



## Reactive extraction of acetic acid and propionic acid using supercritical carbon dioxide



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### ABSTRACT

The paper presents the results of investigations of reactive extraction of acetic and propionic acids from aqueous solutions using supercritical carbon dioxide (scCO<sub>2</sub>) and tri-*n*-octylamine (TOA). The experimental results of reactive extraction were compared with those of physical extraction. The experiments were conducted in both batch mode and semi-continuous mode. The effect of the initial carboxylic acid and amine concentration, pressure, temperature and process time on the extraction efficiency was investigated. The reactive extraction using TOA was found to significantly enhance the efficiency of acetic and propionic acids recovery as compared to physical extraction. It is recommended to perform the reactive extraction using scCO<sub>2</sub> in the semi-continuous mode. It was shown that performing the process in a relatively high pressure is favourable for obtaining a high efficiency of reactive extraction of carboxylic acids. In the case of reactive extraction longer process time results in increase in process efficiency. The highest reactive extraction efficiency 94.7% was obtained for propionic acid (1.04 mol dm<sup>-3</sup>, 35 °C, 16 MPa, 60 min).

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### 1. Introduction

In recent years, the biological production of different carboxylic acids by fermentation technology has been investigated as an alternative to the petrochemical-based process for the production of, e.g., propionic acid, lactic acid, acetic acid, citric acid, succinic acid, etc. [1,2]. Until recently, most carboxylic acids were produced on an industrial scale by synthesis via the petrochemical route. However, in the past few decades the high prices of petrochemical products, uncertain supply and eventual depletion of world petroleum reserves as well as problems concerning environmental protection and requirements for the development of new, environmentally friendly technologies have led to a search for alternative methods of carboxylic acid production [2,3].

With the current trend of the growing importance of carboxylic acid production by fermentation, it is of high importance to develop a new, efficient method of carboxylic acid separation from the fermentation broth or substantial improvement in the existing recovery technology. Even more than half of the total production costs are costs associated with downstream processing. The conventional industrial method of carboxylic acid separation is

precipitation using calcium hydroxide, which is environmentally unfriendly and expensive, as it requires large amounts of sulphuric acid and generates solid waste in the form of calcium sulphate. A number of methods have been investigated for the recovery and purification of carboxylic acids, e.g., electrodialysis, membrane separation, adsorption, liquid–liquid extraction, ion exchange, reverse osmosis, etc. [2,4]. All of these methods have their own disadvantages, e.g., high costs, low efficiency, complexity of operation, high chemical and energy consumption. Reactive extraction using organic solvents has shown promising features as method of carboxylic acid separation from the fermentation broth or waste water and has received increasing attention [5]. However, the application of organic solvents is associated with several disadvantages, among which toxicity, negative environmental impact, reduction of process safety, high costs and difficult regeneration of the solvent should be emphasised.

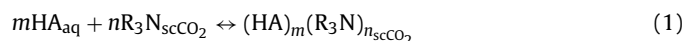
Therefore, the idea of eliminating hazardous organic solvents from industrial extraction processes and of replacing them with safe and green media, e.g. supercritical carbon dioxide (scCO<sub>2</sub>), has been the basis for the dynamic research of industrial technologies using supercritical fluids in recent years. Supercritical carbon dioxide is the most intensively used green medium due to the following properties: non-toxicity, non-flammability, inexpensive, low critical point ( $p_c = 7.38$  MPa,  $T_c = 31.1$  °C), availability, and good transport properties. Recently, effective applications of supercritical fluids in chemical processes have attracted much attention.

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Reactive extraction using  $\text{scCO}_2$  has been used for recovery of metals from aqueous solutions [6], biodiesel production [7] and trioxane synthesis [8].

The application of  $\text{scCO}_2$  as a solvent for the reactive extraction of carboxylic acids from aqueous solution is innovative and still under development. This method has potential as an effective and environmentally friendly alternative method to the traditional technology of carboxylic acid recovery. The solubility of hydrophilic carboxylic acids in non-polar  $\text{scCO}_2$  is low [9,10]. An increase in extraction efficiency can be achieved by adding suitable extractants (high molecular weight aliphatic amines, phosphorus-bonded oxygen bearing extractants) to the  $\text{scCO}_2$  phase. Tertiary aliphatic amines are known to be effective extractants for carboxylic acids [5,11,12]. These reactants react with the acids forming complexes and enhance their solubility. Primary and secondary amines are excessively soluble in water [5] and react with  $\text{CO}_2$  to form carbamates [12,13]. Tertiary amines do not react with  $\text{CO}_2$  [12,14]. The overall reaction between  $m$  molecules of carboxylic acid and  $n$  molecules of tertiary amines to form complexes can be described as:



The formation of acid–amine complex is reversible reaction. It is known that tertiary amines react only with the undissociated form of carboxylic acid [5]. It was observed that reactive extraction efficiency decreases along with an increase in the temperature, as the formation of a complex makes the system more ordered and entropy decreases [15]. Reactive extraction using tertiary amines diluted in organic solvents used for the recovery of carboxylic acids from the fermentation broth and waste water has been widely studied [5,16–20]. However, there are few reports in the literature on the extraction of carboxylic acids using  $\text{scCO}_2$  as a solvent. The phase behaviour of carboxylic acids in  $\text{scCO}_2$  has been reported by Byun et al. [21] and Pappa et al. [22]. Panagiotopoulos et al. [23] studied phase equilibria in ternary systems with  $\text{scCO}_2$ , water and carboxylic acids. On the basis of the data, it can be concluded and confirmed that the solubility of organic acids in  $\text{scCO}_2$  is low. Garrett et al. [24] performed physical extraction of acetic acid from real and model solutions of cow rumen fluid using the flow of  $\text{scCO}_2$ . Very few papers exist in the literature and little effort has been made regarding research on the reactive extraction of carboxylic acids using  $\text{scCO}_2$ . Reactive extraction of lactic and acetic acid using tri-*n*-hexylamine, Hostarex A327 and Amberlite LA-2 dissolved in  $\text{scCO}_2$  was investigated by Hartl and Marr [25]. Kapucu et al. [9] studied the reactive extraction of citric and acetic acid from aqueous solution using  $\text{scCO}_2$  and Alamine 336 and Hostarex A327 as reactants. The solubilities of citric and acetic acids, amines and acid–amine complexes in  $\text{scCO}_2$  were examined. It was found that the use of an extractant significantly enhanced the extraction efficiency of citric and acetic acids as compared to physical extraction. The separation of citric acid was investigated using  $\text{scCO}_2$  and a mixture of tertiary amine Hostarex A327 and oleyl alcohol [26]. Rahmanian and Ghaziaskar [12] performed reactive extraction of maleic acid and phthalic acid from their mixture using a continuous flow of  $\text{scCO}_2$  saturated with trioctylamine. Wang et al. [10] reported an investigation regarding the increase in solubility of benzoic, citric and lactic acid in  $\text{scCO}_2$  using TBP as a Lewis base carrier.

Acetic acid and propionic acid are monocarboxylic acids that are widely used in chemical, food and pharmaceutical industries. Acetic acid is an important chemical reagent used in the production of cellulose acetate, polyvinyl acetate, acetic anhydride and esters. In the food industry, acetic acid has been applied for years as an acidity regulator and a vinegar. Propionic acid is applied in the manufacture of plastic, pesticides, pharmaceuticals, flavours and perfumes. It is an important carboxylic acid for the food industry and is used

in mould preservation of food, mainly bread and cakes. Propionic acid is also consumed as a preservative in silage, hay and animal feed [27]. Due to the wide applications of acetic and propionic acid, it is important to conduct an investigation on extraction of these monocarboxylic acids using  $\text{scCO}_2$ .

In this work, reactive extraction of acetic acid and propionic acid from aqueous solutions using  $\text{scCO}_2$  was investigated. The results of reactive extraction of carboxylic acids were compared with those of physical extraction. Tri-*n*-octylamine (TOA) as a reactant forming a complex with undissociated form of acid was applied in reactive extraction experiments. The results of previous investigations of organic solvents suggest that TOA is the most recommended extractant for the monocarboxylic acids examined here [16–19]. To date, no experimental work concerning the use of  $\text{scCO}_2$  and TOA as reactant for reactive extraction of acetic acid and propionic acid from aqueous solutions has been conducted. In the literature, little data has been reported on the physical extraction of acetic acid using  $\text{scCO}_2$  [9,24] and the phase equilibria of mixtures containing  $\text{CO}_2$  and monocarboxylic acids [21–23]. Moreover, the shortcomings of previous works are: the lack of uniform operating conditions, no effect of the reactants' concentrations and no comparison of efficiency for batch and continuous systems. In the present work, the effectiveness of using TOA in supercritical reactive extraction process as compared to physical extraction of carboxylic acids was evaluated. The experiments were conducted in batch mode and in semi-continuous mode, i.e., with the flow of  $\text{scCO}_2$ . The semi-continuous mode allowed to eliminate the limitation of process efficiency in the batch mode. The effect of the initial carboxylic acid and amine concentration, pressure, temperature and process time on extraction efficiency is reported here. The equilibria and distribution coefficient values for reactive and physical extraction have also been determined. Potential application of reactive extraction using  $\text{scCO}_2$  for the separation of carboxylic acids, in particular monocarboxylic acids, from aqueous solutions is discussed.

## 2. Materials and methods

### 2.1. Materials

Acetic acid (Chempur, 99.9%) and propionic acid (Merck, 99.9%) were used to prepare aqueous solutions of various concentrations. The initial concentrations of acetic acid and propionic acid in their solutions were 0.07, 0.13, 0.26, 0.39, 0.52 and 1.04 mol dm<sup>-3</sup> and corresponded to concentrations of acids in fermentation broth and waste streams [16–19,28,29]. Tri-*n*-octylamine (TOA) with a purity of 93% was purchased from Merck. The initial concentration of TOA in  $\text{scCO}_2$  for batch mode system experiments was set at 0.07 mol dm<sup>-3</sup>, which was limited by the solubility of TOA in  $\text{scCO}_2$  [14]. Carbon dioxide with a purity of 99.995% was purchased from Linde Gaz.

### 2.2. Supercritical fluid extraction experiments

The experimental system for supercritical extraction is shown in Fig. 1. In the experiments performed in the batch mode, 50 cm<sup>3</sup> of carboxylic acid solution was added to a high-pressure reactor (4) of volume 100 cm<sup>3</sup> (Amar Equipments, India). In the reactive extraction experiments, amine was placed in a high-pressure reactor (4). Liquid  $\text{CO}_2$  was subsequently pumped from the tank with a siphon tube (1) into the reactor (4) with a pump (2) (SFT-10, Supercritical Fluid Technologies, USA). The experimental conditions were set at 35 °C and 16 MPa. The extraction time was 60 min and was experimentally checked to be sufficient to reach equilibrium state [30]. The experiments were performed for a stirrer speed of 500 rpm [30]. After the extraction was completed, samples of the aqueous

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