

PROCESS OPTIMIZATION FOR SUPERCRITICAL CONCENTRATION OF ORANGE PEEL OIL

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Abstract— This work addresses modeling, simulation and optimization of countercurrent deterpenation of orange peel oil, modeled as a model mixture of limonene-linalool, with supercritical carbon dioxide as solvent. Binary and ternary systems are modeled with a group contribution equation of state, and vapor-liquid equilibria and selectivity predictions are compared to experimental data from different sources. A nonlinear programming model is proposed for the maximization of net profit. Process simulations are carried out at conditions reported in the literature and component purity and recovery in the output streams are contrasted against laboratory-scale process results. Optimization results provide operating conditions and equipment size to maximize net profit.

Keywords— optimization, supercritical carbon dioxide, orange oil, extraction, equation of state

I. INTRODUCTION

Citrus essential oils are mainly composed of hydrocarbon terpenes and oxygenated compounds. They are obtained from fruit peel through a cold press process and they are used in food products, perfumes and pharmaceuticals. Oxygenated components from “cold pressed” orange peel oil can be concentrated by supercritical extraction of terpene hydrocarbons, as these compounds can decompose and produce unpleasant flavors.

Experimental studies on pilot plant deterpenation processes have been reported by Gerard (1984), Stahl and Gerard (1985), Sato *et al.* (1996) and Reverchon *et al.* (1997). More recently, Budich *et al.* (1999) and Budich and Brunner (1999) have provided phase equilibrium data for the pseudo binary system orange peel oil – carbon dioxide. These authors have also carried out countercurrent column experiments and flooding point measurements.

Vapor liquid equilibrium predictions for the system under study have been performed by Temelli *et al.* (1990) and Espinosa *et al.* (2000) with group contribution methods. Some authors have also used cubic equations of state (Sato *et al.*, 1996; Vieira de Melo *et al.*, 1999). Diaz *et al.* (2000, 2003) and Espinosa *et al.* (2000) have performed simulation and optimization of

citrus peel oil deterpenation process, through the integration of nonlinear programming techniques and thermodynamic predictions with the Group Contribution Equation of State (GC-EOS, Skjold-Jorgensen, 1988).

In this work, the design and optimization of a supercritical deterpenation process for orange peel oil is addressed for the production of a 5-fold concentrate. Even though the concentration is relatively moderate, the low ratio of flavor to terpene fraction in this natural oil requires high flow of solvent, pressures and recycle flow rate and several equilibrium stages. Therefore, an economically feasible supercritical deterpenation process is strongly dependent on the determination of optimal operating conditions. Numerical simulation results have been favorably compared to pilot plant reported data.

II. THERMODYNAMIC MODELING

In orange peel oil, the main oxygenated compounds are linalool and decanal and the main terpenes are limonene and α -pinene. However, this peel oil can be accurately modeled as a binary mixture made up of limonene ($C_{10}H_{16}$) and linalool ($C_{10}H_{17}OH$). Solubility and equilibrium predictions have been made with the Group Contribution Equation of State (GC-EOS, Skjold-Jorgensen, 1988), whose parameter table has been updated for the groups used in this work (Espinosa *et al.*, 2000, Diaz *et al.*, 2005). Details on pure group and binary interaction parameters between groups are given in Appendix A. Distribution coefficients (defined as the ratio between each component molar composition in the vapor and liquid phase) predicted with GC-EOS are plotted for binary and ternary mixtures against experimental data from the literature. Figures 1a and 1b show our predictions for the binary systems limonene + carbon dioxide (experimental data from Iwai *et al.*, 1994) and linalool + carbon dioxide, (Iwai *et al.*, 1996) respectively, in logarithmic scale. Figure 2 shows calculated distribution coefficients (K_{limonene} , K_{linalool}) for key components in the ternary mixture limonene + linalool + CO_2 and experimental data from Morotomi *et al.* (1999). Moreover, separation selectivity, calculated as K_{limonene} to K_{linalool} ratio in the ternary mixture, is in agreement with experimental results from Sato *et al.* (1996), Morotomi *et al.* (1999) and Fonseca *et al.* (2003).

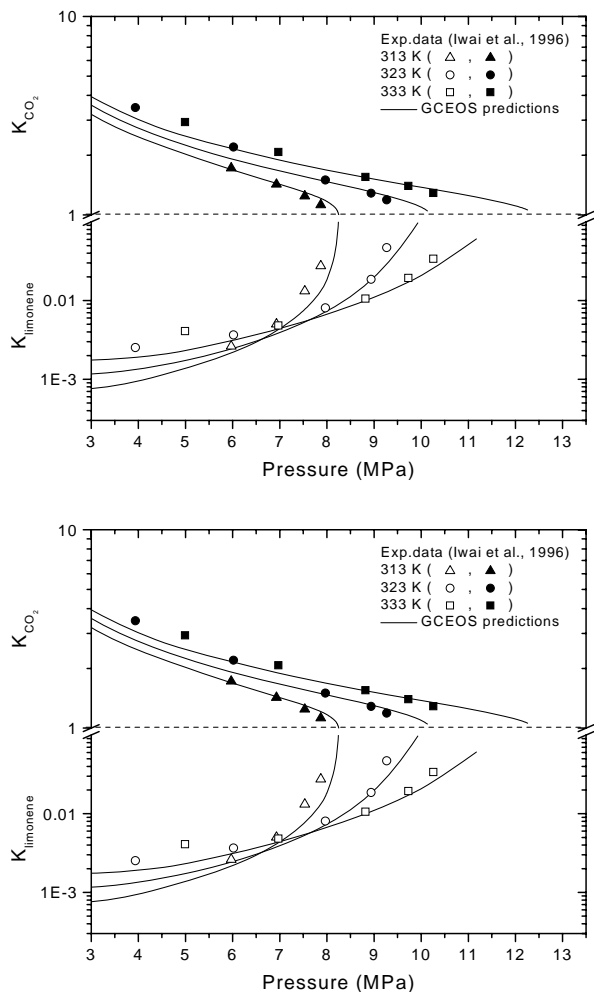


Fig. 1. Distribution coefficients for a) CO₂ + limonene; b) CO₂+linalool

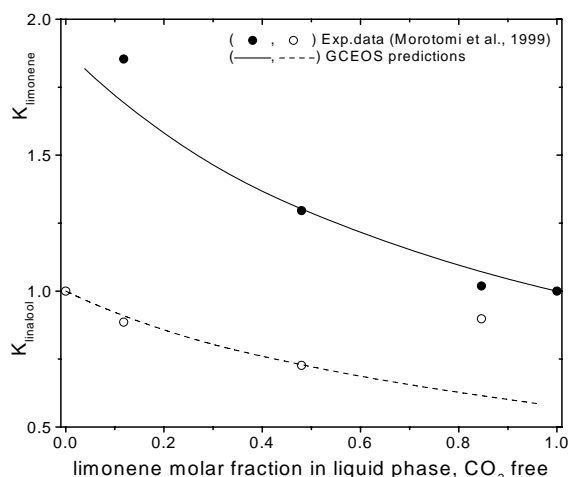


Fig. 2. Experimental and calculated distribution coefficients (CO₂ free base) for orange key components in the ternary system CO₂ + limonene + linalool at 333 K and 10 MPa.

Vapor liquid equilibrium predictions for the pseudo-binary system CO₂ + natural orange peel oil (modeled as a 98/2 wt% limonene/linalool mixture) have also been favorably compared to experimental data from Budich and Brunner (1999) and Morotomi *et al.* (1999). Further detail on orange oil thermodynamic modeling is given in Espinosa *et al.* (2003) and Diaz *et al.* (2005).

III. PROCESS MODELING AND OPTIMIZATION

In a supercritical extraction process (Figure 3), orange peel oil is fed to an extraction column in counter-current with high-pressure carbon dioxide. The aroma (linalool concentrate) constitutes the raffinate. The extract, mainly limonene and carbon dioxide, is heated before expanding and sent to a solvent recovery unit; the vapor is the recovered solvent and the liquid is partly returned to the extractor as reflux and partly recovered as limonene product after a second expansion to ambient pressure. In this work, a pump mode has been considered in the solvent cycle.

Main units in the supercritical deterpenation process are rigorously modeled: a high-pressure multistage extractor (Brignole *et al.*, 1987) and a multiphase flash (Michelsen, 1982), supported by the Group Contribution Equation of State (GC-EOS) thermodynamic predictions. Pump, valve and heat exchanger models have also been included in the solvent cycle. This model is formulated within a Fortran environment as a sequential modular simulator that is integrated to the optimization algorithm in a black box way. However, recycle streams are not converged within the simulation model but at the optimization level, in an infeasible path optimization strategy.

A nonlinear programming problem has been formulated, where the objective function is profit maximization calculated as:

$$Net\ profit = (price * production)_{5-fold\ aromal} + (price * production)_{limonene} - (cost * consumption)_{orange\ oil} - \Sigma(Operating\ Costs) - \Sigma(Investment\ Costs),$$

Alternatively, the objective function can be set to minimize solvent to feed ratio.

Equality constraints: process units simulation model, reflux convergence in extraction column, solvent recycle convergence and the specification of 5-fold concentrate as raffinate.

Inequality constraints: terpene purity specifications ($\geq 99.70\%$ wt), recycled solvent purity ($\geq 99.90\%$ wt) and operating bounds on variables.

Optimization variables: extraction pressure ($9.0 \leq P_{ext} \leq 10.0$ MPa) and temperature ($329 \leq T_{ext} \leq 335$ K), solvent recovery unit pressure ($1.0 \leq P_{ext} \leq 2.0$ MPa), solvent flowrate ($700.0 \leq S \leq 1200.0$ Km³/h) and reflux ratio ($1.0 \leq R \leq 1.5$), components flowrates in reflux and recycled solvent streams.

To avoid formulating an MINLP, the number of stages (N) is fixed in the optimization problem. How-

ever, several optimizations for different values of N have been performed to select the best value. Column diameter is estimated from hydraulic behavior of the packed tower. Process units capital costs curves have been obtained from Ulrich (1984), Peters and Timmerhaus (1968) and Institut Français du Pétrole (1981). A propane refrigeration cycle has been considered to condense carbon dioxide and related capital costs curves have been implemented from Institut Français du Pétrole (1981). Investment cost has been annualized considering a project life of three years. Operating costs include electrical motor consumption of pump driver, cooling water and steam consumption. A detailed description of cost correlations and flooding point calculations is given in Diaz *et al.* (2005), Appendix B.

The nonlinear programming problem is solved with a Successive Quadratic Programming algorithm (Biegler and Cuthrell, 1985).

IV. DISCUSSION OF RESULTS

Simulation and optimization of the deterpenation of orange peel oil process with supercritical carbon dioxide is carried out. A 5-fold concentrate is to be obtained as raffinate because it represents a current market specification for this product. Furthermore, a 5-fold aroma is more stable than the corresponding natural orange peel oil, maintaining its characteristic flavor. In our economic analysis, prices for a 5-fold orange peel oil have

been considered. A 25-stage countercurrent extraction column ($P=10$ MPa, $T=333$ K) with reflux, fed with 25 kg/h of a 98.25 wt % limonene-1.75 wt % linalool mixture. The high-pressure separator operates at 5 MPa and 303 K. Simulation has been performed at these conditions to allow comparison with laboratory-scale process data reported by Budich *et al.* (1999). Simulation has been carried out specifying 99.64 wt% limonene purity in top product and calculated results are in close agreement with experimental data requiring a slightly higher solvent to feed ratio (108 against 100 kg solvent/kg feed), with an aroma purity of 8.11% wt and a net profit of 10.57 \$/kg product.

In all cases, reported net profit has been calculated taking into account incomes from the sale of the 5-fold concentrate (limonene top product has not been included). Orange peel oil cost is 2 U\$S /kg and 5-fold orange oil, 33 U\$S/kg (www.bestdeal.org, Sept/2003).

Simulation results for the production of a 20-fold concentrate are shown in Table 1. In this case, a 100 kg/h of a limonene/linalool feed is considered and a 99.7 wt% purity of terpenes in top product is imposed. The higher concentration required in the 20-fold specification has rendered an aroma purity of 32.76%wt in the raffinate, together with a higher solvent to feed (126 kgCO₂/kgFeed) and reflux ratios (2.6). Numerical results are in agreement with scale-up estimations reported by Budich *et al.* (1999).

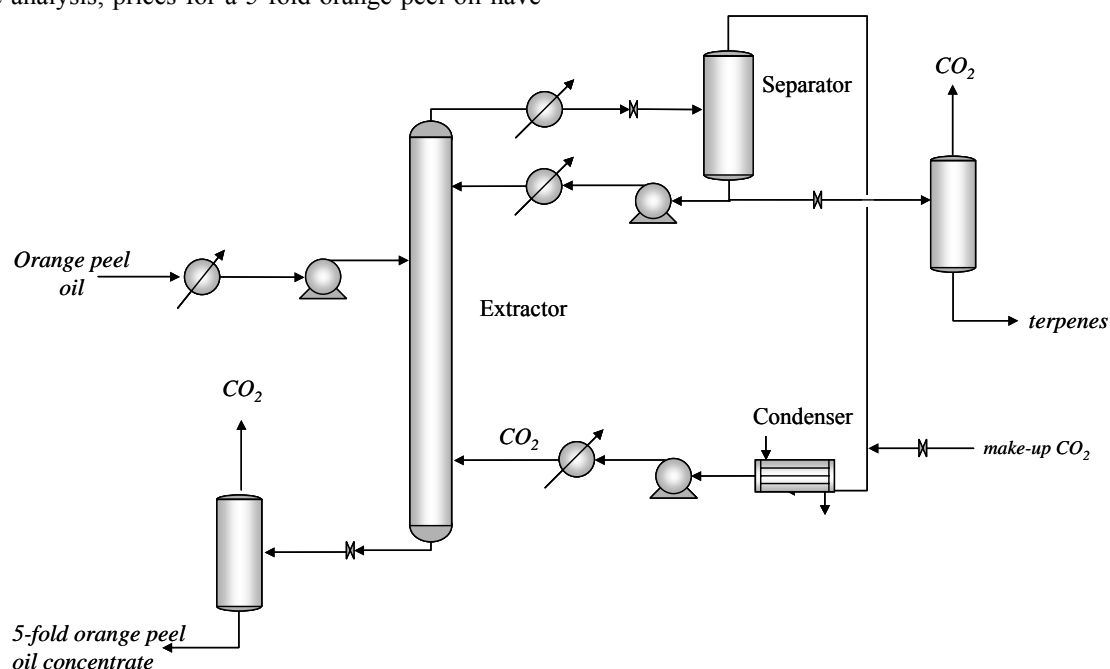


Fig. 3. Supercritical process deterpenation flowsheet.

As a second step, process optimization has been performed. The resolution of the optimization model provides process operating conditions that maximize net profit in the production of a 5-fold concentrate. Inequality constraints impose a lower bound on limonene purity in top product (>99.7 wt%) and recycled solvent purity

(>99.9 wt%). Optimization variables and main process and economic variables are shown in Table 2, for a pump cycle. As compared to experimental data (Budich *et al.*, 1999), the nonlinear programming (NLP) model determines a slightly different operating point: lower extractor temperature (330 against 333 K) and pressure

(9.93 instead of 10 MPa) and lower pressure in the separation tank (4.41 against 5 MPa). These conditions lead to a better separation (aroma purity to 8.34% wt. and terpene purity in top product to 99.70% wt.) and an increase in profit per product mass unit, mainly due to the lower obtained solvent to feed ratio (106.28 against 108 kg solvent/kg feed).

Table 1. Simulation of a 100 kg/h feed, 20-fold concentrate.

Variable	Simulation Results
Extractor Pressure (MPa)	10.7
Extractor Temperature (K)	333
Separator Pressure (MPa)	5.0
Separator Temperature (K)	303
Reflux Ratio	2.6
Solvent-to feed ratio (mass)	129
Terpene in Top Product, CO ₂ free (wt%)	99.70
Aroma recovery (%)	85.47
Aroma in Raffinate, CO ₂ free (wt%)	32.76
Extractor diameter (m)	0.52
Extractor height (m)	14.8

Table 2. Continuous optimization variables and main costs for optimal deterpenation conditions (25 theoretical stages, 5-fold concentrate)

Variable	NLP Optimum
Extractor Pressure (MPa)	9.93
Extractor Temperature (K)	330.0
Separator Pressure (MPa)	4.41
Separator Temperature (K)	300
Reflux Ratio	1.34
Solvent-to feed ratio (mass)	106.28
Linalool in Raffinate, CO ₂ free (wt%)	8.34
Linalool Recovery (%)	87.23
Limonene in Top Product (wt%)	99.70
Limonene Recovery (%)	81.32
CO ₂ in Sep. Vapor (wt%)	99.90
Extractor diameter (m)	0.21
Extractor height (m)	15.68
Flooding gas load (kg/(hs m ²))	77351
Pump consumption (Kw)	5.19
Condenser area (m ²)	2.40
Heat exchanger area (m ²)	6.74
Capital Cost (\$/kg product)	9.00
Operating cost (\$/kg product)	3.27
Profit (\$/kg product)	10.72

Finally, the effect of scale-up on net profit has been studied. Figure 4 shows optimization results when increasing flowrates of natural orange peel oil (modeled as a mixture of limonene: 98.25 wt% + linalool: 1.75 wt%) are fed to the extractor. In all cases, a 5-fold concentrate is obtained as product and limonene with 99.7

wt% purity is the top stream. A steep increase in profit can be seen when increasing feed flowrate up to 100 kg/h (20 kg/h in raffinate), as a result of a 50 % decrease in investment costs and a 30 % decrease in operating costs, per kg of concentrated oil (compared to a 5 kg/h aroma production). This behavior is due to logarithmic cost dependence on equipment capacity.

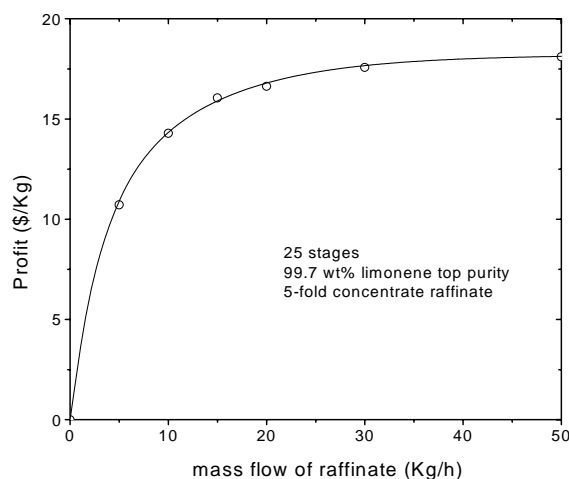


Fig. 4. Optimal net profit as function of product mass flow obtained as product and limonene with 99.7 wt% purity in top stream (5-fold concentrate)

V. CONCLUSIONS

A nonlinear programming model has been formulated for the design and optimization of the concentration of orange peel oil with supercritical carbon dioxide, based on group contribution equation of state predictions and successive quadratic programming techniques. Binary parameters for the equation of state have been updated and it has been shown that vapor liquid equilibrium predictions and process simulation results are in close agreement with reported experimental data. The optimization of the concentration process has given a slight increase in net profit as compared to available pilot plant data, together with the optimal design of process units. Finally, a scale-up study has been performed to analyze costs behavior for an industrial process. The integration of group contribution methods for thermodynamic predictions to nonlinear programming techniques has proved to be a versatile tool for process design and scale-up of supercritical processes.

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

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APPENDIX A

Table A1. Pure group parameters

Group	T*(K)	q	g*	G'	g''	CO ₂	Limonene	Linalool
CH ₂	600	0.54	356080	-0.8755	0	0	0	2
C=CH	600	0.676	546780	-1.0966	0	0	0	1
CH=CH ₂	600	1.176	337980	-0.6764	0	0	0	1
CH ₃ (B)/WSCH ₃ (B)	600	0.7891	316910	-0.9274	0	0	1	3
CYCH ₂	600	0.54	466550	-0.6062	0	0	3	0
CYCH	600	0.228	466550	-0.6062	0	0	1	0
ACH	600	0.4	723210	-0.606	0	0	1	0
C=CH ₂	600	0.988	323440	-0.6328	0	0	1	0
ACCH ₃	600	0.968	506290	-0.8013	0	0	1	0
COH ^(a)	512.6	0.7138	1207500	-0.6441	0	0	0	1
CO ₂	304.2	1.261	531890	-0.578	0	1	0	0

(a) Tertiary alcohol joined to an olefinic group

Table A2 Binary interaction parameters (above diagonal) and temperature dependence of binary interaction parameters (below diagonal)

Group	CH ₂	C=CH	CH=CH ₂	CH ₃ (B)	CYCH ₂	CYCH	ACH	C=CH ₂	ACCH ₃	COH	CO ₂
CH ₂	1	0.977	0.977	1	1	1	1.041	1	0.975	0.682	0.874
C=CH	0	1	1.094	0.977	1	1	1	1.094	1.040	0.773	1
CH=CH ₂	0	0	1	0.977	1	1	0.984	1.094	1.034	1.04	0.948
CH ₃ (B)	0	0	0	1	1	1	1.041	1	0.975	0.715	0.898
CYCH ₂	0	0	0	0	1	1	0.98	1.040	0.994	0.719	0.928
CYCH	0	0	0	0	0	1	0.98	1.040	0.994	0.719	0.928
ACH	0.094	0	0	0.094	0	0	1	1.040	1.007	0.826	1.060
C=CH ₂	0	0	0	0	0	0	0	1	1.040	0.769	1.057
ACCH ₃	0	0	0	0	0	0	0	0	1	0.774	0.938
COH	0	0	0	0	0	0	0	0	0	1	0.785
CO ₂	0	0	0	0	0.21	0.21	0	0	0	0	1

Table A3. Binary nonrandomness parameters

Group	CH ₂	C=CH	CH=CH ₂	CH ₃ (B)	CYCH ₂	CYCH	ACH	C=CH ₂	ACCH ₃	COH	CO ₂
CH ₂	0	0	0	0	0	0	0.392	0	0	1.471	4.683
C=CH	0	0	0	0	0	0	0	0	0	1.376	0
CH=CH ₂	0	0	0	0	0	0	0	0	0	0	0
CH ₃ (B)	0	0	0	0	0	0	0.392	0	0	1.471	4.683
CYCH ₂	0	0	0	0	0	0	0	0	0	1.471	0
CYCH	0	0	0	0	0	0	0	0	0	1.471	0
ACH	0.392	0	0	0.392	0	0	0	0	0	4.091	-6.888
C=CH ₂	0	0	0	0	0	0	0	0	0	0.603	0
ACCH ₃	0	0	0	0	0	0	0	0	0	0.784	-14.93
COH	10.22	1.376	0	10.22	10.22	10.22	20.74	0.603	20.74	0	0.22
CO ₂	4.683	0	0	4.683	0	0	-3.329	0	-3.94	-1.18	0

Received: August 19, 2004

Accepted for publication: May 5, 2005

Recommended by Subject Editor J. Pinto