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Reactive Distillation

Status and Future Directions

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Status and Future Directions

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Prof. Dr.-Ing. Kai Sundmacher,
Prof. Dr.-Ing. Achim Kienle
Max Planck Institute for Dynamics
of Complex Technical Systems
Sandtorstraße 1
39106 Magdeburg
Germany

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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].

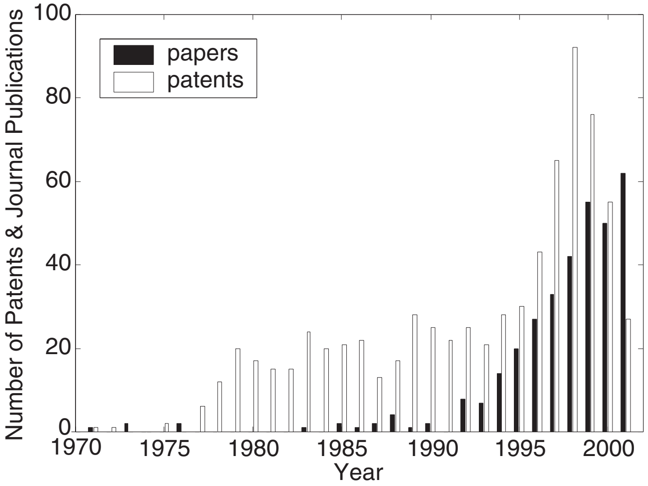

Fig. 1. Journal publications on reactive and catalytic distillation over the last three decades according to the Science Citation Index and patents in these fields according to the Deutsches Patent- und Markenamt (www.depatis.net)

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 co-current 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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Max-Planck-Institut für Dynamik
komplexer technischer Systeme
Magdeburg, Germany
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Kai Sundmacher
and Achim Kienle

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List of Contributors

B. Bessling
BASF Corporation
Wyandotte, MI, USA

N. Chadda
Department of Chemical Engineering
University of Massachusetts
Amherst, MA 01003-3110, USA

M. F. Doherty
Department of Chemical Engineering
University of California
Santa Barbara, CA 93106, USA
mfd@engineering.ucsb.edu

T. Frey
Lehrstuhl für Fluidverfahrenstechnik
Technische Universität München
85747 Garching, Germany

S. B. Gadewar
Department of Chemical Engineering
University of Massachusetts
Amherst, MA 01003-3110, USA

H. Hasse
Institute of Thermodynamics
and Thermal Process Engineering
University of Stuttgart
70550 Stuttgart, Germany
hasse@itt.uni-stuttgart.de

U. Hoffmann
Institut für Chemische Verfahrenstechnik
Technische Universität Clausthal
Leibnitzstr. 17
38678 Clausthal-Zellerfeld, Germany

A. Kienle
Max Planck Institute for Dynamics
of Complex Technical Systems
Sandtorstr. 1
39106 Magdeburg, Germany
kienle@mpi-magdeburg.mpg.de

R. Krishna
Department of Chemical Engineering
University of Amsterdam
Nieuwe Achtergracht 166
1018 WV Amsterdam, The Netherlands
krishna@science.uva.nl

U. Kunz
Institut für Chemische Verfahrenstechnik
Technische Universität Clausthal
Leibnitzstr. 17
38678 Clausthal-Zellerfeld, Germany

S. M. Mahajani
Department of Chemical Engineering
Indian Institute of Technology
Bombay, Powai, Mumbai, India 400 076

M. F. Malone
Department of Chemical Engineering
University of Massachusetts
Amherst, MA 01003-3110, USA

W. Marquardt
Lehrstuhl für Prozesstechnik
RWTH Aachen
Turmstrasse 46
52064 Aachen, Germany
secretary@lfpt.rwth-aachen.de

F. Nierlich
Oxeno Olefinchemie GmbH
45764 Marl, Germany

T. Pöpken
Process Technology & Engineering
Degussa AG
45764 Marl, Germany

Z. Qi
Max Planck Institute for Dynamics
of Complex Technical Systems
Sandtorstr. 1
39106 Magdeburg, Germany
qi@mpi-magdeburg.mpg.de

D. Reusch
Process Technology & Engineering
Degussa AG
45764 Marl, Germany

H. G. Schoenmakers
Process Engineering
BASF AG
67056 Ludwigshafen, Germany

M. M. Sharma
Jawaharlal Nehru Centre
for Advanced Research
502 Saurabh
Plot No. 39
Kunger Marg, Swastik Park
Chembur, Mumbai, India 400 071
mmsharma@bom3.vsnl.net.in

J. Stichlmair
Lehrstuhl für Fluidverfahrenstechnik
Technische Universität München
85747 Garching, Germany

K. Sundmacher
Max Planck Institute for Dynamics
of Complex Technical Systems
Sandtorstr. 1
39106 Magdeburg, Germany
sundmacher@mpi-magdeburg.mpg.de

R. Taylor
Department of Chemical Engineering
Clarkson University
Potsdam, NY, 13699–5705 USA
taylor@clarkson.edu

A. Tuchlenski
Process Technology & Engineering
Degussa AG
45764 Marl, Germany
axel.tuchlenski@degussa.com

Part I
Industrial Applications

1

Industrial Applications of Reactive Distillation

M. M. Sharma and S. M. Mahajani

1.1

Introduction

Reactive distillation (RD) is a combination of separation and reaction in a single vessel. The concept of combining these two important functions for enhancement of overall performance is not new to the chemical engineering world. The recovery of ammonia in the classic Solvay process for soda ash of the 1860s may be cited as probably the first commercial application of RD, as shown in Fig. 1.1. Many old processes have made use of this concept. The production of propylene oxide, ethylene dichloride, sodium methoxide, and various esters of carboxylic acids are some examples of processes in which RD has found a place in some form or the other, without attracting attention as a different class of operation. It was not until the 1980s, thanks to the enormous demand for MTBE (methyl *tert*-butyl ether), that the process gained separate status as a promising multifunctional reactor and separator.

The commercial success of RD for the production of MTBE was immediately followed by another remarkable achievement with the Eastman Kodak process that condensed the whole chemical plant for methyl acetate in a single RD unit that accepts reactants and delivers pure products. Since this demonstration of its ability to render cost-effectiveness and compactness to the chemical plant, RD has been explored as a potentially important process for several other chemicals and reactions. Along with esterifications and etherification, other reactions such as acetalization, hydrogenation, alkylation, and hydration have been explored. This chapter gives an overview of the efforts being made in this direction and suggests some potentially important processes for RD. The objectives of existing and potential applications of RD are to: surpass equilibrium limitation, achieve high selectivity towards a desired product, achieve energy integration, perform difficult separations, and so on. One or more of these benefits are offered by the processes in which RD

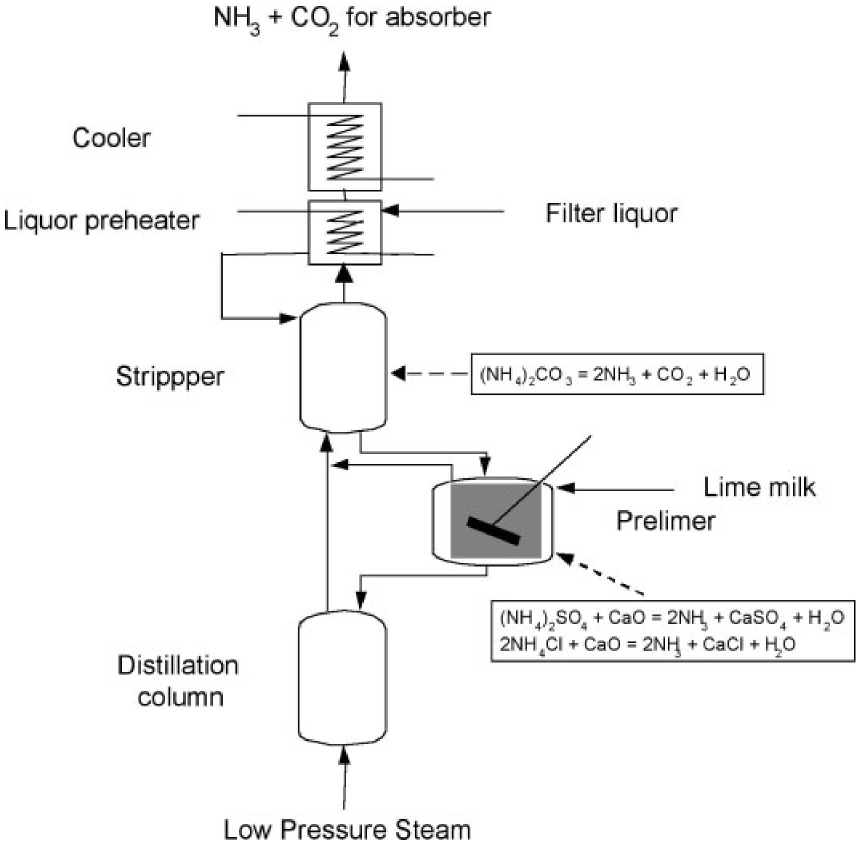

Fig. 1.1 Ammonia recovery in Solvay process

is used. Tab. 1 gives a comprehensive list of the reactions that have been investigated as candidates for RD. Tab. 2 suggests some potentially important reactions that should be investigated. Because of the large number of such reactions, it is not possible to describe each reacting system in detail here. The application of RD to the most important reactions is described here to give an overview of the issues related to industrial use of RD.

Table 1.1 Industrially important reactions, either implemented on a commercial scale or have been investigated on laboratory scale, using RD.

Reaction	*Catalyst/column internals etc.*	*Remarks on motives and achievements*	*Reference*
Etherification			
methanol + isobutene = methyl *tert* butyl ether (MTBE)	Amberlyst-15	to enhance the conversion of isobutene and achieve separation if isobutene from C_4 stream	[1, 2]
methanol + isoamylene = *tert* amyl methyl ether (TAME)	ion-exchange resin	to enhance the conversion of isoamylene	[1, 3]
ethanol/bioethanol + *tert* butyl alcohol = ethyl *tert* butyl ether (ETBE) + water	Amberlyst-15 pellet structured Amberlyst-15	to effectively utilize bioethanol and surpass equilibrium conversion	[4]
isopropanol + propylene = diisopropyl ether (DIPE)	ZSM 12, Amberlyst-36 Zeolite	a two-stage process that uses water and propylene as feed	[5]
Esterification with alcohols/olefins			
acetic acid + methanol = methyl acetate + water	Dowex 50 W X-8	recovery of acetic acid from dilute streams (30–60 % w/w)	[6]
	Amberlyst-15 (baskets on trays)	recovery of acetic acid from dilute streams (2.5–10 % w/w)	[7]
	Katamax packing		[8]
	sulfuric acid	recovery of dilute acetic acid in carbonylation process	[9]
		manufacture of methyl acetate; overcomes azeotrope formation; enhances conversion (> 99 %)	[12]
butanol + acetic acid = butyl acetate + water	cation exchange resin	for recovery of acetic acid from dilute aqueous solutions	[13, 14]
2-methyl propanol + acetic acid = 2-methyl propyl acetate	Katapak-S	manufacture of 2-methyl propyl acetate	[15]
lactic acid + methanol = methyl lactate + water	Dowex 50-W	for recovery of lactic acid from fermentation broth	[16]
myristic acid + isopropanol = isopropyl myristate + water		for recovery of myristic acid	[17]

Table 1.1 (continued)

Reaction	*Catalyst/column internals etc.*	*Remarks on motives and achievements*	*Reference*
Esterification with alcohols/olefins			
silylated compounds + sulfuric acid = silylated sulfuric acid ester	non-reactive packings	for recovery of silylated compounds from pharmaceutical wastes	[18]
propane diol monoalkyl ether + carboxylic acid = propylene glycol monoalkyl ether carboxylate	acidic catalyst; toluene as an entrainer		[19]
acetic acid/acrylic acid/formic acid + cyclohexene = cyclohexyl carboxylate	ion-exchange resin bags		[20]
Synthesis of vinyl acetate			
acetaldehyde + acetic anhydride = vinyl acetate		improved safe process with high yields	[21]
Transesterification			
polytetramethylene glycol diacetate + methanol = polytetramethylene glycol + methyl acetate			[22]
dialkyl carbonate + phenol/ethanol = diaryl carbonate + alcohol	lead compound/zeolites; phenol as entrainer	alternative to the conventional process that uses phosgene; effective removal of alcohol to improve yields	[23, 24]
acetic acid + vinyl stearate = stearic acid + vinyl acetate			[25]
Hydrolysis			
methyl acetate + water = methanol + acetic acid	ion-exchange resin bags	recovery of acetic acid and methanol in polyvinyl alcohol (PVA) and terephthalic acid (PTA) manufacture	[26, 27]
	fluidized RD		[28]
	cation exchanger on inert	recovery of acetic acid in PVA manufacture	[29]
acrylonitrile to acrylamide	copper oxide catalyst	less side product formation	[30]

Table 1.1 (continued)

Reaction	*Catalyst/column internals etc.*	*Remarks on motives and achievements*	*Reference*
Acetalization			
methanol + aqueous formaldehyde = methylal + water	ion-exchange resins zeolites, ion-exchange resins	to surpass equilibrium conversion; to remove formaldehyde as an impurity (e. g., from 1,2-butyne diol)	[31, 32, 33]
ethanol + aqueous formaldehyde = ethylal + water	ion-exchange resins	recovery of formaldehyde and synthesis of ethylal	[34]
ethylene glycol + formaldehyde	ion-exchange resins	recovery of formaldehyde and synthesis of acetal	[35]
propylene glycol + acetaldehyde/formaldehyde	ion-exchange resin	recovery of propylene glycol	[36]
MeCOCHO + methanol = methyl glyoxal dimethyl acetal + water	acid catalyst, preferably ion exchanger; azeotropic separation of water	to enhance rate and conversion	[37]
Aldol condensation followed by dehydration			
acetone to diacetone alcohol (DAA) and mesityl oxide	anion exchange resin	high selectivity towards DAA; enhanced conversion level	[38]
n-butaraldehyde to 2-ethyl hexenal	aqueous alkaline solution	formation of trimers/tetramers of aldehyde is avoided	[39]
Hydration/dehydration			
ethylene oxide + water = ethylene glycol	cationic/anionic exchange resins	to enhance selectivity towards MEG and avoid formation of diethylene glycol (DEG); attain better temperature control over the exothermic reaction	[40, 41, 42]
isobutene + water = *tert* butyl alcohol	cationic exchange resin	to overcome equilibrium limitation	[43, 44]
hydration of propylene to isopropanol	cationic exchange resin	to overcome equilibrium limitation	[45]
hydration of isoamylene to *tert*-amyl alcohol	Amberlyst-15 (catalytic-bales)	enhanced yield and selectivity	[5]
hydration of cyclohexene to cyclohexanol	SiO_2/Ga_2O_3	surpass equilibrium conversion	[46]

Table 1.1 (continued)

Reaction	*Catalyst/column internals etc.*	*Remarks on motives and achievements*	*Reference*
Alkylation/trans-alkylation/dealkylation			
benzene + propylene = cumene	Union Carbide- LZY-82 molecular sieves	use of exotherm of reaction; high purity cumene	[48, 44]
	suspended catalyst process	suitable for dilute benzene and dilute olefin	[49]
m-xylene (MX) + di-*tert*-butyl benzene (TBB) = *tert* butyl *m*-xylene (TBMX) + *tert*-butyl benzene and TBB + MX = TBMX + benzene		separation of *m*-xylene and *p*-xylene	[50]
benzene + ethylene/propylene = alkyl benzene	zeolite-β	suitable for dilute benzene and dilute olefin	[51, 52]
benzene (from refinery stream) + ethylene/propylene = alkyl benzene		to reduce amount of benzene from gasoline	[53]
alkylation of aromatics with C_4 to C_{15} olefins and dealkylation of the alkylated product	molecular sieves	the product is considered to be the best motor octane component of gasoline; indirect skeletal isomerization of olefins	[54]
isobutane + propylene/butylene = highly branched paraffins	Lewis acid promoted inorganic oxide catalyst	selectivity for C_7/C_8 branched alkanes	[55]
Isomerization			
α-isophorone = β-isophorone	adipic acid, ZSM-5, alumina	to surpass the equilibrium conversion	[56]
butene-2 = butene-1	alumina-supported palladium oxide	to upgrade C_4 stream and get high conversion	[57]
butene-1 = butene-2	standard hydrogenation catalyst	for separation of isobutylene from C_4 stream	[58]
n-paraffin to *iso*-paraffins	Chlorinated alumina catalyst, presence of hydrogen ($<$ 8 bar)	To increase the octane value of paraffin stock	[59]
Chlorination			
dichlorobenzene to trichlorobenzene		to increase selectivity towards trichlorobenzene	[60]
dichlorodimethyl silane to dichloro (chloromethyl) silane	photochlorination	increased yields towards monochlorinated product	[61]