

# Intensifying the Recovery of Carboxylic Acids by Reactive Extraction

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**Abstract.** It can be observed from the worldwide economy of the chemical and allied industries, there has been a revitalization of interest in large production of fermentation chemicals. A new energy-efficient fermentation technology is receiving growing attention because of the sharp increase in petroleum costs. Fermentation chemicals are still limited in the current market in large part due to difficulties in recovery of carboxylic acids. Hence, 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 chemicals widely used in pharmaceutical, food and other allied industries. Due to some specific applications such as controlled drug delivery or artificial prostheses, draws attention towards the development of new recovery processes for carboxylic acids production. 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.

**Keywords:** Reactive extraction, Intensification, Carboxylic acid, Recovery.

## 1. Introduction

It can be observed from the worldwide economy of the chemical and allied industries, there has been a revitalization of interest in large production of fermentation chemicals. A new energy-efficient fermentation technology is receiving growing attention because of the sharp increase in petroleum costs. Fermentation chemicals are still limited in the current market in large part due to difficulties in recovery of carboxylic acids. Hence, 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 chemicals widely used in pharmaceutical, food and other allied industries. Due to some specific applications such as controlled drug delivery or artificial prostheses, draws attention towards the development of new recovery processes for carboxylic acids production.

Many separation processes are available like, stripping, adsorption, electrodialysis, liquid-liquid extraction, pertraction, pervaporation, and membrane solvent extraction. All these processes have their own advantages and disadvantages. 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

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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, the approach brings to the process flow sheet. These operations are also coveted for the investment and operating cost savings garnered on successful scale up to commercial operations.

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. However, commercialization of reactive separation processes is desired, which can be achieved by the mutual working of chemists and engineers. Reactive extraction links chemical 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 recycles streams.

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 the fermentation product in one continuous step and reduce down stream processing load and recovery cost. 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 further for the recovery of carboxylic acid from aqueous solutions and model solutions having close resemblance to the fermentation broth. The numerous advantages of reactive extraction initiated to use it as a method of intensification for the recovery of carboxylic acid. The reactive substance or extractant forms the reversible complex with acid, which promotes the transfer of the polar acid from the aqueous phase to the nonpolar organic phase. Results show that process intensification is a vital tool to realize an improved process. Further, the reactive extraction process does not affect the thermal stability of bioproducts, and energy demand is substantially low.

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.

## 2. Physical Extraction

Generally physical extraction involves the extraction of solute into inert non reacting hydrocarbons and substituted hydrocarbons and is relatively free of complexities. Two factors need to be accounted to show the influence of diluents on the extraction: (a) partial dissociation of the acids in aqueous phase and (b) dimerization in the hydrocarbon phase.

## 3. Chemical Extraction

Separation involving reactive extraction i.e. extraction with reversible chemical complexation are gaining wide importance owing to the high capacities and high selectivity for dilute solutes. In these processes, the mixture is contacted with a second phase containing a complexing agent that reacts reversibly with the solute of interest. The separation by reactive extraction tends to be more attractive for cases of relatively low solute concentration. In addition to high capacity at low solute concentration, the other major potential advantage of reactive separation is selectivity. Since the complexation reaction can be selective for solutes with particular groups, these processes have the potential to separate only certain solutes from complex mixtures. Reactive extraction employing specific extractant can also give less coextraction of water than separations with more conventional solvents. 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. The amine interacts with acid to form acid - amine complex and thus provide high distribution of acid. The high affinity of acid to the base provides an additional advantage of high selectivity over the non acidic components in the mixture.

## 4. Kinetics

In order to exploit the principle of reactive extraction and for simulation and design of reactive extraction unit for practical application, knowledge of the extraction kinetics is important. Since extraction was found to depend on the type of extractant and diluents, kinetic study is important to explain the nature of process. Jet apparatus, stirred cell, mechanically agitated contactor and stirred contactor are some of the setups successfully employed to carry out kinetic studies of fluid-fluid systems. However, in liquid-liquid system it would be desirable to use a stirred cell or a small mechanically agitated contactor. Kinetics of lactic acid extraction with quaternary ammonium salt (tri-n-octylmethylammonium chloride) was investigated. It was found that the species were in equilibrium at the interface in stirred cell and the extraction rate was limited by mass transfer. It was concluded that the extraction rate was mainly controlled by a chemical reaction occurring at the organic side of the liquid-liquid interface. The intrinsic rate constants for the formation and dissociation of the acid complexes were determined and a possible reaction mechanism was proposed.

## 5. Effect of Temperature

Temperature effect is an important subject of study in the reactive extraction process in view of operating temperature and back extraction/regeneration step. 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. The relatively large differences in enthalpy and entropy loss between the two diluents for (1:1) complexation are consistent with the conclusion that interaction of chloroform with the complex is specific hydrogen bonding. The association of chloroform with the complex is exothermic and increases the order (decreases in entropy) of the system.

## 6. Effect of pH

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. It was found that in intermediate pH range, distribution coefficient decreased with increasing the equilibrium pH of the aqueous phase; however, at extremely high and low pH ranges, distribution coefficient remained unchanged with pH. Pure Aliquat 336 was found to provide higher extractions than Alamine 336 at all pH values, when used alone without any diluent. However, when used with diluents, kerosene and 2-octanol, TOA provides higher extraction than Aliquat 336 in these diluents.

## 7. Effect of Salt and Substrate

Lowering of extraction by NaCl and no effect on extraction by lactose was found in extraction of lactic acid. Effect of pH (2.0 and 2.5) and inorganic salts ( $\text{Na}_2\text{SO}_4$  and NaCl) on extraction of different carboxylic acids (acetic acid, propionic acid, butyric acid, valeric acid and caproic acid) using TBP was studied.

## 8. Water Coextraction

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 10% with corresponding decreases in the aqueous phase when Aliquat 336 was used.<sup>62</sup> On the other hand, Yang et al. observed no significant volume change when Alamine 336 was used. 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. 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 backextraction, and therefore it has little effect upon process viability.

## 9. 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. These methods were compared and 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.

## 10. 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.

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