



## Equilibrium partition of rapeseed oil between supercritical CO<sub>2</sub> and prepressed rapeseed



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### ABSTRACT

The equilibrium partition of a vegetable extract between supercritical (SC) CO<sub>2</sub> (fluid phase) and a vegetable substrate (solid phase) is commonly best-fitted in the mathematical simulation of extraction curves. The aim of this study was to develop and apply an experimental methodology to measure the equilibrium partition of rapeseed oil between SC CO<sub>2</sub> and prepressed rapeseed. We measured and modelled sorption isotherm/isobar curves using a methodology that intersperses extraction (to reduce oil content) and equilibration (by recirculation of the SC CO<sub>2</sub> phase) steps, with oil being sampled in each step. Oil desorption was a two-stage process; when rapeseed contains more than ~70–80 g kg<sup>-1</sup> oil/substrate the SC CO<sub>2</sub> phase gets saturated with oil ( $C_f = C_{sat}$ ), whereas when it contains less oil this is bound to the solid matrix in such a way that  $C_f$  dips below  $C_{sat}$ . Increasing pressure from 22 to 28 MPa at constant temperature (40 °C) increases  $C_f$ . The effect of the increase in pressure is less pronounced when SC CO<sub>2</sub> density is kept constant (857.1 kg/m<sup>3</sup>) by simultaneously increasing temperature from 40 to 50 °C. The heat of desorption of the oil is ~100 kJ/mol which suggests it is bound to the prepressed seed by van der Waals interaction forces. However experimental values in this region are uncertain due to propagation of uncertainties to estimate  $C_s$ .

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## 1. Introduction

Industry requires reliable mathematical descriptions of Supercritical (SC) Fluid (SCF) Extraction (SCFE) to facilitate process design, scale-up, and costing. SCFs, particularly carbon dioxide (CO<sub>2</sub>) above its corresponding critical temperature and pressure, have been successfully applied to extract high-value-added compounds for the food, cosmetic, and pharmaceutical industries [1]. Reliable mathematical descriptions of SCFE of vegetable substrates depend critically on the determination of equilibrium and mass transfer parameters, including those characterizing solute partition between SC CO<sub>2</sub> and the pretreated substrate. Mass transfer parameters include an axial dispersion coefficient ( $D_L$ ) describing solute migration in the SCF phase moving along the packed bed, a film mass transfer coefficient ( $k_f$ ) describing transport of the solute

from solid particles to the SCF phase through a thin layer of SCF stationed next to the particles, and an internal mass transfer coefficient (e.g., effective diffusivity,  $D_e$ ) describing the transport of solute within solid particles under the influence of solute gradients imposed by the removal of solute at the surface of the particles [2,3]. Equilibrium parameters correspond to those of a sorption isotherm/isobar equation relating solute concentration in the SC CO<sub>2</sub> phase ( $C_f$ ) with solute concentration in the solid (pretreated vegetable substrate) phase ( $C_s$ ) [4]. Parameters  $D_L$  and  $k_f$  can be estimated using dimensionless correlations for packed beds operating with SCFs [2,3]. On the other hand,  $D_e$  and the parameter(s) of a simple sorption isotherm/isobar equation (e.g., a constant partition coefficient  $K$ ) are usually estimated by best-fitting integral extraction curves (plots of cumulative yield, e.g., grams of solute per kilogram of substrate, versus specific solvent consumption, e.g., kilograms of CO<sub>2</sub> per kilogram of substrate) obtained in laboratory or pilot-plant units. Although it may be possible for a mathematical model that does not fit reality to describe integral extraction plots when model parameters are best-fitted to experimental data, the best-fitted model will probably fail in simulating extractions at larger scales, including industrial extractions [4].

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## Nomenclature

$a_s$	specific surface area ( $\text{m}^2$ )
$b$	model parameter in Eq. (12c) (K)
$df_c$	degrees of freedom of complete model (–)
$df_r$	degrees of freedom of reduced model (–)
$d_p$	particle diameter (m)
$f_p$	value of Fisher–Snedecor function for ( $df_r - df_c$ ) degrees of freedom in the numerator, $df_c$ degrees of freedom in the numerator, and a significance level $p$ (–)
$k_f$	film mass transfer coefficient ( $\text{m s}^{-1}$ )
$k_p$	global mass coefficient using a linear driving force ( $\text{m s}^{-1}$ )
$n$	isotherm/isobar curve parameter in Eq. (5)
$p$	significance level (–)
$t$	extraction time (s)
$u(y)$	variance of variable $y$
$z$	axial position along the bed (m)

### Upper case letters

$A$	isotherm/isobar curve parameter in Eqs. (9) and (12c), or cross sectional area of extraction vessel ( $\text{m}^2$ )
$A^\circ$	value of parameter $A$ at reference temperature $T^\circ$ (313.2 K) in Eq. (12c)
$C_f$	oil concentration in SC $\text{CO}_2$ ( $\text{g kg}^{-1}$ oil/ $\text{CO}_2$ )
$C_{f(i)}$	oil concentration in SC $\text{CO}_2$ in equilibration period 'i' ( $\text{g kg}^{-1}$ oil/ $\text{CO}_2$ )
$C_f^\circ$	oil concentration in saturated SC $\text{CO}_2$ phase equilibrated with oilseed at reference temperature $T^\circ$ (313 K) ( $\text{g kg}^{-1}$ oil/ $\text{CO}_2$ )
$C_{f^* z,t}$	oil concentration in SC $\text{CO}_2$ film in equilibrium with oil in oilseed ( $\text{g kg}^{-1}$ oil/ $\text{CO}_2$ )
$C_{fo}$	oil concentration in SC $\text{CO}_2$ phase following static equilibration period ( $\text{g kg}^{-1}$ oil/ $\text{CO}_2$ )
$C_{f z,t}$	oil concentration in SC $\text{CO}_2$ phase at position $z$ and time $t$ ( $\text{g kg}^{-1}$ oil/ $\text{CO}_2$ )
$C_s$	average oil concentration in oilseed or adsorbed onto it ( $\text{g kg}^{-1}$ oil/substrate)
$C_{s(i)}$	average oil concentration adsorbed onto oilseed after equilibration period 'i' ( $\text{g kg}^{-1}$ oil/substrate)
$C_{s(n)}$	residual oil content in oilseed after final equilibration period ( $n$ ) measured by Soxhlet extraction ( $\text{g kg}^{-1}$ oil/substrate)
$C_{\text{sat}}$	oil concentration in saturated SC $\text{CO}_2$ phase ( $\text{g kg}^{-1}$ oil/ $\text{CO}_2$ )
$C_{\text{sat}}^\circ$	oil concentration in saturated SC $\text{CO}_2$ phase at reference temperature $T^\circ$ (313 K) and reference density $\rho^\circ$ ( $857.1 \text{ kg m}^{-3}$ ) ( $\text{g kg}^{-1}$ oil/ $\text{CO}_2$ )
$C_{so}$	oil content in oilseed following a static equilibration period ( $\text{g kg}^{-1}$ oil/substrate)
$C_{s z,t}$	concentration of oil in oilseed in position $z$ and time $t$ ( $\text{g kg}^{-1}$ oil/substrate)
$D$	diameter of the extraction vessel (m)
$D_{12}$	binary diffusion coefficient of oil in SC $\text{CO}_2$ ( $\text{m}^2 \text{ s}^{-1}$ )
$D_e$	effective diffusion coefficient of oil in oilseed ( $\text{m}^2 \text{ s}^{-1}$ )
$D_L$	axial dispersion coefficient of oil in packed bed ( $\text{m}^2 \text{ s}^{-1}$ )
$F$	statistical distribution (–)
$F_M$	microstructural (correction) factor for $D_{12}$ , to account for mass transfer resistance in oilseed (–)
$J_{ z,t}$	overall extraction rate ( $\text{kg m}^{-2} \text{ s}^{-1}$ )

$K$	equilibrium partition when there is no interaction between oil and the solid matrix ( $\text{kg kg}^{-1} \text{ CO}_2/\text{substrate}$ )
$L$	length of extraction vessel (m)
$M_o$	oil-free substrate (kg)
$N$	number of axial nodes in finite difference scheme to solve differential mass balance equations (–)
$P$	equilibration pressure of system (MPa)
$P'$	atmospheric pressure (MPa)
$Q$	volumetric flow rate of $\text{CO}_2$ in the extraction vessel ( $\text{m}^3 \text{ s}^{-1}$ )
$R$	universal gas constant ( $0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$ )
$Re$	dimensionless Reynolds number (–)
$S_{(i)}$	oil removed in period 'i' (g)
$S_o$	initial oil content in oilseed sample (g)
$Sc$	dimensionless Schmidt number (–)
$SSE_C$	Sum of squared errors of complete model
$SSE_R$	Sum of squared errors of reduced model
$T$	equilibration temperature of system (K)
$T'$	temperature of expanded $\text{CO}_2$ in volumetric gas meter (K)
$T^\circ$	reference absolute temperature (313.2 K)
$U$	superficial velocity of SC $\text{CO}_2$ in the extraction vessel ( $\text{m s}^{-1}$ )
$V$	volume ( $\text{m}^3$ )
$V_{\text{cell}}$	empty volume of equilibrium cell ( $\text{m}^3$ )
$V_{\text{CO}_2}$	volume of expanded $\text{CO}_2$ samples ( $\text{m}^3$ )
$V_{\text{loop}}$	total volume of equilibration system ( $\text{m}^3$ )

### Greek letters

$\alpha$	isotherm/isobar curve parameter in Eqs. (9) and (12b) ( $\text{kg g}^{-1}$ substrate/oil)
$\alpha^\circ$	value of parameter $\alpha$ at reference temperature $T^\circ$ (313.2 K) in Eq. (12b) ( $\text{kg g}^{-1}$ substrate/oil)
$\Delta H$	total heat of solvation and sorption of oil ( $\text{kJ mol}^{-1}$ )
$\Delta H_{\text{solv}}$	heat of solvation of oil ( $\text{kJ mol}^{-1}$ )
$\Delta H_{\text{sorp}}$	heat of desorption of oil ( $\text{kJ mol}^{-1}$ )
$\Delta t$	time interval in finite difference scheme to solve differential mass balance equations (s)
$\Delta z$	height interval in finite difference scheme to solve differential mass balance equations (m)
$\varepsilon$	(inter-particle) porosity of the packed bed (–)
$\varepsilon'$	(inter-particle) porosity of the packed bed and other elements in equilibration system (–)
$\varepsilon_p$	(intra-particle) porosity of the solid substrate (–)
$\mu$	viscosity of $\text{CO}_2$ (Pa s)
$\rho$	density of $\text{CO}_2$ in the equilibrium system ( $\text{kg m}^{-3}$ )
$\rho'$	density of expanded $\text{CO}_2$ ( $\text{kg m}^{-3}$ )
$\rho_b$	bulk (apparent) density of oilseed in equilibrium cell ( $\text{kg m}^{-3}$ )
$\rho_s$	(true) density of oilseed ( $\text{kg m}^{-3}$ )

There is a need to experimentally measure equilibrium parameters to limit best-fitting of integral extraction curves to estimate a single parameter ( $D_e$ ) representing inner mass transfer within the pretreated substrate [4]. However, to the best of the authors' knowledge there are experimental reports in literature only for the partition of oil between partially-extracted canola seeds [5] or neat rapeseeds [6] and SC  $\text{CO}_2$ , and of phenanthrene between spiked soil samples and pure or methanol-modified SC  $\text{CO}_2$  [7]. In their experiments, Bulley et al. [5] reduced the initial oil content of canola samples to various extents by partial extraction with hexane, and estimated corresponding equilibrium concentrations in  $\text{CO}_2$  from

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