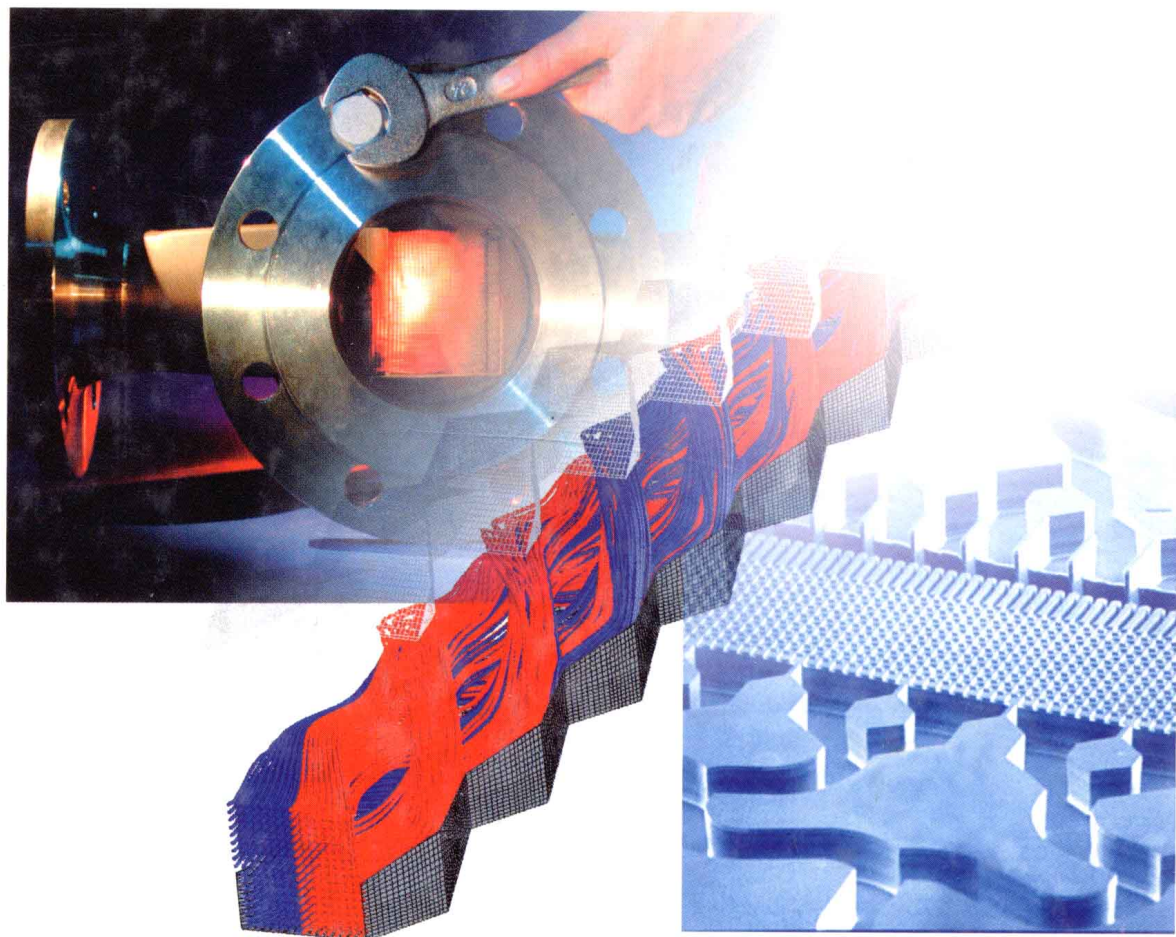


Volker Hessel, Steffen Hardt,
Holger Löwe

 WILEY-VCH

Chemical Micro Process Engineering

Fundamentals, Modelling and Reactions



Dr. Volker Hessel

Dr. Steffen Hardt

Dr. Holger Löwe

IMM – Institut für Mikrotechnik Mainz GmbH
Carl-Zeiss-Straße 18–20
55129 Mainz
Germany

Cover Illustration

Upper left: Production- and pilot-scale gas/ gas counter-flow heat exchanger comprising microstructured channel arrays. The device (including flanges about 36 kg heavy and 54 cm long), made of stainless steel, is designed for gas throughput in the range of m^3/min at 100 mbar pressure drop for a power of about 10 kW. The internals consist of a stack of microstructured plates having multi-channel arrays of a channel width of 2 mm, depth of 250 μm , and length of 240 mm. Totalling, 6685 micro channels are operated in parallel in this device. The flange-type connection allows installation in large-scale industrial plants (IMM Mainz-Hechtsheim, Germany).

Center: CFD simulation of streamlines of a liquid flow in a caterpillar micro mixer. This device utilizes the split-recombine principle leading to distributive mixing. It is seen that by multiple repetition of this principle the entanglement of the streams increases (IMM Mainz-Hechtsheim, Germany).

Lower right: Cross-flow catalyst screening device with multiple short mini-fixed beds. The fixed-bed catalyst section is fed by bifurcation-channel flow architectures that serve for flow equipartition. This device is a typical example for the class of smart chip reactors, widely employed for analytical-chemistry, kinetic studies and process/catalyst screening purposes on a lab-scale level, and is fabricated using MEMS technology based on silicon micromachining (Courtesy K. S. Jensen, MIT Cambridge, USA).

This book was carefully produced. Nevertheless, authors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: Applied for.

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

Bibliographic information published by

Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the internet at <http://dnb.ddb.de>.

© 2004 Wiley-VCH Verlag GmbH & Co.
KGaA, Weinheim

All rights reserved (including those of translation in other languages). No part of this book may be reproduced in any form – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Printed in the Federal Republic of Germany.
Printed on acid-free paper.

Composition Manuela Treindl, Laaber

Printing betz-druck GmbH, Darmstadt

Bookbinding Buchbinderei J. Schäffer
GmbH & Co. KG, Grünstadt

ISBN 3-527-30741-9

V. Hessel, S. Hardt, H. Löwe

**Chemical Micro Process
Engineering**

Related Titles

V. Hessel, S. Hardt, H. Löwe

Chemical Micro Process Engineering

Processing, Applications and Plants

2004

ISBN 3-527-30998-5

T. Gh. Dobre, J. G. Sanchez Marcano

Chemical Engineering Modelling, Simulation and Similitude

2004

ISBN 3-527-30607-2

W. Ehrfeld, V. Hessel, H. Löwe

Microreactors

New Technology for Modern Chemistry

2000

ISBN 3-527-29590-0

K. Sundmacher, A. Kienle (Eds.)

Reactive Distillation

Status and Future Directions

2003

ISBN 3-527-30579-3

W. Menz, J. Mohr, O. Paul

Microsystem Technology

2001

ISBN 3-527-29634-4

S. P. Nunes, K.-V. Peinemann (Eds.)

Membrane Technology in the Chemical Industry

2001

ISBN 3 527 28485-0

J. G. Sanchez Marcano, Th. T. Tsotsis

Catalytic Membranes and Membrane Reactors

2002

ISBN 3-527-30277-8

Preface

Carrying out chemical reactions in volumes as small as possible is *a priori* not a completely new idea. In the beginnings of chemical experimentation, dating back to the age of alchemy, chemical substances like sulphuric acid or ammonia were much more valuable than gold, and very small reaction vessels were used to economize on the precious materials. When analytical chemistry was established as a second, independent discipline, the desire to make do with ever less material was very strong in order to avoid consuming large portions of the product for analysis. Establishing increasingly sensitive analytical techniques has therefore been one of the most significant driving forces in analytics research.

The beginning of the industrial age saw a substantial increase in demand for basic materials and chemicals, and the chemical industry was established to satisfy these demands for high production volumes. The tall and impressive silhouettes of modern chemical plants dominate industrial estates, visible from afar as symbols for the vast capabilities and capacities of today's chemical industry. Without this industry and its equipment of enormous proportions, our economic wealth would be quite inconceivable.

Bearing all this in mind, what is the purpose of Chemical Micro Process Technology?

Conventionally, the development of chemical manufacturing processes takes place subsequently *via* a sequence of different intermediate stages. Approaching the final process design, the reaction volume is successively increased from laboratory scale to reaction vessel dimensions suitable for production outputs of several kilotons *per annum*. This procedure, known as "scale-up", is expensive and time-consuming. During the scale-up, new and previously unencountered problems often crop up and have to be solved. It may even occur that the complete development process has to be re-initiated in order to circumvent severe obstacles. Furthermore, the developed industrial process is laid out for a specific, predefined throughput, a fact which constrains the later flexibility of production significantly.

The solution of these problems is based on a simple idea: the developed laboratory-scale process is used for manufacturing of a chemical product by parallelization of many small units. Although promising great advantages over scale-up, this procedure, denoted "numbering-up", is not trivial by far. It cannot be carried out in a simple way due to the tremendous technological effort necessary: a chemical plant with hundreds or even thousands of small-scaled vessels, stirrers, heaters, pumps,

etc. would be impractical. A new way of engineering and new technologies had to be developed to combine the advantages of lab-scale processing with the necessities associated with production-scale throughput. First steps into this direction have been taken, and despite some remaining throughput restrictions, first successes have become visible. Also, economical and ecological reasons create increasing demand for further steps in process intensification and sustainable development.

The present book is devoted to both the experimentally tested micro reactors and micro reaction systems described in current scientific literature as well as the corresponding processes. It will become apparent that many micro reactors at first sight “simply” consist of a multitude of parallel channels. However, a closer look reveals that the details of fluid dynamics or heat and mass transfer often determine their performance. For this reason, besides the description of the equipment and processes referred to above, this book contains a separate chapter on modeling and simulation of transport phenomena in micro reactors.

Using specific examples of gas-phase, gas/liquid and liquid-phase reactions, the advantages of microstructured reactors are highlighted in comparison to conventional equipment. At the same time, known problems are pointed out and some processes are listed for which micro reactors so far failed to show superior performance. Furthermore, the book is conceived as a compendium. Processes, microstructured reactors and chemical reactions are described in an integrated manner, providing in each case the relevant original citations. Equipped with the data given in this book, readers will be able to identify the most suitable reactor to successfully perform a given chemical reaction on the micro scale.

By now, Chemical Micro Process Technology has been established as an independent discipline, bringing forth over 1500 publications in the last few years, and an end is not foreseeable. The surge of scientific cognitions encouraged the authors to write this book, which should provide a deeper insight into this new and fascinating subject.

We are very grateful to those who helped this project become reality. In particular, we would like to mention K. Bouras, T. Hang, C. Mohrmann, and L. Widarto, who prepared electronic versions of many of the figures appearing in this book. We also wish to thank C. Mohrmann and L. Widarto for handling the copyright transfer formalities and T. Hang for taking pictures of some of IMM’s micro devices. A special thanks goes to B. Knabe and R. Schenk for helping us with literature retrieval. Last but not least, we are indebted to K. S. Drese and F. Schönfeld for the thorough checking of parts of our manuscript.

Mainz, November 2003

The authors

Contents

Preface V

List of Symbols and Abbreviations XXXI

1	A Multi-faceted, Hierarchic Analysis of Chemical Micro Process Technology	1
1.1	Micro-reactor Differentiation and Process Intensification	3
1.1.1	Structure or Being Structured? Miniature Casings and Micro Flow	3
1.1.2	Symmetry and Unit Cells	3
1.1.3	Process Design Dominates Equipment Manufacture and Choice	4
1.1.4	Micro-reactor and Chemical-micro-processing Differentiation	5
1.1.5	Numbering-up	6
1.1.5.1	Progressive Increase in Capacity by Addition of Modules	6
1.1.5.2	Internal vs. External Numbering-up: Scaling-out of Elements or Devices	7
1.1.5.3	Issues to be Solved; Problems to be Encountered	10
1.1.5.4	Limits of Mini- and Micro Plants for Scale-up	11
1.1.5.5	First Large-capacity Numbered-up Micro-flow Devices Reported	11
1.1.5.6	First Complete Test Station for Multiple-micro-reactor testing	12
1.1.6	Process Intensification	13
1.1.6.1	Definitions	13
1.1.6.2	Matching Fluidics to Physico-chemical Requirements of a Reaction	13
1.1.6.3	Relationship of and Difference between of PI and Micro-reaction Technology	14
1.1.6.4	Process Intensification Achieved by Use of Micro Reactors	15
1.1.7	The Multi-scale Concept	15
1.1.8	A Word of Caution on the Probability of a Deductive Analysis	17
1.1.9	Other Concepts Related to or Relevant for Chemical-Micro Processing	17
1.1.9.1	mTAS: Micro Total Analysis Systems	17
1.1.9.2	Green Chemistry	17
1.1.9.3	Sustainable Development and Technology Assessment	17
1.1.9.4	Microfluidic Tectonics (μ FT)	18

1.1.9.5	Compact Flow-through Turbulent Reactors, also Termed Microreactor (MR) Technology	18
1.1.9.6	Supramolecular Aggregates, Also Termed Micro Reactors	19
1.1.10	Some Historical Information on Micro-reactor Evolution	21
1.1.11	Micro-reactor Consortia/Forums	22
1.1.11.1	The Laboratory on a Chip Consortium (UK)	22
1.1.11.2	MicroChemTec and IPmVT (D)	22
1.1.11.3	NeSSI (USA)	23
1.1.11.4	Micro Chemical Process Technology, MCPT (J)	23
1.1.11.5	CPAC Micro-reactor Initiative (USA)	24
1.2	Consequences of Chemical Micro Processing	25
1.2.1	Limits of Outlining Top-down Impacts for Micro Reactors	25
1.2.2	Categories of 'Micro-reactor Fundaments and Impacts'	25
1.2.3	Comprehensive Reviews and Essays	26
1.2.4	Reviews and Essays on Physical Fundaments and the Impact on Chemical Engineering and Process Engineering	27
1.2.5	Reviews and Essays on the Impact on Process Results, Society/Ecology and the Economy	27
1.2.6	Reviews and Essays on Application Topics and Microfabrication	27
1.2.7	Reviews and Essays on Institutional Work	28
1.3	Physical and Chemical Fundaments	28
1.3.1	Size Reduction of Process Equipment	28
1.3.2	Scaling Effects Due to Size Reduction: Hydrodynamics	29
1.3.3	Chemical Fundaments	31
1.4	Impact on Chemical Engineering	32
1.4.1	Basic Requirements on Chemical Engineering from an Industrial Perspective	32
1.4.2	Top-down and Bottom-up Descriptions	32
1.4.3	A Top-down Description of Chemical Engineering Impacts	32
1.4.3.1	A Case Study on Gas-phase Reactions	33
1.4.3.2	Energy Gain from Microstructuring	33
1.4.3.3	Residence-time Distributions	36
1.4.3.4	Heat Transfer: Safety in Operation	37
1.4.3.5	Potential for Size Reduction	40
1.4.3.6	Proposing a Methodology for Micro-reactor Dimensioning and Layout	42
1.4.4	A Bottom-up Description of Chemical Engineering Impacts	45
1.4.4.1	Mixing	45
1.4.4.2	Heat Transfer	48
1.4.4.3	Microfluidics	49
1.4.5	Fouling	50
1.5	Impact on Process Engineering	51
1.5.1	Laboratory-scale Processing	51
1.5.1.1	Provision of a Multitude of Innovative Reactor Designs	51
1.5.1.2	Quality of Information – More Accurate and In-depth	51
1.5.1.3	Quantity of Information – Speed of Experimentation	51

1.5.1.4	Shrinkage of Total System	52
1.5.1.5	Integratability of Sensing and Other Functions	52
1.5.2	Industrial Process Development and Optimization	53
1.5.2.1	Information on Industrial Large-scale Chemical Manufacture: Time to Market	53
1.5.2.2	Pharmaceutical and Organic Synthesis Process Development	54
1.5.2.3	Approval by Public Authorities	55
1.5.3	Pilot-stage Processing and Centralized Production	55
1.5.3.1	Production as a Challenge for Micro Reactors	55
1.5.3.2	Micro Reactors as Information Tools for Large-scale Production	56
1.5.3.3	Micro Reactors for Specialty-chemicals Production	56
1.5.3.4	Intensification of Transport – Reduction of Equipment Size	58
1.5.4	Distributed, On-Site Production	59
1.5.4.1	An Existing Distributed Small-scale Plant for Phosgene Synthesis	59
1.5.4.2	Distributed Manufacturing – A Conceptual Study of Future Scenarios	59
1.5.4.3	Central Role of Control Systems and Process Models	61
1.5.4.4	Off-shore Gas Liquefaction	61
1.5.4.5	Energy Generation and Environmental Restoration	61
1.5.4.6	Desk-top Pharmacies, Home Factories and More	62
1.5.4.7	Production of Chemical Weapons?	63
1.5.4.8	Standardization	63
1.5.5	The Shape of Future Plants/Plant Construction	63
1.5.5.1	The Outer Shape of Future Chemical Manufacture Plants	63
1.5.5.2	Today's Shape of Micro-reactor Bench-scale Plants: Monolith vs. Hybrid/Multi-scale? Specialty vs. Multi-purpose?	65
1.5.5.3	Methodology of Micro/Mini-plant Conception	66
1.5.5.4	Highly Integrated Systems	66
1.6	Impact on Process Results	66
1.6.1	Selection Criteria for Chemical Reactions for Micro Reactors	66
1.6.2	Conversion, Selectivity, Yield	67
1.6.2.1	Conversion	67
1.6.2.2	Selectivity	67
1.6.2.3	Yield	69
1.6.3	Reaction Time – Reaction Rate	69
1.6.3.1	Reaction Time	69
1.6.3.2	Reaction Rate	70
1.6.4	Space–Time Yield	70
1.6.5	Isomerism	71
1.6.5.1	Cis–Trans Isomerism of Double Bonds	71
1.6.5.2	Regioisomerism in Condensed Aromatics	72
1.6.5.3	Regioisomerism in Aromatics with One Substituent	72
1.6.5.4	Keto–Enol Isomerism	72
1.6.6	Optical Purity	73
1.6.6.1	Enantiomeric Excess (<i>ee</i>)	73
1.6.6.2	Racemization	73

1.6.7	Reaction Mechanism	73
1.6.7.1	Preferring One Mechanism Among a Multitude	73
1.6.7.2	Tuning Bulk Reactions to Surface Control	74
1.6.8	Experimental Protocols	74
1.6.8.1	Residence Time	74
1.6.8.2	Reaction Temperature	74
1.6.8.3	Type of Reactants and Auxiliary Agents	75
1.6.9	Safety Profits	75
1.6.9.1	Share of Safety-relevant Industrial Processes	75
1.6.9.2	Safe Micro-reactor Operations in the Explosive Regime or for Otherwise Hazardous Processes	76
1.6.10	New Process Regimes	76
1.6.10.1	Essentially Novel Processes	77
1.6.10.2	Known Processes that Become Entirely Better or Otherwise Different	77
1.6.10.3	Processes Known, but not Used for Safety Reasons	77
1.7	Impact on Society and Ecology	79
1.7.1	The 'Control Circuit' for Chemical Micro Processing	79
1.7.2	Social Acceptance via Education and Awareness	81
1.7.3	Ecologic Acceptance via Environmental Acceptability	81
1.7.4	Environmental Restoration	83
1.7.5	The Micro-reactor Echo in Trade Press and Journal Cover Stories	83
1.7.6	The Micro-reactor Echo in Newspaper Press and Magazines	90
1.8	Impact on Economy	91
1.8.1	Market Development/Commercial Implementation	91
1.8.1.1	A Historical Description of the Interplay between Technology Push and Market Pull	91
1.8.1.2	PAMIR – A Market Study Giving First Insight	93
1.8.1.3	Market Evaluation	94
1.8.1.4	Start-up Companies and User–Supplier Platforms	95
1.8.2	Device Fabrication and Quality Control	96
1.8.2.1	Cost Estimation from Mass-manufacture Scenarios for Chip-based Microfabrication	96
1.8.2.2	Quality Control	96
1.8.3	Cost Savings for the Chemical Industry	96
1.9	Application Fields and Markets for Micro Reactors	97
1.9.1	Transportation/Energy	97
1.9.1.1	How Far is the Development? A Critical Review	98
1.9.2	Petrochemistry	98
1.9.2.1	How Far is the Development? A Critical Review	98
1.9.3	Catalyst Discovery and Optimization via High-throughput Screening	99
1.9.3.1	How Far is the Development? A Critical Review	99
1.9.4	Bulk Chemicals and Commodities	100
1.9.4.1	How Far is the Development? A Critical Review	100
1.9.5	Fine Chemicals and Functional Chemicals	100
1.9.5.1	Fine Chemicals – Drivers and Trends	100

1.9.5.2	Fine Chemicals – State of the Art of Micro-reactor Use	102
1.9.5.3	Functional Chemicals	103
1.9.5.4	How far is the Development? A Critical Review	103
1.9.6	Cosmetics and Foods	104
1.9.6.1	How Far is the Development? A Critical Review	104
1.9.7	Extra-terrestrial Processing	104
1.9.7.1	How Far is the Development? A Critical Review	105
1.9.8	Chemical Analysis, Analyte Separation, Assays and Further Diverse Applications in the Bio Field	105
1.9.8.1	How Far is the Development? A Critical Review	105
	<i>References</i>	106

2 Modeling and Simulation of Micro Reactors 125

2.1	Introduction	125
2.2	Flow Phenomena on the Micro Scale	127
2.2.1	Gas Flows	127
2.2.1.1	Slip Flow Regime	129
2.2.1.2	Transition Flow and Free Molecular Flow	131
2.2.2	Liquid Flows	136
2.2.2.1	Boundary Slip of Liquids	138
2.2.2.2	Electric Double Layers	139
2.2.2.3	Nano Flows	141
2.2.3	Multiphase Flows	142
2.2.3.1	Phase Transitions in Confined Spaces	143
2.2.3.2	Wetting and Spreading Phenomena	144
2.3	Methods of Computational Fluid Dynamics	146
2.3.1	Fundamentals of the Finite-volume Method	149
2.3.2	Solution of the Navier–Stokes Equation	156
2.3.3	Computational Grids	161
2.3.4	Solution Methods for Linear Algebraic Systems	165
2.4	Flow Distributions	169
2.4.1	Flow in Rectangular Channels	170
2.4.2	Generalized Channel Cross-Sections	171
2.4.3	Periodic and Curved Channel Geometries	172
2.4.4	Multichannel Flow Domains	176
2.5	Heat Transfer	182
2.5.1	Fundamental Equations of Heat Transport	182
2.5.2	Heat Transfer in Rectangular Channels	184
2.5.3	Generalized Channel Cross-sections	185
2.5.4	Periodic Channel Geometries	185
2.5.5	Viscous Heating	188
2.5.6	Micro Heat Exchangers	189
2.5.7	Thermal Optimization of Micro reactors	196
2.6	Mass Transfer and Mixing	197
2.6.1	Transport Equation for Species Concentration	198

2.6.2	Special Numerical Methods for Convection-Dominated Problems	198
2.6.3	Mixing Channels	200
2.6.4	Estimation of Mixing Efficiency by Flow-field Mapping	206
2.6.5	Multilamination Mixers	207
2.6.6	Active Micro Mixing	209
2.6.7	Hydrodynamic Dispersion	214
2.7	Chemical Kinetics	218
2.7.1	Kinetic Models	218
2.7.2	Numerical Methods for Reacting Flows	220
2.7.3	Reacting Channel Flows	222
2.7.4	Heat-exchanger Reactors	224
2.7.5	Periodic Processing	228
2.8	Free Surface Flow	230
2.8.1	Computational Modeling of Free Surface Flows	231
2.8.2	Micro Flows of Droplets and Bubbles	236
2.9	Transport in Porous Media	240
2.9.1	Morphology of Porous Media	241
2.9.2	Volume-averaged Transport Equations	242
2.9.3	Computation of Transport Coefficients	244
2.9.4	Reaction-diffusion Dynamics inside Pores	247
	<i>References</i>	249
3	Gas-phase Reactions	257
3.1	Catalyst Coating in Micro Channels: Techniques and Analytical Characterization	258
3.2	Micro Reactors for Gas-phase Reactions	261
3.2.1	Housing-encased Single-platelet and Multi-platelet Stack Micro Reactors	261
3.2.1.1	Reactor 1 [R 1]: Reactor Module with Different Multi-channel Micro Reactors	262
3.2.1.2	Reactor 2 [R 2]: Steel Multi-plate-stack Reactor with Micro Mixer	263
3.2.1.3	Reactor 3 [R 3]: Modular Multi-plate-stack Reactor	264
3.2.1.4	Reactor 4 [R 4]: Multi-plate-stack Micro Reactor with Diffusers	266
3.2.1.5	Reactor 5 [R 5]: Cross-flow Multi-Plate Stack Micro Reactor	268
3.2.1.6	Reactor 6 [R 6]: Counter-flow Multi-plate Stack Micro Reactor	270
3.2.1.7	Reactor 7 [R 7]: Multi-Plate Stack Micro Reactor in Heatable Holding Unit	272
3.2.1.8	Reactor 8 [R 8]: Ceramic Platelet Micro Reactor	273
3.2.1.9	Reactor 9 [R 9]: Micro Heat Transfer Module	274
3.2.2	Chip Micro Reactors	275
3.2.2.1	Reactor 10 [R 10]: Catalyst Membrane Si-chip Micro Reactor with Sensing and Heating Functions	276
3.2.2.2	Reactor 11 [R 11]: Single-channel Chip Reactor	278
3.2.2.3	Reactor 12 [R 12]: Multi-channel–One-plate Chip Reactor	278
3.2.2.4	Reactor 13 [R 13]: Micro-strip Electrode Reactor	279

3.2.2.5	Reactor 14 [R 14]: Self-heating Chip Micro Reactor	280
3.2.2.6	Reactor 15 [R 15]: Modular Multi-functional Chip Reaction System	281
3.2.3	Mini Fixed-bed Micro Reactors	281
3.2.3.1	Reactor 16 [R 16]: Wide Fixed-bed Reactor with Retainer Structures, Pressure-drop Channels and Bifurcation-cascade Feed/Withdrawal	282
3.2.3.2	Reactor 17 [R 17]: Mini Packed-bed Reactor	283
3.2.4	Thin-wire and mGauze Micro Reactors	285
3.2.4.1	Reactor 18 [R 18]: Modular Integrated 3D System with Electrically Heated μ Gauze	285
3.2.4.2	Reactor 19 [R 19]: Catalyst-wire-in-channel Micro Reactor	287
3.2.5	Thin-membrane Micro Reactors	288
3.2.5.1	Reactor 20 [R 20]: Permeable-separation Membrane Chip Reactor	288
3.2.6	Micro Reactors without Micro Channel Guidance – Alternative Concepts	289
3.2.6.1	Reactor 21 [R 21]: Filamentous Catalytic-bed Membrane Reactor	289
3.2.6.2	Reactor 22 [R 22]: Various Other Reactor Designs	290
3.3	Oxidations	291
3.3.1	Drivers for Performing Oxidations in Micro Reactors	291
3.3.2	Beneficial Micro Reactor Properties for Oxidations	292
3.3.3	Oxidation of Ammonia	293
3.3.3.1	Drivers for Performing the Oxidation of Ammonia	293
3.3.3.2	Beneficial Micro Reactor Properties for the Oxidation of Ammonia	293
3.3.3.3	Typical Results	294
3.3.4	Oxidation of Ethylene – Ethylene Oxide Formation	299
3.3.4.1	Drivers for Performing Ethylene Oxide Formation	299
3.3.4.2	Beneficial Micro Reactor Properties for Ethylene Oxide Formation	299
3.3.4.3	Typical Results	300
3.3.5	Oxidation of 1-Butene – Maleic Anhydride Formation	309
3.3.5.1	Drivers for Performing Maleic Anhydride Formation in Micro Reactors	309
3.3.5.2	Beneficial Micro Reactor Properties for Maleic Anhydride Formation	309
3.3.5.3	Typical Results	309
3.3.6	Oxidation of Methanol – Formaldehyde Formation	311
3.3.6.1	Drivers for Performing Formaldehyde Synthesis in Micro Reactors	311
3.3.6.2	Beneficial Micro Reactor Properties for Formaldehyde Synthesis	312
3.3.6.3	Typical Results	312
3.3.7	Oxidation of Derivatized Alcohols – Derivatized Aldehyde Formation	314
3.3.7.1	Drivers for Performing Derivatized Aldehyde Synthesis in Micro Reactors	314
3.3.7.2	Beneficial Micro Reactor Properties for Derivatized Aldehyde Synthesis	314
3.3.7.3	Typical Results	315
3.3.8	Oxidation of Propene to Acrolein	316
3.3.8.1	Drivers for Performing the Oxidation of Propene to Acrolein	316

- 3.3.8.2 Beneficial Micro Reactor Properties for the Oxidation of Propene to Acrolein 316
- 3.3.8.3 Typical Results 317
- 3.3.9 Oxidation of Isoprene – Citraconic Anhydride Formation 318
- 3.3.9.1 Drivers for Performing Citraconic Anhydride Formation 318
- 3.3.9.2 Beneficial Micro Reactor Properties for Citraconic Anhydride Formation 318
- 3.3.9.3 Typical Results 318
- 3.3.10 Partial Oxidation of Methane – Syngas Generation 322
- 3.3.10.1 Drivers for Performing Syngas Generation 322
- 3.3.10.2 Beneficial Micro Reactor Properties for Syngas Formation 323
- 3.3.10.3 Typical Results 323
- 3.3.11 Oxidation of Carbon Monoxide to Carbon Dioxide 327
- 3.3.11.1 Drivers for Performing the Oxidation of Carbon Monoxide to Carbon Dioxide 327
- 3.3.11.2 Beneficial Micro Reactor Properties for the Oxidation of Carbon Monoxide to Carbon Dioxide 327
- 3.3.11.3 Typical Results 327
- 3.3.12 Andrussov Process 329
- 3.3.12.1 Drivers for Performing the Andrussov Process 329
- 3.3.12.2 Beneficial Micro Reactor Properties for the Andrussov Process 329
- 3.3.12.3 Typical Results 330
- 3.3.13 Hydrogen/Oxygen Reaction 332
- 3.3.13.1 Drivers for Performing the Hydrogen/Oxygen Reaction 332
- 3.3.13.2 Beneficial Micro Reactor Properties for the Hydrogen/Oxygen Reaction 332
- 3.3.13.3 Typical Results 333
- 3.3.14 Oxidation of Formamides – Synthesis of Methyl Isocyanate 339
- 3.3.14.1 Drivers for Performing the Synthesis of Methyl Isocyanate 339
- 3.3.14.2 Beneficial Micro Reactor Properties for the Synthesis of Methyl Isocyanate 340
- 3.3.14.3 Typical Results 340
- 3.4 Hydrogenations 340
- 3.4.1 Cyclohexene Hydrogenation and Dehydrogenation 340
- 3.4.1.1 Drivers for Performing the Cyclohexene Hydrogenation and Dehydrogenation 340
- 3.4.1.2 Beneficial Micro Reactor Properties for Cyclohexene Hydrogenation and Dehydrogenation 340
- 3.4.1.3 Typical Results 341
- 3.4.2 Hydrogenation of *c,t,t*-1,5,9-Cyclododecatriene to Cyclododecene 346
- 3.4.2.1 Drivers for Performing the Hydrogenation of *c,t,t*-1,5,9-Cyclododecatriene to Cyclododecene 346
- 3.4.2.2 Beneficial Micro Reactor Properties for the Hydrogenation of *c,t,t*-1,5,9-Cyclododecatriene to Cyclododecene 346
- 3.4.2.3 Typical Results 347

3.4.3	Hydrogenation of 1,5-Cyclooctadiene to Cyclooctene	349
3.4.3.1	Drivers for Performing the Hydrogenation of 1,5-Cyclooctadiene to Cyclooctene	349
3.4.3.2	Beneficial Micro Reactor Properties for the Hydrogenation of 1,5-Cyclooctadiene to Cyclooctene	349
3.4.3.3	Typical Results	350
3.4.4	Hydrogenation of Benzene	351
3.4.4.1	Drivers for Performing the Hydrogenation of Benzene	351
3.4.4.2	Beneficial Micro Reactor Properties for the the Hydrogenation of Benzene	351
3.4.4.3	Typical Results	351
3.5	Dehydrogenations	352
3.5.1	Non-oxidative Dehydrogenation of Propane to Propene	352
3.5.1.1	Drivers for Performing the Non-oxidative Dehydrogenation of Propane to Propene	352
3.5.1.2	Beneficial Micro Reactor Properties for the Non-oxidative Dehydrogenation of Propane to Propene	353
3.5.1.3	Typical Results	353
3.5.2	Oxidative Dehydrogenation of Propane to Propene	355
3.5.2.1	Drivers for Performing the Oxidative Dehydrogenation of Propane to Propene	355
3.5.2.2	Beneficial Micro Reactor Properties for the Oxidative Dehydrogenation of Propane to Propene	355
3.5.2.3	Typical Results	355
3.5.3	Dehydrogenation of Cyclohexane to Benzol	358
3.5.3.1	Drivers for Performing the Dehydrogenation of Cyclohexane	358
3.5.3.2	Beneficial Micro Reactor Properties for the Dehydrogenation of Cyclohexane	358
3.5.3.3	Typical Results	358
3.6	Substitutions	358
3.6.1	Chlorination of Alkanes	358
3.6.1.1	Drivers for Performing the Chlorination of Alkanes	358
3.6.1.2	Beneficial Micro Reactor Properties for the Chlorination of Alkanes	359
3.6.1.3	Typical Results	359
3.7	Eliminations	360
3.7.1	Dehydration of 2-Propanol to Propene	360
3.7.1.1	Drivers for Performing the Dehydration of 2-Propanol to Propene	361
3.7.1.2	Beneficial Micro Reactor Properties for the Dehydration of 2-Propanol to Propene	361
3.7.1.3	Typical Results	361
3.8	Additions and Coupling Reactions	364
3.8.1	Phosgene Formation	364
3.8.1.1	Drivers for Performing Phosgene Formation	364
3.8.1.2	Beneficial Micro Reactor Properties for Phosgene Formation	364
3.8.1.3	Typical Results	365

3.8.2	Oxidative Coupling of Methane	366
3.8.2.1	Drivers for Performing the Oxidative Coupling of Methane	366
3.8.2.2	Beneficial Micro Reactor Properties for the Oxidative Coupling of Methane	367
3.8.2.3	Typical Results	367
	References	368
4	Liquid- and Liquid/Liquid-phase Reactions	379
4.1	Micro Reactors for Liquid-phase and Liquid/Liquid-phase Reactions	379
4.1.1	Tube Micro Reactors	379
4.1.1.1	Reactor 1 [R 1]: Electrothermal Tubing-based Micro Reactor	379
4.1.1.2	Packed-bed Tube or Capillary Micro Reactors	380
4.1.2.1	Reactor 2 [R 2]: Packed-bed Capillary Micro fFlow Reactor	380
4.1.2.2	Reactor 3 [R 3]: Porous-polymer Rod in Tube Micro Reactor	381
4.1.3	Chip Micro-reactor devices	382
4.1.3.1	Reactor 4 [R 4]: Chip Reactor with Micro-channel Mixing Tee(s)	382
4.1.3.2	Reactor 5 [R 5]: Chip Micro Reactor with Multiple Vertical Injections in a Main Channel	384
4.1.3.3	Reactor 6 [R 6]: Chip Micro Reactor with Multiple Micro Channel–Mixing Tees	386
4.1.3.4	Reactor 7 [R 7]: Chip Micro Reactor with Z-type Flow Configuration	386
4.1.3.5	Reactor [R 8]: Chip Micro Reactor with Extended Serpentine Path and Ports for Two-step Processing	387
4.1.3.6	Reactor 9 [R 9]: Chip System with Triangular Interdigital Micro Mixer–Reaction Channel	387
4.1.3.7	Reactor 10 [R 10]: 2 × 2 Parallel Channel Chip Reactor	389
4.1.3.8	Reactor 11 [R 11]: Bifurcation-distributive Chip Micro Mixer	390
4.1.3.9	Reactor 12 [R 12]: Micro Y-Piece Micro-channel Chip Reactor	391
4.1.3.10	Reactor 13 [R 13]: Triple Feed Continuous Multi-phase Chip Reactor	391
4.1.3.11	Reactor 14 [R 14]: Chip with Bi-/Tri-layer Flow Configuration Using Y-type Contact	392
4.1.3.12	Reactor 15 [R 15]: Single-channel Chip Micro Reactor	392
4.1.4	Chip–Tube Micro Reactors	393
4.1.4.1	Reactor 16 [R 16]: Liquid-Liquid Micro Chip Distributor–Tube Reactor	393
4.1.4.5	Reactor 17 [R 17]: Fork-like Chip Micro Mixer–Tube Reactor	395
4.1.5	3-D Microfab Reactor Devices	396
4.1.5.1	Reactor 18 [R 18]: Interdigital Micro Mixers	396
4.1.6	3-D Microfab Mixer–Tube Reactors	399
4.1.6.1	Reactor 19 [R 19]: Slit-Type Interdigital Micro Mixer–Tube Reactor	399
4.1.6.2	Reactor 20 [R 20]: Triangular Interdigital Micro Mixer–Tube Reactor	400
4.1.6.3	Reactor 21 [R 21]: Caterpillar Mini Mixer–Tube Reactor	401
4.1.6.4	Reactor 22 [R 22]: [Separation-layer Micro Mixer; Tube] – Reaction System	402
4.1.6.5	Reactor 23 [R 23]: [Impinging-jet Micro Mixer; Tube] – Reaction System	403

4.1.7	3-D Microfab Micro Mixer–Micro Heat Exchangers	404
4.1.7.1	Reactor 24 [R 24]: System with Series of Micro Mixers–Cross-Flow Reactor Modules	404
4.1.8	2-D Integrated Total Systems with Micro Mixing and Micro Heat Exchange Functions	405
4.1.8.1	Reactor 25 [R 25]: CPC Micro Reaction System CYTOS™	405
4.1.8.2	Reactor 26 [R 26]: Chip Micro Reaction System with Parallel Mixer–Reaction Channels	406
4.1.8.3	Reactor 27 [R 27]: [Bi-layer Contactor; High-aspect-ratio Heat Exchanger] – Reaction System	407
4.1.8.4	Reactor 28 [R 28]: Multi-channel Integrated Mixer-Heat Exchanger	409
4.1.9	Electrochemical Micro Reactors	410
4.1.9.1	Reactor 29 [R 29]: Multi-sectioned Electrochemical Micro Reactor	410
4.1.9.2	Reactor 30 [R 30]: Electrochemical Diaphragm Micro Flow Cell	411
4.1.9.3	Reactor 31 [R 31]: Electrochemical Capillary Micro Flow Reactor	411
4.1.9.4	Reactor 32 [R 32]: Electrochemical Sheet Micro Flow Reactor	412
4.1.9.5	Reactor 33 [R 33]: Electrochemical Plate-to-Plate Micro Flow Reactor	413
4.1.9.6	Reactor 34 [R 34]: Ceramic Micro Reactor with Interdigitated Electrodes	414
4.1.10	Photochemical Micro Reactors	416
4.1.11	Complete Parallel-synthesis Apparatus	417
4.2	Aliphatic Nucleophilic Substitution	418
4.2.1	Hydroxydehalogenation – Hydrolysis of Chlorides and Acid Chlorides	418
4.2.1.1	Drivers for Performing Chloride Hydrolysis in Micro Reactors	418
4.2.1.2	Beneficial Micro Reactor Properties for Chloride Hydrolysis	418
4.2.1.3	Chloride Hydrolysis Investigated in Micro Reactors	419
4.2.1.3	Experimental Protocols	419
4.2.1.4	Typical Results	420
4.2.2	Cyanodehalogenation – Preparation of Nitriles	421
4.2.2.1	Drivers for Performing Preparation of Nitriles in Micro Reactors	421
4.2.2.2	Beneficial Micro Reactor Properties for Preparation of Nitriles	422
4.2.2.3	Preparation of Nitriles Investigated in Micro Reactors	422
4.2.2.4	Experimental Protocols	422
4.2.2.5	Typical Results	422
4.2.3	Thiocyanatodehydrogenation – Thiocyanation	422
4.2.3.1	Drivers for Performing Thiocyanation in Micro Reactors	422
4.2.3.2	Beneficial Micro Reactor Properties for Thiocyanation	422
4.2.3.3	Thiocyanation Investigated in Micro Reactors	422
4.2.3.4	Experimental Protocols	423
4.2.3.5	Typical Results	423
4.2.4	Azidodehalogenation – Formation of Azides	423
4.2.4.1	Drivers for Performing Azide Substitutions in Micro Reactors	423
4.2.4.2	Beneficial Micro Reactor Properties for Azide Substitutions	423
4.2.4.3	Azide Substitutions Investigated in Micro Reactors	423
4.2.4.4	Experimental Protocols	423