

PART 1

FUNDAMENTALS AND TOOLS

COPYRIGHTED MATERIAL



CHAPTER 1

INTRODUCTION

An azeotrope is a mixture of chemical components that has identical compositions of the liquid and vapor phases in equilibrium with each other. This azeotropic phenomenon occurs because of molecular interactions between different chemical components. If the components contain similar elemental molecules and structure, the molecular interaction is very slight and azeotropes do not occur. Mixtures of hydrocarbons (propane, butane, pentane, etc.) are important examples. These mixtures have phase equilibrium behavior that is close to ideal and often have relative volatilities that are almost constant. However, if the components are dissimilar, the molecules can exhibit either repulsion or attraction. Repulsion increases the effective vapor pressures of the components at a given temperature and can produce minimum-boiling azeotropes. In terms of liquid-phase activity coefficients, discussed in detail in Chapter 2, repulsion produces activity coefficients greater than unity. If the repulsion is large enough, the repulsive forces can lead to the formation of heterogeneous minimum-boiling azeotropes (two liquid phases). The azeotrope boils at a temperature that is lower than the boiling point of the lighter component.

The methanol–water mixture is an example of a system that exhibits modest nonideality. The OH end of the methanol molecule is similar to the OH end of the water molecule, but the hydrocarbon CH₃ end of the methanol molecule is different from water. So the system exhibits a modest amount of nonideality, which can be represented by the change in relative volatility as liquid composition changes.

If we add another CH₂ group and move to the ethanol–water system, there is more repulsion because the CH₃–CH₂ end of the ethanol molecule is quite different from the OH end of the water molecule. The system exhibits more nonideality and a minimum-boiling azeotrope occurs. This azeotrope is homogeneous (only one liquid phase in equilibrium with a vapor phase). If we add two more CH₂ groups and move to the *n*-butanol–water system, the

repulsion is even more extreme. The result is the formation of a *heterogeneous* minimum-boiling azeotrope with two liquid phases in equilibrium with a vapor phase.

In other chemical systems, the molecules can *attract* instead of repulse. The results can be the formation of *maximum*-boiling azeotropes because the molecular attraction reduces the effective vapor pressures of the components. Examples include nitric acid–water, acetone–chloroform, formic acid–water, and *n,n*-dimethyl acetamide–acetic acid.

Chapter 2 is devoted to a detailed discussion of the vapor–liquid–liquid phase equilibrium of azeotropic systems. In this chapter we provide some historical perspective of the field, discuss several typical and important applications, and provide some journal references in the area of control of azeotropic distillation systems.

Also included is an example of one of the important complexities in trying to deal with azeotropic distillation systems. These systems are highly nonlinear and exhibit the phenomenon of multiple steady states.

1.1 HISTORY

The existence of azeotropes has been known for many years, probably as long as man has made ethanol. Designing chemical engineering processes to separate azeotropes has been dealt with in some of the earliest chemical engineering books. The first chemical engineering textbook used by the senior author was the 1937 *Principles of Chemical Engineering*,¹ authored by three of the very early workers in the field of chemical engineering. On page 526 of that pioneering book, the *xy* curve for ethanol–water was presented. Subsequent pages showed curves for typical homogeneous minimum and maximum-boiling azeotropes.

The earliest book that concentrated on distillation as a unit operation *Elements of Fractional Distillation*,² was first published in 1922 and was into its fourth edition by 1950. Chapter 10 of this work discussed extractive and azeotropic distillation. In an era before computers, the authors presented how plate-to-plate component and phase equilibrium equations can be solved manually (mechanical calculator or slide rule) to design several extractive distillation systems. One interesting example was the maximum-boiling nitric acid–water system using sulfuric acid as the heavy entrainer (solvent). They also presented a detailed design of azeotropic distillation of ethanol–water using benzene as the light entrainer. Ternary diagrams and composition profiles were presented. The labor-intensive calculations probably took a hard-working graduate student many days or weeks to complete. We are fortunate to now have the tools to perform these calculations in seconds.

The earliest book that concentrated exclusively on extractive and azeotropic distillation was published in 1964 by E. J. Hoffman.³ Ternary diagrams for many azeotropic systems were discussed, including the concepts of residue curves, and alternative flowsheet configurations were presented.

One of the pioneers in developing a method for separating azeotropic mixtures was Donald F. Othmer, who worked for Eastman Kodak before moving to Brooklyn Polytechnic University. Othmer's many papers and patents in the 1930s and 1940s were major contributions to the field. His early paper,⁴ discussed the use of azeotropic distillation to facilitate the separation of acetic acid and water (which do not form an azeotrope but which exhibit a severe pinch in the high-water region) by the addition of a light entrainer (ethylene dichloride). Othmer developed these process designs without the aid of modern tools.

The advent of computer technology greatly enhanced our ability to explore azeotropic systems in a quantitative manner. Two of the early workers in developing and applying modern computational tools were Michael Doherty and Michael Malone at the University of Massachusetts. They demonstrated how ternary diagrams and the concepts of residue curves and distillation boundaries could be effectively used to aid in the conceptual design of azeotropic systems. They developed the Mayflower simulation software for performing azeotropic distillation calculations, which was later commercialized by Hyprotech into the DISTIL program and by AspenTech into the SPLIT program. Some of these tools are discussed and demonstrated in Chapter 2.

The early workers in the area of azeotropic separation concentrated on phase equilibrium issues and steady-state designs. There was much less work in the area of control of azeotropic systems. A pioneering paper by Prokopakis and Seider⁵ dealing with the dynamic simulation of azeotropic distillation columns was published in 1983. One of the earliest papers that dealt with both design and control was published in 1985.⁶ Several early papers by Morari and co-workers considered both design and control of azeotropic systems.⁷⁻⁹

A comprehensive review paper by Widagdo and Seider,¹⁰ summarized the literature as of that date concerning the design, simulation, and control aspects of azeotropic systems. More recent control papers are reviewed in Section 1.3.

1.2 APPLICATIONS

There are many important industrial applications of azeotropic separations, which employ a variety of methods. In this book we discuss several of these chemical systems and demonstrate the application of alternative methods of separation. The methods presented include pressure-swing distillation, azeotropic distillation with a light entrainer, extractive distillation with a heavy entrainer (solvent), and pervaporation. The chemical systems used in the numerical case studies included ethanol–water; tetrahydrofuran (THF)–water, isopropanol–water, acetone–methanol, isopentane–methanol, *n*-butanol–water, acetone–chloroform, and acetic acid–water. Economic and dynamic comparisons between alternative methods are presented for some of the chemical systems, for example azeotropic distillation versus extractive distillation for the isopropanol–water system.

The systems discussed in this book are typical of many azeotropic systems. So the techniques demonstrated in subsequent chapters should be applicable to a wide range of systems.

1.3 LITERATURE

The literature dealing with azeotropes is vast with hundreds of journal articles. There are several excellent textbooks that deal with the conceptual design of azeotropic systems. Most notable are the books by Doherty and Malone¹¹ and Stichlmair and Fair.¹² Both of these books give examples of azeotropic separation phase equilibrium and flowsheets in both binary and ternary systems. The chapter by Doherty and Knapp “Azeotropes,” in the *Kirk–Othmer Encyclopedia of Chemical Processes* provides an excellent discussion of VLE fundamentals and conceptual design of a number of azeotropic systems.

The vast majority of the literature deals with phase equilibrium and steady-state design aspects of azeotropic separation. Papers dealing the control of azeotropic systems are far fewer in number. Some more recent journal articles are listed in the references 13–32.

1.4 MULTIPLE STEADY STATES

The nonlinear algebraic equations that describe a steady-state distillation column consist of component balances, energy balances, and vapor–liquid phase equilibrium relationships. These equations are nonlinear, particularly those describing the phase equilibrium of azeotropic systems. Unlike a linear set of algebraic equations that have one unique solution, a nonlinear set can give multiple solutions; therefore, the possibility of multiple steady states exists in azeotropic distillation.

With exactly the same input variables fixed (feed flow and composition, reflux flowrate, and distillate flowrate), there may be completely different values for the compositions and temperatures throughout the column. This is called “output multiplicity.” If this occurs it adds significant complexity to the design and control of these systems. Problems in converging the steady-state program in Aspen Plus frequently are encountered and can be challenging to overcome.

To provide an example of this phenomenon, let us consider the azeotropic distillation column shown in Figure 1.1. This is the first column in a two-column azeotropic distillation system to separate a binary mixture of ethanol and water. Benzene is used as the light entrainer that carries the water overhead and produces a bottoms product of high-purity ethanol. The column has an organic reflux (OR) stream fed to the top tray, which comes from a downstream decanter. A recycle stream from the second column is also fed to the azeotropic column. The overhead vapor is condensed and goes to a decanter. The organic phase is refluxed back to the first column. The aqueous phase is fed to a recovery column whose bottoms product is high-purity water and whose distillate is recycled back to the azeotropic column. Note that the azeotropic column is a stripper with no condenser. Once the

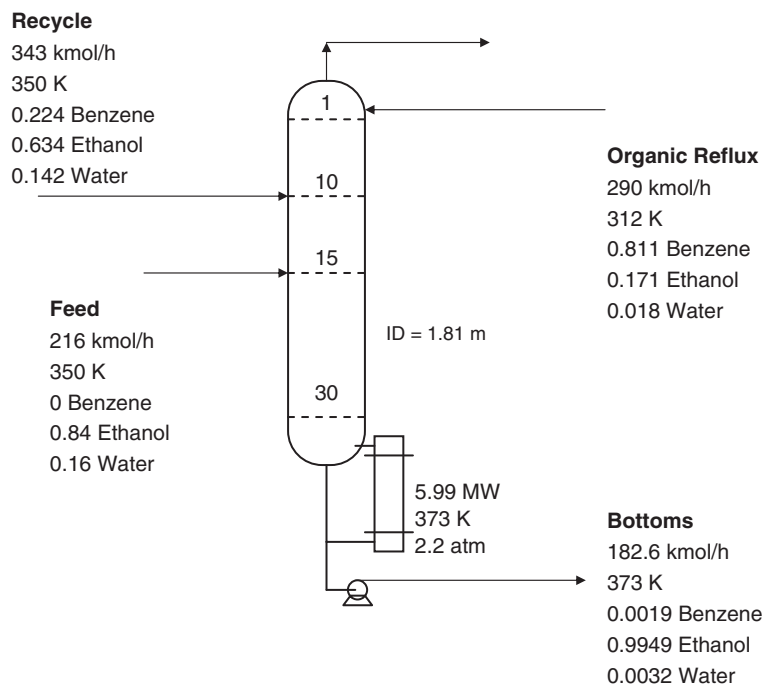


Figure 1.1 Azeotropic column.

number of stages, the feed locations, the pressure, and the feed conditions (composition, flowrate and temperature) have been fixed, the stripper has only one degree of freedom. This is selected as the bottoms flowrate.

To illustrate what happens when running Aspen Plus with this column, we fix the bottoms flowrate at 182.6 kmol/h and vary the reflux flowrate over a range of values, starting first at low values and then starting at high values. Figure 1.2 gives the results of these positive and negative scans.

If we start at a small value of reflux and gradually increase the flowrate, the resulting trajectories of the benzene and water compositions of the bottoms are shown in the solid lines. For small reflux flowrates, there is not enough benzene being fed, so there is a high concentration of water $x_{B(W)}$ in the bottoms as shown in the lower graph. Of course, there is also very little benzene in the bottoms.

As the reflux is gradually increased, a point is reached at about 315 kmol/h where the water concentration in the bottoms drops abruptly to very small values, while the concentration of benzene begins to gradually increase. Now there is enough benzene in the column to drive the water overhead; however, to have a high-purity ethanol product, there should be very small amounts of both benzene and water.

Once the point of this sharp change has been passed, we can reverse the sequence of cases and begin to reduce the reflux flowrate. These are the dashed lines in Figure 1.2. The benzene concentration gradually decreases; the water concentration remains very low until a reflux flowrate of about 280 kmol/h is reached, where another abrupt change occurs. The column “goes over the cliff” at 315 kmol/h when moving up in reflux, and it again “goes over the cliff” at 280 kmol/h when moving down in reflux. Operating with any reflux flowrate between these two values can yield two possible steady-state conditions.

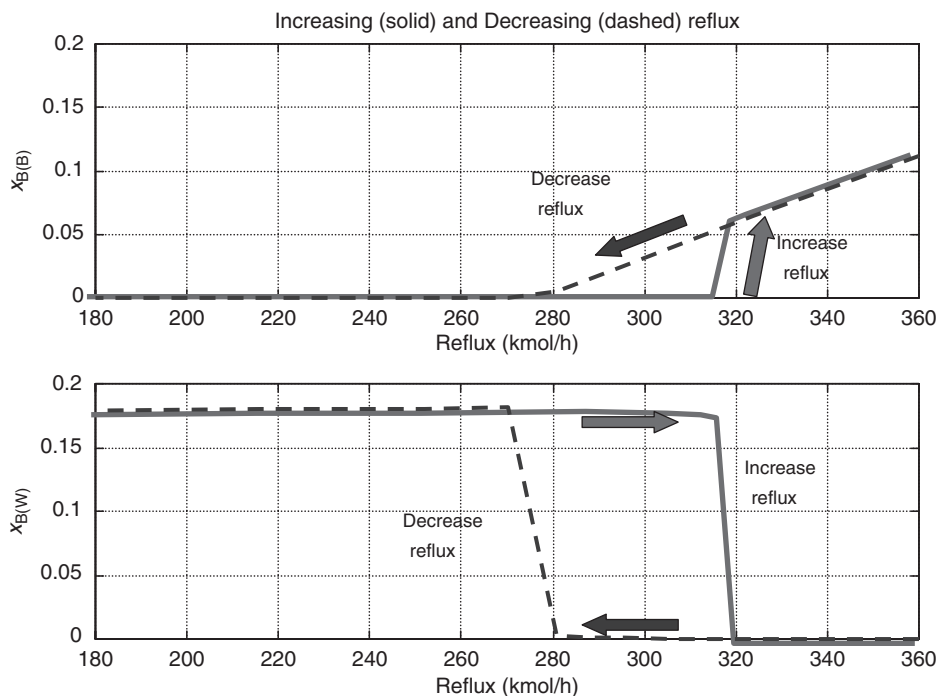


Figure 1.2 Steady-state convergence.

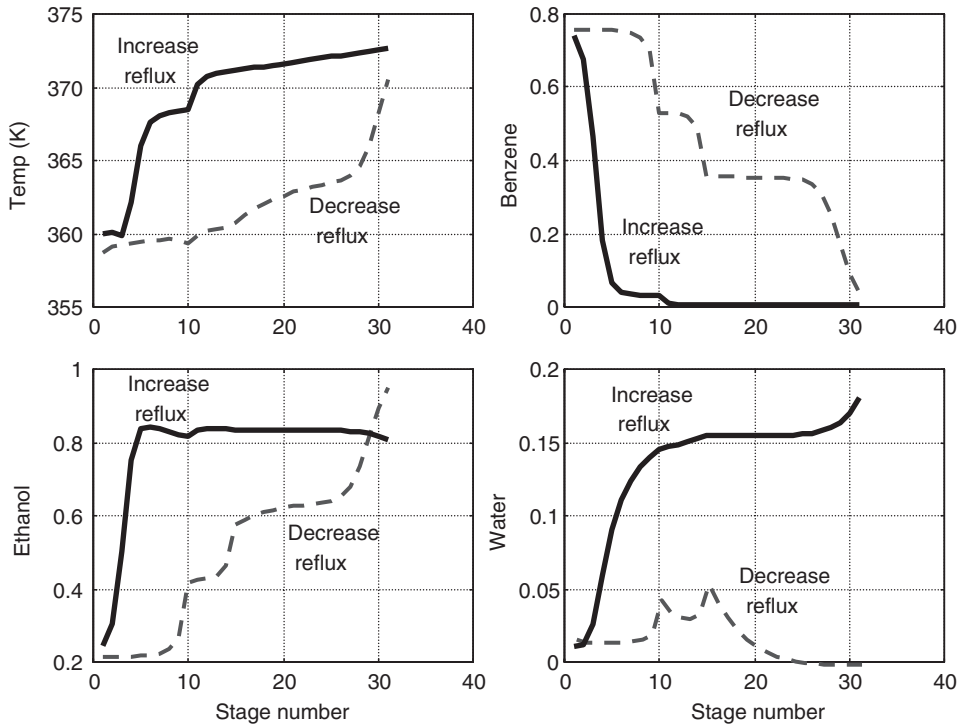


Figure 1.3 Multiple steady-state profiles; $R = 300$ kmol/h.

Figure 1.3 shows the resulting temperature and compositions profile for two steady-state solutions. Both have exactly the same reflux flowrate (300 kmol/h) and bottoms flowrate (182.6 kmol/h), but the profiles are very different. The solid lines correspond to the case when the reflux has been slowly *increased* to 300 kmol/h from a lower value. There is little benzene in the bottoms but lots of water. Temperatures are high throughout the column.

The dashed lines correspond to the case when the reflux has been slowly *decreased* to 300 kmol/h from a higher value. Now there is little water in the bottoms but increasing values of benzene. Temperatures are low throughout the column.

The desired steady-state design produces a high-purity ethanol bottoms product. Figure 1.1 shows that this is achieved with a reflux flowrate of 290 kmol/h, which is inside the multiple steady-state region (280 to 315 kmol/h). Under these conditions, the bottoms composition is 0.19 mol% benzene, 99.49 mol% ethanol, and 0.32 mol% water.

These results clearly illustrate some of the complexities of dealing with azeotropic distillation. We will encounter these problems and also other issues in dealing with azeotropic systems in subsequent chapters, which make design and control challenging.

REFERENCES

1. Walker W. H., W. K. Lewis, and E. R. Gilliland, *Principles of Chemical Engineering*, Third Edition, McGraw-Hill, New York, 1937.
2. Robinson C. S. and E. R. Gilliland, *Elements of Fractional Distillation*, McGraw-Hill, New York, 1958.
3. Hoffman E. J., *Azeotropic and Extractive Distillation*, Interscience Publisher, New York, 1964.

4. Othmer D. F., Azeotropic distillation for dehydrating acetic acid. *Chemical and Metallurgical Engineering*, 91–94 (June 1941).
5. Prokopakis G. J. and W. D. Seider, Dynamic simulation of azeotropic distillation towers, *AIChE J.*, **29**, 1017–1029 (1983).
6. Abu-Eishah S. I. and W. L. Luyben, Design and control of a two-column azeotropic system, *Ind. Eng. Chem. Process Des. Dev.*, **24**, 132–140 (1985).
7. Jacobsen E. W., L. Laroche, M. Morari, S. Skogestad, and H. W. Andersen, Robust control of homogeneous azeotropic distillation columns, *AIChE J.*, **37**, 1810–1824 (1991).
8. Andersen H. W., L. Laroche, and M. Morari, Dynamics of homogeneous azeotropic distillation columns, *Ind. Engng. Chem. Res.*, **30**, 1846–1855 (1991).
9. Laroche L., M. Morari, and H. W. Anderson, Effect of design on the operation of homogeneous azeotropic distillation, *Comput. Chem. Engng.*, **19**, 105–122 (1995).
10. Widagdo S. and W. D. Seider, Journal review: azeotropic distillation, *AIChE J.*, **42**, 96–130 (1996).
11. Doherty M. F. and M. F. Malone, *Conceptual Design of Distillation Systems*, McGraw-Hill, New York, 2001.
12. Stichlmair J. G. and J. R. Fair, *Distillation Principles and Practices*, Wiley-VCH, New York, 1998.
13. Kurooka T., Y. Yamahsita, H. Nishitani, Y. Hashimoto, M. Yoshida, and M. Numata, Dynamic simulation and nonlinear control system design of a heterogeneous azeotropic distillation column, *Comput. Chem. Engng.*, **24**, 887–892 (2000).
14. Phimister J. R. and W. D. Seider, Semicontinuous, middle-vessel, extractive distillation, *Comput. Chem. Engng.*, **24**, 879–885 (2000).
15. Phimister J. R. and W. D. Seider, Semicontinuous, pressure-swing distillation, *Ind. Engng. Chem. Res.*, **39**, 122–130 (2000).
16. Chien I. L., C. J. Wang, D. S. H. Wong, C. H. Lee, S. H. Cheng, R. F. Shih, W. T. Liu, and C. S. Tsai, Experimental investigation of conventional control strategies for a heterogeneous azeotropic distillation column, *J. Process Control*, **10**, 333–340 (2000).
17. Chien I. L., W. H. Chen, and T. S. Chang, Operation and decoupling control of a heterogeneous azeotropic distillation column, *Comput. Chem. Engng.*, **24**, 893–899 (2000).
18. Chien I. L., K. L. Zeng, and H. Y. Choa, Design and control of a complete heterogeneous azeotropic distillation column system, *Ind. Engng. Chem. Res.*, **43**, 2160–2174 (2004).
19. Rueda L. M., T. F. Edgar, and R. B. Eldridge, A novel control methodology for a pilot plant azeotropic distillation column, *Ind. Engng. Chem. Res.*, **45**, 8361–8372 (2006).
20. Luyben W. L., Control of a multi-unit heterogeneous azeotropic distillation process, *AIChE J.*, **52**, 623–637 (2006).
21. Luyben W. L., Plantwide control of an isopropyl alcohol dehydration process, *AIChE J.*, **52**, 623–637 (2006).
22. Arifin S. and I. L. Chien, Combined preconcentrator/recovery column design for isopropyl alcohol dehydration process, *Ind. Engng. Chem. Res.*, **46**, 2535–2543 (2007).
23. Arifin S. and I. L. Chien, Design and control of an isopropyl alcohol dehydration process via extractive distillation using dimethyl sulfoxide as an entrainer, *Ind. Engng. Chem. Res.*, **47**, 790–803 (2008).
24. Luyben W. L., Design and control of a fully heat integrated pressure-swing azeotropic distillation system, *Ind. Engng. Chem. Res.*, **47**, 2681–2695 (2008).
25. Luyben W. L., Comparison of extractive distillation and pressure-swing distillation for acetone-methanol separation, *Ind. Engng. Chem. Res.*, **47**, 2696–2707 (2008).
26. Luyben W. L., Effect of solvent on controllability of extractive distillation, *Ind. Engng. Chem. Res.*, **47**, 4425–4439 (2008).
27. Luyben W. L., Control of maximum-boiling acetone/chloroform azeotropic distillation system, *Ind. Engng. Chem. Res.*, **47**, 6140–6149 (2008).

28. Luyben W. L., Control of the heterogeneous azeotropic *n*-butanol/water distillation system, *Energy and Fuels*, **22**, 4249–4258 (2008).
29. Luyben W. L., Control of a column/pervaporation process for separating the ethanol/water azeotrope, *Ind. Engng. Chem. Res.*, **48**, 3484–3495 (2009).
30. Wu Y. C., I. L. Chien, and W. L. Luyben, Two-stripper/decanter flowsheet for methanol recovery in the TAME reactive-distillation process, *Ind. Engng. Chem. Res.*, **48**, 10532–10540 (2009).
31. Wu Y. C. and I. L. Chien, Design and control of heterogeneous azeotropic column system for the separation of pyridine and water, *Ind. Engng. Chem. Res.*, **48**, 10564–10576 (2009).
32. Hsu K. Y., Y. C. Hsiao, and I. L. Chien, Design and control dimethyl carbonate-methanol separation via extractive distillation in the dimethyl carbonate reactive-distillation process, *Ind. Engng. Chem. Res.*, **49**, 735–749 (2010).