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INFLUENCE OF MIXING ON THE COURSE  
OF REACTIVE EXTRACTION OF CITRIC ACID  
USING SUPERCRITICAL CO<sub>2</sub>

WPŁYW MIESZANIA NA PRZEBIEG REAKTYWNEJ  
EKSTRAKЦИИ KWASU CYTRYNOWEGO  
Z UŻYCIEM CO<sub>2</sub> W STANIE NADKRYTYCZNYM

Abstract

This paper presents the investigation results of mixing effects on the course of reactive extraction of citric acid from an aqueous solution, with the use of supercritical CO<sub>2</sub> and tertiary aliphatic amines. The influence of the mixing rate and the mixing time on the efficiency of the considered process has been studied. This paper also presents the influence of the tertiary amine chain length and the molar ratio of reactants on the efficiency of the process.

*Keywords: reactive extraction, supercritical CO<sub>2</sub>, citric acid*

Streszczenie

W artykule przedstawiono badania dotyczące wpływu mieszania na przebieg procesu ekstrakcji reaktywnej kwasu cytrynowego z roztworu wodnego z zastosowaniem CO<sub>2</sub> w stanie nadkrytycznym oraz trzeciorzędowych alifatycznych amin. Zbadano wpływ szybkości i czasu mieszania na efektywność rozważanego procesu. Zaprezentowano również wyniki badań wpływu długości łańcucha trzeciorzędowej aminy i stosunku molowego reagentów na efektywność procesu.

*Słowa kluczowe: ekstrakcja reaktywna, CO<sub>2</sub> w stanie nadkrytycznym, kwas cytrynowy*

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## 1. Introduction

Nowadays, modern chemical engineering is directed at the design of efficient and environmentally friendly industrial technologies. An increase of the efficiency of the applied technologies can be achieved by the integration of the following step processes: chemical reaction and simultaneous separation of products from the reaction environment. Reactive extraction is an example of such a process. Its application allows for a significant intensification of transport processes by increasing the rates of mass transfer and chemical reactions. In addition, this method allows for beneficial changes in the equilibrium position of a reversible chemical reaction, and therefore, increases its efficiency and selectivity for the desired product.

The production of carboxylic acids recently became of high interest to the chemical industry. Organic acids play an important role as pharmaceuticals and chemical intermediates, additives in the food industry, precursors of synthetic resins and biodegradable polymers. Recently, fermentation technology has been found to be an attractive and effective process for producing carboxylic acids. However, the product must be recovered from fermentation broth. The recovery of carboxylic acids from the fermentation broth is an important step in the production process, and it generates most of the economic and environmental problems. About 60% of the total production costs are created by downstream processing. The conventional industrial method of the separation of carboxylic acids from a fermentation broth is still acid precipitation in the form of insoluble calcium salts. The main disadvantages of this method are the high amount of by-product calcium sulphate and the high consumption of sulphuric acid [1]. Reactive extraction of acid using various suitable extractants has been found to be an alternative and effective method, when compared to the conventional process. The conventional reactive extraction processes are performed with the use of organic solvents. However, the use of organic solvents is a significant burden for the environment, it reduces the safety of the process, and it may also adversely affect the activity of the biochemical reagents. Therefore, eliminating organic solvents from industrial extraction processes and replacing them with safe media, e.g. supercritical CO<sub>2</sub>, is the basis for the dynamic development of industrial technologies using supercritical fluids.

Reactive extraction using supercritical fluids has a great potential as a new, efficient and clean method, in comparison with conventional methods of extraction. Moreover, its application is consistent with the principles of green chemistry and technology. Supercritical carbon dioxide is the most commonly used fluid due to its specific properties: non-toxicity, non-flammability, inertness and a low critical point ( $P_c = 7.38$  MPa,  $T_c = 304.3$  K). Supercritical fluids are of densities in-between those of liquids and gases, while their viscosities and diffusivities are closer to that of gases. Supercritical fluids also offer advantageous physicochemical properties by being good solvents. The application of reactive extraction using supercritical CO<sub>2</sub> for the separation of carboxylic acids from an aqueous solution is an innovative technology that is still under development.

This paper is dedicated to the reactive extraction process of citric acid (HOOC-CH<sub>2</sub>-C(OH)(COOH)-CH<sub>2</sub>-COOH) from an aqueous solution using supercritical CO<sub>2</sub> and tertiary aliphatic amines. The influence of the mixing rate and the mixing time on the efficiency of the considered process is presented. This paper presents the influence of the tertiary amine chain length and the molar ratio of reactants on the efficiency of the process.

## 2. Background of the process

### 2.1. Principles of reactive extraction of carboxylic acids

Reactive extraction of carboxylic acids is based on complex formation, in which the extractant soluble in the supercritical CO<sub>2</sub> phase reacts with carboxylic acid in the aqueous phase, and the formed complex is solubilised into the supercritical fluid phase. The solubility of carboxylic acids in supercritical CO<sub>2</sub> is very low because carboxylic acids are polar and CO<sub>2</sub> is nonpolar [2]. In order to increase solubility, polar entrainers or reactants are added to the supercritical fluid phase. There are two categories of extractants used in reactive extraction of carboxylic acids: high molecular weight aliphatic amines and phosphorus bonded oxygen bearing extractants [3]. For the reactive extraction of carboxylic acid from an aqueous solution, long chain aliphatic primary, secondary and tertiary amines are known to be efficient and selective extractants. In the considered system, tertiary amines are used because primary amines are soluble in the aqueous phase and secondary amines react irreversibly with carboxylic acids, which makes stripping difficult [4]. Moreover, primary and secondary amines react with CO<sub>2</sub> at low temperatures and pressures to form carbamates [5].

### 2.2. Mechanism of acid-amine complex formation

The stoichiometry of acid and amine in the acid-amine complex varies with the properties and concentrations of the amine, acid and diluents [6]. The notation (p,q) of the complex denotes p as the number of acid molecules, and q as the number of amine molecules. For example, the extraction of citric acid with trioctylamine dissolved in organic solvents is followed by the formation of acid-amine complexes of the (1,1) and (1,2) type, or their aggregates – (2,3) complex. The formation of the acid-amine complex is a reversible reaction.

Two possible structures of the citric acid-amine complex are shown in Fig. 1. Two major mechanisms have been reported for the extraction of carboxylic acids using amine: ion-pair formation and hydrogen bonds. Interaction between the first acid and the amine molecules is different from the interaction between the second acid and the (1,1) complex. The first acid forms an ion pair or a hydrogen bond with the amine, while the second acid forms a hydrogen bond to the carboxylate of the first acid [7].

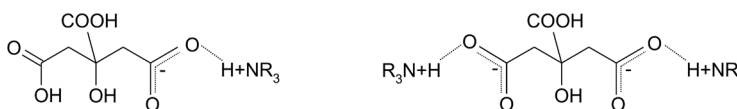


Fig. 1. Structure of a) (1,1) and b) (1,2) citric acid-amine complexes

## 3. Experimental

### 3.1. Materials

Citric acid with purity of > 99% was purchased from Merck. As the extractants formed complexes with citric acid, tertiary aliphatic amines have been applied: tripropylamine (TPA, Merck, > 98%), tributylamine (TBA, Merck, > 99%), trioctylamine (TOA, Merck, > 93%).

Liquid CO<sub>2</sub> with purity of more than 99.995% was purchased from Linde Gas. The aqueous solution of citric acid with an initial concentration equal to 0.014 mol dm<sup>-3</sup> was prepared by diluting citric acid with distilled water.

### 3.2. Apparatus and experimental procedure

The schematic diagram of the system for the supercritical CO<sub>2</sub> reactive extraction experiments is shown in Fig. 2.

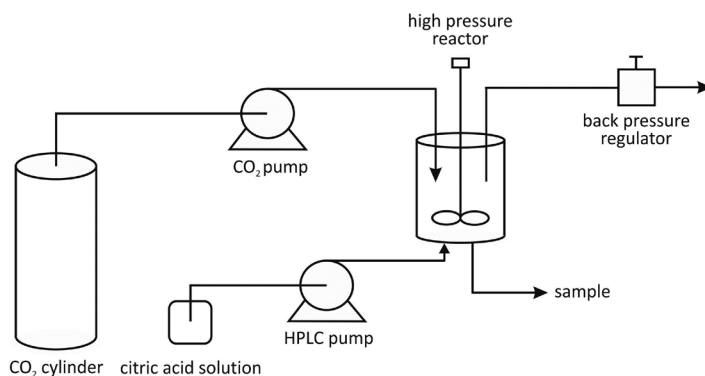


Fig. 2. Schematic diagram of the system for supercritical fluid reactive extraction

The main component of the apparatus consists of a high pressure reactor (Amar Equipments, 100 cm<sup>3</sup>, max. pressure 20 MPa). A piston pump (Supercritical Fluid Technologies, SFT-10) is used to deliver CO<sub>2</sub> to the high pressure reactor. During experiments on the influence of the amine chain length and the molar ratio of reactants, 50 cm<sup>3</sup> of citric acid solution (0.014 mol dm<sup>-3</sup>) and a specific volume of tertiary amine (TPA, TBA, TOA) was placed in the reactor, in order to keep a constant initial amine concentration of 0.014, 0.028, 0.042, 0.056 mol dm<sup>-3</sup> (molar ratio amine and acid 1:1, 2:1, 3:1, 4:1). Liquid CO<sub>2</sub> was subsequently purged into the system. The experiments were performed in a batch system for 60 minutes at a pressure of 16 MPa, a temperature of 308 K, and stirrer speed of 500 rpm.

During the experiments, according to the influence of the mixing rate, tertiary amine TPA with a constant initial concentration of 0.056 mol dm<sup>-3</sup> was placed in the reactor. Liquid CO<sub>2</sub> was subsequently purged into the system and the back pressure regulator was closed for the CO<sub>2</sub> pressurising process in the reactor with the pump. When the system pressure reached the desired value of 16 MPa, amine (TPA) and carbon dioxide were heated and mixed to reach the desired temperature of 308 K. The back pressure regulator was opened to enable CO<sub>2</sub> flow. When the pressure and the temperature reached the desired conditions, 50 cm<sup>3</sup> of citric acid solution (0.014 mol dm<sup>-3</sup>) was purged into the reactor with the HPLC pump (Knauer, Smartline 1000). An equal volume 50 cm<sup>3</sup> of the aqueous phase and the supercritical CO<sub>2</sub> phase were then agitated (250, 350, 500 rpm). All experiments were performed as batch reactive extractions, at a pressure of 16 MPa and a temperature of 308 K. Samples of the aqueous phase were taken after 1, 5, 10, 20 and 60 min. using the valve at the bottom of the reactor.

The applied experimental conditions were limited by the solubility of tertiary amines, in particular of trioctylamine, in supercritical CO<sub>2</sub>. The concentration of citric acid in the aqueous phase was determined by titration with aqueous sodium hydroxide, in the presence of phenolphthalein as the indicator.

#### 4. Results and discussion

The efficiency of reactive extraction of citric acid using tertiary amine and supercritical CO<sub>2</sub> ( $E$ ) is defined as:

$$E = \frac{C_{A0} - C_A}{C_{A0}} \cdot 100\% \quad (1)$$

where:

$C_{A0}$  – the initial concentration of citric acid in the aqueous phase,

$C_A$  – the concentration of citric acid in the aqueous phase after the process.

The results of the performed experiments are presented in Fig. 3, 4 and 5.

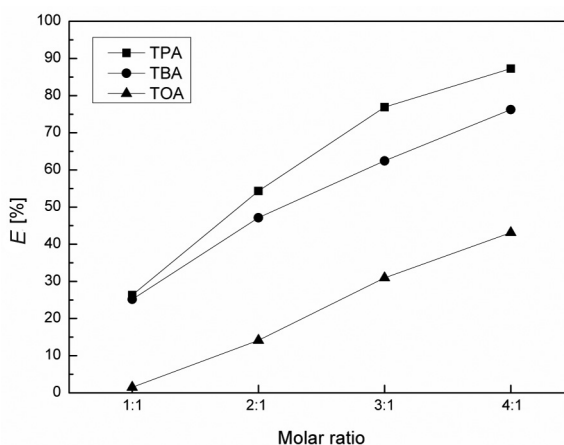


Fig. 3. Influence of the tertiary amine chain length and the molar ratio of reactants on the process efficiency (16 MPa, 308 K, 60 min, 500 rpm)

The aim of the performed experiments was to determine the influence of the molar ratio of the amine and acid reactants (1:1, 2:1, 3:1, 4:1), and the type of tertiary amine, on the final efficiency of the reactive extraction process. The results of experiments show that the molar ratio of citric acid and the amine is an important parameter affecting the efficiency of the process. It has been shown that an increase of the mole ratio of the amine, according to the concentration of citric acid, increases the process efficiency. The highest process efficiency, regardless of the amine, was obtained with a 4:1 molar ratio of the reactants. The highest efficiency of 87.28% was obtained using tripropylamine with 4:1 molar ratio. In the case of trioctylamine, a 4-fold increase of the concentration of amine allows to increase the process efficiency to 43.13%.

As shown in Fig. 3, the reactive extraction efficiency of carboxylic acids depends on the chain length of the tertiary aliphatic amine. The efficiency of the process using supercritical CO<sub>2</sub> increases with decrease of the amine chain length. The highest efficiency was obtained for tripropylamine at all molar ratios, while the least efficient process was using trioctylamine. The extraction efficiency increases with the chain length of tertiary amines in an active (polar) diluent, such as 1-octanol, however, it decreases with the chain length in an inactive (nonpolar) diluent, such as n-heptane [8,9]. The value of the dipole moment of a tertiary amine increases with the number of carbon atoms in the amine chain. The basicity of amines increases with their dipole moments. In the case of an active diluent with increasing polarity of the formed acid-amine complex, with an increasing amine chain length in the complex, the solubility and efficiency of the process increases. In the case of a nonpolar diluent, the more inert the diluent, the more unfavourable it is for polar complexes.

Carbon dioxide is a nonpolar, inactive solvent. Therefore, the efficiency of the reactive extraction of citric acid using supercritical CO<sub>2</sub> increases with the decrease of number of carbon atoms in the aliphatic tertiary amine chain (Fig. 3). In the case of a 1:1 molar ratio of reactants, for trioctylamine, an efficiency equal to zero was observed, while the use of tripropylamine allows to achieve an efficiency of 24.86%. The process efficiency obtained by the use of tripropylamine is 2-fold higher than in the case of trioctylamine, while maintaining a 4:1 molar ratio of the reactants.

The aim of the second part of the performed experiments was to investigate the effect of the mixing rate on the course of the process. The obtained results are shown in Fig. 4 and Fig. 5. In Fig. 4, the change of concentration of acid in the aqueous phase after the process versus the time is presented. In Fig. 5, the efficiency of the process versus the time is shown. The experiments have been performed at stirrer speeds of 250, 350 and 500 rpm.

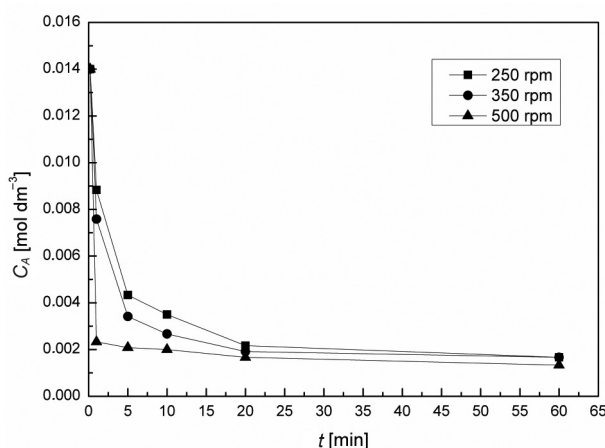


Fig. 4. Effect of stirrer speed on the concentration of citric acid in the aqueous phase versus the time (16 MPa, 308 K,  $C_{A0} = 0.014 \text{ mol dm}^{-3}$ ,  $C_{TPA} = 0.056 \text{ mol dm}^{-3}$ )

As shown in Fig. 4, an increase of the stirrer speed increases the reactive extraction process rate. A positive effect of the high mixing rates on the course of the reactive extraction process is clearly observed in the case of stirrer speeds of 250, 350 and 500 rpm. For example, at

500 rpm, the equilibrium concentration of acid in the aqueous phase was achieved already after 20 min. An increase of the stirrer speed leads to an increase of the process rate, so the final efficiency is obtained in a shorter period of time (Fig. 5). An increase in the stirrer speed leads to an increase of dispersion of the heterogeneous mixture and to a reduction of the mass transfer resistance between the phases of the system, which contributes to an increase of the process efficiency. The application of a stirrer speed of 500 rpm allows for an efficiency of 83.72% after 1 min, while the use of 250 rpm and 350 rpm results in an efficiency of 38.37% and 47.09%, respectively. This effect demonstrates the very fast reaction of acid-amine complex formation and mass transfer in a heterogeneous system.

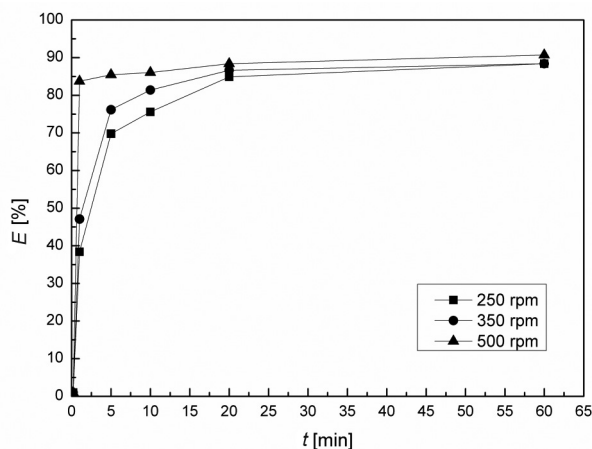


Fig. 5. Effect of stirrer speed on the efficiency of citric acid reactive extraction versus the time (16 MPa, 308 K,  $C_{A0} = 0.014 \text{ mol dm}^{-3}$ ,  $C_{TPA} = 0.056 \text{ mol dm}^{-3}$ )

## 5. Conclusions

The obtained results indicate the legitimacy of the application of supercritical  $\text{CO}_2$  in the reactive extraction process in order to recover citric acid from an aqueous solution. The supercritical reactive extraction process of carboxylic acid can be controlled by changing the type of tertiary amine, the molar ratio of reactants, and the mixing rate in the system. A concentration of amine that is higher than the concentration of acid, and a decrease of the tertiary amine chain length, result in the highest efficiency of the reactive extraction of citric acid from an aqueous solution. More intensive mixing intensifies the process and increases its final efficiency in a shorter period of time. For a high stirrer speed, the reactive extraction process is controlled by kinetics of the reaction of complex formation.

In the batch mode, the efficiency of the considered process is limited by the solubility of the reactant forming a complex with an acid in supercritical  $\text{CO}_2$ . Therefore, the obtained efficiencies of the process performed for higher acid concentrations could be relatively low. An increase of the process efficiency can be achieved by the application of a continuous system, in which the flow of supercritical  $\text{CO}_2$  is saturated with an extractant.

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