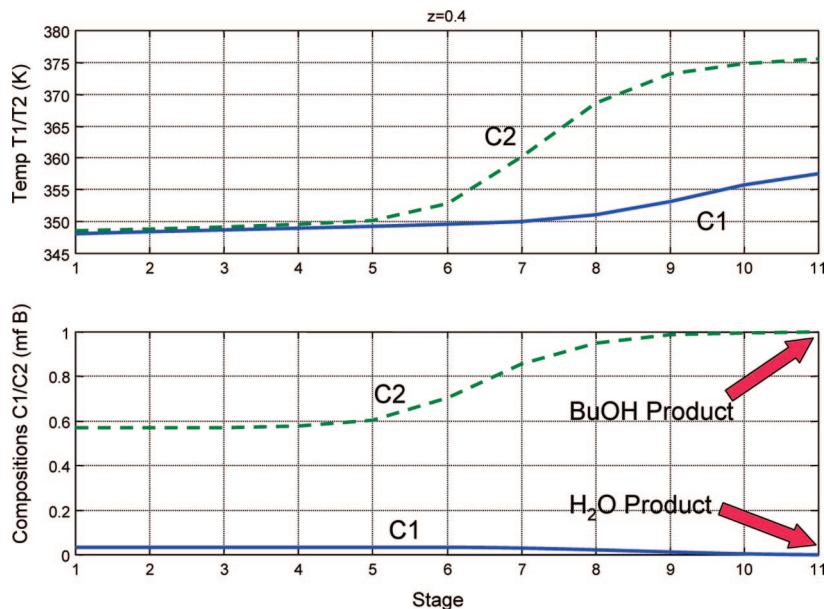


Figure 6. Temperature and composition profiles for 40 mol % case.

is counter-intuitive. For example, in the design for a 2 mol % butanol feed and an operating pressure of 0.5 atm, the reboiler energy requirements are $Q_{R1} = 2.237$ MW and $Q_{R2} = 0.3222$ MW when each column has 20 trays. When each column has 10 trays, the reboiler energy requirements are $Q_{R1} = 2.203$ MW and $Q_{R2} = 0.3183$ MW. On the other hand, the removal requirement in the overhead condenser Q_C increases from 1.215 MW with 20 trays to 1.243 MW with 10 trays. These small changes have little effect on the economics. Because the capital cost of the 10-tray column is lower, this design is selected.

Operating the columns at a pressure of 1 atm gives higher energy consumption: $Q_{R1} = 2.431$ MW and $Q_{R2} = 0.3257$ MW. The operation at 0.5 atm still permits the use of cooling water in the

condenser because the decanter temperature of 343 K is sufficiently higher than the available cooling water temperature.

The final designs for the different feed compositions are shown in Figures 3–5. As feed composition increases, the diameter of the first column decreases, the diameter of the second column increases, and the size of the decanter increases. Also, as feed

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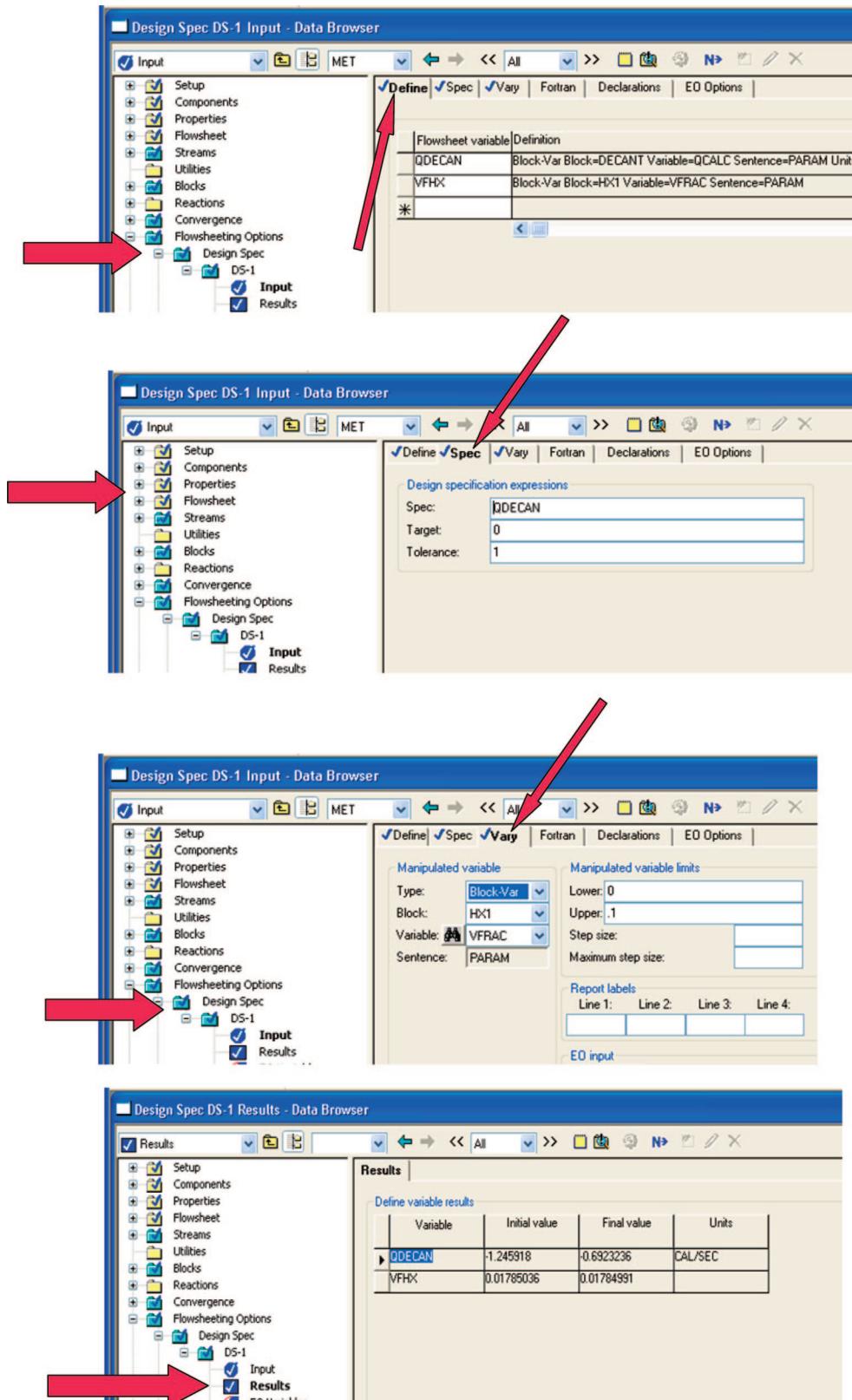


Figure 7. Design spec to achieve adiabatic decanter.

composition increases, the reboiler energy in the first column decreases, while the reboiler energy in the second column increases. Temperature and composition profiles in the two columns are quite similar in all cases. Figure 6 gives these profiles in both columns for a feed composition design of 40 mol % *n*-butanol.

The compositions of the two bottom products are fixed at 99.9 mol % purity of their respective component. The design spec/vary feature of Aspen Plus is used to hold these compositions by varying the flow rates of the two bottom product streams. Each column block uses one design spec/vary. A third design spec/vary (in *Flowsheeting Options*) is used to achieve an adiabatic decanter.

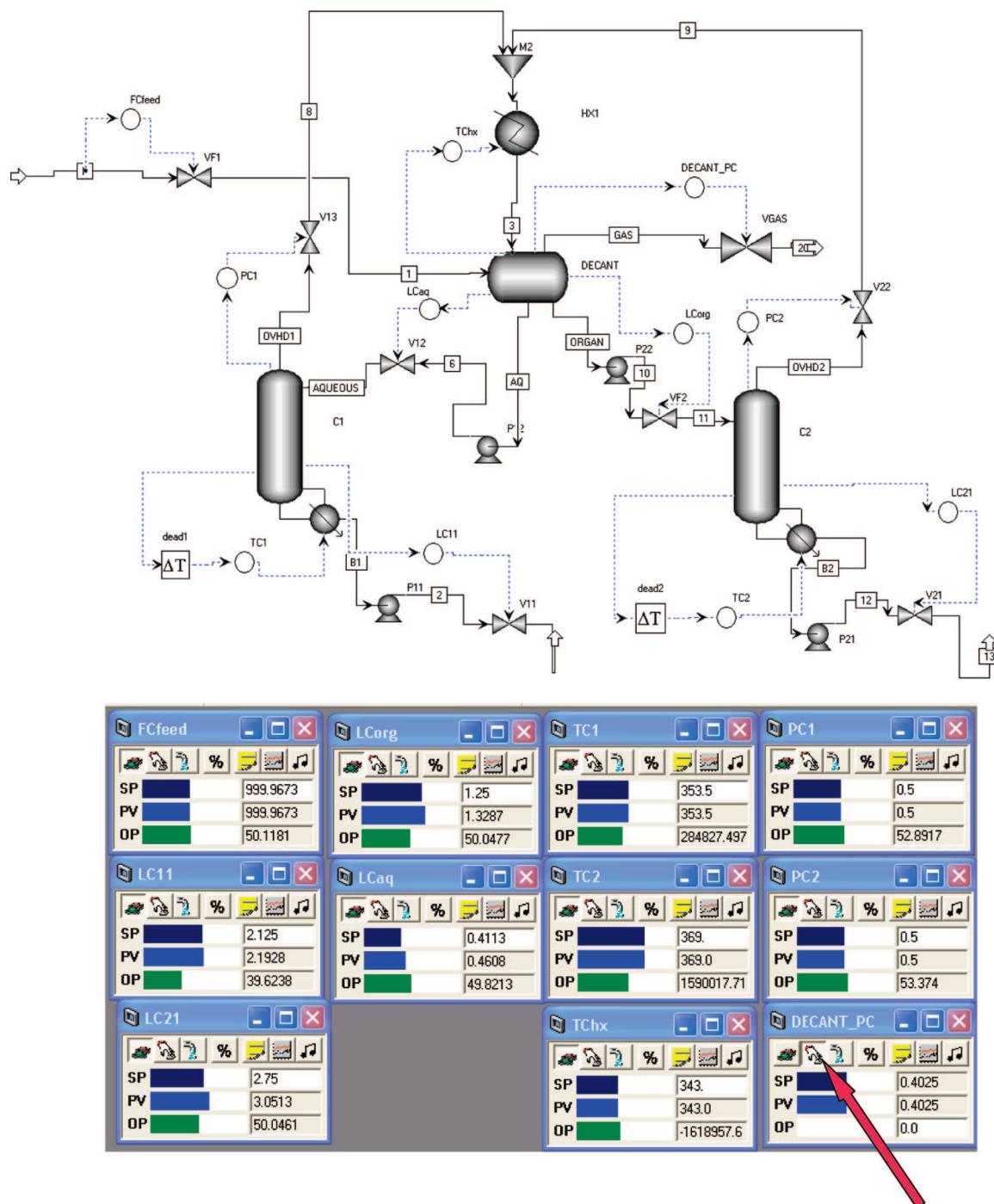


Figure 8. Control structure and controller face plates.

This is illustrated in Figure 7. The heat input in the decanter “QDECAN” is specified to be driven to zero by varying the vapor fraction “VFHX” in the condenser (~ 0.018).

One important feature of the flowsheet shown in Figure 1 is a vapor stream leaving the decanter. There are two liquid–liquid models available in Aspen Plus. The first is “DECANTER” that has only two liquid streams leaving the vessel. The second is “FLASH3” that has two liquid streams and a vapor stream. Both of these models work in the steady-state simulations conducted in Aspen Plus. However, in the dynamic simulations conducted in Aspen Dynamics, we found that the “FLASH3” model works well, but the “DECANTER” model predicted that the organic level steadily increased and could not be controlled. The reason for this problem is unclear.

The decanter model using “FLASH3” requires two specifications. The first is selected as pressure, and the second is specified to be

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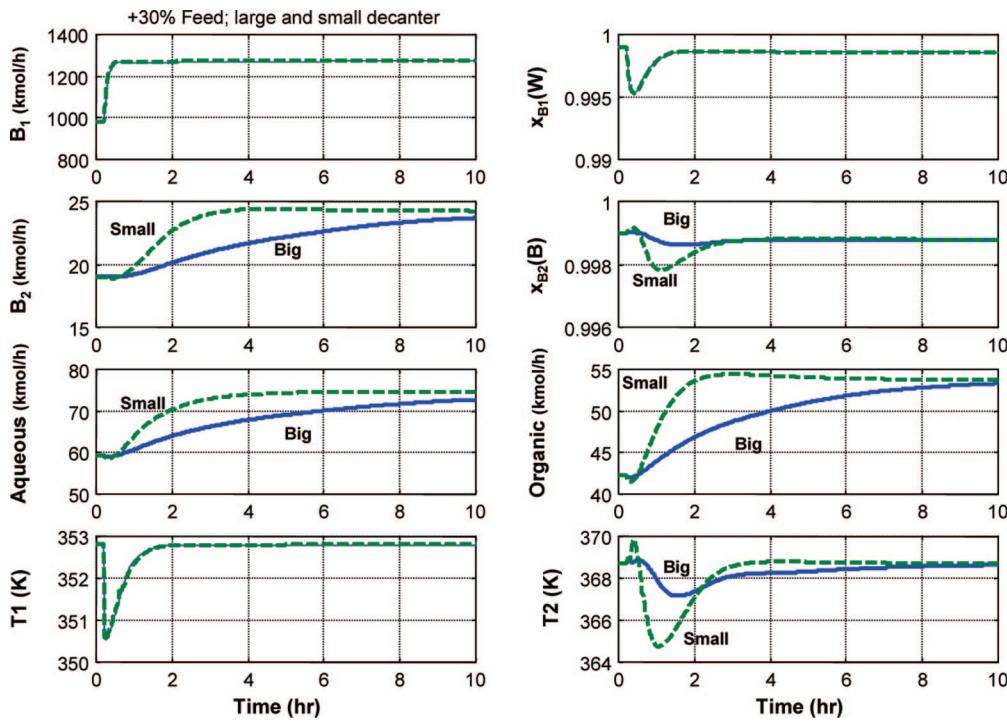


Figure 9. Effect of the decanter size.

a very small vapor fraction (0.0001). During the dynamic simulations, the control valve on the vapor stream is completely shut by putting the decanter pressure controller on manual and setting its output signal at 0%.

3. Dynamics and Control

Each of the three designs is exported to Aspen Dynamics after the volumes of the column bases and the decanter have been specified. A holdup time of 10 min in the bottom of each column is used. A holdup time of 20 min is used in the decanter. The effect of using larger decanter holdups is explored in the results given below. Control valves and pumps are sized to give the rangeability required to handle the large disturbance tested later in the dynamic simulations. If a valve becomes wide open, the appropriate pump work is increased²⁶ and a new steady-state is used for initial conditions. The resulting controller output signals under steady-state conditions are lower than the default

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value of 50% that is used to size the control valve in Aspen Plus for the given flow rate and pressure drop over the valve.

3.1. Control Structure. Figure 8 shows the control structure developed for this two-column/decanter system. Conventional PI controllers are used. The features of the loops are outlined below:

- (1) The feed is flow-controlled.
- (2) The pressure in each column is controlled by a valve in its overhead vapor line.
- (3) The base level of each column is controlled by manipulating the bottom flow rate.
- (4) The temperature of one tray in each column is controlled by manipulating the reboiler heat input in that column.
- (5) The aqueous interface in the decanter is controlled by manipulating the flow rate of the aqueous stream to the top tray of the first column.
- (6) The organic level in the decanter is controlled by manipulating the flow rate of the organic stream to the top tray of the second column.
- (7) The temperature of the decanter is controlled by manipulating the heat removal in the condenser.
- (8) The pressure controller on the decanter is on manual with the vapor valve shut.

All level controllers are proportional only with a gain of 2. The trays selected for temperature control are located near the bottom of the columns where the temperatures are changing the most rapidly from tray to tray (see Figure 6). A 1 min deadtime is inserted in each temperature loop. Relay-feedback tests and Tyreus–Luyben tuning are used to obtain controller tuning parameters in the column temperature loops. Table 1 gives tuning constants for the three design cases. Controller face plates are shown at the bottom of Figure 8.

3.2. Results. To test the effectiveness of this control structure for each of the cases, disturbances in feed flow rate and feed composition are made. In Figure 9, the effect of using different size decanters is illustrated. The design is for the 2 mol % *n*-butanol feed. Results for the normal 20 min decanter are the dashed lines. Results for a decanter with twice the holdup are

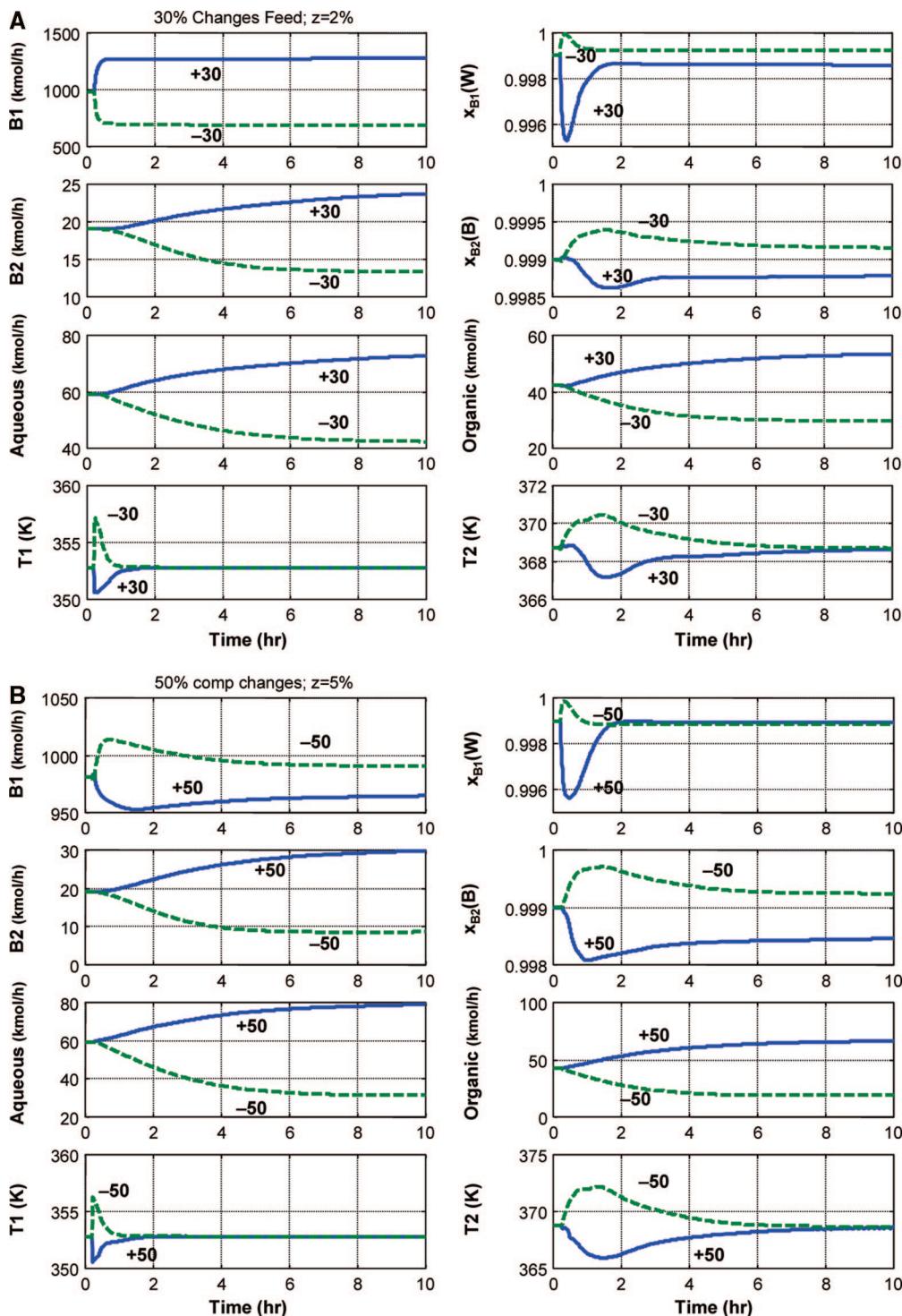


Figure 10. (A) 30% changes in feed flow rate for 2 mol % case. (B) 50% changes in feed composition for 2 mol % case.

the solid lines. The disturbance is a large 30% increase in feed flow rate. The large decanter reduces the transient peak change in the composition of the *n*-butanol product $x_{B2(B)}$ from the base of the second column. This occurs because the flow rate of the feed to this column, the organic stream, does not change as quickly and the temperature controller can hold tray temperature closer to the desired value.

Figure 10 give results for the 4 mol % butane feed case, with a 20 min holdup decanter. In Figure 10A, the disturbances are very large, with 30% changes in feed flow rate. The solid lines are for a 30% increase at time equal 0.2 h. The dashed lines

are for a 30% decrease. Stable regulatory control is achieved. The compositions of the two product streams ($x_{B1(W)}$) and $x_{B2(B)}$) are held quite close to the desired values. Notice that the stream leaving the bottom of the first column undergoes a larger transient deviation than the deviation seen in the bottom of the second column. This occurs because the first column sees a step change in feed flow rate because the feed is introduced into this column for the 2 mol % feed composition case. The second column sees a more gradual change in the flow rate of the stream entering the column (the organic). The use of a steam/feed ratio system in the first column would help to reduce this transient

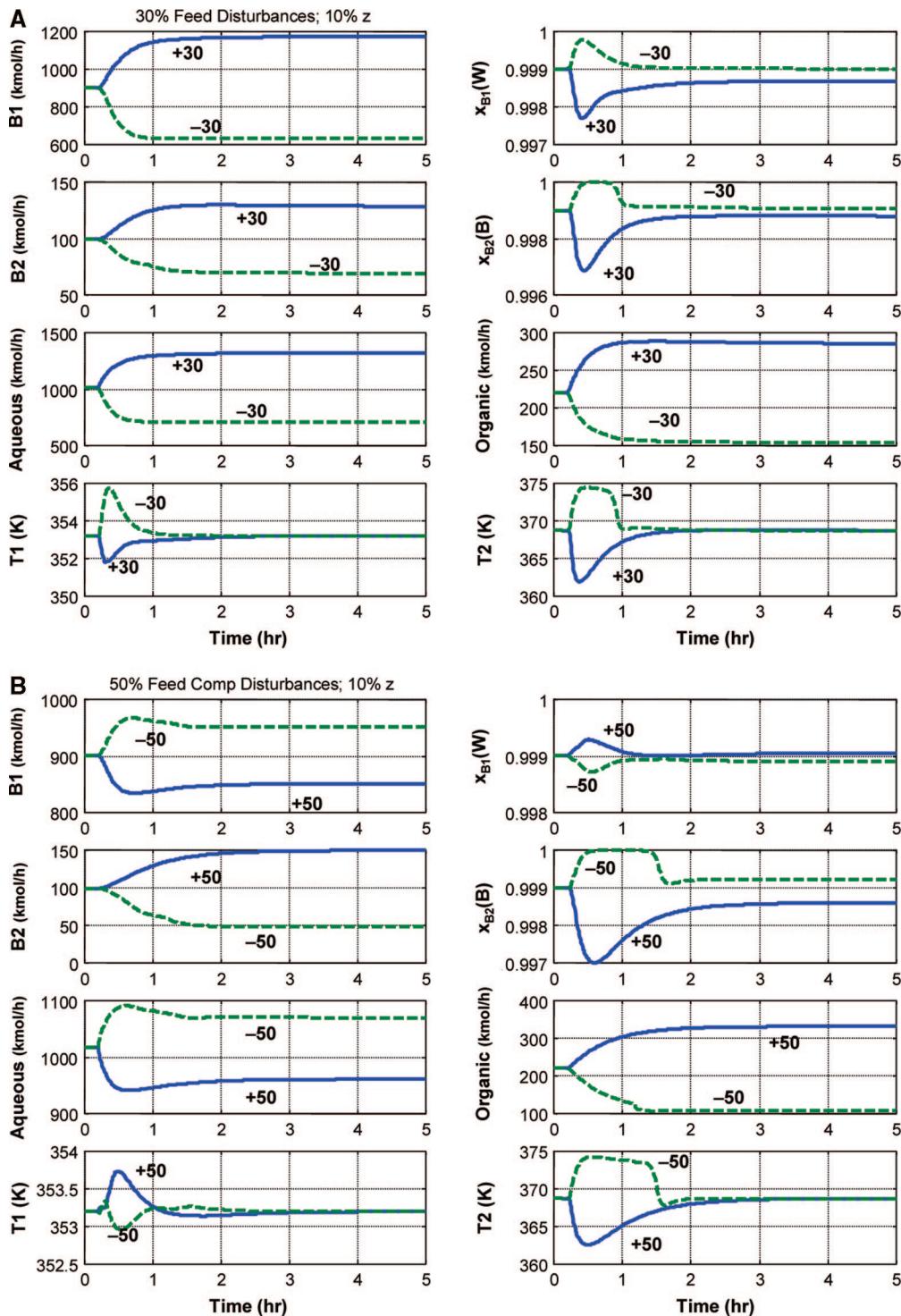


Figure 11. (A) 30% changes in feed flow rate for 10 mol % case. (B) 50% changes in feed composition for 10 mol % case.

deviation. Notice that it takes almost 10 h for this system to come to its new steady state.

Figure 10B shows results for very large 50% feed composition disturbances. The solid lines are for a step change at 0.2 h from 2 to 3 mol %. The dashed lines are for a step change from 2 to 1 mol %. Stable regulatory control is achieved, and product purities are held close to the desired value. The increase in *n*-butanol in the feed causes a transient drop in the purity of the water product stream from the bottom of the first column $x_{B2(W)}$ down to about 99.6 mol %, but the composition returns to 99.9 mol % in about 2 h. There is a

small offset in the purity of the *n*-butanol stream from the bottom of the second column.

Similar dynamic results are observed in Figures 11 and 12 for the other cases. Figure 11 gives results for the 10 mol % case, and Figure 12 gives results for the 40 mol % case. Notice that the time scale is smaller for these cases. Transients die out in about 2 h. Notice also that the transient deviations in $x_{B1(W)}$ for feed flow rate disturbances are smaller than those seen in the 2 mol % case. This occurs because the feed is entering the decanter and not the column. The column sees a more gradual disturbance in the aqueous stream instead of a step change.

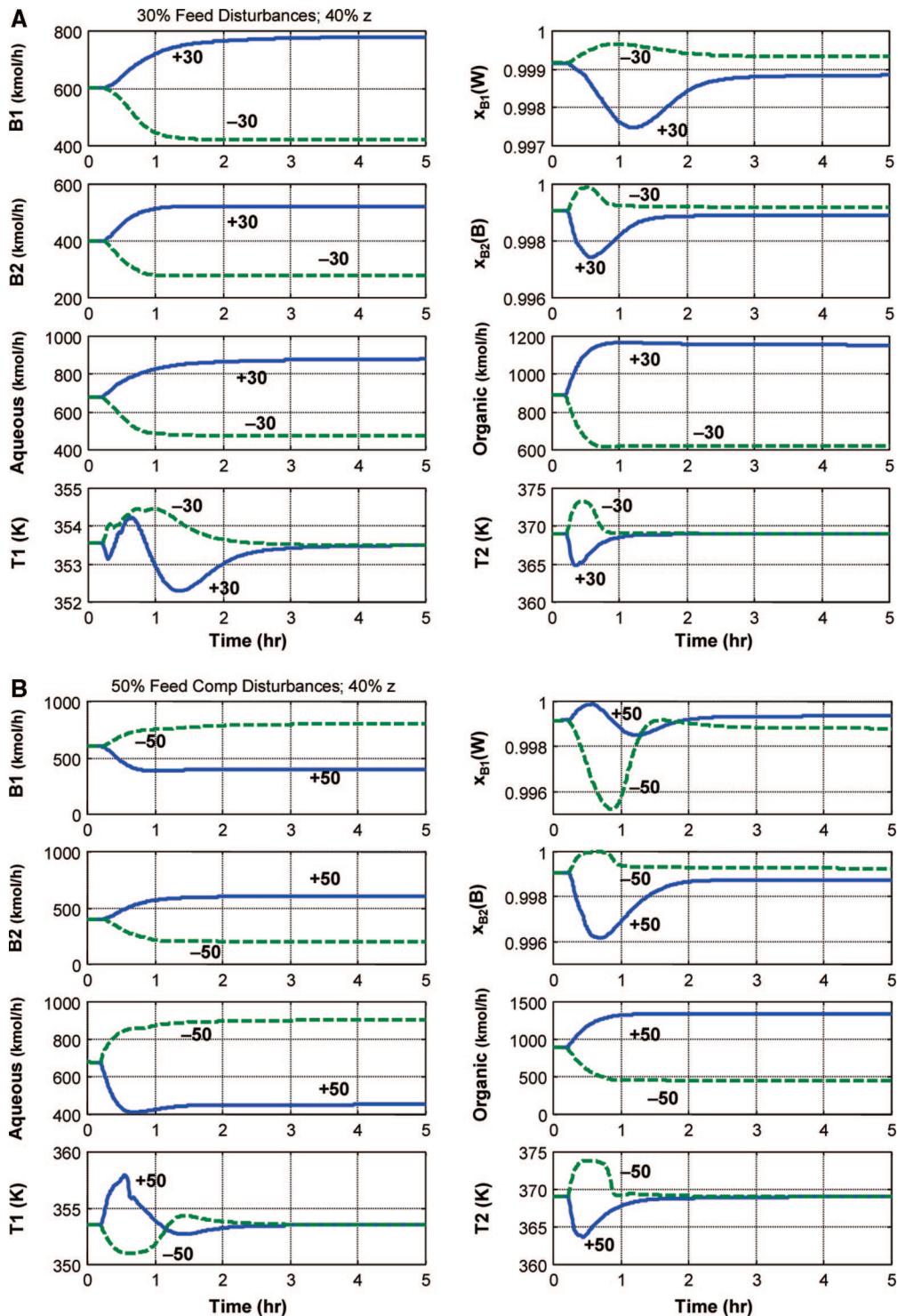


Figure 12. (A) 30% changes in feed flow rate for 40 mol % case. (B) 50% changes in feed composition for 40 mol % case.

The 40 mol % case has somewhat slower dynamics than the 10 mol % case and exhibits more sensitivity to disturbances in feed composition. The peak deviations in product purities are larger.

4. Conclusion

A simple control structure has been developed and demonstrated to be remarkably robust for the separation of the binary

heterogeneous azeotropic *n*-butanol/water system. The process configuration consists of two stripping columns, a decanter and a single condenser. A tray temperature is controlled in each column. Very large disturbances in feed flow rate and feed composition are effectively handled, with product compositions maintained close to the desired values.