

CHEMICAL ENGINEERING MONOGRAPHS 13

Chemical Reactor Design in Practice

L.M. ROSE



0062430

1551CHA

Chemical Reactor Design in Practice

L.M. ROSE

*Privatdozent, Technisch-Chemisches Laboratorium,
Eidgenössische Technische Hochschule, Zürich, Switzerland*



ELSEVIER SCIENTIFIC PUBLISHING COMPANY
Amsterdam — Oxford — New York 1981

ELSEVIER SCIENCE PUBLISHERS B.V.
Molenwerf 1
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Distributors for the United States and Canada:

ELSEVIER SCIENCE PUBLISHING COMPANY INC.
52, Vanderbilt Avenue
New York, NY 10017, U.S.A.

First edition 1981 (hardbound)
Second impression 1983 (hardbound)
Third impression 1985 (paperback)

ISBN 0-444-42018-5 (Vol. 13, hardbound)
ISBN 0-444-42476-8 (Vol. 13, paperback)
ISBN 0-444-41295-6 (Series)

© Elsevier Science Publishers B.V., 1981

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, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science Publishers B.V./Science & Technology Division, P.O. Box 330, 1000 AH Amsterdam, The Netherlands.

Special regulations for readers in the USA — This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the USA. All other copyright questions, including photocopying outside of the USA, should be referred to the publishers.

Printed in The Netherlands

0042430

1551CHA

Chemical Reactor Design in Practice

McGraw-Hill Chemical Engineering Series
McGraw-Hill Book Company, New York, New York

0045000

CHEMICAL ENGINEERING MONOGRAPHS

Edited by Professor S.W. CHURCHILL, Department of Chemical Engineering,
University of Pennsylvania, Philadelphia, Pa. 19104, U.S.A.

- Vol. 1 Polymer Engineering (Williams)
- Vol. 2 Filtration Post-Treatment Processes (Wakeman)
- Vol. 3 Multicomponent Diffusion (Cussler)
- Vol. 4 Transport in Porous Catalysts (Jackson)
- Vol. 5 Calculation of Properties Using Corresponding State Methods
(Sterbacek et al.)
- Vol. 6 Industrial Separators for Gas Cleaning (Storch et al.)
- Vol. 7 Twin Screw Extrusion (Janssen)
- Vol. 8 Fault Detection and Diagnosis in Chemical and Petrochemical
Processes (Himmelblau)
- Vol. 9 Electrochemical Reactor Design (Pickett)
- Vol. 10 Large Chemical Plants (Froment, editor)
- Vol. 11 Design of Industrial Catalysts (Trimm)
- Vol. 12 Steady-state Flow-sheeting of Chemical Plants (Benedek, editor)
- Vol. 13 Chemical Reactor Design in Practice (Rose)
- Vol. 14 Electrostatic Precipitators (Böhm)

To Jane

Preface

This text was compiled as a result of an invitation from Helsinki University of Technology to give a lecture course in "Practical Reactor Design", to follow on from their existing undergraduate introductory course as a senior course, also open to industrial participation.

There are a number of texts on reactor design now available, all of which cover the basic principles of the subject and discuss the present state of the art in various aspects of reactor engineering research. However, since reactor engineering research has moved from solving problems of practical interest to solving problems demanding high intellectual challenge, the available texts do not contain enough practical information to teach students how to design and specify reactors, or even to know the techniques by which this is done in technically advanced companies.

It is this void that this text is trying to fill.

In practice, reactor design usually starts by obtaining laboratory data from a new reaction system. It then sorts out the important factors, predicts a full-scale performance, and if this is attractive the pilot reactor is designed and operated. Data from the pilot reactor are then used in addition to laboratory data to design and predict the performance of a full-scale reactor that will work as optimally as possible, based on an economic criterion, and be easily operable and safe.

The engineer is best confronted with reactor problems at an early stage, when the chemist is going to look for good operating conditions, or even before, when he is thinking about the "reaction mechanism". The engineer can contribute to the search for optimum conditions, since he can bring economic factors into the picture and often has a numerate training which helps in the experimental planning and analysis of results.

The engineer produces a model from the laboratory results and uses this model for the design of his pilot and full-scale plant, for the choice of optimum conditions and for the stability analysis.

Reactor design in practice is concerned with the laboratory determination of data, their analysis, the development of models of the chemical and physical processes occurring, their optimization, the hardware dimensioning, and the definition of the necessary control and safety systems.

A text describing these activities touches on a multitude of disciplines - statistics, economics, optimization, control, and safety, as well as those subjects traditionally thought of as reactor design. This is an advantage for a senior course in that it is bringing together separate earlier courses, to show how, in practice, they are all needed to solve real problems.

The text was prepared for a 36 hours course plus nine two-hour exercise sessions. Since much of the course emphasized computer methods, the majority of the exercises were computer-based and run interactively with three or four students at each terminal. The nine exercises are included as Appendix 3, together with the programs used for the computer-based exercises.

The questions included at the end of each chapter are simply to emphasize the main point of that chapter and can be used by the reader to check that he has grasped the points that were being made.

It was the intention to compile a text of about 450 pages surveying the whole area of reactor design. When this is divided into topics and then further subdivided to produce a balanced text, it is surprising how few pages remain for the subjects that occupy volumes in the research literature because of the few recommendations that result from this activity. Whenever possible, only industrially tested techniques are described. When untried though promising methods are presented, a warning is given in the text. Since this is not a research text, no effort is made to substantiate the points made by reference to original literature. "Further Reading" lists are given where most points can be found discussed in more detail, and references are given only when the work would otherwise be difficult to find.

This "textbook" appears as a monograph because of the general feeling that not many teachers will be able to integrate this type of material into their present "reactor engineering" courses. If those teachers who do achieve this would contact the publishers, this would give some indication of the need for a textbook edition.

I would like to record my thanks to the staff of TKK Helsinki who made my stay in Finland so interesting and enjoyable - particularly to Professors B-son Bredenberg and Järveläinen, who arranged for the reactor design course to take place, and J. Aitamaa, who put much of his time into preparing the programs for the computer exercises.

Particular thanks are due to Elfriede Kilian for taking the major typing load and to Sirpa Pauni, who transferred some of my hand-written notes to typed text by a very novel, though somewhat laborious process.

Zürich, May 1981

L.M. Rose

Notation

a	empirical constant	-
a	interfacial area/unit volume	m^{-1}
A	cross-section area	m^2
A_i	pre-exponential factor (of reaction i)	$Kmol^{(1-n)} m^{3(n-1)} s^{-1}$
A'	heat-transfer area	m^2
b	empirical constant	-
c	empirical constant	-
c_i	cash flow for year i	\$
c_p	mass specific heat at constant pressure	$kJ kg^{-1} K^{-1}$
C_A	molar concentration (of component A)	$kmol m^{-3}$
d (d_p, d_B, d_t, d_I, d_e)	diameter of particle, bubble, tube, impeller or equivalent diameter	m
D	reactor diameter	m
D_A	molecular diffusivity (of component A)	$m^2 s^{-1}$
E_i	activation energy (of reaction i)	$kJ kmol^{-1}$
E'	enhancement factor	-
f	fanning friction factor	-
f	fraction capital costs incurred annually	-
F	molar flowrate	$kmol s^{-1}$
F	objective function	-
F'	tax factor	-
g	gravitational constant	$9.81 m s^{-2}$
g_g	heat generation/unit reactor volume	$kJ m^{-3}$
g_r	heat removed/unit reactor volume	$kJ m^{-3}$
G	mass flowrate (gas)	$kg s^{-1}$
G	free energy	$kJ kmol^{-1}$
h	single film heat-transfer coefficient	$kW m^{-2} K^{-1}$
H	enthalpy	$kJ kmol^{-1}$
H'	Henry's law solubility constant	$bar m^3 kmol^{-1}$
ΔH_i	heat of reaction (of i^{th} reaction)	$kJ kmol^{-1}$
I	investment cost	\$
k_i	reaction rate constant (of i^{th} reaction)	$kmol^{(1-n)} m^{3(n-1)} s^{-1}$
k_g	gas film mass-transfer coefficient	$kmol m^{-2} bar^{-1} s^{-1}$
k_L	liquid film mass-transfer coefficient	$m s^{-1}$
K (K_a, K_c)	equilibrium constant (based on activity, concentration)	-
K_g	overall gas mass-transfer coefficient	$kmol m^{-2} bar^{-1} s^{-1}$

xx

K_A	absorption coefficient	bar^{-1}
K', K'', K'''	miscellaneous constants	-
L	length	m
$L_{\frac{1}{2}}$	catalyst life (number of half lives)	-
L	project life	years
L'	mass flowrate (liquid)	kg s^{-1}
m	lifetime for taxation purposes	years
M_A	molecular weight (of A)	kg kmol^{-1}
n_A	number of kmoles (of A)	kmol
\dot{n}_A	molar flowrate (of A)	kmol s^{-1}
N	stirrer speed (RPS)	s^{-1}
N	number of tubes, number of beds, number of tanks	-
N_{Ca}	dimensionless group in Calderbank's surface area equations	-
N_p	agitator power number	-
N_{Re}	Reynolds number	-
p_A	partial pressure (of A)	bar
P	total pressure	bar
P', P'_g	agitator power (ungassed and gassed)	kW
P''	power supplied by gas	kW
Q	volumetric flowrate	$\text{m}^3 \text{s}^{-1}$
r	fractional rate of interest	-
r	recycle rate	kmol s^{-1}
r_i	molar reaction rate/unit reactor volume	$\text{kmol m}^{-3} \text{s}^{-1}$
r_t	fractional taxation rate	-
R	gas constant	$8.314 \text{ kJ kmol}^{-1} \text{ K}^{-1}$ or $0.08314 \text{ bar m}^3 \text{ kmol}^{-1} \text{ K}^{-1}$
s	tube pitch	m
s'	stirrer tip speed	m s^{-1}
S	entropy	$\text{kJ K}^{-1} \text{ kmol}^{-1}$
S	selectivity	-
t	time	s
$t_{\frac{1}{2}}$	half-life time	s
t_F	residence time in the film	s
t_R	residence time of the reaction	s
\bar{t}	mean residence time of a distribution	s
T	temperature	K
T'	production	kmol s^{-1} or tons year^{-1}
u	velocity	m s^{-1}
u_s, u_t, u_m	superficial, terminal, minimal velocity	m s^{-1}

U	overall heat-transfer coefficient	$\text{kW m}^{-2} \text{K}^{-1}$
V	volume	m^3
V_R	reactor volume	m^3
w	width	m
W	weight	tons
x	independent variable	-
x_A	mole fraction in liquid (of A)	-
X_A	fractional conversion (of A)	-
y	dependent variable	-
y_A	mole fraction in gas (of A)	-
Z	film thickness	m

GREEK LETTERS

α	empirical constant	-
ϵ_g	gas hold up in gas/liquid dispersions	-
ϵ_p	void fraction in packed bed	-
λ	thermal conductivity	$\text{kW m}^{-1} \text{K}^{-1}$
θ	reduced time	-
μ	dynamic viscosity	$\text{kg m}^{-1} \text{s}^{-1}$
ν	stoichiometric coefficient (-ve for reactants)	-
σ	surface tension	kg s^{-2}
π	3.1416	-
ρ	mass density	kg m^{-3}
τ	space time	s
η	effectiveness factor (gas/solid reactions)	-
β	pellet temperature rise factor	-
ϕ	Thiele modulus	-

SUBSCRIPTS

A, B ...	for components A, B ...
amb	ambient conditions
b	in bulk (fluid)
g	in gas phase (or in presence of gas)
i	for i^{th} reaction
in	of inlet
j	for j^{th} species
J	of jacket
L	in liquid phase
0	at initial (or reference) condition

out	of outlet
R	of reactor
s	at solid surface, of solid
S	for standard case
U	for utilities
w	at wall

GENERAL NOTE ON UNITS

SI units have been used throughout, but in order to be able to deal with conveniently sized numbers the following have been consistently used: m, kg, kmol, kJ, kW, s, K, bar.

CONTENTS

Preface	vii
Notation	xix
Chapter 1 CHEMICAL KINETICS AND REACTOR DESIGN PRINCIPLES	1
1.1 THE SINGLE CHEMICAL REACTION	1
a Predictions of heats of reaction	4
1.2 SIMULTANEOUS REACTION SYSTEMS	6
a Reversible reactions	6
b Consecutive reactions	9
c Parallel reactions	10
d Catalytic reactions	10
1.3 REACTION MECHANISMS	13
a Partial-order kinetics as a result of simultaneous reaction	18
1.4 TYPES OF REACTOR	21
a The batch reactor	21
b The semi-batch reactor	22
c The continuous stirred tank reactor	23
d The plug-flow reactor	25
1.5 THE SELECTIVITIES SHOWN BY THE FOUR REACTOR TYPES IN SIMULTANEOUS REACTION SYSTEMS	26
a Consecutive reactions	26
b Parallel reactions	27
1.6 MODELLING OF SIMULTANEOUS REACTION SYSTEMS	28
a Batch and plug-flow reactors	28
b Continuous and stirred tank reactors	29
c Semi-batch reactors	30
1.7 SOME ANALYTICAL SOLUTIONS	31
1.8 INTRODUCTION OF HEAT EFFECTS INTO REACTOR MODELS	36
a Batch, semi-batch, and plug-flow reactors	36
b Continuous stirred tank reactors	37
1.9 THE ROLE OF MASS TRANSFER	38
1.10 THE NEED FOR COMPLEX MODELS	39
FURTHER READING	39
QUESTIONS	40

Chapter 2	MODELLING OF REACTORS	41
2.1	WHY MODEL REACTORS ?	42
2.2	THE MODEL EQUATIONS	44
2.3	THE CHOICE OF COMPUTER AND SOFTWARE	47
	a Choice between analog and digital computers	47
	b The numerical techniques	48
	(i) Simultaneous algebraic equations	48
	(ii) Differential equations	49
2.4	EXAMPLES OF REACTOR MODELS	50
	a Example 1: A model of a CSTR reactor	50
	b Example 2: A model of a tubular catalytic reactor	57
	c Example 3: Modelling of PFR reactors when changes occur with time	60
2.5	FITTING PARAMETERS TO MODELS	62
2.6	LINEAR REGRESSION	64
	a Analysis of variance	66
	b Parameter confidence limits	66
	c Prediction of correlation between parameters	67
	d Confidence limits for a model prediction	68
	e The elements of the $[X^T X]$ matrix	68
	f Improving the linear model	70
2.7	NON-LINEAR REGRESSION	72
	a Non-linear regression-theory	72
	b Non-linear regression-practice	74
2.8	MULTIPLE RESPONSE NON-LINEAR REGRESSION	78
	a Weighting	79
2.9	THE ROLE OF STATISTICS IN MODEL FITTING	80
	FURTHER READING	80
	QUESTIONS	81
Chapter 3	REACTOR LABORATORY STUDIES IN PROCESS DEVELOPMENT	82
3.1	THE OBJECTIVE OF PROCESS DEVELOPMENT	82
	a Scale-up	82
	b Safety	84
	c Low cost process	84
3.2	TYPES OF LABORATORY EXPERIMENTAL REACTOR	85
3.3	LABORATORY REACTORS FOR MEASURING CHEMICAL KINETICS	86
	a Chemical kinetics determination - liquid phase	87
	Ampoules in a thermostat	87
	Small scale batch reactor	88
	Micro-reactor	91

b	Rate measurements in two phase systems with mass transfer resistance	91
c	Chemical kinetics determination - gas phase	92
	Gas stirred reactor	92
	Stirred gas-solid reactor	93
	Differential reactor	95
	Weighed pellet	96
d	Chemical kinetics measurement on solid reactions	97
3.4	LABORATORY EQUIPMENT FOR MEASURING TOTAL REACTOR PERFORMANCE	97
a	Batch reactor with cooling	97
b	Heat calorimeter reactors	99
c	Autoclave reactors	99
d	CSTR with cooling	102
e	Gas/liquid and liquid/liquid reactors	102
f	Tubular reactors	102
g	Tubular fluid bed	104
3.5	LABORATORY MEASUREMENT OF HEAT OF REACTION	105
3.6	THE CONTRIBUTION OF MODELLING TO PROCESS DEVELOPMENT STUDIES	105
a	The development of an acrolein process	106
b	The development of a pyridine process	110
	FURTHER READING	111
	QUESTIONS	112
Chapter 4	THE PLANNING OF EXPERIMENTS	113
4.1	GENERAL CONSIDERATIONS	113
4.2	SCREENING EXPERIMENTS	114
a	Planning	114
b	Evaluation of screening experiments	117
c	Problems associated with screening experiments	119
4.3	EXPERIMENTAL DESIGN TECHNIQUES AFTER THE SCREENING STAGE	120
a	Experimental design methods for location of optima	120
	Response surface methods	120
	The Box-Wilson method	120
	EV-OP methods	123
	Mechanistic modelling methods	125
b	Experimental design techniques to define the mechanistic model	125
4.4	NON-LINEAR EXPERIMENTAL PLANNING - A CASE STUDY	130
	Experimental	130
	A comparison of existing algorithms	131
	A proposed algorithm	134

4.5	CONCLUDING REMARKS	137
	FURTHER READING	139
	QUESTIONS	139
Chapter 5	THE PILOT STAGE	140
5.1	THE FUNCTIONS OF A PILOT PLANT	140
	a The production of material for evaluation and market development	140
	b The definition of effluent problems and the testing of methods of their solution	141
	c To check the feasibility of continuous operation	141
	d Checking the effects of concentration build-ups and other long term effects	142
	e Checking that the process can be "scaled up"	142
	Surface to volume ratios	142
	Mixing in tank reactors	143
	Tubular reactor - diameter changes	143
	Tubular reactor - length changes	143
	Tubular reactor - multiple tubes	143
	f Checking materials of construction	144
	g Design information for unit operations	144
	h The overlooking or misinterpretation of important factors	144
	i Developing confidence in those in control of finance	145
5.2	TYPES OF PILOT PLANT	146
5.3	PILOT PLANT DESIGN	148
5.4	PILOT PLANT INSTRUMENTATION	148
	a Flow control	148
	b Flow measurement	150
	c Temperature measurement	150
	d Analysis	151
5.5	USE OF COMPUTERS ON PILOT PLANTS	151
5.6	PILOT PLANT OPERATION	152
5.7	SOME CASE STUDIES	152
	Example 1 - Acrolein reactor development	153
	Example 2 - Chlorination of ethylene	154
	Example 3 - Methyl chloride reactor	155
	Example 4 - Pyridine process development	156
	Example 5 - Process integration by use of HCl	157
	Example 6 - Development of a carbon tetrachloride process	159
	Example 7 - Scale up of kinetic data for a gas/solid catalyzed reaction	160

FURTHER READING	162
QUESTIONS	162
Chapter 6 THE LOCATION OF OPTIMUM CONDITIONS	163
6.1 THE OBJECTIVE FUNCTION	164
a The reactor alone	164
b The reactor plus an estimation of other plant costs	165
c Total process optimization	166
6.2 ECONOMIC CRITERIA	166
a Modified economic criteria for optimization studies	168
b The inclusion of tax	169
c The effect of inflation	171
6.3 OPTIMIZATION METHODS	172
a The case study approach	172
b Sensitivity studies	173
c The use of non-linear optimization methods	173
Constraints	174
6.4 TOTAL PROCESS MODELS	175
a Individual equipment models	176
b Specific process models	176
c Generalized flowsheet programs	179
Types of standard reactor model	179
d Optimization with process models	181
6.5 TIME PROFILES	183
a Batch and semi-batch reactors	183
b Time profiles in continuous reactors	189
c Length profiles for continuous plug flow reactors	192
6.6 ALLOWING FOR UNCERTAINTY	192
a Reactor design safety factors	193
6.7 WHEN TO OPTIMIZE	194
FURTHER READING	194
QUESTIONS	195
Chapter 7 THE DESIGN OF STIRRED TANK REACTORS	196
7.1 MIXING IN STIRRED TANKS	196
a Stirrer type selection	197
b Determination of stirrer speed	200
Impeller pumping rates	200
Batch mixing time	201
Mixing criteria to achieve adequate heat and mass transfer	201