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Oil extraction from macauba pulp using compressed propane

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ABSTRACT

In this study, the extraction of macauba pulp oil (MPO) using compressed propane as a solvent was investigated, and compared with conventional (Soxhlet) extraction. Extractions with propane were carried out in order to investigate the effects of temperature (333–373 K) and pressure (4–12 MPa) on the oil yield and the chemical composition of the products. The effects of temperature and pressure on the yield were negative and positive, respectively, with a maximum yield of 23.08 wt% being obtained at 333 K and 12 MPa. The use of propane allowed a fast extraction with a yield of ~86% in the conventional extraction. The fatty acids composition showed a predominance (~85%) of oleic and palmitic acids. The β-carotene and flavonoid contents were affected by the compressed-solvent extraction conditions and extraction method. Oil obtained using compressed-solvent extraction showed higher levels of phytosteroids and tocopherols and, consequently, a longer oxidation induction time.

1. Introduction

Macauba (*Acrocomia aculeata*) oil is an important resource with a productivity of 4–6 tons of oil per hectare [1]. The most economically significant part of the plant is the fruit, because it has ~30% of oil in its composition [2,3]. However, macauba oil can also be extracted from the pulp and amond, and pulp has oil contents of 18.70–32.76% [4–8].

The oil extracted from the pulp has an orange-yellow color, with a high concentration of oleic and palmitic acids [7,9–11]. Macauba pulp oil has active compounds in its composition, such as tocopherols [4,12,13], phytosterols [8,11] and β-carotene and flavonoids [5,8,14,15].

As an alternative to the conventional methods of extraction using solvent and pressing, the extraction of vegetable oils using pressurized fluids under sub- or supercritical conditions has been reported. This extraction technique is flexible, due to the possibility of continuous modulation of the solvent power to adjust the selectivity of the supercritical fluid [16]. Also, the high diffusivity of the fluid ensures rapid extraction and the oil extracted with this technique is less subject to oxidation [17,18]. Additionally, the degradation of bioactive compounds is reduced or eliminated, resulting in a final product free of toxic solvent residues [19,20].

Carbon dioxide is generally used as the extraction solvent under supercritical conditions, but a limiting factor for its use is that it is associated with a low solubility of triacylglycerides [21]. Thus, relatively high pressures and longer extraction times are required to provide satisfactory yields [22–24]. Propane (pressure and temperature critical of 369.67 K and 4.3 MPa, respectively), provides higher extraction yields than carbon dioxide, due to its high solvation power in relation to triacylglycerides at low pressures [21,22,25]. This results in shorter extraction times and higher oil yields can be obtained with a smaller volume of solvent [22,26–28]. Additionally, it has been reported that propane is more efficient in the extraction of active compounds, such as phytosterols and tocopherols [16,29–33] and also carotenoids [31,34,35], compared to carbon dioxide, and provides extracts with high thermal stability [28,32].

Publications in the literature report oil extraction from *Acrocomia aculeata* pulp using solvent extraction in a Soxhlet [3–5,7,9,12,36], pressing [7,37,38] and low-pressure extraction [8]. However, no previous studies on obtaining this oil using compressed propane as the solvent could be found. Recently, Nascimento et al. [24] reported the extraction of oil from macauba pulp (variety *Acrocomia intumescens* Drude) using supercritical carbon

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dioxide as the solvent. They obtained low oil yields with higher pressure (200 bar) and long extraction times (~200 min).

In this context, the aim of this study was to obtain macauba pulp oil (MPO) using compressed propane as the solvent and investigate the effects of temperature and pressure in the oil yield. At the same time, extracts were obtained by the conventional Soxhlet technique, using n-hexane and dichloromethane as solvents, for comparative purposes. The extracts obtained applying the two techniques were characterized and compared in terms of their chemical compositions.

2. Materials and methods

2.1. Sample preparation

Fruits of *Acrocomia aculeata* harvested in the Araripe Plateau (Global Positioning System coordinates 38°0′ and 41°55′ W; 70°10′ and 7°50′ S), Cariri region, Ceara State, Brazil were used in the experiments. The fruits were sanitized followed by the separation of the pulp, which was dried at 60 °C for 8 h (Marconi, MA035), obtaining a moisture content of 3.6 ± 0.1 wt%. The dried material was milled in an electric mill (Marconi, MA 750) and classified using Tyler sieves (Bertel, ASTM). Particles with an average diameter of 0.5 mm were selected to conduct the experiments.

2.2. Reagents and standards

Propane P.A. 99.5% (White Martins), *n*-hexane 99% (F. Maia) and dichloromethane 99.5% (Vetec) was used in the extractions. For β-carotene and flavonoid content, β-carotene standard >99.9% (Sigma–Aldrich), *n*-hexane (F Maia), ethanol 95% (Anidrol) and hydrochloric acid 37% (Nuclear) were used. For the determination of the tocopherol content, α, γ and δ-tocopherol standards >99.9% (Sigma–Aldrich), isopropanol (JT Baker, grau HPLC), methanol (JT Baker, grau HPLC) and ultrapure water (Milli-Q) were used. For determination of fatty acid composition and free glycerol compounds were used derivatizing agents BF3-methanol and N,O-bis (trimethylsilyl) trifluoro-acetamide-BSTFA with trimethylchlorosilane-TMCS, potassium hydroxide P.A. (Biotec), methanol PA (Vetec) and heptane 99.6% (F Maia), and internal standards of 5α-cholestane and methyl heptadecanoate >99.9% (obtained from Sigma–Aldrich). Oxygen 99.9% (White Martins) were used in DSC analysis.

2.3. Oil extraction

Propane was used as a solvent in the extraction, which was conducted with the experimental apparatus shown in Fig. 1 and applying the procedure described in detail by Santos et al. [25]. The laboratory-scale unit consists of a gas cylinder, two thermostatic baths, syringe pumps (Teledyne ISCO 500 D), and a jacketed extraction vessel (1.95 cm of diameter and 19.4 cm of height) with a capacity of 58 cm^3.

To evaluate the effects of pressure and temperature, a 22 factorial design was adopted, with triplicates at the central point, where the pressure ranged from 4 to 12 MPa and temperature from 333 K to 373 K. The pressure and temperature levels choice had as reference the phase behavior of the pseudo-binary system was performed for the {Propane (1) + *Moringa oleifera* oil (2)} system [39]. The content of oleic acid (18:1) present in macauba pulp oil (MPO) and *Moringa oleifera* oil extracted with the pressurized propane are like, 76% and 61%, respectively. It is worth mentioning that the monounsaturated fatty acids have higher selectivity with compressed propane under low pressure. The solvent was pumped at a constant flow rate of 3 mL min^{-1} and for each extraction the extraction vessel was loaded with ~17 g of pulp to form a bed of solids supported by two 200-mesh wire disks at both ends.

The oil was collected in an amber glass vessel and its mass was determined at time intervals of 5 (0–30 min), 10 (30–60 min) and 20 (60–80 min) of extraction. The yields were calculated as the ratio of the extracted oil mass to the initial macauba pulp mass. The analysis of the experimental data, at the 95% confidence level, was performed using the Statistica 8.0 software program (STATSOFT™, Inc.)

The conventional oil extraction was performed in a Soxhlet apparatus, as recommended by Institute Adolfo Lutz [40], in order to compare the yield and characteristics of the oil with that obtained applying the compressed-solvent extraction technique. Dichloromethane and *n*-hexane were employed as solvents at their boiling points, for 480 min, and ~5 g of sample was used in each test.

2.4. Oil characterization

For the determination of the β-carotene content, samples were solubilized in *n*-hexane and a calibration curve was constructed from the dilution of a β-carotene standard to concentrations of 1.0–100 mg L^{-1}, which showed a regression coefficient of 0.998. The results were expressed in mg of β-carotene per 100 g of oil.

The total flavonoid content was determined according to the procedure reported by Francis [41]. The oil (~1 g) was solubilized in 50 mL of ethanol/HCl (1.5 mol L^{-1}). The sample was homogenized, the solution was cooled and left to stand protected from the light for 12 h and then the absorbance was determined. The results were expressed in mg of flavonoids per 100 g of oil, using 76.6 as the flavonoids conversion factor.

The β-carotene and flavonoids contents were determined based on the absorbance reading for the samples at 450 nm and 374 nm, respectively, using UV spectrophotometry (Femto, 700 plus).

The α, γ and δ-tocopherols were determined in a high performance liquid chromatograph (LC-20AT, coupled to a UV–VIS detector SPD-20 A, Shimadzu) equipped with a C-18 column (Shimpack CLC-ODS M, 25 cm × 4.6 mm, 5 μm). The method employed was that described by Freitas et al. [42] using methanol and ultrapure water as the mobile phase (96% of methanol and 4% of water). Samples were injected at 298 K with a loop of 50 μL, mobile phase flow rate of 1 mL min^{-1} and detection at 292 nm. Approximately 30 mg of the oil was solubilized in 1 mL of isopropanol, filtered through a nylon syringe filter (Analytical, 13 mm and 45 μm). To quantify the tocopherols in the samples, standard curves were constructed using chromatographic standards at concentrations of 0.5–5 mg L^{-1} for α and γ, and 0.2–5 mg L^{-1} for δ.

The fatty acids composition and glycerol-free compounds were determined using a gas chromatograph coupled with a mass detector (Thermo-Finnigan), fitted with a capillary column Agilent HP-5MS (30 m × 0.25 mm × 0.25 μm), with the injection of 0.4 μL in split mode 1:10 and helium as the carrier gas at a flow rate of 1 mL min^{-1}. The identification of the components present in the samples was performed using the Xcalibur software program (ThermoElectron).

To determine the fatty acids composition, samples were derivatized following the methodology of AOAC Ce 2–66 [43] and analyzed applying the chromatographic conditions described by Trentini et al. [8], using methyl heptadecanoate as the internal standard. For the determination of free glycerol compounds, approximately 30 mg of oil was derivatized with 20 μL of BSTFA/TMCS with subsequent addition of 5α-cholestane and methyl heptadecanoate to quantify the phytosterols and free fatty acids, respectively. The solution remained for 30 min at 333 K. The analysis was performed applying the conditions reported by Santos et al. [25].

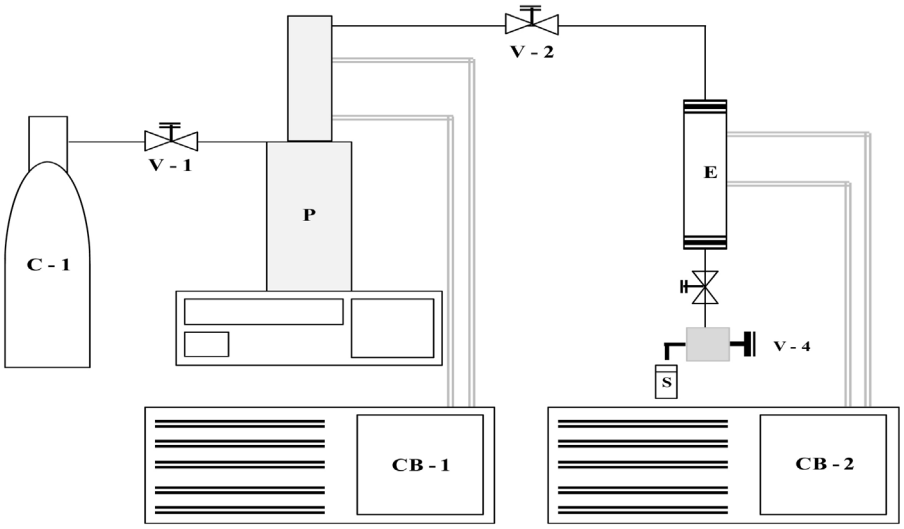

Fig. 1. Schematic diagram of the extraction unit used in this study: C-1 carbon dioxide and propane cylinder; CB-01 and CB-02 circulation baths; P syringe pump; E extractor; S sampling trap; V-1 ball valve; V-2 and V-3 needle valves; V-4 micro-metering needle valve.

The oxidative stability of the MPO was determined in a differential scanning calorimeter (DSC Shimadzu-60). In this analysis, 5 mg of oil was placed in an aluminum pan and then subjected to a flow of oxygen at 50 mL min^{-1}. Each sample was submitted to four different temperatures (383, 393, 403 and 413 K). The oxidation induction time (t_0) was obtained from the oxidation curve, corresponding to the intersection of the baseline and the tangent line at the edge of the isotherm.

All of the analyses for the oil characterization were performed in duplicate, and the results are presented as mean values ± standard deviation. The data collected were subjected to ANOVA using Excel 2010 and Tukey tests (with a 95% confidence interval) to evaluate differences between the results.

3. Results and discussion

3.1. Oil extraction

Table 1 shows the experimental conditions and results for the oil yield obtained in the conventional and compressed-solvent extraction of oil from macauba pulp. Analysis of the data obtained on the experimental conditions using propane, in the experimental range evaluated, indicates that the use of higher pressures at low temperatures favors the oil extraction ($p < 0.05$). An increase in the temperature at constant pressure (compare runs 1 and 3) results in a decrease in the yield, due to a reduction in the solvent density. Under the conditions of run 1, the propane is in the gaseous state and its extractor power is lower compared with the other conditions evaluated.

It can be seen from the data reported in Table 1 that the interaction between the temperature and pressure (experiments 2–5) had a moderate effect on the solvent density when compared to run 1, and similar yields were obtained ($p > 0.05$).

The extraction kinetics curves obtained with the use of compressed propane are shown in Fig. 2, it was verified that extraction yield reached a plateau after a short extraction time (30 min for runs 2–5 and 20 min for run 1), which indicates the high solubility of the macauba pulp oil in this solvent. This behavior is one of the characteristics of the use of compressed propane as a solvent in the extraction of vegetable oils [39,44,45].

Soxhlet extraction using *n*-hexane and dichloromethane as solvents resulted in similar yields ($p > 0.05$) of 25.64% and 26.83%, respectively. The extraction with propane provided achieving ~86% of the yield obtained by Soxhlet. However, it is noteworthy that in this case the extraction time was 30 min while for the conventional extraction it is 480 min, verifying that a high oil yield can be obtained with short extraction times using propane.

Table 1
Experimental conditions and results for MPO extraction yields obtained by compressed-solvent and conventional (Soxhlet) extraction techniques.

Run	Solvent	T (K)	P (MPa)	p^1 (g cm^{-3})	Time (min)	Oil yield (wt%)
1	Propane	373	4	0.11	80	9.77^{a}
2	Propane	373	12	0.41	80	22.69^{b}
3	Propane	333	4	0.44	80	22.86^{b}
4	Propane	333	12	0.47	80	23.08^{bA}
5	Propane	353	8	0.42	80	$22.8^{b} \pm 0.23^{2}$
6	*n*-Hexane	342	–	–	480	$25.64^{B} \pm 0.59^{2}$
7	Dichloromethane	313	–	–	480	$26.83^{C} \pm 0.10^{2}$

Means followed by the same lower case letters (comparison of runs with compressed propane) and uppercase letters (comparison of conventional and compressed extractions) indicates no significant difference ($p > 0.05$).
[1] Propane density.
[2] Average value for three replicate runs ± standard deviation.

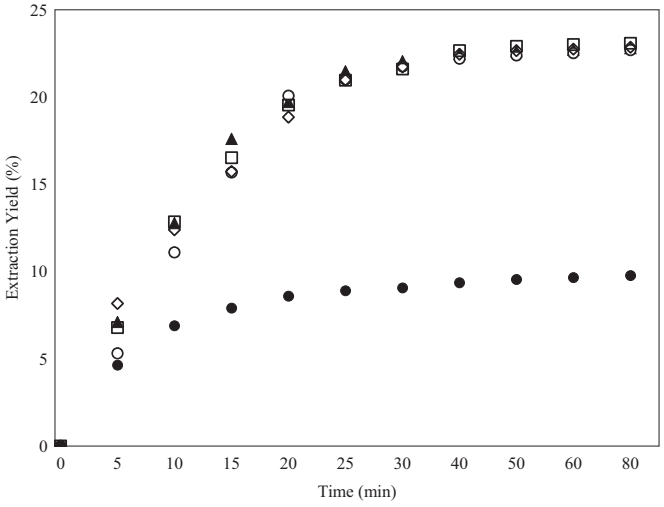

Fig. 2. Kinetics of the extraction of macauba pulp oil (MPO) using compressed propane (353 K/8 MPa), (373 K/12 MPa), (373 K/4 MPa), (333 K/12 MPa), (333 K/4 MPa).

Table 2
Fatty acids composition of MPO obtained with compressed propane, *n*-hexane (HEX) and dichloromethane (DIC) as solvents.

Fatty acids[1]	Compressed propane					HEX	DIC
	373 K 4 MPa	373 K 12 MPa	333 K 4 MPa	333 K 12 MPa	353 K 8 MPa		
8:0	0.28 ± 0.02^{a}	0.25 ± 0.08^{a}	0.22 ± 0.07^{a}	0.30 ± 0.01^{a}	0.30 ± 0.02^{a}	–	–
10:0	0.10 ± 0.05^{a}	0.10 ± 0.02^{a}	0.07 ± 0.0^{a}	0.08 ± 0.01^{a}	0.05 ± 0.0^{a}	0.10 ± 0.01^{a}	0.05^{a}
12:0	0.13 ± 0.00^{a}	0.12 ± 0.02^{a}	0.08 ± 0.02^{a}	0.09 ± 0.00^{a}	0.09 ± 0.00^{a}	0.26 ± 0.03^{a}	0.15^{a}
14:0	0.21 ± 0.02^{a}	0.26 ± 0.06^{a}	0.24 ± 0.04^{a}	0.27 ± 0.0^{a}	0.31 ± 0.07^{a}	0.02 ± 0.00^{b}	0.24^{a}
16:0	27.43 ± 0.33^{ac}	26.72 ± 0.08^{a}	28.12 ± 0.68^{a}	27.87 ± 0.35^{ac}	29.16 ± 1.45^{a}	20.93 ± 0.15^{b}	29.75^{c}
18:0	1.89 ± 0.09^{a}	2.28 ± 0.26^{a}	1.49 ± 0.25^{a}	1.31 ± 0.09^{a}	2.56 ± 0.65^{a}	2.08 ± 0.10^{a}	1.66^{a}
18:1n-9	60.85 ± 0.33^{a}	61.12 ± 0.32^{a}	61.16 ± 0.40^{a}	60.46 ± 0.42^{a}	59.33 ± 1.87^{a}	63.21 ± 0.05^{b}	56.50^{c}
18:2n-6	6.18 ± 0.08^{ac}	6.29 ± 0.16^{ac}	5.63 ± 0.39^{a}	6.60 ± 0.17^{ac}	5.42 ± 0.43^{a}	8.47 ± 0.31^{b}	8.55^{c}
18:3n-3	2.93 ± 0.02^{ab}	2.86 ± 0.05^{a}	3.02 ± 0.15^{a}	3.02 ± 0.15^{a}	2.78 ± 0.13^{b}	1.32 ± 0.07^{c}	3.19^{d}
SFA[2]	30.04	29.73	30.18	29.92	32.47	23.39	31.85
UFA[3]	69.96	70.27	69.81	70.08	67.53	73.00	68.24
MUFA[4]	60.85	61.12	61.16	60.46	59.33	63.21	56.50
PUFA[5]	9.11	9.15	8.65	9.62	8.20	9.79	11.74

Means followed by the same letter (in each row) indicate no significant difference ($p > 0.05$).
[1] Results in g $100\,g^{-1}$ of oil.
[2] Saturated fatty acids.
[3] Unsaturated fatty acids.
[4] Monounsaturated fatty acids.
[5] Polyunsaturated fatty acids.

In this study, the oil yields are higher than those reported by Hiane et al. [9] and Oliveira et al. [5] who used Soxhlet extraction with petroleum ether as the solvent and obtained oil yields of 19.3% and 18.70%, respectively. Recently, Rodrigues et al. [46] and Trentini et al. [47] reported obtaining 49.2% and 44.78% of oil from macauba pulp for ultrasonic assisted extraction and pressurized liquid extraction, respectively, using ethanol as a solvent.

3.2. Oil characterization

3.2.1. Fatty acids

The fatty acids compositions of the oils obtained are shown in Table 2. The macauba pulp oil contained higher concentrations of monounsaturated fatty acids, and the major fatty acids identified were oleic (20.93–29.75%) and palmitic (56.50–63.21%) acids. The polyunsaturated fatty acids identified were linoleic and linolenic acids.

The statistical analysis showed a significant difference between the different solvents used in relation to the fatty acids composition, particularly the amount of oleic and palmitic acids extracted. The extraction of fatty acids may be related to the polarity of the solvents used, and long-chain fatty acids with at least one double bond, such as oleic acid, have lower polarity compared to other fatty acids. This characteristic explains the higher yield in the extraction of this compound when using low polarity solvents [48]. As can be observed in the extraction with dichloromethane, a solvent with higher polarity, less oleic acid is extracted, while with the use of solvents of lower polarity (like propane and *n*-hexane) the yields are greater. In the case of medium-chain fatty acids, such as palmitic acid, the solvents with high polarity demonstrate greater extraction efficiency.

In studies reported by Jesus et al. [22], Pessoa et al. [27] and Silva et al. [4] on the extraction of oils from palm, pequi and *Mucuna aterrima* using propane, the different conditions applied in the extraction did not influence the fatty acids composition of the oils.

The fatty acids composition of the macauba pulp oil obtained in the study reported herein is similar to others reported in the literature, for instance, Lescano et al. [7], Trentini et al. [8], Coimbra and Jorge [36], Navarro-Díaz et al. [38], Rodrigues et al. [46] and Trentini et al. [47]. In these studies, the levels of oleic and palmitic acid varied from 52.6 to 70.28% and from 17.65 to 27.39%, respectively.

3.2.2. Free glycerol compounds

The contents of free fatty acids (FFA) and phytosterols (PHY) in the MPOs obtained are shown in Table 3. The FFA content of the oils ranged from 0.493 to 1.66%, and the lowest levels were observed in the extractions with *n*-hexane and dichloromethane.

Other authors have reported FFA contents of 0.83–9.43% for macauba pulp oil [5,9,36,49]. The differences observed may be associated with the region in which the fruits were harvested, climatic conditions, the time and temperature of the pulp drying before the oil extraction, and even the extraction method used, which can accelerate the formation of these compounds [3,36].

As can be seen in Table 3, the phytosterols present in the macauba pulp oil were campesterol, estigmasterol and β-sitosterol. The total content of phytosterols was influenced by the experimental conditions, where the application of lower pressure and temperature favors the extraction of these compounds ($p < 0.05$). Thus, 188.17 mg of PHY per 100 g of oil were obtained at 333 K and 4 MPa.

An increase in temperature causes a decrease in the efficiency of phytosterol extraction, which can be attributed to an increase in the vapor pressure of the active compounds in the oil, negatively influencing the extraction of phytosterols [50].

All of the extractions performed with propane led to a higher content of total phytosterols ($p < 0.05$) when compared with the Soxhlet extraction. The average amounts of each phytosterol in the macauba pulp oil obtained in this study were 18.5, 7.9 and 73.6% for campesterol, stigmasterol and β-sitosterol, respectively, the best conditions providing 188.17 mg of PHY per 100 g of MPO. This content is comparable with recent reports for other vegetable oils obtained from the extraction with compressed propane, such as oils from crambe [25], perilla [28], flaxseed [51] and sacha inchi [20], with values of 201.05, 101.92, 146.98 and 177.68 mg of PHY per 100 g of oil, respectively, being reported. Specifically for macauba pulp oil, Trentini et al. [8] reported 104.15 mg of PHY per 100 g of oil, applying extraction at low pressure using isopropanol as the solvent.

3.2.3. Tocopherols

The results for the quantification of the tocopherols (α, γ and δ) present in the macauba pulp oil obtained applying different extraction methods are presented in Table 4. The major tocopherol obtained in all extractions was γ-tocopherol, which is consistent with studies by Costa et al. [52], Przygoda and Wejnerowska [53]

Table 3
Free fatty acids (FFA) and phytosterol (PHY) in MPOs obtained with compressed propane, *n*-hexane (HEX) and dichloromethane (DIC) as solvents.

	FFA content (%)	Phytosterol (mg of PHY per 100 g of oil)			
		Campesterol	Stigmasterol	β-Sitosterol	Total
Compressed propane					
373 K; 4 MPa	1.66 ± 0.03^{aA}	33.87 ± 3.70	13.77 ± 2.03	132.97 ± 0.58	180.61 ± 2.25^{a}
373 K; 12 MPa	1.40 ± 0.05^{b}	25.88 ± 1.43	13.13 ± 0.19	121.59 ± 1.91	160.60 ± 0.66^{b}
333 K; 4 MPa	1.30 ± 0.02^{b}	26.75 ± 0.84	11.76 ± 1.60	149.65 ± 1.59	188.17 ± 0.83^{cA}
333 K; 12 MPa	1.34 ± 0.01^{b}	30.67 ± 2.13	15.26 ± 0.81	125.94 ± 0.73	171.87 ± 2.05^{d}
353 K; 8 MPa	1.34 ± 0.10^{b}	31.31 ± 1.15	12.05 ± 0.17	130.45 ± 1.40	173.81 ± 0.43^{d}
Conventional (Soxhlet) extraction					
HEX	0.493 ± 0.01^{B}	2.84 ± 0.18	3.24 ± 0.66	17.31 ± 2.78	23.39 ± 1.94^{B}
DIC	0.524 ± 0.07^{B}	6.71 ± 1.07	4.81 ± 1.72	35.34 ± 1.84	46.86 ± 0.95^{C}

Means followed by the same lower case letters (comparison of runs with compressed propane) and uppercase letters (comparison of conventional and compressed extractions) indicate no significant difference ($p > 0.05$).

Table 4
Tocopherols (α, γ and δ) content in MPOs obtained with compressed propane, *n*-hexane (HEX) and dichloromethane (DIC) as solvents.

	Tocopherol (mg per 100 g oil)			
	α	γ	δ	Total
Compressed propane				
373 K; 4 MPa	1.92 ± 0.02	14.57 ± 0.30	2.17 ± 0.02	18.66 ± 0.31^{aA}
373 K; 12 MPa	2.02 ± 0.01	10.42 ± 0.10	1.84 ± 0.01	14.28 ± 0.10^{b}
333 K; 4 MPa	1.71 ± 0.02	9.97 ± 0.02	2.47 ± 0.01	14.15 ± 0.02^{b}
333 K; 12 MPa	1.84 ± 0.01	10.06 ± 0.16	2.05 ± 0.01	13.95 ± 0.16^{b}
353 K; 8 MPa	1.85 ± 0.05	10.72 ± 0.13	1.74 ± 0.03	14.31 ± 0.21^{b}
Conventional extraction (Soxhlet)				
HEX	2.36 ± 0.01	10.13 ± 0.19	0.67 ± 0.03	13.16 ± 0.18^{B}
DIC	1.73 ± 0.03	10.24 ± 0.21	0.72 ± 0.02	12.69 ± 0.21^{B}

Means followed by the same lower case letters (comparison of runs with compressed propane) and uppercase letters (comparison of conventional and compressed extractions) indicate no significant difference ($p > 0.05$).

Table 5
β-Carotene and total flavonoid contents in MPOs obtained with compressed propane, *n*-hexane (HEX) and dichloromethane (DIC) as solvents.

	β-Carotene (mg per 100 g of oil)	Flavonoid (mg per 100 g of oil)
Compressed propane		
373 K; 4 MPa	136.66 ± 1.65^{a}	11.03 ± 0.07^{a}
373 K; 12 MPa	185.03 ± 1.55^{b}	12.34 ± 0.10^{b}
333 K; 4 MPa	303.70 ± 1.89^{c}	12.21 ± 0.04^{b}
333 K; 12 MPa	356.05 ± 1.67^{dA}	13.12 ± 0.10^{cA}
353 K; 8 MPa	347.21 ± 4.65^{d}	11.06 ± 0.06^{a}
Conventional extraction (Soxhlet)		
HEX	213.33 ± 1.97^{B}	12.32 ± 0.07^{B}
DIC	282.41 ± 1.57^{C}	11.36 ± 0.04^{C}

Means followed by the same lower case letters (comparison of runs with compressed propane) and uppercase letters (comparison of conventional and compressed extractions) indicate no significant difference ($p > 0.05$).

and Santos et al. [25] for oils extracted from buriti pulp, quinoa and crambe seeds, respectively.

In the extractions carried out with propane under the conditions of higher temperature and lower pressure (333 K and 4 MPa), associated with a lower propane density, provided a higher concentration of total tocopherols ($p < 0.05$). For the other conditions applied (runs 2–5 of Table 1), alterations in the temperature and pressure did not influence the solvent density and the extraction of these compounds ($p > 0.05$). Silva et al. [28] evaluated the tocopherols content in perilla oil extracted using compressed propane and reported similar values under the conditions investigated, which were associated with a moderate variation in the solvent density, as observed in this study.

In comparison with the concentration of tocopherols obtained with propane and in extractions using *n*-hexane and dichloromethane, oils obtained by Soxhlet extraction provided lower tocopherol contents, as also observed in studies by Zanqui et al. [51], Silva et al. [28] and Silva et al. [54] on oil extraction from flaxseed, perilla and pinhão endosperm, respectively. According to Nimet et al. [55] the lower concentration of tocopherols in oils obtained by Soxhlet extraction may be related to the long extraction time allowing the degradation of these compounds.

3.2.4. β-Carotene and flavonoids

The β-carotene and flavonoids content in the extracts obtained by Soxhlet extraction and compressed-solvent extraction are shown in Table 5. Higher concentrations of β-carotene and flavonoids were obtained from the extraction with propane, which again can be attributed to the short extraction time, the long Soxhlet extraction time allowing the degradation of these compounds [56,57]. Furthermore, it was shown that propane is an excellent solvent for the extraction of β-carotene [22,31].

With the use of propane as a solvent, the extraction of β-carotene was favored by increasing the pressure and reducing the extraction temperature ($p < 0.05$). Thus, the oil obtained at a higher solvent density, 333 K and 12 MPa, contained 356.05 mg of β-carotene per 100 g of oil. Trentini et al. [47] reported for pressurized liquid extraction with ethanol as solvent, obtaining 232.44 mg of β-carotene per 100 g of oil.

As reported by Lu et al. [58], increasing the temperature at constant pressure causes a reduction in the solvent density, reducing its solvating power. Mustapa et al. [59] noted that the maximum solubility of β-carotene can be achieved using conditions where the solvent has a higher density, allowing the solvent to penetrate the vegetable matrix and dissolve this compound, which is located deep within the solid particles. The increased solubility of β-carotene in propane with the use of higher pressure is also reported elsewhere in the literature [34,35].

In relation to the flavonoid contents, these varied from 11.03 to 13.12 mg per 100 g of oil, and a higher content of these compounds was favored by the application of low temperature and high pressure (333 K and 12 MPa). The oil extracted with propane contained higher contents of flavonoids, followed by the oil samples obtained using *n*-hexane and dichloromethane. Flavonoids vary in polarity and less polar solvents are efficient in the extraction of flavonoid aglycones [56].

3.2.5. Thermal stability

The thermal stability was evaluated using the oil samples extracted by the Soxhlet method, using *n*-hexane and dichloromethane, and the oil sample which contained the highest amount of total tocopherols obtained with compressed propane (333 K, 12 MPa). Table 6 shows the oxidation induction times (t_0) as well as the adjusted equations for the relationship between T and

Table 6
Oxidation induction times obtained by DSC analysis for MPOs extracted with propane, *n*-hexane (HEX) and dichloromethane (DIC).

Solvent	t_0 (min)				Regression equation	R^2
	383 K	393 K	403 K	413 K		
Propane	120.68	52.55	24.21	9.45	$T = 167.08 - 27.32 * \log_{10} t_0$	0.998
HEX	42.70	19.80	8.84	–	$T = 157.75 - 29.24 * \log_{10} t_0$	0.999
DIC	65.70	28.24	9.40	–	$T = 153.29 - 23.55 * \log_{10} t_0$	0.991

t_0, proposed by Tan et al. [60], and their determination coefficients (R^2), obtained for the samples analyzed. The oxidation induction time (t_0) was obtained from the oxidation curve considering the intersection of the baseline and the tangent line at the edge of the isotherm (Supplementary Material).

The MPO extracted with propane showed a longer oxidation induction time (120.68 min at 383 K) compared with the Soxhlet extraction. This result is a characteristic of oils obtained by extraction using compressed propane, as evidenced in studies by Santos et al. [25], Zanqui et al. [51] and Zanqui et al. [18]. These authors reported oxidation induction times, at 333 K, of 420.2, 49.4 and 89.5 for crambe, flaxseed and chia oils, respectively.

4. Conclusions

Macauba pulp oil (MPO) was obtained using compressed-solvent and conventional (Soxhlet) extraction techniques. With the use of compressed propane the best results were obtained by applying high pressure and low temperature (12 MPa and 333 K), with a yield of 23.08 wt% being obtained under these conditions. The extraction of MPO with subcritical propane provides satisfactory extraction yields within 30 min, which represents ~86% of the yield obtained applying conventional extraction. Palmitic and oleic acids were predominant in the fatty acids composition of the oils obtained applying the different methods and conditions. The free fatty acids content was low (~2%), and β-sitosterol and γ-tocopherol were the predominant phytosterol and tocopherol in the MPOs, respectively. The compressed-solvent extraction favored the extraction of β-carotene and flavonoids. The oil extracted with subcritical propane had the longest oxidation induction time.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.supflu.2017.02.018.

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