

INTERNATIONAL JOURNAL OF CHEMICAL REACTOR ENGINEERING

Volume 2

2004

Review R1

Industrial Applications of Reactive Distillation: Recent Trends

Rameshwar S. Hiwale*

Nitin V. Bhate†

Yogesh S. Mahajan‡

Sanjay M. Mahajani**

*Indian Institute of Technology, Bombay, rameshwar@che.iitb.ac.in

†Indian Institute of Technology, Bombay, nvbhate@che.iitb.ac.in

‡Indian Institute of Technology, Bombay, yogmaha@iitb.ac.in

**Indian Institute of Technology, Bombay, sanjaym@che.iitb.ac.in

ISSN 1542-6580

Copyright ©2004 by the authors.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher, bepress.

Industrial Applications of Reactive Distillation: Recent Trends

Rameshwar S. Hiwale, Nitin V. Bhate, Yogesh S. Mahajan, and
Sanjay M. Mahajani

Abstract

Last few years have seen a dramatic rise in the number of applications of reactive distillation (RD). This useful technology is now being applied for any scale of operation- from manufacture of fine chemicals to that of bulk chemicals. This article reviews the very recent applications and serves as a supplement for the exhaustive review on this subject by Sharma and Mahajani (2003). It not only furnishes the information on the ongoing research in the existing applications but also elaborates the newly discovered applications such as manufacture of phenol, linear alkyl benzene, carbonates, chlorosilane derivatives and chiral chemicals. Multiple reactions in RD, failure of RD in some cases and new RD configurations to increase the overall yields are some of the additional aspects being covered.

KEYWORDS: Reactive distillation, Catalytic Distillation, Etherification, Hydrogenation, Esterification

1 INTRODUCTION

Reactive Distillation (RD) is a combination of reaction and distillation in a single vessel owing to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. Improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes are a few of the advantages that reactive distillation offers. The introduction of an *in situ* separation in the reaction zone or vice versa leads to complex interactions between vapor–liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for design and synthesis of these systems. RD being a relatively new field, the research on various aspects such as modeling and simulation, process synthesis, column hardware, non-linear dynamics and control etc. is in progress. The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products, reaction and distillation temperatures etc. and hence, the use of RD for every reaction may not be feasible. Exploring the candidate reactions for RD, itself is an area that needs considerable attention to expand the domain of RD processes.

RD has been successfully used and investigated in the past for several reactions such as etherification, esterification, hydrogenation, hydrodesulfurisation and polymerization. Various reviews have been published on this aspect (Doherty and Buzad, 1992; Podrebarac et al., 1997; Taylor and Krishna, 2000; Mahajani and Chopade, 2001; Sharma and Mahajani, 2003 and Ng and Rempel, 2003). However, even after the recent review by Sharma and Mahajani (2003) that was presented in the first international workshop on reactive distillation held at Magdeburg, Germany in 2001, an increasing number of articles have appeared in the last couple of years. Figure 1, which is an updated version of the recently published statistics (Malone and Doherty, 2000), shows that there are around 180 papers and 100 patents published in the last two years on reactive distillation alone. This clearly reveals the increasing interest in this area. Apart from the theoretical aspects of RD, we see the research being performed mainly in two different directions, firstly, in improving the performance of RD for the existing applications and secondly, in exploring new applications. Hence, considering the growing rate of publications, we felt it necessary to review this voluminous information shortly after the gap of about 2-3 years. The present article is intended to serve as a supplement to the review by Sharma and Mahajani (2003) which we feel the reader to go through as well, in order to get an idea of the entire spectrum of reactions that comes under the umbrella of reactive distillation.

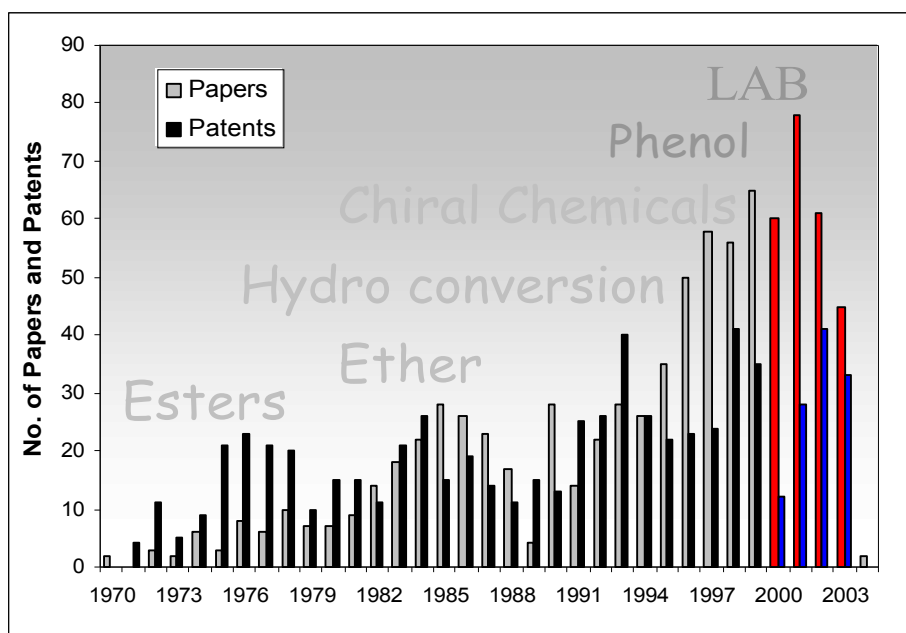


Figure 1: An updated statistics of patents and publications

An exhaustive list of recently investigated reactions with references is given in Table 1. It mainly includes the literature reports on the existing and new applications in the last three years. Table 2 highlights the potential of reactive distillation to conduct multiple reactions. Reactive distillation may not always be a feasible option since it has its own limitations. Some of these cases are listed in Table 3. It is not possible to discuss every reaction from this list in detail here and hence only a few representative systems have been discussed in the following sections.

2 ESTERIFICATION

The commercial successes of reactive distillation for the production of methyl acetate and MTBE are living examples to highlight the strong domain of reactive distillation. Esterification and etherification reactions are associated with reactive distillation right from its early days and the discussion on commercial applications cannot be complete without the due coverage to these reactions. Following is a brief discussion on the recent work on RD for various esterification reactions.

2.1 Synthesis of $C_4 - C_5$ acetates

Esterification of acetic acid with alcohols like *n*-butanol, isobutyl alcohol, amyl alcohol and hexanol fall in a typical class of the reacting systems (Eq. 1). The alcohols are sparingly soluble in water and the ester is almost insoluble. Another interesting feature of this system is that it is associated with the formation of a minimum boiling azeotrope, which is heterogeneous in nature. Hence, in a typical reactive distillation column that consists of both reactive and non-reactive zones, the heterogeneous azeotrope can be removed as the top product. Moreover, the aqueous phase that forms after the condensation of the vapor is almost pure water. It can be conveniently withdrawn as a product and the organic phase can be recycled back as reflux. The bottom product is also a pure ester, which is the least volatile component in the system. A typical reactive distillation column used for these reacting systems is shown in Figure 2.

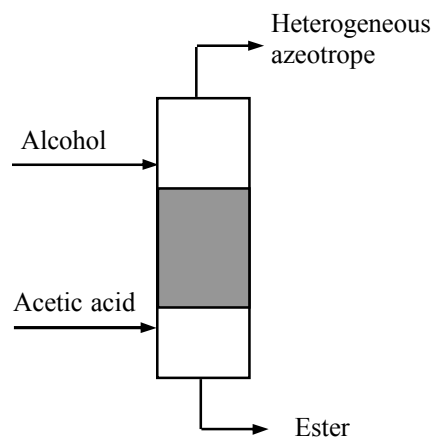
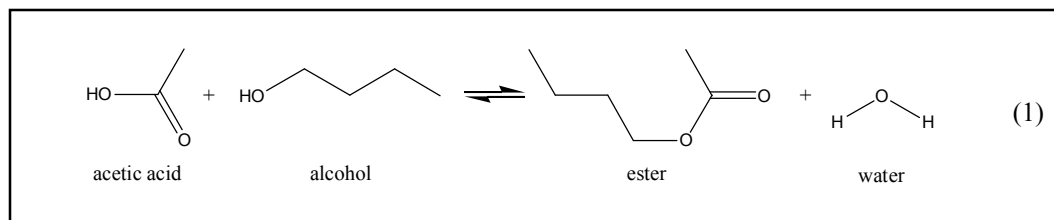


Figure 2: Synthesis of C_4-C_5 acetates with reactive distillation

Butyl acetate is an important chemical with an application as a versatile solvent. It is used in large quantities as a useful solvent for various applications. Synthesis of butyl acetate is commonly carried out by esterification of *n*-butanol with acetic acid in the presence of a suitable acid catalyst. The reaction is reversible in nature making it difficult to produce required product purity, despite the equilibrium constant favoring the production of butyl acetate. Simultaneous removal of product(s) during the course of the reaction is beneficial to obtain enhanced conversion. For this purpose various methods, such as reactive distillation and reactive extraction have been adopted. Butyl acetate synthesis using homogenous catalyst is still being practiced. However, problems like difficulty in separation of catalyst from product stream, corrosion and disposal problems are likely to occur in homogenous catalyzed processes. Hence, solid cation exchange resin is considered to be an important catalyst for liquid phase reactions. Recently, the esterification of *n*-butanol with acetic acid using reactive distillation has been investigated (Hanika et al., 1999 and Lederer et al., 2002). This reaction is also being studied in the author's laboratory (Gangadwala, 2002; Hiwale et al., 2002; Hiwale, 2003 and Gangadwala et al., 2003). Conversion close to 100% is realized with almost stoichiometric ratio of butanol to acetic acid. The work has also brought forward an important limitation of reactive distillation in this specific case. Because of the typical concentration and temperature profiles along the length of the column one gets *n*-dibutyl ether as an undesired side product that is not known to form otherwise in the slurry or fixed bed reactor. However, this strongly depends on the feed location.

Amyl acetate which is another important solvent ester that may be synthesized using RD. Chiang et al. (2002) present a comparison between two better alternatives for this process, coupled reactor/column and reactive distillation. Their results, in terms of the total annual cost, indicate that reactive distillation is four times more efficient than the other alternative for this process. A possible control system for the process by reactive distillation has also been suggested.

Due to its unique ability to dissolve both polar and non-polar compounds, methyl isopropyl acetate finds an important place as a solvent and component in paints and adhesives. The reaction of acetic acid and 2-methyl propanol carried out in a reactive distillation column containing ion exchange resins and the simulation studies show good agreement and report almost 100% conversion (Smejkal et al., 2001 and Hanika et al., 2001). However, to meet the market specifications, the ester needs to be separated from acetic acid by subsequent distillation steps.

2.2 Synthesis of methyl acetate/ethyl acetate

Methyl acetate is used as an intermediate in the manufacture of a variety of polyesters such as photographic film base, cellulose acetate, Tenite cellulosic plastics and Estron acetate. The conventional processes before 1980's used multiple reactors with large excess of one of the reactants to achieve high conversion of the ester. Sharma and Mahajani (2003) have discussed in detail the process for the manufacture of methyl acetate by reactive distillation. The process developed by Eastman Kodak, uses near stoichiometric mole ratio of methanol and acetic acid to obtain high purity and ultra-pure methyl acetate. In this process, at low reflux ratio, separation is poor whereas at high reflux ratio the reactant methanol tends to get separated through enrichment of azeotrope of methanol and methyl acetate. A sufficient conversion is possible only through a double feed strategy because acetic acid as a separate feed stream, acts as an entrainer and helps separate water effectively. Along with MTBE synthesis, this reaction has been and is being used by many researchers as a model reaction for experimental and modeling studies on Reactive Distillation.

A number of articles and patents have been published in the recent years containing excellent material on various aspects of the methyl acetate synthesis process like characterization of the various catalysts used, effect of change in operating conditions on the performance and hydrolysis of methyl acetate (Fernholtz et al., 2000; Kolodziej et al., 2001 and Poepken et al., 2001). Extensive work has been done on ethyl acetate as well in the recent years (Vora and Dautidis, 2001 and Lee and Westerberg, 2001). Okur and Bayramoglu (2001) have studied the effect of the liquid-phase activity model on the simulation of ethyl acetate production by reactive distillation. The potential of homogeneously catalyzed reactive distillation to increase conversion and improve selectivity has been highlighted by Kenig et al. (2001).

2.3 Esterification of Fatty acids

Esterification of high boiling acids and/or alcohols is an interesting application of reactive distillation. The boiling temperatures involved in such processes are relatively high and can adversely affect the catalyst life. Efforts are being made to use efficient catalyst and entrainer to obtain best performance in reactive distillation column (Omota et al., 2003a; Omota et al., 2003b; Steinigeweg and Gmehling, 2003 and Dimian et al., 2004).

3 TRANSESTERIFICATION

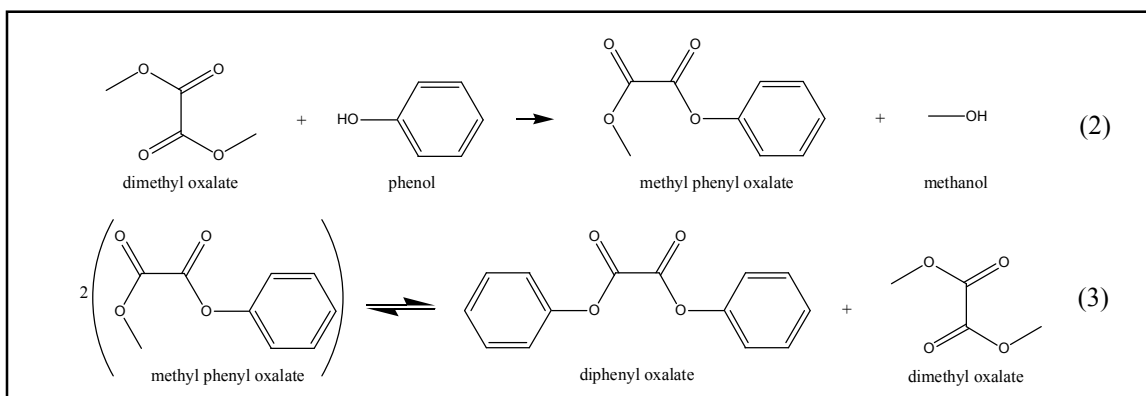
3.1 Production of butyl acetate

Sometimes transesterification can be a beneficial alternative to hydrolysis as it does not involve formation of water and moreover, it brings out value addition through formation of another ester. Jimenez and Lopez (2002) applied a new strategy called extractive reactive distillation for the production of butyl acetate.

The raw material, a byproduct from the polyvinyl alcohol process is a mixture of methanol and methyl acetate (30 wt% methyl acetate). It is first concentrated to 80% methyl acetate and then reacted with *n*-butanol to form butyl acetate and methanol by reactive distillation. To eliminate the azeotropes (especially the methanol-methyl acetate) *o*-xylene is used as an entrainer. The authors studied kinetics and chemical equilibrium of transesterification with polymeric acid resin as a catalyst. Based on dynamic modeling, controller implementation was also considered. Using this technique high purity butyl acetate and 100% yield of *n*-butanol have been reported. However, in addition to above advantages, preliminary economic survey revealed that the use of combined reactive and extractive distillation strategy is not profitable.

3.2 Production of oxalates

Diaryl oxalates, such as diphenyl oxalate, find an important place in the production of carbamates. Conventional processes use diaryl carbonate as a starting material, which is expensive. Moreover, many undesired by-products are formed which makes the separation further difficult. In addition to this, these processes have extremely low rates of reaction. The state-of-the-art process based on reactive distillation using homogeneous catalyst has been proposed by Nishihira et al. (2000). Alkyl phenyl oxalate, the starting material for the synthesis of diphenyl oxalate is obtained by the ester interchange reaction of dialkyl oxalate with a phenol compound in a reactive distillation column (Eq. 2). This is followed by the disproportionation of alkyl phenyl oxalate to diphenyl oxalate and dialkyl oxalate (Eq. 3) and their efficient separation which is either carried out in the same column or a separate column. The catalyst system based on organic tin compounds and Lewis acid compounds is common for both the reactions. The major advantage of reactive distillation is reduction in the formation of by-products as compared to the conventional process.



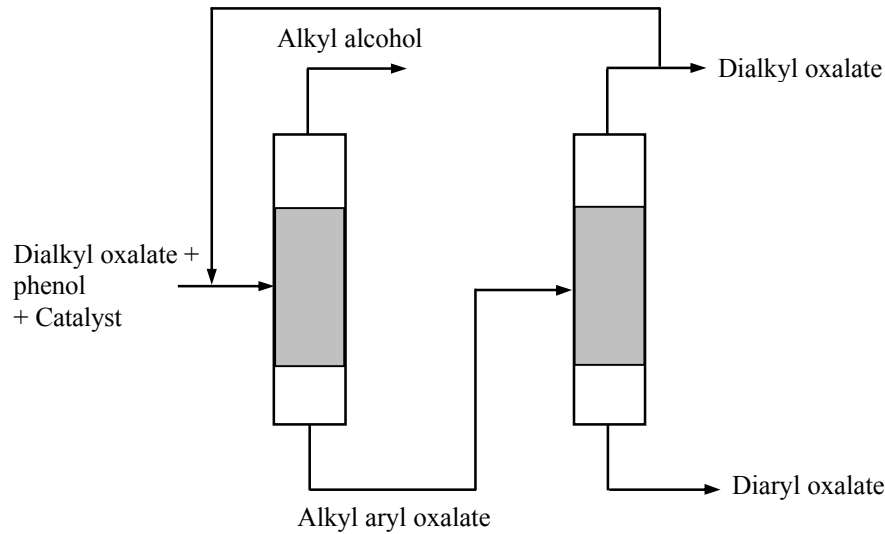


Figure 3: Synthesis of Diaryl Oxalate (Nishihira et al., 2000)

Reactive distillation has also been used for synthesis of high molecular weight esters. Substituted hydroxy-hydro-cinnamate esters were prepared by continuous transesterification of the corresponding lower alkyl monoester with an alkanol or polyol using reactive distillation (Schaerfl et al., 2001). The continuous reaction results in improved product throughput and product quality compared to the known batch-type process.

4 HYDROLYSIS

4.1 Hydrolysis of methyl acetate

Methyl acetate is produced in great amounts as a byproduct from purified terephthalic acid (PTA) plants and polyvinyl alcohol (PVA) plants. Since methyl acetate is a less valuable solvent, methyl acetate is sold at a low price or hydrolyzed to methanol and acetic acid, which are more valuable, by a hydrolysis reaction followed by conventional distillation processes.

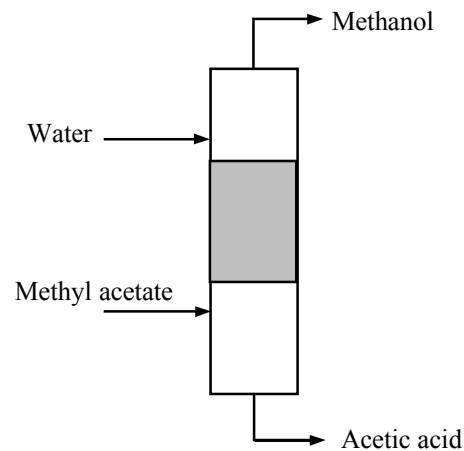


Figure 4: Hydrolysis of Methyl Acetate (Hoyme and Holcombe, 2002)

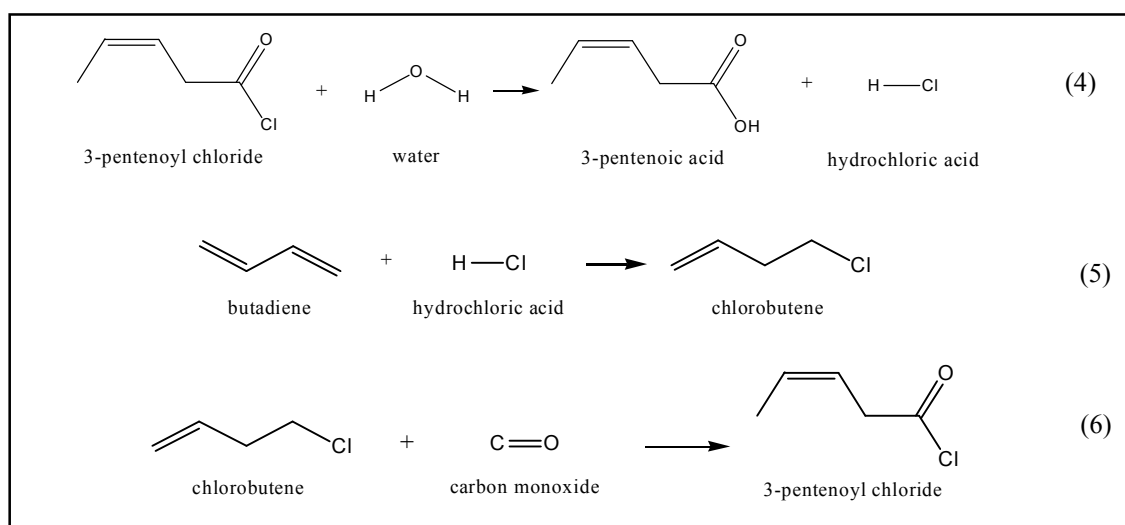
The conversion is unfavorable at equilibrium (equilibrium constant 0.14 – 0.2) and a large amount of unconverted methyl acetate needs to be separated and recycled as the low equilibrium constant and presence of interfering azeotrope inhibit the hydrolysis of methyl acetate via conventional processes. The early work by Fuchigami (1990) on reactive distillation is considered to be pioneering and is well discussed by Sharma and Mahajani (2003). Methyl acetate is fed to a reaction zone (Fig. 4) of a reactive distillation column wherein reaction zone is at a temperature and pressure required to preferentially hydrolyze methyl acetate to produce acetic acid and dimethyl ether, which can be produced by the dehydration of methanol by using an alumina catalyst (Hoyme and Holcombe, 2002). The hydrolysis of methyl acetate has also been recently studied by a number of researchers and the conversions close to 100% have been reported (Poepken et al., 2001; Von et al., 2001; Von et al., 2002; Xiao et al., 2001 and Wang, 2001). In another process, etherification and hydrolysis take place simultaneously in a RD column. The ether thus formed may further be converted back to the alcohol (Wang, 2001).

4.2 Hydrolysis and alcoholysis of alkyl halides

3-pentenoic acid synthesized by hydrolysis of 3-pentenoyl chloride (Eq. 4) is an important intermediate in the preparation of adipic acid from butadiene. Ester of pentenoic acid can be obtained by alcoholysis of pentenoyl chloride. Hydrolysis of pentenoyl chloride in the presence of 75% (w/w) chlorobutenes is a mass transfer limited reaction requiring excess aqueous phase. However, minimum quantity of water and methanol is desired to minimize the formation of side products viz. chlorovaleric acid and methyl chloride.

The reaction, if carried out in a reactive distillation column as shown in Fig 5, can do the needful by keeping hydrochloric acid separate from the product acid or methanol (Murphree and Ozer, 1996). Usually, the feed stream to the column consists of a mixture of pentenoyl chloride and chlorobutenes. Thus, if butadiene is introduced near the top of the reactive distillation column, the hydrochloric acid produced during the process can react to form chlorobutene (Eq. 5) which can subsequently undergo carbonylation in presence of a suitable catalyst to give 3-pentenoyl chloride (Eq.6).

Use of RD for dehydrohalogenation reactions has also been successfully demonstrated recently for the manufacture of neo-hexene through the reaction of *tert*-butyl bromide and ethylene by Lin et al. (2003).



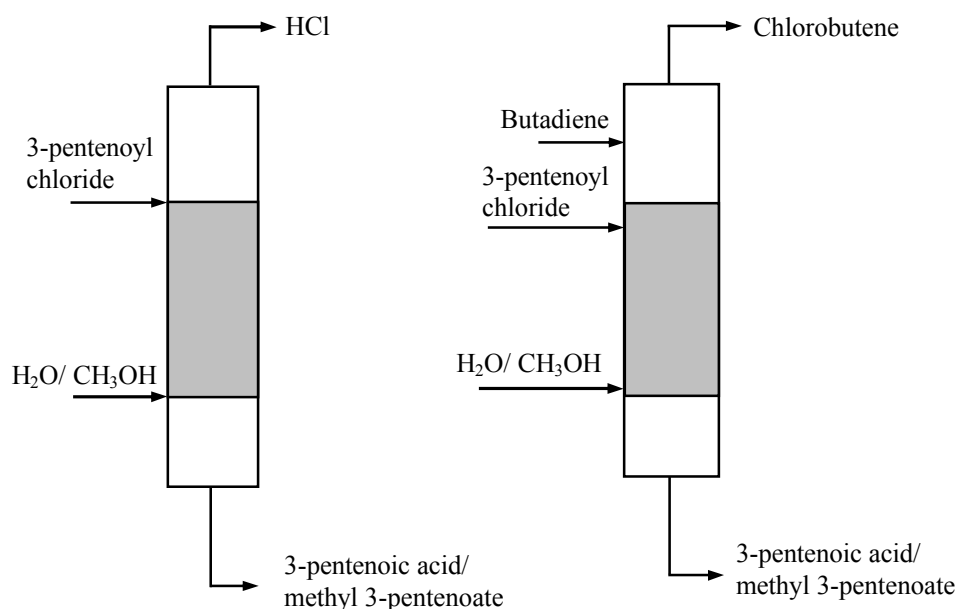
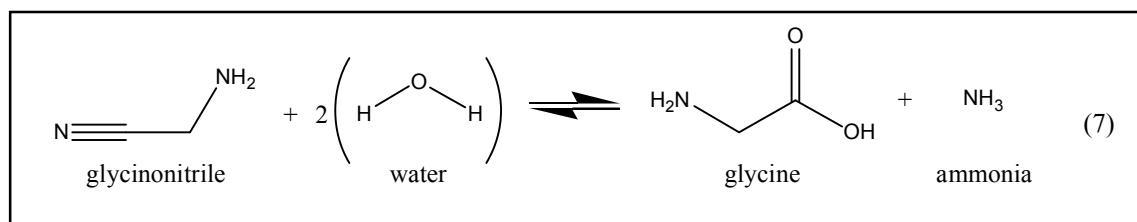


Figure 5: Different schemes for the synthesis of Pentenoic acid (Murphree and Ozer, 1996)

4.3 Reactive distillation for the manufacture of glycine from glycinonitrile



In practice, prior to carrying out acid hydrolysis of amino nitriles, the amino group is first trapped using strong acids so as to prevent its reaction with the acid catalyst. However, after hydrolysis the salt formed is converted back to the respective amine group using a suitable base. All these lead to waste disposal problems.

RD has the potential to make most of the conventional processes salt-free and eliminate the waste disposal problems. Manufacture of glycine from glycinonitrile is one such process that is promoted by removal of ammonia by reactive distillation (Eq. 7). The salt free RD process does not require the addition of acid, alkali, and buffer solution to adjust the pH. Reactive distillation is carried out at reduced pressure and/or in the presence of inert gas (Aoki and Otsubo, 2001).

5 ETHERIFICATION

5.1 Production of MTBE, ETBE and TAME

Etherification, especially the synthesis of methyl *tert*-butyl ether (MTBE) has been probably the most studied reacting system in RD as is evident in the previous reviews (Taylor and Krishna, 2000 and Sharma and Mahajani, 2003). It is a well-known fact that MTBE and other fuel ethers are promising fuel additives. The tremendous demand for these ethers in the last two decades along with the suitability of RD technology

for these products has truly given a boost to the research in the field reactive distillation on every front. Even after the recent ban on MTBE in USA and some other countries, the research work continues to flow and a number of patents and articles have appeared alone on RD for fuel ethers in the recent part. About 99.9% of isobutene with 98% pure MTBE as a bottom product from the RD column have recently been reported by Rix et al. (2003).

Several workers have studied the reactive distillation processes for production of ethers including MTBE, ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME) using ion exchange resin as catalyst. Many researchers report excellent work on modeling, control studies in detail. Detailed study of the MTBE production has been presented by a large number of researchers (Stein et al., 2000; Baur et al., 2000; Chen et al., 2000; Baur et al., 2001a; Baur et al., 2001b; Giessler et al., 2001; Lee and Westerberg, 2001; Beckmann et al., 2002; Chen et al., 2002; Grund et al., 2002 and Noeres et al., 2003). Also, studies on ETBE process have been presented (Tian and Tade, 2000a; Tian and Tade, 2000b; Quitain et al., 2000; Sneesby and Tade, 2000; Al-Arfaj and Luyben, 2000; Bisowarno and Tade, 2002; Li et al., 2003a and Li et al., 2003b) and TAME production process using reactive distillation has been studied (Li et al., 2003a; Li et al., 2003b; Baur and Krishna, 2002; Peng et al., 2002 and Baur et al., 2003).

Improvisation of the etherification of methanol and isobutene has also been attempted using β -Zeolite-coated catalytic packing in a reactive distillation column. The study of the steady state composition profiles and of the characteristics of the reaction reveals that the optimal operating conditions are a pressure of 0.7 MPa, a methanol/isobutene feed molar ratio of unity and a reflux of more than 3. Reactive distillation is found to achieve high conversion whereas in conventional systems the overall yield of the process is less due to the non-ideality in the vapor-liquid equilibrium of the reactive system which leads to incomplete separation of isobutene (Li et al., 2002).

5.2 Separation of isobutene from hydrocarbon mixture

The C₄ fraction of hydrocarbon generally contains 1-butene, 2-butene, *n*-butane, butadiene and isobutene. Butadiene is separated by extractive distillation. However, the separation of remaining components is economically not favored because of small difference in the boiling points. The existing process for the isolation of isobutene is based on reacting C₄ stream with primary C₃ or C₄ alcohol in the presence of ion exchange resins to give corresponding tertiary ether (Eq. 8). The reaction is conducted in a cascade of three reactors with an excess of primary alcohol to achieve satisfactory conversions. The ether formed is then separated from the remainder of C₄ stream by distillation. Isobutene is obtained after catalytic cleavage of the ether (Eq. 9).

A modified process combines the reaction and the separation steps in a single column by employing reactive distillation (Fig. 6). The C₃ or C₄ alcohol and C₄ hydrocarbon mixture are fed to the column above and below the reaction zone respectively. The reaction zone contains Bayer Levatit.R ion exchange resins. The remaining C₄ stream and ether are separated from isobutanol in the rectification and stripping zone respectively. The top and the bottom products contain < 1.5% and 0.3% by weight of isobutene respectively. The separated ether is then cleaved to subsequent alcohol and isobutene by the conventional process (Bessling et al., 2002).

The possibility of using etherification as separation tool for the C₄ streams has also been explored recently by Baur et al. (2001b). In the first column, isobutene and methanol react to form MTBE hence separating the inert C₄ component, while in the second column MTBE splits back to methanol and isobutene. Methanol is recycled back to MTBE formation column and isobutene is obtained as a pure product. This coupled reaction would be useful if no side reactions occur. The side products like diisobutene, *di*-methyl ether and water; if present; these affect the purity of methanol. Thus, the outlet of the splitting column must first be separated before recycling. Selectivity of the product is also affected by factors like reflux ratio. If reflux ratio increases, the amount of byproducts formed increases thus affecting the selectivity of isobutene. Even though RD could increase the selectivity of the desired product by selective reaction, this is not so always.

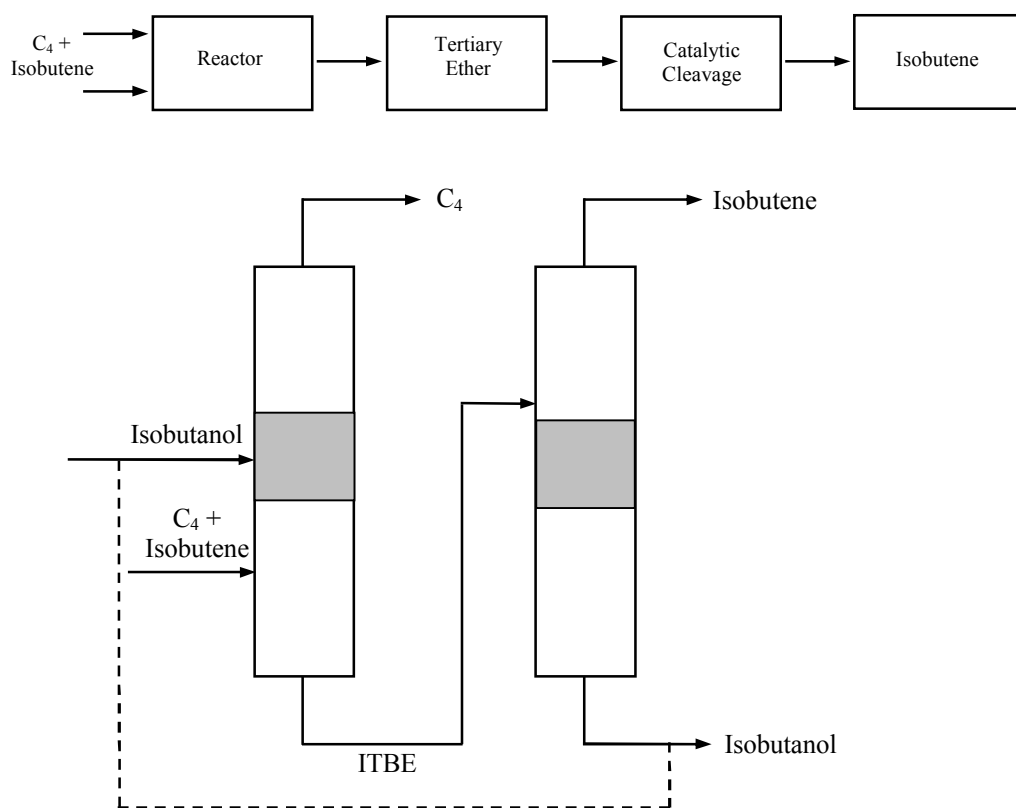
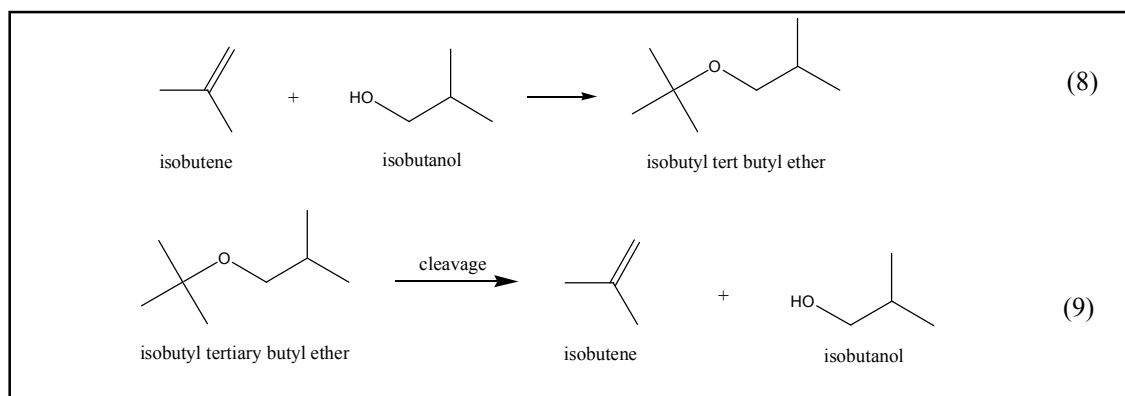


Figure 6: Isolating isobutene from hydrocarbon (Li et al., 2002)

5.3 Higher Ethers

3-methyl-2-pentene (3M2P) and 2-ethyl-1-butene (2E1B) are important precursors for the preparation of 2-ethyl-2-methylbutanoic acid (EMBA), a high value neoacid. Even a small percent of any other C₆ olefins results in unacceptable mixture of neoacids and neoacid esters that is extremely difficult to separate by distillation. Conventional tools for the manufacture of 3M2P suitable for EMBA include co-dimerizing ethylene with *n*-butenes over supported sodium or potassium metal catalysts. However, these products contain isomers of hexane making them unsuitable for the preparation of EMBA. It can also be synthesized

by etherification of 2E1B to 3-methoxy-3-methylpentane (Eq.10) followed by decomposition to 3M2P (Eq. 11) as reported by Hendriksen et al. (1998). The etherification can be conducted in a reactive distillation column containing acid ion-exchange catalysts as shown in Fig.7. The advantage of employing reactive distillation is enhancement in conversion of 2E1B to 3M2P. Etherification of isobutylene dimer and methanol can also be used as fuel additive. The use of RD for this reaction has been recently explored by Rihko-Struckmann et al. (2004).

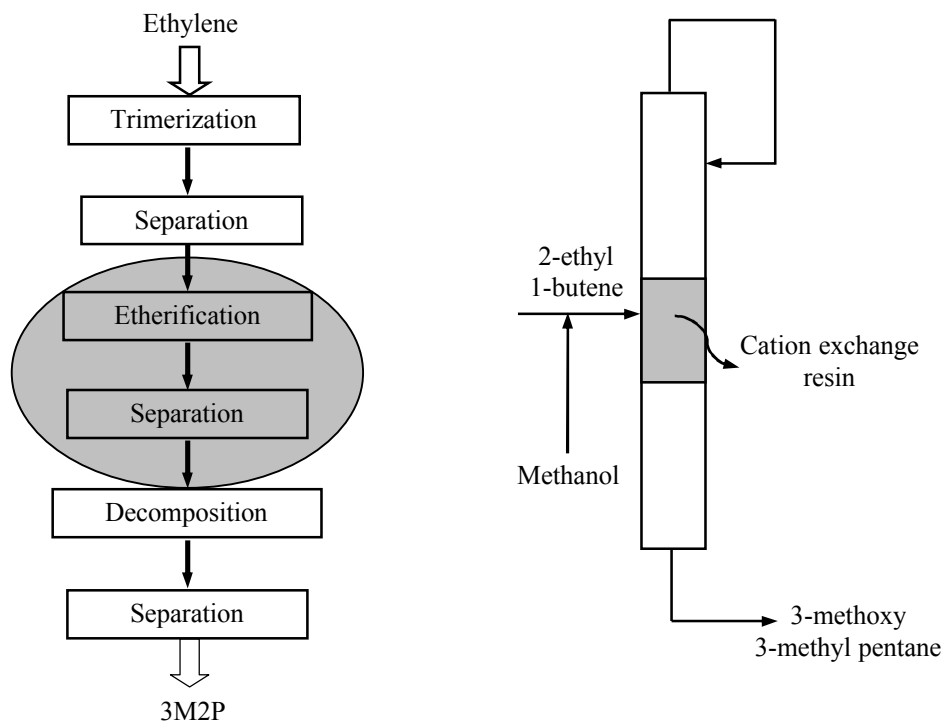
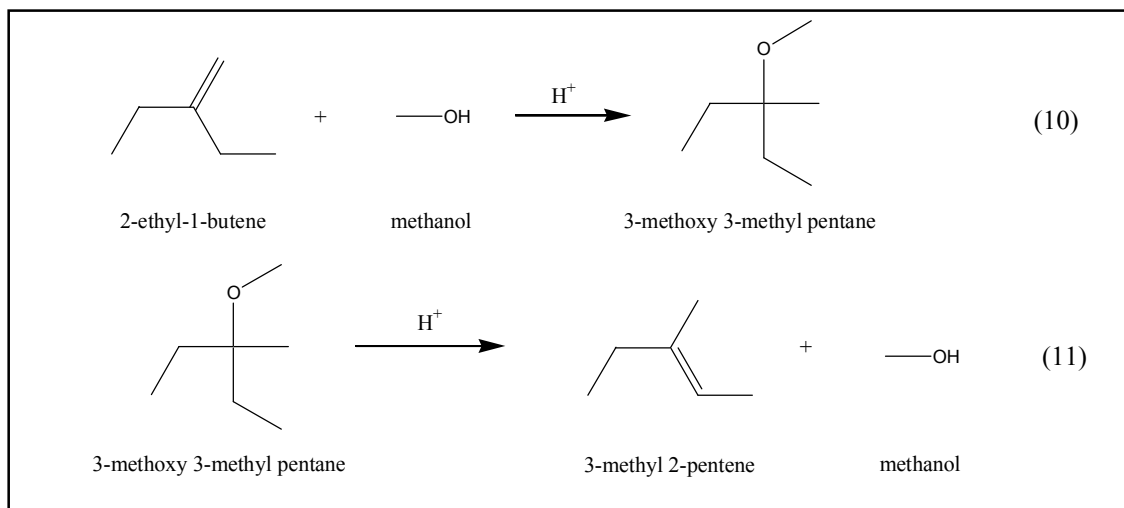


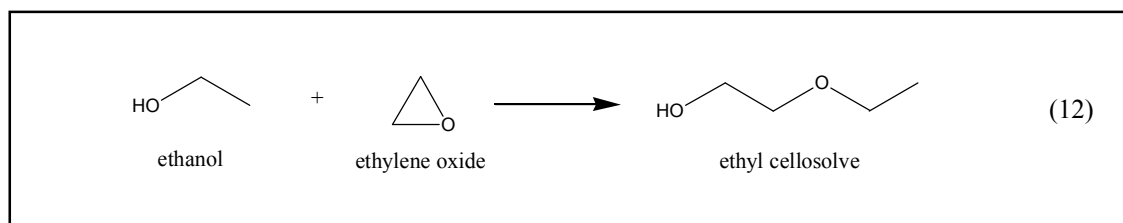
Figure 7: Synthesis of 3-methoxy-3-methylpentane (Hendriksen et al., 1998)

Polyoxymethylene dimethyl ethers are also recognized as suitable components for blending into fuel having improved qualities for use in diesel engines. Methanol can be reacted with formaldehyde in the presence of

a catalyst comprising of copper and zinc and a soluble condensation-promoting component capable of activating a heterogeneous catalyst in a reactive distillation unit in which there is a section containing an anion exchange resins to produce polyoxymethylene dimethyl ethers. An essentially acid-free product is obtained. Advantageously, methylal and higher polyoxymethylene dimethyl ethers are also formed (Hagen and Spangler, 2002).

5.4 Synthesis of alcoxy alkanol using reactive distillation

A process for the synthesis of ethyl cellosolve (EC) has recently been studied by Zheng et al. (2003a). Ethyl cellosolve is used as an organic solvent used in ink, resin and coating manufacturing etc. and especially in brake fluids. The conventional process employs the reaction of ethanol with ethylene oxide (Eq. 12) in a batch reactor or a fixed bed reactor as follows.



EC further reacts with ethylene oxide to give dimers and oligomers. Exothermicity of the reaction needs continuous cooling and the ethanol used in excess requires a separation unit after the reactor. Unlike the conventional process, reactive distillation system eliminates the cooling system and the reduced pressure conditions. High ethanol conversion (89.1%) and high EC selectivity (98.8%) have been reported. A non-equilibrium model developed has been validated using the experimental data.

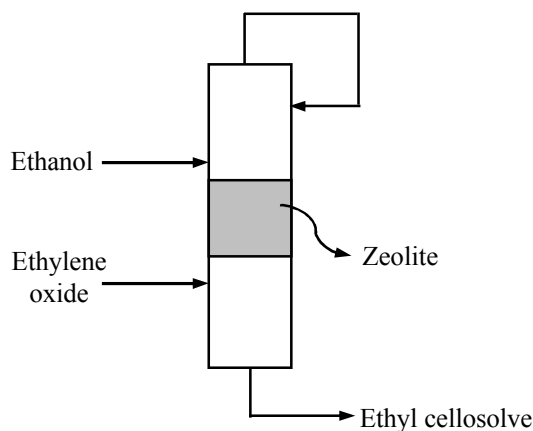


Figure 8: Synthesis of ethyl cellosolve by reactive distillation (Zheng et al., 2003a)

In another work by Zhang and Wan (1991) this reaction was conducted in a reactive distillation column using zeolite catalyst to give high yield (90%) and conversion (93%). Similarly, propylene glycol mono-ethyl ether (PGME) can be produced from ethyl alcohol and propylene oxide in a catalytic distillation column containing β -zeolite catalyst. Reactive distillation enhances the conversion of propylene oxide and offers high selectivity towards propylene glycol mono-ethyl ether (Wen et al., 2001).

6 HYDROGENATION

This reaction has long been known and is usually carried out at super atmospheric pressures and moderate temperatures using a large excess of hydrogen over a metal catalyst. Recently many hydrogenation reactions have been investigated and commercialized successfully using reactive distillation. Peculiarity of these reactions is that they can be conveniently conducted along with other reactions in RD. Some examples are given in Table-2. Following are few important examples.

6.1 Hydrogenation of Benzene

Cyclohexane being the main precursor for the production of nylon products, its demand will always remain on the rise. It was first obtained by the direct fractional distillation of suitable crude petroleum refinery streams. Hydrogenation of benzene (Eq. 13) was carried out at moderate temperature and pressure conditions in a RD column using heterogeneous catalyst to produce almost pure (99.9%) cyclohexane (Gildert, 2001). Group VIII metals on suitable support is the preferred catalyst system. Reactive distillation facilitates efficient contact of hydrogen with benzene, proper utilization of the heat of reaction, and good temperature control. Higher conversion (90%) of benzene and almost 100% selectivity to cyclohexane has been reported. The schematic of the process is shown in Fig. 9. Moreover, the “washing effect” due to the internal reflux, reduces the possibility of polymer build-up and coking.

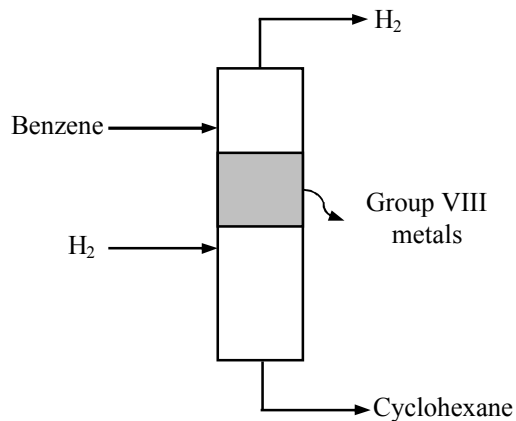
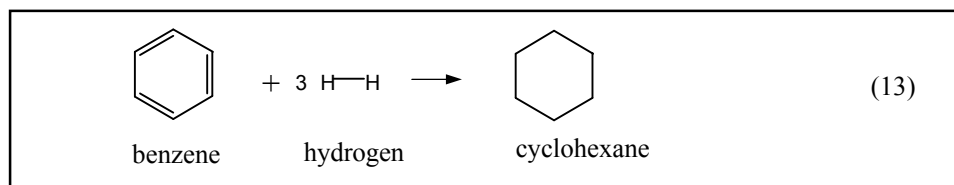


Figure 9: Hydrogenation of benzene to cyclohexane (Gildert, 2001)

6.2 Production of cyclopentane or cyclopentene

Cyclopentane is used as a solvent and blowing agent. The conventional process employs cracking of dicyclopentadiene (DCPD) to produce cyclopentadiene (CPD) (Eq. 14), hydrogenation to cyclopentane/cyclopentene (Eq. 15), followed by separation using distillation. This high-pressure process (>13.6 atm) is circumvented by using low pressures (~0.5 atm) single reactive distillation column (Fig.10). This column also replaces the hydrotreating unit and two distillation columns used in the conventional set-up. The central catalytic zone consists of a heterogeneous hydrogenation catalyst bed or catalyst embedded in the structured packing. The preferred catalyst system may include metals like nickel, platinum, palladium etc. on alumina, silica alumina or carbon support. DCPD is cracked to CPD in the bottom-

cracking zone, which is subsequently hydrogenated to cyclopentane or cyclopentene. Selective distillation of the same gives cyclopentane with 97-98% purity (Silverberg et al., 2000).

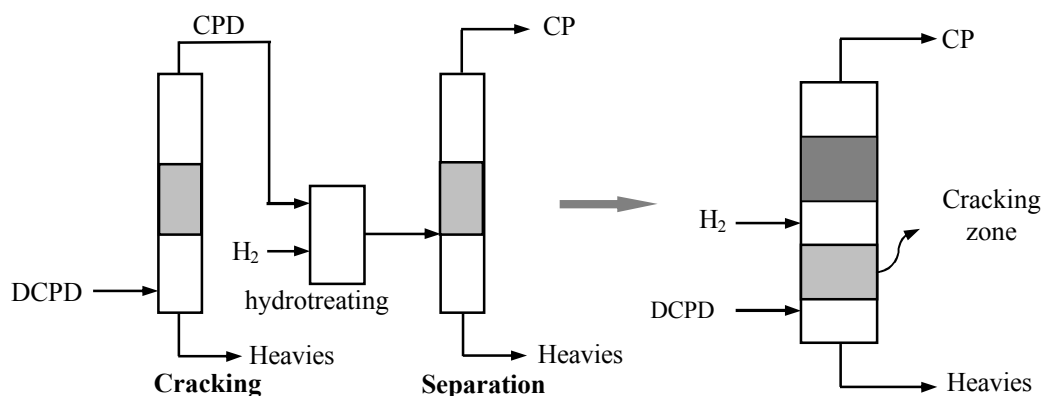
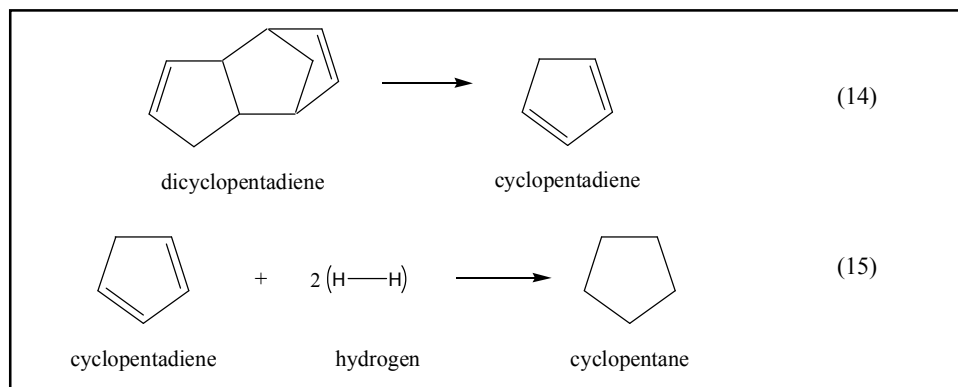


Figure 10: Reactive distillation to produce cyclopentane/cyclopentene (Silverberg et al., 2000)

6.3 Synthesis of iso-octane from isobutylene

Hydrogenation of Diisobutene (DIB) was carried out in a RD column using a dimerisation catalyst (acidic cation exchange resins or zeolites) (Eq. 16) and a hydrogenation catalyst (alumina and palladium and cobalt) (Eq. 17) to produce C_8 alkanes, especially 2, 2, 4-trimethyl pentane (isooctane) as is reported by Gildert and Loescher (2001). Isooctane is an important industrial chemical commonly used in the synthesis of various organic molecules, as a solvent and more importantly, with the recent ban on MTBE, it is being looked upon as an alternative fuel additive (Kolah and Mahajani, 2001). The traditional route for the production of isooctane consists of a multi step process requiring higher temperature and pressure conditions. However, a single reactive distillation column operating at moderate temperature and pressure has manifold advantages over the traditional process. The condensation of a portion of the vapor provides intimate contact of the oligomer with hydrogen in the presence of a catalyst. Better temperature control can be achieved by regulating pressure. Unlike the conventional process, isooctane is produced by combining concurrent dimerization and hydrogenation in the single reactive distillation column (Gildert and Loescher, 2001) The dimerization catalyst is an acidic cation exchange resin or zeolite and the hydrogenation catalyst consists of Group VIII metals on suitable support. Both these catalysts may be contained in alternating beds or used as a mixture. The un-reacted isobutene and hydrogen are removed as overheads from the RD column and diisobutene and C_8 alkanes are removed as bottoms from the RD column.

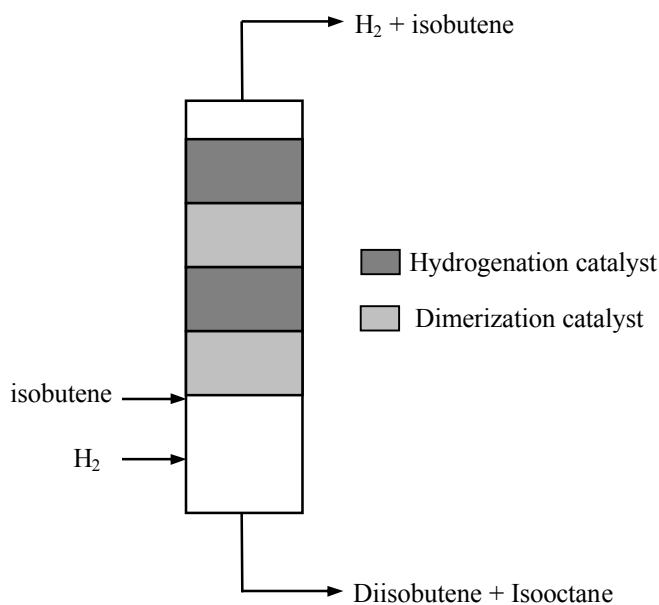
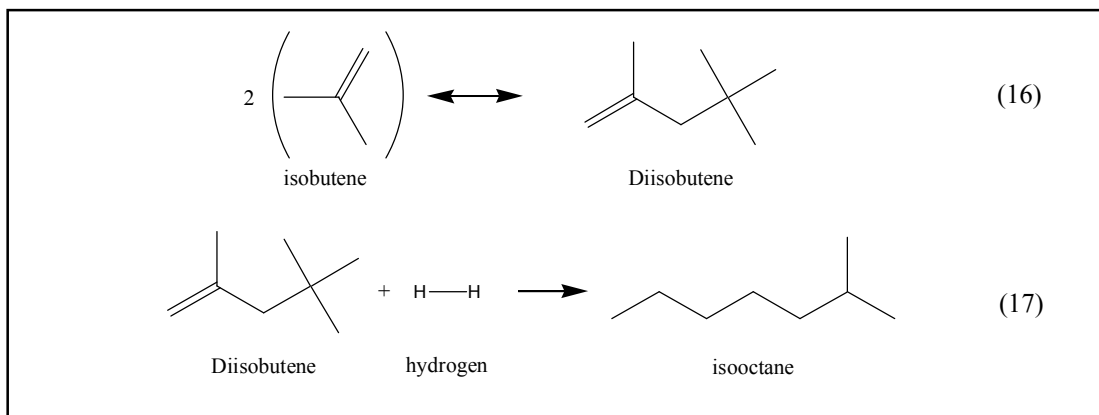


Figure 11: Synthesis of Isooctane (Gildert and Loescher, 2001)

Instead of hydrogenation of the dimer one can etherify the same with methanol in RD column to obtain the corresponding ether which is also considered to be an attractive gasoline oxygenates (Rihko-Struckmann et al., 2004).

6.4 Removal of methyl acetylene/propadiene (MAPD) from hydrocarbon streams

In the recent years, hydrogenation coupled with reactive distillation has been shown to be an effective tool for the purification of process streams from undesired olefinic/diolefinic impurities. The MAPD compounds are highly reactive contaminants in a propylene stream. The most common method of removal is by selective hydrogenation, using a single pass fixed bed reactor (FBR) containing hydrogenation catalyst. A portion of methyl acetylene and propadiene react in vapour phase with hydrogen to produce propylene. Thus, in addition to the removal of impurities, a valuable product like propylene is obtained. The effluent from the FBR is fed to a reactive distillation column and contacted with hydrogen in a reaction zone containing a hydrogenation catalyst, such as supported palladium oxide catalyst, in the form of a catalytic distillation structure. In the RD column, unreacted MAPD is converted to propylene, which is then

separated by simultaneous fractional distillation. The separated propylene along with any propane and lighter compounds, including any unreacted hydrogen, from the reactive distillation column is taken as an overhead product. The reactive distillation column enhances conversion and selectivity to propylene (Stanley and Gildert, 2002). Hydrogenation of olefins to propylene in a series of reactive distillation columns containing palladium based catalyst to enable maximum conversion to propylene and isomerization of 1-butene to 2-butene has also been investigated (Gartide and Gildert, 2002).

Conventionally it is more difficult to remove both dienes and olefins than dienes alone. Higher temperature cannot be used to prevent oligomerization. However, stepwise use of reactive distillation in presence of palladium based catalyst system can effectively separate dienes and olefins from the hydrocarbon mixture. The unsaturated compounds comprising diolefins are hydrogenated in the first reactive distillation column to remove diolefins, followed by removal of mono olefins in the second column. This not only reduces side reactions leading to undesired products but the washing effect in the column reduces polymer build-up and coking (Maraschino, 2002).

6.5 Hydrogenation of acetone

The process in which acetone and hydrogen are fed to the reaction zone of the RD column to produce methyl isobutyl ketone (MIBK) has been reported. Some of the acetone is converted to mesityl oxide (MSO), water and optionally, di-acetone alcohol (DAA) and/or other byproducts. A product stream containing MSO, water or DAA and unreacted acetone are withdrawn from the catalytic distillation zone. In the reaction zone of distillation column, MSO and hydrogen react to form MIBK (Podrebarac et al., 1998 and Saayman et al., 2003).

6.6 Hydrodesulfurization

Petroleum distillate streams contain a variety of organic chemical components. The organic sulfur compounds are almost always considered to be contaminants which generally depend on the crude source and the boiling range of a given stream. Generally the lower boiling range fractions contain mercaptans while the higher boiling fractions contain thiophenic and heterocyclic sulfur compounds. Reactive distillation column containing hydrodesulfurization catalyst bed when operated counter-currently can be successfully employed to convert the organic sulfur compounds to H_2S (Groten and Loescher, 2002). Similarly, dehydrogenation of naphtha using reactive distillation reduces hydrogenation of olefins, deactivation of catalyst giving sulfur content less than 50 ppm (Podrebarac et al., 2001).

6.7 Hydroconversion

The usefulness of reactive distillation in hydrocracking has already been highlighted (Sharma and Mahajani, 2003). Cracking of heavy petroleum stock to lighter hydrocarbons and subsequent hydrogenation can be conveniently performed in a single reactive distillation column (Mukherjee and Louie, 2003). The lighter compounds thus formed can be recycled back to the crude distillation unit. However, the lighter compounds formed in the column can undergo further cracking which is undesired. Recently, Tung (2002) has suggested an important modification in the reactive distillation technology to avoid such an adverse effect on selectivity. A *stripped reactive distillation* (SRD) column as shown in Fig.12 can be used effectively to avoid the re-entry of the lighter product in the reactive zone. Hence, the liquid entering the reactive zone has considerably less concentration of the product formed. Simulation studies have shown considerable improvement in performance. Such an approach may find a general application when one wants to avoid consecutive reaction. A *rectified reactive distillation* (RRD) column can be used if the product formed is heavier than the reactants.

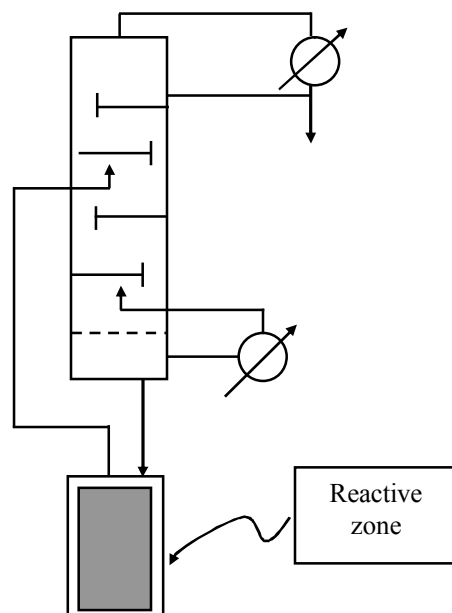
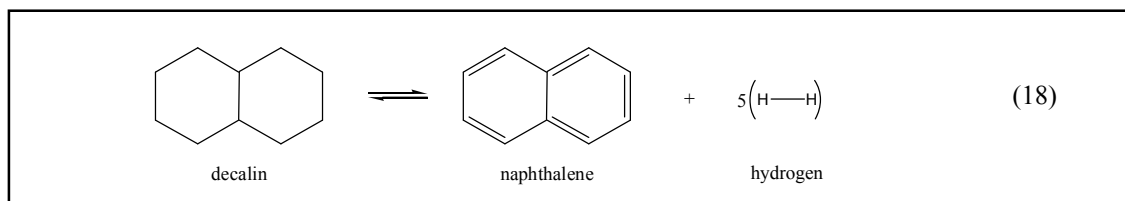


Figure 12: Stripped reactive distillation column (Tung, 2002)

7 DEHYDROGENATION

Use of RD in chemical heat pump by dehydrogenation and hydrogenation of acetone and isopropanol respectively has already been discussed in the earlier review by Sharma and Mahajani (2003) though few more studies are reported in the recent literature (Mukherjee and Louie, 2003). Recently, a novel application of reactive distillation concept has been suggested for generation of hydrogen for fuel cells (Shinya et al., 2003). Naphthalene can be hydrogenated off board to decalin which on dehydrogenation (Eq. 18) can act as a source of hydrogen on board.



Dehydrogenation being reversible can be effectively performed in a compact liquid-film type reactor operated under reactive distillation conditions in the presence of Pt/C catalyst. Preliminary experimental studies evaluate this as an excellent hydrogen source with a desired evolution rate under relatively mild conditions (250°C) for fuel cells. The naphthalene produced by dehydrogenation can be removed from the vehicle for off-board hydrogenation.

8 ALKYLATION

8.1 Alkylation of benzene/toluene with propylene by catalytic distillation

Alkylation of benzene to cumene is one of the earliest reactions studied in reactive distillation. Isopropyl benzene is mainly used as an intermediate required for the production of phenol, acetone, and alpha-methyl

styrene, which are widely used in plastic resins, as fuel additive and solvent. Shoemaker and Jones (1987) were the first to introduce the reactive distillation concept for alkylation reactions. RD facilitates effective utilization of reaction exotherm.

Propylene gas is fed nearer to the bottom while benzene or toluene is fed from the top of the distillation column containing β -zeolite, FX-01, as catalyst to produce isopropyl benzene or isopropyl toluene. The residual gas components are discharged from the top of the reactive distillation column and the product solution from the bottom of the reactive distillation column (Zhang et al., 2001a). Advantage of reactive distillation column is that, it enhances the propylene conversion to 99% and also gives about 90% selectivity for isopropyl benzene or isopropyl toluene. The production of cumene catalyzed by FHI-01 in a reactive distillation column has also proven advantageous due to enhanced conversion (99%) and higher selectivity (98%) towards cumene (Li et al., 2001).

In a novel catalytic distillation process alkylation of benzene is carried out with propylene in the presence of suspended catalyst to produce cumene. 100% conversion of propylene with more than 90% selectivity to cumene is realized. Cumene obtained is of extremely high purity with both *n*-propyl benzene and C_8 aromatics less than 100 ppm (Wen et al., 2000).

8.2 Alkylation of benzene with ethylene in dry gas by catalytic distillation

Ethyl benzene is one of the most useful starting materials for various polymers. In most of the conventional processes, alkylation is carried out at relatively high benzene to ethylene molar ratio. This high molar ratio increases the amount of unreacted benzene and thus its recovery and recycling back to the process become disadvantageous from an industrial viewpoint. In the conventional process, fixed bed liquid phase alkylation is carried out in a trickle bed region by the use of a β -zeolite as catalyst. This process reports high productivity with a disadvantage that the catalytic activity is greatly changed in the initial stage of the reaction and is difficult to control.

Ethyl benzene produced in a RD column overcomes the above limitation. The unreacted benzene is recovered from the top of the column as vapor (Netzer, 2001). In addition to this, it is possible to remove the generated heat of reaction easily and suppress the abnormal rise of the temperature of the catalyst layer even at a very low benzene and ethylene molar ratio, so that ethylated benzene can be produced with very high yield and selectivity. Moreover, ethylene can be completely converted, and decrease in activity of the catalyst can be suppressed. An improved arrangement of rectified reactive distillation (RRD) described in the earlier section has been recommended by Tung (2002) to avoid the formation of dialkylated or polyalkylated products.

8.3 Synthesis of linear alkyl benzene

Reactive distillation can be successfully employed in the manufacture of linear alkyl benzenes (LABs). Linear alkyl benzenes containing more than 80% 2-phenyl isomer content form the basic starting material for the manufacture of detergents. Traditionally they are synthesized by the alkylation of detergent-range olefins and benzene using either Lewis acid or liquid hydrofluoric acid (HF) or solid acid as catalysts. HF catalyzed process gives selectivity of only 17-18%. Use of reactive distillation in presence of HF treated mordenite catalysts is reported to give LAB of more than 80% 2-phenyl isomer with 74-84% selectivity and less than 0.5 bromine number. Continuous removal of aqueous product from the reaction system ensures long catalyst life (Knifton et al., 2003).

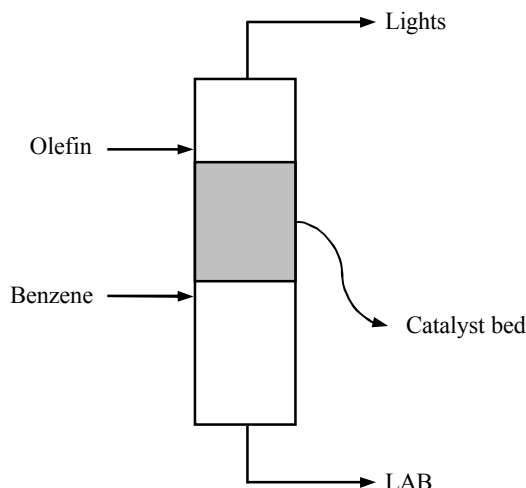


Figure 13: Synthesis of LAB (Knifton et al., 2003)

In another study by Lei et al. (2003) suspension catalytic distillation (SCD) column has been effectively used for the synthesis of C_{12} alkyl benzene by alkylation of benzene with 1-dodecene. In this work, a supported heteropoly acid catalyst was used and conversion and selectivity close to 100% have been reported.

Like alkylation, sulfonation of aromatics has also been studied in RD for the synthesis of *p*-toluene sulfonic acid (Kim et al., 2002).

9 METATHESIS AND DISPROPORTIONATION

The metathesis of olefins is conventionally carried out in either fixed bed, stirred bed, fluid bed or a fluidized bed reactor operated in batch or continuous mode using alumina based catalyst. The reaction mass is then subjected to a series of distillation operations for the separation of products and the unreacted components. The possibility of using reactive distillation for the metathesis reaction has already been reported in the literature (Sharma and Mahajani, 2003). The problem of catalyst deactivation retards the potential of this process to be applied at the industrial level. However, according to the recent finding, continuous or separate injection of an aluminum compound makes it possible to reduce considerably the deactivation of the catalyst.

The metathesis of butene-2 rich olefinic C_4 fraction with ethylene takes place in the reaction zone of the reactive distillation column containing catalyst (Fig. 14). Ethylene and olefin feed stocks are introduced respectively at the bottom and top of the reactive distillation column. Aluminium compound as stabilizing agent is introduced along with the olefin feed stock. The ethylene-propylene mixture obtained at the top of the column is separated in a distillation column, with ethylene recycled back to the reactive distillation column. An auxiliary column separates the unreacted C_4 fraction from the by-products and heavy ends formed at the bottom of the reactive distillation column. The use of reactive distillation eliminates a series of reactors coupled with distillation columns, thus, substantially bringing down the equipment and energy cost (Commereuc and Mikitenko, 2002). Similarly metathesis of 1-butene and 2-butene to propene and 2-pentene and subsequent metathesis of 2-pentene to propene and 1-butene in two reactive distillation columns arranged in series has been discussed (Schwab et al., 2002). Since, both these reactions are equilibrium limiting, fast removal of products in reactive distillation column promotes higher conversions unlike the conventional process.

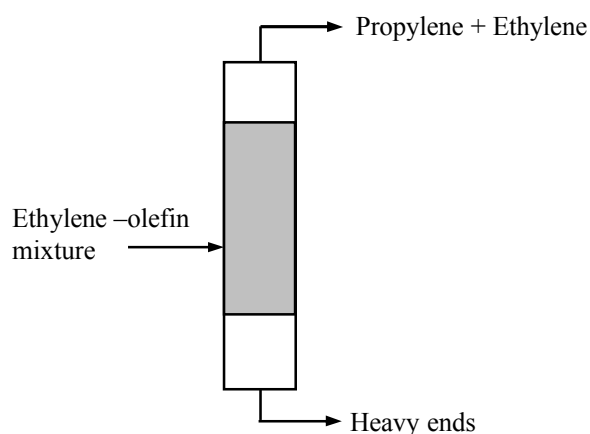


Figure 14: Metathesis of olefins (Commereuc and Mikitenko, 2002)

9.1 Toluene dis-proportionation

Stitt (2002) has presented the economic evaluation of toluene dis-proportionation to benzene and xylene in RD column (Eq. 19). His investigations reveal that this process does not prove to be a fruitful development opportunity for RD. His observations as a result of a comparison with the conventional process (Vapor phase process at 400-425°C and 20-25 bars in presence of a catalyst) and a RD process (Fig.15) are that though RD allows a considerable flow sheet simplification, both the plants have similar capital and fixed costs. RD has a lower variable cost but the high pressure required for the RD process tends to negate this advantage.

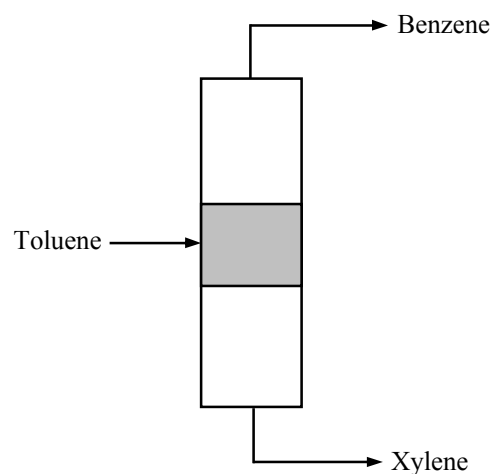
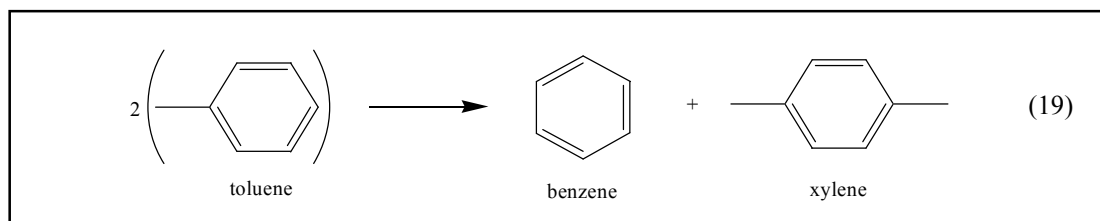


Figure 15: Toluene dis-proportionation via reactive distillation (Stitt, 2002)

9.2 Preparation of triflic anhydride

Triflic anhydride is manufactured from trifluoromethanesulfonic (triflic) acid and is widely used in the synthesis of organic molecules of research and commercial interest. The yield of a conventional process may be enhanced by addition of phosphorous compounds. However, the generation of non-recyclable by-products makes the process non-suitable to be applied on industrial level. An improved two-step process that eliminates the use of phosphorus reagent comprises of forming a mixed anhydride by contacting triflic acid with a ketene based carboxyl compound followed by dis-proportionation to triflic anhydride and carboxyl acid anhydride using reactive distillation (Hembre and Lin, 2002). Trifluoro-methanesulfonyl isobutyrate (isobutyryl triflate) derived from triflic acid and dimethylketene is the most preferred mixed anhydride for the continuous production of triflic anhydride. Strong acid such as sulfuric acid or cation exchange resins can be used.

As an alternative the process may be carried out in a single column by introducing triflic acid and dimethylketene directly into a reactive distillation column, wherein they react to form a mixed anhydride which undergoes dis-proportionation to form triflic anhydride and carboxylic anhydride (Eq. 20). Reactive distillation, in addition to elimination of phosphorus can also substantially lower the equipment cost and offer better temperature control and heat utilization.

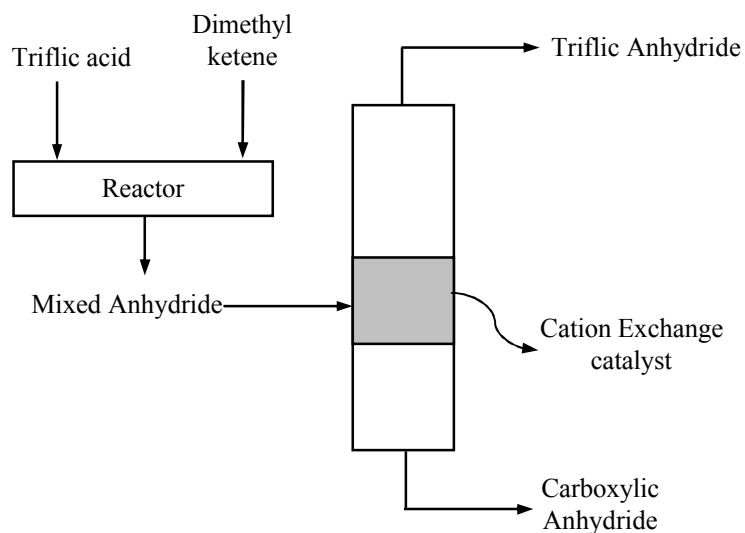
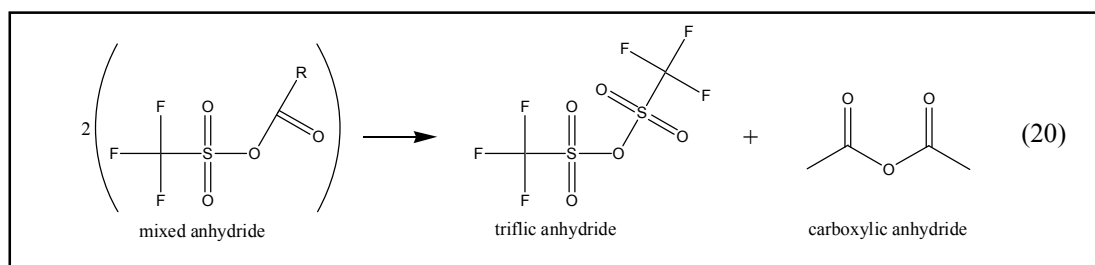


Figure 16: Preparation of triflic anhydride (Hembre and Lin, 2002)

10 HYDRATION / DEHYDRATION

Hydration of ethylene oxide by reactive distillation to produce ethylene glycol has also received considerable attention due to possible benefits that RD can offer. The exothermic heat of reaction can be effectively utilized to optimize the boil-up requirement. Moreover, efficient temperature control can avoid diethylene glycol formation. Recent studies by Liu et al. (2002a) show that the mole proportion of water to ethylene oxide may be reduced from 15-20:1 to 3:1. The conversion obtained is approximately 100% and the selectivity towards ethylene glycol is 98.58%. Hydration of cyclohexene (Fig. 17) is also an important candidate for RD. Water and cyclohexene (Eq. 21) may be fed to the reactor together with very fine catalyst particles and the resulting slurry is separated in the decanter leading to an organic phase and an aqueous phase (Frank et al., 2002). The catalyst particles can be recovered quantitatively in the aqueous phase, and recycled back to the reactive distillation column. The organic phase is composed of cyclohexanol as the reaction product, unreacted cyclohexene as well as benzene and cyclohexane which are impurities coming from the preceding benzene hydrogenation step. Due to the very close boiling points of benzene (80.10°C), cyclohexene (82.98°C) and cyclohexane (80.74°C), they are difficult to be separated by conventional distillation. Cyclohexanol, on the other hand, has a significantly higher boiling point of 161.1°C at normal pressure and is therefore easily separated from the rest of the mixture in a reactive distillation column.

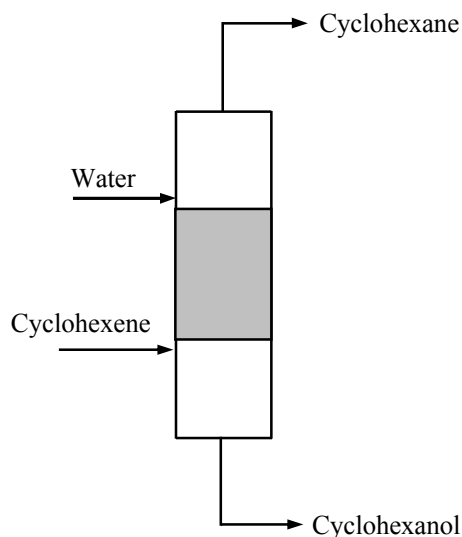
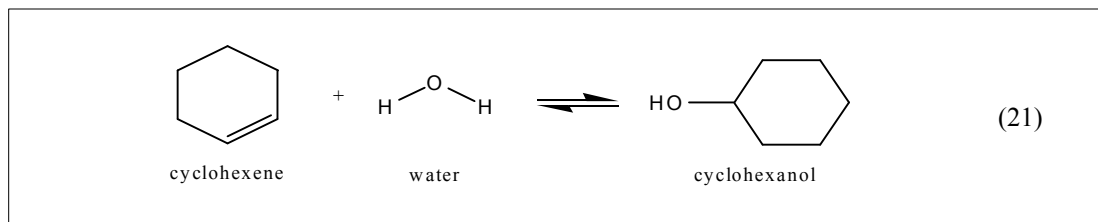
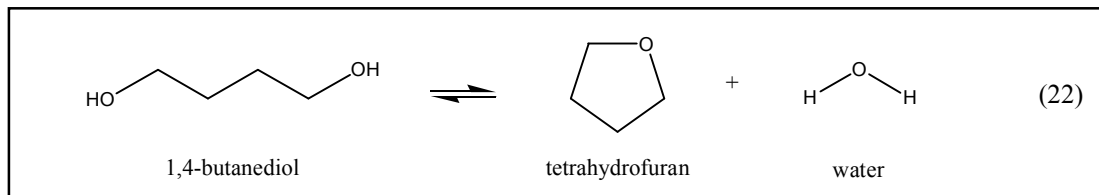


Figure 17: Synthesis of Cyclohexanol by reactive distillation (Frank et al., 2002)

Among dehydrations, *tert*-butanol dehydration is the well studied reaction in RD. Anhydrous isobutylene product is recovered as overhead fraction and co-product water as bottoms fraction. The β -zeolites, hydrogen-fluoride-treated β -zeolites and HF-treated montmorillonite clays can be used as acid catalyst. Advantage of RD over conventional methods is that it enhances the conversion of *tert*-butanol (Abella et al., 1999 and Gotze et al., 2001).

10.1 Synthesis of tetrahydrofuran from butanediol



Tetrahydrofuran of more than 98% purity was synthesized from butanediol (Eq. 22) in the reactive distillation column containing cation exchange resins. The possibility of using a novel technique of pressure-sensitive reactive distillation to get high purity product was studied (Liu and Xiao, 2001 and Liu et al., 2002b). It has been noted that this can be achieved by using a dual-column reactive distillation scheme operating at different pressures.

11 CARBONYLATION

11.1 Synthesis of Acetic Acid

Acetic acid, an important chemical commodity used as an intermediate and solvent is synthesized by carbonylation of methanol (Eq. 23) in a homogeneous catalytic medium using stirred reactor. Group VIII metal compounds, preferably rhodium or iridium along with a halide promoter comprises the catalyst system. The accumulation of hydrogen iodide and the separation of acetic acid from the reaction mass make the process economically unfavorable due to higher energy consumption and capital investment.

Carbonylation of methanol, dimethyl ether (DME) or other reactive derivatives can be conveniently carried out in a RD column (Voss, 2001) as shown in Fig.18. Carbon monoxide and oxygenate feeds are introduced below the reaction zone. The stripping of unconverted carbon monoxide, hydrogen and inert gases and distilling off acetic acid from the remaining components can be done simultaneously.

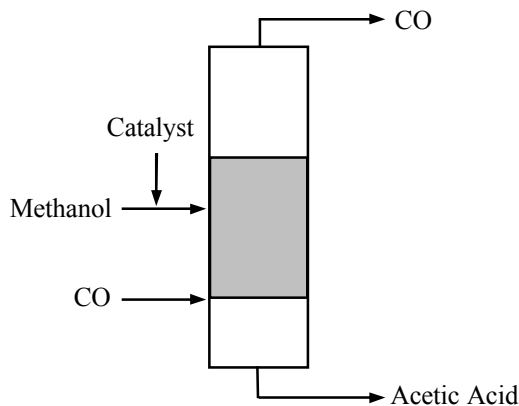
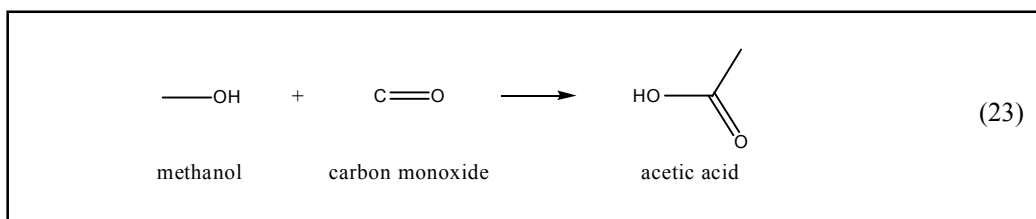


Figure 18: Synthesis of Acetic Acid (Voss, 2001)

The major advantage of the reactive distillation column is that it replaces several operation units of the conventional scheme, like stirred reactor, flash vessel, light end column, dehydration column, absorber etc. and related piping. The heat of reaction from the highly exothermic reaction is recovered in a steam boiler heated by the pump-around stream. Moreover, since flash vaporization is eliminated, catalyst deactivation, precipitation and losses are prevented. In addition to this, because of introduction of oxygenate feed to the distillation at the right location the “critical water limit” of the column is eliminated which prevents the accumulation of hydrogen iodide as observed in the conventional process.

12 PRODUCTION OF POLYMERS

12.1 Production of polyamides by reactive distillation

In the conventional process, the polyamides are prepared by direct hydrolytic polymerization of amino nitriles to produce incomplete hydrolyzed intermediates. However, these intermediates hinder the formation of high molecular weight product and cause adverse effects on the quality of the polyamide. Moreover, they cause incomplete removal of the ammonia produced in the reaction from the polymer melt. The conventional industrial solution is a single-phase process for the hydrolysis and pre-polymerization. This requires high operating pressures to keep volatile components-especially ammonia-in the solution.

However, the objective is achieved by carrying out the reaction in a RD column in the presence of Bronsted acid based catalyst as shown in Fig. 19. Ammonia and water (steam) along with low molecular weight compounds are taken off as overheads while high molecular weight product is discharged from the bottom of the column (Leemann et al., 2002).

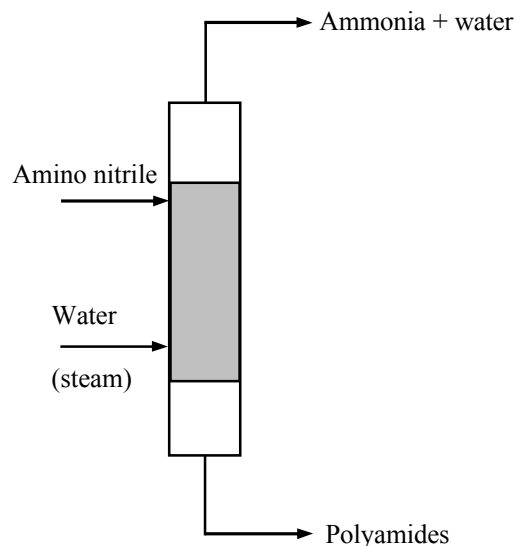


Figure 19: Production of polyamides by reactive distillation (Leemann et al., 2002)

12.2 Process for the production of nylon-6

Nylon 6 is produced commercially using caprolactam as the starting material in a VK tube at atmospheric pressure. However, the product contains 7-10% caprolactam, removal of which adds considerably to the cost. Another process for the conversion of 6-aminocapronitrile to nylon-6 uses a pipeline reactor. Major

disadvantage of this process is that it requires long residence times, which may lead to product degradation. However, use of multistage reactive distillation column (Fig. 20) reduces the excessively long residence times and eliminates the purification step (Cohen et al., 2002).

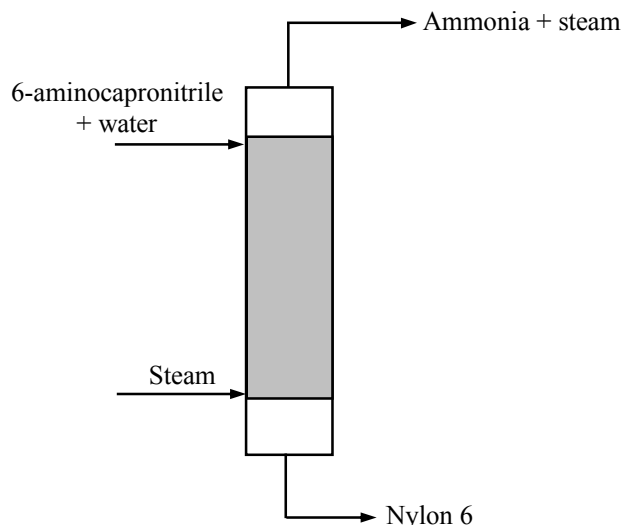


Figure 20: Process for the production of nylon-6 (Cohen et al., 2002)

13 REACTIVE DISTILLATION FOR ALCOXY/ACYLOXY-SILANES AND THEIR DERIVATIVES

Alcoxysilanes and alcoxysilane-based compositions (Eq. 24) have wide variety of applications such as adhesion promoters, crosslinking agents in polymers, release agents, additives in paints and coatings, etc. Acyloxy-silanes (Eq. 25) are well known cross-linking agents for vulcanizable silicone rubber compositions. Common acyloxysilane cross-linking agents include methyltriacetoxysilane and ethyltriacetoxysilane. Reactive distillation has also been considered as an important process for the manufacture of organo-silanes or siloxanes through the reaction of chlorosilane with corresponding alcohol or carboxylic acid (Nitzsche et al., 1974; John et al., 1979; Tolentino, 1982; Bank and Petrisko, 1990 and Lowenberg et al., 2001). In these reactions, hydrogen chloride is formed as a co-product, which is required to be separated immediately from the reaction mixture as it leads to insufficient conversion and formation of side products. Typically a reactive distillation configuration consisting of the feeds of chlorosilane and alcohol/acid at different locations as shown in Fig. 21 is employed. The high boiling alcoxy/acyloxy silane is removed from the bottom and hydrogen chloride is withdrawn as a top product.

A notable drawback of reactive distillation is the attainment of considerably high temperatures especially in the bottom zone of the column, which may lead to the formation of dimers of organosilanes or formation of gel that may plug the column. In order to overcome these limitations, several other attempts have been made such as the use of reactive falling-film type evaporators (Bank and Meindersma, 1994 and Rasmussen et al., 1995). Recently, some patents claim that reactive extraction with a proper solvent that can remove hydrogen chloride effectively, finds an edge over reactive distillation process due to less severe diffusion limitations and mild conditions (Bade and Robers, 2000). However, reactive distillation can still be an attractive alternative for transesterification of alcoxyorganosilanes (Bowman et al., 2002). The various applications of organo-functional silicon compounds require alkoxy groups derived from other alcohols for reasons of reactivity, stability, toxicity, volatility, solubility, and flammability. The synthesis of higher alcoxysilanes is not as easy as that of methoxy/ethoxy organosilanes and transesterification of lower organosilanes (Eq. 26) with higher alcohols is desired and reactive distillation can be conveniently used here, as one needs to separate lower alcohols (instead of hydrogen chloride in esterification) to drive the reaction in forward direction.

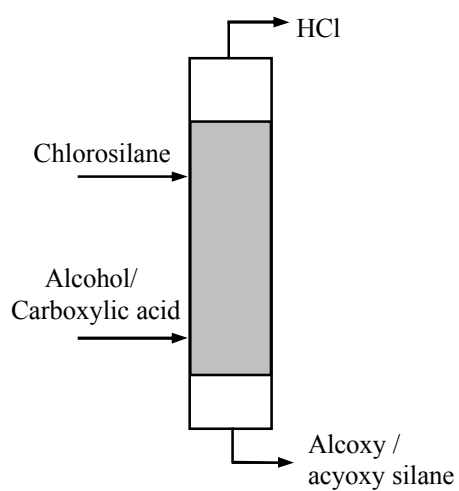
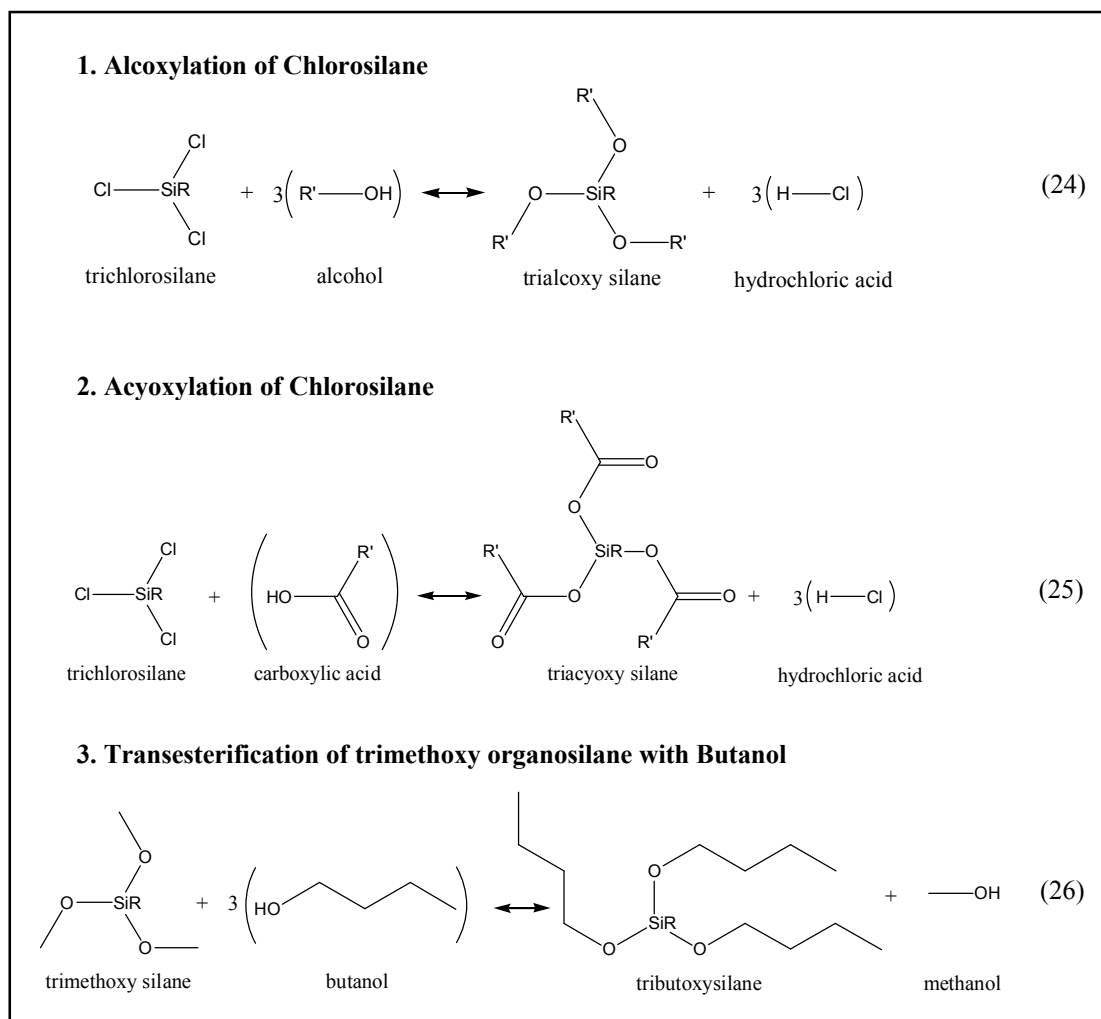
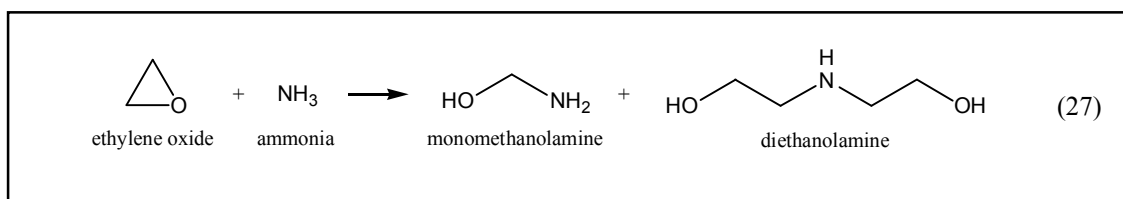


Figure 21: Synthesis of Alkoxy /acyoxy silane by Reactive Distillation

14 CHLORINATION/AMINATION

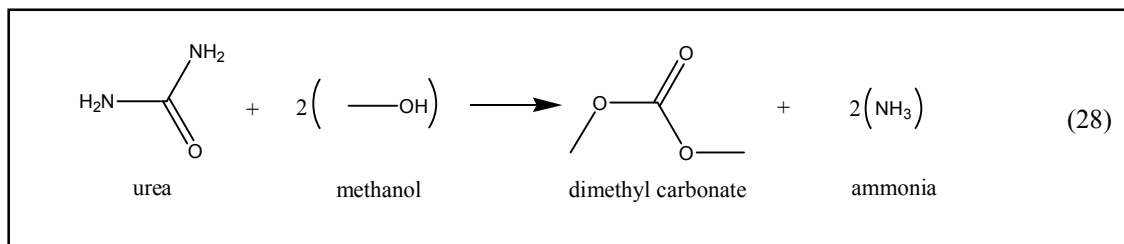
Chlorination and amination are associated with the formation of di-, tri-chlorinated or amino products; some of which are not desired. The use of RD in chlorination of aromatics for selectivity improvement has already been reported (Sharma and Mahajani, 2003). Recently, mono-chloro-acetones which are used as couplers for colour photography, enzyme in-activator, insecticides, etc. have been produced in RD column. The formation of poly-chloro-acetone is suppressed effectively. The concentration of poly-chloro-acetone is less than 0.5% and almost pure product is obtained. The concentration of mono-chloro-acetone is greater than 98% (Zhang et al., 2001b). Similarly ethanalamines like monomethanolamine (MEA), diethanolamine (DEA), trimethanolamine (TEA) are produced by reacting ethylene oxide (EO) with aqueous ammonia at sub-atmospheric pressure (Eq. 27). They are extensively used for scrubbing acid gases, synthesis of ammonia, pharmaceuticals and intermediates, in emulsion, paints and polishes, etc. In the reaction to produce DEA, a desired product, the selectivity is over 90% in the absence of a catalyst. Also good temperature control is achieved. Thus all the conventional advantages of reactive distillation are realized (DiGuilio and McKinney, 2000).



15 SYNTHESIS OF CARBONATES

15.1 Dimethyl carbonate

Dimethyl carbonate (DMC) is an important chemical commodity of commercial importance. It is extensively used as a methylating and carbonylating agent and also as a solvent to replace halogenated solvents such as chloro-benzene. Although the current price of dimethyl carbonate makes it expensive to be used as fuel additive, it may be used as oxygenate in reformulated gasoline and an octane component as it has high oxygen content and pleasant odor. In a commercial process, dimethyl carbonate is produced from methanol, carbon monoxide, molecular oxygen and cuprous chloride *via* oxidative carbonylation in a two-step slurry process. The major shortcomings of this process are the low production rate, high cost for the separation of products and reactants, formation of by-products, high recycle requirements and the need for corrosion resistant reactors and process lines. Dialkyl carbonates can be synthesized using reactive distillation. In the reaction zone a portion of the methanol and urea react (Eq. 28) in the presence of organotin compound (dibutyltin dimethoxide) and high boiling electron donor atom containing solvent (triethylene glycol dimethyl ether) to produce dimethyl carbonate (Ryu and Gelbein, 2002). The dimethyl carbonate and ammonia are removed from reaction zone as vapors (Fig. 22). The complexing agent and the solvent are preferably the same compound. The product DMC is stripped from the reaction mixture with methanol.



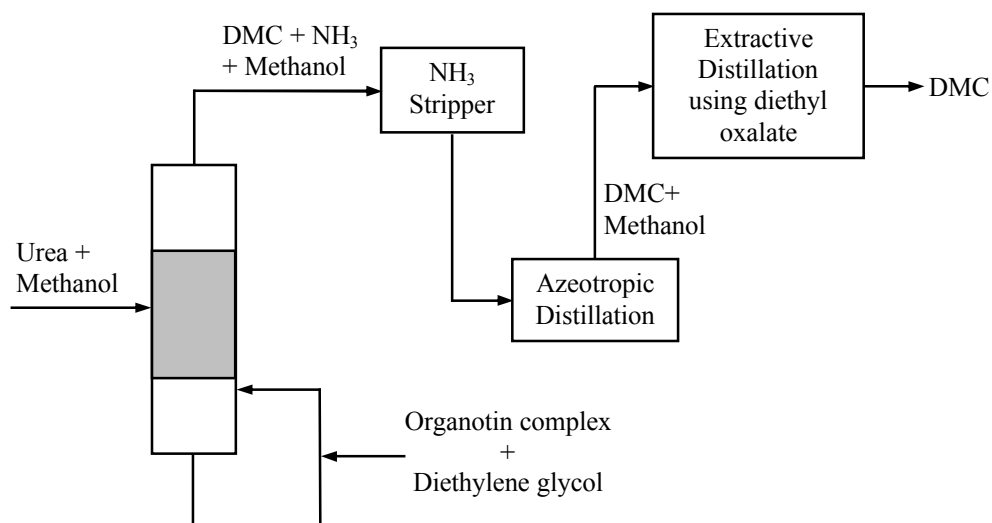


Figure 22: Production of DMC by reactive distillation (Ryu and Gelbein, 2002)

15.2 Diethyl carbonate

Luo and Xiao (2001) developed a process for diethyl carbonate by transcarybonylation of dimethyl carbonate with ethanol. Diethyl carbonate is used as a solvent for nitrocellulose, natural and synthetic resins and also as a starting material for organic synthesis. Effects of the feed locations of the two reactants and the reflux ratio on the performance of the column are discussed.

15.3 Diaryl carbonate

Diaryl carbonate which is an important raw material for the manufacture of polycarbonate resins can also be conveniently synthesized in a series of RD columns and conventional distillation columns maintained at different temperatures and pressures (Bruin et al., 2001) as shown in Fig. 23. This methodology facilitates high rates of production coupled with convenient recovery of unreacted starting materials and side reaction products for recycle within the process for making diaryl carbonates or for utilization in parallel reactions such as in the manufacture of diakyl carbonates.

In the first reactive distillation column, the dialkyl carbonate (e.g. DMC) and phenol are reacted in the presence of the transesterification catalyst to produce alkyl aryl carbonate and alcohol (Eq. 29). The dialkyl carbonate and alcohol are recovered as the top stream. The first bottom stream containing alkyl aryl carbonate is then fed to a second reactive distillation column to produce diaryl carbonate by disproportionation of the alkyl aryl carbonate (Eq. 30). The third reactive distillation column is used to further enhance the yield of the unreacted DMC and alkyl aryl carbonate.

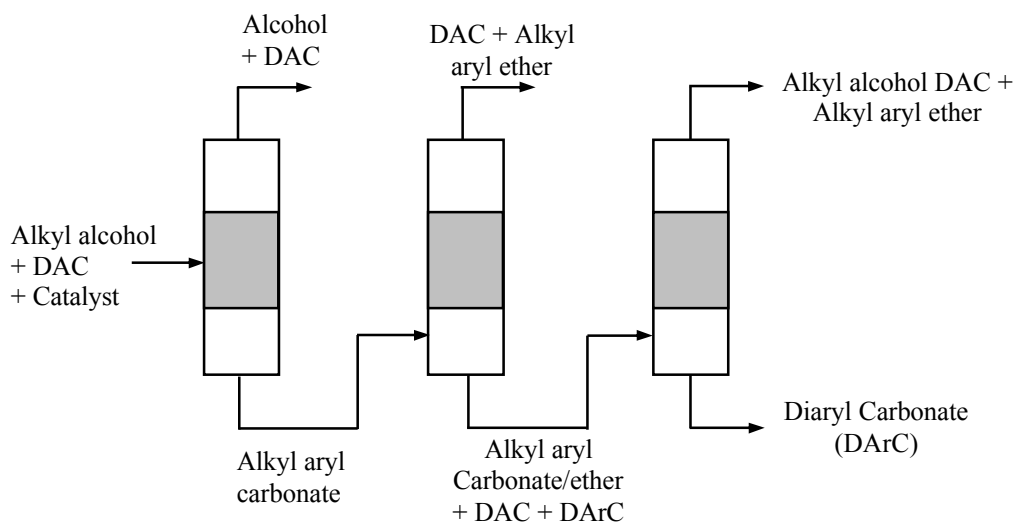
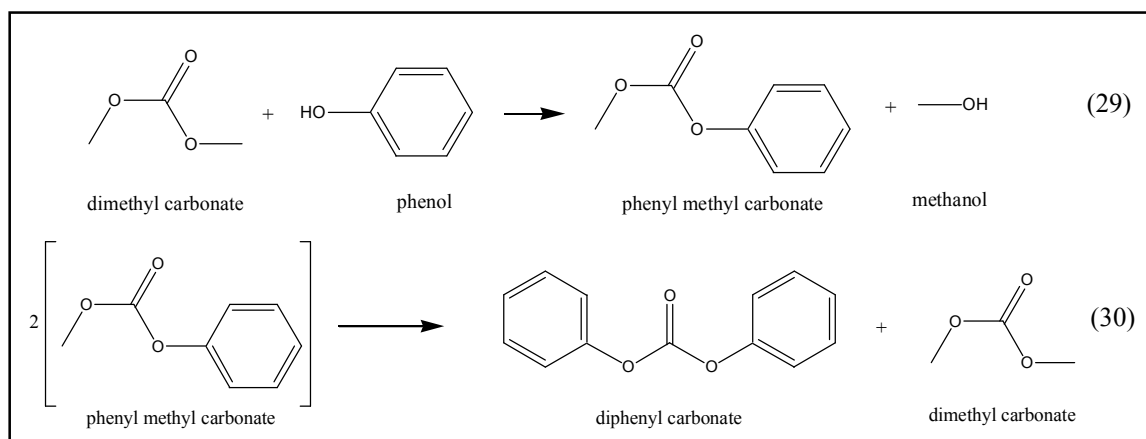


Figure 23: Continuous production of diaryl carbonates using RD (Bruin et al., 2001)

16 APPLICATION OF RD FOR CHIRAL SEPARATION

Enantiomers are difficult to separate from their racemic mixtures by conventional techniques as they possess similar properties. The usual methods adopted for such separation include kinetic resolution with chiral catalyst which exploits the difference in reactivity of these enantiomers. Typically, the undesired enantiomer reacts faster than the other. The desired one that reacts slower is separated from the reaction mixtures later by conventional techniques like distillation. The residue is left with the enantiomeric product(s) and the efficient separation of them also may add a tremendous value in this multi-billion dollar business. A recent article by Okasinski and Doherty (2003) brings out this fact and shows how RD can be advantageously used for the chiral separation that yields both, the enantiomer from the racemate and the corresponding product of kinetic resolution. Both the *yield* and *enantiomeric excess* can be improved

remarkably in RD compared to that obtained in either conventional batch reactor or CSTR. RD not only overcomes equilibrium limitations here but also expedites the reaction of undesired enantiomer by simultaneously removing the corresponding product and thereby increasing the yield. Table 1 gives the list of various reversible reactions like hydration, transesterification, transketalization etc. that can be effectively performed in RD for kinetic resolution. As mentioned by the authors, RD for this application will be only useful when the reaction and distillation conditions match and the reactants, products and catalysts are not temperature sensitive. Fig. 24 gives the schematic for kinetic resolution of propylene oxide in RD given by them. The side reactor is employed to provide required additional hold up as the reaction is relatively slow.

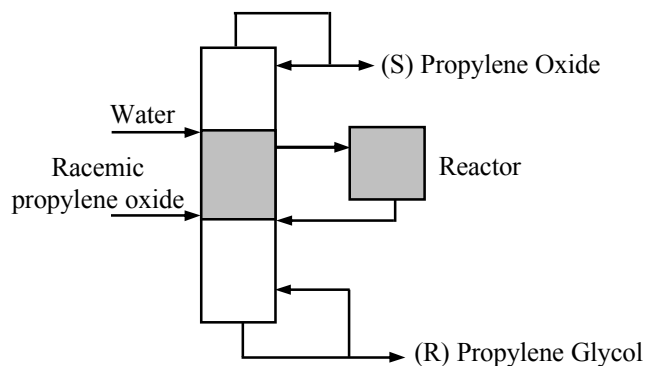


Figure 24: Reactive distillation column schematic for propylene oxide – propylene glycol (Okasinski and Doherty, 2003)

17 RECOVERY OF CHEMICALS

17.1 Lactic acid recovery

Lactic acid is potentially an important raw material for biodegradable polymers such as polylactide. The conventional methods for the recovery of lactic acids are precipitation, extraction with a solvent, electrodialysis, and adsorption. However these recovery processes are not economical because of high cost and low purity of the recovered lactic acid. Lactic acid in high purity from aqueous solutions can be recovered by reactive distillation process. This process gives a good yield of lactic acid by carrying out esterification reaction, distillation and hydrolysis reaction simultaneously. The concept of reactive distillation for recovery of lactic acid by carrying out reaction and distillation is not new. This technique was first applied by Schopmeyer and Arnold (1944) for the continuous process. In this process the crude lactic acid reacts with low boiling aliphatic alcohol (methanol) in the presence of a homogeneous catalyst (sulfuric acid). Due to the corrosion and separation problems along with the occurrence of side reactions posed by the use of homogeneous catalyst this process it is difficult to use it on industrial level. Choi and Hong (1999) have developed batch reactive distillation system using cation exchange resins to overcome the above problem. The system consists of esterification and hydrolysis reactor along with a fractionating column as shown in Fig. 25.

Esterification of crude lactic acid with methanol is takes place in the esterification reactor. The vapors containing unreacted methanol, water and product methyl lactate pass through the fractionating column. Methyl lactate and water being low volatiles get condensed in the partial condenser and flow downward towards the hydrolysis reactor. Hydrolysis of methyl lactate gives methanol and lactic acid. Lactic acid being non-volatile remains in the reactor, but methanol vapors move upward and get condensed in the total condenser. This methanol is recycled back to the esterification reactor. Yield of lactic acid thus

obtained is 95%. In our opinion, this is a novel concept and can be effectively used for recovery of many high boiling compounds obtained in biochemical or chemical reaction.

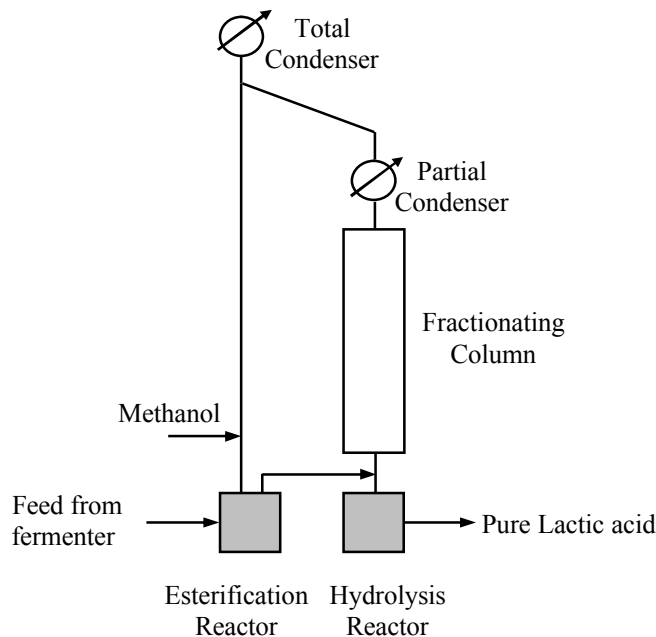
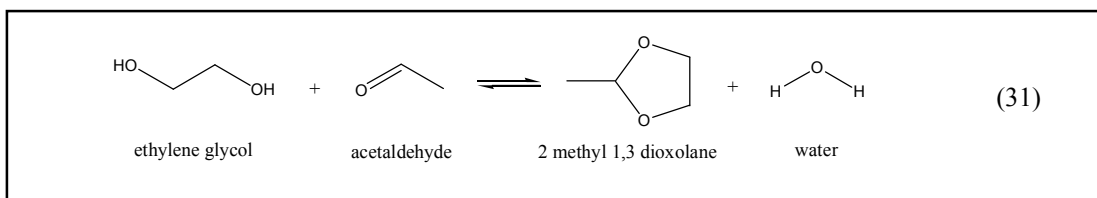


Figure 25: A conceptual block flow diagram for lactic acid recovery from the fermentation product (Choi and Hong, 1999)

17.2 Recovery of polyols

Chopade et al. (2003) have invented a novel reactive distillation based process for the recovery of ethylene and propylene glycol from a mixed polyol aqueous solution resulting from hydrogenolysis of sugars or sugar alcohols to polyols. Fig. 26 shows a reactive distillation column which is fed with polyol and acetaldehyde streams at appropriate locations. Acetaldehyde reacts with polyols to yield the corresponding cyclic acetals (Eq. 31) in the acetalization section. The acetals of EG and PG being more volatile rise through the column and are collected as distillate and further hydrolysed back to EG and PG in separate columns. The acetals of other polyols like glycerol being less volatile than water move towards the bottom and get hydrolysed back to acetaldehyde and glycerol on their way in the hydrolysis section. Two non-reactive enriching and stripping sections are provided at top and bottom for better purity.



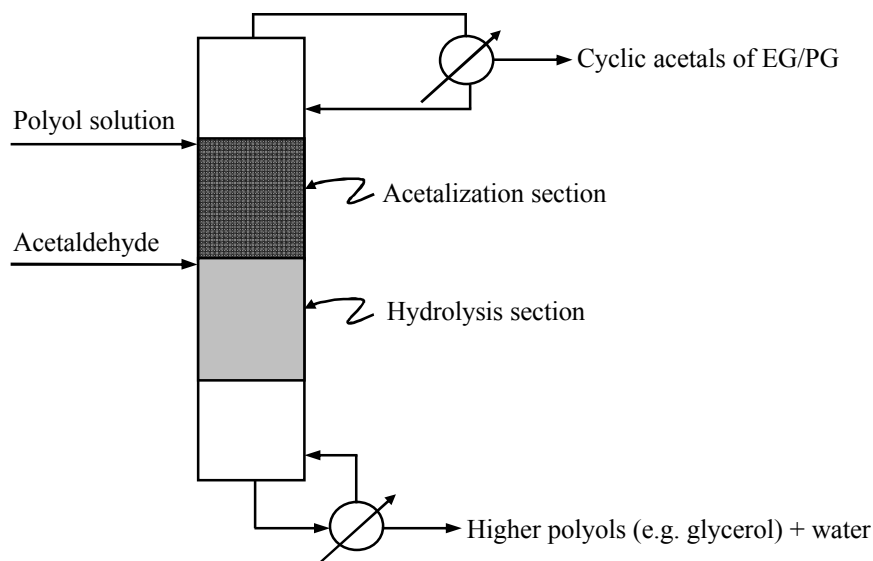
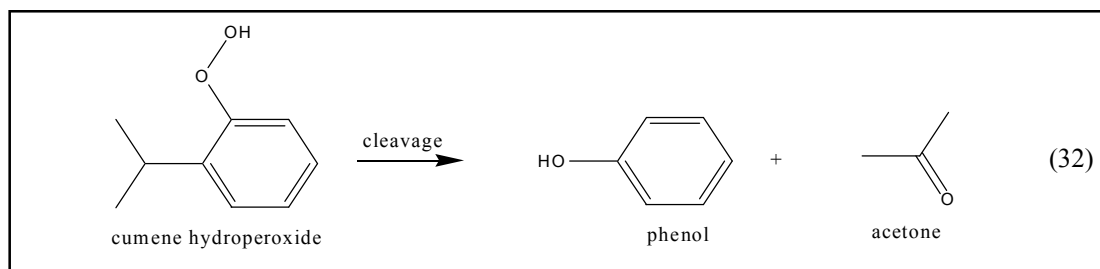


Figure 26: Process for the recovery of a polyol (Chopade et al., 2003)

18 MISCELLANEOUS REACTIONS

18.1 Production of phenol using reactive distillation

Phenol is an important organic chemical with a wide variety of industrial uses. It is used, in the production of phenolic resins, bisphenol-A and caprolactam. Traditionally phenol is produced from cumene. The basic reaction involved in this process is the cleavage of cumene hydroperoxide (Eq. 32) to give phenol and acetone (Levin and Santiesteban, 2002). In a reactive distillation process cumene hydroperoxide is fed into a reactive distillation column comprising at its upper portion a distillation column and at its lower portion a catalyst bed, at a point above or at an upper portion of catalyst bed as shown in Fig. 27. The exothermic decomposition of cumene hydroperoxide takes place in presence of catalyst to form product. The product comprises of a heavy fraction, which is predominantly phenol, and the vaporized light fraction comprising acetone. Heavy fractions are withdrawn from bottom and vaporized light fractions flow upwards through the catalyst bed and are condensed. Introduction of acetone at various locations and in the feed reduces formation of heavy compounds and helps maintain isothermal conditions. Near 100% conversion of cumene hydroperoxide and high selectivity to phenol with minimal production of heavy ends is realized. Moreover, the exothermicity of the reaction substantially reduces the reboiler duty, thus, making the process cost effective.



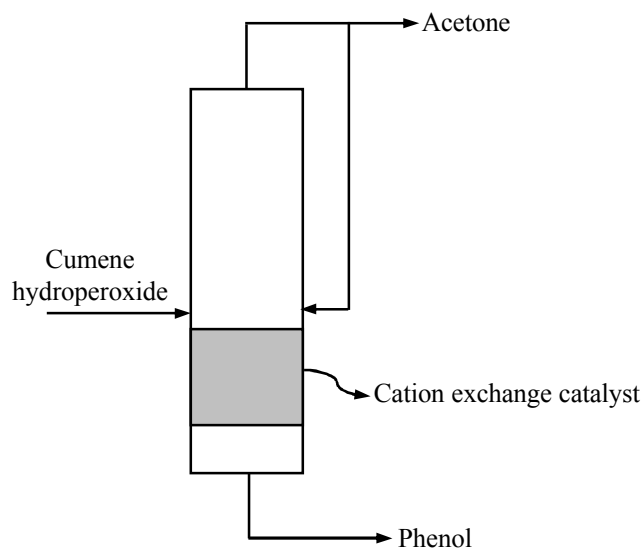
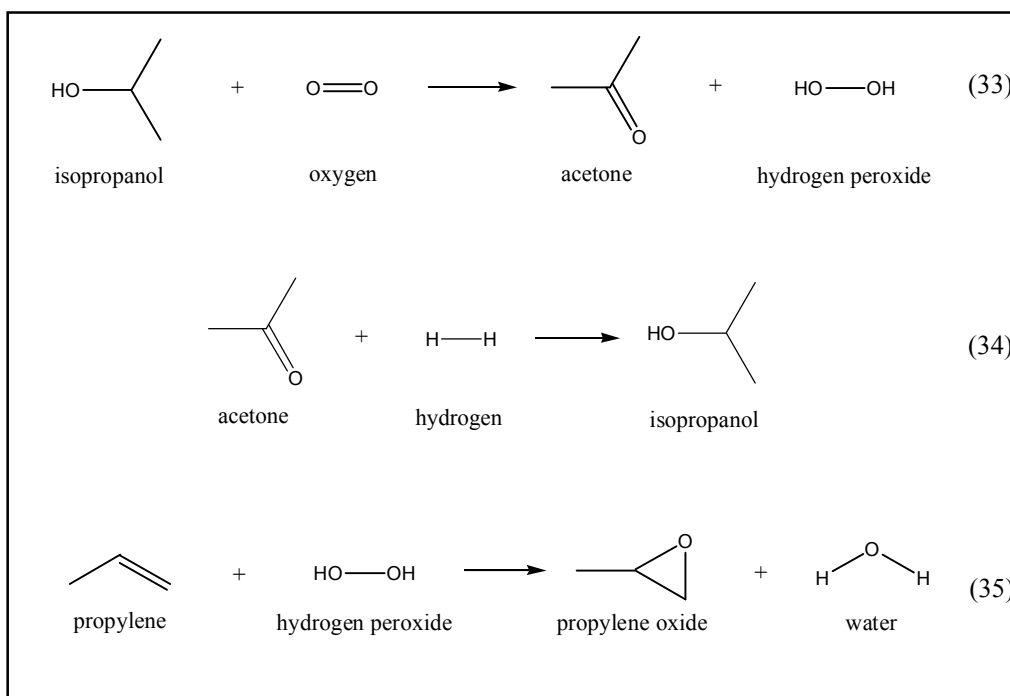


Figure 27: Production of phenol using reactive distillation (Levin and Santiesteban, 2002)

18.2 Propylene oxide process

The epoxidation of propylene to propylene oxide (Eq. 35) requires hydrogen peroxide as one of the reactants. Oxidation of isopropanol (Eq. 33) in a reactive distillation column gives hydrogen peroxide and acetone as shown in Fig. 28. The acetone stream containing water is subjected to second reactive distillation to convert it back to isopropanol by hydrogenation (Eq. 34). The hydrogen peroxide obtained contains only 1-2 wt% acetone and the separation of acetone from water-isopropanol stream is not required prior to hydrogenation (Gelbein, 2002).



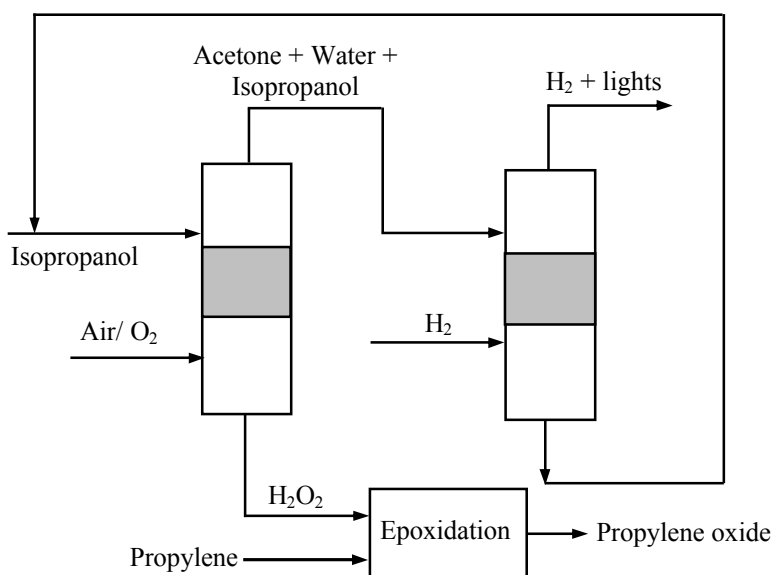
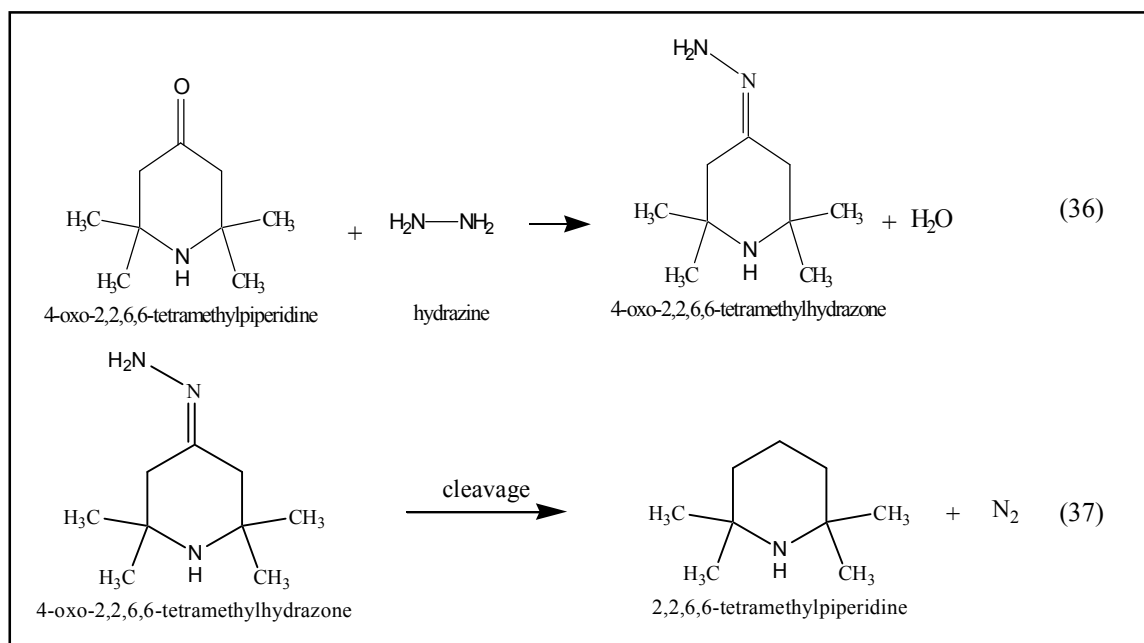


Figure 28: Synthesis of propylene oxide (Gelbein, 2002)

18.3 2, 2, 6, 6-tetramethyl piperidine

2,2,6,6-tetramethyl piperidine due to its strong basic nature, is used as a light stabilizer for polyolefins, co-catalyst in olefin polymerization (Ziegler catalysts) and dichloroacetyl chloride, a building block for the synthesis of pharmaceuticals and crop protection products etc. It is synthesized by reduction of triacetonamine using hydrazine hydrate to hydrazone (Eq. 36) followed by cleavage (Eq. 37) in presence of KOH and ethylene glycol as a solvent. The known processes give lower yields (60-70%) and are expensive to be exploited on industrial level. According to Kampmann and Stuhlmuller (1997), cleavage carried out in the reactive distillation column as shown in Fig. 29, not only results in higher yields (>90%) and purity (>99%) but also substantially reduces the amount of alkali and the solvent used and increases the selectivity of 2,2,6,6-tetramethyl piperidine as well. Moreover, it is also possible to carry out reduction of triacetonamine with hydrazine in a reactive distillation column.



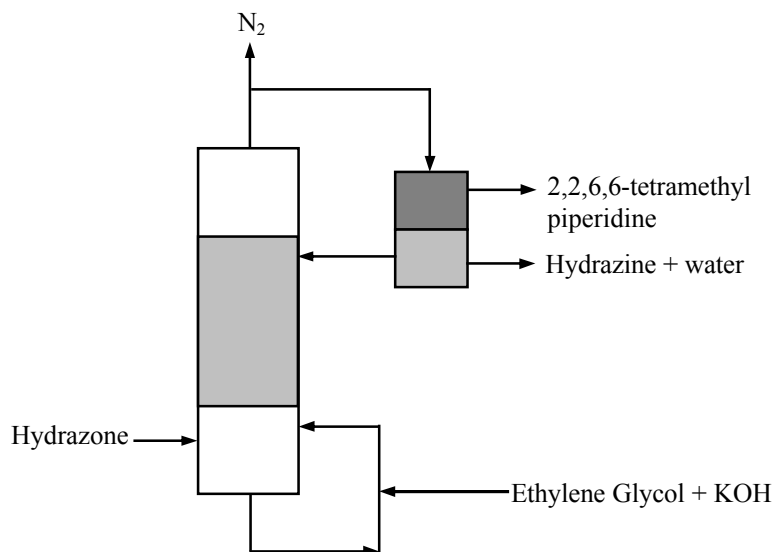


Figure 29: Preparation of 2, 2, 6, 6-tetramethyl piperidine (Kampmann and Stuhlmuller, 1997)

18.4 Synthesis of vinyl acetate

A novel RD process for the manufacture of vinyl acetate from acetic acid and ethylene in the presence of palladium promoted metal alkali catalyst has been recently patented (Adams et al., 2003). The use of non-condensable reacting/non-reacting (oxygen/nitrogen) in reactive distillation is the special feature of this reaction.

CONCLUSION

The application domain of reactive distillation is increasing fast and will continue to remain on the rising trend. In the last few years, reactive distillation has entered in the well-established technologies for the manufacture of carbonates, phenols, and linear alkyl benzenes etc. It also seems to be a promising technology in the lucrative business of chiral chemicals and to some extent in the production of organosilicon derivatives. The idea of coupling more than one reactions in a single column is taking shape especially for various hydrogenation reactions. However, the recent work for some reactions, if not many, has revealed the important limitations of RD especially when the side products are formed at high temperatures near reboiler or because of the depletion of one of the reactants in the reactive zones. Though there is a scope to overcome this limitation by a prudent choice of operating parameters, this may be considered as an important threat to conventional reactive distillation column and modifications like stripped or rectified RD units, side reactor concept are likely to be inevitable in future.

Acknowledgement

The authors would like to acknowledge Prof. M. M. Sharma for the valuable suggestions, guidance and motivation during the preparation of this manuscript.

Table 1: Recent industrially important reactions

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
ESTERIFICATION				
1	Acetic acid + <i>n</i> -butanol = <i>n</i> -butyl acetate + water	Solid acid catalyst, 360-393 K, 1bar Amberlyst-15, KATAPAK-S Indion 130 KATAPAK-S, Amberlyst- 15, 352 K	Purity > 99% 100% conversion Recovery of acetic acid 98.5% conversion, 96.9% purity	Lederer et al. (2002) Gangadwala (2002); Hiwale et al. (2002); Hiwale (2003); Gangadwala et al. (2003) Saha et al. (2000) Steinigeweg et al. (2002)
2	Acetic acid + amyl alcohol = amyl acetate + water	Amberlyst-15, 373- 423 K, 1bar	Four times more efficient than the conventional process based on annual cost	Chiang et al. (2002)
3	Acetic acid + 2-methyl propanol = 2-methyl propyl acetate + water	KATAPAK-S, Solid acid catalyst, 380 K Ion exchange resin, 343 K, 1bar	High conversion Conversion close to 100%.	Smejkal et al. (2001) Hanika et al. (2001)
4	Acetic acid + methanol = Methyl acetate + water	MULTIPAK MULTIPAK KATAPAK-S, Amberlyst-15	High conversion 82.7% conversion 97.1% conversion, 97.5% purity	Gorak and Hoffmann (2001) Kolodziej et al. (2001) Poepken et al. (2001)
5	Acetic acid + ethanol = ethyl acetate + water	MULTIPAK Sulfuric acid	High conversion and purity 99.5% purity,	Vora and Daoutidis (2001); Lee and Westerberg (2001); Von et al. (2001); Von et al. (2002); Kloeker et al. (2003a) Tang et al. (2003)
6	Acetic acid + <i>n</i> -hexanol = <i>n</i> -hexyl acetate + water	KATAPAK-S, MULTIPAK-2, 304-420 K, 0.3-0.5 bar KATAPAK-S, Amberlyst CSP-2, 370-444 K, 1.013 bar	High purity product, >89% conversion ~94% conversion, 99.5% purity	Kloeker et al. (2003b) Kloeker et al. (2003a) Schmitt et al. (2004);
7	<i>n</i> -butanol + acrylic acid = <i>n</i> - butyl acrylate + water	Not available	High yield above 99%	Yang et al. (2000)

Table 1 continued

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
8	Dodecanoic acid + 2-ethyl hexanol = 2-ethylhexyl dodecanoate + water	Super acidic sulfated zirconia catalyst, 343-473 K, 0.32 bar	More uniform and higher reaction rate, high conversion and 99.9% purity	Omota et al. (2003a); Omota et al. (2003b)
	Dodecanoic acid + methanol = methyl dodecanoate + water	KATAPAK-S and KATAPAK-SP (Amberlyst 15), 300-333 K, 3 bar	99% purity	Steinigeweg and Gmehling (2003)
	Dodecanoic acid + 1- propanol = 1-propyl dodecanoate + water	Sulfated zirconia catalyst, 453 K	50% reduction in catalyst requirement	Dimian et al. (2004)
9	Propanol + acetic acid = Propyl acetate + water	Not available	94.8% yield	Li et al. (2003c)
10	hydroxy acid + C1-C8 alcohol = hydroxycarboxylate esters	KATAPAK- S	Production of hydroxycarboxylate esters	Hildebrandt et al. (2003)
11	Lactic acid + methanol = methyl lactate + water	Cation exchange resin	95% yield obtained	Choi and Hong, 1999
TRANSESTERIFICATION				
1	Methyl acetate + <i>n</i> -butanol = butyl acetate + methanol	Amberlyst-15	High purity products and 100% yield	Jimenez and Costa-Lopez (2002)
		KATAPAK-S and KATAPAK-SP (Amberlyst 15), 327-389 K, 1-1.02 bar	Conversion close to 100% Combination of RD and pervaporation	Steinigeweg and Gmehling (2004)
2	Dialkyl oxalate + phenol = alkyl phenyl oxalate	Homogeneous organotin Compounds, 398-498 K	Reduction in by-product formation	Nishihira et al. (2000)
3	Butyl acrylate + dimethyl amino ethanol = dimethylaminoethyl acrylate + butanol	Tetradimethylaminoethyl titanate	Synthesis of dimethylaminoethyl acrylate	Geisendoerfer et al. (2002)
HYDROLYSIS				
1	Methyl acetate + water = dimethyl ether + acetic acid	Acid catalyst	Increase in yield and selectivity	Hoyme and Holcombe (2002)
2	Pentenoyl chloride + water = pentenoic acid + HCl	Not available, 323-398 K, 0.1-2 bar	Minimizes formation of methyl chloride and chloro-valeric acids	Murphree and Ozer (1996)
3	Methyl formate + water = formic acid + methanol	Ion exchange, 311-373 K, 1-30 bar	Better separation, better productivity	Saari et al. (2002)

Table 1 continued

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
4	Hydrolysis of heavy acrylic esters	Sulfuric acid, toluene sulfonic acid, strong acid ion exchange resin,	For production of high purity butyl acrylate	Bauer et al. (2001)
5	Methyl lactate + water = Lactic acid + Methanol	Cation exchange resin	Recovery of lactic acid	Choi and Hong, 1999
6	Glycinonitrile + water = glycine + ammonia	Acientobacter/Rhodococcus maris enzyme catalyst	Salt free process	Aoki and Otsubo (2001)
7	3,3-dimethyl butyl ester + water = 3,3-dimethyl butanol	Not available	Production of 3,3-dimethyl butanol	Jerry et al. (2003)
ETHERIFICATION				
1	Methanol + isobutene = methyl <i>tert</i> butyl ether	KATAMAX Beta- zeolite Ion exchange catalyst, 559-569 K, 7.4-8 bar	99.9% conversion, 98% purity Enhances conversion Higher selectivity towards product	Rix et al. (2003) Li et al. (2002) Qi et al. (2002)
2	C ₄ hydrocarbon mixture (containing isobutene) + isobutanol = isobutyl <i>tert</i> -butyl ether	Levatit ion exchange resins	Higher selectivity towards product, <1.5% by weight isobutene present in the treated C ₄ stream	Bessling et al. (2002)
3	2-ethyl-1-butene + methanol = 3-methoxy-3-methylpentane	Amberlyst RTM 15, 15C Lewatit SPC 118, 118BG Dowex M-31,32, DR-2040	Enhances conversion	Hendriksen et al. (1998)
4	Ethanol + <i>tert</i> butyl alcohol = ethyl <i>tert</i> butyl ether + water	Amberlyst- 15 Beta- zeolite	Conversion 99.9% 95% isobutene conversion	Quitain et al. (2000) Yu et al. (2003)
5	Methanol + 2,4,4-trimethyl pentenes = 2-methoxy-2,4,4-trimethyl pentane	Amberlyst-35, 323-383 K, 1-8 bar	Increase in octane value, higher conversion	Rihko-Struckmann et al. (2004)
6	Methanol + formaldehyde = methylal + water	Ion exchange resin	Separation of formaldehyde from polyoxymethylene dimethyl ether	Hagen and Spangler (2002)
7	Ethylene oxide + ethanol = 2 ethoxyethanol	Zeolite (NKC-01)	Conversion of ethane oxide is 93%	Zhang and Wan (1991)
8	Ethanol + propylene oxide = propylene glycol monoethyl ether	Beta- zeolite	To enhance conversion	Wen et al. (2001)
9	<i>Tert</i> -amyl alcohol + ethanol = <i>tert</i> -amyl ethyl ether + water	Amberlyst-15, Zeolite NaA membrane 348-379 K, 1 bar	Combination of RD and pervaporation	Aiouache and Goto (2003)

Table 1 continued

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
10	Methanol + isoamylene = tert amyl methyl ether	MULTIPAK-2	Production of TAME	Kloeker et al. (2003c)
11	1-butanol + Acetylene = butyl vinyl ether	Potassium hydroxide 408-433 K, 1.4-1.5 bar	Production of butyl vinyl ether	Pisarenko et al. (2002)
HYDROGENATION				
1	Benzene + hydrogen = cyclohexane	Nickel supported on a mixture of titanium dioxide	Higher conversion with 100% selectivity to cyclohexane	Gildert (2001)
2	MAPD + hydrogen = propylene	Palladium oxide, 310-394 K, 15-22 bar	To enhance conversion and selectivity.	Stanley and Gildert (2002)
3	C ₃ to C ₆ = propylene	Pd based catalyst system, 360-383 K, 10-13 bar	Maximizes propylene production	Gartide and Gildert (2002)
4	Hydrogenation of olefins	Palladium based catalyst	Effective separation of dienes from olefins and reduction in by-products	Maraschino (2002)
5	Acetone + hydrogen = MIBK	Not available	Production of MIBK	Saayman et al. (2003)
6	Acetone + hydrogen = isopropanol	Not available, 393-463 K, 19-24 bar	Production of isopropanol	Gelbien (2002)
7	Hydrocracked oil fraction + H ₂ = hydrotreated fraction	Ni/Pd/Co on suitable support 630 K, 131 bar	Significant reduction in hydrogen consumption	Mukherjee and Louie (2003)
HYDRODESULFURISATION				
1	A diesel boiling range petroleum fraction + hydrogen = hydrogen sulphide + sulfur free petroleum fraction	Group VIII metals on suitable support 588-688 K, 42-205 bar	Production of low sulfur diesel	Groten and Loescher (2002)
2	Naphtha + hydrogen = hydrogen Sulphide + sulfur free naphtha	Group VIII metals on suitable support 588-688 K, 42-205 bar	<50 ppm sulfur content, reduced olefin loss	Podrebarac et al. (2001)
DEHYDROGENATION				
1	3,3-dimethyl butanol = 3,3-dimethyl butanal + hydrogen	Not available, 473-673 K, 7.8 bar	Production of 3,3-dimethyl butanal	Jerry et al. (2003)
2	Decalin = naphthalene + hydrogen	Carbon supported platinum catalyst, 473-573 K	A promising source for fuel cell	Shinya et al. (2003)
3	2-propanol = acetone + hydrogen	Ru -Pd/C catalyst	Use in chemical heat pump	Gaspillo et al. (1998)

Table 1 continued

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
ALKYLATION				
1	Benzene or toluene + propylene = cumene / Isopropyltoluene	Beta- zeolite Not available FHI – 01 Cation exchange resin FX-01, 433 K, 8 bar	Propylene conversion 99% and selectivity 90%. 100% conversion of propylene and more than 90% selectivity towards Cumene 99% conversion of propylene and 98% selectivity towards Cumene production of Cumene 98% propylene conversion 94% selectivity of cumene	Zhang et al. (2001a) Wen et al. (2000) Sy (2003) Zhang et al. (2003)
2	Benzene + ethylene = ethyl benzene	Beta- zeolite, 403-468 K, 21-27 bar	Complete conversion of ethylene with high selectivity	Netzer (2001)
3	Benzene + α -olefins = LAB	Mordenite zeolites	High conversion and selectivity	Knifton et al. (2003); Wang and Li (2003); Winder et al. (2003); Barry et al. (2003); Prakasa and George (2003)
4	Benzene + 1-dodecene = C-12 alkylbenzene	Silica gel supported on Tungstophosphoric acid 358-398 K, 1.0-1.6 bar	100% conversion and selectivity	Lei et al. (2003)
METATHESIS/DISPROPORTIONATION				
1	Alkyl phenyl oxalate = diphenyl oxalate + dialkyl oxalate	Homogeneous organotin compounds	Reduction in by-product formation	Nishihira et al. (2000)
2	2-butene + ethylene = propylene	Rhenium based porous mineral substrate and aluminum compound based stabilizer	Reduction in de-activation of catalyst	Commereuc and Mitenko (2002); Podrebarac (2003)
3	C ₁₅ olefins + C ₉ olefins = detergent grade olefins	Co/Mo/Rh based oxides	High conversion and selectivity towards desired olefin	Podrebarac (2003)
4	Isobutylene + isobutylene = tetramethyl ethylene	Cation exchange resin	Better control of product distribution, conversion and diisobutene oligomerization	Podrebarac (2003)

Table 1 continued

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
5	Diisobutylene + ethylene = neohexene	Cation exchange resin	Better temperature control, Higher conversion, Minimization of undesirable side products	Podrebarac (2003)
6	1-butene + 2-butene = propene + 2-pentene	Ru and Re based catalyst on suitable support	Fast removal of products Higher conversion	Schwab et al. (2002); Peter and Michael (2003)
7	Mixed anhydride = triflic anhydride + carboxylic anhydride	Cation exchange resins (NAFION/DUOLITE), 343-423 K, 1 bar	Elimination of phosphorus reagent, lower equipment cost, efficient heat utilization	Hembre and Lin (2002)
HYDRATION/DEHYDRATION				
1	<i>tert</i> -butanol = isobutylene + water	Beta- zeolite, 353-393 K, ~1 bar	To enhance conversion	Knifton et al. (2003)
2	Ethylene oxide + water = Ethylene glycol	Not available	Conversion is close to 100% and >98% selectivity	Liu et al. (2002a)
3	Cyclohexene + water = Cyclohexanol	Hydrophilic zeolite catalyst, (H-ZSM 5, high Si /Al ratio), 323-443 K, 1bar	Minimal formation of by-products	Frank et al. (2002)
4	Dehydration of <i>tert</i> butyl ether	KATAPAK-SP, S	To enhance conversion	Gotze et al. (2001)
5	<i>tert</i> -butyl alcohol = isobutene + water	Amberlyst 15	For use in Chemical Heat Pump	Abella et al. (1999)
6	Butanediol = tetrahydrofuran + water	Not available, Acid resin containing silica	High purity product Purity of Tetrahydrofuran > 98%	Liu and Xiao (2001) Liu et al. (2002b)
7	Isobutene + water = <i>tert</i> -butyl alcohol	Amberlyst-15, 323-353 K	To enhance the yield of <i>tert</i> -butyl alcohol	Zhang et al. (2003)
CARBONYLATION				
1	Methanol + carbon monoxide = acetic acid	Homogeneous catalyst system comprising of Group VIII compounds with a halide promoter, 423-553 K, 25-40 bar	Prevents precipitation and deactivation of catalyst and accumulation of hydrogen iodide	Voss (2001)
POLYMERS				
1	Amino nitrile + water = polyamide + ammonia	Heterogeneous Bronsted Acid catalyst	Higher conversion and reduces cost of starting material and energy consumption	Leemann et al. (2002)
2	Caprolactam + water = nylon 6	Oxygen containing Phosphorous compounds	Eliminates costly purification step of an intermediate product	Cohen et al. (2002); Stuart et al. (2002)
CHLORINATION/AMINATION				
1	Ethylene oxide + ammonia = diethanol amine, monoethanol amine, tri ethanol amine, ethylene glycol	Absence of catalyst	> 90% selectivity towards Diethaneolamine	DiGuilio and McKinney (2000)

Table 1 continued

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
SYNTHESIS OF CARBONATES				
1	Methanol + urea and / or alkyl carbonate = dimethyl carbonate	Dibutyltin dimethoxide, Tetraphenytin 420-466 K, 3-11 bar	Improve the selectivity towards dimethyl carbonate	Ryu and Gelbein (2002)
2	Dialkyl carbonate + phenol = alkyl phenyl carbonate	Homogeneous catalyst	High production and efficient recovery of unreacted species	Bruin et al. (2001)
3	ethylene carbonate + methanol = 2-hydroxyethyl methyl carbonate HEMC + methanol = dimethyl carbonate + ethylene glycol	Ion exchange resins	High yield, high purity minimization of hydroxy alkyl carbonate	Scott et al. (2003)
APPLICATION OF RD FOR CHIRAL SEPARATION				
1	Propylene oxide (r,s) + water = Propylene glycol (r) + Propylene oxide (s)	Cobalt based chiral catalyst, 349-371 K, 1 bar	The enantiomeric reactant (s-form) and the product (r-form) are valuable chemicals	Okasinski and Doherty (2003)
2	R-OH (r,s) + ethyl acetate = R-acetate (r) + ethanol + R-OH (s)	Chiral catalyst, 349-371 K, 1 bar	Ethanol and R-OH (r) can be removed as top products or a side-stream distillation column can be used	Okasinski and Doherty (2003)
3	Ethanol + methyl phenyl ketone(r,s) = phenyl ethyl alcohol (r) + acetone	Chiral bidentate Schiff Bases, 349-371 K, 1 bar	A very fast reaction. The products are lowest and highest boiling and hence can be conveniently separated in the same RD column and quantitative yields may be realized	Okasinski and Doherty (2003)
ACETALIZATION				
1	Ethylene glycol + acetaldehyde = 2-methyl-1,3-dioxolane + water	KATAMAX, Amberlyst 15 335-376 K, 1bar	Recovery of polyols	Chopade et al. (2003)
MISCELLANEOUS REACTIONS				
1	Cumene hydroperoxide = phenol + acetone	Sulfonic ion exchange resin	Close to 100% conversion and high selectivity towards phenol	Levin and Santiesteban (2002); Doron and Jose (2002)
2	Preparation of Monochloroacetone	Not available	Pure product and the concentration of monochloroacetone is 98%	Zhang et al. (2001b)
3	Acetone = diacetone alcohol	Amberlite IRA-900 anion exchange resin	To enhance conversion	Podrebarac et al. (1998); Zheng et al. (2003b)

Table 1 continued

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
4	Ethanol + dimethyl carbonate = diethyl carbonate	K ₂ CO ₃ , 348-405 K, 1 bar	Side reactions minimized	Luo and Xiao (2001)
5	hydrazone = 2,2,6,6-tetramethyl-piperidine + N ₂ (cleavage)	Not available, 448-468 K	>90% yield, >99% purity, Increased selectivity	Kampmann and Stuhlmüller (1997)
6	<i>tert</i> -butyl bromide + ethylene = 1-neohexyl bromide = neohexene	AlCl ₃	Purity of product > 98%, Yield of product up to 88%	Lin et al. (2003)
7	Maleic anhydride + methanol = di-methyl maleate	DNW-1 Solid acid catalyst	Conversion of maleic anhydride close to 100% and yield of di-methyl maleate > 99% High conversion	Hao et al. (2003) Anonymous
8	(<i>Oxyacylation</i>) Acetic acid + ethylene + oxygen = vinyl acetate + water	Palladium based catalyst 338-420 K, 2-5 bar	Side reactions minimized Reduction in polymer built-up and coking	Adams et al. (2003)
9	isobutene + isobutene = diisobutene	Cation exchange resin	Production of diisobutene	Mitchell (2003)
10	(<i>Fischer Tropsch</i>) CO + H ₂ = hydrocarbons and oxygenates	Not available	Efficient handling of heat releases, better purity products	George (2000)

Table 2: Multiple Reactions in Reactive Distillation Columns

Sr. No.	Reaction	Product of Interest	References
1	a) Dicyclopentadiene = Cyclopentadiene b) Cyclopentadiene + hydrogen = Cyclopentane	Cyclopentane/cyclopentene	Silverberg et al. (2000)
2	a) Isobutene = diisobutene b) Di isobutene + hydrogen = isooctane	Isooctane	Gildert and Loescher (2001)
3	a) Butadiene + HCl = Chlorobutene b) 3-pentenoyl chloride +water = 3-pentenoic acid + HCl	3-pentenoic acid	Murphree and Ozer (1996)

Table 3: Limitations of RD

Sr. No.	Reaction	Catalyst, Operating conditions etc.	Remarks on motive and achievements	References
Limitations based on Selectivity				
1	Acetic acid + <i>n</i> -butanol = <i>n</i> -butyl acetate + water	Amberlyst-15, KATAPAK-S	Formation of <i>n</i> -di-butyl ether	Gangadwala (2002); Hiwale et al. (2002); Hiwale (2003); Gangadwala et al. (2003)
2	Alcoxylation and aceoxylation of chloro silanes	Not available	Undesired by-products due to high temperature zones near reboiler	Bade and Robers (2000)
Limitations based on Cost Effectiveness				
1	Methyl acetate + <i>n</i> -butanol = butyl acetate + methanol	Amberlyst-15	Economic study reveals that the process has no profitability	Jimenez and Costa-Lopez (2002)
2	Toluene = benzene + (o/m/p) xylene	Not available	High pressure requirement	Stitt (2002)
3	acetone = diacetone alcohol diacetone alcohol = mesityl alcohol + water	Anion exchange resin	High catalyst-liquid mass transfer resistance	Nicol (2003)

References

- Abella L.C., Gaspillo P. D., Itoh H. and Goto S., "Dehydration of *tert*-butyl alcohol in reactive distillation", *J. Chem. Eng. Japan*, Vol. 32, No. 6, 742-746, *cf* CA 132:166555 (1999).
- Adams J., Groten W., and Nemphos S., "Process for vinyl acetate", US Pat. 6,620,465 (2003).
- Aiouache F., and Goto S., "Reactive distillation-pervaporation hybrid column for *tert*-amyl alcohol etherification with ethanol", *Chem. Eng. Sci.*, Vol. 58, No. 12, 2465 – 2477 (2003).
- Al-Arfaj M. A. and Luyben W. L., "Effect of number of fractionating trays on reactive distillation column performance", *AIChE J.*, Vol. 46, No. 12, 2417-2425, *cf* CA 134: 43968 (2000).
- Aoki T. and Otsubo K., "Reactive distillation for manufacture of glycerin from glycinonitrile", *Jpn. Kokai Tokkyo Koho*, *cf* CA 135:225949 (2001).
- Anonymous, Davy process technology, "Esters to alcohols and back again": <http://www.davyprotech.com/pdfs/8.204-Esters%20to%20Alcohols%20&%20Back.pdf> (Last cited in May 2003).
- Bade S. and Robers U., "Process for preparing alkoxysilanes", US Pat. 6,150,550 (2000).
- Bank H. M. and Meindertsma R. D., "Process for organooxylation of Cyanoalkylchlorosilanes", US Pat. 5,374,757 (1994).
- Bank H. M. and Petrisko R. A., "Method for preparation of organoalkoxysilanes", US Pat. 4,924,022 (1990)
- Barry W., Donald W., John S., Mary B., Joy M., Richard H., Wayne S. and Daniel S., "Reactive distillation process for the alkylation of aromatic hydrocarbons", US Pat. 6,642,425 (2003).
- Bauer J. W., Chapman J. T., Mirabelli M.G. and Venter J. J., "Process for producing butyl acrylate", U.S. Pat. 6,180,819 (2001).
- Baur R. and Krishna R., "Hardware selection and design aspects for RD columns. A case study on the synthesis of TAME", *Chem. Eng. and Processing*, Vol. 41, No. 5, 445- 462 (2002).
- Baur R., Higler A. P., Taylor R. and Krishna R., "Comparison of equilibrium stage and non- equilibrium stage models for Reactive Distillation", *Chem. Eng. J.*, Vol. 76, No. 1, 33-47 (2000).
- Baur R., Taylor R. and Krishna, R., "Dynamic behavior of reactive distillation columns described by a non equilibrium stage model", *Chem. Eng. Sci.*, Vol. 56, No. 6, 2085-2102 (2001b).
- Baur R., Taylor R. and Krishna, R., "Influence of column hardware on the performance of reactive distillation column", *Catal. Today*, Vol. 66, No. 2-4, 225-232 (2001a).
- Baur R., Taylor R. and Krishna R., "Bifurcation analysis for TAME synthesis in a reactive distillation column: Comparison of pseudo- homogeneous and heterogeneous reaction kinetics models", *Chem. Eng. and Processing*, Vol. 42, No. 3, 211-221 (2003).
- Beckmann A., Nierlich F., Popken T., Reusch D., von Scala C. and Tuchlenski, A., "Industrial experience in the scale-up of reactive distillation with examples from C₄-chemistry", *Chem. Eng. Sci.*, Vol. 57, No. 9, 1525-1530 (2002).
- Bessling B., Knab J., Brox W. and Lohe B., "Method and device for obtaining isobutenes from conjugated hydrocarbons", US Pat. 6,362,386 (2002).

Bisowarno B. H. and Tade M. O., "The comparison of disturbance properties of the point control schemes for ETBE reactive distillation", *Chem. Eng. Comm.*, Vol. 189, No. 1, 85-100 (2002).

Bowman M. P., Childres T. E., Mendicino F. D and Warren R. I., "Continuous transesterification process for alkoxyorganosilicon compounds", US Pat. 6,489,500 (2002).

Bruin P. R., Law J.S. and Vriens V.A., "Method and apparatus for the continuous production of diaryl carbonate", US Pat. Appli. 20010021786 (2001).

Chen F., Huss R. S., Doherty M. F. and Malone M. F., "Multiple steady states in reactive distillation: Kinetic effects", *Comp. and Chem. Eng.*, Vol. 26, No. 1, 81-93 (2002).

Chen F., Huss R.S., Malone M. F. and Doherty, M. F. "Simulation of kinetic effects in reactive distillation", *Comp. and Chem. Eng.*, Vol. 24, No. 11, 2457- 2472 (2000).

Chiang, S., Kuo, C., Yu, C., Wong and David S.H., "Design alternatives for the amyl acetate process: Coupled Reactor/column and reactive distillation", *Ind. Eng. Chem. Res.*, Vol. 41, No. 13, 3233- 3246 (2002).

Choi J. and Hong W. N., " Recovery of Lactic acid by batch distillation with chemical reactions using ion exchange resins", *Jr. of Chem. Eng. Japan*, Vol. 32, No. 2, 184-189, *cf* CA 131:60286 (1999).

Chopade S.P., Dhale A. D., Kiesling C. W., Clark A. M., Jackson J. E. and Miller D. J., "Process for the recovery of a polyol from an aqueous solution", U S Pat. 6,548,681 (2003).

Cohen J.D., Fergusson S.B., Marchildon E.K., Marks D.N. and Mutel A.T., "Process for the production of nylon 6", US Pat. 6,437,089 (2002).

Commereuc D. and Mikitenko P., "Process for metathesis of olefins in the presence of a stabilizing agent of the catalyst", US Pat. 6,437,209 (2002).

DiGuilio R. M., and McKinney M. W., "Selective production of diethanolamine", US Pat. 6,075,168 (2000).

Dimian A., Omota F., and Bliet A., "Entrainer-enhanced reactive distillation", *Chem. Eng. Proc.*, Vol. 43, No. 3, 411-420 (2004).

Doherty, M.F. and Buzad G, "Reactive distillation by design", *Chem. Eng. Res. and Design, Transactions of the Institution of Chem. Engineers*, Part A, Vol. 70, 448-458 (1992).

Doron L. and Jose S., "Apparatus for producing phenol using reactive distillation", US Pat., 6,441,252 (2002).

Fernholtz G., Engell S., Kreul L. and Gorak A., "Optimal operation of a semi-batch RD column", *Comp. and Chem. Eng.*, Vol. 24, No. 2-7,1569-1575 (2000).

Frank S., Zhiwen Q. and Sundmacher K., "Synthesis of cyclohexanol by three-phase reactive distillation: influence of kinetics on phase equilibria", *Chem. Eng. Sci.*, Vol. 57, No. 9, 1511-1520 (2002).

Fuchigami Y., "Hydrolysis of methyl acetate in distillation column packed with reactive packing of ion exchange resin", *J. Chem. Eng., Japan*, Vol. 23, No. 3, 354-359, *cf* CA 113:80919 (1990).

Gangadwala J., "Synthesis of butyl acetate in the presence of ion exchange resins as catalysts", *M. Tech Dissertation*, IIT Bombay (2002).

Gangadwala J., Mankar S., Mahajani S. M., Kienle A. and Stein E., "Synthesis of butyl acetate in the presence of ion exchange resins as catalysts", *Ind. Eng. Chem. Res.*, Vol. 42, No. 10, 2146-2155 (2003).
Gartide R. and Gildert G., "Cracked gas processing and conversion for propylene production", US Pat. 6,420,619 (2002).

Geisendoerfer M., Nestler G., Schroeder J., and Vandenmersch H., "Transesterification process for the manufacture of basic (meth) acrylate esters from alkyl (meth) acrylates", *cf CA 137:109609* (2002).

Gelbein A. P., "Three stage propylene oxide process", US Pat. 6,337,412 (2002).

Giessler S., Danilov R. Y., Pisarenko R. Y., Serafimov L. A., Hasebe S. and Hashimoto I., "Systematic structure generation for reactive distillation processes", *Comp. and Chem. Eng.*, Vol. 25, No. 1, 49-60 (2001).

Gildert G. R. and Loescher M.E., "Catalytic distillation process for the production of C8 alkanes", US Pat. 6,274,783 (2001).

Gildert G.R., "Hydrogenation of benzene to cyclohexane", US Pat. 6,187,980 (2001).

Gorak A. and Hoffmann A., "Catalytic distillation in structured packings: methyl acetate", *AIChE J.*, Vol. 47, No. 5, 1067-1076 (2001).

Gotze L., Bailer O., Moritz P. and Von S. "Reactive distillation with KATAPACK", *Catal. Today*, Vol. 69, No. 1-4, 201-208 (2001).

Groten W.A. and Loescher M.E., "Process for the production of an ultra low sulfur", US Pat. 6, 416,659 (2002).

Grund G., Rix A. and Bueschken W., "Etherification and reactive distillation processes for the manufacture of high-purity methyl *tert*-butyl ether and an isobutylene-free C4 hydrocarbon mixture", Eur. Pat. Appl., *cf CA 136:327382* (2002).

Hagen G. P. and Spangler M. J., "Preparation of polyoxymethylene dialkane ethers, by catalytic conversion of formaldehyde formed by dehydrogenation of methanol or dimethyl ether", US Pat. 6,350,919 (2002).

Hanika J., Kolena J. and Smejkal Q., "Butyl Acetate via Reactive Distillation: Modeling and Experiment", *Chem. Eng. Sci.*, Vol. 54, No. 21, 5205-5209 (1999).

Hanika J.; Smejkal Q. and Kolena J; "2-methylpropylacetate synthesis via reactive distillation", *Catal. Today*, Vol. 66, No. 2-4, 219-223 (2001).

Hao X., Dong L., Yu Z., Wang W. and Wang W. C., "Synthesis of di-methyl maleate by catalytic distillation", *Shiyou Huagong*, Vol. 32, No. 3, 187-190, *cf CA 139:38187* (2003).

Hembre R. and Lin R., "Process for the preparation of triflic anhydride", US Pat. 6,469,206 (2002).

Hendriksen D. E., McGlamery G. G., Keenan M. J. and Pete D. D., "Process for preparing 3-methyl-2-pentene", US Pat. 5,731,486 (1998).

Hildebrandt R., Vollmer S., Alscher A., and Hoeltmann W., "Esterification processes for the preparation of hydroxycarboxylate esters via the reactive distillation of an α -hydroxycarboxylic acid with a C₁-C₈ alcohol in the presence of an esterification catalyst", Eur. Pat. Appl., *cf CA 138:289362* (2003).

Hiwale R.S., Naphade P.S. and Mahajani S.M., "Synthesis of butyl acetate through reactive distillation", *Chemcon conference paper*, Hyderabad, India (2002).

Hiwale R.S., "Synthesis of butyl acetate by reactive distillation", *M. Tech Dissertation*, IIT Bombay (2003).

Hoyme C.A. and Holcombe E.F., "Reactive distillation process for hydrolysis of esters", US Pat. Appli. 20020077501 (2002).

George J. A., "Fisher-Tropsch synthesis via Reactive Distillation", http://pep.sric.sri.com/Public/Reports/Phase_2000/RW2000-13/RW2000-13.html (cited in June 2003)

Gaspillo P., Abella L. and Goto S., "Dehydrogenation of 2-propanol in reactive distillation column for chemical heat pump", *J Chem. Eng. Jap.*, Vol. 31, No. 3, 440-444 (1998).

Jerry E., Zhi G., Arnold H., Loraine K., William M., Mark P. and Indra P., "Process for the preparation of 3, 3-dimethylbutanal", US Pat., 6,573,409 (2003).

Jimenez, L., and Costa-Lopez J., "The Production of butyl acetate and methanol via reactive and extractive distillation II. Process modeling, dynamic simulation, and control Strategy", *Ind. Eng. Chem. Res.*, Vol. 41, No. 26, 6735-6744 (2002).

John P., Feichtner W., Graf W. and Frey V. "Process for preparing acyloxysilanes and acyloxysiloxanes", US Pat. 4,176,130 (1979).

Kampmann D. and Stuhlmuller G., "Process for the continuous preparation of 2, 2, 6, 6-tetramethylpiperidine", US Pat. 5,663,351 (1997).

Kenig E. Y., Bader H., Gorak A., Bessling B., Adrian T. and Schoenmaker H., "Investigation of ethyl acetate reactive distillation process", *Chem. Eng. Sci.*, Vol. 56, No. 21-22, 6185-6193 (2001).

Kim J., Lim C., Hant M. and Kim B., "Preparation of p-toluene sulfonic acid using reactive distillation", *Hwahak Konghak*, Vol. 40, No. 5, 565-571, *cf* CA 139:69013 (2002).

Kloeker M., Keing E., Schmitt M., Althaus K., Shoenmaker H., Markusse A. and Kwant G., "Influence of operating conditions and column configuration on the performance of reactive distillation columns with liquid-liquid separators", *Can. J. Chem. Eng.*, Vol. 81, No. 3-4, 725-730 (2003a).

Kloeker M., Kenig E. and Gorak A., "On the development of new column internals for reactive separations via integration of CFD and process simulation", *Catal. Today*, Vol. 79-80, 479-485 (2003b).

Kloeker M., Kenig E., Gorak A., Fraczek K., Salacki W. and Orlikowski W., "Experimental and theoretical studies of the TAME synthesis by reactive distillation", *Computer-Aided Chem. Eng.*, *cf* CA 139:278386 (2003c).

Knifton J. F., Anantaneni P. R., Eugene Dai P.E. and Stockton M. E., "Reactive distillation for sustainable, high 2-phenyl LAB production", *Catal. Today*, Vol. 79-80, 77-82 (2003).

Kolah A. K., Qi Z. and Mahajani S. M., "Dimerized isobutene: An alternative to MTBE", *Chem. Innovation*, 15-21 (2001).

Kolodziej A., Jaroszynski M., Hoffmann A.; and Gorak A., "Determination of catalytic packing characteristics for reactive distillation", *Catal. Today*, Vol. 69, No. 1-4, 75-85 (2001).

Lederer J., Kolena J., Hanika J., Levering W. W., Bailer O., Moravek P., Smejkal Q. and Macek V., "Process and apparatus for the production of butylacetate and isobutylacetate", US Pat. 6,458,992 (2002).

Lee J. W. and Westerberg A. W., "Graphical design applied to MTBE and methyl acetate reactive distillation processes", *AIChE J.*, Vol. 47, No. 6, 1333-1345 (2001).

Leemann M., Hildebrandt V., Thiele H. and Espig S., "Production of polyamides by reactive distillation", US Pat. 6,358,373 (2002).

Levin D. and Santiesteban J.G., "Production of phenol using reactive distillation", US Pat. 6,410,804 (2002).

Li D., Cao G., Zhang J., Song S., Wang Z. and Yu X., "Pilot plant test for the synthesis of cumene by catalytic distillation" *Shiyou Huagong*, Vol. 30, No. 5, 351-354, *cf* CA 135:197150 (2001).

Li D., Zhi-gang T., and Zhan-ting D., "Production of propyl acetate by reactive distillation", *Jingxi Huagong*, Vol. 20, No. 9, 532-534 (2003c).

Li Y., Huang S., Wu S. and Yuan X., "Preparation and Catalytic Distillation Testing of an Acidic Zeolite Film Catalytic Packing for Synthesis of ETBE", *Catal. Letters*, Vol. 87, No. 1-2, 31-35 (2003a).

Li Y., Yu S., Yuan X. and Wang H., "The etherification of methanol and isobutene in a catalytic distillation column packed with zeolite-beta-coated catalytic packing", *Ind. Eng. Chem. Res.*, Vol. 41, No. 20, 4936-4940 (2002).

Li Y., Yuan X. and Wu S., "Zeolite film packing: Application to synthesis of ETBE in a catalytic distillation column", *Abstracts of papers*, 225th ACS National meeting, New Orleans, LA United States, *cf* AN 2003:182540 (2003b).

Lin F., Li C. and Chen, X., "Synthesis of neohexene", *Huaxue Fanying Gongcheng Yu Gongyi*, Vol. 19, No. 1, 40-44, *cf* CA 139:53342 (2003).

Liu H., Qu Y. and Wang W., "Simulation of hydration process of water and ethylene oxide by reactive distillation to produce glycol", *Beijing Huagong Daxue Xuebao*, *cf* CA 137:156380 (2002a).

Liu Q. and Xiao J., "Synthesis of tetrahydrofuran from butanediol by pressure-sensitive reactive distillation", *Jisuanji Yu Yingyong Huaxue*, *cf* CA 135:94243 (2001).

Liu Q., Zhang F. and Gao H., "Synthesis of tetrahydrofuran from butanediol by reactive distillation", *Huaxue Gongcheng*, Vol. 30, No. 2, 75-78, *cf* CA 138:289287 (2002b).

Lowenberg P., Schlosser T., Horn M., Loven R. and Monkiewicz J., "Process for the preparation of alkoxysilanes", US Pat. 6,323,356 (2001).

Luo H.P. and Xiao W.D., "A reactive distillation process for a cascade and azeotropic reaction system: Carbonylation of ethanol with dimethyl carbonate", *Chem. Eng. Sci.*, Vol. 56, No. 2, 403-410 (2001).

Mahajani S. M. and Chopade S. P., "Reactive Distillation: Processes of Commercial Importance", in *Encyclopedia of Separation Science* by Wilson I. D., Edlard T. R., Poole C. A. and Cooke M. (Eds.), Academic Press, London, UK, 4075-4082 (2001).

Malone M.F. and Doherty M.F., "Reactive Distillation", *Ind. Eng. Chem. Res.*, Vol. 39, No. 11, 3953-3957 (2000).

Maraschino M. J., "Apparatus and process for hydrogenations", US Pat. 6,407,300 (2002).

Mitchell L., "Recovery of tertiary butyl alcohol", US Pat., 6,596,913 (2003).

Mukherjee U., and Louie W., "Hydrocracking of vacuum gas and other oils using post-treatment reactive distillation system" US Pat. 6,547,956 (2003).

Murphree, B. and Ozer, R., "Preparation of pentenoic acid", US Pat. 5,536,873 (1996).

- Netzer D., "Method for producing ethyl benzene", US Pat. 6,252,126 (2001).
- Ng F., and Rempel G., "Catalytic Distillation", *Encyclopedia of Catalysis*, John Wiley and Sons, Vol. 2, 477-505 (2003).
- Nicol W., "Comparing catalytic distillation to separate reaction and distillation for the production of diacetone alcohol", *Chem. Eng. Res. Des.*, Vol. 81 (A8), 1026-1032 (2003).
- Nishihira K., Tanaka S. and Nishihida Y., "Process for producing a diaryl oxalate", US Pat. 6,018,072 (2000).
- Nitzsche S., Zeller N., Graf W. and Bauer I., "Process for the manufacture of alkoxy silanes and alkoxy polysiloxanes", US Pat. 3,792,071 (1974).
- Noeres C., Kenig E. Y. and Gorak A., "Modelling of reactive separation processes: reactive absorption and reactive distillation", *Chem. Eng. and Processing*, Vol. 42, No. 3, 157-178 (2003).
- Okasinski M. J. and Doherty M. F., "Simultaneous kinetic resolution of chiral propylene oxide and propylene glycol in a continuous reactive distillation column", *Chem. Eng. Sci.*, Vol. 58, 1289 (2003).
- Okur H. and Bayramoglu M., "The effect of the liquid phase activity model on the simulation of ethyl acetate production by reactive distillation", *Ind. Eng. Chem. Res.*, Vol. 40, No. 16, 3639 – 3646 (2001).
- Omota F., Dimian A., and Blik A., "Fatty acid esterification by reactive distillation. Part1: equilibrium-based design", *Chem. Eng. Sci.*, Vol. 58, No. 14, 3159 – 3174 (2003a).
- Omota F., Dimian A., and Blik A., "Fatty acid esterification by reactive distillation. Part2: Kinetic based design for sulfated zirconia catalyst", *Chem. Eng. Sci.*, Vol. 58, No. 14, 3175 – 3185 (2003b).
- Peng J., Lextrait S., Edgar T. F. and Eldridge, R. B. "A comparison of steady state equilibrium and rate based models for packed reactive distillation columns", *Ind. Eng. Chem. Res.*, Vol. 4, No. 11, 2735-2744 (2002).
- Peter S and Michael S., "Preparation of propene", US Pat., 6,646,172 (2003).
- Pisarenko O., Yu A., Serafimov L., Timofeev V., "Method for the manufacture of butyl vinyl ether from 1-butanol and acetylene", Russ. Pat., *cf CA* 138:304678 (2002).
- Podrebarac G. G., Gildert G. R. and Groten, W. A., "Process for desulfurization of petroleum feeds", US Pat. 6,303,020 (2001).
- Podrebarac G. G., Ng F. T. T. and G.L. Rempel, "The production of diacetone alcohol with catalytic distillation. Part I. Catalytic Distillation", *Chem. Eng. Sci.*, Vol. 53, No. 5, 1067-1075 (1998).
- Podrebarac G., "Olefin metathesis in a distillation column reactor", US Pat., 6,583,329 (2003).
- Podrebarac G., Ng F., and Rempel G., "More uses for Catalytic Distillation", *CHEMTECH*, Vol. 27, No. 5, 37-45, *cf CA* 126: 344747 (1997).
- Poepken T., Steinigeweg S., and Gmehling J., "Synthesis and hydrolysis of methyl acetate by reactive distillation structured catalytic packings: Experiments and simulation", *Ind. Eng. Chem. Res.*, Vol. 40, No. 6, 1566-1574 (2001).
- Prakasa A. and George S., "Fuel and oil detergents", US Pat., 6,630,430 (2003).

Qi Z., Sundmacher K., Stein E., Kienle A. and Kolah A., "Reactive separation of isobutene from C₄ crack fractions by catalytic distillation processes", *Sep. Pur. Tech.*, Vol. 26, No. 2-3, 147-163, *cf* CA 136:403945 (2002).

Quitain A. T., Itoh H. and Goto S., "Reactive distillation for synthesizing ETBE from bioethanol", *Reaction Engineering for Pollution Prevention*, *cf* CA 133: 107039 (2000).

Rasmussen E. T., Schroeder B. A. and Walker M. A., "Process for preparing Acyloxysilanes", US Pat. 5,387,706 (1995).

Rihko-Struckmann L. K., Karinen R. S., Krause A. O., Jakobsson K. and Aittamaa J. R. "Process configurations for the production of the 2-methoxy-2,4,4-trimethylpentane—a novel gasoline oxygenate", *Chem. Eng. And Proc.*, Vol. 43, No. 1, 57-65 (2004).

Rix A., Grund G. and Bueschken W., "Process for preparing highly pure raffinate II and Methyl tert-butyl ether", US Pat. 6,657,090 (2003).

Ryu J. Y. and Gelbein A. P., "Process and catalyst for making dialkyl carbonates", US Pat., 6,392,078 (2002).

Saari K., Tirronen E., Vuori A. and Lahtinen M., "Method for preparing formic acid", U.S. Pat. 6,429,333 (2002).

Saayman N., Kindermans S. and Lund G. J., "Process for production of MIBK using catalytic distillation technology", US Pat. 6,518,462 (2003).

Saha B., Chopade S. P. and Mahajani S. M., "Recovery of dilute acetic acid through esterification in a reactive distillation column", *Catal. Today*, Vol. 60, No. 1-2, 147-157 (2000).

Schaerfl R. A., Jr. Day M. J., Piecuch S.P. and Tellier R.R., "Preparation of substituted hydroxyhydrocinnamate esters by continuous transesterification using reactive distillation", US Pat. 6,291,703 (2001).

Schmitt M., Hasse H., Althaus K., Schoenmakers H., Gotze L., and Moritz P., "Synthesis of *n*-hexyl acetate by reactive distillation", *Chem. Eng. Proc.*, Vol. 43, No. 3, 397-409 (2004).

Schopmeyer H. H. and Arnold C. R., "Lactic acid purification", US Pat. 2,350,370 (1944).

Schwab P., Breitscheidel B., Oost C., Schulz R. and Schulz M., "Preparation of propene and, if desired, 1-butene", US Pat. 6,433,240 (2002).

Scott B., Jose S., and Zhaozhong J., "Co-production of dialkyl carbonates and diols with treatment of hydroxyl alkyl carbonates", US Pat., 6,573,396 (2003).

Sharma M. M. and Mahajani S.M., "Industrial applications of reactive distillation (A review), in "Reactive Distillation" by Sundmacher K. and Kienle A. (Eds), Wiley VCH, Germany, pp 1-29 (2003).

Shinya H., Hiroshi A., Shigeki T., and Yasukazu S., "Catalytic decalin dehydrogenation/naphthalene hydrogenation pair as a hydrogen source for fuel-cell vehicle", *Int. J. of Hydrogen Energy*, Vol. 28, 1255-1262 (2003).

Shoemaker J. D. and Jones E. M., "Cumene by catalytic distillation", *Hydro. Proc.*, Vol. 66, No. 6, 57-58 (1987).

Silverberg S., Sanchez L. and Lattner J., "Use of catalytic distillation to produce cyclopentane or cyclopentene", US Pat. 6,100,435 (2000).

Smejkal Q., Hanika J. and Kolena J., "2-methylpropylacetate synthesis in a system of equilibrium reactor and reactive distillation column", *Chem. Eng. Sci.*, Vol. 56, No. 2, 365-370 (2001).

Sneesby M.G., and Tade M. O., "A multi-objective control scheme for an ETBE reactive distillation column", *Chem. Eng. Res. and Des.*, Vol. 78 (A2), 283-292 (2000).

Stanley S.J. and Gildert G. R., "Process for the removal of MAPD from hydrocarbon streams", US Pat. 6, 414,205 (2002).

Stein E., Kienle A. and Sundmacher K., "Separation using coupled reactive distillation columns", *Chem. Eng.*, Vol. 107, No. 13, 68-72 (2000).

Steinigeweg S., and Gmehling J., "Esterification of fatty acid by reactive distillation", *Ind. Eng. Chem. Res.*, Vol. 42, No. 15, 3612-3619 (2003).

Steinigeweg S., and Gmehling J., "*n*-Butyl Acetate Synthesis via Reactive Distillation: Thermodynamic Aspects, Reaction Kinetics, Pilot-Plant Experiments, and Simulation Studies", *Ind. Eng. Chem. Res.*, Vol. 41, No. 22, 5483-5490 (2002).

Steinigeweg S., and Gmehling J., "Transesterification processes by combination of reactive distillation and pervaporation", *Chem. Eng. Proc.*, Vol. 43, No. 3, 447-456 (2004).

Stitt E. H., "Reactive distillation for toluene disproportionation: a technical and economic evaluation", *Chem. Eng. Sci.*, Vol. 57, No. 9, 1537-1543 (2002).

Stuart F., Ernest M., Ahmet M., "Process for converting caprolactam to nylon 6", US Pat., 6,479,620 (2002).

Sy A., "Catalytic distillation reactor in combination with a multibed catalytic reactor having individual feed inlets", US Pat., 6,620,387 (2003).

Tang Y., Huang H. and Chien I., "Design of complete ethyl acetate reactive distillation column system", *Computer-Aided Chem. Eng., cfCA*: 139:216221 (2003).

Taylor R. and Krishna R., "Modeling reactive distillation", *Chem. Eng. Sci.*, Vol. 55, No. 22, 5183-5229 (2000).

Tian Y. and Tade M. O., "Conversion Inference for ETBE reactive distillation", *Sep. Pur. Tech.*, Vol. 19, No. 1-2, 85-91, *cfCA* 132:295884 (2000a).

Tian Y. and Tade M.O., "Inference of conversion and purity of ETBE reactive distillation", *Braz. J. of Chem. Eng., cfCA* 135; 21170 (2000b).

Tolentino L. A., "Process for preparing acyloxysilanes", US Pat. 4,332,956 (1982).

Tung P., "Dimensions in reactive distillation technology", US Pat. 6,500,309 (2002).

Von S. C., Gotze L. and Moritz P., "Acetate technology using reactive distillation. Chemical reaction and distillative product separation", *Chem. Plants + Processing, cfCA* 138:57776 (2002).

Von S.C., Gotze L. and Moritz P., "Acetate technology using reactive distillation", *Sulzer Technical Review, cfCA* 136:87692 (2001).

Vora N. and Daoutidis P., "Dynamics and control of an ethyl acetate reactive distillation column", *Ind. Eng. Chem. Res.*, Vol. 40, No. 3, 833-849 (2001).

Voss, B., "Acetic acid reactive distillation based on DME/methanol carbonylation", US Pat. 6,175,039 (2001).

Wang C., "Study on hydrolysis of methyl acetate in a catalytic distillation column", *Chinese J. of Chem. Eng.*, Vol. 9, No. 4, 382-387, *cf* CA 136:218599 (2001).

Wang E., and Li C., "Simulation of suspension catalytic distillation for the synthesis of linear alkyl benzene", *Chinese J. Chem. Eng.*, Vol. 11, No. 5, 520-525, *cf* AN 2003:908600 (2003).

Wen L., Liu X., Li J., Cui F. and Li M., "Beta zeolite catalyst for the manufacture of propylene glycol monoethyl ether by catalytic distillation" *Shiyou Huagong*, *cf* CA 136:71510, (2001).

Wen L., Min E., Pang G. and Yu W., "Synthesis of cumene by suspension catalytic distillation process" *Huagong Xuebao*, Vol. 51, No. 1, 115-119, *cf* CA 132:295355 (2000).

Winder J., Wharry D., Schell J., Brown M., Murray J., Howe R., Sorensen W., and Szura D., "Reactive distillation processes for the alkylation of aromatic hydrocarbons with straight chain C₆-C₁₈ olefins", US Pat. Appli. 2003171630 (2003).

Xiao J., Liu J., Li J., Juntai X. and Zhang Z., "Increase MeOAc conversion in PVA production by replacing the fixed bed reactor with a catalytic distillation column", *Chem. Eng. Sci.*, Vol. 56, No. 23, 6553-6562 (2001).

Yang M., Han Y., Zhang Q., Jin Z. and Ding B., "Synthesis of n-butyl acrylate using catalytic distillation tower", *Jilin Huagong Xueyuan Xuebao*, Vol. 17, No. 1, 22-24, *cf* CA 134:281157 (2000).

Yu S., Li Yand Chen H., "ETBE reactive distillation on supported Beta- zeolite membrane", *Shiyou Jiagong*, Vol. 19, No. 5, 58-62 (2003).

Zhang C. M., Adesina A.A and Wainwright M.S., "Isobutene hydration over Amberlyst-15 in a slurry reactor", *Chem. Eng. and Proc.*, Vol. 42, No. 12, 985-991 (2003).

Zhang D., Li D., and Zhang J., "Synthesis of cumene by catalytic distillation", *Ziran Kexueban*, Vol. 23, No. 1, 34-39, *cf* AN 2003:790827 (2003).

Zhang J., Li D. and Cao G., "Apparatus and method for alkylation of benzene/toluene with propylene by catalytic distillation", *Faming Zuanli*, *cf* CA137: 95516 (2001a).

Zhang W. and Wan Y.L., "Synthesis of 2-ethoxyethanol using catalytic distillation", *App. catal.* Vol. 74, No. 2, N 20 (1991).

Zhang Y., Yan S. and Shen J., "Preparation of monochloroacetone in reaction distillation column", *Jiangsu Shiyou Huagong Xueyuan Xuebao*, Vol. 13, No. 3, 20-22, *cf* CA 136:296492 (2001b).

Zheng Y., Ng. F. and Rempel G., "Modeling of the catalytic distillation process for the synthesis of ethyl cellosolve using a three-phase non-equilibrium model", *Int. J. Chem. Reactor Eng.*, Vol. 1, No. 1-17, (2003a).

Zheng Y., Ng F. and Rempel G., "Process analysis for the production of diacetone alcohol via catalytic distillation", *Ind. Eng. Chem. Res.*, Vol. 42, No. 17, 3962-3972 (2003b).