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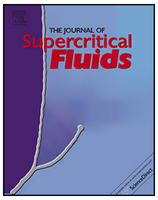

Fractionation of aqueous isopropanol mixtures in a countercurrent packed column using supercritical CO_2

R. Lalam [a], S. Chamali [b], S. Camy [b,*], D. Rouzineau [b], R. Kessas [a], J.-S. Condoret [b]

[a] *Université des Sciences et de la Technologie d'Oran – Mohamed Boudiaf, BP 1505 El-M'Naouar, Oran, Algeria*
[b] *Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique UMR CNRS 5503, 4, Allée Emile Monso, F-31030 Toulouse, France*

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ABSTRACT

Purification of isopropanol aqueous mixtures by supercritical CO_2 was realized in the continuous mode using a packed column. The aim of the study was to experimentally and theoretically evaluate the separation performance of this packed contactor. Experiments were performed in a column of 2 m height and 17 mm diameter, in the range (10–20 MPa) and (40–60 °C) with a solvent to feed ratio varying from 4 to 11. Two types of packing, spring shape packing and metallic foam, were tested. The IPA composition of the feed was varied between 5% and 60% (w/w). The experimental results were compared to simulation of the process using the process simulation software Prosim Plus. The column modelling was based on the concept of theoretical equilibrium stages. Thermodynamic behaviour of the CO_2–IPA–water system under pressure was represented on the whole range of conditions corresponding to the process, using the Soave–Redlich–Kwong equation of state (SRK) modified by Boston Mathias with PSRK mixing rules and UNIQUAC activity coefficient models. This model gave the best predictions, after the twelve interaction coefficients (four for each binary subsystem) were identified from the literature equilibrium experimental data. From the modelling, rather high values of the Height of a Theoretical Stage (HETS) were obtained (larger than 1 m) and these values were shown to diminish when the IPA feed composition was increased.

1. Introduction

Isopropanol (IPA) is a secondary alcohol currently used as a chemical feedstock in particular for acetone production and also as a solvent in many consumer products [1]. Although IPA is currently obtained via indirect or direct hydration of propylene, some alternative bio-processes are under investigations. These alternatives routes have to meet the recent green chemistry requirements which encourage the use of bio sourced chemicals. Fermentation routes for IPA have been investigated with several species of *Clostridium* leading to so-called bio-isopropanol. Nevertheless, IPA concentrations obtained with these strains were very low because clostridia produce butanol together with IPA [2], although Inokuma et al. [3] have recently shown that fermentation of glucose using metabolically engineered *Escherichia coli* strain TA76, could lead to IPA aqueous solution. Nevertheless, recovery of IPA from fermentation broth is usually proposed by distillation of the azeotropic isopropanol/water mixture. This route implies a high energy consumption and alternative downstream processes for purification of these bio alcohols need to be proposed.

Use of supercritical fluids for fractionation of ethanol–water mixtures has been studied for long, considering the interest to propose alternative processes to the azeotropic distillation for this mixture. This was envisaged for applications such as dealcoholisation of beverages [4], extraction of aromatic compounds from alcoholic solutions [5] or purification of bioethanol [6]. This kind of separation can be operated in continuous mode, in spray, packed or sieve-tray columns, where liquid phase to be fractionated flows counter-currently with the supercritical solvent, in a similar way as liquid–liquid extraction. Also, supercritical fractionation has been proposed, at laboratory or pilot scales, for deacidification of edible oils [7], fish oils fractionation [8], deterpenation of citrus oils [9], or fractionation of perfluorinated oligomers [10]. Although still underexploited, the potential of this technology for industrial applications is thus significant, but a better understanding of the process is still needed for its full development, as recently stated by Brunner [11].

Specific studies above mass transfer performances in countercurrent fractionation columns, for processing aqueous solutions of alcohols with supercritical carbon dioxide or other solvents, are available in the literature. For instance, Rathkamp et al. [12]

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* Corresponding author. Tel.: +33 5 34 32 37 13.
E-mail address: severine.camy@ensiacet.fr (S. Camy).

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and Lahiere and Fair [13] studied separation of ethanol/water and isopropanol/water with supercritical CO_2 in spray, sieve tray and Rashig ring packed columns (1.2 m height and 2.54 cm internal diameter). Values of global mass transfer parameters such as Height and Number of Transfer Unit (HTU/NTU) and Height Equivalent to a Theoretical Stage (HETS) have been deduced from experimental results and compared to conventional liquid–liquid systems. The authors pointed out that, despite high mass transfer coefficients in the supercritical phase, important resistance to mass transfer occurred in that phase due to low partition coefficients of alcohols. Several mass transfer studies have been done about the CO_2/water/ethanol system such as the one of Bernad et al. [14] using a countercurrent 1.4 m height and 54 mm internal diameter column, packed with stainless steel BX 64 Sulzer packing. Commercial, so as home-made simulation softwares were used by the authors to estimate HETS of the contactor and comparison of two contacting modes (trickle bed and bubble column) was done. HETS values were found to range between 0.5 and 1.5 m depending on experimental conditions and contacting mode, the packed bubble column being the most efficient. Also, Lim et al. [15], using a 3.175 cm internal diameter and 1.52 m height Knit mesh elements packed column, extensively studied this system and showed that conventional mass transfer models used for liquid–liquid extraction could be used with a reasonable accuracy to predict overall mass transfer coefficient. Using the graphical Ponchon–Savarit method, Budich and Brunner [16] showed that it was theoretically possible to obtain anhydrous ethanol when operating extraction at 333 K and 10 MPa, where the ternary system exhibits so-called type II thermodynamic behaviour (taking advantage of the ethanol–CO_2 partial immiscibility). The CO_2–1-butanol–water system was studied by Laitinen and Kaunisto [17] who showed the feasibility of the separation using scCO_2 at 10 MPa and 313 K in a mechanically agitated Oldshue-Rushton-type column (2 m high and 35 mm internal diameter). From the HTU–NTU approach, they deduced values of overall mass transfer coefficients of the system and HETS were found to be in the range 0.4–0.5 m. Moreover, they evidenced that mechanical agitation had no effect on the column efficiency at the selected extraction conditions.

A better understanding of mass transfer should arise from the knowledge of hydrodynamics of high pressure countercurrent contactors but such studies are very scarce, mainly due to experimental difficulties for measuring pressure drops or visualizing flow patterns in high pressure systems. Most studies have concerned measurements of liquid hold-up in the column using static methods [15] and analysis of flooding of the column was done with a column equipped with sapphire windows and pressure drop transducers [16]. These studies essentially highlighted that hold-up is greater in packed columns as compared to spray columns. Also, flooding conditions were shown to be influenced by the ethanol content in the feed, because of its influence on fluid properties.

Most engineering studies have utilized conventional chemical engineering tools, similar to those for liquid–liquid extraction, but, when thermodynamic behaviour of the mixture can be satisfactorily described using standard thermodynamic models, such as cubic equations of state, commercial process simulation softwares are useful tools to model a fractionation column and/or the entire process, including solute recovery and solvent recycling. Bernad et al. [14] used the ProSim software to estimate HETS values of their experimental set-up in the case of ethanol recovery from aqueous solutions. The ASPEN Plus software was successfully used by Brunner [18] and Riha and Brunner [19] to evaluate the number of theoretical stages of their experimental set-up and to predict the concentration profiles in a column used to process a mixture of ethyl esters of fatty acids. They showed that Aspen Plus led to similar HETS values than those obtained from conventional graphical Mc Cabe and Thiele or Ponchon–Savarit methods. Recently, Fiori et al. [20] used the same software to investigate and optimize the fractionation of omega-3 lipids from fish oil by supercritical CO_2. Similarly, the HYSIS software was used by Moraes et al. [21] in order to optimize a process for dehydration of ethanol using supercritical propane. Typically, with these approaches, counter-current contactors are represented by a succession of equilibrium theoretical stages. With a proper thermodynamic model, these tools provide information on separation performances, together with other information such as energy consumption of the process or optimized experimental conditions for solute recovery. Considering the ongoing improvements of these tools, with implementation of novel thermodynamic models, use of simulation softwares in the design and optimization of operating conditions of such processes appear now as unavoidable.

Indeed, the objective of our work was to consider the CO_2 fractionation of aqueous IPA mixtures to give an analysis of experimental separation results using a process simulation software (here the ProSim Plus software), fed with the adapted thermodynamic model. For that purpose, specific effort was done to model the ternary fluid phase equilibrium of the CO_2–water–IPA system. Use of an adapted thermodynamic model is indeed expected to improve description of the column operation since, in previous works about fractionation of aqueous isopropanol mixtures [12,13] the thermodynamics behaviour of the system was represented by a simplified approach based on the use of a constant partition coefficient.

2. Materials and methods

2.1. Materials

Carbon dioxide was supplied by Air Liquide (≥purity 99.98%) and isopropanol is from Sigma–Aldrich (≥purity 99.8%). Distilled water was used for aqueous mixtures preparation.

2.2. Experimental set-up

The experimental set up (Fig. 1) was purchased from the Separex Company (Champigneulles, France). This device consists of a 2 m high column with 17 mm internal diameter, filled with random packing made of “spring” shaped stainless steel elements (see photo in Table 1) whose dimensions are 5 mm length and 3 mm diameter. The wire diameter of the spring is 0.55 mm and its extended length is 62 mm. The specific surface of this packing was theoretically evaluated from the number of elements per unit volume (experimentally determined by manual counting) and computation of the surface of an element. If it is assumed to evaluate the specific surface considering the entire surface of the wire constituting the spring, the value of the specific surface of the packing is then computed at $a = 1184\ m^2/m^3$. The void fraction ε was experimentally measured at 0.75. This measurement was done in a tube of the same diameter as the column, thus including wall effects.

In this work an original packing made of open cellular metallic (FeCrAlY) foam (5 Pores per Inches, characteristic dimension of pores 4 mm) was also tested. It is composed of 5 cm high, 17 mm diameter cylindrical pieces that were cut out from blocs of metallic foam (using water jet technology) and stacked inside the column. Its void fraction is 0.92 and its specific surface is equal to $a = 610\ m^2/m^3$, evaluated elsewhere [37]. Characteristics of both packings are gathered in Table 1.

The column is equipped with four type J temperature sensors (±1 °C) distributed along the column wall and temperature is regulated by an electrical heating device. Pressure is measured by a 0–400 bar manometer (±2 bar). A specific device made of two automatic valves in series, alternatively closed and opened by a