# Control of the Maximum-Boiling Acetone/Chloroform Azeotropic Distillation System

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The literature contains a number of papers that study the control of azeotropic distillation systems. Both homogeneous and heterogeneous azeotropes have been considered, but all of the systems considered in these control papers deal only with minimum-boiling azeotropes. These azeotropes are caused by molecular *repulsion* between different types of chemical components and are more common than systems in which molecular *attractions* occur that result in maximum-boiling azeotropes. There appears to be no papers that study the control of this type of azeotropic system. This paper explores the design and control of the maximum-boiling azeotropic acetone/chloroform distillation system. The normal boiling points of the two pure components are 329.4 and 334.3 K, while the azeotropic boils at 337.6 K at 1 atm with a composition of 34.09 mol % acetone. A two-column extractive distillation process is used with dimethyl sulfoxide as the solvent. The two components are separated into 99.5 mol % pure products leaving in the distillate streams from two distillation columns. The solvent flowrate that minimizes total energy consumption is determined. A control structure that is capable of handling very large disturbances in throughput and feed composition is developed. The control of two tray temperatures in the extractive column is found to be necessary to handle feed composition disturbances.

## 1. Introduction

Many textbooks discuss azeotropic distillation systems[1,2] from the standpoint of steady-state design. Control structures for many of these systems have been presented in a number of papers. Design and control of the THF/water system was presented in one of the earliest papers[3] using pressure-swing distillation and was recently revisited[4] to explore the effect of heat-integration on controllability. The methanol/pentane system has been studied using pressure-swing distillation[5] and extractive distillation.[6] The acetone/methanol system has been studied[7,8] using both pressure-swing and extractive distillation.

The ethanol/water system is probably the most widely studied azeotropic system. Several types of light entrainers have been used to produce a heterogeneous ternary azeotrope so that a decanter can be employed to cross the distillation boundaries. A control study[9] with benzene as the entrainers has appeared. Control of the isopropanol/water system has been the subject of a number of papers by Chien and co-workers[10–15] using cyclohexane as an entrainer. A plantwide control study[16] of the same system used an ethylene glycol entrainer. Control of the minimum-boiling heterogeneous butanol/water has recently been studied.[17] Chien et al.[18–22] considered the water/acetic acid system, which does not form an azeotrope but has a severe pinch that makes conventional distillation very energy and capital intensive. Adding an entrainer to form a heterogeneous azeotrope produces a less expensive process.

The azeotropes studied in all these papers are minimum-boiling, either homogeneous or heterogeneous. There appears to be no papers that explore the control of maximum-boiling azeotropes. That is the primary purpose of this paper. The specific system selected as an example is acetone/chloroform. Uniquac physical properties are used in the Aspen simulations.

## 2. Acetone/Chloroform System

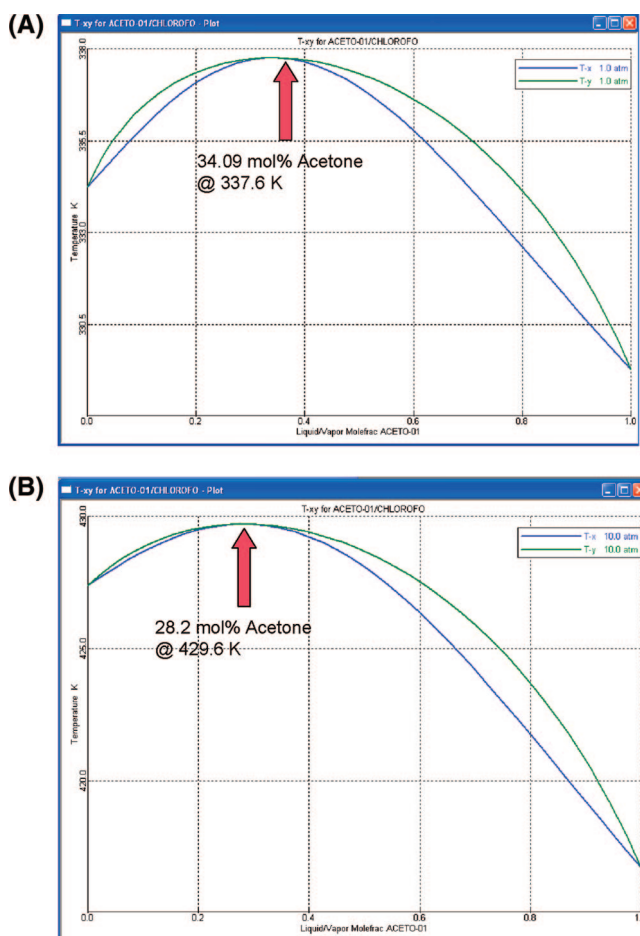Acetone and chloroform have very similar boiling points (329.4 and 334.3 K), despite having molecular weights that are



**Figure 1.** (A) *Txy* diagram at 1 atm for acetone/chloroform; (B) *Txy* diagram at 10 atm for acetone/chloroform.

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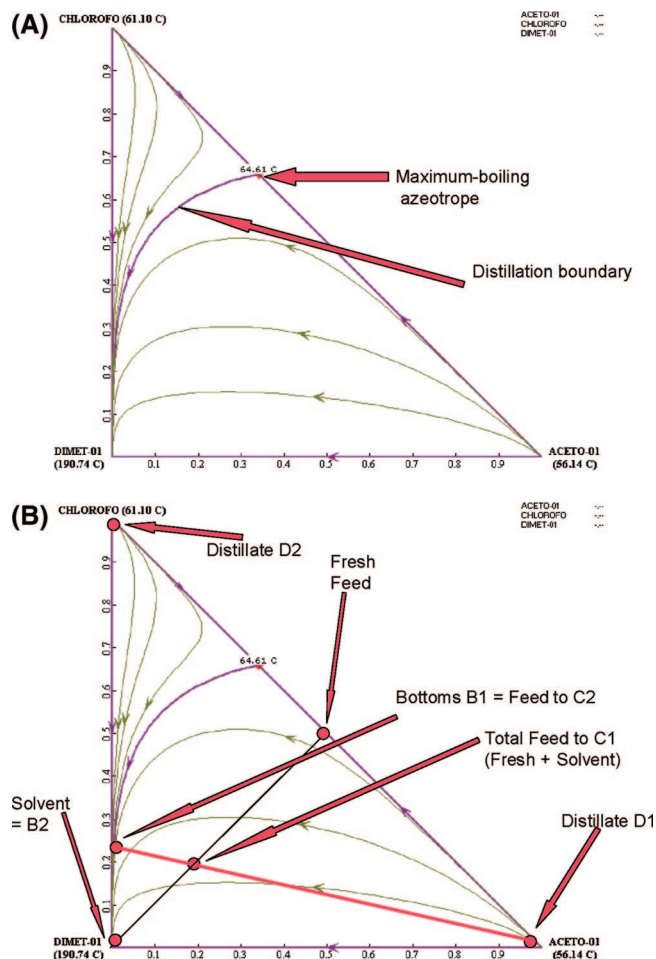
**Figure 2.** (A) Ternary diagram for acetone/chloroform/DMSO; (B) feed, product, and solvent points.

considerably different (58.08 and 117.4 kg/kmol). These molecules have an attraction for each other, which results in a maximum-boiling azeotrope. Figure 1 gives *Txy* diagrams for the system at two different pressures. At 1 atm the azeotropic composition is 34.09 mol % acetone and the temperature is 337.6 K. Note that this is higher than the boiling point temperature of either pure component.

These diagrams show that the effect of pressure on the azeotrope is small, so we would expect pressure-swing distillation to be unattractive. This would be the case for minimum-boiling azeotropes because the circulating streams are the distillates of the two columns that must be vaporized, which translates into high energy consumption, large heat exchangers, and large diameter columns. However, in the maximum-boiling case, the circulating streams are the bottoms of the two columns. The distillate streams are the two product streams. The large recycle streams are liquids that do not have to be vaporized. Therefore, if the azeotrope is maximum boiling, a pressure-swing system may be feasible despite having relatively small changes in the azeotropic composition with pressure. This inherent difference between minimum-boiling and maximum-boiling systems could be quite significant in terms of flowsheet selection. Investigation of a pressure-swing distillation process for acetone/chloroform indicated that columns with a large number of trays and high reflux ratios are required because of the very small relative volatilities between the two components on both sides of the azeotrope. However, extractive distillation was found to be effective for this separation.

## 3. Steady-State Design

Several solvents were explored using Aspen Plus simulations (water, chlorobenzene, ethylene glycol, and xylene), but the only one found that achieved the desired separation was dimethyl sulfoxide (DMSO). The ternary diagram for the acetone/chloroform/DMSO system is given in Figure 2A. There is a distillation boundary that separates the diagram into two regions. Notice that the residue curves follow paths that start at either of the light components (acetone or chloroform) and move to the heavy component (DMSO).

In the extractive distillation column, the solvent is essentially pure DMSO and is fed in the upper part of the extractive column. The fresh feed mixture of acetone and chloroform is fed lower in the column. The total feed point shown in Figure 2B corresponds to a fresh feed flowrate of 100 kmol/hr of 50 mol % acetone and 50 mol % chloroform with a solvent flowrate of 164 kmol/hr of DMSO. The ternary diagram shows that a distillate of quite pure acetone can be produced from the top of the extractive column, and the bottoms product will contain very small amounts of acetone. The bottoms stream is essentially a
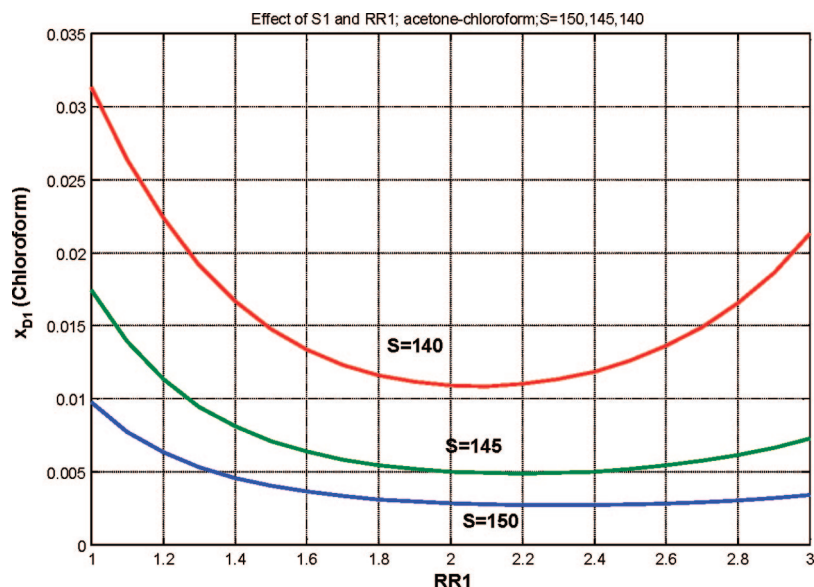


**Figure 3.** Effect of reflux ratio and solvent on chloroform impurity in acetone product.
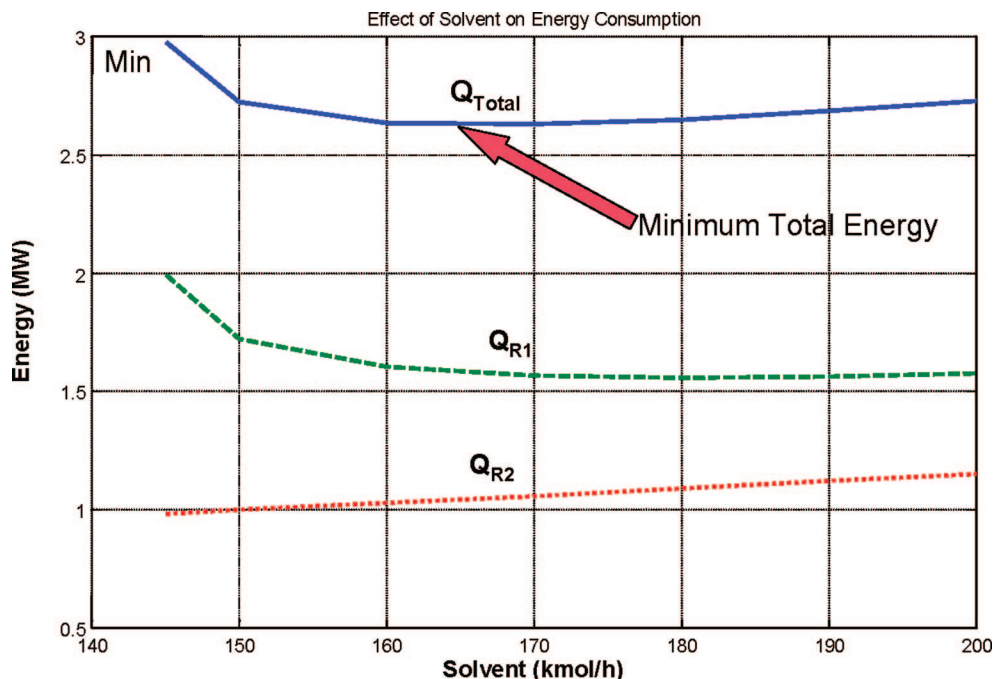
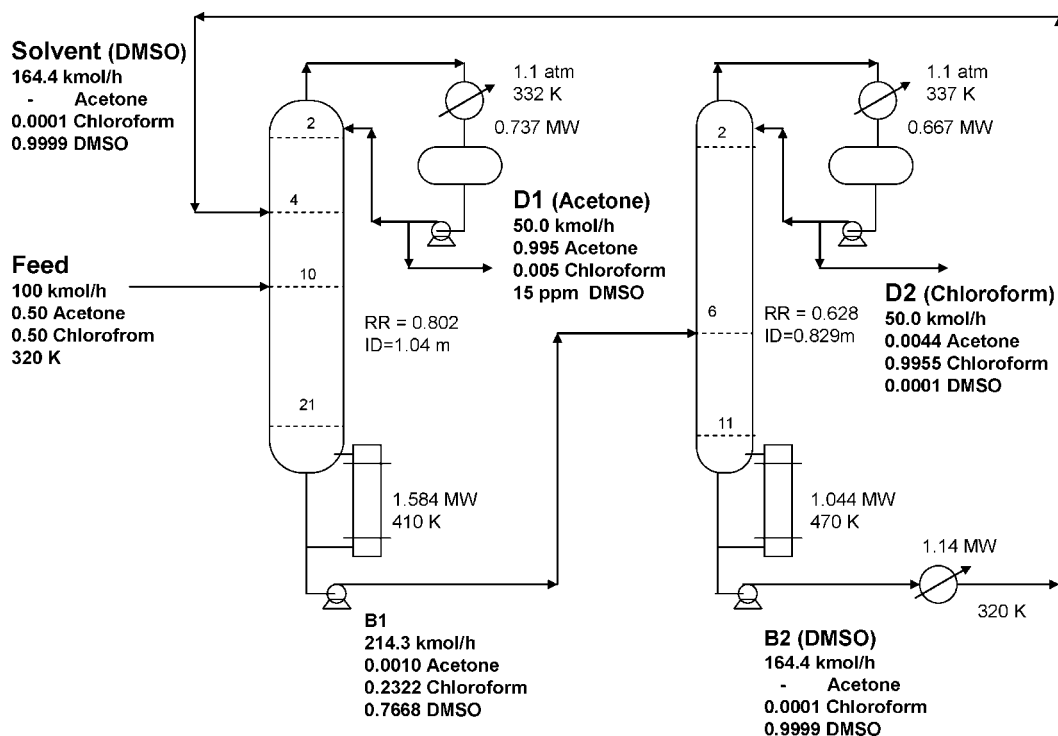**Figure 4.** Minimum energy consumption.



**Figure 5.** Extractive distillation; acetone/chloroform/DMSO; $S = 164.4$.

binary mixture of chloroform and DMSO that can be easily separated in a recovery column. The chloroform goes overhead in the distillate and the DMSO leaves in the bottoms, which is recycled back to the extractive column.

It may seem confusing that the feed point of the recovery column (the bottoms B1 from the first column) is slightly outside the region in which the distillate D2 and bottoms B2 points lie in the ternary diagram (Figure 2B). This is physically possible because the distillation boundary is curved. Therefore the feed point can lie outside the region in which the two product streams are located.

The extractive column has several design degrees of freedom. In addition to the number of trays and fresh feed and solvent feed tray locations, the amount of solvent and the reflux ratio can be varied to achieve the desired purities of the distillate and bottoms streams while minimizing energy consumption. A 22-stage extractive column is used in this study since adding more trays was found to have little effect on the amount of solvent required and the energy consumed. The fresh feed is introduced on Stage 10, and the solvent on Stage 4 (using Aspen tray numbering with the reflux drum Stage 1). A 12-stage solvent recovery column is used that is fed on Stage 6. These feed
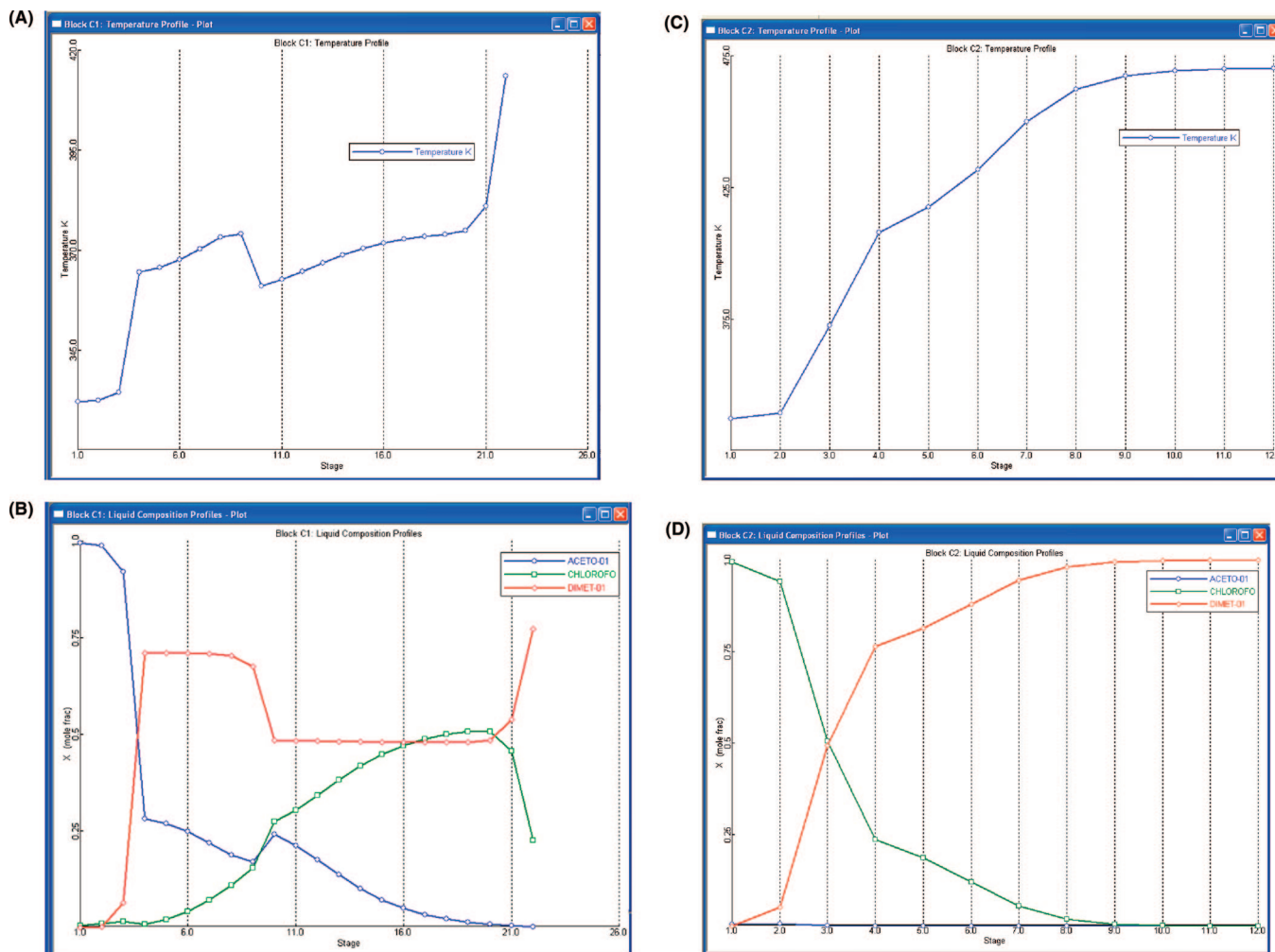
**Figure 6.** (A) Temperature profile in extractive column; (B) composition profiles in extractive column; (C) temperature profile in solvent recovery column; (D) composition profiles in solvent recovery column.

locations were found empirically by observing their effects on reboiler energy consumptions.

The separation in the extractive column depends on the amount of solvent circulating around the system. Figure 3 shows that high solvent flowrates reduce the impurity of chloroform in the distillate acetone product. For each solvent flowrate, there is a nonmonotonic effect of reflux ratio. To achieve the desired distillate purity of 99.5 mol % acetone, the minimum solvent flowrate is 145 kmol/hr (solvent-to-feed ratio of 1.45). These results are obtained with the impurity of acetone in the bottoms held at 0.1 mol % acetone using the design spec/vary feature of Aspen Plus and manipulating distillate flowrate.

The optimum solvent flowrate is found by determining the minimum total energy required in the reboilers of the two columns ($Q_{R1}$ and $Q_{R2}$), using four design spec/vary specifications. In the extractive column, the distillate impurity is held at 0.5 mol % chloroform and the bottoms impurity is held at 0.1 mol % acetone by varying distillate flowrate $D_1$ and reflux ratio $RR_1$. In the solvent recovery column, the distillate impurity is held at 0.01 mol % DMSO and the bottoms impurity is held at 0.01 mol % chloroform by varying distillate flowrate $D_2$ and reflux ratio $RR_2$. Figure 4 shows that the reboiler duty in the extractive column $Q_{R1}$ decreases as solvent flowrate increases, but the reboiler duty in the solvent recovery column $Q_{R2}$ increases. The solvent flowrate that minimizes total energy consumption is 164 kmol/hr.

Figure 5 gives the flowsheet with stream conditions, heat duties, reflux ratios, and column diameters. Both columns operate at 1.1 atm. Reflux drum temperatures are 332 and 337 K, which permit the use of cooling water in the condensers. The reflux ratios are fairly small (0.802 and 0.628), which indicates that the separations are not difficult and columns with relatively few trays are required. Notice that a heat exchanger is installed to cool the solvent from the bottom of the solvent recovery column before introducing it into the extractive column. Figure 6 gives temperature and composition profiles for the two columns.

## 4. Dynamics and Control

Several alternative control structures were investigated. Figure 7A shows one control structure CS1, which handled feed rate disturbances fairly well but did not maintain product purities for feed composition changes. A second control structure is developed later in this section that handles both types of disturbances effectively.

**4.1. CS1 Structure.** The features of control structure CS1 shown in Figure 7A are listed below. All controllers have conventional PI action except level controllers, which are proportional only.

1.  Feed is flow controlled.
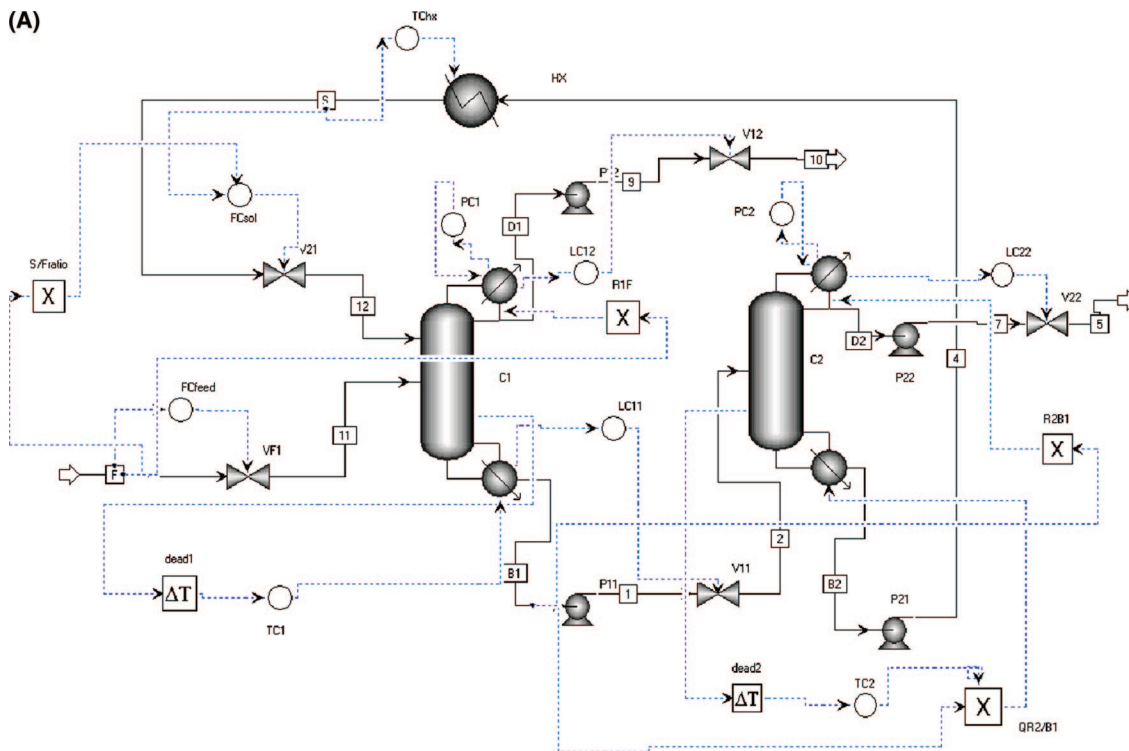2.  Solvent is ratioed to feed.

**(A)**



**(B)**



**Figure 7.** (A) Control structure CS1; (B) controller faceplates.

**Table 1. Controller Tuning Parameters**

|  | CS1 | CS2 |
|---|---|---|
| | Extractive Column C1 | |
| controlled variable | $T_{13} = 334.2$ K | $T_{13} = 334.2$ K |
| manipulated variable | $Q_{R1}$ | $R/F$ |
| transmitter range | 300–400 K | 300–400 K |
| controller output range | 0 to $0.824 \times 10^6$ cal/sec | 0 to $1.5 \times 10^6$ cal/sec |
| $K_c$ | 5.4 | 1.35 |
| $\tau_I$ | 7.9 min | 6.6 min |
| controlled variable | | $T_{115} = 369.6$ K |
| manipulated variable | | $Q_{R1}/F$ |
| transmitter range | | 300–400 K |
| controller output range | | 0–0.1 |
| $K_c$ | | 2.0 |
| $\tau_I$ | | 9.2 |
| | Solvent Recovery Column C2 | |
| controlled variable | $T_{23} = 372.6$ K | $T_{2AVG} = 372.6$ K |
| manipulated variable | $Q_{R2}/B1$ | $Q_{R2}/B1$ |
| transmitter range | 300–500 K | 300–500 K |
| controller output range | 0–0.04 | 0 to $0.80 \times 10^6$ cal/sec |
| $K_c$ | 0.12 | 0.76 |
| $\tau_I$ | 21 min | 21 min |

3. Reflux flowrate in each column is ratioed to its feed flowrate. In the extractive column the ratio is $R1/F$. In the solvent recovery column the ratio is $R2/B1$.

4. Reflux drum level in each column is controlled by manipulating distillate.

5. Base level in the extractive column is controlled by manipulating bottoms.

6. Base level in the solvent recovery column is not controlled because the solvent losses are almost negligible. A periodic addition of fresh solvent would be required to make up for these very small losses, but this would not be part of the basic regulatory control structure.

7. Pressure in each column is controlled by manipulating condenser heat removal.

8. The temperature of the solvent entering the extraction column is controlled by manipulating heat removal in the cooler.

9. Reboiler heat input in the solvent recovery column is ratioed to the feed to the column (stream B1).
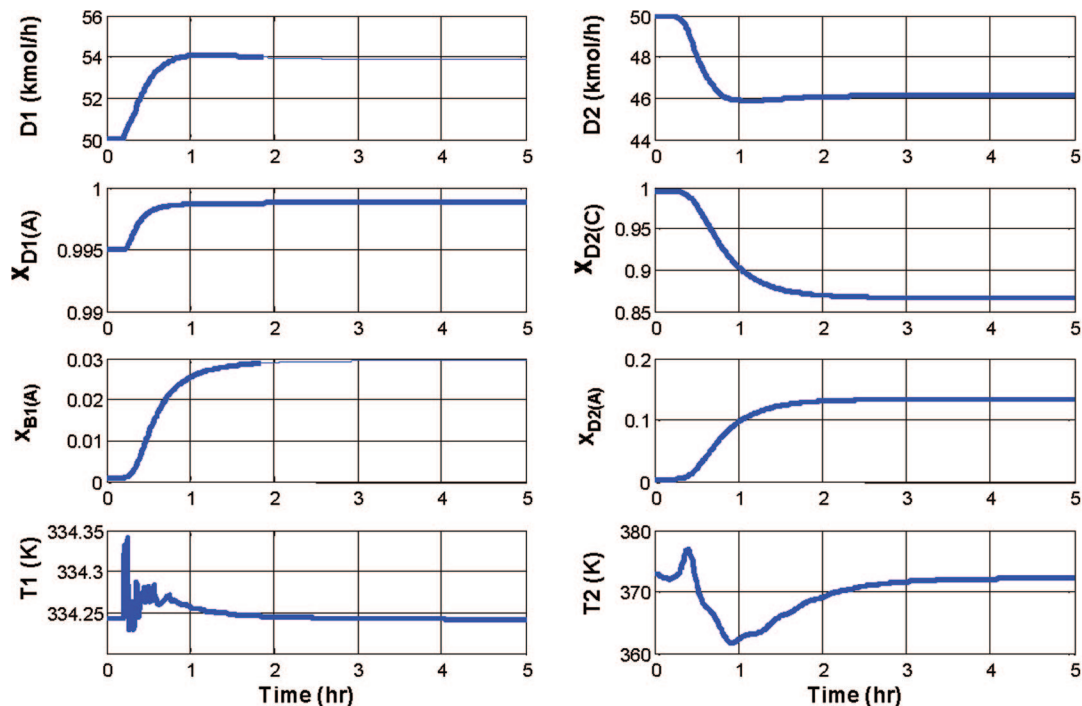
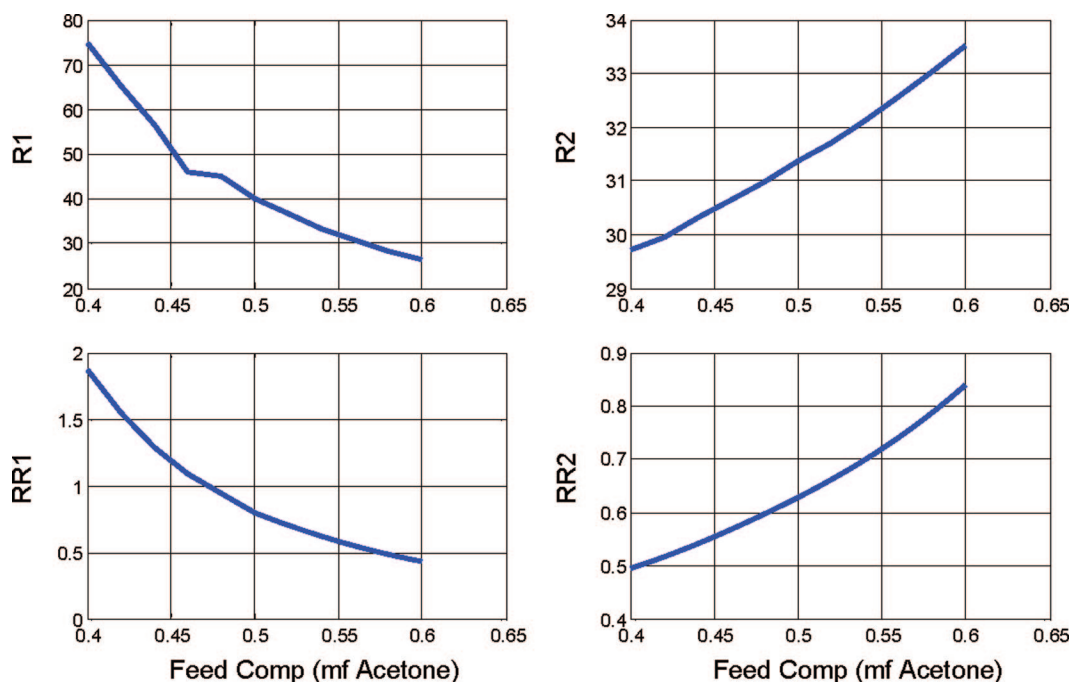**Figure 8.** CS1; feed composition 50 to 60 mol% acetone.



**Figure 9.** Effect of feed composition on required $R$ and RR.

10. A temperature in the extractive column is controlled by manipulating reboiler heat input.

11. A temperature in the solvent recovery column is controlled by manipulating the ratio of the reboiler heat input to the feed to the column.

Since both product streams are the distillates from the two columns, conventional process control wisdom suggests that a tray temperature near the top of each column should be selected in order to hold product purities. As shown in Figure 6A, holding Stage 3 temperature at 334 K in the extractive column should maintain acetone purity $x_{D1(A)}$ of the distillate $D_1$. Figure 6C shows the holding Stage 3 temperature at 372 K in the solvent recovery column should maintain chloroform purity $x_{D2(C)}$ of

the distillate $D_2$. Notice that there is a very large temperature difference between the top and bottom of the solvent recovery column (337 to 470 K). The implications of this on temperature control are considered later in this paper. Deadtimes of 1 min are inserted in each temperature loop. Relay-feedback tests and Tyreus−Luyben tuning are used to find the temperature controller tuning constants given in Table 1.

Notice in the controller faceplates shown Figure 7B that the "$F_{Csol}$" controller is on "cascade" with its setpoint coming from the multiplier "$S/F_{ratio}$". The output signal from the "$T_{C1}$" controller is the reboiler heat input in the extractive column. The output signal from the "$T_{C2}$" controller is the ratio of reboiler
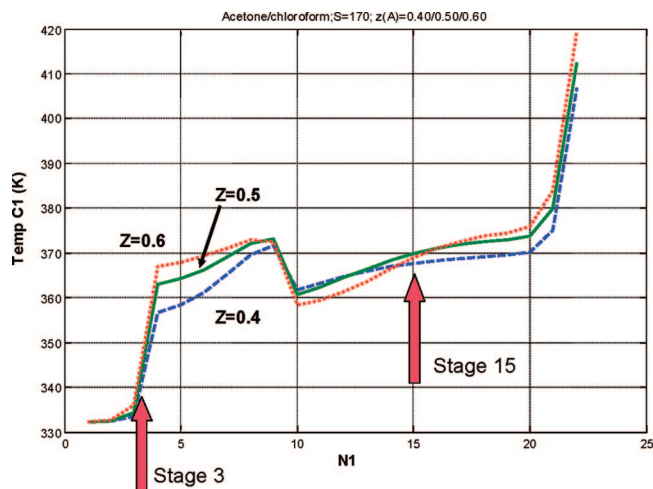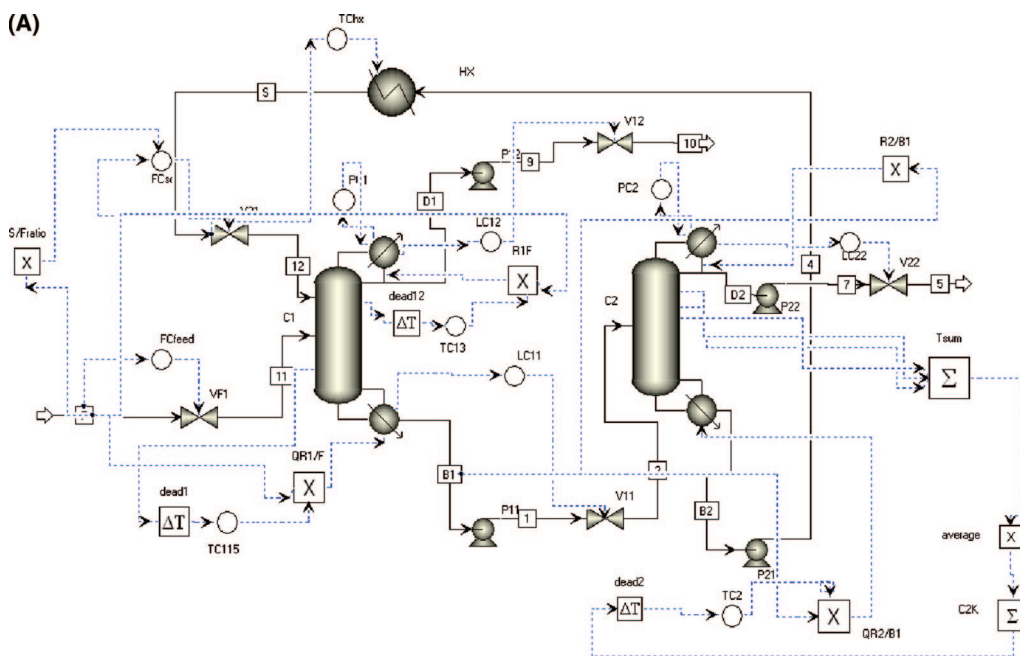
**Figure 10.** Temperature profiles for feed composition changes.

heat input in the solvent recovery column to the feed to the column "$Q_{R2}$/B1".

This control structure handled feed flowrate changes fairly well. However, as Figure 8 shows, the response of the system

for a feed composition disturbance is very poor. At time equals 0.2 h, the feed composition is changed from 50/50 molar ratio of acetone to chloroform to a 60/40 ratio. The temperatures on Stage 3 in both columns are controlled. The purity $x_{D1(A)}$ of the acetone product distillate stream from the extractive column increases, but the purity $x_{D2(C)}$ of the chloroform product distillate stream from the solvent recovery column drops drastically from 99.5 to 86 mol % chloroform. This occurs because acetone drops out the bottom of the extractive column. The bottoms composition in the extractive column climbs to $x_{B1(A)} = 3$ mol % acetone, and all of this acetone goes overhead in the solvent recovery column.

Holding a single temperature constant near the top of the extractive column maintains acetone product purity, but it does not prevent acetone from moving down the column and appearing in the chloroform product from the solvent recovery column. We need to find a control structure that keeps chloroform from leaving out of the top and acetone from leaving out of the bottom. This implies a dual composition or dual temperature control structure.



**Figure 11.** (A) Control structure CS2; (B) controller faceplates.

**Figure 12.** Setting up average temperature control in solvent recovery column.

fore a control structure that holds a constant reflux ratio or a constant reflux-to-feed ratio cannot maintain product purities in the face of feed composition changes.

The required changes in the solvent recovery column are fairly large but not excessive. The changes in the reflux $R2$ are only about 10% over the range of feed compositions from 40 to 60 mol % acetone. This suggests that a reflux-to-feed ratio scheme with one temperature controller should be effective in the solvent recovery column.

However, in the extractive column the required changes in both reflux and reflux ratio are very large, changing by a factor of 3 over the range of feed compositions from 40 to 60 mol % acetone. Therefore the control structure must be able to adjust these variables, which suggests that a dual temperature structure is required in this column.

The next issue is to decide what two temperatures to control. Figure 10 illustrates one approach to answering this question. The temperature profiles in the extractive column are plotted for feed compositions of 40, 50, and 60 mol % acetone when the products are all held at their specified values. If there are locations where temperatures do not change much as feed composition changes, these tray locations are candidates for temperature control. Figure 10 indicates that Stage 3 and Stage 15 in the extractive column satisfy this criterion.

**4.3. CS2 Control Structure.** Figure 11 shows the second control structure developed. It differs from the CS1 structure shown in Figure 7 in the following ways. The rest of the loops are unchanged.

1. The temperature on Stage 3 in the extractive column is controlled by manipulating the reflux-to-feed ratio.
2. The temperature on Stage 15 in the extractive column is controlled by manipulating the reboiler heat input-to-feed ratio.
3. An average temperature in the solvent recovery column is calculated using Stages 3, 4, and 5. This becomes the process variable in the temperature controller "$T_{C2}$" that changes the reboiler heat input-to-feed ratio.

An average temperature is used in the solvent recovery column because of the large temperature gradient in this column.[23] Using multiple temperatures is an effective method

The alternative of selecting the control tray in the stripping section was evaluated and found to be ineffective because the purity of the distillate was not maintained.

**4.2. Analysis for Dual Temperature Control.** To understand why the CS1 control structure fails for feed composition disturbances, a series of runs are made using steady-state simulations in Aspen Plus. Feed composition is varied from its design value of 50 mol % acetone. The distillate and bottoms compositions are held constant in both columns at their desired values by using four design spec/vary features. The resulting values of reflux flowrate and reflux ratio for each column are plotted in Figure 9. It is clear that all of these variables have to change significantly as feed composition changes in order to maintain product purities. There-
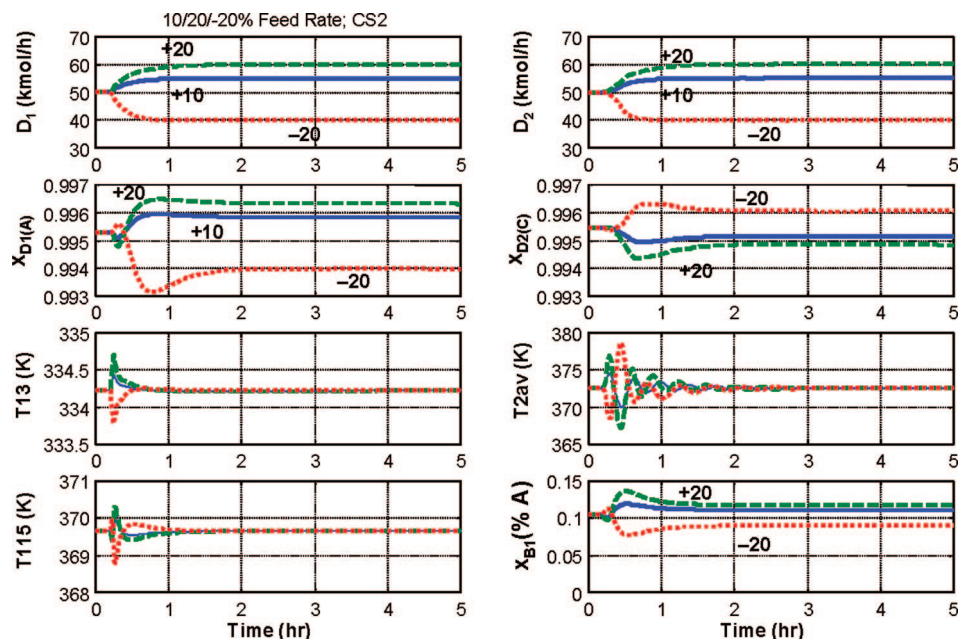


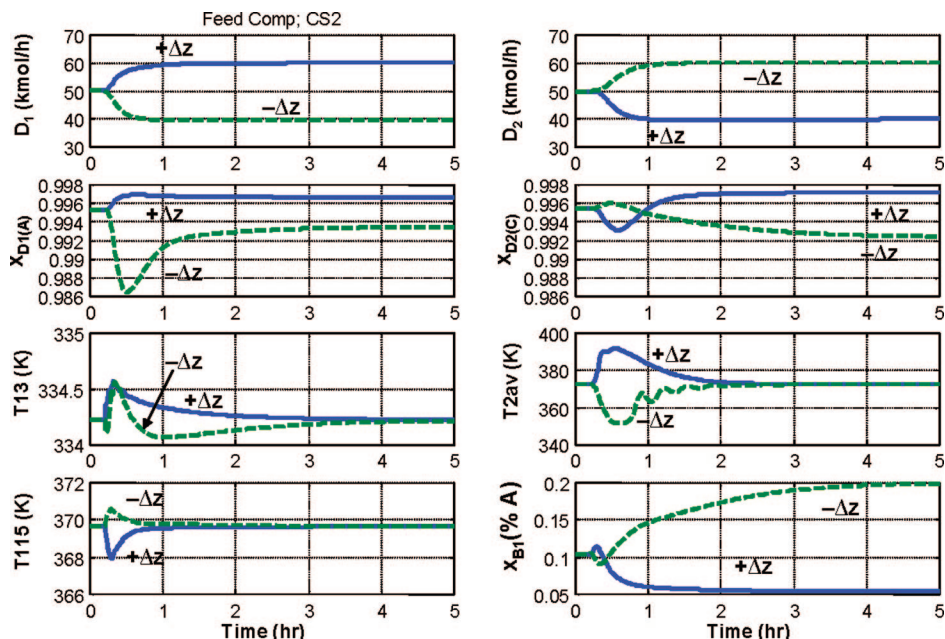**Figure 13.** CS2: feed flowrate disturbances.

**Figure 14.** CS2: feed composition disturbances.

to achieve profile position control. The temperature profile can be tracked as it moves up and down the column. The process gain is reduced, which permits a larger controller gain. The control structure using multiple temperatures also avoids saturation of the process variable signal, which occurs when a single temperature at only one tray is measured.

Setting up the average temperature in Aspen Dynamics is illustrated in Figure 12. The temperatures on the three stages are added together in "$T_{\mathrm{sum}}$". The output signal is the sum of the three temperatures in Celsius because Aspen Dynamics uses metric units. This signal is multiplied by 0.3333 in "average" and finally a constant 273 is added to convert the average temperature to Kelvin before feeding into the deadtime element.

Figures 13 and 14 give responses for feed flowrate and feed composition disturbances. Stable regulatory control is shown with product purities held close to their specifications for all of these large disturbances. Figure 13 gives the responses of the system for step changes in the setpoint of the feed flow controller at 0.2 h. The solid lines are for a 10% increase, the dashed lines are for a 20% increase, and the dotted lines are for a 20% decrease. Increasing feed results in increases in both distillate product streams, as expected. The two temperatures in the extractive column are held at their setpoint values after a short transient period, as is the average temperature in the solvent recovery column. The purities of the two products are held quite close to their desired values. The largest offset in the acetone product purity occurs for the 20% decrease in feed flowrate where it drops to 94.4 mol%. The system comes to a new steady state in less than 2 hours.

Figure 14 gives the responses of the system for step changes in feed composition at 0.2 h. The solid lines are for an increase from 50 to 60 mol % acetone in the feed with a corresponding reduction in chloroform. The dashed lines are for a decrease from 50 to 40 mol % acetone in the feed. Feed more acetone and less chloroform produces an increase in $D_1$ and a decrease in $D_2$ as expected. There is a fairly large transient drop in acetone product purity $x_{D1(A)}$ down to 98.6 mol % when less acetone is fed, but the steady-state purity recovers to 99.3 mol %. The chloroform purity is maintained quite close to specification. The system comes to a new steady state in about 3 hours.

These results illustrate that the dual-temperature control structure provides effective regulatory control of this maximum-boiling azeotropic system in the face of very large disturbances.

## 5. Conclusion

This paper has studied the control of a maximum-boiling azeotropic system. Extractive distillation is shown to be capable of producing quite pure products. A conventional control structure is developed that provides effective disturbance rejection for both production rate and feed composition changes.

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