

## Modeling and Simulation Tools for Supercritical Fluid Processes

S. Diaz, S. Espinosa and E. A. Brignole

Planta Piloto de Ingenieria Quimica - PLAPIQUI (UNS-CONICET)  
Camino La Carrindanga Km 7 - 8000 Bahia Blanca - Argentina  
e-mail: [ebrignole@plapiqui.edu.ar](mailto:ebrignole@plapiqui.edu.ar), [sdiaz@plapiqui.edu.ar](mailto:sdiaz@plapiqui.edu.ar), [espinosa@plapiqui.edu.ar](mailto:espinosa@plapiqui.edu.ar)

### ABSTRACT

The application of an upgraded group contribution equation of state combined with rigorous simulation and optimization to supercritical processes is reviewed and new applications are presented for vegetable oil purification and separation of fatty acid alkyl esters.

### 1. INTRODUCTION

Chemical processes with supercritical fluids have received increasing interest during the past decade. Experimental data are scarce and difficult to obtain. Several laboratory experiments with supercritical fluids have been reported, but there is still much research to be done on near critical fluid property predictions, rigorous unit simulations and synthesis and optimum design of these processes. Commercial process simulators provide a wide range of thermodynamic models for nonideal mixtures at high pressures. However, in many cases these models fail to give a realistic and quantitative description of the phase behavior, for example in mixtures of gases with associating components (Gros *et al.*, 1997) or with a wide range of component molecular weights (gases with tryglicerides) (Bottini *et al.*, 1999).

Gros *et al.* (1998) demonstrated the potential of rigorous process optimization and simulation to the synthesis and optimization of process schemes and conditions for oxychemicals recovery and dehydration from aqueous solutions, using the dual solvent effect (extraction and dehydration) of near critical light hydrocarbon gases. The synthesis problem of the extraction-dehydration has been solved as a mixed integer nonlinear programming problem, where the objective function represents the process energy consumption. Optimum process schemes depend on the oxychemical to be recovered, supercritical fluid used as solvent and feed composition (Diaz *et al.*, 1999).

Amaro *et al.* (1998) have applied a similar approach for the synthesis of operating schemes and selection of process conditions for the Gas Antisolvent (GAS) Crystallization Process of organic salts from aqueous solutions. In GAS a near critical gas is dissolved in the solution and the solute precipitates due to the gas strong antisolvent effect. However, organic salts are soluble in aqueous solutions, but nonpolar gases are not. Therefore a cosolvent is required to increase the gas solubility in the mixture. An operating scheme is found to achieve a high loading of salt in the crystallizer and complete miscibility of water in the gas antisolvent - cosolvent mixtures. Several cosolvents were identified and process conditions that maximize the water solubility in the crystallizer were proposed. The results were confirmed by crystallization experimental studies.

In this work the purification of vegetable oils from liposoluble contaminants is discussed; near critical propane and CO<sub>2</sub> are analyzed as potential solvents. Furthermore, the separation of fatty acid esters is studied with the use of supercritical CO<sub>2</sub> as a high-pressure entrainer. The process is based on the high solubility of long chain fatty acid alkyl esters in supercritical CO<sub>2</sub>. The process conditions depend on the main column pressure, temperature and CO<sub>2</sub>/feed ratio. The column reflux is obtained by heating and pressure reduction of the extract. The selection of optimum process conditions for this

separation process is illustrated for the separation of methyl myristate (C14:0) and ethyl stearate (C18:0) and for the recovery of EPA (C20:5) from a fish oil fatty acids mixture. The observed behavior may be applicable to other problems of purification or refining of fatty oils like removal of cholesterol from butter and milk fat.

## 2. THERMODYNAMIC MODELING OF SUPERCRITICAL PROCESSES

The GC-EOS model was proposed by Skjold-Jorgensen (1988) to study gas solubilities in nonideal mixtures at high pressures. This model was applied for the prediction and correlation of solubilities of solvents in supercritical fluids by Brignole *et al.* (1987). The original model takes into account only repulsive and dispersive interactions. Gros *et al.* (1997) have extended the capability of this model to treat associating mixtures (GCA-EOS) in mixtures of water and alcohols with non polar gases, like propane or CO<sub>2</sub>. Natural oils and derivatives are complex mixtures of glycerides with fatty acids of different chain length and degree of saturation. However, their molecular structure can be characterized with a few functional groups. The development of supercritical processes for the purification of triglycerides or derivatives requires the prediction of phase equilibrium compositions and conditions for mixtures of high molecular weight components with gases at high pressure. The use of the SRK equation or similar equations of the van der Waals family has proven to be unsuccessful to predict and correlate the complex phase equilibrium behavior observed in those systems. An upgraded version of the GCA-EOS model has been developed for the correlation and simulation of vegetable oils and derivatives processing with near critical fluids (Bottini *et al.*, 1999). In the application to high molecular weight compounds, the component critical diameter is adjusted from activity coefficient data at infinite dilution of alkanes in the heavy compounds. In the oil molecules, the number of methyl plus methylene groups are in the range of 40 to 60. For molecules of this size, even with moderate energetic interactions, it is very important to revise the binary energy parameters of CO<sub>2</sub> with (CH<sub>2</sub>) and (CH<sub>3</sub>) in order to avoid degeneration of the predictions with a large increase in molecular size (number of CH<sub>2</sub> groups). The same observation is valid for other interaction parameters like aromatic groups with (CH<sub>2</sub>) and (CH<sub>3</sub>). Bottini *et al.* (1999) and Espinosa *et al.* (1999) give revised sets of parameters for the application of the GCA-EOS for natural oils and derivatives. The model is able to describe multicomponent vapor-liquid, liquid-liquid and liquid-supercritical fluid equilibria.

## 3. MATHEMATICAL MODELING OF SUPERCRITICAL PROCESSES

The determination of operating conditions for different supercritical processes has been solved as Nonlinear Programming (NLP) problems. Design variables have been selected to represent main continuous decisions associated to each particular process. Equality constraints represent the process mathematical model and they are solved within a sequential process simulator. This program includes rigorous models for a high-pressure multistage extractor (Kehat and Ghitis, 1981), low and high pressure distillation columns (Naphtali and Sandholm, 1971), and a multiphase flash (Michelsen, 1982). The GCA-EOS has been integrated as thermodynamic support for these model unit simulation routines. Inequality constraints include process specifications, operating bounds and bounds on potential units. Depending on the type of process, different optimization goals have been analyzed.

The optimization program interacts with a rigorous sequential modular process simulator in a black box way and non-linear programming problems have been solved with OPT (Biegler and Cuthrell, 1985). The use of a black box simulator for function evaluation does not guarantee problem convexity and may converge to locally optimal solutions. Reported numerical results have been obtained running the program with different initial points that converged to the same optimum; this fact does not guarantee that the solution is the global optimum, but it enforces the fact that it is a strong local minimum.

#### 4. ANALYSIS OF SUPERCRITICAL EXTRACTION PROCESSES

##### 4.1. Removal of contaminants or valuable products from natural oils

Natural oils are prone to contamination with liposoluble pollutants. The use of CO<sub>2</sub> for the removal of pollutants or valuable substances from natural oils is a promising approach. CO<sub>2</sub> is an environmentally benign solvent and fatty oils have very low solubility in liquid or near critical CO<sub>2</sub>. Propane has greater solvent power than CO<sub>2</sub> for organic solutes, but has the disadvantage of being flammable. Besides, the liquid-liquid immiscibility between vegetable oils and propane is observed under a limited range of pressures and temperatures (Bottini *et al.*, 1999). Under these conditions the solubility of the oils in the propane phase is also very low. The removal of pollutants with near critical solvents from vegetable or animal oils or oils containing natural matrices, also requires the determination of optimal operating conditions. In this case, the solubility of the pollutants in the near critical phase should be increased keeping the solubilities of the TAGs in the extract phase at very low values. In addition, the density difference between the oil and the extract phase should be adequate when countercurrent operation is required.

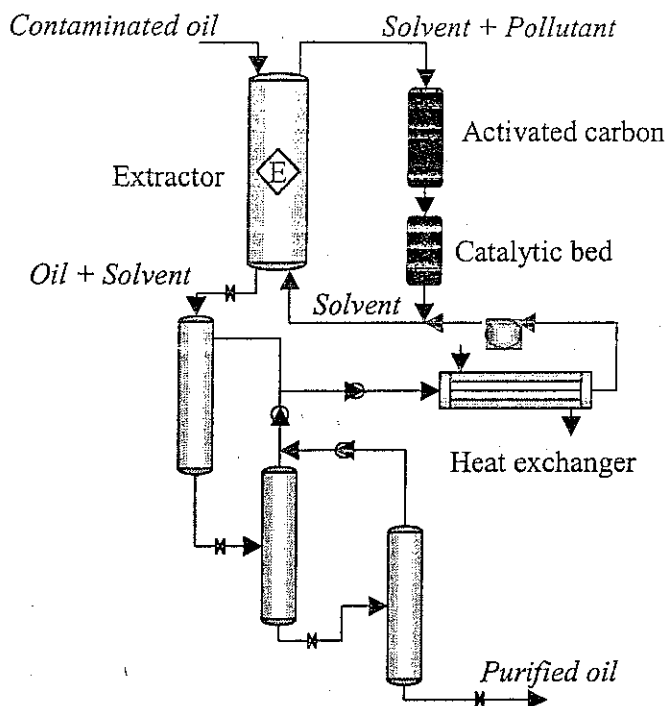


Figure 1. NCF extraction process flow diagram.

The extraction cycle and the solvent recovery system are shown in Fig. 1. An isothermal extractor of 15 stages is used. The concentration of solutes in the oil is studied in the diluted range: 1% for hexane and 0.01% for other pollutants. The objective is to minimize solvent-to-feed ratio (S/F) subject to an oil weight concentration in the extract lower than 0.05% and purity specifications (less than 5 ppm for hexane, less than 0.01 ppm for aromatics and chloroaromatics).

**Extraction with CO<sub>2</sub>:** The system vegetable oil - CO<sub>2</sub>, shows phase immiscibility under near critical and supercritical conditions. This immiscibility region extends to very high pressures. Therefore, the two-phase behavior, required for countercurrent removal of pollutants with CO<sub>2</sub> is observed over all foreseeable operating conditions. The optimization of operating conditions is performed for temperatures in the range  $303 \leq T \text{ (K)} \leq 340$  and for pressures  $7 \leq P \text{ (MPa)} \leq 20$  to minimize solvent-to-feed ratio. Table 1 shows optimization results for the extraction of different pollutants.

**Extraction with Propane.** For the class of solutes studied in the present work, propane is a better solvent than CO<sub>2</sub>. The use of propane requires working with temperatures above the lower critical end point (LCEP) of mixtures of propane with TAGs. At temperatures below the LCEP, propane and oil are completely miscible. However when the liquid phase splits, the solubility of the oil in the propane phase decreases sharply. Under these conditions propane is a feasible solvent for the purification/refining of fatty oils. The temperature of the upper critical end point (UCEP) for these systems is very close to the critical temperature of propane (370 K). In 340-400 K temperature range, liquid - liquid equilibrium is observed at pressures above the propane saturation pressure. At supercritical temperatures a dense gas phase and an oil phase are obtained. The heterogeneous region of the oil-propane binary mixtures decreases at all temperatures with increasing pressure and for each

isotherm there is a maximum pressure at which complete miscibility is obtained. Therefore, to keep the solubility of the oil in the propane phase at very low values, operating pressures should be below the maximum pressure for each isotherm. The process behavior is similar to the one with CO<sub>2</sub>. Optimal conditions for the removal of different pollutants with propane are also given in Table 1. The optimal pressure and temperature combination is the same for each solvent and it is independent of the extracted pollutant due to the very low pollutant concentrations and the tight constraint imposed on oil loss in the extract.

Table 1. Optimal operating conditions for the removal of pollutants with propane as solvent.

Pollutant	T <sub>extr</sub> (K)		P <sub>extr</sub> (MPa)		S (Kmol)		S/F		Pollutant ppm
	CO <sub>2</sub>	C3	CO <sub>2</sub>	C3	CO <sub>2</sub>	C3	CO <sub>2</sub>	C3	
Hexane	333.7	399.4	16.	7.0	376.	18.50	2.6	1.28	5.
Benzene	333.	400	16.	7.15	70.	55.83	4.58	3.65	0.01
Toluene	333.	400	16.	7.15	88.	67.88	5.75	4.43	0.01
Chlorobenzene	333.	400	16.	7.15	200.5	107.15	13.08	6.99	0.01
Naphtalene	332.8	400	15.9	7.15	206.3	200.23	13.44	13.05	0.01
Dichlorobenzene	n.a.	400	n.a.	7.15	n.a.	215.90	n.a.	14.06	0.01
Biphenyl	n.a.	400	n.a.	7.15	n.a.	322.17	n.a.	20.98	0.01

#### 4.2. Supercritical Fluid Fractionation of Fish Oils

Nilsson (1996) has recently reviewed the supercritical fluid extraction and fractionation of fish oils. Fish oils typically contain straight-chain fatty acids (C14-C22), often unsaturated having from one to six double bonds. The high degree of unsaturation of these oils, of great pharmaceutical interest, precludes the application of vacuum distillation because these components are highly thermally labile. Among the components of interest derived from fish oils are concentrates of EPA (eicosapentanoic acid) and DHA (docosahexaenoic acid) in the form of ethyl esters. Eisenbach (1984) proposed the fractionation of fatty acid ethyl esters using CO<sub>2</sub> as a high-pressure entrainer in a semi batch fractionation process. In this scheme, a hot finger in the top of the column decreases the esters solubility in the gas phases and acts as a partial condenser. A continuous high pressure (extraction and fractionation column) of the process is also proposed by Eisenbach (1984). Brunner (1994) discusses this separation problem in detail, however he points out that the selection of process conditions by rigorous computational solution is not available.

The upgraded version of the GCA-EOS is able to predict with good accuracy the high pressure vapor - liquid equilibria of fatty acid alkyl esters with CO<sub>2</sub> in the entire range of operation for fractionation, solute recovery and CO<sub>2</sub> separation process. In this work, we have determined design and operating conditions for different optimization goals such power consumption, product specification or a combination of them. The approach is illustrated for the separation of methyl myristate (C14:0) and ethyl stearate (C18:0), straight chain fatty acids ethyl esters and for EPA recovery from a C14, C18, C20 mixture.

##### 4.2.1. Separation of a methyl myristate – ethyl stearate mixture

An extractor-separator system is studied for the separation of a methyl myristate – ethyl stearate mixture (54 and 46% weight, respectively) with carbon dioxide. The objective function is the maximization of C14 recovery. Main optimization variables are: CO<sub>2</sub> recirculation rate, column operating pressure and temperature, the solvent recovery unit temperature and reflux ratio, subject to given constraints on components recovery and purity. Optimization results are given in Table 2 for an extraction temperature of 340.15 K.

Table 2. Optimal operating conditions for the fractionation of methyl myristate (C14:0) and ethyl stearate (C18:0)

Variables	Lower bound	Upper bound	Optimum
Pextractor (Mpa)	12.00	17.00	16.80
Tflash (K)	378.00	390.00	378.00
Reflux to Column/Liq. Top Product	0.40	0.80	0.57
Solvent/Feed (wt)	17.00	22.00	21.85
Solvent Purity (%)	99.98	100.00	99.98
C14 Purity (%)	80.00	100.00	84.30
C18 Purity (%)	99.00	100.00	99.87
C14 Recovery (%)			98.80

#### 4.2.2 EPA recovery from fatty acid alkyl esters

EPA (eicosapentanoic acid or 20:5 $\omega$ 3) is a fish oil derivative that has pharmaceutical value. In this work, a urea-adducted ethyl ester derived from fish oil (C14, 14.1%; C18, 9.7%; C20, 74.9%, wt.) is fractionated in a supercritical fluid extraction train, as shown in Fig. 2, to obtain an EPA concentrate.

Optimization variables are: extractors pressure, solvent flowrate in each column, separators temperature and refluxed fractions. Additionally, an infeasible path strategy has been applied for the convergence of recycles of separators liquid streams to the extractors. Results are shown in Table 3.

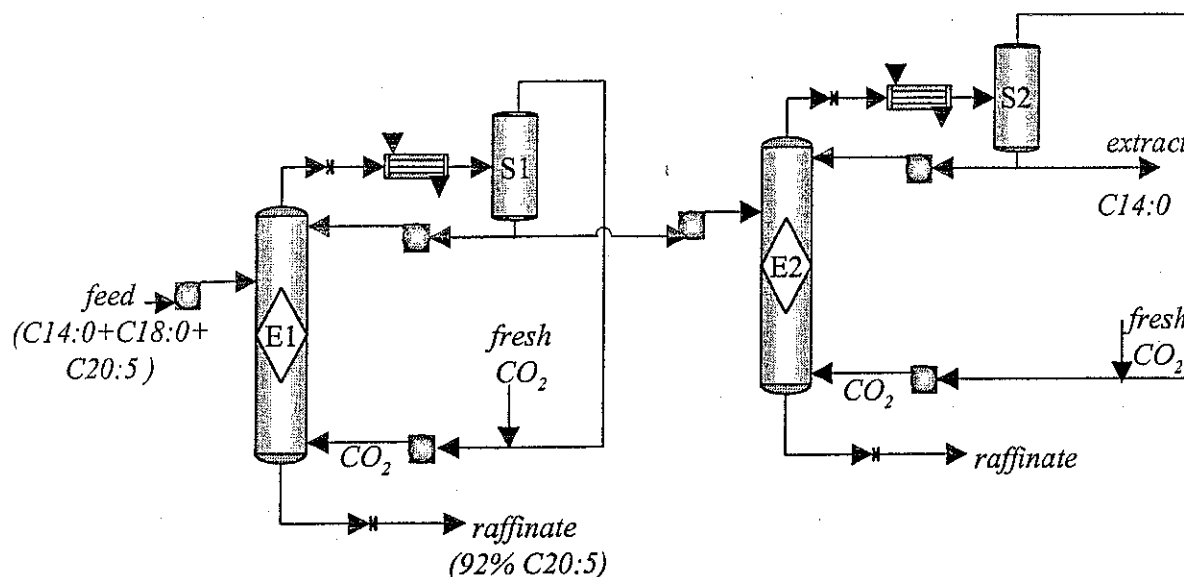


Figure 2. Fatty acids alkyl esters fractionation process.

Table 3. EPA recovery with supercritical carbon dioxide

Variables	Lower bound	Upper bound	Optimum
Pextr (E1) (Mpa)	12.00	17.00	13.83
Tflash (S1) (K)	358.00	390.00	377.3
Solvent/Feed E1 (wt)	17.00	60.00	45.05
Solvent Purity (S1 & S2) (%)	99.98	100.00	99.99
C14 Recovery (%)	90.00	100.00	100.00
EPA in Raffinate (%)	92.00	100.00	92.01
EPA Recovery (%)			90.00

A 92% EPA stream (solvent free basis) is obtained as the raffinate in the first extractor with 90% EPA recovery. These results are comparable to experimental values reported by Nilsson (1996) with an increase in recovery and purity.

## 5. CONCLUSIONS

Optimum operating conditions for the purification of vegetable oils with near critical CO<sub>2</sub> and propane have been identified with the help of reliable predictions of phase equilibria using the GCA-EOS model. The problem of fractionation of fish oil fatty acids ethyl esters has also analyzed. Rigorous thermodynamic modeling and process optimization have been applied to a great variety of problems for processing, refining and purification of natural oils with high-pressure gases. In this way, a better understanding has been gained on the selection of process conditions for these non-conventional separation processes.

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