biotechnologicallly acquired pharmacological receptor proteins to generate drug–receptor interaction data and by applying QSRR analysis, the preselection of drug candidates can be facilitated and experiments on animals reduced.

See also: **II/Chromatography: Liquid:** Mechanisms: Reversed Phases.

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REACTIVE DISTILLATION

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Introduction

Reactive distillation is a combination of separation and reaction in a single process. Commercial reactive distillation processes for the manufacture of methyl *t*-butyl ether (MTBE) and methyl acetate were successfully commissioned in 1981 and 1983, respectively. These processes have a distinct edge over their conventional predecessors. The reactive distillation process is particularly advantageous in the case of reversible reactions where the conversion is limited by thermodynamic equilibrium. Some of the important benefits of reactive distillation are: reduced capital cost; employment of low mole ratios of reactants; energy saving owing to utilization of the heat of reaction; and automatic temperature control and elimination of hot spots. The commercial process of MTBE manufacture has shown that heterogeneous catalysts such as ion exchange resins can be advantageously used in reactive distillation columns. Innovative techniques of confining the small size resin particles (0.3–2 mm) in the column, allowing efficient solid–liquid contact and high void fraction, have been developed by CDTech, Sulzer, Koch Engineering and BASF. An alternative approach is to prepare a catalyst in the form of conventional column packing and pack it directly into the reactive distillation column.

Recognizing the potential of reactive distillation for a particular process is a difficult task, as not all the reactions can be conducted effectively in this way. Once its potential has been identified, the next step is to design the reactive distillation column for the required task. The simultaneous existence of multiple processes such as mixing, mass transfer and reaction are involved, and the design method requires thorough knowledge of both chemical and physical equilibria as well as the reaction kinetics. Graphical representations of liquid phase compositions, called residue curve maps or distillation maps, are commonly used to analyse the reactive distillation process. Though some efforts have been made to study the underlying theory of the design method, the work is still at its preliminary stage. Another approach to understanding the behaviour of this process is to perform computer simulations and predict the performance of a column of known configuration.

In this article the important aspects of commercial reactive distillation processes of MTBE and methyl acetate manufacture are described in detail. Recent trends in the experimental and theoretical investigations in this area are also outlined. The potential importance of reactive distillation in some industrial processes such as hydrolysis of methyl acetate and recovery of chemicals from aqueous streams is discussed.

MTBE Production

The area of particular interest where reactive distillation can be used is the production of fuel ethers such as MTBE. Gasoline reformulation using these ethers as environmentally benign octane boosters has been driven by various Clean Air Acts, which have boosted MTBE production to a new level. By 2001 the production of MTBE is expected to be 25×10^6 tonnes per annum worldwide. *t*-Amyl methyl ether (TAME) and ethyl *t*-butyl ether (ETBE) are also emerging as promising fuel additives. In addition to its property as an antiknock agent to enhance the octane number of the fuel, MTBE improves the water tolerance limit of the fuel and has a higher calorific value than that of other additives such as methanol.

Another important aspect of carrying out the etherification to near complete conversion is its efficient use in separating the *iso*-olefins from the refinery stream containing both normal and secondary butenes (C_4 or C_5), which are otherwise very difficult to isolate. A reactive distillation column can handle the mixed olefins quite effectively and exploits the presence of inert butenes to improve performance. This separation is necessary because *n*-butenes are required in the pure form for homopolymerization and as a feed for the oxidative production of butadiene.

Reaction Details

MTBE is a product of the liquid-phase reaction of isobutylene and methanol, catalysed by a strong acidic macroreticular ion exchange resin. The reaction is highly selective, so that methanol reacts only with isobutylene in the presence of other C_4 olefins [I].

$$\underset{\text{methanol}}{CH_3OH} + \underset{\text{isobutylene}}{(CH_3)_2C{=}CH_2} \Leftrightarrow \underset{\text{MTBE}}{(CH_3)_3COCH_3} \quad [I]$$

$$\Delta H^0_{298} = -37.7\ \text{kJ mol}^{-1}$$

The favourable temperature and pressure ranges for the reaction to occur are 323–373 K and 5–15 atm, respectively. The useful side reactions are the dimerization and oligomerization of isobutylene and butadiene as well as the formation of codimers. Since, until recently, only butadiene-extracted C_4 refinery streams were used for MTBE production, the only important by-product is diisobutylene, which consists of the isomers 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. The other side reactions, which are of less importance, are formation of *t*-butanol by reaction of isobutylene with water present as a feed impurity, the formation of traces of dimethyl ether by methanol condensation, and the double bond isomerization of 1-butene. Amberlyst 15®, a macroporous cation exchange resin, is widely used as a catalyst for this reaction. Numerous investigations on the kinetics of this reaction system have been reported in the literature. A model based on systematic studies of reaction kinetics (eqn [1]) and equilibrium of this system incorporating the activities of the compounds has been developed and is used by many investigators for column simulation studies.

$$r = m_{\text{cat}}\, q_{\text{acid}} k_{\text{f}} \left(\frac{a_{\text{IB}}}{a_{\text{MeOH}}} - \frac{1}{K_{\text{eq}}} \frac{a_{\text{MTBE}}}{a^2_{\text{MeOH}}} \right) \quad [1]$$

In eqn [1], m_{cat} is the catalyst loading, q_{acid} is the ion exchange capacity and a_i is the activity coefficient of the corresponding component (IB, isobutylene, MeOH, methanol). The forward reaction rate constant k_{f} and the equilibrium constant K_{eq} have been fitted experimentally. As a result of the high polarity of methanol, the reaction mixture is highly nonideal and involves formation of two binary azeotropes and one ternary reactive azeotrope. The activities of the components can sometimes be up to 20 times their mole fractions.

Commercial Process

Conventional processes for the manufacture of MTBE (see **Figure 1**) use a catalytic reactor with a slight excess of methanol (methanol/isobutylene = 1.05–2). The products correspond to the near-equilibrium conversion of about 90–95%. The reaction mixture is separated using distillation, but suffers from complications resulting from the formation of binary azeotropes methanol–MTBE and isobutylene–methanol. The unreacted isobutylene is also difficult to separate from other volatile C_4 products. With the reactive distillation process, almost complete conversion of isobutylene is obtained, thereby eliminating the separation and recycle problems. **Figure 2** provides a schematic representation of this process. A fixed-bed pre-reactor is used to achieve near-equilibrium conversion. The product stream equivalent to the equilibrium conversion is fed to the reactive distillation column, wherein, the residual amount of isobutylene is reacted with methanol. The reactive distillation column is composed of three sections, the middle of which is a reactive zone packed with a solid catalyst. The top nonreactive rectifying section performs the separation of inert gases and

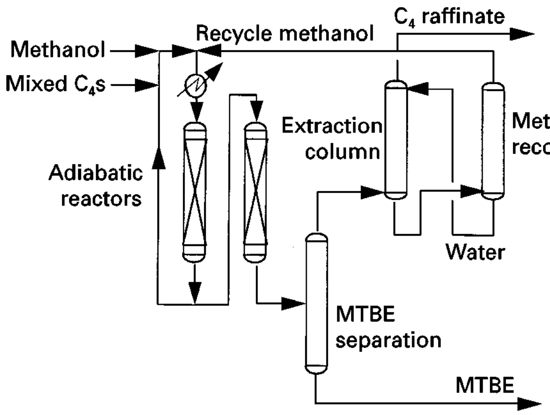

Figure 1 Conventional process for MTBE manufacture.

excess methanol, while the bottom section separates out MTBE in pure form. The boiling points of MTBE and methanol are 328 K and 337.5 K, respectively. This may seem surprising, as MTBE is the bottom product while unreacted high boiling methanol is collected through the distillate. The behaviour is caused by the formation of an MTBE–methanol low boiling azeotrope, which lifts methanol from the stripping section of the column.

The pioneering work to commercialize this technology was performed by Smith from Chemical Research and Licensing Company, who has been awarded several patents for different catalyst structures, column internals design and flow schemes. Some patents have also been assigned to researchers from ELF who claim to have used alternating catalytic and noncatalytic zones successfully to carry out the etherification. The efforts in these studies were directed towards minimizing the pressure drop in the catalyst bed and providing maximum residence time for the liquid in the catalytic zone. This was achieved by providing separate free passage to the up flowing vapour stream either by packing the catalyst in the downcomers or by providing annular space in the catalyst bed, thereby isolating reaction and distillation zones in a single column. UOP, Koch Engineering and Hüls AG have jointly developed the Ethermax process for producing ethers by reactive distillation. The process uses Koch Engineering's Katamax packing, where a solid acid catalyst is confined in screen envelopes.

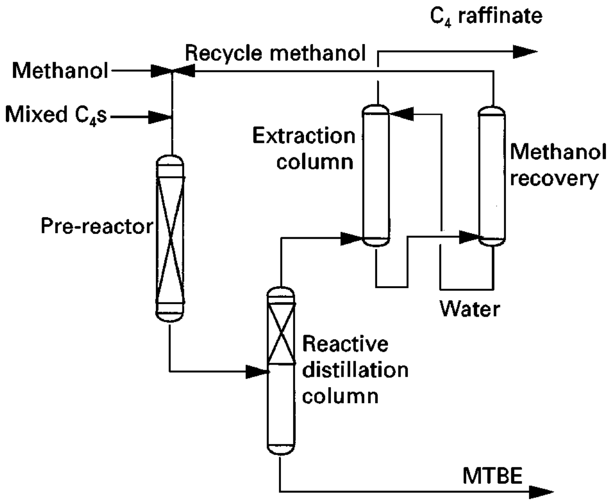

Figure 2 Reactive distillation process for MTBE manufacture.

Simulation Studies

Following the successful commercialization of the MTBE process, numerous studies simulating a catalytic distillation column have appeared in the literature. The basic idea behind simulation studies is to predict the overall conversion of either isobutylene or methanol, and examine the product purity at a steady state for a known column configuration and feed composition. Various software packages such as ASPEN PLUS, SPEEDUP, etc, have been used effectively for this purpose.

The interesting discovery of multiple steady states for a column operated under identical conditions has attracted the attention of many researchers in the recent past. Several studies examining the reasons for the existence of these steady states have been reported. Experimental findings confirmed this fact and showed that the same column configuration operated under similar conditions can give rise to two different conversions. Simulation studies using an ASPEN PLUS flowsheet simulator for a column with a total of 17 reactive and nonreactive stages, operated at 11 atm with two different feed streams of methanol and butenes, result in either 36% or 99% isobutylene conversion when methanol is fed to the 10th stage. The methanol feed plate was varied by following either top-to-bottom or bottom-to-top sequence and it was found that only at certain feed plates (9–12) were multiple conversions realized (see **Figure** 3). The steady-state conversion in this multiplicity region depends upon which sequence is followed to simulate the column. In the upgoing sequence low conversions are obtained, while the downgoing sequence is associated with high conversions. Subsequent efforts on column simulation have confirmed this finding. Installation of the methanol feed at more than one location has been suggested to avoid the unwanted steady state caused by column misoperation.

A mechanistic explanation has been provided as to why MTBE production by reactive distillation may yield multiple solutions. It was found that the initial estimates for temperature and composition profiles

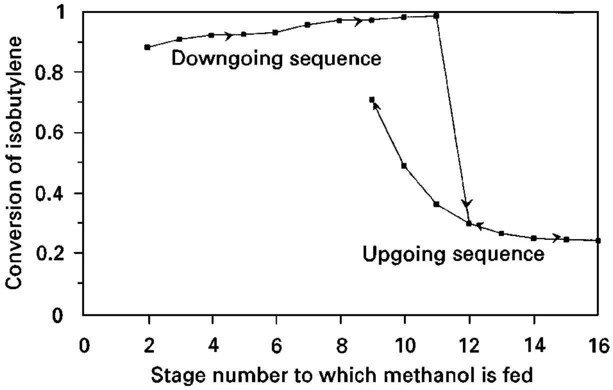

Figure 3 Steady-state multiplicity behaviour of the MTBE process.

decide whether a steady-state simulation would converge to a high conversion or a low conversion solution. In order to obtain a high conversion solution, the lower section of the column must contain sufficient MTBE to lift the entire amount of methanol to the reactive zone. Second, in the reactive zone, the reaction mixture must be diluted to avoid a substantial amount of MTBE decomposition. Initial estimates of the composition at the lowest stage in the reactive zone are crucial in deciding the nature of the steady state. This is expected to be due to the inherent coupling between 'lift' and 'dilution' effects that takes place on this stage.

Recent simulation studies on reactive distillation of MTBE and TAME indicate two types of multiple steady states. The first, discussed above, arises out of the interaction between reaction and vapour–liquid equilibrium. The second multiple steady state is related exclusively to the chemical reaction and arises because of the highly nonlinear concentration dependence of methanol activity at low operating pressures. The only experimental evidence of multiple steady states reported so far comes from work on etherification for TAME synthesis in a pilot plant of Nestle Oy. It is therefore necessary to perform dynamic simulations during the first steps of the design process in order to avoid dynamic surprises.

Another interesting finding of MTBE simulation studies is the oscillatory behaviour of the reactive distillation column. Sustained oscillations of boiling temperature and reflux have been reported in experimental studies on reactive distillation. It has been proved that the nonreactive and nonideal interactions between methanol and isobutylene are responsible for these effects.

Methyl Acetate Production

Methyl acetate is another high volume commodity chemical that is manufactured commercially using reactive distillation. It finds applications as an intermediate in the manufacture of a variety of polyesters such as photographic film base, cellulose acetate, Tenite cellulosic plastics and Estron acetate.

Reaction Details

The reaction of methanol and acetic acid to give methyl acetate (reaction [II]) has equilibrium limitations.

$$\underset{\text{methanol}}{CH_3OH} + \underset{\text{acetic acid}}{CH_3COOH} \Leftrightarrow \underset{\text{methyl acetate}}{CH_3COOCH_3} + \underset{\text{water}}{H_2O} \qquad [II]$$

$$\Delta H^0_{298} = -8.0\ \text{kJ mol}^{-1}$$

$$K_{eq} = \frac{a_{MeOAc}a_{H_2O}}{a_{AcOH}a_{MeOH}} = 5.2 \qquad [2]$$

Equation [2] gives the equilibrium constant K_{eq} as a function of the activity coefficients a_{MeOAc} (methyl acetate), a_{H_2O} (water), and a_{AcOH} (acetic acid).

Thus the reaction product will contain all four components even if one of the reactants is used in excess. The reaction can be conducted in the temperature range 310–393 K and at a pressure of 1 atm. The only important side reaction is the formation of dimethyl ether by the condensation of methanol. This reaction is predominant at high temperatures.

Though the reaction has been commercialized in a reactive distillation column, it is surprising that a systematic study on the kinetics of this reaction in the presence of sulfuric acid as catalyst is not evident in the open literature. As in the MTBE system, the rate expression in the form of activities is strongly preferred because the high polarity of water and methanol compared to that of methyl acetate leads to strongly nonideal solution behaviour. Because of the commercial success of reactive distillation and the proven potential of the ion exchange resins, some efforts have been made to propose a rate expression for an ion exchange resin-catalysed reaction. The expression for the rate, r, based on kinetic data generated over a range of molar feed ratios more typical of reactive distillation conditions, is given by:

$$r = \frac{k(a_{HOAc}a_{MeOH}(-a_{MeOAc}a_{H_2O}/K_{eq}))}{(1 + K_{HOAc}a_{HOAc} + K_{MeOH}a_{MeOH} + K_{MeOAc}a_{MeOAc} + K_{H_2O}a_{H_2O})} \qquad [3]$$

where k is the rate constant, K_{eq} is the equilibrium constant and the K_is are the adsorption coefficients involved in the Langmuir–Hinshelwood/Hougen–Watson model (HOAc, methyl acetate, MeOH, methanol; MeOAc, methyl acetate, H_2O, water). The expression has been successfully used to verify the experimentally observed residue curve maps of this system. The residue curve maps shows no distillation boundaries and hence, ultrahigh purity methyl acetate and water can be obtained through a proper design of reactive distillation column.

Commercial Process

Conventional processes before the 1980s used multiple reactors with a large excess of one of the reactants to achieve high conversion of the other. The product is difficult to purify because of the formation of methyl acetate–methanol and methyl acetate–water azeotropes. Different means to break the methyl acetate–methanol azeotrope were employed, such as use of several atmospheric and vacuum distillation columns or extractive distillation. A typical process contained two reactors and eight distillation columns, making it complex and capital intensive.

Eastman Kodak has developed a reactive distillation process for the manufacture of high purity and ultrahigh purity methyl acetate. The remarkable factor is that, in spite of the reaction having unfavourable equilibrium limitation, high purity product is obtained using a near-stoichiometric mole ratio of methanol and acetic acid. The reactive distillation column used in the process is shown in **Figure 4**. In order to explain the process, the column can be divided in four stages starting from the top as: (1) methyl acetate enrichment; (2) water extraction; (3) reaction; and (4) methanol stripping. The reaction occurs in the middle section (section 3) in a series of countercurrent flashing stages with sulfuric acid as the catalyst. In section 2, acetic acid acts as an extracting agent and extracts water (breaking the methyl acetate–water azeotrope) and some methanol. Acetic acid and methyl acetate are separated above the acetic acid feed, in the methyl acetate-enriching section (section 1), allowing pure methyl acetate to be recovered as the overhead product. Methanol is stripped from water in the bottom section (section 4) and water is the bottom product. Some intermediate boiling compounds are formed because of the impurities present in feed. Hence, a small stream is withdrawn just above the catalyst feed point and treated separately in an impurity-removal system. The impurities are stripped and concentrated, and the methanol + methyl acetate stream is recycled to the reaction zone. The reactive distillation column has been successfully operated at a near-stoichiometric mole ratio of acetic acid and methanol, yielding high purity methyl acetate as the product. The whole process is integrated in a single column, eliminating the need for a complex distillation column system and recycle of the methanol–methyl acetate azeotrope. A single reactive distillation column at Eastman Kodak's Tennessee plant produces 180 000 metric tons per year of high purity methyl acetate. The composition profile of the column shown in **Figure 5** demonstrates that the methyl acetate can be manufactured in a single column without need for additional purification steps.

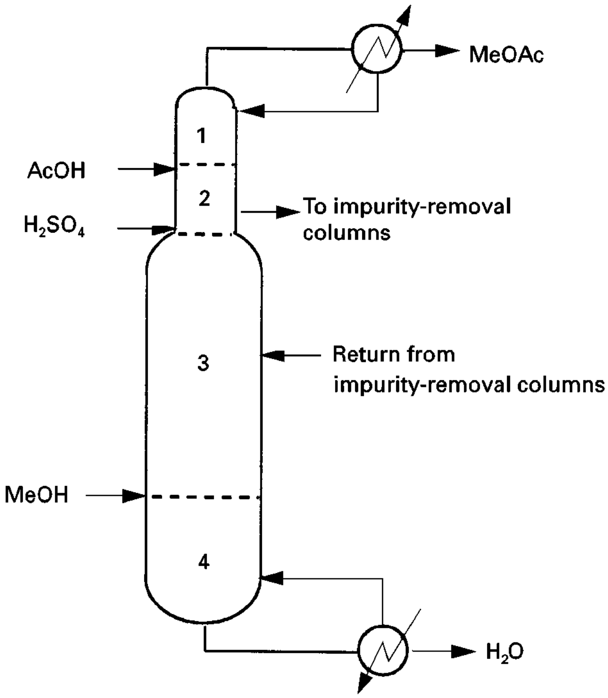

Figure 4 Reactive distillation process for methyl acetate manufacture.

Hydrolysis of Methyl Acetate

Methyl acetate–water mixture is produced in large quantities from purified terephthalic acid (PTA) plants. The manufacture of poly(vinyl alcohol) (PVA) also produces large quantities of methyl acetate (1.68 kg per kg PVA). Since methyl acetate is a comparatively low value solvent, it has to be sold at a lower price; hence it would be a better idea to hydrolyse it economically and recover methanol and acetic acid for reuse in the process.

Conventional processes for the hydrolysis of methyl acetate use a fixed-bed reactor followed by a complex arrangement of several distillation/extraction columns. The conversion is limited by unfavourable equilibrium (equilibrium constant 0.14–0.2) and a large amount of unconverted methyl

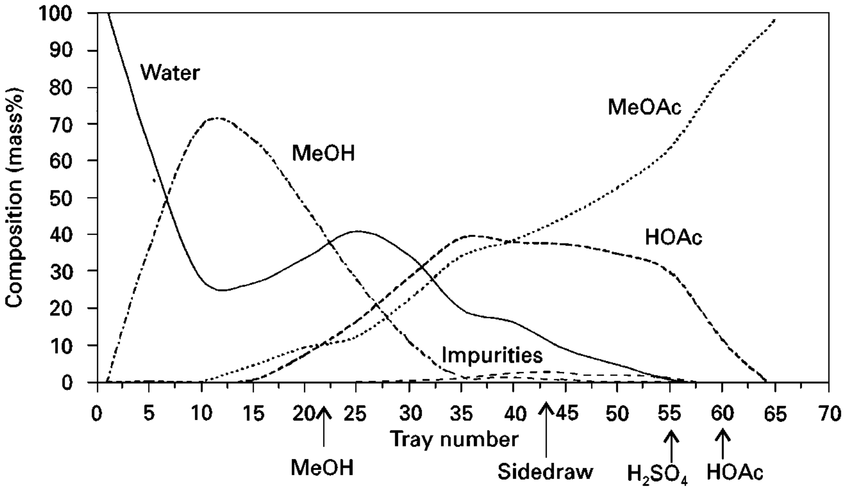

Figure 5 Composition profile in methyl acetate reactive distillation column.

acetate has to be separated and recycled. A schematic diagram of a typical conventional process is given in **Figure 6**. The reaction is carried out in a fixed-bed reactor and the product stream contains all four components. Four additional columns are required to separate methanol and acetic acid streams and recycle unconverted methyl acetate, along with methanol, to the reactor.

The above has shown how reactive distillation simplifies the process in the case of the manufacture of methyl acetate. A similar concept can be applied to the hydrolysis reaction. A reactive distillation process has been developed on a laboratory scale for the hydrolysis of methyl acetate using an ion exchange resin catalyst in a special form. Converting the process from conventional to reactive distillation offers the possibility of eliminating many complicated steps. The use of solid acid catalysts obviates the need for recovery of the spent acid and the use of exotic construction materials. Resin was moulded into 7 mm × 7 mm pellets using polyethylene powder. The distillation column was directly packed with these pellets, which played the role of both catalyst and packing.

A schematic diagram of the proposed reactive distillation process is shown in **Figure 7**. Water is fed at the top of the reactive section and methyl acetate is introduced at the bottom of the reactive section. The column is operated under total reflux of methyl acetate–methanol azeotrope. The stripping section strips all the methyl acetate and the bottom product is essentially free of methyl acetate. The bottom product, which now contains only methanol, water and acetic acid, can be easily separated using two distillation columns in series giving methanol and acetic acid as products. Thus, this process eliminates two main pieces of equipment from the conventional process: (1) a water wash column for the separation of methanol from methyl acetate, and (2) a methanol-enriching

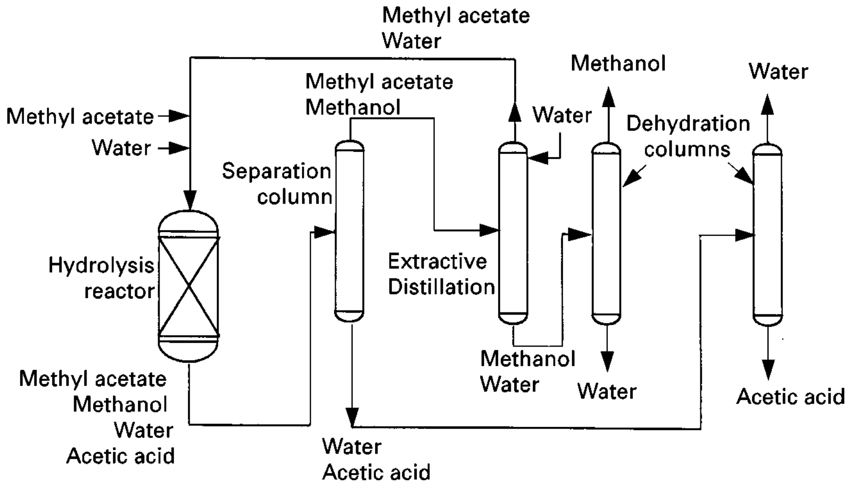

Figure 6 Conventional process for hydrolysis of methyl acetate.

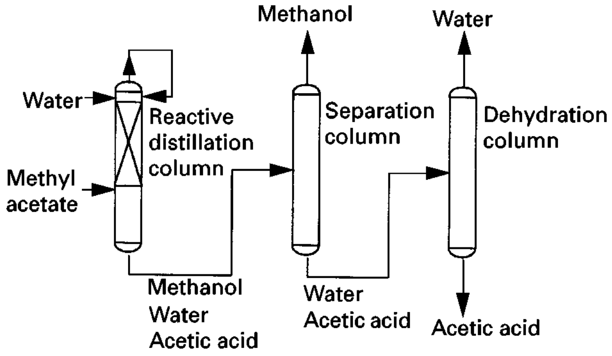

Figure 7 Reactive distillation process for hydrolysis of methyl acetate.

column for recovery of water-diluted methanol. Conversions to the tune of 99% are achieved in this process. The estimated heat savings are 50% that of the conventional process.

Recovery and Purification of Chemicals

The esterification reaction has also been successfully employed for the recovery of acetic acid from aqueous streams. Dilute acetic acid is produced in large quantities in many processes, such as the manufacture of cellulose esters, terephthalic acid and dimethyl terephthalate; and also in reactions such as acetylation and nitration. The recovery of acetic acid from these streams is a daunting problem. The conventional methods for recovery are azeotropic distillation, simple distillation and liquid–liquid extraction. With the advent of reactive distillation processes, esterification of acetic acid with methanol seems an attractive alternative. Laboratory experiments have been carried out to recover acetic acid in a reactive distillation column. The column contained commercially available ion exchange resin along with Rashig rings. The use of a solid acid catalyst offers noncorrosive conditions so that a less expensive construction material can be used. Up to 84% recovery of acetic acid as methyl acetate was achieved. Hoechst Celanese Corporation has recently described a reactive distillation process for the recovery of acetic acid from aqueous solutions as methyl acetate. With the use of acidic ion exchange resin as catalyst, more than 90% recovery from 5–30% aqueous acetic acid is claimed. They also suggest the use of Koch Engineering's Katamax packing as catalyst.

Reactive distillation can be applied for the recovery of many other chemicals from dilute streams. The polymer industry is often faced with the challenge of treatment of aqueous formaldehyde solutions, as it is a nuisance to the environment and it is difficult to remove trace quantities of formaldehyde. Reactive distillation with methanol, ethanol or ethylene glycol not only brings down the formaldehyde concentration to the ppm level, but also yields useful acetal products. Similarly, nonboiling chemicals such as glyoxal and glyoxylic acid can be recovered from their aqueous solutions through the formation of their corresponding acetals or esters, which can be separated by distillation. CDTech has recently developed a reactive distillation process for hydrodesulfurization, called the CDHDS process, which is aimed at producing low sulfur fuels to meet stringent future environmental regulations at the lowest cost.

Reactive distillation has reportedly been employed for the purification of bisphenol A of polycarbonate grade, where impurities in the form of carbonyl compounds such as acetone, mesityl oxide, hydrotropaldehyde, etc., have to be reduced from about 3000 ppm to <10 ppm. A continuous reactive distillation column has been claimed to be a versatile method to achieve this objective.

Concluding Remarks

Reactive distillation offers several benefits over conventional processes for MTBE and methyl acetate manufacture. The commercial success of MTBE manufacture by reactive distillation has led to numerous investigations in the recent past on almost every aspect of this process. The generation of kinetic and equilibrium data at boiling temperatures, simulation and design studies, control strategies and identification of new reactions as candidates for reactive distillation, are some of the areas being investigated. Simulation studies of catalytic distillation for etherification have highlighted the important aspects of steady state multiplicity. This concept carries a special significance and plays an important role in design methods. Future work on simulation will see other reactions displaying this unusual phenomenon. Eastman Kodak has demonstrated the feasibility and advantages of reactive distillation at the commercial scale for methyl acetate manufacture. The process has scope for improvement in the sense that solid acid catalyst can be employed instead of sulfuric acid. Different techniques of confining the small beads of ion exchange resin in fibre glass cloth, wire mesh or structured packing have been developed. These catalysts offer very good vapour–liquid contact and activity but replacing the deactivated catalyst would be labour-intensive and time-consuming. The future focus should be on development of a catalyst in the form of a conventional column packing, such as Rachig rings, which would have good mechanical strength, activity and stability under the reaction conditions. Reactive distillation may find a place in many other processes such as hydrolysis of methyl acetate, recovery of carboxylic acid from their aqueous solutions, hydrodesulfurization and purification of phenols.

See also: **II/Distillation:** Energy Management; Historical Development; Instrumentation and Control Systems; Theory of Distillation.

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RESINS AS BIOSORBENTS: ION EXCHANGE

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Introduction

The term biosorbent is usually applied to solid polymeric media employed in the purification, separation or isolation of biotechnological products. To assure