Contents lists available at ScienceDirect

Food and Bioproducts Processing

journal homepage: www.elsevier.com/locate/fbp

Supercritical CO_2 extraction of cupuassu butter from defatted seed residue: Experimental data, mathematical modeling and cost of manufacturing

Rodrigo N. Cavalcanti[*], **Carolina L.C. Albuquerque**, **M. Angela A. Meireles**

LASEFI/DEA/FEA (School of Food Engineering)/UNICAMP (University of Campinas), Monteiro Lobato 80, Campinas, SP, 13083-862, Brazil

ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form 3 October 2015
Accepted 30 October 2015
Available online 10 November 2015

Keywords:
Oil-seed
Green technology
Supercritical fluid extraction
Free fatty acids
Tocopherol
Manufacturing cost

ABSTRACT

The aim of this work was to perform a techno-economic feasibility study of the supercritical CO_2 ($scCO_2$) extraction for obtaining solvent-free cupuassu butter from cold-pressing by-product of cupuassu seeds and assess the influence of thermodynamic and kinetic variables on the yield, chemical composition, and manufacturing cost of the extracts. Phenolic content (0.47–2.82 mg/g) was much lower than those found in the literature (20–23 mg/g). The high contents of alpha (7.72–18.05 mg/g), gamma (233–365 mg/g), and delta (11.84–44.10 mg/g) tocopherols, as well as the high levels of unsaturated fatty acids (48%) compared to the saturated fatty acids (52%), give the cupuassu butter obtained by supercritical fluid extraction (SFE) a solvent-free product with high value-added and great potential for use as an ingredient in food, pharmaceutical and cosmetic industries. Optimal conditions for SFE of butter regarding extraction kinetics, chemical composition and production costs were 30–35 MPa and 50 °C.

1. Introduction

Cupuassu (*Theobroma grandiflorum* Shum.) is a fruit tree native to Brazilian Amazon rainforest phylogenetically close to cocoa (*Theobroma cacao* L.), member of the Sterculiaceae family, with remarkable flavour and high agro-economic potential (Oliveira and Genovese, 2013; Salgado et al., 2011). The fruit has the form of a drupe with a strong and pleasant smell; the endocarp contains 25–50 superposed seeds in five rows surrounded by creamy-yellowish-white pulp, which corresponds to 45.5 ± 3.5% of the fruit (Rogez et al., 2004; Salgado et al., 2011). Cupuassu pulp is not usually consumed directly due to its strong acidity (average pH of 3.4); therefore, it is often manufactured to produce fresh juice, jam, wine, liquor, candies and ice-cream (Quijano and Pino, 2007; Rogez et al., 2004). The fresh seeds contain about 84% moisture and the fat content is approximately 60% of the dry weight (Azevedo et al., 2003). The fat is comprised by triacylglycerols mainly formed by palmitic, linoleic, arachidic, stearic and oleic acids (Quast et al., 2011). The seeds are often fermented, dried, roasted, milled, and pressed to obtain cupuassu butter in yields of approximately 45% and a residue around 55% (Salgado et al., 2011). This product has been used as cocoa butter substitute in a variety of products in food, pharmaceutical and cosmetic industry (Oliveira and Genovese, 2013). The seeds can also be processed to yield a chocolate-like product called “cupulate” that has a good market potential as an exotic replacement for chocolate (Oliveira et al., 2004; Pugliese et al., 2013). The seeds are also sources of bioactive compounds such as (+)-catechin, (−)-epicatechin, isoscutellarein 8-O-β-D-glucuronide, hypolaetin 8-O-β-glucuronide, quercetin 3-O-β-D-glucuronide, quercetin 3-O-β-D-glucuronide6″-methyl ester, quercetin, kaempferol, isoscutellarein 8-O-β-D-glucuronide 6″-methyl ester, theograndins I and II (Pugliese et al., 2013),

---

[*] *Corresponding author.* Tel.: +55 1935214053; fax: +55 1935214027.
E-mail address: rodrigoncavalcanti@gmail.com (R.N. Cavalcanti).

http://dx.doi.org/10.1016/j.fbp.2015.10.004
0960-3085/

Nomenclature

a_1, a_2, a_3	adjustable parameters of spline model (kg/s)
b_0	adjustable parameter of spline model (kg)
b_i	adjustable parameter of Martínez model (no physical meaning) (s^{-1})
db	dry basis
d_B	bed diameter (cm)
d_p	mean particle diameter (mm)
D_{ef}	effective diffusion coefficient of the solute within the solid matrix (m^2/s)
F	mass of feed material (g)
H_B	bed height (cm)
k_{Xa}	solid phase mass transfer coefficient (s^{-1})
k_{Ya}	fluid phase mass transfer coefficient (s^{-1})
M_{CER}	extraction rate of the of the constant extraction rate (CER) period (kg/s)
MSE	mean square error (%)
Q_{CO_2}	solvent flow rate (kg/s)
R_{CER}	extraction yield of the CER period
S	mass of solvent (%, kg extract/kg feed material)
S/F	solvent to feed mass ratio (kg CO_2/kg feed material)
S/F_{CER}	solvent to feed mass ratio of the CER period (kg CO_2/kg feed material)
S/F_{FER}	solvent to feed mass ratio of the falling extraction rate (FER) period (kg CO_2/kg feed material)
t_{CER}	time that marks the end of the CER period (min)
t_{CER}^{*}	time that marks the end of the CER period obtained from Sovová's model (min)
t_D	dynamic extraction time (min)
t_{FER}	time that marks the end of the FER period (min)
t_{mi}	adjustable parameter of Martínez model (s)
t_{RES}	residence time of the solvent into the solid matrix (min)
t_S	static extraction time (min)
X_0	global yield (kg extract/kg feed material)
X_k	intect cells solute ratio (hardly accessible solute) (kg extract/kg feed material)
Y	mass ratio of solute in the fluid phase (kg extract/kg CO_2)
Y_{CER}	Y at the bed outlet during the CER period (kg extract/kg CO_2)
ε	bed porosity (dimensionless)
ρ_a	apparent bed density (kg/m^3)
ρ_{CO_2}	CO_2 density (kg/m^3)
ρ_p	true density of particles

which may have different antioxidant potential against oxidative stress associated with chronic diseases (Oliveira and Genovese, 2013; Salgado et al., 2011). In spite of that, very few studies have emphasized the potential use of agro-industrial by-products of cupuassu in the development of new functional ingredients for food enrichment to provide an economic alternative for industries, agriculture families and sustainability for the environment.

Nowadays, the conventional industrial technologies used for obtaining fats and oils include hydraulic pressing, screw pressing and solvent extraction with organic solvents (Willems et al., 2008). Utilization of mechanical processes is advantageous for production of high quality oils, but product yield is relatively low. On the other hand, higher yields are achieved using solvent extraction methods; however, they yield low quality oils. In the majority of cases, they employ solvents such as *n*-hexane, sodium hydroxide or petroleum ether, which are dangerous to handle and unacceptable as they are quite harmful to human health and environment (Azevedo et al., 2003; Chan and Ismail, 2009). $scCO_2$ is the most commonly used solvent in SFE because of its advantageous characteristics, such as non-toxic, non-explosive, chemically inert, cheap and readily available. Furthermore, its low critical parameters (7.39 MPa and 31.1 °C) allow isolation of supercritical extracts at relatively low pressures and near room temperature; thus, preventing degradation of thermolabile and volatile compounds (Chan and Ismail, 2009). Tuning of the processing conditions (pressure and temperature) enables adjustment of $scCO_2$ solvent power and its easy and complete separation from the final extract. Extracts obtained by SFE are superior to extracts obtained by conventional methods since they contain no organic solvent residues and have aromatic profile similar to the fresh plant material (Brunner, 2005; Herrero et al., 2010). SFE of fats and oils from various natural sources (vegetable, nuts, seeds, spices, meat products, marine products, skin, etc.) has been widely reported and reviewed in the literature (de Melo et al., 2014; Hierro and Santa-María, 1992; Martínez and de Aguiar, 2014; Temelli, 2009). Nevertheless, study on SFE of cupuassu seed oil has been poorly reported in literature (Azevedo et al., 2003). This is the first report on SFE of cupuassu butter from defatted seeds residue, which is often discarded in the soil or added to animal feed.

The main objective of this work was to perform a techno-economic feasibility study of the $scCO_2$ extraction for obtaining solvent-free cupuassu butter from cold-pressing by-product of cupuassu seeds and assess the influence of thermodynamic and kinetic variables on the yield, chemical composition, and manufacturing cost of the extracts.

2. Material and methods

2.1. *Sample characterization and preparation*

The raw material consisted of defatted cupuassu seeds, donated by Croda do Brazil Ltda. (Campinas, SP, Brazil), obtained as residue of cold-pressing process from “cupulate” production. The raw material was ground in a mill (Tecnal, TE631, Piracicaba, Brazil), packaged in polyethylene bags and stored in a domestic freezer (Metalfrio, DA420, São Paulo, Brazil) at −18 °C. The methods recommended by the AOAC (1995) were used to determine ash, crude lipid, carbohydrate, crude fiber and protein contents. The particle size analysis was performed using a vibratory sieve system (Model N1868, Bertel, Caieiras, Brazil) using sieves from 16 to 80 mesh (Model ASTME-11, W.S. Tyler, Wheeling, WV, USA). Particles of 24–48 mesh were selected for the SFE assays. The mean particle diameter (d_p) was determined by the ANSI/ASAE Standard S319.3 method (ASAE, 2000) according to the following equation:

$$d_p = \log^{-1}\left[\frac{\sum_{i=1}^{n}\left(w_i \log \bar{d}_i\right)}{\sum_{i=1}^{n} w_i}\right] \tag{1}$$

$\bar{d}_i$ is geometric mean diameter or median size of particles on ith sieve, mm, or is $(d_i \times d_{i+1})^{1/2}$; where d_i is nominal sieve aperture size of the ith sieve, mm and d_{i+1} is