

REFERENCE

- Al-Arfaj, M.; and Luyben, W.L. Comparison of Alternative Control Structures for an Ideal Two-Product Reactive Distillation Column. *Ind. Eng. Chem. Res.* 39(2000): 3298-3307.
- Al-Arfaj, M.; and Luyben, W.L. Control Study of Ethyl *tert*-Butyl Ether Reactive Distillation. *Ind. Eng. Chem. Res.* 41(2002a): 3784-3796.
- Al-Arfaj, M.; and Luyben, W.L. Comparative control study of ideal and methyl acetate reactive distillation. *Chem. Eng. Sci.* 57(2002b): 5039-5050.
- Bianchi, C.L.; Ragaini, V.; Pirola, C.; Carvoli, G. A new method to clean industrial water from acetic acid via esterification. *Appl. Catal., B* 40(2003): 93-99.
- Ciric, A.R.; and Gu, D. Synthesis of nonequilibrium reactive distillation by MINLP optimization. *American Institute of Chemical Engineers Journal*, 40(1994): 1479-1487.
- Doherty, M.F.; and Buzad, G. Reactive distillation by design. *Chemical Engineering Research and Design, Transactions of the Institution of Chemical Engineers, Part A*, 70(1992): 448-458.
- Gangadwala, J.; Kienle, A.; Stein, E.; Mahajani, S. Production of Butyl Acetate by Catalytic Distillation: Process Design Studies. *Ind. Eng. Chem.* 43(2004): 136-143.
- Gangadawala J.; Mankar S.; Mahajani S. Esterification of Acetic Acid with Butanol in the Presence of Ion-exchange Resins as Catalysts. *Ind. Eng. Chem. Res.* 42(2003): 2146-2155.
- Groggins, P.H. *Unit Processes in Organic Synthesis*, 2nd ed., New York, McGraw-Hill Book, 1938.
- Hanika, J.; Kolena, J.; Smejkal, Q. Butyl acetate via reactive distillation: Modeling and Experiments. *Chem. Eng. Sci.* 54(1999): 205-5209.

- Hung, W.J.; Lai, I.K.; Chen, Y.W.; Hung, S.B.; Huang, H.P.; Lee, M.J.; Yu, C.C. Process Chemistry and Design Alternatives for Converting Dilute Acetic Acid to Esters in Reactive Distillation. *Ind. Eng. Chem. Res.* 45(2006a): 1722-1733.
- Hung, W.J.; Lai, I.K.; Hung, S.B.; Huang, H.P.; Lee, M.J.; Yu, C.C. Control of Reactive Distillation Columns for Amyl Acetate Production using Dilute Acetic Acid. *Journal of the Chinese Institute of Engineers*, 29(2006b): No.2, 319-335.
- Karpilovskiy, O.L.; Pisarenko, Yu.A.; Serafimov, L.A. Multiple Solutions in Single-Product Reactive Distillation. *Distill. Adsorpt.* 97 (1997): 685-694.
- KMPS Extraction Technology Group, Recovery of tightly Hydrogen-Bonded Organics from Water, Liquid-Liquid Extraction Column Design Karr, Scheibel, RDC, Pulsed, Static & More.
- Leyes C.E.; and Othmer D.F. Esterification of Butanol and Acetic Acid. *Ind. Eng. Chem.* 37(1945): 968-977.
- Loning, S.; Horst, C.; Hoffmann, U. Theoretical Investigations on the quaternary System *n*-Butanol, *n*-Butyl acetate, Acetic Acid and Water. *Chemical Engineering Technology*, 23(2000): 789-794.
- McKetta, J.J. *Encyclopedia of Chemical Processing and Design*; Marcel Dekker: New York, 19(1983): 381-402.
- Neumann, R.; and Sasson, Y. Recovery of Dilute Acetic Acid by Esterification in a Packed Chemorectification Column. *Ind. Eng. Chem. Process Des. Dev.* 23(1984): 654-659.
- Noeres, C.; Kenig, E.Y.; Gorak, A. Modelling of reactive separation processes: reactive absorption and reactive distillation. *Chemical Engineering and Processing*, 42(2003): 157-178.
- QVF Process Systems Ltd. Tollgate Industrial Estate, The Recovery of Acetic Acid by Liquid-Liquid Extraction.
- Saha, B.; Chopade, S.P.; Mahajani, S.M. Recovery of Dilute Acetic Acid through Esterification in a Reactive Distillation Column. *Catal. Today*. 60(2000): 147-157.

- Sirola, J.J. An industrial perspective on process synthesis. *AIChE Symp. Ser.* No. 304, 91(1995): 222-233.
- Singh, A.; Tiwari, A.; Mahajani, S.M.; Gudi, R.D. Recovery of Acetic Acid from Aqueous Solutions by Reactive Distillation. *Ind. Eng. Chem. Res.* 45(2006): 2017-2025.
- Shoemaker, J.D., and Jones, E.M. Cumene by catalytic distillation. *Hydrocarbon Processing*, 66(1987): 57-58.
- Smejkal, Q. et al. Comparison of computer simulation of reactive distillation using ASPEN PLUS and HYSYS software. *Chemical Engineering and Processing*, 41(2002): 413-418.
- Steinigeweg, S.; and Gmehling, J. n-Butyl acetate synthesis via Reactive Distillation: Thermodynamic Aspects, Reaction Kinetics, Pilot-Plant Experiments, and Simulation Studies. *Ind. Eng. Chem.* 41(2002): 5483-5490.
- Sundmacher, K.; Zhand, R.S.; Hoffmann, U. Mass transfer effects on kinetics of nonideal liquid phase ethyl tert-butyl ether formation. *Chemical Engineering and Technology*, 18(1995) 269-277.
- Taylor, R.; and Krishna, R. Modelling reactive distillation. *Chem. Eng. Sci.* 55(2000): 5183-5229.
- Venimadhavan, G.; Malone, M.F.; Doherty, M.F. A Novel Distillate Policy for Batch Reactive Distillation with Application to the Production of Butyl Acetate. *Ind. Eng. Chem. Res.* 38(1999): 714-722.
- Wang, S.J.; Wong, D.S.H.; Lee, E.K. Control of a Reactive Distillation Column in the Kinetic Regime for the synthesis of n-Butyl Acetate. *Ind. Eng. Chem. Res.* 42(2003): 5182-5194.
- WIKIPEDIA THE FREE ENCYCLOPEDIA, [http://en.wikipedia.org/wiki/Acetic acid](http://en.wikipedia.org/wiki/Acetic_acid)
- Xu, Z. P.; Afacan, A.; Chuang, K.T. Removal of Acetic Acid from Water by Catalytic Distillation. Part 1: Experimental Studies. *Can. J. Chem. Eng.* 77(1999): 676-681.

Zeng, K.L.; Kuo, C.L.; Chien, I.L. Design and control of butyl acrylate reactive distillation column system. *Chem. Eng. Sci.* 61(2006): 4417-4431.

APPENDICES

APPENDIX A

NRTL METHOD

Theoretical developments in the molecular thermodynamics of liquid-solution behavior are often based on the concept of local composition.

The NRTL (Non-Random-Two-Liquid) equation, proposed by Renon and Prausnitz in 1968, is an extension of the original Wilson equation. It uses statistical mechanics and the liquid cell theory to represent the liquid structure. These concepts, combined with Wilson's local composition model, produce an equation capable of representing VLE, LLE and VLLE phase behavior.

The NRTL is thermodynamically consistent and can be applied to ternary and higher order systems using parameters regressed from binary equilibrium data. It has accuracy comparable to the Wilson equation for VLE systems.

The NRTL equation in HYSYS contains five adjustable parameters (temperature dependent and independent) for fitting per binary pair. The NRTL combines the advantages of the Wilson and van Laar equations, and, like the van Laar equation, it is not extremely CPU intensive and can represent LLE quite well. It is important to note that because of the mathematical structure of the NRTL equation, it can produce erroneous multiple miscibility gaps.

The NRTL equation in HYSYS has the following form:

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \left[\tau_{ij} - \frac{\sum_{m=1}^n \tau_{mj} x_m G_{mj}}{\sum_{k=1}^n x_k G_{kj}} \right] \quad (\text{A-1})$$

$$G_{ji} = \exp[-\tau_{ij}\alpha_{ji}] \quad (\text{A-2})$$

$$\tau_{ij} = A_{ij} + B_{ij}/T(\text{K}) \quad (\text{A-3})$$

where	γ_i	=	activity coefficient of component i
	x_i	=	mole fraction of component i
	T	=	temperature (K)
	n	=	total number of components
	A_{ij}	=	binary parameters of NRTL equation
	B_{ij}	=	binary parameters of NRTL equation
	α_{ij}	=	relative volatility of component i with respect to component j for VLE ($\alpha_{ij} = \alpha_{ji}$)
	G_{ji}	=	binary interaction parameter in NRTL equation
	τ_{ij}	=	binary interaction parameter

The equation uses parameter values are shown in Table A-1.

Table A-1 Binary parameters α_{ij} and τ_{ij}

Component i	H ₂ O	H ₂ O	H ₂ O	BuOAc	BuOAc	BuOH
Component j	BuOAc	BuOH	HOAc	BuOH	HOAc	HOAc
A_{ij}	5.563	1.807	-1.667	-1.637	-5.226	-7.338
A_{ji}	-1.677	-1.170	-3.895	-0.167	4.927	5.735
B_{ij}	157.21	628.99	813.48	661.5	2044.38	2797.74
B_{ji}	903.22	682.68	1601.61	222.88	-1801.49	-2268.36
α_{ij}	0.25	0.45	1.7	0.45	0.3	0.2

APPENDIX B

AN INTEGRATED APPROACH FOR DESIGN OF DISTILLATION COLUMN CONTROL SYSTEM

Rigorous dynamic simulation is clearly a more accurate way of evaluating process response and the dynamic performance of various control structure. By making use of its solving efficiency, we can employ a steady state technique to screen out unattractive control structures and suggest viable candidates. Then, using rigorous dynamic simulation, we can discriminate among the smaller number of remaining alternatives.

We present an integrated distillation control design procedure that involves both steady state and dynamic simulation. The steady state design methodology presented is useful for suggesting viable distillation control candidates and screening out clearly unworkable schemes. The design procedure is composed of the following steps:

- Step 1 Develop design basis
- Step 2 Select a candidate control scheme
- Step 3 Open loop test using model to fine a candidate temperature sensor location
- Step 4 Close loop test candidate control scheme for feed rate and feed composition disturbances

Step 1 Develop Design Basis

As with any design effort, it is important to begin by establishing all of the important criteria that the final design must satisfy. This includes, but may not be limited to identifying and understanding:

- what the product draw composition specs are

- whether the specifications are one- or two-sided
- which stream is the demand stream
- what the expected disturbances to the column are
- what the operating constraints are
- what the base case or normal operating condition for the column is

It is particularly important to understand the nature of the disturbances that are likely to upset the column. Accurate predictions of feed rate and feed composition disturbances are a key element to eventually developing a robust and workable control structure. It is perhaps worth mentioning here as well, that if the design is for an upgrade or expansion to an existing process, it is important to understand the existing control structure and why it is implemented the way it is. Reasons for a particular control structure may be very subtle, yet critically important to the plant-wide operability. On the other hand, many controls are left-overs from old designs and have not been changed simply because no one has bothered to improve them.

Step 2 Selecting candidate control schemes

The second step in the steady state procedure is to select a candidate control structure. Two-product distillation is typically viewed as a 5×5 control problem. There are five degrees of freedom in a typical two-product distillation column, represented by:

1. feed valve
2. reflux valve
3. distillate valve
4. heat input valve
5. bottom valve

We do not consider pressure controls here since we are normally able to achieve tight pressure control via inerts blanketing and venting, or with low-boiler venting.

Under such conditions, pressure may be considered fixed, and thus does not affect the degrees of freedom available for the remaining controls.

In a 5×5 system, there are $5!$ or 120 possible single-input, single-out control combinations. However, once all of the constraints of the process are considered, normally only a few combinations are left.

First, we must determine which of the streams in the demand stream: the one which is set by some upstream or downstream process and thereby sets the production rate for the column. Typically the feed is the demand stream; however, occasionally we see the distillate or the bottoms being set independently.

Next we examine the overhead and bottoms inventory controls in light of the base case, or normal operating conditions. We compare the relative magnitude of the reflux vs. distillate, and bottom vs. boilup. If the

Step 3 Open loop testing

The third step in the process involves evaluating the open loop sensitivity of temperature (composition) to the candidate composition control variable. The goal here is to identify a sensitive region in the column for temperature measurement. By holding all other inputs constant and running a number of case studies with different values of the manipulated variable, we can generate a family of temperature profiles around the base case. Typically, changes in the manipulated variable of $\pm 1\%$, $\pm 2\%$, $\pm 5\%$, and $\pm 10\%$ are sufficient.

Examining the curves, we look for sensor locations where temperature changes are significant, and linear. We can often control temperatures accurately to within $\pm 0.5^\circ\text{C}$. Thus a temperature change of 1°C , while not ideal, is often significant enough. By linear, we mean that temperature changes are roughly equal in magnitude when the manipulated variable is changed by the same amount in both directions around the base case.

Figure B-1 shows a group of temperature profiles for an industrial column currently in operation. One where the distillate flow is increased by 1 %, and one where the distillate flow is decreased by 1 %. As you can see, when the distillate flow is increased, some tray temperatures increase. This is because the concentration of the high boiling point material is higher in the distillate which shifts the composition profile up, producing higher temperatures in the top trays. When we decreased the distillate, the opposite effect occurs. Using the criteria described above, we might select tray 38 for temperature control. Tray 10 would be a poor location as there is no sensitivity to negative changes in the manipulated variable.

In general we prefer to measure temperature for control purposes nearer to the end of the column with the most important purity specification. Additionally, the temperature at the sensor location ought to be reasonably sensitive to changes in the manipulative variable, and should vary linearly with increasing and decreasing values of the manipulative variable. We have found that in some cases we can control tray temperature to within a half of a degree centigrade. Based on this performance, we consider a plus or minus one degree change at a given location to be sufficient for temperature control.

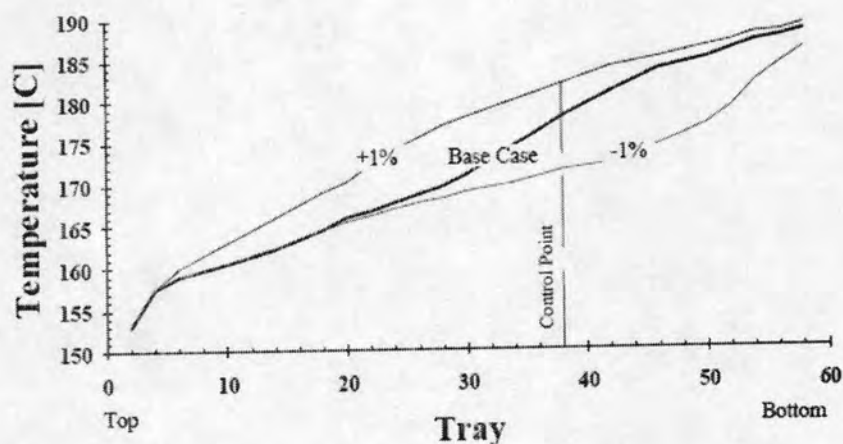


Figure B-1 Temperature Sensitivity

Step 4 Close loop test candidate control scheme for feed rate and feed composition

The last step in the design procedure is to perform what we have termed “closed loop” testing. In this step, we use the steady model to simulate the candidate control strategy and test it for feed composition and feed flow changes.

The control strategy is simulated by setting the model solution specifications to mimic the way the column is controlled. For example, if we are considering a control strategy where the reflux flow is fixed and a tray temperature is controlled with steam flow, then steady state model solution conditions would be to set the mass reflux flow and tray temperature.

The first step is to find a set of operating conditions that meet or exceed the product composition specifications for all expected feed rates and compositions. This can be a b iterative process; however, in many situations we can use out knowledge of distillation to help find these conditions. Again, if we are fixing the reflux flow, we need to find the feed conditions that require the highest reflux flow to satisfy the product composition specifications. The reflux flow will then be set at this value for all other feed rate and feed composition combinations. We also must find a temperature setpoint that will keep the top and bottom product compositions at or below specifications for all expected conditions.

Next we test the model with these operating conditions for various feed composition and feed rate combinations. We recommend that a minimum, a middle, and a maximum feed rate and feed composition be selected which defines nine cases to be simulated. For some multicomponent cases, more than one feed composition may need to be varied independently. If two compositions are varied then 27 cases must be simulated. The case study features of the steady state models make it easy to run the large m\number of cases needed. If the top and bottom product specifications are met or exceeded for all cases, then we have found an acceptable control strategy for the column. The last step in the closed loop testing procedure is to compare the energy consumption of the candidate scheme, the ratio alternative, and the minimum.

The minimum energy consumption is found by setting the top and bottom product purities exactly at the specifications. If the energy cost difference is large between the minimum, the candidate control scheme and the ratio alternative, then another candidate control scheme should be evaluated to see if a more energy efficient scheme exists.

APPENDIX C

EQUIPMENT SIZING

In conventional distillation, tray holdup has no effect on the steady-state design. In reactive distillation, tray holdup (or amount of catalyst) can be a critical design parameter because of its effect on reaction rates. Tray holdup is not important if the forward and reverse reaction rates are so fast that chemical equilibrium occurs on each tray. However, if reactions are kinetically limited, not equilibrium limited, tray holdup is critically important. Tray holdup depends on both the diameter of the column and weir height. The latter is limited by pressure drop. The former depends on vapor rates, which vary with tray holdup because of the interplay between reaction and separation in reactive distillation columns. Therefore, column sizing becomes more complex than is the case in conventional distillation.

A. Column Diameter

The calculation of the diameter of the column in reactive distillation column is more complex than in conventional distillation because of its effect on liquid holdup or weight of catalyst on each tray. The depth of liquid on a reactive tray cannot be too large because of hydraulic limitations (excessive pressure drop). This limits the holdup on individual trays for a given diameter column. But the smaller the holdup, the more reactive trays required in the design and/or the higher the reflux ratio required to achieve the desired conversion.

The diameter of a column is set by the maximum vapor velocity. The vapor rate and vapor density at tray 1 and tray 30 are needed to calculate the maximum vapor velocity from Eq. (B-1).

$$V_{\max} = \frac{F - \text{Factor}}{\sqrt{\rho_V}} \quad (\text{B-1})$$

Then the cross-sectional areas of the columns at these two locations are calculated from Eq. (B-2).

$$\text{Area} = \frac{\text{Volumetric Flow}}{\text{Velocity}} \quad (\text{B-2})$$

The larger of these two areas must be used to calculate the column diameter.

$$D = \sqrt{\frac{4(\text{Area})}{\pi}} \quad (\text{B-3})$$

B. Reflux Drum and Column Base

Using the heuristic of 10 minutes of total holdup, we can calculate the volumes in the reflux drum and in the column base. Both of the total flowrate and density of organic phase and aqueous phase leaving the reflux drum are needed to calculate reflux drum volume. Therefore, reflux drum volume can be calculated from Eq. (B-4). Whereas, column base (reboiler) volume can be calculated from Eq. (B-5).

$$V = \frac{(\text{organic or aqueous flowrate})(\text{holdup})}{(\text{organic or aqueous density})} \quad (\text{B-4})$$

$$V = \frac{(\text{liquid entering reboiler flowrate})(\text{holdup})}{(\text{liquid entering reboiler density})} \quad (\text{B-5})$$

C. Control Valve Sizing

All valves are designed to be 50 % open except for the valves on the condenser. Nominal pressure drops are used.

VITA



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