

Chapter

Macauba (*Acrocomia aculeata*): Biology, Oil Processing, and Technological Potential

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Abstract

The global production of vegetable oil has increased since the beginning of the century, reaching a peak of 209 million tons in 2020/2021 and is projected to continue to increase due to population growth and the impact of the biodiesel industry. In this context, palm oil and soybean oil have stood out. However, both palm oil and soybean oil production chains are not fully sustainable, leading to socioeconomic and environmental challenges, which have driven the search for new raw materials with sustainability potential. Macauba [*Acrocomia aculeata* (Jacq.) Lodd. Ex Mart.] is an oleaginous palm distributed mainly in Central and South America, and most of the Brazilian territory. It is one of the species with greater potential for economic exploitation due to its high oil productivity and use of by-products from oil extraction and processing. This chapter addresses the most up-to-date information in biology, oil production, and oil processing from fruit to oil applications.

Keywords: *A. aculeata*, macauba, oil extraction, oil refining, biofuel

1. Introduction

The world population growth brings great challenges regarding food security and environmental sustainability [1]. In this scenario, increasing the production of vegetable oils by developing resilient and sustainable cropping systems may be a promising approach. The global production of vegetable oil is dependent on the production of tropical perennial oilseed plants, in particular the African palm (*Elaeis guineensis*) [2]. In 2019–2020, over 81.1 Mt of *E. guineensis* oil was produced worldwide, of which 72.3 Mt consisted of palm oil (mesocarp), and 8.8 Mt. of kernel oil (endocarp) [3]. However, the cultivation of this species requires specific soil and climate conditions, leading to the deforestation of large areas of the rainforests, with considerable environmental impact and competition for land intended for food cultivation [4].

In this context, the identification of oilseed plant species that contain oils with triacylglycerol composition similar to palm oil, high production yield, and greater resistance to adverse edaphoclimatic conditions is a challenge. Macauba [*Acrocomia aculeata* (Jacq.) Lodd. Ex Mart.] is an endemic palm species of the Americas that

presents all these peculiarities, becoming a promising alternative for the development of a sustainable production chain of oils and co-products of industrial interest [5–7].

A. aculeata is popularly known as macauba, macaíba, macaiuva, mocaja, mocuja, mucaja, bacaiuva, bocaiuva, coco-de-catarro, coco-de-espinho, imbocaia, and umbocaiuva, depending on the region of occurrence [8]. Analyses of the productive capacity of macauba crops in Brazil indicate that approximately 5000 kg of pulp oil and 1500 kg of kernel oil can be produced per hectare per year. In addition, macauba is considered the second-largest oleaginous source after palm oil concerning the production yield [5, 9, 10].

This plant species grows preferably in tropical and subtropical regions with high rainfall and solar irradiation [11]. However, it is able to adapt well to other environments, including subtropical and semiarid conditions [9]. In Brazil, there is a large quantity of degraded land or land in process of degradation or desertification caused by human action or natural phenomena. Land degradation is the loss of productivity due to factors such as soil erosion, reduction of soil fertility, and loss of natural vegetation [12]. The fact that macauba has a great capacity to adapt to extreme edaphoclimatic conditions has led to the proposal that this plant could contribute to the recovery of degraded lands [13].

The energy capacity of macauba is due to the high productivity and quality of the pulp and kernel oils. Macauba oils have a different fatty acid profile and minority compounds. The pulp oil has a predominance of unsaturated fatty acids and bioactive compounds, such as carotenoids and tocopherols [14]. In turn, kernel oil is rich in saturated fatty acids, mainly lauric acid. These notable differences confer distinct market potential for both products [15].

In the last decade, studies on *A. aculeata* have intensified due to its characteristics and applications, mainly as an alternative feedstock for biodiesel production [16]. Soybean oil, canola oil, rapeseed oil, cottonseed oil, and palm oil are examples of noble and edible feedstocks used for biodiesel production [17]. In 2020, soybean oil accounted for 71.4% of biodiesel production in Brazil [18]. Studies have shown a similar profile of fatty acid esters in biodiesel from macauba oil when compared to soybean oil [19], highlighting the fundamental role of macauba as a potential feedstock with high availability and productivity for use in the biodiesel industry [5].

Due to the essentially extractive nature of macauba cultivation, in many cases, good practices for harvesting and storing the raw material are not followed, and this directly impacts the quality of the fruits and oils obtained [10]. In Brazil, there are several commercial cultivation programs demonstrating that it is a viable strategy, although it is still far from competing with commodities. The processing of macauba oils begins with the process of extraction by continuous pressing to obtain the crude oil [20]. Subsequently, the oils must undergo a refining process in order to eliminate undesirable substances that compromise both the oxidative stability of these oils and their organoleptic qualities [20]. Once refined, oils can have several applications both in the food and oleochemical areas and can still undergo modifications to expand their range of applications [15]. **Figure 1** outlines the complete macauba oil production chain from the palm tree to the lipid modified.

Excellent studies on the biology of macauba have been reported, including the factors that influence productivity, domestication processes, and genetic improvement, aiming for the development of commercial crops, and genetic variability, among others. Recently, Vargas-Carpinteiro et al. have published an exhaustive review on *Acrocomia*, showing that studies on harvesting, postharvest, crude oil extraction, refining, and deodorization are among the most incipient topics [7]. Therefore, the

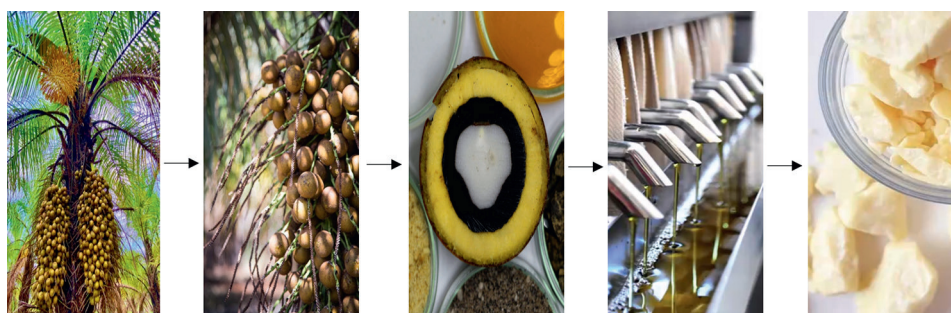


Figure 1.
 Representation of the macauba oil production chain: Palm, fruit bunches, open fruit, processing of oils, and lipids modification (photos source: S. Oleum).

present study addresses the biology of *A. aculeata*, with emphasis on the processing steps from fruit to oil, as well as the main applications of macauba oils.

2. Biology

2.1 Taxonomic classification and distribution

Macauba is a palm species that belongs to the Arecaceae family, which includes approximately 189 genera and about 3000 species, which are classified into five subfamilies, as follows: Calamoideae, Nypoideae, Coryphoideae, Ceroxyloideae, and Arecoideae [21]. The latter is the most representative family since it contains species of great economic interest such as *Elaeis guineensis* (African palm), *Cocos nucifera*, *Euterpe oleracea*, and the emerging species *Acrocomia aculeata* (macauba) [21]. The great phenotypic diversity among individuals of *A. aculeata* (Jacq.) Lodd. ex-Mart has led to a misunderstanding about the number of species that belong to the genus *Acrocomia*. For this reason, there is still no consensus on the taxonomy of this genus [22]. Recent studies using both morphoanatomical characteristics of the plant and fruit biometrics have contributed to the understanding of the taxonomy of this group [23–27].

Currently, nine species are included within the genus *Acrocomia* that occur in the Neotropical region, including *A. aculeata*, *A. crispa*, *A. emensis*, *A. corumbaensis*, *A. glaucescens*, *A. hassleri*, *A. intumescens*, *A. media*, and *A. totai* [22]. Fossil studies and the great phenotypic diversity of the genus *Acrocomia* suggest that Brazil may be the center of origin and dispersal of these species [28], probably due to both weathering processes and human activity in the Americas [22]. The species *A. aculeata* is endemic to Brazil and has been distributed to islands in the Caribbean, Central America, and South America [22]. In Brazil, this palm occurs in most of the territory, mainly in the states of Minas Gerais, São Paulo, Goiás, Mato Grosso, and Mato Grosso do Sul, in the Cerrado [22, 29]. It can also be found in tropical and subtropical forests, and dry forests of Caatinga [23, 30], with good adaptation to sandy soils and regions with low water availability [24].

2.2 Morphology and reproduction

Macauba is a perennial, halophytic, tree-like palm species with a solitary, aerial, cylindrical, and spindle-shaped stem that can reach 10–15 m in height and 20–30 cm in diameter. The stipe is often covered by the bases of the petioles, which remain

attached for many years. The node region is covered with dark and sharp spines and is approximately 10 cm long [31].

The *A. aculeata* genome has 2.8 Gbp distributed on 15 pairs of chromosomes ($2n = 30$) with an AT base content of 58.3% [32]. This palm is monoecious and presents interfoliate and branched spadix-like yellow inflorescences 50–80 cm long. It presents a large number of staminate flowers at the base and pistillate flowers originate triad at the top of the inflorescence [30, 33]. Although the reproductive system is cross-pollination between different individuals, the species is self-compatible [33]. Entomophily is the main pollination route, and anemophily plays a secondary role. Scariot et al. suggested that the combination of these two types of pollination with a flexible reproductive system is related to the wide distribution of the species [33].

Macauba flowering is seasonal and annual. In Brazil, it blooms from September to February, with peak flowering in November and December [33]. However, fruiting occurs throughout the year and the fruits mature approximately 1 year after fertilization [33]. Macauba generates inflorescences with bulky clusters that contain 300–600 drupaceous fruits, weighing about 66 g/each, resulting in a highly productive plant [13].

The fruits can be 3.0–5.0 cm in diameter, are edible, spherical, and do not ferment immediately after ripening [5]. The fruit contains approximately 20% epicarp (peel), 40% mesocarp (pulp), 33% endocarp, and 7% kernel [34]. The epicarp ruptures easily when ripe. The mesocarp is fibrous, mucilaginous, sweet-tasting, edible, and rich in glycerides, yellow or whitish in color. The endocarp is strongly adhered to the pulp, with a black bony wall, and an edible oily kernel covered by a thin layer of the tegument. Each fruit usually contains a seed surrounded by a hard, dark endocarp approximately 3-mm thick [30, 35]. Macauba has two economically important kinds of oil, stored in the fruit pulp and its kernel. The pulp contains up to 75% of the total lipids, while the kernel may contain up to 65%, both on a dry basis [34]. **Table 1** shows the proximate composition of *A. aculeata* pulp and kernel.

2.3 Domestication and plant breeding

Macauba, like most palm species, has an essentially extractive cultivation system, leading to habitat fragmentation, increasing inbreeding, and decreasing genetic diversity [37]. Both the domestication process and the development of breeding programs for *A. aculeata* are still at an incipient stage [27, 38]. However, its domestication

	Kernel %	Pulp %
Dry matter	83.11	42.65
Ash	1.29	2.03
Crude protein	5.66	1.15
Lipids	47.76	32.05
Crude fiber	62.79	51.70
Mineral matter	0.39	0.66
Carbohydrates	33.40	18.10
Moisture	3.18	45.42

Table 1.
Proximate composition of macauba fruit. Source: Lira et al. [36].

should be integral and systematic due to the socioeconomic impact of the cultivation of this palm and the application prospects [7]. The success of the domestication process depends on genetic improvement programs that are directly related to the choice of genotypes with the best agronomic characteristics [39]. Knowledge about the genetic diversity of *A. aculeata* is fundamental to guiding the selection of the most promising materials for use in the crop, maximizing genetic gains, and contributing to the creation of commercial cultivars [38]. Colombo et al. pointed out the main guidelines for the improvement of *Acrocomia* plants, including obtaining varieties with optimized height, greater drought tolerance, and higher oil productivity [5].

There is great morphometric and genetic variability among macauba plants native to the Brazilian Cerrado and Pantanal regions of Brazil and Costa Rica, characterized by fruit biometry and oil yield [34, 40, 41]. However, these factors are not correlated [40]. Biometric studies of Costa Rican varieties have suggested a possible environmental effect on oil composition and yield [41]. Dos Santos et al. [42] studied the accumulation of metabolites in fruits coming from three Brazilian regions (Southeast, Northeast, and Midwest) characterized by having different lipid contents. The authors concluded that, despite the anatomical differences between mesocarp and endocarp, in both tissues, a similar trend of metabolite accumulation was observed toward ripening. In the mesocarp, total soluble proteins, free amino acids, sucrose, starch, and total lipids accumulate toward maturity, with a decrease in glucose and fructose contents. The endosperm differed from the mesocarp only for the amino acid contents, which decreased in mature fruits. The results pointed out that fruits from the Southeast region (Minas Gerais) may be of interest for breeding studies due to their higher lipid contents [42].

Genomics-based strategies allow access to the genetic potential of natural populations, germplasm characterization, phylogenetic analysis, etc. [38]. The availability of public databases (www.ncbi.nlm.nih.gov) of genomic sequences of *A. aculeata* has enabled great advances in genetic variability studies in the last decade. Those studies confirm the high genetic diversity among varieties, allowing the identification of genotypes with the highest agronomic potential, the abiotic factors related to increased oil production, and the efficiency of biosynthesis, evolution, and phylogeny of this species [32, 40, 43–45].

The embryo culture of *A. aculeata* allows the achievement of high germination rates, solving the deep seed dormancy that causes low germination rates [46]. However, the acclimation process restricts seedling growth. Recent histological studies have pointed to impaired development of the haustoria, root system, and leaves as the possible causes of this phenomenon [18]. Souza et al. [47] evaluated the effects of climate seasonality on the longevity and dormancy of diaspores of macauba palm. That approach is critical for establishing soil seed banks that allow for the conservation of natural populations and extractive management. The authors reported that the longevity of macauba seeds in the soil depends on several factors, including the maintenance of structural protection of the embryo, tolerance to water deficits, and control of oxidative stress. In turn, the overcoming of dormancy is related to the gradual weakening of the containment tissues and the strength of the embryo [47].

In this context, the development of genetic improvement programs for macauba to allow systematic cultivation and commercialization on a large scale in the near future is required. Initiatives to cultivate macauba in Brazil for commercial purposes have been undertaken, including the programs Entaban Brazil, Solea, and Inocas, with production destined for national consumption [5].

3. From macauba fruit to refined oil: modifications

3.1 Fruit processing

The harvest and storage stages of fruits are determinants of the quality of agricultural products. Both the harvest method and the development stage of macauba fruit at the time of harvest directly impact the quality of the oil [16]. The storage time of the fruits before the oil extraction also has a great impact on the product quality, which is determinant in humid tropical countries [37]. In the extractive cultivation system of macauba, the fruits are collected directly from the soil, after the natural fall at the end of the fruiting period, and stored with no controlled humidity and temperature conditions, resulting in low-quality oils and yield [16].

Data have shown an increase in oil content at the end of the maturation period of macauba fruits, thus harvesting bunches at the end of this phase is recommended. However, the proportions of fatty acids and triacylglycerols of both pulp and kernel oils do not vary [48]. A very important peculiarity of the macauba fruit is the additional oil synthesis after abscission, which differentiates it from other palm species, including *E. guineensis*. Studies have shown that such production can reach up to 35% after 40 days of storage under ambient conditions [16]. Therefore, the harvest and postharvest stages of macauba fruits are crucial in the productivity and quality of crude oil, mainly concerning the acidity index and oxidative stability.

The acidity index is a measure of the free fatty acids content in the oil. Oils with acidity levels >5% expressed as free fatty acids compromise the later stages of processing and commercialization [49]. The increase in free fatty acids in the oil from the mesocarp is due to the action of lipases (E.C. 3.1.1.3; glycerol ester hydrolases) that hydrolyze triacylglycerols in the presence of water. These enzymes are produced by plants, animals, and microorganisms [50], and the latter are recognized as potential producers of extracellular lipases [51]. Cavalcanti-Oliveira et al. analyzed the origin of lipases involved in the hydrolysis of macauba pulp oil [52]. The results suggested that the oil from the mesocarp is hydrolyzed by lipases produced by microorganisms that contaminate the fruit when in contact with soil, rather than the action of endogenous lipases. Some authors have reported that macauba fruits harvested directly from the bunch or naturally fallen fruits with no contact with the soil can be stored under ambient conditions for up to 20 days, without exceeding 5% acidity [16, 18, 53]. However, a varied microbiota can be found in the epicarp and mesocarp of macauba fruits without contact with the soil [16].

Thus, efficient harvesting methods and rapid fruit processing are required to slow pulp decomposition and oil acidification [54]. Fresh macauba fruit has high-quality mesocarp oil, even when it is dried immediately after harvest, provided that good harvesting and processing practices are applied [55]. Drying the fruit after harvest decreases the moisture content and reduces the hydrolysis efficiency of lipases in addition to facilitating pulping with simultaneous separation of the peel [56]. The combination of drying and autoclaving processes of macauba fruits allowed the storage of crude oil for 180 days, preserving the original acidity and the triacylglycerol profile [52]. It is worth noting that under good harvesting and storage practices, the acidification process of macauba pulp oil is slower than palm oil [55]. Other methods of treating the fruit immediately after harvest have been used to extend the shelf life of the fruit and the oil quality, including the use of ozone gas, irradiation, and different drying methods [53, 57, 58].

Evaristo et al. [16] reported a significant increase in the oil content of the meso-carp after the fruits were detached from the bunch, suggesting that macauba has climacteric behavior. The authors showed that harvesting macauba fruit directly from the bunch and the immediate storage under controlled humidity and temperature conditions, as well as the treatment with fungicides, resulted in higher fruit quality and therefore longer postharvest shelf life [16].

Improvements in fruit processing steps that positively impact the quantity and quality of the extracted oil can increase productivity and make the macauba more commercially competitive [56].

3.2 Obtaining crude oil

Three important steps should be considered for obtaining the crude oil, which directly affects the oil quality and product yield, including the storage of the raw material, preparation, and extraction of the crude oil. The variation in moisture content and temperature during fruit storage can trigger enzymatic and oxidation reactions, leading to a reduction in the quality of the oil extracted due to the increase in free fatty acids and other degradation compounds, known as peroxides [20].

The proximate composition of the macauba fruit consists of 47.76% and 32.05% lipids in the kernel and pulp, respectively; thus, continuous pressing is the most suitable method for oil extraction due to the high lipid contents [36, 59].

The screw-type press, also known as screw expeller, is a continuous press in which the fruit pulp or kernel is fed into a thick-walled cylinder containing a rotating, polished screw with gradually decreasing size. The oil from the plant cell is in the form of globules covered by a cell membrane. A typical characteristic of plant cells is the presence of thick cell walls; thus, the cell wall should be broken down to get the oil globules out. For that, the pulp or kernel cluster is fed continuously into the press and compressed at high pressure (4–35 MPa). In turn, while the oil is extracted, the compressed fruit cake is discarded at the end of the stretch. The high-energy consumption generated during shearing can considerably increase the temperature of both the oil and cake [20].

3.3 Physicochemical characterization of macauba oils

3.3.1 Composition of saponifiable and unsaponifiable fractions

Chemically, oils and fats are mixtures composed mainly of triacylglycerols formed from a glycerol molecule esterified with three fatty acids. The crude oil usually contains monoacylglycerols, diacylglycerols, free fatty acids, waxes, phospholipids, sphingolipids, glycolipids, terpenes, sterols, tocopherols, and carotenoids as minority compounds [20]. The unsaponifiable matter consists of solubilized minority compounds in oils and fats that are extractable with organic solvents after saponification [60]. Nunes (2013) found 0.76% unsaponifiable matter in crude macauba pulp oil, while Breves (2018) found 2% unsaponifiable matter in crude macauba kernel oil [61, 62].

3.3.2 Fatty acid composition

The macauba kernel oil is characterized by the predominance of oleic acid and lauric acid, and presents a translucent aspect, while the pulp oil has an orange color and is characterized by a high concentration of oleic acid and carotenoids, which may

Fatty acids		Pulp (%)	Kernel (%)
C4:0	Butyric	Traces	0.91
C6:0	Caproic	0.22	0.27
C8:0	Caprylic	0.11	3.67
C10:0	Capric	Traces	2.79
C12:0	Lauric	0.39	32.58
C14:0	Myristic	0.38	9.71
C16:0	Palmitic	24.6	8.25
C16:1	Palmitoleic	4.27	—
C18:0	Stearic	1.08	2.24
C18:1	Oleic	52.57	36.27
C18:2	Linoleic	13.80	3.82
C18:3	Linolenic	2.26	—
C20:0	Arachidic	Traces	—
C22:0	Behenic	Traces	—
C24:0	Lignoceric	0.32	—
Σ saturated	—	27.10	59.92
Σ unsaturated	—	72.90	40.09

Table 2.

Fatty acid profile of macauba oils (pulp and kernel). Source: Coimbra and Jorge [14].

provide high oxidative stability [63, 64]. **Table 2** presents the fatty acids profile of macauba pulp and kernel oils.

The low content of polyunsaturated fatty acids (linoleic—C18:2 and linolenic—C18:3) can also affect the oxidative stability of the pulp oil, corresponding to 15%. On the other hand, the kernel oil presents a peculiar fatty acid composition, because although it has 32.58% of lauric acid (C12:0), which is a lower level when compared to conventional lauric oils, such as coconut, palm kernel, and babassu, it has more than 35% of oleic acid, an unusual content among all vegetable oils of this class.

3.3.3 Triacylglycerol composition

The macauba pulp oil presents a smaller range of carbon groups, comprising 48–54 carbon groups. Fourteen distinct triacylglycerols were identified, corresponding to 17.07% OOO, 6.36% OOL, 28.53% POO, and 10.53% PLP [65]. Lieb et al. analyzed macauba pulp oil from Costa Rica and found 20.8% OOO, 10.4% OOL, 13.0% POO, and 1.5% PLP (P: palmitic; Po: palmitoleic, S: stearic; O: oleic; L: linoleic) [48]. This divergence of values is due to the different origins of the fruits and the extraction method used to obtain the crude oil.

3.3.4 Tocopherols, carotenoids, and phenolic compounds

Natural antioxidants found in vegetable oils, such as tocopherols and tocotrienols, have four isomers, designated as alpha (α), beta (β), gamma (γ), and delta (δ),

	Macauba pulp oil (mg kg ⁻¹)	Macauba kernel oil (mg kg ⁻¹)
Phenolic compounds	2.21	4.38
Total carotenoids	300.1	1.82
Total tocopherol	221.95	23.10
α-Tocopherol	143.70	14.35
β-Tocopherol	3.25	0.85
γ-Tocopherol	57.83	—
δ-Tocopherol	8.15	7.90

Source: Coimbra and Jorge [14].

Table 3.
Tocopherols, carotenoids, and phenolics concentrations in macauba oils.

depending on the number and position of methyl groups in a chromanol ring. Tocopherols are characterized by a saturated side chain, while tocotrienols present an unsaturated side chain, and they also have a vitamin E activity in humans. They are also recognized for slowing down the lipid oxidation process. The antioxidant activity of tocopherols in food increases progressively for the δ, β, γ, and α isomers. On the other hand, tocotrienols are less effective than their corresponding isomers [66].

Carotenoids constitute a diverse group of lipophilic compounds that provide yellowish to red color to oils and are also known as bioactive compounds with proven health benefits [66].

Coimbra and Jorge characterized the macauba kernel and pulp oils for the concentration of phenolic compounds, carotenoids, and tocopherols, and the findings are shown in **Table 3** [14].

3.3.5 Oxidative stability

Factors that affect or catalyze the lipid oxidation include the presence of unsaturated or double bonds in fatty acids, light, temperature, prooxidants and antioxidants, enzymes, and storage conditions. In addition, the oxidative stability reflects the quality of the raw material from harvest to processing, leading to undesirable flavors that reduce the quality and shelf life of oils [67].

Breves [62] studied the oxidative stability of macauba kernel and pulp oils according to ISO 6886, and reported 41.35 and 16.36 min at 110°C, respectively. It is worth noting that the stability of the pulp oil is relatively lower than that of the kernel oil, due to the higher number of unsaturated fatty acids [62].

3.3.6 Oil refining

Refining can be defined as a series of distinct steps aimed at reducing undesirable substances from crude oils that can affect the stability and sensory properties. It removes colloidal substances, phosphatides, free fatty acids, natural pigments, such as chlorophyll and carotenoids, inorganic substances, such as calcium salts, metals, and phosphates, among others, and volatile compounds, such as peroxides, hydrocarbons, alcohols, aldehydes, ketones, and low-molecular weight esters, and water [20].

The selection of the adequate refining process is directly related to the free fatty acid content (%) of the crude oil and can be done through a chemical or physical process.

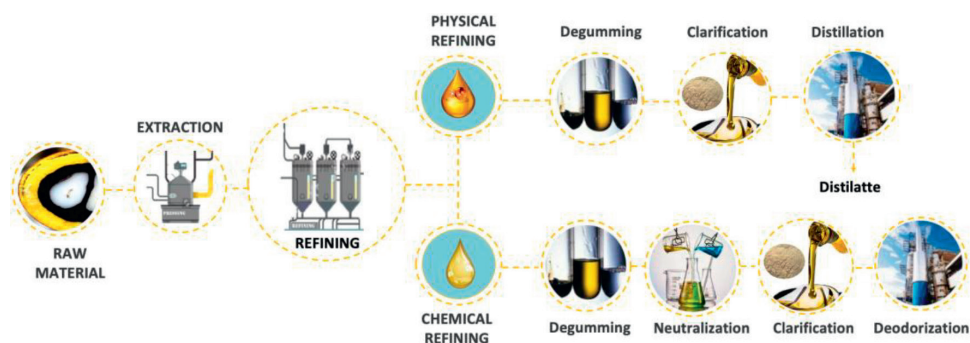


Figure 2.
Schematic diagram of the typical process for obtaining refined oil from the raw material of interest.

The chemical process is not indicated for high acidity oils since significant losses of neutral lipids may occur due to saponification or soapstock dragging. For acidic oils, physical refining is indicated and should be performed under high temperature and low pressure, volatilizing and removing free fatty acids with reduced loss of neutral lipids [68].

In addition, phospholipid contents are the second factor to be considered before selecting the refining process. Chemical refining is indicated for high phosphorus levels, while the physical refining process is more usual for oils with low phosphorus levels [60]. For macauba pulp oil, both types of refining can be used due to its non-standardization as acidic oil (**Figure 2**).

Degumming is the first step for obtaining the refined oil, either for physical or chemical processes, in which phospholipids are converted into oil-insoluble hydratable gums that are easily separated by sedimentation, filtration, or centrifugation through the addition of water and/or acid solution. This step is important for the removal of phospholipids, which can precipitate during the storage, affecting the quality of the oil and the subsequent refining steps. Additionally, it is possible to obtain lecithin, which is a by-product of high commercial value due to its emulsifying effect [20, 60].

Neutralization is carried out during the chemical refining and consists of neutralizing and thus reducing the free fatty acids content by adding an alkaline solution. Diluted caustic soda is usually used in concentrations between 10 and 24° Bé (degrees Baumé). The concentration of caustic soda and its excess is dependent on the free fatty acids (FFA) content of the degummed oil to be neutralized, avoiding saponification of the oil [69].

The next step is known as clarification or bleaching. Its main objective is to remove pigments to obtain clear oils (an important factor for commercialization), in addition to removing other constituents, such as oxidation products, metal traces, phospholipids, and soaps, resulting from the chemical refining. According to Kaynak et al. [70], these impurities, when present in the oil, can contaminate the hydrogenation and interesterification catalysts, darken the oil, and decrease oxidative stability [20, 70].

The efficiency of the process is determined by adding clarifying clays, either natural or activated, via adsorption. Part of the pigments is adsorbed onto the clarifying clay through surface attraction forces, known as “Van de Waals forces.” Other components are chemically bound to the surface of the clarifying clays by covalent or ionic bonds. Part of the impurities present in the oil is removed by trapping their molecules in the pores of the clay. Some minor components, such as oxidation compounds and pigments, are chemically altered during clarification due to the catalytic activity of some clays [69].

Deodorization is the last step of chemical refining, with the elimination of volatile compounds such as remaining free fatty acids and peroxides that give the oil an unpleasant aroma and flavor. The deodorization is done through steam distillation, removing volatile substances through a high vacuum [69].

In physical refining, the last step consists of distillation, with oil deacidification through the removal of free fatty acids, volatiles, and oxidation products [69]. The process is carried out through the association of high temperature and low absolute pressure, favoring the acceleration of distillation and preserving the oil from atmospheric oxidation [61].

According to the CODEX Alimentarius CXS 210-199 for vegetable oils, refined oils should have a maximum acidity of 0.6 mg KOH/g oil and up to 10 mEq O₂ kg⁻¹ [71].

3.3.7 Refining the by-product: deodorizing the distillate

It is estimated that a great amount of industrialized vegetable products, corresponding to 15–20%, are not used. The volume of these residues can reach even higher levels depending on the raw material, the processing applied, equipment used, and process yield, among others. All these factors induce the generation of by-products for food, fertilization, and feed production. Researchers have attempted to use by-products from the processing of vegetable raw materials, including vegetable oils, and once besides adding value to the by-products, it reduces the disposal in nature, helps in the environmental preservation, and promotes the integral use of the vegetable sources [72].

In addition to the refined oil, the distillate is obtained during the refining process, known as vegetable oil deodorization distillate (VODD). It is a by-product of the industrial processing of vegetable oils and is considered a low-cost source rich in health-giving components, such as tocopherols and phytosterols, in addition to FFA with numerous industrial applications. The distillates from physical refining have FFA contents above 70% and lower levels of unsaponifiable materials [73].

The research team of the Laboratory of Oils and Fats of the Faculty of Food Engineering—UNICAMP, Campinas, Brazil, studied the distillates from the deodorization of macauba kernel and pulp oils from physical refining. The kernel distillate presented 14.49 mg/100 g of γ -tocopherol and 0.79 mg/100 g of γ -tocotrienol. In turn, the pulp distillate presented 80.27 mg/100 g of γ tocopherol, 25.84 mg/100 g of β tocopherol, and 5.64 mg/100 g of γ tocotrienol (unpublished data).

According to Tay et al. [74], the free fatty acid content of palm oil deodorized distillate ranged from 72.7% to 92.6%. The author studied the co-product of palm oil refining and found VODD content of 86.4% [74]. These valuable components can be used in food, pharmaceutical, and cosmetic formulations [73].

3.4 Emerging technologies

The great potential of macauba has led to the development of several processing technologies for kernel and pulp oils. Favaro et al. studied the aqueous extraction of oil from fresh macauba pulp using the commercial enzyme Cellic® CTec3 and reported that the aqueous extraction was effective for obtaining high-quality oil [75]. Rosa et al. evaluated the effectiveness of ethyl acetate as a solvent in macauba kernel oil extraction by ultrasound-assisted extraction. Increasing the amount of solvent, the higher temperatures, and longer extraction times led to a higher amount of oil extracted [76]. Trentini et al. extracted macauba pulp oil by low-pressure solvent extraction and reported higher yields by using isopropanol as a solvent [77]. Prates-Valério et al. [78] studied

different mechanical extraction conditions for obtaining pulp oil, aiming to produce an extremely productive raw material. The fruit pressed at 34°C resulted in higher oil quality when compared to other temperatures studied [78]. Favaro et al. evaluated the extraction efficiency and quality of pulp oil extracted using aqueous media from wet fruits and reported an acidity of 0.45% oleic acid [79]. Malaquias et al. estimated macauba yield by regression models using the variables bunch volume, length, and length/diameter ratio [80]. Colombo et al. studied the physicochemical characteristics of macauba and reported the high potential of this fruit [5].

3.5 Lipid modification processes

To meet market demands and provide varied and uniform raw materials, lipid modification processes allow flexibility and contribute to reducing the gap between production site, demand, and availability. The most commonly used modification processes include hydrogenation, fractionation, and interesterification, using analytical or computational methods to ensure process efficiency [20, 69].

3.5.1 Fractionation

The fractionation process consists of a thermomechanical separation in which the lipid material is separated into two or more fractions with different physical and chemical properties, due to the difference in the melting point of triacylglycerols. A fraction called olein is obtained, composed of a greater amount of triacylglycerols with a lower melting point, which is present in liquid form, and a semisolid fraction called stearin, composed of triacylglycerols with a higher melting point [81, 82]. Magalhães et al. [83] performed the fractionation of macauba kernel oil and evaluated the olein and stearin fractions for thermal behavior and consistency. The authors concluded that fractionation allowed obtaining fractions with different degrees of oxidative stability and different physical properties for various applications [83].

3.5.2 Hydrogenation

The presence of double bonds interferes with the chemical and physical properties of oils and fats. The hydrogenation reaction is a physicochemical process that leads to the saturation of the double bonds of unsaturated fatty acids through the addition of hydrogen atoms [20, 69].

Hydrogenation takes place in hermetic tanks, in which hydrogen gas is mixed with the raw material in the presence of a nickel catalyst, at high temperatures and high pressure. During partial hydrogenation, part of the double bonds of fatty acid is saturated, while some *cis* double bonds undergo isomerization and are converted to *trans*. A fully hydrogenated oil or fat is obtained after the hydrogenation of all double bonds. Fully hydrogenated vegetable oils are currently the technological alternative to produce fats with specific functional properties through both chemical and enzymatic interesterification reactions [84].

Various harmful effects have been associated with the consumption of *trans* fat in foods since these isomers are structurally similar to saturated fats, competing with essential fatty acids in complex metabolic pathways. In addition, they are cited as lipids that act as risk factors for coronary artery disease. Several countries have established changes in legislation, including Brazil through the Resolution (RDC) 332/2019, which sets limits on industrial fats for the food industry, with a ban on

the use of partially hydrogenated fat until 2023 [85, 86]. The Pan American Health Organization launched an action plan to eliminate industrial *trans* fatty acids between 2020 and 2025, and in 2018 the World Health Organization warned the world about the need to remove these fats from the global food supply [87].

3.5.3 Interesterification

The interesterification of liquid oils and fully hydrogenated vegetable oils has been the main alternative to produce fats with specific properties [84]. During the reaction, although the fatty acids remain unchanged, there is a redistribution of fatty acids in the triacylglycerol molecules, leading to changes in the triacylglycerol composition [88].

Two technological processes can be used for the interesterification of oils, including chemical and enzymatic interesterification. The chemical interesterification uses an alkaline catalyst, with no control over the fatty acid distribution, that is, it has a random nature. In turn, the enzymatic interesterification uses lipases with specific activities and selectivity, thus with greater control over the fatty acid distribution in triacylglycerol molecules [89]. Our research group developed interesterified fractions from macauba oil, which led to a patent application with the National Institute of Intellectual Property (INPI), registered under the number BR 102020 026665 9 [89].

4. Potential for macauba applications

A. aculeata, in growing regions, is widely used by the local population, from the stem, leaves, and thorns to all parts of the fruit (epicarp, mesocarp, and endocarp) for food, medicinal, and craft purposes [90], while the medicinal applications of macauba palm as an analgesic, hypotensive, and diuretic are empirical [90]. Recently, a phytochemical study of the components of *A. totai* spines allowed the identification of eight bioactive compounds with anticancer, antiparasitic, antibacterial, and antiviral activities [91].

The macauba potential for industrial applications is due to the high productivity and quality of pulp and kernel oils and can be grouped into four industrial segments, such as pharmaceuticals, cosmetics, food, and energy [15].

Both the macauba pulp and kernel are edible and have high nutritional value, allowing their insertion into the food industry [15]. The pulp can be added directly to food or as flour [92]. Other parts of the fruit can also be used. The biomass resulting from the macauba oil extraction is pressed to form cakes as an alternative for animal feed, as they do not present toxic components [93]. The pulp cake contains 9% protein, while the kernel cake has 32% [15]. Residues from the oil extraction from the macauba endocarp have been used for the production of higher quality vegetable carbon when compared to carbon from eucalyptus, with wide application in the steel industry [5, 94].

The differential composition of macauba pulp and kernel oils concerning the fatty acid profile and minor components (tocopherols, carotenoids, antioxidants, and phenolic compounds) provides a differentiated market for both products [15]. Pulp oil has a higher content of oleic and linoleic acids, with a recognized role in disease prevention and health promotion, including the role of oleic acid in the prevention of breast cancer and linoleic acid in the cognitive abilities of the elderly [95, 96]. Additionally, the macauba pulp oil has a higher content of carotenoids and tocopherols when compared to kernel oil. Traesel et al. reported no cytotoxic, genotoxic, or mutagenic effects of macauba pulp oil in rats [97].

Studies have shown that pulp oil, both in its raw and microencapsulated form, has diuretic and anti-inflammatory potential. It was also found that the microencapsulated pulp oil maintained the stability of the active ingredient and exhibited antiedematogenic activity [98]. Recent research has suggested that macauba pulp oil can be a promising high-quality raw material for the production of functional ingredients and foods with nutraceutical properties [99].

The kernel oil presents high content of saturated fatty acids (74%) with a predominance of lauric acid (44%) [99], which can be a promising approach for use in the pharmaceutical and cosmetic industries [9]. Studies have shown the hypoglycemic effect of kernel oil in rats with type 2 diabetes when administered orally [100]. Dario et al. showed that kernel oil can be an alternative adjuvant in the development of a nanocarrier, enhancing the photoprotective activity [101]. Macauba kernel oil has also shown potential for use as a lipid ingredient in margarines and mayonnaises [102].

The macauba mesocarp oil is a promising raw material for biodiesel production due to the predominance of unsaturated fatty acids ($\pm 73\%$), mainly oleic acid ($\pm 52\%$) [14]. Biodiesel is defined as methyl esters of long-chain fatty acids derived from vegetable oils or fats [103]. As reported by Coimbra and Jorge, biodiesel derived from *A. aculeata* pulp oil is mainly composed of intermediate alkyl esters (16- and 18-carbon fatty acid chains) consisting of more than 50% monounsaturated alkyl esters, and approximately 25% palmitic acid esters [14]. This chemical composition ensures the desired thermo-oxidative stability and viscosity [104]. Currently, the industrial production of biodiesel is accomplished by alkali-catalyzed transesterification of vegetable oils in the presence of short-chain alcohol to form fatty acid esters and glycerol [105]. Meanwhile, macauba pulp oil has been used for the synthesis of ethyl esters by transesterification using both heterogeneous and homogeneous acid catalysts [106, 107]. Enzymatic transesterification reactions have also been used as a sustainable alternative to the chemical process for the production of biofuels from macauba pulp oil and ethanol [108]. Non-catalytic transesterification of macauba pulp oil in supercritical alcohols also generates quality products and environmental benefits [109]. These methodologies are more tolerant to high levels of oil acidity, which is common in macauba oil, while basic transesterification requires a maximum acidity of 0.5% (w/w) [105].

Xavier and Costa [15] performed a scientific and technological mapping on the characteristics and applications of macauba oil, showing the important contribution of Brazil in this area, and the participation of Brazilian universities in the valorization of native raw material. The technological segments most represented in this analysis of patents were energy, cosmetics, and agriculture [15].

5. Conclusions

Macauba is an emerging species with scientific interest concerning the distribution and genetic diversity of the species, plant development, oil production, crop management, harvest techniques and fruit treatment, extraction, processing, and modification of oils to obtain more plastic lipid bases for various applications. The high productivity of the macauba and the resilience of the crop along with the need to search for vegetable oils with potential use as alternative raw materials for biofuel production have encouraged further studies on this species. Although it is a very promising plant for the sustainable production of vegetable oil on a large scale, there are still scientific and technological challenges. The main challenges include

obtaining commercial varieties, developing sustainable cultivation models, efficient fruit processing techniques, standardized refining protocols, and effective analytical techniques for oil characterization. This chapter summarizes the recent studies on *A. aculeata* biology, oil processing, and technological applications. To the best of our knowledge, this is the first comprehensive review of all the processing steps of *A. aculeata* oils (pulp and kernel) from fruit to refined oils, and the characterization of by-products of the refining distillate, thus addressing the entire macauba oil production chain.

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Conflict of interest

The authors declare no conflict of interest.

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