

CHAPTER 1

INTRODUCTION

1.1 CONTEXT AND SIGNIFICANCE

In virtually any chemical process, whether it is in the food, pharmaceutical, biological or fuel industries, one or more chemical reactions take place to manufacture a wide range of products. Unfortunately, as nature would have it, these reactions invariably produce by-products which severely affect the quality and therefore the final market value of the final product. This generally means that some sort of separation scheme has to be devised to remove unwanted impurities and to upgrade the purity of the wanted component(s). Over the course of the past few decades, many technologies have become available and have been sufficiently developed to accomplish this task, including distillation, membrane separation, crystallization, and solvent extraction, among others. However, of all these methods of separations, distillation remains by far the most common, mainly because it is (relatively) well understood, and its economic properties on a large scale are at the present moment the most favorable. In short, distillation is a method of purifying binary and multicomponent mixtures into purer products by exploiting the difference in boiling points between the respective components.

In order to exploit the difference in boiling point temperatures (or vapor pressures), a distillation column generally requires heating. On a large scale this heating is not insignificant. In fact, Soave and Feliu have reported that in 1995 there were approximately 40,000 distillation columns in the United States [1], accounting for 90% of all industrial separations and consuming around 2.87×10^{18} J (2.87 million TJ), which is equivalent to 54 million tons of crude oil or a continuous

power consumption of 91 GW [2]. In another study, it has been estimated that energy inputs into distillation columns in the United States accounts for approximately 3% of the entire country's energy consumption [3]. It is evident that by saving or recovering only 1% of the energy used by distillation columns, the impact would be significant. Apart from the obvious opportunities in reducing the energy requirements of a distillation train, it is also important to consider the capital investments associated to a particular separation, that is, the cost to physically construct the column, which is a strong function of the steel price at the time of construction. Capital and energy costs are generally opposing objectives, namely an energy-intensive column usually requires a smaller capital investment, and vice versa. A typical *simple*, one-feed-two-product continuous distillation column is shown in Figure 1.1.

The column shown in Figure 1.1 generally accepts an impure or mixed feed, and purifies it into two product streams, namely the *distillate* and *bottoms* streams. The distillate stream has a higher purity in low-boiling components while the bottoms stream is richer in high-boiling components.

Due to the tremendous costs associated to distillation, it is essential that a design engineer fully knows and understands the phenomena and processes at work. As such, graphical methods for designing distillation schemes have been especially

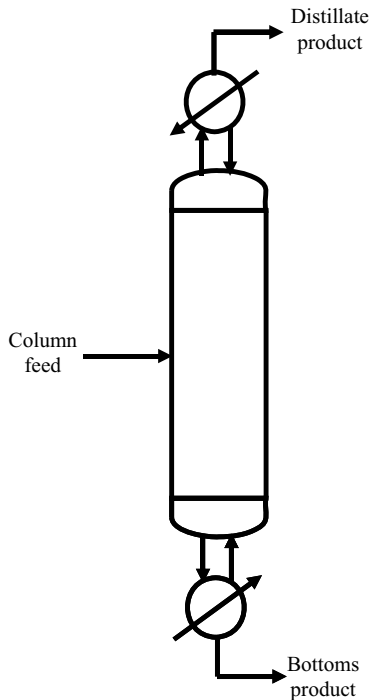


FIGURE 1.1 A typical continuous distillation column.

popular. In 1925, McCabe and Thiele published a landmark paper on a graphical design method for binary distillation [4], still used today as a quick means of understanding the relationship between energy and capital costs for simple distillation. Multicomponent distillation columns have been traditionally designed through the Underwood set of equations [5]. These equations assume constant relative volatility between all components, constant molar overflow, and a sharp separation between product streams, that is, one or more of the components are completely depleted in at least one of the products (sharp splits) [6]. These assumptions are very good approximations for a large number of industrial applications and these equations have been applied by numerous authors to a plethora of distillation structures [7–16].

Residue curve maps and distillation line maps have also been a useful graphical technique for screening ternary separation feasibility, especially for simple columns [17]. These maps are basically a range of trajectories that track the liquid compositions of the chemical species over time in a simple batch distillation operation and conveniently present the relationship between liquid and vapor phases, allowing one to quickly analyze potential splits, even for highly nonideal systems. Although these maps can tell much about the feasibility of separation, they have limitations in that they only give information at rather impractical conditions for the design engineer: infinite energy requirements when in continuous operation. This will become apparent especially in Chapters 2 and 3.

Numerous other design techniques have evolved over the years with varying degrees of complexity. One of these is the shortest stripping line method proposed by Lucia et al. [18], which states that the shortest stripping line will generally lead to the structure with lowest heat duty. Another technique, proposed in the 1980s by Doherty and coworkers, modeled sections above and below the feed stage of a simple column with a set of ordinary differential equations [19–23]. This approach, named the boundary value method, is relatively simple to employ (with modern day computers and mathematical software) and accepts virtually any phase equilibrium behavior and product distributions.

Other, so-called nonequilibrium models or rate-based models [24–28] have also received considerable attention. In short, these models do not assume perfect equilibrium on each stage in the distillation column, but rather use mass and heat transfer coefficients to compute the degree of fractionation. Although the nonequilibrium model is unquestionably more rigorous and precise, it may not allow the same insight and understanding afforded by its simpler, equilibrium counterpart. For the vast majority of distillation problems, the equilibrium model is quite sufficient, especially when the designer is still in the conceptual or “idea-generation” stage of the design.

Even advanced simulation packages such as Aspen Plus[®] or Hysys, although having undoubted modeling capabilities, have not provided much insight into the design of complex distillation systems. This is largely due to the fact that these packages require precise initialization values to ensure convergence to the specified product purities. Furthermore, because of the “black box” nature of these packages, the user often does not have any insight into the final solution and how one might go about improving it. Without the necessary experience or advanced knowledge of the

problem at hand, rigorously determining a column's feasibility or optimal point(s) of operation is a time-consuming, if not impossible, task.

Recently, in a series of papers by the Centre of Material and Process Synthesis (COMPS) at the University of the Witwatersrand, Johannesburg, a new distillation design technique was proposed, Column Profile Maps (CPMs) [29,30]. CPMs were derived from an adaptation of ordinary differential equations for simple columns first proposed by Doherty and coworkers [19–23]. The graphical, generalized CPM method has been shown to be extremely useful for designing and analyzing distillation systems, especially complex distillation systems [31,32]. As with the boundary value method, the CPM method is an equilibrium model, and does not require any simplifying assumptions regarding the phase equilibrium behavior, that is, the ideality of the liquid–vapor phase or the product distribution. Furthermore, highly insightful design parameters, such as the feed and product placements, are a product of the design and do not require the designer to specify them blindly beforehand. However, it is thought that the CPM method is perhaps most useful in devising new, previously unthought-of structures, since it is completely generalized and not limited to any particular piece of equipment.

The CPM method is furthermore not only confined to classical distillation schemes like those mentioned above but also the distillation research group at COMPS have used the original CPM ideas to design and analyze reactive distillation systems (Chapter 8) [33], hybrid membrane-distillation systems (Chapter 9) [34,35], experimental validation of thermodynamic models and column behavior (Chapter 4) [36–38], and fundamental work in the behavior of columns [39,40]. This book aims to summarize some of the key ideas the group have developed over the past few years, with the hope that other researchers, students, and engineers may come up with new and interesting configurations, or at the very least, understand the underlying workings of a particular distillation column.

Although this book primarily advocates distillation synthesis using the CPM method and can be read on its own, the reader should be aware that it is by no means an all encompassing text on distillation. Among the books that are considered by the authors to be a useful addition to this book are *Distillation Design* [41] and *Distillation Operation* by Henry Kister [42], *Conceptual Design of Distillation Systems* by Doherty and Malone [43], *Separation Process Principles* by Seader and Henley [44], and *Distillation Theory and its Application to Optimal Design of Separation Units* by Petlyuk [45]. All these works present different perspectives on the separation synthesis problem. Specifically, the book by Doherty and Malone shows the fundamental roots of the CPM method, that is modeling distillation columns with differential equations.

1.2 IMPORTANT DISTILLATION CONCEPTS

This book has been compiled for the student, engineer, or researcher that understands the fundamental concepts of distillation, or has at least attended an introductory course on the subject. The reader should be familiar with key vapor–liquid

equilibrium concepts, how industrial distillation is performed and basic design techniques such as the McCabe–Thiele method. For the sake of completeness and clarity however, we give a brief overview here of core concepts that the reader should be aware of and that are often used in this book.

1.2.1 A Typical Column

As evident from Figure 1.1, heat is added to the column through a *reboiler*, which vaporizes material and causes a vapor stream to travel upward in the column. Moving upward in the column, this vapor stream becomes richer in low-boiling component (s). For an efficient separation to occur, the vapor stream at the top of the column is condensed, at the *condenser*, and a portion of the condensed liquid is sent back down the column. This recycling of material is a key design parameter in distillation and is known as *reflux*, or the *reflux ratio*, and is directly proportional to the energy requirement of the column, that is, the higher the reflux ratio of the column, the higher the heating and cooling loads of the column are. Therefore, from a purely energetic perspective, one would like to operate as close to the minimum column reflux as possible.

A column can be either *packed* or *trayed*, as shown in Figure 1.2a and b, respectively. Separation occurs continuously throughout the length of a packed column, and occurs in a more step-by-step fashion in trayed columns. In general, this book deals with packed columns but the behavior of these two types of columns are fundamentally similar and the results can be interpreted interchangeably. We will refer to the spatial coordinate representing the position down the length of the column as stage number, represented by the variable n . The total number of stages

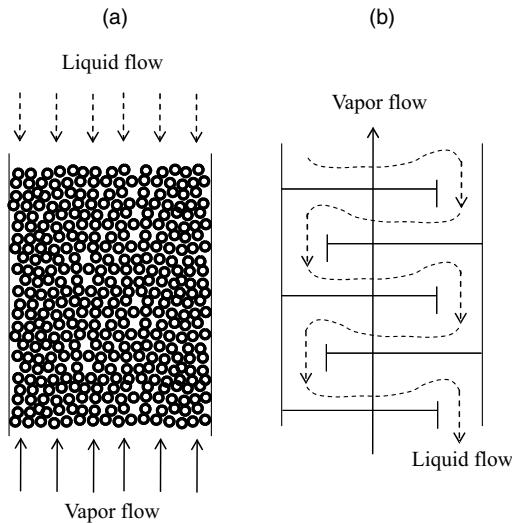


FIGURE 1.2 (a) Packed column and (b) trayed column.

required to affect the separation is thus related to the height of the column, which is indicative of the capital costs. It should be noted that the entry point of the feed stream occurs at the *feed stage*. Determining the feed stage is also an important design factor as it has a significant impact on the final product distribution of the column.

1.2.2 Complex Columns

Complex columns are in a broad sense all columns that are not simple columns, like the column shown in Figure 1.1. Complex columns may have multiple feeds, side product streams, stream transfers between two column units (thermally coupled columns), simultaneous chemical reaction(s) within the column body, hybrid membrane-distillation columns, and so on. Each of these columns present unique opportunities for cost saving. Typical complex columns are shown in Figure 1.3a–d.

Due to the tremendous costs associated to distillative separations, many alternate schemes to the simple column shown above have been proposed over the past several years both to improve on some of its inherent costs. Traditionally, when purifying a multicomponent mixture, an entire series of distillation columns are used in series, and the way in which these columns are sequenced may make a tremendous difference in the eventual process costs. However, due to the large energy requirements of even the most optimal sequence, more complex column arrangements have been proposed and subsequently utilized. These arrangements include thermally coupled columns such as side rectifiers and strippers, the fully thermally coupled columns (often referred to as the Petlyuk and Kaibel columns),

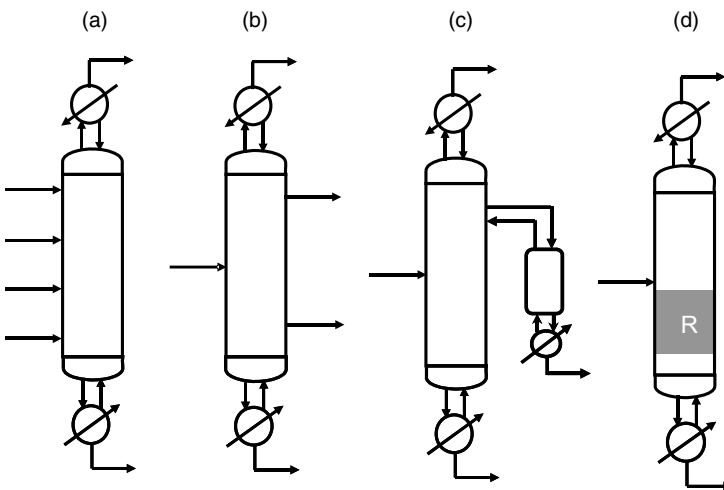


FIGURE 1.3 Examples of complex columns (a) distributed feed, (b) side-draw columns, (c) thermally coupled side stripper, (d) reactive distillation column with reaction zone (R).

prefractionating columns, and multieffect arrangements [9,10]. Up to 50% savings in energy expenditures have been reported with these thermally coupled arrangements [10,11,46–48].

Side stripping columns have found widespread use in the petrochemical industry to produce various cuts of petroleum products [49]. On the other hand, side rectifying columns have found application in air separation [45] as well as replacing entrainer regeneration columns in extractive distillation operations [50]. Even more complex columns such as the Petlyuk column or dividing wall column for separating a given feed into three products in a single distillation unit, requires only a single heat addition and removal, thereby reducing the energy costs of the separation. Despite the apparent advantages that these complex configurations offer, simple distillation columns are overwhelmingly more utilized in industry. One factor contributing to the underutilization of the complex arrangements is, possibly, a lack of understanding of these columns. Simple columns, on the other hand, are extremely well understood. Current research in distillation has therefore largely been directed toward complex column design.

1.2.3 Vapor–Liquid Equilibrium

The fundamental driving force for a separation to occur via distillation is that a mixture of components has different vapor and liquid compositions due to differences in vapor pressures. In other words, low-boiling components tend toward the vapor phase quicker than high-boiling components. Obviously, this difference in composition across coexisting vapor and liquid phases is dependent on the mixture being dealt with. From a modeling and design point of view, the relationship between the vapor composition of component i (y_i) and its liquid compositions (x_i) are centrally important, as it is ultimately this relationship which determines the design and operation of a distillation structure. In general, the relationship between vapor and liquid compositions can be expressed as

$$y_i = K_i x_i \quad (1.1)$$

Depending on the system at hand, the equilibrium ratio K_i may be either constant (as in Henry's law), or a function of temperature, pressure, and/or composition. In this book, the following phase equilibrium models are primarily models dealt with (1) constant relative volatilities, (2) ideal solutions using Raoult's law, and (3) nonideal solutions using a modified Raoult's law and the NRTL activity coefficient model, although other activity coefficient models are also applicable. Each of these three models is briefly discussed here.

- (1) *Constant Relative Volatilities*. The constant relative volatility model is the simplest model for relating vapor and liquid compositions with each other. Essentially, this model assumes that the volatility of components with respect

to each other remain constant, and are independent of temperature or composition. The relative volatility (α_i) of a component i is defined simply as

$$\alpha_i = \frac{K_i}{K_r} \quad (1.2)$$

where r is a reference component in the system and α_i is a constant. The reference component is usually taken as the highest boiling component and its relative volatility will be unity, subsequently all other relative volatilities in the system will be greater than one. This is the convention used in this book, but any component can of course be taken as the reference component. Using the unity summation properties of both vapor and liquid compositions, elucidated in Equation 1.3, the relationship in Equation 1.4 can be derived

$$\sum_{i=1}^{nc} x_i = 1 \quad \text{and} \quad \sum_{i=1}^{nc} y_i = 1 \quad (1.3)$$

$$y_i = \frac{\alpha_i x_i}{\sum_{j=1}^{nc} \alpha_j x_j} \quad (1.4)$$

where nc is the total number of components in the system. Equation 1.4 shows that the vapor composition in equilibrium with its liquid composition is only a function of the liquid composition and the relative volatilities that have been assumed. Obviously, the higher the value for α is for a particular component, the greater its tendency is to escape to the vapor phase. The assumption of constant relative volatility is generally, but not always, acceptable when the species being dealt with are all from the same functional group. For example, benzene and toluene have constant volatilities of approximately 5.28 and 2.24 with respect to the higher boiling *p*-xylene, respectively. Figure 1.4 shows the effect of the relative volatility on vapor and liquid compositions for binary systems. Here, component 1 is the low-boiling component, that is, most volatile, and component 2 is the highest boiling component, that is, least volatile with volatility of 1.

Figure 1.4 clearly indicates that higher the volatility is between two components, the greater the difference is between vapor and liquid compositions at equilibrium. Since it is exactly this difference between liquid and vapor compositions, that is, the driving force for distillative separation, higher volatility mixtures are consequently “easier” to separate than low volatility mixtures.

(2) *Ideal Solutions.* The constant relative volatility assumption is often very good for a large number of systems. However, in many systems the equilibrium ratio is not constant but a function of temperature and pressure. Such a system may be modeled with Raoult’s law, assuming that the vapor phase is an ideal

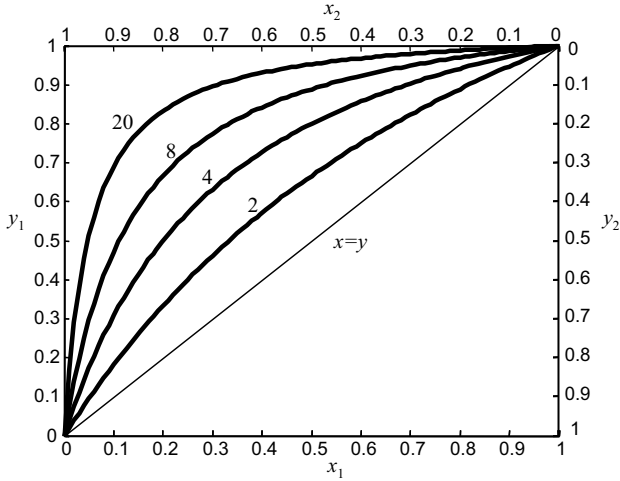


FIGURE 1.4 The effect of the relative volatility (α) on vapor and liquid compositions in a binary system.

gas and the liquid is an ideal solution (typically when liquid phase molecules are of the same size and chemically similar). In such instances, the equilibrium ratio is given by

$$K_i = \frac{P_i^{\text{VAP}}}{P} \quad (1.5)$$

where P is the total system pressure, and P_i^{VAP} is the vapor pressure of species i and a function of temperature using the familiar Antoine equation, which has the general form shown in Equation 1.6

$$\ln(P_i^{\text{VAP}}) = A_i - \left(\frac{B_i}{T + C_i} \right) \quad (1.6)$$

Coefficients A_i , B_i , and C_i are constants unique to specie i , and T is the boiling (or bubble) temperature of the mixture. The temperature at which a liquid with a particular composition is in equilibrium with its vapor may be calculated by combining Equations 1.1, 1.3, 1.5, and 1.6, ultimately yielding Equation 1.7

$$\sum_{i=1}^{nc} y_i = 1 = \sum_{i=1}^{nc} K_i x_i = \frac{1}{P} \sum_{i=1}^{nc} P_i^{\text{VAP}} x_i \quad (1.7)$$

If the system pressure (P), the liquid composition and the Antoine coefficients are known for all components, temperature is the only remaining variable in Equation 1.7. Solving for the temperature in Equation 1.7 requires an iterative numerical technique. Once the temperature (and therefore the equilibrium ratio) is known, the vapor in equilibrium with its liquid may be obtained quite

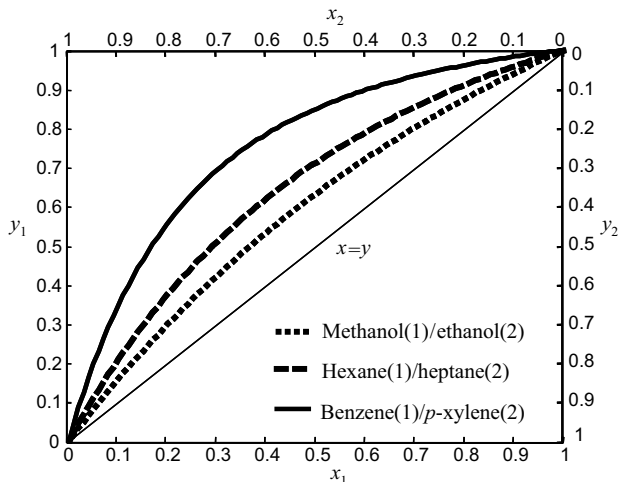


FIGURE 1.5 Behavior of selected binary systems' vapor and liquid compositions using Raoult's law at 1 atm.

simply through Equation 1.1. Examples of selected binary systems are shown in the $x - y$ diagram in Figure 1.5

- (3) *Nonideal Solutions.* The level of complexity for modeling the relationship between vapor and liquid compositions accounts for nonideal interactions in the liquid phase. The equilibrium ratio is still used for such systems, but in this instance it is defined as

$$K_i = \frac{\gamma_i P_i^{\text{VAP}}}{P} \quad (1.8)$$

where γ_i is known as the activity coefficient of component i , and takes into account deviations from ideal, Raoult's law behavior. It is evident that Raoult's law in Equation 1.5 is a special case of Equation 1.8 where the activity coefficients are assumed to be one. Thus, Equation 1.8 is known as the modified Raoult's law. The activity coefficient is a function of both temperature and composition and calculating it can be quite intricate. There are many models used to calculate activity coefficients (Wilson, Margules, UNIQUAC, NRTL, and so on), and certain models may be better suited to a certain system than others. In this book, however, we primarily focus on the NRTL (non-random-two-liquid) model because it is quite widely applicable to a large number of systems. The NRTL activity coefficient may be modeled through Equations 1.9 and 1.10

$$\gamma_i = \exp \left[\frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \right] \quad (1.9)$$

$$\text{where } \tau_{ij} = a_{ij} + \left(\frac{b_{ij}}{T(\text{K})} \right) \quad \text{and} \quad G_{ij} = \exp(-c_{ij}\tau_{ij}) \quad (1.10)$$

The coefficients a_{ij} , b_{ij} , and c_{ij} are binary interaction parameters specific to components i and j . A list of binary interaction parameters and Antoine coefficients for systems prominently featured systems in the book are given in Appendix B. Evidently, modeling nonideal systems can be rather laborious and computationally intensive, but the solution strategy is exactly the same to the one outlined for ideal solutions in Equation 1.7, and simply incorporating the activity coefficients. Activity coefficient models can account for azeotropes, that is, where vapor and liquid compositions are equal, while neither Raoult's law nor the constant volatility model is able to. Examples of binary nonideal systems modeled with the NRTL equation are shown in Figure 1.6.

Figure 1.6 shows a very different curvature when compared to the “well-behaved” mixtures in Figures 1.4 and 1.5. Specifically, the acetone/chloroform and ethyl acetate/water systems form azeotropes where the vapor and liquid compositions become equal and the equilibrium curve intersects the $y = x$ line. Systems with azeotropes present challenging design problems because it is no longer possible to obtain two high purity products in a single distillation unit. There are of course ways to overcome this problem, notably through adjusting the pressure for so-called pressure swing distillation (notice from Equation 1.8 that the $y - x$ relationship is system pressure dependent), or through creative material recycling [43]. The acetone/water system, on the other hand, does not have azeotropic behavior, but it is still quite nonideal, as evident from the asymmetric nature of its $y - x$ curve.

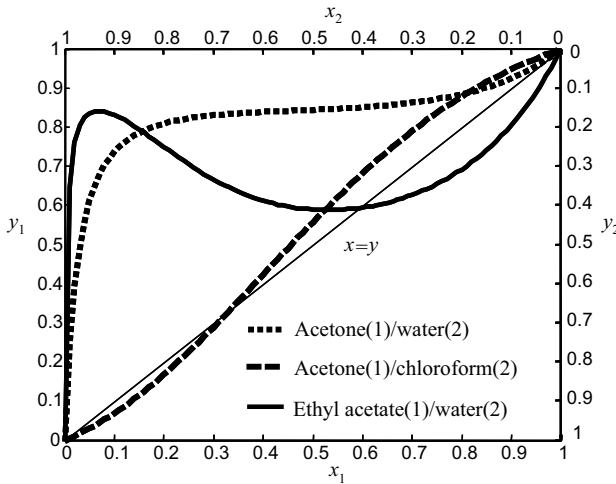


FIGURE 1.6 Behavior of selected binary systems' vapor and liquid compositions using a modified Raoult's law at 1 atm.

None of the systems in Figure 1.6 are, therefore, good candidates for modeling with either constant volatility or ideal solution models.

1.3 SUMMARY

It is hoped that from this chapter the reader understands the context and importance of industrial distillation, and realizes why efficient and insightful design techniques are so important. Although it is a comparatively old separation technique, there is still much room for improvement, especially in the area of complex distillation. The CPM technique that is presented in this book will aid in understating simple and complex distillation systems more clearly. Although the premise of the CPM technique is reasonably easy to follow and comprehend, it is a rather advanced technique, not recommended as a reader's first introduction to the field of distillation.

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