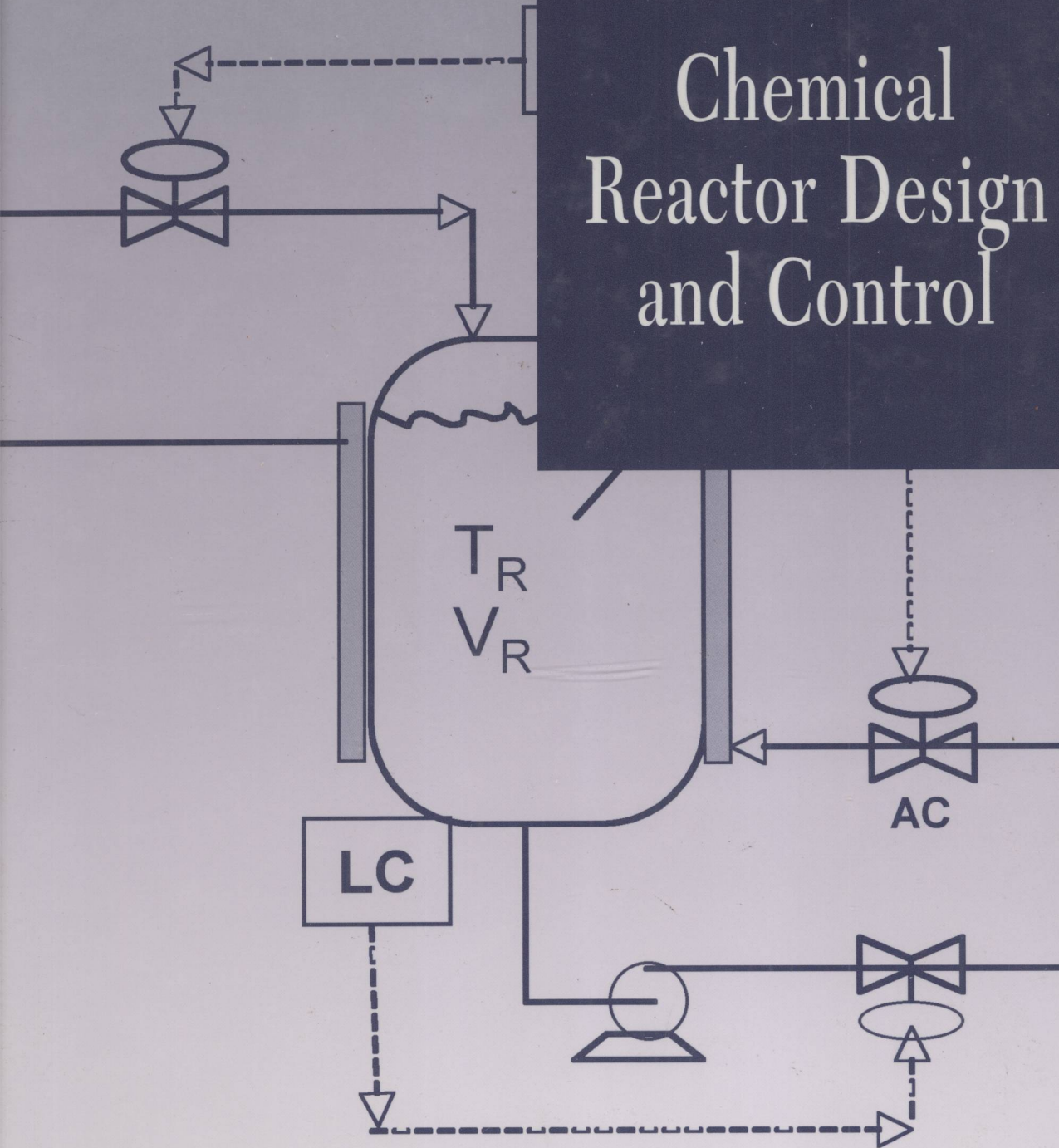


# Chemical Reactor Design and Control



*William L. Luyben*

AICHE®

---

# CHEMICAL REACTOR DESIGN AND CONTROL

---

**WILLIAM L. LUYBEN**

Lehigh University

**AIChE®**



**WILEY-INTERSCIENCE**  
**A JOHN WILEY & SONS, INC., PUBLICATION**

Copyright © 2007 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey  
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-750-4470, or on the web at [www.copyright.com](http://www.copyright.com). Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, 201-748-6011, fax 201-748-6008, or online at <http://www.wiley.com/go/permission>.

**Limit of Liability/Disclaimer of Warranty:** While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at 877-762-2974, outside the United States at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at [www.wiley.com](http://www.wiley.com).

Wiley Bicentennial Logo: Richard J. Pacifico.

***Library of Congress Cataloging-in-Publication Data:***

Luyben, William L.

Chemical reactor design and control/William L. Luyben.

p. cm.

Includes index.

ISBN 978-0-470-09770-0 (cloth)

1. Chemical reactors—Design and construction. I. Title.

TP157.L89 2007

600'.2832--dc22

2006036208

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

# CHEMICAL REACTOR DESIGN AND CONTROL



---

#### THE WILEY BICENTENNIAL—KNOWLEDGE FOR GENERATIONS

---

Each generation has its unique needs and aspirations. When Charles Wiley first opened his small printing shop in lower Manhattan in 1807, it was a generation of boundless potential searching for an identity. And we were there, helping to define a new American literary tradition. Over half a century later, in the midst of the Second Industrial Revolution, it was a generation focused on building the future. Once again, we were there, supplying the critical scientific, technical, and engineering knowledge that helped frame the world. Throughout the 20th Century, and into the new millennium, nations began to reach out beyond their own borders and a new international community was born. Wiley was there, expanding its operations around the world to enable a global exchange of ideas, opinions, and know-how.

For 200 years, Wiley has been an integral part of each generation's journey, enabling the flow of information and understanding necessary to meet their needs and fulfill their aspirations. Today, bold new technologies are changing the way we live and learn. Wiley will be there, providing you the must-have knowledge you need to imagine new worlds, new possibilities, and new opportunities.

Generations come and go, but you can always count on Wiley to provide you the knowledge you need, when and where you need it!

**WILLIAM J. PESCE**  
PRESIDENT AND CHIEF EXECUTIVE OFFICER

**PETER BOOTH WILEY**  
CHAIRMAN OF THE BOARD

*Dedicated to 40 classes of  
Lehigh Chemical Engineers*

# PREFACE

---

Chemical reactors are unquestionably the most vital parts of many chemical, biochemical, polymer, and petroleum processes because they transform raw materials into valuable chemicals. A vast variety of useful and essential products are generated via reactions that convert reactants into products. Much of modern society is based on the safe, economic, and consistent operation of chemical reactors.

In the petroleum industry, for example, a significant fraction of our transportation fuel (gasoline, diesel, and jet fuel) is produced within process units of a petroleum refinery that involve reactions. Reforming reactions are used to convert cyclical saturated naphthenes into aromatics, which have higher octane numbers. Light C4 hydrocarbons are alkylated to form high-octane C8 material for blending into gasoline. Heavy (longer-chain) hydrocarbons are converted by catalytic or thermal cracking into lighter (shorter-chain) components that can be used to produce all kinds of products. The unsaturated olefins that are used in many polymerization processes (ethylene and propylene) are generated in these reactors. The polluting sulfur components in many petroleum products are removed by reacting them with hydrogen.

The chemical and materials industries use reactors in almost all plants to convert basic raw materials into products. Many of the materials that are used for clothing, housing, automobiles, appliances, construction, electronics, and healthcare come from processes that utilize reactors. Reactors are important even in the food and beverage industries, where farm products are processed. The production of ammonia fertilizer to grow our food uses chemical reactors that consume hydrogen and nitrogen. The pesticides and herbicides we use on crop fields and orchards aid in the advances of modern agriculture. Some of the drugs that form the basis of modern medicine are produced by fermentation reactors. It should be clear in any reasonable analysis that our modern society, for better or worse, makes extensive use of chemical reactors.

Many types of reactions exist. This results in chemical reactors with a wide variety of configurations, operating conditions, and sizes. We encounter reactions that occur in solely the liquid or the vapor phase. Many reactions require catalysts (homogeneous if

the catalyst is the same phase as the reactants or heterogeneous if the catalyst has a different phase). Catalysts and the thermodynamic properties of reactants and products can lead to multiphase reactors (some of which can involve vapor, multiple liquids, and solid phases). Reactions can be exothermic (producing heat) or endothermic (absorbing heat). An example of the first is the nitration of toluene to form TNT. A very important example of the second is steam–methane reforming to produce synthesis gas.

Reactors can operate at low temperature (e.g., C4 sulfuric acid alkylation reactors run at 10°C) and at high temperatures (hydrodealkylation of toluene reactors run at 600°C). Some reactors operate in a batch or fed-batch mode, others in a continuous mode, and still others in a periodic mode. Beer fermentation is conducted in batch reactors. Ammonia is produced in a continuous vapor-phase reactor with a solid “promoted” iron catalyst.

The three classical generic chemical reactors are the batch reactor, the continuous stirred-tank reactor (CSTR), and the plug flow tubular reactor (PFR). Each of these reactor types has its own unique characteristics, advantages, and disadvantages. As the name implies, the *batch reactor* is a vessel in which the reactants are initially charged and the reactions proceed with time. During parts of the batch cycle, the reactor contents can be heated or cooled to achieve some desired temperature–time trajectory. If some of the reactant is fed into the vessel during the batch cycle, it is called a “fed-batch reactor.” Emulsion polymerization is an important example. The reactions conducted in batch reactors are almost always liquid-phase and typically involve slow reactions that would require large residence times (large vessels) if operated continuously. Batch reactors are also used for small-volume products in which there is little economic incentive to go to continuous operation. In some systems batch reactors can provide final product properties that cannot be achieved in continuous reactors, such as molecular weight distribution or viscosity. Higher conversion can be achieved by increasing batch time. Perfect mixing of the liquid in the reactor is usually assumed, so the modeling of a batch reactor involves ordinary differential equations. The control of a batch reactor is a “servo” problem, in which the temperature and/or concentration profiles follow some desired trajectory with time.

The CSTR reactor is usually used for liquid-phase or multiphase reactions that have fairly high reaction rates. Reactant streams are continuously fed into the vessel, and product streams are withdrawn. Cooling or heating is achieved by a number of different mechanisms. The two most common involve the use of a jacket surrounding the vessel or an internal coil. If high conversion is required, a single CSTR must be quite large unless reaction rates are very fast. Therefore, several CSTRs in series are sometimes used to reduce total reactor volume for a given conversion. Perfect mixing of the liquid in the reactor is usually assumed, so the modeling of a CSTR involves ordinary differential equations. The control of a CSTR or a series of CSTRs is often a “regulator” problem, in which the temperature(s) and/or concentration(s) are held at the desired values in the face of disturbances. Of course, some continuous processes produce different grades of products at different times, so the transition from one mode of operation to another is a servo problem.

The PFR tubular reactor is used for both liquid and gas phases. The reactor is a long vessel with feed entering at one end and product leaving at the other end. In some applications the vessel is packed with a solid catalyst. Some tubular reactors run adiabatically (i.e., with no heat transferred externally down the length of the vessel). The heat generated or consumed by the reaction increases or decreases the temperature of the process



material as it flows down the reactor. If the reaction is exothermic, the adiabatic temperature rise may produce an exit temperature that exceeds some safety limitation. It may also yield a low reaction equilibrium constant that limits conversion. If the reaction is endothermic, the adiabatic temperature change may produce reactor temperatures so low that the resulting small chemical reaction rate limits conversion.

In these cases, some type of heat transfer to or from the reactor vessel may be required. The reactor vessel can be constructed like a tube-in-shell heat exchanger. The process fluid flows inside the tubes, which may contain catalyst, and the heating/cooling medium is on the shell side. Variables in a PFR change with both axial position and time, so the modeling of a tubular reactor involves partial differential equations. The control of a PFR can be quite challenging because of the distributed nature of the process (i.e., changes in temperature and composition variables with length and sometime radial position). Tubular reactor control is usually a regulator problem, but grade transitions can lead to servo problems in some processes.

The area of reactor design has been widely studied, and there are many excellent textbooks that cover this subject. Most of the emphasis in these books is on steady-state operation. Dynamics are also considered, but mostly from the mathematical standpoint (openloop instability, multiple steady states, and bifurcation analysis). The subject of developing effective stable closedloop control systems for chemical reactors is treated only very lightly in these textbooks. The important practical issues involved in providing reactor control systems that achieve safe, economic, and consistent operation of these complex units are seldom understood by both students and practicing chemical engineers.

The safety issue is an overriding concern in reactor design and control. The US Chemical Safety Board (CSB) published a report in 2002 in which they listed 167 serious incidents involving uncontrolled chemical reactivity between 1980 and 2001. There were 108 fatalities as a result of 48 of these incidents. The CSB has a number of reports on these and more recent incidents that should be required reading for anyone involved in reactor design and control. In 2003 the American Institute of Chemical Engineers published *Essential Practices for Managing Chemical Reactivity Hazard*, which is well worth reading.

There are hundreds of papers dealing with the control of a wide variety of chemical reactors. However, there is no textbook that pulls the scattered material together in a cohesive way. One major reason for this is the very wide variety in types of chemistry and products, which results in a vast number of different chemical reactor configurations. It would be impossible to discuss the control of the myriad of reactor types found in the entire spectrum of industry. This book attempts to discuss the design and control of some of the more important generic chemical reactors.

The development of stable and practical reactors and effective control systems for the three types of classical reactors are covered. Notice that “reactors” are included, not just control schemes. Underlying the material and approaches in this book is my basic philosophy (theology) that the design of the process and the process equipment has a much greater effect on the successful control of a reactor than do the controllers that are hung on the process or the algorithms that are used in these controllers. This does not imply that the use of models is unimportant in reactor control, since in a number of important cases they are essential for achieving the desired product properties.

The basic message is that the essential problem in reactor control is temperature control. Temperature is a dominant variable and must be effectively controlled to achieve the desired compositions, conversions, and yields in the safe, economic, and

consistent operation of chemical reactors. In many types of reactors, this is achieved by providing plenty of heat transfer area and cooling or heating medium so that dynamic disturbances can be handled. Once temperature control has been achieved, providing base-level stable operation, additional objectives for the control system can be specified. These can be physical property specifications (density, viscosity, molecular weight distribution, etc.) or economic objectives (conversion, yield, selectivity, etc.).

The scope of this book, like that of all books, is limited by the experience of the author. It would be impossible to discuss all possible types of chemical reactors and presumptuous to include material on reactors with which I have little or no familiarity. Despite its limitations, I hope the readers find this book interesting and useful in providing some guidance for handling the challenging and very vital problems of chemical reactor control.

The many helpful comments and suggestions of Michael L. Luyben are gratefully acknowledged.

WILLIAM L. LUYBEN

# CONTENTS

---

## PREFACE

xiii

## 1 REACTOR BASICS

1

- 1.1 Fundamentals of Kinetics and Reaction Equilibrium / 3
  - 1.1.1 Power-Law Kinetics / 3
  - 1.1.2 Heterogeneous Reaction Kinetics / 7
  - 1.1.3 Biochemical Reaction Kinetics / 10
  - 1.1.4 Literature / 14
- 1.2 Multiple Reactions / 14
  - 1.2.1 Parallel Reactions / 15
  - 1.2.2 Series Reactions / 17
- 1.3 Determining Kinetic Parameters / 19
- 1.4 Types and Fundamental Properties of Reactors / 19
  - 1.4.1 Continuous Stirred-Tank Reactor / 19
  - 1.4.2 Batch Reactor / 21
  - 1.4.3 Tubular Plug Flow Reactor / 22
- 1.5 Heat Transfer in Reactors / 24
- 1.6 Reactor ScaleUp / 29
- 1.7 Conclusion / 30

vii

**2 STEADY-STATE DESIGN OF CSTR SYSTEMS****31**

- 2.1 Irreversible, Single Reactant / 31
  - 2.1.1 Jacket-Cooled / 33
  - 2.1.2 Internal Coil / 44
  - 2.1.3 Other Issues / 48
- 2.2 Irreversible, Two Reactants / 48
  - 2.2.1 Equations / 49
  - 2.2.2 Design / 50
- 2.3 Reversible Exothermic Reaction / 52
- 2.4 Consecutive Reactions / 55
- 2.5 Simultaneous Reactions / 59
- 2.6 Multiple CSTRs / 61
  - 2.6.1 Multiple Isothermal CSTRs in Series with Reaction  $A \rightarrow B$  / 61
  - 2.6.2 Multiple CSTRs in Series with Different Temperatures / 63
  - 2.6.3 Multiple CSTRs in Parallel / 64
  - 2.6.4 Multiple CSTRs with Reversible Exothermic Reactions / 64
- 2.7 Autorefrigerated Reactor / 67
- 2.8 Aspen Plus Simulation of CSTRs / 72
  - 2.8.1 Simulation Setup / 73
  - 2.8.2 Specifying Reactions / 80
  - 2.8.3 Reactor Setup / 87
- 2.9 Optimization of CSTR Systems / 90
  - 2.9.1 Economics of Series CSTRs / 90
  - 2.9.2 Economics of a Reactor–Column Process / 91
  - 2.9.3 CSTR Processes with Two Reactants / 97
- 2.10 Conclusion / 106

**3 CONTROL OF CSTR SYSTEMS****107**

- 3.1 Irreversible, Single Reactant / 107
  - 3.1.1 Nonlinear Dynamic Model / 108
  - 3.1.2 Linear Model / 109
  - 3.1.3 Effect of Conversion on Openloop and Closedloop Stability / 111
  - 3.1.4 Nonlinear Dynamic Simulation / 117
  - 3.1.5 Effect of Jacket Volume / 121
  - 3.1.6 Cooling Coil / 125
  - 3.1.7 External Heat Exchanger / 126

- 3.1.8 Comparison of CSTR-in-Series Processes / 130
- 3.1.9 Dynamics of Reactor–Stripper Process / 133
- 3.2 Reactor–Column Process with Two Reactants / 137
  - 3.2.1 Nonlinear Dynamic Model of Reactor and Column / 137
  - 3.2.2 Control Structure for Reactor–Column Process / 139
  - 3.2.3 Reactor–Column Process with Hot Reaction / 142
- 3.3 AutoRefrigerated Reactor Control / 148
  - 3.3.1 Dynamic Model / 148
  - 3.3.2 Simulation Results / 150
- 3.4 Reactor Temperature Control Using Feed Manipulation / 154
  - 3.4.1 Introduction / 154
  - 3.4.2 Revised Control Structure / 156
  - 3.4.3 Results / 157
  - 3.4.4 Valve Position Control / 159
- 3.5 Aspen Dynamics Simulation of CSTRs / 162
  - 3.5.1 Setting up the Dynamic Simulation / 165
  - 3.5.2 Running the Simulation and Tuning Controllers / 172
  - 3.5.3 Results with Several Heat Transfer Options / 184
  - 3.5.4 Use of RGIBBS Reactor / 192
- 3.6 Conclusion / 196

## 4 CONTROL OF BATCH REACTORS

197

- 4.1 Irreversible, Single Reactant / 199
  - 4.1.1 Pure Batch Reactor / 199
  - 4.1.2 Fed-Batch Reactor / 206
- 4.2 Batch Reactor with Two Reactants / 210
- 4.3 Batch Reactor with Consecutive Reactions / 212
- 4.4 Aspen Plus Simulation Using RBatch / 214
- 4.5 Ethanol Batch Fermentor / 224
- 4.6 Fed-Batch Hydrogenation Reactor / 227
- 4.7 Batch TML Reactor / 231
- 4.8 Fed-Batch Reactor with Multiple Reactions / 234
  - 4.8.1 Equations / 236
  - 4.8.2 Effect of Feed Trajectory on Conversion and Selectivity / 237
  - 4.8.3 Batch Optimization / 240
  - 4.8.4 Effect of Parameters / 244
  - 4.8.5 Consecutive Reaction Case / 246
- 4.9 Conclusion / 249

**5 STEADY-STATE DESIGN OF TUBULAR REACTOR SYSTEMS 251**

- 5.1 Introduction / 251
- 5.2 Types of Tubular Reactor Systems / 253
  - 5.2.1 Type of Recycle / 253
  - 5.2.2 Phase of Reaction / 253
  - 5.2.3 Heat Transfer Configuration / 254
- 5.3 Tubular Reactors in Isolation / 255
  - 5.3.1 Adiabatic PFR / 255
  - 5.3.2 Nonadiabatic PFR / 260
- 5.4 Single Adiabatic Tubular Reactor Systems with Gas Recycle / 265
  - 5.4.1 Process Conditions and Assumptions / 266
  - 5.4.2 Design and Optimization Procedure / 267
  - 5.4.3 Results for Single Adiabatic Reactor System / 269
- 5.5 Multiple Adiabatic Tubular Reactors with Interstage Cooling / 270
  - 5.5.1 Design and Optimization Procedure / 271
  - 5.5.2 Results for Multiple Adiabatic Reactors with Interstage Cooling / 272
- 5.6 Multiple Adiabatic Tubular Reactors with Cold-Shot Cooling / 273
  - 5.6.1 Design–Optimization Procedure / 273
  - 5.6.2 Results for Adiabatic Reactors with Cold-Shot Cooling / 275
- 5.7 Cooled Reactor System / 275
  - 5.7.1 Design Procedure for Cooled Reactor System / 276
  - 5.7.2 Results for Cooled Reactor System / 276
- 5.8 Tubular Reactor Simulation Using Aspen Plus / 277
  - 5.8.1 Adiabatic Tubular Reactor / 278
  - 5.8.2 Cooled Tubular Reactor with Constant-Temperature Coolant / 281
  - 5.8.3 Cooled Reactor with Co-current or Countercurrent Coolant Flow / 281
- 5.9 Conclusion / 285

**6 CONTROL OF TUBULAR REACTOR SYSTEMS 287**

- 6.1 Introduction / 287
- 6.2 Dynamic Model / 287
- 6.3 Control Structures / 291
- 6.4 Controller Tuning and Disturbances / 293
- 6.5 Results for Single-Stage Adiabatic Reactor System / 295
- 6.6 Multistage Adiabatic Reactor System with Interstage Cooling / 299

- 6.7 Multistage Adiabatic Reactor System with Cold-Shot Cooling / 302
- 6.8 Cooled Reactor System / 308
- 6.9 Cooled Reactor with Hot Reaction / 311
  - 6.9.1 Steady-State Design / 311
  - 6.9.2 Openloop and Closedloop Responses / 314
  - 6.9.3 Conclusion / 318
- 6.10 Aspen Dynamics Simulation / 319
  - 6.10.1 Adiabatic Reactor With and Without Catalyst / 319
  - 6.10.2 Cooled Tubular Reactor with Coolant Temperature Manipulated / 323
  - 6.10.3 Cooled Tubular Reactor with Co-current Flow of Coolant / 331
  - 6.10.4 Cooled Tubular Reactor with Countercurrent Flow of Coolant / 337
  - 6.10.5 Conclusions for Aspen Simulation of Different Types of Tubular Reactors / 343
- 6.11 Plantwide Control of Methanol Process / 344
  - 6.11.1 Chemistry and Kinetics / 345
  - 6.11.2 Process Description / 349
  - 6.11.3 Steady-State Aspen Plus Simulation / 351
  - 6.11.4 Dynamic Simulation / 356
- 6.12 Conclusion / 368

## **7 HEAT EXCHANGER/REACTOR SYSTEMS**

**369**

- 7.1 Introduction / 369
- 7.2 Steady-State Design / 371
- 7.3 Linear Analysis / 373
  - 7.3.1 Flowsheet FS1 without Furnace / 373
  - 7.3.2 Flowsheet FS2 with Furnace / 375
  - 7.3.3 Nyquist Plots / 375
- 7.4 Nonlinear Simulation / 379
  - 7.4.1 Dynamic Model / 380
  - 7.4.2 Controller Structure / 382
  - 7.4.3 Results / 383
- 7.5 Hot-Reaction Case / 387
- 7.6 Aspen Simulation / 391
  - 7.6.1 Aspen Plus Steady-State Design / 396
  - 7.6.2 Aspen Dynamics Control / 399
- 7.7 Conclusion / 405

<b>8</b>	<b>CONTROL OF SPECIAL TYPES OF INDUSTRIAL REACTORS</b>	<b>407</b>
8.1	Fluidized Catalytic Crackers /	407
8.1.1	Reactor /	408
8.1.2	Regenerator /	409
8.1.3	Control Issues /	409
8.2	Gasifiers /	410
8.3	Fired Furnaces, Kilns, and Driers /	412
8.4	Pulp Digesters /	413
8.5	Polymerization Reactors /	413
8.6	Biochemical Reactors /	414
8.7	Slurry Reactors /	415
8.8	Microscale Reactors /	415
	<b>INDEX</b>	<b>417</b>



# CHAPTER 1

---

## REACTOR BASICS

---

In this chapter we first review some of the basics of chemical equilibrium and reaction kinetics. We need to understand clearly the fundamentals about chemical reaction rates and chemical equilibrium, particularly the effects of temperature on rate and equilibrium for different types of reactions. Reactions are generally categorized as exothermic (releasing energy) or endothermic (requiring energy), as reversible (balance of reactants and products) or irreversible (proceeding completely to products), and as homogeneous (single-phase) or heterogeneous (multiphase).

One major emphasis in this book is the focus of reactor design on the control of temperature, simply because temperature plays such a dominant role in reactor operation. However, in many reactors the control of other variables is the ultimate objective or determines the economic viability of the process. Some examples of these other properties include reactant or product compositions, particle size, viscosity, and molecular weight distribution. These issues are discussed and studied in subsequent chapters.

Many polymer reactions, for example, are highly exothermic, so the temperature control concepts outlined in this book must be applied. At the same time, controlling just the temperature in a polymer reactor may not adequately satisfy the economic objectives of the plant, since many of the desired polymer product properties (molecular weight, composition, etc.) are created within the polymerization reactor. These key properties must be controlled using other process parameters (i.e. vessel pressure in a polycondensation reactor or chain transfer agent composition in a free-radical polymerization reactor).

Many agricultural chemicals (pesticides, fungicides, etc.), for another example, are generated in a series of often complex batch or semibatch reaction and separation steps. The efficacy of the chemical often depends on its ultimate purity. Operation and control of the reactor to minimize the formation of undesirable and hard-to-separate byproducts