Reactive extraction of citric acid using supercritical CO_2 and trioctylamine

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The paper is dedicated to the integrated process of the reactive extraction of citric acid from aqueous solution using supercritical CO_2 and trioctylamine. The aim of this study is to investigate the influence of process parameters (concentration of reactants in phases, pressure, temperature, mixing rate, mixing time) on the course of the reactive extraction process. The increase of the initial concentration of amine (0.04-0.07 mol·dm^{-3}) results in the higher efficiency of reactive extraction. The influence of pressure (12-18 MPa) on the process is negligible. The process efficiency decreases with temperature (308-328 K). The increase of stirrer speed (250-500 rpm) leads to increase of process rate, so the final efficiency is obtained in shorter time.
Keywords: reactive extraction, supercritical CO_2, citric acid, trioctylamine

Introduction

Production of carboxylic acids is recently of high interest to the chemical industry. Carboxylic acids play an important role as the precursors of synthetic resins, biodegradable polymers, pharmaceuticals and chemical intermediates and as the additives in the food industry. Fermentation technology using microorganisms has been found to be an effective process to produce carboxylic acids. The product must be recovered from fermentation broth. More than half of the total production costs are generated by downstream processing. The industrial method for separation of carboxylic acids from fermentation broth is a precipitation. The main disadvantages of this method are the production of high amount of by-product calcium sulphate and high consumption of sulphuric acid [1]. For that reason, alternative and effective methods of carboxylic acids separation have to be developed. The reactive extraction of carboxylic acids with the use of organic solvents is an alternative method for recovery of carboxylic acids from fermentation broth. However, the use of organic solvents is significant burden for the environment, reduces the safety of the process, and may also adversely affect the activity of the biochemical reagents. Therefore, the elimination of organic solvents from industrial extraction processes and replacement them with safe media e.g. supercritical CO_2 are the basis for dynamic development of industrial technologies. The application of supercritical fluid as a green solvent in reactive extraction process allows the elimination of disadvantages of the use of organic solvents. Supercritical CO_2 is the most common used fluid due to its specific properties: non-toxicity, non-flammability, inertness and low critical point (P_c=7.38 MPa, T_c=304.3 K). The use of supercritical CO_2 as a green solvent in the reactive extraction and replacement of organic solvents applied in the traditional method in separation processes is a part of the latest trend in the design of industrial technologies in agreement with the principles of „Green Chemistry". In this context supercritical fluid reactive extraction has a great potential as a clean and efficient method compared to the conventional methods of separation. Its application allows a significant intensification of transport processes by increasing the rates of mass transfer and chemical reactions.

Solubility of carboxylic acids in supercritical CO_2 is very low, because carboxylic acids are polar and CO_2 is nonpolar. To increase solubility, entrainers or reactants are added to the supercritical fluid phase. The reactive extraction of carboxylic acids using supercritical CO_2 is based on complex formation, in which the extractant soluble in supercritical CO_2 phase reacts with carboxylic acid of aqueous phase and the formed complex is solubilised into the supercritical fluid phase. The two categories of extractants are applied in reactive extraction of carboxylic acids, long-chain aliphatic amines and organophosphorous compounds [2]. For the reactive extraction of carboxylic acid from aqueous solution long chain aliphatic primary, secondary and tertiary amines are known to be efficient and selective extractants. In the considered reactive extraction process the tertiary amines, for example trioctylamine, are used. The primary amines are soluble in aqueous phase and secondary amines react irreversibly with carboxylic acids

[3]. Moreover, in the case of primary and secondary amines the carbamates with CO_2 are formed [4]. In the considered system the long-chain aliphatic tertiary amines, for example trioctylamine, are effective reactants for the extraction of carboxylic acids. In the process using CO_2 the acid-amine complex can be recovered by simply depressurizing of the system. The carboxylic acid can be recovered from complex using various regeneration methods e.g. using NaOH or by temperature swing.

This paper is dedicated to reactive extraction process of citric acid from aqueous solution using supercritical CO_2 and trioctylamine. The research of the reactive extraction of carboxylic acids using supercritical CO_2 has been presented in our previous work [5,6]. The aim of this study is to investigate the influence of process parameters on the course of the reactive extraction process. The influence of concentration of reactants in phases, pressure and temperature on the final efficiency of the process has been investigated. The influence of mixing rate and mixing time on the course of the considered process has been presented. The obtained results will allow identification of elementary mechanisms of the process, chemical reaction kinetics and formulation of modeling method of the process.

Materials and methods

Citric acid with purity 99% was purchased from Sigma-Aldrich. Trioctylamine with purity 93% and 1-octanol with purity 99% were obtained from Merck. The purity of CO_2 was more than 99.995% and was purchased from Linde Gas. Aqueous solution of citric acid was prepared by diluting a citric acid with distilled water.

The experiments were performed with the use of the high pressure system. The schematic diagram of the system for the supercritical CO_2 reactive extraction experiments is shown in Figure 1.

The main component of the apparatus is high pressure reactor (Amar Equipments, 100 cm^3, max. pressure 20 MPa). A piston pump (SFT-10, Supercritical Fluid Technologies) is used to deliver CO_2 to high pressure reactor. During all experiments trioctylamine is placed in reactor. Liquid CO_2 is purged into the reactor and the back pressure regulator

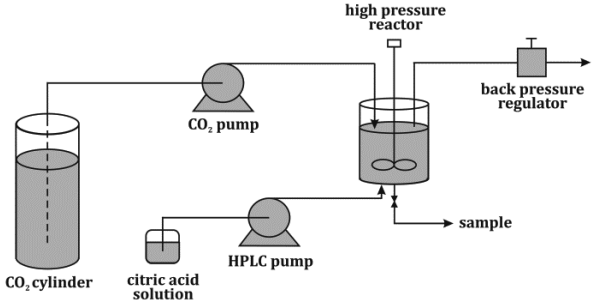

Figure 1. Schematic diagram of the system for supercritical fluid reactive extraction

(Tescom) is closed for pressurizing CO_2 in system with the pump. When the pressure of the system reaches the desired value, extractant and CO_2 are heated and mixed to reach desired temperature. The trioctylamine is solubilised in supercritical CO_2. When the pressure and the temperature reach the desired conditions, the carboxylic acid solution is delivered into the reactor with the HPLC pump (Knauer). All experiments were performed in batch system. After desired time samples of the aqueous phase were taken with the use of the valve at the bottom of the reactor.

The concentration of carboxylic acid in aqueous phase (before and after reactive extraction process) was determined by titration method with 0.1 N sodium hydroxide aqueous solution in the presence phenolphthalein as the indicator. The concentration of the acid in supercritical CO_2 phase was calculated by a mass balance. The initial concentration of citric acid in aqueous phase (C_{A0}) was 0.02-0.04 mol·dm^{-3} and the initial concentration of trioctylamine in supercritical CO_2 (C_{B0}) was 0.04-0.07 mol·dm^{-3}. The pressure was varied in the range 12-18 MPa and the temperature in the range 308-328 K. The stirrer speed was 250 and 500 rpm. The applied experimental conditions were limited by solubility of trioctylamine in supercritical CO_2 [6]. The results obtained for supercritical reactive extraction were compared with those obtained using organic solvent, 1-octanol.

Results and discussion

The efficiency of reactive extraction of citric acid using trioctylamine and supercritical CO_2 or 1-octanol (E) is defined as:

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

where C_{A0} – the initial concentration of citric acid in the aqueous phase [mol·dm^{-3}], C_A – the concentration of citric acid in the aqueous phase after process [mol·dm^{-3}]. The initial concentration of trioctylamine in supercritical CO_2 is denoted as C_{B0} [mol·dm^{-3}].

The results of performed experiments are presented in Figures 2-4 and summarized in table 1. The obtained results indicate that supercritical reactive extraction process of carboxylic acid can be controlled by change of concentration of reactants, pressure and temperature in the system. The influence of concentration of reactants on the process efficiency is shown in Figure 2. The results obtained using supercritical CO_2 are compared with results obtained using organic solvent 1-octanol. The increase of the initial concentration of amine (0.04 and 0.07 mol·dm^{-3}) results in the higher efficiency of reactive extraction of citric acid from aqueous solution. The process efficiency obtained using 1-octanol is higher than efficiency of the process performed with the use of supercritical CO_2.

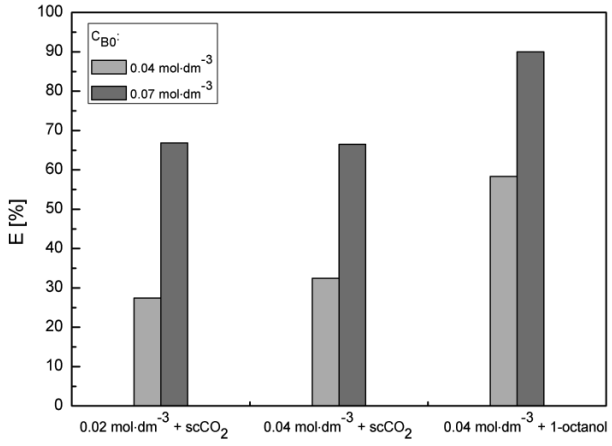

Figure 2. Influence of concentration of reactants on the process efficiency (16 MPa, 308 K, 60 min, 500 rpm)

Table 1. Influence of pressure on the process efficiency (308 K, 60 min, 500 rpm, C_{A0}=0.04 mol·dm^{-3}, C_{B0}= 0.04 mol·dm^{-3})

p [MPa]	E [%]
12	35.8
14	35.8
18	32.5

In Table 1 the influence of pressure on the process efficiency using supercritical CO_2 is shown. The experimental data showed that influence of pressure on the process is negligible. However, the higher pressure is more favorable for the reactive extraction of the citric acid due to higher solubility of trioctylamine in supercritical CO_2 [6].

The influence of temperature on the course of the supercritical reactive extraction process is presented in Figure 3. With the increase of temperature the efficiency of the considered process decreases. The reaction of complex

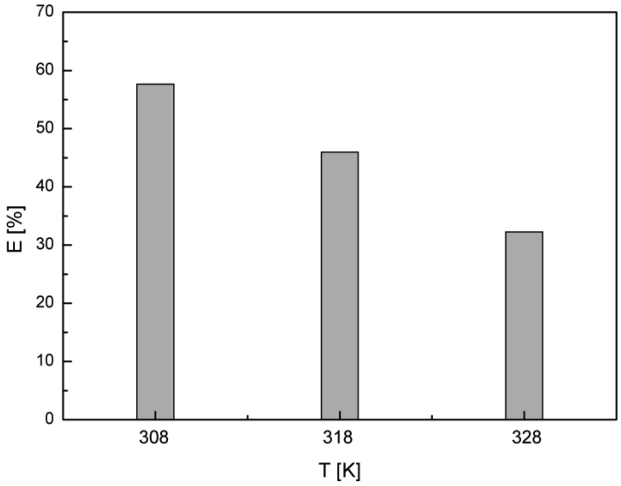

Figure 3. Influence of temperature on the process efficiency (C_{A0}=0.04 mol·dm^{-3}, C_{B0}=0.07 mol·dm^{-3}, 18 MPa, 60 min, 500 rpm)

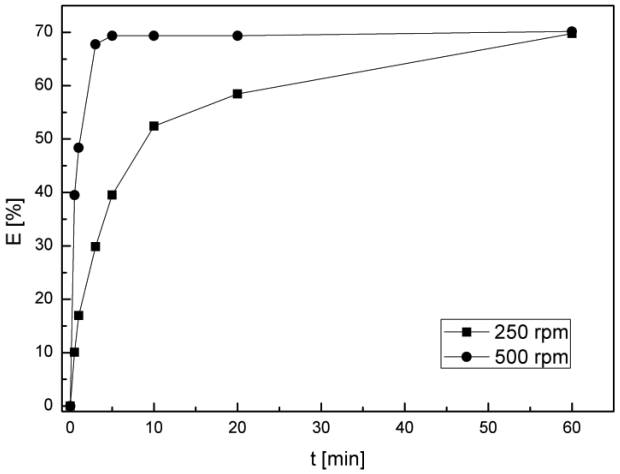

Figure 4. Effect of stirrer speed on the process efficiency versus time (C_{A0}=0.04 mol·dm^{-3}, C_{B0}=0.07 mol·dm^{-3}, 16 MPa, 308 K)

formation between carboxylic acid and amine is exothermic. Therefore, as the temperature is increased, the process efficiency decreases. With the increase of temperature the acid-amine complex is decomposed. The equilibrium at higher temperature is shifted and favors the transfer of the acid to the aqueous phase.

In Figure 4 the effect of stirrer speed and time on the course of reactive extraction process using supercritical CO_2 is presented. The increase of stirrer speed intensifies the process and leads to increase of process rate, so the final efficiency is obtained in shorter time. At 250 rpm the equilibrium concentration of acid in aqueous phase was achieved in 60 min, at 500 rpm already in 5 min. The increase of stirrer speed leads to increase of dispersion of heterogeneous mixture and to reduce the mass transfer resistance between the phases of the system, and the extraction process gets accelerated significantly.

For high value of the stirrer speed the effect of mixing intensity on the process rate is eliminated. The process rate is dependent on the rate of complex formation reaction.

Conclusions

The obtained results indicate that reactive extraction of citric acid using supercritical CO_2 and trioctylamine can be controlled by change of concentration of acid and amine in the system, pressure and temperature. The mixing rate and mixing time influence also the course of the process. The application of concentration of trioctylamine higher than concentration of citric acid results in higher process efficiency. The supercritical reactive extraction of citric acid should be performed at low temperature, high pressure and stirrer speed. In batch mode the efficiency of the considered process is limited by the solubility of the reactant forming a complex with an acid in supercritical CO_2. Therefore, the obtained efficiencies of the process per-

formed for higher acid concentrations could be relatively low. The increase of process efficiency can be achieved by application of continuous system, in which flow of supercritical CO_2 saturated with extractant is applied. The described problem can be additionally eliminated by recirculation of CO_2 in the system.

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