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Mapping of Alternative Oilseeds from the Brazilian Caatinga and Assessment of Catalytic Pathways toward Biofuels Production

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Abstract: Biofuels are increasingly important renewable resources in the world's energy matrix that have challenged the scientific community as well as small and large farmers to develop alternatives to fossil fuels in order to achieve the aims of energy transition. In particular, Brazil's proven competitiveness in agribusiness together with its rich biodiversity put the country in a key position in the biofuels market. The semiarid Caatinga of northeastern Brazil, an exclusive biome rich in many oilseed species suitable for potential energy purposes, is of particular interest in this field. Nowadays, soybeans are the main feedstock used for the production of biodiesel, but, due to the increasing demand for biofuels, the search for alternative sources of oil from tropical flora with high productivity is crucial. Under this premise, this systematic review focuses on mapping Caatinga's vegetable oil crops that could be used as alternative raw materials for biofuels' production in Brazil, in addition to traditional soybeans and sugarcane. To gain more detailed insight into these matrices, their main properties, including oil content, fatty acid profile and physicochemical properties, are discussed. Moreover, an overview is provided of processes to synthesize different types of biofuels, particularly biodiesel and aviation biokerosene, including the routes employing homogeneous, enzymatic and mainly heterogeneous catalysts. Finally, future prospects and challenges for renewable biofuels and the Caatinga biome are addressed.

Keywords: Brazilian tropical flora; Caatinga biome; feedstock; vegetable oils; biodiversity; catalysis; biodiesel; biojet; biofuels



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1. Introduction

As is known, renewable biofuels are vitally important for the world's energy matrix. Rapid population growth, combined with the worrying scenario of COVID-19 (SARS-CoV-2) implications, political instability in some countries, and industrial and technological advances, is boosting the use of highly polluting petroleum-derived fuels (crude oil and coal), which have been quickly depleting in the last past decades due to high global energy demand, leading to the current energy crisis [1,2]. Consequently, the growing concern about the environment has challenged the scientific community as well as small and large farmers to develop renewable alternatives to fossil fuels. According to the International Energy Agency, among these alternatives biofuels are considered a highly sustainable source of energy [2]. Biodiesel is a biofuel produced from vegetable oils, waste vegetable oils or animal fats that are chemically made up of alkyl mono esters produced by esterification of free fatty acids or by transesterification of triacylglycerols with short-chain alcohols, essentially methanol and ethanol [1–3].

In this scenario, the proven competitiveness of Brazil in agribusiness together with its rich biodiversity puts the country in a key position in the biofuels market. In particular,

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Caatinga—an exclusively Brazilian biome—is a semi-arid ecosystem corresponding to about 10% of the Brazilian territory and 60% of the northeastern region that stands out due to unique environmental and chemical characteristics (dry and spiny shrub/forest vegetation) with several plant species that may be used as renewable oil sources for energy purposes and nutrition [4,5].

Much interest has been focused on the evaluation of the production potential of this biome, which contains more than 5344 plant species, many of which are not found anywhere else in the world [4]. A crucial point in this context is the bioprospecting of plant species present in the Brazilian Caatinga [6–14], among which are endemic ones that can be potentially useful as sources of valuable oil crops with potential applications for biofuel purposes. This perspective is in fact expected to add value to them and, at the same time, to contribute to food needs and to their sustainable use. Some representative oilseeds present in the Caatinga are shown in Figure 1.



Figure 1. Representatives of some oilseeds occurring in the Brazilian Caatinga that can be potentially used as alternative crops for energy purposes. (a) *Syagrus cearensis*; (b) *Syagrus coronata* (Mart.) Becc.; (c) *Attalea speciosa* Mart. ex Spreng.; (d) *Acrocomia aculeata* (Jacq.) Lodd. ex Mart.; (e) *Jatropha curcas* L.; (f,g) *Calophyllum brasiliense* Cambess. All images are from authors' original photo collection.

Based on this background, the aim of this review is the mapping of alternative vegetable oil crops present in the Caatinga biome, as well as an in-depth evaluation of the catalytic routes that could be used to exploit them as candidate feedstocks for biofuels production in Brazil. Moreover, to obtain a more detailed picture of these matrices, their main properties such as their oil contents and fatty acid profiles are presented. An overview of the synthesis processes of the different types of biofuels, particularly biodiesel and aviation biokerosene, is also presented and discussed, with emphasis on heterogeneous catalysts. Finally, the future outlook for renewable biofuels and the Caatinga biome is addressed.

2. Materials and Methods

To develop this review article, an extensive literature survey was performed on studies focused on alternative oilseed crops occurring in the Caatinga biome to be used for biofuel production in Brazil. A bibliographic and exploratory search for scientific papers was performed, regardless of the publication period, using five search databases, namely ScienceDirect (http://www.sciencedirect.com (accessed on 12 August 2022)), PubMed (https://pubmed.ncbi.nlm.nih.gov/ (accessed on 12 August 2022)), Google Scholar

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(https://scholar.google.com.br/ (accessed on 12 August 2022)), Scielo (https://scielo.org/ (accessed on 12 August 2022)) and Portal de periódicos CAPES (https://www.periodicos.capes.gov.br/ (accessed on 12 August 2022)), and the terms "oil seeds", "Caatinga" and "biofuels" as keywords. The collected results were checked and filtered (title, summary and methodology) based on information related to oil yield (>50%) and fatty acid composition as inclusion criteria.

In addition, the online platforms "Flora e Funga do Brasil" from Reflora (https://reflora.jbrj.gov.br/ (accessed on 12 August 2022)) and International Plant Names Index—IPNI (https://www.ipni.org (accessed on 12 August 2022)) were used to consult the scientific name of species in the selected articles and to obtain further information such as occurrence, botanical synonyms, among others. Figure 2 graphically summarizes the study methodology.

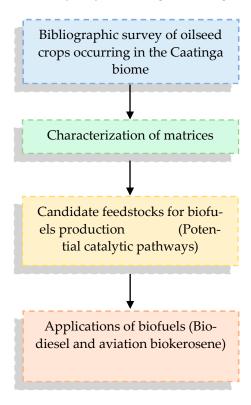


Figure 2. Research methodology flowchart.

3. Results

3.1. Biofuels as Renewable Energy Sources

Brazil has pledged to reduce greenhouse gas emissions together with the other countries participating in the Paris Agreement in 2015 (COP21), then confirmed in Glasgow in 2021 (COP26). Brazil's main role in this scenario is to preserve the Amazon through the control of deforestation. Moreover, among the various alternatives to mitigate greenhouse gas emissions, the most important is the one that directly concerns the energy matrix, i.e., the replacement of fossil fuels with renewable energy sources [15,16].

Brazilian public policies to encourage the use of biofuels began in the 1970s with the National Alcohol Program (Programa Nacional do Álcool—Proálcool). Biodiesel production gained importance in the 2000s with the National Biodiesel Production and Use Plan (Plano Nacional de Produção e Uso do Biodiesel—PNPB) in 2005, which established the gradual addition of biodiesel to fossil diesel, starting with 2% in 2004 (not yet mandatory) up to 13% in 2021 (mandatory); however, this proportion is not always fulfilled due to economic and political variables [17,18].

The PNPB also aims that biodiesel producers acquire raw material from small farmers, which guarantees them the Social Biofuel Seal. This allows the insertion of family farming

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and the diversification of potential raw materials in specific regions of the country, such as the Caatinga biome in the Northeast region [17].

In addition, the 2017 National Biofuels Policy (Política Nacional de Biocombustíveis—Renovabio) aims to ensure fuel supply, promote biofuels in the Brazilian energy matrix and reduce greenhouse gas emissions. Finally, in November 2021 the Biokerosene National Program (Programa Nacional do Bioquerosene) was established to encourage research and promote biomass-based energy production, aiming at the sustainability of Brazilian aviation [17,18].

This program meets international environmental impact mitigation policies such as the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA), which imposed in 2019 the measurement of carbon emissions of airlines on behalf of the International Civil Aviation Organization (ICAO); however, Brazil foresees to enter this stage only in 2027 [19].

Regarding the production and consumption of biofuels, Brazil stands out with bioethanol and biodiesel, being the second largest producer in the world with 27% of production, behind only the United States (42%). According to the data of the 2021 Brazilian Statistical Yearbook of the National Agency of Petroleum, Natural Gas and Biofuels (Anuário Estatístico Brasileiro de 2021 da Agência Nacional do Petróleo, Gás Natural e Biocombustíveis—ANP) [20], national biodiesel production has grown progressively since 2005, reaching approximately 6.8 million m³ in 2021, with an especially significant increase in the last 10 years (Figure 3).

Biodiesel Production - Brazil (m3)

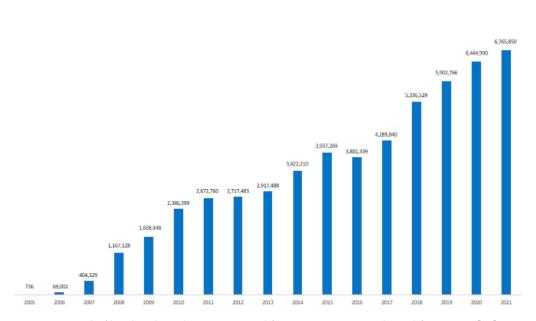


Figure 3. Trend of biodiesel production in Brazil from 2005 to 2021. Adapted from ANP [20].

It is important to note that plants would be able to ensure higher levels of production as they are operating below their nominal capacity (Figure 4) due to poor biodiesel demand. However, with the increase in the percentage of biodiesel in diesel, which is currently 13%, the complete operation of the plants will be reached [21].

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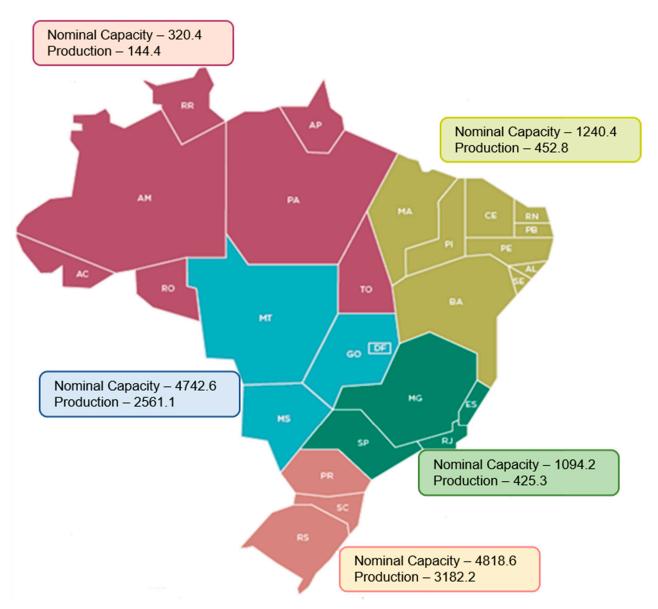


Figure 4. Nominal capacity and biodiesel (B100) production in the different Brazilian regions (thousands of m³/year). Adapted from ANP [20]. The different regions are highlighted with different colors (between rounds brackets): North (red), area: 3,853,676.9 km²; Northeast (dark yellow), area: 1,558,196 km²; Southeast (green), area: 924,511.3 km²; South (light brown), area: 576,409.6 km²; Center-West (light blue), area: 1,612,077.2 km².

The map of Figure 4 also reveals that the southern region has the highest biodiesel productivity (47%); however, so that production reaches its total capacity and, especially, covers the whole territory of the country, a diversification of the matrices is needed from which to extract vegetable oils. The southern and center-western regions lead production using soybean oil (72%) as the main matrix, followed by frying oil—waste made up of residual soybean oil (13%), animal fat (cattle, chicken and pig) (11%), and other vegetable oils—and by cotton, canola, sunflower, macaúba, corn, palm and palmist (4%) oils (Figure 5) [20].

Today, both bioethanol and biodiesel serve the road market (mainly cars and trucks), leaving a gap in the production of sustainable aviation fuels (SAFs). However, factors such as large agroindustrial production, and consequently large availability of bio-waste, vast territory and a well-developed internal air transport market place the country in a privileged position for SAF production. For a better understanding of the terms used

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to refer to SAFs, which are generically defined as fuels derived from renewable sources for use in aircraft, it is worth remembering that expressions such as "aviation biofuel", "alternative aviation kerosene" (alternative Jet) and "aviation biokerosene" (Biojet) are often indifferently adopted, among which the latter has been chosen in this study because it is the most common. In addition, according to ICAO, the features of aviation biokerosene are such that it can be mixed with fossil kerosene in any proportion (drop-in) without change in quality and without adaptation of aircraft engines, which allows use of the existing storage and transport infrastructure [22].

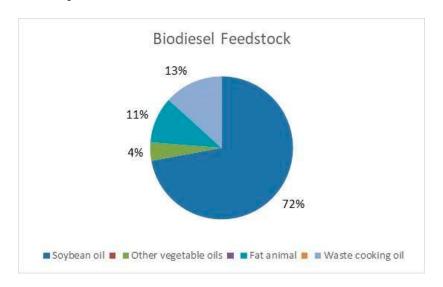


Figure 5. Matrices used in Brazil for biodiesel production. Adapted from ANP [20].

In Brazil, ANP regulates the production and distribution of aviation biokerosene through Resolution No. 856 of 22 October 2021 [23], which imposes that only one type of Biojet can be added to fossil kerosene (named Jet A) to prepare aviation kerosene (named Jet C) or simply Biojet, in maximum proportions established according to the synthesis processes described in Section 3.3.

Market analyses regarding the production and consumption of Biojet are organized by interest groups, such as universities, research centers, farmers' cooperatives, producers' associations, airlines and regulatory agencies making up the Brazilian Alliance for Biojet (ABRABA) and the Brazilian Biojet Platform (BBP), which lead research and join efforts to advance production, especially in the states of Minas Gerais, Pernambuco and Rio Grande do Sul [24,25].

In Pernambuco, the goal by 2030 is the "recovery of the semiarid zone to Caatinga" through (a) the revitalization of watersheds, aiming at the recovery of springs in permanent preservation areas, legal reserves and riparian forests, (b) the exploitation of oilseeds from the Caatinga and Atlantic Forest biomes, and (c) the insertion of familiar agriculture to promote the sustainable production of biomass for the biofuels segment. This objective is in accordance with both the Brazilian Forest Code (Law No. 12,651, of 25 May 2012) and the CORSIA criteria [24,25].

This scenario reinforces our effort in this work to map oilseeds of the Caatinga biome with potential for biodiesel and aviation biokerosene production as well as catalytic routes that may contribute to the technological development required by the Brazilian northeast region.

3.2. Mapping of Alternative Vegetable Oil Crops Occurring in the Caatinga Biome as Candidate Feedstocks for Biofuels Production

The data survey through the five search databases allowed identifying 123 species in 61 articles found in the literature, among which, after careful evaluation, only 16 species met the inclusion criteria established for this review, which means that about 87% of

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the species found were excluded. However, eight of them [Allagoptera arenaria (Gomes) Kuntze—guriri/paissandu, Cnidoscolus urens (L.) Arthur—urtigão/pinha-queimadeira, Arachis pusilla Benth.—mandubim, Scaevola plumieri (L.) Vahl—mangue-da-praia, Trichilia elegans A.Juss.—pau-ervilha, Trichilia hirta L.—catiguá, Agonandra brasiliensis Benth. & Hook.f.—pau-marfim, and Agonandra excelsa Griseb.—pau-cascudo/pau-marfim], investigated by Harand et al. [26] as alternative oilseeds from northeastern Brazil, despite showing satisfactory oil extraction yields (>50%), did not have their oils characterized in terms of fatty acid composition; therefore, they were disregarded in the present study as well.

Examining all the 14 scientific articles taken for analysis, oils from 11 plant species belonging to 7 different families (Table 1) have already been reported for use in biofuels, namely *Acrocomia aculeata* (Jacq.) Lodd. ex Mart.—macaúba, *Attalea speciosa* Mart. ex Spreng. formerly known as *Attalea vitrivir* Zona—babassu [8], *Caryocar brasiliense* Cambess.—pequi, *Cascabela thevetia* (L.) Lippold. synonym *Thevetia peruviana*—chapéu-de-napoleão, *Jatropha curcas* L.—pinhão-manso, *Syagrus cearensis*—catolé, *Syagrus coronata* (Mart.) Becc.—licuri, *Serjania caracasana* (Jacq.) Willd.—cipó-leiteiro, *Serjania salzmanniana* Schltdl.—cipó-timbó, *Virola surinamensis* (Rol. ex Rottb.) Warb.—ucuúba, and *Ximenia americana* L.—ameixado-mato), while the other 5 species, belonging to 5 different families, namely *Pachira retusa* (Mart.) Fern.Alonso formely known as *Bombacopsis retusa* (Mart. and Zucc.) A. Robyns [27], *Calophyllum brasiliense*—guanandi, *Platonia insignis* Mart.—bacuri, *Fevillea trilobata* L.—gindiroba, and *Virola sebifera* Aubl.—mucuíba, have not been used so far in this field.

The applicability of oil from plants depends on several factors, such as seed oil content and fatty acid profile. Considering these properties, it is possible to have a first glimpse of the performance of the analyzed plants as alternative sources of oil from tropical flora (Table 1).

According to this table, the oil extraction yields of the reviewed species ranged from 50 to 78%. For instance, Iha et al. [28], Lieb et al. [29], Pascoal et al. [2] and Oliveira et al. [30] obtained yields of oil extraction from licuri/ouricuri, macaúba/macaíba, catolé/coco-babão and babassu/babaçu of 50, 56, 57 and 65%, respectively, while Faria-Machado et al. [31] reported a yield of 78% from pequi.

It is also possible to observe that the oilseeds have different fatty acid compositions (Table 1), with a predominance of oleic acid (C18:1) in the oils of ameixa-do-mato (72.09%), pequi (64.66—67.59%) and pinhão-manso (55.7%), of lauric acid (C12:0) in those of babassu (50.8%), licuri (48.0%) and catolé (45.66%), myristic acid (C14:0) in those of mucuíba (71.0%) and ucuúba (71.66%), and gadoleic acid (C20:1) in those of cipó-leiteiro (69.4%) and cipó-timbó (64.7%). In addition, palmitic (C16:0), linoleic (C18:2) and linolenic (C18:3) acids were the major fatty acids in the oils of *P. retusa* (Mart.), guanandi and gindiroba, averaging 59.98, 41.32 and 39.0%, respectively.

Taken as a whole, these compositions are in agreement with the widespread conviction [1,4,32,33] that exotic plants occurring in the semi-arid Caatinga of northeastern Brazil have potential as renewable oil sources for diffrent biofuels, particularly biodiesel and aviation biokerosene, which will be the focus of the following sections of this review.

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Table 1. Characterization of matrices occurring in the Caatinga biome as potential feedstocks for biofuels production.

Family <i>Species</i> (Popular Name)	Studied Part	Occurrence	Vegetation Type	Oil Yield	Major Components ^a	Extraction Technique	Reference
Apocynaceae Cascabela thevetia (L.) Lippold., synonym Thevetia peruviana (chapéu-de-napoleão) Arecaceae	Seed	NE, N, S, SE, CW	Shrub	60–65%	18:1 (43.4%)	Soxhlet, Hexane	[34]
Arecaceae Acrocomia aculeata (Jacq.) Lodd. ex Mart. (macaúba/macaíba/mucajá) Attalea speciosa Mart. ex	Seed	N, NE, CW, SE	Arboral /palm	56.1%	12:0 (42.9%)	Soxhlet, Hexane	[29]
Spreng., formerly known as Attalea vitrivir Zona, synonym Orbignya phalerata (babassu/babaçu)	Almonds	N, NE, CW, SE	Arboreal /palm	65.0%	12:0 (50.8%)	Mechanical pressing	[8,30]
Syagrus cearensis (catolé/coco-babão)	Almonds	NE	Arboreal /palm	57.0%	12:0 (45.66%)	Hydraulic press, Ultrasonic-assisted in situ transesterification	[2]
Syagrus coronata (Mart.) Becc. (licuri/ouricuri) Bombacaceae	Nuts/Almonds	NE, SE	Arboreal /palm	50.0%	12:0 (48.0%)	Pressing by hydraulic press	[28]
Pachira retusa (Mart.) Fern.Alonso, formerly known as Bombacopsis retusa (Mart. & Zucc.) A. Robyns, (ND)	Seeds	NE, SE	Arboreal/Tree	55.60%	16:0 (59.98%)	Soxhlet, Hexane	[27,35]
Calophyllaceae Calophyllum brasiliense Cambess. (guanandi) Caryocaraceae	Almonds	N, NE, CW, SE, S	Arboreal	58.20%	18:2 (41.32%)	Maceration, Hexane	[36]
Caryocar brasiliense Cambess. (pequi)	Pulp	N, NE, CW, SE, S	Shrub, Tree, Sub-shrub	78.5%	18:1 (64.66–67.59%)	Soxhlet, Petroleum ether	[31]

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 Table 1. Cont.

Family <i>Species</i> (Popular Name)	Studied Part	Occurrence	Vegetation Type	Oil Yield	Major Components ^a	Extraction Technique	Reference
Clusiaceae Platonia insignis Mart. (bacuri)	Seeds	N, NE	Arboreal	63.0%	18:1 (27.59%)	Soxhlet, Hexane	[37]
Cucurbitaceae Fevillea trilobata L. (gindiroba)	Almonds	NE, CW, SE, S	Liana	65–66%	18:3 (39.0%)	Soxhlet	[38]
Euphorbiaceae Jatropha curcas L. (pinhão-manso/pinhão- branco/pião-branco) Myristicaceae	Seeds	N, NE, CW, SE, S	Arboreal	53.4%	18:1 (55.7%)	Soxhlet, Hexane	[39]
Virola sebifera Aubl. (mucuíba/bicuíba/ucuúba)	Almonds	N, NE, CW, SE	Arboreal	69.0%	14:0 (71.0%)	Soxhlet, Hexane	[40]
Virola surinamensis (Rol. ex Rottb.) Warb. (ucuúba)	Seeds	N, NE, CW	Arboreal	64.39%	14:0 (71.66%)	Supercritical CO ₂	[41]
Olacaceae Ximenia americana L. (ameixa-do-mato) Sapindaceae	Seeds	N, NE, CW, SE, S	Shrub, Tree	49.9%	18:1 (72.09%)	Soxhlet, Petroleum ether	[42]
Serjania caracasana (Jacq.) Willd. (cipó-leiteiro/timbó)	Seeds	N, NE, CW, SE, S	Liana	66.6%	20:1 (69.4%)	Soxhlet, Hexane	[39]
Serjania salzmanniana Schltdl. (cipó-timbó)	Seeds	N, NE, CW, SE	Liana	67.4%	20:1 (64.7%)	Soxhlet, Hexane	[39]

ND: Not determined; ^a Fatty acids: C18:1 = oleic acid; C12:0 = lauric acid; C16:0 = palmitic acid; C18:2 = linoleic acid; C18:3 = linolenic acid; C14:0 = myristic acid; C20:1 = gadoleic acid. CW = Center-West; N = North; NE = Northeast; S = South; SE = South-East.

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3.3. Biofuel Catalytic Routes for Selected Oil Seeds Occurring in the Caatinga Biome

3.3.1. Biodiesel Synthesis Processes

In this survey of catalytic routes for biodiesel production, it is important to provide a brief explanation of each of them, i.e., esterification (usually a pretreatment), transesterification, pyrolysis, ultrasound process and reactive distillation, with the first two, approved by ANP, being used by the main Brazilian factories in this field.

i. Esterification

Biodiesel is a biofuel derived from renewable feedstocks obtained by esterification, which consists of the reaction of free fatty acids with an alcohol (more often methanol or ethanol) with formation of an alkyl ester and water (Figure 6). The reactivity of different fatty acids as well as the use of different catalysts is often the focus of experimental studies.

Figure 6. General chemical equation of the esterification reaction.

The esterification process makes use of lower-cost raw materials compared to the transesterification one. It is a process that can be catalyzed by acids; in the presence of a strong acid such as sulphuric acid (H_2SO_4) or hydrochloric acid (HCl) and an alcohol at reflux temperature, it reaches equilibrium in a short time with formation of an ester as a product with good yield [43].

ii. Transesterification

The transesterification process consists of the reaction of triacylglycerides (also called triacylglycerols) (TAGs) with an alcohol (methanol or ethanol) (Figure 7). This process leads to the synthesis of methyl or ethyl esters of fatty acids (biodiesel) and glycerol as a byproduct, which is removed by decantation. Fatty acid esters formed have less viscosity than triacylglycerols used as raw material.

Figure 7. General chemical equation of the transesterification reaction.

As for esterification, the reactivity of different TAGs is often studied employing different catalysts to accelerate the reaction. Among the homogeneous catalysts, the most commonly used alkaline catalysts are sodium hydroxide (NaOH) and potassium hydroxide (KOH), while sulfuric acid (H_2SO_4), sulfurous acid (H_2SO_3) and hydrochloric acid (HCl) are the acidic counterparts; on the other hand, heterogeneous catalysts include metal oxides, mixed or doped metal oxides, zeolites, layered double hydroxides, organic bases, ion exchange resins, as well as natural catalysts such as enzymes (lipases) [44].

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iii. Pyrolysis

The pyrolysis process, employed for energy generation, consists of thermal degradation, under high temperature and in the presence of little or no oxygen, of any organic material. This process, which leads to the rupture of the original molecular structure of a given compound by the action of heat, can be used for the TAGs' conversion, under external heating, into alkanes, alkenes, alkadienes, aromatic compounds and carboxylic acids, in the presence or not of a catalyst. It is usually performed at a temperature of around 300 °C until the beginning of intensive gasification under atmospheric pressure.

Pyrolysis has significant advantages over other methods, including raw material flexibility, no need of pretreatment to remove impurities, cheap catalysts and low environmental impact features, among which are reduced greenhouse gas emissions. For these reasons, pyrolysis is considered one of the most promising processes to refine TAGs [45].

iv. Ultrasound Process

By interacting with matter, ultrasound radiation causes physical and chemical transformations that occur due to the interaction of radiation with matter. Ultrasound is a vibration of the same physical nature as sound, but with frequencies above the ones perceived by human hearing. This process is used in chemical reactions to develop or improve reaction outcomes, such as increasing yield and/or reducing time. Among the numerous reactions to which it can be applied, the transesterification reaction stands out. Because the transesterification reaction occurs at the interface of two liquid–liquid phases that are immiscible with each other, it is necessary to create the same time late to achieve the stability of the mixture before the beginning of the reaction. Therefore, the function of ultrasound is to provide mechanical energy for the mixture and activation energy necessary to initiate the transesterification reaction.

With the advent of environmental sustainability, ultrasounds can be used at various stages of biodiesel synthesis aiming at green chemistry. Ultrasounds can be divided into two groups based on frequency and power: ultrasounds of high frequency and low power are mainly used in medicine, while those of low frequency and high power in chemistry. Ultrasound-assisted reactions are aided by the presence of cavitation and can be divided into four large categories according to the type of induction, namely, particle, optic, acoustic and hydrodynamic cavitation. Cavitation can be defined as formation, growth and collapse of a bubble inside a liquid, releasing a large amount of energy in a small area around it [46].

v. Reactive Distillation

Reactive distillation is a process intensification technique that combines chemical reaction and separation by distillation into a single equipment, and is therefore considered a multifunctional unit process. Because these two operations usually happen separately and in sequence in chemical process industries, their integration can increase the global performance of the production line.

This technique, which can be applied to reactions such as hydrogenation, isomerization, hydrolysis, alkylation, esterification and transesterification among others, can be an alternative to conventional processes [47].

3.3.2. Biodiesel Production from the Selected Oil Seeds Occurring in the Caatinga Biome

Regarding the catalytic routes described in the literature for the selected oilseeds occurring in the Caatinga biome, the most important results are summarized here on the use of the 11 species already reported for biofuels production, which were listed in Section 3.2.

i. Macaúba (Acrocomia aculeata)

Iha et al. [28] conducted a study on the production and characterization of biodiesel from macaúba ($Acrocomia\ aculeata$) oil using either H_2SO_4 or KOH dissolved in methanol as a catalyst. Souza et al. [48] evaluated the stability to oxidation of biodiesel produced

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from the same oil using H_2SO_4 dissolved in ethanol as a catalyst, while in a similar study Santos et al. [49] compared the process performance using ethyl and isopropyl alcohols.

As for heterogeneous catalysis, Prado et al. [50] investigated biodiesel production from macaúba oil using a mixture of calcium and aluminum oxides (CaO/Al_2O_3) as catalyst in both methanol and ethanol. On the other hand, Ramos et al. [51] employed *Burkholderia cepacia* lipase immobilized in silica–polyvinyl-alcohol and ethanol for biodiesel production via enzymatic catalysis from the same oil.

ii. Babassu (Attalea speciosa)

Paiva et al. [52] reported good biodiesel yields for babassu (*Attalea speciosa*) oil transesterification with ethanol using KOH or NaOH as catalyst either in a conventional magnetically stirred reactor or in another with ultrasound irradiation. Ferrari and Soler [53] synthesized biodiesel from the same oil with ethanol using sodium methoxide (NaOCH₃) as a catalyst, while, in a similar study, Girardi et al. [54] also tested natural additives such as isoamyl alcohol, camphor and limonene to improve biodiesel production. Oliveira et al. [55] first studied the effect of alcohol chain length from C1 to C8 on biodiesel production from babassu oil, and then, using ethanol, tested different catalysts such as KOH, H₂SO₄ and *p*-toluenesulfonic acid to obtain ethyl esters.

For heterogeneous catalysis, Carvalho et al. [56] used strontium oxide (SrO), strontium carbonate (SrCO₃) and strontium hydroxide [Sr(OH)₂] as catalysts to produce biodiesel from both babassu oil and a mixture of this oil with other oilseed oils. For the enzymatic route, Andrade et al. [57] employed seven different lipases as catalysts for biodiesel production from the same oil using ethanol, while Da Rós et al. [58] reported an enzymatic route in which *B. cepacia* lipase immobilized in silica–polyvinyl-alcohol was applied using either the conventional method with magnetic stirring or microwave irradiation. Differently, Moreira et al. [59] used residual babassu oil, ethanol and lipase extracted from the *Candida antarctica* yeast as a catalyst.

iii. Pequi (Caryocar brasiliense)

Several authors reported the production of biodiesel from oils of pequi (*Caryocar brasiliense*) and of its seed using KOH and NaOCH₃ as catalysts and methanol [60–63], while Guimarães [64] and Santos et al. [49] studied the effect of the type of alcohol (methanol, ethanol or isopropanol) on the same production from the seed oil using H_2SO_4 as a catalyst.

On the other hand, Souza et al. [65] reported the pyrolytic production of biodiesel from pequi oil, pretreated by H_2SO_4 -catalyzed esterification of free fatty acids, using cerium dioxide (CeO₂), cobalt oxide (CoO) and HUSY zeolite as catalysts, while Guimarães et al. [66] employed a synthetic zirconium-based catalyst for transesterification with ethanol.

iv. Chapéu-de-napoleão (Cascabela thevetia)

As usually occurs in homogeneous catalysis, also the transesterification of chapéude-napoleão (*Cascabela thevetia*) oil was performed with methanol or ethanol employing alkaline catalysts (NaOH and KOH) and, when necessary, pretreatment with H₂SO₄ [67–71].

A very promising class of heterogeneous catalysts under study is that of catalysts derived from natural sources, also called biocatalysts, which are obtained for example from eggshells, snail shells, and barks of plants such as noz-de-cola (*Cola acuminata*) and banana trees [72–74]. Some authors have developed an innovative methodology to prepare heterogeneous catalysts from trunk barks of *Musa balbisiana* and *Musa paradisiaca*, two banana species, to be used for biodiesel production from chapéu-de-napoleão oil. Characterization by particle-induced X-ray emission (PIXE) of dried bark powder revealed, after calcination at 500 °C for 3.5 h, the presence of Al, Si, P, S, Cl, K, Ca, Mn, Fe, Zn, Rb and Sr in its chemical composition [75,76]. In addition to these natural catalysts, metal oxides are also reported to produce biodiesel from the same oil, including a nanostructured zinc oxide catalyst supported in titanium/zinc oxide (TiO₂-ZnO) [77], CaO and calcium carbonate (CaCO₃) [78,79] for biodiesel production from the same oil.

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v. Pinhão-manso (Jatropha curcas L.)

To perform a complete analysis of the life cycle of biodiesel from pinhão-manso (Jatropha~curcas~L.), Prueksakorn and Gheewala [80] investigated the energy consumption of the transesterification reaction with NaOH and methanol for a period of 20 years, thus showing the importance of investment in the cultivation of this species to produce biodiesel. Many other authors employed NaOH or KOH as catalyst [81–85], while only a few opted for the acidic catalysis with HCl or H_2SO_4 [86–90], to investigate different reaction parameters, such as temperature, catalyst dosage, types of solvent, co-solvent and alcohol, as well as the effect of stabilizers.

ANR et al. [91] reported biodiesel production from the oil of pinhão-manso using nanostructured CaO heterogeneous catalysts in the methyl route. Transesterification of this oil has widely been tested using lipases from *Chromobacterium viscosum*, *Candida rugosa*, *C. antarctica*, *B. cepacia* and porcine pancreas, in conventional systems or using ultrasounds. Typical advantages of this route are the low reaction temperature and consequently the low energy expenditure [92–94], but as enzymes are often expensive and sensitive to the reaction environment [95–98], a careful assessment of reaction parameters and applicability is required.

vi. Catolé (Syagrus cearensis)

Only traditional homogeneous catalysts such as NaOH, KOH, HCl and H_2SO_4 have so far been employed in studies on production of biodiesel from catolé (*Syagrus cearensis*) oil by the methyl route and its characterization, with the only difference in conditions being between the use of conventional and ultrasound-assisted transesterification [2,99].

vii. Licuri (Syagrus coronata)

To date, the synthesis of biodiesel from licuri ($Syagrus\ coronata$) oil via the methyl route has been investigated using only traditional homogeneous catalysts, either alkaline, namely NaOH, KOH and NaOCH₃, or acid, such as $H_2SO_4\ [28,100,101]$.

viii. Cipó-leiteiro (Serjania caracasana Willd.) and Cipó-timbó (Serjania salzmanniana Schltdl.)

Coutinho et al. [39] investigated the production of biodiesel by the methyl route from six different oilseeds oils, including those of cipó-leiteiro ($Serjania\ caracasana$) and cipó-timbó ($Serjania\ salzmanniana$), for which either H_2SO_4 or KOH was used as catalyst.

ix. Ucuúba (Virola surinamensis (Rol. ex Rottb.) Warb.)

Lacerda, Jr. [102] reported biodiesel production from the oil of ucuúba (*Virola surinamensis*) using both homogeneous catalysis, with HCl or KOH, and heterogeneous catalysis, with ferric sulfate $[Fe_2(SO_4)_3]$.

x. Ameixa-do-mato (Ximenia americana L.)

Shentil et al. [103] conducted an interesting study on biodiesel production from ameixado-mato (*Ximenia americana*) oil through a two-step process consisting of one step via heterogeneous catalysis and another via homogeneous catalysis. In the former step, the esterification of free fatty acids was catalyzed using a zeolite modified by reaction with phosphoric acid (H_3PO_4), while in the latter the transesterification was catalyzed with KOH. Indeed, in 2009 Hariharan et al. were successful already in transesterifying the oil of this oilseed with KOH at 70 °C without agitation for 1 h [104].

A summary of this information on the various oilseed matrices and the results in terms of percentage yield of biodiesel are gathered in Table 2.

It can be seen in the table that the use of most catalysts resulted in very high biodiesel yields, often above 75%. Among the homogeneous, heterogeneous and enzyme catalysts, the homogeneous ones are still the most common, but their number is rather limited; on the other hand, heterogeneous and enzyme catalysts come from a wide variety of materials or species, respectively, whose number is continuously growing thanks to the promising results of innovative research in this field. In particular, heterogeneous catalysts offer the

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opportunity to resort to materials with various structures, including metal oxides, zeolites, mesoporous materials, clay, resins, lamellar materials and nanoparticles, or can be used as supports for homogeneous catalysts, with the additional advantage of allowing their easy separation and reuse.

Table 2. Conditions of biodiesel production from oils of oilseeds occuring in the Caatinga biome and
related results in terms of percentage yield of biodiesel.

Feedstock	Homogeneous Catalyst	Heterogeneous Catalyst	Enzyme Catalyst (Lipase)	Catalyst Dosage (%)	Temperature (°C)	Time (h)	Yield (%)	Ref.
Macaúba	KOH, H ₂ SO ₄	CaO, Al ₂ O ₃	Burkholderia cepacia	1–10	25–115	1.5–16	94–98	[48–51]
Babassu	KOH, H ₂ SO ₄ , NaOCH ₃	SrO, SrCO ₃ , Sr(OH) ₂	Burkholderia cepacia Candida antartica	0.05-20	30–100	0.2–120	16–99	[52–59]
Pequi	KOH, NaOCH ₃ , H ₂ SO ₄	CeO ₂ , CoO, Zeolite HUSY, PRZr	_	1–50	30–100	0.5-24	67–96	[60–66]
Chapéu-de- napoleão	NaOH, KOH, H ₂ SO ₄	Musa balbisiana Musa paradisiacal CaCO ₃ , CaO, TiO ₂ -ZnO, Cola acuminata	_	0.1–20	30–70	0.2–5	66–97	[67–77]
Pinhão-manso	NaOH, KOH, H ₂ SO ₄ , HCl,	CaO, Co-Mo/Al ₂ O ₃ , Ni-Mo/Al ₂ O ₃	Candida rugosa Chromobacterium viscosum Porcine pancreas Candida antartica	0.01–30	30–200	0.3–48	80–98	[80–98]
Catolé	KOH, NaOH, HCl	_	_	1–5	60-65	0.5-2	97–99	[2,99]
Licuri	KOH, NaOH, NaOCH ₃ , H ₂ SO ₄	ZnO	_	5–20	30	0.6-4	91–98	[28,100,101]
Cipó-leiteiro	KOH, H ₂ SO ₄	_	_	0.5-1	60	1	97	[39]
Cipó-timbó	KOH , H_2SO_4		_	0.5–1	60	1	97	[39]
Úcuúba Ameixa-do-mato	HCl, KOH KOH	$Fe_2(SO_4)_3$	_	0.5–2 1	80–90 70	2–4 1	20–88 92	[102] [103,104]

3.3.3. Biojet Synthesis Processes

Figure 8 shows, in a schematic way, the Brazilian national evolution in the production of aviation biokerosene, with a timeline of regulatory acts representing when each process was approved by ANP and the last update having been published in ANP Resolution No. 856 of 22 October 2021 [23].



Figure 8. Timeline of ANP approval of processes for the production of aviation biokerosene in Brazil.

This 2021 resolution considers as aviation fuels: (a) JET A or JET A-1 aviation kerosene (maximum freezing point of -40 or -47 °C, respectively), either of fossil origin, (b) alternative aviation kerosene (alternative JET), a fuel derived from alternative sources, such as biomass, vegetable oils, animal fat, residual gases, solid waste, coal or natural gas, and (c) JET C aviation kerosene, a "drop-in" fuel composed of a single type of alternative JET mixed with JET A or JET A-1 in proportion depending on the type of alternative JET process, but not exceeding 50%.

Aviation biokerosene has the advantage of combining biofuels production with agriculture and livestock, both strongly developed in the country; therefore, a huge amount of organic waste can be used as a raw material in different aviation biokerosene processes, which are described below.

i. SPK-FT (Synthetic Paraffinic Kerosene—Fischer-Tropsch). The raw materials used in this process are urban solid waste, agricultural and forest waste, as well as natural gas and coal. First, biomass is gasified in an oxidizing atmosphere to

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generate syngas (mainly CO and H_2), which is then converted to hydrocarbons mainly employing cobalt- or iron-based catalysts supported or not on zeolites or mesoporous materials. The former, more efficient at high temperatures, lead to the formation of n-paraffins, while the latter, used at low temperatures, produce α -olefins and oxygenated compounds. Steps of deoxygenation and fractionation are required to produce liquid paraffins similar to those of petroleum-based kerosene (C9–C15) and that can be mixed with it in various proportions up to a maximum percentage of 50% [105].

- ii. SPK-HEFA (Synthetic Paraffinic Kerosene—Hydroprocess of Esters Fatty Acids). The hydrogenation of free fatty acids and fatty acid esters or vegetable and animal fats is basically the deoxygenation of triglycerides under conditions of temperature between 250 and 450 °C and hydrogen pressure between 10 and 300 bar in the presence of specific catalysts. After this step, isomerization is performed to adjust carbon chains in the desired hydrocarbon fractions, thus leading to an alternative biokerosene that can be mixed up to 50% with aviation kerosene. Since most of the oilseeds that serve as raw materials, such as licuri, catolé, macaúba, babassu, etc., are found in the Caatinga biome, this process has great potential to be applied in the northeast region of Brazil. In addition, the oil of these raw materials, which is the fraction of interest to produce aviation biokerosene, often has lauric acid (C12:0) as one of its main components, which can reduce the need for the above-mentioned isomerization step [106].
- iii. SPK/A (Synthetic Paraffinic Kerosene—Aromatic). The SPK-FT process described above usually does not produce cyclic and aromatic hydrocarbons, which are typically found in oil-based aviation fuel; therefore, the process can be complemented by the addition of light aromatics, while the raw materials used for gasification are the same, i.e., urban or agroforestry solid waste. The addition of aromatic structures, mainly obtained by benzene alkylation, prevents fuel leaks, as it ensures the quality of seals in the aircraft components. Since the biokerosene produced by this process is made up of the same components found in the fossil kerosene, its full replacement would be technically possible if a 50% maximum blend were not imposed [105].
- iv. SPK/ATJ (Synthetic Paraffinic Kerosene—Alcohol to Jet). Biomass employed in the alcoholic fermentation of starch and sugars includes beets, sugarcane, corn, saccharine, sweet sorghum and tubers or derivatives of cellulosic biomass obtained by lignocellulose hydrolysis. Alcohol can also originate from biochemical conversion of other forms of hydrogen and carbon through the action of organisms able to convert CO, H₂ and CO₂. Processing of ethyl or isobutyl alcohol occurs through successive dehydration and oligomerization reactions followed by hydrogenation and fractionation. The step of alcohol dehydration employs acidic catalysts such as alumina, silica-alumina, zeolites (e.g., ZSM-5 and Y), silicoaluminophosphates and ion exchange resins such as Amberlyst and Nafion, while Ziegler-Natta-type catalysts, i.e., organometallic complexes and organoaluminum catalysts, are traditionally used for oligomerization. Even the biokerosene produced by this process can be mixed with aviation kerosene in a maximum proportion of 50% [107].
- v. SIP (Synthetic Isoparaffins). The biochemical route known as "Direct Sugar to Hydrocarbon" consists of sugar fermentation followed by hydrogenation performed by genetically modified strains of the yeast *Saccharomyces cerevisiae*, which allow directly obtaining hydrocarbons. The process leads to farnesene hydrogenation to farnesane (Figure 9), which is later mixed with aviation kerosene in a 10% maximum blend, as it is made up only of iso-paraffins [108].

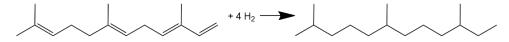


Figure 9. Reaction of farnesene hydrogenation to farnesane.

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vi. CHJ (Catalytic Hydrothermolysis to Jet). Similar to SPK-HEFA, catalytic hydrothermolysis uses vegetable or animal fatty acids and fatty acid esters as raw materials to produce a bio-oil, which is then submitted to hydrotreatment, hydrocracking or hydroisomerization and other conventional refinery steps, including fractionation, thus resulting in a biokerosene composed of *n*-paraffins, iso-paraffins, cycloparaffins and aromatic compounds. Even so, a maximum proportion of 50% is established for its blend with aviation kerosene [109].

vii. SPK-HC-HEFA ou SPK-HH (Hydroprocess of Hydrocarbons and Esters Fatty Acids). In this process, also similar to SPK-HEFA, only hydrocarbons (tri-terpenes) and fatty acid esters of the microalga *Botryococcus braunii* are hydroprocessed. The process consists of the extraction of hydrocarbons, deoxygenation (or hydrogenation) to remove oxygen and other undesirable compounds, cracking and isomerization. This alternative kerosene can be added to oil-based aviation kerosene up to a maximum proportion of 10% [110].

Table 3 summarizes the processes to produce aviation biokerosene in Brazil, with indication of the starting biomass, the pretreatment step and the steps of conversion with the main catalysts employed.

Process	Feedstock (Biomass)	Pre-Treatment	Intermediate Product	Conversion Process	Catalysts	Blend (%)	Ref.
SPK-FT SPK-FT/A	Solid waste (agricultural or urban)	Gasification	Syngas (CO + H ₂)	Hydrocracking/ distillation	Fe, Co sup. zeolites; mesoporous materials	50	[105]
SPK-HEFA	Vegetable and animal fats	Neutralization	Hydrocarbons	Hydrocracking/ distillation	Pd, Ni, Pt sup. activated carbon; zeolites	50	[106]
SPK-ATJ	Sugar, starch and cellulose	Fermentation	Ethanol and isobutanol	Dehydration/ oligomerization/ hydrogenation/ distillation	Ziegler-Natta catalysts, zeolites; ionic resins	50	[107]
SIP	Sugar cane	Extraction	Sugar	Fermentation/ hydrogenation	Ni, Pt, Rh, Pd complexes	10	[108]
СНЈ	Vegetable and animal fats	Catalytic hydrothermol- ysis	Bio-oil	Hydrogenation/ distillation	Ni and Pt supported on activated carbon	50	[109]
SPK-HH	Microalga Botryococcus braunii	Extraction	Bio-derived hydrocarbons	Hydrogenation/ cracking/ Isomerization	Ni, Mo, Co, Pd, Pt, Ru supported on zeolites	10	[110]

Table 3. Summary of processes in use in Brazil to produce Biojet.

Technological routes are complex and involve many additional steps, but it is important to understand that these steps depend on starting biomass, and for this reason the choice of the raw material is crucial. Moreover, the type of raw material chosen for the process influences the potential gains in terms of greenhouse gas reduction, because when considering the life cycle of cultivated species, all emissions associated with production should be accounted for. In this sense the option of using waste, in general of agricultural origin, is always an advantage [22].

To get an idea of this influence on greenhouse gas emissions, Carvalho analyzed the life cycle of two processes for aviation biokerosene production in Brazil, i.e., the SPK-FT process applied to wood waste that allowed a 94% reduction in emissions, and the SPK-HEFA one using soybean oil whose reduction was 52% compared to the use of fossil kerosene [111].

It is also noteworthy that the cost of raw material, which accounts for 60 to 75% of the total cost of production, is considered the main barrier to a sustainable economy [112]; therefore, the most viable alternatives would be the use of industrial and agricultural waste and, for the processes employing plant oils, the diversification of oilseeds.

Even though the six processes approved by ANP and summarized in Table 3 are more complex than presented here, all of them have the possibility of being employed in the current refineries of the country. This is especially true for the SPK-HEFA and CHJ

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processes, as they would diversify oilseed agriculture according to the biome of each region of the country, especially that of Caatinga in the Northeast, which shows the great Brazilian potential to expand the production of aviation biokerosene. The processes employed to produce aviation biokerosene are marked by growing technological advances to meet the market demand, so debate by the whole community involved in the production chain is essential.

Regarding the availability of raw materials in Brazil to produce aviation biokerosene, there are recent studies considering either wastes, such as sugarcane bagasse and straw, wooden waste, exhausted frying oil, bovine tallow, and Linz-Donawitz gas, or even specific biomass, including sugarcane, pinhão-manso, soy and eucalyptus [22,113]. This survey opens a window to the biodiversity of oilseeds, especially taking into account the regional context of the Brazilian Northeast in the selection of species occurring in the Caatinga biome.

3.3.4. Oilseeds with Potential for Use in Biojet Synthesis in Brazil

Studies on the use of macaúba (*A. aculeata*), babassu (*A. speciosa*), pinhão-manso (*J. curcas* L.) and licuri (*S. coronata*) to produce aviation biokerosene are reviewed in this section.

i. Macaúba (A. aculeata)

Moreira et al. [114] carried out the synthesis of biokerosene by the SPK-HEFA process from macaúba pulp oil using cobalt supported on commercial (Co/CAC) or macaúba endocarp-derived (Co/EAC) activated charcoal as a catalyst. The deoxygenation reaction was performed in dodecane for 2 h at 350 °C and 30 bar H_2 , under agitation at 300 rpm, using a 1:3 (w/w) oil:solvent ratio and a 10% (w/w) catalyst dosage. The use of Co/EAC as a catalyst allowed a 96% degree of deoxygenation, with 94% of products being hydrocarbons, as well as the exploitation of both macaúba mesocarp and endocarp in the production of aviation biokerosene.

Freitas et al. [115], after preliminary hydrolysis for 30 min in ethanol under reflux at a 1:5 (w/v) oil:KOH ratio, utilized the same process to deoxygenate macaúba pulp oil for 3 h at 350 °C and 10 bar H₂, under agitation at 700 rpm using Beta (25 Si/Al ratio; B25) and ZSM-5 (50 Si/Al ratio; Z50) zeolites as catalysts. The authors observed, with the former catalyst, a 100% deoxygenation degree and the formation of aromatic and saturated compounds, with predominance of pentadecane (compatible with biokerosene), while a lower deoxygenation degree (80%) was obtained with the latter, with the prevalent formation of aromatic compounds such as o-xylene and p-xylene.

Vilalva [116] performed the synthesis of biodiesel from macaúba almond oil followed by distillation to obtain biokerosene. Transesterification occurred in methanol via homogeneous catalysis with 1% (w/w) NaOH at a 1:6 molar ratio with respect to oil and 60 °C, under agitation for 2 h. Atmospheric distillation of methyl esters, performed at 214–266 °C on a conventional system with a Vigreux column, allowed recovering mainly (82%) C8–C14 hydrocarbons, with prevalence (67%) of C12. Azevedo [117] also obtained biokerosene through biodiesel production and fractional distillation, but from macaúba pulp oil. Transesterification was done in methanol via acidic catalysis with 1% (w/w) H₂SO₄, using a 1:8 mass ratio with respect to oil, at 74 °C, under agitation for 4 h, reaching a 96% yield. In subsequent fractional distillation under atmospheric pressure at 110–224 °C, a 60% yield in biokerosene hydrocarbons was obtained.

ii. Babassu (A. speciosa)

Llamas et al. [118] studied the production of biokerosene from biodiesel obtained from babassu oil by homogeneous catalysis. The oil was processed by esterification with p-toluenesulfonic acid and transesterification with 25% (w/w) NaOCH $_3$ in methanol, and the resulting biodiesel was subjected to fractional distillation (124–359 °C; 2.66 × 10 $^{-3}$ bar) that allowed separating a major fraction (69%) of methyl laurate (C12). Analyzing the main features, it was added to fossil kerosene in blends of 5, 10 and 20% (v/v), with the intermediate one being the most viable in compliance with ASTM D1655-09 standards.

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Oliveira [119] produced biokerosene by molecular distillation of babassu biodiesel obtained by homogeneous catalysis via transesterification with methanol (alcohol:oil ratio of 6:1) and 1.5% (w/w) NaOH at 60 °C for 1 h. Biodiesel, obtained with 97% yield, was distilled under vacuum in Kugelrohr apparatus (140 °C; 3 × 10⁻⁵ bar), thus leading to a distillate with 80% methyl esters in the desired C8–C16 range, mainly C12.

Likewise, Ranucci et al. [120] investigated the transesterification of babassu oil with 1.0% (w/w) NaOH and 50% (v/v) methanol with respect to oil. The mixture remained under constant agitation at 65 °C for 5 h, reaching an 82% yield. Vacuum distillation of biodiesel (115–157 °C; 0.19 bar) in a Vigreux column resulted in a distilled fraction of compounds up to C16 of 74%, with methyl laurate as the main component.

Although the method employed by these authors, i.e., biodiesel synthesis followed by distillation, is not among those approved by ANP in Brazil, it could be adapted to the SPK-HEFA process. In addition, only homogeneous catalysts were tested, essentially NaOH, leaving room for the application of heterogeneous catalysis.

iii. Pinhão-manso (J. curcas L.)

This is one of the most investigated species in the last 10 years and also the one that originated aviation biokerosene added to fossil kerosene in the early tests on commercial flights in 2011 by Interjet (blend 23/73), Aeroméxico (blend 25/75) and Lufthansa (blend 50/50) airlines and in 2012 by United Airlines (blend 40/60) [121].

Alherbawi et al. [122] performed the synthesis of aviation biokerosene by the SPK-FT process, consisting of pinhão-manso oil hydroprocessing, through the hydrogenation and deoxygenation steps with Ni/Al₂O₃ as a catalyst (300 °C and 45 bar H₂), hydrocracking with Ni/ZSM-5 (350 °C and 80 bar H₂) and isomerization with Pt/ γ Al₂O₃. Gasification for syngas production, performed at 1000 °C and atmospheric pressure, was followed by the SPK-FT process with Co/Al₂O₃ (240 °C and 25 bar H₂) and by reforming with Ni/Al₂O₃ (900 °C and 15 bar H₂). These catalytic routes led to a 77.5% yield in liquid hydrocarbons, 46.5% of which being biokerosene.

Altalhi et al. [123] used the SPK-HEFA process by catalytically cracking pinhão-manso oil for 4 h at 350 °C, using as catalyst (0.2%~w/w) MMT-MS-SO₃H and a montmorillonite clay chemically modified with 3-mercaptopropyl trimethoxysilane and sulfuric acid. The subsequent distillation step at 250 °C allowed obtaining biokerosene with 79% yield, which was added in 10% proportion to aviation kerosene, forming a 10/90 blend (B10) compatible with the physicochemical properties and specifications established by ASTM. Muharam et al. [124] also utilized the SPK-HEFA process to prepare biokerosene using a trickle-bed reactor for hydrocracking of the same oil using (5%~w/w) Ni-W/SiO₂Al₂O₃ as a catalyst at 500 °C, 80 bar H₂ and a 105.5 H₂/oil molar ratio in the reactor feeding. From this reaction, a 99% triglyceride conversion and a 79.5% biokerosene yield were obtained.

Romero-Izquierdo et al. [125] have recently proposed a biorefinery scheme for the exploitation of whole pinhão-manso fruit. Of the peels, 10% would be gasified to produce H₂ and 90% treated by acid hydrolysis with co-fermentation to produce ethanol. Oil extracted from the seeds would follow two biokerosene routes, i.e., the STK-ATJ process from ethanol, through the dehydration, oligomerization and hydrogenation steps with 40% yield, and the SPK-HEFA one from oil, through oil hydrocracking and distillation, with biokerosene yield of 47.5%.

iv. Licuri (S. coronata)

Araújo et al. [101] synthesized biokerosene by the SPK-HEFA process, consisting of licuri oil transesterification to obtain biodiesel and subsequent deoxygenation of esters. The transesterification step, performed in methanol via homogeneous catalysis with KOH at 30 °C for 40 min using a 1:6 oil:alcohol molar ratio, achieved a 92% yield. Biodiesel then underwent deoxygenation at 300 °C, 14.3 bar He/H₂, under agitation at 1000 rpm for 4 h, using palladium supported on activated charcoal (5% w/w). Although the yield in C7–C17 n-alkanes was 39%, the authors stressed that isomerization and fractional distillation are still necessary to obtain aviation biokerosene.

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Oliveira et al. [126] conducted a study on the catalytic pyrolysis of licuri oil, using the CHJ process with 1% zinc oxide supported on vermiculite (VZN1) as a catalyst. The products obtained by adding 10% (w/w) in pyrolyser coupled to CG-MS at 500 °C, underwent deoxygenation and decarbonylation, resulting in a yield in C11–C15 hydrocarbons of 53.5%, which is proper to biokerosene.

The reaction conditions and characteristics of aviation biokerosene produced by the authors mentioned in this section are gathered in Table 4.

Table 4. Catalytic routes described in the literature for the production of aviation biokerosene from oilseeds occurring in the Caatinga biome.

Feedstock	Process	Catalyst	Reaction Conditions	Hydrocarbons Yield (%)	Reference
	SPK-HEFA	Co/activated carbon	350 °C, 30 bar H ₂ , 2 h	94	[114]
	SPK-HEFA	Beta/ZSM-5 zeolite	350 °C, 10 bar H ₂ , 3 h	100/80	[115]
Macaúba	Transesterification Distillation	NaOH *	60 °C, 2 h, 1:6 methanol/oil Distillation: 214–266 °C	82	[116]
	Transesterification Distillation	H ₂ SO ₄ *	74 °C, 4 h, 1:8 methanol/oil Distillation: 110–224 °C	60	[117]
	Transesterification Distillation	NaOCH ₃ *	Distillation: 124–359 °C; $2,66 \times 10^{-3}$ bar	69	[118]
Babassu	Transesterification Distillation	NaOH *	60 °C, 1 h, 1:6 methanol/oil Distillation: 140 °C; 3×10^{-5} bar	80	[119]
	Transesterification Distillation	NaOH *	65 °C, 5 h, 1:2 methanol/oil Distillation: 115–157 °C; 0.19 bar	74	[120]
	SPK-FT	Ni/Al_2O_3 Ni/ZSM-5 $Pt/\gamma Al_2O_3$ Co/Al_2O_3 Ni/Al_2O_3	Hydrogenation (300 °C, 45 bar H ₂) Hydrocracking (350 °C, 80 bar H ₂) Isomerization Fischer-Tropsch (240 °C, 25 bar H ₂) Reforming (900 °C, 15 bar H ₂)	77.5	[121]
Pinhão-manso	SPK-HEFA	Sulfonated montmorillonite	Cracking (350 °C, 4 h) Distillation 250 °C	79	[123]
	SPK-HEFA	Ni-W/SiO ₂ Al ₂ O ₃	$500 ^{\circ}$ C, $80 \text{bar} \text{H}_2$	79.5	[124]
	ATJ SPK-HEFA	Ni Pd/activated carbon	Oligomerization (120 °C, 35 bar H_2) Hydrogenation (100 °C, 30 bar H_2) Hydroprocessing (320 °C, 80 bar H_2)	40 (ATJ) 47 (SPK-HEFA)	[125]
Licuri	Transesterification SPK-HEFA	KOH * Pd/activated carbon	30 °C, 40 min, 1:6 methanol/oil Hydrodeoxygenation (300 °C, 14.3 bar He/H ₂ , 4 h)	39	[101]
	CHJ	ZnO/vermiculite	Pyrolysis/deoxygenation (500 °C)	53.5	[126]

^{*} catalyst used in the transesterification reaction.

The data from Table 4 show that the most used catalytic route to produce biokerosene from oilseeds is the SPK-HEFA process, approved by ANP, while the most frequently used catalysts are heterogeneous and composed of transition metals, especially Ni, Co, Pd, Pt and Zn, supported on materials such as activated charcoal, zeolites, alumina and clay. However, there are processes that integrate biodiesel production and fractional distillation in which only an alkaline homogeneous catalyst is used for the transesterification.

These data reveal that there are few studies on oilseeds and there is, therefore, a lot of space for research on the production of aviation biokerosene, with special reference to catalytic routes. All these processes do in fact require knowledge of many chemical reactions and require catalysts and specific conditions so that this biofuel meets quality standards.

4. Conclusions and Future Prospects

Currently, biodiesel production is based on oils obtained from agronomic commodities (especially soybean in Brazil), which increases the environmental burden and limits food stocks for human use. Investments in alternative oil sources decrease environmental pressure by diversifying starting raw materials and has great economic potential thanks to the development of new production lines. With climate change, plant species that resist high temperatures and long drought periods, such as those belonging to the biome of the semiarid Caatinga of northeastern Brazil, are increasingly desirable because they are

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already naturally adapted to these adverse conditions, have a high biofuel yield and do not need investments in soil management.

Brazilian flora, especially that of Caatinga, has an extremely rich diversity. Among the species of this biome, the ones taken into consideration in this systematic review stand out as alternative oilseed crops thanks to their high oil content and interesting properties, which make them promising renewable resources for production of biodiesel and aviation biokerosene.

Research and development efforts on sustainable management of bioresources using the biorefinery concept are needed to optimize biomass exploitation with the aim of facing global challenges such as mitigating the effects of climate change and achieving the so-called energy transition by the second half of this century. In this context, these alternative oilseed crops would provide renewable carbon sources whose full exploitation is expected to (a) establish integrated local biorefineries, (b) promote the circular bioeconomy, (c) contribute to landscape valorization and biodiversity conservation, and (d) add value to the oilseeds themselves, thus improving the income and quality of life of the local population. At the same time, it will serve a consumer market increasingly concerned with urgent strategies, especially in the field of renewable energies as well as clean and new ecofriendly products, to face the current worrying world scenario. To this purpose, possible catalytic routes to produce biodiesel and aviation biokerosene have been reviewed herein, with a special look at those adopting heterogeneous catalysts.

However, some limitations of this study can be highlighted, which are due to the typical rigidity of systematic reviews using exclusion criteria. Among them, an underestimation of the overall potential of plants or plant residues with oil contents lower than 50%, which, although disregarded in this review, may have other important characteristics such as higher growth rate under specific conditions able to counterbalance this drawback. Another limitation, linked to the focus on the desired biofuels, is to ignore other equally important characteristics of excluded raw materials, including their potential as food or as source of fatty acids of great interest for other industrial sectors such as those of fine chemicals, pharmaceuticals and cosmetics.

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References

- 1. Bergmann, J.C.; Tupinambá, D.D.; Costa, O.Y.A.; Almeida, J.R.M.; Barreto, C.C.; Quirino, B.F. Biodiesel production in Brazil and alternative biomass feedstocks. *Renew. Sustain. Energy Rev.* **2013**, 21, 411–420. [CrossRef]
- 2. Pascoal, C.V.P.; Oliveira, A.L.L.; Figueiredo, D.D.; Assunção, J.C.C. Optimization and kinetic study of ultrasonic-mediated in situ transesterification for biodiesel production from the almonds of *Syagrus cearensis*. *Renew. Energy* **2020**, 147, 1815–1824. [CrossRef]
- 3. Ramos, M.D.N.; Milessi, T.S.; Candido, R.G.; Mendes, A.A.; Aguiar, A. Enzymatic catalysis as a tool in biofuels production in Brazil: Current status and perspectives. *Energy Sustain. Dev.* **2022**, *68*, 103–119. [CrossRef]
- 4. Lisboa, M.C.; Wiltshire, F.M.S.; Fricks, A.T.; Dariva, C.; Carrière, F.; Lima, A.S.; Soares, C.M.F. Oleochemistry potential from Brazil northeastern exotic plants. *Biochimie* **2020**, *178*, 96–104. [CrossRef] [PubMed]
- 5. Sánchez, A.S.; Almeida, M.B.; Torres, E.A.; Kalid, R.A.; Cohim, E.; Gasparatos, A. Alternative biodiesel feedstock systems in the Semi-arid region of Brazil: Implications for ecosystem services. *Renew. Sustain. Energy Rev.* **2018**, *81*, 2744–2758. [CrossRef]

Energies **2022**, 15, 6531 21 of 25

6. Gbif. Sistema Global de Informação Sobre Biodiversidade (Global Biodiversity Information Facility). Catolé (*Syagrus cearensis*). 2022. Available online: https://www.gbif.org/species/5293881 (accessed on 27 July 2022).

- 7. Reflora. *Syagrus in* Flora e Funga do Brasil. Jardim Botânico do Rio de Janeiro. Licuri (*Syagrus coronata* (Mart.) Becc.). 2022. Available online: https://floradobrasil.jbrj.gov.br/FB15736 (accessed on 27 July 2022).
- 8. Reflora. *Attalea in* Flora e Funga do Brasil. Jardim Botânico do Rio de Janeiro. Babassu (*Attalea speciosa* Mart. ex Spreng., Formerly Known as *Attalea vitrivir* Zona). 2022. Available online: https://floradobrasil.jbrj.gov.br/FB15686 (accessed on 27 July 2022).
- 9. Publisher iNaturalist. Babassu/Babaçu (*Attalea speciosa*). Available online: https://www.inaturalist.org/taxa/364354-Attalea-speciosa/browse_photos (accessed on 27 July 2022).
- 10. Publisher iNaturalist. Pequi (*Caryocar brasiliense*). Available online: https://www.inaturalist.org/taxa/464113-Caryocar-brasiliense/browse_photos (accessed on 27 July 2022).
- 11. Publisher iNaturalist. Macúba (*Acrocomia aculeata*). Available online: https://www.inaturalist.org/taxa/244459-Acrocomia-aculeata/browse_photos (accessed on 27 July 2022).
- 12. Reflora. *Platonia in* Flora e Funga do Brasil. Jardim Botânico do Rio de Janeiro. Bacuri (*Platonia insignis* Mart.). 2022. Available online: https://floradobrasil.jbrj.gov.br/FB16880 (accessed on 27 July 2022).
- 13. Reflora. *Calophyllum in* Flora e Funga do Brasil. Jardim Botânico do Rio de Janeiro. Guanandi (*Calophyllum brasiliense* Cambess.). 2022. Available online: https://floradobrasil.jbrj.gov.br/FB6827 (accessed on 27 July 2022).
- 14. Reflora. *Serjania in* Flora e Funga do Brasil. Jardim Botânico do Rio de Janeiro. Cipó-timbo (*Serjania salzmanniana* Schltdl.). 2022. Available online: https://floradobrasil.jbrj.gov.br/FB20977 (accessed on 27 July 2022).
- 15. Eskander, S.; Fankhauser, S. Reduction in greenhouse gas emissions from national climate legislation. *Nat. Clim. Chang.* **2020**, 10, 750–756. [CrossRef]
- 16. Tucki, K.; Orynycz, O. Bioenergy and Biofuels. Sustainability 2021, 13, 9972. [CrossRef]
- 17. Rodrigues, A.C.C. Policy, regulation, development and future of biodiesel industry in Brazil. *J. Clean. Prod.* **2021**, *4*, 100197–100209. [CrossRef]
- 18. de Souza, T.A.Z.; Pinto, G.M.; Julio, A.A.V.; Coronado, C.J.R.; Perez-Herrera, R.; Siqueira, B.S.; da Costa, R.B.R.; Roberts, J.J.; Palacio, J.C.E. Biodiesel in South American countries: A review on policies, stages of development and imminent competition with hydrotreated vegetable oil. *Renew. Sustain. Energy Rev.* 2022, 153, 111755–111769. [CrossRef]
- Madsen, R.; Henkes, J.A. A aviação civil e a inserção do bioquerosene no Brasil. Rev. Bras. Aviação Civ. Ciências Aeronáuticas 2021, 1, 6–34.
- Anuário Estatístico Brasileiro do Petróleo, Gás Natural e Biocombustíveis: 2021/Agência Nacional do Petróleo, Gás Natural e Biocombustíveis.—Rio de Janeiro: ANP. 2008. Available online: https://www.gov.br/anp/pt-br/centrais-de-conteudo/publicacoes (accessed on 12 August 2022).
- 21. Cremonez, P.A.; Feroldi, M.; Nadaleti, W.C.; de Rossi, E.; Feiden, A.; de Camargo, M.P.; Cremonez, F.E.; Klajn, F.F. Biodiesel production in Brazil: Current scenario and perspectives. *Renew. Sustain. Energy Rev.* **2015**, 42, 415–428. [CrossRef]
- 22. Milanez, A.Y.; Maia, G.B.; Guimarães, D.D.; Ferreira, C.L.A. Aviation biofuels in Brazil: An agenda of sustainability. *R. BNDES* **2021**, *28*, 361–398.
- 23. BRASIL. Resolução nº 856, de 22 de Outubro de 2021. Estabelece as Especificações do Querosene de Aviação; Diário Oficial da União: Brasília, Brazil, 2021; Volume 1, p. 89.
- 24. De Souza, L.M.; Mendes, P.A.S.; Aranda, D.A.G. Assessing the current scenario of the Brazilian biojet market. *Renew. Sustain. Energy Rev.* **2018**, *98*, 426–438. [CrossRef]
- 25. Walter, A.; Seabra, J.; Rocha, J.; Guarenghi, M.; Vieira, N.; Damame, D.; Santos, J.L. Spatially Explicit Assessment of the Feasibility of Sustainable Aviation Fuels Production in Brazil: Results of Three Case Studies. *Energies* **2021**, *14*, 4972. [CrossRef]
- 26. Harand, W.; Pinho, R.S.; Felix, L.P. Alternative oilseeds for Northeastern Brazil: Unrevealed potential of Brazilian biodiversity. *Braz. J. Bot.* **2016**, *39*, 169–183. [CrossRef]
- Reflora. Pachira in Flora e Funga do Brasil. Jardim Botânico do Rio de Janeiro. Castanha (Pachira retusa (Mart.) Fern. Alonso, Formerly Known as Bombacopsis retusa (Mart. & Zucc.) A. Robyns). 2022. Available online: https://floradobrasil.jbrj.gov.br/FB25757 (accessed on 27 July 2022).
- 28. Iha, O.K.; Alves, S.C.F.C.; Suarez, P.A.Z.; de Oliveira, M.B.F.; Meneghetti, S.M.P.; Santos, B.P.T.; Soletti, J.I. Physicochemical properties of *Syagrus coronata* and *Acrocomia aculeata* oils for biofuel production. *Ind. Crops Prod.* **2014**, 62, 318–322. [CrossRef]
- 29. Lieb, V.M.; Schex, R.; Esquivel, P.; Jiménez, V.M.; Schmarr, H.-G.; Carle, R.; Steingass, C.B. Fatty acids and triacylglycerols in the mesocarp and kernel oils of maturing Costa Rican *Acrocomia aculeata* fruits. *NFS J.* **2019**, *14*, 6–13. [CrossRef]
- 30. Oliveira, R.A.D.; Conceição, N.S.; Ribeiro, L.M.; Nascimento, L.P.S.; Silvério, F.O. Storage, oil quality and cryopreservation of babassu palm seeds. *Ind. Crops Prod.* **2016**, *91*, 332–339. [CrossRef]
- 31. Faria-Machado, A.F.; Tres, A.; van Ruth, S.M.; Antoniassi, R.; Junqueira, N.T.V.; Lopes, P.S.N.; Bizzo, H.R. Discrimination of pulp oil and rernel oil from pequi (*Caryocar Brasiliense*) by fatty acid methyl esters fingerprinting, using GC-FID and multivariate analysis. *J. Agric. Food Chem.* **2015**, *63*, 10064–10069. [CrossRef]
- 32. Pinho, R.S.; Oliveira, A.F.M.; Silva, S.I. Potential oilseed crops from the semiarid region of Northeastern Brazil. *Bioresour. Technol.* **2009**, *100*, 6114–6117. [CrossRef]
- 33. Girardi, J.C.; Bariccatti, R.A.; Souza, S.N.M.; Amaral, C.Z.; Guedes, C.L.B.; Bauni, J.; Bertosse, C.M. Potential of babassu biofuels use as aviation fuel. *Res. Soc. Dev.* **2022**, *11*, e51911125226. [CrossRef]

Energies **2022**, *15*, 6531 22 of 25

34. Sut, D.; Chutia, R.S.; Bordoloi, N.; Narzari, R.; Kataki, R. Complete utilization of non-edible oil seeds of *Cascabela thevetia* through a cascade of approaches for biofuel and by-products. *Bioresour. Technol.* **2016**, 213, 111–120. [CrossRef]

- 35. Pereira, N.P. Extraction, determination of the fatty profile and potential application of oil from the seeds of *Bombacopsis retusa* (Mart. & Zucc.) A. Robyns. *Acta Sci. Technol.* **2013**, *35*, 573–579. [CrossRef]
- 36. Bernabé-Antonio, A.; Álvarez, L.; Salcedo-Pérez, E.; López-Dellamary Toral, F.A.; Anzaldo-Hernández, J.; Cruz-Sosa, F. Fatty acid profile of intact plants of two different sites and callus cultures derived from seed and leaf explants of *Calophyllum brasiliense* cambess: A new resource of non-edible oil. *Ind. Crops. Prod.* 2015, 77, 1014–1019. [CrossRef]
- 37. Oliveira, M.D.A.; Alves, P.S.; Sousa, H.G.; da Costa Silva, C.; Rai, M.K.; Lima, N.M.; Andrade, T.J.A.S.; Feitosa, C.M.; Costa Júnior, J.S. Genotoxic and cytotoxic activities of hexane extract in seeds from *Platonia insignis* Mart. *Res. Soc. Dev.* **2022**, *11*, e13911225504. [CrossRef]
- 38. Gentry, A.H.; Wettach, R.H. Fevillea-a new oil seed from Amazonian Peru. Econ. Bot. 1986, 40, 177–185. [CrossRef]
- 39. Coutinho, D.J.G.; Barbosa, M.O.; de Souza, R.J.C.; da Silva, A.S.; da Silva, S.I.; de Oliveira, A.F.M. Comparative study of the physicochemical properties of FAME from seed oils of some native species of Brazilian Atlantic Forest. *J. Am. Oil Chem. Soc.* **2016**, 93, 1519–1528. [CrossRef]
- 40. Rocha Filho, G.N.; Bentes, M.H.S.; Brodzki, D.; Djéga-Mariadassou, G. Catalytic conversion of *Hevea brasiliensis* and *Virola sebifera* oils to hydrocarbon fuels. *J. Am. Oil Chem. Soc.* **1992**, *69*, 266–271. [CrossRef]
- 41. Cordeiro, R.M.; Silva, A.P.d.S.; Pinto, R.H.H.; da Costa, W.A.; da Silva, S.H.M.; de Souza Pinheiro, W.B.; Arruda, M.S.P.; Carvalho Junior, R.N. Supercritical CO₂ extraction of ucuúba (*virola surinamensis*) seed oil: Global yield, kinetic data, fatty acid profile, and antimicrobial activities. *Chem. Eng. Commun.* **2019**, 206, 86–97. [CrossRef]
- 42. Eromosele, C.O.; Eromosele, I.C. Fatty acid compositions of seed oils of *Haematostaphis barteri* and *Ximenia americana*. *Bioresour*. *Technol*. **2002**, 82, 303–304. [CrossRef]
- 43. Changi, S.; Pinnarat, T.; Savage, P.E. Mechanistic Modeling of Hydrolysis and Esterification for Biofuel Processes. *Ind. Eng. Chem. Res.* **2011**, *50*, 12471–12478. [CrossRef]
- 44. Long, F.; Liu, W.; Jiang, X.; Zhai, Q.; Cao, X.; Jiang, J.; Xu, J. State-of-the-art technologies for biofuel production from triglycerides: A review. *Renew. Sustain. Energy Rev.* **2021**, *148*, 111269. [CrossRef]
- 45. Chandrasekaran, S.R.; Murali, D.; Marley, K.A.; Larson, R.A.; Doll, K.M.; Moser, B.R.; Scott, J.; Sharma, B.K. Antioxidants from slow pyrolysis bio-oil of birch wood: Application for biodiesel and biobased lubricants. *ACS Sustain. Chem. Eng.* **2016**, *4*, 1414–1421. [CrossRef]
- 46. Mahamuni, N.N.; Adewuyi, Y.G. Optimization of the synthesis of biodiesel via ultrasound-enhanced base-catalyzed transesterification of soybean oil using a multifrequency ultrasonic reactor. *Energy Fuels* **2009**, *23*, 2757–2766. [CrossRef]
- 47. Kiss, A.A.; Dimian, A.C.; Rothenberg, G. Biodiesel by catalytic reactive distillation powered by metal oxides. *Energy Fuels* **2008**, 22, 598–604. [CrossRef]
- 48. Souza, G.K.; Scheufele, F.B.; Pasa, T.L.B.; Arroyo, P.A.; Pereira, N.C. Synthesis of ethyl esters from crude macauba oil (*Acrocomia aculeata*) for biodiesel production. *Fuel* **2016**, *165*, 360–366. [CrossRef]
- 49. Santos, R.C.M.; Gurgel, P.C.; Pereira, N.S.; Breves, R.A.; de Matos, P.R.R.; Silva, L.P.; Sales, M.J.A.; Lopes, R.V.V. Ethyl esters obtained from pequi and macaúba oils by transesterification with homogeneous acid catalysis. *Fuel* **2020**, 259, 116206. [CrossRef]
- 50. Prado, R.G.; Almeida, G.D.; de Oliveira, A.R.; de Souza, P.M.T.G.; Cardoso, C.C.; Constantino, V.R.L.; Pinto, F.G.; Tronto, J.; Pasa, V.M.D. Ethanolysis and methanolysis of soybean and macauba oils catalyzed by mixed oxide Ca—Al from hydrocalumite for biodiesel production. *Energy Fuels* **2016**, *30*, 6662–6670. [CrossRef]
- 51. Ramos, L.; Martin, L.S.; Santos, J.C.; de Castro, H.F. Combined use of a two-stage Packed bed reactor with a glycerol extraction column for enzymatic biodiesel synthesis from macaw palm oil. *Ind. Eng. Chem. Res.* **2017**, *56*, 1–7. [CrossRef]
- 52. Paiva, E.J.M.; da Silva, M.L.C.P.; Barboza, J.C.S.; de Oliveira, P.C.; de Castro, H.F.; Giordani, D.S. Non-edible babassu oil as a new source for energy production—a feasibility transesterification survey assisted by ultrasound. *Ultrason. Sonochem.* **2013**, 20, 833–838. [CrossRef]
- 53. Ferrari, R.A.; Soler, M.P. Obtention and characterization of coconut babassu derivatives. Sci. Agric. 2015, 72, 291–296. [CrossRef]
- 54. Girardi, J.C.; Barricatti, R.A.; de Sousa, R.N.M.; do Amaral, C.Z.; Guedes, C.L.B. Natural compounds as antifreeze additives to improve babassu biodiesel. *Fuel* **2021**, 289, 119746. [CrossRef]
- 55. Oliveira, V.F.; Parente, E.J.S., Jr.; Manrique-Rueda, E.D.; Cavalcante, C.L., Jr.; Luna, F.M.T. Fatty acid alkyl esters obtained from babassu oil using C1–C8 alcohols and process integration into atypical biodiesel plant. *Chem. Eng. Res. Des.* 2015, 160, 224–232. [CrossRef]
- Carvalho, L.M.G.; Abreu, W.C.; Silva, M.G.O.; Lima, J.R.O.; Oliveira, J.E.; Matos, J.M.E.; Moura, C.V.R.; Moura, E.M. Heterogeneous Catalysis Afford Biodiesel of Babassu, Castor oil and Blends. J. Braz. Chem. Soc. 2013, 24, 550–557. [CrossRef]
- 57. Andrade, G.S.S.; Freitas, L.; Oliveira, P.C.; de Castro, H.F. Screening, immobilization and utilization of whole cell biocatalysts to mediate the ethanolysis of babassu oil. *J. Mol. Catal. B Enzym.* **2012**, *84*, 183–188. [CrossRef]
- 58. Da Rós, P.C.M.; Silva, W.C.; Grabaukas, D.; Perez, V.H.; de Castro, H.F. Biodiesel from babassu oil: Characterization of the product obtained by enzymatic route accelerated by microwave irradiation. *Ind. Crops Prod.* **2014**, *52*, 313–320. [CrossRef]
- 59. Moreira, K.S.; Moura Junior, L.S.; Monteiro, R.R.C.; de Oliveira, A.L.B.; Valle, C.P.; Freire, T.M.; Fechine, P.B.A.; de Souza, M.C.M.; Fernandez-Lorente, G.; Guisan, J.M.; et al. Optimization of the Production of Enzymatic Biodiesel from Residual Babassu Oil (Orbignya sp.) via RSM. *Catalysts* **2020**, *10*, 414. [CrossRef]

Energies **2022**, *15*, 6531 23 of 25

60. Borges, K.A.; Batista, A.C.F.; Rodrigues, H.S.; Terrones, M.H.; Vieira, A.T.; de Oliveira, M.F. Production of methyl and ethyl biodiesel fuel from Pequi oil. *Chem. Technol. Fuels Oils* **2012**, *48*, 83–89. [CrossRef]

- 61. Oster, V.V. Influência do Tempo de Extração e da Razão Amostra: Solvente no Processo de Extração do Óleo do Caroço do Pequi Visando a Produção de Biodiesel. Master's Thesis, Universidade Federal de Tocantins, Palmas, Brazil, 2013. Available online: http://hdl.handle.net/11612/547 (accessed on 12 August 2022).
- 62. Silva, T.A.; de Assunção, R.M.N.; Vieira, A.T.; de Oliveira, M.F.; Batista, A.C.F. Methylic and ethylic biodiesels from pequi oil (*Caryocar brasiliense* Camb.): Production and thermogravimetric studies. *Fuel* **2014**, *136*, 10–18. [CrossRef]
- 63. Ferreira, E.N. Utilização de Pequi (*Caryocar brasilienses* Camb.) Para Produção Sustentável de Combustíveis e Lubrificantes. Master's Thesis, Universidade Federal do Ceará, Fortaleza, Brazil, 2019. Available online: http://www.repositorio.ufc.br/handle/riufc/53435 (accessed on 12 August 2022).
- 64. Guimarães, M.G. *Produção de Biocombustível Líquido a Partir de Resíduo Agroindustrial: Caroço de Pequi*; Universidade de Brasília: Brasilia, Brazil, 2015. Available online: https://bdm.unb.br/handle/10483/11245 (accessed on 12 August 2022).
- 65. Souza, M.G.S.; Guimarães, M.G.; Macedo, J.L.; Rodrigues, J.P.; Ghesti, G.F. Characterization and Use of Pequi Residual Oil (*Caryocar brasiliense*) in the Production of Liquid Biofuels. *RIPE* **2019**, *5*, 41–49. [CrossRef]
- 66. Guimarães, M.G.; Evaristo, R.B.W.; de Macedo, J.L.; Ghesti, G.F. Extraction and characterization of pequi seed oil for biodiesel production: A green management of waste to biofuel using ethanol and heterogeneous catalysis. *J. Braz. Chem. Soc.* **2022**, 33, 327–339. [CrossRef]
- 67. Dhoot, S.B.; Jaju, D.R.; Deshmukh, S.A.; Panchal, B.M.; Sharma, M.R. Extraction of *Thevetia peruviana* seed oil and optimization of biodiesel production using alkali-catalyzed methanolysis. *JoAEST* **2011**, *2*, 8–16.
- 68. Olatunji, O.M.; Akor, A.J.; Abowei, M.F.N. Modeling the chemical kinetics of milk bush (*Thevetia peruviana*) oil transesterification process for biodiesel production. *Cont. J. Eng. Sci.* **2012**, *7*, 40–48.
- 69. Oseni, M.I.; Obetta, S.E.; Orukotan, F.V. Evaluation of fatty acids profile of ethyl esters of yellow oleander and groundnut oils as biodiesel feedstock. *Am. J. Sci. Ind. Res.* **2012**, *3*, 62–68. [CrossRef]
- 70. Yarkasuwa, C.I.; Wilson, D.; Michael, E. Production of Biodiesel from Yellow Oleander (*Thevetia peruvian*) Oil and its Biodegradability. *J. Korean Chem. Soc.* **2013**, 57, 377–381. [CrossRef]
- 71. Yadav, A.K.; Khan, M.E.; Pal, A.; Dubey, A.M. Biodiesel production from Nerium oleander (*Thevetia peruviana*) oil through conventional and ultrasonic irradiation methods. *Energy Sources A Recovery Util. Environ. Eff.* **2016**, *38*, 3447–3452. [CrossRef]
- 72. Sanjay, B. Heterogeneous Catalyst Derived from Natural Resources for Biodiesel Production: A Review. *Res. J. Chem. Sci.* **2013**, *3*, 95–101. Available online: https://www.cabdirect.org/cabdirect/abstract/20133301549 (accessed on 6 August 2022).
- 73. Ogunkule, O.; Oniya, O.O.; Adebayo, A.O. Yield response of biodiesel production from heterogeneous and homogeneous catalysis of milk bush seed (*Thevetia peruviana*) oil. *Energy Policy Res.* **2017**, *4*, 21–28. [CrossRef]
- 74. Osakwe, E.U.; Ani, I.J.; Akpan, U.G.; Olutoye, M.A. Kolanut Pod Husk as a Biobase Catalyst for Fatty Acid Methyl Ester Production Using *Thevetia peruviana* (Yellow oleander) Seed Oil. *IOP Conf. Ser. Earth Environ. Sci.* **2018**, 173, 012008. Available online: https://iopscience.iop.org/article/10.1088/1755-1315/173/1/012008/meta (accessed on 6 August 2022). [CrossRef]
- 75. Deka, D.C.; Basumatary, S. High quality biodiesel from yellow oleander (*Thevetia peruviana*) seed oil. *Biomass Bioenergy* **2011**, 35, 1797–1803. [CrossRef]
- 76. Betiku, E.; Ajala, S.O. Modeling and optimization of *Thevetia peruviana* (yellow oleander) oil biodiesel synthesis via *Musa paradisiacal* (plantain) peels as heterogeneous base catalyst: A case of artificial neural network vs. response surface methodology. *Ind. Crops. Prod.* **2014**, *53*, 314–322. [CrossRef]
- 77. Borah, M.J.; Devi, A.; Das, V.; Deka, D. Catalytic Conversion of *Thevetia peruviana* Oil into Biodiesel by TiO₂-ZnO Nanocatalyst. *Int. J. Res. Eng. Technol.* **2017**, *6*, 56–60. Available online: https://ijret.org/volumes/2017v06/i13/IJRET20170613012.pdf (accessed on 6 August 2022).
- 78. Arun, S.B.; Suresh, R.; Avinash, E. Optimization of biodiesel production from yellow oleander (*Thevetia peruviana*) using response surface methodology. *Mater. Today* **2017**, *4*, 7293–7301. [CrossRef]
- 79. Oyekunle, D.T.; Oyekunle, D.O. Biodiesel Production from Yellow Oleander Seed Oil via Heterogeneous Catalyst: Performance Evaluation of Minitab Response Surface Methodology and Artificial Neural Network. *J. Mater. Environ. Sci.* **2018**, *9*, 2468–2477. Available online: https://www.jmaterenvironsci.com/Document/vol9/vol9_N8/271-JMES-3784-Oyekunle.pdf (accessed on 6 August 2022).
- 80. Prueksakorn, K.; Gheewala, S.H. Full chain energy analysis of biodiesel from *Jatropha curcas* L. in Thailand. *Environ. Sci. Technol.* **2008**, 42, 3388–3393. [CrossRef]
- 81. Diwani, G.E.; Attia, N.K.; Hawash, S.I. Int. Development and evaluation of biodiesel fuel and by-products from jatropha oil. *J. Environ. Sci. Tech.* **2009**, *6*, 219–224. [CrossRef]
- 82. Patil, P.D.; Gude, V.G.; Deng, S. Biodiesel production from *Jatropha Curcas*, waste cooking, and *Camelina sativa* oils. *Ind. Eng. Chem. Res.* **2009**, *48*, 10850–10856. [CrossRef]
- 83. Mascal, M.; Nikitin, E.B. Co-processing of carbohydrates and lipids in oil crops to produce a hybrid biodiesel. *Energy Fuels* **2010**, 24, 2170–2171. [CrossRef]
- 84. Shuit, S.H.; Lee, K.T.; Kamaruddin, A.H.; Yusup, S. Reactive extraction of *Jatropha curcas* L. seed for production of biodiesel: Process optimization study. *Environ. Sci. Technol.* **2010**, *44*, 4361–4367. [CrossRef]

Energies **2022**, *15*, 6531 24 of 25

85. Kumar, G.R.; Ravi, R.; Chadha, A. Kinetic studies of base-catalyzed transesterification reactions of non-edible oils to prepare biodiesel: The effect of co-solvent and temperature. *Energy Fuels* **2011**, 25, 2826–2832. [CrossRef]

- 86. Joshi, G.; Lamba, B.Y.; Rawat, D.S.; Mallick, S.; Murthy, K.R.S. Evaluation of additive effects on oxidation stability of *Jatropha curcas* biodiesel blends with conventional diesel sold at retail outlets. *Ind. Eng. Chem. Res.* **2013**, 52, 7586–7592. [CrossRef]
- 87. Fernandes, A.M.A.P.; El-Khatib, S.; Cunha, I.B.S.; Porcari, A.M.; Eberlin, M.N.; Silva, M.J.; Cunha, V.S.; Daroda, R.J.; Alberici, R.M. Chemical characterization of *Jatropha curcas* L. seed oil and its biodiesel by ambient desorption/ionization mass spectrometry. *Energy Fuels* **2015**, 29, 3096–3103. [CrossRef]
- 88. Sitoé, B.V.; Mitsutake, H.; Guimarães, E.; Gontijo, L.C.; Santos, D.Q.; Neto, W.B. Quality control of biodiesel content of B7 blends of methyl jatropha and methyl crambe biodiesel using mid-infrared spectroscopy and multivariate control charts based on net analyte signal. *Energy Fuels* **2016**, *30*, 1062–1070. [CrossRef]
- 89. Chang, C.C.; Teng, S.; Yuan, M.H.; Ji, D.R.; Chang, C.Y.; Chen, Y.H.; Shie, J.L.; Ho, C.; Tian, S.Y.; Tacca, C.A.A.; et al. Esterification of Jatropha oil with isopropanol via ultrasonic irradiation. *Energies* **2018**, *11*, 1456. [CrossRef]
- 90. Hossain, A.K.; Hussain, A. Impact of Nanoadditives on the performance and combustion characteristics of neat Jatropha biodiesel. *Energies* **2019**, 12, 921. [CrossRef]
- 91. ANR, R.; Saleh, A.A.; Islam, M.S.; Hamdan, S.; Maleque, M.A. Biodiesel production from crude Jatropha oil using a highly active heterogeneous nanocatalyst by optimizing transesterification reaction parameters. *Energy Fuels* **2016**, *30*, 334–343. [CrossRef]
- 92. Shah, S.; Sharma, S.; Gupta, M.N. Biodiesel preparation by lipase-catalyzed transesterification of jatropha oil. *Energy Fuels* **2004**, *18*, 154–159. [CrossRef]
- 93. Akoh, C.C.; Chang, S.W.; Lee, G.C.; Shaw, J.F. Enzymatic approach to biodiesel production. *J. Agric. Food Chem.* **2007**, *55*, 8995–9005. [CrossRef] [PubMed]
- 94. Jothiramalingam, R.; Wang, M.K. Review of recent developments in solid acid, base, and enzyme catalysts (heterogeneous) for biodiesel production via transesterification. *Ind. Eng. Chem. Res.* **2009**, *48*, 6162–6172. [CrossRef]
- 95. Adewale, P.; Dumont, M.J.; Ngadi, M. Enzyme-catalyzed synthesis and kinetics of ultrasonic-assisted methanolysis of waste choice white grease for fatty acid methyl ester production. *Energy Fuels* **2015**, 29, 6412–6421. [CrossRef]
- 96. Gao, J.; Yin, L.; Feng, K.; Zhou, L.; Ma, L.; He, Y.; Wang, L.; Jiang, Y. Lipase immobilization through the combination of bioimprinting and cross-linked protein-coated microcrystal technology for biodiesel production. *Ind. Eng. Chem. Res.* **2016**, 55, 11037–11043. [CrossRef]
- 97. Moussavou, R.W.M.; Brunschwig, C.; Baréa, B.; Villenevue, P.; Blin, J. Assessing the enzyme activity of different plant extracts of biomasses from sub-saharan africa for ethyl biodiesel production. *Energy Fuels* **2016**, *30*, 2356–2364. [CrossRef]
- 98. Gusniah, A.; Veny, H.; Hamzah, F. Ultrasonic assisted enzymatic transesterification for biodiesel production. *Ind. Eng. Chem. Res.* **2019**, *58*, 581–589. [CrossRef]
- 99. Melo, K.R.B.; Lopes, G.C.; Coelho, D.G.; Soletti, J.I. Liquid-liquid equilibrium for systems composed by biodiesel from catolé oil (*Syagrus cearensis*), methanol and glycerol. *Chem. Ind. Chem. Eng. Q.* **2020**, *26*, 21–29. [CrossRef]
- 100. La Salles, K.T.S.; Meneghetti, S.M.P.; de La Salles, W.F.; Meneghetti, M.R.; dos Santos, I.C.F.; da Silva, J.P.V.; de Carvalho, S.H.V.; Soletti, J.I. Characterization of *Syagrus coronata* (Mart.) Becc. oil and properties of methyl esters for use as biodiesel. *Ind. Crops Prod.* **2010**, *32*, 518–521. [CrossRef]
- 101. Araújo, P.H.M.; Maia, A.S.; Cordeiro, A.M.T.M.; Gondim, A.D.; Santos, N.A. Catalytic deoxygenation of the oil and biodiesel of licuri (*Syagrus coronata*) to obtain *n*-alkanes with chains in the range of biojet fuels. *ACS Omega* **2019**, *4*, 15849–15855. [CrossRef]
- 102. Lacerda, O.S., Jr. Gordura de Ucuúba: Caracterização Química e Síntese de Biodiesel. Master's Thesis, Universidade Federal do Amazonas, Manaus, Brazil, 2009. Available online: https://tede.ufam.edu.br/handle/tede/3351 (accessed on 6 August 2022).
- 103. Senthil, R.; Sivakumar, E.; Silanbarasam, R.; Pranesh, G. Performance and emission characteristics of using sea lemon biodiesel with thermal barrier coating in a direct-injection diesel engine. *Biofuels* **2016**, *8*, 235–241. [CrossRef]
- 104. Hariharan, V.S.; Reddy, K.V.; Rajagopal, K. Study of the Performance, Emission and Combustion Characteristics of a Diesel Engine Using Sea Lemon Oil Based Fuels. *Indian J. Sci. Technol.* **2019**, *2*, 43–47. Available online: https://ijabe.org/index.php/ijabe/article/view/116 (accessed on 6 August 2022). [CrossRef]
- 105. Meurer, A.; Kern, J. Fischer-Tropsch synthesis as the key for decentralized sustainable kerosene production. *Energies* **2021**, *14*, 1836. [CrossRef]
- 106. Monteiro, R.R.C.; dos Santos, I.A.; Arcanjo, M.R.A.; Cavalcante., C.L., Jr.; de Luna, F.M.T.; Fernandez-Lafuente, R.; Vieira, R.S. Production of jet biofuels by catalytic hydroprocessing of esters and fatty acids: A review. *Catalysts* **2022**, *12*, 237. [CrossRef]
- 107. Wang, W.C.; Tao, L. Bio-jet fuel conversion technologies. Renew. Sustain. Energy Rev. 2016, 53, 801–822. [CrossRef]
- 108. Vogelsang, D.; Faßbach, T.A.; Kossmann, P.P.; Vorholt, A. Terpene-derived highly branched C30-amines via palladium-catalysed telomerisation of β-farnesene. *Adv. Synth. Catal.* **2018**, *360*, 1984–1991. [CrossRef]
- 109. Eswaran, S.; Subramaniam, S.; Geleynse, S.; Brandt, K.; Wolcott, M.; Zhang, X. Techno-economic analysis of catalytic hydrothermolysis pathway for jet fuel production. *Renew. Sustain. Energy Rev.* **2021**, *151*, 111516–111527. [CrossRef]
- 110. O'Neil, G.W.; Knothe, G.; Reddy, C.M. Jet biofuels from algae. In *The Biomass, Biofuels and Biochemicals*, 2nd ed.; Pandey, A., Chang, J., Soccol, C.R., Lee, D., Chisti, Y., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 359–395. [CrossRef]
- 111. Carvalho, F.M. Evaluation of the Brazilian Potential for Producing Aviation Biofuels through Consolidated Routes. Master's Thesis, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil, 2017.

Energies **2022**, *15*, 6531 25 of 25

112. Goh, B.H.H.; Chong, C.T.; Ong, H.C.; Seljak, T.; Katrasnik, T.; Jozsa, V.; Ng, J.; Tian, B.; Karmarkar, S.; Ashokkumar, V. Recent advancements in catalytic conversion pathways for synthetic jet fuel produced from bioresources. *Energy Convers. Manag.* **2022**, 251, 114974–114998. [CrossRef]

- 113. Escalante, E.S.R.; Ramos, L.S.; Coronado, C.J.R.; Carvalho, J.A., Jr. Evaluation of the potential feedstock for biojet fuel production: Focus in the Brazilian context. *Renew. Sustain. Energy Rev.* **2022**, *153*, 111716–111738. [CrossRef]
- 114. Moreira, J.B.D.; Rezende, D.B.; Pasa, V.M.D. Deoxygenation of macauba acid oil over Co-based catalyst supported on activated biochar from macauba endocarp: A potential and sustainable route for green diesel and biokerosene production. *Fuel* **2020**, 269, 117253–117265. [CrossRef]
- 115. Freitas, L.N.S.; Souza, F.P.; Carvalho, A.R.; Pasa, V.M.D. Study of direct synthesis of bio-hydrocarbons from macauba oils using zeolites as catalysts. *Fuel* **2021**, *287*, 119472–119483. [CrossRef]
- 116. Vilalva, J.B. *Produção de Ésteres Leves Derivados de Óleo de Amêndoa da Macaúba Para Potencial Aplicação Como Biocombustível de Aviação*; Final Project; Universidade Estadual Paulista: Rosana, Brazil, 2021.
- 117. Azevedo, W.J. Inventário do Ciclo de Vida da Produção de Bioquerosene Para Aviação Utilizando a Macaúba Como Fonte de Matéria-Prima. Master's Thesis, Universidade Federal dos Vales do Jequitinhonha e Mucuri, Diamantina, Brazil, 2021.
- 118. Llamas, A.; Al-Lal, A.; Hernandez, M.; Lapuerta, M.; Canoira, L. Biokerosene from babassu and camelina oils: Production and properties of their blends with fossil kerosene. *Energy Fuels* **2012**, *26*, 5968–5976. [CrossRef]
- 119. Oliveira, V.F. Estudo da Obtenção de Bioquerosene a Partir da Destilação Molecular de Biodiesel de Babaçu; Final Project; Universidade Federal do Ceará: Fortaleza, Brazil, 2016.
- 120. Ranucci, C.R.; Alves, H.J.; Monteiro, M.R.; Kugelmeier, C.L.; Bariccatti, R.A.; Rodrigues, C.O.; da Silva, E.A. Potential alternative aviation fuel from jatropha (*Jatropha curcas* L.), babassu (*Orbignya phalerata*) and palm kernel (*Elaeis guineensis*) as blends with Jet-A1 kerosene. *J. Clean. Prod.* 2018, 185, 860–869. [CrossRef]
- 121. Alherbawi, M.; McKay, G.; Mackey, H.R.; Al-Ansari, T. Jatropha curcas for jet biofuel production: Current status and future prospects. *Renew. Sustain. Energy Rev.* **2021**, *135*, 110396–110415. [CrossRef]
- 122. Alherbawi, M.; McKay, G.; Mackey, H.R.; Al-Ansari, T. A novel integrated pathway for Jet Biofuel production from whole energy crops: A *Jatropha curcas* case study. *Energy Convers. Manag.* 2021, 229, 113662–113683. [CrossRef]
- 123. Altalhi, A.A.; Mohamed, E.A.; Morsy, S.M.; Abou Kana, M.T.H.; Negm, N.A. Catalytic manufacture and characteristic valuation of biodiesel-biojet achieved from *Jatropha curcas* and waste cooking oils over chemically modified montmorillonite clay. *J. Mol. Liq.* 2021, 340, 117175–117183. [CrossRef]
- 124. Muharam, Y.; Dianursanti; Wirya, A.S. Modeling of jatropha oil hydrocracking in a trickle-bed reactor to produce green fuel. *Int. J. Chem. Eng.* **2021**, *1*, 7079459. [CrossRef]
- 125. Romero-Izquierdo, A.G.; Gutiérrez-Antonio, C.; Gómez-Castro, F.I.; Hernández, S. Synthesis and intensification of a biorefinery to produce renewable aviation fuel, biofuels, bioenergy and chemical products from *Jatropha curcas* fruit. *IET Renew. Power Gener.* 2022, 1, 1–21. [CrossRef]
- 126. Oliveira, J.L.F.; Batista, L.M.B.; dos Santos, N.A.; Araújo, A.M.M.; Fernandes Junior, V.F.; Araújo, A.S.; Alves, A.P.M.; Gondim, A.D. Clay-supported zinc oxide as catalyst in pyrolysis and deoxygenation of licuri (*Syagrus coronata*) oil. *Renew. Energy* **2021**, 168, 1377–1387. [CrossRef]