ANALYSIS, SYNTHESIS, AND DESIGN OF CHEMICAL PROCESSES

FIFTH EDITION

RICHARD TURTON | JOSEPH A. SHAEIWITZ
DEBANGSU BHATTACHARYYA| WALLACE B. WHITING

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The second specification shows that both specifications can be achieved without violating the material balance. The top product contains 99% of the feed benzene (105.2 kmol/h) and 0.4 kmol/h toluene, which gives a top composition of 99.6 mol% benzene. The bottoms product contains 1.0% of the feed benzene (1.1 kmol/h) and 34.6 kmol/h of toluene.

When giving the top and bottom specifications for a distillation column, make sure that the specifications do not violate the material balance.

If problems continue to exist, one way to ensure that the simulation will run is to specify the top reflux rate and the boil-up rate (reboiler duty). Although this strategy will not guarantee the desired purities, it will allow a base case to be established. With subsequent manipulation of the reflux and boil-up rates, the desired purities can be obtained. Another strategy that may be useful when a high purity is needed is to start with a lower purity and then increase the purity specification in steps to the desired purity. This only works if the simulation is not "reset" after each run, that is, the previous result is used as the starting point each time.

Absorbers and Strippers. Usually these units are simulated using the rigorous distillation module given above. The input streams and the number of equilibrium stages are specified, and the outlet streams are obtained. The main difference in simulating this type of equipment is that condensers and reboilers are not normally used. In addition, there are two feeds to the unit: one feed enters at the top and the other at the bottom. It may also be necessary to toggle a setting to indicate that an absorber/stripper is being simulated.

Liquid-Liquid Extractors. A rigorous tray-by-tray module is used to simulate this multistaged equipment. The input streams and the number of equilibrium stages are specified, and the outlet streams are obtained. It is imperative that the thermodynamic model for this unit be capable of predicting the presence of two liquid phases, each with appropriate liquid-phase activity coefficients. This module is usually different from the module that simulates vapor-liquid systems, like distillation, absorption, and stripping.

13.2.6 Selection of Output Display Options

Several options will be available to display the results of a simulation. Often, a report file can be generated and customized to include a wide variety of stream and equipment information. In addition, a simulation flowsheet (not a PFD); *T-Q* diagrams for heat exchangers; vapor and liquid flows; temperature and composition profiles (tray-by-tray) for multistaged equipment; temperature and composition profiles along a tubular reactor; scheduling charts for batch operations; environmental parameters for exit streams; and a wide variety of phase diagrams for streams can be generated. The user manual should be consulted for the specific options available for the simulator you use.

13.2.7 Selection of Convergence Criteria and Running a Simulation

For equipment requiring iterative solutions, there will be user-selectable convergence and tolerance criteria in the equipment module. There will also be convergence criteria for the whole flowsheet simulation, which can be adjusted by the user.

The two most important criteria are number of iterations and tolerance. These criteria will often have default values set in the simulator. These default values should be used in initial simulations. If problems arise, these values should be adjusted, but it may also be necessary to choose a different convergence method.

If the simulation has not converged, the results do not represent a valid solution and should not be used.

When convergence is not achieved, three common causes are as follows:

1. The problem has been ill posed. This normally means that an equipment specification has been given incorrectly. For example, see the first specification in Example 13.2 for the rigorous column module.
2. The tolerance for the solution has been set too tightly, and convergence cannot be obtained to the desired accuracy no matter how many solution iterations are performed.
3. The number of iterations is not sufficient for convergence. This occurs most often when the flowsheet has many recycle streams. Rerunning the flowsheet simulation with the results from the preceding run may give a converged solution. If convergence is still not obtained, then one way to address this problem is to remove as many recycle streams as possible. The simulation is then run, and the recycle streams are added back, one by one, using the results from the preceding simulation as the starting point for the new one. This method is discussed in more detail in Section 13.3.

Of the three reasons, the first one is by far the most common.

The most common reason for the failure of a simulation to converge is the use of incorrect or impossible equipment specifications.

13.2.8 Common Errors in Using Simulators

As mentioned previously, simulators perform some calculations that are not physically correct, and some unit operations in simulators do not correspond to acutal equipment. Two examples were previously mentioned. One is that mixing streams will be at the same pressure, not the lower of the pressures of the mixing streams, which is what simulators assume. It is the user's responsibility to add valves to the higher-pressure streams so that mixing streams are at the same pressure. Another example is the "flash" tank that operates at a different temperature from the feed stream without a heat exchanger. In reality, the "flash" operation is a partial vaporization or partial condensation, which requires a heat exchanger. The correct equipment configuration is a heat exchanger followed by a tank to disengage the vapor and liquid phases. The tank can be modeled in a simulator as a flash operating at the same conditions as the feed stream, which is the exit stream from the heat exchanger. It is also important to make use of the information available within a simulator, for example, temperature and composition profiles in tubular reactors and *T-xy* diagrams for heat exchangers.

Table 13.1 summarizes some common errors made by students when using process simulators.

Table 13.1 Commonly Observed Simulation Errors

Physical Situation	Error Observed	Correct Method
Incorrect use of flash unit simulation	Including flash unit with heat load, so temperature changes "magically"	Simulate as heat exchanger followed by flash unit operating at inlet conditions
Mixing points	Mixing streams at different pressures, outlet stream at lowest pressure (simulator default)	Add valves to input streams to mixer as appropriate to ensure mixing streams at same pressure
Zoned analysis required	For phase change operations, only one zone used with one heat transfer coefficient	Simulate each zone as separate heat exchanger with separate heat transfer coefficient, but PFD shows one heat exchanger (some simulators allow zoned analysis in heat exchange unit if each zone's heat transfer coefficient is provided)
LMTD correction factor required but ignored	Standard configuration in industry is 1-2 exchanger	Check approach temperatures to see if more shell passes are needed, often occurs if heat integration used
Inappropriate reactor size	Desired product rate approaches constant value or starts to decrease	Examine reactor profiles to determine if reactor is oversized or if selectivity is decreasing
Real vs. actual trays	Column design and cost calculated for number of equilibrium trays	Include tray efficiency in simulation or add trays when performing cost calculation
Column pressure drop	Column assumed to be at constant pressure or pressure drop chosen does not correspond to reality	Include pressure drop and make sure pressure drop per tray roughly corresponds to weir height, and that weir height is not too small or not more than 50% of tray spacing; or assume weir height (typically 4-6 in and less than half of tray spacing) and include pressure drop in simulation

13.3 HANDLING RECYCLE STREAMS

Recycle streams are very important and common in process flowsheets. Computationally, they can be difficult to handle and are often the cause for unconverged flowsheet simulations. There are ways in which the problems caused by recycle streams can be minimized. When a flowsheet is simulated for the first time, it is wise to consider carefully any simplifications that may help the convergence of the simulation. Consider the simulation of the DME flowsheet illustrated in Figure B.1.1, Appendix B. This flowsheet is shown schematically in Figure 13.5(a). The DME process is simple, no by-products are formed, the separations are relatively easy, and the methanol can be purified easily prior to being recycled to the front end of the process. In attempting to simulate this process for the first time, it is evident that two recycle streams are present. The first is the unreacted methanol that is recycled to the front of the process, upstream of the reactor. The second recycle loop is due to the heat integration scheme used to preheat the reactor feed using the reactor effluent stream. The best way to simulate this flowsheet is to eliminate the recycle streams as shown in Figure 13.5(b). In this figure, two separate heat exchangers have been substituted for the

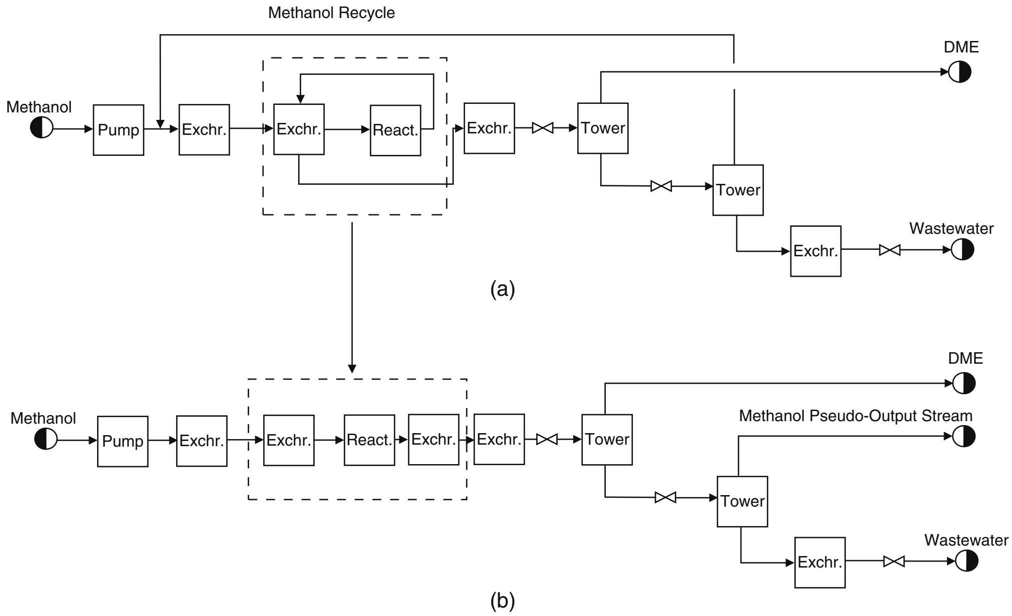

Figure 13.5 Block Flow Diagram for DME Process Showing (a) Recycle Structure and (b) Elimination of Recycles

heat integration scheme. These exchangers allow the streams to achieve the same changes in temperature while eliminating the interaction between the two streams. The methanol recycle is eliminated in Figure 13.5(b) by producing a methanol pseudo-output stream. The simulation of the flowsheet given in Figure 13.5(b) is straightforward; it contains no recycle streams and will converge in a single flowsheet iteration. Troubleshooting of the simulation, if input errors are present, is very easy because the flowsheet converges very quickly. Once a converged solution has been obtained, the recycle streams can be added back. For example, the methanol recycle stream would be introduced back into the simulation. The composition of this stream is known from the preceding simulation, and this will be a very good estimate for the recycle stream composition. The simulation is then run with the preceding simulation as the starting point. Once the simulation has been run successfully with the methanol recycle stream, the heat integration around the reactor can be added back and the simulation run again. Although this method may seem unwieldy, it does provide a reliable method for obtaining a converged simulation.

For the DME flowsheet in Figure 13.5, the unreacted methanol that was recycled was almost pure feed material. This means that the estimate of the recycle stream composition, obtained from the once-through simulation using Figure 13.5(b), was very good. When the recycle stream contains significant amounts of by-products, as is the case with the hydrogen recycle stream in Figure 1.5 (Streams 5 and 7), the estimate of the composition using a once-through simulation will be significantly different from the actual recycle stream composition. For such cases, when purification of the recycle stream does not occur, it is best to keep this recycle stream in the flowsheet and eliminate all other recycle streams for the first simulation. Once a converged solution is reached, the other recycle streams can be added back one at a time.

Often, a series of case studies will need to be run using a base-case simulation as a starting point. This is especially true when performing a parametric optimization on the process (see Chapter 14). When performing such case studies, it is wise to make small changes in input parameters in order to obtain a converged simulation. For example, assume that a converged simulation for a reactor module at 350°C has been obtained, and a case study needs to be run at 400°C. When the equipment temperature in the reactor module is changed and the simulation is rerun, it may be found that the simulation does not converge. If this is the case, then, for example, start with the base-case run, change the reactor temperature by 25°C, and see whether it converges. If it does, then the input can be changed by another 25°C to give the desired conditions, and so on. The use of small increments or steps when simulating changes in flowsheets often produces a converged simulation when a single large change in input will not.

Often when simulating a process, it is the flowrate of products (not feeds) that is known—for example, production of 60,000 tonne/y of chemical X, with a purity of 99.9 wt%. If a converged solution has been found in which all the product specifications have been met except that the flowrate of primary product is not at the desired value, it is a simple matter to multiply all the feeds to the process by a factor to obtain the desired flowrate of the product; that is, the solution is scaled up or down by a constant factor and the simulation rerun to get the correct equipment specifications.

For more advanced simulation applications, such as optimizing or simulating existing plants, it may be necessary or useful to use controller modules (also called design specifications, depending on the simulator) in the simulation to obtain a desired result. For example, in a recycle loop, it might be required that the ratio of two components entering a reactor be set at some fixed value. A controller module could be used to adjust the purge flowrate from the recycle stream to obtain this ratio. A controller module can also be used to specify the feed necessary for the product flowrate to be at a specific value. The use of controller modules introduces additional recycle loops. The way in which specifications for controllers are given can cause additional convergence problems, and this topic is covered in detail by Schad [10].

13.4 CHOOSING THERMODYNAMIC MODELS

The results of any process simulation are never better than the input data, especially the thermodynamic data.

Everything from the energy balance to the volumetric flowrates to the separation in the equilibrium-stage units depends on accurate thermodynamic data.

If reaction kinetics information is missing, the simulator cannot calculate the conversion from a given reactor volume. Because such a calculation is not possible, only equilibrium reactor modules and those with specified conversions can be used.

Only a few, readily available data are required to estimate the parameters in simple thermodynamic models. If the critical temperature and critical pressure are known for each pure component, the parameters for simple, cubic equations of state can be estimated. Even if these critical properties are unknown, they in turn can be estimated from one vapor pressure and one liquid density. Group-contribution models require even less information: merely the chemical structure of the molecule. However, these estimations can never be as accurate as experimental data. In thermodynamics, as elsewhere, *you get only what you pay for—or less!*

Using the default thermodynamics packages in a process simulator will often lead to an erroneous solution.

Compounding this problem is the development and implementation of expert systems to help choose the thermodynamic model. These methods are a good starting point but verification through comparison with real data is always necessary.

A safe choice of thermodynamic model requires knowledge of the system, the calculation options of the simulator, and the margin of error. In this section, guidance on choosing and using a thermodynamic model is given. In an academic setting, the choice of thermodynamic model affects the answers but not the ability of the student to learn how to use a process simulator—a key aspect of this book. Therefore, the examples throughout this book use simplistic thermodynamic models to allow easy simulation. In any real problem, where the simulation will be used to design or troubleshoot a process, the proper choice of thermodynamic model is essential. This section focuses on the key issues in making that choice, in using experimental data, and in determining when additional data are needed.

It has been assumed that the reader understands the basics of chemical engineering thermodynamics as covered in standard textbooks [4–6]. As pointed out before, it is extremely important that the chemical engineer performing a process simulation understand the thermodynamics being used. In a course, the instructor can often provide guidance. The help facility of the process simulator provides a refresher on details of the model choices; however, these descriptions do not include the thermodynamics foundation required for complete understanding. If the descriptions in the help facility are more than a refresher, the standard thermodynamics textbooks should be consulted.

If the thermodynamic option used by the process simulator is a mystery, the meaning of the results obtained from the simulation will be equally mysterious.

13.4.1 Pure-Component Properties

Physical properties such as density, viscosity, thermal conductivity, and heat capacity are generally not difficult to predict accurately in a simulation. The group-contribution methods are reasonably good, and simulator databanks include experimental data for more than a thousand substances. Although these correlations have random and systematic errors of several percent, this is close enough for most purposes. (However, they are not sufficient when paying for a fluid crossing a boundary based on volumetric flowrate.) As noted in Section 13.2.2, it is important always to be aware of which properties are estimated and which are from experimental measurements.

13.4.2 Enthalpy

Although the pure-component heat capacities are calculated with acceptable accuracy, the enthalpies of phase changes often are not. Care should be taken in choosing the enthalpy model for a simulation. If the enthalpy of vaporization is an important part of a calculation, simple equations of state should be used with caution. In fact, the “latent heat” or “ideal” options often give more accurate results. If the substance is above or near its critical temperature, equations of state must be used, but the user must beware, especially if polar substances such as water are present.

13.4.3 Phase Equilibria

Extreme care must be exercised in choosing a model for phase equilibria (sometimes called the fugacity coefficient, *K*-factor, or fluid model). Whenever possible, phase-equilibrium data for the