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 cavitational reactors and subsequent industrial applications based on the theoretical and experimental analysis of the net cavitational 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.

References

- 1 Hüther, A.; Geißelmann, A.; Hahn, H.: Chem. Ing. Tech., **77** (2005), 1829
- 2 Kleemann, G.; Hartmann, K.: Wiss. Z. Tech. Hochschule "Carl Schorlemmer", Leuna Merseburg, **20** (1978), 417
- 3 Ramshaw, C.: Chem. Eng. (London), **389** (1983), 13
- 4 Cross, W.T.; Ramshaw, C.: Chem. Eng. Res. Des., **64** (1986), 293
- 5 Stankiewicz, A.I.; Moulijn, J.A.: Chem. Eng. Prog., **96** (2000), 22
- 6 BHR Group: www.bhrgroup.com/pi/aboutpi.htm
- 7 see Chapter 2, this book
- 8 Machhammer, O.: Chem. Ing. Tech., **77** (2005), 1635
- 9 Stankiewicz, A.I.; Moulijn, J.A. (Eds.): Re-engineering the chemical processing plant: process intensification, Marcel Dekker, New York (2004)
- 10 Hessel, V.; Hardt, S.; Löwe, H.: Chemical Micro Process Engineering, Wiley-VCH, Weinheim (2004)
- 11 Marcano, J.G.S.; Tsotsis, T.T.: Catalytic Membranes and Membrane Reactors, Wiley-VCH, Weinheim (2002)
- 12 Koch, M.V.; VandenBussche, K.M.; Christman, K.M.: Micro Instrumentation in High Throughput Experimentation and Process Intensification, Wiley-VCH, Weinheim (in preparation, January 2007)
- 13 Wang, Y.; Holladay, J.D. (Eds.): Microreactor Technology and Process Intensification (ACS Symposium Series No. 914), ACS Publ. (2005)

- 14 Jachuck, R. (Ed.): *Process Intensification in the Chemical and Related Industries*, Blackwell, Oxford (in preparation)
- 15 Charpentier, J.-C.: *Chem. Eng. Technol.*, **28** (2005), 255
- 16 Jachuck, R.: *Chem. Eng. Res. Des.*, **80** (2002), 233
- 17 Nigam, K.D.P.; Larachi, F.: *Chem. Eng. Sci.*, **60** (2005), 5880
- 18 Agar, D.: *Chem. Eng. Sci.*, **54** (1999), 1299
- 19 Burns, J.R.; Jamil, J.N.; Ramshaw, C.: *Chem. Eng. Sci.*, **55** (2000), 2401
- 20 Kreutzer, M.T.; Kapteijn, F.; Moulijn, J.A.; Heiszwolf, J.: *Chem. Eng. Sci.*, **60** (2005), 5895
- 21 Liu, T.; Gepert, V.; Vesper, G.: *Chem. Eng. Res. Des.*, **83** (2005), 611
- 22 Gavriilidis, A.; Angeli, P.; Cao, E.; Young, K.K.; Wan, Y.S.S.: *Eng. Chem. Res. Des.*, **80** (2002), 3
- 23 Matlosz, M.: *Chem. Ing. Tech.*, **77** (2005), 1393
- 24 Kreutzer, M.T.; Kapteijn, F.; Moulijn, J.; Ebrahimi, S.; Kleerebezem, R.: *Ind. of Eng. Chem. Res.*, **44** (2005), 9646
- 25 Drioli, E.; di Profio, G.; Fontananova, E.: *Fluid/Particle Separ. J.*, **16** (2004), 1
- 26 Iliuta, J.; Larachi, F.: *Can. J. Chem. Eng.*, **81** (2003), 776
- 27 Muthukumaram, S.; Kentish, S.E.; Stevens, G.W.; Ashokkumar, M.: *Rev. Chem. Eng.*, **22** (2006), 155
- 28 Keil, F.J.; Swamy, K.M.: *Rev. Chem. Eng.*, **15** (1999), 85
- 29 van Eldik, R.; Hubbard, C.D. (Eds.): *Chemistry under Extreme and Non-classical Conditions*, Wiley & Spektrum Akademischer Verlag, New York, Heidelberg (1997)