1

INTRODUCTION

1.1 INTRODUCTION

This book is concerned with a field of study called *attainable regions* (ARs), which is a set of ideas intended to address a generalized problem, often encountered in chemical reactor and process design. Although the problem can become quite detailed if we allow it, the basic idea is simple to understand. This chapter serves to articulate the type of problems AR theory could help address. To gain a sense of the scientific discipline that we are interested in, many (but not all) of the problems we are concerned with can be represented by Figure 1.1.

Assume that we are supplied feed material of a known state (i.e., composition, temperature, and flow rate) and asked to design a process that optimizes the production of a desired product. The system in question is represented by a single block, a "black box." This is a process that accepts a feed and converts it into something of higher economic or social value, chiefly via *reactive* unit operations. The block could be a batch or continuous process. In this book, we will mainly focus on continuous reactors. Products from the block are given by a single effluent stream. In reality, this could come about from a number of intricate recycles and bypass streams, occurring amongst a vast set of unit operations within the block—that is, the physical process represented by the block in Figure 1.1 is likely to be very complex in reality.

For many problems, we might specifically wish to find the best concentration of a desired component exiting the network, or perhaps the total cost of equipment to meet a minimum level of production—at a minimum product quality—within the network. For now, we shall leave these descriptions open so that we can describe the central problem that is related to them all.

A relevant question to ask in this context is the following: How do we best design the internals of the block given in Figure 1.1? Since we are specifically interested with reactive processes, how do we best design a process involving reaction? There is no assumption of a predefined design inside the block. We are concerned with the generalized design of the internals, and not simply the optimization of a set design. (Some readers may recognize this as *synthesis*.) These questions often constitute what is referred to as the *reactor network synthesis problem*. Moreover, once we have synthesized a design, how do we measure a "good" design from other competing designs? Although it may appear as the former problem is our chief concern, it is actually the latter problem that we interested in. Our goal in this book is to understand how we find and measure "good" designs using AR theory.

AR theory is hence a set of ideas in chemical reactor design that aims to understand the reactor network synthesis problem. But to understand this problem will ultimately require us to understand a broader problem of what it means to be "the best," for various designs within the block may achieve the same outcome. This is our primary concern in AR theory. It is related to the reactor network synthesis problem, but it is also distinct.

1.2 MOTIVATION

1.2.1 Toluene Production as a Case Study

To motivate why AR theory is useful, let us begin with a story, involving a team of three young engineers, who are interested in the production of toluene. We would like to gain a sense of some of the typical design considerations encountered by the team, which may also be addressed with AR theory. Sections 1.2.2–1.2.5 describe the team's story, whereas Section 1.2.6 explains the story in relation to AR theory. Sections 1.3 and 1.4 are intended for readers who are already familiar with the rudiments of chemical reactor design.

Sam, Alex, and Donald are promising young engineers working for a large chemical company that produces toluene ($C_6H_5CH_3$) as one of its products. One day, their boss asks

Attainable Region Theory: An Introduction to Choosing an Optimal Reactor, First Edition. David Ming, David Glasser, Diane Hildebrandt, Benjamin Glasser, and Matthew Metzger.

Companion website: http://attainableregions.com

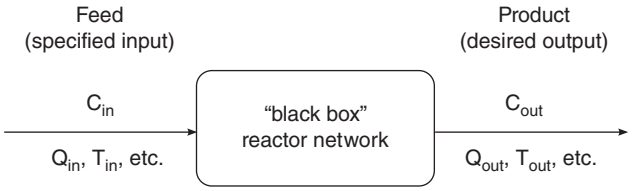

Figure 1.1 Overview of reactor network.

them to investigate how the company could improve the quality of their toluene product. Specifically, he asks:

How can we maximize the amount of toluene produced from a feed of 0.5 moles of ethylene and 1.0 moles of benzene?

Although there are potentially many unit operations that might improve the amount of toluene in the system, we are mainly interested in unit operations that involve reaction. The objective may be refined slightly to say that we wish to find a *reactive* system that maximizes the amount of toluene produced.

The three engineers decide to first conduct a number of experiments in the company's lab, as a way to gain a deeper understanding of the system of reactions. The discussions given in the following text chronicle their experimental process, their discoveries, and ultimately their recommendations in addressing this problem.

1.2.2 Part One: Initial Investigations

Having no prior knowledge or experience with toluene and its production, Sam first consults one of the senior chemists in the company, and gathers information regarding the reaction chemistry. The following set of reactions explain the system, including all significant products and by-products.

$$C_6H_6 + \frac{1}{2}C_2H_4 \leftrightarrow C_6H_5(CH_3) \tag{1.1a}$$

Benzene + $^1/_2$ ethylene $\leftrightarrow$ toluene

$$C_6H_5(CH_3) + \frac{1}{2}C_2H_4 \leftrightarrow C_6H_4(CH_3)_2 \tag{1.1b}$$

Toluene + $^1/_2$ ethylene $\leftrightarrow$ xylene

$$2C_6H_6 \leftrightarrow C_6H_5C_6H_5 + H_2 \tag{1.1c}$$

2 benzene $\leftrightarrow$ diphenyl + hydrogen

Benzene (B) reacts with ethylene (E) to form toluene (T). Toluene and ethylene further react to form xylene (X). At the same time, benzene reacts to form two side-products in a competing side reaction: diphenyl (D) and hydrogen (H). This system may be classified as a series–parallel reaction, with toluene as an intermediate product, which shall hereafter be referred to as the BTX system.

TABLE 1.1 Sam's First Few Experiments

Experiment	Reaction Time (h)	Toluene Concentration (mol/L)
1	5.0	0.0087
2	2.1	0.0373
3	1.1	0.0560
4	0.1	0.0361

For the purposes of the investigation, the BTX reaction is independent of both temperature and pressure. It is assumed that the toluene concentration inside the reactor is simple to measure, so that concentrations are easily recorded, and that it is also possible to initiate and terminate the reaction easily.

Sam then begins her investigation in the simplest manner possible: by experimenting in a batch reactor (a beaker) in the lab, using an initial feed concentration of 0.5 mol/L ethylene and 1.0 mol/L benzene.

She starts by carrying out the experiment for a number of (arbitrary) reaction times using the same initial conditions each time, and then by recording the associated toluene concentration achieved after each run. Sam conducts four experiments in total, and a summary of her results is displayed in Table 1.1.

From the data, there appears to be an ideal reaction time, between 0.1 and 2.1 h, where the toluene concentration is maximized. Using this insight, Sam carries out a series of additional experiments, attempting to isolate the exact reaction time that maximizes toluene concentration. In effect, her approach is to use reaction time as a parameter to find the maximum toluene concentration.

After many experiments, Sam finds that a reaction time of 35.4 min (0.59 h) produces the highest toluene concentration: 0.0619 mol/L. Confident in her results, Sam reports back to her boss with the good news.

OBSERVATION: Initial investigations

Many of us tend to begin our investigations in a similar manner to Sam's approach—with little previous knowledge or known insight, we simply begin with that *is* known and then attempt to improve the current performance of the system using known parameters. This is a reasonable approach, but additional insight into the system might bring about further improvements.

1.2.3 Part Two: Iterative Improvement

1.2.3.1 Accidental Improvement Happy with Sam's initial results, the team decides to run the reaction on a larger scale. The reaction is predictable and simple to operate, and they manage to consistently achieve the toluene

concentration expected with little complications. A standard operating regime is eventually developed, involving four steps: filling, reacting, emptying, and cleaning.

One day, whilst preparing the reactor for the following day, Alex forgets to empty the entire contents of the reactor vessel, and a small portion of the reactor product is retained in the reactor overnight. Alex enters the lab the next day, ready to complete a new set of batches, unaware of his mistake the previous day. He fills the reactor with fresh feed material, and runs a new batch.

To his surprise, when he expects to obtain the same toluene concentrations as in the previous experiments, he realizes that the toluene concentration has changed. It has *increased*.

Indeed, his absentmindedness has turned out be something of great interest—not only is it possible to adjust the reaction time of a particular batch, but it is also possible to adjust the starting concentration of the batch, using product from a previous run. With this vision, Alex proposes a new three-step reaction procedure as follows:

1. First, running a fresh batch with feed material for a restricted period;
2. Then, retaining a small fraction of product;
3. Last, refilling the reaction vessel with fresh feed again, thereby altering the starting concentration of the next batch. This batch is then run to the desired exit concentration.

Alex runs the reaction with the new operating procedure (for an arbitrary reaction time and mixture concentration) and finds that he is able to achieve a toluene concentration of 0.0652 mol/L in the following batch, which is an improvement over what Sam could achieve.

1.2.3.2 Experimenting with Different Combinations

Noting Alex's achievement, Donald begins to experiment with different retained fractions, in an attempt to find further improvements. He begins with an arbitrary combination of reaction times and mixing fraction, but he finds that some combinations produce *worse* results, whereas others offer moderate improvements. He writes down his results in a matrix format, which are illustrated in Figure 1.2.

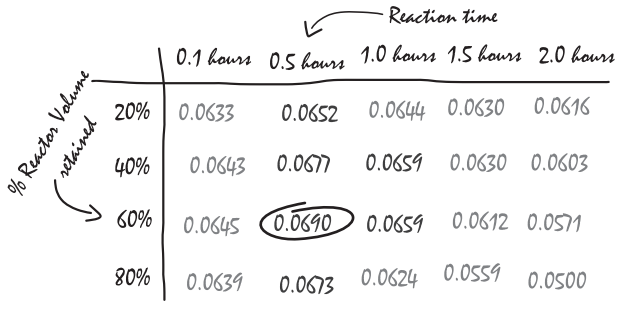

Figure 1.2 Donald's investigation, summarized in a matrix for the maximum toluene concentration achieved.

The optimal combination from Donald's finding suggests that 60% of the reactor product volume must be retained and a reaction time of 0.5 h must be used. This gives a toluene concentration of 0.0690 mol/L, or approximately 11% over Sam's investigation. Happy with this result, Sam, Alex, and Donald report back to their boss with the updated operating procedure.

> **OBSERVATION: Refining the approach**
>
> Although Donald, Sam, and Alex have managed to improve the toluene concentration, finding improvements are becoming more complicated in general. This procedure now involves finding an optimal combination of parameters, as opposed to just one parameter with Sam's investigation.

1.2.4 Part Three: Coffee

One morning, Donald walks into the office kitchen to make a cup of coffee. He likes his coffee strong and black. He sits the cup down on the counter and accidentally brushes past a nearby jug of milk. The jug knocks over and some of the milk spills into Donald's cup, mixing with the coffee and changing the color of its contents slightly.

Donald notes the change in the color of the coffee. Rather than discarding it and pouring a new cup, he realizes that his cup is like a beaker, and the addition of milk has changed the beaker's contents. An interesting idea appears in Donald's mind—could material be added into the toluene reactor *during* reaction? He realizes that Sam and Alex have been constraining themselves to the operation of standard batches only. But the reaction could be carried out in a *fed-batch reactor*, such as in Figure 1.3.

Donald sets out to see if he can improve the toluene concentration using fed-batch reaction. He allows material to flow into the reactor and mix with the reactor contents for the entire duration of the run, recording the maximum toluene concentration achieved after each run. After many experiments, Donald believes that he has found the optimum toluene concentration: 0.0761 mol/L; obtained by feeding at a constant rate of 1.0 L/h during reaction. This result is again an improvement over previous methods.

> **SIDE NOTE: New options available**
>
> The introduction of a new mode of operation has opened up a wider choice of potential operating approaches to pursue.

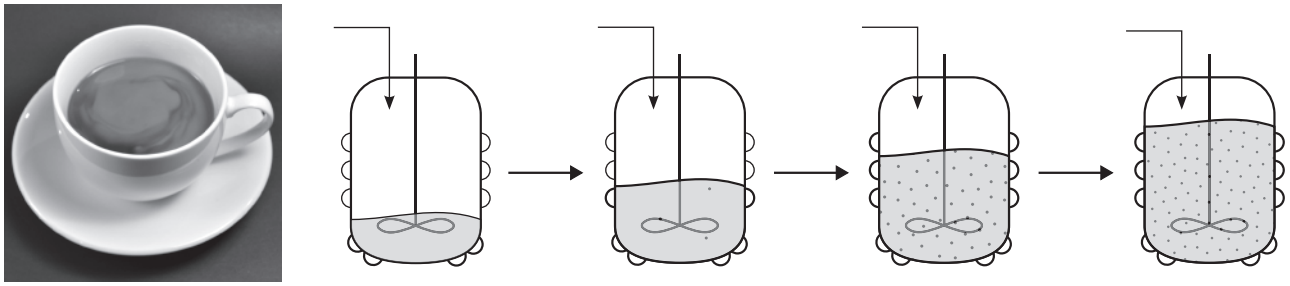

Figure 1.3 Coffee and fed-batch reactors.

1.2.5 Part Four: Additional Improvements

The team believes that they are close to reaching a point where no further improvements can be made. One day, Sam forgets to switch off the reactor just after a batch has reacted. She turns off the feed to the fed-batch reactor but forgets to turn off the reactor itself, and the reaction proceeds with a feeding rate of zero.

To her surprise, an even higher toluene concentration is obtained. Sam has, in effect, created an operating *sequence* involving the following two distinct reaction steps:

1. Reaction period involving fed-batch operation;
2. Reaction period of standard batch operation with no additional feeding.

The team discovers that if the fed-batch portion of the sequence is allowed to run for 1.6 h with a feeding rate of 1.0 L/h, followed by period of no feeding for another 15.6 min (0.26 h) as a standard batch, then a maximum toluene concentration of 0.0793 mol/L may be achieved, which again is an improvement. A summary of all the team's discoveries and recommendations for this investigation is provided in Table 1.2.

The team has managed to improve the toluene concentration by 28%: starting from 0.0619 mol/L, initially obtained by a standard batch reactor, to 0.0793 mol/L, obtained by a combined fed-batch and batch sequence. Satisfied with their progress—as well as a little tired of having to do so many experiments—Sam, Alex, and Donald report their findings as final recommendations.

SIDE NOTE: Additional modifications

Note that concepts from Section 1.2.4 could also be incorporated into this operating sequence. Depending on how long we react, and how much product is mixed, the result might be improved even further. Each time a new discovery is found, many more combinations with existing procedures can be explored.

1.2.5.1 A Change in Objective Sam, Alex, and Donald's boss is so impressed with their findings; he proposes another problem for them to tackle (one that the company has not yet been able to fully understand): instead of seeking to maximize toluene concentration, what can be done to minimize the production of hydrogen as a by-product?

Although the team has developed useful insights from their toluene experiments, a new set of experiments must now be carried out for hydrogen, and they have little understanding that could elicit an immediate recommendation for this new objective. Their boss' request leaves them feeling a bit bewildered, and they walk away hoping that they will be as fortunate with their new investigation as they were with the previous experiments.

TABLE 1.2 All Discoveries and Recommendations Made by Sam, Alex, and Donald

	Toluene Concentration (mol/L)	Associated Method Used
Part One	0.0619	Standard batch reactor. Optimized for reaction time.
Part Two	0.0690	Repeated batch with partial mixing. Optimized for reaction time and starting concentration.
Part Three	0.0761	Fed-batch reactor at 1.0 L/h. Optimized for feeding rate.
Part Four	0.0793	Fed-batch for 1.6 h at 1.0 L/h, followed by a standard batch optimized for 15.6 min (0.26 h).

ILLUSTRATION: Results from a number of random experiments

When the objective of the investigation is modified, a new set of experiments must be carried out. Perhaps the team can use what they have learnt previously for the new investigation, but it is unclear whether the same techniques will also work with hydrogen.

Suppose that a new set of experiments are carried out, in an attempt to understand the hydrogen minimization problem, and that Table 1.3 provides a summary of those experiments. These data originate from the same BTX reaction used in the previous sections.

Which experiments would you recommend for further investigation? How much more improvement do you think is possible?

TABLE 1.3 Experiments for Minimum Hydrogen Production

Attempt	Operating Method	Hydrogen Concentration (mol/L)	Toluene Concentration (mol/L)
1	Batch reactor (0.3 h)	0.4042	0.0563
2	Batch reactor (1.5 h)	0.4396	0.0484
3	Fed-batch reactor with 0.1 L/h, 5 h	0.3682	0.0641
4	Fed-batch reactor with 1.0 L/h, 5 h	0.3677	0.0676
5	Batch reactor (0.55 h), followed by a fed-batch (0.7 h, 0.2 L/h)	0.3621	0.0685
6	Standard batch (0.5 h) mixed with 15% fresh feed at the end	0.3601	0.0522

1.2.6 What this Book is About

1.2.6.1 Attainability The challenges faced by Sam, Alex, and Donald might also be commonly encountered by those who work in a design and experimental environment. Not only is it important for Sam, Alex, and Donald to understand how to improve the reaction, but it is also important for them to understand *what* procedure should be improved and *why* it is needed. Had they been aware of this knowledge from the start, they may have arrived at their final recommendation much quicker and been more confident in their recommendations overall.

What is known in the present moment influences our thinking—in terms of what improvements are currently possible—and how these improvements should be carried out. We may be accustomed to a certain way of thinking, and sometimes our decisions depend on events that were not originally planned. Hindsight is often hard-earned. Furthermore, sometimes we do know what design or procedure should be followed, but they cannot be implemented due to financial or physical constraints. Do we always understand what impact these constraints have in terms of a potential loss, an opportunity cost?

Could we have foreseen these challenges from the beginning? How do we find these limits? And what tasks must be done in order to achieve them? There is a theme of *attainability* that runs through these questions, and AR theory provides a framework for helping to address these questions in chemical reactor networks.

1.2.6.2 Performance Targets AR theory is concerned with problems related to the attainability of certain states. Understanding what states are attainable and what states are not allows for *performance targets* to be established, which may be incorporated into the design process. Examples of common performance targets in reactor design might include the following:

- Minimizing the production of CO_2 or other unwanted by-products from the reactor;
- Finding the smallest reactor volume needed to meet a desired output;
- Achieving the highest production rate of a biological product from a batch reactor;
- Maximizing the profit from the sale of a reactor product;
- Determining the maximum operating temperature within the reactor.

AR theory also helps us to understand what equipment is needed to achieve these targets. In relation to reactive equipment, this means providing insight into what type of reactor should be used, and how different reactor types should be

arranged to achieve a certain target, such as concentration, conversion, yield, and profit.

SIDE NOTE: Optimal result still unknown

We have not yet confirmed whether a toluene concentration of 0.0793 mol/L, achieved in Section 1.2.5, is the highest concentration possible. In Chapter 7, we shall solve this problem again and show that a toluene concentration of 0.0807 mol/L is achievable. Moreover, we can also answer the hydrogen minimization problem, described in Section 1.2.5.1, using previous calculations involving the toluene maximization problem. Hence, both questions may be addressed without the need for additional work to be carried out.

1.3 REACTOR NETWORK SYNTHESIS

In Section 1.2, we described how Sam, Alex, and Donald approached the BTX problem from an experimental perspective. How might our approach change if we are given mathematical expressions for the rates of reaction? In the following sections, we wish to describe some common ideas and approaches in theoretically designing a network of reactors (the reactor network synthesis problem), and also describe a central challenge faced in reactor network synthesis, even when mathematical and optimization techniques are available. For example, suppose that kinetics is also available for the BTX reaction and assumed to follow the data in Table 1.4:

TABLE 1.4 Rate Expressions for the BTX System

Component	Rate Expression
Benzene (r_B)	$-k_1 c_B c_E^{0.5} - 2k_3 c_B^2$
Ethylene (r_E)	$-0.5k_1 c_B c_E^{0.5} - 0.5k_2 c_T c_E^{0.5}$
Toluene (r_T)	$k_1 c_B c_E^{0.5} - k_2 c_T c_E^{0.5}$
Xylene (r_X)	$k_2 c_T c_E^{0.5}$
Diphenyl (r_D) = Hydrogen (r_H)	$k_3 c_B^2$

where $k = 1.0\,L^{0.5}/(mol^{0.5}.h)$, $k_2 = 1.0\,L^{0.5}/(mol^{0.5}.h)$, and $k_3 = 10.0\,L/(mol.h)$; c_i represents the concentration of component i in the system. Since expressions for species reaction rates are known, it is possible to model the BTX reaction, and hence mathematical optimizations may be carried out.

Perhaps, as a first attempt, the BTX reaction could be compared using a number of different, common, reactor models, such a continuous-flow stirred tank reactor (CSTR). One could solve the CSTR equation and then compare the toluene concentration achieved in a CSTR to that achieved in a standard batch reactor (or equivalently in a plug flow reactor or PFR). Figure 1.4 illustrates the results of this approach using the BTX kinetics given in Table 1.4. Different reactor types behave uniquely, and thus each reactor type could be separately optimized for maximum toluene production.

SIDE NOTE: Reactor equations

If the density is assumed to be constant, a steady-state mass balance over a CSTR gives the following expression[1]:

$$Q(c_i^{out} - c_i^{in}) = V_{CSTR} r_i \tag{1.2a}$$

Here, c_i^{in} and c_i^{out} are the inlet and exit concentrations of component i, respectively. Variables Q and V_{CSTR} are the volumetric flow rate and CSTR vessel volume, respectively. Similarly, the equation for a constant volume batch reactor follows the differential equation:

$$\frac{dc_i}{dt} = r_i \tag{1.2b}$$

where t is the reaction time of the batch. Solving Equation 1.2a and 1.2b produces the toluene concentration profiles in Figure 1.4.

In this case, the CSTR achieves a higher toluene concentration, but are there perhaps other reactor types (i.e., a packed bed reactor) that could outperform the CSTR? Additionally, are there *combinations* of reactors—as a *network of reactors*—that could achieve better?

To demonstrate the potential complexity involved when dealing with multiple reactor designs, consider Figure 1.5, which proposes a number of different reactor configurations (reactor structures) that might be used. For simplicity, the configurations are limited to combinations of a maximum of three reactors, using PFRs and CSTRs only.

How do we determine which reactor configuration is best? In this example, we could potentially solve each system and find the best configuration from the size options. However, we can always devise new configurations that may be superior. A number of additional design choices must be made when considering reactor structures, even for simple configurations such as in Figure 1.5. Some of these considerations might include the following:

- How many individual reactors do we consider in each structure?
- What reactor types do we consider?

[1] A summary of fundamental reactor types is provided in Appendix A.

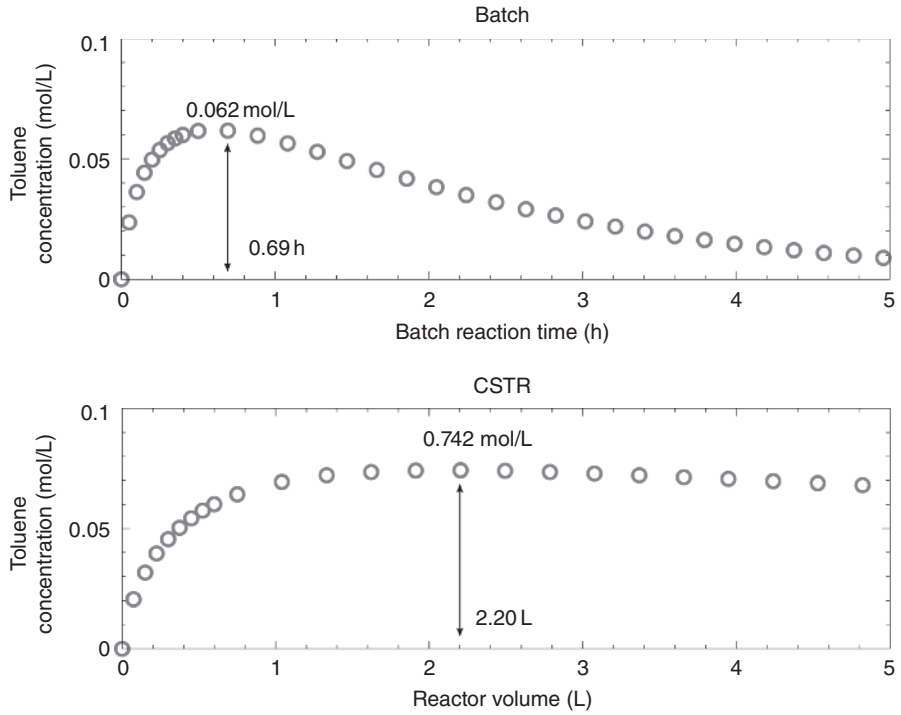

Figure 1.4 Toluene concentration data obtained in a batch experiment and a continuous-flow stirred tank reactor (CSTR).

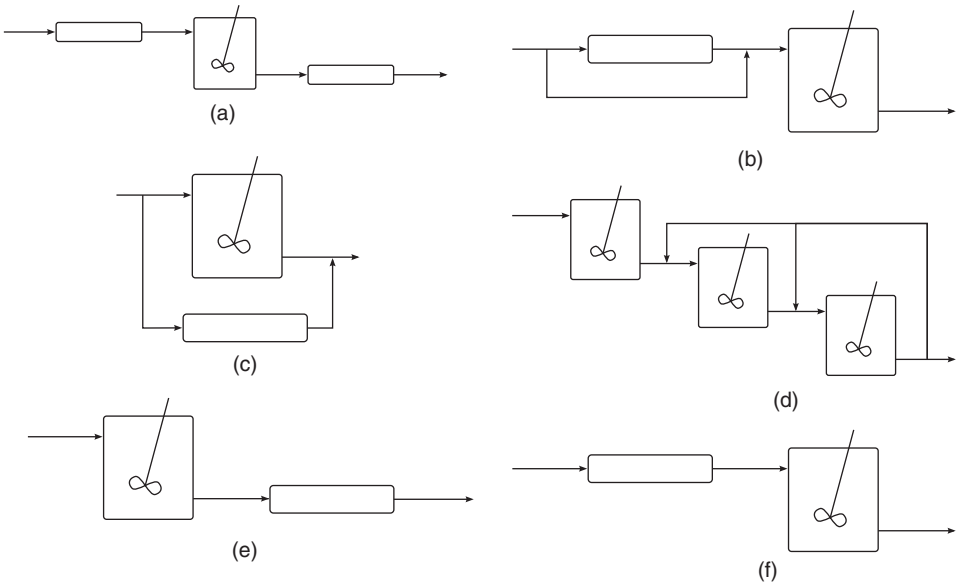

Figure 1.5 Options (a)–(f) represent a number of different reactor configurations. Only PFRs and CSTRs are used with a maximum of three reactors per configuration.

- Do we include recycle and bypass streams? If so, where are they placed within the structure?
- How many parallel reactors are included?
- How many reactor structures should be considered?

How should one select the best reactor structure from a pool of many reactor configurations? Nominating specific combinations in an exhaustive fashion is not feasible because we could always devise a different configuration that may perform better. Yet again, we are presented with a

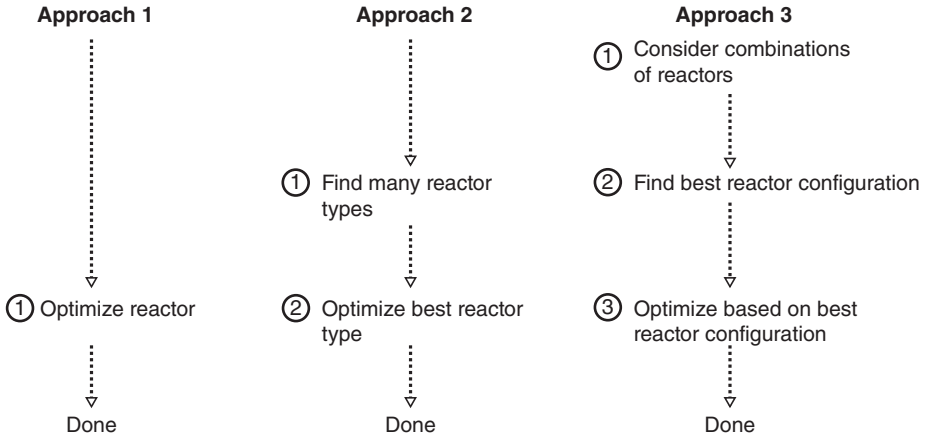

Figure 1.6 Overview of different approaches. Each approach will terminate in an optimal design, although the particular design achieved may differ depending on the order of steps taken.

similar question as in Section 1.2.6—*when do we know we are the best?*

CONCEPT: Reactor structures

By a *reactor structure*, we have in mind a well-defined arrangement of reactors (a reactor network) that produces a particular output. The network might typically be composed of various reactor types. The kinds of problems that we will investigate in this book all fall into this category. We will be interested in looking at how combinations of reactors (as opposed to a single reactor) can often provide meaningful improvements to a problem.

Figure 1.6 proposes a number of general approaches to the reactor synthesis problem, starting from the simplest and most constrained approach, to the most general (and difficult) approach. In AR theory, we are ultimately concerned with problems involving reactor structures that produce the best performance, and thus AR theory falls into Approach 3 of Figure 1.6.

ILLUSTRATION: Are multiple reactors necessary?

Consider the following two reactions:

$$6.21\mathrm{A} + 0.145\mathrm{B} \rightarrow 1.001\mathrm{C} + 10\mathrm{D} + 0.1\mathrm{F} + 2.15\mathrm{G} \tag{1.3a}$$

and

$$2\mathrm{A} + \mathrm{C} \rightarrow 1.5\mathrm{B} \rightarrow 0.25\mathrm{C}$$

$$2\mathrm{C} + 3.6\mathrm{D} \rightarrow 3\mathrm{D} + 6\mathrm{E}$$

$$2\mathrm{E} + \mathrm{F} + 0.17\mathrm{B} \rightarrow \mathrm{B} + 1.5\mathrm{C} + \mathrm{G} \tag{1.3b}$$

How would you build a reactor that maximizes the production of component C according to Equation 1.3a? How would you optimize for the same scenario if Equation 1.3b occurred in the reactor instead?

In Equation 1.3a, the reaction is "simple": although multiple components participate in the reaction, there is only one reaction, and hence there is only one pathway that reactants may proceed to form products (all components are linked by a common extent of reaction). The choice of reactor type *may* have a significant influence on system performance, although it is possible to achieve the same performance with different reactor types.

By comparison, Equation 1.3b contains the same number of individual components, yet these are split over a number of different reaction paths. Equation 1.3b is hence more complex: each path could be individually pursued, resulting in a number of different product mixtures depending on which reactions are dominant, the initial concentration of species, and the intrinsic behavior of different reactor types to these reactions. Consequently, the choice of reactor type may have a significant influence on performance. One reactor type may only achieve a small portion of all possible product states, favoring one reaction over other competing reactions—a CSTR might favor the first two reactions, whereas a PFR might favor the last reaction. Utilizing different reactor types may expose a larger set of possible outputs, but the opportunity for different reactions to occur means that the underlying reactors must be sufficiently generalized to target the operating point of interest. In order to achieve these states, reactor structures are more suitable.

ILLUSTRATION: Biological reactions

Consider the metabolic pathway diagram in Figure 1.7 for the production of nattokinase (and other biological products) by glucose and glycerol. Here, there are *many* reactions occurring. Each arrow displayed in the schematic represents a reaction.

The diagram given in Figure 1.7 is common in biological systems. Complex recycling of intermediate products, and the possibility for compounds to traverse along many divergent paths, means that it is often not straightforward to predict how the flow of material is best arranged along a certain pathway, or what the best pathway is for the production of a desirable intermediate product. Modeling the reactions present in a biological system is complex, and optimizing for a bioreactor that maximizes the production of a specific byproduct is hence a challenging task.

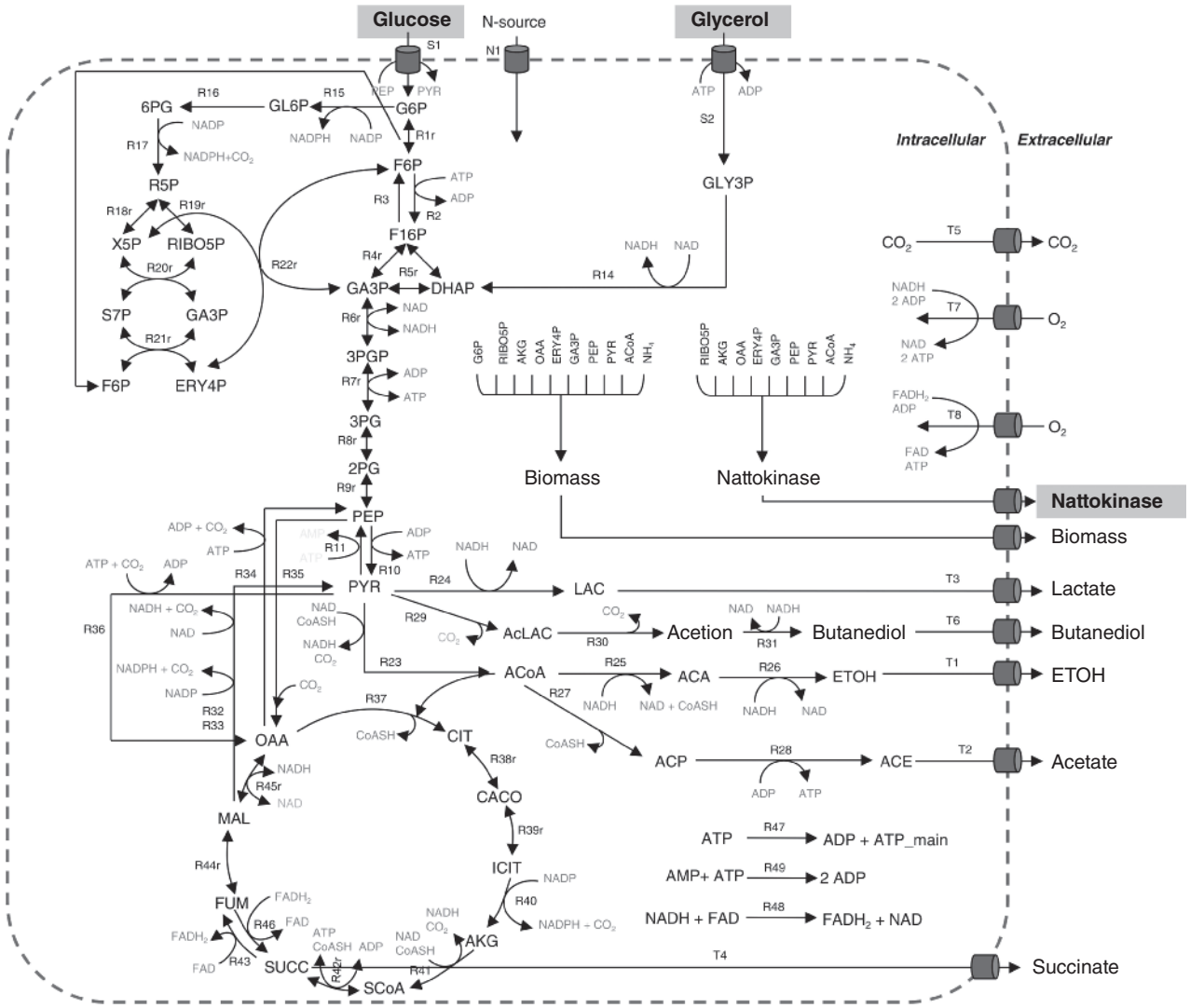

Figure 1.7 Metabolic pathway showing how glucose and glycerol are converted in a series of complex biological reactions to produce a number of different by-products. Unrean and Nguyen (2013). Reproduced with permission of Springer.

There is again an opportunity here to use multiple reactor types to maximize a desired product, yet in practice, simplifications are often applied (i.e., lumped reaction models) to make the problems more tractable. The design of the reactors themselves are also often of a simpler nature, employing a single CSTR (chemostat) or fed-batch reactor with biomass recirculation (Nielsen et al., 2011). Utilizing one reactor in one configuration may limit the possible combination of pathways, which may limit performance as a result.

Although multiple reactors can be used for single reaction systems, they are potentially not required. For systems involving multiple reactions, reactor structures may be *essential*—unlocking certain states that would not be possible with a single reactor type. However, solving reactor network synthesis problems is more difficult than single reactors, because reactor structures introduce more complexity into the design.

SIDE NOTE: Multiple reactions and multiple reactors

We find that methods such as AR theory are required not because of problems involving multiple reactors, but because of problems involving multiple reactions. Many of these methods are unnecessary when the reactions are inherently simple. The reactor network synthesis problem arises often as a result of complexities in the system from multiple reactions.

When the reaction is complex, the best performance is often achieved in a reactor network (a combination of reactors). AR theory deals with reactor problems involving *more than one reactor*.

1.4 SOLVING THE REACTOR NETWORK SYNTHESIS PROBLEM

1.4.1 Reactor Superstructures

1.4.1.1 Description A popular approach to solving the reactor network synthesis problem is by use of *reactor superstructures*. A reactor superstructure is a reactor configuration where many simpler reactor types are arranged in a specific pattern and connected via a network of bypass and recycle streams, so that various outcomes can be achieved from a single structure. Reactor superstructures thus represent a superset of all possible outputs, wherein an optimal answer is a subset of the superstructure.

ILLUSTRATION: Examples of reactor superstructures

Consider how a series of CSTRs might act as potential building blocks that approximate other reactor types.

For PFR approximation, CSTRs can be connected in series, as in Figure 1.8(a). A variety of different outputs may be produced from a single reactor type in the appropriate arrangement. More complex reactor structures have been published in the scientific literature. One example is provided in Figure 1.8(b) (Rooney and Biegler, 2000).

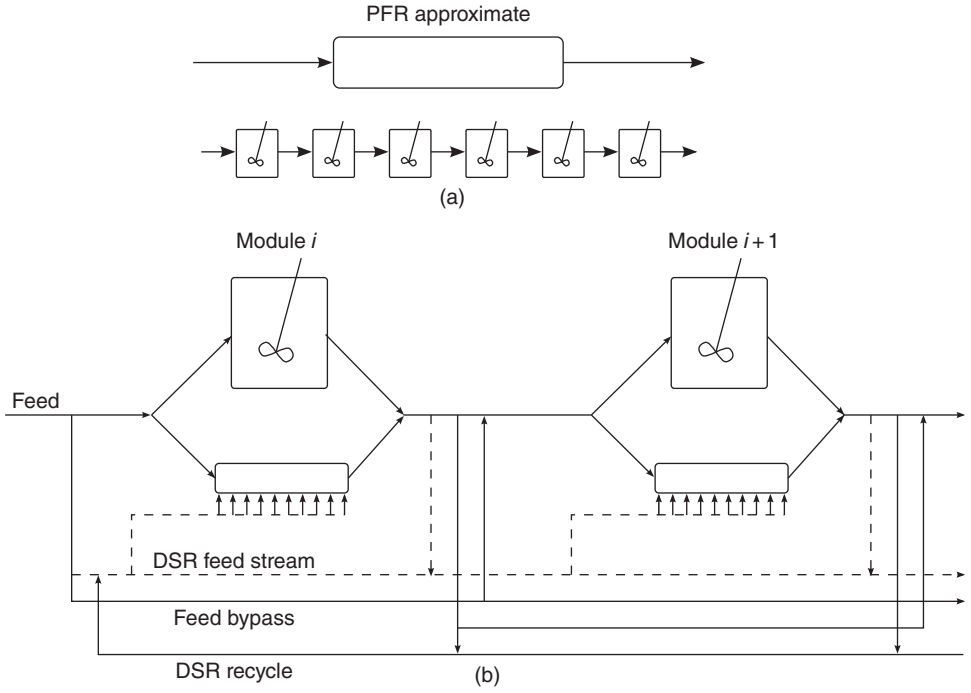

Figure 1.8 (a) A CSTR configuration that approximates a plug flow reactor (PFR). Kauchali et al. (2002). Reproduced with permission of Elsevier. (b) Example of a reactor superstructure. Rooney and Biegler (2000). Reproduced with permission of Elsevier.

Combinations of basic reactor types, such as CSTRs and differential sidestream reactors (DSRs), are arranged in a specific pattern to produce a building block structure for the creation of more sophisticated reactor structures. These superstructures allow for the description of a wider variety of different achievable states.

Using the superstructure approach, nonreactive unit operations (i.e., separation) may be included into the design as well, which allows for a wide range of optimization scenarios to be solved for. The superstructure approach is a powerful method to reactor network design, as a large amount of detail and flexibility can be incorporated into the configuration.

SIDE NOTE: The power of the superstructure approach

Superstructure methods are a powerful and popular approach to the reactor network synthesis problem, as well as to the generalized problem of process synthesis (the design of entire processes). An advantage of superstructures is that they interface easily with existing plants—that is, it is often possible to mathematically model the operation of plants that have already been designed and built, which once represented as a mathematical model, can be optimized with standard optimization methods. This makes the superstructure approach highly useful in industry, as existing plants can be modeled and optimized directly, making results much easier to relate to real-life performance.

1.4.1.2 Solving Optimal Reactor Superstructures With a large number of interlinked bypass and recycle streams, amongst a number of different reactor types, reactor superstructures are expressed in a large mathematical model—a system of differential algebraic equations (DAEs)—which can be solved using mathematical optimization techniques. To solve the model, the parameters of the superstructure model are adjusted and checked against an appropriate objective function to determine optimal performance. Optimization follows the generalized form:

Maximize/minimize:	Objective function (i.e., volume, concentration, time or operating costs)
Subject to:	Parameters and constraints (i.e., time, reactor model equations, flow rates and mixing fractions)

The complexity of modeling and optimizing the superstructure is then related to the complexity of the superstructure itself. Parameters in the model act like switches on a switchboard, and a solution to the optimization problem is a specific combination of switches that achieves the desired result. A balance must be established between practicality and accuracy: the superstructure must be adequately generalized (more complex) to describe many outcomes, yet computationally simple to allow for solution of the associated problem in a reasonable time.

Solutions are based on the objective function specified. A change in the objective function introduces a change in the superstructure configuration, which might require re-solving the problem for the new objective function. (When Sam, Alex, and Donald are asked to minimize the production of hydrogen in the BTX reaction, this signals a change in objective function.)

Two important questions that arise when dealing with the optimization of reactor superstructures thus arise:

1. Are there similar superstructure configurations that achieve the same result? (*Are there multiple solutions?*)
2. Does a better superstructure exist? (*Is the answer globally optimal?*)

More generalized structures, capable of describing a wider variety of solutions, may require additional complexity in the superstructure model. Additional complexity in the design also leads to increased complexity in the solution of the equations describing the superstructure, which may make the problem more difficult to solve. (Figure 1.8(b) might be able to describe more complex problems and solutions based on Figure 1.8(b) may offer better performance than Figure 1.8(a), but it is also more difficult to solve.)

ILLUSTRATION: Word combinations

How many unique English words can you form from the following set of letters? Not all letters in the set need be used:

{C, X, A, H, T}

Suppose now that the letter "E" is included into the set. How many more words can you find? What if letters "D" and "O" are added to the set?

With the help of a computer, we can show that there are approximately 11 unique words that can be formed from the set {C, X, A, H, T}, 32 unique combinations are possible from the set {C, X, A, H, T, E}, and 83 words are possible from {C, X, A, H, T, E, D, O}. Indeed, it is evident that with each addition of a new letter, there

are many more words that can be generated. (If we were to add the letter "R" to the set for instance, the number of unique combinations would increase to roughly 211 words!)

Each time additional variations are introduced, many new combinations are possible, and complexity explodes. This phenomenon is also observed with reactor superstructures—with highly generalized superstructures, there is a greater possibility of obtaining many configurations of the base design. Many of these designs may even result in the same output. The mathematical models associated with these superstructures are also more difficult to solve. But there may also be many other solutions for which the superstructure does *not* acknowledge. The set of solutions obtained might therefore only be a *subset* of all possible outcomes in the system.

1.4.2 AR Theory

In AR theory, we have an interest in the reactor network synthesis problem, but it is not our chief interest. It is sometimes not possible to generate an optimal reactor structure using AR theory, but it is still possible to generate important information that may help to understand what the optimal reactor structure might be. Let us refer back to the following two points from Section 1.4.1.2:

1. Are there multiple solutions?
2. Is the solution globally optimal?

In both of these questions, we must begin with knowledge of the final answer *before* the reactor structure is devised—we must know, beforehand, of all possible solutions (for all possible structures) to understand if multiple solutions exist, and the same information must be known to understand if our structure is globally optimal.

This ordering of tasks is depicted graphically in Figure 1.9. In a "classical" (non-AR theory) approach, reactor structures are first formulated, solved, and then optimized to produce a particular output. An output exists for a particular reactor structure, and the exact output obtained is as a result of the specific path taken in the approach. The typical workflow is then from left to right. In contrast, we wish to first find many answers at once with AR theory, and then utilize these answers to optimize the specific problem at hand. This is done without a specific impression of a particular reactor structure in mind. Rather, the reactor structure is an outcome of the answer and not the other way around, and the workflow in this instance then proceeds from right to left. All possible answers to all possible problems are generated first, and only after this task has been accomplished is the reactor structure for a particular duty found.

As a precursor to the following chapters, we wish to leave with a number of scenarios that AR theory could help to address. These scenarios are related to the BTX problem discussed earlier. It is important to keep these questions in mind, for they shape the approach we would like to adopt with AR theory.

1. *A Known Achievable Point*: Consider if it were known (because an oracle tells you) that a toluene concentration of 0.09 mol/L is achievable *without* knowing what particular piece of equipment or method is needed to achieve it. Would it be possible to utilize this piece of information to deduce what equipment or methods would be needed? Simply knowing that 0.09 mol/L is an achievable concentration may incentivize investigation to determine an appropriate reactor that achieves it.
2. *Multiple Solutions*: Suppose that various sets of reactors could all achieve the same toluene concentration of 0.09 mol/L, but that some reactor arrangements are able to achieve this concentration in a smaller total reactor volume. Is your design still appropriate? Understanding the range of different options available to us is useful in selecting the most appropriate reactor configuration for our needs.
3. *Globally Optimal Solution*: Now imagine that the maximum toluene concentration ever achievable is 0.1 mol/L. Would there be any attempt to improve the system further? What if the maximum concentration is 1.5 mol/L instead? This information is useful to the designer, as now appropriate performance targets

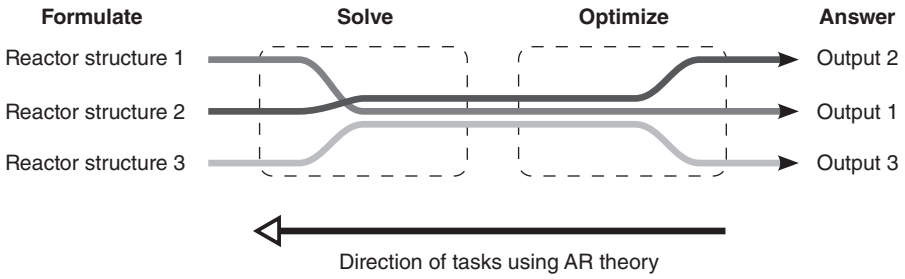

Figure 1.9 Order of tasks using the AR approach.

may be set and used to justify whether additional optimization effort is required.

4. *A Different Global Optimum for a Different Objective*: Imagine further that xylene is now the desired component and not toluene, and that we also wish to minimize the consumption of ethylene. How do we achieve this new objective and is our old design still appropriate? If it is possible to compute a *set* of achievable available concentrations, for many reactor configurations, then a change in objective function is easily incorporated into the new analysis.

1.4.3 Attainability Problems Outside of Reactor Design

We end this chapter with a number of open-ended anecdotes. The topics described are not specific to reactor design, but many of them are simply the same challenge disguised under a different context. All situations seek to understand the same kind of question: *How do we know that we are the best?*

1.4.3.1 Fishing Two friends, Bob and Jim, go fishing on a trout farm and hold a friendly competition to see who can catch the biggest fish by the end of the day. They find a quiet spot by the lake in the morning, settle in, and cast their lines into the lake at the same time. The two spend the rest of the day attempting to outdo each other by catching the largest fish.

The two take their catches back to be weighed and recorded at the end of the day. On this occasion, Bob has managed to catch the largest fish. When they arrive at shore, spectators are astounded by the size of Bob's catch. The lake owner comments that Bob's fish is the largest he had seen in his entire career. He adds that it may even be the largest fish in the entire lake!

But how would we know if Bob's catch is indeed the biggest fish in the lake? Perhaps larger fish exist that have not yet been caught. It is simply not feasible to see all the fish in the lake for one to know with absolute certainty. We would first need to find and measure *all* the fish in the lake. The question is then: how do we find all the fish in the lake?

SIDE NOTE: Colossal squid

Colossal squid—measuring in excess of 10 m in length—are sometimes caught by fishing boats, or are found when they wash up on shore. The only colossal squid that we know of are the few specimens that scientists have observed near the ocean surface, yet they exist in parts of the deep ocean that human society cannot fully explore at present. It is likely that there are even bigger squid that exist deep in the ocean. How would we find these creatures if they reside in a part of the ocean that we cannot reach?

1.4.3.2 Olympic Records On August 16, 2008, during the Summer Olympic Games, Usain Bolt set a new world record for the men's 100 m sprint, achieving a time of 9.69 s. One year later, on August 16, 2009, during the International Association of Athletics Federations or IAAF World Championship in Athletics, Bolt again broke the world record by running a time of 9.58 s (*IAAF World Championships: IAAF Statistics Handbook. Daegu 2011*, 2011).

Indeed, Usain Bolt's successive achievements have made us question something deeper in the sport—what is the shortest time a human being could *ever* run 100 m? Are we close to reaching this point, or will someone run a faster time in the future?

ILLUSTRATION: A maze puzzle

Consider how you might approach solving the maze puzzle in Figure 1.10. The aim is to start at a predefined location and then travel through the maze to reach a desired exit point. A number of potential paths may be pursued, resulting in many final states.

1. Suppose that you wish to terminate your journey at point 1 in Figure 1.10. How would your solution be affected if you started from:
   a. The point labeled "Start" and worked to point 1?
   b. Point 1 and worked backward to the start?
2. Suppose we wish to end at point 7 instead. Would it be easier to start from the beginning or the end of the maze?
3. Imagine that now all the exits are hidden and are only known when they are reached. That is, we do not know that there are a total of eight exit points initially. At the end of each exit, a reward is placed (i.e., a pot of gold). Each exit holds a different reward value, but exit 6 contains the largest reward out of all eight exits (it is the global optimum). If only one exit can be reached on any given journey, how would you go about finding all exit points and simultaneously know that exit 6 is the overall best? If you were to end at exit 3 instead, how would you know if there is a larger reward elsewhere?

This example, although simple, illustrates a fundamental challenge often encountered in reactor network synthesis problems. Each exit in the maze could be considered a final objective. An answer is achieved from an initial state, but various outcomes may be realized from a single starting point. When attempting to solve reactor network synthesis problems, we often do not

know how many possible outcomes could be achieved. When an exit is found, how do we know if it is the best? There is certainty only when *all* possible exits have been identified, but this is difficult when we do not start with this information in hand. We seek to understand the *attainability* of all points in a system.

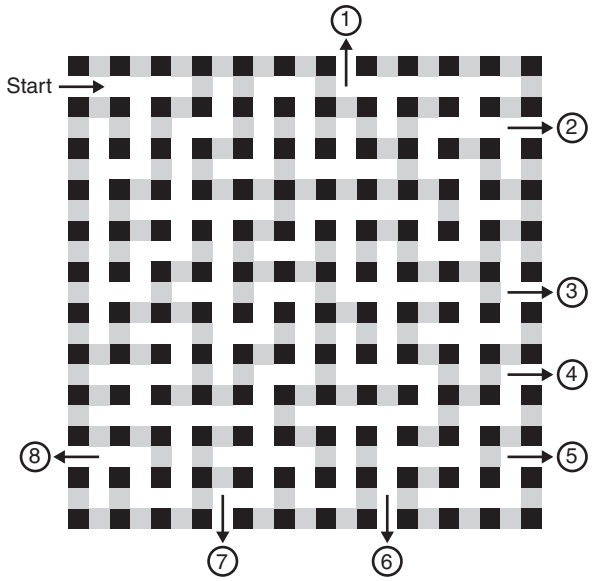

Figure 1.10 A maze with one entry point and multiple exit points.

Note the differences when performing tasks with these two different approaches:

1. In the first (non-AR theory) approach, the answer is obtained by proposing a structure.
2. In the second (AR theory) approach, it is first assumed that a certain answer is achievable, and then we determine what is required to achieve it.

If the best answer is known beforehand, then the same procedure may be carried out to find the corresponding best reactor configuration. It is often difficult to know when a good design has been achieved when we first devise a design and then attempt to find a solution, because it is not clear whether a superior design exists. The order in which tasks are carried out is significant. AR theory attempts to generate answers first. This approach offers us a different way of viewing and solving reactor problems.

IMPORTANT: Attainability and performance targeting

Knowing what is achievable beforehand is useful, for it provides guidance on how one should proceed with a design. With attainability information, it is possible to set appropriate and realistic *performance targets*—you may want not improve your current design if you knew that you were 99% to perfection, but you may wish to do something if you were only 50% of the best instead.

1.5 CHAPTER REVIEW

OBSERVATION: Finding your way in the dark

In the absence of any previous knowledge, we often think that carrying out a design (or conducting an experiment) is similar to how we wonder in the dark: It is straightforward to navigate a room at night when the lights are switched on. It is more challenging when the power goes off, and we are caught in the dark—attempting to avoid the furniture—searching for a flashlight. When the power returns, everything is put into context, and it is again simple to see how everything fits together.

Without any previous knowledge, we often follow a similar procedure in design: only after discovering what works is it clear how different units should fit together, and why certain designs work better than others. Although it is easy to see what to do next once it is known (optimizing for reaction time, feeding rates, etc.), carrying out modifications provides little satisfaction if these improvements are replaced with more effective ones.

We write this book out of a need to understand a very basic question—*when do we know we have achieved the best?* AR theory is an approach that seeks to help answer this question for chemical reactor networks (reactor structures). In this chapter, we described how problems of this nature arise when attempting to optimally produce toluene in the BTX reaction. In general, three approaches to the solution of this problem emerged, which are summarized pictorially in Figure 1.11.

Each of the approaches displayed are useful. One could always begin with a generalized approach, and then focus on specific issues during the investigation. Truly effective designs, we believe, are ones that incorporate all three strategies into the design process, although it is the *ordering* of tasks that is important.

Although we wish to motivate improvements by use of reactor structures (combinations of reactors), there are challenges associated with this approach. It is often not clear how to formulate and optimize systems involving complex combinations, and simply listing many combinations always leads us to ponder if there are other designs that may be better.

With ARs, we want to approach problems from the mindset of looking at the answer first, and then focusing on how

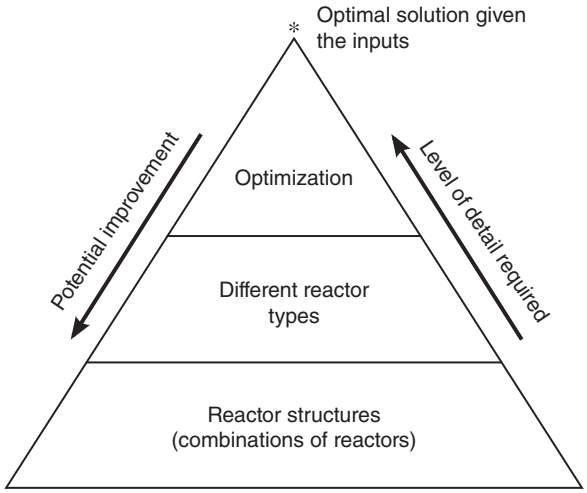

Figure 1.11 Hierarchy of design for reactors.

to achieve this from a known starting point. In this sense, the approach is top-down as opposed to bottom-up, starting from the biggest changes through structure, and refining until the most appropriate design is identified. From then on, optimizations may be carried out with the knowledge that improvements are performed on the best possible reactor structure for the problem.

From this perspective, AR theory should not be viewed as a competing method to optimization or superstructure methods, but rather as complementary tool used to benchmark current designs. Superstructures can be used in conjunction with AR theory to both set reactor performance targets and design the reactors needed to achieve these targets.

We do not wish to stumble in the dark, only identifying our position in the room once we have reached it. Rather, we hope that the ideas of AR theory will act as a flashlight, illuminating aspects of the unknown so that it is easier to advance forward. It is the awareness that these ideas are important that eventually promotes improvement. In short, *we cannot fix what we do not know*. The most useful feature that we would like to generate with AR theory is *hindsight*.

SIDE NOTE: A roadmap for discussing future questions

Throughout this book, we wish to introduce a set of ideas and perspectives that will ultimately allow us to address the challenges faced by Sam, Alex, and Donald. Many of the questions raised by them will be examined in subsequent chapters. We include a number of these questions in the following text, as a roadmap for the reader.

- *How should the problem be interpreted?*

  These fundamental concepts are introduced in Chapter 2. Here, the reader will learn how a change in perspective can allow for more complex concepts, such as the AR, to be described.
- *Is the answer unique? Could I do better? What is the absolute best?*

  Understanding what is the absolute best starts by understanding the AR itself. This concept is described in Chapter 3.
- *What procedure or method is required to achieve a certain performance target?*

  The specific reactor type used, and why it is needed, is described in Chapter 4. A number of worked problems, using AR theory, are given in Chapter 5.
- *How should multiple objectives be handled?*

  A change in perspective does not generally influence how we approach the analysis in AR theory. This concept is described in Chapters 3 and 4. Similar questions arise when there is a change in conditions, such as a change in the reactor feed, or if a different reaction is used. Again, this may give rise to a different recommendation, but the fundamental approach in AR theory remains unchanged. A worked example demonstrating this concept is given in Chapter 5.

REFERENCES

IAAF World Championships: IAAF Statistics Handbook. Daegu 2011, 2011. IAAF Media & Public Relations Department, Monte Carlo.

Kauchali, S., Rooney, W.C., Biegler, L.T., Glasser, D., Hildebrandt, D., 2002. Linear programming formulations for attainable region analysis. Chem. Eng. Sci. 57, 2015–2028.

Nielsen, J., Villadsen, J., Lidén, G., 2011. Design of fermentation processes, in: Bioreaction Engineering Principles. Springer, New York, pp. 383–458. http://link.springer.com/book/10.1007%2F978-1-4419-9688-6 (accessed May 18, 2016).

Rooney, W.C., Biegler, L.T., 2000. Multiperiod reactor network synthesis. Comput. Chem. Eng. 24, 2055–2068.

Unrean, P., Nguyen, N.H., 2013. Metabolic pathway analysis and kinetic studies for production of nattokinase in *Bacillus subtilis*. Bioprocess Biosyst. Eng. 36, 45–56.