Process Integration of Supercritical Fluid Extraction and Membrane Separation to Recover “Vegetal” Squalene from Olive Oil Residues

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ABSTRACT

Vapor liquid equilibrium data are reported for the ternary system oleic acid– squalene – carbon dioxide in the temperature range of 313 – 333 K and in the pressure range of 10 – 22 MPa. Experiments were performed in a continuous-type equilibrium apparatus by using a static mixer ensemble to promote the equilibrium between the gas and liquid phases.

INTRODUCTION

One of the most promising applications of supercritical fluids (SF) is the extraction of high value natural compounds from residues of the food industry. Squalene is one of these compounds, used as a health-food or refined to squalane, a product used in pharmaceuticals and cosmetics. For the past decades the main source of squalene has been the liver oil of deep-sea sharks, where it is present at concentrations of 40 to 80% by weight. Strong environmental concerns with regard to the protection of the marine life, however, have focused the attention onto other sources, in particular to the residues from olive oil processing industries. Such residues, stemmimg from the olive oil deodorizer distillation, can contain up to 40% by eight of squalene and 30 to 40% by weight of free fatty acids. The processing of such effluents can hence add value to both the food industry and to the environment. Using supercritical carbon dioxide technology for the separation of squalene from free fatty acids, however, has been rendered difficult since, for example, in supercritical carbon dioxide their solubility is very similar. This work aims at surmounting this shortcoming by combining SF technology with a membrane separation process in order to separate squalene from fatty acids. The intention is to provide a novel hybrid process based on separation units that rely on different separation principles, and hence yield an increased overall degree of freedom for the optimised process design.

The first part of this work will be focused to the vapour-liquid equilibria of the ternary system squalene, oleic acid and carbon dioxide. This data was achieved in a static mixer apparatus that promotes the contact between the two fluid phases; the separation of both phases occurs in a gravimetric separation cell and samples from the gas and the liquid were collected and analysed.

Results are presented for different initial feed compositions in terms of the solubility of oil in supercritical carbon dioxide.

APPARATUS AND METHOD.

A schematic diagram of the apparatus used to obtain the phase equilibria data is showed in figure 1. The experimental runs were carried out by first bringing the apparatus to steady state conditions with respect to the carbon dioxide flow rate (pumped by means of a liquid metering pump, P01), and temperatures and pressures of the static mixer, SM, and separation column, GS. Then, the oil mixture was introduced in the apparatus via metering pump P02. The carbon dioxide and the oil feed were put in contact in a "tee" joint just prior to the SM entrance. Gas and liquid phase flows passed co-currently through the static mixer and, if certain flow conditions were followed, equilibrium was reached at the end of the static mixer. Separation of the two equilibrium phases was subsequently accomplished in a gravimetric separation cell, GS. The liquid phase was precipitated and collected at regular time intervals through valve V8 and into low pressure collector vessel CV01. Temperature and pressure of this vessel was continuously monitoring during this process. Functioning of valve V8 was controlled by direct observation of the liquid phase amount in the gravimetric cell due to a sapphire window located at the bottom of the cell. The carbon dioxide dissolved in the liquid phase was flashed from the oil, through valve V9, and measured by means of a gas flowmeter, GFM. This amount was later compared with the mass of oil collected in CV01 to determine the concentration of carbon dioxide in the liquid phase. The gas phase, exiting GS via the top, was expanded through air-driven valve EV into low pressure collector vessel CV02. Oil extract was recovered at regular time intervals through valve V12. Oil-free carbon dioxide phase was then recirculated back to the metering pump. The respective amount of carbon dioxide in the equilibrium gas phase was determined by subtracting the CO_2 mass quantity in the liquid phase (determined as above) to the total mass of CO_2 flowed through static mixer (given by the coriolis mass flowmeter MFM01). This value was subsequently compared with the mass of oil collected in CV02 to determine the oil solubility in high pressure carbon dioxide.

A Kenics static mixer (model 37-04-065) was used in these experiments, with an internal diameter of 4.928 mm, length of 178 mm, and 21 helical mixing elements.

The intrinsically dynamic process of this static mixer method to measure the phase equilibria of mixtures at high pressure conditions presents some sources of errors that must be outlined prior to execute the experimental runs. The main errors are an insufficient oil flow rate to achieve saturation of the gas phase, and a possible variation of the oil solubility with carbon dioxide flow rate. Other possible sources of error, like non-isothermal conditions in the SM plus separation column ensemble was carefully eliminated by a correct scale-up of the respective temperature control system. Also, pressure variations in the gravimetric column, GS, were set to a minimum by means of air-driven controlled valve, EV (Badger Meter RCV 807). The liquid flow rate was fixed throughout the equilibrium trials, at a value around 4-5 grams per minute, to assure that an excess of oil required to that to achieve saturation of the gas phase was always verified. Apparent solubilities of oil mixture in the carbon dioxide were measured at some random chosen conditions of pressure and temperature; experiments were carried out at a fixed oil feed flow rate and increasing gas flow rate. The standard fixed CO_2 flow rate was determined by checking the critical value where the solubility of oil in gas phase would start to decrease, due to a non-enough contact time in the static mixer ensemble. The actual equilibrium measurements were performed at a gas flow rate lower than the critical value.

Each experiment consisted of four measurements of the oil composition in the gas and liquid phases; only the last three samples were considered for the calculations. The reproducibility of the method was checked by randomly selecting a pair of pressure and temperature conditions and repeating the experimental trial several times. Reproducibility varies by less than 2% of the mean value. The experimental error for the solubility of oil in carbon dioxide was estimated to be at most ±0.001 g of oil/kg of CO_2 and that for carbon dioxide in oil to be ±0.01 wt %.

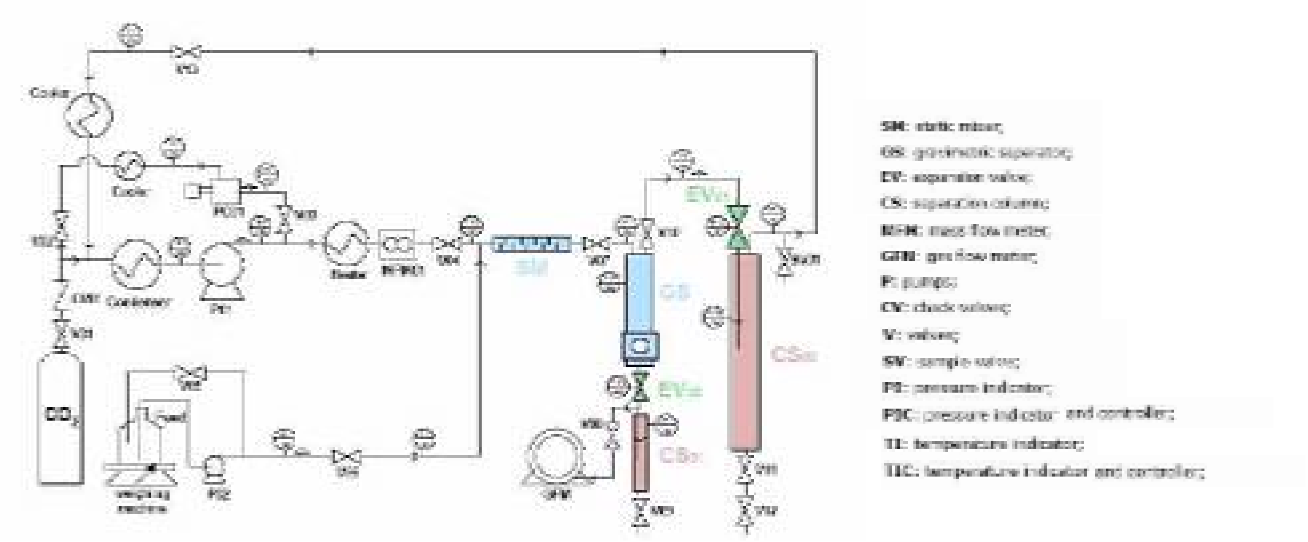

figure 1. Schematic diagram of the apparatus used to obtain the phase equilibria data

MATERIALS AND ANALYSIS

Carbon dioxide was supplied by Air Liquide with a purity of 99.995%. Squalene was supplied by Sigma (98% by weight) and Oleic Acid was supplied by Riedel-deHaën (88% by weight). The squalene content of oil in the liquid and gas phases was determined by Gas Chromatography.

RESULTS

The isothermal phase equilibria data of the ternary system is represented in figures 1 and 2 as the pseudo-binary system oil/ carbon dioxide; the mass fraction of CO2 in the liquid and vapour phases is plotted as a function of the extraction pressure, for the various feed compositions (figure 2.) and isothermal curves (figure 3.), it can be observed that:

- the amount of oil dissolved in the liquid phase increases with the pressure as well as the carbon dioxide composition in the liquid phase;

- an increase in the initial squalene content of the feed mixture causes an enlargement of the two-phase region;

- the oil solubility in the gas phase decreases as the mixture become richer in squalene (this can indicate that squalene is more soluble in carbon dioxide than oleic acid);

- as the temperature increases the total amount of carbon dioxide diminishes.

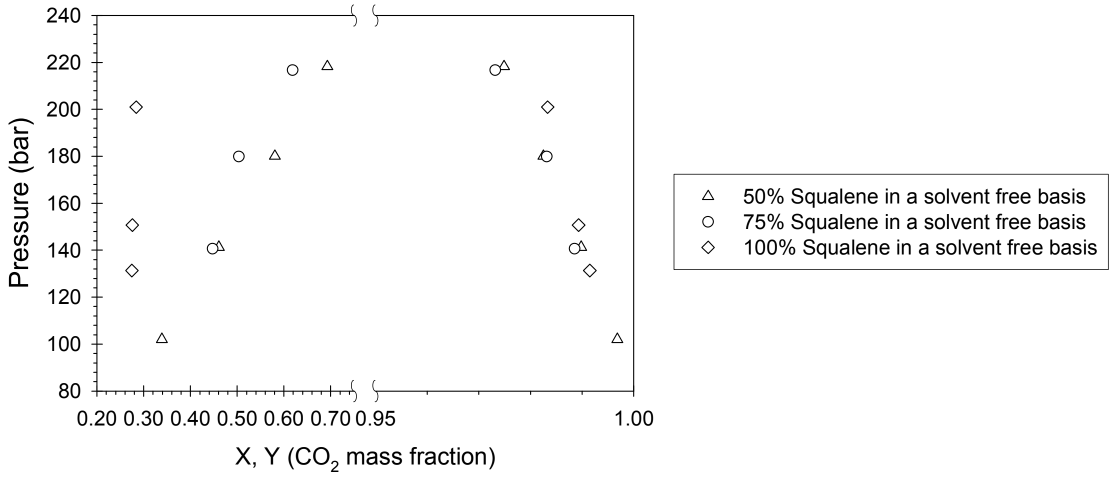

figure 2. Measured mass fraction of carbon dioxide (CO2) in liquid and vapour phases at 40ºC for several mixtures of different overall mass composition.

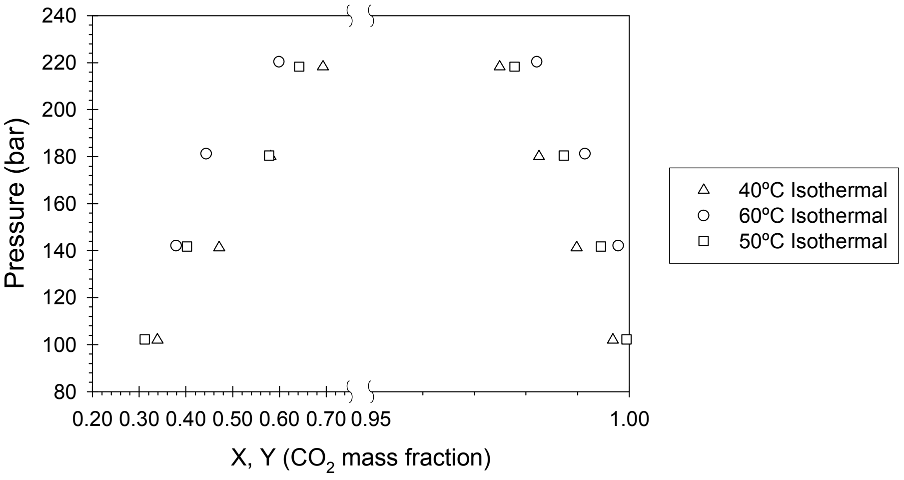

figure 3. Measured mass fraction of carbon dioxide (CO2) in liquid and vapour phases for an oil mixture with an overall mass composition of 50%wt fraction of Squalene (solvent free basis) at different isothermal curves.

The expected selectivity of supercritical carbon dioxide towards the squalene compound is better seen by the respective separation factor. This parameter is useful to identify the capacity of the supercritical solvent to separate two compounds at a given extraction condition. The selectivity is calculated from the respective compositions of squalene and oleic acid in the vapour and liquid phases

Representing the isothermal curves of selectivity as a function of pressure and for the oil mixture of 50wt% in squalene (figure 4), it is possible to see that carbon dioxide is more selective to squalene than for oleic acid, although that difference is not significant (their solubility is very similar with values of selectivity not higher than 3).

Based on these results, is possible to conclude that a simple extraction step is not sufficient to separate squalene from oleic acid.

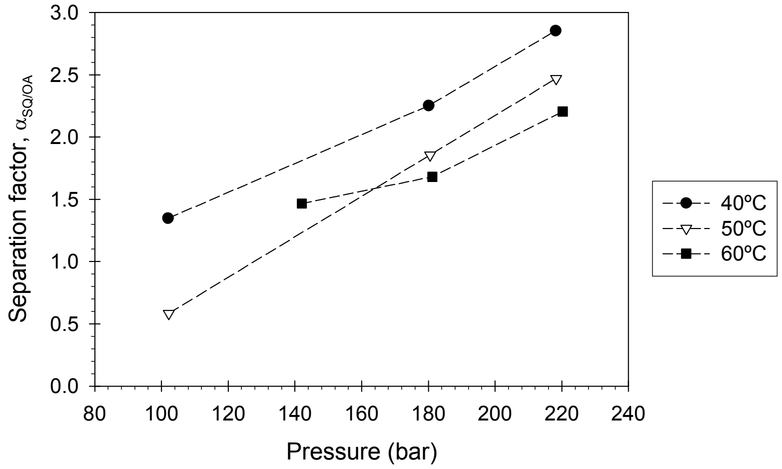

figure 4. Separation factor between squalene and oleic acid as a function of pressure for an oil mixture with an overall mass composition of 50%wt in squalene

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