

CHAPTER 1

INTRODUCTION

The development of the chemical industry over the last two centuries has provided modern civilization with a whole host of products that improve the well-being of the human race. The result has been a better quality of life, longer life expectancy, more leisure time, rapid transportation to anywhere in the world (and outer space), healthier food, more comfortable homes, better clothing, and so forth.

A major factor in this development has been inexpensive energy and inexpensive raw materials. Coal was the major energy source in the 19th century. Petroleum and natural gas were the major sources in the 20th century. Crude oil offers definite advantages over coal in terms of ease of production and transportation from its origins to the points of consumption. Natural gas also has an inherent advantage over coal because of the hydrogen to carbon ratio. Natural gas is mostly methane (CH_4) with an H/C ratio of 4, but coal's H/C ratio is approximately 1. This means that coal produces much more carbon dioxide when these fuels are burned. Therefore, as an energy source, coal contributes more to greenhouse gases and global warming problems. In addition, coal contains sulfur compounds that require expensive stack-gas cleanup facilities.

Only a fool (or weatherman or economist) would dare to predict what lies ahead. However, the era of inexpensive energy is definitely over because of the rapid growth in demand in developing countries and the increasing difficulty and expense of finding and producing new supplies. It is clear that our modern society must undergo dramatic and perhaps painful changes in lifestyle that will sharply reduce per capita energy consumption in order to achieve a sustainable supply of energy.

The end of the era of cheap energy has had a major impact in the chemical industry. Significant modifications of the processes to produce chemicals have been made to reduce energy consumption. New and innovative processing methods have been developed

and commercialized. Extensive use of heat integration has cut energy consumption in some processes by factors of 2 or 3.

Reactive distillation is an excellent example of process innovation. In a conventional chemical plant, there are reaction sections and separation sections. These have their own vessels and equipment, but they are often linked together by material and energy recycles. In reactive distillation, separation and reaction occur in the same vessel. This can result in significant reductions in both energy and equipment in systems that have appropriate chemistry and appropriate vapor–liquid phase equilibrium.

In this chapter we introduce the subject of reactive distillation by covering some of the basic aspects of this interesting and challenging process.

1.1 HISTORY

As mentioned in the Preface, a small number of industrial applications of reactive distillation have been around for many decades. One of the earliest was a DuPont process in which dimethyl terephthalate was reacted with ethylene glycol in a distillation column to produce methanol and ethylene terephthalate. The reactants were fed into the middle of the column where the reversible reaction occurred. The more volatile, low-boiling methanol product was removed from the top of the column, and the high-boiling ethylene terephthalate product was removed from the bottom. The removal of the products from the reaction zone drove the reversible reaction toward the product side. This is one of the fundamental advantages of reactive distillation. Low chemical equilibrium constants can be overcome and high conversions achieved by the removal of products from the location where the reaction is occurring.

There were few early applications of reactive distillation. About two decades ago, engineers at Eastman Chemical published a very influential paper.¹ This seminal paper produced a surge of interest in reactive distillation in both industry and academia.

The Eastman reactive distillation column (see Preface, Fig. P.1) has reactant feedstreams of methanol and acetic acid. Methanol is more volatile than acetic acid and is fed into the lower part of column. The heavier acetic acid is fed into the upper part of the column. As the lighter methanol works its way up the column, it comes in contact with the heavier acetic acid that is coming down the column. The two react to form methyl acetate and water. Methyl acetate is the most volatile component in the system, so it goes into the vapor stream flowing up the column. This keeps the concentration of methyl acetate low in the liquid phase where the reversible reaction is occurring. Thus, the reaction is driven toward the product side and high conversion is achieved despite a modest equilibrium constant.

Jeff Sirola reports that this single reactive column replaced a conventional multiunit process that consumed 5 times more energy and whose capital investment was 5 times that of the reactive column.² The methyl acetate reactive distillation column has become the prize example of the application of reactive distillation. It provides an outstanding example of innovative chemical engineering.

Over the last two decades there have been a number of other industrial applications of reactive distillation. The most important from the standpoint of the number of installations

¹V. H. Agreda, L. R. Partin, and W. H. Heise, High-purity methyl acetate via reactive distillation, *Chem. Eng. Prog.* **86**(2), 40–46 (1990).

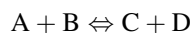
²J. J. Sirola, Industrial applications of chemical process synthesis, *Adv. Chem. Eng.* **23**, 1062 (1996).

and production capacity is methyl tertiary butyl ether (MTBE), which is used in gasoline blending. A mixed C4 hydrocarbon stream from a refinery light-ends debutanizer column contains isobutene and other C4 components (isobutane, *n*-butane, and *n*-butene), which are not involved in the reaction. This mixed C4 stream is fed into a reactive distillation column along with methanol. The isobutene reacts with the methanol to form MTBE. The heavy MTBE is removed at the bottom, and the chemically inert C4s go out the top. The use of MTBE in gasoline is being phased out because of environmental problems. Other similar esters are being substituted [ethyl tertiary butyl ether (ETBE) and *tert*-amyl methyl ether (TAME)], which are also produced using reactive distillation. All of these applications will be discussed in detail in subsequent chapters.

1.2 BASICS OF REACTIVE DISTILLATION

Reactive distillation is attractive in those systems where certain chemical and phase equilibrium conditions exist. We will discuss some of its limitations in Section 1.4. Because there are many types of reactions, there are many types of reactive distillation columns. In this section we describe the ideal classical situation, which will serve to outline the basics of reactive distillation.

Consider the system in which the chemical reaction involves two reactants (A and B) producing two products (C and D). The reaction takes place in the liquid phase and is reversible.



For reactive distillation to work, we should be able to remove the products from the reactants by distillation. This implies that the products should be lighter and/or heavier than the reactants. In terms of the relative volatilities of the four components, an ideal case is when one product is the lightest and the other product is the heaviest, with the reactants being the intermediate boiling components.

$$\alpha_C > \alpha_A > \alpha_B > \alpha_D$$

Figure 1.1 presents the flowsheet of this ideal reactive distillation column. In this situation the lighter reactant A is fed into the lower section of the column but not at the very bottom. The heavier reactant B is fed into the upper section of the column but not at the very top. The middle of the column is the reactive section and contains N_{RX} trays. Figure 1.2 shows a single reactive tray on which the net reaction rate of the reversible reaction depends on the forward and backward specific reaction rates (k_F and k_B) and the liquid holdup (or amount of catalyst) on the tray (M_n). The vapor flowrates through the reaction section change from tray to tray because of the heat of the reaction.

As component A flows up the column, it reacts with descending B. Very light product C is quickly removed in the vapor phase from the reaction zone and flows up the column. Likewise, very heavy product D is quickly removed in the liquid phase and flows down the column.

The section of the column above where the fresh feed of B is introduced (the rectifying section with N_R trays) separates light product C from all of the heavier components, so a distillate is produced that is fairly pure product C. The section of the column below where the fresh feed of A is introduced (the stripping section with N_S trays) separates

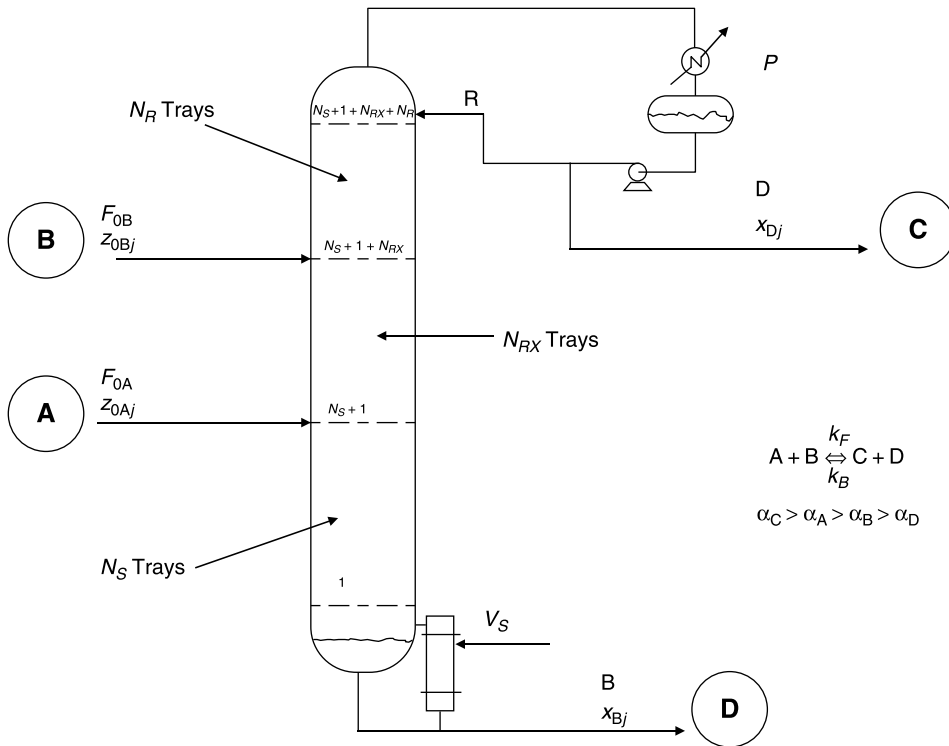
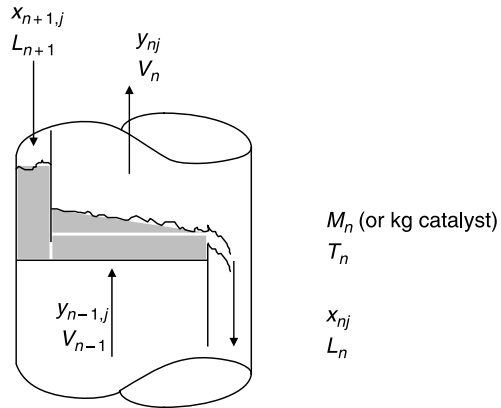


Figure 1.1 Ideal reactive distillation column.



$$R_n = M_n (k_{F(T_n)} x_{nA} x_{nB} - k_{B(T_n)} x_{nC} x_{nD})$$

$$V_n = V_{n-1} + \frac{-\lambda R_n}{\Delta H_v}$$

Figure 1.2 Reactive tray.

heavy product D from all of the lighter components, so a bottom is produced that is fairly pure product D. The reflux flowrate and the reboiler heat input can be manipulated to maintain these product purities. Figure 1.3 gives typical composition profiles for this ideal case. The specific numerical case has 30 total trays, consisting of 10 stripping trays, 10 reactive trays, and 10 rectifying trays. Trays are numbered from the bottom. Note that the concentrations of the reactants peak at their respective feed trays (tray 11 for A, tray 20 for B). The purities of the two products are both 95 mol%, with B the major impurity in the bottoms and A the major impurity in the distillate.

One of the most important design parameters for reactive distillation is column pressure. Pressure effects are much more pronounced in reactive distillation than in conventional distillation. In normal distillation, the column pressure is selected so that the separation is made easier (higher relative volatilities). In most systems this corresponds to low pressure. However, low pressure implies a low reflux-drum temperature and low-temperature coolant. The typical column pressure is set to give a reflux-drum temperature high enough (49 °C, 120 °F) to be able to use inexpensive cooling water in the condenser and not require the use of much more expensive refrigeration.

In reactive distillation, the temperatures in the column affect both the phase equilibrium and chemical kinetics (Fig. 1.4). A low temperature that gives high relative volatilities may

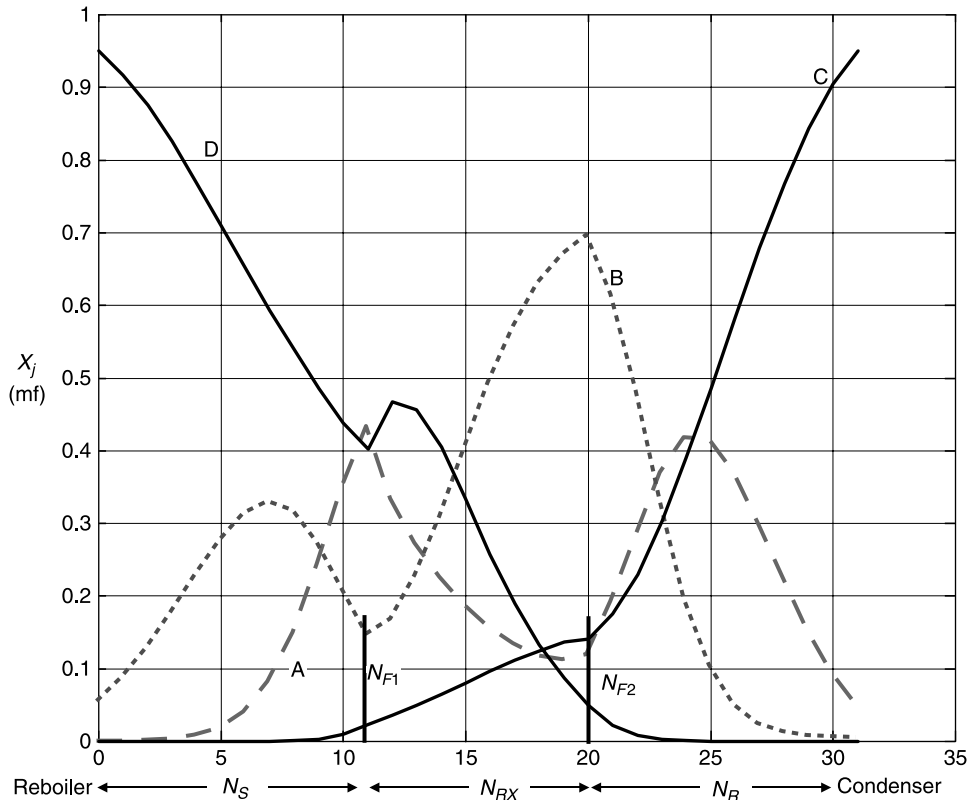


Figure 1.3 Base case composition profiles (95% purities).

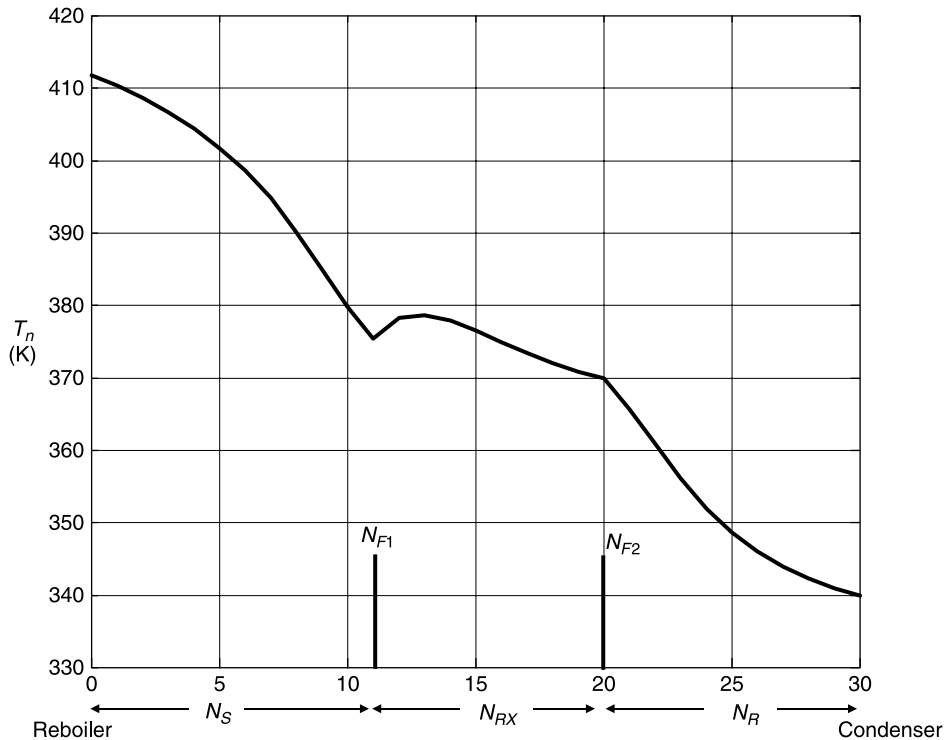


Figure 1.4 Temperature profile.

give small specific reaction rates that would require very large liquid holdups (or amounts of catalyst) to achieve the required conversion. In contrast, a high temperature may give a very small chemical equilibrium constant (for exothermic reversible reactions), which makes it more difficult to drive the reaction to produce products. High temperatures may also promote undesirable side reactions. Thus, selecting the optimum pressure in a reactive distillation column is very important. This will be illustrated in subsequent chapters.

Reactive distillation is also different from conventional distillation in that there are both product compositions and reaction conversion specifications. The many design degrees of freedom in a reactive distillation column must be adjusted to achieve these specifications while optimizing some objective function such as total annual cost (TAC). These design degrees of freedom include pressure, reactive tray holdup, number of reactive trays, location of reactant feedstreams, number of stripping trays, number of rectifying trays, reflux ratio, and reboiler heat input.

Another design aspect of reactive distillation that is different from conventional is tray holdup. Holdup has no effect on the steady-state design of a conventional column. It certainly affects dynamics but not steady-state design. Column diameter is determined from maximum vapor-loading correlations after vapor rates have been determined that achieve the desired separation. Typical design specifications are the concentration of the heavy key component in the distillate and the concentration of the light key component in the bottoms. However, holdup is very important in reactive distillation because reaction rates directly depend on holdup (or the amount of catalyst) on each tray. This means that the

holdup must be known before the column can be designed and before the column diameter is known. As a result, the design procedure for reactive distillation is iterative. A tray holdup is assumed and the column is designed to achieve the desired conversion and product purities. The diameter of the column is calculated from maximum vapor-loading correlations. Then the required height of liquid on the reactive trays to give the assumed tray holdup is calculated. Liquid heights greater than 10–15 cm (4–6 in.) are undesirable because of hydraulic pressure-drop limitations. Thus, if the calculated liquid height is too large, a new and smaller tray holdup is assumed and the design calculations repeated. An alternative, which may be more expensive in terms of capital cost, is to make the column diameter larger than that required by vapor loading.

1.3 NEAT OPERATION VERSUS EXCESS REACTANT

The reactive distillation column described in the previous section was designed to operate “neat” (precisely the correct amounts of reactants are fed to the column to satisfy the stoichiometry of the chemistry and there are only small amounts of unreacted reactants that leave in the streams leaving the column). Only a single column is required, so both capital investment and energy cost are minimized. However, it can be difficult to control a reactive column that operates in this neat mode. The problem is the need to feed in exactly enough of both reactants, down to the last molecule, to make sure that there is no excess of either reactant. If the balance is not absolutely perfect, the reactant that is in excess will gradually build up in the column, and it will not be possible to maintain product purities. This build-up may take hours or days, but eventually the column control structure will not be able to hold the products at their specified compositions.

One might think that this problem can be very easily overcome by simply ratioing the flowrates of the two fresh reactant feeds. This strategy works in computer simulations, but it does not work in a real plant environment. The reasons why ratio schemes are not effective are inaccuracies in flow measurements, which are always present, and/or changes in the compositions of the feedstreams. Either cause will result in an imbalance of the stoichiometry. Therefore, it is necessary to have some way to determine the amount of at least one of the reactants inside the column so that feedback control can be used to adjust a fresh feed flowrate. Sometimes temperatures or liquid levels can be used. Sometimes a direct composition measurement on a tray in the column is required. This issue is the heart of the reactive distillation control problem and will be quantitatively studied in detail in subsequent chapters.

An alternative flowsheet, which is more costly but easier to control, uses two distillation columns. As illustrated in Figure 1.5, the first is a reactive distillation column into which an excess of one of the reactants is fed (component B), along with the second fresh feed of component A. The total B fed to the reactive column is 10–20% in excess of the stoichiometric amount needed to react with the moles of A being fed. The amount of this excess is determined by the variability in the compositions of the two fresh feeds and by the flow measurement inaccuracies. Reactant A is the “limiting reactant” in this column and its conversion is high. The conversion of reactant B is not high in the reactive column. Because not all of the B is consumed by the reaction, the excess comes out of the bottom of the column with product component D. This binary mixture is fed to the second distillation column, the recovery column, which produces component D out the bottom and component B out the

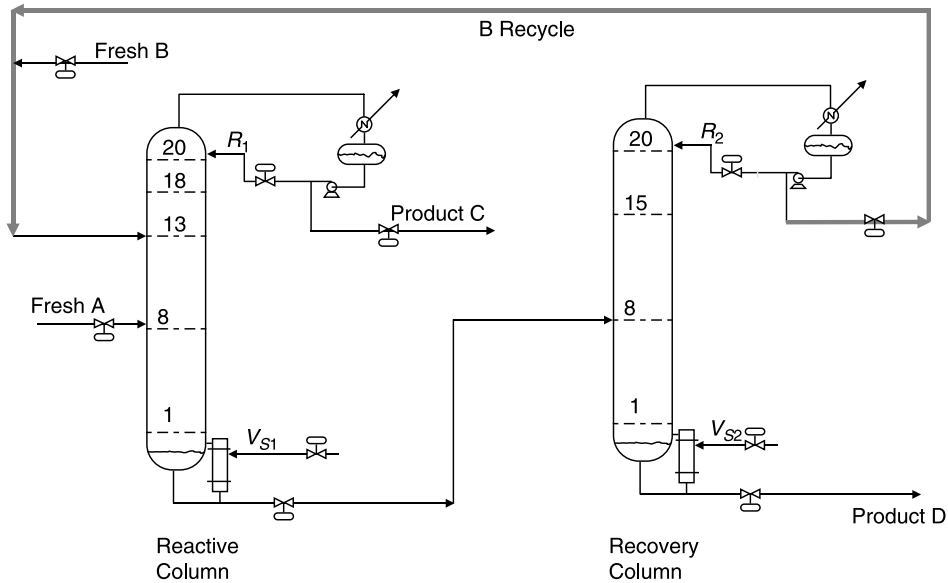


Figure 1.5 Two-column process with excess reactant.

top. The distillate is recycled back to the reactive column, the fresh feed of B is added to the recycle stream, and the total is fed to the reactive column.

The control of this system is easy because the inventory of B in the system can be inferred from the liquid level in the reflux drum of the recovery column. If too much B is being fed into the system, it will accumulate in the reflux drum because the total B fed to the reactive column is fixed. Thus, a simple level controller on the recovery column reflux drum adjusting the flowrate of the fresh feed of B into the system can achieve the required balancing of the stoichiometry. Note that the overall conversion of B is high, considering the entire process, despite having a low “per pass” conversion in the reactive column.

These two alternative flowsheets (neat vs. excess) are quantitatively compared in Chapter 4 in terms of steady-state design and in Chapter 11 in terms of dynamic controllability.

1.4 LIMITATIONS

Although reactive distillation sounds like a great idea, its area of application is fairly restricted. Both the chemistry and the vapor–liquid equilibrium phase equilibrium must be suitable.

1.4.1 Temperature Mismatch

The principle limitation is that there must be no mismatch in the temperatures that are favorable for reaction and the temperatures that are favorable for separation. Because reaction and separation both occur in a single vessel at essentially a single pressure, the

temperatures throughout the column are fixed by tray compositions. Both the reactions and vapor–liquid equilibrium see the same temperatures.

Contrast this with what can be done in a conventional multiunit flowsheet. The reactors can be operated at their optimum pressures and temperatures that are selected to be the most favorable for their given chemical kinetics. The distillation columns can be operated at their optimum pressures and temperatures that are selected to be the most favorable for their vapor–liquid equilibrium properties.

1.4.2 Unfavorable Volatilities

The second major limitation for the application of reactive distillation is that the relative volatilities of the components must be such that the reactants can be contained in the column and the products can be easily removed from the top and/or from the bottom.

For example, suppose we wished to produce acetic acid and methanol from methyl acetate and water (the reverse of the methyl acetate process). Now the reactant methyl acetate is the lightest, and it would be very difficult to keep it in the reactive zone and not have much of it escape into the distillate with the methanol that is being produced. This process would not be suitable for reactive distillation.

1.4.3 Slow Reaction Rates

Another limitation for reactive distillation is the need for reasonably large specific reaction rates. If the reactions are very slow, the required tray holdups and number of reactive trays would be too large to be economically provided in a distillation column.

1.4.4 Other Restrictions

Reactive distillation is limited to liquid-phase reactions because there is very little holdup in the vapor phase. The heats of reaction must be modest to prevent large changes in vapor and liquid rates through the reactive zone. A highly exothermic reaction could completely dry up the trays.

1.5 SCOPE

Any book reflects the experiences and prejudices of the authors. We both come from a background of design and control with an emphasis on practical engineering solutions to real industrial problems. Thus, this book contains no elegant mathematics or complex methods of analysis.

Our emphasis is on rigorous simulations, not approximate methods. Rigorous models are used for steady-state design and dynamic analysis of a variety of different types of reactive distillation columns. Several types of ideal systems are studied as well as several real chemical systems.

Steady-state designs of reactive distillation columns are developed that are economically “optimum” in terms of total annual cost, which includes both energy and capital costs. The economics of reactive distillation columns are quantitatively compared with conventional multiunit processes over a range of parameter values (chemical equilibrium constants,

specific reaction rates, and relative volatilities). Then effective control structures are developed for these types of reactive distillation columns.

1.6 COMPUTATIONAL METHODS

The rigorous steady-state and dynamic models used in this book are solved using Matlab programs or Aspen Technology simulation software (Aspen Plus and Aspen Dynamics).

1.6.1 Matlab Programs for Steady-State Design

For the ideal chemical cases, a dynamic model is simulated in Matlab. This model consists of ordinary differential equations for tray compositions and algebraic equations for vapor–liquid equilibrium, reaction kinetics, tray hydraulics, and tray energy balances. The dynamic model is used for steady-state design calculations by running the simulation out in time until a steady state is achieved. This dynamic relaxation method is quite effective in providing steady-state solutions, and convergence is seldom an issue.

Specifying the conversion usually sets the product purities. The unreacted reactants will be impurities in the product streams. For the base case $A + B \rightleftharpoons C + D$ system, the distillate will contain most of the unreacted A, and the bottoms will contain most of the unreacted B. For example, suppose 100 mol of both A and B are fed. If the conversion is 95%, there will be 5 mol of A and B that will leave the column in the products. Most of the lighter reactant A will leave in the distillate with product C. Most of the heavier reactant B will leave in the bottoms. There will be some B in the distillate and some A in the bottoms. However, there will be essentially no D in the distillate and no C in the bottoms.

If the distillate and bottoms impurity levels are equal, there will be 5 mol of impurities in each product stream in this example. Then, the total distillate will be 100 mol. The amount of C in the distillate will be 95 mol, so the composition of the distillate is 95 mol% C. Likewise, the total bottoms will be 100 mol. The amount of D in the bottoms will be 95 mol, so the composition of the bottoms is 95 mol% D.

With all feed conditions and the column configuration specified (number of trays in each section, tray holdup in the reactive section, feed tray locations, pressure, and desired conversion), there is only one remaining degree of freedom. The reflux flowrate is selected. It is manipulated by a distillate composition controller to drive the distillate composition to 95 mol% C. The vapor boilup is manipulated to control the liquid level in the base. Note that the distillate and bottoms flowrates are known and fixed as the dynamic model is converged to the steady state that gives a distillate composition of 95 mol% C. The composition of the bottoms will be forced by the overall component balance to be 95 mol% D.

Similar approaches are used for other chemical systems with different stoichiometry. In most cases the columns converged to steady-state conditions in about 15–20 h of process time, which takes about 5–10 min on current personal computers.

1.6.2 Aspen Simulations

Aspen Plus is used for the steady-state designs of the real chemical systems. Convergence problems can occur because of the difficulty of trying to solve the large set of very nonlinear simultaneous algebraic equations. Another problem is that the current version of

Aspen Plus does not permit the use of activities in the reaction rate expressions. “User subroutines” are used to incorporate this feature when necessary.

Aspen Dynamics is used to study dynamics and control of the real systems. The type of reactions that can be used are limited (they must be kinetic and of power law form). These restrictions make the use of Aspen products somewhat less convenient than we would like.

1.7 REFERENCE MATERIALS

There are many reactive distillation systems and many recent publications and patents. Doherty and Malone give 61 chemical systems (see their table 10.5) and cite 134 references in their chapter on reactive distillation.³ An updated literature survey shows that there were 1105 publications and 814 US patents between 1971 and 2007.

Figure 1.6 is an updated version of a figure by Malone and Doherty.⁴ The numbers in the figure are search results from the Engineering Index and the U.S. Patent Office using the following keywords: reactive distillation, catalytic distillation, catalytic reactive distillation, reactive rectification, reactive separation, reactive packing, reaction column, and reacting distillation.

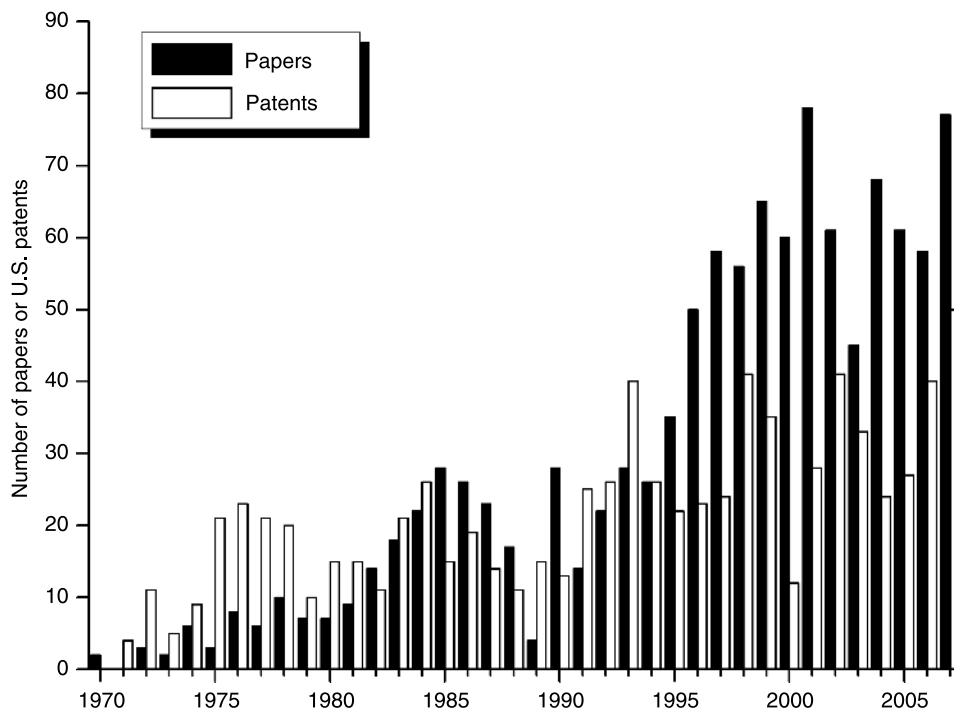


Figure 1.6 Publications or U.S. patents of reactive distillation for the period 1971–2007 as listed in the Engineering Index and U.S. Patent Office (through December 31, 2007).

³M. F. Doherty and M. F. Malone, *Conceptual Design of Distillation Systems*, McGraw-Hill, New York, 2001, Chapter 10.

⁴M. F. Doherty and M. F. Malone, Reactive distillation, *Ind. Eng. Chem. Res.* **39**, 3953 (2000).

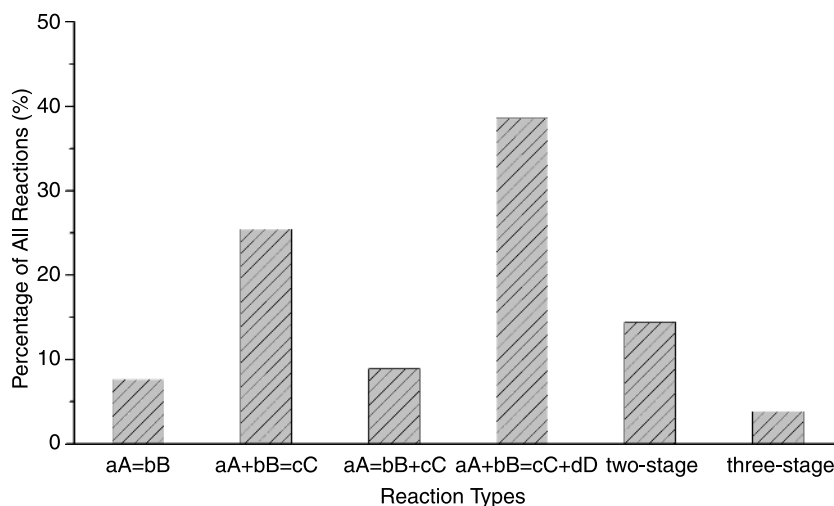


Figure 1.7 Percentage of different reaction types using reactive distillation in the literature.

A literature search using Compendex showed some interesting chronological features. The search was limited to only journal articles in English. From 1969 to 1994 there were only 35 citations in reactive distillation design and a mere six in reactive distillation control. From 1995 to 2007 there were 435 citations in reactive distillation design and 106 in reactive distillation control. This clearly indicates the recent level of interest, particularly in control.

For reactive distillation, a literature survey shows a total of 236 reaction systems. If these are classified into reaction types, 91 systems belong to the $aA + bB = cC + dD$ class (e.g., $A + B = C + D$, $A + 2B = C + 2D$, etc.), 60 are of the form of the general $aA + bB = cC$ class, 21 systems belong to the $aA = bB + cC$ class, and 18 of them are of the form $aA = bB$. The remaining 33 reaction systems fall into the category of a two-stage reaction (e.g., $A + B = C + D$ and $B + C = D + E$) or a three-stage reaction (e.g., $A + B = C$, $C + B = D$, $D + B = E$). These are illustrated in Figure 1.7. A complete listing of these reactions is given in the Appendix.

There are four books that deal with reactive distillation, among other subjects:

1. *Distillation, Principles and Practice* by Stichlmair and Fair⁵
2. *Conceptual Design of Distillation Systems* by Doherty and Malone³
3. *Reactive Distillation—Status and Future Directions* by Sundmacher and Kienle⁶
4. *Integrated Reaction and Separation Operations* by Schmidt-Traub and Gorak⁷

These books deal primarily with the steady-state design of reactive distillation columns. Conceptual approximate design approaches are emphasized. There is little treatment of rigorous design approaches using commercial simulators. The issues of dynamics and control

⁵J. G. Stichlmair and J. R. Fair, *Distillation, Principles and Practice*, Wiley-VCH, New York, 1998.

⁶K. Sundmacher and A. Kienle, Editors, *Reactive Distillation—Status and Future Directions*, Wiley-VCH, New York, 2003.

⁷H. Schmidt-Traub and A. Gorak, *Integrated Reaction and Separation Operations*, Springer, New York, 2006.

structure development are not covered. Few quantitative economic comparisons of conventional multiunit processes with reactive distillation are provided. Schmidt-Traub and Gorak discuss the control of a batch reactive distillation column and give experimental results. Some aspects of the control of reactive distillation systems are discussed in *Distillation Design and Control Using Aspen Simulation* by Luyben.⁸

⁸W. L. Luyben, *Distillation Design and Control Using Aspen Simulation*, Wiley, New York, 2006, Chapter 9.

