

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 (C₁₀H₁₆) and linalool (C₁₀H₁₇OH). 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 + CO₂ 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).