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CHEMICAL SCIENCES

Valorization of *Carapa guianensis* Aubl. seeds treated by compressed *n*-propane

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Abstract: This study evaluated the oil content obtained from andiroba seeds by pressurized *n*-propane at different conditions of temperature (25, 35, and 45 °C) and pressure (40, 60, and 80 bar), and conventional extraction technique using *n*-hexane as the solvent. Kinetic extraction curves were fitted using Sovová's mathematical model. The chemical characterization of the oil was reported as well as the protein content in the extraction by-product. Pressurized extractions conducted at 25 °C provided the highest oil recovery (~45 wt%) from the seeds. The increase in pressure at 25 ºC favored obtaining oil with higher Stigmasterol contents, however, the Squalene content was higher in the oil obtained at 40 bar. The oils with the highest concentration phenolic compounds and antioxidant activity were obtained at 80 bar. Extraction with *n*-propane provided oils with higher levels of phenolic compounds, however, with antioxidant activity similar to conventional extraction. For all evaluated extractions, the product showed a predominance of oleic and palmitic acids, with similar values of oxidative stability. The extraction of the by-product with the highest soluble protein content was obtained under mild processing conditions (25 °C and 40 bar) with *n*-propane.

Key words: Andiroba seed, oleic acid, palmitic acid, squalene.

INTRODUCTION

There is a growing interest from the scientific community and the chemical industry in obtaining compounds with phytochemical properties derived from plant matrices. *Carapa guianensis* Aubl., popularly known as Andiroba, is a large tree of the Meliaceae family, commonly found in the Amazon region (Oliveira et al. 2018). Trees can produce about 190 kg of seed per year (Ferraz et al. 2002, Lima 2010), requiring ~22 kg to obtain 1 liter of oil (Tonini & Kaminski 2009). However, the great genetic variability for individuals of this species, as well as climatic factors and biodiversity, can cause variations in the size of the fruits and seeds of its trees (Lourenço et al. 2017), modifying the annual productivity. Stem bark, leaves and seeds of Andiroba are recognized in traditional medicine for having therapeutic properties (Silva et al. 2021) and have been used in cosmetics (Narvaez et al. 2022).

Andiroba seed oil (ASO) has properties that can be related to health benefits that can fight inflammation and allergies (Wanzeler et al. 2018), as well as healing and analgesic capacity, resulting from its biologically active constituents (Krist 2020). Its main components in fatty acids are oleic, palmitic and linoleic acids (Araujo-Lima et al. 2018). The biological properties of the oil are mainly associated with the presence of limonoids (Oliveira et al. 2018) and minor components such as squalene, stigmasterol and sitosterol (Bataglion et al. 2014). It has been reported that squalene has emollient, anti-inflammatory, detoxifying, antioxidant and photoprotective properties (Gaforio et

al. 2015), inducing the immune system against various diseases (Yarkent & Oncel 2022), acts as a cancer chemopreventive agent, being proven to be a precursor of vitamin D (Chanioti & Tzia 2019) and excellent drug administration agent (Lozano-Grande et al. 2018), even used as an adjuvant for COVID vaccines (Yarkent & Oncel 2022). Sterols, such as stigmasterol and sitosterol, are reported to have anti-inflammatory, antibacterial, antifungal, and antioxidant activity (Sánchez-Machado et al. 2004, Yuan et al. 2015). Studies report that ASO is free from toxicity (Melo et al. 2018), no mutagenic, hemotoxic or genotoxic effect (Milhomem-Paixão et al. 2017), demonstrated therapeutic effect on oral mucositis in children undergoing chemotherapy (Soares et al. 2021), in addition to the chemical profile being compatible with phytogenic substances (Abdelli et al. 2021).

Given the relevance of composition, obtaining the ASO has become of interest with the development of new processing technologies. Extraction is traditionally carried out mechanically (Souza et al. 2006, Mendonça et al. 2020), including cooking, drying under the sun, enzymatic action and fermentation (Shanley & Londres 2011, Nardi et al. 2016). However, these techniques involve expensive steps, which can result in loss of oil quality and low extraction yields. Therefore, extraction using pressurized fluids, at supercritical or subcritical conditions, is attractive from an environmental and operational point of view, in which the solvent is removed by depressurizing the system and can be recovered (Bubalo et al. 2015, Saldaña et al. 2002). The *n*-propane solvent is reported to be effective in extracting vegetable oils without any toxicity. Due to its high density and low viscosity, it allows operation at mild temperatures, which minimizes the thermal degradation of the target compounds (Hrnčič et al. 2018), in addition to providing high solvation capacity, therefore requiring lower operating conditions compared to other solvents, such as supercritical carbon dioxide (Trentini et al. 2019, Iwassa et al. 2021). These properties have been previously demonstrated in obtaining biologically active compounds such as phenolic compounds (Guedes et al. 2018), squalene and tocopherol (Zanqui et al. 2020), phytosterols and carotenoids, also providing extracts with high thermal stability (Trentini et al. 2019, Iwassa et al. 2021).

The extraction of andiroba seed oil through different methods is still incipient, with reports of Reis et al. (2021) and Novello et al. (2015), using ultrasound-assisted extraction and extraction with pressurized *n*-butane, respectively, as strategies for obtaining oil involving emerging techniques. Therefore, the objective of this study was to determine how extraction using pressurized *n*-propane affected the composition of the oil from *Carapa guianensis* Aubl. seeds (ASO) compared to extraction via Soxhlet using *n*-hexane as the solvent. The extraction process parameters (temperature and pressure) were evaluated in terms of yield, fatty acid profile, minority compound content and oxidative stability to confirm the possible use of the extracted oils in the cosmetic industry.

MATERIALS AND METHODS

Sample preparation

Fruits of *Carapa guianensis* Aubl. harvested in the coastal plain (Global Positioning System coordinates Lat: -1.1662617 and Lng: -48.2339978), Santa Bárbara do Pará region, Pará State, Brazil were used in the experiments. The fruits were sanitized followed by drying at 60 °C for 8 h (MA035, Marconi, Piracicaba, São Paulo, Brazil), obtaining a moisture content of 8.0 ± 0.1 wt%. The dried material was ground using

an electric mill (Marconi, MA 750) and classified using Tyler sieves (Bertel, ASTM, Caieiras, São Paulo, Brazil). Particles with an average diameter of 0.8 mm were selected to conduct the experiments.

Reagents

In the extractions, *n*-propane (99.5% purity, White Martins, Rio de Janeiro, Brazil) and *n*-hexane (98.5% purity, Synth, Diadema, São Paulo, Brazil) were used as solvents. For the characterization analysis of the oil were used: sodium hydroxide (≥97.0% purity, Anidrol, Diadema, São Paulo, Brazil), sulfuric acid (>95.0% purity, Anidrol) and heptane (99.0% purity, Synth), N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA, ≥99.0% purity, Sigma-Aldrich, São Paulo, Brazil), 5-α-Cholestane (98% purity, Sigma-Aldrich), Folin-Ciocalteu reagents (Dinâmica, Indaiatuba, São Paulo, Brazil), sodium carbonate (≥99.5% purity, Anidrol), gallic acid monohydrate (≥98.0% purity, Sigma-Aldrich), methanol (99.9% purity, Panreac), *n*-hexane (98.5% purity, Synth), 2,2-Diphenyl-1pikrylhydrazyl (DPPH radical, ≥95% purity, Sigma-Aldrich), (±)-6-Hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox, 97% purity, Sigma-Aldrich), ethanol (≥99.9% purity, Honeywell, Barueri, São Paulo, Brazil).

To determine the content of soluble proteins in the defatted meal, the following reagents were used: sodium citrate (90% purity, Anidrol), sodium hydroxide (≥97.0% purity, Anidrol), sodium carbonate (≥99.5% purity, Anidrol), copper sulfate (>98.0% purity, Anidrol), Folin-Ciocalteu 2N (Sigma-Aldrich) and bovine sérum albumin (≥98.0% purity, Sigma-Aldrich).

Oil extraction

Extractions were carried out using *n*-propane as the solvent, according to the experimental methodology previously described (Trentini et al. 2017). A syringe-type pump (Teledyne ISCO 500 D) was used to pressurize the *n*-propane to the desired pressure. A micrometric valve, inserted in a heated aluminum block to prevent cooling in the depressurization process, was used to manually control the mass flow rate of solvent at 1.0 $g \cdot min^{-1}$ to the extractor (Wenceslau et al. 2021). The temperature of the extraction vessel was controlled using a thermostatic bath (Julabo, F25-HE, precision of 0.01 °C Seelbatch, Germany). The extractor, 304 L stainless steel, had an internal diameter of 1.9 cm and a height of 19 cm, which was filled with 20 g of sample in each extraction. The oil samples were collected in amber flasks at 10 min intervals until completion of 50 min. The total mass of the extracted oil was quantified, and the oil yield was determined according to the mass of oil obtained and the mass of seeds fed into the extractor.

Extractions were carried out at 25, 35 and 40 °C, with pressures of 40, 60 and 80 bar. These operating conditions were selected based on previous studies of andiroba seeds oil obtained from pressurized *n*-butane (Novello et al. 2015) and oil extraction of macauba pulp with *n*-propane (Trentini et al. 2017). The contents of the primary fatty acids (oleic and palmitic acids) in macauba pulp oil and andiroba seed oil evaluated were similar. The analysis of the experimental data, at the 95% confidence level, was performed using the Statistica 8.0 software program (StatSoft™, Inc., Tulsa, Oklahoma, United States of America).

Soxhlet extraction was carried out using *n*-hexane as the solvent, at its boiling temperature (~69 °C), using a solvent to sample mass ratio of 30 $mL \cdot g^{-1}$ for 480 min (Stevanato & Silva 2019).

Mathematical modeling

The kinetics data obtained for the oil extraction were described by the mathematical model of Sovová (1994). The equations used to describe the model are presented below, where (m) was the extracted mass as a function of the extraction time (t). The Software Maple® was used. Apparent solubility values (S_b) were determined from experimental data from the initial part of the extraction curve, in which the rate can be represented by an equation of the straight line.

For $t < t_{CER}$ (time when the extraction of the difficult-to-access oil starts):

$$m(t) = \dot{m}_F S_b t[1 - \exp(-Z)] \quad (1)$$

For $t_{CER} \leq t < t_{FER}$ (time when the extraction of the easy-to-access oil fraction ends):

$$m(t) = \dot{m}_F S_b \{t - t_{CER} exp[\frac{Z S_b}{W q_0} ln[\frac{1}{1-r}(exp^{\frac{W\dot{m}_F}{m_S}}(t - t_{CER}) - r)] - Z]\} \quad (2)$$

For $t \geq t_{FER}$:

$$m(t) = m_S\{q_0 - \frac{S_b}{W} \ln[1 + (\exp(\frac{W q_0}{S_b}) - 1)exp(\frac{W\dot{m}_F}{m_S}(t_{FER} - t))r]\}) \quad (3)$$

t_{CER} and t_{FER} are:

$$t_{CER} = \frac{(1-r)m_S q_0}{S_b Z \dot{m}_F} \quad (4)$$

$$t_{FER} = t_{CER} + \frac{m_S}{W\dot{m}_F} ln[r + (1-r)exp(\frac{W q_0}{S_b})] \quad (5)$$

where, t_{CER} is the time (min) at which the extraction of the oil of difficult access starts, t_{FER} is the time (min) at which the extraction of the easily accessible oil fraction ends, $\dot{m}_F$ is the solvent mass flow rate ($g \cdot min^{-1}$), S_b is the apparent solubility of the oil in the solvent ($g_{oil} \cdot g_{solvent}^{-1}$), Z and W are the adjustable model parameters, q_0 is the initial fraction of oil, m_S is the solid mass on an oil-free basis, and r is the less accessible oil fraction, an adjustable parameter of the model.

The values of the dimensionless parameters Z and W depend on the operating conditions of the extraction (temperature and pressure), as these parameters are related to the mass transfer resistances in the external and intraparticle film. The parameter r is related to the amount of oil that is difficult to access, so this parameter depends on the pre-treatment conditions of the seeds (grinding, and chemical treatment). As all seeds were submitted to the same type of pre-treatment, it was assumed that this parameter was the same in all extraction conditions.

The adjustable parameters Z and W were estimated using objective functions, and the volumetric mass transfer coefficients (min^{-1}) in the fluid (K_{Fa}) and solid phase (K_{Sa}) can be obtained using the following equations:

$$Z = \frac{K_{Fa} m_S \rho_F}{\dot{m}_F \rho_{bed}} \quad (6)$$

$$W = \frac{m_S K_{Sa}}{\dot{m}_F(1-\varepsilon)} \quad (7)$$

where, ρ_F is the solvent density (g·cm^{-3}), ρ_{bed} is the bed density (g·cm^{-3}) obtained from the ratio between m_S and the bed volume, and ε is the bed porosity, obtained from: $\varepsilon = 1 - \rho_{bed}/\rho_S$.

The adjustable parameter r was calculated by minimizing the objective function given by Equation 8 using the golden-search method. The parameters Z and W were estimated by minimizing the objective function given by Equation 9 where the downhill simplex method was used.

$$F = \sum_{i=1}^{n\_exp} \sum_{j=1}^{N} \left(m_j^{calc} - m_j^{exp}\right)^2 \quad (8)$$

$$F = \sum_{j=1}^{N} \left(m_j^{calc} - m_j^{exp}\right)^2 \quad (9)$$

where, N is the number of experimental data in the kinetic curves, n_exp is the number of extraction experiments, $m\ j\ calc$ is the mass of oil calculated by the model, and $m\ j\ exp$ is the guariroba oil mass obtained experimentally.

Oil characterization

Fatty acid profile and content of minor compounds

The fatty acid (FA) profile and content of minor compounds were analyzed using a gas chromatograph coupled to a mass spectrometer (Shimadzu, GC-MS QP2010 SE, Kyoto, Japan) equipped with an automatic injector. Helium was used as the carrier gas at a flow rate of 1.0 mL·min^{-1} with a split ratio of 1:40 and an injection volume of 2 µL. The injection temperature and the GC-MS interface temperature were maintained at 250 and 280 °C, respectively, for analysis of FA and minor compounds. The temperature of the ionic source was 260 °C for both analyses. Mass spectra were recorded at 70 eV with a range of m/z 50 to 550. Compound identification was performed from the library databases NIST14.lb and NIST14.lbs.

The FA profile was determined after oil derivatization (Gonzalez et al. 2013) and dilution in heptane. The percentage of each FA were expressed as the normative area of the peak of each FA. For minority analysis, the samples were derivatized with BSTFA for 30 min at 60 °C (Stevanato & Silva 2019). The 5α-cholestane standard was added to the derivatized samples for quantification of the compounds, and after that, the dilution with heptane was carried out. The prepared samples were analyzed using heating ramp of the column reported by Iwassa et al. (2021).

Total phenolic content and antioxidant activity

The extraction of phenolic compounds was performed as described by Santos et al. (2017) and the content of compounds in the obtained extract was determined by Folin-Ciocalteu method (Singleton et al. 1999). The absorbance of the samples was determined at 760 nm (UV-1900i UV-Vis Spectrophotometer, Shimadzu Scientific, Tokyo, Japan) and quantified using a calibration curve prepared with gallic acid ($R^2 \geq 0.996$).

The antioxidant capacity was determined according to the DPPH radical assay (Gu et al. 2019). The sample was diluted in ethanol (10 mg·mL^{-1}) and 1 mL of this solution was incubated with 4 mL of the ethanolic reagent DPPH (0.004%) for 60 min at room temperature in the absence of light. Absorbance was determined at a wavelength of 517 nm (Shimadzu, UV-1900) and quantified using a calibration curve made with Trolox ($R^2 \geq 0.998$).

Oxidative stability

The oxidative stability was determined by transferring the samples (~3.0 g) to the reaction vessel, which were placed in the heating block of the Professional Biodiesel Rancimat equipment (Model 893, Metrohm, Herisau, Switzerland). The analysis were conducted at constant temperature and airflow of 110 °C and 20 $L{\cdot}h^{-1}$, respectively (Pattnaik & Mishra 2021). Exhaust gases were collected in an electrical conductivity measurement vessel containing 50 mL of deionized water with an initial conductivity lower than 5 $\mu S\ cm^{-1}$ as an absorption solution. The induction time (IT) provided by the measurement of a sudden increase in conductivity after the formation of volatile acids under accelerated conditions, was determined from the second derivative of the conductivity curve, provided automatically by the StabNet 1.1 software.

Characterization of partially defatted meal

Initially, the proteins were extracted, in which a mixture of 70 $mL{\cdot}g^{-1}$ of meal and aqueous NaOH solution was placed in a refrigerated incubator (Marconi, MA 830/A) for 45 min at 60 °C and 200 rpm (Wani et al. 2006). Subsequently, the mixture was filtered through a qualitative filter (160.0 µm) and the obtained extract was centrifuged (Q222MT1, Quimis®, São Paulo, Brazil). To determine the soluble protein content, the supernatant, named protein extract, was analyzed according to the method reported by Lowry et al. (1951). The absorbance of the samples was determined at 750 nm (Shimadzu, UV-1900) and quantification was performed using a calibration curve prepared with bovine serum albumin ($R^2 \geq 0.990$), with the results expressed as soluble protein content.

Data analysis

Samples were analyzed in triplicate and results were expressed as mean ± standard error of the mean. Data collected were subjected to analysis of variance (one-way ANOVA) using Statistica 8.0 software program (StatSoft™, Inc.) the Tukey test (with a 95% confidence interval), to evaluate differences between the results.

RESULTS AND DISCUSSION

Oil yield

Table I shows the experimental conditions and results obtained for the extractions using subcritical *n*-propane and Soxhlet extraction with *n*-hexane. The total lipid content obtained by Soxhlet extraction was ~62.0 wt%, a higher value than those reported in literature of 56.4-61.5 wt% (Araujo-Lima et al. 2018, Nascimento et al. 2019).

The analysis of variance (ANOVA) study showed that only temperature, in the evaluated experimental range, significantly affected the oil yield ($p<0.05$), as shown in Table II. The values of ASO solubility ranged from 0.238 to 0.362 (g oil·g solvent), where the highest values were obtained at 25 ºC, regardless of the operating pressure.

The increase in temperature, in the evaluated experimental range from 25 to 45 °C, under constant pressures (40 and 80 bar), resulted in a decrease in the density of the compressed solvent, therefore reduced its solvation power, decreasing the solubilization of the oil, and consequently, its removal from the pores of the matrix (Fetzer et al. 2021, Saldaña et al. 2002). Trentini et al. (2019) used the

same *n*-propane density range (0.46–0.51 g cm^{-3}) to obtain macauba kernel oil and found that, in the investigated range, temperature (30 to 60 °C) and pressure (80 to 120 bar) exerted little influence on the solubility of the oil in the extracting solvent, resulting in a small difference in the yields obtained. Wenceslau et al. (2021) reported that with increasing temperature (40 to 60 °C), a decrease in the solvent density was observed, also reducing the apparent solubility and viscosity of this compressed fluid, facilitating the intracellular penetration of the solvent. In extractions with subcritical propane, the effect of pressure is considerably low or negligible (Azevedo et al. 2022), however, its properties as a solvent can be impacted, generating an increase in its density, solvation power and vapor pressure, which results in obtaining higher extraction yields (Barbi et al. 2019, Cuco et al. 2019).

The values of the adjusted parameters of the Sovová model and the correlation coefficient are presented in Table III. The experimental results of the extraction curve and predicted by the Sovová model are shown in Figure 1. For the modeling, it was considered that the initial amount of oil (q_0) was 0.823 (mass of oil per mass of oil-free raw material), which corresponded to the condition where the highest yield was obtained. The model adequately represented the behavior in all conditions evaluated, this is also proven by the values of the correlation coefficient (0.99) close to one, indicating a good fit of the model.

The experimental data of the extraction curve (Figure 1) showed a typical behavior, a linear region and another with a decreasing rate. The values of the external film mass transfer parameters (K_{ya}) ranged from 0.32 to 3.2 min^{-1}, while the intraparticle mass transfer parameter (K_{sa}) ranged from 0.004 to 0.032 min^{-1}. Mass transfer parameters varied with oil composition, solvent transport properties, in

Table I. Experimental conditions and results of oil yield from Andiroba seed extracted with pressurized *n*-propane (50 min) and Soxhlet extraction (480 min).

Run	Conditions	ρ ($kg \cdot m^{-3}$)	S_b ($g\ oil \cdot g^{-1}$ solvent)	Oil yield (wt%)	Recovery (%)	
	T (°C)	P (bar)				
1	25	40	0.50113	0.362	45.14	72.58
2	25	80	0.51076	0.322	44.50	71.55
3	45	40	0.46933	0.238	32.82	52.77
4	45	80	0.48301	0.248	33.41	53.72
5-7[1]	35	60	0.49188	0.260	34.90 ± 1.30	56.11 ± 2.10
Soxhlet[1]	69	1	nd	nd	62.19 ± 0.50	100

[1]Experiment performed in triplicate. ρ: solvent density. S_b: apparent solubility of the oil in the solvent. nd: not determined.

Table II. Effect of the variables on the oil extraction of *Carapa guianensis* seeds obtained by pressurized *n*-propane.

	Effect	Standard Error	*p**
Intercept	37.22	0.493	<0.001
Temperature (T)	-11.70	1.306	0.012
Pressure (P)	-0.025	1.306	0.986
T × P	0.615	1.306	0.684

*Statistical significance p < 0.05.

addition, K_{Ya} parameter depended on the solvent flow velocity, while the K_{sa} parameter depended on the structure of the solid. The mass transfer parameters obtained were of the same order of magnitude of other studies, where *n*-propane was used as a solvent in the extraction of lipids (Wenceslau et al. 2021, Santos et al. 2015).

Based on the parameter *r*, estimated by the model, the fraction of easily accessible oil (1– *r*) was 0.603. The mass of subcritical *n*-propane in contact with the raw material during the static period was ~20 g and the removal of all this solvent after opening the micrometric valve occurred in ~20 min (mass flow rate was 1 g min^{-1}). The values obtained by the model for t_{FER} (extraction of the entire fraction of easily accessible oil ends) were from 22.78 to 24.95 min. That is, the solvent removed in this stage corresponded to that used in the static period. Thus, the solvent confined with the andiroba particles for 20 min was able to solubilize the high fraction of the oil obtained, as evidenced in Figure 1.

Oil characterization

The oil extracted from *Carapa guianensis* seeds, using pressurized *n*-propane and *n*-hexane, was characterized in terms of the fatty acid profile, minority compounds, total phenolic compounds, antioxidant capacity and induction time. The results obtained are summarized in Table IV.

Table III. Parameters obtained from the mathematical modeling applied to the kinetics of Andiroba seed oil extraction.

T (ºC)	P (bar)	Z	W	r	t_{CER} (min)	t_{FER} (min)	K_{ya} (min^{-1})	K_{sa} (min^{-1})	R^2
25	40	9.13	1.706	0.397	1.756	24.950	0.318	0.0321	0.9974
25	80	87.58	1.318	0.397	0.193	24.139	3.198	0.0265	0.9974
45	40	15.33	0.108	0.397	1.389	24.208	0.653	0.0023	0.9995
45	80	39.61	0.122	0.397	0.528	23.062	1.602	0.0026	0.9976
35	60	21.27	0.187	0.397	0.925	22.785	0.856	0.0040	0.9966

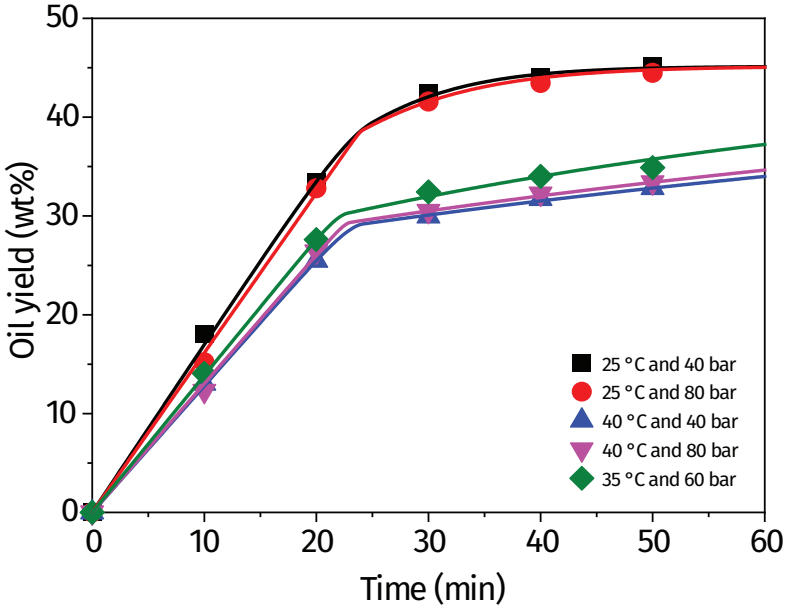

Figure 1. Experimental kinetic curves for Andiroba seed oil extraction with pressurized n-propane fitted using the Sovová model.

Fatty acid profile

The fatty acid profile showed the predominance of oleic, palmitic, stearic and linoleic acids, which represent ~95% of the composition, among all the conditions studied. The identification of these fatty acids in ASO is in line with what was previously reported (Novello et al. 2015, Milhomem-Paixão et al. 2016), however, quantitatively in different proportions, which may be related to the type of solvent and extraction method used (Juhaimi et al. 2019). This is because the exposure of fatty acids to long process times and temperatures, mainly due to conventional extraction methods, can cause adverse effects on oil quality, such as the degradation of this class of compounds. In addition, the type of solvent can negatively affect the solubility and extractability of the target compounds, due to the lack of affinity regarding the polarity of these analytes, resulting in insufficient extraction (Nde & Foncha 2020).

Table IV. Experimental conditions and Andiroba seed oil composition extracted with pressurized *n*-propane and Soxhlet extraction with *n*-hexane.

Property		Experimental conditions					Soxhlet
		25 °C and 40 bar	25 °C and 80 bar	45 °C and 40 bar	45 °C and 80 bar	35 °C and 60 bar	
Fatty acid (%)[1]	Myristic	0.08 ± 0.009^{a}	0.08 ± <0.01^{b}	0.08 ± <0.01^{ab}	0.07 ± <0.01^{ab}	0.06 ± <0.01^{ab}	0.06 ± <0.01^{a}
	Palmitic	29.04 ± 0.090^{a}	30.07 ± 0.07^{b}	28.88 ± 0.03^{a}	28.45 ± 0.05^{c}	28.19 ± 0.03^{c}	31.00 ± 0.17^{d}
	Palmitoleic	0.99 ± 0.003^{a}	0.95 ± <0.01^{a}	0.93 ± <0.01^{a}	0.94 ± 0.01^{a}	0.95 ± 0.01^{a}	0.84 ± 0.03^{b}
	Stearic	11.29 ± 0.042^{a}	11.13 ± 0.04^{a}	11.25 ± <0.01^{a}	11.57 ± 0.01^{ab}	12.18 ± 0.11^{c}	12.08 ± 0.31^{bc}
	Oleic	46.05 ± 0.039^{ab}	45.66 ± 0.05^{ab}	46.33 ± 0.04^{ab}	46.24 ± 0.05^{ab}	45.31 ± 0.21^{a}	46.87 ± 0.85^{b}
	Linoleic	9.17 ± 0.014^{ab}	8.78 ± <0.01^{a}	9.18 ± <0.01^{ab}	9.30 ± 0.01^{bc}	9.61 ± 0.08^{c}	5.52 ± 0.23^{d}
	Linolenic	0.21 ± 0.003^{a}	0.20 ± 0.01^{a}	0.19 ± 0.01^{a}	0.19 ± <0.01^{a}	0.20 ± <0.01^{a}	0.07 ± <0.01^{b}
	Arachidic	1.81 ± 0.018^{a}	1.76 ± 0.01^{a}	1.78 ± <0.01^{a}	1.87 ± <0.01^{ab}	2.09 ± 0.02^{bc}	2.17 ± 0.14^{c}
	Behenic	0.44 ± 0.008^{a}	0.45 ± <0.01^{ab}	0.46 ± <0.01^{ab}	0.48 ± <0.01^{ab}	0.57 ± 0.02^{c}	0.54 ± 0.05^{bc}
	Others	0.93 ± 0.004^{a}	0.90 ± <0.01^{a}	0.92 ± 0.01^{a}	0.89 ± <0.01^{a}	0.80 ± 0.03^{a}	0.69 ± 0.02^{a}
Minority compounds (mg 100 g^{-1} of oil)	Squalene	49.03 ± 0.26^{a}	36.67 ± 0.21^{b}	54.64 ± 0.51^{c}	38.88 ± 0.19^{d}	53.55 ± 0.94^{c}	20.36 ± 0.48^{e}
	Stigmasterol	17.89 ± 0.77^{a}	23.44 ± 0.95^{b}	14.06 ± 0.34^{c}	15.99 ± 0.01^{ac}	10.99 ± 0.57^{d}	20.43 ± 0.21^{e}
Total phenolic compounds (mg GAE 100 g^{-1} oil)[2]		31.49 ± 0.24^{a}	34.39 ± 0.37^{b}	37.35 ± 0.37^{c}	41.43 ± 0.62^{d}	26.57 ± 0.44^{e}	27.06 ± 0.12^{e}
Antioxidant capacity (µmol Trolox g^{-1} oil)		52.62 ± 0.05^{ab}	55.18 ± 0.14^{ab}	52.28 ± 0.09^{ab}	46.42 ± 0.04^{d}	49.51 ± 1.62^{ad}	52.96 ± 0.05^{a}
Induction time (h)		3.01 ± 0.03^{a}	2.40 ± 0.17^{bc}	2.42 ± 0.01^{bc}	2.51 ± 0.10^{bcd}	2.17 ± 0.08^{bc}	2.61 ± 0.20^{abcd}

[1]Normative area; [2]GAE: gallic acid equivalent. Means followed by the same letters (on the same line) do not differ statistically (p>0.05).

Oils rich in oleic acid have shown modulatory effects on broad physiological functions, suggesting a beneficial effect on autoimmune and inflammatory diseases, in addition to their ability to facilitate wound healing (Sales-Campos et al. 2013), thus, it is the most used liquid lipid as a precursor for topical drug administration (Atef et al. 2022). Oils with a high concentration of palmitic acid, such as sea buckthorn pericarp oil (29-36%), are known to promote the epithelization of the skin and mucosal tissue (Poljšak et al. 2020). Stearic acid is linked to bacteriostatic and anti-inflammatory activities (Cornily et al. 2010), and linoleic acid increases neovascularization, extracellular remodeling, cell migration and differentiation, presenting antioxidant activity (Rekik et al. 2016).

Minority compounds

Squalene and stigmasterol were identified as minor compounds in ASO. Squalene is an important component in vegetable oils due to its antioxidant properties, reducing serum cholesterol concentrations, photoprotection, anticancer, and antitumor (Gutiérrez-Luna et al. 2022). The ASO obtained showed a higher content of squalene (54.64 mg per 100 g oil) compared to the oils of chia seed (40.73 mg per 100 g oil) (Scapin et al. 2017), soybean (4.56 mg per 100 g oil), sunflower (8.91 mg per 100 g oil) (Shen et al. 2021) and moringa (3.56 mg per 100 g oil) (Gutiérrez-Luna et al. 2022). The use of *n*-propane proved to be more efficient in obtaining oils with higher levels of squalene compared to the extraction by Soxhlet at all conditions tested, being a lower pressure (40 bar) indicated for removal of this compound from andiroba seeds.

The presence of stigmasterol confers antioxidant, antiparasitic, antifungal, antibacterial, anticancer, antidiabetic, anti-osteoarthritis, anti-inflammatory, immunomodulatory and neuroprotective activity to vegetable oils (Bakrim et al. 2022). The ASO with the highest stigmasterol content was obtained at 25 ºC and 80 bar, which was ~14% higher than the value obtained by conventional extraction (20.43 ± 0.21 mg per 100 g oil). Additionally, the results obtained indicate that the extraction of stigmasterol was favored with the increase in pressure at 25 ºC and that the increase in temperature did not contribute to increase its extraction.

Minority compounds are accumulated at the interfaces of plant cells, especially in the pores of the matrix membranes, places that are difficult for the solvent to access and therefore more difficult to extract (Spanova & Daum 2011). Achieving permeability, the selectivity of the extraction method becomes crucial to promote the removal of these compounds (Hawthorne et al. 2000). In addition, under pressurized conditions, efficiency is conditioned to the simultaneous action of operating temperature and pressure. The lowest pressure (50 bar) evaluated by Scapin et al. (2017) allowed obtaining the highest content of squalene in chia seed oil using liquefied petroleum gas (composed of a mixture of gases with 50.3 wt% propane). The highest stigmasterol content reported by Lopes et al. (2020) in the *Pachira aquatica* seed oil, extracted with compressed *n*-propane was obtained with the combination of the lowest temperature and highest pressure of 30 °C and 80 bar, respectively.

Total phenolic compounds

Phenolic compounds are the most prominent constituents with reported bioactivity, and their presence in ASO may indicate antioxidant potential. All samples resulting from the extraction with pressurized *n*-propane showed phenolic content, ranging from 26.5 to 41.4 mg GAE $100\,g^{-1}$ oil, with differences between assays and contents up to 53% higher than those obtained by Soxhlet extraction. The

efficiency of pressurized *n*-propane in extracting these compounds compared to Soxhlet extraction has been previously reported (Guedes et al. 2018, Azevedo et al. 2022).

The highest TPC content (41.4 mg GAE 100 g $^{-1}$ oil) was obtained in the extraction condition of 45 °C and 80 bar, corresponding to the maximum temperature and pressure conditions investigated, in line with what was previously reported for blackberry seed oil (Correa et al. 2021) and cumaru seed oil (Fetzer et al. 2021). For andiroba seed oil, Novello et al. (2015) using pressurized *n*-butane reported that the maximum value of TPC (35.6 mg GAE 100 g^{-1} oil) was obtained under the lowest investigated temperature and pressure conditions (25 °C and 13 bar). However, for *n*-propane, the ability to extract more phenolic compounds at higher temperatures without causing thermal degradation may be attributed to the increased solubility of these compounds in the solvent, which was favored by this variable (Cuco et al. 2019). Increasing the pressure increased the solvent density, resulting in greater solvation power (Scapin et al. 2017), allowing the obtainment of ASO with higher phenolic compounds content.

Antioxidant capacity

The DPPH radical scavenging activity of ASO samples obtained with compressed *n*-propane ranged from 46.4 to ~55.2 μmol Trolox g^{-1} oil, with higher values obtained at 25 °C (Table IV). This result may be linked to the increase in recovery of the stigmasterol content under the same processing conditions. Although squalene was present in greater quantity in the content of minor compounds of ASO, verified in this study and by Milhomem-Paixão et al. (2016), stigmasterol was the compound that has been identified with more active biological activities in plant matrices (Ashraf & Bhatti 2021). The lowest temperature also resulted in the highest antioxidant activity in the investigations reported by Barbi et al. (2019) for the extraction of inajá pulp oil with subcritical *n*-propane, evaluating the temperature in the range of 20 to 60 °C at 100 bar. In addition, it is worth mentioning that phenolic compounds are important plant constituents due to their ability to eliminate free radicals, due to their hydroxyl groups (Vuolo et al. 2019), directly reflecting on the antioxidant action. The data in Table IV revealed a relationship between antioxidant activity and the TPC content of ASO, suggesting that the antioxidant action results from the contribution of the phenolic content present in this oil, as previously reported for favela seed oil (Santos et al. 2021).

It can be observed that the oil resulting from the process using pressurized *n*-propane resulted in similar antioxidant capacity than the oil obtained by Soxhlet extraction (52.96 μmol Trolox g^{-1} oil). Despite of the lower contents, in the range of temperature studied, it did not cause thermal degradation of the compounds, since the temperatures investigated are lower than those used in Soxhlet extraction (~69 °C), demonstrating that the results obtained may be linked to incomplete extraction of compounds responsible for the antioxidant activity. Correa et al. (2021) reported 14.4% higher antioxidant capacity in blackberry seed oil, resulting from Soxhlet extraction, when compared to the extraction process with pressurized *n*-propane conducted at 50 °C and 50 bar. Although *n*-hexane showed greater extraction capacity for obtaining compounds that result in greater antioxidant capacity, all ASO samples resulting from extraction with *n*-propane showed activity antioxidant activity against DPPH radical assay. Corroborating the operational conditions involved in the aforementioned processes, the non-toxicity of the solvent used and consequently the quality of

the product obtained, the best choice for obtaining these compounds in ASO is through the use of compressed *n*-propane.

Induction time

Based on the results shown in Table IV, it can be seen that, in general, the oils obtained from the tests using with compressed *n*-propane showed similar resistance to oxidation (2.1 to 3.0 h) when compared to the oil resulting from Soxhlet extraction (2.6 h). Considering the Soxhlet data as a reference, as it is an exhaustive process that occurs until the complete removal of lipids from the matrix (López-Bascón & Castro 2020), it can be seen that the oils extracted under pressurized conditions showed good oxidation stability, considering less time (50 min) and temperatures (25 to 45 °C) applied (480 min at ~69 °C, respectively). Teixeira et al. (2018) also reported similarity in the data obtained for oxidative stability of the oil from sapucaia (*Lecythis pisonis*) nuts extracted with compressed *n*-propane and Soxhlet extraction. Vegetable oils have their functional attributes altered by the chemical composition of the raw material or the sensitivity of its lipids, which can undergo autoxidation, thermal oxidation and photooxidation (Santos et al. 2013a, b). Considering that biologically active compounds present beneficial action on compounds harmful to the cell matrix, giving it greater resistance, it is possible to link the oxidative stability of oils obtained with pressurized *n*-propane to its composition in squalene and stigmasterol, as well as to its content of phenolic compounds. Roszkowska et al. (2015) reported that the oxidative stability of commercial rapeseed oils was mainly related to phenolic compounds. Therefore, phenolic lipids are essential for various applications (Ciftci & Saldaña 2012). Furthermore, this is an important attribute that confers properties for cosmetic use of the oil (Bialek et al. 2016), since it is linked to an important source of antioxidant resources, with healing potential and pro and anti-inflammatory properties, it suggests capacity for topical use.

Defatted meal characterization

The soluble protein content of partially defatted meal from Andiroba seeds obtained as a by-product of extraction with pressurized *n*-propane and Soxhlet is presented in Table V.

For successful application in skin care products, proteins are usually concentrated, targeting proper functionality and technological properties (Rommi et al. 2015). In this context, the influence of operating conditions applied for oil extraction must be considered, as they directly interfere in the solubility of proteins, which were concentrated in the meal. From the data presented in Table V, it can be observed that removing the oil with *n*-propane at 40 bar, made it possible to obtain a by-product with a higher content of soluble proteins. However, comparing the result of Soxhlet extraction, it is possible to verify that the conventional technique resulted in a ~53% higher concentration in the defatted material, indicating greater protein solubility in pressurized *n*-propane than in *n*-hexane.

Although extraction with *n*-hexane effectively removed oil from Andiroba seeds, the process requires high temperature (69 °C) and considerable long time (480 min), which can promote the denaturation of proteins (Sawada et al. 2014). In addition, solvent traces, which compromise the quality of the material obtained, mainly due to its toxicity, limit its usability, making subsequent treatments necessary for its elimination. On the other hand, the defatted meal after extraction with compressed *n*-propane was a fast process, carried out under mild conditions that can avoid protein denaturation, in addition to not requiring subsequent processing treatments.

Table V. Characterization of partially defatted meal of Andiroba pulp.

Extraction technique	Condition	Soluble protein (wt%)
Compressed propane	25 °C and 40 bar	17.89 ± 0.02[a]
	25 °C and 80 bar	15.23 ± 0.08[b]
	45 °C and 40 bar	17.89 ± 0.04[a]
	45 °C and 80 bar	16.61 ± 0.02[c]
	35 °C and 60 bar	17.35 ± 0.09[d]
Soxhlet using hexane	69 °C and 1 bar	27.32 ± 0.06[e]

Means followed by the same letters do not differ statistically (p>0.05).

The need for proteins with functional properties is growing due to the high consumer demand for their use in diverse sectors of the industry. The properties depend on the behavior of these molecules in liquids, which are important due to their influence on other characteristics, such as the formation of emulsions, lotions and gels (Xi et al. 2018). For products designed for skin care, this attribute may promote water's ability to combine with the skin's cuticle and its appendages, playing a role in its lightening (Turowski & Adlmann-Grill 1985). Soluble proteins might be sources of peptides, promising different applications with biological activities such as antioxidant, antimicrobial and anti-inflammatory action (Vasconcellos et al. 2016). In addition, the proteins concentrated or isolated in the defatted meal may contain phytoactives, with suitable properties for incorporation in topical formulations (Plundrich et al. 2013), such as lotions, gels, and creams (Teglia & Secchi 1999). Therefore, the recognition of the absence of any risk, associated with its potential use, has renewed interest in investigations into the use of the by-product of oil extraction as an ingredient for the formulation of phytocosmetics, an interesting alternative for sustainable cultivation, with low environmental impact and suitable functional properties.

CONCLUSIONS

Compressed *n*-propane can be considered as a promising alternative for oil extraction, as it requires lower temperature and pressure conditions than when using the Soxhlet processs, without compromising the quality of the oil obtained. It was observed that the high level of fatty acids associated with the lipid induction time prevents the enzymatic degradation of the oil, and this high-quality oil guarantees its use by the cosmetic industry without the need for the chemical refining of the oil. The oil obtained presented squalene and stigmasterol as minority compounds in its composition. Therefore, technically this process is advantageous due to the small amount of solvent required, short extraction time, elimination of post-processing steps and high potential to promote the healthiness of the products. In addition, the by-product represented by the defatted meal resulting from the extraction with compressed *n*-propane does not require subsequent treatments for later use and can avoid any protein denaturation due to its low temperature and pressure conditions. For the implementation of emerging technologies and with sustainable demands, as a suggestion for future work, we indicate conducting studies assisted by technoeconomic analysis

and dangerousness, due to the flammable characteristics of pressurized n-propane, as well as environmental impact studies, which benefit the process with an additional focus on scalability, factors that configure the main challenges in expanding the use of this technology.

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