

Carbon dioxide supercritical extraction provides low operating temperatures (that avoid product thermal degradation) and no solvent residue. The terpeneless oxygenated aroma, of high commercial value, is obtained as the raffinate. Equilibrium predictions have been performed with the Group Contribution Equation of State (GC-EOS, Skjold-Jorgensen, 1984; Brignole *et al.*, 1984). In this work, aldehyde pure group parameters have been calculated for GC-EOS, together with binary interaction parameters between this new group and paraffins, carbon dioxide and aromatics. Pure group and interaction parameters for olefin groups (Pusch and Schmelzer, 1993) and carbon dioxide and aromatics binary interaction groups (Bamberger *et al.*, 1994) have been added to original GC-EOS parameters. Figure 2 shows binary phase equilibrium predictions for the system citral-carbon dioxide, with GC-EOS, which are in good agreement with experimental data (Marteau *et al.*, 1995).

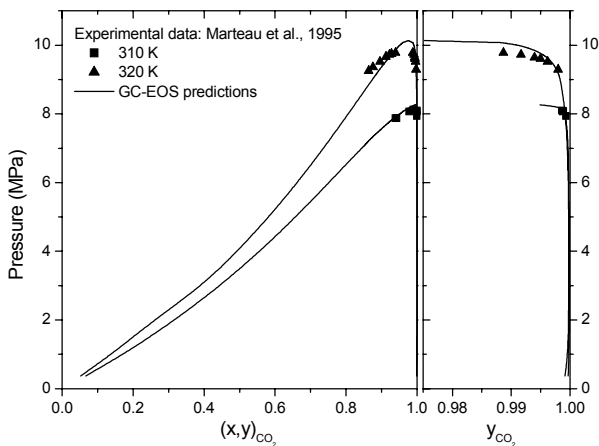


Figure 2. Vapor-liquid equilibria for CO₂ – Citral mixture

The quality of ternary predictions has also been tested; Fig. 3 shows a pressure-composition diagram for a model lemon oil mixture (75% limonene and 25% citral), prepared by Kalra *et al.* (1987), with CO₂, and our predictions at three isotherms.

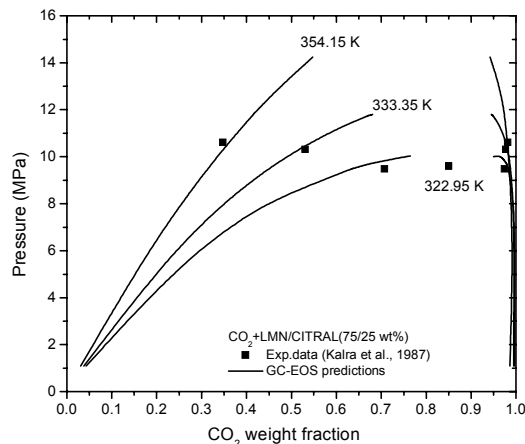


Figure 3. Pressure-composition diagram for the ternary mixture CO₂-Limonene-Citral

Figure 4 shows a comparison between GC-EOS vapor - liquid equilibrium predictions and the same experimental data for the ternary. Finally, solubility data for an actual lemon oil-CO₂ mixture (Kalra *et al.*, 1987) have been compared to GC-EOS predictions for a 75% limonene-25% citral (weight) mixture in CO₂, as it is shown in Fig. 5, at three different temperatures. Lemon peel oil can be accurately modeled as a binary mixture composed of limonene-citral (75-25 weight %) and process simulation and optimization have been performed for this lemon oil feed composition.

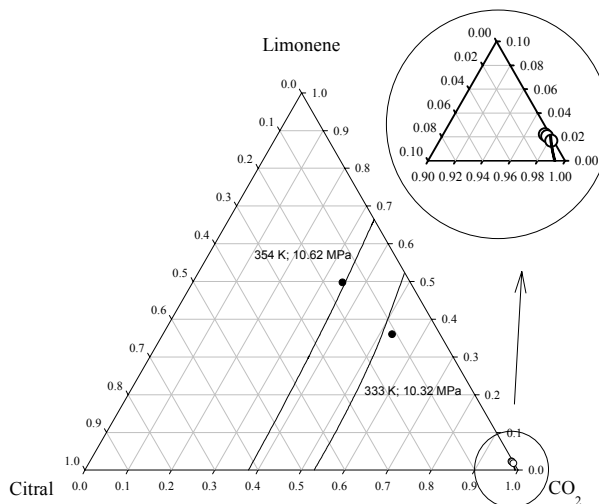


Figure 4. Vapor-liquid ternary equilibrium diagram for CO₂-Citral-Limonene mixture. (symbols: experimental data; lines: GC-EOS predictions)

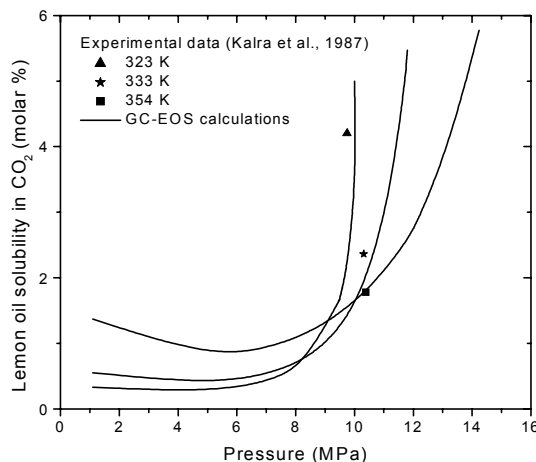


Figure 5. Predictions and experimental data for lemon oil solubility in CO₂

III. OPTIMIZATION MODEL

The determination of optimal solvent cycle scheme and operating conditions for the supercritical deterpenation of lemon oil has been formulated as the following

Mixed Integer Nonlinear Programming (MINLP) model:

$$\begin{aligned}
 & \text{Max}_{x,y} f(x,y) \\
 & \text{s.t.} \\
 & h(x,y) = 0 \\
 & c(x) = 0 \\
 & g(x,y) \leq 0 \\
 & x \in \mathfrak{R}^n, x_L \leq x \leq x_U, \quad y \in \{0,1\}^m
 \end{aligned}$$

where vector x corresponds to continuous optimization variables: extraction pressure, solvent recovery unit pressure, solvent flowrate and reflux ratio. Binary vari-

ables y have been associated to potential units in the process and the solvent recovery system. Equality constraints, h , represent the process mathematical model. It is solved within a sequential process simulator which includes rigorous models for a high-pressure multistage extractor (Brignole *et al.*, 1987) and a multiphase flash (Michelsen, 1982). The GC-EOS has been integrated as thermodynamic support for these model unit simulation routines. Additional equality constraints c correspond to reflux recycle, as the nonlinear optimization subproblem has been solved in an infeasible-path way. Inequality constraints, g , include product purity and recovery specifications, solvent purity and operating bounds.

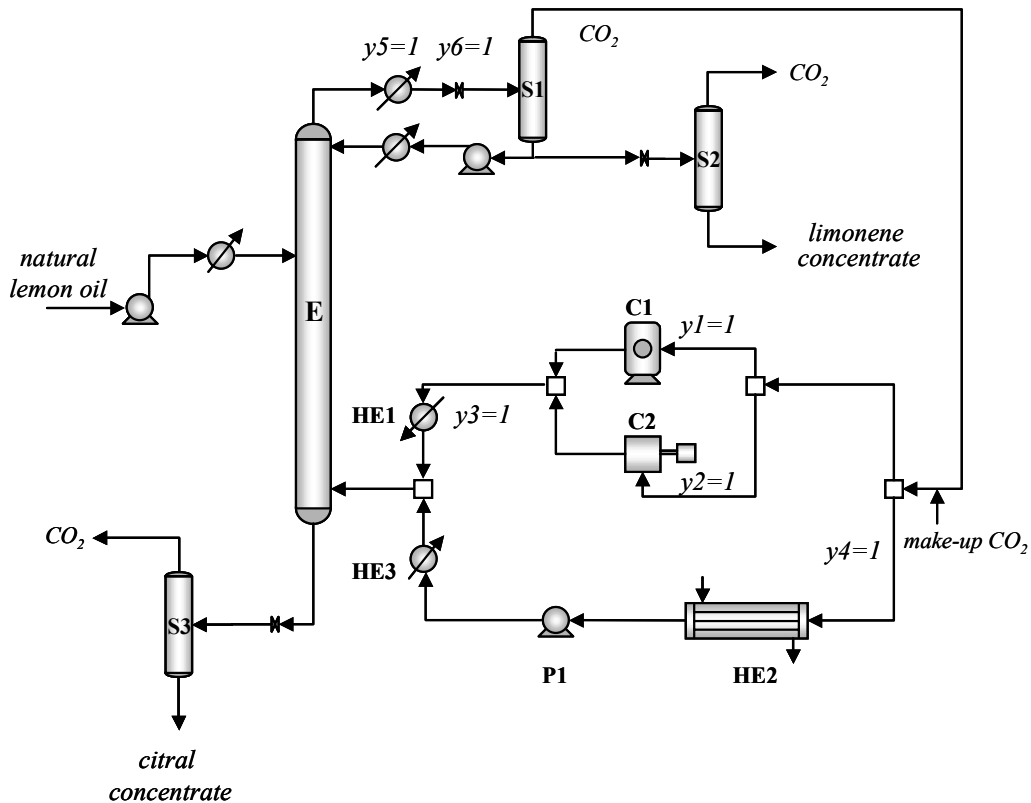


Figure 6. Supercritical deterpenation scheme with solvent cycle superstructure

Figure 6 shows the deterpenation process together with the solvent recovery system superstructure. In the extraction column (E), lemon oil is fed at the sixth stage in countercurrent with supercritical carbon dioxide; citral is the raffinate. Limonene and carbon dioxide constitute the extract, which may be heated ($y_5=1$) and/or expanded through a Joule-Thomson valve ($y_6=1$) to reduce solute solubility in supercritical carbon dioxide. This stream is then sent to a solvent recovery unit (S1); 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 further expansion to ambient pressure. Other alternative to separate the extract from the solvent is to change temperature in order to reduce solute solubility in carbon dioxide at constant

pressure, so the valve (V1, $y_6=1$) is also optional; however solvent purity for reuse cannot be achieved in this option. In compression mode, the recovered carbon dioxide is compressed (C1, centrifugal, $y_1=1$ or C2, reciprocal, $y_2=1$) to extraction pressure and then it is cooled to extraction temperature (HE1, $y_3=1$). In pumping mode ($y_4=1$), the recovered solvent is condensed (HE2), pumped (P1) and heated (HE3) to extraction pressure and temperature respectively. In pumping mode, a propane refrigeration cycle has been considered to condense carbon dioxide; the solvent is heated in HE3 with low-pressure steam to extractor temperature. In compressor mode, the solvent is cooled (HE1) to extractor temperature with cooling water. The objective is to maximize net profit.

IV. DISCUSSION

Optimal solvent recovery scheme for the deterpenation of lemon peel oil has been determined for supercritical extraction with carbon dioxide together with optimal operating conditions. The plant processes 20 kg/h feed oil, which is composed of 75% limonene and 25% citral (weight basis), a mixture that closely represents natural lemon oil. A twenty-stage column has been selected. Nonlinear constraints, which correspond to process specifications, are shown in Table 1.

Table 1. Nonlinear constraints

Nonlinear constraint	Lower Bound
Citral purity (CO ₂ free) (% mole)	99.00
Citral recovery (%)	95.00
Limonene purity (CO ₂ free) (% mole)	98.00
Limonene recovery (%)	87.00
Carbon dioxide in vapor (% mole)	99.97

A simple countercurrent scheme has been studied as a first step, but none of the nonlinear constraints could be fulfilled with this process scheme. An 89 % product purity (carbon dioxide free) with 66.50% citral recovery could be obtained, together with 97.4% and 89.70% limonene recovery and purity in top product, respectively. Extractor operating conditions were 93.22 bar and 345 K. The addition of external reflux to the extraction step, as it is shown in Fig. 6, increases both product recovery and purity. The objective function, net profit maximization, has been calculated as :

$$\text{Net profit} = (\text{price} * \text{production})_{\text{terpeneless lemon oil}} + (\text{price} * \text{production})_{\text{limonene}} - (\text{cost} * \text{consumption})_{\text{lemon oil}} - (\text{Operating Costs} + \text{Capital Costs}),$$

where operating costs include electrical motor consumption, either as pump or compressor driver, cooling water and steam consumption. Capital cost models are of the general form: $C_i = a_i y_i + b_i w_i^{\eta_i}$, where a_i , b_i and η_i are cost parameters. These functions are defined over the entire domain of the design variable w_i (which stands for heat exchanger area, power consumption in pumps and compressors, etc.) and they have been derived for each unit in the superstructure based on graphical correlations from Ulrich (1984) and Institut Français du Pétrole (1981). In the MILP master problem, these functions have been replaced with linear underestimators. Also, for a variable w_i , associated to unit or path i , the following inequality constraints have been written:

$$w_i - M_i y_i \leq 0,$$

$$w_i \geq 0,$$

where M_i is a known upper bound on w_i ; therefore, for a non-existing unit i ($y_i = 0$), the associated variable w_i must be zero. If $y_i = 1$, the upper bound holds on w_i .

The MINLP problem has been solved with an implementation of the Outer Approximation algorithm (Duran and Grossmann, 1986) that can interface a process simulator (Diaz and Bandoni, 1996); NLP subproblems have been solved with an SQP algorithm (Biegler and Cuthrell, 1985) and MILP problems, with LINDO (Schrage, 1987).

Lemon oil is corrosive so stainless steel process units are required. The extraction column is a structured packed column with Sulzer packing (Mellapack 250). Shell and tube heat exchangers, compressors and reciprocating pump costs curves have been obtained from Ulrich (1984). Capital cost curves for the extraction column have been obtained from Institut Français du Pétrole (1981). Investment cost has been annualized considering a project life of three years. Raw material cost is 28 \$/kg (Chemical Market Reporter, Apr/01) and product prices strongly depend on product purity. Terpeneless lemon oil (citral, in this work) price is 847 \$/kg (TGSC, www.execpc.com/~goodsent/, Apr/01). Limonene price has been considered as 1.44 \$/kg (Chemical Market Reporter, Apr/01).

The MINLP optimum corresponds to a solvent recovery system in compression mode. Numerical results, which are reported in Table 2, show that a compressor cycle is the best option because this process operates at pressure below 300 bar (Brunner, 1994). Terpeneless lemon oil high-commercial value justifies working with larger solvent-to-feed ratio. Figure 7 shows a comparison between solvent cycle consumption in compressor mode and in pump mode for the optimal determined conditions, in a T-S diagram. It can be clearly seen that a compressor is the option with lower energy consumption at this pressure level.

Table 2. Continuous optimization variables and main costs for the countercurrent extraction with reflux at solvent cycle MINLP optimum

Variable	MINLP Opt.
Extractor Pressure (bar)	95.00
Extractor Temperature (K)	333.14
Separator Pressure (bar)	44.60
Reflux Ratio	0.586
Solvent-to feed ratio (mass)	125.31
Citral in Raffinate, CO ₂ free (%mole)	99.98
Citral Recovery (%)	96.03
Limonene in Top Product (%mole)	98.72
Limonene Recovery (%)	91.54
CO ₂ in Sep. Vapor (% mole)	99.98
Extractor volume (m ³)	0.15
Compressor consumption (KW)	30.00
Pumps consumption (KW)	0.13
Heat exchanger area HE1 (m ²)	4.94
Capital cost (\$/Kg product)	8.09
Operating cost (\$/Kg product)	0.62
Profit (\$/Kg product)	721.80

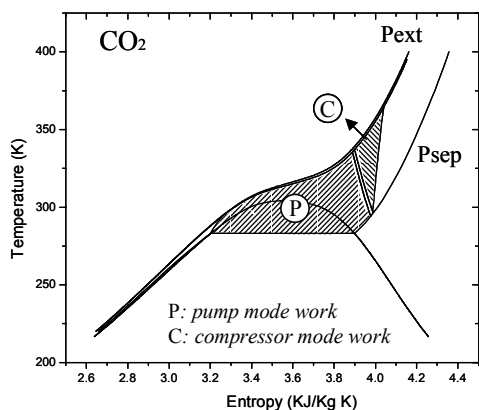


Figure 7. T-S diagram for CO₂ recycle.

V. CONCLUSIONS

The problem of optimal solvent cycle design has been addressed as an MINLP problem for the supercritical deterpenation of lemon oil. Argentina is lemon first world producer and a nontoxic technology for the production of a high commercial value aroma, as citral seems to be of great interest. The MINLP model includes reliable thermodynamic predictions with a Group Contribution Equation of State and rigorous unit models. The close agreement between experimental equilibrium and solubility data for the ternary system limonene-citral-CO₂ and thermodynamic predictions, together with rigorous process simulation models guarantee optimal process schemes and operating conditions. A better insight has been obtained as regard process feasibility, operating conditions and solvent cycle design when performing economic evaluation through a detailed cost analysis.

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