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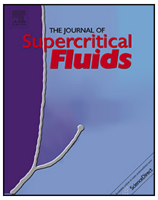

Multi-scale experimental study and modeling of the supercritical fractionation process

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ABSTRACT

In this work, the fractionation of water–ethanol mixtures by supercritical carbon dioxide at 333 K and 10.1 MPa was used as a model system to compare experimental extract and raffinate compositions and overhead loadings at laboratory, pilot and industrial scales to contribute toward a sizing methodology for counter-current supercritical fractionation columns. A series of three columns with an internal diameter of 19, 58 and 126 mm and with a height of 2, 4 and 8 m respectively were used for the different scales, meaning scaling factors from 9 to 44 between columns. The massic solvent-to-feed ratio was varied between 5.2 and 78.8. Experimental results at the different scales are analyzed and compared from the thermodynamic, mass transfer and column hydrodynamics points of view; and also using process simulation by equilibrium-stage models. In total, 42 successful experimental runs are taken into account, including 6 at a pilot scale unit and 2 at an industrial scale.

1. Introduction

The supercritical fractionation process allows the separation of liquid mixtures by use of a solvent under supercritical conditions. It relies on the difference of solubility of the feed components in a solvent. Supercritical fractionation of a feed mixture can be implemented in a continuous mode, contrary to supercritical extraction from solid matrices. In order to put in contact the feed and the solvent, a counter-current column setup can be used. In this configuration, the lighter solvent-rich phase, *i.e.* the overhead, is recovered at the top of the column. Then, depressurization of the overhead produces the condensation of the extract, whereas the raffinate, which corresponds to the highest density phase, is recovered directly at the bottom of the column [1,2].

The long-term goal of this research is to provide a reliable method for the conception of an industrial-scale fractionation of fatty acid esters derived from microalgal oil. Although the feasibility of the enrichment of several oil components has been previously attested in literature [3–7], the prediction of the throughput capacity of a counter-current column has received less attention [2]. The operation feasibility utterly depends on the solvent selectivity toward the targeted compounds, which is a thermodynamic variable obtainable from vapor–liquid equilibrium (VLE) data. However, hydrodynamic and mass transfer factors must also be taken into account for the conception and sizing of supercritical fractionation units. These factors are affected in turn by process variables such as the feed and solvent flow rates; fluid properties such as feed and solvent densities, viscosities, individual component diffusivities and interfacial tension; and equipment considerations such as the column diameter, height and absence or presence of packing elements and their characteristics. Most literature on the subject has focused on proving the feasibility of difficult separations, such as the purification or concentration of eicosapentaenoic acid and dodecahexaenoic acid (EPA and DHA, respectively) from fish oil [3,8–10]; breaking of azeotropes, *i.e.* water/ethanol [11–13] and water/2-propanol [11,14]; dealcoholization of beverages [15–17]; the separation of heavy waxes from petroleum residues [18,19]; the purification of essential citrus oil [20–27] and the recovery of high-value products from natural matter (principally α-tocopherol and squalene) [28–32]. In most cases, carbon dioxide is used as the working solvent given its low critical temperature (31.06 °C), moderate critical pressure (7.38 MPa), large availability at low cost and low reactivity. It has also been given a “Generally Recognized As Safe” (GRAS) status by the U.S. Food and Drug Administration, encouraging its use in the pharmaceutical and food industries. Although the operation has shown to be of promise, no widely implemented industrial application is found even if industrial fractionation units do exist.

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The purpose of this work was to explore the reliability of laboratory-scale experiments for the conception of a large-scale fractionation unit. To do so, small-scale experimental data have been compared to experiments carried out in larger-scale units. Also, experiments carried on larger fractionation units have provided more information about the influence of the solvent apparent velocity and of the nature of the packing on the efficiency of the operation.

In order to be able to extent the discussion to the hydrodynamics and mass transfer aspects of the operation and not only to limit it to the thermodynamic modeling of the equilibrium concentrations, a widely studied system was chosen to determine the limits and working range of the column and validate the experimental procedure for further studies. The ethanol–water fractionation by supercritical carbon dioxide was selected, being the most studied operation of its kind. This process drew the attention of the scientific community as a mean to overcome the thermodynamic restraints on distillation processes to obtain pure ethanol in a single step imposed by the existence of the water–ethanol azeotrope [12,33–35]. In order to take advantage of the equilibrium data of Budich and Brunner [35], Lim et al. [36], and Furuta et al. [37] working temperature and pressure of 333 K and 10.1 MPa, respectively, were chosen.

Supercritical fractionation of ethanol–water mixtures by carbon dioxide has been previously modeled by Budich and Brunner [35] using the Ponchon–Savarit method, however, little experimental fractionation data was available and no comparison was drawn between experimental and simulated data. The McCabe–Thiele method was also portrayed by Brunner and Machado [7] for the fractionation of edible oils, and in this case a good agreement between experimental and simulated data was found.

In this work, three fractionation columns were used with internal diameters of 19, 58 and 126 mm and heights of 2, 4 and 8 m respectively. Experimental results at the different scales are analyzed and compared from the thermodynamic, mass transfer and column hydrodynamics points of view; and also using process simulation by equilibrium-stage models. In particular, experimental extract and raffinate compositions as well as overhead loadings at different scales are compared and discussed.

2. Materials and methods

2.1. Chemicals

Double-distilled water and technical-grade anhydrous ethanol (>99.8%) from Carlo Erba Reagents (France) were used. Technical grade carbon dioxide (>99.8%) used was provided by Air Liquide Méditerranée (France).

2.2. Experimental conditions

Through all experiments, the fractionation column temperature was kept at 333 K and pressure was regulated at 10.1 MPa. These conditions were chosen based on available experimental VLE data. According to the solvent-to-feed ratio, the liquid feed was selected as the dispersed phase.

2.3. Analytical methods

All water–ethanol compositions were determined by density measurements. Samples were treated by ultrasound in order to remove excess carbon dioxide. Compositions were obtained from literature density tables [38]. All reported values were obtained with an Anton Paar DMA 4500 unit (Austria).

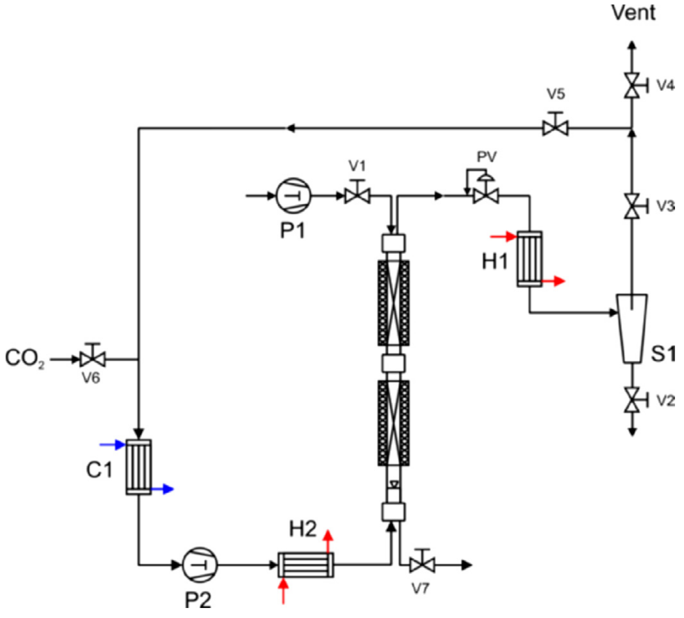

Fig. 1. Schematic diagram of the laboratory-scale fractionation column.

2.4. Laboratory-scale unit

2.4.1. Description

A simplified schematic diagram of the laboratory-scale fractionation set-up is shown in Fig. 1. This fractionation unit supplied by Separex (France) includes a packed column with an internal diameter of 19 mm and 2 m height with a viewing cell located at the bottom of the column, below the solvent injection nozzle. The column is able to withstand pressures up to 35 MPa, and its temperature is controlled by means of two independent heating jackets. The column is filled with 10 mm Interpack random packings from VFF (Germany), with a measured apparent density of 588 kg m^{-3}, a specific surface area of 580 m^{-1} and a void fraction of 0.917 in order to improve mass transfer efficiency.

During operation, carbon dioxide under roughly 4.5 MPa is cooled to 275 K in a double tube heat exchanger (C1) before being pumped and then heated to the working temperature (H2). A high pressure piston pump (P2) from Separex (France) with a top capacity of 15 L h^{-1} of liquid carbon dioxide and a maximum attainable pressure of 35 MPa delivers the supercritical solvent at the suitable flow rate. When the supercritical solvent leaves the column, the overhead current is depressurized through a backpressure regulator (PV) to recover the extract in a pressurized cyclonic separator (S1). The recovered solvent is then recycled and condensed into the cooler (C1) to reduce carbon dioxide consumption. The liquid mixture is fed by a Gilson 307 HPLC piston pump (P1) (France), with a 20 mL min^{-1} ($\sim$1.2 kg h^{-1}) maximum capacity. The carbon dioxide flow rate is controlled by a Rheonik RHE 14 mass flowmeter (Germany), while the liquid feed flow rate is directly controlled by the pump speed.

The extract and raffinate are collected from the bottom of the cyclonic separator and column, respectively, by manual regulation of the corresponding valves (V2 and V7). Under high feed rates, the liquid is continuously withdrawn, while an accumulation and purge method is preferred for small liquid rates. In the case of continuous withdrawal of raffinate, the liquid level in the column is kept constant by adjustment of the corresponding valve and observation through the windows at the bottom of the column. The corresponding dead volume is estimated to be 40 mL.