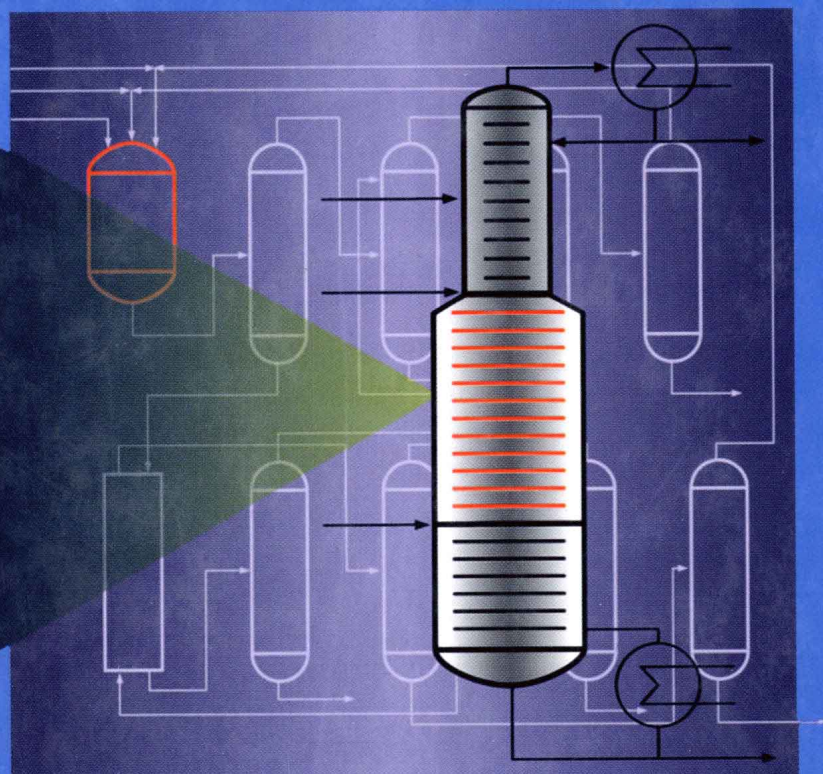


Reactive Distillation

Status and Future Directions

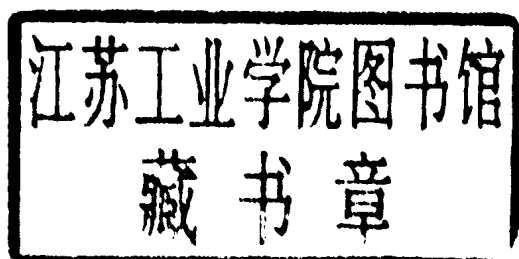
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Kai Sundmacher and Achim Kienle (Eds.)

Reactive Distillation

Status and Future Directions



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Preface

In the chemical process industries, chemical reaction and the purification of the desired products by distillation are usually carried out sequentially. In many cases, the performance of this classic chemical process structure can be significantly improved by integration of reaction and distillation in a single multifunctional process unit. This integration concept is called 'reactive distillation' (RD); when heterogeneous catalysts are applied the term 'catalytic distillation' is often used.

As advantages of this integration, chemical equilibrium limitations can be overcome, higher selectivities can be achieved, the heat of reaction can be used in situ for distillation, auxiliary solvents can be avoided, and azeotropic or closely boiling mixtures can be more easily separated than in non-RD. Increased process efficiency and reduction of investment and operational costs are the direct results of this approach. Some of these advantages are realized by using reaction to improve separation; others are realized by using separation to improve reaction.

Most important industrial applications of RD are in the field of esterification processes such as the famous Eastman Chemical Co.'s process for the synthesis of methyl acetate [1]. This process combines reactive and non-reactive sections in a single hybrid RD column and thereby replaces a complex conventional flowsheet with 11 process units. With this RD technology investment and energy costs were reduced by factor five [2]. Another success story of RD was started in the 1980s by using this technology for the preparation of the ethers MTBE, TAME, and ETBE, which are produced in large amounts as fuel components because of their excellent antiknock properties [3].

Nowadays, many research and development activities are under way to introduce RD into other chemical processes. But despite the convincing success of RD in esterification and etherification applications, it is important to note that RD is not always advantageous. In some cases it is not even feasible. Therefore, the development of reliable tools for the conceptual design of RD processes is one of the most important fields of current research activities.

Due to the interaction of reaction and distillation in one single apparatus, the steady-state and dynamic operational behavior of RD can be very complex. Therefore, suitable process control strategies have to be developed and applied, ensuring

optimal and safe operation. This is another very important area of current and future research and development.

Today, RD is discussed as one part of the broader area of reactive separation, which comprises any combination of chemical reaction with separation such as distillation, stripping, absorption, extraction, adsorption, crystallization, and membrane separation. In the next decade, unifying approaches to reactive separators should be developed allowing the rigorous selection of the most suitable type of separation to be integrated into a chemical reactor.

Despite the fact that the basic idea of combining reaction and distillation is old, there has been an enormously growing interest in the design and operation of RD processes in recent years. Fig. 1 shows the number of journal papers that have appeared on the subject during the last 30 years. It is worth noting that the total number of publications including the papers in conference proceedings and so on is a multiple of the number of publications in scientific journals. In an analogous manner, the industrial interest in applying this attractive process technology has increased continuously. This is reflected by the steadily growing number of patents applied since 1970.

Despite the large number of publications only a few review papers have been written on this topic so far. Podrebarac et al. [4] highlighted the advantages of RD and gave an overview on potential uses of catalytic distillation. The review by Taylor and Krishna [5] focused mainly on the modeling aspects of RD. Doherty and Malone [6] gave valuable commentaries on future trends and challenges in this field of research. Gorak and co-workers [7] summarized rate-based modeling techniques for RD and also for reactive absorption. Book chapters on RD are available in volumes on distillation technology by Stichlmair and Fair [8], and by Doherty and Malone [9], and also in a recent book on reactive separations [10].

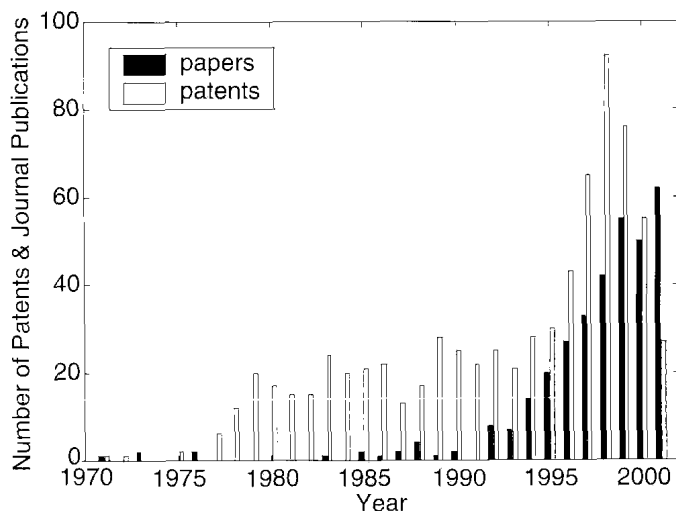


Fig. 1. Journal publications on reactive and catalytic distillation over the last three decades according to the Science Citation Index and patents in these fields according to the Deutsches Patent- und Markenamt (www.depatris.net)

Moreover, since RD is going to become a more established technology, it has found its way into classic chemical engineering encyclopedias [11, 12].

However, a comprehensive volume covering all aspects of application, design, analysis, and control of RD processes is still missing. To fill this gap, the present book was prepared. Its chapters are written by leading international experts from both academic institutions and industrial companies. They summarize the present state of knowledge and give an outlook on challenging issues in the future.

The book is divided into four parts: Part I surveys various industrial applications and covers both established large-scale processes as well as new chemical reaction schemes with high future potential. Part II provides the vital details for analysis of reactive phase equilibria, and discusses the importance of chemical reaction kinetics, while Part III focuses on identifying feasible column configurations and the design of their internal structure. Analysis and control of the complex dynamic and steady-state behavior of RD processes are described in Part IV.

Part I Industrial Applications

Chapters 1–3 give a survey of chemical reaction schemes that are performed successfully in RD columns and present ideas for new applications. Sharma and Mahajani (Chapter 1) point out that RD has acquired its new status only recently in spite of the fact that the concept has been used in various processes since 1860s. Over the last two decades, especially after the commissioning of large-scale plants for MTBE and methyl acetate production, RD has been seen as a promising reactor/separator that can fulfill multiple objectives simultaneously. With respect to applications, engineers and chemists have started looking beyond the classic esterification and etherification reactions. Hydrogenation, hydrodesulfurization, isomerization, and oligomerization are some of the unconventional examples to which RD has been successfully applied on a commercial scale. Moreover, hydrolysis, alkylation, acetalization, hydration, and transesterification have also been identified as potential candidates for RD. Another important area of application is the removal of small amounts of impurities to obtain high quality product (e.g., phenol). RD can also be used for the recovery of valuable products like acetic acid, glycols, lactic acid, and so on from waste streams.

Schoenmakers and Bessling (Chapter 2) give an overview of the tools that are available today and the methods that are now introduced in the industrial practice of chemical companies. A process synthesis procedure gives good qualitative reference points. Simulation tools have been developed that are mainly based on equilibrium models. But there are further steps to go on the way to the realization of an industrial plant. The scale-up from the miniplant scale used for the experimental validation of a new process is well known for conventional distillation, but complicated by several facts for RD especially in the case of heterogeneous catalysis. To overcome these problems either reference plant experience on an industrial scale or (if not available) further research is required. Other options both for homogeneous and heterogeneous catalysis are possible and are discussed

in the contribution. The authors emphasize that the combination of reaction and distillation not necessarily has to be operated in a counter-current column. For slower reactions a broad variety of equipment not necessarily containing columns can be used.

In Chapter 3, Tuchlenski and colleagues illustrate a procedure for process design on an industrial scale using the decomposition of the fuel ether MTBE into methanol and isobutene as an important example. Based solely on thermodynamic considerations, a plausible column configuration is derived. In order to study the scale-up of structured packing, experiments were performed on the lab scale as well as on the pilot scale. While lab scale experiments could be described satisfactorily with a simple equilibrium stage model, the same approach failed in the case of pilot plant experiments. Hydrodynamics, maldistribution and/or mass-transfer limitations might be a reasonable explanation and are worth more thorough investigation. The authors conclude that pilot plant operation is indispensable to establish a heterogeneously catalyzed RD process.

Part II Physicochemical Fundamentals

Chapters 4 and 5 are dedicated to the thermodynamic and kinetic fundamentals of RD processes. In Chapter 4, Hasse reviews the fundamentals of thermodynamic modeling of simultaneous phase and reaction equilibria. The author emphasizes the importance of consistency of phase equilibrium models. Thermodynamic consistency provides a sound basis for developing predictive reaction models for RDs, which are valid over a wide range of concentrations. To develop phase equilibrium models, reliable experimental data of phase equilibria in reactive systems have to be available. For successful measurements, suitable experimental techniques are needed, which are briefly summarized in this chapter. Criteria for their selection are also given.

Sundmacher and Qi (Chapter 5) discuss the role of chemical reaction kinetics on steady-state process behavior. First, they illustrate the importance of reaction kinetics for RD design considering ideal binary reactive mixtures. Then the feasible products of kinetically controlled catalytic distillation processes are analyzed based on residue curve maps. Ideal ternary as well as non-ideal systems are investigated including recent results on reaction systems that exhibit liquid-phase splitting. Recent results on the role of interfacial mass-transfer resistances on the attainable top and bottom products of RD processes are discussed. The third section of this contribution is dedicated to the determination and analysis of chemical reaction rates obtained with heterogeneous catalysts used in RD processes. The use of activity-based rate expressions is recommended for adequate and consistent description of reaction microkinetics. Since particles on the millimeter scale are used as catalysts, internal mass-transport resistances can play an important role in catalytic distillation processes. This is illustrated using the syntheses of the fuel ethers MTBE, TAME, and ETBE as important industrial examples.

Part III Process Design

Chapters 6–8 focus on process design, i. e. determining suitable column configurations, suitable operating conditions, and suitable column internals. Chapter 6 by Doherty and co-workers is concerned with conceptual process design. Geometrical methods are provided, which allow at the initial stages of process development to decide quickly whether RD is likely to be a good process concept. The attainable region approach for reaction-mixing systems is applied to systems with simultaneous reaction and separation in order to assess the possible selectivity-yield-conversion benefits of this technology. Feasible direct and indirect sharp splits are predicted with a model in which each column section is represented by a series of concurrent isobaric flashes. In the limits of no reaction, or of chemical equilibrium, the model reduces to conventional models for distillation lines, and each column section can be represented by the same equations. However, at intermediate rates of reaction the models for the column sections are different, and new results are obtained. A bifurcation study shows the limits of feasibility including the influence of flow rate, catalyst level and holdup. Unlike distillation without reaction, limited ranges of feasibility in all of these variables are found.

Chapter 7 by Krishna is concerned with hardware selection and design for RD columns. An overview on available hardware for homogeneously as well as heterogeneously catalyzed RD processes is given. Criteria for suitable hardware selection are discussed and illustrated by different case studies. It is shown that the requirements for hardware selection are different from conventional non-RD. The author concludes that especially for heterogeneously catalyzed RD processes it is almost impossible to reconcile the conflicting requirements and introduces the side reactor concept as a promising alternative to overcome many of these conflicting hardware issues.

Chapter 8 by Kunz and Hoffmann introduces a special catalyst technology developed by the authors. State of the art in industrial catalyst technology is to use catalyst particles with a size in the millimeter range and to sew these particles into a wire mesh or glass-fiber clothing to form structured packing. The manufacturing process makes this type of packing expensive. In contrast to this, unstructured packing materials like Raschig rings are much cheaper. However, so far, Raschig rings with comparable catalytic activity are not commercially available. In the present contribution the authors introduce various methods for the preparation of catalytically active rings by polymerization of ion-exchange resin into the pores of a carrier material. Application is tested for MTBE synthesis. Based on this technology monolithic polymer/carrier materials were developed, which can be used for other reactive separation processes like reactive chromatography and polymer-assisted solution-phase organic synthesis.

Part IV Modeling and Process Control

Chapters 9 and 10 are on modeling, dynamics, and control of RD processes. The contribution by Taylor and Krishna (Chapter 9) deals with the modeling of homogeneously and heterogeneously catalyzed RD processes. The focus of this contribution is on steady-state behavior. First, the equilibrium stage model is introduced, which is readily obtained from the non-reactive case by adding reaction terms. Afterwards, non-equilibrium stage models are introduced as a more rigorous approach. It is shown that different types of non-equilibrium models apply to homogeneously and heterogeneously catalyzed processes. In the homogeneous case, further distinction has to be made between slow and fast liquid-phase reactions. In the heterogeneous case distinction between negligible and finite intraparticle diffusion inside the catalyst is essential. Finite intraparticle diffusion can be modeled with the dusty fluid model, which is an extension by the authors of the well-known dusty gas model. Finally, cell models are introduced to account for non-ideal flow patterns on distillation trays and maldistribution in packed columns. Equilibrium and non-equilibrium models are compared for different process applications including MTBE, TAME, and ethylene glycol synthesis and a perspective on the use of non-equilibrium models in RD process design is given.

The final contribution by Kienle and Marquardt (Chapter 10) gives an overview of the present knowledge of non-linear dynamics and control of RD columns. First, focus is on open-loop dynamics. It is shown that RD processes can sometimes show an intricate non-linear dynamic behavior, a profound understanding of which is not only of scientific interest but also very important for improved process design and operation. Basic terminology, methods, and tools are introduced for analyzing and understanding non-linear dynamics. Three different types of reaction systems are introduced including esterification, etherification, and the ethylene glycol system. Different patterns of behavior are identified depending on the reaction systems and the operating conditions. In the equilibrium regime of the chemical reaction the dynamic behavior of a RD column is qualitatively similar to a non-RD column, whereas in the kinetic regime the chemical reaction rate is dominating. For closely boiling mixtures, like in many etherification processes, the behavior in the kinetic regime is very similar to a single phase isothermal reactor. Additional effects arise for mixtures of components with completely different boiling points as for the ethylene glycol system, for example. In the second part, available guidelines for control structure selection and control system design are summarized. Emphasis is on the equilibrium regime. Here, similar methods as in non-RD apply. Additional complexity is introduced in inferential control schemes, where temperature is used as a cheap, fast, and reliable measurement instead of concentration. The authors conclude that control studies for kinetically controlled processes are missing to a large extent.

Book History and Acknowledgments

The present book is the outcome of the *1st International Workshop on Reactive Distillation* held at the Max Planck Institute for Dynamics of Complex Technical Systems in Magdeburg, Germany, on 2–3 July 2001. The goal of this workshop was to bring together world-renowned pioneering scientists and leading industrial experts in the field of RD on a common platform. The workshop was organized by the editors and their colleagues with financial support from the Kompetenznetz Verfahrenstechnik Pro3 e. V., Germany, which is gratefully acknowledged.

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Contents

Preface *XI*

List of Contributors *XIX*

Part I Industrial Applications

1 Industrial Applications of Reactive Distillation 3

- 1.1 Introduction 3
- 1.2 Etherification: MTBE, ETBE, and TAME 14
- 1.3 Dimerization, Oligomerization, and Condensation 15
- 1.4 Esterification: Methyl Acetate and Other Esters 16
- 1.5 Hydrolysis of Esters 18
- 1.6 Hydration 20
- 1.7 Hydrogenation/Hydrodesulfurization/Hydrocracking 20
 - 1.7.1 Benzene to Cyclohexane 21
 - 1.7.2 Selective Hydrogenation of C₄ Stream 21
 - 1.7.3 Hydrogenation of Pentadiene 21
 - 1.7.4 C₄ Acetylene Conversion 22
 - 1.7.5 Hydrodesulfurization, Hydrodenitrogenation, and Hydrocracking 22
 - 1.7.6 Miscellaneous Hydrogenations 22
- 1.8 Chlorination 23
- 1.9 Acetalization/Ketalization 23
- 1.10 Recovery and Purification of Chemicals 24
- 1.11 Difficult Separations 25
- 1.12 Chemical Heat Pumps 26
- 1.13 RD with Supercritical Fluids 26
- 1.14 Conclusions 26

2 Reactive Distillation Process Development in the Chemical Process Industries 30

- 2.1 Introduction 30
- 2.2 Process Synthesis 32
- 2.3 Process Design and Optimization 35

2.4	Limitations of the Methods for Synthesis and Design: the Scale-Up Problem	37
2.5	Choice of Equipment	38
2.6	Some Remarks on the Role of Catalysis	46
2.7	Conclusions	46
2.8	Acknowledgments	47
2.9	Notation	47
3	Application of Reactive Distillation and Strategies in Process Design	49
3.1	Introduction	49
3.2	Challenges in Process Design for Reactive Distillation	51
3.2.1	Feasibility Analysis	51
3.2.2	Catalyst and Hardware Selection	51
3.2.3	Column Scale-Up	51
3.3	MTBE Decomposition via Reactive Distillation	52
3.3.1	Conceptual Design	52
3.3.2	Model Development	54
3.3.2.1	Catalyst Selection and Reaction Kinetics	55
3.3.2.2	Phase Equilibrium Model	55
3.3.2.3	Steady-State Simulation	56
3.3.3	Lab-Scale Experiments	57
3.3.4	Pilot-Plant Experiments	58
3.4	Conclusions	61
Part II	Physicochemical Fundamentals	
4	Thermodynamics of Reactive Separations	65
4.1	Introduction	65
4.2	Process Models for Reactive Distillation	66
4.2.1	Outline	66
4.2.2	Case Study: Methyl Acetate	66
4.3	Equilibrium Thermodynamics of Reacting Multiphase Mixtures	70
4.4	Fluid Property Models for Reactive Distillation	74
4.4.1	Outline	74
4.4.2	Examples	75
4.4.2.1	Hexyl Acetate: Sensitivity Analysis	75
4.4.2.2	Methyl Acetate: Prediction of Polynary Vapor–Liquid Equilibria	77
4.4.2.3	Butyl Acetate: Thermodynamic Consistency	81
4.4.2.4	Ethyl Acetate: Consequences of Inconsistency	82
4.4.2.5	Formaldehyde + Water + Methanol: Intrinsically Reactive Complex Mixture	83
4.5	Experimental Studies of Phase Equilibria in Reacting Systems	88
4.5.1	Outline	88
4.5.2	Reactive Vapor–Liquid Equilibria	90
4.5.2.1	Batch Experiments	90
4.5.2.2	Flow Experiments	91

4.5.2.3	Recirculation Experiments	92
4.6	Conclusions	92
4.7	Acknowledgments	93
4.8	Notation	93
5	Importance of Reaction Kinetics for Catalytic Distillation Processes	97
5.1	Introduction	97
5.2	Reactive Ideal Binary Mixtures	98
5.2.1	Reaction-Distillation Process with External Recycling	100
5.2.1.1	(∞, ∞) -Analysis	101
5.2.1.2	(∞, N_{\min}) -Analysis	102
5.2.2	Distillation Column with Reactive Reboiler	103
5.2.3	Fully Reactive Distillation Column	106
5.3	Kinetic Effects on Attainable Products	109
5.3.1	Singular Point Analysis	110
5.3.2	Ideal Ternary Mixtures	112
5.3.2.1	Case a: $\alpha_{AC} = 0.2$, $\alpha_{BC} = 3.0$	112
5.3.2.2	Case b: $\alpha_{AC} = 5.0$, $\alpha_{BC} = 3.0$	112
5.3.3	Non-Ideal Mixtures	115
5.3.3.1	Synthesis of MTBE	115
5.3.3.2	Synthesis of TAME	117
5.3.4	Systems with Liquid-Phase Splitting	121
5.3.5	Systems with Interfacial Mass-Transfer Resistances	126
5.4	Determination and Analysis of Reaction Kinetics	129
5.4.1	Physicochemical Transport Phenomena	129
5.4.2	Process Evaluation by Dimensionless Numbers	131
5.4.3	Formulation of Reaction Rate Expressions	133
5.4.4	Importance of Transport Resistances for Column Operation	135
5.5	Conclusions	138
5.6	Acknowledgments	139
5.7	Notation	140
Part III	Process Design	
6	Feasibility and Process Alternatives for Reactive Distillation	145
6.1	Introduction	145
6.2	Motivation	147
6.3	Flash Cascade Model	153
6.4	Feasibility Hypothesis	156
6.5	Bifurcation Analysis of the Flash Cascade Model	160
6.6	Conclusions	165
6.7	Notation	165