

Modeling of Process Intensification

Edited by

Frerich Johannes Keil



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**Modeling of Process
Intensification**

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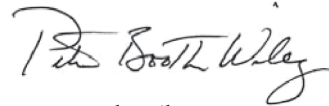
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Frerich Johannes Keil



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The Editor

Prof. Dr. Dr. h.c. Frerich J. Keil

Hamburg University of Technology
Institute of Chemical Reaction Engineering
Eißendorferstr. 38
21073 Hamburg
Germany

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Contents

Preface *XI*

List of Contributors *XIII*

- 1 Modeling of Process Intensification – An Introduction and Overview** *1*
Frerich J. Keil
- 2 Process Intensification – An Industrial Point of View** *9*
Robert Franke
- 2.1 Introduction *9*
- 2.1.1 Remarks on the Term Process Intensification *9*
- 2.1.2 Management Aspects *10*
- 2.2 Microreaction Technology *11*
- 2.2.1 Principal Features *11*
- 2.2.2 Catalytic Wall Reactors *12*
- 2.3 Simulation *15*
- 2.3.1 Introduction *15*
- 2.3.2 Molecular Simulations *16*
- 2.3.2.1 Quantum-chemical Calculations *16*
- 2.3.2.2 COSMO-RS Calculations *18*
- 2.3.2.3 Molecular-dynamics Calculations *19*
- 2.3.3 Monte Carlo Simulations in Project Valuation under Risk *20*
- 3 Modeling and Simulation of Microreactors** *25*
Steffen Hardt
- 3.1 Introduction *25*
- 3.2 Flow Distributions *30*
- 3.2.1 Straight Microchannels *30*
- 3.2.2 Periodic and Curved Channel Geometries *32*
- 3.2.3 Multichannel Flow Domains *34*
- 3.3 Heat Transfer *39*

3.3.1	Straight Microchannels	39
3.3.2	Periodic and Curved Channel Geometries	41
3.3.3	Multichannel Flow Domains	43
3.3.4	Micro Heat Exchangers	47
3.4	Mass Transfer and Mixing	50
3.4.1	Simple Mixing Channels	51
3.4.2	Chaotic Micromixers	53
3.4.3	Multilamination Micromixers	59
3.4.4	Hydrodynamic Dispersion	62
3.5	Chemical Kinetics	66
3.5.1	Numerical Methods for Reacting Flows	66
3.5.2	Reacting Channel Flows	68
3.5.3	Heat-exchanger Reactors	71
3.6	Conclusions and Outlook	74
4	Modeling and Simulation of Unsteady-state-operated Trickle-flow Reactors	79
	<i>Rüdiger Lange</i>	
4.1	Introduction	79
4.2	Modeling	82
4.3	Reactor Model	85
4.4	Simulation	88
4.5	Conclusion	93
5	Packed-bed Membrane Reactors	99
	<i>Ákos Tóta, Dzmitry Hlushkou, Evangelos Tsotsas, and Andreas Seidel-Morgenstern</i>	
5.1	Introduction	99
5.1.1	The PBMR Principle	101
5.1.2	Case Study	101
5.1.3	Porous Membranes	102
5.1.4	Outline	103
5.2	One-dimensional Modeling of Packed-bed Membrane Reactors	103
5.2.1	One-dimensional Pseudohomogeneous Model	103
5.2.2	Cofeed (FBR) vs. Distributed Dosing of Reactants (PBMR) – Nonreactive Conditions	105
5.2.3	Comparison between FBR and PBMR – Reactive Conditions	107
5.2.4	Nonisothermal Operation	111
5.3	Two-dimensional Modeling of Packed-bed Membrane Reactors	114
5.3.1	Two-dimensional Model of PBMR – The Momentum-balance Equation	115
5.3.2	Two-dimensional Model of PBMR – The Mass-balance Equation	117
5.3.3	Two-dimensional Model of PBMR – The Energy-balance Equation	118
5.3.4	Boundary Conditions	119
5.3.5	Numerical Solution of the Two-dimensional Model	121

5.3.6	Velocity Field in a Packed-bed Membrane Reactor	122
5.3.7	The Influence of Membrane Permeability on the Boundary Conditions	123
5.3.8	Effect of Porosity Profile	126
5.3.9	Effect of Radial Mass-transport Limitations	127
5.3.10	Comparison of the $l(r)$ - and a_w -model Concepts – Temperature Profiles in a PBMR	129
5.4	Three-dimensional Modeling of a Packed-bed Membrane Reactor	132
5.4.1	Introduction to the Large-scale Simulation Methods in Fluid Mechanics and Mass Transport	132
5.4.2	Pressure and Velocity Field (Varying the Flow Distribution) – Comparison between FBR and PBMR	133
5.4.3	Advective-diffusive Mass Transport in PBMR	137
5.5	Summary and Conclusion	140
6	The Focused Action of Surface Tension versus the Brute Force of Turbulence – Scaleable Microchannel-based Process Intensification using Monoliths	149
	<i>Michiel T. Kreutzer, Annelies van Diepen, Freek Kapteijn, and Jacob A. Moulijn</i>	
6.1	Introduction	149
6.2	Monoliths – A Scalable Microchannel Technology	150
6.3	Power Required for Gas–Liquid Dispersion	152
6.3.1	Turbulent Contactors	152
6.3.2	Laminar Contactors	154
6.4	Physical Adsorption of Oxygen	156
6.5	Three-phase Processes	158
6.6	Discussion	160
6.6.1	Design Considerations for Intensified Monolith Processes	160
6.7	Conclusions	161
7	Chemical Reaction Modeling in Supercritical Fluids in Special Consideration of Reactions in Supercritical Water	165
	<i>Andrea Kruse and Eckhard Dinjus</i>	
7.1	Introduction	165
7.2	Properties of Supercritical Fluids	167
7.3	The C—C-bond Splitting of Tert.-butylbenzene	169
7.3.1	Experimental	170
7.3.2	Modeling	170
7.4	Total Oxidation in Supercritical Fluids	173
7.4.1	Is Oxidation in CO ₂ the same as Oxidation in Water?	175
7.4.2	Experimental	176
7.4.3	Modeling	177
7.5	Glycerol Degradation	179
7.5.1	Modeling	180
7.6	Conclusion	186

8	Ultrasound Reactors	193
8.1	Some Fundamentals of Ultrasonics and the Design of High Energy Density Cravice Reactors	193
	<i>Christian Horst</i>	
8.1.1	Introduction	193
8.1.2	Bubble Behavior in Acoustic Fields	196
8.1.2.1	Equations for the Motion of the Bubble Wall	196
8.1.2.2	Cavitation Thresholds	200
8.1.2.3	Influence of Parameters on Cavitation Behavior	202
8.1.2.4	Cavitation near Solid Boundaries	204
8.1.2.5	Finite Amplitude Waves and Shock Waves	205
8.1.2.6	Streaming	206
8.1.2.7	Bjerknes Forces	206
8.1.2.8	Forces on Small Particles	207
8.1.2.9	Sonochemical Effects	207
8.1.3	Modeling of Sound Fields	209
8.1.4	Examples of Sound Fields in Ultrasound Reactors	214
8.1.4.1	High-amplitude–High Energy Density Conical Reactor	214
8.1.4.2	Low-amplitude–High Energy Density Crevice Reactor	217
8.1.5	Modeling of Sonochemical Effects in Ultrasound Reactors	218
8.1.6	Summary	225
8.2	Design of Cavitational Reactors	226
	<i>Parag R. Gogate and Aniruddha B. Pandit</i>	
8.2.1	Introduction	226
8.2.2	Theoretical Approach	228
8.2.2.1	Identification of Stable or Transient Cavitation	231
8.2.2.2	Effect of Compressibility of Medium	233
8.2.2.3	Optimization of Operating Parameters	235
8.2.2.4	Development of Design Equations	235
8.2.3	Distribution of the Cavitational Activity in the Reactors	240
8.2.4	Intensification of Cavitational Activity in the Sonochemical Reactors	247
8.2.4.1	Use of Process-intensifying Parameters	249
8.2.4.2	Use of Combination of Cavitation and Advanced Oxidation Processes	250
8.2.5	Design of a Pilot-scale Reactor and its Experimental Evaluation	252
8.2.5.1	Rational for the Design of a Reactor	252
8.2.5.2	Actual Design of the Novel Reactor	253
8.2.5.3	Comparison of the Efficacy of the Hexagonal Flow-cell Reactor with Conventional Designs	254
8.2.6	Hydrodynamic Cavitation Reactors	257
8.2.6.1	Engineering Design of Hydrodynamic Cavitation Reactors	258
8.2.7	Comparison of Cavitational Yields in Acoustic and Hydrodynamic Cavitation	268
8.2.8	Qualitative Considerations for Reactor Choice, Scaleup and Optimization	268

8.2.9	Efforts Needed in the Future	271
8.2.10	Concluding Remarks	272
9	Modeling of Simulated Moving-bed Chromatography	279
	<i>Monika Johannsen</i>	
9.1	Introduction	279
9.2	From Elution Chromatography to Countercurrent Chromatography	280
9.2.1	The TMB Process	281
9.2.2	The SMB Process	282
9.3	Applications of SMB Chromatography	284
9.4	Modeling of Chromatographic Processes	287
9.4.1	Modeling of Single-column Chromatography	288
9.4.1.1	Ideal Model	290
9.4.1.2	Dispersive Model	291
9.4.1.3	Equilibrium Dispersive Model	292
9.4.1.4	Linear Driving Force (LDF) Model	293
9.4.1.5	General Rate Model	294
9.4.1.6	Initial and Boundary Conditions for Single-column Chromatography	295
9.4.2	Modeling of SMB Chromatography	296
9.4.2.1	Model Classification	296
9.4.2.2	Modeling of the TMB Process	297
9.4.2.3	Modeling of the SMB Process	299
9.4.2.4	Solution of the TMB Model with the Triangle Theory	299
9.4.2.5	Consideration of Different Adsorption Coefficients in the Zones	303
9.4.2.6	Modeling of Pressure Gradient in SFC	306
9.4.3	Numerical Algorithms	307
9.5	Simulations of SMB-SFC Chromatography	308
9.5.1	Separation of Cis/trans-Isomers of Phytol	308
9.5.2	Separation of Enantiomers of (R,S)-Ibuprofen	311
9.5.3	Separation of Tocopherols	314
9.6	Conclusion	317
10	Modeling of Reactive Distillation	323
	<i>Eugeniy Y. Kenig and Andrzej Górak</i>	
10.1	Introduction	323
10.2	Characteristics of Reactive Distillation	324
10.2.1	Column Internals for Reactive Distillation	324
10.3	Modeling Principles of Reactive Distillation	326
10.3.1	General Aspects	326
10.3.2	Equilibrium-stage Model	328
10.3.3	Rate-based Approach	329
10.3.3.1	Balance Equations	330
10.3.3.2	Mass Transfer and Reaction Coupling in the Fluid Film	332
10.3.3.3	Nonideal Flow Behavior in Catalytic Column Internals	333

10.3.3.4	Dynamic Modeling	336
10.4	Case Studies	336
10.4.1	Methyl Acetate Synthesis	336
10.4.1.1	Process Description	336
10.4.1.2	Process Modeling	338
10.4.1.3	Results and Discussion	339
10.4.2	Methyl Tertiary Butyl Ether	341
10.4.2.1	Process Description	341
10.4.2.2	Process Modeling	341
10.4.2.3	Results and Discussion	342
10.4.3	Ethyl Acetate Synthesis	343
10.4.3.1	Process Description	343
10.4.3.2	Process Modeling	347
10.4.3.3	Results and Discussion	347
10.4.4	Dymethyl Carbonate Transesterification	350
10.4.4.1	Process Description	350
10.4.4.2	Process Modeling	351
10.4.4.3	Results and Discussion	352
10.5	Conclusions and Outlook	355
11	Experimental and Theoretical Explorations of Weak- and Strong-gradient Magnetic Fields in Chemical Multiphase Processes	365
	<i>Faiçal Larachi</i>	
11.1	Background	365
11.1.1	Nonmagnetic Fluids	366
11.1.2	Magnetic Fluids	367
11.2	Nonmagnetic Fluids	368
11.2.1	Principle	368
11.2.2	Theory	370
11.2.3	Experimental Results and Discussion	371
11.3	Magnetic Fluids	378
11.3.1	Principle	378
11.3.2	Theory	380
11.3.2.1	Local Description	380
11.3.2.2	Upscaling	381
11.3.2.3	Closure Problem	384
11.3.2.4	Zero-order Axisymmetric Volume-average Model	386
11.3.3	Results and Discussion	386
11.4	Concluding Remarks	394
	Index	401

Preface

Process intensification has been on the upswing since a review written by A. Stankiewicz and J. Moulijn was issued in 2000. Meanwhile, companies and academia are addressing problems in process intensification, organizing workshops and even establishing departments on this subject. Process intensification is a very broad discipline and includes expertise in many diverse fields. It is applied to the development of novel apparatuses and techniques that either dramatically improve chemical or biological processes with respect to reduced equipment size, increased energy efficiency, less waste production, improved inherent safety, or even break new ground in process engineering by introducing newly developed equipment and production procedures. The present book focuses on modeling in process intensification. Experts in various areas of process intensification, from both industry and academia, have contributed to this book, which does not cover all the developments in this field; rather it demonstrates the activities in modeling for some representative problems. New equipment like microreactors, membrane reactors, ultrasound reactors, and those in simulated moving-bed chromatography, magnetic fields in multiphase processes or reactive distillation, requires new modeling approaches. The same applies to nonstationary process operation or the use of supercritical media. Process intensification is an emerging discipline that will result in many surprising developments in the future.

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F. J. Keil
Hamburg, January 2007

List of Contributors

Eckhard Dinjus

Forschungszentrum Karlsruhe
Institut für Technische Chemie
P.O. Box 36 40
76021 Karlsruhe
Germany

Robert Franke

Degussa AG
Creavis Technologies & Innovation
Project House Process
Intensification
Rodenbacher Chaussee 4
63457 Hanau
Germany

Parag R. Gogate

Institute of Chemical Technology
Chemical Engineering Department
Matunga, Mumbai-400019
India

Andrzej Gorak

Universität Dortmund
Lehrstuhl für Thermische
Verfahrenstechnik
FB Chemietechnik
44221 Dortmund
Germany

Steffen Hardt

Leibniz Universität Hannover
Institut für Nano- und
Mikroprozesstechnik
Callinstr. 36
30167 Hannover
Germany

Dzmitry Hlushkou

Otto von Guericke University
Magdeburg
Institute of Process Engineering
Chair of Thermal Process
Engineering
P.O. Box 4120
39106 Magdeburg
Germany

Christian Horst

Infraserv Gendorf
84504 Burgkirchen
Germany

Monika Johannsen

Technische Universität
Hamburg-Harburg
Institut für Thermische
Verfahrenstechnik
Eißendorferstraße 38
21073 Hamburg
Germany

Freek Kapteijn

University of Technology
Reactor/Cat. Engineering Group
Julianalaan 136
2628 BL Delft
The Netherlands

Eugen Y. Kenig

Universität Dortmund
Lehrstuhl für Thermische
Verfahrenstechnik
FB Chemietechnik
44221 Dortmund
Germany

Frerich J. Keil

Hamburg University of Technology
Institute of Chemical Reaction
Engineering
Eißendorferstraße 38
21073 Hamburg
Germany

Michiel T. Kreutzer

University of Technology
Reactor/Cat. Engineering Group
Julianalaan 136
2628 BL Delft
Netherlands

Andrea Kruse

Forschungszentrum Karlsruhe
Institut für Technische Chemie
P.O. Box 36 40
76021 Karlsruhe
Germany

Rüdiger Lange

Technische Universität Dresden
Verfahrenstechnik / Zi. A208
Münchener Platz 3
01062 Dresden
Germany

Faical Larachi

Laval University
Department of Chemical
Engineering
Cité Universitaire
Avenue de la Médecine
Pouliot Building
G1K 7P4 Quebec
Canada

Jacob A. Moulijn

University of Technology
Reactor/Cat. Engineering Group
Julianalaan 136
2628 BL Delft
The Netherlands

Andreas Seidel-Morgenstern

Otto von Guericke University
Magdeburg
Institute of Process Engineering
Chair of Chemical Process
Engineering
P.O. Box 4120
39106 Magdeburg
Germany

Aniruddha B. Pandit

Chemical Engineering Department
Institute of Chemical Technology
Matunga, Mumbai-400019
India

Ákos Tóta

Otto von Guericke University
Magdeburg
Institute of Process Engineering
Chair of Thermal Process
Engineering
P.O. Box 4120
39106 Magdeburg
Germany

Evangelos Tsotsas

Otto von Guericke University
Magdeburg
Institute of Process Engineering
Chair of Chemical Process
Engineering
P.O. Box 4120
39106 Magdeburg
Germany

Annelies van Diepen

University of Technology
Reactor/Cat. Engineering Group
Julianalaan 136
2628 BL Delft
The Netherlands

1

Modeling of Process Intensification – An Introduction and Overview

Frerich J. Keil

As noted by Hüther et al. [1], the term “process intensification” (PI) was probably first mentioned in the 1970s by Kleemann et al. [2] and Ramshaw [3]. Ramshaw, among others, pioneered work in the field of process intensification. What does “process intensification” (PI) mean? Over the last two decades, different definitions of this term were published. Cross and Ramshaw defined PI as follows: “Process intensification is a term used to describe the strategy of reducing the size of chemical plant needed to achieve a given production objective” [4]. In a review of PI, Stankiewicz and Moulijn [5] proposed: “Any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology is process intensification”. The BHR Group describes PI as follows [6]: “Process Intensification is a revolutionary approach to process and plant design, development and implementation. Providing a chemical process with the precise environment it needs to flourish results in better products, and processes which are safer, cleaner, smaller, and cheaper. PI does not just replace old, inefficient plant with new, intensified equipment. It can challenge business models, opening up opportunities for new patentable products and process chemistry and change to just-in-time or distributed manufacture”. To bring forward PI, Degussa established a so-called “project house” whose research activities are focused on PI. Degussa expanded the meaning of the concept “process intensification”: “Process intensification defines a holistic approach starting with an analysis of economic constraints followed by the selection or development of a production process. Process intensification aims at drastic improvements of performance of a process, by rethinking the process as a whole. In particular it can lead to the manufacture of new products which could not be produced by conventional process technology. The process-intensification process itself is “constantly financially evaluated” [1, 7]. As can be recognized from the above definitions, process intensification is a developing field of research and far away from a mature status. The chemical industry and academia are very interested in PI developments. For example, some German chemical engineering associations (DECHEMA, VDI-GVC) established a subject division on process intensification, which has already more than 180 members. In the opening session of this division

several sceptical questions arose, like: “Are any new options offered by PI which are not known already from other fields of chemical engineering, e.g. optimization or process integration?” “How large should be the improvement of a process for PI?” “What is the difference between the aims of PI and neighbouring disciplines?” [8]. There is an agreement that PI is an interdisciplinary field of research that needs an integrated approach. In PI, the journey is the reward.

PI has inspired already many new developments of equipment, process-intensifying methods and design approaches. As thermodynamic equilibrium and reaction kinetic properties are fixed values for given mixtures under fixed conditions like temperature, pressure and catalysts, most efforts were directed towards the improvement of transport properties, alternative energy resources, and process fluids. Examples of new equipment are the Sulzer SMR static mixer, which has mixing elements made of heat-transfer tubes, Sulzer’s open-crossflow-structure catalysts, so-called Katapaks, monolithic catalyst supports covered with washcoat layers, microreactors, ICI’s High Gravity Technology (HIGEE), HI-GRAVITEC’s rotating packed beds, centrifugal adsorbers made by Bird engineering, BHR’s improved mixing equipment and HEX reactors, high-pressure homogenizers for emulsifications, the spinning-disc reactor (SDR) developed by Ramshaw’s group at Newcastle University, and the supersonic gas/liquid reactor developed by Praxair Inc. (Danbury). Various ultrasonic transducers and reactors are now commercially available. The efforts in PI have been compiled in several books [9–14]. A general introductory paper was presented by Stankiewicz and Moulijn [5]. Process intensification by miniaturization has been reviewed by Charpentier [15]. Jachuck [16] reviewed PI for responsive processing. Other subjects related to process intensification have also been reviewed, for example, trickle-bed reactors [17], multifunctional reactors [18], rotating packed beds [19], multiphase monolith reactors [20], heat-integrated reactors for high-temperature millisecond contact-time catalysis [21], microengineered reactors [22, 23], monoliths as biocatalytic reactors [24], membrane separations [25], two-phase flow under magnetic-field gradients [26], and applications of ultrasound in membrane separation processes [27].

In Fig. 1.1 an overview of equipment and methods employed in PI is presented. PI leads to a higher process flexibility, improved inherent safety and energy efficiency, distributed manufacturing capability, and ability to use reactants at higher concentrations. These goals are achieved by multifunctional reactors, e.g. reactive distillation or membrane reactors, and miniaturization that can be done by employing microreactors and/or improving heat and mass transfer. Microfluidic systems enable very high heat- and mass-transfer rates so that reactions can be executed under more severe conditions with higher yields than conventional reactors. New reaction pathways, for example, direct fluorination of aromatic compounds, are possible, and scaleup of reactors is easier. This feature may enhance instationary reactor operation, like reverse flow, in industrial applications. These are just a few examples.

Intensification of heat and mass transfer can be achieved by using supersonic flow, strong gravitational magnetic fields, improved mixing, among other ap-

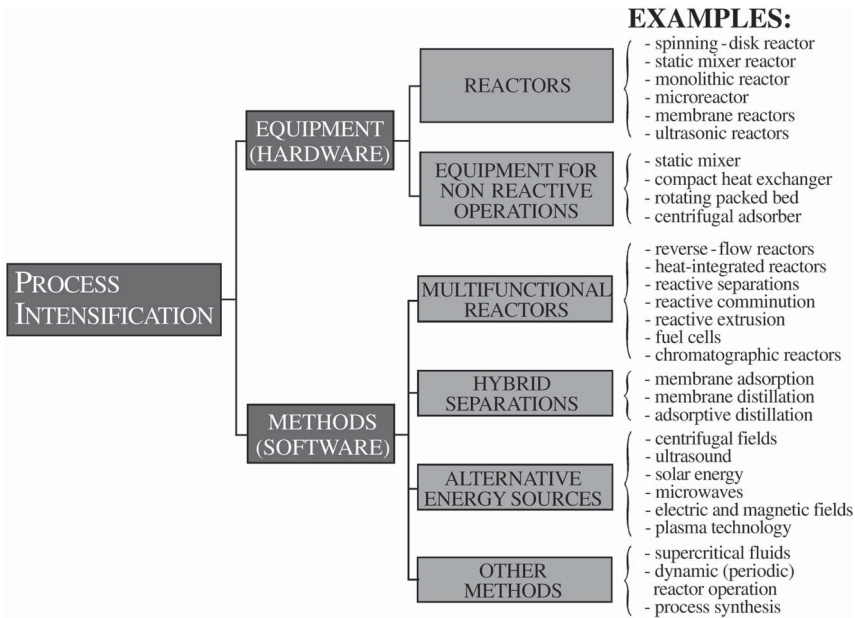


Figure 1.1 Tools of Process Intensification.

proaches. For example, the spinning-disc reactor technology utilizes the effects of high centrifugal force, which is capable of producing highly sheared films on the surface of rotating discs/cones. Convective heat-transfer coefficients as high as $14 \text{ kW m}^{-2} \text{ K}$ and mass transfer coefficients, K_L values as high as $30 \times 10^{-5} \text{ m s}^{-1}$ and K_G values as high as $12 \times 10^{-8} \text{ m s}^{-1}$, can be achieved whilst providing micro-mixing and an appropriate fluid dynamic environment for achieving faster reaction kinetics.

A further possibility is offered by external magnetic fields that exert a body force on electrically nonconducting magnetically permeable fluids, and this force can be used to compensate or to amplify the gravitational body force, which can be employed to influence two-phase flow in, for example, trickle-flow reactors.

Ultrasound can either be used for enhancing mass transfer or reaction engineering [28]. Cavitation generates conditions of locally very high temperatures ($>6000^\circ\text{C}$) and pressure (>10000 bars) along with the release of active radicals, which results in intensification of many of the physical and chemical transformations. Sonochemistry opened new possibilities for chemical synthesis. Sonoreactors can be thought of as high-energy microreactors. A compilation of chemistry and extreme and nonclassical conditions was edited by van Eldik and Hubbard [29].

The present book reviews recent developments in modeling of process intensification. It is divided into eleven chapters. After an introduction and overview, Robert Franke from Degussa AG describes in Chapter 2 the efforts on PI from an industrial point of view in their “project house”. A special feature is the use

of molecular simulations on various levels, like quantum chemistry, and classical molecular dynamics or Monte Carlo simulations. For liquid/liquid equilibria COSMO/RS is in use. Cash-flow analysis and project valuation under risk are investigated by Monte Carlo approaches.

Chapter 3 has been written by Steffen Hardt from Darmstadt University of Technology on modeling and simulation of microreactors. Flow distributions and heat transfer in various microchannels are described. Fast mass transfer and mixing are key aspects of microreactors. Modeling of micromixers is discussed in detail. The chapter is completed by a review of reacting flows in microchannels. The discussion of modeling and simulation techniques for microreactors shows that the toolbox available at present is quite diverse and goes well beyond the standard capabilities of CFD methods available in commercial solvers. Most of the effects are described by the standard continuum equations, but there are a number of problems that are extremely difficult, and require very fine computational grids. Among these problems is the numerical study of mixing in liquids that often severely suffers from discretization artefacts.

Chapter 4 by Rüdiger Lange from the University of Technology Dresden is on modeling and simulation of unsteady-state operated trickle-flow reactors. The behavior of these three-phase reactors is rather complex due to cocurrent flow of gas and liquid downward through a catalyst packing. Periodic change of reactant-feed concentration and/or volumetric flow rate are suitable for a considerable improvement of reaction conversion. A review of unsteady-state operated trickle-flow reactors is presented and a dynamic reactor model developed by Lange's group, based on an extended axial dispersion model, is described in detail.

Andreas Seidel-Morgenstern's group from the Max-Planck-Institute in Magdeburg presents in Chapter 5 an extensive review of packed-bed membrane reactors (PBMR), and analysis of the properties of this type of reactors by means of models developed in their group. In contrast to conventional tubular fixed-bed reactors, where all reactants together are fed into the reactor inlet, packed-bed membrane reactors allow one or several reactants to be dosed via membranes over the reactor wall along the axial reactor coordinate. Computational results, based on realistic data originating from the important class of partial oxidation reactions, are presented. The oxidative dehydrogenation of ethane to ethylene using a vanadium oxide catalyst was considered. Different membrane permeabilities were studied in the range of currently available porous materials. Investigations by a two-dimensional reactor model revealed that flow maldistribution, caused by increased bed porosity close to the membrane wall, leads to local temperature profiles that result in performance predictions different from an integral reactor. Results of a three-dimensional model using the lattice Boltzmann method are also presented.

In Chapter 6 Jacob Moulijn's group from the Delft University of Technology discusses the advantages and disadvantages of using segmented flow in microchannels to intensify catalytic processes. Once bubbles are formed in microchannels, they can no longer coalesce, and hence no energy is required to break up larger bubbles. As a result, the same gas-liquid mass-transfer behavior can be

obtained at an order of magnitude lower power input. This flow pattern can be used for biochemical conversions using cell cultures, provided the channels are not too small, and the operating conditions are such that biofilm formation is suppressed. If the segmented flow pattern is used for a reaction catalyzed at the walls of the capillary channels, then the mass transfer is actually improved by reducing the amount of energy that is dissipated in the system. This allows the simultaneous achievements of two goals of process intensification: reduction of energy requirement and reduction of equipment size.

Chapter 7 focuses on chemical-reaction modeling in supercritical fluids, in particular in supercritical water. This contribution is from Eckhard Dinjus' group at the Research Center Karlsruhe. The contribution gives detailed presentations of modeling of systems by elementary reactions and their reaction engineering.

Chapter 8 consists of two parts. The first contribution by Christian Horst explains some fundamentals of cavitation and its modeling applied to a so-called "High Energy Density Crevice Reactor". The Grignard reaction of chlorobutane isomers was used as an example. The sound field inside sonochemical reactors can be modeled by treating the liquid bubble mixture as a pseudofluid. The Kirkwood–Bethe–Gilmore equations were used to calculate the bubble motions of bubbles with different sizes. Knowing the bubble-size distribution at a given sound pressure by calculating cavitation thresholds and using this information in an equation for the local total bubble number, the calculation of the complex bulk modulus of the bubbly mixture is possible. The resulting sound velocities and the damping coefficients can be used for calculating the sound field by finite-element codes. The simulation results have been employed to optimize reactor geometries and to interpret some surprising effects. Sonochemical effects for Grignard reactions were also modeled.

The second contribution, written by Pareg Gogate and Anniruddha Pandit from the Institute of Chemical Technology in Mumbai, stresses important factors for efficient scaleup of cavitation reactors and subsequent industrial applications based on the theoretical and experimental analysis of the net cavitation effects. Guidelines for selection of an optimum set of operating parameters have been presented and hydrodynamic cavitation has also been discussed.

Chapter 9 on simulated moving-bed chromatography has been written by Monika Johannsen at Hamburg University of Technology. Simulated moving-bed (SMB) chromatography is a powerful purification process allowing the continuous separation of a feed mixture into two product streams. Most of these separations are performed using liquid chromatography. The complexity of preparative chromatography results in highly complex models for the quantitative description compared to analytical chromatography. The models are based on the adsorption theory and the theory of nonlinear chromatography. Various simulation tools for the SMB technique have been developed, which can be used for optimization of the column length, column configuration, flow rates, feed concentration, and switch times. Applications of SMB chromatography and modeling of this process are reviewed.

Chapter 10 reviews modeling of reactive distillation. This contribution is written by Kenig and Gorak at the University of Dortmund (Germany). In reactive distillation, reaction and distillation take place within the same zone of a distillation column. Reactants are converted to products with simultaneous separation of the products and recycle of unused reactants. The process basics and peculiarities are discussed in detail. Up-to-date applications, reactive distillation modeling and design issues are presented. The theoretical description is illustrated by several case studies and supported by the results of laboratory-, pilot- and industrial-scale experimental investigations. Both, steady-state and dynamic issues are treated, and the design of column internals is addressed. An outlook on future research requirements is given.

Façal Larachi from the Laval University in Quebec (Canada) presents in Chapter 11 experimental and theoretical investigations on artificial gravity (micro- or macrogravity) generated by strong gradient magnetic fields that could potentially open up attractive applications, especially in multiphase catalytic systems where a number of factors can be optimized in an original manner for improving process efficiency. For example, inhomogeneous and strong fields applied to trickle-bed reactors are capable of affecting their hydrodynamics. Liquid holdup can be improved that results in better contacting between a liquid and a catalyst surface. Additionally, a theoretical framework is developed based on the application of the volume-averaging theorems in multiphase porous media to analyze the flow of ferrofluids in a special class of porous media presenting pronounced effects of wall-bypass flows. Limitations of the present models are discussed.

To sum up, process intensification is a rapidly developing field that has already inspired many ideas in modeling and design of new equipment and operating modes, and whose potential is by far not fully tapped.

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2

Process Intensification – An Industrial Point of View

Robert Franke

2.1

Introduction

Process intensification aims at drastic improvements in performance of a process by rethinking the process as a whole. Modeling of process intensification relies partly on well-established engineering software tools that include process simulators and codes on computational fluid dynamics. However, process intensification goes beyond process optimization making the modeling tools – or the modeling Ansätze generally – much more versatile. This chapter will begin with a brief discussion of process intensification from the conceptual and management points of view. In the second section we will report on process-intensification strategies for gas-phase processes based entirely on relatively simple model calculations. Finally we will discuss molecular and financial simulation approaches that are important in the practical work on process-intensification projects.

2.1.1

Remarks on the Term Process Intensification

The definition of process intensification is still an ongoing process. In 1986 Cross and Ramshaw offered the definition: “Process intensification is a term used to describe the strategy of reducing the size of chemical plant needed to achieve a given production objective” [1]. In 2000 Stankiewicz and Moulijn proposed: “Any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology is process intensification” [2]. These definitions restrict process intensification to *engineering* methods and equipment and explicitly exclude the development of a new chemical route or the change in composition of a catalyst (see, e.g., [2]). We are convinced that these narrow definitions are inadequate for the description of process-intensification projects in industry. Following Hüther et al. [3] our working definition is: process intensification defines a *holistic* approach starting with an analysis of economic constraints followed by the selection or development of a production process. As

stated above, process intensification thus aims at drastic improvements of performance of a process, by rethinking the process *as a whole*. In particular, it can lead to the manufacture of new products which could not be produced by conventional process technology. The process-intensification process itself is constantly financially evaluated. In view of this definition, modeling in process intensification also includes the employment of methods such as computer-assisted organic synthesis or financial modeling software suites.

2.1.2

Management Aspects

A central precondition of process intensification is creative thinking. Creativity is an active process by which a genuinely new idea takes form. Creativity needs to be distinguished from innovation. In industry, an innovation is the introduction of new products or application processes or services *to the market*. It characterizes the generation of new ideas in order to produce a new product, process or service. Creativity is required if innovation is to be possible. In industrial R&D creativity is usually a product of prior knowledge and thinking, but truly creative acts in science are mostly unplanned. This does not mean that they happen by chance but that they are quite unpredictable and not guaranteed. Although exceptions may exist, significant inventions are usually the results of many years of constant research in a certain field and the accumulation of vast amounts of data. An enormous number of publications exist that discuss how to create an environment for creativity and innovation (see, e.g., [4] and references therein). Since R&D in industry takes place almost exclusively in teams, team work is the key for running a successful research process. Two types of teams seem to be particularly suitable for creative R&D work: crossfunctional and multidisciplinary teams. Crossfunctional teams consist of members who have different functions and specialisms, for instance in research, marketing, controlling and production. In these teams expertise in developing *and* launching new products or technologies are linked. Multidisciplinary teams are especially suited to developing new technologies by pooling the expertise of, for instance, chemists, physicists and engineers.

The organization of R&D addressed to process intensification can be briefly illustrated by considering Degussa's approach where it is realized in the form of a so-called "project house". Project houses have been developed by Degussa for multiunit research. They are a part of *Creavis Technologies & Innovation*, the Degussa R&D unit that attends to crosscompany and crossportfolio research activities to develop new fields of business and technologies. Project houses are formed for a limited time period of three years with the participation of several Degussa business units and Creavis and are linked into internal and external research networks. They include multidisciplinary project teams whose members are recruited from different business and service units. Since process intensification addresses the drastic improvement of a process using novel technologies by rethinking processes as a whole, knowledge of actually existing and realized

technologies and products must be brought together with special knowledge in novel equipment and process technology. The concept of project houses is ideally tailored to these requirements. Sustainability is guaranteed because at the end of a project house's existence, either the business units market the results generated in the form of new products and processes or (in cases where concepts cannot be developed within the business units) internal start-ups for business development are founded.

2.2

Microreaction Technology

2.2.1

Principal Features

Microreaction technology is based on chemical microprocessing that is characterized by a continuous flow of matter through well-defined structures with dimensions that characteristically lie in the interval 0.1–1000 μm . When comparing microreaction technology with (conventional) reaction technology the distinguishing phenomena are usually described as “microeffects” or “scaling effects”. Important microeffects are the strongly intensified heat and mass transport in directions of the small lateral dimensions of the apparatus due to diffusion and heat conduction. These are no longer negligible in comparison to convection and are responsible for drastically enhanced heat and mass transfer. Both result in specific advantages over conventional process technology. For example, the usage of microreactors prevents the occurrence of hot spots due to the greatly improved heat dissipation. This makes possible higher reactant concentrations, higher catalyst loading or the use of highly active catalysts when dealing with exothermic reactions. For a comprehensive introduction we refer to [5].

Microreaction technology is used in each of the three phases of product or process development. In the development laboratory it is especially useful in providing precisely defined conditions. Another advantage is its usage in high-throughput experiments. In process development the characteristics mentioned above turn microreaction systems into powerful tools even if the process itself is to be realized using conventional technology. Microreaction technology is particularly useful here in searching for optimal process parameters and in providing benchmarks. A drastically accelerated process development is possible if microstructured equipment is used in production. It is not necessary to perform time-consuming studies for the scale up because the production scale can be realized *in principle* by parallelization; i.e. by multiple repetitions of the microstructured *elements* (“numbering up” the elements). To date, such chemical microprocesses have only been built as pilot plants, largely due to the formidable challenges that must be overcome in the development of technical concepts, and that go beyond the requirements for conventional processes.

2.2.2

Catalytic Wall Reactors

This section offers a short overview of research and process development in a field that is the target of one of the key projects in Degussa's project-house process intensification. Most of this survey has been published recently by Hüther et al. [3].

Partial oxidations are one of the most important classes of gas-phase reactions in the chemical industry. Usually these reactions are highly exothermic and solid catalysts are used. Since the product is generated by an only partial oxidation of the reactant, total oxidation has to be avoided as either a side reaction or an elementary step in a series of reactions. The control of residence time and especially reaction temperature are essential for the enhancement of the selectivity of partial oxidations. A brief look at the reaction enthalpies of ethylene oxide, one of the major intermediate products based on ethylene (in 1999 the world capacity was 14.5 million tonnes per year [6]) illustrates the crucial importance of heat control. The reaction enthalpy of the partial oxidation of ethylene to ethylene oxide is -105 kJ/mol, while the total oxidation of ethylene resulting in carbon dioxide and water is more than one order of magnitude larger at -1327 kJ/mol. Consequently this side reaction causes the occurrence of regions of extremely high temperatures (hot spots) with negative impact on the selectivity and the lifetime of catalysts.

In order to enhance space-time yields of catalytic gas-phase reactions, two strategies are in principle possible: the improvement of catalyst activity or the implementation of more intense process conditions. This usually leads to an increase of heat production that can only be partially released, if at all, using conventional reactor technology.

A simple estimation of the temperature profile inside a tube reactor starts from an energy balance for the system [7]. Since we are particularly interested in the performances of a tube reactor and a catalytic wall reactor the following simplifying assumptions are made:

1. A constant heat conduction and viscosity is achieved.
2. Heat conduction in the longitudinal direction is neglected.
3. Friction in the bed of solid catalyst pellets is neglected.
4. It is assumed that the reactor is an ideal tubular flow reactor.
5. The temperature dependence of the reaction is neglected.

The final assumption is a drastic simplification that leads to an *underestimation* of the temperature increase. The temperature T of an arbitrary point in the catalytic bed may be related to the effective thermal conductivity λ , the heat of reaction ΔH_R and the rate of reaction \tilde{r} by the differential equation

$$\lambda \left(\frac{\partial^2 T}{\partial r^2} \right) - \Delta H_R \cdot \tilde{r}(c, T) = 0 \quad (2.1)$$