

Control of Reactive Distillation Production of High-Purity Isopropanol by Hydration of Propylene

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Abstract

The process characteristics and control strategy of a high-purity IPA reactive distillation column are investigated. The problems of input/output state multiplicities and high nonlinearity are resolved by a systematic procedure proposed in the study. Output multiplicity is eliminated by feeding excess propylene. The stage temperature and propylene composition with one-to-one relationship with reboiler duty and propylene feed, respectively are selected to avoid the control problem caused by input multiplicity. High nonlinearity of the selected input-output relation is overcome by using variable transformation approach. Dynamic simulations demonstrate that such a transformed control scheme is capable of maintaining the desired steady state and provides much superior control performance than the untransformed one.

1. Introduction

Reactive distillation column has become an attractive unit operation in recent years due to its ability to reduce energy consumption and the number of equipment unit, as well as its ability to break azeotropes. Research and development of reactive distillation has been comprehensively reviewed by Doherty and Buzad [1] and Taylor and Krishna [2]. One of the main disadvantages of a reactive distillation column is that the process exhibits nonlinear characteristics such as multiple steady states and high sensitivity to operating variables due to the coupling between separation and chemical reaction [3-13]. Hence special consideration must be given to the design of its control system. For example, two-point control scheme [14], nonlinear control strategy [15, 16], adaptive control [17] and robust PI [18] control configuration were used in controlling ETBE, ethylene glycol, and ethyl acetate reactive distillation processes, respectively.

The keys to controlling a reactive distillation column are to maintain the product composition as

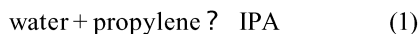
well as stoichiometric balance between the reactant feeds. When there is no measurement bias of the absolute feed flow rate, a ratio control of the feed flow rates coupled with the usual temperature control for distillation product purity is sufficient for the reaction in an equilibrium control regime. However, Al-Arfaj and Luyben [19] pointed out that such a feed-ratio control scheme is a feedforward one with no assurance that correct stoichiometric balance is maintained in case of feed flow measurement bias. The use of a composition analyzer in the reactive zone to maintain stoichiometric balance was advocated. They also have studied a number of reactive distillation columns [20-24] and found that effective control can be provided by the simple PI control schemes. Using a MTBE synthesis column as an example, Wang et al. [25] found that interaction multiplicity between stoichiometric balance and product quality control loops must be eliminated for such a linear control strategy to work. Furthermore, set-point adjustment of the internal composition control loop by either final product purity feedback [26] or direct

throughput rate feedforward control [27] becomes necessary when the reaction is kinetically controlled.

Isopropanol (IPA) is a widely used solvent in chemical and cosmetics industries. It is used as a feedstock for the manufacture of acetone and other compounds. Direct or indirect hydration of propylene are the methods used widely for the manufacture of IPA [28]. Direct hydration process is the preferred process to produce IPA because it avoids some corrosion and environment problems encountered using indirect hydration process. However, the use of complex distillation columns is still required to recover IPA. The synthesis reaction of IPA is a typical equilibrium-limited reaction. Therefore, reactive distillation can be used to improve conversion. In this study, the process characteristics and control strategy of a reactive distillation for the production of high-purity IPA (99.9 mol%) by direct hydration of propylene are investigated. The main purpose is to show that a simple control strategy coupled with a nonlinear variable transformation, will keep the IPA column operating at high product purity even though the overall process exhibits steady multiplicities and highly nonlinear dynamics.

2. Base case column design

The reactive distillation column shown in Figure 1 is used as the basis of process characteristic and control study. A similar column has been studied by Xu et al. [29]. It consists of 28 stages, including a total condenser, a partial reboiler, and 26 column stages. The column is operated at 20 atmosphere and its pressure drop is assumed to be 0.135 atmosphere. There are three zones in the column: rectification zone (stages 1 and 2) and stripping zone (stages 6 to 28) purifying top and bottom products. Pure water and propylene, high and low boiling reactants, at 298 K and 20 atm are fed to the stages 3 and 5, respectively, numbering from column top. IPA is formed in the reaction zone between stages 3 and 5 according to the following reversible reaction:



and is withdrawn from column bottom. Diisopropyl ether (DIPE), a by-product, is produced by the following reaction:



The simulation of the IPA column is carried out using the rigorous distillation model provided by ChemCad software. The liquid phase activities

were calculated by using UNIFAC. Redlich-Kwong equation of state was used to predict the nonideal vapor phase behavior. The IPA yield is strongly limited by the equilibrium conversion. The reversible reaction needs to be catalyzed by strong acids. The following two equations given by Xu [30], using Amberlyst 38 as a catalyst, are used to represent the temperature dependence of reaction equilibrium constants in Equations (1) and (2), respectively

$$\ln K_{a1} = -18.46 + \frac{7592}{T} \quad (3)$$

$$\ln K_{a2} = 133.7 - \frac{46103}{T} \quad (4)$$

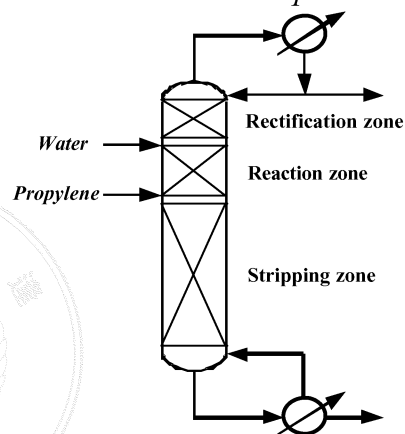


Figure 1. Configuration of reactive distillation column for IPA synthesis.

where K_{a1} and K_{a2} represent reaction equilibrium constants for the main and side reactions, respectively, and T is temperature with unit of degree K. Every stage is assumed to be in chemical reaction equilibrium.

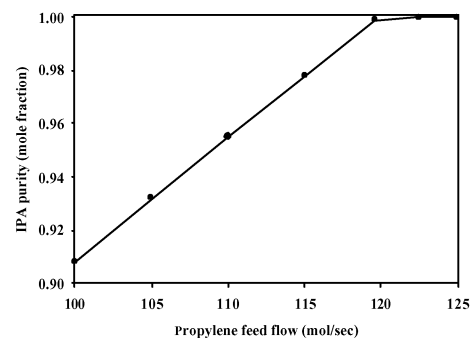


Figure 2. Maximum achievable IPA product purity for various propylene feed flow rates.

Water and propylene feeds are initially designed at 100 mole/s, respectively, for which stoichiometric balance is satisfied. Reflux ratio is

fixed at 30. A maximum achievable IPA product purity can be obtained from steady-state analysis by varying reboiler duty. However, IPA product purity with only 90.8 mol% is achieved under stoichiometric balance condition. Figure 2 shows the maximum achievable IPA product purity for various propylene feed flow rates. When propylene feed increases, the maximum achievable IPA product purity also increases. The maximum achievable IPA product purity with 99.9 mol% can be obtained if propylene feed is designed at 119.6 moles/s.

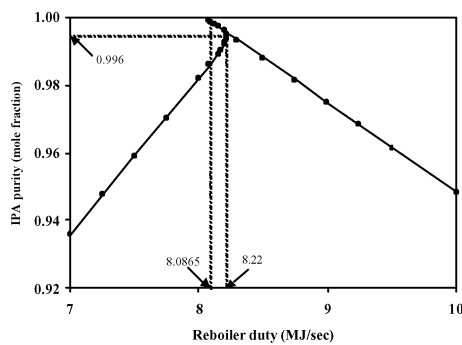


Figure 3. Relationship between reboiler duty and IPA product purity for propylene feed of 119.6 mole/s.

Reactive distillation processes often exhibit multiple steady states. Multiplicity of steady states can be classified as either “input multiplicity” or “output multiplicity”. With reference to control structures, input variables are those that can be manipulated by control valves or other actuating devices. Output variables are those that are either controlled or measured to describe the conditions of the process. Input multiplicity occurs when two or more sets of input variables produce the same output variable. Output multiplicity occurs when one set of process input variables results in two or more sets of process output variables. Figure 3 shows the relationship between reboiler duty and bottom IPA product purity at a propylene feed of 119.6 moles/s. Both input and output multiplicities occur under this feed condition. For reboiler duties below 8.0865 MJ/s (the required amount to IPA product with 99.9 mol%) or above 8.22 MJ/s, there is only one solution corresponding to a reboiler duty. However, for reboiler duties between 8.0865 MJ/s and 8.22 MJ/s, there are two solutions corresponding to exactly the same reboiler duty, i.e. output multiplicity. Similarly, the same value of IPA product purity below 99.6 mol% can be obtained with two different values of reboiler duty,

i.e. input multiplicity can be found. The presence of input and output multiplicities may cause operation and control problems. Output multiplicity is, by definition, a “true” multiplicity phenomenon. Oscillation between steady states can occur even without observable disturbances. When the desired controlled variable exhibits input multiplicity that results in the change in the sign of process gain leading to control instability, alternative controlled variable that has one-to-one relation with the manipulated variable should be identified.

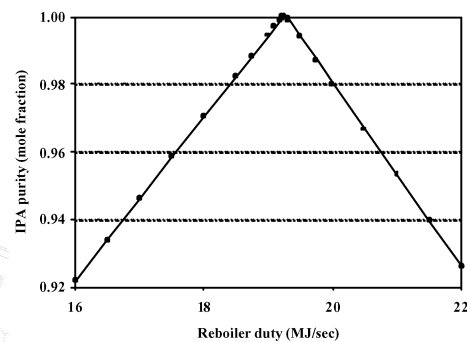


Figure 4. Relationship between reboiler duty and IPA purity for propylene feed of 150 mole/s.

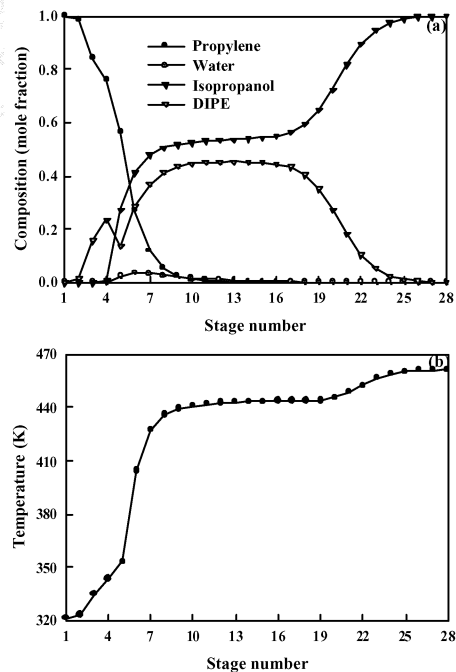


Figure 5. Composition and temperature profiles at nominal operating condition.

To eliminate output multiplicity, we try to increase propylene feed flow to examine its impact on the multiplicity. Figure 4 shows the relationship

between reboiler duty and IPA product purity for propylene feed of 150 mole/s. We found that output multiplicity of the IPA column can be eliminated by increasing propylene feed flow above 150 mole/s. The column to produce 99.9 mol% IPA from bottom needs less reboiler duty for propylene feed of 150 mole/s, which is thus chosen as the nominally operating value. Figure 5 shows the composition and temperature profiles in the column at nominal operating condition. The excess propylene feed is withdrawn from column top. Side product, DIPE, is mainly retained in the middle of the column and can therefore reduce the effect of side reaction.

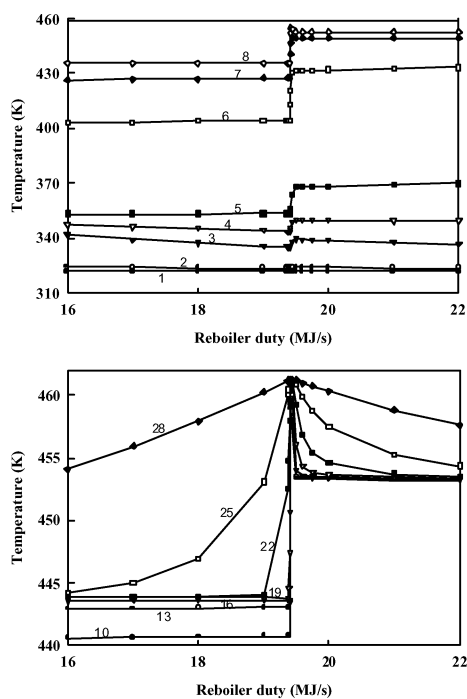


Figure 6. Relationship between reboiler duty and stage temperature.

3. Temperature + Feed Ratio Control

The primary objective of the column is to produce a bottom IPA product with high-purity. Reflux ratio is fixed and reboiler duty is manipulated to maintain IPA product purity. The bottom IPA product purity is, however, non-monotonic with respect to the reboiler duty due to input multiplicity. The changes in sign of the process gain and dead time of the composition analyzer made direct control of IPA purity difficult. An alternative candidate for the controlled variable can be the stage temperature. The relationship between stage temperature and

reboiler duty with reflux ratio fixed at 30 is shown in Figure 6. Very low sensitivity and near-constant value of temperature can be found at stages 1 and 2. Input multiplicity occurs at the temperatures of stages 3 and 4 and between the temperatures of stages 7 and 28 around nominal operating condition. Temperatures of stages 5 and 6 are the only two variables that have one-to-one relationship with reboiler duty. Both temperatures show very strong nonlinearity. They have low sensitivity when reboiler duty is below 19.405 MJ/s and above 19.450 MJ/s, but very high sensitivity when reboiler duty is between 19.405 MJ/s and 19.450 MJ/s. The temperature of stage 5 has slower response to reboiler duty than that of stage 6, which is thus chosen as the controlled variable of temperature control loop.

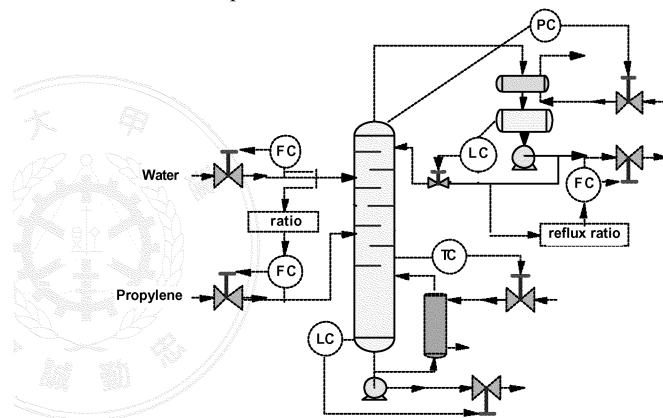


Figure 7. Temperature + feed-ratio control scheme at constant reflux ratio, with set point of propylene flow loop adjusted by feed ratio control.

When operating the reactive distillation column for IPA synthesis, the propylene and water feeds are kept at 1.5:1 ratio in order to eliminate output multiplicity. The simplest way to maintain this ratio is to use feed ratio control. Figure 7 is a feed-ratio control scheme in which both feeds are flow controlled. The set point of propylene flow loop is adjusted to 1.5 times that of the water flow by ratio control. Column pressure is controlled by manipulating coolant flow rate. Reflux-drum level and base level are maintained by changing reflux flow rate and bottom flow rate respectively. Reflux ratio is controlled by manipulating distillate flow rate. Temperature control loop is implemented by manipulating vapor boilup. Temperature of stage 6 is used as the controlled variable of the loop. All control valves are designed to be half open at the

initial steady state. Dead time of five seconds is assumed for the temperature measurement with a transmitter span of 100°C . Dead time of five minutes is assumed for the concentration measurement. The transmitter span of composition measurement is taken as 0.6. The flow measurement has no dead time and a span equals to the difference of 1.5 and 0.5 time the nominal operating flow.

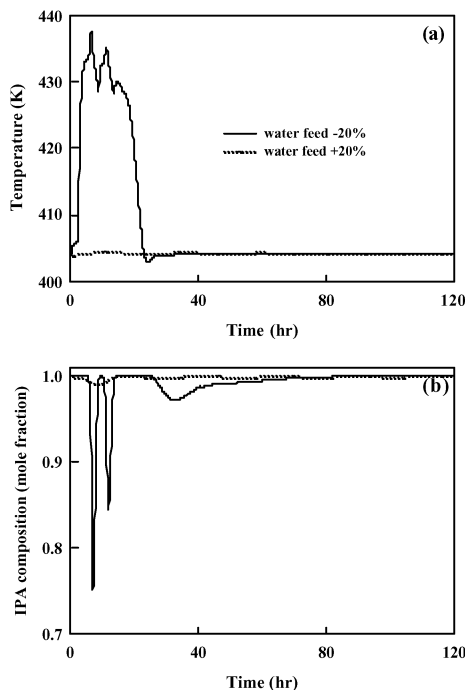


Figure 8. Dynamic responses of temperature + feed-ratio control scheme at constant reflux ratio, with set point of propylene flow loop adjusted by feed ratio control.

Figure 8 shows the dynamic responses of the control scheme in Figure 7 when the set point of the water flow loop is changed by $\pm 20\%$ with no bias in feed flow measurement. In the case of feed flow increase, the temperature of stage 6 is initially decreased and the column is driven into the region with low sensitivity but linear behavior as described in Figure 6. Large control action is allowed to reject the external disturbance. Thus the controlled stage temperature and bottom IPA product purity can quickly be settled at their set point and designed operating value, respectively. However, in the case when feed flow decreases, the temperature of stage 6 is initially increased and the column is driven from the low sensitivity region into

the high sensitivity one, that is, the column is operated within the region with highly nonlinear behavior. Thus only very smaller control action is allowed to compensate for the external disturbance and isn't sufficient to quickly draw the controlled stage temperature back its set point. The controlled stage temperature then jumps from low temperature plateau to high temperature one shown in Figure 6. It takes about 20 hours at high temperature plateau. In the meantime, bottom IPA product oscillates between the peak purity and its right-hand region as shown in Figure 4. Once the controlled stage temperature is drawn back to the low temperature plateau, the IPA product can fall into the left-hand region of the peak purity and then takes a long time to gradually return to its designed value.

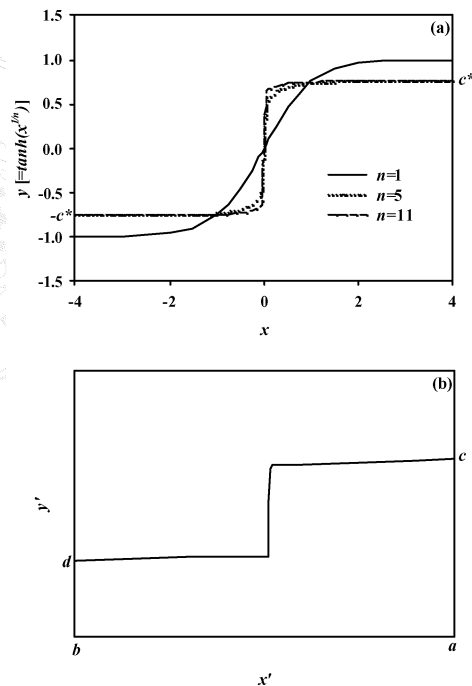
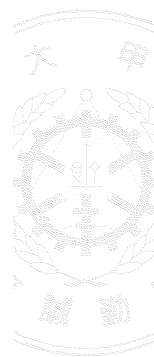


Figure 9. Comparison of the relationship between x and $\tanh(x^{1/n})$ with different n and the relationship between reboiler duty and temperature of stage 6.

4. Variable Transformation

The temperature of stage 6 exhibits highly nonlinear characteristic with reboiler duty. The use of nonlinear control element becomes necessary for performance improvement. Bequette [31] surveyed nonlinear control system techniques ranging from ad hoc or process-specific strategies to predictive control approaches. One of nonlinear

control techniques is variable transformation approach, which is used in the study. To transform the nonlinear controlled variable to a linear one, we try to search for a mathematic function where the relation of dependent variable and independent variable is similar to that of the temperature of stage 6 and reboiler duty. Figure 9a shows the relationship between $y=\tanh(x^{1/n})$ and x for different odd numbers n . Figure 9b shows the relationship between temperature of stage 6 as y' and reboiler duty as x' . a and b represent the extreme values of possible operating range of reboiler duty, while c and d are the corresponding temperature of stage 6 when reboiler duties are equal to a and b , respectively. It can be found that the relation between temperature and reboiler duty most resembles the function $y=\tanh(x^{1/11})$, which is thus used as the basic form of variable transformation. By comparing Figures 9a and 9b, the following form of variable transformation can be derived by algebraic calculation

$$50 \cdot \left\{ \operatorname{arctanh} \left[\frac{1}{23.639} (T_6 - 417.89) \right] \right\}^{11} + 420 \quad (5)$$

Figure 10 shows the relationship between reboiler duty and original temperature and transformed temperature of stage 6. It can be found the transformed temperature has more linear behavior with reboiler duty than the original one.

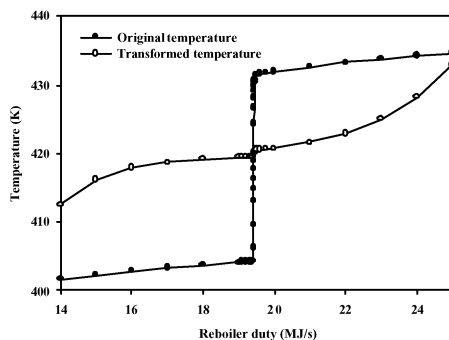


Figure 10. Relationship between reboiler duty and original temperature and transformed temperature of stage 6.

To compare the control performance of linear control scheme, shown in Figure 8, with that of the control scheme with transformed temperature loop, the dynamic responses of original temperature and bottom IPA purity are shown in Figure 11. For the transformed temperature loop, the controller was tuned using a sequential design approach [32]. Relay-feedback test [33] is performed to obtain

ultimate gain and ultimate frequency. The following equations are then used to calculate the tuning parameters of PI controllers:

$$K_c = K_{cu} / 3 \quad (6)$$

$$T_I = P_u / 0.5 \quad (7)$$

where K_c and T_I represent proportional gain and integral time respectively, and K_{cu} and P_u are ultimate gain and ultimate period respectively. Much larger control action of transformed temperature loop than original temperature loop is allowed to compensate for the external disturbance and avoid the temperature of stage 6 to jump from low temperature plateau to high temperature plateau. From these two figures, it is obvious that the control scheme with transformed temperature control loop provides much superior control performance.

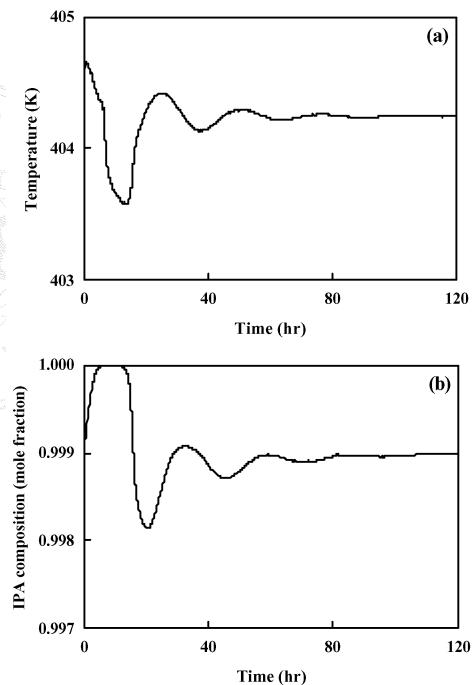


Figure 11. Dynamic responses of transformed temperature + feed-ratio control scheme at constant reflux ratio, with set point of propylene flow loop adjusted by feed ratio control.

5. Temperature + Composition Control

Al-Arfaj and Luyben [19] pointed out that a feed-ratio control scheme is a feedforward scheme, that has no guarantee of the final product quality. When there is a measurement bias in feed flow rate, the feed-ratio control scheme will not be able to keep the desired feed ratio. The results by steady state analysis, shown in Figure 12, explains the effect of measurement bias of propylene feed on the IPA

product purity when the temperature of stage 6 is kept as its initial value. Very pure IPA product is obtained for negative measurement bias of propylene feed, while substantial decrease in IPA purity occurs for the case of positive measurement bias. Figure 13 shows the dynamic responses of transformed temperature + feed ratio control scheme to feed flow measurement bias $\pm 3\%$ and large throughput rate change -20% . The bottom IPA purity cannot return to its designed value, even though the controlled stage temperature can settle at its set point.

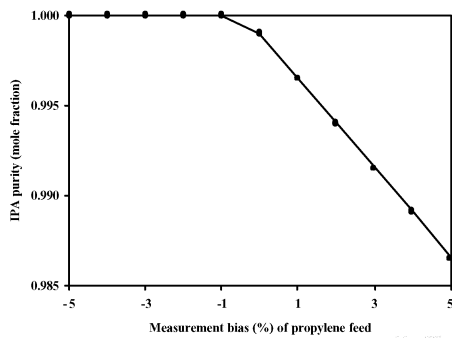


Figure 12. Relationship between IPA purity and measurement bias of propylene feed when temperature of stage 6 is kept as its initial value.

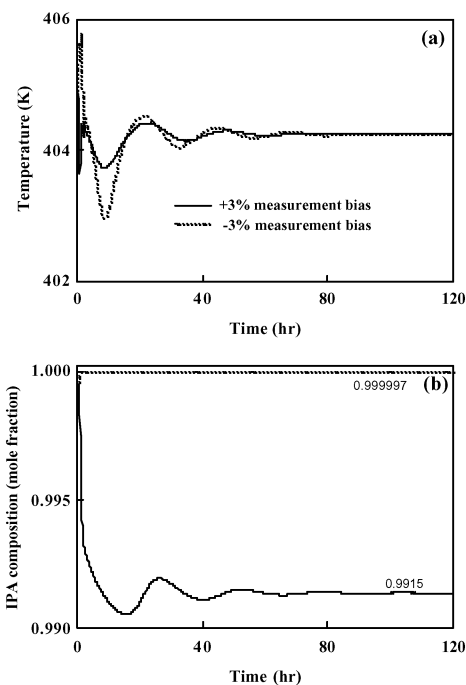


Figure 13. Responses of transformed temperature + feed ratio to propylene feed flow measurement bias $+3\%$ and large throughput rate change -20% .

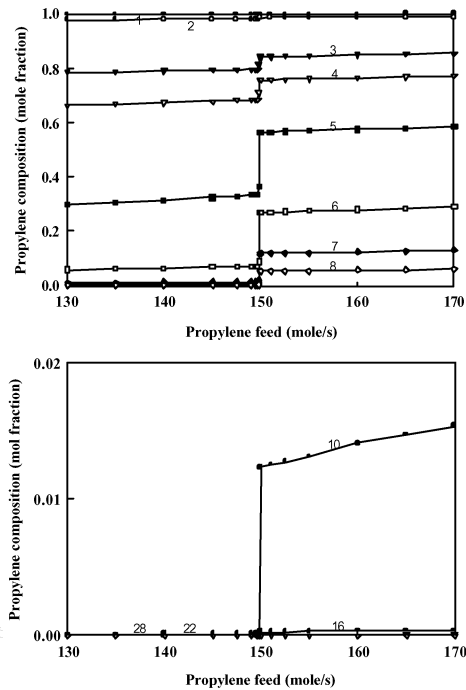


Figure 14. Effect of propylene feed flow on propylene concentration at different stages.

To overcome the shortcomings of a feed ratio control, Al-Arfaj and Luyben [19] suggested that the composition of some column stage be controlled by the feed flow. Although online composition measurement is more expensive and has a longer dead time, it does not depend on the absolute value of the measurement. However, the problem is to find a proper candidate for controlled variable. Water concentrations are low in the column at the nominal operating condition as shown in the Figure 5. Propylene composition of some column stage is then selected as the controlled variable. Figure 14 shows the effect of propylene feed on propylene compositions at different stages. Very low sensitivity and near-constant value of propylene composition can be found at stages 1 and 2. Very low propylene composition exists at stages 8 to 28 around nominal operating condition. Figures 15 and 16 show the effect of reboiler duty on propylene concentration and the effect of propylene feed flow on temperature at different stages, respectively. It can be found that interaction multiplicity occurs between reboiler duty and propylene compositions of stages 3 and 4. Thus propylene compositions of stages 5 to 7 are the only candidates for the controlled variables of the composition loop. The propylene composition of stages 6 and 7 has slower

response to propylene feed flow. Hence the propylene composition of stage 5 is chosen as the controlled variable of composition loop. Very strong nonlinearity also occurs around nominal operating condition between propylene composition of stage 5 and propylene feed flow. To have better control performance, the propylene composition of stage 5, c_5 , is transformed by the similar procedures as those for the variable transformation of stage temperature by using the following equation.

$$\left\{ \arctan h \left[\frac{1}{0.235} (c_5 - 0.435) \right] \right\}^{11} + 0.45 \quad (8)$$

Figure 17 shows the difference between original composition and transformed composition. Much linear behavior is obtained for the transformed composition.

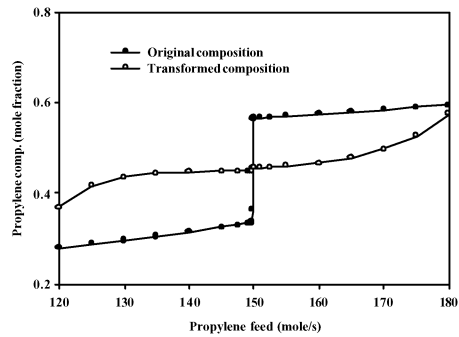


Figure 17. Relationship between propylene feed and original propylene composition and transformed propylene composition of stage 5

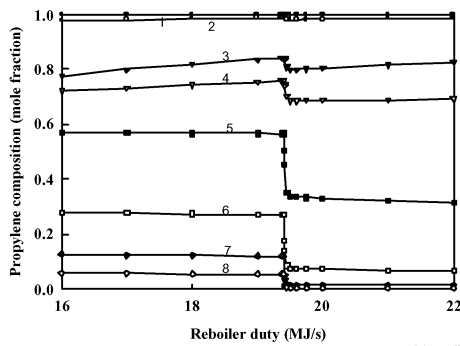


Figure 15. Effect of reboiler duty on propylene concentration at different stages.

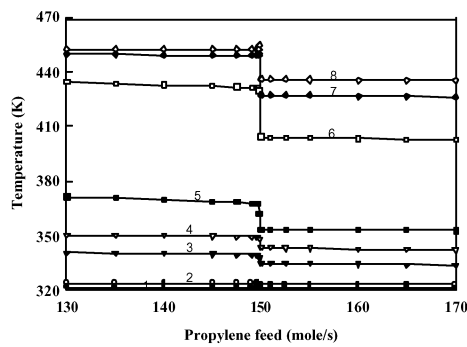


Figure 16. Effect of propylene feed flow on temperature at different stages.

The dynamic responses under the transformed temperature and composition control scheme are shown in Figure 18 when there is a -20% change in water flow rate. Bottom IPA composition can return to its nominal operating value under both temperature and composition control. Therefore the control scheme works well when there is a feed flow disturbance.

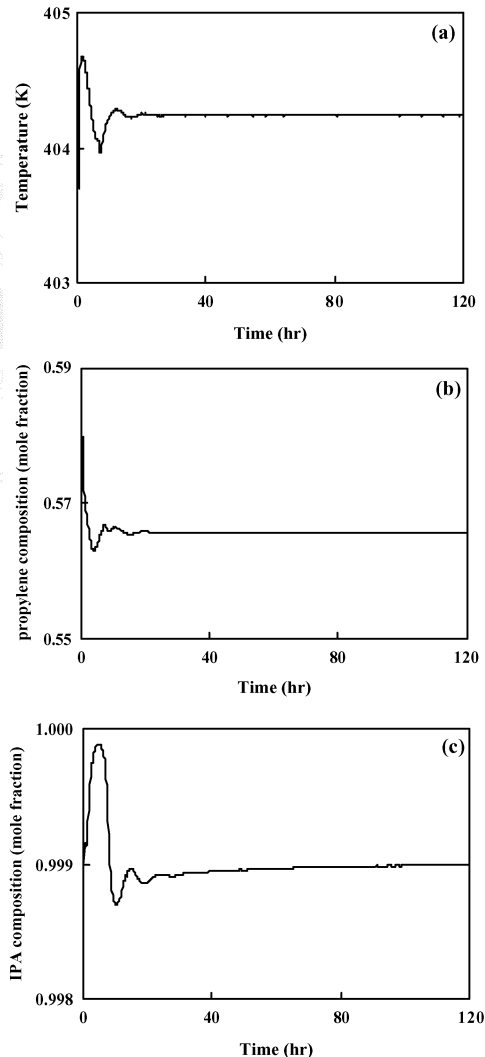


Figure 18. Responses of transformed temperature + composition control scheme to a -20% change in water feed flow.

6. Conclusion

In this study, we have used the steady-state analysis to investigate the process characteristics and control strategy of a reactive distillation column for IPA synthesis by direct hydration of propylene. The keys of controlling the column are to maintain the quality of the bottom product and to maintain a proper ratio between the feeds. Quality can be maintained by controlling the temperature of some column stage. Maintenance of feed ratio can be implemented by internal composition control. Although both input and output state multiplicities occur in the column, output multiplicity is eliminated by increasing propylene feed flow and input multiplicity is avoided by choosing the stage temperature and propylene composition that has monotonic relationship with reboiler duty and propylene feed, respectively. Variable transformation is used to overcome the strong nonlinearity existing in temperature and composition loops. Simulation results show that the transformed temperature and composition control scheme can provide superior control performance for feed flow disturbances.

Acknowledgments

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Nomenclature

a = right extreme value of possible operating range of reboiler duty
 b = left extreme value of possible operating range of reboiler duty
 c = temperature of stage 6 when reboiler duty is equal to a
 c^* = corresponding y value of the right extreme value of x
 d = temperature of stage 6 when reboiler duty is equal to b
 K_a = reaction equilibrium constant
 K_c = proportional gain
 K_{cu} = ultimate gain
 n = odd number
 P_u = ultimate period
 T = temperature (K)
 T_I = integral time
 x = independent variable
 x' = reboiler duty

y = dependent variable

y' = temperature of stage 6

\hat{y} = transformed temperature

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