Supercritical CO_2 fractionation of ethanol-water mixtures

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Supercritical fractionation is a unitary operation of separation involving two immiscible phases, a liquid mixture as feed and a supercritical solvent. This process can be conducted continuously using a counter-current column and the use of supercritical carbon dioxide as solvent enables to operate a compact unit at low temperatures with a selective and safe solvent which may open many potential outlets for the supercritical CO_2 fractionation in different industrial fields. Currently, fractionations using supercritical CO_2 of alcoholic solutions, essential oils or lipid mixtures are the most widely studied in the literature [1]. However, supercritical CO_2 fractionation is still few widespread in industry and the development of reliable tools for its scaling up should allow easier deployment. To this end, an experimental campaign for the supercritical CO_2 fractionation of ethanol-water mixtures was carried out. Indeed, this mixture is of industrial interest for ethanol regeneration or beverage dealcoholization. Moreover, the CO_2-ethanol-water ternary system is close to a model system due to numerous thermodynamics data [2]. In addition, such fractionation studies performed at different scales could encourage industrials to invest in this process [3]. Preliminary measurements of interfacial tensions and contact angles with stainless steel of ethanol-water mixture in high pressure CO_2 were performed to take these properties into account in future modeling work [4]. The fractionation unit includes a packed column with an internal diameter of 19 mm and 2 m height; a separator allows to collect the extract and a view cell at the bottom of the column allows to manage the recovery of the raffinate. The CO_2 used was recycled after its separation with the extract by simple depressurization. After ultrasonic treatment to release the dissolved CO_2, ethanol mass fraction of extract and raffinate was determined by density measurements with a densimeter Anton Paar DMA 5000M. Fractionation process efficiency was studied as a function of several parameters such as the mass fraction of ethanol in the feed, working pressure and temperature, and solvent over feed flow rate ratio (S/F). The studied mixtures had ethanol mass fractions of 0.25, 0.50, and 0.75; working pressures and temperatures were of 10.1 and 15.1 MPa, 40 and 60 °C, respectively; finally, S/F ratios were around 9, 24 and 80. An experimental design was set up to determine the right operating conditions according to the targeted application. Globally, for beverage dealcoholization, the highest pressure, temperature, and S/F ratio, of 15.1 MPa, 60°C, and 80 respectively, led to the poorest ethanol mass fraction in the raffinate with less than 0.08 whatever the feed composition (Fig. 1a). Conversely, for ethanol regeneration, the highest ethanol mass fraction in the extract, at least of 0.87, was attained under the lowest pressure and temperature of 10.1 MPa and 40°C and at moderate S/F ratio between 9 and 24 whatever the feed composition (Fig. 1b).

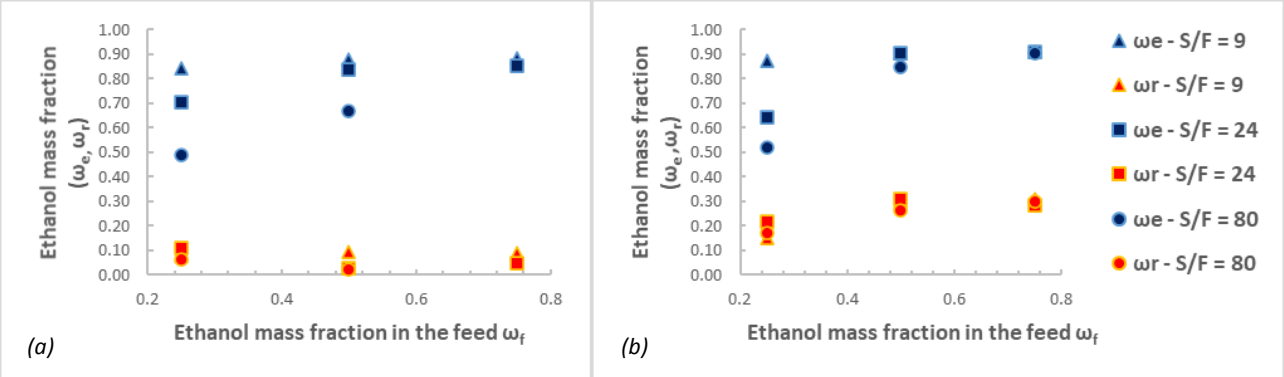

Figure 1 Ethanol mass fraction in the extract ω_e and in the raffinate ω_r versus the composition of the feed ω_f for different S/F ratios (a) 15.1 MPa and 60 °C; (b) 10.1 MPa and 40 °C

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