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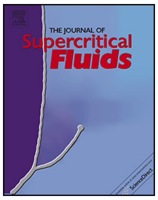

# Extraction of natural compounds using supercritical $CO_2$: Going from the laboratory to the industrial application

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## ABSTRACT

Despite industrial application for almost four decades, there is reluctance in some world regions to adopt supercritical (sc) $CO_2$ extraction because of the wrong perception that it is not fully competitive. To refute this misconception, this manuscript analyzes economics of $scCO_2$ extraction of vegetable oil from prepressed seeds. Selection of this application was due to the availability of a predictive mathematical model of the extraction process applicable for simulation purposes; inner microstructural changes of oilseeds during prepressing allow their extraction according to a shrinking core hypothesis. The predictive model has as its single parameter a particle-size and $scCO_2$-condition-independent microstructural mass transfer factor that can be best-fitted to laboratory extractions, existing literature correlations to estimate other model parameters, such as the axial dispersion in packed beds operating with supercritical fluids, and the solubility of vegetable oils in $scCO_2$. On the other hand, there is a need to correlate literature data for the film mass transfer coefficient to unveil the factors responsible for experimental data scattering. Because laboratory or pilot plant runs in single-extraction-vessel units cannot produce the simulated countercurrent contact in an industrial plant having $\geq 3$ extraction vessels, mathematical simulation provides the relationship between oil yield and extraction time that can anchor precise estimations of extraction cost. Analysis of results unveiled differences in optimal extraction time (for minimal extraction cost) between production costs estimated in this work and the operational costs informed before. Because the operational cost does not include the capital cost of the industrial plant, the need appears to reduce its contribution to the total cost by increasing plant productivity. This is achieved reducing extraction time, which negatively influences oil yield.

To make further progress in the optimization of industrial $scCO_2$ extraction processes, this manuscript proposes refining the mathematical simulation approach, and studying those technical constraints whose manifestations become more prevalent on scale-up. Mathematical simulation can be adapted to alternative, sample-pretreatment dependent mass transfer mechanisms in the solid matrix. It can be refined also to account for the size distribution of the substrate, radial changes in superficial $scCO_2$ velocity, axial changes in pressure, and radial/axial changes in temperature resulting from heterogeneous packing, pressure drop, and/or heat transfer from/to extraction vessel walls that may influence large-scale extractions. Large-scale experiments will allow studying these phenomena, as well as technical constraints to the decrease in particle size, increase in $scCO_2$ velocity, and decrease in extraction time imposed by the agglomeration and decrease in packed bed permeability of the substrate, and thermal effects during reconditioning of extraction vessels. The latter effects should be included as restrictions in the optimization of the extraction process, which may limit the extraction rate and the size or number of extraction vessel that impact economics positively. Close collaboration with industry will facilitate tackling large-scale problems, as well as refining estimates of plant cost as a function of its size and/or configuration.

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## Nomenclature

*Variables and parameters*

| | |
|---|---|
| $C$ | Solute concentration in the supercritical phase (g/kg oil/$CO_2$) |
| $C_B$ | cost of a batch per unit volume of the extraction vessel (USD/$m^3$) |
| $C_B^{CO_2-\text{in}-\text{oil}}$ | unitary cost of dissolved $CO_2$ lost with recovered solute in separator (USD/kg extracted oil) |
| $C_C$ | unitary cost of eliminated heat (USD/GJ) |
| $C_{CO_2}$ | unitary cost of $CO_2$ (USD/kg) |
| $C_H$ | unitary cost of heat (USD/GJ) |
| $C_{DP}$ | unitary cost of depressurization (USD/kg $CO_2$) |
| $C_E$ | unitary cost of electricity (USD/GJ) |
| $C_H$ | unitary cost of heat (USD/GJ) |
| $C_I$ | annual cost of the installed SFE plant (USD) |
| $C_L$ | unitary annual cost of labor (USD/yr per worker) |
| $C_{RP}$ | unitary cost of repressurization (USD/kg $CO_2$) |
| $C_{oil}$ | solute content in the substrate at the end of the extraction (kg/kg oil/substrate) |
| $C_{oil}^o$ | initial solute content in the substrate (kg/kg oil/substrate) |
| $C_S$ | cost of the substrate (USD/yr) |
| $C_{sat}$ | solubility of oil in $scCO_2$ at extraction conditions (g/kg oil/$CO_2$) |
| $C_{sat}^o$ | solubility of oil in $scCO_2$ at reference ($T_o$, $\rho_o$) conditions (g/kg oil/$CO_2$) |
| $C_{SC}$ | unitary cost of the solvent cycle (USD/kg $CO_2$) |
| $C_{sep}$ | solubility of oil in $CO_2$ at separation conditions (g/kg oil/$CO_2$) |
| $D$ | inner diameter of the extraction vessel (m) |
| $D_{12}$ | binary diffusivity of the solute in $scCO_2$ ($m^2$/s) |
| $D_c$ | cell size in seed tissue (m) |
| $D_e$ | effective diffusivity of the solute in the substrate ($m^2$/s) |
| $D_L$ | axial dispersion coefficient of $scCO_2$ in the packed bed ($m^2$/s) |
| $d_p$ | particle diameter of the substrate (m) |
| $e_C$ | cold media requirement of the solvent cycle (kJ/kg $CO_2$) |
| $e_E$ | electric power requirement of the solvent cycle (kJ/kg $CO_2$) |
| $e_H$ | heat requirement of the solvent cycle (kJ/kg $CO_2$) |
| $F_M$ | microstructural correction factor (–) |
| $g$ | earth's standard acceleration due to gravity (9.81 m/$s^2$) |
| $Gr$ | dimensionless Grashof number (–) |
| $h_i$ | specific enthalpy of the $CO_2$ stream in condition "i" of the solvent cycle (kJ/kg $CO_2$) |
| $H$ | height of the extraction vessel (m) |
| $I$ | cost of a SFE plant (USD) |
| $I_r$ | cost of a reference SFE plant having two 1000-L extraction vessels and a solvent cycle operating with 6000 kg/h of $CO_2$ (USD) |
| $k$ | association number ($CO_2$ molecules forming a solvato complex with a single solute molecule) |
| $k_f$ | external (film) mass transfer coefficient (m/s) |
| $M$ | molecular weight of the lipid molecule (g/mol) |
| $n$ | number of extraction vessels in a SFE plant |
| $N$ | number of extraction batches produced in a year |
| $n_L$ | number of workers required to operate the SFE plant |
| $P$ | pressure of extraction or separation (MPa) |
| $P_o$ | reference pressure (30 MPa) |
| $Q$ | mass flow rate of $CO_2$ in the solvent cycle (t/h) |
| $r$ | annual rate of discount (%) |
| $R$ | universal gas constant (8.314 J/(mol K)$^{-1}$) |
| $Re$ | dimensionless Reynolds number (–) |
| $Sc$ | dimensionless Schmidt number (–) |
| $Sh$ | dimensionless Sherwood number (–) |
| $s_i$ | specific entropy of the $CO_2$ stream in condition "$i$" of the solvent cycle (kJ/kg $CO_2$) |
| $t$ | Extraction time (h) |
| $T$ | temperature of extraction or separation (°C) |
| $t_e$ | optimal extraction time in the SFE plant (h) |
| $t_p$ | annual production time of the SFE plant (h) |
| $t_s$ | optimal switch time in the SFE plant (h) |
| $T_o$ | reference temperature (313 K) |
| $U$ | superficial velocity of the $CO_2$ in the packed bed (m/s) |
| $V_E$ | volume of the extraction vessels ($m^3$ or L) |
| $w_{CO_2}^{oil}$ | weight fraction of $CO_2$ in the oil at separation conditions (kg/kg $CO_2$/oil) |
| $Y$ | yield of extraction (% of oil) |

*Greek letters*

| | |
|---|---|
| $\alpha$ | fraction of free solute in pretreated seed (–) |
| $\beta$ | fraction of the cost of a reference SFE plant having two 1000-L extraction vessels and operating using 6000 kg/h of $CO_2$ that is due to the solvent cycle (–) |
| $\delta$ | thickness of superficial layer of broken cells in milled seeds (m) |
| $\Delta H$ | total (vaporization plus dissolution) heat required to synthesize a solvato complex (J/mol) |
| $\Delta\rho$ | density difference between a supercritical fluid phase saturated with solute and the pure solvent (kg/$m^3$) |
| $\varepsilon$ | void fraction of the packed bed (intraparticle porosity) (–) |
| $\varepsilon_{oil}$ | absolute volume fraction of oil in the packed bed (–) |
| $\bar{\varepsilon}^o$ | volume fraction of oil in the substrate in a void-free basis (–) |
| $\varepsilon_p^o$ | initial void fraction of the substrate (intraparticle porosity) (–) |
| $\varepsilon_s$ | absolute volume fraction of nonfat solids in the substrate in the packed bed (–) |
| $\bar{\varepsilon}_s$ | volume fraction of nonfat solids in the substrate in a void-free basis (–) |
| $\varepsilon_T$ | absolute void volume fraction (inter-plus intraparticle porosity) of the bed (–) |
| $\varepsilon^o$ | initial value of $\varepsilon_T$ (–) |
| $\eta_e$ | electric efficiency of the motor of the pump or compressor (%) |
| $\eta_i$ | isoentropic efficiency of the pump or compressor (%) |
| $\rho$ | density of $CO_2$ (kg/$m^3$) |
| $\rho_{app}$ | apparent density of the substrate (kg/$m^3$) |
| $\rho_{app}^{max}$ | true density of the substrate (kg/$m^3$) |
| $\rho_b$ | bulk density of the bed (kg/$m^3$) |
| $\rho_o$ | density of $CO_2$ at reference ($T_o$, $P_o$) conditions (910 kg/$m^3$) |
| $\rho_{oil}$ | density of the oil (kg/$m^3$) |
| $\rho_s$ | density of the nonfat solids in the substrate (kg/$m^3$) |
| $\rho_{sat}$ | density of a supercritical fluid phase saturated with solute (kg/$m^3$) |
| $\rho_v$ | density of expanded $CO_2$ in the extraction vessel at buffer tank pressure (kg/$m^3$) |