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Supercritical CO_2 extraction of oil from green coffee beans: Solubility, triacylglycerol composition, thermophysical properties and thermodynamic modelling

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ABSTRACT

The aim of this study was to measure the experimental solubility of green coffee oil (GCO) in supercritical CO_2 ($scCO_2$). Solubility was measured by static method under temperatures from 313.15 to 353.15 K and pressures of 30 and 35 MPa. The fatty acid (FA) profile was determined by gas chromatography-mass spectrometry (GC/MS). From these results, the triacylglycerol (TAG) profile was estimated by statistical methodology based on the FA composition. The thermophysical properties of the TAGs were estimated by group contribution methods The experimentally calculated equilibrium data were correlated using the Peng-Robinson equation of state (PR-EoS) with the van der Waals mixing rule. The experimentally measured solubility ranged from 12.4 to 26 g oil/kg CO_2. The results showed that solubility increased with increasing temperature under isobaric conditions. However, the effect of temperature showed different behavior at 343.15 and 353.15 K, depending on the pressures.

1. Introduction

Supercritical fluid (SCF) techniques have been largely used in the extraction of compounds present in nature with nutrient, antioxidant, anticancer, and antimicrobial properties, amongst others (commercial high-value compounds) [1–3], during the last decades especially in food, pharmaceutical, and cosmetic industries [4]. One of these compounds is the green coffee oil (GCO) rich in diterpenes (cafestol and kahweol), valued for its beneficial physiological activity important for health [5]. Therefore, some researchers have studied GCO in order to extract and/or isolate its main functional compounds (cafestol and kahweol) using the cold mechanical press and solvent extraction [6,7], supercritical carbon dioxide extraction [8–12], molecular distillation [13], microwave-assisted extraction [14], and pressurized liquid extraction [15]. Carbon dioxide is often promoted as a sustainable solvent because of its unique properties and numerous advantages including, non-explosive, nonflammable, relative low toxicity, low cost, natural abundance [4,16,17], easy removal from extracted materials [4], in addition to being non-polar and Generally Recognized as Safe (GRAS) for use in food products [18,19].

Oil, one of the major constituents of green coffee, is located in the endosperm of the beans and represents 7–17% of dry weight. The main components of GCO arabica are triacylglycerols (75.2%), esters of diterpene alcohol and fatty acids (18.5%), free diterpenes (0.4%), steroid esters and fatty acids (3.2%), free sterols (2.2%), tocopherol (0.04–0.06%), phosphatides (0.1–0.5%), and caffeine (~0.3%) [20–22]. The major fatty acids in triglycerides are: linoleic acid (43.1%), palmitic acid (31.1%), oleic acid (9.6%), stearic acid (9%), arachidic acid (3%), linolenic acid (1.8%), and behenic acid (0.7%) [12,26–28], and diterpenes (cafestol and kahweol) belonging to the kauran family that account for up to 19% of total oil [23–25] are of interest because of their physiological impact on human health, including anticarcinogenic [29,30] and antioxidant [31,32] effects.

The lipidic fraction is the primary interest in this type of raw material with functional properties. Recent efforts have focused on more profitable, economic, and clean isolation and/or extraction. Consequently, the supercritical carbon dioxide extraction technique proves to be an alternative to conventional processes such as solvent extraction (high cost of organic solvents), distillation separation (high temperatures), and mechanical pressing (low yield) for the extraction of

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Nomenclature

GCO	Green coffee oil
SFE	Supercritical fluid extraction
TAGs	Triacylglycerols
FA	Fatty acid
T_b	Normal boiling point [K]
T_c	Critical temperature [K]
P_c	Critical pressure [MPa]
ω	Acentric factor
$scCO_2$	Supercritical CO_2
X_0	Overall extraction yield
S	Solubility [g oil/kg CO_2]
ρ	CO_2 density [kg/m^3]
Δy	Relative error
ΔP	Pressure differential
FAME	Fatty acid methyl esters
SCF	Supercritical fluids
M	Molar mass [kg/mol]
n_A	Number of atoms
S_i	Solubility of the component (i)
x_i	Mole fraction in heavy (liquid) phase
y_i	Mole fraction in light (SCF) phase
Ka_{ij} and Kb_{ij}	Binary interaction parameters
φ	Fugacities coefficient
φ_i^L	Fugacity coefficient of the i-th component in the liquid phase
$\varphi_i^{V(SCF)}$	Fugacity coefficient of the i-th component in the SCF phase
PR-EoS	Peng-Robinson equation of state.

oils and other materials. The supercritical extractions offers a number of advantages such as excellent quality products, reduction of operational steps, automation, safe operation due to the use of non-organic solvents, and the use of moderate temperatures favorable for thermally labile compounds, in addition to recovery of extracts between 97% and 100% [4]. Knowledge of certain properties such as solubility and implicit values in the liquid–supercritical fluid equilibrium of the oils is considered necessary and important for the modelling and simulation processes [33].

The solubility of compounds in supercritical fluids depends mainly on two factors. One refers to the pressure, which increases the density of the supercritical fluid, thereby increasing its solvent power or its solubilizing ability. The other relates to the temperature, which influences the properties of the solvent, density, and also the properties of the solute, especially vapor pressure. The increase in temperature decreases the density of the solvent (low solubility) and increases the vapor pressure of the solute (higher solubility). Meeting this double influence on solubility requires compensation of these two opposite effects [34–36]. However, there is also discussion about the influence of cellulosic structure on solubility for plant material/CO_2 systems, as stated by Brunner [34]. This author also showed that the solubility of pure caffeine in CO_2 (binary system) is about 20 times higher than the solubility of caffeine measured for the system of coffee beans/CO_2 (cellulosic structure + solute/solvent).

The objective of this study was to measure the experimental solubility of GCO in $scCO_2$ under predetermined pressure (P) and temperature (T) conditions and, from the experimental data, to establish thermodynamic models that use the PR-EoS and the van der Waals mixing rule to predict phase equilibrium. The influence of operating conditions (P and T) of SFE on the FA profile and overall extaction yield were analyzed as well.

2. Materials and methods

2.1. Chemicals

The solvent used in SFE was CO_2 (Linde, São Paulo, Brazil) with 99.0% purity. Hexane (Synth, São Paulo, Brazil) with 98.5% purity was used for the atmospheric pressure extraction. All the other solvents and chemicals used were of analytical grade.

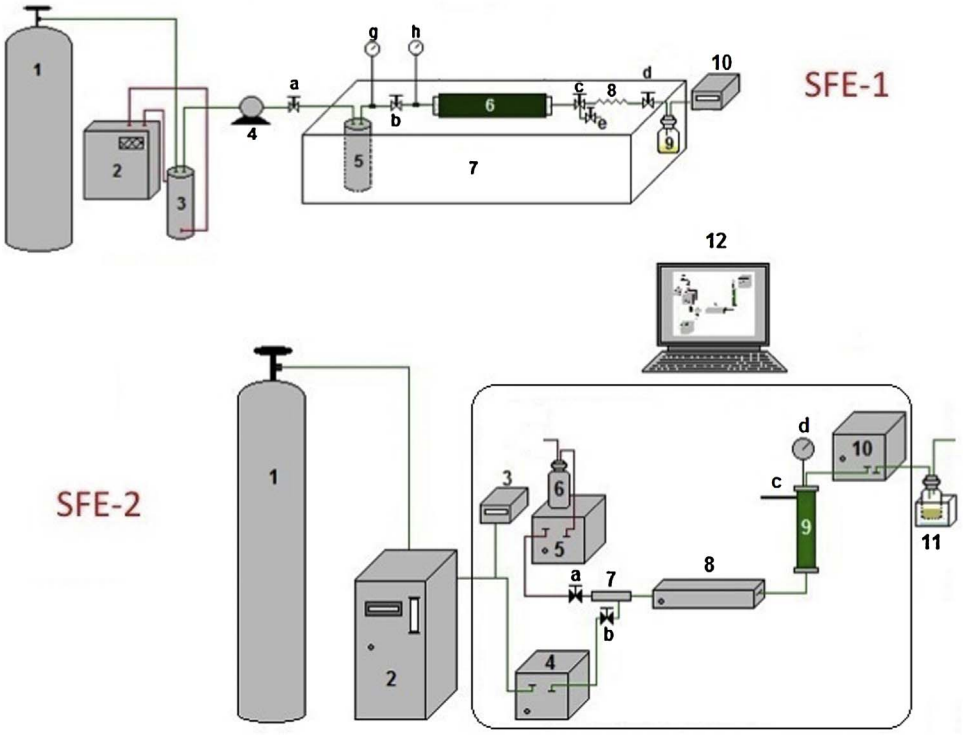

Fig. 1. Supercritical fluid extraction systems, SFE-1 (CO_2 cylinder (1), refrigerated bath (2), CO_2 cooling tank (3), high-pressure pump (4), lung tank (5), needle valve (a)–(c) and (e), two bourdon-type manometers (g) and (h), cylindrical extractor (6), temperature-controlled water bath (7), known volume collector (8), micrometering needle valve (d), glass bottle collector (9) and flow meter (10)) and SFE-2 (CO_2 cylinder (1), cooling bath (2), flow meter (3), high-pressure pump (4), co-solvent pump (5), co-solvent glass bottle (6), needle valve (a) and (b), solvent mixer (7), heat exchanger (8), cylindrical extractor (9), thermostat (c), bourdon-type manometer (d), automated back-pressure regulator (ABPR) (10), glass bottle collector (11) and Thar SFC software (12)).