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Study of the Physicochemical and Mechanical Properties of Oil and Macadamia Walnut Shell

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***Abstract**. The present work, advances in the characterization of the macadamia nut are shown. The study started from the fact that the diffusion in the cultivation and processing of macadamia nut inside the country is not fully developed; On the other hand, its exploitation can be technified through a sustainable use and of low environmental impact. The objective of this research is to propose alternatives of integral use of this fruit. The methodology used included physicochemical and instrumental analysis (infrared spectroscopy). In the case of oil, the peroxide, saponification and acidity indices were obtained. In relation to the shell of the walnut, the infrared spectra of both the ground and dry material were obtained, as well as of a composite material in which the walnut constitutes the reinforcement. The results suggested that macadamia nut can be fully exploited within the scope of green technologies.*

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I. Introduction

Macadamia nut comes from the *proteaceae* family, which is native to Australia. Only two species are widely distributed in the world *M. tetraphylla* and *M. integrifolia,* both species are characterized by having excellent properties for human consumption, highlighting their flavor and high nutritive value [1].

The seed of the walnut is covered by a thick shell. It is one of the exotic crops with better growth prospects in Mexico. Since 1968 its cultivation was officially introduced in the country as an alternative due to the crisis generated by the dropped in coffee prices and the spread of pests in crops. The main nut producing states within Mexico are: Puebla, Veracruz, Chiapas and Michoacán [2].

1.1. Macadamia nut and the dried fruit

The dried fruit, including Macadamia, are natural foods that offer high nutritional value. In previous decades, there was a belief that regular consumption of nuts contributed significantly to increase body weight, however, such prejudice was poorly founded, as it has been shown that such increases are not as dramatic as was assumed, in addition to that, the inclusion of nuts in controlled diets has been shown to promote weight loss.

From a nutritional point of view, the nuts have a combination of nutrients that make them a very complete food, and they have a great energetic contribution, as they contain diverse nutrients, vitamins, minerals and bioactive substances.

Recently, it has been found that nuts have additional positive health effects. The high content of monounsaturated fatty acids has a cardioprotective effect. They have a high antioxidant power, which in the case of nuts, these components are mainly lodged in the edible layer. Nuts, after whole grains, are the foods with the highest fiber content, which the main effect is to reduce cardiovascular risks. Folic acid is also part of its composition, its presence in the body helps prevent the development of atherosclerosis. Phytosterols together with fats or oils are able to decrease the build-up of lipids in the arterial walls.

Finally, due to their composition, this type of food can intervene in the prevention of cancer; however, there is currently insufficient evidence [3]. The oil extracted from the fruit of macadamia is the only vegetable oil that contains a large amount of palmitoleic acid, a monounsaturated fatty acid that is responsible for the metabolism of lipids. Because of its high content of monounsaturated fatty acids, walnut oil is used in the cosmetic industry for the manufacture of emollient creams and soaps, as it is a vegetable oil that is easily absorbed by the skin. It has a high cost but fortunately, this oil is stable, so it has a longer shelf life compared to other oils.

According to studies conducted in Japan, the fatty acids contained in the oil can help lower blood cholesterol levels and reduce the incidence of heart disease [4]. With regard to cancer, one of the most feared diseases and the leading causes of death in the world; the possible pathophysiological relationship between this disease and the alterations found in lipid metabolism and lipid peroxidation has been described; so, antioxidants also play a predominant role in preventing different types of cancer [5]. Although, there is no history of such studies with macadamia oil.

1.2. Macadamia nuts and composite materials

Composite materials have always been present in human activity: wood, concrete, woven straw and bitumen, bricks reinforced with straw and horse hair, etc. The fibers are responsible for the mechanical properties of the material, they serve to resist traction, the matrix is responsible for the physical and chemical properties to resist deformations, and the materials present (including any aggregate) contribute to the resistance to compression effects [6].

The twentieth century is considered the era of composite materials because great strides have been made in this field. Approximately 180 million kilograms of composite materials on the market, 4% correspond to natural reinforcing fibers such as flax, kenaf, hemp and jute. These fibers are often a substitute for fiberglass. The main thrust for the use of these fibers is that they are recyclable.

Toyota and Mitsubishi since 2003 have experimented with biodegradable plastic matrices such as PLA (Polylactic Acid)and PBS (Polybutylene Succinate)by combining them with kenaf and bamboo fibers. More recently, Ford motor company used wheat straw as a reinforcement for internal parts of its Flex Crossover [7]. In addition, in 2004, Mercedes Benz began using a blend of thermoplastic polypropylene (PP) and abaca yarn in parts of the body of its cars. To produce abacáfiber, about 60% less energy is needed than for the production of fiberglass [8].

The mechanical properties of the composite materials can be modified by some methods such as: selection of the matrix constituent material with better tenacity, improvement of the interface between the components, orientation of the dispersion of the fibers, improvement of the length / diameter ratio of the reinforcing fibers, fiber size optimization and percentage composition of each material [9].

On the other hand, the inner shell of the walnut is extremely hard, its thickness varies between 0.15 and 0.62 cm, represents about 33% of the walnut shell, so it could be ideal in the production of materials reinforced with natural fiber [10]. Macadamia nut shells are considered a waste in the oil production process, however, given their mechanical properties, they can be used in the production of plastics that are environmentally friendly.

At the present investigation, the composition of the oil and macadamia nut flour was determined, in addition, volumetric tests of physicochemical characterization were applied to the oil. Finally, the shell was subjected to a treatment with sodium hydroxide (mercerization) and, subsequently, the effectiveness of this treatment was verified through Infrared (IR) spectroscopy.

The main objective is to study the properties of *M. tetraphylla* and *M. integrifolia*, for their application in the development of new products of low environmental impact, with different applications and seeking as far as possible, that are included within the scope of green technologies.

II. Methodology

2.1 Materials

The Macadamia nut that was used as raw material was acquired from local producers in the state of Michoacán. The polyester resin with which the composite was obtained is of commercial grade purchased from a local polymer resin company.

2.2 Conditioning of the raw material

The clean nuts were cracked manually with a nutcracker to obtain the fruit. The oil was obtained by cold pressing the fruit, using a handler press, once the oil was obtained, it was exposed to centrifugation at 8000 rpm for 10 minutes at 20 °C in order to separate the largest number of suspended solids, the supernatant was recovered also. The oil was placed in amber flasks and stored refrigerated at 4 °C for use in the characterization tests.

2.3 Milling, mercerizing and sieving

The shell from the breaking step was subjected to grinding and sieving using 1.4 mm, 850 µm and 250 µm particle size sieves, followed by alkaline treatment [11]: in an aqueous 10% w/V the ground shell was added until saturation and the mixture was heated at 80 °C for 4 hours. After contact time with the basic solution, the treated solid was washed with copious water to a pH of 7 and spread in a tray to dry at room temperature for 48 h, thereafter the solid was oven dried for 5 hours at 80 °C. This was done in order to break up the fiber and particle agglomerations and leave the cellulose free of hydrophilic compounds, in addition to promoting better adhesion with the polymer matrix when composing materials.

2.4 Physicochemical characterization

2.4.1 Physicochemicalanalysis.

The fatty acid profile study was performed by GC-MS (Gas chromatography coupled to mass spectrometry) according to the standard NMX-F-490-1999-NORMEX for determination of the composition of fatty acids from the C6. The physicochemical analysis of walnut meal was carried out according to NMX-F-083-1986 standards for food moisture determination, NMX-F-608-NORMEX-2011 for protein determination in foods, NMX-F- 607-NORMEX-2013 for ash determination in foods, NMX-F-615-NORMEX-2004 for the determination of ethereal extract (Soxhlet method) and NMX-F-613-NORMEX-2003 for determination of crude fiber in food.

2.4.2 Stability study. Determinations of the acid number, peroxide index and oil saponification index were made according to the methods specified in the United States Pharmacopeia for olive oil [12].

2.5 FT-IR Spectroscopy

For the analysis of samples using infrared spectroscopy with Fourier transform (FT-IR), a NICOLET iS10 equipment was used, the spectra were obtained in the range of 400 to 4250 cm^{-1} with 16 scans. The obtained spectra were compared with published data of frequencies of the main functional groups.

2.6 Preparation of the composite material

The silicone molds were prepared to obtain the compression and impact specimens (test specimens) according to ASTM D 695-15 and D 256-10, respectively, using polyester resin matrix and reinforcing the macadamia nut shell with a composition of 20% by mass.

III. Analysis Of Results

3.1 Characterization of Macadamia Nut Oil and flour

The oil extracted in cold presents significant differences in the organoleptic characteristics compared to the commercial oil. The oil extracted in cold is practically colourless, transparent and with a soft and pleasant smell, whereas the commercial oil exhibited a yellowish colour besides having a smell of burnt, which suggests that the extraction process possibly was realized in a hot environment that may have altered its properties.The fatty acid composition of the cold pressed oil obtained in the present research is shown in table 1.

Table 1. Fatty acid profile of macadamia nut.

Determination	% in mass
Stearic	3.39
Oleic	31.74
Palmitic	13.61
Linoleic	1.21
Linolenic	0.08

The results show that the oil has a high content of oleic acid (31.74%), this monounsaturated fatty acid, commonly known as omega 9, is responsible for the metabolism of lipids and the decrease of LDL levels in the bloodstream as LDL (Low-density lipoproteins) carry cholesterol to different tissues of the body and, if they become too much, can accumulate in the walls of veins and arteries causing various Health problems such as cardiovascular diseases [15].

The remaining flour from the pressing process was also analysed according to the norms mentioned in the methodology, the results obtained are concentrated in Table 2.

Table 2. Composition of walnut flour.

Determination	% in mass
Humidity	1.84
Protein	8.94
Ashes	1.72
Fats (ethereal extract)	70.73
Total carbohydrates	16.77
Raw fiber	8.75

The flour has a high percentage of fats, which can make it useful in the processing of products like soap and even be used to enrich foods due to its content of proteins, carbohydrates and raw fiber [16]. The results of the volumetric tests that were applied to the oil are presented in Tables 3 and 4.

Table 3. Acidity (fatty acid) index of macadamia nut oil.

Sample	Amount of sample (g)	Volume of NaOH 0.1 N (mL)	Acidity index (mg KOH/g oil)	Degree of acidity
1	3.35	1	1.675	0.843
2	3.32	0.9	1.521	0.766
3	3.37	0.7	1.165	0.587
Average	3.3467	0.8667	1.454	0.732
Standard Deviation	0.0252	0.1528	0.261	0.132

A high value of the degree of acidity in an oil indicates its deterioration and has initialized the roasting processes. The degree of acidity is of great importance as this is categorized the quality of the oils. It should be noted that the oil examined, according to the results shown in Table 3, can be considered edible and of great quality, since these oils have less than 1% free acid (grade 1 acidity) [17].

Regarding the saponification index, the only experimental value available was 313 mg of KOH/g of oil. The value of the saponification index was well above that obtained by Rodríguez *et al*. in 2011, which was 233.65 mg KOH/g oil, since it was not performed in triplicate, it is not considered reliable [18].

The results of the tests for the peroxide index, shown in Table 4, are well below the limit value of the United States Pharmacopeia [12], the value of which should not exceed 4 meq O_2/kg of oil, this is an indication that during the extraction process and until the moment of the analysis there was very little oxidative degradation. Therefore, the oil meets this quality parameter.

Table 4. Index of peroxides of macadamia nut oil.

Sample	Amount of sample (g)	Volume used of $Na_2S_2O_3$0.01 N (mL)	Peroxide index (O2 meq / kg oil)
1	5.1695	12	0.232
2	5.0458	7	0.139
3	5.1023	7	0.137
Average	5.106	8.667	0.169
Standard Deviation	0.062	2.887	0.054

Figure 1 shows the IR spectra obtained from the treated and untreated walnut fiber. In the Y axis are found the characteristic absorbance values of the components of the macadamia nut shell.

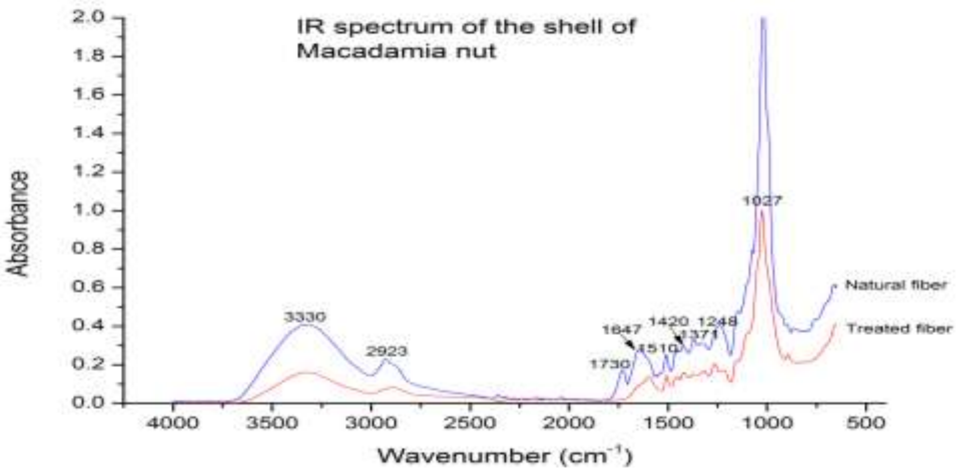

Figure 1. IR spectra of the treated and untreated shell of macadamia nut.

The samples analysed have two main absorption regions: the first in the range of 700 to 1750 cm^{-1} and the second in 2700 to 3600 cm^{-1}. The peak observed at 3330 cm^{-1} may be OH groups characteristic of cellulose. The signal at 2923 cm^{-1} corresponds to stretching vibration of the C-H bonds. The absorbance signal observed at 1730 cm^{-1} is due to C=O bonds of unconjugated ketones of hemicellulose, which disappears after the alkaline treatment [19,20]. Between 1630 and 1650 cm^{-1} a signal belonging to the O-H bond of water is observed.

The signal obtained between 1500 and 1650 cm^{-1} corresponds to the characteristic peaks of lignin due to the vibration of aromatic rings [20], which is mostly diminished in the spectrum of the treated fiber, due to the alkaline treatment, where different fiber impurities such as lignin, waxes and oils are removed by breaking the hydrogen bonds, increasing the outer surface of the cell wall to achieve a better adhesion to the polymer matrix [21]. Finally, the characteristic absorption bands of the hemicellulose, present between 1740 and 1250 cm^{-1}, likewise decreased once the alkaline treatment was carried out on the walnut shell.

The signal at 1027 cm^{-1} corresponds to the stretching vibration of the C-OH bond, specifically of a primary alcohol (between 1075 and 1025 cm^{-1}). It is a flexion in the plane, this type of signals is only complementary, since the stretches C-C, C-N and C-O fall in the same region (1225 - 950 cm^{-1}). These are weak but sharp signals, which increase significantly in the presence of polar groups. Several signals appear depending on the number of hydrogens.The IR spectroscopy technique allows analysing and characterizing the chemical structure of a sample by identifying the functional groups that compose it. Natural fibers such as sugar cane, jute, hemp, lily, macadamia nut shell, among others, mainly contain cellulose, hemicellulose and lignin whose characteristic functional groups are alkanes, esters, ketones, alcohols and aromatic rings.

IV. Conclusions

In the oil were found the essential fatty acids: omega-6 (linoleic) and omega-9 (oleic acid). However, according to the analysis, the proportion of monounsaturated (oleic) acids is higher than that of polyunsaturated (linoleic and linolenic), besides containing a very low proportion of saturated fatty acids (palmitic acid, stearic acid); Palmitic acid is responsible for raising blood cholesterol levels. According to these results, macadamia oil can be consumed as a good natural source of omega-6; however, its intake must be balanced with other sources of omega-3 (alpha-linolenic acid), since the ideal proportion to be saved between linoleic and alpha-linolenic is 4: 1. The current rhythm of life coupled with the type of fast food rich in saturated fat, low exercise and accumulation of stress contribute strongly to diseases such as diabetes and those related to overweight will continue to proliferate massively. Therefore, the consumption of this type of food is very low processed that help to reduce the negative effects of current eating habits.The acidity, peroxide (indicative of the presence of antioxidants) and the lipid profile make the oil can be a source of very valuable raw material for the production of cosmetics: oleic acid has regenerative and moisturizing properties, linoleic acid helps to prevent the loss of transepidermal water, phytosterols have healing properties and make the oil have a high penetration ability in the skin. The alkaline treatment helps to obtain better composite materials by allowing a better distribution of resins on the surface of the fiber was carried out on the walnut shell.

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