

DESIGN AND CONTROL OF BUTYL ACRYLATE REACTIVE DISTILLATION COLUMN SYSTEM

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Abstract. In this study, the design and control of a reactive distillation column system for the production of butyl acrylate has been investigated. The proposed design is quite simple including only one reactive distillation column and an overhead decanter. The optimal design is selected based on the minimization of Total Annual Cost (TAC) for the overall system. At this optimized flowsheet condition, output multiplicity was found with reboiler duty as the bifurcation parameter. The highest purity stable steady state was selected as the base case condition for the control study. The overall control of this system is achieved with no on-line composition measurements. Tray temperature control loop will be designed to infer final product purity. From Aspen Dynamics simulation, the proposed control strategy performs very well in rejecting various disturbances while maintaining butyl acrylate product at high purity. *Copyright © 2005 IFAC*

Keywords: Butyl Acrylate; Reactive Distillation; Column Simulation; Design and Control

1. INTRODUCTION

Reactive distillation has demonstrated its potential for capital productivity improvements, selectivity improvements, reduced energy use, and the reduction or elimination of solvents in the process (cf. Malone and Doherty, 2000). From this review paper, there are a total of 562 publications of reactive distillation for the period of 1970-1999. According to a chart in that review paper, exponential rate of growth in the literature is exhibited. For the five-year period (2000-2004) after that review paper has been published, there are another 272 publications in the research area of reactive distillation. This shows the rapid progress in this technology sector in recent years.

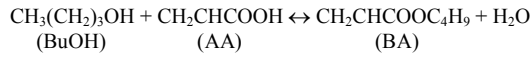
Butyl acrylate is widely used in industry as a precursor for varnishes, adhesive, and finishes of papers and textiles. This important ester can be produced directly from n-butanol and acrylic acid via esterification reaction with the presence of acid ion exchange resin as catalyst. Even though in recent year there are many papers investigate design and control aspects of reactive distillation columns, no

paper on design and control of this system has been reported in open literature to the best of our knowledge.

In this paper, design and control of a reactive distillation column system for the production of butyl acrylate will be investigated. Section 2 shows the proposed simple design of the overall system with only one reactive distillation column and an overhead decanter. The optimal design flowsheet is determined by minimizing TAC of the overall system. In Section 3, output multiplicity of this system is demonstrated with reboiler duty as the bifurcation parameter. The highest purity stable steady state is selected as the base case condition for the control study. Section 4 shows the overall control strategy development of this system. Only tray temperature (not on-line composition analyzer) is used in the overall control strategy. The closed-loop dynamic simulations of the proposed control strategy in the face of various disturbances are illustrated in this section. Finally, some concluding remarks are drawn in Section 5.

2. PROPOSED PROCESS DESIGN

The reaction taking place in the reactive distillation column can be seen as below:



The kinetics of this reaction was assumed to behave according to a Langmuir Hinshelwood Hougen Watson (LHHW) mechanism. The kinetics parameters from Schwarzer and Hoffmann (2002) are used in this study. The reaction rate expression is shown below:

$$r_{AA}(\text{kmol}/\text{m}^3 \cdot \text{s}) = K_1 \exp\left(-\frac{K_2}{RT}\right) \frac{a_{\text{BuOH}} a_{\text{AA}} - \frac{1}{K_a} a_{\text{BA}} a_{\text{H}_2\text{O}}}{\left(K_3 a_{\text{BuOH}} + a_{\text{AA}} + K_4 a_{\text{H}_2\text{O}}\right)^2} \quad (1)$$

with

$$K_1(\text{kmol}/\text{m}^3 \cdot \text{s}) = 8.12 \cdot 10^9, \quad K_2(\text{J}/\text{mol}) = 8.37 \cdot 10^4, \quad K_3 = 1.864, \quad K_4 = 1.308$$

$$\ln K_a = -8.805 + 0.05743(T/K) - 6.429 \cdot 10^{-5}(T/K)^2 + 3.821 \cdot 10^{-9}(T/K)^3$$

The NRTL-HOC thermodynamic model is used to describe vapor-liquid and vapor-liquid-liquid equilibrium. Aspen Plus[®] built-in thermodynamic model parameters are used in the simulation. For the two model pairs (butyl acrylate–acrylic acid, and butyl acrylate–water) that do not have the Aspen Plus[®] built-in NRTL parameters, the Dortmund modified UNIFAC group contribution estimation method (Weidlich and Gmehling, 1987) was used to obtain the remaining thermodynamic model parameters.

This system includes two homogeneous azeotropes (acrylic acid–butanol and butyl acrylate–acrylic acid) and two two-component heterogeneous azeotropes (butyl acrylate–water and butanol–water) and one three-component heterogeneous azeotrope (butyl acrylate–butanol–water). The normal boiling point of the azeotropes and pure components as predicted by the NRTL-HOC thermodynamic model parameters are given in Table 1.

Table 1: Boiling point of azeotropes and components

Azeotropes or components	Boiling point (°C)
H ₂ O	100.0
BuOH	117.7
AA	141.2
BA	147.4
BuOH+AA	141.3
BA+AA	147.8
BuOH+H ₂ O (hetero.)	92.5
BA+H ₂ O (hetero.)	95.2
BuOH+ BA+H ₂ O (hetero.)	92.3

The proposed design of the reactive distillation column is to produce high purity butyl acrylate product (>99.5 mol %) at the column bottom and to have top vapor composition near three-component heterogeneous azeotrope. This top vapor after condensation can be formed into two liquid phases to be separated in a decanter. The organic phase containing mixture of butanol, butyl acrylate and

some water will be refluxed back to the reactive distillation column. The aqueous phase containing high-purity water (over 95 mol %) can be discharged out of the system. The feasibility of the design can be illustrated by the following two residue curve maps (RCMs). Figure 1 shows the BuOH-BA-H₂O three-component RCM which can be used toward the top of the reactive distillation column where acrylic acid is negligible. Figure 2 shows the AA-BuOH-BA three-component RCM which can be used toward the bottom of the reactive distillation column where water is negligible.

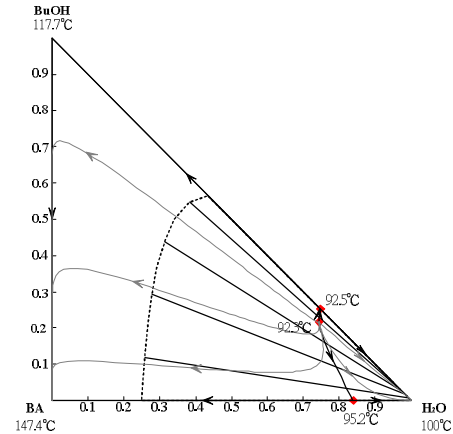


Figure 1. BuOH-BA-H₂O three-component RCM.

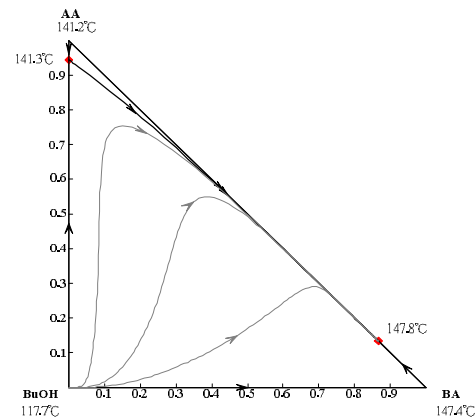


Figure 2. AA-BuOH-BA three-component RCM.

The proposed design of the overall system including a reactive distillation column and an overhead decanter can be seen in the following Figure 3.

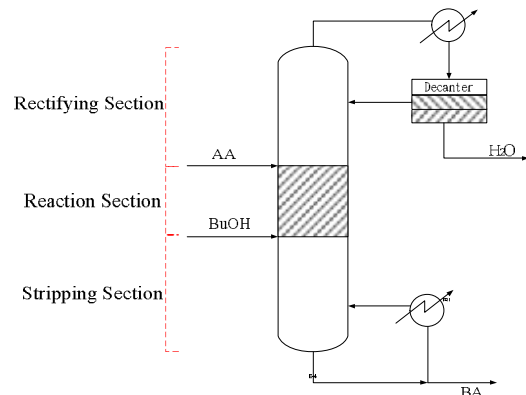


Figure 3. Proposed overall process design.

The design and operating variables need to be optimized are: total stages of the reactive distillation column, acrylic acid feed stage, butanol feed stage, reboiler heat duty, and acrylic acid (AA) feed flow rate. The butanol feed flow rate is selected as the throughput manipulator of this process to be set at 1.5 g-mol/s. In the remaining two operating variables (reboiler heat duty and AA feed flow rate), one will be used to specify the bottom product purity to be at 99.5 mol %. From sensitivity analysis by varying AA feed flow rate or reboiler heat duty, it was found that the bottom product purity is more sensitive to the AA feed flow rate. Therefore, in the Aspen Plus simulation runs, the specification of bottom product purity at 99.5 mol % BA is achieved by varying the AA feed flow rate while reboiler heat duty is fixed in all the simulation runs. A minimum reboiler heat duty can be found for a certain set of design variables (total stages of the reactive distillation column, acrylic acid feed stage, and butanol feed stage) which meets bottom product purity specification.

Since there are three design variables need to be determined, iterative optimization procedure will be followed to find the best set of design variables. Total Annual Cost (TAC) is used for the comparison of various feasible simulation runs. The best set of design variables is the one that minimize TAC while meets bottom product purity specification and also having lowest reboiler heat duty. Another issue needs to be careful in the optimization procedure is that the reaction tray holdup used in the dynamic component balance equations needs to be consistent with the one obtained from tray sizing calculation. After many exhaustive simulation runs by varying two feed locations with fixed number of total stages, the minimized TAC can be found. From Figure 4 below, the final optimized number of total stages for the reactive distillation column is 22. Note that for each total stage, the one in the figure is selected as the minimized TAC with varying two feed locations. The optimized feed locations for AA and BuOH are at 5th stage and 18th stage, respectively.

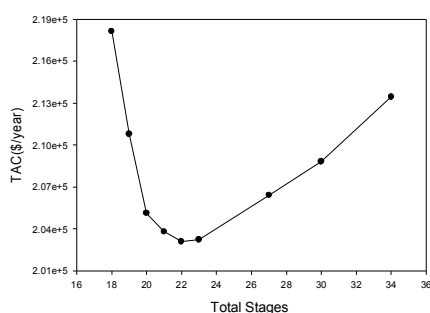


Figure 4. Minimized TAC at each fixed number of total stages.

3. OUTPUT MULTIPLICITY OF THIS SYSTEM

After the optimized process design has been found, an investigation is made to see if output multiplicity

exists in this system. Using the homotopy continuation capability in Aspen Dynamics, the following Figure 5 can be generated with reboiler heat duty as the bifurcation parameter. From the figure, the point marked at SS1 (Steady-state 1) is the steady-state which was found in previous section with bottom product purity specified at 99.5 mol% BA. From this bifurcation analysis, we observe that there is another steady-state with the same set of system inputs which can achieve even higher bottom product purity. This steady-state was marked as SS2. At SS2, the achievable bottom product purity is at 99.83 mol% BA. There is a third steady-state with the same reboiler duty of 305 KW which results in much lower product purity (not shown in Fig. 5), thus this steady-state is unattractive for process design purpose.

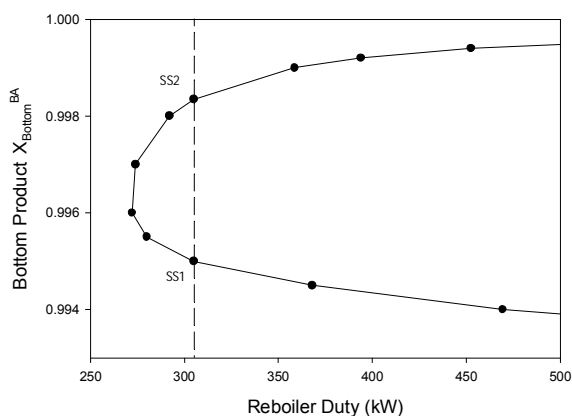


Figure 5. Bifurcation plot.

A dynamic simulation run is made to start the system at SS1 (lower purity) with a hypothetical bottom composition control loop in automatic mode which fixed bottom product purity at 99.5 mol% BA. At time = 100 hr, the composition control loop is put in manual mode and a small positive pulse of the reboiler heat duty is made from 305KW to 305.3KW, and then after an hour this duty is back to 305KW again. The system outputs are gradually moved from that of SS1 to SS2. This dynamic response can be seen in Figure 6. Notice about the time scale differences in the upper and lower plots. A similar dynamic simulation run is made to start the system at SS2 with a small negative pulse test. Unlike the dynamic response in Fig. 6, the system outputs are returned back to the values of the original SS2 after some initial deviations from the steady-state values.

These dynamic simulation runs demonstrate that the steady-state at SS1 is actually open-loop unstable, while that of SS2 is open-loop stable. Since the rigorous process simulation is very complex with many ordinary differential equations coupled with algebraic equations, eigenvalue analysis in finding the stability of the steady-states is impossible to perform. The steady-state operating condition at SS2 is easier to control (because of open-loop stable) and also achieves higher product purity, thus this operating condition will be selected as the base case for further control strategy study.

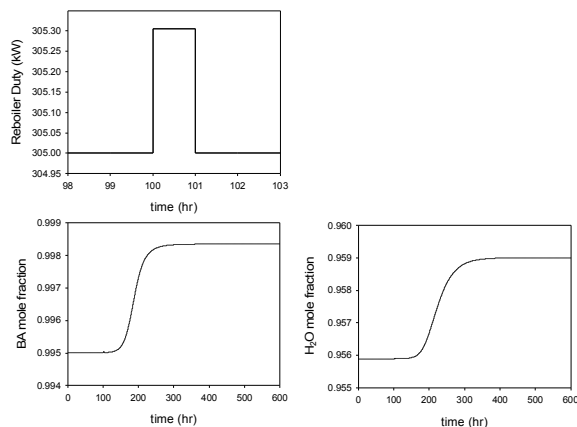


Figure 6. Dynamic transient from SS1 to SS2 with pulse input.

The final process design variables and steady-state operating condition can be found in Table 2 with the liquid composition and temperature profile inside the reactive distillation column as shown in Figure 7. Notice that in the table and the figure, the stages are counting from top down with decanter as stage 1 and reboiler as stage 22.

Table 2: Process design and steady-state condition

Total stages (including decanter and reboiler)	22
AA feed stage	5
BuOH feed stage	18
AA feed flow rate(g-mol/s)	1.4377
BuOH feed flow rate(g-mol/s)	1.5
Reboiler heat duty (KW)	305
Organic reflux flow rate (g-mol/s)	5.1560
Organic molar composition	BA: 7.38% BuOH: 54.43% AA: 0.03% H ₂ O: 38.16%
Aqueous outlet flow rate (g-mol/s)	1.4988
Aqueous molar composition	BA: 0.05% BuOH: 4.05% AA: 1.89E-3% H ₂ O: 95.90%
Bottom product flow rate (g-mol/s)	1.4389
Bottom molar composition	BA: 99.83% BuOH: 0.14% AA: 0.03% H ₂ O: 2.38E-9%

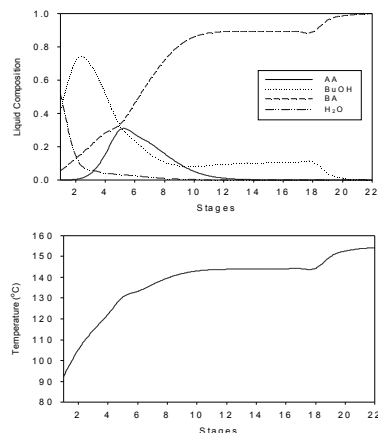


Figure 7. Liquid composition and temperature profile of steady-state 2 (SS2)

4. CONTROL STRATEGY DEVELOPMENT

The above steady-state condition, SS2, will be used in this section to investigate the proper overall control strategy of the system. The overall control strategy needs to hold bottom product at high purity in the face of various disturbance changes. The disturbances considered in this study include: throughput changes via BuOH feed flow rate; composition changes of two reactants with some water impurity; and catalyst decay by multiplying a factor in the forward rate constant K_f . In the control strategy development, we will assume that no online composition measurement is available. The product composition loop will be inferred by some tray temperature control loop.

The inventory control loops are determined first. Decanter aqueous phase level is manipulated by the aqueous outlet flow. Organic phase level is manipulated by the organic reflux flow. The column bottom level is manipulated by the bottom product flow. The pressure at the top of the reactive distillation column is manipulated by the top vapor flow. The temperature at decanter is maintained at 40 °C by the condenser duty.

After the inventory control loops have been determined, there are three manipulated variables left and can be used in the product purity control loop. These three manipulated variables are: AA feed flow; BuOH feed flow; and reboiler heat duty. Since BuOH feed flow has been selected as the throughput manipulator of the system, there are two remaining manipulated variable left (reboiler heat duty and AA feed flow). In the control strategy development, we will try to keep the strategy as simple as possible for wider industrial applications. Hence, single tray temperature control loop will be investigated first. For the manipulated variable not used in the tray temperature control loop, some ratio scheme will be implemented to keep the ratio of this manipulated variable to the BuOH feed flow at a constant value.

Two alternative control strategies have been investigated for their closed-loop performance. The

first control strategy is to control tray temperature at 8th stage by manipulating the reboiler heat duty while keeping the ratio of AA/BuOH feed at a constant value. The second control strategy is to control tray temperature at 6th stage by varying AA/BuOH feed ratio while keeping the ratio of reboiler heat duty to the BuOH feed flow at a constant value. The temperature control points in the alternative control strategies are determined via sensitivity analysis to pick one tray temperature at maximum sensitivity while still exhibits near linear dynamic behavior.

The first control strategy fails during unmeasured feed composition changes. The controlled tray temperature can not be maintained at setpoint during this feed composition disturbance. The manipulated variable (reboiler heat duty) will continuously increase until control valve fully open. On the other hand, the second control strategy performs well for all the disturbances tested. Table 3 summarizes the proposed control strategy with controller tuning constants used in the dynamic simulation. For all the level control loops, P-only control form is selected with $K_c=2$ for maximum flow smoothing. The tuning constants for the critical tray temperature control loop are determined by IMC-PI tuning rules of Chien and Fruehauf (1990). In order to obtain the PI controller tuning constants, open-loop step test was performed on the control loop and then the dynamic of the loop was modeled as an integrator plus deadtime system.

Table 3. Lists of the control loops in the proposed control strategy

Controlled Variable	Manipulated Variable	Controller tuning constants
6 th stage temperature	AA/BuOH feed ratio	$K_c=4.59$ $\tau_i=54$ min
Organic level	Organic reflux flow	$K_c=2.0$
Aqueous level	Aqueous outlet flow	$K_c=2.0$
Column bottom level	Bottom product flow	$K_c=2.0$
Column top pressure	Top vapor flow	$K_c=20$ $\tau_i=12$ min

The Aspen Dynamics closed-loop simulation results of the proposed control strategy will be shown next. The first disturbance considered is the AA feed composition changes. At time = 1h, the AA feed composition is changed from pure AA to either 95 mol% AA or 90 mol% AA. The impurity of the AA feed stream is water. The closed-loop simulation result is shown in Figure 8. The top part of the figure is the controlled and manipulated variables of the tray temperature control loop. From the figure, the 6th tray temperature is controlled back to setpoint value within three hours with smoothing increase of the AA to BuOH feed ratio. The bottom BA and top water compositions are shown in the bottom part of the figure. It is shown that the bottom product purity

is return back to tight specification after this disturbance changes.

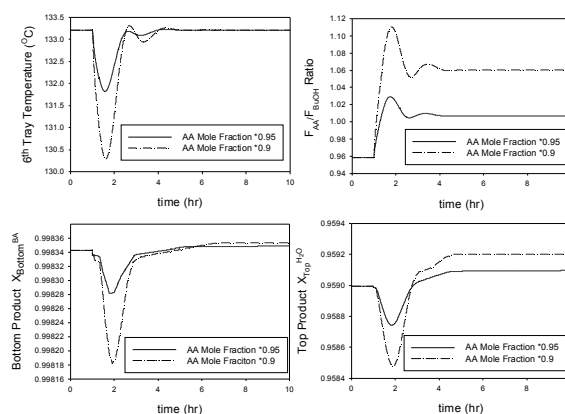


Figure 8. Closed-loop responses with AA feed composition changes.

The next disturbance to test is the unmeasured BuOH feed composition changes. The closed-loop response is shown in Figure 9. At time = 1h, the BuOH feed composition is changed from pure BuOH to either 95 mol% or 90 mol%. The impurity of the BuOH feed stream is again water. Since the impurity of the feed which we used as the throughput manipulator is increased, this means that the actual key reactant into the system is decreased. Therefore, we'd anticipate a dropping of the AA to BuOH feed ratio to cope with this disturbance change. The proposed control strategy is able to do exactly the same thing as we expected via 6th tray temperature control loop. Since there is no direct bottom product composition control loop, the bottom BA purity is slightly dropped from 99.83 mol% to 99.79 mol% during the more severe BuOH feed composition change. This small dropping of the bottom product purity is considered to be quite acceptable since no on-line composition measurement is used in the proposed control strategy. The top aqueous outlet composition is returned closely to the original steady-state value despite the disturbance changes.

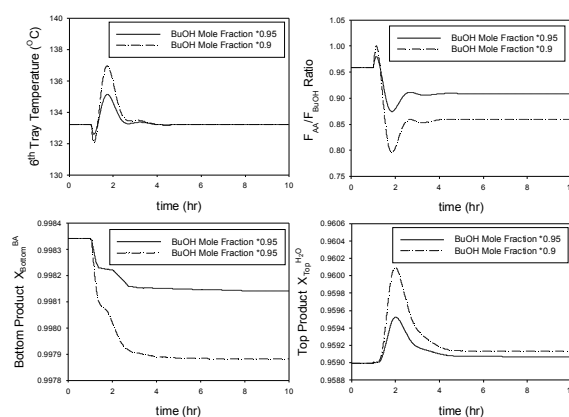


Figure 9. Closed-loop responses with BuOH feed composition changes.

The proposed control strategy should be able to hold the product purity specification despite of the

reasonable range of the throughput changes. Since the throughput manipulator of the system is selected as the BuOH feed flow rate, the next closed-loop simulation is to adjust this feed flow rate upward or downward and to see if the proposed control strategy performs adequately or not. Figure 10 shows the closed-loop simulation results with $\pm 20\%$ changes in the BuOH feed flow rate at time = 1h. The crucial bottom BA purity is held very close to the original purity of 99.83 mol% with only a small dropping of the purity to 99.80 mol% during +20% BuOH feed flow rate change. Notice that in this load change situation, the reboiler heat duty will also increase or decrease accordingly because of the ratio scheme in the proposed control strategy.

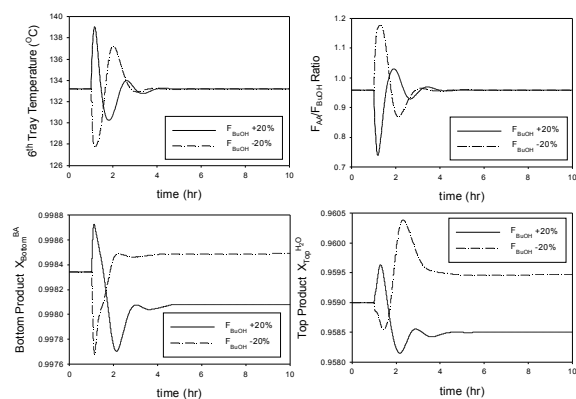


Figure 10. Closed-loop responses with $\pm 20\%$ changes in the BuOH feed flow rate.

The last disturbance in the closed-loop simulation is to simulate the cases with catalyst decay. The life of the catalyst packed in the reaction section of the reactive distillation column was assumed to be one year in the TAC calculation. The reaction rate will be somewhat different when the catalyst is new or toward the end of the year before replacement. This situation is simulated with a more severe disturbance of cutting K_1 in the rate expression to 90% or 80% of the original value. The closed-loop simulation of the proposed control strategy is shown in Figure 11. The bottom BA product purity only dropped slightly to 99.76 mol% with this very severe cutting of the K_1 value to 80%.

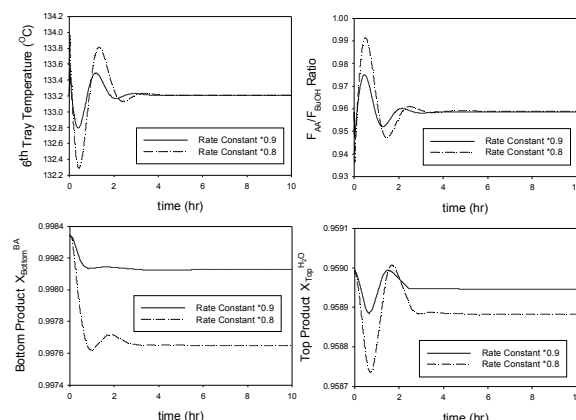


Figure 11. Closed-loop responses with catalyst decay.

The above simulation runs show that this simple proposed control strategy is capable of rejecting all major disturbances. Therefore, there is no need to investigate more complicate dual temperature control loop strategy. Notice that to maintain the product composition at high-purity, no on-line composition analyzer is needed, thus this proposed control strategy can be easily implemented in industry.

5. CONCLUSIONS

In this study, the design and control of a reactive distillation column system producing butyl acrylate has been investigated. No other design and control study of this system has been reported in open literature. The proposed design of the system contains only one reactive distillation column with an overhead decanter. High purity butyl acrylate product at 99.83 mol% can be obtained from the bottom of the reactive distillation column. The other outlet stream of the system is the aqueous draw from the decanter. The purity of this stream is also high enough at 95.9 mol% H_2O .

The optimum design and operating condition is obtained by minimizing TAC of the system. Output multiplicity is observed at this optimized design and operating condition. The stable steady-state which achieves highest purity is selected as the base case for the control study. The proposed overall control strategy of this system is very simple containing only one tray temperature control loop to control 6th stage tray temperature by varying AA/BuOH feed ratio while keeping the ratio of reboiler heat duty to the BuOH feed flow at a constant value. No on-line composition measurement is needed in the proposed control strategy. This control strategy is able to hold product specification at high purity despite various feed flow rate, feed composition, and catalyst decay load disturbance changes.

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