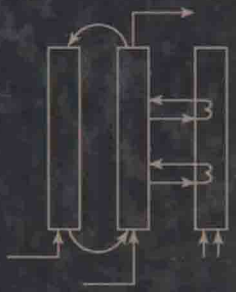
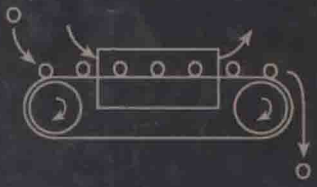
The Engineering of Chemical Reactions





Lanny D. Schmidt

THE ENGINEERING OF CHEMICAL REACTIONS

LANNY D. SCHMIDT
University of Minnesota

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Cover Photos: The *upper photo* shows a view across the Mississippi River of the Exxon refinery in Baton Rouge, Louisiana. This is one of the largest refineries in the world, converting over 400,000 barrels per day of crude oil into gasoline and diesel fuel. This refinery also produces petrochemicals for products such as polymers and plastics. The *lower photo* shows three new types of products made by chemical engineers. These are foods (Cheerios), pharmaceuticals (aspirin), and microelectronics (memory chips). The skills which have been developed in petroleum and petrochemicals have enabled chemical engineers to expand into new processes such as these.

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PREFACE

I learned about chemical reactors at the knees of Rutherford Aris and Neal Amundson, when, as a surface chemist, I taught recitation sections and then lectures in the Reaction Engineering undergraduate course at Minnesota. The text was Aris' *Elementary Chemical Reaction Analysis*, a book that was obviously elegant but at first did not seem at all elementary. It described porous pellet diffusion effects in chemical reactors and the intricacies of nonisothermal reactors in a very logical way, but to many students it seemed to be an exercise in applied mathematics with dimensionless variables rather than a description of chemical reactors.

We later used Octave Levenspiel's book *Chemical Reaction Engineering*, which was written with a delightful style and had many interesting figures and problems that made teaching from it easy. Levenspiel had chapters on reactions of solids and on complex reactors such as fluidized beds, topics to which all chemical engineering students should be introduced. However, the book had a notation in which all problems were worked in terms of the molar feed rate of one reactant F_{Ao} and the fractional conversion of this reactant X. The "fundamental equations" for the PFTR and CSTR given by Levenspiel were $V = F_{Ao} \int dX/r_A(X)$ and $V = F_{Ao}X/r_A(X)$, respectively. Since the energy balance is conventionally written in terms of spatial variations of properties (as is the general species balance), there was no logical way to solve mass and energy balance equations simultaneously, as we must do to consider nonisothermal and nonideal reactors. This notation also prohibits the correct handling of multiple reaction systems because there is no obvious X or r_A with multiple reactions, and Levenspiel could only describe selectivity and yield qualitatively. In that notation, reactors other than the perfect plug flow and the perfectly stirred reactor could not be handled because it did not allow consideration of properties versus position in the reactor. However, Levenspiel's books describe complex multiphase reactors much more thoroughly and readably than any of its successors, certainly more than will be attempted here.

We next used the texts of Hill and then Fogler in our chemical reactors course. These books are adapted from Levenspiel, as they used the same notation and organization, although they reduced or omitted reactions of solids and complex reactors, and their notation required fairly qualitative consideration of nonisothermal reactors. It was our opinion that these texts actually made diffusion in porous pellets and heat effects seem more complicated than they need be because they were not sufficiently logically or mathematically based. These texts also had an unnecessary affinity for the variable density reactor such as $A \rightarrow 3B$ with ideal gases where the solutions require dealing with high-order polynomials and partial fractions. In contrast, the assumption of constant density (any liquid-phase reactor or gases with diluent) generates easily solved problems.

At the same time, as a chemist I was disappointed at the lack of serious chemistry and kinetics in reaction engineering texts. All beat $A \rightarrow B$ to death without much mention that irreversible isomerization reactions are very uncommon and never very interesting. Levenspiel and its progeny do not handle the series reactions $A \rightarrow B \rightarrow C$ or parallel reactions $A \rightarrow B$, $A \rightarrow C$ sufficiently to show students that these are really the prototypes of all multiple reaction systems. It is typical to introduce rates and kinetics in a reaction engineering course with a section on analysis of data in which log–log and Arrhenius plots are emphasized with the only purpose being the determination of rate expressions for single reactions from batch reactor data. It is typically assumed that any chemistry and most kinetics come from previous physical chemistry courses.

Up until the 1950s there were many courses and texts in chemical engineering on "Industrial Chemistry" that were basically descriptions of the industrial processes of those times. These texts were nearly devoid of mathematics, but they summarized the reactions, process conditions, separation methods, and operating characteristics of chemical synthesis processes. These courses in the chemical engineering curriculum were all replaced in the 1950s by more analytical courses that organized chemical engineering through "principles" rather than descriptions because it was felt that students needed to be able to understand the principles of operation of chemical equipment rather than just memorize pictures of them. Only in the Process Design course does there remain much discussion of the processes by which chemicals are made.

While the introduction of principles of chemical engineering into the curriculum undoubtedly prepared students to understand the underlying equations behind processes, succeeding generations of students rapidly became illiterate regarding these processes and even the names and uses of the chemicals that were being produced. We became so involved in understanding the *principles of* chemical engineering that we lost interest in and the capability of dealing with *processes*.

In order to develop the processes of tomorrow, there seems to be a need to combine principles and mathematical analysis along with applications and synthesis of these principles to describe processes. This is especially true in today's changing market for chemical engineers, where employers no longer are searching for specialists to analyze larger and larger equipment but rather are searching for engineers to devise new processes to refurbish and replace or retrofit old, dirty, and unsafe ones. We suggest that an understanding of how and why things were done in the past present is essential in devising new processes.

Students need to be aware of the following facts about chemical reactors.

1. The definition of a chemical engineer is one who handles the engineering of chemical reactions. Separations, fluid flow, and transport are details (admittedly sometimes very

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important) in that task. Process design is basically reactor design, because the chemical reactors control the sizes and functions of other units.

2. The most important reactor by far in twentieth century technology is the fluidized catalytic cracker. It processes more chemicals than any other reactor (except the automotive catalytic converter), the products it creates are the raw materials for most of chemical technology, and this reactor is undoubtedly the largest and most complex piece of equipment in our business. Yet it is very possible that a student can receive a B.S. degree in chemical engineering without ever hearing of it.
3. Most industrial processes use catalysts. Homogeneous single reaction systems are fairly rare and unimportant. The most important homogeneous reaction systems in fact involve free radical chains, which are very complex and highly nonlinear.
4. Energy management in chemical reactors is essential in reactor design.
5. Most industrial reactors involve multiple phases, and mass transfer steps between phases are essential and usually control the overall rates of process.
6. Polymers and their monomers are the major commodity and fine chemicals we deal with; yet they are considered mostly in elective polymer chemistry and polymer properties courses for undergraduates.
7. Chemical engineering is rapidly changing such that petroleum processing and commodity chemical industries are no longer the dominant employers of chemical engineers. Polymers, bioprocesses, microelectronics, foods, films, and environmental concerns are now the growth industries needing chemical engineers to handle essential chemical processing steps.
8. The greatest safety hazard in chemical engineering operations is without question caused by uncontrolled chemical reactions, either within the chemical reactor or when flammable chemicals escape from storage vessels or pipes. Many undergraduate students are never exposed to the extremely nonlinear and potentially hazardous characteristics of exothermic free radical processes.

It is our belief that a course in chemical reaction engineering should introduce all undergraduate students to all these topics. This is an ambitious task for a one-semester course, and it is therefore essential to focus carefully on the essential aspects. Certainly, each of these subjects needs a full course to lay out the fundamentals and to describe the reaction systems peculiar to them. At the same time, we believe that a course that considers chemical reactors in a unified fashion is essential to show the common features of the diverse chemical reactors that our students will be called on to consider.

Perhaps the central idea to come from Minnesota is the notion of modeling in chemical engineering. This is the belief that the way to understand a complex process is to construct the simplest description that will allow one to solve the problem at hand. Sometimes a single equation gives this insight in a back-of-the-envelope calculation, and sometimes a complete simulation on a supercomputer is necessary. The chemical engineer must be prepared to deal with problems at whatever level of sophistication is required. We want to show students how to do simple calculations by capturing the essential principles without getting lost in details. At the same time, it is necessary to understand the complex problem with sufficient clarity that the further steps in sophistication can be undertaken with confidence. A modeling

approach also reveals the underlying beauty and unity of dealing with the engineering of chemical reactions.

Chemical reaction engineering has acquired a reputation as a subject that has become too theoretical and impractical. In fact, we believe that reaction engineering holds the key in improving chemical processes and in developing new ones, and it requires the greatest skills in both analysis and intuition. Students need to see these challenges and be equipped to solve the next generation of challenges.

OVERALL ORGANIZATION

The book starts with a review of kinetics and the batch reactor in Chapter 2, and the material becomes progressively more complex until Chapter 12, which describes all the types of multiphase reactors we can think of. This is the standard, linear, boring progression followed in essentially all textbooks.

In parallel with this development, we discuss the chemical and petroleum industries and the major processes by which most of the classical products and feedstocks are made. We begin in Chapter 2 with a section on "The Real World," in which we describe the reactors and reactions in a petroleum refinery and then the reactions and reactors in making polyester. These are all catalytic multiphase reactors of almost unbelievable size and complexity. By Chapter 12 the principles of operation of these reactors will have been developed.

Then throughout the book the reactions and reactors of the petroleum and commodity chemical industries are reintroduced as the relevant principles for their description are developed.

Along with these topics, we attempt a brief historical survey of chemical technology from the start of the Industrial Revolution through speculations on what will be important in the twenty-first century. The rise of the major petroleum and chemical companies has created the chemical engineering profession, and their current downsizing creates significant issues for our students' future careers.

Projection into the future is of course the goal of all professional education, and we at least mention the microelectronic, food, pharmaceutical, ceramic, and environmental businesses which may be major employers of chemical engineering students. The notion of evolution of technology from the past to the future seems to be a way to get students to begin thinking about their future without faculty simply projecting our prejudices of how the markets will change.

Finally, our goal is to offer a compact but comprehensive coverage of all topics by which chemical reactors are described and to do this in a single consistent notation. We want to get through the fundamental ideas as quickly and simply as possible so that the larger issues of new applications can be appreciated. It is our intent that an instructor should then have time to emphasize those topics in which he or she is especially knowledgeable or regards as important and interesting, such as polymerization, safety, environment, pharmaceuticals, microelectronics, ceramics, foods, etc.

At Minnesota we cover these topics in approximately 30 lectures and 20 recitations. This requires two to four lectures per chapter to complete all chapters. Obviously some of the material must be omitted or skimmed to meet this schedule. We assume that most instructors will not cover all the industrial or historical examples but leave them for students to read.

We regard the "essential" aspects of chemical reaction engineering to include multiple reactions, energy management, and catalytic processes; so we regard the first seven chapters as the core material in a course. Then the final five chapters consider topics such as environmental, polymer, solids, biological, and combustion reactions and reactors, subjects that may be considered "optional" in an introductory course. We recommend that an instructor attempt to complete the first seven chapters within perhaps 3/4 of a term to allow time to select from these topics and chapters. The final chapter on multiphase reactors is of course very important, but our intent is only to introduce some of the ideas that are important in its design.

We have tried to disperse problems on many subjects and with varying degrees of difficulty throughout the book, and we encourage assignment of problems from later chapters even if they were not covered in lectures.

The nonlinearities encountered in chemical reactors are a major theme here because they are essential factors, both in process design and in safety. These generate polynomial equations for isothermal systems and transcendental equations for nonisothermal systems. We consider these with graphical solutions and with numerical computer problems. We try to keep these simple so students can see the qualitative features and be asked significant questions on exams. We insert a few computer problems in most chapters, starting with $A \rightarrow B \rightarrow C \rightarrow D \rightarrow \ldots$, and continuing through the wall-cooled reactor with diffusion and mass and heat transfer effects. We keep these problems very simple, however, so that students can write their own programs or use a sample Basic or Fortran program in the appendix. Graphics is essential for these problems, because the evolution of a solution versus time can be used as a "lab" to visualize what is happening.

The use of computers in undergraduate courses is continuously evolving, and different schools and instructors have very different capabilities and opinions about the level and methods that should be used. The choices are between (1) Fortran, Basic, and spreadsheet programming by students, (2) equation-solving programs such as Mathematica and MathCad, (3) specially written computer packages for reactor problems, and (4) chemical engineering flowsheet packages such as Aspen. We assume that each instructor will decide and implement specific computer methods or allow students to choose their own methods to solve numerical problems. At Minnesota we allow students to choose, but we introduce Aspen flowsheets of processes in this course because this introduces the idea of reactor-separation and staged processes in chemical processes before they see them in Process Design. Students and instructors always seem most uncomfortable with computer problems, and we have no simple solutions to this dilemma.

One characteristic of this book is that we repeat much material several times in different chapters to reinforce and illustrate what we believe to be important points. For example, petroleum refining processes, NO_x reactions, and safety are mentioned in most chapters as we introduce particular topics. We do this to tie the subject together and show how complex processes must be considered from many angles. The downside is that repetition may be regarded as simply tedious.

This text is focused primarily on chemical reactors, not on chemical kinetics. It is common that undergraduate students have been exposed to kinetics first in a course in physical chemistry, and then they take a chemical engineering kinetics course, followed by a reaction engineering course, with the latter two sometimes combined. At Minnesota we now have three separate courses. However, we find that the physical chemistry course

contains less kinetics every year, and we also have difficulty finding a chemical kinetics text that covers the material we need (catalysis, enzymes, polymerization, multiple reactions, combustion) in the chemical engineering kinetics course.

Consequently, while I jump into continuous reactors in Chapter 3, I have tried to cover essentially all of conventional chemical kinetics in this book. I have tried to include all the kinetics material in any of the chemical kinetics texts designed for undergraduates, but these are placed within and at the end of chapters throughout the book. The descriptions of reactions and kinetics in Chapter 2 do not assume any previous exposure to chemical kinetics. The simplification of complex reactions (pseudosteady-state and equilibrium step approximations) are covered in Chapter 4, as are theories of unimolecular and bimolecular reactions. I mention the need for statistical mechanics and quantum mechanics in interpreting reaction rates but do not go into state-to-state dynamics of reactions. The kinetics with catalysts (Chapter 7), solids (Chapter 9), combustion (Chapter 10), polymerization (Chapter 11), and reactions between phases (Chapter 12) are all given sufficient treatment that their rate expressions can be justified and used in the appropriate reactor mass balances.

I suggest that we may need to be able to teach all of chemical kinetics within chemical engineering and that the integration of chemical kinetics within chemical reaction engineering may have pedagogical value. I hope that these subjects can be covered using this text in any combination of courses and that, if students have had previous kinetics courses, this material can be skipped in this book. However, chemistry courses and texts give so little and such uneven treatment of topics such as catalytic and polymerization kinetics that reactors involving them cannot be covered without considering their kinetics.

Most texts strive to be encyclopedias of a subject from which the instructor takes a small fraction in a course and that are to serve as a future reference when a student later needs to learn in detail about a specific topic. This is emphatically not the intent of this text. First, it seems impossible to encompass all of chemical reaction engineering with less than a Kirk–Othmer encyclopedia. Second, the student needs to see the logical flow of the subject in an introductory course and not become bogged down in details. Therefore, we attempt to write a text that is short enough that a student can read all of it and an instructor can cover most of it in one course. This demands that the text and the problems focus carefully. The obvious pitfall is that short can become superficial, and the readers and users will decide that difference.

Many people assisted in the writing of this book. Marylin Huff taught from several versions of the manuscript at Minnesota and at Delaware and gave considerable help. John Falconer and Mark Barteau added many suggestions. All of my graduate students have been forced to work problems, find data and references, and confirm or correct derivations. Most important, my wife Sherry has been extremely patient about my many evenings spent at the Powerbook.

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PART I

FUNDAMENTALS

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