Integrated Chemical Processes

Synthesis, Operation, Analysis, and Control

Edited by
Kai Sundmacher,
Achim Kienle and
Andreas Seidel-Morgenstern

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Contents

Preface

In the chemical industries, the pretreatment of educts, their chemical conversion into valuable products, and the purification of resulting product mixtures in downstream processes are carried out traditionally in sequentially structured trains of unit operations. In many cases, the performance of this classical chemical process structure can be significantly improved by an integrative coupling of different process units.

The integration of unit operations to form multifunctional processes very often gives rise to synergetic effects which can be technically exploited. By suitable process design, an efficient and environmentally benign process operation can be achieved. Possible advantages of process integration include:

- higher productivity;
- higher selectivity;
- reduced energy consumption;
- improved operational safety; and
- improved ecological harmlessness by avoidance of auxiliary agents and chemical wastes.

Due to the interaction of several process steps in one apparatus, the steady-state and the dynamic operating behavior of an integrated process unit is often much more complex than the behavior of single, non-integrated units. Therefore, suitable methods for the design and control must be developed and applied, ensuring optimal and safe operation of the considered integrated process.

The major objectives of current research activities in this highly interesting domain of chemical engineering are to develop new concepts for process integration, to investigate their efficiency, and to make them available for technical application. The importance of this field is reflected by the increasing number of articles in journals and book contributions that have been published during the past three decades (Fig. 1).

Among these published articles and books, some excellent reviews have appeared which focused on specific aspects of the process integration. Agar and Ruppel [1] were among the first to investigate the whole area of integration of heat-exchanging functions in chemical reactors, whilst Agar [2] later also surveyed other innovative integration concepts in chemical reactor engineering. According to the present editors' knowledge, the first review which covered a broader range of integration concepts including heat exchange, separation and also mechanical unit operations, was published in 1997 by Hoffmann and Sundmacher [3]. The cited works refer to integrated chemical processes as "multifunctional reactors", which is often used as a

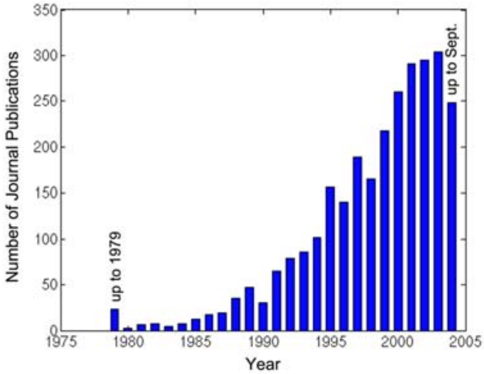

Fig. 1. Journal publications on integrated chemical processes according to the Science Citation Index.

synonym. Multifunctional reactors can be seen as a very important sub-class of the area of "process intensification" which was summarized by Stankiewicz and Moulin [4].

A comprehensive volume covering all aspects of integrated chemical processes including heat exchange, separations and mechanical unit operations is still missing, however, and as a consequence the present book was prepared to fill this gap. The book's chapters have been authored by leading international experts, and provide overviews on the present state of knowledge and on challenging future issues.

The book is divided into three parts. Part I surveys concepts for heat-integrated chemical reactors, with special focus on coupling reactions and heat transfer in fixed beds and in fuel cells. Part II is dedicated to the conceptual design, control and analysis of chemical processes with integrated separation steps, whilst Part III focuses on how mechanical unit operations can be integrated into chemical reactors.

Part I:
Integration of Heat Transfer and Chemical Reactions

Chapters 1 to 3 discuss two recent and important applications of heat-integrated chemical reactions. Chapter 1, by Kolios et al., is concerned with high-temperature endothermic processes in *heat integrated fixed-bed reactors*. Emphasis is placed on reforming processes, which are widely used for the production of basic chemicals and fuels from fossil feed stocks. These processes require large amounts of heat at temperatures up to 1000 °C. In conventional solutions, only about half of the heat supplied at high temperatures is transferred into the endothermic reaction. Emerging applications such as decentralized hydrogen production for residential and mobile power generation require considerable improvement in specific productivity and thermal efficiency. Therefore, this topic is currently the subject of vivid research activities in industry and academia alike. Chapter 1 also includes an introduction to the fundamentals of heat-integrated processes, an overview on recent trends in process and apparatus design, and an analysis of the state of the art, with special emphasis on the steam reforming of methane.

The focus in Chapters 2 and 3 is on *high-temperature fuel cells with internal reforming*. In particular, special attention is given to the Molten Carbonate Fuel Cell (MCFC) which is increasingly used for decentralized power generation. In Chapter 2, Heidebrecht and Sundmacher use a simple model of an MCFC to discuss the pros and cons of alternative reforming concepts in high-temperature fuel cells.

The *temperature management in a fuel cell stack* is a key issue in the operation of high-temperature fuel cells. In Chapter 3, prepared by Mangold and colleagues, it is shown that the temperature-dependence of the electrolyte's electrical conductivity is a potential source of instabilities, hot spots, and spatial temperature patterns.

Part II: Integration of Separation Processes and Chemical Reactions

Due to fact that chemical reactions typically do not deliver the desired product alone and that separation processes are always required, a wide range of efforts have long been undertaken to combine these two processes into a single apparatus. Although a comprehensive overview was published recently [5], nine chapters of the present book describe and discuss the possibilities of integrating separation processes and chemical reactions.

In Chapter 4, Sundmacher et al. – in the first contribution – analyze in detail the thermodynamic and kinetic effects relevant to an understanding of *reactive distillation processes*. Although a comprehensive volume on this type of process integration was published in 2003 [6], Chapter 4 focuses on the *a priori* determination of products that can be obtained using such processes.

In exploiting the equilibrium theory, Kienle and Grüner present in Chapter 5 a general analysis of the development and propagation of *nonlinear waves* in reaction separation processes. Besides considering reactive distillation as one example, these authors also analyze reactive chromatography.

In Chapter 6, Morbidelli et al. describe *chromatographic separations combined with chemical reactions*, the focus of their contribution being to present possibilities of performing such processes in a continuous manner.

An analysis of reactors where *adsorbents* are used *as a regenerative source or sink* for one or several of the reactants is discussed systematically by Agar, in Chapter 7.

In cases where reactive distillation cannot be applied because some of the reactants are temperature-sensitive, *reactive stripping* might be an efficient alternative, and the current state of the application of this technology is reviewed by Kapteijn and colleagues in Chapter 8.

Another powerful concept is to combine *absorption processes with chemical reactions*, and a large number of possible concepts for this approach is presented in Chapter 9 by Kenig and Górak.

In addition, *extraction processes* can be performed with reacting species, and several advantages of this technique may be realized compared to conventional consecutive processes, as discussed by Bart in Chapter 10.

Based on a thorough analysis of *reactive crystallization*, Ng and colleagues, in Chapter 11, demonstrate that such integrated processes can also be performed efficiently with solid phases involved.

In the final chapter of Part II, Seidel-Morgenstern presents two examples of how *membrane reactors* might become an alternative to conventional technology.

Part III: Integration of Mechanical Unit Operations and Chemical Reactions

The last four chapters of the book are dedicated to the successful combination of chemical reactions and mechanical process operations. In Chapter 13, Janssen elucidates that *reactive extrusion* has emerged from a scientific curiosity to an industrial process. Nonlinear effects in this process can give rise to instabilities that are of thermal, hydrodynamic, or chemical origin.

In Chapter 14, Hoffmann and colleagues provide a survey on the status and directions of *reactive comminution*. In this type of process integration, mechanical stress exerted in mills is used to enhance the chemical reactions of solids with fluids. Simultaneously, chemical reactions can generate cracks in solid particles and thereby enhance their comminution.

Filtration and chemical reactions can be usefully integrated in order to separate diesel soot particles efficiently from motor exhaust gases, and this is illustrated by Rieckmann and Völker in Chapter 15, together with a series of other examples of reactive filtration processes which are realized in the chemical industries.

In the final chapter, Mörl and coworkers analyze the complex interaction of particle *granulation and/or agglomeration with chemical reactions* in fluidized beds. For the description of the particle property distribution, a population balance approach is recommended which is mathematically challenging but which provides valuable insight into the steady-state and dynamic process operating behavior.

The Book's History, and the Editors' Acknowledgments

The present book is the outcome of the International Max Planck Symposium on Integrated Chemical Processes held in Magdeburg, Germany, on 22–24 March, 2004. At this symposium, renowned scientists met to discuss the current state and future trends in the field of integrated chemical processes. The conference was organized by this book's editors and their colleagues at the Max Planck Institute for Dynamics of Complex Technical Systems, with financial support from the Kompetenznetz Verfahrenstechnik Pro3 e.V. in Germany, which is gratefully acknowledged.

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References

1. D. W. Agar, W. Ruppel, Multifunktionelle Reaktoren für die heterogene Katalyse, *Chem. Ing. Tech.* **1988**, *60,* 731–741.
2. D. W. Agar, Multifunctional Reactors: Old Preconceptions and New Dimensions, *Chem. Eng. Sci.* **1999**, *54,* 1299–1305.
3. U. Hoffmann, K. Sundmacher, Multifunktionale Reaktoren, *Chem.-Ing.-Tech.* **1997**, *69,* 613–622.
4. A. I. Stankiewicz, J. A. Moulin, Process Intensification, *Chem. Eng. Progress,* **2000**, *Jan.,* 22–34.
5. S. Kulprathipanja, (Ed.) *Reactive Separation Processes,* Taylor & Francis, New York, 2002.
6. K. Sundmacher, A. Kienle, (Eds.), *Reactive Distillation, Status and Future Directions,* Wiley-VCH, Weinheim, 2003.

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