

REVIEW PAPER

## Recovery of acids from dilute streams : A review of process technologies

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**Abstract**—Chemical process industries convert raw materials into useful products. Acids, among other chemicals, are used in many industries as reactants, solvents and also as catalysts in a few instances as well. Resulting streams are dilute, from which the acids must be recovered. For recovery, many technologies can be used by which acids can be regained as such or can be converted into other value-added products like esters. Membrane processes and biological processes are being researched academically and practiced industrially. These have their own advantages and disadvantages in view of conversion, energy consumption etc. These are not always advantageous and hence an alternate process technology is necessary like reactive separation (RS). RS is advantageous especially when the acid is to be converted to other useful products by reaction, due to additional advantages or because no other technology is well suited or due to cost considerations alone. Conventional process technologies use the reactor configuration followed by the subsequent separation sequence. This approach can sometimes suffer from lesser conversion, difficulties in separation etc. To overcome these problems, RS has an edge over other processes in terms of the recovery of the useful compounds. Reactive distillation (RD), reactive extraction (RE) and reactive chromatography (RC) are the separation technologies that can be useful for acid recovery in an economically feasible way. This review covers the various processes of acid recovery along with the recent work in the field of reactive separations.

Keywords: Recovery, Reactive Distillation, Reactive Chromatography, Membrane Processes, Separation

### INTRODUCTION

Chemical process industries convert raw materials into useful products. Acids, among other chemicals, are used in many industries for several purposes such as reagents, reactants, solvents and also as catalysts. The recovery of acids from aqueous streams is a major problem in the petrochemical, pharmaceutical and fine chemical industries. Dilute solutions containing acids along with various metals/salts emerge as waste streams in a number of industrial processes. The disposal of these waste streams or recovery of the valuable chemicals from them is an acute problem for the processing industry. Until recently, the waste acids have been subjected to neutralization without any proper treatment resulting in environmental and financial problems. The effective recovery of the acids from the waste streams in a pure or relatively concentrated form, suitable for recycling to the main process, could amply cover up the separation costs. Furthermore, the removal of bulk of the free acids would greatly simplify any further treatment of the waste stream as well [1].

Various acids have been recovered in the past from their dilute aqueous mixtures. Dilute acetic acid is a by-product from many chemical processes like production of terephthalic acid, dimethyl terephthalate, glyoxal and cellulose acetate. The concentration of dilute acetic acid in aqueous solution varies up to 35% and sometimes even up to 65 wt%. Due to such a large acid content, the recovery

of acetic acid becomes environmentally and economically important [2]. Although a number of methods are reported in the literature, these are not entirely satisfactory. Till date, no mature technology has been reported that can handle recovery of all possible concentrations of acetic acid. This problem becomes more difficult when the concentration of acetic acid becomes low [3]. Lactic acid is recovered from its dilute aqueous solution [4]. Trifluoroacetic acid (TFA) has been recovered from its very dilute solutions recently [5]. Other acids like lactic acid, adipic acid, myristic acid, succinic acid, chloroacetic acid and glycolic acid can also be recovered from their dilute solutions in the same manner with a properly designed RD system [6].

Solutions containing strong mineral acids mixed with various metals/salts come out as waste/intermediate stream in some industrial processes. The disposal of these waste streams is also an acute environmental problem of the processing industry. Chemical etching is used during the manufacture of silicon wafers. Mixed acids (hydrofluoric, nitric and acetic acid) are used for the purpose. It has been attempted to recover these acids with a view to recycle to the main process and to cover the separation costs. Sulfuric acid has also been recovered from the metal industry, which helps in disposal of spent liquor [7].

Several process technologies are available for the recovery of these acids, some of which are physical and some are chemical. Conventional, well-practiced physical separation methods such as distillation and extraction suffer from several drawbacks. Distillation is generally uneconomic when dilute aqueous streams are to be separated because of the high costs involved in vaporizing water (the more volatile component) that exists in high proportion possessing

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large latent heat of vaporization. Extraction is limited by phase separation and distribution of the components involved in the reacting system. Note that extraction alone cannot be a complete remedy for recovery although distillation can be. Due mainly to cost considerations, extraction followed by distillation is practiced industrially. In view of these constraints, it is appropriate to explore alternative methods of recovering the valuable chemicals, especially the acids [8]. Some of these include ion exchange/adsorption, biological processes and membrane processes. The recent addition in this list is reactive separation (RS). Although known for several decades, its usefulness for recovery has been brought forth only recently. The following sections discuss the details of many of the above mentioned process technologies along with the merits and demerits of each.

## MEMBRANE PROCESSES

Membrane technology has emerged as one of the sustainable separation processes. Since membranes allow selective permeation of a component from a multi-component mixture, these can help enhance the conversion of reactants for thermodynamically or kinetically limited reactions [1]. However, the cost of membranes, especially for bipolar membranes, is quite a bit higher, and relatively high energy consumption is also reported [9]. While selecting to choose a membrane-assisted separation process, these factors need to be taken into consideration. Electro-dialysis, reverse osmosis, pervaporation and also the membranes made up of ion exchangers are the important sub-processes that are discussed below. Many membrane processes need pretreatment, and due to fouling behavior of membrane it is not sometimes feasible or economical. Cost of the membranes is also an issue that should be looked into, especially for bipolar membrane.

## ELECTRO-DIALYSIS (ED)

Electro-dialysis in many cases represents a powerful technology, when charged compounds have to be separated from a solution. It is an environmentally friendly alternative to the technology currently in use. In recent years, electro-dialysis has been widely used for the purification and recovery of organic acid solutions [10]. Many researchers have reported that it can be used for acid recovery. Electro-dialysis is promising if its temperature range can be increased and if it can be made cost effective.

Senad et al. [9] recovered organic acids with molecular weight 200 kg/kmol or more. The organic acids separated were gluconic and citric acid. They used electro-dialysis with bipolar membranes (EDB) in a three compartment arrangement. One of the problems lies in the coupled system between anion exchange membranes and bipolar membranes. To reduce the bipolar membrane area, a high transport rate through the anion exchange membranes is necessary. They found that mass transfer (conversion rate) was rather low and energy consumption was relatively high. They tried to improve the process by splitting the three compartment EDB into conventional ED, and a two compartment system with bipolar and cation exchange membranes. With this, they could significantly reduce the necessary bipolar membrane area thereby favoring economic aspects.

Lixin et al. [3] worked on bipolar membrane electro-dialysis to recover acetic acid in dilute wastewater containing 0.2 wt% acetic

acid. Experimental results show that the method is technically feasible, and that large percent recovery is possible. Experiments also show that the back molecular diffusion of acetic acid through an ion exchange membrane is one reason for the low electric current efficiency (around 40%). Low current efficiency and the high energy consumption are the two problems that are reported.

Zhixin et al. [10] proposed the possibility of recovery of organic acids from waste salt solution, derived from the manufacture of cyclohexanone, by means of single anion-exchange membrane electro-dialysis. Some key parameters such as voltage, current density, pH value, current efficiency and specific energy consumption are studied and analyzed in detail. They further illustrated that single anion exchange membrane electro-dialysis can be effectively used for the recovery of organic acids, especially, butyric and adipic acids.

Weier [11] worked on recovery of acetic and propionic acids produced by fermentation. In this process, acid recovery is important both for producing a concentrated product from the broth and also for removing acid from the broth to reduce product inhibition during the fermentation. The use of electro-dialysis for producing a concentrated acid product is not promising unless salt levels in the medium can be reduced and acid levels increased. However, electro-dialysis can be used to maintain low acid levels in the fermenter during extractive fermentation.

Eszter et al. [12] studied the recovery of galacturonic acid from sugar beet pulp's pectin hydrolyzate by electro-dialysis. In this work, 94% of the initial galacturonate concentration was recovered by the electro-dialysis cell and more than 25% galacturonate content in the concentrate solution was achieved. Cifuentes et al. [13] used two lab-scale electro-hydrolysis (EH) cells to study the effectiveness of this method in the recovery of sulfuric acid from copper-containing electrolytes such as those present in copper electro-refining.

## PERVAPORATION

Pervaporation is a versatile membrane-based separation process with major applications in the separation of azeotropes. Separation by pervaporation is independent of the vapor-liquid equilibrium, because the transport resistance depends on the sorption equilibrium and mobility of the permeate components through the membrane [14]. Several applications of pervaporation are known in the recovery of the acids, some of which are discussed below.

Kun et al. [15] showed the separation of acetic acid from *n*-butyl acetate, *n*-butanol in from aqueous solutions by pervaporation using a poly-(ether block amide) membrane. Initially, the separations of binary (i.e., *n*-butyl acetate - water, *n*-butanol - water and acetic acid - water) mixtures were investigated, followed by separation studies of quaternary mixtures comprising all the four components that are relevant to *n*-butyl acetate production by esterification via reactive distillation. The membrane permeability was found to follow the order of *n*-butyl acetate > *n*-butanol > acetic acid > water.

Benedict et al. [16] studied reactors coupled with membrane separation, such as pervaporation, to help enhance the conversion of reactants for thermodynamically or kinetically limited reactions via selective removal of one or more product species from the reaction mixture. Esterification of lactic acid ( $C_3H_6O_3$ ) and succinic acid ( $C_4H_6O_4$ ) in dilute aqueous solutions with ethanol ( $C_2H_5OH$ ) to generate ethyl lactate ( $C_5H_{10}O_3$ ) and diethyl succinate ( $C_8H_{14}O_4$ ), respectively, is

studied in well-mixed reactors with solid catalysts (Amberlyst XN 1010 and Nafion NR50) and two pervaporation membranes in detail. The efficacy of pervaporation-aided esterification is reported by attainment of near total utilization of the stoichiometrically limiting reactant within a reasonable time. Protocols for recovery of ethyl lactate and diethyl succinate from pervaporation retentate are discussed and simultaneous esterification of lactic and succinic acids, which is an attractive and novel concept, is proposed.

Jiang et al. [17] presented the application of an integrated pervaporation process to improve the pervaporation for removal of acetic acid from water. This integrated pervaporation process was based on a plain poly-dimethylsiloxane (PDMS) membrane with a hydrophobic ionic liquid composed of a heterocyclic cation and PF<sub>6</sub> anions. They found that the ionic liquid as an extractant prior to pervaporation was favorable for improving the permeate selectivity and the permeate flux of acetic acid compared with using only a plain PDMS membrane.

### REVERSE OSMOSIS (RO)

The reverse osmosis membranes processes are a developing technology for new desalination installations, and they are applied to a variety of salt water resources using pretreatment and membrane

system. The use of membrane for desalination is practiced because the quality of materials has improved and costs have decreased [18].

Ibanez et al. showed [19] that membrane water desalination processes generate high salinity concentrates containing inorganic salts that may be further purified to increase their commercial value. These concentrates are beneficial to reuse and using RO some acids can be recovered. Bipolar membrane electro-dialysis has been the selected technology for the conversion of RO concentrates into acid and base products.

Ahsan et al. [20] reported the recovery and concentrating acetic acid from pre-hydrolysis liquor (PHL) of the Kraft-based dissolving pulp process prior to fermentation of hemi-cellulosic sugars, by the combination of activated carbon adsorption, nano-filtration (NF) and reverse osmosis (RO) processes. To reduce fouling, PHL was subjected to adsorption on activated carbon, then the treated PHL (TPHL) was passed through a nano-filtration (NF DK) membrane to retain the sugars, and the permeate of acetic acid rich solution was passed through a reverse osmosis membrane. For the reverse osmosis process, 68% of acetic acid retention was achieved at pH 4.3 and 500 psi pressure and the acetic acid concentration increased from 10 to 50 g/L.

Masuda et al. [21] worked on the evaporation drain of sulfite pulp spent liquor containing few volatile fatty acids, most of which is

**Table 1. A summary sheet of membrane processes**

Process conditions	Acid recovered	Results	Reference
Organic acids of molecular weights around 200 kgkmol <sup>-1</sup> or more are recovered using electrodialysis with bipolar membranes, cation exchange membrane.	Gluconic acid and citric acid.	Conversion rate is low and energy consumption is relatively high. A high transport rate through the anion exchange membranes is necessary to reduce the bipolar membrane area.	[9]
Recovery of organic acids from waste salt solutions by electrodialysis, The anion exchange membrane Ionac MA-3475 used.	Butyric acid and adipic acid. 20% waste salt solution.	Butyric and adipic acids are separated from waste salt solution by one-step electrodialysis The concentration of organic acids increases with increasing applied potential, but it also leads to low current efficiency and high energy consumption.	[10]
Catalyst Amberlyst XN-1010, Nafion NR50, ethanol, Vacuum 10 <sup>-3</sup> Torr.	Lactic acid and succinic acid.	Pervaporation-assisted esterification of lactic and succinic acids with ethanol studied. High water flux through the pervaporation membrane obtained by maintaining high recirculation rate for the reactor and low permeate pressure.	[16]
A plain Poly-dimethylsiloxane (PDMS) membrane with a hydrophobic ionic liquid composed of a heterocyclic cation and PF <sub>6</sub> anions.	Acetic acid.	The ionic liquid as an extractant prior to pervaporation was favored the permeate selectivity and the permeate flux of acetic acid compared using a plain PDMS membrane. Scale-up for process may be possible.	[17]
Combination of activated carbon adsorption, nanofiltration (NF) and reverse osmosis (RO) processes, prehydrolysis liquor of the kraft-based dissolving pulp process used.	Acetic acid.	the permeate of acetic acid rich solution was passed through a reverse osmosis membrane, 80 to 90% of acetic acid permeated, 68% of acetic acid retention achieved at pH 4.3 and 500 psi pressure.	[20]
Sulfite pulp spent liquor contains acetic acid, cellulose acetate membrane, reverse osmosis employed.	Acetic acid.	Concentration by reverse osmosis was successfully carried out with the suitable pretreatment. The recovery of acetic acid reported 95.6, 90.5 and 98.2% for Na-, NH <sub>4</sub> -, and Ca-drain, respectively.	[21]
Wastewater containing 0.2% acetic acid, pH 4-7, Bipolar membrane electrodialysis.	Acetic acid.	70% (wt%) acetic acid solution can be obtained. At low electric current efficiency (around 40%) noted the molecular diffusion back of acetic acid through the anion-exchange membrane.	[3]

acetic acid. The main objective of this study is to recover acetic acid as the concentrated solution (about 4%), which could be used as a culture medium of the yeast. As acetic acid can easily pass through the cellulose acetate membrane, the drains neutralized by NaOH,  $\text{NH}_4\text{OH}$  and  $\text{Ca}(\text{OH})_2$  were used as the feed solutions. In all cases, concentration by reverse osmosis was successfully carried out. In addition, the recovered, permeated water may be used for industrial purpose.

A summary of membrane separation for recovery of various acids is given in Table 1.

## BIOLOGICAL PROCESSES

Biotechnological production processes can be characterized mostly as using moderate temperatures, low substrate and product concentrations and a neutral pH range. As a direct consequence of this, many of these suffer from low productivity, dilute product streams and/or high recovery costs. Certain microbes have been observed to be capable of working at higher than usual temperatures and also at other than neutral pH. However, since these are presently at development stage, the same are not yet been industrially used. The biological processes are fast becoming the ones that will replace all other processes. However, presently progress in this important area is underway and hence needs more time to become the leader in the list. Nevertheless, it certainly needs to be mentioned. Indeed, the survival range of useful microbes can be extended but not without limitations and consequences [22].

Lactic acid was recovered from fermentation broths in the presence of citric acid and acetic acid with various carriers: modifier: solvent combinations [23]. Secondary amine (Hoe F 2562), a tertiary amine (Hostarex A 327) as well as a phosphine oxide as carriers and butyl acetate and kerosene as solvents were used for the purpose. The effects of the type and concentration of the carrier and modifier and the temperature on the equilibrium distribution were evaluated.

Hyohak et al. [24] reported use of *M. succiniciproducens* LPK7 strain, which produces succinic acid as a major fermentation product while producing much reduced by-products. For the recovery of succinic acid from the fermentation broth of LPK7 strain, a simple process composed of a single reactive extraction, vacuum distillation, and crystallization yielded highly purified succinic acid (greater than 99.5% purity, wt%) with a high yield of 67.05 wt%.

Mostafa [25] proposed the production of volatile fatty acids (VFAs) by anaerobic fermentation of wheat milling waste residues (akalona) either as a solid or hydrolyzate, and whey was studied using fresh rumen fluid as a mixed culture for anaerobic digestion of the organic residues. VFAs recovery from fermentation broth by liquid-liquid extraction using a mixed solvent (tri-n-octylphosphine oxide in kerosene) followed by a pure solvent was studied. Experiments were done covering the extraction of tri-n-octylphosphine in diluent kerosene under the optimum conditions.

Yonghui et al. [26] studied the reaction between  $\text{SO}_2$  and calcium acetate, which potentially can be used to recover acetic acid from the anaerobic fermentation broth with an  $\text{SO}_2$  waste stream. The conversion of given amounts of calcium acetate to acetic acid was evaluated under different reaction temperatures and flow rates of  $\text{SO}_2$ . Analyses of concentrations of the produced acetic acid indicated that the reactions between  $\text{SO}_2$  and calcium acetate were com-

pleted under all experimental conditions.

## ION EXCHANGE/ADSORPTION

Ion exchange is a simple technique widely used in the demineralization and purification of water streams. In addition, many ion exchange resin manufacturers provide more selective and chemical and mechanical resistant resins, which increases the application fields of ion exchange. In addition, the simplicity of ion exchange operation makes it attractive to the chemical purification field. It is observed that most adsorption processes are limited by the pH of the solution.

Yue et al. [27] measured the selective adsorption of acetic acid from aqueous solutions onto activated carbons and polymeric sorbents. For styrene-di-vinyl-benzene macro-reticular resins, they report that adsorption behavior is dominated by aqueous-phase non-idealities. Differences in the degree of surface heterogeneity are probably also important. Munson [28] worked on recovery of acetic acid from low-pH aqueous solution onto polymeric adsorbents and activated carbons and report that surface area and chemical nature of the adsorbent plays important role in acid recovery. Activated carbons and pyrolyzed polymers show better selectivity.

Frierman et al. [29] investigated solvent leaching as a method of regeneration for activated carbons and polymer sorbents loaded with acetic acid by contact with aqueous solutions. Batch-equilibration and fixed-bed experiments were conducted. Methanol, methyl acetate, and acetone are found to be suitable regeneration solvents for most activated carbons. Methanol provides still more efficient regeneration for macro-reticular styrene-divinyl-benzenes adsorbents.

Wang and Jinli [30] investigated the ability of the macroporous resin, H-103, in adsorbing and recovery sorbic acid. Adsorption thermodynamics and kinetics of sorbic acid by H-103 resin was studied through static experiments. Adsorption kinetics was found to follow first-order reversible model expression.

Fernandez et al. [31] performed an experimental study of the purification of dilute hydrofluoric acid (5 wt%) by ion exchange. Fernandez et al. [32] showed the purification of two commercial dilute HF samples by ion exchange by investigating a two column purification system and two resins from Dow Company, strong acid resins, Dowex HCR-W2, and a weak basic resin, Dowex M43.

## REACTIVE SEPARATION

Reactive separation is an emerging technology for the recovery purpose as well. Here, reaction and separation occur in a single unit. Under the larger umbrella of reactive separation, various unit separation-operations like distillation, extraction, and chromatography can be combined with the reaction step. Generally, when reaction is combined with a separation step, various advantages can be realized. But some challenges can also be forced on the process. Improved conversion and selectivity, lesser separation duty and better economy can be achieved. But sometimes, the impregnation of these two steps may put forth unforeseen constraints. Hence before opting for such an option it needs to be effectively weighed up. Distillation (RD), Extraction (RE) and Chromatography/Adsorption (RC) are the major players in the list. These are discussed in the following section in greater details. Reactive Separation is especially useful when the acid in question needs to be converted to another value

added product. Whenever applicable, Reactive separation can work wonders for the given separation.

## REACTIVE DISTILLATION

Reactive distillation (RD) is possibly the most important method

of separation for the recovery of many acids. There has been an increasing effort to combine downstream/upstream separation with reaction to improve the process performance. RD is an emerging technology that has considerable potential as an alternative process for carrying out equilibrium limited liquid phase chemical reactions. It is a unit operation that combines simultaneous chemical reaction

**Table 2. A summary sheet of reactive distillation processes**

Title	Process conditions	Comments	Result	Reference
Use of RD for n-butyl acetate production from dilute acetic acid.	For pervaporation: 30 to 100 °C at 1 atm. For RD Column: 1 atm. pressure, temperature of feed stream 25 °C, same feed flow rate of alcohol and acid solution of 35 mol/h.	A hybrid pervaporation - reactive distillation is used. Requires lower energy than both the conventional distillation - reactive distillation system and the single reactive distillation.	With dilute acetic acid as feed for esterification in RD, more reboiler heat duty is required. An increase in acid concentration in feed is required for better RD performance. For RD - pervaporation an increase in operating temperature provides higher recovery.	[2]
Recovery of dilute acetic acid through esterification in RD.	Catalyst: Indion - 130, 368 K.	Conversion of acetic acid is inversely proportional to feed rate because the residence time is lowered. The reactions was equilibrium limited.	Conversion of 52.7% of acetic acid was achieved at 1 : 2 mole ratio of acid to alcohol. A slight increase in conversion was observed when recycle was used.	[8]
Entrainer-enhanced reactive distillation using n-propyl acetate as entrainer.	Temperature 380-453 K, saturated vapor at 1.3 bar.	The entrainer enhances the reaction rate, Minimum and maximum entrainer ratios were identified.	Increase in the entrainer moves the alcohol to the reaction zone. The use of entrainer leads to 50% reduction in catalyst needed.	[36]
Heterogeneously catalysed esterification of acetic acid with iso-amyl alcohol.	Catalyst: Purolite CT-175, 333-363 K.	The reaction is the rate limiting step.	Conversion of acetic acid increases slightly with temperature. Size of catalyst has no appreciable effect on rate of reaction.	[35]
Production of n-propyl acetate by RD experimental and theoretical study.	Catalyst: A-15, experiments were performed using a homogeneous strong acid catalyst in a packed column.	Simulation result matches with experimental data.	The strong influence of the composition of the initial charging in the decanter noted and an initial charging of the two-phase top product indicated the fastest startup.	[39]
Recovery of trifluoroacetic acid (TFA) from dilute aqueous solutions by RD.	Temperature 70-90 °C, ratio of alcohol-IPA to TFA 1.4 : 1 for BRD runs without catalyst.	Experimentation and subsequent simulation results showed that an appropriately designed recovery system can yield 97% recovery. TFA is reasonably a strong acid to act as a self-catalyst.	The reaction rate increases with an increase in mole ratio of alcohol to acid. Total 70 stages are required to achieve conversion of 96.4%. Effect of process parameters investigated.	[5]
Diethyl succinate synthesis by RD.	Catalyst: Amberlyst 70. KATA-PAK SP-11 structured packing.	Good agreement between experimental and simulation results was observed.	Succinic acid conversions reached to 100%, and diethyl succinate yields up to 98%.	[37]
Fatty acid esterification by RD.	Catalyst: Sulfated zirconia, temperature 373-440 K.	Catalyst is highly selective for high alcohol/acid ratios. The operating temperatures beyond 373 K preferred.	To avoid catalyst deactivation, liquid - liquid segregation into an organic and an aqueous phase must be prevented.	[38]
Esterification of formic acid, acrylic acid and methacrylic acid with Cyclohexene.	Catalyst: Indion 130, A - 15, Amberlite IR-120. Temperature 343-373 K.	The optimum conditions were investigated.	With an increase in the ratio of formic acid to cyclohexene, the conversion of cyclohexene increased but selectivity decreased. Conversion and selectivity increased with an increase in temperature.	[40]

and multi-component distillation in the same vessel, which in turn reduces reactor and recycle costs. Ion-exchange resins (IERS) find application in reactive distillation columns (RDCs) where they play a dual role of catalyst as well as a part of tower packing [8]. RD can be used for either equilibrium reactions or non-equilibrium (irreversible) reactions. In the first case, the withdrawal of products as they are formed results in an increased conversion. This increase is achieved through a shift in equilibrium, based on Le Chatelier's principle. In the second case, it is generally applied to systems where products may react with reactants, causing a decrease in product yield in conventional reactors [5]. The extractive etherification is an interesting method to simultaneously purify water and product ester having a good commercial value [33].

### 1. Possible Advantages and Disadvantages [34]

1. Effecting distillation and reaction simultaneously can reduce the capital costs and can yield benefits like reduction of recycle, optimization of separation, lower requirements of pumps, instrumentation and piping.

2. An equilibrium reaction can be driven to completion by separation of the products from reaction mixture (i.e., the reactant conversions can approach 100%). This is advantageous when equilibrium conversion is particularly low.

3. Elimination of possible side reaction by removal of the products from reaction zone. This can serve to increase selectivity.

4. Savings associated with energy costs, through use of the energy released by exothermic reactions for vaporization. This reduces the reboiler heat duty for boil up that is supplied normally by steam.

5. Non-reactive azeotropes may disappear under reactive distillation condition.

6. Mismatch of reaction and distillation conditions. The temperature and pressure ranges for reaction and separation must overlap.

7. Reactions may form reactive azeotropes. These azeotropes are induced by the reaction affecting separation.

8. Technical constraints such as adequate catalyst characteristics.

A large number of recoveries have been effected by use of RD. Acetic acid, lactic acid, propionic acid, formic acid, acrylic acid and methacrylic acid, trifluoroacetic acid, succinic acid and fatty acids have all been successfully recovered using RD in the past. The yields thus obtained and the conversion efficiency have been observed to be large. Table 2 gives details of a few characteristic recovery processes using RD.

### REACTIVE CHROMATOGRAPHY (RC)

It is a reaction-separation unit called the chromatographic reactor that utilizes differences in adsorptivity of the different components involved rather than differences in their volatility as in RD. It is especially attractive as an alternative to RD when the species involved are either non-volatile or sensitive to temperature, as is the case, for example, in some fine chemical or pharmaceutical applications, or exhibit small volatility differences. Chromatographic reactors are competitive when the involved chemical species are thermally sensitive or when higher purities are required that are better achieved by chromatography [41]. These reactors are typically operated in the batch mode, although better performances can be achieved through continuous-mode operation, as, for example, in simulated moving bed reactors.

### POSSIBLE ADVANTAGES AND DISADVANTAGES

1. It utilizes differences in adsorptivity of the different components involved rather than differences in their volatility. This requires that suitable differences in adsorptivity are necessary.

2. The process is less corrosive and is opposite to homogeneous ones so does not require a further step of separation and neutralization.

3. Cost reduction and high product purity is obtained.

4. Chromatographic reactors are competitive when the involved chemical species are thermally sensitive or when required purities are better achieved by chromatography.

5. In batch chromatographic operations, where large quantity of eluent is needed to perform the separation, highly diluted products are formed. However this problem is solved in continuous chromatographic reactors in order to decrease the solvent consumption and to enhance the productivity.

6. The main difficulty is that a reaction and separation must be conducted at same conditions which in general may not be optimal for both.

7. The scale up of these reactors to industrial size is still an open problem [41].

Gelosa et al. [41] carried out the synthesis of triacetine, starting from glycerol and acetic acid, using reactive chromatography on acidic polymeric resins from dilute solutions. The study first characterized the adsorption equilibria of the involved multicomponent mixtures and then studied the kinetics of the relevant reactions using a batch reactor. Next, the separation-reaction process was investigated using a fixed-bed chromatographic column. The obtained data were compared with the predictions of a mathematical model, its kinetic and equilibrium parameters were estimated from the batch experiments mentioned above. It is shown that, although this synthesis requires three steps in series, the chromatographic reactor can produce high-purity (i.e., food-grade) triacetine with high conversions. The presence of water in the mixture and in the resin at the end of the regeneration step had a strongly detrimental effect on the final triacetine purity.

Lode et al. [42] studied reactive simulated moving bed chromatography (SMBR), a continuous and counter-current operation combining chemical reaction and adsorptive separation within one single apparatus. Its application promises substantial improvements in process performance, especially for equilibrium limited reactions involving heat-sensitive products, as, for example, fine chemicals or pharmaceuticals. In their work, a general approach towards the design of an SMBR process is illustrated using the synthesis of methyl acetate, catalyzed by a sulfonated poly (styrene divinyl-benzene) resin, as a model system. Starting from a suitable mathematical representation of the experimentally determined adsorption thermodynamics and reaction kinetics, a model for a reactive chromatographic column is developed and validated.

Deshmukh et al. [43] studied chromatographic reactor operation of esterification of butyl cellosolve with dilute acetic acid using cation exchange resin Amberlyst-15, in a chromatographic reactor. The study involves determining the appropriate kinetic model for the reaction by performing experiments at different temperatures, mole ratio of the reactants, catalyst loading and stirring speeds. Characterization of the adsorption capacity of the resin for different com-

ponents involved in the reaction was performed through adsorption experiments for the nonreactive binaries. The combined separation-reaction process was experimentally investigated using a fixed bed chromatographic column.

### REACTIVE EXTRACTION

Reactive extraction with specified extractant giving a higher distribution coefficient has been seen to be a promising technique for the recovery of carboxylic and hydroxyl-carboxylic acids. This method is advantageous for alcohol and organic fermentations [44]. Reactive extraction involves use of an extractant - diluent system to extract the acid. Organic solvents used for the extraction of carboxylic acids are categorized as (i) conventional oxygen bearing and hydrocarbon extractants (ii) organo-phosphorous compounds and (iii) high molecular weight aliphatic amines. Conventional solvents like ketones, ethers, aliphatic hydrocarbons are found to be inefficient in the extraction of carboxylic acids from dilute solutions. The reason of this may be the low activity of these acids in these conventional solvents resulting in low distribution coefficients [45].

### POSSIBLE ADVANTAGES AND DISADVANTAGES [44]

1. Increased productivity.
2. Ease in pH control without requiring base addition.
3. Use of a high-concentration substrate as the process feed to reduce process wastes and production costs. This method may also allow the process to produce and recover the fermentation products. Among various methods, extractive recovery of carboxylic acids from dilute aqueous solution such as fermentation broth and waste water, has been receiving increasing attention.

Nikhade et al. [46] worked on equilibria and kinetics for the extraction of citric acid by Alamine 336 in cyclohexanone as diluent are reported. The theory of extraction accompanied by a chemical reaction was used to obtain the intrinsic kinetics of extraction of citric acid. The reaction was found to be first order in both Alamine 336 and citric acid.

Wasewar and Shende [47] studied the recovery of carboxylic acid from dilute solutions. They reported the study of reactive extraction equilibrium of caproic acid using tri-n-butyl phosphate (TBP, extractant), an organo-phosphorous compound, in benzene and tol-

**Table 3. A summary sheet of Reactive extraction processes**

Purpose	Process conditions	Result	Comments	Reference
Recovery of propionic acid.	Mixing time 12 hrs Aliquat 336 with 1-octanol, room temperature.	The study shows that propionic acid is recovered from aqueous solution to organic solvent. Solvent can be regenerated to give pure acid.	Physical and chemical equilibria for propionic acid extraction by Aliquat 336 dissolved in 1-decanol have been determined.	[44]
Recovery of propionic acid by RE using quaternary amine (Aliquat 336).	Aliquat-336, methyl-tri-caprylammonium-chloride, n-heptane, petroleum ether, 1-decanol, and 1-octanol were used as diluents at 305 K for 12 h.	Chemical extraction was found to be better than physical extraction. The overall distribution coefficient (KD), loading ratios, and equilibrium complexation constants were evaluated.	The data obtained is useful in the designing of reactive extraction process for the recovery of propionic acid.	[45]
Recovery of Nicotinic acid.	Temperature 298 K, time 8 hours tri-n-octyl phosphine oxide (TOPO) concentrations are varied in the range of 0.10 to 0.60 mol/l.	The effects of diluent, extractant (TOPO) Composition and initial acid concentration on extraction efficiency studied.	Optimum values of equilibrium extraction constant and number of extractant reacting molecules have been found when optimization procedure (differential evolution algorithm) is used to solve the model equations.	[48]
Extraction of lactic acid into sunflower oil and its recovery into an aqueous solution.	Lactic acid, Aliquat 336 and tri-octylamine (as carriers) and tributyl phosphate and sunflower oil (as solvents). Time 24 h, pH 2.4, effect of various parameter was studied.	An increase in operating temperature yields an increase in the distribution coefficient in the organic phase.	Cheap and non-toxic solvents such as sunflower oil with less environmental impact can be used alone or in combination with tri-butyl phosphate (TBP) for extraction of lactic acid.	[49]
RE of lactic acid using alamine 336.	Room temperature at 25 °C, Shaking time 24 h, two phase settling time 30 min alamine 336 concentration and speed of agitation effects studied.	Extraction efficiency increased with an increase in alamine 336 concentration. There was no effect of speed of agitation on the specific rate of extraction, the reaction is first order with respect to lactic acid.	These data may be useful in the design of extraction processes.	[50]

**Table 3. Continued**

Purpose	Process conditions	Result	Comments	Reference
A comparison between tris 2-ethyl hexyl amine (TEHA) and Cyanex 923 on the separation and the recovery of sulfuric acid from aqueous solutions.	Initial concentrations of sulfuric acid in the aqueous phase varied from 12.5 to 250 g/L. TEHA 43%vol (1 M) agitated at temperatures of 20, 35, 50 and 70 °C time 45 min.	The total time needed for equilibrium extraction of sulfuric acid with both TEHA and Cyanex 923 was 1.5 min, approximately. The results showed that a maximum extraction percent occurred in the range of 50 to 65 when initial concentration of sulfuric acid was around 100 g/L.	The recovery of sulfuric acid from aqueous media using TEHA is more feasible than Cyanex 923.	[51]
RE of aspartic acid from water in hollow fiber.	Feed concentration of Asp (5 mol/m <sup>3</sup> ) and different feed pH (3-5), carrier concentrations (100-500 mol/m <sup>3</sup> ), and strip acidities (100-2000 mol/m <sup>3</sup> ). The flow rates range 120-420 cm <sup>3</sup> /min, 180-480 cm <sup>3</sup> /min for organic phase.	A steady-state mass transfer model was developed that considers all possible diffusion resistances to predict time changes of the extent of Asp extraction in these two hollow fiber modules.	The rate-controlling mechanisms of such non-dispersive solvent extraction processes were identified.	[52]
RE of maleic acid and phthalic acid by supercritical carbon dioxide saturated with trioctylamine.	Temperature range of 308-328 K the pressure range of (100-350) bar and flow rate of 0.2 mL min <sup>-1</sup> of liquid CO <sub>2</sub> .	The amount of extraction of maleic acid and phthalic acid increased with pressure up to 250 and 200 bar, respectively.	The method was established as a selective and green extraction method for dicarboxylic acids such as maleic and phthalic acids.	[53]
RE of amino acids and dipeptides using an extra-flow hollow-fiber module.	The membrane module is 2.5 cm diameter × 20 cm long. The feed and organic solutions were circulated on the fiber side and shell side, respectively.	The experimental data has been shown to be able to calculate the overall mass transfer coefficient of the extraction process.	The value of the overall mass transfer coefficient is similar to those in the literature and has been found to be significantly affected by the solute type and feed solution pH.	[54]
Extraction of aqueous malic acid by trioctylamine extractant in various diluents.	Five different alcohols (isoamyl alcohol, hexan-1-ol, octan-1-ol, nonan-1-ol, and decan-1-ol) and two different ketones (diisobutyl ketone (DIBK) and methyl isobutyl ketone (MIBK).	The most effective solvent was determined as isoamyl alcohol with a distribution value coefficient of 17.81.	A linear solvation energy relationship (LSER) was accurately regressed to the experimental distribution coefficients.	[55]
RE of salicylic acid and D, L-phenylalanine in a bench-scale pulsed sieve plate column.	Secondary amine (Amberlite LA-2) in xylene, quaternary ammonium salt (Adogen 464) in xylene.	For reactive extraction, the measured and calculated degrees of extraction agreed well.	The longitudinal concentration profiles of the solute are not in agreement. The cause of this has not been evaluated yet.	[56]

uene (diluents). Equilibrium parameters such as distribution coefficients, loading ratio, degree of extraction, and equilibrium complexation constants were presented. The data obtained are useful in understanding the equilibrium characteristics and efficient design of the reactive extraction process for the recovery of caproic acid.

Several other recoveries have also been achieved via reactive extraction. A summary of reactive extraction for recovery of various acids is given in Table 3.

### MISCELLANEOUS METHODS FOR RECOVERY

In addition to the various methods discussed above, there are a few other processes/methods which may not be categorized under the above classification. These are discussed below.

Emrah et al. [57] worked on anaerobic acidification of sugar beet

processing wastes and investigated subsequent liquid-liquid extraction of produced fermentation metabolites. The simple extraction experiments assessed the influence of pH and extractant (trioctylphosphine oxide (TOPO) in kerosene) concentrations on the recovery of volatile fatty acids (VFAs) from fermentation broth. Depending on the type of the acid extracted (acetic, butyric, propionic and valeric acids) and the concentration of TOPO in kerosene (5-20%), the percent recovery of VFAs changed from 43 to 98%.

Chang et al. [1] developed a solvent extraction technique to recover nitric acid from the waste stream of the wafer industry. Tri-butyl phosphate (TBP) was selected among several solvents because of its better selectivity towards HNO<sub>3</sub>. The HNO<sub>3</sub> was recovered with a purity of 99.8%.

Samadi et al. [58], explored the use of carbon dioxide gas to exploit the pH-dependent solubility of L-aspartic acid for its separa-

tion from aqueous solution. Experimental data were obtained for the aqueous solubility of L-aspartic acid at 25 °C over the pH range from 2 to 6. It was noticed that solubility increased from the iso-electric pH to higher and lower pH values.

Hogle et al. [59] studied the recovery of itaconic acid (IA) from mixed aqueous solutions of citraconic acid (CA) and succinic acid (SA). Here itaconic acid was produced via condensation of succinates with formaldehyde. Chang et al. [1] showed how solvent extraction process is exploited for acetic acid recovery from the waste etching solution discharged from silicon wafer manufacturing process. In the batch process 96.3% acid recovery was reported. To assess the feasibility of the process continuous operations were carried out for 100 h using mixer-settler.

Huang et al. [60] worked out the recovery of carboxylic acids from fermentation broths, especially pyruvic acid, since acidity of pyruvic acid ( $pK_a=2.49$ ) is stronger than that of normal carboxylic acids. Brown [61] showed the pickling with sulfuric acid; the waste pickle liquor is neutralized and the harmless products disposed of satisfactorily. Xu and Yang [62] reported sulfuric acid recovery from titanium white waste liquor. Anion exchange membranes were practiced for the processes of bromination, chlomethylization and amination. It was noted that acid recovery and selectivity was improved by benzyl and aryl substitution, respectively. Fatmehsari et al. [51] reported sulfuric acid recovery from tris 2-ethyl hexyl amine (TEHA) and Cyanex 923 by solvent extraction process. It was noted that sulfuric acid concentration in aqueous phase was reduced using this extraction.

## SPECIFIC EXAMPLES OF ACID RECOVERY

Thus, many methods have been used for recovery of various acids. Extensive work has been reported for recovery of acetic acid and lactic acid through various processes especially esterification, and these are discussed below.

### 1. Acetic Acid

Gelosa et al. [41], using reactive chromatography, examined the synthesis of triacetine, starting from glycerol and acetic acid on acidic polymeric resins. They found that the presence of water in the resin at the end of the regeneration step has a highly unfavorable effect on the final purity of triacetine.

Singh et al. [63] developed a reactive distillation column by varying different parameters. The reactive distillation can be employed for the recovery process.

Amornchai et al. [2] proposed to produce *n*-butyl acetate via esterification with butanol in a reactive distillation, which is presented by using Aspen Plus. It was noticed that a hybrid pervaporation-reactive distillation requires lower energy than both the conventional distillation-reactive distillation system and the single reactive distillation.

Deshmukh et al. [43] studied esterification of butyl cellosolve with acetic acid using cation exchange resin Amberlyst-15. In their work the experimental and predicted data match each other and a high conversion can be obtained with a comparatively high purity of the product.

Yonghui Shi et al. [26] studied the recovery of acetic acid from the anaerobic fermentation broth with a  $SO_2$  waste stream. The reaction between  $SO_2$  and calcium acetate was carried out. The con-

version of given amounts of calcium acetate to acetic acid was estimated, under different reaction temperatures and flow rates of  $SO_2$ .

Jiang et al. [17] presented the application of an integrated pervaporation process to improve the pervaporation performance of acetic acid over water. This pervaporation process was based on a plain poly-dimethylsiloxane (PDMS) membrane with a hydrophobic ionic liquid composed of a heterocyclic cation and  $PF_6^-$  anions.

Lixin et al. [3] worked on acetic acid recovery using bipolar membrane electro-dialysis in dilute wastewater containing 0.2% (wt%) of acetic acid. Experimental results showed up to 70% (wt%) acetic acid solution can be obtained.

Kun et al. [15] showed the application of pervaporation using a poly-(ether block amide) membrane for the recovery of acetic acid from the mixture of *n*-butyl acetate, *n*-butanol and acetic acid from aqueous solutions. The membrane permeability was in the order of *n*-butyl acetate > *n*-butanol > acetic acid > water.

Masuda et al. [21] worked on the recovery of acetic acid from the evaporation drain of sulfite pulp spent liquor containing few volatile fatty acids, along with acetic acid. Cellulose acetate membrane was used to pass acetic acid and maximum 98.2% recovery was reported.

Munson [28] worked on recovery of acetic acid from low-pH aqueous solution onto polymeric adsorbents and activated carbon, and reported that surface area and chemical nature of the adsorbent plays important role in acid recovery. Activated carbons and pyrolyzed polymers showed better selectivity.

Yue et al. [27] worked on the selective uptake of acetic acid from aqueous solutions onto activated carbons and polymeric sorbents. For styrene-di-vinyl-benzene macro-reticular resins, they reported that adsorption behavior is dominated by aqueous-phase non-idealities. It was noted that the differences in the degree of surface heterogeneity are probably important.

Frierman et al. [29] developed a solvent leaching method of regeneration for activated carbon and polymer sorbents loaded with acetic acid contaminated with aqueous solutions. It was noted that Poly-benzimidazole, a weaker base, gives higher recoveries of acetic acid when leached by solvents.

Aqueous solutions of acetic acid is produced in the production of cellulose esters, terephthalic acid and dimethyl terephthalate [64]. The post process streams contain up to 13-35% acetic acid. Because of large amount of water contained, distillation requires long columns. It has been shown that extraction is not sufficient when used alone; hence it is also necessary to find various means to recover acetic acid. Table 4 gives a summary sheet of acetic acid recovery.

### 2. Lactic Acid

Kumar and Mahajani [4] carried out esterification of lactic acid with *n*-butanol to synthesize *n*-butyl lactate or to recover lactic acid from its aqueous solution. The applicability of reactive distillation for the reaction was evaluated through experimentation.

Seo et al. [65] suggested the recovery of lactic acid by two reactions, esterification and hydrolysis by batch reactive distillation using cation exchange resin as a catalyst. The yield of lactic acid is dependent on the boiling temperature of the reaction mixture in the esterification reaction.

Kim et al. [66] showed purification of lactic acid, batch distillation using esterification reaction of lactic acid with methanol to produce methyl lactate and water followed by hydrolysis of methyl

**Table 4. A summary sheet of acetic acid recovery**

Process conditions	Results obtained	Reference
For pervaporation: 30 to 100 °C at 1 atm. For column: 1 atm. pressure, temperature of feed stream 25 °C, same feed flow rate of alcohol (butanol) and acid solution of 35 mol/h.	With dilute acetic acid as feed for esterification in RD, more reboiler heat duty was required. An increase in acid concentration in feed is required for better RD performance. For RD - pervaporation, an increase in temperature provides higher recovery.	[2]
Bipolar membrane electro-dialysis in dilute wastewater containing 0.2% (wt%) of acetic acid.	Experimental results showed up to 70% (wt%) acetic acid solution can be obtained.	[3]
Catalyst: Indion - 130, 368 K.	Maximum conversion of 52.7% of acetic acid was achieved at 1 : 2 mole ratio of acid to alcohol using RD. Conversion increases when recycle is used.	[8]
The separation of n-butyl acetate, n-butanol and acetic acid from aqueous solutions by pervaporation using a poly-membrane. Temperature 60 °C.	The effects of feed composition and operating temperature on the separation performance were investigated. The organic phase can be recycled to the distillation column for reprocessing, while the aqueous phase can be recycled to the pervaporation unit for further treatment.	[15]
Integrated pervaporation process based on a plain Poly-dimethylsiloxane (PDMS) membrane with a hydrophobic ionic liquid composed of a heterocyclic cation and PF6 anions.	The ionic liquid as an extractant prior to pervaporation was favorable for improving the permeate selectivity and the permeate flux of acetic acid compared by using PDMS membrane. Extraction of a real effluent containing acetic acid from an antibiotic pharmaceutical plant was carried out using the above integrated pervaporation, and results showed that it can be scaled up.	[17]
The reaction between SO <sub>2</sub> and calcium acetate, the anaerobic fermentation broth with a SO <sub>2</sub> waste stream, temperature 60 °C , Time 80 min.	SO <sub>2</sub> concentration and reaction temperature had no effect on the concentrations of acetic acid produced sulfur dioxide can be used to recover acetic acid from calcium acetate solutions.	[26]
Catalyst: Purolite CT-175, 333-363 K.	Conversion of acetic acid increases slightly with temperature. Size of catalyst has no appreciable effect on rate of reaction.	[35]
Fixed-bed chromatographic reactor, A-15, 60-80 K, time 100 min.	The chromatographic reactor can produce high-purity (food-grade) triacetate with high conversions using RC. The predicted results and the experimental data were matched for the chromatographic reactor which shows the reliability of the model.	[41]
A-15 esterification of butyl cellosolve with acetic acid using cation exchange resin in a chromatographic reactor at different parameters.	It is shown that the experimental and predicted data closely follow each other and that the high conversion can be obtained using RC with a relatively high purity of the product.	[43]
A RD column developed by varying different parameters.	RD can be employed for the recovery process of dilute aqueous solution (30% w/w). Experimental work is validated with modeling and simulation.	[63]

lactate and water to reproduce lactic acid and methanol.

Kumar et al. [67] did batch reactive distillation of lactic acid, to separate from its aqueous solution. Because of a non-boiling compound it is necessary to convert it to the relatively volatile ester and the separation of the ester, followed by hydrolysis which is suggested for a desirable recovery.

Frieling and Schugerl [23] recovered lactic acid from fermentation broths in the presence of citric acid and acetic acid. Due to the toxicity of the carriers and modifiers, in situ extraction of lactic acid was not possible. In a multistage process only the separation of the acids is possible.

Kumar et al. [68] showed separation and purification of lactic acid from the fermentation broth are difficult due to non-volatile nature and the presence of other organic acids. Continuous removal of the volatile component (i.e. methanol) from the reaction zone increases conversion of lactic acid.

Hyohak Song et al. [24] indicated producing lactic acid by fermentation of several natural and engineered bacterial strains. Man-

nheimia succiniciproducens MBEL55E was isolated from bovine rumen

Benedict et al. [16] studied the esterification of lactic acid (C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>) and with ethanol (C<sub>2</sub>H<sub>5</sub>OH) to generate ethyl lactate (C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>) using solid catalysts (Amberlyst XN 1010 and Nafion NR50) and two pervaporation membranes (GFT-1005 and T1-b).

Lactic acid is typically obtained in fermentation broths. The percentage of lactic acid in these broths is varying and typically contains 1-20% in dilute aqueous solution. Along with water several other fermentation products are present in these broths. Naturally, separation of lactic acid is difficult. Industrially, lactic acid is a precursor for different important chemicals like methyl lactate; hence recovery of lactic acid is very important. Table 5 gives a summary sheet for lactic acid recovery processes.

## CONCLUDING REMARKS

- The review has attempted to cover the majority of the process

**Table 5. A summary sheet of Lactic acid recovery**

Process conditions	Results obtained	Reference
Esterification of lactic acid with n-butanol from its aqueous solution. Cation-exchange resins as a catalyst.	An equilibrium stage model is formulated, and simulation results are compared with the experimental results. The applicability of RD for the reaction was evaluated through experimentation.	[4]
Lactic acid recovered from fermentation broths in the presence of citric acid and acetic acid, reactive extraction carried out, temperature 80 °C.	Due to the toxicity of the carriers and modifiers, in situ extraction of lactic acid was not possible. In a multistage process only the separation of the acids is possible. Experiments were performed using a secondary amine (Hoe F 2562), a tertiary amine (Hostarex A 327) as well as a phosphine oxide as carriers and butyl acetate and kerosene as solvents.	[23]
Catalyst cation exchange resin esterification and hydrolysis reactions were carried out.	The effects of operating variables such as catalyst loading, reactant mole ratio, feed concentration, type of alcohols and condenser temperature on the yield were studied.	[65]
Batch distillation with the simultaneous reaction was used.	Esterification reaction of lactic acid with methanol produced methyl lactate and water. The effect of the number of stages in column on the recovery yield was also investigated.	[66]
Esterification, distillation and hydrolysis performed in a batch reactive distillation unit.	An unsteady state mathematical model based on an equilibrium stage developed. The applicability of reactive distillation assessed.	[67]
A continuous process for the recovery of lactic acid by RD in a two-phase CSTR, ion-exchange resin used for esterification, operated under boiling conditions.	Ester separated from the aqueous solution is hydrolyzed in a RD column. Conversion increases because of continuous removal of the volatile component methanol.	[68]

technologies available for recovery of acids, mainly organic acids, although other acids including mineral acids have also been referred to.

- Biological processes are indicated to have several limitations presently like temperature rise and toxicity of the stream or effluents where the processes are not viable, but this is a very promising technique for the future.

- Many membrane processes need pretreatment and due to fouling behavior of membranes it is not sometimes feasible or economical. Cost of the membranes is also an issue that should be looked into, especially for bipolar membrane. Electrodialysis is a promising technique if its temperature range can be increased and can be made cost effective.

- It is observed that most adsorption processes are limited by the pH of the solution.

- Recovery of acetic acid from dilute aqueous solutions is studied by almost every group of researchers. However, no mature technology is reported, especially when concentrations are low.

- Reactive separation has under its umbrella, several unit operations possibly coupled with reaction step. Reactive separation is especially useful when the acid in question needs to be converted to another value-added product. Whenever applicable, reactive separation can work wonders for the given separation.

- This brief review indicates that there is a definite need of efforts in this important field. The number of systems studied is limited and so the work in this important area needs to be strengthened.

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