EXTRACTION OF PEQUI (*Caryocar coriaceum*) PULP OIL USING HIGH PRESSURE PROPANE: DETERMINATION OF CHEMICAL PROFILE AND ANTIOXIDANT POTENTIAL

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Abstract. Brazil is rich in oil plants that have natural antioxidants in its constitution and among them stands "pequi", a fruit represented by several species and the most common in the Northeasters Brazilian States as Ceará and Pernambuco is *Caryocar coriaceum*. The use of pressurized fluids as extraction solvents exploits the solvents properties such as density, viscosity and diffusivity, for the purpose of extracting the compounds of interest from a raw material. Therefore the objective of this study was to extract "pequi (*Caryocar coriaceum*) pulp oil" using different extraction techniques in order to evaluate the yield. The experiments were conducted using propane as solvent at pressures of (5, 10 and 15) MPa and temperatures of (303.15, 318.15 and 333.15) K. Extractions at 10 MPa and 318.15 K were also performed using propane and ethanol in different concentrations of (10% and 25%, m/m). The extraction yields with propane and with propane combined with ethanol ranged from 39.36% to 45.55%. The variation in density is very small under these conditions. It was noticed an yield increase with enhancing temperature due to the increased vapor pressure of the extract and increasing diffusivity. It was observed that with the use of ethanol there was an increase in yield due to high solubility of polar compounds.

Keywords: pressurized propane, pequi pulp oil, *Caryocar coriaceum*

1. Introduction

The pequi is a species occurring in the Brazilian *cerrado* that belongs to the family *Caryocaraceae*. In Brazil, its fruit is known as *pequi, piqui, piquiá-bravo, amêndoa-de-espinho, grão-de-cavalo, pequiá, pequiá-pedra, pequerim e suari* [1]. Regions between the states of Ceará, Piauí and Pernambuco occurs the species *Caryocar coriaceum*, which performs an important socioeconomic function in these regions [2].

There is virtually no industrialization of fruit and therefore their trade is very limited. The most common form of industrialization is the oil extraction by families that make pequi a means of survival. With unique characteristics for flavor and nutritional value, pequi represents a potential source for food [3]. Pulp and almond pequi can be extracted an oil that has great versatility as to its use, with applications ranging from regional cuisine to the cosmetic industry, for the production of soaps and creams [4].

Most used technique for obtaining vegetable oils is the use of mechanical press followed by extraction with further solvent where the solvent used is hexane. This procedure may produce undesirable residues and removal of the solvent can cause oxidative changes in the oil resulting in a low quality oil [5].

The conventional extraction often requires solvents, extracting long period and high temperature, such as Soxhlet extraction, which can destroy some bioactive compounds. Extraction methods such as supercritical fluid have been used for oil extraction [6]. The supercritical fluid extraction technology (SFE) has been widely studied for the extraction of seed oil [5, 7, 8, 9]. The SFE, often operating at low temperature and short extraction time, can minimize the degeneration of bioactive compounds and improve the properties of the extracted oil.

Among the several advantages of supercritical extraction [6] include the following: supercritical fluids have a relatively low viscosity and high diffusivity, which results in a shorter time of extraction. The solvent power of the fluid can be manipulated by changing the pressure and/or temperature. The solutes dissolved in supercritical fluid can be readily separated by depressurization. The supercritical extraction is generally carried out at low temperatures, which is good to study thermally labile compounds.

Although in the supercritical extraction the CO_2 is the most widely solvent used, there are some studies [5, 8, 9, 10, 11] comparing extraction using supercritical CO_2 and subcritical propane. In these studies is affirmed the greater power of solvation of propane at pressures below the lowest used with CO_2 and shorter extraction time.

Despite the existence of some studies about supercritical extraction with CO_2 from various oilseed, the literature lacks information extraction using propane as solvent at high pressure. The aim of this study was to extract the oil from the pulp pequi (*Caryocar coriaceum*) using different extraction techniques in order to evaluate the productivity, the effect of temperature and pressure on the extraction yield using subcritical propane and describe the kinetics of extraction.

2. Materials and Methods

2.1 Sample collecting

The pequi fruits were collected during the harvest period (December 2011 and January 2012) in the municipalities of Crato and Barbalha, State of Ceará, Brazil. Fruits were selected at random, intact soil to ensure that they were mature. The pequi fruits were frozen and transported to the UNIT University, Aracaju, State of Sergipe, Brazil, washed in running water, immersed for 5 minutes in a solution of sodium hypochlorite at 50 ppm and then peeled. The pulp was extracted manually with stainless steel knife, cut into chips, packed in polyethylene bags and frozen in the freezer at 253.15 K.

2.2 Sample preparation

To reduce the water content was performed pequi pulp drying in an oven with air circulation (Nova Ética, model 400/4N), with a temperature of 313.15 K for 19 h [12].

After drying, the seeds were crushed in household blender, and then the particles were classified as to size by sieving. Samples with grain size -8 /+32 mesh were selected. After this procedure the samples were analyzed for water content in the oven at 378.15 K until constant mass [13].

2.3 Process of oil extraction

Soxhlet extraction: The Soxhlet extraction was conducted according to AOAC method 920.39C [13] using hexane and ethanol. About 5 g of the pequi pulp were placed in cartridge filter paper and inserted into the extractor. A flask with 150 mL of solvent was connected to the extractor and by means of a heating mantle kept at boiling temperature of the solvent for 6 h.

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

$$X_0 = 100 \times \frac{m_e}{m_i} \tag{1}$$

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

Subcritical propane extraction: The extraction was performed in an experimental module consisting of a reservoir for the solvent, a syringe pump (Isco, model 500D) and two thermostatic baths. 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 cooled and the liquid phase, the solvent was pumped and placed in the system, entering the extraction cell. The pressure monitoring was done through the pressure indicator (Novus, model N1500) connected to the absolute pressure transducer (Smar, model A5). After 30 min (time to stabilize the system) a micrometering valve (HIP, model 1511 AF2) placed at the outlet of the extractor is carefully open occurring the flow of mixture solvent/solute. The flow rate used was 2 mL·min^{-1} in each experiment. At the output of the extractor occurred separation from oil and solvent due to depressurization.

3. Results and Discussion

3.1 Water content

The water content of the samples for extraction was performed in triplicate as described in section 2.2. The water content was 4.73 ± 0.07%.

3.2 Extraction yield

Table 1 shows the results of extraction yield (Equation 1) of pequi pulp oil with propane, propane and cosolvent and hexane (Soxhlet). The extraction with hexane was carried out for 6 h at its boiling point and had a yield of 49.58 ± 0.16%.

To evaluate the effect of pressure and temperature on the performance of pequi pulp oil extraction with propane, experiments were performed combining these two parameters with fixed values for the propane flow and particle diameter. The flow used was 2 mL·min^{-1}, average particle diameter of 0.62 mm and the real density of particles of 1.082 g·cm^{-3}. Also extractions were conducted with ethyl acetate and ethanol as cosolvents at concentrations (m/m) of 10 and 25%.

The density of propane was obtained using the HBT equation proposed by Hankinson and Thompson [14] and extended compressed liquid by Thomson et al. [15] and Reid et al. [16]. It can be seen from Table 1 that the temperature has a positive effect on yield. This effect can be further evaluated by observing the extractions 1, 3 and 5, where the density presents values closest. This behavior becomes clearer when the Figure 1 is observed which present the extraction curves for these experiments.

This phenomenon can be explained because the increase in temperature occur an increase of the vapor pressure of the extracts and an increase in diffusivity and decreases the viscosity of the solvent. The behavior of the curves is similar at the beginning of extraction where the solvent is saturated with the extract. After a time, the curves begin to separate. The Figure 1 shows that this phenomenon is more pronounced at higher temperature.

Table 1. Extraction yield of pequi pulp oil with propane at high pressure.

Extraction	Solvent	Temperature (K)	Pressure (MPa)	Density of solvent (g·cm^{-3})	Extraction time (min)	Yield (%, m/m)
1	Propane	303.15	5	0.497	80	39.81
2	Propane	303.15	15	0.521	80	39.36
3[a]	Propane	318.15	10	0.490	80	40.80 (±0.86)
4	Propane	333.15	5	0.446	80	41.65
5	Propane	333.15	15	0.484	80	43.69
6	Propane/ethanol (10%)	318.15	10	0.490	80	43.97
7	Propane/ethanol (25%)	318.15	10	0.490	80	44.99
8	Propane/ethyl acetate (10%)	318.15	10	0.490	80	42.55
9	Propane/ethyl acetate (25%)	318.15	10	0.490	80	43.06
10[a]	Hexane (soxhlet)	–	–	–	360	49.58 (±0.16)

[a] Average value of three extractions.

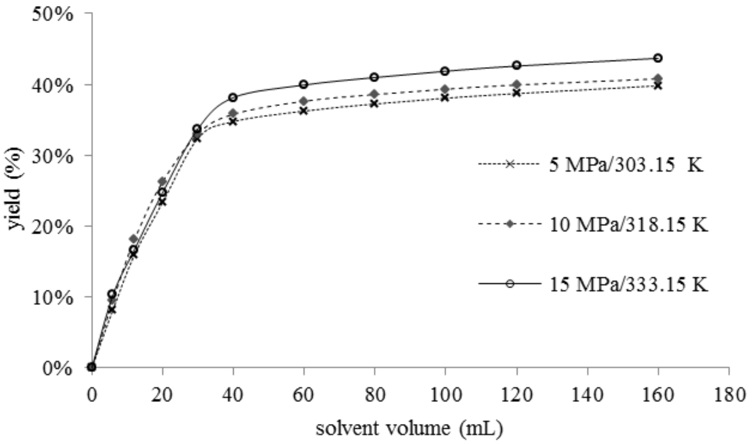

Figure 1. Extraction curves using propane in the density conditions with similar values.

According to Figure 1, the pressure has little significant effect. Figure 2A shows that at 303.15 K the pressure does not influence the yield. The temperature of 333.15 K (Fig. 2B) shows that an increase in pressure produces a small increase in yield. Similar effects observed for temperature and pressure were checked by Corso et al. [10] to extract oil from sesame seeds using propane.

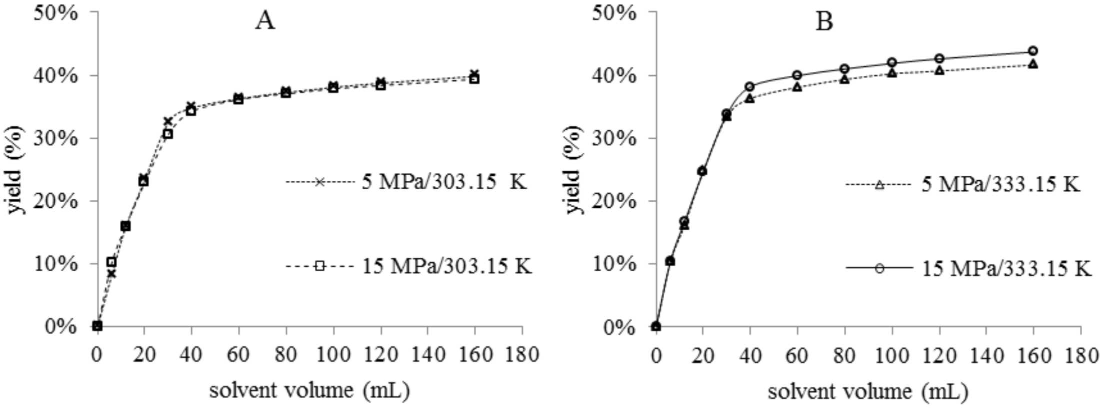

Figure 2. (A) Extraction curves using propane at 303.15 K; (B) Extraction curves using propane at 333.15K

The extractions with ethanol as a cosolvent were performed at pressure of 10 MPa and temperature of 318.15 K and the values obtained for the total yield was 43.97% with 10% ethanol and 45.55% with 25% ethanol. The higher yields observed with the presence of ethanol is due to the fact ethanol increase the solubility of polar compounds. Figure 3A presents the comparison of the extraction curves for pure propane and extractions performed with ethanol as cosolvent. It shows that increasing the ethanol ratio in the solvent mixture does not produce a significant increase in final yield; however the solubility decreases at the beginning of the process.

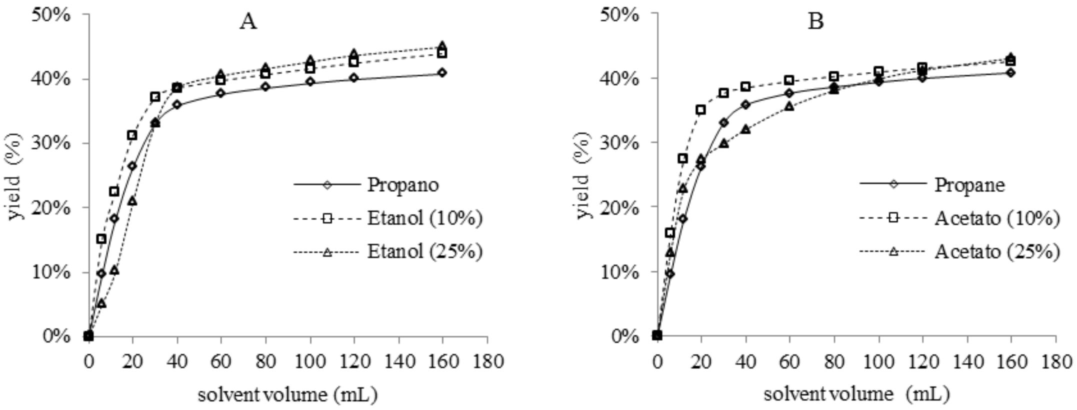

Figure 3. (A) Extraction curves using propane and ethanol at 318.15 K and 10 MPa; (B) Extraction curves using propane and ethyl acetate at 318.15 K and 10 MPa.

In extractions made with ethyl acetate as cosolvent have a behavior similar to that seen in the extraction with ethanol (Figure 3B) where no difference in the total final yield occurred, however, there is a greater solubility at the beginning of the process to the proportion low acetate. The total yields obtained with ethyl acetate were of 42.55% in the proportion of 10% and 43.06% in the proportion of 25%. These values are higher than those obtained with pure propane, however, lower than the values attained with ethanol due to lower polarity of ethyl acetate.

3.3 Mathematical Modeling

For the modeling of extraction curves (cumulative mass of extract versus extraction time) were used three models; a model based on heat transfer analogy, the diffusion model proposed by Crank [17] and presented by Reverchon [7] and two models based on the equation of differential mass balance, the Sovová model [18] and the logistic model, presented by Martínez et al. [19].

Crank model [17]: Presents supercritical extraction as a phenomenon of heat transfer where each particle is considered a hot sphere in a uniform way [7]. Applying Fick's second law of diffusion for the mass balance on the internal surface of the particle can be solved analytically to give Equation 2.

$$m_{ext} = m_0\left[1-\left(\frac{6}{\pi^2}\right)\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 Dt}{r^2}\right)\right] \tag{2}$$

Where: m_{ext} = mass of extract (g); m_0 = initial mass of solute (g); t = time (min); D = diffusion coefficient ($m^2 \cdot min^{-1}$); r = radium of solid particle (m).

Sovová model [18]: This model describes a condition with axial solvent flow with superficial velocity through a bed of milled vegetal material in a cylindrical extractor. The temperature and pressure are considered constant. The solid bed is homogeneous as regards both the particle size distribution as for the initial and solute. Also believes that the solute is directly exposed to the solvent due to the breakdown of cell walls by grinding the sample.

The analytical solution Sovová model is given by three different equations corresponding to the mechanism which control mass transfer.

$$m_{ext} = m_F S_b t[1-\exp(-Z)] \qquad \text{para } 0 \le t \le t_{CER} \tag{3}$$

$$m_{ext} = m_F S_b t[t - t_{CER}\exp(Z_m(t)-Z)] \qquad \text{para } t_{CER} \le t \le t_{FER} \tag{4}$$

$$m_{ext} = m_S \left\{ q_0 - \frac{S_b}{W} \ln\left[1 + \left(\exp\left(\frac{W_{q0}}{S_b} \right) - 1 \right) \exp\left(\left(\frac{W_{m_F}}{m_S} \right) (t_{CER} - t \right) r \right] \right\} \text{ para } \; t \geq t_{CER} \tag{5}$$

$$Zm(t) = \frac{ZS_b}{W_{q_0}} \ln\left\{ \frac{1}{1-r} \left[\exp\left[\left(\frac{W_{m_F}}{m_S} \right) (t - t_{CER}) \right] - r \right] \right\} \tag{6}$$

$$Z = \frac{K_F a m_S \rho_F}{m_F \rho_{bed}} \tag{7}$$

$$W = \frac{m_S k_S a}{m_F (1 - \varepsilon)} \tag{8}$$

$$t_{CER} = \frac{(1-r) m_S q_0}{S_b Z m_F} \tag{9}$$

$$t_{FER} = t_{CER} + \frac{m_S}{W m_F} \ln\left[r + (1-r) \exp\left(\frac{W q_0}{S_b} \right) \right] \tag{10}$$

Where: m_f = mass flow rate of the solvent; S_b = solubility of the oil in solvent (g oil/g of solvent); t = time of extraction; q_0 = initial concentration of oil in the solid matrix (g oil/g solid); m_s = mass of solid oil-free basis; q_{bed} = bed density; q_F = solvent density; K_FA = mass transfer coefficient of solvent (min^{-1}); ε = bed porosity; K_Sa = mass transfer coefficient of the solid phase (min^{-1}); r = fraction of oil easily accessible; t_{CER} = oil extracting time of the interior of the particles (min); t_{FER} = final time of the extraction of solute easily accessible (min). Z, Y and r are dimensionless parameters of Sovová model.

Martínez model [19]: considers the extract as a pseudocomponent (a mixture of substances or groups of components with similar chemical structure). The model is based on the mass balance of the bed of extraction, and despises the accumulation and dispersion in the fluid phase for these phenomena are not presenting significant influence on the process when compared to the effect of convection [20, 21]. When the solute is considered a pseudocomponent, the mass of solute can be described according to Equation 11.

$$m_{ext}(h = H, t) = \frac{m_0}{\exp(bt_m)} \left\{ \frac{1 + \exp(bt_m)}{1 + \exp[b(t_m - t))} - 1 \right\} \tag{11}$$

With: $m_0 = x_0 m_t$

Where: m_{ext} = mass of extract (g); m_0 = initial total mass of solute in the bed extraction (g); x_0 = initial mass ratio of solute extracting; m_t = total mass of solid in the extraction column; t = extraction time (s); b and t_m = adjustable parameters of the model.

The equations of the models used were solved with the software Mass Transfer developed at the Laboratory of Thermodynamics and Supercritical Extraction, UFSC, Florianópolis, Brazil, which uses the maximum likelihood method to minimize the sum the squares of the deviations calculated [20].

Some process variables are needed for application models such as: density of solvent, density of solid, particle diameter, porosity of bed, height and radius of extractor, solubility and content of oil that can be extracted. The solubility value used for modeling curves extracted was 0.428 g oil/g propane. The adjusted parameters for the Sovová model are listed in Table 2 and the adjustable parameters for Martínez model (b *e* t_m) and Crank model (D) in Table 3.

Table 2. Adjusted parameters for Sovová model.

Extraction	M_{CER} ($g \cdot min^{-1}$)	Y_{CER} ($g \cdot g^{-1}$)	t_{CER} (min)	X_k ($g \cdot g^{-1}$)	k_{ya} (min^{-1})	k_{xa} (min^{-1})
1	0.3993	0.3790	8.5680	0.1045	0.1461	0.0355
2	0.4004	0.3792	7.5673	0.1549	0.1399	0.0362
3	0.3700	0.3571	9.3464	0.0578	0.1787	0.0303
4	0.4032	0.3933	8.7926	0.0679	0.1836	0.0332
5	0.4169	0.3926	7.9545	0.1760	0.1739	0.0316

In according to Table 2, it is observed that the values of the mass transfer coefficient in the solid phase (K_{xa}) were lower than the mass transfer coefficient from the fluid phase (K_{ya}). This highlights the greater influence of the convective process in the pequi pulp oil extraction.

Table 3. Adjustable parameters for Martínez and Crank models.

Extraction	b (min^{-1})	t_m (min)	D ($m^2 \cdot min^{-1}$)
1	0.107	-12.08	$5.02 \cdot 10^{-10}$
2	0.097	-26.25	$5.06 \cdot 10^{-10}$
3	0.107	-9.94	$4.9 \cdot 10^{-10}$
4	0.097	-41.36	$5.3 \cdot 10^{-10}$
5	0.097	-18.93	$4.8 \cdot 10^{-10}$

It is observed in Table 3 that the values of the parameter t_m have negative values. This parameter indicates the point where the extraction rate is maximum, negative values indicate that the extraction rate is decreasing from the beginning (t = 0) [19]. Table 4 presents the average errors between the experimental data and from models.

Table 4. Average errors (%) between the experimental data and calculated curves for the pequi pulp oil extraction.

Extraction	Sovová	Martínez	Crank
1	0.0499	0.0332	0.2122
2	0.0472	0.0177	0.1369
3	0.0711	0.0261	0.2607
4	0.1174	0.0478	0.1425
5	0.0580	0.0274	0.2158

The data in this table show that the experiment that had the lowest average errors was conducted at 15 MPa and 303.15 K and the model that best fits the conditions was Martínez et al. [19]. The Crank model [17] presents the highest values of average errors probably believes that the extraction process is controlled by diffusion alone, disregarding the mechanism of mass transfer by convection.

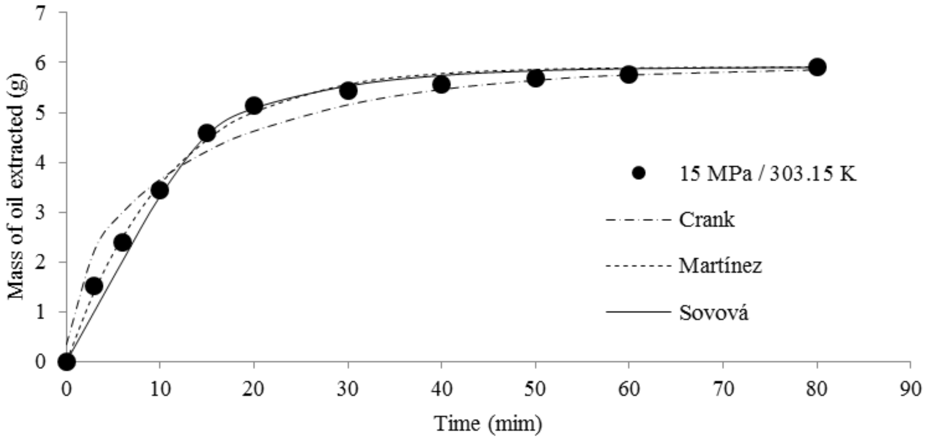

Figure 4. Experimental and calculated curves of the pequi pulp oil extraction to 15 MPa and 303.15 K, flow rate of 2 $mL \cdot min^{-1}$ of propane.

4. Conclusions

The extraction yield with hexane (Soxhlet) was higher than those obtained in the pressurized solvent extraction, however, the use of cosolvent increased the yield by about 10% when ethanol is used. An increase in the proportion of cosolvent did not increase the extraction yield. The best result for the extraction yield with propane was obtained under the condition of 15 MPa and 333.15 K.

The model that obtained the best fit to the experimental data (lower mean square error) was the Martínez model, followed by Sovová model. The Crank model not submitted a satisfactory adjustment.

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