DYNAMIC STUDIES ON A SCF COUNTERCURRENT EXTRACTION PROCESS

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The development of computational tools to describe industrial processes has increased in the last decades. Such tools are helpful to understand the flowsheet plants and/or just a single unit operation in a process.

The consistent design of a supercritical fluid (SCF) extraction process involving countercurrent packed columns requires reliable and robust steady state and dynamic state models; the usage of tough computational tools that are able to simulate a SCF process can be very valuable to evaluate its viability.

Here, we intend to present a dynamic simulation model of a countercurrent packed column operating at high pressure conditions. This model takes into account phase equilibria considerations, mass transfer and hydrodynamic characteristics. The model was developed and applied to a case study involving the fractionation of a model mixture of olive oil deodorised distillates. The composition profiles of the outlet streams from the packed column as well as hydrodynamic and mass transfer parameters were evaluated and their behaviour with time described by the dynamic model. Validation of the model was done by carrying out a series of experiments in a lab-scale continuous SCF extraction unit.

INTRODUCTION

Supercritical fluids have been largely applied in the field of separation processes, particularly in the extraction of high-value substances from natural products. The design and analysis of SFE processes require reliable computational tools to predict steady-state and dynamic process behavior. With a dynamic study it is possible to obtain information on the behavior of the whole process of extraction when subjected to disturbances in the load variables.

The current work has been developed to obtain a dynamic simulation model of a SFE countercurrent packed column for the extraction of liquid mixtures. This model can be used in the future for design, analysis, and optimization of SFE processes.

The proposed model was validated by performing a series of extraction experiments in a home-made supercritical fluid extraction lab-scale apparatus, equipped with structured gauze packing elements. The case study used in these validation experiments was the fractionation of a model mixture of methyl oleate and squalene by supercritical carbon dioxide. This mixture partly emulates the residues obtained from the olive oil refining process.

The dynamic model was developed by making use of a commercially available dynamic simulation software, gProms$^®$. This software allows the resolution of differential equations in order to time and position by using mathematical calculation procedures.

The simulation model incorporates a system of differential equations corresponding to the momentum material balances over the packed column and algebraic equations describing the mass transfer kinetics of the process, the hydrodynamic behaviour of the structured packing at high pressure conditions and the thermodynamic equilibria of the system under consideration. The material balances are made for a finite length of

packing and integrated to the overall packing height. The thermodynamic relations and the mass transfer and hydrodynamic equations were developed from experimental data previously collected [1-3]. Physical and transport properties of the gas and liquid phases flowing through the column are allowed to vary along the packed column and extraction time. A series of correlations for the density, viscosity, diffusion coefficient and surface tension of the studied system were developed for this work.

The input variables of the model are the initial pressure and temperature of operation, the flowrate and the composition of the supercritical solvent and liquid feed streams entering the packed column. The model allows the prediction of the composition and flowrate profiles of the extract and raffinate streams as a function of extraction time and position in the packed bed. It is also possible to quantify the residence time of liquid drops inside the packed (by calculating the extraction time it takes to come the first drops of raffinate on the bottom of the column) and the required time to reach steady state conditions (determined as the time when composition and flowrate profiles of all checked variables tend to a constant value). The pressure drop of the gas phase across the packed bed and the dispersed phase holdup can be traced during a simulated extraction run, as well as the effective interfacial area and the mass transfer coefficients.

The material balances for component i in the liquid phase and gas phase in each discrete packing section p are shown in the following equations

$$\frac{d}{dt}\{h_L \cdot (A \cdot e \cdot dz) \cdot r_{mL} \cdot X_i\}_p = L_{p+1} \cdot X_{p+1\_i} - L_p \cdot X_{p\_i} - J_{p\_i} \cdot dz$$

and

$$\frac{d}{dt}\{(1-h_L) \cdot (A \cdot e \cdot dz) \cdot r_{mG} \cdot Y_i\}_p = G_{p-1} \cdot Y_{p-1\_i} - G_p \cdot Y_{p\_i} + J_{p\_i} \cdot dz$$

where X and Y are the molar fractions of component i in the liquid and gas phase respectively, L and G the liquid and gas phase molar flowrates, z and t the dimensional time and position variables, h_L the dispersed phase holdup, and J_i the mass transfer flux of component i as given by

$$J_{p\_i} = r_{mG} \cdot K_{oG} \cdot a_e \cdot A \cdot (1 - e) \cdot \left(Y_{eqi} - Y_i\right)_p$$

with K_{oG} the overall mass transfer coefficient, a_e the effective mass transfer area, and Y_{eqi} the molar fraction of component i in the gas phase when in equilibrium with respective liquid phase.

EXPERIMENTAL

The extraction experiments carried out to validate the simulation model were made in a lab-scale plant for supercritical fluid extraction of liquid mixtures. In Figure 1 it is shown a schematic diagram of the apparatus.

This apparatus was modified for the purpose of performing the dynamic studies. A data acquisition system was installed in the SFE apparatus allowing the online acquisition of the pressure, temperature and mass flows all over the apparatus.

Materials

Carbon dioxide was supplied by Air Liquide with a purity of 99.995 wt%. Squalene was supplied by Sigma (98% by weight) and methyl oleate was supplied by Aldrich (70% by weight).
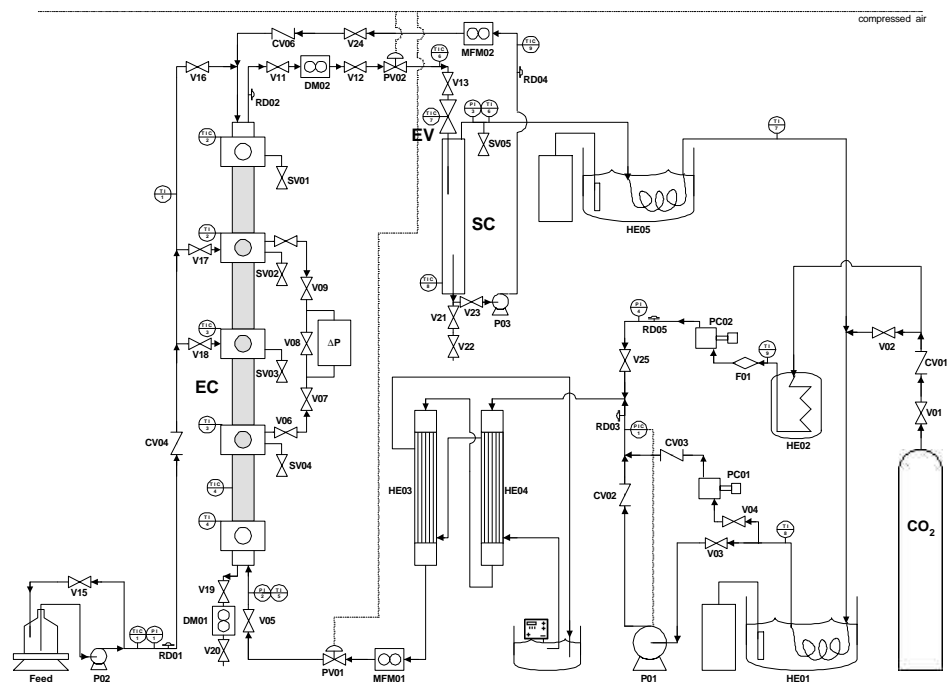
Figure 1. Schematic diagram of the experimental apparatus: CV#, check valve; EC, extraction column; EV, expansion valve; F#, line filter; HE#, heat exchanger; MFM#, mass flow meter; P#, pump; PC#, compressor; PI#, pressure indicator; PIC# pressure controller; PV#, pneumatic valve; RD#, rupture disc; SC, separation column; SV#, sample valve; TI#, temperature indicator; TIC#, temperature controller; V#, valve; DP, differential pressure transducer.

RESULTS AND DISCUSSION

The key parameters that were chosen to be continuously measured during an extraction run were the pressure in the extraction and separation columns, the temperature in a series of points along the apparatus (along the packing bed of the extraction column, in the separation column, in the gas compressor and in the expansion valve), and the mass flowrates of the carbon dioxide and liquid feed entering the packed column.

An example of a temperature profile obtained in a SFE experiment can be seen in Figure 2. A typical PID profile is observed.
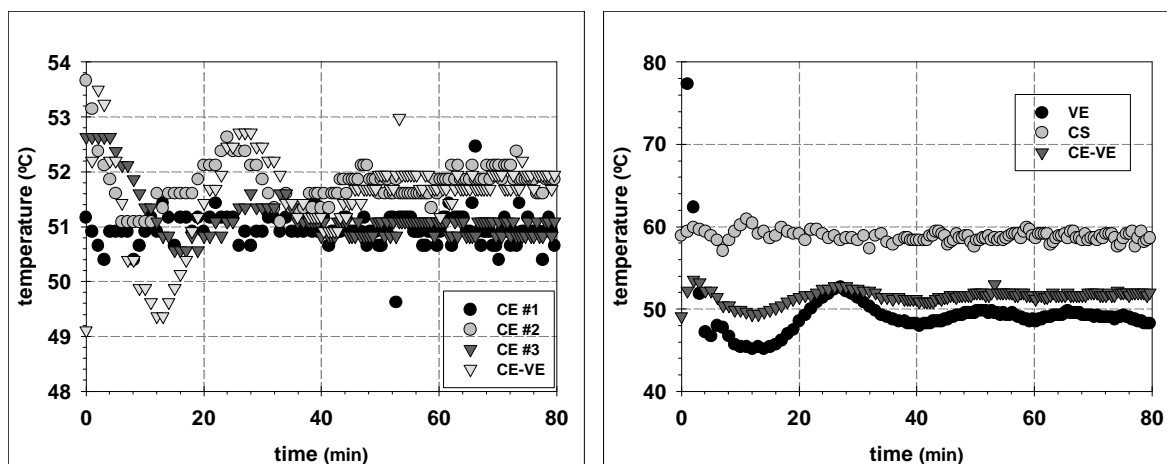
Figure 2. Temperature profiles in the SFE apparatus during carbon dioxide recirculation. CE: extraction column; VE: expansion valve; CS: separation column.

The dynamic model was validated by performing a series of extraction runs in the experimental apparatus and comparing the results thus obtained with the results predicted by the model.

For the extraction experiments two feed mixtures were studied, one with 40% by weight in squalene and the other with 70% by weight in squalene. The mass flow ratio between solvent and liquid feed in the packed column was varied in the range of 10 – 80; the pressure and temperature conditions of fractionation were 12.0 MPa / 313K, 12.0 MPa / 323K and 15.0 MPa / 323K.

Samples of the raffinate and extract streams were collected during constant time intervals from the beginning of experience and their composition analyzed for the squalene content by refractive index (RI). The RI method was previously checked against gas chromatography and was found to be a useful and rapid tool for data analysis.

In Table 1 we compare the experimental values of the weight fraction compositions of the raffinate and extract phases obtained at steady state to the predicted ones for several

extraction conditions. The mass flowratio was set at a value of 10 for an initial feed composition of 40% by weight of squalene.

Table 1. Weight fraction ccomposition of raffinate (X) and extract (Y) phases at steady state for several extraction conditions (MO: methyl oleate, SQ: squalene, CO2:carbon dioxide)

	X_{MO}	X_{SQ}	X_{CO2}	Y_{MO}	Y_{SQ}	Y_{CO2}
12.0 MPa / 313K						
Experimental	0.270	0.360	0.370	0.0201	0.0026	0.9773
Predicted	0.317	0.302	0.381	0.0186	0.0005	0.9809
12.0 MPa / 323K						
Experimental	0.379	0.281	0.340	0.0061	0.0004	0.9935
Predicted	0.358	0.283	0.359	0.0098	0.0002	0.9901
15.0 MPa / 323K						
Experimental	0.250	0.360	0.390	0.0242	0.0039	0.9720
Predicted	0.281	0.325	0.394	0.0252	0.0008	0.9740

A comparison between the experimental results obtained for the fractionation of a feed mixture with 40% by weight of squalene at 12.0 MPa and 323K and the predicted results by the simulation model is shown in Figure 3 in terms of the raffinate phase composition along the extraction run.

The agreement between the model and the experimental data is reasonable good. Still, the model predicts a residence time for the dispersed liquid phase within the packed bed lower than that experimentally observed. This can be attributed to an imprecise correlation for the dispersed holdup. Work has currently being done to correct this deviation.
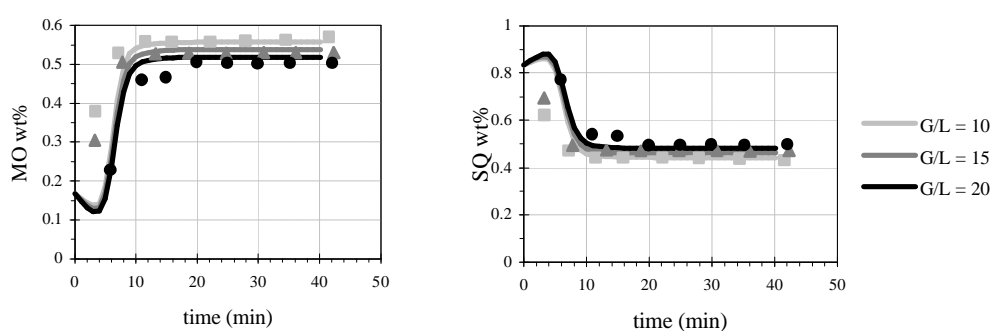

Figure 3. Composition profile of the raffinate phase for an extraction at 12.0 MPa and 323K; points: experimental data, lines: as predicted by the model. Compositions are expressed as weight fraction in a solvent free basis.

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