

THIRD
EDITION

COULSON & RICHARDSON'S **CHEMICAL ENGINEERING**

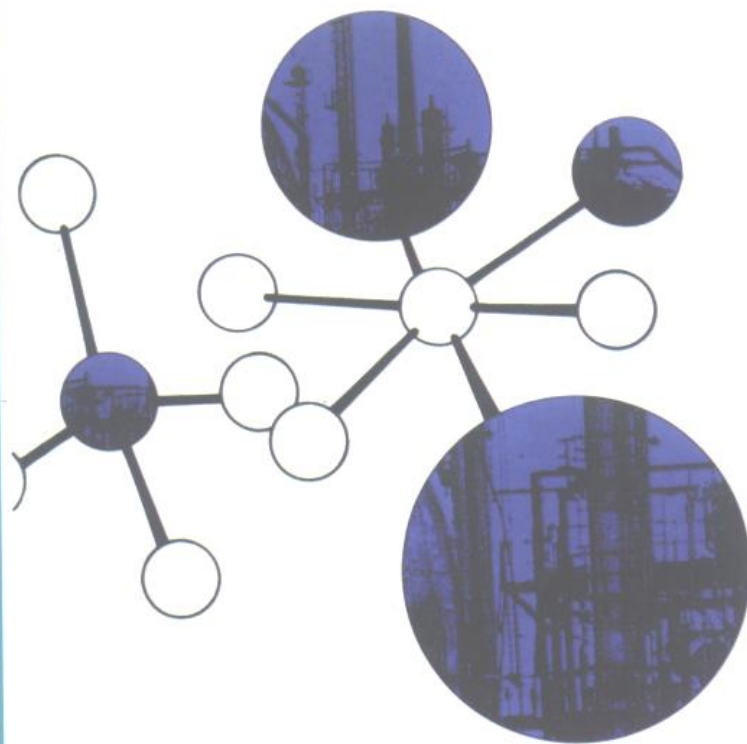
化学工程

第3卷 第3版

J F Richardson
& D G Peacock

VOLUME 3

3



Chemical & Biochemical Reactors & Process Control

Butterworth
Heinemann

世界图书出版公司

Coulson & Richardson's

CHEMICAL ENGINEERING

VOLUME 3

THIRD EDITION

*Chemical & Biochemical Reactors &
Process Control*

EDITORS OF VOLUME THREE

J. F. RICHARDSON

*Department of Chemical Engineering
University of Wales Swansea*

and

D. G. PEACOCK

The School of Pharmacy, London

PERGAMON

世界图书出版公司

书 名: Chemical Engineering Vol.3 3rd ed.

作 者: J.F.Richardson & D.G.Peacock

中译名: 化学工程 第3卷 第3版

出 版 者: 世界图书出版公司北京公司

印 刷 者: 北京中西印刷厂

发 行: 世界图书出版公司北京公司 (北京朝内大街 137 号 100010)

开 本: 1/24 711×1245 印 张: 33.5

出版年代: 2000 年 6 月

书 号: ISBN 7-5062-4728-3/T·15

版权登记: 图字 01-2000-1224

定 价: 130.00 元

世界图书出版公司北京公司已获得 Butterworth-Heinemann 授权在中国境内独家重印发行。

U.K. Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington,
Oxford, OX5 1GB, U.K.

U.S.A. Elsevier Science Inc., 660 White Plains Road, Tarrytown,
New York 10591-5153, U.S.A.

JAPAN Elsevier Science Japan, Tsunashima Building Annex,
3-20-12 Yushima, Bunkyo-ku, Tokyo 113, Japan

Copyright © 1994 J C Lee W J Thomas R Lovitt
M Jones & A P Wardle

All rights Reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic tape, mechanical, photocopying, recording or otherwise, without permission in writing from the publishers.

First edition 1971

Reprinted 1975

Second edition 1979

Reprinted with corrections 1982, 1987, 1991

Third edition 1994

Library of Congress Cataloging in Publication Data
(Revised for vol. 3)

Coulson, J. M. (John Metcalfe)

Chemical engineering.

Includes bibliographical references and index.

Contents: v. 1. Fluid flow, heat transfer, and mass transfer — v. 2. Unit operations — v. 3. Chemical and biochemical reactors and process control.

1. Chemical engineering. I. Richardson, J. F. (John Francis). II. Title.

TP155.C69 1977 660 75-42295

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the
British Library

ISBN 0-08-041002-2 (Hardcover)

ISBN 0-08-041003-0 (Flexicover)

First published by © Butterworth Heinemann [a division of Reed Educational &
Professional Publishers]-1994

For sale in mainland of China only. Not for export elsewhere

Titles in the Chemical Engineering Series by

J M COULSON & J F RICHARDSON

Chemical Engineering, Volume 1, Fourth edition
Fluid Flow, Heat Transfer and Mass Transfer
(with J R Backhurst and J H Harker)

Chemical Engineering, Volume 2, Fourth edition
Particle Technology and Separation Processes
(with J R Backhurst and J H Harker)

Chemical Engineering, Volume 3, Third edition
Chemical & Biochemical Reactors & Process Control
(edited by J F Richardson and D G Peacock)

Chemical Engineering, Volume 4, Second edition
Solutions to the Problems in Volume 1
(J R Backhurst and J H Harker)

Chemical Engineering, Volume 5, Second Edition*
Solutions to the Problems in Volumes 2 and 3
(J R Backhurst and J H Harker)

Chemical Engineering, Volume 6, Second edition
Chemical Engineering Design
(R K Sinnott)

Related Pergamon Journals

Chemical Engineering Science
Computers & Chemical Engineering
International Communications in Heat and Mass Transfer
International Journal of Heat and Mass Transfer

***In preparation**

Full details of all Elsevier Science publications and free specimen copies of any Elsevier Science journal are available on request from your nearest Elsevier Science office.

Coulson & Richardson's

CHEMICAL ENGINEERING

**VOLUME 3
THIRD EDITION**

*Chemical & Biochemical Reactors &
Process Control*

Preface to Third Edition

The publication of the Third Edition of *Chemical Engineering* Volume 3 marks the completion of the re-orientation of the basic material contained in the first three volumes of the series. Volume 1 now covers the fundamentals of Momentum, Heat and Mass Transfer, Volume 2 deals with Particle Technology and Separation Processes, and Volume 3 is devoted to Reaction Engineering (both chemical and biochemical), together with Measurement and Process Control.

Volume 3 has now lost both Non-Newtonian Technology, which appears in abridged form in Volume 1, and the Chapter on Sorption Processes, which is now more logically located with the other Separation Processes in Volume 2. The Chapter on Computation has been removed. When Volume 3 was first published in 1972 computers were, by today's standards, little more than in their infancy and students entering chemical engineering courses were not well versed in computational techniques. This situation has now completely changed and there is no longer a strong case for the inclusion of this topic in an engineering text book. With some reluctance the material on numerical solution of equations has also been dropped as it is more appropriate to a mathematics text.

In the new edition, the material on Chemical Reactor Design has been re-arranged into four chapters. The first covers General Principles (as in the earlier editions) and the second deals with Flow Characteristics and Modelling in Reactors. Chapter 3 now includes material on Catalytic Reactions (from the former Chapter 2) together with non-catalytic gas-solids reactions, and Chapter 4 covers other multiphase reactor systems. Dr J. C. Lee has contributed the material in Chapters 1, 2 and 4 and that on non-catalytic reactions in Chapter 3, and Professor W. J. Thomas has covered catalytic reactions in that Chapter.

Chapter 5, on Biochemical Engineering, has been completely rewritten in two sections by Dr R. L. Lovitt and Dr M. G. Jones with guidance from the previous author, Professor B. Atkinson. The earlier part deals with the nature of reaction processes controlled by micro-organisms and enzymes and is prefaced by background material on the relevant microbiology and biochemistry. In the latter part, the process engineering principles of biochemical reactors are discussed, and emphasis is given to those features which differentiate them from the chemical reactors described previously.

The concluding two chapters by Dr A. P. Wardle deal, respectively, with Measurement, and Process Control. The former is a completely new chapter describing the

various in-line techniques for measurement of the process variables which constitute the essential inputs to the control system of the plant. The last chapter gives an updated treatment of the principles and applications of process control and concludes with a discussion of computer control of process plant.

January 1994

J F RICHARDSON
Department of Chemical Engineering
University of Wales Swansea
Swansea SA2 8PP
UK

D G PEACOCK
School of Pharmacy
London WC1N 1AX
UK

Preface to Second Edition

Apart from general updating and correction, the main alterations in the second edition of Volume 3 are additions to Chapter 1 on Reactor Design and the inclusion of a Table of Error Functions in the Appendix.

In Chapter 1 two new sections have been added. In the first of these is a discussion of non-ideal flow conditions in reactors and their effect on residence time distribution and reactor performance. In the second section an important class of chemical reactions—that in which a solid and a gas react non-catalytically—is treated. Together, these two additions to the chapter considerably increase the value of the book in this area.

All quantities are expressed in SI units, as in the second impression, and references to earlier volumes of the series take account of the modifications which have recently been made in the presentation of material in the third editions of these volumes.

Preface to the First Edition

Chemical engineering, as we know it today, developed as a major engineering discipline in the United Kingdom in the interwar years and has grown rapidly since that time. The unique contribution of the subject to the industrial scale development of processes in the chemical and allied industries was initially attributable to the improved understanding it gave to the transport processes—fluid flow, heat transfer and mass transfer—and to the development of design principles for the unit operations, nearly all of which are concerned with the physical separation of complex mixtures, both homogeneous and heterogeneous, into their components. In this context the chemical engineer was concerned much more closely with the separation and purification of the products from a chemical reactor than with the design of the reactor itself.

The situation is now completely changed. With a fair degree of success achieved in the physical separation processes, interest has moved very much towards the design of the reactor, and here too the processes of fluid flow, heat transfer and mass transfer can be just as important. Furthermore, many difficult separation problems can be obviated by correct choice of conditions in the reactor. Chemical manufacture has become more demanding with a high proportion of the economic rewards to be obtained in the production of sophisticated chemicals, pharmaceuticals, antibiotics and polymers, to name a few, which only a few years earlier were unknown even in the laboratory. Profit margins have narrowed too, giving a far greater economic incentive to obtain the highest possible yield from raw materials. Reactor design has therefore become a vital ingredient of the work of the chemical engineer.

Volumes 1 and 2, though no less relevant now, reflected the main areas of interest of the chemical engineer in the early 1950s. In Volume 3 the coverage of chemical engineering is brought up to date with an emphasis on the design of systems in which chemical and even biochemical reactions occur. It includes chapters on adsorption, on the general principles of the design of reactors, on the design and operation of reactors employing heterogeneous catalysts, and on the special features of systems exploiting biochemical and microbiological processes. Many of the materials which are processed in chemical and bio-chemical reactors are complex in physical structure and the flow properties of non-Newtonian materials are therefore considered worthy of special treatment. With the widespread use of computers, many of the design problems which are too complex to solve analytically or graphically are now capable of numerical solution, and their application to chemical

engineering problems forms the subject of a chapter. Parallel with the growth in complexity of chemical plants has developed the need for much closer control of their operation, and a chapter on process control is therefore included.

Each chapter of Volume 3 is the work of a specialist in the particular field, and the authors are present or past members of the staff of the Chemical Engineering Department of the University College of Swansea. W. J. Thomas is now at the Bath University of Technology and J. M. Smith is at the Technische Hogeschool, Delft.

J. M. C.

J. F. R.

D. G. P.

Acknowledgements

The authors and publishers acknowledge with thanks the assistance given by the following companies and individuals in providing illustrations and data for this volume and giving their permission for reproduction. Everyone was most helpful and some firms went to considerable trouble to provide exactly what was required. We are extremely grateful to them all.

Butterworth-Heinemann for Fig. 3.16

Cambridge University Press for Fig. 3.22.

John Wiley for Fig. 3.24.

McGraw-Hill for Table 3.1.

Endress and Hauser Ltd, Manchester, U.K. for Fig. 6.2*b*, Fig. 6.19*b*.

Foxboro, Great Britain Ltd., Crawley, U.K. for Figs. 6.19*a*, 6.20, 6.52, 6.77.

MTS Systems Corp., North Carolina, U.S.A. for Fig. 6.33*b*.

Schlumberger Industries, Farnborough, U.K. for Fig. 6.36.

Precision Scientific Inc., Chicago, Illinois, U.S.A. for Fig. 6.39.

Mettler-Toledo Ltd, Leicester, U.K. for Fig. 6.40.

Servomex plc., Crowborough, U.K. for Figs 6.42, 6.49, 6.57, 6.58.

Anacon Corp., Thame, U.K. for Fig. 6.45.

Nome Co., Metuchen, New Jersey, U.S.A. for Fig. 6.41.

J. Winter, Gwent Tertiary Campus, Newport, U.K. for Example 6.3.

Fisher Controls Ltd, Rochester, U.K. for Fig. 7.103.

Kent Process Control Ltd, Luton, U.K. for Fig. 7.108.

Samson AG, Frankfurt, Germany for Figs 7.119, 7.121.

W84728
18

List of Contributors

Chapter 1—Reactor Design—General Principles

J. C. LEE (*University of Wales Swansea*)

Chapter 2—Flow Characteristics of Reactors—Flow Modelling

J. C. LEE (*University of Wales Swansea*)

Chapter 3—Gas-Solid Reactions & Reactors

J. C. LEE (*University of Wales Swansea*)

& W. J. THOMAS (*Bath University of Technology*)

Chapter 4—Gas-Liquid & Gas-Liquid-Solid Reactors

J. C. LEE (*University of Wales Swansea*)

Chapter 5—Biochemical Reaction Engineering

R. LOVITT (*University of Wales Swansea*)

& M. JONES (*University of Wales Swansea*)

Chapter 6—Sensors for Measurement & Control

A. P. WARDLE (*University of Wales Swansea*)

Chapter 7—Process Control

A. P. WARDLE (*University of Wales Swansea*)

Contents

PREFACE TO THIRD EDITION	xiii
PREFACE TO SECOND EDITION	xv
PREFACE TO FIRST EDITION	xvi
ACKNOWLEDGEMENTS	xviii
LIST OF CONTRIBUTORS	xix
1. Reactor Design—General Principles	1
1.1 Basic objectives in design of a reactor	1
1.1.1 Byproducts and their economic importance	2
1.1.2 Preliminary appraisal of a reactor project	2
1.2 Classification of reactors and choice of reactor type	3
1.2.1 Homogeneous and heterogeneous reactors	3
1.2.2 Batch reactors and continuous reactors	3
1.2.3 Variations in contacting pattern—semi-batch operation	5
1.2.4 Influence of heat of reaction on reactor type	6
1.3 Choice of process conditions	10
1.3.1 Chemical equilibria and chemical kinetics	10
1.3.2 Calculation of equilibrium conversion	11
1.3.3 Ultimate choice of reactor conditions	14
1.4 Chemical kinetics and rate equations	15
1.4.1 Definition of reaction rate, order of reaction and rate constant	16
1.4.2 Influence of temperature. Activation energy	17
1.4.3 Rate equations and reaction mechanism	18
1.4.4 Reversible reactions	20
1.4.5 Rate equations for constant-volume batch reactors	21
1.4.6 Experimental determination of kinetic constants	24
1.5 General material and thermal balances	24
1.6 Batch reactors	27
1.6.1 Calculation of reaction time; basic design equation	27
1.6.2 Reaction time—isothermal operation	28
1.6.3 Maximum production rate	30
1.6.4 Reaction time—non-isothermal operation	31
1.6.5 Adiabatic operation	32
1.7 Tubular-flow reactors	34
1.7.1 Basic design equations for a tubular reactor	36
1.7.2 Tubular reactors—non-isothermal operation	40
1.7.3 Pressure drop in tubular reactors	41
1.7.4 Kinetic data from tubular reactors	42

1.8	Continuous stirred-tank reactors	43
1.8.1	Assumption of ideal mixing. Residence time	43
1.8.2	Design equations for continuous stirred-tank reactors	44
1.8.3	Graphical methods	47
1.8.4	Autothermal operation	49
1.8.5	Kinetic data from continuous stirred-tank reactors	50
1.9	Comparison of batch, tubular and stirred-tank reactors for a single reaction.	
	Reactor output	51
1.9.1	Batch reactor and tubular plug-flow reactor	52
1.9.2	Continuous stirred-tank reactor	52
1.9.3	Comparison of reactors	54
1.10	Comparison of batch, tubular and stirred-tank reactors for multiple reactions. Reactor yield	55
1.10.1	Types of multiple reactions	56
1.10.2	Yield and selectivity	57
1.10.3	Reactor type and backmixing	57
1.10.4	Reactions in parallel	58
1.10.5	Reactions in parallel—two reactants	61
1.10.6	Reactions in series	63
1.10.7	Reactions in series—two reactants	67
1.11	Further reading	68
1.12	References	68
1.13	Nomenclature	68
2.	Flow Characteristics of Reactors—Flow Modelling	71
2.1	Non-ideal flow and mixing in chemical reactors	71
2.1.1	Types of non-ideal flow patterns	71
2.1.2	Experimental tracer methods	71
2.1.3	Age distribution of a stream leaving a vessel—E-curves	73
2.1.4	Application of tracer information to reactors	75
2.2	Tanks-in-series model	78
2.3	Dispersed plug-flow model	80
2.3.1	Axial dispersion and model development	80
2.3.2	Basic differential equation	83
2.3.3	Response to an ideal pulse input of tracer	84
2.3.4	Experimental determination of dispersion coefficient from a pulse input	88
2.3.5	Further development of tracer injection theory	93
2.3.6	Values of dispersion coefficients from theory and experiment	96
2.3.7	Dispersed plug-flow model with first-order chemical reaction	98
2.3.8	Applications and limitations of the dispersed plug-flow model	102
2.4	Models involving combinations of the basic flow elements	104
2.5	Further reading	105
2.6	References	105
2.7	Nomenclature	106
3.	Gas-Solid Reactions and Reactors	108
3.1	Introduction	108
3.2	Mass transfer within porous solids	111
3.2.1	The effective diffusivity	112
3.3	Chemical reaction in porous catalyst pellets	115
3.3.1	Isothermal reactions in porous catalyst pellets	116
3.3.2	Effect of intraparticle diffusion on experimental parameters	122
3.3.3	Non-isothermal reactions in porous catalyst pellets	124
3.3.4	Criteria for diffusion control	128

CONTENTS

vii

3.3.5	Selectivity in catalytic reactions influenced by mass and heat transfer effects	129
3.3.6	Catalyst de-activation and poisoning	139
3.4	Mass transfer from a fluid stream to a solid surface	143
3.5	Chemical kinetics of heterogeneous catalytic reactions	144
3.5.1	Adsorption of a reactant as the rate determining step	146
3.5.2	Surface reaction as the rate determining step	148
3.5.3	Desorption of a product as the rate determining step	148
3.5.4	Rate determining steps for other mechanisms	148
3.5.5	Examples of rate equations for industrially important reactions	150
3.6	Design calculations	151
3.6.1	Packed tubular reactors	151
3.6.2	Thermal characteristics of packed reactors	172
3.6.3	Fluidised bed reactors	180
3.7	Gas-solid non-catalytic reactors	181
3.7.1	Modelling and design of gas-solid reactors	182
3.7.2	Single particle unreacted core models	183
3.7.3	Types of equipment and contacting patterns	186
3.8	Further reading	190
3.9	References	190
3.10	Nomenclature	192
4.	Gas-Liquid and Gas-Liquid-Solid Reactors	196
4.1	Gas-liquid reactors	196
4.1.1	Gas-liquid reactions	196
4.1.2	Types of reactors	196
4.1.3	Equations for mass transfer with chemical reaction	197
4.1.4	Choice of a suitable reactor	202
4.1.5	Information required for gas-liquid reactor design	204
4.1.6	Examples of gas-liquid reactors	205
4.1.7	High aspect-ratio bubble columns and multiple-impeller agitated tanks	216
4.1.8	Axial dispersion in bubble columns	218
4.1.9	Laboratory reactors for investigating the kinetics of gas-liquid reactions	223
4.2	Gas-liquid-solid reactors	229
4.2.1	Gas-liquid-solid reactions	229
4.2.2	Mass transfer and reaction steps	230
4.2.3	Gas-liquid-solid reactor types: choosing a reactor	231
4.2.4	Combination of mass transfer and reaction steps	235
4.3	Further reading	248
4.4	References	248
4.5	Nomenclature	249
5.	Biochemical Reaction Engineering	252
5.1	Introduction	252
5.1.1	Cells as reactors	254
5.1.2	The biological world and ecology	255
5.1.3	Biological products and production systems	256
5.1.4	Scales of operation	257
5.2	Cellular diversity and the classification of living systems	259
5.2.1	Classification	260
5.2.2	Prokaryotic organisms	262
5.2.3	Eukaryotic organisms	265
5.2.4	General physical properties of cells	269
5.2.5	Tolerance to environmental conditions	270

5.3	Chemical composition of cells	271
5.3.1	Elemental composition	271
5.3.2	Proteins	273
5.3.3	Physical properties of proteins	275
5.3.4	Protein purification and separation	277
5.3.5	Stability of proteins	277
5.3.6	Nucleic acids	278
5.3.7	Lipids and membranes	278
5.3.8	Carbohydrates	278
5.3.9	Cell walls	278
5.4	Enzymes	279
5.4.1	Biological versus chemical reaction processes	279
5.4.2	Properties of enzymes	279
5.4.3	Enzyme kinetics	281
5.4.4	Derivation of the Michaelis–Menten equation	282
5.4.5	The significance of kinetic constants	285
5.4.6	The Haldane relationship	286
5.4.7	Transformations of the Michaelis–Menten equation	287
5.4.8	Enzyme inhibition	289
5.4.9	The kinetics of two-substrate reactions	291
5.4.10	The effects of temperature and pH on enzyme kinetics and enzyme de-activation.	294
5.4.11	Enzyme de-activation	295
5.5	Metabolism	298
5.5.1	The roles of metabolism	298
5.5.2	Types of reactions in metabolism	298
5.5.3	Energetic aspects of biological processes	302
5.5.4	Energy generation	304
5.5.5	Substrate level phosphorylation	304
5.5.6	Aerobic respiration and oxidative phosphorylation	309
5.5.7	Photosynthesis	315
5.6	Strain improvement methods	315
5.6.1	Mutation and mutagenesis	316
5.6.2	Genetic recombination in bacteria	318
5.6.3	Genetic engineering	320
5.6.4	Recombinant DNA technology	320
5.6.5	Genetically engineered products	325
5.7	Cellular control mechanisms and their manipulation	326
5.7.1	The control of enzyme activity	326
5.7.2	The control of metabolic pathways	327
5.7.3	The control of protein synthesis	334
5.8	Stoichiometric aspects of biological processes	337
5.8.1	Yield	339
5.9	Microbial growth	342
5.9.1	Phases of growth of a microbial culture	342
5.9.2	Microbial growth kinetics	345
5.9.3	Product formation	352
5.10	Immobilised biocatalysts	354
5.10.1	Effect of external diffusion limitation	356
5.10.2	Effect of internal diffusion limitation	360
5.11	Reactor configurations	364
5.11.1	Enzyme reactors	364
5.11.2	Batch growth of micro-organisms	365
5.11.3	Continuous culture of micro-organisms	367
5.12	Estimation of kinetic parameters	386
5.12.1	Use of batch culture experiments	386
5.12.2	Use of continuous culture experiments	393