



Review

Modeling and optimization of supercritical fluid processes

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ARTICLE INFO

Article history:

Received 30 July 2008

Received in revised form

10 September 2008

Accepted 11 September 2008

Keywords:

Supercritical fluid extraction

Simulation model

Thermodynamic modeling

ABSTRACT

In this work, we discuss recent advances on thermodynamic modeling, process simulation and optimization of supercritical extraction and fractionation processes. The increasing availability of experimental data, as well as the need for estimation of economical viability, has encouraged the development of supercritical processes computer models. This review will discuss main approaches on phase equilibrium thermodynamic modeling of high-pressure processes, as well as process simulation. In this case, two main supercritical processes are considered: extraction of valuable products from solids and countercurrent fluid–fluid extraction and fractionation. In the latter process, again two main approaches are considered: rigorous models based on equilibrium stages and mass transfer models in packed columns. Finally, optimization procedures will be reviewed, both based on rigorous models and on experimental data.

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1. Introduction

The computer aided design, simulation and optimization of chemical processes has had an impressive growth during the last 50 years. During the same period supercritical fluids technology, mainly based on carbon dioxide, has found applications in many fields, from separations, chemical reactions to particle micronization and materials processing, due to its tunable solvent power, good transport properties and very low interfacial tensions. From bench scale to pilot plant and industrial size a wealth

of experimental information on supercritical processes is nowadays available. At the same time the development of supercritical processes was accompanied by improved models to describe the phase equilibrium of multicomponent mixtures at high pressures, and the prediction of physicochemical properties, viscosities, diffusivities and thermal conductivities in supercritical media. The combination of these methods together with rigorous mathematical modeling of different unit operations opens the way to the application of computer modeling and optimization of supercritical processes, which is of great interest, considering the cost of high-pressure pilot plant facilities and industrial scale experimentation.

The present review will cover advances in thermodynamic modeling, simulation and optimization of supercritical extraction and fractionation processes in the last 20 years.

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2. Phase equilibrium in natural product mixtures

The analysis of supercritical fluid processes requires the support of simulation tools based on rigorous modeling of complex phase equilibrium behavior. In these processes a new dimension, the *solvent density*, is added to tune the operating conditions and process scheme to the separation needs. This property is highly sensitive to changes in pressure, temperature and supercritical solvent composition. The development of thermodynamic models to describe the phase equilibrium in supercritical processes has been possible thanks to the wealth of experimental data that have been presented in the literature on high-pressure phase equilibria. A very extensive review of systems studied and the applied experimental techniques has been presented by Christov and Dohrn [1]. The experimental techniques can be classified as dynamic or flow, analytic (fixed or variable volume cell), synthetic, etc., examples of apparatus for different techniques are given by Richon [2].

Group contribution equations of state have been widely used for predicting thermodynamic equilibrium in supercritical fluid processes, as a great variety of natural products can be represented with a limited number of functional groups. The Group Contribution Equation of State (GC-EOS) model was proposed by Skjold-Jorgensen [3,4] to study gas solubilities in non-ideal mixtures at high pressures. This model was applied for the prediction and correlation of solubilities of solvents in supercritical fluids by Brignole et al. [5]. Temelli et al. [6] studied the thermodynamic modeling of the deterpenation of citrus peel oils with supercritical carbon dioxide and presented phase equilibria data at temperatures from 40 to 70 °C and pressures from 8.3 to 12.4 MPa. Experimental data were correlated with a simple model using vapor fugacity coefficients from the GC-EOS and unsymmetric convention activity coefficients. The original model takes into account only repulsive and dispersive interactions. Gros et al. [7] extended its capability to treat associating compounds (GCA-EOS) in mixtures of water and alcohols with non-polar gases, like propane or CO₂.

Natural oils and derivatives are complex mixtures of glycerides with fatty acids of different chain length and degree of saturation, but their molecular structure can be characterized with a few functional groups. Bottini et al. [8] and Espinosa et al. [9] proposed an upgraded version of the GCA-EOS, as well as revised sets of parameters for the use of this equation of state in the simulation of natural oils and derivatives processing with near critical fluids. Diaz et al. [10–12] tuned the Group Contribution Equation of State to predict thermodynamic properties for mixtures composed of citrus peel oils key components and carbon dioxide for representing supercritical deterpenation of lemon and orange peel oil, respectively. Fig. 1 shows a good agreement between GC-EOS predictions in multicomponent vapor liquid equilibrium [12] and experimental data [13,14] for the system orange peel oil, modeled as a mixture of linalool and limonene, and carbon dioxide. Sato et al. [15] used the Peng–Robinson equation of state (PR-EOS) [16] with two binary temperature dependent parameters to describe the phase equilibrium properties of limonene and linalool and they also discussed the process selectivity. Soave [17] applied the Soave–Redlich–Kwong equation of state [18] with Huron–Vidal mixing rules to describe the solubility of solids in supercritical solvents, using two adjustable parameters, vapor pressure and an interaction factor in the expression for its fugacity coefficient in the gas phase.

Raeissi and Peters [19] studied the double-domed retrograde vaporization phenomenon using the original Peng–Robinson equation of state [16] for the binary systems of ethane + limonene and ethane + linalool. Espinosa et al. [20] applied the GC-EOS model to predict the double retrograde behavior of ethane + limonene and ethane + linalool. In a later study, Raeissi and Peters [21] showed

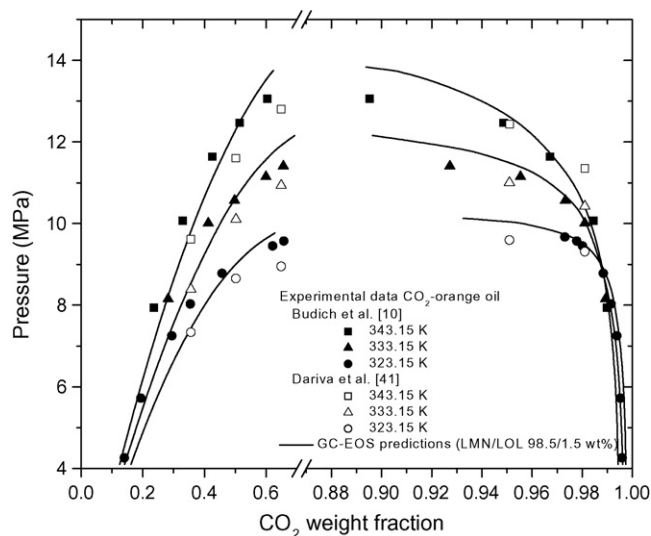


Fig. 1. GC-EOS predictions and experimental data for CO₂-orange peel oil.

that the Peng–Robinson equation of state, using the one-fluid van der Waals mixing rules, provided good qualitative predictions of double retrograde vaporization behavior for the ternary system CO₂ + limonene + linalool. At certain conditions, this phenomenon can cause the decrease in solubility of the less soluble component, while having no adverse effects on the solubility of the component to be extracted. More recently, Raeissi et al. [22] used the Soave–Redlich–Kwong [18] equation of state (SRK EOS) together with the classical one-fluid van der Waals mixing rules as the thermodynamic model for orange peel oil deterpenation with supercritical fluids. They tuned SRK adjustable binary interaction parameters to a combination of different literature data sets consisting of binary isothermal P–x,y, ternary constant composition P–T, and ternary isothermal isobaric x–y data of representative citrus oil component(s), limonene and linalool, with not only CO₂ as solvent but also with ethane.

Several approaches have been proposed for the prediction of thermodynamic equilibrium in mixtures of fatty acid ethyl esters with carbon dioxide. Coniglio et al. [23] studied phase equilibrium predictions of supercritical carbon dioxide with fish oil derivatives. They explored the combination of the Huron–Vidal first order (MHV1) and second order (MHV2) mixing rules [24,25] to combine the Soave–Redlich–Kwong equation of state with different excess Gibbs energy-based models such as UNIFAC/UNIQUAC and van der Waals models. They concluded that the MHV1 mixing rules used with modified UNIFAC [26,27] and a quadratic expression for the co-volume in the equation of state with a universal constant for all systems rendered very satisfactory results. Riha and Brunner [28] measured and modeled phase equilibrium of 13 different fatty acid ethyl ester mixtures and pointed out the need for further work on the thermodynamic modeling of these multicomponent systems, especially if separation of a real mixture is to be rigorously simulated and optimized. Espinosa et al. [9] modeled multicomponent vapor–liquid, liquid–liquid and vapor–liquid–liquid equilibrium of fish oil fatty acid ethyl esters with carbon dioxide with the extended GC-EOS. They introduced new pure groups for representing esters (CH₃COO and CH₂COO) and estimated binary interaction parameters with the remaining groups. Additionally, Espinosa et al. [29] proposed a strategy for the determination of hard sphere diameter for long chain esters with different degree of unsaturation as a function of pure esters van der Waals volume and the number of CH = CH groups in the molecule. These authors modeled phase equilibrium for multicomponent mixtures made up of thirteen fish oil FAEE

representing fish oils esters and carbon dioxide. A comparison with experimental data reported by Staby et al. [30] and Borch-Jensen et al. [31] showed good agreement with GC-EOS predicted values.

An alternative approach to equations of state to describe solute solubilities in supercritical fluids is the use of empirical models. Chrastil [32] proposed a linear log–log functionality between solute concentration in the supercritical fluid phase and its density. He derived this expression applying chemical equilibrium and entropy concepts. He reported agreement between predicted and experimental solubilities in supercritical carbon dioxide for several compounds, including stearic acid, oleic acid, behenic acid, tributyrin, tripalmitin, triolein, trilinolein, palmityl behenate, behenyl behenate, α -tocopherol, cholesterol, water, cafestol, naphthalene, anthraquinone and *p*-chloriodobenzene. Adachi and Lu [33] proposed a modification to Chrastil's equation in which the association number was calculated as function of solvent density. In a recent paper, del Valle and Aguilera [34] suggested a further modification by accounting for variations in the solute's heat of vaporization with temperature. They validated the model with experimental data for several vegetable oils in a wide range of pressure and temperature.

3. Process simulation models

3.1. Extraction of valuable products from solids

An important application of supercritical fluids is the extraction of one or more components from natural solid matrices. In most cases, this technology constitutes a cleaner alternative to the traditional industrial techniques, which are based on hexane extraction. Mass transfer processes take place when a solute is extracted from a fixed bed of a disintegrated vegetable material, with a solvent in supercritical or near-critical state. The pressurized solvent flows continuously through the bed of particles. After extraction, pressure is reduced and, consequently, solubility decreases and the solute precipitates in a separator. The process is characterized by an extraction curve, the plot of the cumulated extract versus the extraction time or the amount of solvent required in the extractor. The different approaches to mathematical modeling of extraction from solids range from models based on experimental data [35] or based on heat and mass transfer analogy [36,37] to the formulation of differential mass balances [38–42]. In the differential mass balances formulation, time dependent concentration profiles are obtained for fluid and solid phase through integration and the extraction curve is later calculated from the solute concentration at the extractor outlet stream. Sovova [41] presented a simple model which divides the extraction curve into three main sections. The first part, where extraction rate is constant, is controlled by the thermodynamic equilibrium between solute and solvent and external mass transfer. The last section considers the internal diffusion controls. The midsection is the only nonlinear section and represents the period where both internal and external mass transfer controls the extraction process. Martinez and Martinez [43] proposed global optimization strategies for parameter estimation in Sovova's model. Lu et al. [44] adjusted parameters of Sovova's model for the extraction of borage seed oil by compressed CO₂, based on their experimental data. They also studied the effects of the most important operating parameters (pressure, temperature, flow rate and bed length) on the rate of extraction.

Reverchon and De Marco [45] presented a comprehensive and critical overview of the analytical, processing and modeling aspects on supercritical fluid extraction and fractionation. They covered around 250 applications that range from extraction from solids to liquid feed processing and antisolvent extraction, focusing on the selection of operating parameters, examples of application and

mathematical modeling. Regarding solids processing, they reported more than 35 applications for the extraction of seed oils, essential oils or volatile compounds and to the adsorption/desorption of terpenic model mixtures, based on the three mentioned modeling approaches. Meireles [46] performed an exhaustive review on papers providing information on process parameters required for economical analysis of supercritical fluid extraction from solids, which is required to decide whether SFE can be considered among the feasible alternatives to produce high added value natural extracts. Experimental data were classified into two types, according to the extractor vessel size. For capacities greater than 50 ml, the SFE units were considered as process units, and for capacities lower than 50 ml, as analytical ones. She reviewed almost 40 applications for process vessels and more than 15 for analytical ones. Del Valle and De La Fuente [47] presented an exhaustive review on mechanisms of oil transport within the solid matrix, including desorption from the solid, formation of a shrinking core of condensed oil in a non-adsorbing porous matrix, and diffusion in a homogenous medium. They discussed on several simplifications of a general mass transfer as well as more complex two-stage models. They also analyzed trends for the external mass transfer coefficient and effective diffusivity in the solid matrix from studies on supercritical carbon dioxide extraction of oil from vegetable substrates. Furthermore, they analyzed the high-pressure vegetable oil-carbon dioxide phase equilibrium in connection with its influence on the mass transfer process.

More recently, and based on the model developed by Cocero and Garcia [48] considering the mass balance of solute into the SC phase and linear equilibrium, Lucas et al. [42] proposed a physicochemical model for the description of supercritical extraction, adsorption and impregnation processes. The model considers two parameters: convective flow transport between particles and bulk phase (supercritical solvent) modeling with an external mass transfer coefficient (k_f), and linear equilibrium on the matrix surface (h). In supercritical fluid extraction and adsorption processes parameter h considers two mass transfer steps (internal diffusion and adsorption/desorption equilibrium). In impregnation processes, this parameter represents the partition coefficient. These authors propose an analytical solution to model equations for simultaneously determining temporal and spatial profiles for solute concentration, both in the fluid and in the solid phase.

Zizovic et al. [49,50] introduced micro-scale mathematical models of essential oil supercritical fluid extraction process based on the hypothesis that essential oil extraction processes should be dependent on the type of secretory structure. Their objective was to verify the phenomena on the micro-scale and to optimize the supercritical fluid extraction process according to the behavior of specific secretory structure during the extraction. Supercritical carbon dioxide extraction confirmed previously reported phenomenon that particle size does not affect the evolution of extraction yield of some Asteraceae and Apiaceae family species.

3.2. Countercurrent fluid–fluid processes

3.2.1. Models based on equilibrium stages at steady state

In a typical supercritical extraction/fractionation scheme, the mixture to be fractionated is fed to an extraction column in countercurrent with carbon dioxide at high pressure. The extract is expanded and sent to a separator tank, where the condensed solute is obtained. The recovered solvent is recycled to the extraction unit after compression or pumping. Cygnarowicz and Seider [51] proposed a model for the dehydration of acetone with supercritical carbon dioxide. Both the extractor and the distillation column were modeled as equilibrium stages and thermodynamic properties have been calculated with the Group Contribution Equation of State [3,4].

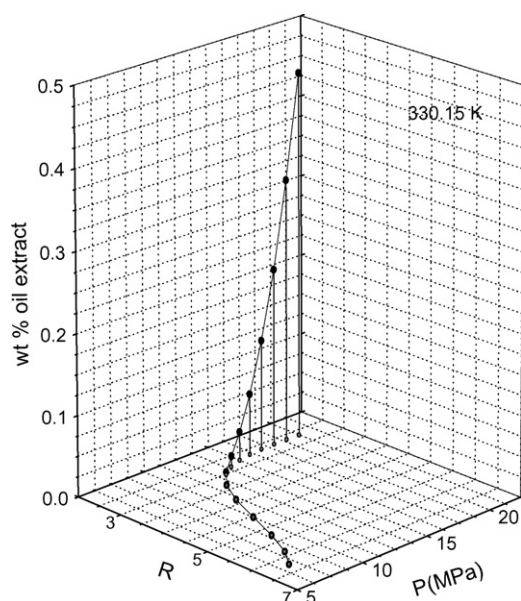


Fig. 2. Hexane extraction with CO₂ (R: solvent/feed weight ratio).

The model was developed within program SEPSIM [52] and the nonlinear program has been solved with a Successive Quadratic Programming algorithm [53].

Several authors [5,54,55] have proposed the use of light hydrocarbons at near critical conditions for the recovery of dehydrated oxychemicals from azeotropic or dilute aqueous mixtures. The process is based on a cycle in which the aqueous mixture is fed to an extractor and the solvent and the extracted product are separated in a solvent recovery column. This is the simplest two-column (extraction + distillation) separation process, typical of liquid or supercritical extraction. A main feature of this process is that the distillation column not only performs solvent recovery, but also completely removes water from the bottom product. In this way, dehydrated products can be obtained without additional columns. The hydrocarbon solvent shows good selectivity for the oxychemical recovery and also exhibits a water entrainment effect (water-solvent relative volatility greater than one in the solvent recovery column). Moreover, no azeotrope formation between the solvent and the extracted product is required. A thorough study of process alternatives for the recovery of ethanol from water using propane as supercritical solvent was presented by Gros et al. [56] through the formulation of simulation models based on equilibrium stages for the countercurrent extractor and the distillation column, as well as thermodynamic predictions with a Group Contribution with Association Equation of State [57]. The simulation program included rigorous models for a high-pressure multistage extractor [58], low and high-pressure distillation columns [59], and a multiphase flash [60].

Espinosa et al. [61] developed a rigorous simulation model based on the above mentioned unit models [58–60] to study the use of CO₂ for the removal of liposoluble pollutants or valuable substances from natural oils. Both CO₂ and propane were considered as SC solvents; the latter one with greater solvent power than CO₂ for organic solutes, but with the disadvantage of being flammable. Fig. 2 shows concentration of oil in the extract as a function of pressure and solvent to feed ratio (*R*) required for achieving treated oil specifications (5 ppm for hexane in raffinate). It can be seen that *R* is almost constant (2.7), when operating above 15 MPa. However, when pressure increases from 15 to 20 MPa there is a drastic increase in oil concentration in the extract.

Another application of supercritical fluids in countercurrent processes is the selective entrainment in the fractionation of fish oil fatty acid ethyl esters (FAEE). Numerous experimental studies have been reported and, therefore, several authors have proposed mathematical models of different complexity. Krukoniš et al. [62] proposed a two-column scheme and presented simplified simulation results for the continuous recovery of eicosapentaenoic acid (EPA) and docohexaenoic acid (DHA) esters from urea-adducted menhaden oil ethyl esters. Espinosa et al. [29] extended their rigorous simulation model [61], integrated to GC-EOS [8] to represent a fractionation scheme for a 13 component FAEE mixture, consisting of three consecutive supercritical columns with reflux for the production of highly concentrated streams of EPA and DHA esters from both natural and urea-adducted fish oil FAEE. More recently, Espinosa et al. [63] proposed a single column scheme for the production of pharmaceutical grade concentrates of eicosapentaenoic acid and docohexaenoic acid esters, within an optimization environment. They compared ethane and carbon dioxide as supercritical solvents, concluding that ethane shows a better performance, with higher selectivity to EPA and DHA among the esters with the same number of carbon atoms, together with higher solubility of these esters in ethane.

Supercritical fluid fractionation by extraction with carbon dioxide is also an attractive alternative for the deterpenation of citrus peel oils, as it combines low operating temperatures that prevent products from thermal degradation, and a benign solvent. In citrus deterpenation, the main issue is to produce desirable flavors for processed orange peel oil and to minimize undesirable features such as bitterness. Budich et al. [13] and Budich and Brunner [64] carried out a thorough study on the deterpenation of orange peel oil with supercritical carbon dioxide, reporting phase equilibrium data, countercurrent column experiments and flooding point measurements. They also formulated a simplified model, based on vapor liquid equilibrium data, to perform stage calculations and a preliminary scale-up of the deterpenation process. Citrus peel oil extraction optimization has been addressed in our group using different fractionation schemes and alternative supercritical fluids [11,12,65]. A discussion on optimization models and results is given in Section 4.

Castier and co-workers have developed the simulation software program *Thermat*, based on *Mathematica*®, and integrated to Fortran routines for the calculation of thermodynamic properties. Process models were developed for the simulation of isothermal extraction columns [66], dynamic simulations of flash drums, parameter fitting interval arithmetic [67] and the simulation of simple and reactive distillation columns [68]. Nogueira et al. [69] extended *Thermat* for the simulation of isothermal and non-isothermal supercritical extraction columns. As an example, they modeled the separation of ethyl acetate, isoamyl alcohol, ethanol and isoamyl acetate, which are present in an enzymatic transesterification reaction, with carbon dioxide as SC solvent. The resulting algebraic equation system was solved with the Newton–Raphson method and phase equilibrium was modeled with the Soave–Redlich–Kwong (SRK) equation of state (EOS) with the Huron–Vidal mixing rule.

Several authors have addressed dynamic simulation of countercurrent supercritical extraction processes. Cygnarowicz and Seider [70] performed a dynamic analysis of β-carotene recovery from fermentation broths by SC CO₂, studying the influence of feed load and vapor flow rate-induced disturbances on product separator pressure. Sato et al. [71] reported the semi-batch deterpenation of orange peel oil with supercritical carbon dioxide; they studied the effect of internal reflux induced by a temperature gradient in the column, on process selectivity and product recovery, using the Peng–Robinson [16] equation of state to estimate the ternary phase

equilibria. These authors also reported laboratory-scale data for the continuous countercurrent extraction of terpenes from orange peel oil. Benvenuti et al. [72] modeled a semi-continuous single-stage process for deterpenation of natural lemon oil, where equilibrium conditions were determined with the Peng–Robinson equation of state [16], assuming that the vapor phase leaving the apparatus was always in equilibrium with the liquid stationary phase inside the vessel. These authors implemented the differential algebraic system representing the SCF process in gPROMS [73] and their predictions are in good agreement with experimental data they have obtained in their laboratory. Additionally, they report simulation results for a steady state countercurrent process, simulated with the commercial simulator Aspen Plus.

3.2.2. Models based on mass transfer approaches

Several authors have proposed mass transfer models for the simulation of extraction columns at high pressure. De Haan and de Graaw [74] developed a mass transfer model for the fractionation of hydrocarbons with supercritical carbon dioxide, in which physical properties were represented by correlations. They reported numerical and experimental results for the separation of hexadecane and 2-methylnaphthalene with carbon dioxide at high pressure and found good agreement between measured and calculated height equivalent of a theoretical plate (HETP). The model was based on a previous one proposed by Bravo et al. [75] for structured packing distillation columns. These authors, Rocha et al. [76], extended the model for packed distillation columns. Ruivo et al. [77] compared the performance of several available mass transfer models in packed columns with experimental results obtained at their laboratory in a countercurrent supercritical extraction packed column of 2 m height and 2.4 cm internal diameter for the fractionation of a squalene/methyl oleate mixture by supercritical carbon dioxide. They concluded that the model proposed by Rocha et al. [76] was appropriate for modeling high-pressure extraction systems with corrugated gauze packing columns.

More recently, Ruivo et al. [78] formulated a dynamic model for the simulation of a SCF extraction column with structured packing for the fractionation of a binary mixture of squalene and methyl oleate, with SC carbon dioxide. The model comprises a set of partial differential equations (PDE) for the differential mass balances on the packed column, algebraic equations for mass transfer, hydrodynamics of the two-phase flow through the packings and thermodynamic equilibrium. They transformed the PDE into an ordinary differential equations system by performing a spatial discretization with finite volumes. The ternary phase equilibrium was calculated with a simplified empirical correlation, as function of pressure, temperature and squalene composition in the liquid phase. Column temperature was assumed constant. The model was implemented in gPROMS [73] and the authors report a good agreement between measured and predicted composition profiles of the outlet streams. Fernandes et al. [79] extended the model to account for non-isothermal conditions in the packed column.

Martin and Coccero [80] developed a rigorous model of a SCF fractionation column, which includes differential mass and energy balances in the column, and coupled mass and heat transfer in the interface between the two fluid phases. Mass transfer is represented by means of the generalized Maxwell–Stefan relations for multicomponent systems and thermodynamic properties are calculated with the Stryjek–Vera Peng–Robinson equation of state [81]. Transport properties (diffusivity, viscosity and interfacial tension) were calculated with correlations. The entire model for the extractor was represented with a differential algebraic equation (DAE) system that was solved in an iterative way to include the calculation of the reflux flash. To solve the DAE, these authors used an ordinary differential equation solver based on an explicit

Runge–Kutta 4–5 formula, implemented in Matlab [82]. At each integration step, an algebraic equation system was solved for mass and energy balances to the interphase at each column height and physical properties calculation. The model was used to simulate the separation of a binary mixture of squalene and methyl oleate, reported by Ruivo et al. [78], and the fractionation of fish oil fatty acid ethyl esters [83]. In this case, long chain fatty acid ethyl esters were lumped into two pseudo components: one representing low molecular weight components (LMC, with carbon numbers from C14 to C18) and a high molecular weight component (HMC, C20–C22). In both cases, carbon dioxide was used as supercritical solvent.

In a recent paper, Varona et al. [84] have addressed modeling and experimental determinations for the separation of linalool and linalyl acetate, main components of lavandin oil, using the previously described model for packed extraction column and flash condenser.

4. Process optimization approaches

As high-pressure processes render important energy consumption, they must be highly integrated to be economically feasible. Special attention must be devoted to solvent cycle scheme [85]. There are different sequences of operations to change the solvent state conditions and composition; they depend on operating conditions of the main process, the nature of the solvent and the scale of the process unit. In supercritical fluid processes, the solvent can be driven either by a compressor or by a pump and it can be recycled either in supercritical or in liquid state. If there is a pump cycle, lower fixed costs are associated to pumps as compared to compressors and energy consumption is lower than the compressor process for pressures higher than 300 bar. As a disadvantage, the pump cycle requires several heat exchangers and condensers and additional heat energy at low extraction pressures. The compressor cycle needs only one heat exchanger and it shows low heat energy consumption but it has higher fixed costs for the compressor, higher electrical energy consumption and lower energy consumption compared to the pump cycle for pressures lower than 300 bar. Solvent cycle determination constitutes an important design problem in supercritical fluid processes.

Cygnarowicz and Seider [51] formulated a nonlinear programming model to minimize either the utility or the annualized cost for the dehydration of acetone with supercritical carbon dioxide. Based on the rigorous simulation models proposed by Gros et al. [56] and within a mixed integer nonlinear programming framework, Diaz et al. [86] formulated models for the optimization of the dehydration of oxychemicals with supercritical light hydrocarbons, associating binary variables to potential process units. The objective function was process energy consumption minimization. They studied several aqueous mixtures with oxychemicals such as ethanol, 2-propanol and acetone at different concentrations and the use of several dual effect solvents, such as propane and isobutane.

Diaz et al. [10] formulated a mixed integer nonlinear programming model for the simultaneous determination of operating conditions and process and solvent cycle scheme, including investment and operating costs for the entire process in the deterpenation of lemon peel oil with supercritical carbon dioxide. The objective was the maximization of net profit, while fulfilling product recovery and purity specifications. Discrete decisions, associated to binary variables (y) were related to the potential existence of units in the solvent recovery system (mainly represented by a compressor or a pump cycle). Fig. 3 shows a deterpenation process superstructure. Rigorous simulation models [58–60] were integrated to the extended GC-EOS [9], while heating, cooling and compression loads in the solvent recovery cycle were calculated with rigorous models

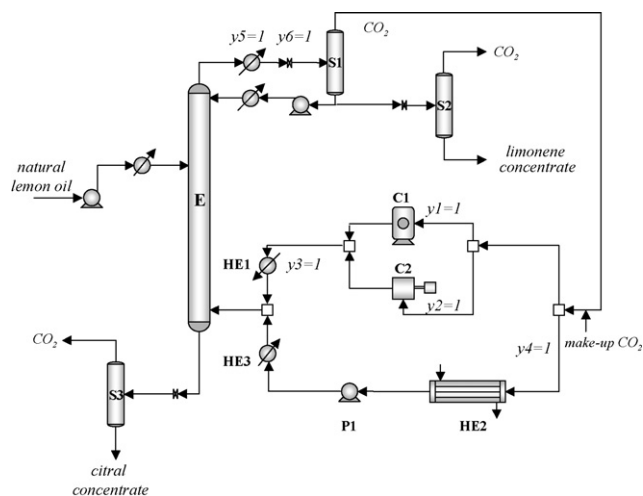


Fig. 3. Supercritical deterpenation scheme with solvent cycle superstructure.

based on SRK [18] predictions (for a single component, carbon dioxide). The mixed integer nonlinear programming model was solved with the Outer Approximations algorithm [87], in which nonlinear problems were solved with a Successive Quadratic Programming algorithm [88] and mixed integer linear problems were solved with LINDO [89] within a Fortran 90 environment. Simulation results were also checked against pilot plant data.

As the main alternatives for the solvent recovery system can be lumped into a pump and a compressor cycle, Diaz et al. [11,12] performed the optimal design of process and solvent cycle for the deterpenation of orange peel oil by formulating and solving two nonlinear programming problems representing the process and solvent cycle for those two cycles, respectively. To perform column sizing, they used correlations for the estimation of the minimum inner diameter derived by Budich and Brunner [64], based on their experimental flooding results for the extraction of orange peel oil with carbon dioxide over a wide range of pressure and temperature [64]. A comparison between optimal profit and costs was performed for the two alternatives, as well as a scale up of the process, as it is shown in Fig. 4 for a compressor cycle process. Nonlinear programming models based on rigorous models were also developed for fish oil fatty acid ethyl esters fractionation with supercritical

carbon dioxide [29] and ethane [63]. More recently, Raeissi et al. [22] proposed nonlinear models for the minimization of solvent flowrate in a deterpenation plant, using the Soave–Redlich–Kwong equation of state [18]. While achieving a fixed level of oil folding, they studied the performance of ethane as supercritical solvent.

Only few authors have addressed process optimization based on rigorous mass transfer models. Fernandes et al. [79] developed a dynamic optimization model for an extraction column, also including energy and momentum balances in the packed bed. They performed process optimization to maximize squalene recovery from a binary mixture composed of squalene and methyl oleate, with supercritical carbon dioxide within program gPROMS [73].

Alternative approaches include process optimization based on experimental data. L'etisse et al. [90] developed a quadratic correlation for the maximization of yield in EPA and DHA production from sardine oil, using carbon dioxide as SC solvent. They performed optimal design of experiments in their laboratory with the Doehlert uniform shell design [91], with five test points evenly distributed over the experimental domain. Independent variables were extraction temperature, solvent flow rate and operating time.

5. Conclusions

The great advances in the last two decades in phase equilibrium modeling, rigorous simulation and optimization of supercritical processing of natural products is opening the way to computer aided optimum design of supercritical plants for the extraction and fractionation of natural products. Phase equilibrium modeling of supercritical processes has been based in several approaches. Extensive use has been made of cubic equations of state in the extraction or fractionation of low to medium molecular weight solutes. When the mixture non-ideality is high, cubic equations of state have been combined with local composition models like UNIFAC. However, in highly asymmetric systems like propane or carbon dioxide with vegetable oils, the use of a more realistic repulsive term in the equation of state has been introduced to describe liquid–liquid and liquid–supercritical solvent phase equilibria. This approach has been used in the GC-EOS and extended for associating systems in the GCA-EOS. When modeling phase equilibrium in systems involving natural products, the use of group contribution methods has been a very efficient procedure to deal with multicomponent natural mixtures that can be described with a reduced set of groups. The use of specific correlations, Chrastil's equation for example, that take into account the effect of temperature and solvent density on solute solubility has found many applications in modeling the extraction from solid matrices. In the extraction of solutes from solids the use of semi-empirical models like Sovova's has been found in many applications. In recent work, rigorous modeling of mass and heat transfer in packed beds has shown promising results for the design and simulation of solid–fluid supercritical extraction, based on first principles. Stage by stage rigorous simulation of countercurrent processes combined with equations of state models has been successful in the synthesis, simulation and optimization of supercritical extraction and fractionation processes. Recently a rigorous approach, based on differential mass, heat and momentum balances equations, more suitable for packed columns, has been applied. Associated to advances in simulation and optimization software, increasingly detailed models can now be formulated to guide the development of industrial applications of supercritical fluid extraction and fractionation processes, especially in the field of high added value compounds, such as pharmaceutical and nutraceutical products.

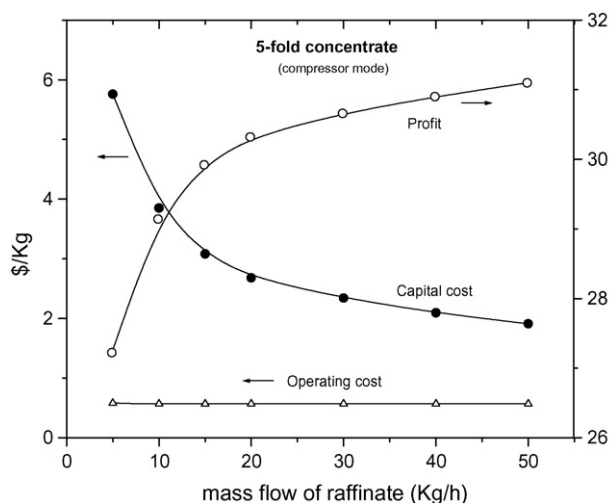


Fig. 4. Plant capacity optimization results for 99.9 wt% limonene purity in top product: compressor mode costs and profit for 5-fold raffinate product.

Acknowledgement

The authors gratefully acknowledge financial support from CONICET, ANPCYT, Universidad Nacional del Sur, Argentina.

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