COMPARATIVE STUDY OF TUCUMÃ OIL QUALITY FROM TWO DIFFERENT SPECIES EXTRACTED BY SUPERCRITICAL CARBON DIOXIDE

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Abstract. The vast Amazon territory presents territorial peculiarities, based on these differences a great diversity of plant species, sometimes of the same botanical family, may have different physical and chemical compositions. Among this variety can highlight the species of tucumã-do-Amazonas (Astrocaryum aculeatum Meyer) and tucumã do Pará (Astrocaryum vulgare, Mart.). The similarities, particularities and potentialities of these oleaginous fruits is the focus of this research which aim is comparative analysis the quality of oils extracted from two species of tucumã, from the Amazonas and Pará States, obtained with supercritical carbon dioxide using different extraction parameters. The results revealed biometric particularities of each species highlighting the tucumã do Amazonas fruit showing highest yield, quality and fatty acids profile with large amount of unsaturations. However, in terms of adding value both showed potential applications in many industrial segments.

Keywords: Tucumã, Oil, Supercritical.

1. Introduction

The Amazon region provide many sources of oleaginous fruits among these stand out two species, the Tucumã-do-Amazonas (*Astrocaryum aculeatum Meyer*) and Tucumã-do-Pará (*Astrocaryum vulgare Mart.*) [6], [19].

These oleaginous fruit pulps have averaging 32-58% lipids, it is a key feature for high energy potential. In its lipid composition there are monounsaturated and polyunsaturated fatty acids, especially the oleic, linoleic and linolenic acids, and the presence of saturated fatty acids such as palmitic acid and stearic and addition of an appreciable amount of carotenoids. These data demonstrate its broad potential applications in many industrial sectors [4], [7].

Technological advances to improve and add value to these compounds in order to implementation and improvement of the industries, should take into account the lipid extraction modes. So many different extraction methods are used for the production of vegetable oils. Among which stand out: the conventional methods, which can use hydraulic and mechanical extraction; the solid-liquid extraction by solvent; the mixed method, joining the previous methods and the unconventional methods, applying gas as the supercritical fluid. Supercritical method has advantages over other methods due its high yield, reduced extraction time, maintaining the quality of extracted material, besides the application in various thermosensitive materials [3], [5], [9], [11], [17] [18].

In the food industry, the most widely used supercritical solvent is carbon dioxide (CO2), wich promotes high efficiency in extraction, atoxicity, low chemical residues and high quality of extracted material [13], [14].

Given the above the objective of this research was to analyze comparatively the oils quality from two varieties of tucumã, from the states of Amazonas (*Astrocaryum aculeatum*) and Pará (*Astrocaryum vulgare*), extracted by supercritical carbon dioxide.

2. Materials and method

2.1 Raw material

Was purchased 10 kg of Tucumã fruit from Augusto Correa, municipality located in Para State, and Rio Preto da Eva, municipality located in Amazonas State, referring to the 2009 harvest. The material was transported in primary packaging (low-density polyethylene) and secondary (cardboard boxes) to the Operations of Separations Laboratory (LAOS) Institute of Technology, Federal University of Pará. The fruits were selected, washed and stored under freezing (about -7 °C) until the experimental procedures start.

2.2 Tucumã oil extraction by supercritical CO_2

The oil extraction experiments by supercritical fluid was performed using the Supercritical Extraction Unit of the Operations of Separations Laboratory at the Federal University of Pará (LAOS / UFPA), charged with carbon dioxide P-4574 (CO2), with purity of 99.9% (White Martins Industry, located in Belém, PA) from a cylindrical reservoir with 30 kg capacity and 70 bar pressure. The samples used in these experiments have an average particle size of 1.20 mm. The fluid is high to the required pressure and then circulated by a compressor membrane (Hoffer, Germany) through a fixed layer of solid material with 6.0 cm diameter and 20 cm height, wrapped in fabric reservoir within the extractor vessel (dimensions of 6.0 cm diameter and 36.0 cm height).

The oil was collected every 10 minutes extraction. The extraction yield was calculated correlating to the total oil mass obtained and the mass of sample. The oils were stored in nitrogen gas atmosphere at -4 °C for further analysis.

2.3 Physicochemical characterization of the oils

The oils obtained from the extractions were characterized by the following analyzes: Acid Value ([1] AOCS Cd 3d-63), Peroxide Index ([1] AOCS Cd 8-53), Saponification Index ([1] AOCS Cd 3 -25) Viscosity (Schott Gerate, Type No. 23 520) ASTM 446-40 ° C, capillary # 200 (ISO 3105, ASTM 446), Melting Point ([1] AOCS Cc 1-25 and Moisture Content ([1] AOCS Ca 2d-25).

The determination of total carotenoids was realized taking about 20 mg of oil and dissolved in 50 ml of hexane/acetone 3:7. The absorbance measurement was realized using a UV/visible spectrophotometer set at 450 nm. The value of carotenes concentration was calculated using Equation 1.

$$\text{Carotenes (ppm)}= \frac{V\ (\text{mL}) x\ A}{2592\ x\ m_0}\ \text{x}\ 10^4 \tag{1}$$

Where:

V is the Total Volume (mL);
m_0 is the Mass sample (g) and
A is the Absorbance.

Fatty acid profile. The determination and quantification of fatty acids present in the oils were obtained by gas chromatography (GC) according to the methodology of the Commission des Communautés Européennes (1977). Triacylglycerols were converted to fatty acid methyl esters using the AOCS EC 266 method [1].

The analysis of fatty acid composition by gas chromatography was performed by a chromatograph VARIAN CP 3800 Autoinjector equipped with a flame ionization detector (FID) and a capillary column CP WAX 52 CB with 30 m length, 0.32 mm internal diameter and 0.25 mm film. Helium was used as the mobile phase at a rate of 1.0 mL/min. The programming of T1 temperature was 80 ° C during 2 minutes, R1 10 ° C / min. T2 180 ° C during 1 minute, R2 of 10 ° C / min, T3 250 ° C during 5 minutes. The fatty acids identification was made by comparison with standards methyl ester (Aldrich Chemical Company, USA). The quantification of fatty acids was performed by normalizing the peak area using W.S Star 6.0 software (VARIAN USA).

2.4 Statistical analysis

The results of the extraction processes and physico-chemical analyzes were analyzed statistically using the Statistica V7.0 software [15], analysis of variance (ANOVA) with 5% level of significance and Tukey test ($p \leq 0, 05$).

3. Results and discussion

The results of the extracted oils by supercritical carbon dioxide at 300 bar pressure, during 180 minutes, and the comparative yield between the two species of Tucumã are expressed in Amazon Tucumã (TA) and Pará Tucumã (TP). The total yield evaluated using the solid-liquid extraction process is 33.1% for TA and 29.8% for TP, as seen in Table 1.

Table 1. Yield from extraction by supercritical CO_2 process

Species	Temperature (^oC)	Extracted oil (g)	Yield (%)
TA	60	$30,52 \pm 0,65^a$	92,0
	50	$31,61 \pm 0,33^a$	95,5
	40	$31,89 \pm 0,32^a$	96,3
TP	60	$23,80 \pm 0,64^a$	79,8
	50	$22,25 \pm 1,14^a$	74,6
	40	$21,05 \pm 0,35^b$	70,6

Different letters in the same column, for each species, represent significant differences between the temperatures studied (Tukey test at 5% significance)

It is noted that the supercritical CO_2 extraction process easily extract more oil contained in the TA than oil contained in the TP. This indicates that the TP oil besides being in less amount inside the solid matrix its cells are less accessible to the supercritical solvent, because the skin proportion of the fruit (skin + pulp) is more rigid and proportionally bigger.

The yield analyses show that the TA yield undergoes small changes with temperature increase and the same occurs in the TP extraction, according to the pressures and temperatures parameters applied in these extractions. The highest relevance point related to yield occurs between 40°C for TA extraction and 60 ºC for TP extraction.

3.1 Oil quality

The Table 2 describes the chemical characteristics of the oils extracted by supercritical CO_2 method, respectively represented by Tucumã do Amazonas (TA) and Tucumã do Pará (TP).

The water content remained below 200 ppm in all extractions and about the extractions at different temperatures, the two species showed different behaviors increasing the water content in TA oil and decreasing the water content in TP oil. There are no parameters defined according to the Brazilian law (RDC 270, September 22, 2005. ANVISA [Brazilian FDA]) that approves technical standards for vegetable oils, for establish maximum water content values in vegetable oils [2], but high values may cause its decay by hydrolysis.

Table 2. Chemical characterizations from oils extracted by supercritical CO_2 process

Temperature °C	Water content (ppm)	Acid value (mg $_{KOH}$/g)	Peroxide index (mEq/kg)	Saponification index (mg $_{KOH}$/g)
TA - 40	85 ± 10[a]	19,1 ± 0,2[a]	11,8 ± 0,0[a]	196,2 ± 0,5[a]
TA - 50	136 ± 5[a]	20,3 ± 0,1[a]	11,8 ± 0,0[a]	196,1 ± 0,2[a]
TA - 60	164 ± 8[a]	20,3 ± 0,1[a]	11,8 ± 0,0[a]	196,3 ± 0,1[a]
TP - 40	192±20[b]	6,4 ± 0,1[b]	13,8 ± 0,0[b]	209,5 ± 0,2[b]
TP - 50	158 ± 6[b]	6,5 ± 0,2 [b]	13,8 ± 0,1[b]	209,9 ± 0,2[b]
TP - 60	104 ± 5[b]	6,5 ± 0,1 [b]	13,8 ± 0,1[b]	208,6 ± 0,2[b]

[a]and [b]in the same row: represent significant differences between the species (Tukey test at 5% significance)

The results about acidity value (IA) and peroxide index (IP) represent parameters related to conservation and quality of the oils. It was observed significant differences of acid value results between the TA and TP oils. The high acid value for the TA oil is possibly due its maturation stage. Also observed significant differences results for peroxide index between the TA and TP oils. However, the three temperature values used in the extraction process did not occur significant differences when they are evaluated for each individual species.

The saponification index (SI) is useful for predicting the glycerides type existing in the oil. The results in Table 3 show significant differences between TA and TP oils at 5% of significance level, indicating that in the TP oil there is a predominance of smaller-chain fatty acids. However, when individually analyzed at different temperatures, there is no significant differences between oils. This results show that the temperature variation applied in the oil extraction process does not dramatically alter its saponification index.

The obtained oil was characterized using the kinematic viscosity analysis and melting point analysis the results are shown in Table 3.

Table 3. Physical characterizations from oils extracted by supercritical CO_2 process

Species	Kinematic viscosity (cSt)	Melting point (^{o}C)
TA - 40	41,8 ± 0,1[a]	19,1 ± 0,2[a]
TA - 50	42,0 ± 0,2[a]	20,3 ± 0,1[a]
TA - 60	42,2 ± 0,1[a]	20,3 ± 0,1[a]
TP - 40	44,2 ± 0,1[b]	19,5 ± 0,7[b]
TP - 50	45,8 ± 0,1[b]	20,5 ± 0,7[b]
TP - 60	46,1 ± 0,4[b]	20,5 ± 0,7[b]

[a] and [b] in the same row: represent significant differences between the species (Tukey test at 5% significance)

The viscosity of vegetable oils depends on the chemical composition, as well as the acid-chain length and its unsaturations. In research on sunflower oil became evident that a less unsaturations number in oils with similar size, results in a higher viscosity [8].

The results in Table 4 show the significant differences between the viscosities of TA and TP oils, at 5% significance level, in accordance with the high presence of unsaturated chain in TA oil. However, the variation of the temperature extraction did not significantly alter the viscosity patterns of the oils extracted from the same species, indicating that this variable does not influence the quality of the extracted product.

The results obtained for the melting point analysis of the oils did not show significant differences between the TA and TP oils, despite the high-unsaturated levels in TA oil, this possibly be due to the presence of smaller compounds, because it is a raw oil. Also, do not differ when evaluated separately under extractions with temperature variations.

The evaluation of total carotenoids (ppm) in tucumã oils is in Table 4.

Table 4. Total carotenes in the tucumã oils

Extraction method		TA oil	TP oil
Supercritical CO_2	60 ºC	1021[a]	2077[b]
	50 ºC	1006[a]	2065[b]
	40 ºC	1065[a]	2101[b]

[a] and [b] in the same row: represent significant differences between the species (Tukey test at 5% significance)

The values of the Table 4 shows significant differences in total carotenoids between the oils extracted from the two tucumã species. However, this behavior does not occur when analyzes each tucumã species individually, the results show no significant difference when the extraction occurs at different temperatures.

Table 5 shows the fatty acid profiles of the oils extracted from the pulp of the TA and TP using the supercritical CO2 process at 40, 50 and 60 ° C.

Table 5. Fatty acid profile of the oils Tucumã do Amazonas (TA) and Tucumã do Pará (TP)

Fatty acids	Fatty acids profile (%)					
	40 °C		50 °C		60 °C	
	TA	TP	TA	TP	TA	TP
Palmitic acid (C16: 0)	8,46	23,10	7,89	26,49	8,04	22,60
Stearic acid (C18: 0)	6,72	5,08	6,07	0,85	6,12	5,16
Oleic acid (C18: 1)	72,50	64,14	71,97	71,77	73,81	65,38
Linoleic acid (C18: 2)	12,14	3,90	11,90	0,0	12,03	3,68
Arachidic acid (C20: 0)	0,0	2,18	1,89	0,0	0,0	2,10
Docosanoic acid (C22: 0)	0,10	0,59	ND	ND	ND	ND
Others not identified	0,08	1,01	0,28	0,90	0,0	1,07
TOTAL	≈ 100	≈ 100	≈ 100	≈ 100	≈ 100	≈ 100

ND – Not determinated

In the results, it can be seen that the oils are predominantly unsaturated, especially with oleic acid with ratios greater than 60% for TP oil and above 70% for TA oil. There is a higher incidence of linoleic acid in the TA oil, with averages around 12% regardless the temperature used in the extraction process, demonstrating that the TA oil is nutritionally superior than TP in this aspect.

About the presence of saturated fatty acids, it is possible to evaluate the differences between the profiles obtained. The presence of palmitic acid is higher in TP oil, averaging between 22.6 and 26.5% regardless the temperature applied in the extraction, confirming the low influence of the temperature extraction for on the quality of the obtained product from both species. The stearic acid from both oils, TA and TP, showed similar values, averaging around 5-6%.

4. Conclusions

- The biometric analysis shows that the pulp yield of the Tucumã do Amazonas is higher than the Tucumã do Pará;
- The oil extracted from TA by supercritical CO2 showed better yield;
- The results of the physicochemical analyzes from both oils, including the carotenes content, showed significant differences between the species;
- The fatty acid profiles showed changes in its relevant aspects of saturation and unsaturation. These results demonstrate the effect of temperature involved in the oils production.

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