The key features and properties of reactive extraction

Science, Chemistry

Introduction:

Any chemical process is the combination of some essential unit operations, and the important one is a chemical reaction and mass transfer. The rate of mass transfer influences many vital aspects of a process like the success rate of how good a process is to implement on a large scale. The simplicity and novelty of reaction and separation as combined operation also make it economically alluring.

In recent years, reactive extraction processes are gaining a lot of importance in response to extreme economic pressure posed by industries as the result of the emergence of new methods 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 sinks to enhance reaction rates, conversions, and selectivity. Since most of the chemical processes are equilibrium driven, removal of the 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 the 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 a reduction in equipment size, elimination of recyclable streams and reductions in utility costs. Reactive separators also lead to safer equipment’s 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 a single bit. We also get a higher distribution coefficient with suitable choice of extractant through reactive extraction which helps in the effective recovery of carboxylic acids. 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 of reactive extraction with fermentation can be summarized as:

Increased reactor productivity.

Ease in reactor pH control without the 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 minimize downstream handling load and recovery cost.

There is a lot of work done in the last few years for the efficient recovery of carboxylic acid from wastewater solution and fermentation broths. Reactive extraction is a clean process, and the extractant used in the process is also recovered easily and reused. There is a lot of scope of reactive extraction because the process is simple and economical. The main problem in the implementation of reactive extraction is the correct choice of the extractant. After resolving this issue, the further process is relatively simple. The highly selective, efficient, economical, clean and straightforward operation of reactive extraction has initiated us to study further for the recovery of carboxylic acid from aqueous solutions and model solutions having a close resemblance to the fermentation broth.

PROCESS PARAMETERS

Physical Extraction

This method does not involve a chemical reaction. Generally, In physical extraction, the solute is extracted into a non reacting, and inert hydrocarbons and substituted hydrocarbons and the process 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 the aqueous phase and

(b) Dimerization in the hydrocarbon phase.

Chemical Extraction

Separation comprising reactive extraction, i. e., extraction with reversible chemical complexation are achieving vast importance owing to the high capacities and high selectivity for dilute solutes. In these processes, the mixture is communicated with a second phase containing a complexing agent that reacts reversibly with the solute of importance. The separation by reactive extraction tends to be more suitable for cases of relatively small solute concentration. In addition to high capacity at small solute concentration, the other critical potential benefit 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 specific solutes from complex mixtures. Reactive extraction employing specific extractant can also give less coextraction of water than separations with more conventional solvents. Different organophosphorus compounds like tri-n-butyl phosphate (TBP), tri-n- octyl phosphine oxide (TOPO) have provided a higher distribution coefficient when utilizing as extractants. Aliphatic amines have been found to be further effective and less expensive than the organophosphorus 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.

Effect of Temperature

The temperature effect is an essential subject of study in the reactive extraction process in view of operating temperature and back extraction/regeneration step. Usually, industrial-scale fermenter for carboxylic acids production runs between the temperature range of 300 to

313 K, so the excellent choice of extractant is always that can operate efficiently under this temperature range. Generally, with the increase in temperature the rate of extraction decrease because the process is exothermic. However, the reduction in extraction efficiency depends upon the extracting medium.

Kanti Kumar Athankar et al., studied reactive extraction of Glutaric acid with TBP in ethyl acetate and hexanol to explain the effect of temperature. Extraction was carried out at a different temperature range of 308-338 K. The reactive extraction results were presented regarding overall distribution coefficients (KD), the degree of extraction (η %), loading ratio (φ), and equilibrium complexation constants (KE). The results showed that an increase in temperature reduced distribution coefficients and extraction efficiency for both diluents used in the organic phase. Moreover, thermodynamic function viz enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) were calculated. The process is exothermic as the extraction results in a negative value of enthalpy.

Hasan Uslu et al., Temperature effect and initial acid concentration are important factors to study in the reactive extraction process. He studied and compared the effect of both temperature and initial acid concentration on the extraction of levulinic acid and malic acid. Extractions have been carried out at the different temperatures 298 K, 318 K, and 328 K. The results showed that an increase in temperature reduced distribution coefficients for all solvents used as the organic phase. He also calculated the enthalpy and entropy of reaction. Reactive extraction of these acids by amines resulted in negative values of enthalpy. Thus, the reactive extraction process is an exothermic process. He also studies the different initial concentrations of both acids have in the range of 0. 08 wt. % to 0. 15 wt. %. For all solvents in the organic phase, the distribution coefficients decreased with increasing initial concentration of acids.

Effect of pH

In the fermentation process, as the reaction proceeds concentration of the acid increase which negatively effects the micro-organism responsible for fermentation. As a resulting pH of medium decrease and inhibits the product formation. So it is necessary to add a neutralizing agent and maintain the required condition for fermentation. Another way is for the continual removal of product acid produced. That is the reason behind the removal of the product in situ and thus enhance the performance and productivity of the bioreactor. The distribution coefficient remains unchanged at extremely high and low pH, however, the distribution coefficient decrease with increasing the equilibrium pH of the aqueous phase in the intermediate pH range. In the case of extraction equilibria, pH change with the progress of extraction of itaconic acid. The range of pH in the extraction experiment was 2. 45 to 3. 43. Equilibrium pH is always higher than initial pH (2. 98 to 3. 32).

Required properties of solute and solvents

Addition of solvent in the aqueous itaconic acid solution leads to form two phases where some itaconic acid transfers from the aqueous phase to organic phase. The extent of transfer depends on both the solute and solvent.

Properties of solute

To use reactive extraction process for removal of solute certain desirable properties of it are recommended so that complexation reactions are favored, such as:

1. Lewis acid or Lewis base functional groups: The solute of interest should have one or more functional group that can help to form a moderately strong complexation. Since most complexation processes involve the interaction of Lewis acid with Lewis bases, acidic and basic functional groups are useful.
2. Low solute concentration: Since complexing agents provide unusually high equilibrium distribution for low solute concentration and tend to saturate stoichiometrically at high concentration, complexation is must attractive for relatively dilute aqueous solutions.
3. Low activity coefficients in water: The complexation separation processes are useful for hydrophilic solutes so that phases should separate perfectly.
4. Low solute volatility: Solutes that are less volatile than water are good candidates for separation by complexation, so that while the time of extraction solute cannot be violated

Properties of solvents

In the process of extraction, separation is obtained by the partition of the solute between two immiscible phases. The two phases should have sufficient density difference and minimum surface tension so that there is a definite phase separation obtained once the phases are made to settle. The affinity of solvent to water should be very less, and hence nonpolar solvents are preferred in the extraction process. The solute should have high solubility in the solvent. The solute should be easily recoverable from the solvent while the conventional separation process is used.

Properties of complex

In the method of reactive extraction, the reaction between the solute and extractant is the prime step. If the reaction produces a product with high bond energy, then it will be difficult to obtain the solute back by some means of reversing the reaction economically. So the choice of the extract is crucial here. It should form a complex with the solute where the bond energy of the complex is low, less the 50kJ/mol and it is same as ordinary associations by van der-Waals forces. A simple complexation reaction is shown below:

Solute + n. extractant « complex

Which is described by an equilibrium constant

K= ([complex])/([solute][extractant]n)

The desirability of the process lies in the removal of solute from relatively low solute concentration since it could lead to higher complexation constant (KE). Another benefit of these complexation reactions is that these are selective for a particular group of solute, and hence, these processes have the potential to separate only specific solutes from complex mixtures. The complexing reaction should have sufficiently fast kinetic in both directions so that equipment size should not become prohibitively large.

Extraction by amine

Recovery of carboxylic acids from aqueous solutions and fermentation broths, where it is present in dilute form (<10%), is always of interest to researchers. Reactive extraction depends on some parameters like types of complexes, distribution coefficient, complexation-equilibrium constant, loading ratio, properties of the solvent, etc. The amine-based extractants and phosphorous based oxygen extractant are the most suitable. Aliphatic amines are efficient and comparatively low-cost extractants that have been used effectively to extract itaconic acid.

Toxicity

Fermentation is overall a proper process however it suffers from the toxicity problem due to the presence of organic solvent and extractant to the microorganism and is a critical issue in extractive fermentation. The degree of toxicity varies according to a combination of microorganism and extractant solution used. The physical microbial and biochemical effects on the catalytic activity of the micro-organisms is affected by the presence of organic solvents in the process. Direct contact of the organism with the extractants should be avoided so that it can substantially reduce the toxic effect. Two type 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 (waste cooking oil, soya bean oil, etc.) can significantly reduce the toxicity. The use of a natural solvent is an excellent choice as it is environmentally friendly and give the extraction in the range of 90% and also do not have any harmful consequences.

Water Coextraction

The concentration and properties of the acid decide the mixing between an aqueous solution and a given solvent at a particular temperature. Mixing between the solvent and aqueous phase cause visible volume change, with weak organic acids. The amount of the volume change is associated with the coextraction of water along with that of the acid. The volume of organic phase increased by about 10% with corresponding decreases in the aqueous phase when Aliquat 336 was used. 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 a diluent, a third emulsion phase was also witnessed 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, the 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.

Extraction equilibrium:

In reactive extraction, the solute reacts with the amine in the organic phase, and the consequential acid-amine complexes are thought to be stabilized due to the hydrogen bonding with the solvent. Because of its hydrophobic nature, the complex formation enriches the extraction of solute from aqueous to the organic phase. The extraction of a carboxylic acid with an amine can be defined by the set of reactions involving the formation of complexes with n acid molecules and one amine molecule

The ionization of carboxylic acid in the aqueous solution.

$HAaq + H_2O \leftrightarrow H_3O^+ + A\text{-}aq$

The partition of undissociated acid between the two phases.

$HAaq \leftrightarrow HAorg$

The complex formation between carboxylic acid and the tertiary amine in the organic phase during reactive extraction

$HAorg + TA\ org \leftrightarrow (HA - TA)\ org$

Where HA is the undissociated carboxylic acid, and TA is the tertiary amine.

According to the ammonium salt is formed by the tertiary amine and undissociated carboxylic acid in the organic phase.

The extraction process is examined using the degree of extraction and distribution coefficient. The distribution coefficient, KD, is evaluated using Eq. 1.

$KD = Corg/Caqu$ ……. (1)

Where, Corg is the total concentration of carboxylic acid in the organic phase and is the Caqu total acid concentration (dissociated and un-dissociated) in the aqueous phase at equilibrium.

The degree of extraction is defined as the ratio of acid concentration in the extracted phase to the initial acid concentration in aqueous solution by assuming no change in volume at equilibrium as given by Equation 2.

$E= Kd/((1+Kd)) *100$ ……. (2)

The extraction equilibrium constant KEn and the number of molecules of extractant are computed by applying the law of mass action that is the ratio between concentrations of reactant molecules and the concentration of product species, according to the general equation of interaction between the extractant and, the extracted species is given by Equation 3

$KEn=([HA\text{-}TA]org)/([TA]org*[HA]n.\ org)$ ….. (3)

KEn is expected to be depending on the properties of the acid and the solvation efficiency of diluent used.

The extent to which the organic phase (extractant and solvent) may be loaded with acid is expressed by the loading ratio, Z (ratio of total acid concentration in the organic phase to the total extractant concentration) as given by Equation 4.

$Z=([HA]org)/([TA]org)$ (4)

The value of Z depends on the extractability of the acid (strength of the acid-base interaction) and its aqueous concentration. The stoichiometry of the complete extraction equilibrium is determined by the loading ratio in the organic phase (Z). If acid does not immensely concentrate the organic phase, i. e., at very low loading ratios (Z < 0. 5), 1: 1 complex of acid and extractant is formed. A plot of Z/ (1-Z) versus [HA] yields a straight line passing through origin with a slope of complexation constant (KE1), for higher loading ratios at least (Z> 0. 5) 2: 1 complex of acid and extractants is formed and plot between Z/ (2-Z) versus [HA]2 produces a straight line passing through origin with a slope KE2.