REVIEW OF REACTIVE EXTRACTION PROCESS FOR RECOVERY OF ACETIC ACID

Abstract

Acetic acid is one of the carboxylic acids which has its importance in industries such as pharmaceutical, food and other industries. The emerging chemical process is looking for technologies that can be used for product separation. Physical Extraction & Reactive extraction is one of the prominent methods of separation. It also provides new scope for extraction which is relatively an economic option. The major advantage is that it can be used for dilute solutions. This technique is used in wastewater treatment and fermentation broth for extracting valuable chemicals from it. This paper aims to present the review of the Physical Extraction & Reactive extraction of acetic acid of the previous works carried out by the researchers. Our efforts have been made to summarize parameters like extraction efficiency, distribution coefficients, the solvent used, and their broad outcome by previous researchers, and to present here as a summary. It was observed that reactive extraction was relatively effective, and it was also emphasized from our study that the selection of suitable solvent, extractant, or diluent stipulates higher capacity and selectivity of acetic acid. So, the review of the physical and reactive extraction will provide one-time insight of the parameters studied by previous researchers and a brief outcome, thereby becoming a reference for the researchers working in the extraction area.

Keywords: Physical Extraction; Reactive extraction; Acetic Acid; Fermentation; Distribution Coefficient; Extraction Efficiency.

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I. INTRODUCTION

Liquid-liquid extraction involves the separation of the desired component in a mixture of liquid based on solubility. In this, we bring the mixture in contact with an immiscible/partially miscible solvent to make it a two-phase mixture. The desired component is miscible in the solvent whereas the other component in the mixture is immiscible. The concentration in which the desired component is high is known as the extract phase(organic) whereas the other immiscible phase is raffinate (aqueous phase). The solubility drives the process and its equilibrium dependent. For reactive extraction, the extractant (in diluent) forms an acetic acid complex, thereby enhancing the reaction rate. For the separation processes previously the processes such as distillation were used. These became energy-consuming and economically cost effective. The reactive or physical extraction is a relatively less energy-consuming process that is done based on the solubility of the component which we want to separate and making it a good alternative for separation by phases and thereby gaining popularity. The reviews published so far are concerned with carboxylic acids, but in this, we made our attempts to focus on acetic acid specifically. The extraction processes are selectivity largely and are dependent on the selection of extractant and diluent (Reactive) or the solvent (Physical). Acetic acid is readily available, cheap, and have used such as in making of vinegar, organic solvent, pharmaceutical industry, etc, which has made researchers focus on developing the extraction principles on this acid. A lot of literature came in and we made our efforts to summarize these and to present very briefly, what has been done by previously published research on this acid until date so that this will become a reference for others who are pursuing research on extraction. We tried to present parameters studied, the solvent used, and its outcome by the researchers. Efforts were also made to present the kinetic studies.

1. **Desirable properties of solvent and the physical principle:** In physical extraction the aqueous solution is added and is mixed with the solvent. The acetic acid gets transferred to the solvent added due to its high solubility. The two phases are organic (solvent + Acetic Acid) and aqueous (water + acetic acid) that are immiscible, can be separated after settling and the concentration of acetic acid in the aqueous phase will be reduced and concentration in the organic phase will be increased. For reactive extraction, the extractant and diluent are mixed to form a solvent. In that case, the acetic acid forms a complex with the extractant which is soluble in the diluent. The above mechanism depends on solvent properties. Ideally the solvent should possess a density variation with aqueous phase. Minimum surface tension is desired. The solubility of acetic acid should be high in solvent compared to aqueous phase. After extraction acetic acid should also be easily recoverable from the organic phase. The interaction affinity with aqueous phase water should be less and if we take nonpolar solvents the separation will be better, because water is a polar solvent.

2. **Extraction by Amine:** The extraction of carboxylic acid using Amine has fascinated researchers for a long time.**[1][2][3]** and **[4]**. For reactive extraction, amine-based extractants are preferred due to high distribution coefficients, easy complex formation, high loading ratio, etc. Aliphatic amines were relatively low cost and can be used for extraction **[5]** efficiently. The amines classification based on its properties are primary, secondary, tertiary, and quaternary. The primary amines are soluble in water. The

secondary and quaternary amines are quite toxic. All of them have a high distribution coefficient value.

3. **Dependency of Distribution Coefficient (K_D):** It depends on the following:

- Nature of the diluents used
- Amine concentration in diluent
- The chain length increases the polarity and basicity (Carbon Number)

The viscosity and density of diluents are key factors to achieve desired composition in which amine extractant is present, thereby the composition effects the equilibrium.

4. **Properties of Complex: The** acetic acid reacts with the extractant present in the diluent to form a complex which is soluble in diluent phase. So, if it forms a strong bond, it will be difficult again to separate the acetic acid from the complex. So, the complex should have lower bond energy. The complex, acetic acid and extractant will be in equilibrium as shown:

$$\text{Acetic Acid + n.Extract} \longleftrightarrow \text{Complex}$$

The equilibrium constant is given by the following equation: $K_D = \frac{[\text{COMPLEX}]}{[\text{Solute}][\text{Extract}]^n}$

5. **Distribution of Acetic Acid at Equilibrium state**: The concentration of acetic acid is measured in organic and aqueous phase. The ratio of acetic acid in organic to aqueous phase is called as distributive coefficient. It is the ability of solvent for extraction. Mathematically it is epitomised as:

$$K_D = \frac{[A]\text{Org}}{[A]\text{Aq}}$$

The benefits of this kind of separation are:

- Operative at high concentration (fermentation extraction).
- Re-extraction of acid and reuse of solvent can be done.
- Enhanced control of pH in the bioreactor.
- Recovery of acid enhances along with product purity.

The three major types of extractants which were categorized by Kertes and King **[10]** are:

- Carbon bonded oxygen.
- Phosphorous bonded oxygen.
- High molecular weight aliphatic amines.

The first two types can extract acid molecules by solvation due to their non-reactive nature. The difference between first two groups is the strength of coordinate bond. The bond is slightly stronger in phosphorous bonded oxygen bearing extractants rather than carbon bonded oxygen bearing extractants. Aliphatic amines of third type can react and by proton transfer can form complex of acid amine. This leads to significant increase in distribution coefficient of carboxylic acids.

Diluents can be generally classified in two groups **[11]**:

- **Active Diluents:** They are polar in nature due to presence of various functional groups which includes chlorinated hydrocarbons, ketones, alcohols, and halogenates aromatic solvents.
- **Inactive Diluents:** They are non-polar in nature and provide very low distribution of acids. This has diluents like benzene, alkanes, alkyl aromatics.

The reactive extraction depends on complexes formed, properties of solvent, temperature, and pH. The tenacity of any method is to achieve a higher distribution coefficient with higher selectivity.There are two stages in extractive separation. First is formation of complex (Acetic acid + extractant). In second stage the acid is stripped off again to obtain pure acetic acid and recover the extractant-diluent (reactive) or solvent(physical).

The two methodologies for regeneration described by Tamada and King **[11]** are:

- Temperature swing
- Diluent swing

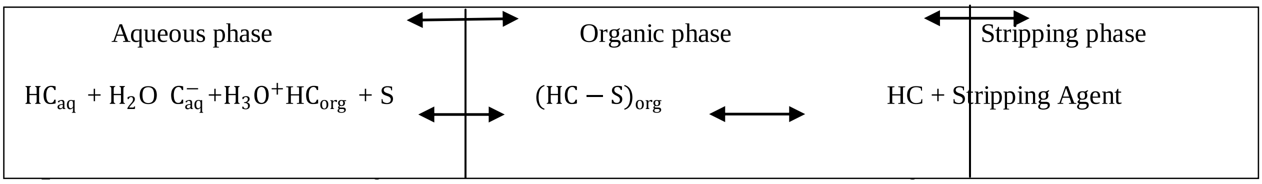

Figure 1: Representation of Physical & Reactive extraction process

Many researchers **[32] [33] and [34]** have tried to optimize the Physical & Reaction.

The following parameters have been considered to predict the kinetic model of extraction:

- Acetic acid concentration (aqueous phase)
- Solvent Type
- Relative amount of solvent
- Extractant used (bond nature)
- Toxicity of solvent phase for micro-organism

6. **Kinetic Studies on Physical & Reactive Extraction of Carboxylic Acids:** For the design of reactive extraction unit, the kinetic studies play a vital role. The kinetic studies were performed on physical & reactive extraction of various carboxylic acids using cylindrical stirring vessel (Lewis's type) which is highly agitated **[12],** hydrophobic microporous membrane stirred cell **[13]** and others. The researchers using kinetic model investigated acid-amine **[14]** complex formation mechanism. The theoretical models were also done along with experimental reaction. The experiments helped to estimate some intrinsic parameters (example rate constants- forward and backward). It was observed that not only composition (organic and aqueous) effects the rate, but some parameters also like- interfacial area, phase volume ratio, agitation speed, hydrodynamic parameters such

as viscosity effects the mass transfer rate. In a study by Jun et al. **[15]** in 2007, it was emphasised that pH and contamination in aqueous phase effect the rate of reaction. It was observed that if pKa is less then pH, the extraction efficiency decreased because of increased disassociation. It was suggested to keep pKa should be higher than pH for effective separation in fermentation broth.

7. **Kinetic Model:** In 1984 Doraiswamy and Sharma **[13]** studied extraction mechanism in a stirred cell -to study the rate of reaction. The reactive extraction regimes were classified as very slow, slow, fast, very fast and instantaneous. This classification was based on film renewal theories.

    - **Reactive extraction setup:** It includes the CSTR and bioreactors for kinetics and the apparatus in which it is done is the Craig Commercial Extractor It is a series of tubes arranged in such a way that the organic/ extractant phase will be transferred to the next one simultaneously and cycle is repeated. The mechanical forces and density difference becomes the principle of operation for this extractor. The stages of extraction are shown in the figure.

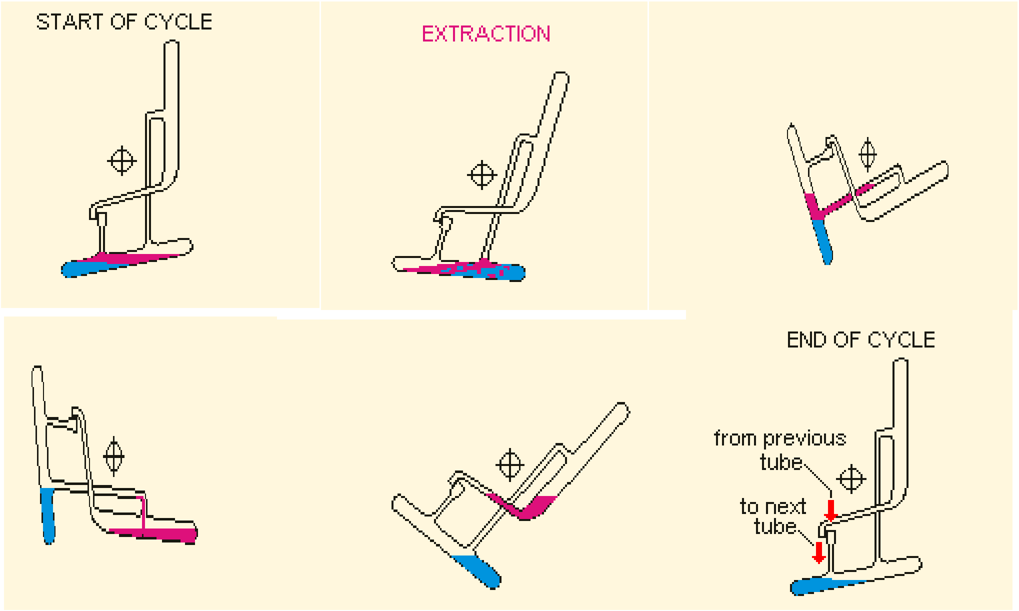

Figure 2: The stages of reactive extraction

Table 1: Kinetic studies of different Carboxylic acids

Sl.No	Carboxylic Acid	Extractant	Diluent	Parameters	Findings	References

1	Benzylpenicillin	Ambertile LA-2	Kerosene	Rotation speed, area of interface of the aqueous and extractant phase, aqueous phase pH concentration penicillin G.	The mass transfer rate constants for forward = 1.64L mol^{-2} s^{-1} and backward = 6.56 × 10 L s^{-1} respectively.	[16]
2	Citric	TOA	iso decanal and paraffins	Concentration of acid, amine, and speed of agitation.	Reaction kinetics were evaluated by proposing elementary kinetic model.	[17]
3	Tartaric	TIOA	iso decanal and kersoene	Concentration of acid, amine and iso decanal.	Modified Langmuir isotherm was proposed, and parameters were inferred by elementary kinetic model.	[18]
4	Lactic	Aliquat 336	Oleyl alcohol	Initial lactate and extractant concentrations in extraction, initial chloride. The complex concentration of lactate-extractant was studied while stripping.	Kinetics was emphasized for stripping and extraction. The RDS (rate determining step) was diffusion in organic film.	[19]
5	Phenyl acetic	Alamine 336	Kerosene and MIBK	Phases volume ratio, concentration of the complex along with acid and amine. Agitation speed also.	Intrinsic kinetics were examined findings were 0 order reaction in alamine 336 and order 1(rate constant 0.9/s) for acid.	[20]
6	Benzylpenicillin	Ambertile LA-2	Kerosene	Concentartion of acid- amine also pH	To investigate the rate step Dankwert and biot numbers were used. (Dispersed - LLE system) LLE- Liquid Liquid Extraction.	[21]

The Stages are shown in clockwise direction for a particular stage. The stage can be repeated for simultaneous accurate extraction. The lighter extract (mobile phase) is shown in red colour (Acetic acid + solvent in physical extraction or acetic acid + extractant in diluent for reactive extraction). The heavier phase is shown with blue colour. At beginning the solvent (physical) or extractant + diluent (Reactive) is added to the aqueous solution. They are thoroughly mixed and then allowed to settle and separate. Then the lighter phase is separated by orientation of tube shown in figure. The lighter phase goes to next stage and the process cycle is repeated. This can be used in commercial as well as lab scale. One unit can be repeated for different stages thus making it like a conatus extractor.

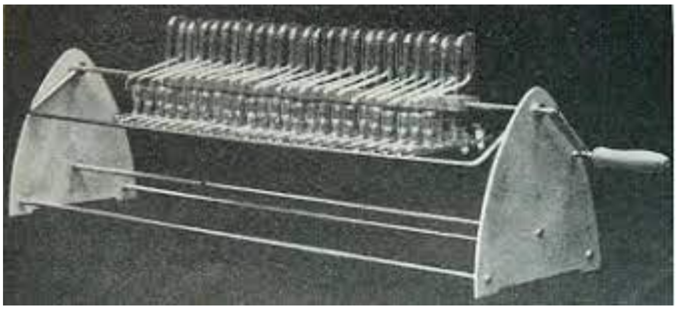

Figure 3: The extractor with simultaneous stages

- **Material balance of Extractor and overview of our idea**

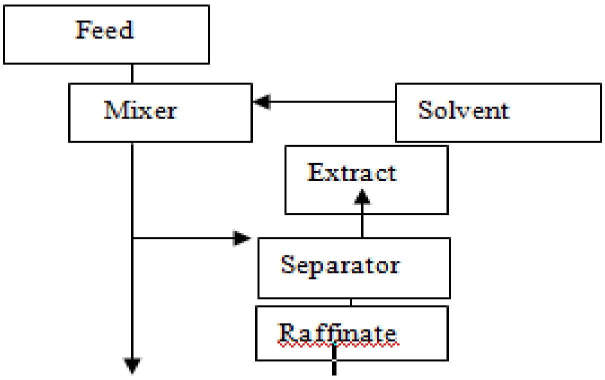

Figure 4: The overview of extractor

Nomenclature:
Moles/ Molar flow rate:
Feed –F
Raffinate-R
Solvent –S
Extract-E
Mole fraction/ Weight Fraction of desired component:
Feed-X_f
Raffinte-X_r
Solvent-X_s
Extract-X_e
Overall material balance:
$F+S=E+R$
Component Balance:

$F.X_f + S.X_s = E.X_e + R.X_r$
Let F+S=M (M indicates mixture)
$M.X_m = F.X_f + S.$ Xs (where X_m is the intial mole fraction after agitation of liquid).
Now Let The components of the mixture be A, B, C. Let C be the desired component. And B be the organic solvent and A be the feed solvent in which C is present initially.
A +C are miscible.
B+C are miscible.
A+B are partially miscible (solubility is very less)
This becomes the driving for extraction.
NOTE: A is known as carrier. Carrier and solvent have some solubility in each other but is very less. Let X_A, X_B, &$X_C$be the mole fractions of A, B, C in a respective phase.
$X_A+X_B+X_C=1$

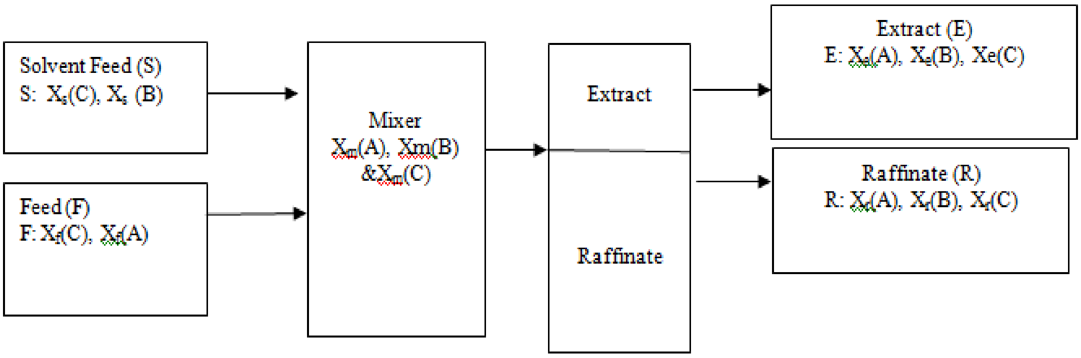

Figure 4: The block diagram of extractor

We find the mole fractions X_A, X_B, &X_C in extract and raffinate phase respectively using titrative methods and generate the ternary diagram. Here degrees of freedom(F)= 2 - NO of phases(pi) + NO of components(N) F=2-2+3=3; This says that it has 3 degrees of freedom, so we maintain T, P constant and vary concentration to get equilibrium solubility. We vary x1(mole fraction of mixed feed and solvent), by varying X_f.

Table 2: Different extractants and diluents used for recovery of carboxylic acids.

Sl. NO	**Carboxylic Acid Type**	**Extractants used**	**Diluents (Physical & Reactive)**	**Parameters Studied**	**Findings**	**Gaps Identified**	**References**
1.	Acetic Acid	Tri –n-octylamine (TOA) (Reactive) Supercritical CO2 (Physical)	Supercritical CO_2	Extraction Efficiency, Temperature and Pressure effects	Efficiency Is High for Reactive Extraction than physical extraction using only $scCO_2$.	Equipment and procedure are very expensive.	[23]
2.	Acetic Acid	Alamine 308 (triisooctylamine) (Reactive) 1-Octanol (Physical)	Benzyl Alcohol, Alcohol, Chloroform, Methylisobutyl Ketone, 1,2 Dichoro Ethane, Xylene	Distribution, Extraction Equilibria, Other parameters at 298K	Highest efficiency is observed for cyclic alcohol/amine. This is done using solvation energy relation (SERAS) and Langmuir equilibrium model and experimental results were found to be close to these models. Distribution is affected by acid structure.	Amine is not good for health, very difficult to handle. Expensive Not a green process.	[24]
3.	Acetic Acid	Alamine 336 (triisooctylamine) (Reactive) Xylene, Toulene, 1- Octanol, 1-decanol (Physical)	Xylene, 1 Octanol	Solvent modification effect on physical and Reactive extraction. Temperature, pH, pressure effects.	Polar modification of solvents increases the recovery efficiency. Xylene (more polar) was better compared to hexane and toluene. Efficiency is also improved by increasing amine concentration. Increase in pH and Temperature decreased KD.	Amine is not good for health, very difficult to handle. Expensive Not a green process.	[25]
4.	Acetic Acid	Tributyal phosphate	Soyabean oil	Shaking time, extraction	Influential parameters of TBP (extractant) were studied and	Phosphate is explosive and	[26]

		(Reactive)		efficiency, optimization, equilibrium studies, temperature studies	reported. Toxicity is reduced. 50% TBP in oil was best for acid recovery.	handling and storage is difficult	
5	Acetic Acid	Tri-n-octylamine (Reactive)	2-ethyl hexanol, 1-octanol, n decane,MIBK,Chloroform, dichloromethane, toluene.	Reactive Pyrolysis oil by TOA is splitted to carry out extraction.	Acid recoveries of (60 ml/min) 51% and 71% were obtained using single stage and two stage cascade contactors at 100HZ. 2 ethyl hexanol is preffered diluents for TOA. (86% efficiency using 40wt % TOA at room temperature).	Amine is not good for health, very difficult to handle. Expensive Not a green process.	[27]
6.	Acetic Acid	Tri-n-octylamine (TOA), (Physical & Reactive) tri-n-octylphosphine oxide (TOPO), (Reactive) tri-n-alkyalphosphine oxide (TAPO) (physical) Ethyl ethanoate (physical)	Alkane (for TOPO), 1-octanol (for TOA)	Observations are made for extraction from fermentation broth by various solvents (to purify ethanol). Done at 298K, with 20.0/g acitic acid 5/g ethanol in broth.	Higher solvent ratio decreased extraction yield. Yield was higher for (TAPO). Lowest was for TOPO. ratio of organic to aqueous was phase is 4:1 respectively., 97% and 92.4% acetic acid can be extracted (extraction by TOPO and TAPO in a single batch) .	Fermentation process is time taking. Yield is not very high. Concentration obtained is low and difficult to extract. Amine is not good for health, very difficult to handle. Expensive Not a green process.	[28]

7.	Acetic Acid	Methyl Isobutyl Ketone (MIBK) (physical) Ethyl acetate (physical) Blend Of both ethyl acetate and MIBK (physical)	-	Combination of Mixed solvent were used for extraction along with different feed concentrations have been studied. and The distribution coefficient is found, and ternary diagram is generated.	The experimental results obtained and the simulation results using RMSD (root mean square deviation, GECEOS and PSRV models using HYSIS software are used to find distribution coefficients. Both are compared and best suited model is duel solvent model with higher concentration of acetic acid in feed.	The real experimental model is not verified. Only simulated study is given. Many real parameters should be considered in real situation.	[29]
8.	Acetic Acid	Ethyl Acetate (Physical extraction from aqueous solution)	-	Extraction using ethyl acetate with and without sonication is done. The correlation between parameters such as mix time, composition of aqueous phase, and aqueous phase to solvent ratio has been investigated.	Increase in solvent to feed ratio improved performance. When solvent to aqueous ratio is increased by 8 times, the amount extracted was doubled. Sonication was effective.	The separation is not very high. Recovery is difficult. Temperature and pressure changes on process are not studied.	[30]
9.	Acetic Acid	Butyl Butyrate, Benzene, di Isopropyl ether (DIPE), Methyl iso butyl ketone	-	Selection of solvents for extraction was investigated. Cloud point is	Order of selectivity of solvents was found to be ethyl acetate, MIBK, DIPE, Benzene, Butyl Butyrate respectively from higher to	The process is not green process. The solvents used are harmful. They are costly also.	[31]

		(MIBK), Ethyl Acetate (All for physical extraction from aqueous solution)		found to generate ternary diagrams.	lower.		
10.	Acetic Acid	Ethyl Acetate (Physical Extraction from aqueous solution)	-	Tie line and ternary diagram are obtained for the system at room temperature.	The reported tie line and binary curves are shown. Plat point is found for water, acetic acid and ethyl acetate. This experiment is done by addition of acid/solvent till turbidity appears and separate layer is resulted	The separation is less compared to Physical & Reactive extraction	[32]
11.	Carboxylic acids	Tertiary Amines (Physical & Reactive)	-	Theory for equilibrium studies and theory on effect of parameter such as solvent, pH is discussed.	Reactive extraction is most efficient compared to physical. pH limitations effect the separation. Nontoxic solvents are preferred.	Amine is not good for health, very difficult to handle. Expensive Not a green process.	[33]
12.	Carboxylic Acids	Tri-n-octylamine (TOA), tri-n-octylphosphine oxide (TOPO), Aliquait 336, tri-n-(octyl-decyl)-amine, aliphatic amines. (for Reactive extraction)	Ethers (for Acetic Acid)	Theory is discussed for novel separation processes.	Reviewed to all other methods of separation (distillation, membrane separation, anion exchange, ultra-filtration, etc) Reactive extraction are found to be environmentally friendly as well as safe with good efficiency. Alipahtic amines and organophosphoric derivatives are found to be most efficient with reduced energy.	Amine is not good for health, very difficult to handle. Expensive Not a green process. Octyl amine is very heavy in Molecular weight.	[34]
13.	Acetic Acid	Tri octyl amine (TOA)	DCM, butyl acetate,	Composition of organic phase	were controlled by polarity of the solvent used. The TOA	Amine is not good for health, very	[35]

		(Reactive)	heptanes, and 1-octanol	and its pH.	compound and interfacial acid formed structures were studied with acetic acid.	difficult to handle. Expensive Not a green process. Octyl amine is very heavy	
14	Acetic, propionic, butyric and valeric	Tri butyal phosphate (TBP) (Reactive)	Cyclohexane, sulfonated kerosene, and 1-octanol	Equilibrium time, temperature and ratio of its phases.	Conditions of extraction and Stripping was found.	TBP is explosive. Needs to be handled carefully. It is not green solvent. Not safe to handle.	[36]
15	Acetic, lactic, succinic, malonic, fumaric, and maleic	Tri-alkyl amine (Alamine 336) (Reactive)	Methyl isobutyl ketone (MIBK), n-heptane, dichloromethane (DCM), and nitrobenzene	The effect on interaction of diluent and complex were studied.	Equilibrium constants, partition coefficient and dimerization constant was determined.	Amine is not good for health, very difficult to handle. Expensive Not a green process.	[37]
16	Carboxylic Acids	Tri-iso-octyl amine (TIOA) (Reactive)	1-octanol and heptane	Effects of modifier and type of acid.	The mechanism of extraction was proposed by considering its types.	Amine is not good for health, very difficult to handle. Expensive Not a green process. Octyl amine is very heavy	[38]
17	Carboxylic Acids	Tri-alkyl phosphine oxide (TRPO) (Reactive)	Kerosene	Aqueous and organic phase compositions	Equilibrium model was established.	TRPO is explosive. Needs to be handled carefully. It is not green solvent. Not safe to handle.	[39]
18	Carboxylic Acids	Tri Butyl Phosphate (TBP) (Reactive)	Do-decane	pH and initial acid concentration	Mechanism of di-carboxylic acids were proposed.	TBP is explosive. Needs to be handled carefully. It is not green	[40]

						solvent. Not safe to handle.	
19	Carboxylic Acids	Tri Butyl Phosphate (TBP) (Reactive)	cyclohexane, sulfonated kerosene, and 1-octanol	Equilibrium time, temperature and phase ratio	The adverse conditions of extraction and stripping were found.	TBP is explosive. Needs to be handled carefully. It is not green solvent. Not safe to handle.	[41]
20	Acetic Acid	Tri-iso-octylamine (Reactive)	Toluene, Petroleum ether, N- Hexane	Distribution coefficients in solvents are determined	The Kd (distribution coefficient) for petroleum-0.79, toluene-1.29 and ether-0.6 respectively. Extractant used was tri-iso-octylamine(40%) in organic solvent. It has shown the highest kd (distribution coefficient) for n-hexane-2.63, petroleum-2.70, toluene-3.65. It was found to be excellent for extraction.	Amine is not good for health, very difficult to handle. Expensive Not a green process. Octyl amine is very heavy.	[42]

II. CONCLUSIONS

It was observed that when reactive extraction was compared to physical extraction, reactive extraction was more effective [23][24][25]. For the reactive extraction most commonly, amine based [40][41][42] extractants were used. For physical extraction, the polar solvents [35] were found to be efficient than nonpolar one. Enhanced recovery in reactive was found when there was the use of polar solvent as diluent [35], and one of the drawbacks was again in the recovery, because in reactive extraction acetic acid complex was having high bond energy and was becoming a challenge to separate it after extraction. Whereas in physical extraction, it can be relatively separated easily after extraction. Moreover, some amine solvents are toxic in nature and not eco-friendly in nature [40][41][42]. So, taking all these parameters into consideration, if we want to separate acetic acid reactive extraction is preferred, but if recovery is needed then, one must select the optimum solvent depending on conditions. So further research can be done on it and moreover the use of eco-friendly green solvents (such as supercritical CO_2) [23] can be carried out to optimize the selectivity and recovery.

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