

Reactive Extraction: An Intensifying Approach for Carboxylic Acid Separation

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Abstract—Since last few decades, there has been a revitalization of attention towards new energy-efficient fermentation technology for large production of fermentation chemicals due to sharp increase in petroleum costs. Carboxylic acid has wide applications in various chemical, food, and pharmaceutical industries. A growing demand for biodegradable polymers, substitutes for both conventional plastic materials and new materials of specific uses such as controlled drug delivery or artificial prostheses, draws attention the need for improvement of conventional processes for carboxylic acids production. Reactive extraction is a multifunctional reactor having reaction and extraction in a single unit. This intensified approach has the closed loop process with sustainability. In present paper, the concept of reactive extraction and effect of various parameters were discussed. These studies are very useful in the view of complete design of a reactive extraction process for the carboxylic acid production.

Index Terms—Reactive extraction, carboxylic acid, intensification, separation, parameters.

I. INTRODUCTION

As per the recent trend of chemical industry, attention towards the production of fermentation based chemicals has been increased due sharp increase in petroleum cost. It is the need of the industry to develop the new energy efficient recovery process or substantial improvements in the existing recovery technology. Carboxylic acids (Lactic, propionic, caproic, lactic, picolinic etc.) can be produced by fermentation and are widely used in pharmaceutical, food and other allied industries. Due to some specific applications it draws attention towards the development of new recovery processes for carboxylic acids production.

Many separation processes are available like, stripping, adsorption, elctrodialysis, liquid-liquid extraction, pertraction, pervaporation, and membrane solvent extraction. All these processes have their own advantages and disadvantages. Reactive extraction is an alternative for the conventional process. In recent few years reactive extraction of lactic acid [1]-[4], caproic acid [5]-[10], picolinic acid [11], nicotinic acid [12], acrylic acid [13], [27], citric acid

[14],[15], phenyl acetic acid [16], propionic acid [17]-[35], benzoic acid [36], pyridine-3-carboxylic acid [36], levulinic [37], butyric acid [27], [38], glycolic acid [40], itaconic acid [40], gluconic acid [41], etc. Also few reviews are available [42]-[45]. In present paper various aspects for the development of reactive extraction process for the recovery of carboxylic acids has been discussed. Physical equilibrium, chemical equilibrium, extraction kinetics, effect of temperature, effect of substrate, effect of salts, effect of pH, back extraction equilibrium and kinetics, regeneration, toxicity, water co-extraction, economical has been analyzed and presented. This paper will be very useful in the context of design of intensifying process for the recovery of carboxylic acid by reactive extraction. The design window of the reactive extraction is shown in Fig. 1.

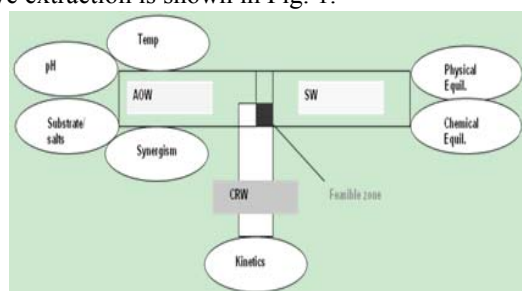


Fig. 1. Design window for reactive extraction AOW: Apparatus operating window, SW:

II. CONCEPT OF REACTIVE EXTRACTION

The basic philosophy of the process intensification methods is to choose the task in a manner such that their combination leads to better overall performance. Since any chemical process involves unit operations for reaction and separation, most of such task combinations fall under the umbrella of reactive separation processes. The combination of reaction and separation is effective when either the reaction substantially improves separation through enhanced mass transfer rates or the separation drives the reaction to higher conversions or both. The fusion of reaction and separation as one combined operation is also prized for its simplicity and novelty. These operations are also coveted for the investment and operating cost savings garnered on successful scale up to commercial operations [44].

In recent years, reactive extraction processes are gaining lot of importance in response to extreme economic pressure posed by industries as the result of emergence of new processes and decline of existing ones, demand of high purity products with low cost and are environmentally safe [19]. However, commercialization of reactive separation processes is desired, which can be achieved by the mutual working of chemists and engineers. Reactive extraction links chemical

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sources and sink to enhance reaction rates, conversions and selectivity. Since most of chemical processes are equilibrium driven, removal of product as soon as it is produced would lead to enhanced reaction rates, increased feed conversions, reduce reaction severity and provide operation under milder conditions. Mass transfer and reaction coupling improves catalyst life, since, high mass transfer forces lead to better catalyst irrigation and surface renewals with transport of catalyst inhibitors away from catalyst surfaces. Further, in reaction and separation operations, the duo would lead to high local driving forces for separation, leading to reduction in equipment size, elimination of recyclable streams and reductions in utility costs. Reactive separators also lead to safer equipments since it reduces the working inventory of reactive chemicals in the equipment. Lower the hazardous chemical, lower will be the chance of its leakage, spills and environmental release. Coupling of reaction and separation also leads to suppression of byproduct reactions which are likely to exhibit runaway behavior and the reactive separator design will increase the inherent safety in the unit against severe process upsets. The combination also provides low cost equipment through the consolidation of multiple pieces of process equipment into single piece and/or through the elimination of process recycle streams [44].

Reactive extraction with a specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic acids. Reactive liquid-liquid extraction has the advantage that acid can be removed easily from the fermentation broth, preventing lowering of the pH. Further, acid can be re-extracted and the extractant recycled to the fermentation process. The advantages for reactive extraction with fermentation can be summarized as: Increased reactor productivity; Ease in reactor pH control without use of base addition; Use of a high-concentration substrate as process feed to reduce process waste and production cost; produce and recover fermentation product in one continuous step and reduce downstream processing load and recovery cost [2], [44].

For the last few decades, there has been intensive work on the reactive extraction for the recovery of carboxylic acid from waste water solutions and fermentation broths. Reactive extraction being a clean process, since the extractant for the recovery of the acid can be completely recovered and reused. The simple and cheap operation has created a lot of scope as an efficient recovery process. The primary hindrance in the establishment of the reactive extraction process for the recovery of the acid is the search for an efficient and selective extractant. When this could be accomplished, the other task like carrying out the process is relatively simple. The highly selective, efficient, economic, simple and clean process of reactive extraction has initiated us to study for the recovery of carboxylic acid from aqueous solutions [3], [7], [9], [15], [43].

III. PROCESS PARAMETERS

A. Physical Extraction

For physical extraction different kind of conventional

solvents can be used as diluents such as: polar-nonpolar, protic-aprotic, inorganic-organic, natural solvents etc. Physical extraction involves the extraction of solute into inert non reacting hydrocarbons and substituted hydrocarbons and is relatively free of complexities. Three factors to be considered for physical extraction [7]-[9], [45]: (a) ionization of the acid in aqueous phase, (b) partial dissociation of the acids between two phases and (c) dimerization of the acid in the organic phase. The concept of physical extraction is presented in Fig. 2. Distribution coefficient (ratio of total acid in organic phase to aqueous phase) can be written in terms of partition coefficient and dimerization coefficient as [3], [5], [45]:

$$K_D^{\text{diluent}} = P + 2P^2D[\text{HA}]_{\text{aq}} \quad (1)$$

where

$$P = [\text{HA}]_{\text{org}}/[\text{HA}]_{\text{aq}} \quad D = [\text{HA}]_{2,\text{org}}/[\text{HA}]_{\text{org}}^2 \quad (2)$$

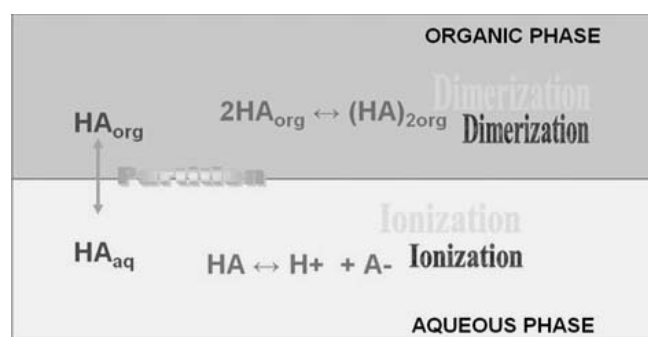


Fig. 2. The concept of physical extraction

B. Chemical Extraction

In chemical process industries, chemical reactions are used far less frequently for separations. The reason for this being that employing chemical reaction often consumes large amount of expensive reactants and the reaction product is usually less valuable than the original compound. These disadvantages are overcome by using a chemical reactant that can reversibly complex with the component of interest in one step and the reaction can be reversed to regenerate the reactant in second step. In order to the reaction being reversible in an economical attractive process, it must have relatively low bond energy. Usually the complexation reactions with bond energy less than 50 kJ/mol are similar to ordinary associations by van der Waals forces in the condensed state and can readily be reversed. However, those having bond energies above 50 kJ/mol are difficult to reverse and require undue expenses [19], [34], [43], [44].

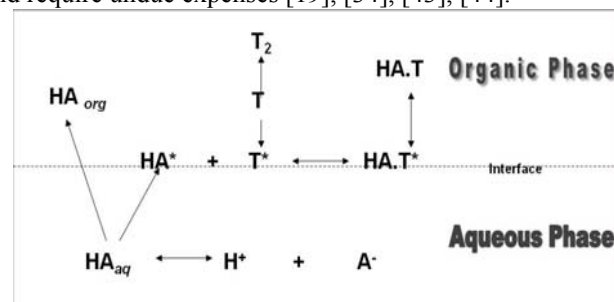
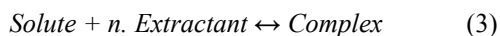


Fig. 3. Mechanism of chemical equilibrium HA: acid, T: extractant

Here, mixture is contacted with a second phase containing an extractant that reacts reversibly with the solute. The choice of complexing agent is based on its strong, specific, yet reversible reaction with the solute. Usually these complexing agents are solid or viscous so they are dissolved in a low molecular weight and low viscosity diluents. The diluents improve the equilibrium through solvation of the complexes and can affect the process in other ways. The mechanism of chemical extraction is explained in Figure 3 and described simple reaction with equilibrium constant as [5], [9], [35], [40]:



$$K_c = \frac{[\text{Complex}]}{[\text{Solute}][\text{Extractant}]^n} \quad (4)$$

Extractants can be categorized as (i) organophosphorous compounds and (ii) high molecular weight aliphatic amines. First category involves the solvation of the acid by donor bonds of some kind which are to be distinguished from strong covalent bonds and from ionic interactions. The second category involves a reaction [2]-[7], [14], [17], [29], [35], [40].

Different organophosphorous compounds like tri-n-butyl phosphate (TBP), tri-n-octyl phosphine oxide (TOPO) have provided higher distribution coefficient when used as extractants. Aliphatic amines have been found to be more effective and less expensive than the organophosphorous compounds. Aliphatic amines (tri-n-octylamine (TOA), Aliquat 336, Alamine 336 etc.) have been widely employed for the extraction of carboxylic acids like lactic, citric, nicotinic, butyric, valeric, glycolic and glyoxylic acids

Usually extractants are solid (tri-n-octylphosphine oxide) or viscous (Aliquat 336 etc), and are employed with diluents. The diluents control the viscosity, density, and interfacial tension of the mixed solvent. With a relatively nonvolatile extractant, the diluent volatility also determines the temperature in the reboiler of the distillation column in a regeneration process. Although the chemistry of acid recovery by reversible chemical complexation is complex, it is possible to treat the extraction by Nernst's distribution law supplemented by sets of mass action law equilibria. The diversity of extraction process stems from the type of reaction governing the transfer, which in general depends solely on the extractants and diluent used [3], [5]-[12], [26].

C. Kinetics

The knowledge of extraction kinetics is important for the design of the reactive extraction process. Since extraction depend on the type of extractant and diluents, kinetic study is important to explain the nature of process. In liquid-liquid system it would be desirable to use a stirred cell for kinetic study [1]-[5], [17], [23]. When the reaction takes place in organic phase, the diluent usually is present in large amount than the reactants such that its concentration remains essentially unchanged during the course of reaction.

The reaction between two molecules in solution can be thought of as involving three steps, (a) diffusion of the reactant molecules to each other; (b) the actual chemical transformation; and (c) the diffusion of the products away

from each other. For most processes, the chemical transformation is much slower than the diffusion process, thus, the overall rate is controlled by the chemical reaction [21]. However, there are some reactions which are vary rapid that they are controlled partly or almost completely by the rate at which the reactants come close together. Thus, the kinetics of reaction in solution could be found by running experiments and studying the effect of different hydrodynamic parameters [27], [31].

Wasewar et al. [1]-[3] studied the kinetics of extraction of lactic acid by Alamine 336 (tertiary amine) in MIBK, octanol, and decanol using stirred cell. The kinetics was found to be fast reaction occurring in diffusion film. The reaction was found to be zero order in Alamine and first order in lactic acid. Similar results were obtained by Gaidhani et al. [16] in extraction of phenyl acetic acid using Alamine 336 in kerosene in a stirred cell. Usually, the reaction was found to be zero order in extractant and first order in acid [1]-[5], [21], [27].

D. Effect of Temperature

In view of operating temperature and back extraction/regeneration step, its study is important. Usually industrial scale fermentor for production of carboxylic acids operates in the temperature range of 305 to 313 K. Thus an extractant can be considered as good only if it could operate efficiently in this operating range. Usually extraction is an exothermic process and a decrease in extraction is expected as the temperature is increased. However, it can be stated that the decrease in extraction is the function of the extractant and diluent chosen i.e. the extracting medium. Further, the variation in climate, feed and bioreactor conditions make the study of temperature effect more important. In most of the cases, extraction decreases (around 50%) with increase in temperature [20], [22], [27], [45].

E. Effect of pH

In carboxylic acid fermentation, the end-product inhibition is the major obstacle in the acid fermentation. During the fermentation, simultaneously with the product inhibition, the pH of the medium decreases, because of acid produced. This leads to the necessity of adding a neutralization agent in order to maintain it in the optimal range of fermentation. Another alternative to this is the continual removal of product acid produced. That is why it is of great importance to remove the product in situ and thus to increase the productivity and the performance of the bioreactor. In reactive extraction, high pH can be maintained by extracting acid as soon as it is formed [3], [7], [15], [37]. In case of phosphorous based extractant (tri-n-octyl phosphoric acid) and high molecular weight tertiary amines (tri-noctyl amine, alamine 336), extraction decreases with increase in pH and in case of quaternary amine it has certain optimum pH [20], [22], [37], [42], [43].

F. Effect of Mixed System

To improve the organic acid extraction various attempts using mixed extractants and/or diluents have been studied. These included use of a mixed diluent system with a single extractant or use of a mixed extractant system in a single or binary diluents [28], [36].

Various active, polar, and proton- or electron-donating

solvents can enhance the extraction, yet they make the back-extraction of free acid into water difficult. Paraffinic, inert diluents, on the other hand, limit the solvent capacity by the third-phase formation at higher acid concentrations in organic phase. Thus, employing binary diluents composed of an inert diluent and an active diluent (modifier) can be used to overcome these difficulties. Between the extraction and back-extraction steps, the composition of the diluent can be changed to promote the efficiencies of both steps. Diluent mixed with polar diluent and nonpolar diluent have been used for reactive extraction of carboxylic acid in order to increase the efficiency of stripping. The active diluent is named as modifier. The advantage of modifier addition is that they prevent the third phase formation which is generally found when an inert diluent is employed with an extractant. The type of modifier can significantly affect the extraction power of the extractants. In general, the polar diluents increase the extraction because they can stabilize the ion-pair formed by hydrogen bonds or by solvation. Mixed extractant, on the other hand, can significantly increase extraction of acid by principle of synergetic extraction in which presence of one can contribute to the increase the performance of the second [28], [36].

G. Effect of Substrates

Since, there was not 100% conversion of feed material in the fermentation broth; the influence of substrate concentrations on reactive extraction is important. Different type of salts and carbon sources are found in fermentation broths owing to the impurities. Since, we are interested in studies of recovery of acid from fermentation broths which usually contains substrate source around 40 g/l, it can be concluded that the presence of substrate does not have any effect on the extraction of acid. The marginal reduction in K_D value can be due to the increased viscosity of the aqueous phase that could have yielded changes in the surface tension at the interface leading to lower complexation and hence lower extraction. However if conversion of substrate of bioreactor is low, i.e. more of substrate is left unconverted (>40 g/l), lower K_D would be expected [22], [43]. It can be found that the presence of various substrates (lactose and dextrose) in any concentration resulted in no significant lowering of K_D . Thus practically these substrate sources do not affect the extraction of acid [22], [43].

H. Effect of Salts

Establishment of reactive extraction on commercial scale requires knowledge of effect of impurities, especially salts like: $NaCl$, Na_2SO_4 , K_2HPO_4 on the extraction. Presence of salt should cause the salting out of acid. Thus, an increase in distribution coefficient should be obtained. However, in contrary to it, a decrease in the distribution coefficient was found. The reason of this may be that the Cl^- , SO_4^{2-} , HPO_4^{2-} ions of $NaCl$, Na_2SO_4 and K_2HPO_4 , respectively, interact with the hydrogen ion of acid to yield HCl , H_2SO_4 and H_3PO_4 in the aqueous phase [22], [43]. The acid in return converts into sodium propionate and potassium propionate. The salting out effect occurs as a result of the formation of salt-liquid phase complexes with water more than that with the acid. The formation of these complexes reduces the

activity of the more attracted component in the solution and increases the activity of the less attracted component which results in expelling or salting out the later from the liquid solution. Thus salting out of HCl , H_2SO_4 and H_3PO_4 occurs more than that of acid [22], [43]. The salted out acid reacts with amine to form complexes in the organic phase. This effect is different for different salt. There is a correlation between the ionic radius and salting out effect. Salting out effect increases with decreased in atomic radius. The smaller ion, allows a closer approach to its charge center, which in turn exerts a stronger attractive force for molecular association in solution. Further, it is expected that salting out effect increases with increasing salt concentration owing to increase in intermolecular forces between the salt and the polar component (water) in the mixture [22], [43].

I. Water Co-Extraction

The mutual solubility between an aqueous solution and a given solvent at a fixed temperature is affected by the nature of the acid and its concentration. With weak organic acids, mutual solubilities cause substantial volume change. The extent of the volume change is, of course, related to the coextraction of water along with that of the acid. The organic-phase volume increased about 2-5% with corresponding decreases in the aqueous phase for aliquot 336. On the other hand, no significant volume change observed for tertiary amines and TBP [9], [11], [20], [43].

For extractions with high concentrations (>25%) of amine in diluent, a third emulsion phase was also observed at the surface between the aqueous and organic phases. Volume change depends on the type of diluent and the type and concentration of extractant as well as temperature. The volume change in the extraction is related with the coextraction of water. Water coextraction, i.e., water that enters the organic phase with the solute, may also affect process economics. For example, it may be necessary to recover pure acid from an aqueous solution produced from the extract during regeneration. Water removal from the organic phase could decrease the solubility of carboxylic acid. This phenomenon was applied for the stripping method of carboxylic acid by the removal of water from the organic phase. In general, selectivity of the acid over water in the extraction by amine extractants is high relative to the results with conventional solvents. The water carried into the extract would be minimal compared to the amount of water used in an aqueous back extraction, and therefore it has little effect upon process viability [9], [11], [20], [43].

J. Toxicity

The presence of an organic solvent can give rise to a series of physical microbial and biochemical effects on the catalytic activity of the microorganisms. Toxicity of the organic solvent and extractant to microbes is the critical problem in extractive fermentation. The degree of toxicity depends on the combination of microbe and extractant solution used. Avoidance of direct contact of the organism with the extractants can substantially reduce toxic effects [8], [11], [14].

Two types of solvent toxicity can be explained: the toxicity of the solvent due to the soluble portion of the solvent

(molecular level toxicity) from that due to the presence of two phases (phase level toxicity). The use of natural solvents (sunflower oil, castor oil, rice bran oil etc.) can significantly reduce the toxicity [8], [11], [14], [25].

K. Back Extraction and Regeneration

The success of the reactive extraction process lies in complete recovery of acid from the loaded organic phase. The second step is referred as regeneration, actually involves reversal of the reaction to recover the acid into a product phase and the acid free extractant, available for recycle. The acid can be back extracted from loaded organic phase using various regeneration methods. These involve using NaOH, HCl or trimethyl amine or by temperature and diluent swing.

Using NaOH: In this method of extraction, the loaded organic phase is contacted with sodium hydroxide solution. Nearly complete recovery of acid can be obtained was obtained, when NaOH in excess of stoichiometric amounts, was used [8], [43].

Using HCl: Concentrated HCl in stoichiometric excess can be used to essentially displace the acid from the loaded organic phase. The acid recovered through back extraction with HCl was in the undissociated form. It is possible to regenerate the solvent by distilling diluent in the dispersed organic phase. This method has the drawback of aqueous HCl being highly corrosive requiring special material of construction (glass lined/graphite) [43].

Temperature-swing regeneration: The extraction has been carried out at relatively low temperature, producing an acid-loaded organic extract and an aqueous raffinate waste stream containing the unwanted feed components. During regeneration, the extract was contacted with a fresh aqueous stream at a higher temperature to produce an acid-laden aqueous product stream and an acid-free organic phase. The concentration of the acid achievable in this stream depends on the amount of change in the extraction equilibrium between temperatures and can be higher than that in the original aqueous feed stream [43].

Using trimethyl amine (TMA): The regeneration of acid extracted in the organic phase using a stronger volatile amine like trimethyl amine (TMA) in aqueous phase has been studied [1], [18], [43]. The advantage of this regeneration technique is that it avoids consumption of chemicals and creation of salt byproduct. The aqueous base, which is volatile, enables thermal decomposition of the acid-base complex in the aqueous back-extract. The decomposition forms carboxylic acid as a product and freebase as a vapor that can be reabsorbed in water and recycled for reuse in back-extraction. The most obvious water-soluble, volatile base is ammonia. However, ammonia and both primary and secondary amines form amides when they are heated in mixtures with carboxylic acids. The amides are sufficiently stable so that it is difficult to reverse the process and recover the amine. In thermal regeneration of TMA, 99% of TMA was removed from trimethylammonium carboxylate aqueous solution. Equilibrium data presented by these researchers show near stoichiometric recovery of acid from amine extract. However, the organic phase, which is recycled to the fermentor, may contain residual dissolved TMA, which can affect the bioactivity of the enzyme [1], [18], [43].

Diluent swing: This is based on a shift of the equilibrium distribution of acid from the aqueous phase to the organic phase between forward and back extraction caused by a change in composition of the diluent with which the extractant is mixed. This diluent composition swing facilitates back extraction of acid into an aqueous product phase. The composition of the acid laden organic phase leaving the extractor is altered, by either removal of the diluent or addition of another diluent, to produce a solvent system that promotes distribution of the acid to the aqueous phase. The altered organic phase is contacted with a fresh aqueous stream in the regenerator to produce the acid laden aqueous product and the acid-free solvent for recycle to the extractor. This approach involving more than one diluent appears to be more complicated than the TMA approach, where an easily removable volatile amine (TMA) is the only externally introduced component. This process has the disadvantage of diluting the extract stream and requiring distillation of large amounts of solvent (after the regeneration) to obtain the same shift in the active/inert diluent ratio [18], [43].

It was found that employing TMA was better among all, yielding nearly complete regeneration of the acid. Kinetics of regeneration of acid was also studied and it was found that in all the cases, the reaction was a fast reaction which signifies that TMA could be successfully employed for the regeneration [18], [43].

IV. DISCUSSION AND CONCLUSION

The rapid industrialization and increasing competitiveness among various sectors of industries in the last few decade have initiated chemical engineers to select a process or unit which is smaller, safer and cheaper; and created less waste generation and requires low energy consumption. Process intensification (PI) emerges as the term for the effort in this direction. Employing PI methods and PI equipments, a considerable improvement can be brought in chemical and allied industries. Separation is an important step in any chemical industry operation. The requirement of current chemical industry is either: improvement of existing separation technologies, introduction of new or improved separation technologies or combination of two or more units into one so that the benefit in terms of scale of operation and cost can be brought in. The last point basically directs towards reactive separations where reaction and separation could be combined in a single step. Reactive extraction is one of the PI method in the category of reactive separation successfully employed in recovery of chemical species from dilute solutions with high selectivity and capacity. Reactive extraction is a clean, simple and cheap operation has created a lot of scope of it as an efficient recovery process.

Carboxylic acids are an important carboxylic acid having wide number of uses in food, chemical and pharmaceutical industries. These can be prepared both by petroleum and fermentation route. Fermentation is advantageous over the former in view of being a clean process and low cost substrate material can be used as feed source. Also the rapid price fluctuation and the depleting feed sources of the petrochemical feed stocks have created the interest of the

production of acid using the bioroute. The challenge in the commercialization of the fermentation technology for the acid recovery is the difficult downstream recovery of dilute concentrations of acid. In view of this reactive extraction is the technique for the recovery of the acid.

In present paper various aspects for the development of reactive extraction process for the recovery of carboxylic acids has been discussed. In this view, physical equilibrium, chemical equilibrium, extraction kinetics, effect of temperature, effect of substrate, effect of salts, effect of pH, back extraction equilibrium and kinetics, regeneration, toxicity, water co-extraction, economical has been analyzed and presented.

This paper will be very useful in the context of design of intensifying process for the recovery of carboxylic acid by reactive extraction.

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