QUALITY PARAMETERS, NUTRITIONAL PROFILE AND THERMAL STABILITY OF SAPUCAIA (*Lecythis pisonis camb.*) OIL OBTAINED BY THE SOLID-LIQUID AND THE SUPERCRITICAL CO2 EXTRACTION PROCESSES

Orquídea Santos[(1)]*, Emmersom Costa[(2)], Raul Carvalho Jr. [(2)], Charles Negrão[(2)] and Nádia Corrêa[(2)]

(1) Centro de Ciências Naturais e Tecnologia
Universidade do Estado do Pará
P.O. 66095-100, Pará, Brasil

(2) Instituto de Tecnologia
Universidade Federal do Pará
P.O. 66075-900, Pará, Brasil

E-mail: orquideavs@usp.br

Abstract. Brazil has a large diversity of plant species, and many in the Amazon region, mainly oleaginous fruits with great potential in the food industry. The sapucaia (*Lecythis pisonis Camb.*) is an almond with considerable lipid content and the focus of this research is determine the quality parameters, nutritional profile and thermal behavior of the sapucaia oil obtained by liquids solvents and supercritical CO2 extraction. The result showed an average yield of 54.50% and 51% respectively. The indexes related to the quality parameters of the oils such as acid value and peroxide index showed better results using supercritical CO2 extraction. These parameters are in accordance with Brazilian law for conservation standards. The values expressed by the fatty acid profile of this oil indicate unsaturated fatty acids predominance at levels above 70%, highlighting omega 3 and 6. The Thermogravimetric analysis demonstrated that the material is stable up to 250 ° C, exothermic peaks characteristic of mass loss, related to lipid oxidation. Based on the results found can be inferred that sapucaia presents great nutritional potential and thermal stability, with qualities applicable in various industrial segments.

Keywords: Sapucaia, Oil, Supercritical, Thermogravimetric.

1. Introduction

The almond of the sapucaia (*Lecythis pisonis Camb.*) is a native oleaginous from the amazon region it has a high calorific value around 700 Kcal, which indicates to be a great source of energy, and it can also be used as raw material for food supplements. Lipids and Proteins are the most prominent nutrients, the lipid portion is very important because of its functionality, with average percentages of relevant fatty acids as omega 3 (0.3%), 6 (48.6%) and 9 (33, 0%) being the first two, from a nutritional point of view, essential for the human organism. With respect to protein content, the almond presents such large quantities with an average of 18.5% [4], [19], [11], [18].

The sapucaia is an oleaginous feedstock with potential application in various industries, being harnessed since its almond until its residue. This oilseed can be used in the food industry for *in natura* consumption and obtainment of vegetable oil (also used by the pharmaceutical industry, dermocosmetic and oleochemical) [10], [15], [14].

One of the ways to increase the implementation and use the oleaginous from the Amazon, such as sapucaia, is using the method of lipid extraction followed by the characterization of oxidative stability, nutritional and functional quality of its oil, and evaluating the quality of its potential applications in various industries [13], [14].

Given the above the objective of this research is to evaluate the quality, nutritional profile and thermal stability of the oils from the almonds of the sapucaia obtained by solid-liquid and supercritical CO2 extractions processes.

2. Materials and method

2.1 Raw material

Sapucaia almonds were acquired, in maturation stage, from the Ver-o-Peso market, located in Belém/Pará (harvest 2012), and transported in low-density polyethylene bags, and then stored under refrigeration.

2.2 Methods

Extração sólido-líquido e por CO2 em estado supercrítico. The solid-liquid extraction was performed in soxhlet apparatus in accordance with the AOAC 948.22 [2] method using petroleum ether as solvent extractor.

The Sapucaia oil extraction by CO2 in supercritical state was performed using the Apllied Separations (Spe-ed SFE, model 7071, Allentown, PA, EUA) equipment. The equipment is located at the Federal University of Pará (UFPA).

The definition of the parameters of temperature and pressure (60 °C and 300 bar) used were based on Santos et al. [14] researches with the same botanical family fruits (Lecythidaceae). Exhaustive extractions were performed to obtain material for successive subsequent analyzes.

The yields from the different extracting processes were evaluated and compared, in the study, using the calculation of the mass of oil extracted divided by total mass of the sample according to the Equation 1.

$$Yield(\%) = \frac{M_{Oil}}{M_{Sample}} \times 100 \qquad (1)$$

Where:
M_{oil} means “Oil mass” and
M_{sample} means “Total mass of the sample”.

Physicochemical characterization of the extracted oils. The oils obtained from the extractions were analyzed by Acid Value AOCS Cd 3d-63), peroxide index (AOCS Cd 8-53), saponification index (AOCS Cd 3-25 and refractive index (AOCS Cc 7-25).

Characterization of the fatty acid profile. The determination of fatty acid profile and preparation of methyl esters of fatty acids followed the methodological recommendations of the international organization for standardization ISO 5509 [6], [8]. The analysis of fatty acid profiles were performed by gas chromatography (GC), Varian brand, coupled with a microcomputer software Galaxie Chomatography. The chromatographic conditions were as follows: fused silica capillary column SP-2560 (SUPELCO USA) with 100 m length and 0.25 m internal diameter containing 0.2 µm polyethylene glycol in its interior.

The qualitative composition were determined by comparison of retention times of the peaks with fatty acid standards. The quantitative composition was performed by normalizing the area being expressed as mass percentage according to the AOCS official method Ce 1-62 [1].

Differential thermal analysis (DTA) / Thermogravimetric analysis (TG-DTG). Were performed on thermobalance Shimadzu - DTG-60 H on the following parameters: air and nitrogen flow: 60 mL / minute, heating ramp: 10 °C / min, in the temperature range 20-600 °C, alumina crucible and 5mg ±0.5 mass.

3. Results and discussion

The oil yield from sapucaia extraction presented averaging moisture around 5%. The average yield from the 2 extraction processes were 54.50% for solvents extraction and 51% for supercritical CO2 extraction.

3.1 Physicochemical characterization

The physicochemical properties of the obtained oils is in Table 1.

Table 1. Physicochemical characterization of sapucaia oil

Analyses	Solid-liquid extraction	Supercritical CO2 extraction
Acid value (mgKOH/g)	1,25 ± 0,85	0,95 ± 0,52
Peroxide index (mEq.kg^{-1})	4,55 ± 0,53	3,97 ± 0,76
Saponification index (mgKOH/g)	186,8 ± 2,41	187,3 ± 2,15
Refractive index (25 °C)	1,45 ± 0,63	1,46 ± 0,85

The results obtained by physical and chemical analysis of oils related to conservation and quality of oil, using parameters such as acid value and peroxide index, indicates that the sapucaia oil obtained via CO2 presented better preservation conditions an average of 0.95 mgKOH / g sample, and the solid-liquid extraction process presented an average of 1.25 mgKOH / g. The peroxide index of the sapucaia oil was 4.55 mEq.kg-1 using solid-liquid extraction and 3.97 mEq.kg-1 using supercritical CO2 extraction. These results can be explained by the presence of some degradation factors, in the way the extraction occurs, such as temperature, light, oxygen and others.

The results are according to the standards set by the Codex Alimentarius [5] that indicates an acid number of 4.0 mg KOH / g for crude oil. The National Health Surveillance Agency (ANVISA) establishing maximum values for unrefined oils of 4.0 mgKOH / g for acid value and 15 mEq.kg-1 for peroxide index [3].

The results for the refractive index observed for sapucaia oil at 25 ° C was 1.45 and 1.46 respectively. This data may show different standards influenced by factors such as the level of free fatty acids, degree of oxidation, heat treatment etc. [7].

The analysis of the fatty acid profiles in different forms of extraction is in Table 2.

Table 2. Fatty acid profile of the sapucaia oil

Chain	Fatty acids	Solid-liquid extraction	Extraction by CO_2
C16:0	Palmitic	13,64±0,10	14,94±0,10
C16:1	Palmitoleic	0,072±0,00	0,052±0,00
C17:0	Heptadecanoic	0,083±0,00	0,095±0,00
C18:0	Stearic	10,93±0,01	11,37±0,01
C18:1	Oleic	59,60±0,00	60,65±0,00
C18:2	Linoleic	14,43±0,01	13,97±0,01
C18:3	Linolenic	0,136±0,00	0,124±0,00
C20:1	Cis-11, eicosenoic	0,125±0,01	0,121±0,01
C22:0	Behenic	0,063±0,00	0,074±0,00
C22:1	Erucic	0,050±0,00	0,053±0,00

The fatty acid profile of the sapucaia oil present variations according to the extraction method used. Analyzing the data is possible to verify the majority presence of the oleic acid approximately of 60% average. Other fatty acids also show some importance as linoleic acid, palmitic and stearic.

The sapucaia oil excels due to high amounts of unsaturated fatty acids such as oleic acid (ω-9) and linoleic acid (ω-6). The oleic acid content, in both forms analyzed, shows higher values than found in sunflower oil, 21.6% [9], Brazil nut with 31.24% [14] and closer to the pecan oil value, 62.5% [11].

The sapucaia almonds showed reasonable amount of linolenic acid, which considered essential, being higher than the values found in researches of [14], about Brazil nut oil, with an average of 0.058% of linolenic acid. These oils shown a high functional relevance for the treatment and prevention of cardiovascular pathologies.

Another peculiar feature evaluated was the thermal behavior of sapucaia oil (SP), which supercritical CO2 extraction represented for "SP CO2" and for Soxhlet apparatus extraction using petroleum ether as solvent is "SP EP Soxhlet". Figures 1, 2 and 3 shows the oil behavior during to progressive increase in temperatures.

The figure 1 shows the behavior of the sapucaia oil from different extraction forms, and a clear continuous mass decay of the oils, followed the same pattern overlapping at temperatures around 250 ° C.

The continuous elevation of temperature shows subtle differences in TG, which best seen in Figure 2, the graphic expression of its first derivative (DTG). The decay mass differentiates between oils is more explicitly at ranges from 350 to 450 °C. Possible solvent residues (EP) present in the oil can explain this fact.

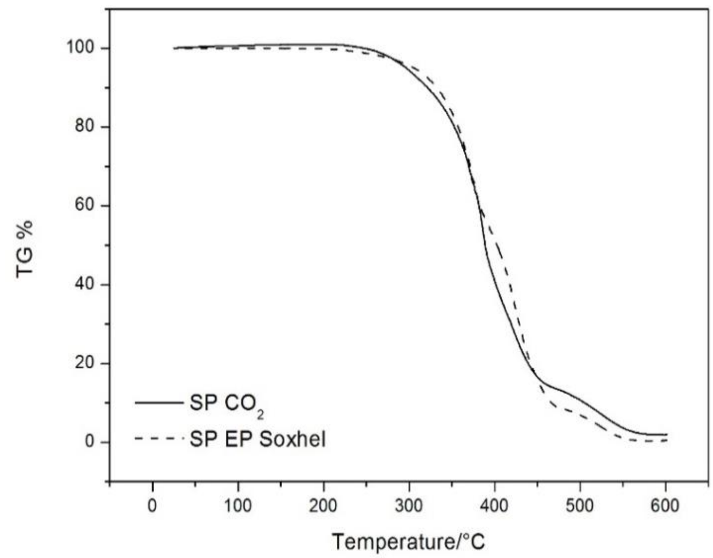

Figure 1. Thermogravimetric analysis

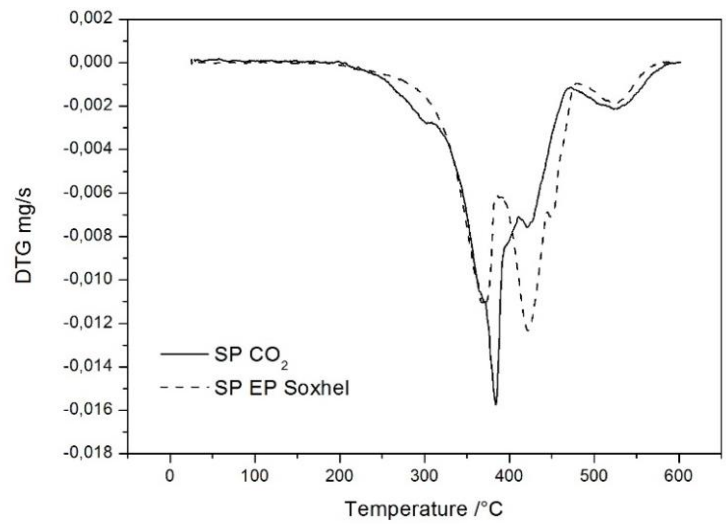

Figure 2. Derivative thermogravimetric analysis

The presence of double bonds in the oil facilitates the oxygen reaction, allowing therefore its rupture and degradation, producing compounds as peroxides, hydroperoxide, peroxide cycle, among others, responsible for the oxidation and rancidity, these events promotes the oil deterioration. The DTA analyse shows that the gradual temperature increase promotes these events releasing energy, which are graphically showed as intense exothermic peaks, as seen in the Figure 3 [14].

The graphic profiles of the DTA curves in oils, related with the extraction processes, showed that the behavior keeps predominantly exothermic with intense peaks at temperature from 350 to 400 °C. This is a common standard for sapucaia oils regardless of its extraction processes showing that the oil is stable at temperatures below 250 ° C. This temperature range is the thermal stability of the sapucaia oil.

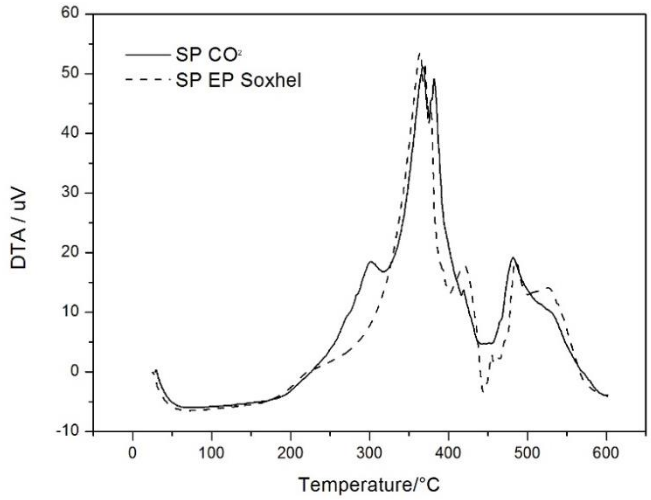

Figure 3. Differential thermal analysis

4. Conclusion

The oil extraction from sapucaia showed an average yield of 52.75%.

The physico-chemical analyses shown parameters of quality and conservation, expressed by its acidity and peroxide, in accordance to the Brazilian law.

The fatty acid profile shows predominantly unsaturated, with emphasis on the content of oleic, linoleic and linolenic.

The thermal analysis showed that the sapucaia oil have a good oxidative stability.

The DTA patterns presents characteristic exothermic peaks of reactions of the thermal and oxidative degradation. However, in temperature levels above the industry standard.

References

[1] American Oil Chemists' Society (AOCS). Official methods and recommended practices of the american oil chemists' society, Champaign, IL., 1997.

[2] American Oil Chemists' Society (AOCS). Official methods and recommended practices of the american oil chemists' society, Champaign, IL., 1998.

[3] Brasil. Resolução RDC/ANVISA/MS nº 270, de 22 setembro de 2005. Regulamento técnico para óleos vegetais, gorduras vegetais e creme vegetal. Diário Oficial da República Federativa do Brasil. Brasília, DF, 23 set. 2005. Seção 1.

[4] Denadai, S.M.S., Hiane, P.A., Marangoni, S., Baldasso, P.A., Miguel, A.M.R., De, O., Macedo, M.L.R. In vitro digestibility of globulins from sapucaia (Lecythis pisonis Camb.) nuts by mammalian digestive proteinases. Ciência e Tecnologia de Alimentos, v. 27, p. 535–543, 2007.

[5] Codex Alimentarius. Codex Standard for Named Vegetable Oils. CODEX STAN 210 (Amended 2003). Codex Alimentarius, Roma: FAO/WHO, 2003.

[6] International Organization for Standardization (ISO 5509). Animal and vegetable fats and oils – Preparation of methyl esters of fatty acids. International Organization for Standardization – ISO, p. 1-6, 1978.

[7] Instituto Adolfo Lutz. Normas Analíticas do Instituto Adolfo Lutz. v. 1: Métodos químicos e físicos para análise de alimentos, 3. ed. São Paulo: IMESP,1985.

[8] Milinsk, M.C.; Matsushita, M.; Visentainer, J. V.; OLIVEIRA, C. C.; SOUZA, N. E. Comparative analysis of esterification methods in the quantitative determination of vegetable oil fatty acid methyl esters (FAME). Journal Brazil Chemistry Society, v.19, n. 8, p.1475-1483, 2008.

[9] Nimet, G. Avaliação dos Solventes Dióxido de Carbono Supercrítico e Propano Subcrítico na Extração do Óleo de Girassol. Dissertação, 119.f (Universidade Estadual do Oeste do Paraná - Centro de Engenharias e Ciências Exatas Programa de Pós-graduação "Stricto Sensu" em Engenharia Química). Toledo – PR, 2009.

[10] Naozuka, J; Vieira, C.E; Nascimento, A.N; Oliveira, P.V. Elemental analysis of nuts and seeds by axially viewed ICP OES. Food Chemistry, v.124, p.1667–1672, 2011.

[11] Oliveira, J.P.C. Estudo químico e farmacológico de Lecythis pisonis Camb. (Lecythidaceae). Teresina, 120 p. Dissertação de Mestrado, Programa de Pós-graduação em Química, Universidade Federal do Piauí. 2010.

[12] Oro, T. Composição nutricional, compostos bioativos e vida de prateleira de noz e óleo prensado a frio de noz-pecã [carya illinoinensis (wangenh.) c. koch] Dissertação, f.105 (Universidade Federal de Santa Catarina, Pós-Graduação em Ciência de Alimentos, Departamento de Ciência e Tecnologia de Alimentos do Centro de Ciências Agrárias) Florianopólis, 2007.

[13] Santos, O. V. et al. Processing of Brazil-nut flour: characterization, thermal and morphological analysis. Ciência e Tecnologia de Alimentos, Campinas, v. 30, supl. 1, p. 264-269, maio. 2010.

[14] Santos, O.V.; Corrêa, N.C.F.; Soares, F.A.S.M.; Gioielli, L.A.; Costa, C.E.F.; Lannes, S.C.S. Chemical evaluation and thermal behavior of Brazil nut obtained by different. Food Research International v.47, p.253-258, 2012.

[15] Souza, V. A. B.; Carvalho, M. G.; Santos, K. S.; Ferreira, C. S. Características físicas de frutos e amêndoas e características químico-nutricionais de amêndoas de acesso de sapucaia. Revista Brasileira Fruticultura, Jaboticabal - SP, v. 30, n. 4, p.946-952, Dezembro 2008.