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Free solute content and solute-matrix interactions affect apparent solubility and apparent solute content in supercritical CO_2 extractions. A hypothesis paper

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ABSTRACT

This manuscript stresses the need of experimental measurements and mathematical models of sorption isotherms/isobars to properly account for mass transfer in the SuperCritical (SC) Fluid Extraction (SCFE) processes. A reliable sorption isotherm/isobar model is a requirement, on one hand, for the determination of relevant inner mass transfer coefficients in SC CO_2 extractions of vegetable substrates and other biological materials at the laboratory scale, and on the other hand, for a simulation tool successfully applicable to describe industrial SCFE process, which should be based both on a reliable mathematical descriptions of SC CO_2 extraction processes. Having a reliable simulation model and model parameters would allow limiting expensive experimental pilot-scale work to validation purposes. Based on simulations of oil extraction from pre-pressed oilseeds using SC CO_2 at 353 K and 90 MPa, this manuscript shows that the initial oil content in the pre-treated seed affects the apparent solubility of the oil, that the partition of the oil between the seed and CO_2 affects oil yield, that it is difficult to discriminate oil partition from inner mass transfer effects, that the best-fit parameters from a mathematical model are adequate only when the model accounts for the true physical picture of the extraction process, and that failure of the mathematical model to account the true physical picture of the extraction process impedes reliable simulations, scale-up, and economical evaluation of industrial SCFE process. Being sorption phenomena of such paramount importance to build a reliable mathematical model for simulation of SCFE processes, this manuscript proposes a mathematical model that fits experimental sorption isotherm/isobars for oil from seeds.

1. Introduction

SuperCritical (SC) Fluids (SCFs) are conveniently applied in environment-friendly extraction processes because of their liquid-like solvent properties and gas-like transport properties, that allow efficient and fast extraction processes, and complete elimination of solvent traces (SCFs are gases under normal conditions) from extracts and treated substrates. Among potential candidates, inexpensive carbon dioxide (CO_2), offers safe and selective SCF Extraction (SCFE) processes at near-environmental temperatures, which justifies commercial applications of SC CO_2 extraction over the last three decades, particularly for high-value compounds in vegetable substrates [1].

Modelling and simulation are important for process design purposes, particularly of SCFE processes. Commercial SCFE plants for vegetable substrates can be designed estimating relevant equilibrium and rate parameters from integral extraction curves obtained in the laboratory [2]. An integral extraction curve is a plot of cumulative yield (e.g., grams of extract per kilogram of substrate) *versus* specific solvent consumption (e.g., kilograms of CO_2 per kilogram of substrate) that, according to Brunner [1], "is of relative simple form . . . (so that) it is not possible to calculate many parameters with significance from such a curve" (p. 181).

Typical integral extraction curves have three zones [3] (Fig. 1). In Zone I the curve has a constant slope having as units, e.g. grams of solute per kilogram of CO_2, which represents a so-called "apparent" solubility of the extract (a multicomponent mixture of solutes in the substrate that can be extracted simultaneously) in SC CO_2 (C_{fo}). When there is free solute on the surface of the substrate particles, this migrates to the interparticle SC CO_2 phase in an amount that is restricted only by the solubility of the solute in SC CO_2 under process conditions. The slope of the integral extraction curve decreases continuously in Zone II because there is no enough free solute on the surface of the particle, there are constraints to mass transfer within the substrate and a stationary film of CO_2 next to the particle, and/or there are equilibrium constraints to the liberation of solute from the substrate to the intra-particle SC CO_2 phase. Finally, in Zone III the integral extraction curve approaches a horizontal asymptote that represents the total amount of solute in the substrate that SC CO_2 can remove under process conditions.

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Nomenclature

a_{s}	specific surface area (m^2)
d_{E}	diameter of the extraction vessel (m)
d_{p}	particle diameter (m)
k_{f}	film mass transfer coefficient (m/s)
k_{p}	global mass coefficient using a linear driving force (m/s)
n	isotherm parameter in Eqs. (18) and (21)
n	N (Appendix)
t	extraction time (s)
t_{res}	residence time of SC CO_2 in the extraction vessel (s)
z	axial position along the bed (m)

Upper case letters

A	isotherm parameter in Eqs. (18) and (21)
Bi	Biot number
C_{f}	concentration of oil in the SC CO_2 (g/kg)
C_{f}^*	concentration of oil in a SC CO_2 film that is in equilibrium with oil in the surface of pre-pressed oilseed (g/kg)
C_{fo}	concentration of oil in the SC CO_2 phase following the static extraction period (g/kg)
$C_{\mathrm{f}}\|_{z,t}$	concentration of oil in the SC CO_2 phase in position z and time t (g/kg)
C_{m}	monolayer concentration of oil in pre-pressed oilseed (g/kg)
C_{s}	average concentration of oil in pre-pressed oilseed or adsorbed onto it (g/kg)
$(C_{\mathrm{s}})_{\mathrm{i}}$	initial concentration of oil in pre-pressed oilseed (g/kg)
C_{sat}	concentration of oil in a saturated SC CO_2 phase (g/kg)
C_{so}	concentration of oil in pre-pressed oilseed following the static extraction period (g/kg)
$C_{\mathrm{s}}\|_{z,t}$	concentration of oil in pre-pressed oilseed in position z and time t (g/kg)
C_{t}	transition concentration of oil in pre-pressed oilseed (isotherm parameter) in Eqs. (8), (20a) and (20b) (g/kg)
D_{12}	binary diffusion coefficient of oil in SC CO_2 (m^2/s)
D_{e}	effective diffusion coefficient of oil in pre-pressed oilseed (m^2/s)
F	microstructural (correction) factor for D_{12}, to account for the resistances to mass transfer in pre-pressed oilseed
J	overall extraction rate (kg/m^2/s)
K	equilibrium coefficient in Eqs. (9a), (9b), (10), (19) and (20b)
L	length of the extraction vessel (m)
N	number of axial nodes in finite difference scheme to solve differential mass balance equations
Pe	Peclet number
Q	mass flow rate of CO_2 in the extraction vessel (kg/s)
U	superficial SC CO_2 velocity in the extraction vessel (m/s)
V	volume of the extraction vessel (m^3)

Greek letters

α	shape factor of particle or isotherm parameter in Eq. (21)
δ	thickness of leaf (μm)
Δt	time interval in finite difference scheme to solve differential mass balance equations (s)
Δz	height interval in finite difference scheme to solve differential mass balance equations (m)
ε	(inter-particle) porosity of the packed bed
ε_{p}	porosity of the solid particle
ε_{t}	total (inter- plus intra-particle) porosity of the packed bed
μ	viscosity of SC CO_2 (Pa s)
ρ	density of SC CO_2 (kg/m^3)
ρ_{b}	bulk (apparent) density of pre-pressed oilseed in the extraction vessel (kg/m^3)
ρ_{oil}	density of oil (kg/m^3)
ρ_{s}	density of pre-pressed oilseed (kg/m^3)
Ψ	sphericity

Integral extraction curves can be used for scaling-up purposes and determining the cost of the SCFE process. Indeed, Rosa and Meireles [4] claim that “the minimum estimated cost (can be) obtained in extraction times close to the end of the constant extraction rate region and thus, in order to have low (cost of manufacturing) the constant extraction rate region should have short time and high yields” (p. 238). This is not entirely true because, as authors’ will show in this manuscript, integral extraction curves may be scale-specific under selected conditions.

The objective of this manuscript is to show the effect of the residual solute content in a vegetable substrate on the apparent solubility and yield of a SC CO_2 extraction process, as well as the implications of solute partition between the substrate and SC CO_2 on kinetics and scale-up of SCFE processes. This is done using mathematical simulations and re-analyzing data in literature.

2. Motivation

According to Brennecke and Eckert [5] “any really widespread applications of SCFE in the future are highly dependent on the ability of engineers to model and predict phase equilibria in the complex systems represented” (p. 1409). This is partially true when applying SCFE to vegetable substrates and other biological substrates because under certain conditions the optimal extraction

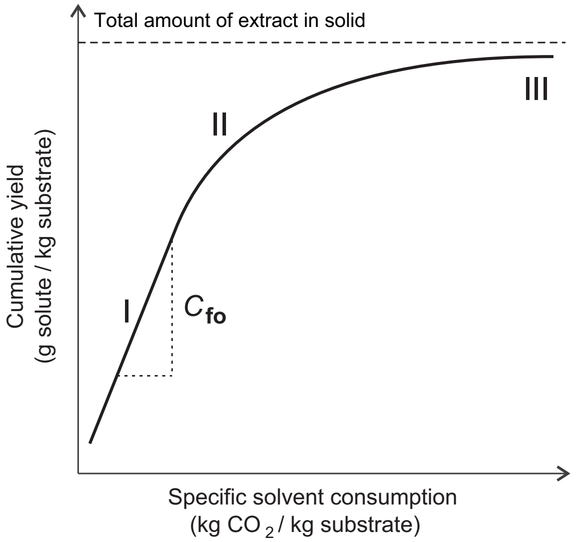

Fig. 1. Main zones of a typical integral extraction curve. Zone I solubility dominated where C_{f0} is the “apparent” solubility, Zone II transition between solubility and mass transfer dominions, Zone III mass transfer dominated where segmented lines C_{s0} represents the “apparent” initial solute content.