Separation Process Of Citric Acid with Tertiary Amines/Diluents in Supercritical CO$_2$

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Reactive extraction of citric acid was investigated at atmospheric and supercritical conditions. The most suitable diluent and amine from among the tertiary amines and eight different diluents were determined at atmospheric conditions. The distribution coefficient values obtained with Hostarex A 327 were higher than those of Alamine 336. The selected amine (Hostarex A327) and the diluent (Oleyl alcohol) were used for reactive extraction of citric acid at supercritical conditions. Separation yields of citric acid were obtained in the temperature ranges of 308 to 328 K and in the pressure ranges of 80 to 180 bars in a supercritical extraction system which is continuous in terms of CO$_2$. It was found that separation yield decreased with increasing extraction pressure at all investigated temperatures. The highest separation yield (28%) was obtained at near the critical pressure. It was observed that the separation yield did not change with increasing temperature in the pressure range of 80 to 180 bars.

Key Words: Citric Acid, Reactive Extraction, Supercritical CO$_2$, Hostarex A 327, Oleyl Alcohol.

Introduction

Citric acid is the most widely used organic acid in the field of foods and beverages as an acidulant as well as in pharmaceutical and chemical products.

Demand for citric acid has increased worldwide, including in Turkey. It is generally produced by surface or submerged fungal fermentation mainly with *Aspergillus niger*. However, the highest citric acid production has been obtained with the submerged fermentation method.

Citric acid is typically purified by a firmly established process known as the method of calcium salt precipitation. Citric acid can be separated from fermentation broths by a series of precipitation and isolation reactions using Ca(OH)$_2$ and H$_2$SO$_4$. However, this process contains several batch treatments, which require large amounts of chemical reagents and a considerable amount of heat. These negative factors have directed many investigators to find new techniques to separate or purify citric acid from fermentation broths.

Recently, reactive extraction with amines and supercritical fluid extraction have been reported in the literature as a new technique. Reactive extraction has proven its applicability in the separation of fermented

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products. The reactive substance, which is added to the organic solvent, enables the phase transfer of the polar acid from the aqueous phase to the nonpolar organic phase. The application of reactive extraction for separation of organic acids based on the use of amine reactants has been investigated intensively[1−10]. Tertiary amines dissolved in organic solvents are effective. In this method, care is necessary when selecting the organic solvent. The distribution coefficient of the solute (K_D), the selectivity factor, and the polarity and toxicity of the solvent are very important factors.

Supercritical fluid extraction has a great potential as a promising and clean alternative method for the conventional recovery of organic acids. CO_2 is the most intensively used solvent due to its critical point (Pc=73 bar, Tc=304 K), non-toxic, inert and non-flammable nature, while remaining an inexpensive and environmentally acceptable substance [11]. Solubilities of organic acids in supercritical CO_2 are very low, because organic acids are polar and CO_2 is apolar. For increasing solubility, polar entrainers are added to the supercritical fluid phase, or reactants that react with acids and increase acid solubility are used.

Studies on supercritical fluid extraction of organic acids have been carried out in several directions. Some researchers have studied the solubilities of organic acids in supercritical $CO_2^{[12−17]}$. Others have investigated the separation of valeric acid from mixed dibasic acids[18] and the extraction of acetic acid from aqueous solution and fermentation broth[19] using supercritical CO_2. Some researchers have investigated the effect of the entrainer on the solubility of organic acid in supercritical $CO_2^{[20−23]}$. Others have carried out reactive extraction of organic acids with amines using supercritical $CO_2^{[24,25]}$. These researchers used lactic and acetic acid as organic acids and tri-n-hexylamine, Hostarex A 327 and Amberlite LA-2 as reactants. It was found that Amberlite LA-2 for lactic acid, and tri-n-hexylamine for acetic acid were suitable reactants. In our previous study, reactive extractions of citric acid and acetic acid were investigated by using supercritical CO_2 (T=313K and P=100 bar) with tertiary amines dissolved in a diluent. Tertiary amines such as Alamine 336 and Hostarex A 327 were used as reactants and oleyl alcohol was used as the diluent[26].

In the first phase of this study, the experiments were carried out at atmospheric conditions in order to determine the amine/diluent system that has the highest distribution coefficient for citric acid. Then the reactive extraction of citric acid was studied with the selected amine/diluent system by supercritical CO_2 at T(=308, 318, 328K) in the pressure range from 80 to 180 bars.

Experimental

Citric acid and isoamyl alcohol were obtained from Sigma Co. Alamine 336 and Hostarex A 327, commercially available tertiary amines, were supplied by Henkel Co. and Clariant Co., respectively. Benzene, toluene, oleyl alcohol, 1-octanol, 1-butanol, methyl isobutyl ketone and chloroform were purchased from Merck Co., as analytical reagent grade. Distilled water was also used in the experiments.

Extraction experiments at atmospheric conditions

These experiments were carried out in order to define the suitable amine and diluent system which has the highest distribution coefficient for citric acid. Alamine 336 and Hostarex A 327 amines and eight different diluents were used. The citric acid solution (aqueous phase) was prepared by dissolving citric acid in distilled water at a concentration of 20 g/L. Amine/diluent mixtures (organic phase) were prepared by diluting Alamine 336 and Hostarex A 327 in eight different diluents (benzene, toluene, oleyl alcohol,

1-octanol, 1-butanol, methylisobutyl ketone, isoamyl alcohol and chloroform) to obtain 15% (v/v) amine concentrations.

Reactive extraction experiments were carried out at the ratio of $V_{a.}/V_{o.} = 2/1$, in glass flasks (150 mL) at 298 K and 150 rpm using an orbital shaker (Stuart Scientific). After equilibrium between two phases was reached, organic and aqueous phases were kept in the separation funnel for 30 min and the phases were separated. Then the organic phases were centrifuged for effective separation at 5000 rpm for 30 min.

Extraction experiments at supercritical conditions

Experiments were carried out at 308, 318, 328 K in the pressure range from 80 to 180 bars at 5 mL/min CO_2 feed rate in a system continuous in terms of CO_2 for 30 minutes. A detailed description of the experimental apparatus and the experimental procedure can be found elsewhere[27,28,29].

Separation yield of citric acid was obtained using Hostarex A 327 as reactant and 1-butanol, chloroform and oleyl alcohol as diluents at supercritical conditions. First, equal volumes (25 mL) of organic phase (Hostarex A 327 (30% , v/v) + Oleyl alcohol (70% , v/v)) and aqueous phase (100 g/L citric acid solution; initial acid concentration) were mixed in the extractor (100 mL). When the temperature and the pressure of the extractor reached the desired conditions, the CO_2 feed rate was adjusted and it was passed through the extractor for 30 minutes. Then the metering valve at the end of the extractor was fully opened and the extractor pressure was decreased to atmospheric pressure. At the end of the extraction, the organic phase in the extractor (rafinate) was used for analysis of citric acid.

The concentrations of acid in the aqueous phase were determined by titration with aqueous sodium hydroxide (0.1 N). The acid concentrations in the organic phase were determined by back extracting the acid into an aqueous solution of sodium hydroxide and titrating the excess amount of sodium hydroxide with hydrochloric acid (0.1 N).

All experimental results given below are the arithmetic averages of three runs.

Results and Discussion

Experimental results at atmospheric conditions

The effect of extraction time on the distribution coefficient is shown in Figure 1. It was found that reactive extraction of citric acid was completed in nearly 30 minutes.
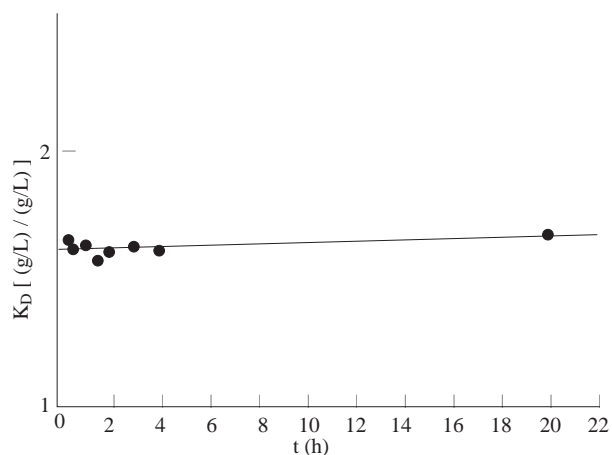
Figure 1. Effect of extraction time on the distribution coefficient of citric acid using Hostarex A 327–Oleyl alcohol

$(C_C=100$ g/L, $C_A = 30\%$, T=308 K, N=150 rpm)

The distribution coefficients for citric acid were obtained with both Alamine 336 and Hostarex A 327 using aqueous citric acid solution. In order to determine the highest distribution coefficient for citric acid eight different diluents were used. The distribution coefficients for citric acid are given in Figures 2a and b.
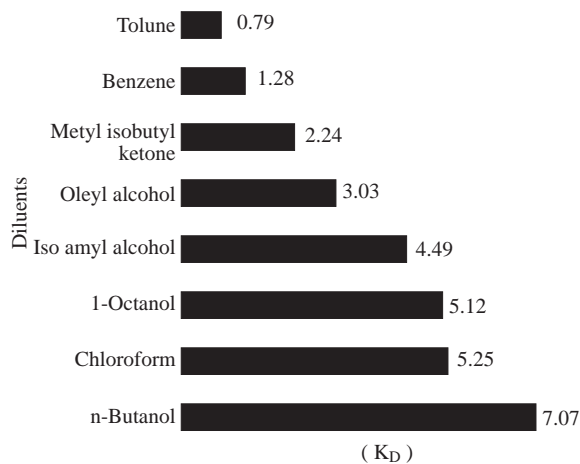

Figure 2a. Effect of diluent on the distribution coefficient for reactive extraction of aqueous citric acid solution with Hostarex A 327.

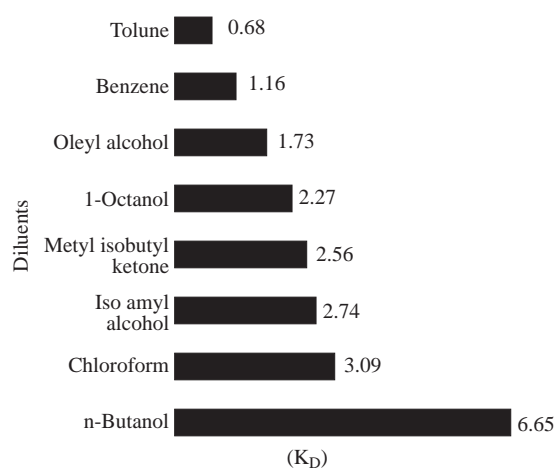$(C_C=20$ g/L, $C_A = 15\%$, T=298 K, N=150 rpm)

Figure 2b. Effect of diluent on the distribution coefficient for reactive extraction of aqueous citric acid solution with Alamine 336.

      (C_C=20 g/L, C_A = 15%, T=298 K, N=150 rpm)

     As shown in Figures 2a and b, the diluent which has the highest distribution coefficient for citric acid is n-butanol for Hostarex A 327 and Alamine 336 and their values are 7.07 and 6.65, respectively. Another suitable diluent is chloroform. It was found that toluene has the lowest distribution coefficient for citric acid. According to the literature the strength of the acid-amine complex solvation decreased in the following order: alcohol > nitrobenzen > proton donating halogenated hydrocarbon > ketone > halogenated aromatic > benzene > alkyl > aliphatic hydrocarbon [30,31]. As shown, our experimental results are confirmed in the literature. Distribution coefficient values obtained with Hostarex A 327 are higher than those of Alamine 336. Although Alamine 336 is a long chain tertiary amine, Hostarex A 327 is a mixture of long chain tertiary amines (1:1 tri n-octyl amine/tri n-decyl amine). It has been reported that these amine mixtures increased extraction power[32].

Experimental results at supercritical conditions

Solubilities of citric acid, Hostarex A 327 and Alamine 336 at supercritical conditions (T=313 K, P=100 bar) were investigated in our previous study[26]. It was observed that their solubility was very low in supercritical CO_2. It was found that the extraction yields were 3.2%, 0.6% and 0.1% for Hostarex A 327, Alamine 336 and citric acid, respectively. The extraction efficiency of citric acid with supercritical CO_2 was enhanced using a reactant dissolved in a diluent. It was found that the extraction yield of citric acid increased from 0.1% to 18% (180-fold) for Alamine 336 and from 0.1% to 15% (150-fold) for Hostarex A 327. For this reason, in this study, reactive extraction of citric acid was investigated with these amines in the presence of three diluents (1-butanol, chloroform and oleyl alcohol) at supercritical conditions.

     Separation yields of citric acid were determined at 308, 318, 328 K in the pressure range from 80 to 180 bars using Hostarex A 327 as the reactant. When 1-butanol and chloroform were used as the diluent, it was observed that these diluents were dragged with supercritical CO_2 to atmosphere and this action caused the loss of diluent. It was found that 1-butanol and chloroform were not suitable diluents at supercritical conditions. For this reason, oleyl alcohol was used in the reactive supercritical extraction experiments as the diluent.

The effect of temperature on the separation yield of citric acid is given in Figure 3. No clear effect was observed while increasing the temperature from 308 to 328 K.
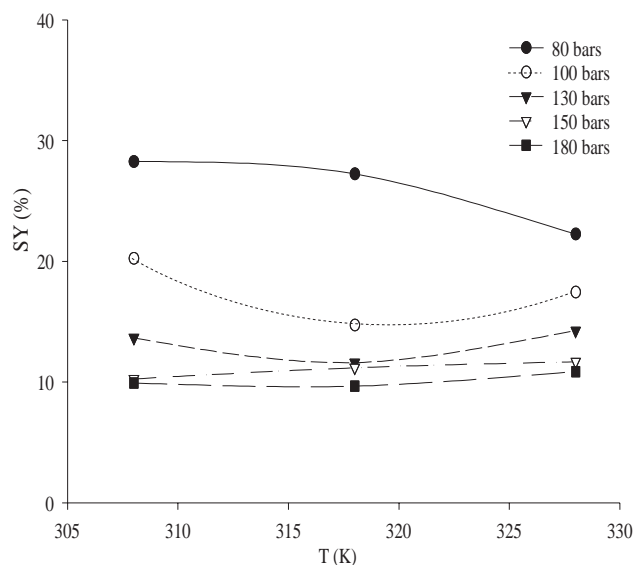

Figure 3. Effect of temperature on the separation yield of citric acid for Hostarex A 327-Oleyl alcohol system. (C_C=100 g/L, C_A = 30%, Q_{CO2}=5mL/min, t=30 min)

The effect of pressure on the separation yield of citric acid is given in Figure 4. It was found that the separation yield decreased with increasing pressure for all temperatures. The highest separation yield (28%) was found at near-critical pressure (P=80 bars, Pc=73 bars), because the density of supercritical CO_2 was near to the normal liquid density at this point and consequently it has a high solvent power[33].
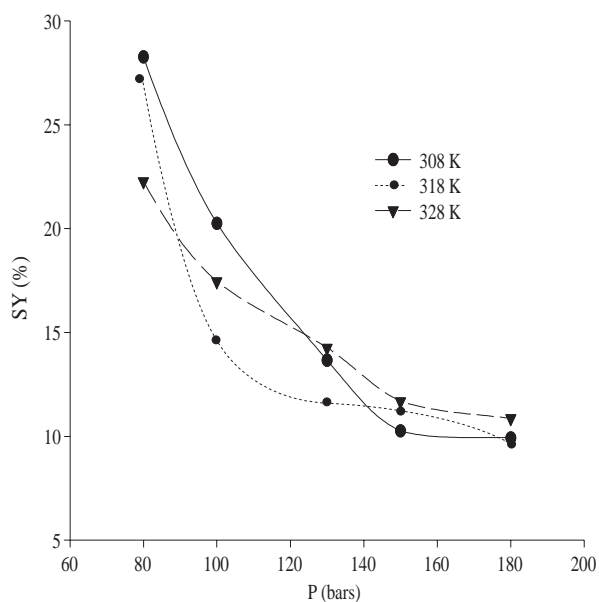

Figure 4. Effect of pressure on the separation yield of citric acid for Hostarex A 327-Oleyl alcohol system. (C_C=100 g/L, C_A = 30%, Q_{CO2}=5 mL/min, t=30 min)

Conclusions

The solubility of organic acid such as citric acid and the solubilities of tertiary amines such as Hostarex A 327 and Alamine 336 are very low in supercritical CO_2. Reactive extraction of citric acid was achieved using the tertiary amine and diluent at supercritical conditions. The highest value of citric acid separation yield (28%) was obtained at near-critical conditions. Reactive extraction of citric acid can be improved by using a mixture of tertiary amines in binary diluents or changing the concentration of amine, extraction parameters such as CO_2 flow rate, and the pH of the solution at supercritical conditions.

Acknowledgments

Nomenclature

C_C Concentration of citric acid in aqueous phase (g/L)

C_A Percentage of amine in organic phase (%, v/v)

K_D Distribution coefficient

$$\left[\frac{\text{Concentration of citric acid in organic phase (g / L)}}{\text{Concentration of citric acid in aqueous phase (g / L)}} \right]$$

N   Agitating rate (rpm)

P   Extraction pressure (bars)

Q_{CO2} Flow rate of liquid CO_2 (mL/min) (T=263 K, P=70 bar)

SY Separation Yield

$$\left[\frac{\text{Amount of citric acid in the initial solution (g) - Amount of citric acid in the raffinate solution (g)}}{\text{Amount of citric acid in the initial solution (g)}} \right]$$

T   Extraction temperature (K)

t   Extraction time (min)

V_a Volume of aqueous phase (mL)

V_o Volume of organic phase (mL)

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