J. of Supercritical Fluids 101 (2015) 95–103

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Extraction of pequi (*Caryocar coriaceum*) pulp oil using subcritical propane: Determination of process yield and fatty acid profile

Alcidênio Soares Pessoa[a], Rossana Podestá[b], Jane Mara Block[b], Elton Franceschi[c], Cláudio Dariva[c], Marcelo Lanza[a,*]

[a] *Laboratory of Thermodynamics and Supercritical Extraction (LATESC), Department of Chemical Engineering and Food Engineering (EQA), Technological Center (CTC), Federal University of Santa Catarina (UFSC), P.O. Box 476, 88040-900 Florianópolis, SC, Brazil*
[b] *Laboratory of Fats and Oils, Department of Food Science and Technology (CAL), Center of Agricultural Sciences (CCA), Federal University of Santa Catarina (UFSC), Rod. Admar Gonzaga, 1346, 88034-001 Florianópolis, SC, Brazil*
[c] *Center for Research on Colloidal Systems (NUESC), Institute of Research and Technology (ITP), Tiradentes University (UNIT), 49032-490 Aracaju, SE, Brazil*

ARTICLE INFO

Article history:
Received 9 December 2014
Received in revised form 13 March 2015
Accepted 14 March 2015
Available online 21 March 2015

Keywords:
Pequi pulp oil
Caryocar coriaceum
Subcritical propane
Extraction
Fatty acids

ABSTRACT

Brazil is rich in oil plants that have natural antioxidants in their constitution, among which "pequi" (*Caryocar coriaceum*) stands out, a fruit represented by several species and the most common in the Northeastern Brazilian states such as Ceará and Pernambuco. This fruit has a lot of oil which can be used for nutritional and medicinal purposes. The aim of this research was to study the oil extraction process from pequi pulp, the quality of the extracts, kinetic modeling, and extraction with subcritical propane. Pequi fruits were extracted and their pulps were dried and ground. The oil extracted with subcritical propane was obtained at a pressure range of 5–15 MPa and temperatures of 303.15–333.15 K. The highest yield was 43.69% for the extraction condition of 15 MPa and 333.15 K. Ethanol and ethyl acetate were used in concentrations of 10–25% (volume) as solvent modifiers to obtain yields up to 44.99%. Soxhlet extractions were performed using ethanol and hexane as solvents and higher yield (52.78%) was obtained with the use of ethanol. The fatty acid analysis showed that different experimental conditions did not impact the fatty acid profile. The fatty acids found at greater proportion were palmitic acid (35.4%, in mass) and oleic acid (60.6%, in mass). The phenolic compound content was determined by the Folin-Ciocalteu method and showed no significant difference among the extraction methods used. Different mass transfer models (Crank, Sovová, and Martinez models) reported in the literature were used to model the extraction curves. The Sovová model had the best fit to the experimental data.

1. Introduction

Pequi is a species occurring in the Brazilian *cerrado*, which is a biome that covers 13 Brazilian states, in an area of about 200 million hectares. In Brazil, its fruit is known as *pequi*, *piqui*, *piquiá-bravo*, *amêndoa-de-espinho*, *grão-de-cavalo*, *pequiá*, *pequiá-pedra*, *pequerim*, and *suari* [1] and belongs to family *Caryocaraceae*. The species *Caryocar coriaceum* occurs in regions comprising the states of Ceará, Piauí, and Pernambuco, where the fruit plays an important socioeconomic role [2].

There is virtually no industrialization of the fruit and, therefore, its trade is very limited. The most common form of industrialization is oil extraction by families that make pequi a means of survival. With unique flavor characteristics and nutritional value, pequi represents a potential food source [3]. A very versatile oil can be extracted from pequi pulp and almond, with applications ranging from regional cuisine to the cosmetic industry, for the production of soaps and creams [4]. This oil is rich in oleic and palmitic acids [5].

According to Specher [6], oleic acid participates in human metabolism and plays an important role in the synthesis of hormones. It is essential in human nutrition and helps lower triglycerides, LDL cholesterol, total cholesterol, and glycemic index. The presence of oleic acid also increases during the oxidation stability of vegetable oil [7].

Conventional extraction, such as Soxhlet extraction (Sox), often requires solvents, long periods, and temperature higher than ambient, which can destroy some bioactive compounds. Extraction methods such as supercritical fluid (SFE) have been used for oil extraction [8]. Among the several advantages this method, supercritical fluids have a relatively low viscosity, high diffusivity and selectivity. The solvent power of the fluid can be manipulated by

* Corresponding author. Tel.: +55 48 3721 2528.
E-mail address: m.lanza@ufsc.br (M. Lanza).

http://dx.doi.org/10.1016/j.supflu.2015.03.006
0896-8446/

changing the pressure and/or temperature. The solutes dissolved in supercritical fluid can be readily separated by depressurization. Supercritical extraction is generally carried out at low temperatures, which is interesting to study thermally labile compounds [8].

SFE is generally carried out at low temperatures, which is good to minimize the degeneration of bioactive compounds, to improve the properties of the extracted oil, and to study thermolabile compounds [9]. The SFE technology has been widely studied for the extraction of seed oil. Although in the supercritical extraction CO_2 is the most commonly used solvent, some studies [8,10–12] have compared extraction using supercritical CO_2 and subcritical propane. These studies report the greater solvation power of propane at pressures below the lowest ones used with CO_2, besides shorter extraction time.

Ndiaye et al. [13] investigated the phase behavior of soybean and olive oil in pressurized propane and n-butane and reported high miscibility at relatively low pressures. Those authors concluded that the compressed propane or butane may be an alternative way to the fractionation of vegetable oils. Despite some studies about supercritical CO_2 extraction of various oilseeds, the literature lacks information on extraction using propane as a solvent at high pressure.

The aim of this study was to extract the oil from pequi (*Caryocar coriaceum*) pulp using different extraction techniques in order to evaluate productivity, the effect of temperature and pressure on extraction yield with subcritical propane, the extraction kinetics, the use of ethanol and ethyl acetate as solvent modifiers, and the quality of extracts (fatty acid profile, total phenolic content, acidity, and moisture).

2. Materials and methods

2.1. Sample collection

The pequi fruits were collected during the harvest period (December and January) in the municipalities of Crato and Barbalha, state of Ceará, Brazil, with geographic coordinates of 7°18′10″ S and 39°33′5″ W. Intact ripe fruits were selected from the ground and were then frozen and transported to UNIT (Tiradentes University), Aracaju, state of Sergipe, Brazil, washed in running water, immersed for 5 min in a 50 ppm sodium hypochlorite solution, and then peeled. The pulp was extracted manually with a stainless steel knife, cut into chips, packed in polyethylene bags, and frozen in a freezer at 253.15 K.

2.2. Sample preparation

To reduce the water content, the pequi pulp was dried in an oven with air circulation (Nova Ética, model 400/4 N), at 313.15 K for 19 h [14]. After drying, the seeds were ground in a household blender and the particles were classified according to size by sieving. Samples with grain size of −8/+32 mesh were selected. After this procedure, the samples were analyzed for moisture content in an oven at 378.15 K until constant mass [15].

2.3. Oil extraction process

2.3.1. Soxhlet extraction

Soxhlet extraction was conducted according to the AOAC method 920.39C [15] using hexane and ethanol. About 5 g of the pequi pulp were placed in a filter paper cartridge, which was inserted into the extractor. A flask with 150 mL of solvent was connected to the extractor and a heating mantle kept the solvent at boiling temperature for 6 h.

Table 1
Operating conditions used in the extraction with subcritical propane.

Variables	−1	0	+1
Pressure	5 MPa	10 MPa	15 MPa
Temperature	303 K	318 K	333 K

The solution obtained in the process above was then concentrated by rotary evaporation (Fisatom, model 802) at 313.15 K under 650 mmHg vacuum and 50 rpm rotation and traces of residual solvent were removed from the oil by washing it with nitrogen. The dried extracts were measured on an analytical balance (Ohaus, model AS200) and the yield (X_0) was calculated by Eq. (1). The experiments were performed in triplicate.

$$X_0 = 100 \times \frac{m_e}{m_i} \quad (1)$$

where m_e is the mass of oil extracted and m_i is the mass of sample used.

2.3.2. Ultrasonic extraction

Ultrasonic extraction was performed by measuring 5 g of sample on an analytical balance (Shimadzu, model AY220) and placing it in a flask to which 150 mL of solvent were added. The flask was adapted to a condenser connected to a refrigerated bath (Micro-Chemical, model MQBMP-01) and dipped into an ultrasound bath (Unique, model USC-700/55 kHz) for 30 min. After extraction, filtration was performed and the filtrate was taken to a rotary evaporator (Fisatom, model 802) at 40 °C under 650 mmHg vacuum and 50 rpm rotation. The traces of residual solvent were removed by drying the oil with nitrogen. The dried extracts were measured on an analytical balance (Ohaus, model AS200) and the yield (X_0) was calculated based on Eq. (1). The experiments were performed in triplicate.

2.3.3. Subcritical propane extraction

Extraction was performed in an experimental module consisting of a reservoir for the solvent, a syringe pump (Isco, model 500D), and two thermostatic baths to maintain the temperature of the extractor (Julabo, model F32 and Quimis, model Q214-M2). The extractor was bundled manually with the aid of a funnel, with approximately 15 g of pequi pulp. Before entering the pump, the solvent was cooled to 280.15 K to prevent vaporization. Once the liquid phase was cooled, the solvent was pumped into the system, entering the extraction cell. Pressure was monitored through a pressure gauge (Novus, model N1500) connected to an absolute pressure transducer (Smar, model A5). After 30 min (time to stabilize the system), a micrometering valve (HIP, model 1511 AF2) placed at the extractor outlet was carefully opened for the solvent/solute mixture to flow. The flow rate used was 2 mL min^{-1} in each experiment. Oil and solvent separated at the extractor outlet due to depressurization.

2.4. Experimental design

To check the influence of pressure and temperature on the global extraction yield with pure propane, a full factorial design with 2 levels and 2 variables (2^2) was used with three replications at the center point as the levels, shown in Table 1. The response variable analyzed in the experimental design was the global yield (X_0). Statistical analysis was performed using the software STATISTICA 8.0® (StatSoft, Inc., Tulsa, USA) by response surface methodology, where the effects of independent variables on the response variable in the extraction process were evaluated, considering 95% confidence level for all variables.

This methodology enabled obtaining a mathematical model for the response using criteria with the percentage of variance