TEMPERATURE CONTROL OF BUTYL PROPIONATE REACTIVE DISTILLATION

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Abstract: In this work, we explore the temperature control of n-butyl propionate reactive distillation. Process characteristics of n-butyl propionate are explored and a systematic procedure is proposed for the design of butyl propionate heterogeneous reactive distillation. Control objective is to product specifications: high purity propionate and ppm level of acid. The control structure design procedure consists of the following steps: (1) selection of manipulated variables, (2) determine temperature control trays, and (3) find controller settings. Since two specifications on the bottoms product have to be met and stochiometric balance has to be maintained, we have a 2x2 control problem with two obvious inputs: reboiler duty and feed ratio. The reactive distillation exhibits unique temperature sensitivities and the non-square relative gain (NRG) successfully identifies temperature control trays. It results in an almost one-way decoupled system. Therefore, decentralized PI controllers are employed. Simulation results indicate good control performance can be achieved with simple control strategy. *Copyright © 2002 IFAC*

Keywords: esterification, n-butyl propionate, reactive distillation, heterogeneous distillation, temperature control

1. INTRODUCTION

Reactive distillation provides an attractive alternative for process intensification, especially for reaction/separation systems with reversible reactions. The literature in reactive distillation has grown rapidly in recent years and the book by Doherty and Malone (2001) gives an updated summary. However, relatively few papers that discuss process control aspects of reactive distillation columns. These are reviewed in a recent paper by Al-Arfaj and Luyben (2000). Al-Arfaj and Luyben (2000, 2002a, 2002b) proposed several control structures for different types of reversible reactions (A+B↔C+D, A+B↔C, and A↔B+C) and consecutive reactions for the product C and by-product D (A+B→C & A+C→D). They have shown that (1) reaction stoichiometric balance is crucial for system with multiple reactants, and (2) simple control strategy works satisfactorily for these complex dynamics.

Similar to the gradual replacement of methyl tert-butyl ether (MTBE) with ethyl tert-butyl ether (ETBE) (Sneesby et al., 1997), this work is a continuous effort to study the production of less volatile solvents to replace light solvents such as methyl acetate or ethyl acetate. In this work, we explore the esterification of propionic acid and n-butanol to form n-butyl propionate (Lee et al., 2002 ; Liu and Tan, 2001). n-Butyl propionate has increasing been used as a cleaning solvent for processing polymers for its relatively low volatility. The process (Huang, 2002) falls into a specific class of reactive distillations: heterogeneous reactive distillation (or three-phase reactive distillation; Chiang et al., 2002). By heterogeneous reactive distillation, we mean two-liquid phase exists in the reflux drum and a decanter is employed to separate the aqueous product from the organic reflux.
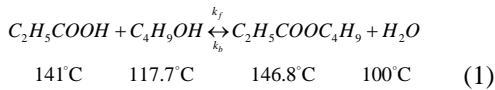
The objective of this work is to devise control structure for n-butyl propionate process and the control objective is to maintain the propionate quality at specification while keeping the acid purity at ppm (part per million) level. This would require two on-line analyzers. Instead of using expensive and less reliable on-line composition analyzers, temperature control of this three-phase reactive distillation is explored.

2. PROCESS

By heterogeneous reactive distillation, we mean two-liquid phase exists in the reflux drum and a decanter is employed to separate the aqueous product from the organic reflux. For esterification reactions, propyl acetate, butyl acetate, and amyl acetate are good examples, because they all share the following characteristics:
(1) a large two-liquid zone exists,
(2) the minimum boiling azeotrope is located in the two-liquid zone,
(3) one end of all tie lines points to the direct of a pure component (typically water for esterification).

n-Butyl propionate typically is synthesized from propionic acid and n-butyl alcohol via an esterification. However, ternary azeotropes were found in the mixture of n-butanol – n-butyl acetate - water. This may lead to difficulty in down-stream separation when the conventional reactor/separator process is employed. Obviously, reaction distillation provides an attractive alternative. The esterification follows the elementary reaction:

$$C_2H_5COOH + C_4H_9OH \overset{k_f}{\underset{k_b}{\leftrightarrow}} C_2H_5COOC_4H_9 + H_2O$$

$$141°C \quad\quad 117.7°C \quad\quad 146.8°C \quad\quad 100°C \quad\quad (1)$$

The normal boiling points (NBP) in Eq. 1 show that the acetate is the highest boiler, the acid is the second highest boiler while water has the lowest NBP. The reaction is catalyzed by acidic cation exchange resin (Amberlyst 35). Quasi-homogeneous model with non-ideal-solution assumption (Lee et al., 2002) is used.

$$r = k_f(a_{HOPr}a_{BuOH} - \frac{a_{BuOPr}a_{H_2O}}{K_{eq}}) \quad (2)$$

where r is the reaction rate per unit volume (Kmol/m³sec), a stands for the activity of corresponding components (Kmol/m³sec). k_f is the forward reaction rate constant

$$k_f = 2.0317 \cdot 10^{11} e^{-\frac{65.74}{8.314T(K)}} \quad (3)$$

with T in Kelvin and K_{eq} is the equilibrium constant with a value of 27.8. This is a reaction with negligible heat effect and the equilibrium constant is around 27.8. The catalyst price is assumed to be 18.5 $/lb and a catalyst life of one year is assumed in this study.

Following Liu and Tan (2001), the nonrandom two liquid (NRTL) activity coefficient model is used for the vapor-liquid-liquid equilibrium (VLLE) for the quaternary system (Table 1). The Hayden-O'Conell second virial coefficient model with association parameters is used to account for the dimerization of acetic acid in the vapor phase. The Aspen Plus built-in association parameters are employed to compute fugacity coefficients.

The quaternary system has three minimum-boiling binary azeotropes (n-butanol - water, n-butyl propionate - water, and water - propionic acid) and one maximum-boiling binary azeotrope (propionic acid - n-butyl propionate). There is one ternary azeotrope for water - butanol - n-butyl propionate which corresponds the lowest boiling azeotropic temperature (92.9°C). Notice that liquid-liquid (LL) envelopes are found in three out of four ternary subsystems and, moreover, a very large LL envelope (type 2) is observed for the water – n-butyl propionate (Fig. 1) and one end of the tie lines are connected to very high purity water. This corresponds to more than 50% of the composition space as shown in Fig. 1. Figure 1 also gives the residue curve maps for these ternary systems. Following the coordinate transformation of Doherty and Malone (2001),

$$X_A = x_{HOPr} + x_{BuOPr} \quad \& \quad X_B = x_{BuOH} + x_{BuOPr} \quad (4)$$

the LL envelop can be visualized in a 2-D plot as shown in Fig. 2. This is a significant two-liquid zone and the ternary azeotrope lies within the LL envelop.

Systematic procedure is devised to design heterogeneous reactive distillation. Here, we extend the approach Chiang et al. (2002) by rearranging feed tray locations. Initially, the arrangement of feed streams is based on reaction kinetics consideration, where the heavy reactant (propionic acid) is fed to the top tray of the reactive zone and the light reactant

(butanol) comes in from the lower section of the reactive zone.

For a system with given specifications on the products and a given production rate, the design steps are:

1. Fix a number of reactive trays (N_{rxn}).
2. Place the heavy reactant feed on the top tray of the reactive zone and the light reactant feed on the lower section of the reactive section.
3. Guess the tray numbers in the rectifying sections (N_R).
4. Find the minimum number of trays of the stripping section ($N_{s,min}$) from the short-cut design with a given specification and set $N_s = 2N_{s,min}$.
5. Adjust reboiler duty until the bottom product specification (99% n-butyl propionate) is met (because organic phase is under total reflux, we have only one degree of freedom).
6. Go back to 3 and change the number of trays in the rectifying section until the total annual cost (TAC, Chiang et al., 2002) is minimized (because of the type II LLE, practically, we do not have control over water purity).
7. Go back to 2 and vary feed tray locations until TAC is minimized with acceptable acid purity in the bottom (<50 ppm).
8. Change the number of reactive trays (N_{rxn}) such that TAC is minimized.

ASPEN Plus was used to carry out steady-state simulations and the residence time of 15 s was assumed for the reactive trays. The TAC calculation was based on the cost models of Douglas (1988) (Chiang et al., 2002). The optimized design is shown in Fig. 3 and Table 2 gives parameters values and costs. The column has a total of 18 trays, with 12 stripping trays, 5 reactive trays (tray 13-17), and 1 rectifying tray (tray 18). The optimum feed tray locations are tray 15 (NF1) and tray 17 (NF2). The acid composition in the bottoms is kept to 7 ppm while maintaining propionate purity at 99%. The phase split in the decanter automatically gives rather high purity water (98.8%). Figure 4A shows most of the stripping section trying to separate propionate from butanol. The acid is consumed early in the reactive zone and its purity is kept low in the stripping section. Significant reaction is observed on trays 16 and 17 as shown in the thick long-dashed line as the fraction of the total reaction. This type of reaction rate profile is within one's expectation, because it is necessary to further react the limiting reactant (acid) in trays 13-15 in order to meet the stringent acid specification in the bottoms. Significant temperature breaks are also observed in the stripping section (trays 2-5) and the reactive zone (trays 15-17) as shown in Fig. 4B. This optimized design results in 10% less energy consumption and also 10 % less TAC as compared to the traditional feed arrangement.

2. CONTROL

The control objective is to maintain bottoms propionate purity while keeping the acid

concentration at ppm level. Instead of control the compositions directly, temperatures are used to infer product composition. This is a multivariable control problem and decentralized PI controllers are used.

A typical multivariable control system design procedure consists of the following steps: (1) selection of manipulated variables, (2) determining measurement locations, (3) variable pairing, and (4) controller tuning.

As pointed out earlier, the organic phase condensate is under total reflux and we are left with only one manipulated input, reboiler duty. The other manipulated variable naturally is the feed ratio (Fig. 3) for this double feed column, because the feed ratio has to be adjusted to maintain stoichiometric balance (Al-Arfaj and Luyben, 2000).

Before looking into measurement selection criterion, let us examine the sensitivity of temperature profiles as manipulated variables change. As the heat input changes ($\pm1\%$), two large changes are observed (Fig. 5A). One is in the stripping section which is typical for conventional distillation and the other is in the reactive zone where significant reaction occurs (cf. Fig. 4). The later comes from the effect of increasing (or decreasing) reaction rate which has not been seen in non-reactive distillation column. Nonlinear behavior can be seen for small change in feed ratio as shown in Fig. 5B. Larger and wider temperature deviation is observed when acid is in excess ($F_{butanol}/F_{acid}=0.99$). The asymmetry in Fig. 5B comes from the fact that the excess acid activates the reaction capability in trays 13-15 and significant amount of propionate (heaviest component) is produced and, subsequently, results in much larger temperature rise. Note that this is not the result of temperature control. Similar behavior can also be seen if we choose to use direct composition control and the real reason is that we deliberately design the column asymmetrically (to maintain trace amount of acid in the bottoms).

Table 2 shows the steady-state gain matrix (K) between the temperatures and two inputs (Q_R and $F_{butanol}/F_{acid}$). The non-square relative gain (NRG) of Chang and Yu (1990) is used for measurement selection.

$$\Lambda^N = K \otimes (K^+)^T \qquad (5)$$

Here, Λ^N stands for NRG, $\otimes$ denotes element-by-element multiplication, the superscripts T and + correspond to transpose and pseudo-inverse, respectively. From the definition, the temperatures with large row sum imply the temperature profile is best maintained by holding corresponding temperatures constant. Based on the row sum of NRG, temperatures on trays 4 and 16 (T_4 and T_{16}) are selected (Table 3). These two temperatures correspond to the locations either with large temperature breaks (Fig. 4) or having high sensitivity. T_4 is located in the stripping section and T_{16} is in the place where largest fraction of total reaction occurs (Fig. 4).

Here, we have a 2x2 multivariable system. The relative gain array (RGA) is used for input-output pairing. For this temperature controlled reactive distillation, the RGA is:

$$\Lambda = \begin{matrix} Q_R & F_{butanol}/F_{acid} \\ \begin{bmatrix} 0.999 & 0.001 \\ 0.001 & 0.999 \end{bmatrix} & \begin{matrix} T_{16} \\ T_4 \end{matrix} \end{matrix} \qquad (6)$$

We have a system with RGA almost equal to 1. Actually, Fig. 5 already reveals that this is a one way decoupled system (i.e., T_{16} is not sensitive to feed ratio change). Therefore, the controller structure becomes: pair T_{16} with reboiler duty and pair T_4 with feed ratio.

Once the control structure is set, decentralized PI controllers are tuned automatically. First, the ultimate gain and ultimate are identified using sequential relay feedback of Shen and Yu (1994) and, then, PI controller settings are obtained following Tyreus and Luyben tuning rule.

Figure 6 shows that good temperature control can be achieved using simple PI controllers. For $\pm10\%$ production rate increase, T_4 and T_{16} return to their set points in less than 100 min. However, butyl propionate composition deviates from its specification because we are controlling temperatures while the acid concentration shows little changes. For $\pm5\%$ measurement errors in feed ratio, good control performance can also be obtained, but asymmetric responses are observed for positive and negative changes as shown in Fig. 7. The reason was pointed out earlier and it can be expected from the temperature sensitivity in Fig. 5B.

4. CONCLUSION

In this work, vapor-liquid-liquid equilibrium behavior of n-butyl propionate, a low volatility solvent, is explored and a systematic procedure is proposed for the design and temperature of the heterogeneous reactive distillation. Significant two-phase zone and a ternary minimum boiling azeotrope lead to a unique separation characteristic. Next, the issue control structure design for heterogeneous reactive distillation is studied. Since two specifications on the bottoms product (propionate purity and ppm level of acid impurity) have to be met and stoichiometric balance need to be maintained, we have a 2x2 control problem with two inputs: heat duty and feed ratio. The reactive distillation exhibits a unique temperature sensitivities, as compared to conventional distillation, and the non-square relative gain (NRG) successfully identifies temperature control trays. It results in an almost one-way decoupled system. Therefore, decentralized PI controllers are employed. The reactive distillation column may become over-capacity as production rate decreases, coordinated control is proposed by the n-butanol feed to a lower feed location. This control system over-design provides the flexibility to handle production rate variations in reactive distillation. Results show the effective control can be achieved over a reasonable range of disturbances.

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Table 1. Steady-state parameters for reactive distillation

total no. of trays (N_T)	18
stripping (N_s)/reactive(N_{rxn})/rectifying(N_R)	12/5/1
propionic acid feed tray	17
n-butanol feed tray	15
n-butanol feed flow rate (Kgmol/h)	49.991
propionic acid feed flow rate (Kgmol/h)	49.991
top product flow rate (Kgmol/h)	50.042
bottoms product flow rate (Kgmol/h)	49.941
distillate	
propionic acid (mole fraction)	0.0108
n-butanol (mole fraction)	0.0004
n-butyl propionate (m.f.)	0.0006
water (m.f.)	0.9882
bottoms	
propionic acid (ppm)	7
n-butanol (mole fraction)	0.0104
n-butyl propionate (m.f.)	0.9900
water (mole fraction)	$<10^{-9}$
heat duty	
condenser (10^7 kJ/h)	0.320
reboiler (10^7 kJ/h)	0.548
column diameter (m)	1.23
heat exchanger area (m^2)	
condenser	18.96
reboiler	42.87
capital cost ($1000)	
column	232.80
trays	17.03
heat exchangers	206.12
operating cost ($1000)	
catalyst	6.24
energy	162.02
total annual cost ($1000)	**333.83**

Table 2. NRG and row sum

| Tray No.	NRG Q	NRG F1/F2	rs(i)	
T19	0.0314	0.0006	0.0320	
T18	0.1032	-0.0006	0.1026	
T17	0.1676	-0.0006	0.1670	
T16	0.3938	0.0025	0.3963	←
T15	0.0012	-0.0002	0.0010	
T14	0.0001	0.0002	0.0003	
T13	0.0002	0.0003	0.0005	
T12	0.0003	0.0004	0.0007	
T11	0.0002	0.0008	0.0010	
T10	0.0001	0.0017	0.0018	
T9	-0.0005	0.0049	0.0044	
T8	-0.0028	0.0160	0.0132	
T7	-0.0115	0.0540	0.0425	
T6	-0.0388	0.1613	0.1225	
T5	-0.0881	0.3313	0.2432	
T4	-0.0579	0.3460	0.2881	←
T3	0.1677	0.1182	0.2859	
T2	0.2323	-0.0191	0.2132	
T1	0.0865	-0.0148	0.0717	
T0	0.0149	-0.0028	0.0121	
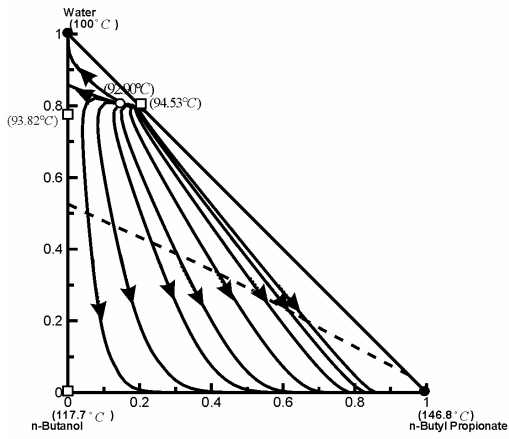
Figure 1. The residue curve maps (RCM) and LLE envelope for water - n-butyl propionate - n-butanol.
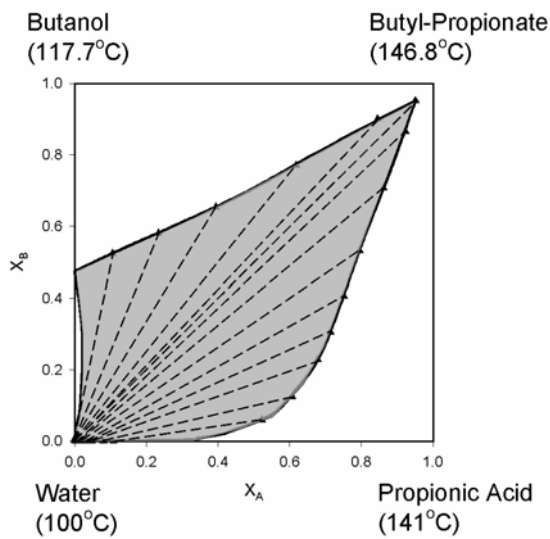

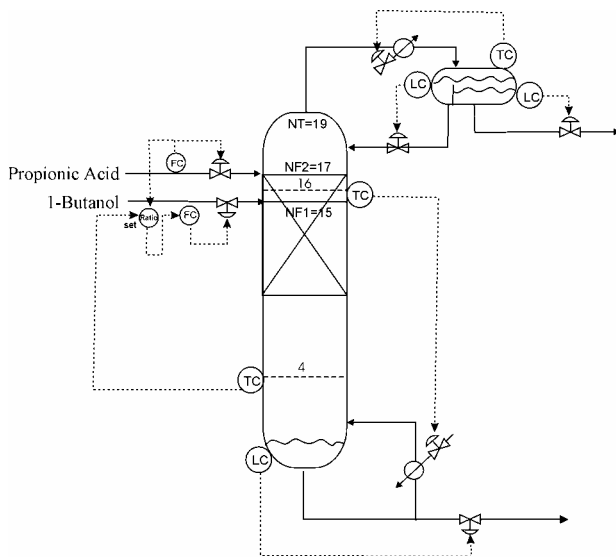**Figure 2.** Two-liquid phase for the quaternary system.

Figure 3. Temperature control scheme for the butyl propionate reactive distillation: feed trays NF1=15 & NF2=17, reactive trays 13-17, temperature control trays T4 & T16.
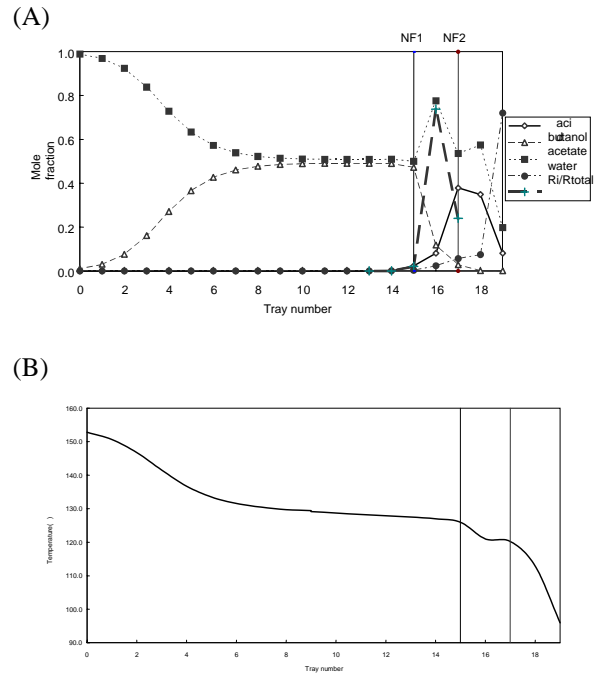

Figure 4. Composition (A) and temperature (B) profiles for optimally designed reactive distillation with $N_R/N_{rxn}/N_S=1/5/12$, NF1/NF2=15/17.
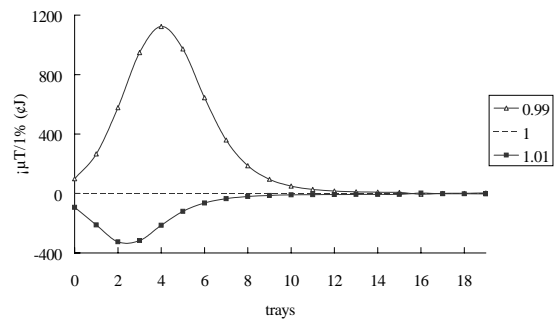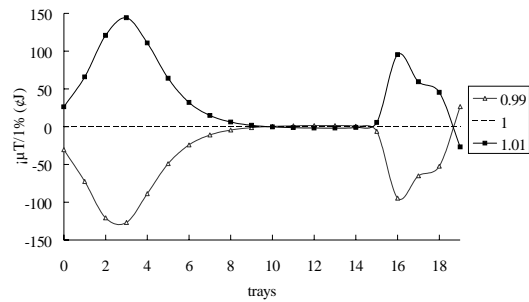

Figure 5. Steady-state gains for 1% changes in reboiler duty (QR) (top) and feed ratio (F_{BuOH}/F_{HOPr}) (bottom)
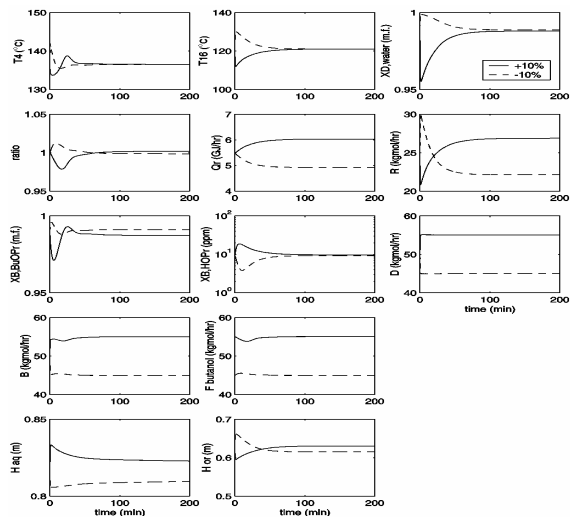
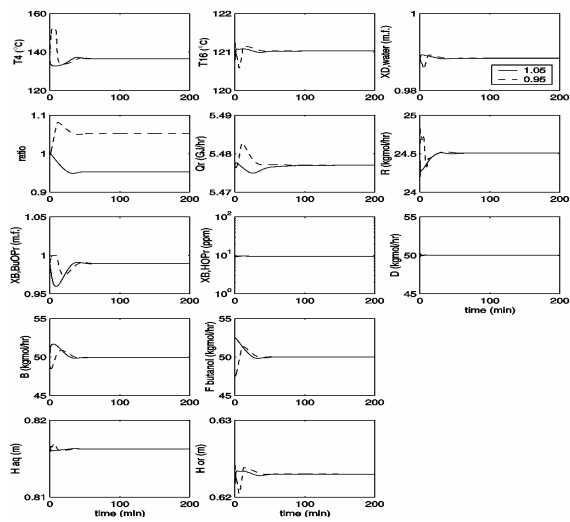**Figure 6.** T_4 and T_{16} temperature control for 10% feed flow disturbances.

Figure 7. T_4 and T_{16} temperature control for 5% feed ratio errors.