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Optimal design of supercritical fluid processes

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Abstract

Optimal schemes and operating conditions are analyzed for the deterpenation of citrus peel oils with supercritical carbon dioxide. The problem is formulated as a mathematical programming model using the group contribution equation of state (GC-EOS) for rigorous phase equilibria predictions. Both thermodynamic predictions and simulation results are found to be in agreement with experimental studies. Optimization results give insight to improve current experimental values of product recovery and purity. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The application of supercritical fluids to a great variety of chemical processes has received increasing interest during the past two decades. Brennecke and Eckert (1989) covered the main developments of the 1980s. More recently, several monographic works have been edited on different fields of application: the extraction of natural products (King & Bott, 1993), food and biomaterials processing (Rizvi, 1994), oil and lipid chemistry (King & List, 1996). Recently, Chemical Reviews edited comprehensive reviews on the state of the art on fundamentals and new fields of applications of supercritical fluids (Noyori, 1999). Although there is a growing number of applications and a wealth of experimental work available, there is still a need for improved property and phase equilibrium predictive methods, rigorous unit simulation, combined with synthesis procedures to optimize industrial applications.

On the other hand, design and synthesis problems have been increasingly solved by formulating mathematical models which involve continuous and integer variables to represent operating conditions and alternative process topologies (Grossmann & Kravanja, 1997). With regards to supercritical processes, Gros, Diaz and Brignole (1998) have addressed the synthesis of optimum extraction and dehydration of oxychemicals processes as a mixed integer nonlinear programming problem.

In this work, the problem of analysis and synthesis of high-pressure deterpenation of cold pressed citrus oil is studied. Citrus essential oils are complex mixtures of more than 200 components, mainly terpene hydrocarbons and derivatives and oxygenated compounds, pigments, waxes, resins and flavonoids. Terpenes hydrocarbons are unsaturated compounds that are readily decomposed by heat, light and oxygen and must be removed to avoid unpleasant flavors. They represent the main aqueous insoluble fraction of the citrus essential oil. The oxygenated compounds, such as aldehydes, alcohols, esters and ketones constitute the flavor fractions. In spite of the mixture complexity, two main components characterize each of the fractions: limonene and linalool. The deterpenation of cold pressed citrus oil is a typical example of the separation of valuable components from a complex natural mixture; another example is the separation of fish oil fatty acid esters. The use of supercritical fluids to deal with this type of separation problems has been intensively studied from an experimental point of view. The separation approach has evolved from simple countercurrent extraction to the use of semibatch and continuous countercurrent extraction with reflux. The use of temperature gradients in the column was introduced to improve the separation of citrus oil components (Gerard, 1984) and fish oil fatty acid ethyl esters (Eisenbach, 1984). Diaz, Espinosa and Brignole (2000) have recently discussed the selection of optimum conditions for the separation of these esters.

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Temelli, O'Connell, Chen and Braddock (1990) studied the thermodynamic modeling of the deterpenation of citrus peel oils with supercritical carbon dioxide. Sato, Goto and Hirose (1996a) experimentally studied the effect of temperature gradients on process recovery and selectivity in a semibatch process. Reverchon, Marciano and Poletto (1997) studied a continuous countercurrent extraction apparatus for the separation of a quaternary mixture. These authors pointed out the need for computational assisted process analysis to optimize operating conditions in terms of oxygenated fraction recovery and separation selectivity. In the present work, mathematical modeling and process optimization give a better understanding of the effect of operating conditions on the citrus oil deterpenation process.

2. Phase equilibria and separation selectivity under near critical conditions

Citrus peel oil is modeled as a mixture of two key components: limonene and linalool. Limonene, a hydrocarbon terpene, is the predominant compound in all peel oils, with concentrations ranging between 30 and 90% weight. Linalool is one of the most represented among oxygenated compounds and it constitutes the flavor fraction. Supercritical carbon dioxide extraction is an interesting alternative for the fractionation of peel citrus oil due to the moderate operating temperatures and no solvent residue. Carbon dioxide extracts the hydrocarbon terpene as top product and the flavor fraction (linalool) is the raffinate product.

The observed decrease in selectivity for the system carbon dioxide–limonene–linalool under near critical conditions has been discussed by Temelli et al. (1990) on the basis of phase equilibrium predictions using the GC-EOS (Brignole, Skjold-Jorgensen & Fredenslund, 1984; Skjold-Jorgensen, 1988). Limonene (hydrocarbon) and linalool (alcohol) show different behavior in a high-pressure liquid phase mixture saturated with carbon dioxide (nonpolar solvent), so their separation factor in near critical extraction is smaller than in distillation.

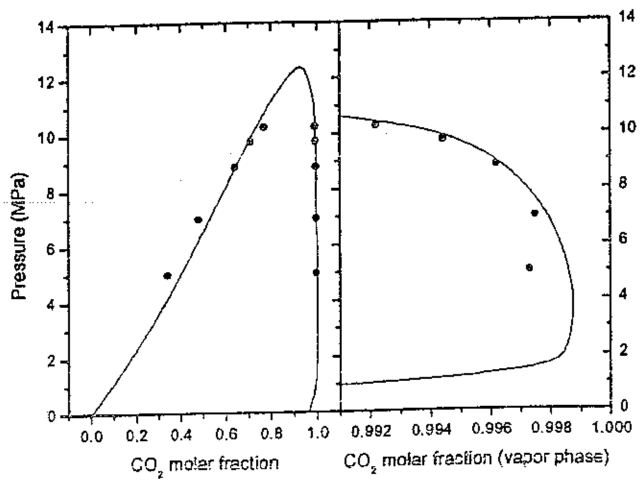
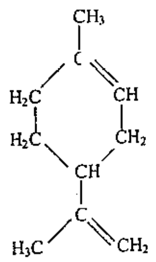


Fig. 1. VLE for the CO-limonene system at 333 K. ● experimental data (Iwai et al., 1996) — GCEOS (this work).

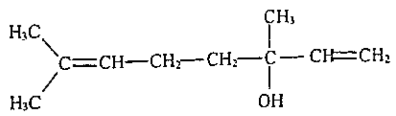
Temelli et al. (1990) concludes that the selectivity is reduced "because the flavor fraction is preferentially attracted to the dense gas phase more than to the liquid phase". Although the conclusion is correct, the reason for the decrease in selectivity lies in an increase of linalool activity coefficient in the carbon dioxide rich liquid phase, more so than in any preferential attraction of this compound to the dense gas phase. Sato et al. (1996a) used the Peng–Robinson equation of state (PR-EOS) with two binary temperature-dependent parameters to describe the phase equilibrium properties of limonene and linalool and they also discussed the process selectivity.

The use of a group contribution approach is justified because a great variety of natural products can be represented with a limited number of functional groups.

In the present work the GC-EOS is used to model phase equilibrium for the system carbon dioxide–limonene–linalool. Chemical structures for these citrus peel oil compounds are:



Limonene



Linalool

Additional pure group and binary interaction parameters for olefinic groups (Pusch & Schmelzer, 1993), for carbon dioxide and aromatics (Bamberger, Schmelzer, Walther & Maurer, 1994) have been considered together with original GC-EOS parameters (Skjold-Jorgensen, 1988). High pressure vapor–liquid equilibrium predictions for the binaries limonene + CO_2 and linalool + CO_2 are compared with experimental data from Iwai, Hosotani, Morotomi, Koga and Arai (1994) and Iwai, Morotomi, Koga, Sacamoto and Arai (1996) in Figs. 1 and 2.

The dense gas phase solubility of both components has a minimum at pressures near the carbon dioxide critical value. At higher pressures, there is an increase in the solubility. The agreement is remarkable considering that neither limonene nor linalool were included in

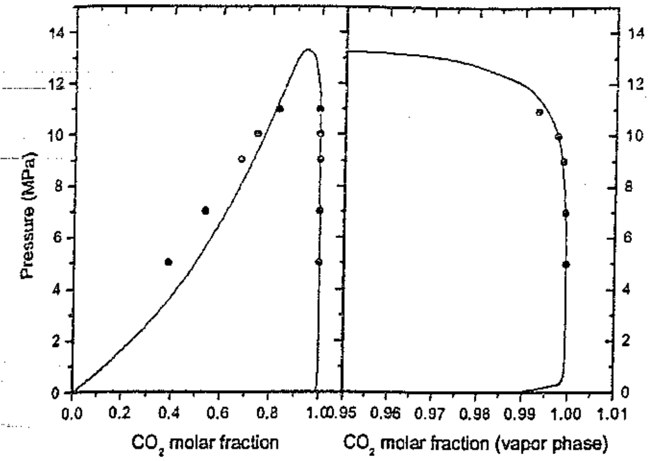


Fig. 2. VLE for the CO_2–linalool system at 333 K. ● experimental data (Iwai et al., 1994) — GC-EOS (this work).

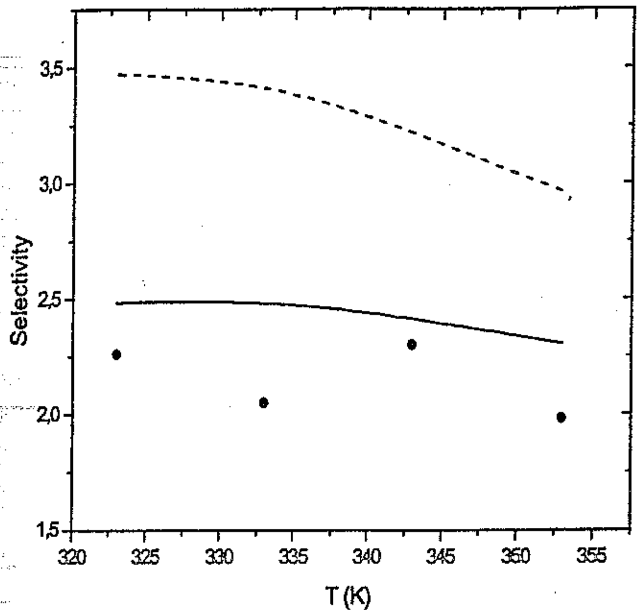


Fig. 3. Limonene–linalool selectivity dependence on temperature at 88 bar. ● experimental data (Sato et al., 1996a) — PR-EOS (Sato et al., 1996a) — GC-EOS (this work).

the original parameter estimation database of the GC-EOS. Furthermore, when selectivity predictions with this equation of state are compared with experimental values determined by Sato et al. (1996a) and with PR-EOS predictions, a good agreement is found with the experimentally observed data, as is shown in Fig. 3.

The solubility of low volatility components, in near critical fluids, exhibits retrograde behavior, i.e., their solubility in the dense phase decrease with increasing temperature over a certain pressure range. This property has been taken into account to propose the generation of internal reflux or hot spots in semibatch extraction. How these effects are tied to linalool purity and recovery and to the different process alternatives requires a full process optimization study under different process constraints.

3. Process analysis and optimization

Four process alternatives have been considered for detailed study: (i) simple countercurrent extraction; (ii) countercurrent extraction with temperature gradients; (iii) countercurrent extraction with external reflux and (iv) a combination of external reflux with temperature gradients. The general process scheme is shown in Fig. 4.

In this figure, continuous lines indicate the countercurrent extraction with or without temperature gradients (alternatives i and ii) and dashed lines indicate alternative paths when external reflux is chosen (alternatives iii and iv). Therefore, the essential oil feed is introduced at the top of the extractor in the countercurrent extraction and a few stages below the top of the extractor when external reflux is used. The supercritical carbon dioxide is fed at the bottom. Limonene is obtained as the top product and linalool constitutes the raffinate. The extract is heated — if there is external reflux — depressurized and sent to a separator; carbon dioxide is pumped and recycled to the extractor. The bottom stream from the separator can be partially recycled to the extractor (external reflux) or obtained, as the limonene extract, in the simple extraction scheme. The optimization problem has been formulated as a nonlinear programming model where optimization variables are: extraction temperature and pressure, reflux ratio, separator temperature and solvent flowrate.

Three alternative objective functions have been considered: (a) maximum recovery of linalool; (b) minimum solvent recirculation and (c) minimum costs. Nonlinear constraints include process unit rigorous models and process specifications. The GC-EOS is the thermodynamic model that supports phase equilibrium

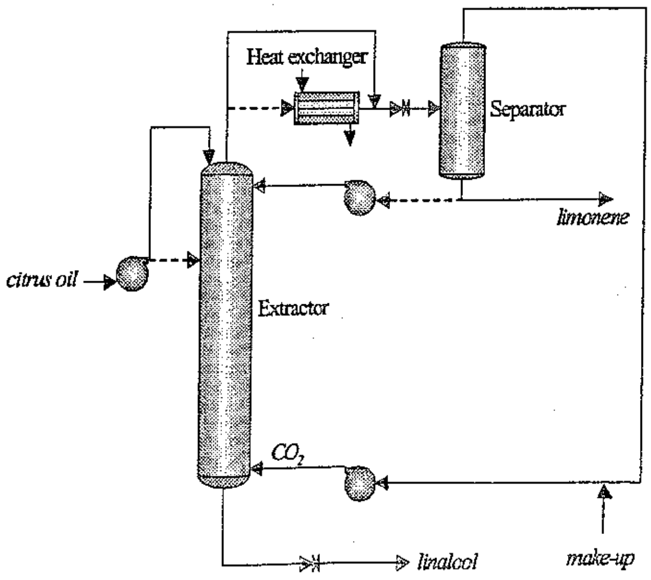


Fig. 4. Supercritical deterpenation process.

Table 1
Nonlinear inequality constraints for the deterpenation process

Equipment	Limitation (%)	Bound
Extractor	Linalool in raffinate (CO_2 free)	≥99.00
Extractor	Linalool recovery	≥92.00
Separator	Limonene in liquid (CO_2 free)	≥98.00
Extr–Sep.	Limonene recovery	≥97.00
Separator	Carbon dioxide in vapor	≥99.99

Table 2
Bounds on optimization variables

Variable	Lower bound	Upper bound
Extractor temperature (K)	313	333
Extractor pressure (bar)	50	95
Reflux ratio	0.40	0.90
Separator temperature (K)	273.15	290.15
Solvent flowrate (Kmol/h)	40.00	100.

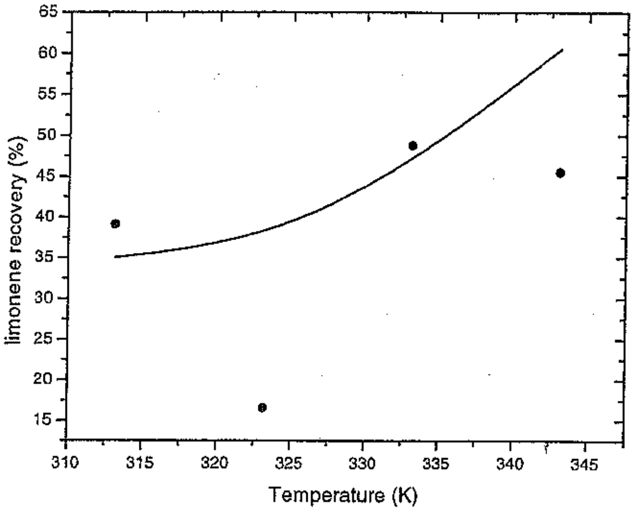


Fig. 5. Limonene recovery dependence on temperature at 75 bar. ● experimental data (Reverchon et al., 1997) — GC-EOS (this work).

predictions. Table 1 shows nonlinear inequalities and their bounds. Nonlinear problems have been solved with OPT (Biegler & Cuthrell, 1985).

4. Discussion of results

In this work, we have studied the deterpenation of citrus peel oil with supercritical carbon dioxide as a mathematical programming problem. The feed consists of 26 kg/h of a model mixture composed of 80% weight limonene and 20% linalool. Different extraction schemes have been studied and optimal operating conditions have been determined for them.

Optimization variables and their bounds are shown in Table 2. Extraction temperature should be below 333–343 K because terpenes (limonene) decompose at higher temperatures. The extractor pressure should not be greater than 100 bar to remain within the two-phase region in that temperature range. The separator pressure is kept at 20 bar.

4.1. Simple countercurrent extraction

This is the simplest extraction scheme, with low product purity and recovery. We have performed process simulations at the same operating conditions (75 bar) as those reported by Reverchon et al. (1997) and the numerical results shown in Fig. 5 are in good agreement with experimental data.

It must be noted that Reverchon et al. (1997) use a model mixture with four key components: limonene (60% wt.), γ-terpinene (10%), linalool (20%) and linalyl acetate (10%) and we have analyzed a limonene–linalool mixture with different compositions (from 75 to 85% wt. limonene). The extractor has six equilibrium stages. As both experimental and numerical product recoveries and purity are low, we have increased the number of theoretical stages and the objective has been the maximization of linalool recovery, subject to 90% molar concentration in the raffinate, in a carbon dioxide free basis. Table 3 shows optimization variables and main process variables for different numbers of ideal stages (N), the extraction temperature is 333.15 K in all cases.

These results show that a rather concentrated linalool can be obtained (90–91% molar, in a carbon dioxide free basis), but with low recovery (50–60%).

Table 3
Optimal operating conditions for simple countercurrent deterpenation

N	Pextr (bar)	Solvent (Kmol/h)	Linalool (%molar)	Recovery (%)	
				Linalool	Limonene
15	85.0	79.90	90.00	50.04	98.00
30	85.5	74.14	90.74	59.78	98.21
40	85.3	74.63	91.96	60.67	98.44

Table 4
Optimal operating conditions for countercurrent extraction with and without temperature gradient

Extractor temperature (K)	Pextr (bar)	Solvent (Kmol/h)	Linalool (%molar)	Linalool recovery (%)	Limonene (%molar)	Limonene recovery (%)
333	85.52	74.14	90.74	59.78	89.25	98.21
343–328	83.71	79.59	88.43	59.37	89.10	97.71

4.2. Countercurrent extraction with temperature gradient in extractor

To improve linalool recovery, a countercurrent operation with internal reflux induced by a temperature gradient in the extractor has been analyzed. Sato et al. (1996a) have experimentally studied a semibatch extraction with and without internal reflux. They have worked with a rectification column in series with an extractor; the temperature gradient is induced in the column with a consequent increase in the separation selectivity. However, Sato, Goto, Kodama and Hirose (1996b) reported that a temperature gradient is not suitable for the continuous process due to the existence of a homogeneous phase at the bottom of the extractor for a 333–313 K gradient from top to bottom, at 88 bar. In this work, we have determined optimal conditions for the extractor in different temperature ranges. Numerical results indicate that there is no improvement with a temperature gradient and linalool purity is slightly lower, as it is shown in Table 4 for the 343–328 K gradient and a uniform extractor temperature of 333 K with 30 theoretical stages.

4.3. Countercurrent extraction with external reflux

In this scheme, the extract is heated before depressurizing and part of the separator liquid is recycled to the extractor. The limonene–linalool mixture is fed into the extractor at the sixth stage in a 40-stage extractor. In the simple extraction cycle, an increase in solvent flowrate improves the separation of the most volatile compound (limonene), but corresponds to a decrease in linalool recovery. The existence of an external reflux increases the liquid flow rate in the column, with a consequent increase in linalool recovery. Numerical results for the minimization of solvent recirculation (operating cost minimization) are shown in Table 5; good product recovery (93.37% linalool and 97.65% limonene) and high purity (99% linalool and 98.52% limonene) have been obtained.

Fig. 6 shows the evolution of extract and raffinate in the extractor at optimal operating conditions (333.15 K and 95 bar). In this ternary system, labels E and R indicate the final composition of extract and raffinate, respectively.

Table 5
Optimal operating conditions for countercurrent extraction with external reflux

Variable	Initial point	NLP optimum
Extractor pressure (bar)	70.00	95.00
Extractor temperature (K)	330.00	333.15
Separator temperature (K)	275.00	273.15
Reflux ratio	0.40	0.54
Solvent flowrate (Kmol/h)	70.00	82.45
Linalool in raffinate, CO_2 free (%molar)	23.54	99.00
Linalool recovery (%)	90.03	93.37
Limonene in sep. bottom (%molar)	98.51	98.52
Limonene recovery (%)	65.07	97.65
CO_2 in sep. vapor (% molar)	99.99	99.99

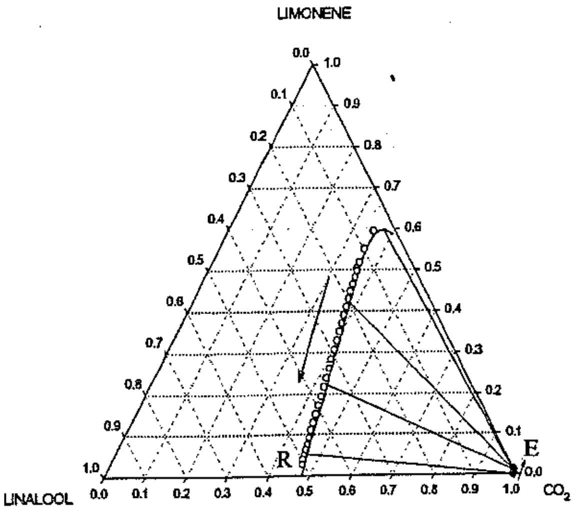


Fig. 6. Evolution of extract (E) and raffinate (R) in extractor with external reflux at optimal operating conditions (333.15 K, 95 bar).

Table 6
Optimal solvent flowrate for different linalool purity specifications in raffinate

Linalool (% molar)	CO_2 flowrate (Kmol/h)	Linalool recovery (%)
80	62.36	88.28
85	65.13	90.00
92	73.93	97.42
95	75.66	96.89

Table 7
Comparison of results for extraction with external reflux, with and without temperature gradient in extractor

Extractor temperature (K)	Pextr (bar)	Solvent (Kmol/h)	Linalool (%molar)	Linalool recovery (%)	Limonene (%molar)	Limonene recovery (%)
343	95	75.75	99.00	95.82	99.06	97.65
343–323	95	82.15	99.00	92.00	98.23	97.76

Table 6 shows the carbon dioxide flowrate as function of required purity in raffinate with external reflux. Bounds on the nonlinear constraint of linalool purity in raffinate have been varied between 80 and 99%; the second column shows optimal solvent flowrate and the third column shows linalool recovery. In all cases, extraction temperature and pressure are at their upper bounds (333 K and 95 bar).

4.4. Countercurrent extraction with external reflux and temperature gradient

In this scheme, an internal temperature gradient of 20 K has been imposed on the extractor and optimal operating conditions have been determined, as shown in Table 7. Conditions have not been improved related to the uniform temperature process. The existence of a hot spot has also been investigated (top stage at higher temperature and the rest of the column at uniform temperature), but neither product recovery nor purity could be improved. Experimental solubility data analysis has demonstrated that when there is a temperature gradient from 333 to 313 K at 95 bar, there is an important decrease in products solubility. However, at 313 K there is an homogeneous phase and linalool cannot be removed. Consequently, higher temperatures must be selected. But the experimental decrease in solubility in the 343–328 K range is negligible and there is no internal reflux. From these considerations, we can conclude that the existence of a temperature gradient can be justified in a semibatch process, but not in a larger scale continuous extraction, where an external reflux is a more effective way to increase process efficiency.

5. Conclusions

Experimental work on deterpenation with supercritical carbon dioxide has been recently reported by several authors; however, the problem of process optimization and design with both reliable thermodynamic models and mathematical programming techniques has not been addressed. In this work, we have determined optimal process schemes and operating conditions for the deterpenation of cold pressed citrus oil with near critical carbon dioxide through the integration of rigorous process unit models, mathematical programming techniques and predictions of phase equilibrium with the group contribution equation of state model (GC-EOS). In this way, a better understanding can be gained on the selection of process conditions for these non-conventional separation processes.

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