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Review

A Review of Tropical Organic Materials for Biodiesel as a Substitute Energy Source in Internal Combustion Engines: A Viable Solution?

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Abstract: In this article, the most important publications on the subject are compiled to highlight the progress in biodiesel production from tropical cultivars, including energy and environmental potential, raw materials, and the advantages and disadvantages of this biofuel. A critical and objective review of biodiesel production as an alternative fuel for power generation systems and its importance in the energy matrix was conducted. A survey of real applications, new computational and experimental trends, and proposals in internal combustion engines employing organic biofuel was performed. The main findings were as follows: (i) there is the possibility of integration and support in the energy matrix of different countries, as well as the competing with and complementing, energetically, other renewable energy sources, such as solar and wind; (ii) *Jatropha curcas*, sunflowers, soybean, *Moringa oleifera*, palm, cottonseed, castor, rubber seed, and coconut are tropical cultivars used to obtained oils into biodiesel; (iii) the findings can be utilized as a theoretical basis for future policies influencing the energy sector through regulatory measures.

Keywords: biodiesel; internal combustion engines; tropical cultivars

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1. Introduction

The need to reduce environmental degradation, enhanced by the use of petroleum-based energy sources and gas emissions that contribute to the aggravation of the greenhouse effect, has stimulated society to search for new fuels with lower environmental impacts and that maintain acceptable efficiency in a context of constant technological advancement, which can be applied in means of transportation or for the generation of electric and thermal energy [1].

The research, development, and application of biofuels, to the detriment of regular fossil fuels, are promising because they present several desirable characteristics, such as being renewable and biodegradable, and emitting low amounts of carbon when burned. When the objective is to drive combustion engines, there are usually two types of biofuels: ethanol, used in the Otto cycle, and biodiesel, used in the diesel cycle [2,3].

Biodiesel is already in widespread use, individually or blended with diesel (which comes from petroleum) in various proportions. Biodiesel is a monoalkyl ester, well established from fatty-acid oil, and it has a low sulfur content. It is formed from vegetable compounds produced on an industrial scale from transesterification. The catalyst facilitates the reaction of triacylglycerols with alcohol, creating biodiesel and glycerol as byproducts in up to 10% of the total mass. The most frequent raw materials for biodiesel synthesis are oilseed plants such as sunflower, rapeseed, or palm, reused cooking oils, and animal fats [3–6].

Tropical countries play an important role in agricultural production. Therefore, they are fundamental to the development and diffusion of biodiesel since many plant compounds from this region of the globe demonstrate predisposition, viability, and quality for fuel oil generation. South America, mainly represented by Brazil, and some Asian countries, located in the tropics, such as Indonesia, in addition to countries on the African continent, contribute relevant portions of the production of biodiesel, and the success of this biofuel depends on the research and production capacity of these locations [7–9]. It is important to emphasize that biofuel production has been a goal for several countries to achieve a renewable energy matrix through the use of raw materials or oil waste, as seen in the literature [10–13].

In this context, numerous published works which contribute to the dissemination of the use of biodiesel [14–17] refer to oils obtained from raw material from tropical regions [2,11,18]; in the face of such a variety of scientific publications, many review articles have synthesized and highlighted the aforementioned scientific production. Souza et al. [19] surveyed public policies, development stage, and aspects related to the competitiveness of biodiesel in South American countries, highlighting Brazil as one of the prominent representatives of tropical biofuel production.

Regarding tropical agricultural cultivars, Anwar et al. [20] reviewed the use of papaya seed and palm kernel for biodiesel oil production in Australia in terms of the challenges needed to enable their use in the transport sector. Osorio-González et al. [8] evaluated the state of the art concerning biodiesel produced from castor oil as a raw material due to its quality and low cost when using this agricultural variety, considering different methods of transesterification processes and technologies for obtaining bio-oil. Related to transesterification to produce biodiesel, Jayakumar et al. [21] reviewed heterogeneous catalysts based on natural resources or biological waste, such as animal hulls and bones, which are low-cost and ecologically beneficial alternatives.

Omonhinmin et al. [5] conducted a review on research repositories such as Google Scholar, Scopus, WorldCat.org, Microsoft Academic, and Science Direct, aiming to highlight the production of oil for biodiesel from *Moringa oleifera*, which is widely cultivated in tropical and subtropical climates, finding that the species present favorable characteristics for the generation of this biofuel; in addition, it is easy to transport and can be stored for long periods. Riayastsyan et al. [22] carried out a review and highlighted the main producers worldwide, as well as the characteristics and performance, of biodiesel obtained from *Jatropha curcas*, also known as jatropha, as a raw material, motivated by the promising scenario predicted for the specie, since it is easy to cultivate and grow in tropical climate regions.

In tropical Asia, there is large-scale rice production due to the monsoon phenomenon. Hoang et al. [23] reviewed the possibility of rice bran biodiesel replacing petroleum-based diesel, considering engine application performance, emission characteristics, and related economic aspects. Ashraf et al. [24] surveyed the actual research of palm oil biodiesel application in the transportation sector in Colombia and Malaysia in terms of the energy supply obtained, available resources, production and consumption, costs, and public policies implemented for the diffusion of this biodiesel.

Supplying sustainable and economical raw materials is critical in the industrialization and dissemination of biodiesel, and one of the most important costs in its production is the oil extraction [25]. In this sense, Bashir et al. [25] reviewed the technologies developed to obtain biodiesel using homogeneous or heterogeneous catalysis, highlighting some more emerging technologies such as plasma, microwave, and ultrasonic radiation. However, in addition to extraction technologies, the technological development of biodiesel internal combustion engines is crucial for more efficient sets of engines in terms of economic, performance, and environmental aspects.

As shown in Figure 1, several review studies concerning biodiesel and covering specific tropical raw materials, directly or indirectly, can be found in the recent literature, forming a huge collection. However, in the face of such a variety of promising tropical species for this purpose, portrayed scientifically and intensely discussed, it is necessary to conduct a review that addresses general aspects related to obtaining oil from tropical agricultural species and their characteristics, with the energy, economic, and environmental performance of biodiesel generated in internal combustion engines.

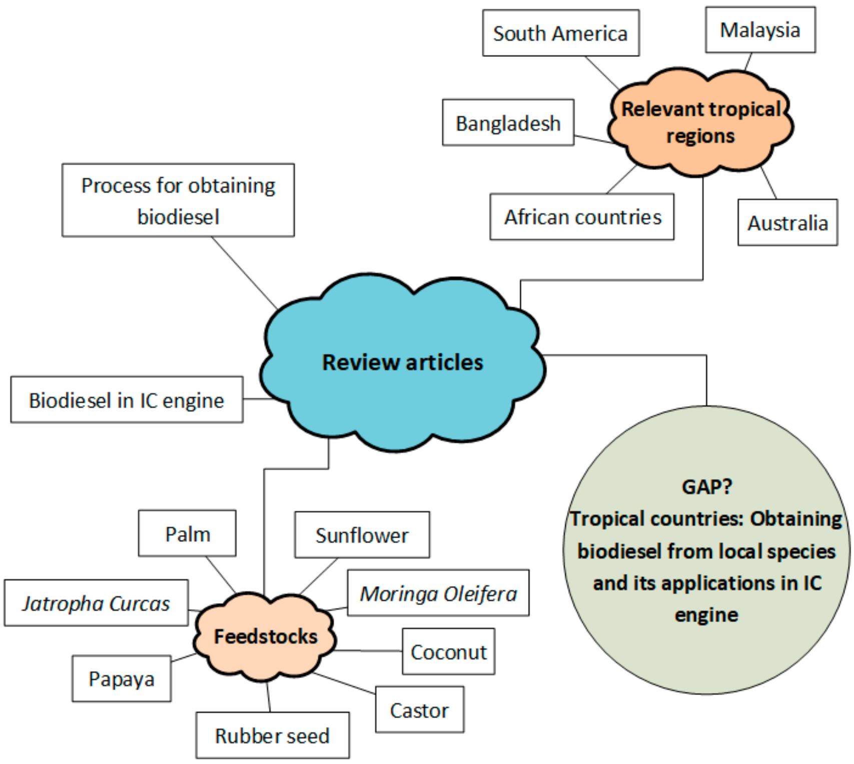


Figure 1. Review studies about the subject.

In this context, the purpose of this review paper is to examine the state of the art in the previous 4 years, regarding tropical raw materials for biodiesel production, and to evaluate characteristics of its transformation process into biofuel, as well as its theoretical and experimental uses in internal combustion engines, including inherent technological novelties.

2. State-of-the-Art Literature Survey

The correlated papers were explored on a scientific repository called Scopus. The main keywords were combined with Boolean operators to find the most appropriate manuscript on the selected topic.

General search keys were first applied, and then the examination continued with more specific words. In Query 1, the search was started with the quest key “biodiesel and internal combustion and engine”. In the general examination, the same keywords used were found. After that, the second query key, Query 2, was used, restricting the results to the tropical climate or country. Lastly, the keyword “feedstock” was added in the hunt query to limit the found results to the specific objective of the present work. The result stratification regarding the document types is presented in Table 1, and the explicit queries, keywords, and Boolean operators are shown in the notes.

Table 1. Overview of the paper founds according to the specified search queries.

Document Type	Query 1	Query 2	Query 3
Article	582	39	9
Conference paper	232	14	4
Review	83	10	6
Conference Review	25	2	0
Book Chapter	44	5	1
Total	966	70	20

Notes: **Query 1**: biodiesel and internal combustion and (motor* or engine*); **Query 2**: biodiesel and internal combustion and (motor* or engine*) and (tropical or (climate* or country*)); **Query 3**: biodiesel and internal and combustion and (motor* or engine*) and (tropical or climate or country*) and (feedstock or material*).

The manuscripts found in the present paper were classified and presented according to the following criteria: (i) biodiesel as an alternative renewable fuel; (ii) biodiesel production and potential: tropical cultivars; (iii) biodiesel applications in internal combustion engines; (iv) final considerations on the use of biodiesel in energy production.

The articles discovered in the literature review were subjected to a critical examination. The publications were scrutinized on the basis of the following characteristics: year of publication, methodology, aims, and important discoveries. Figure 2 groups the articles by class. It can be seen that 44% of the studies were on biodiesel production and related topics, 23% were review papers on different subjects, and 33% were experimental, theoretical/numerical, and real performance studies.

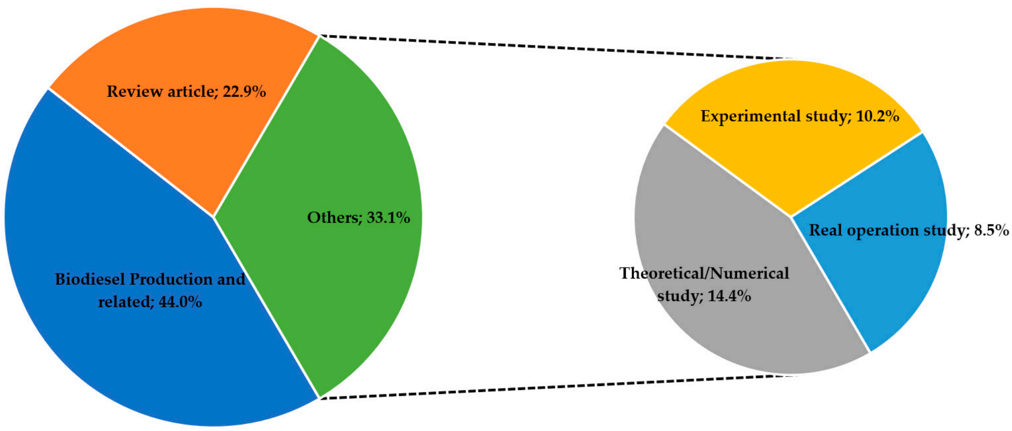


Figure 2. Overview of the articles found in the literature review.

3. Biodiesel as an Alternative Renewable Fuel

Fuel usage is quickly increasing as a result of overpopulation, urbanization, and industrialization, as are other technologies such as electric, hybrid, or even hydrogen-powered transportation. It is known that oil reserves will run out in the future if another alternative fuel is not found. The latest trend in determining alternative fuels has made waste energy conversion an important topic. Therefore, biodiesel has become an interesting alternative fuel since it is of the renewable type, among other relevant aspects, some of which can be seen in Figure 3. It has advantages in the social and economic aspects in the countries because it can promote local development, generate jobs, and help to reduce pollutants by producing biodiesel from local raw materials and recycling, respecting environmental criteria, and generating electricity to attend to the demand in various sectors, such as commercial, residential, transportation, and industrial, with the possibility of sustainable energy self-sufficiency.

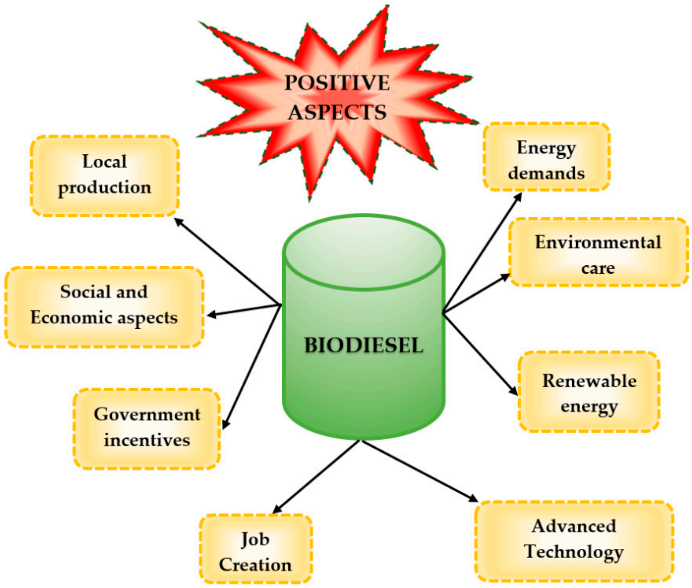
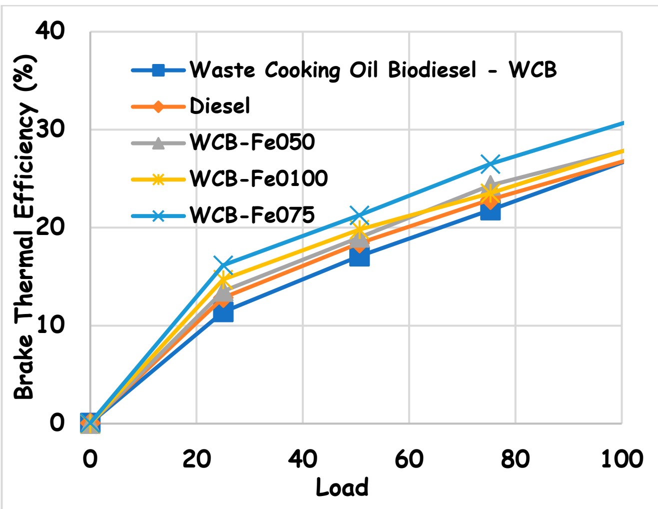
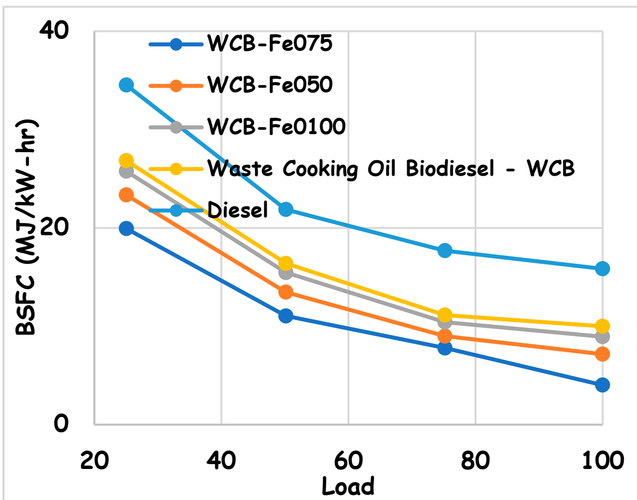


Figure 3. Positive aspects of biodiesel as a renewable fuel.

In this sense, several works have focused on biodiesel production to meet the various energy demands. John et al. [26] presented a study where biodiesel was produced from cooking oil as a total and partial replacement of diesel to verify the influence of performance parameters and impacts of pollutant emissions by adding iron oxide nanoparticles in diesel engines. The biodiesel produced was mixed with various concentrations of iron oxide nanoparticles (25 mL of biodiesel sample at 25 ppm, 50 ppm, 75 ppm, and 100 ppm). The thermal efficiency of the engine was evaluated, as well as the ratio of braking power (BP) and heat supplied by the fuel (BTE). It was observed that engine performance increased with the addition of iron oxide nanoparticles due to their nontoxic nature compared to other catalysts. Furthermore, it was identified that the transesterification conversion process proved to be an effective technique for converting used cooking oil into biodiesel. Regarding the fuel blends, it was observed that waste cooking oil biodiesel (WCB) FeO75 showed better thermal efficiency and lower fuel consumption, as visualized in Figure 4a,b.



(**a**)



(**b**)

Figure 4. (**a**) Brake thermal efficiency versus load. (**b**) Brake-specific fuel consumption versus load. Adapted from John et al. [26].

Furthermore, environmental pollution, climate change, global warming, and ozone layer depletion caused by the combustion of fossil fuels have been the primary causes of air quality degradation and important environmental issues. This fact, in combination with the extensive utilization of fossil fuels in the transportation sector and the production and generation of electricity, has made it difficult, firstly, to supply fossil fuels, and secondly, to mitigate environmental pollution, facts that are negatively linked with the global economic crisis and, most importantly, with human health. The Paris Protocol set a 60% decrease in global emissions by 2050, as well as a limit on the increase in global temperature over the pre-industrialization period. In this context, as a way to face the problems of fossil fuel, the use of alternative fuels can be a fruitful option to meet the energy needs of the planet, as well as reduce emissions. Biodiesel production represents an excellent alternative to meet these energy problems and the climate aspect of emissions of pollutants. Dey et al. [27] indicated that biodiesel production increased from 0.84 billion liters in 2000 to 20.2 billion liters in 2010 and 32 billion liters in 2014, i.e., global demand was strengthened. The fundamental reason for the increased interest in biodiesel is its nontoxic, renewable, sulfur-free nature, natural lubricity, high flashpoint, and ability to significantly reduce pollutant emissions. Several feedstocks may be used to make biodiesel, but palm oil has been shown to be the most dominant biofuel owing to the biggest global contribution (35%), a minimum market price of 660 USD/ton, a maximum oil content (5000 kg oil/ha), and production yield (4.2 MT/ha). Dey et al. [27] also commented that the global palm oil market was growing steadily and was expected to reach a market value of 92.84 billion USD by 2021. However, certain solutions have been proposed to survive the competition and emerge as one of the most important economical edible oils, while addressing the global demand for alternative fuel.

It is important to remember that the raw material and the input depend on each region and must be used to meet social, economic, environmental, and logistical aspects in the development of the country's energy matrix. This type of relationship was addressed by Dey et al. [27], where the use of palm oil as a potential solution for a future renewable fuel was critically discussed. In this regard, oil palm (*Elaeis guineensis*) is a specie of the *Arecaceae* family or palm tree that grows up to 20 to 30 m in height, native to western and southwestern Africa. It is native to Sri Lanka, Madagascar, Malaysia, Indonesia, Thailand, the West Indies, Central America, and various islands in the Indian and Pacific seas. This type of biodiesel produced from palm has an advantage as a remarkable alternative in economics, environment, and energy efficiency. Summarizing this discussion, Table 2 presents some advantages and disadvantages of this type of biodiesel, which can be used as a tool to help choose the type of biodiesel, considering these economical, environmental, and energy aspects.

Another important aspect highlighted with the palm biodiesel blend has been its effectiveness in reducing exhaust emissions such as CO, CO_2, HC, and smoke, compared to basic diesel. Palm oil is highly versatile and can be used for food and as a fuel in various applications. The lower market price compared to other vegetable oils and the diversified use as food, other commodities, and biodiesel make palm oil the most attractive vegetable commodity.

Because of the globe's population and food growth, the world will require more biofuels to reduce carbon emissions in the transportation sector. Therefore, it can be established that palm oil will increase continuously in the coming years due to insufficient production of other oils and fats for food and fuel purposes. Similarly, with more important advantages, such as high production yield, improved waste management, and high employability, palm industries have become one of the most feasible worldwide goods for energy security. Palm oil is still continuously overcoming the food versus fuel obstacle to satisfy the global demand, attending the food and energy balance. Dey et al. [27] also stated that the steady rise of the palm oil industry in recent decades has made this sort of biodiesel an appealing commodity for energy and food demands when compared to other vegetable oils.

Table 2. Advantages and disadvantages of using biodiesel made from oil palm, extracted from Dey et al. [27].

Advantages	Disadvantages
High oil content and higher yield of production with a low market price [28–30]	High viscosity and density of palm biodiesel results in poor fuel atomization and increases the ignition delay [31,32]
Palm biodiesel is ecofriendly, renewable, biodegradable, and nontoxic; it is compatible with any diesel engine without any modification [33,34]	High pour and cloud points, as well as low volatilities [35]
High cetane number of palm biodiesel lowers knocking tendency [32,36]	Early nozzle opening and advanced injection due to higher volume modulus [37]
Palm biodiesel possesses enhanced lubricity property [11]	High oxygen content in palm biodiesel releases a high amount of NOx emission [15,38,39]
Low sulfur content [40]	Several engine defects such as carbon deposit, piston ring sticking, lubricating oil thickening, and injector cooking [10,41]
High flashpoint improves safety [36,42]	Difficulties in cold weather performance due to poor flow properties at lower temperature [43]
Low emissions (CO, CO_2, and HC) and noise [15,44]	Lower energy content compared to diesel, increasing fuel consumption [36]
New job opportunities that improve living standards and social developments [13,28]	Negative impact on the environment due to deforestation of palm oil plantation [45]
Oxygen content (10–12%) in palm biodiesel contributes to better combustion characteristics [16]	

Another feedstock used for biodiesel production has been solketal as a green solvent, commercialized at market prices of >2000 EUR/t [46]. In the work presented by Turck et al. [46], the physical and chemical behavior of solketal in ternary blends with diesel/biodiesel oil was investigated. In biodiesel/solketal blends, hydrotreated vegetable oil (HVO) was employed as a renewable alternative for nonpolar aliphatic diesel fuel. HVO might be thought of as a prototype for other nonpolar fuel components, such as paraffinic fuel streams derived from the Fischer–Tropsch or BtL processes. The biodiesel blend without solketal exhibited a CN of 65.8. The blend, which contained 3% *w*/*w* solketal, had a CN of 64.8, showing that this solvent reduces the CN. In preliminary experiments, 10% solketal was shown to be soluble in diesel in the presence of 40% biodiesel. B20, B30, and B40 biodiesel blends make it possible to use single-phase or HVO diesel with varying solketal content (2% and 10%) at a constant amount of biodiesel. As a positive aspect, no solvent effect on fuel aging was detected. However, blends containing HVO tended to decrease the thermochemical stability compared to diesel fuel. Lastly, the physical features of these blends indicated that the polarity should rise without miscibility issues due to the use of biodiesel as a solubilizer. The need to verify different raw materials to produce biodiesel has encouraged researchers to search for energetically suitable inputs to replace diesel or make blends that can perform adequately and decrease environmental pollution. In this regard, the rice cultivation area in the world in 2016–2017 was 160×10^6 ha, leading to a global rice production of about 500×10^6 tons [23]. Meanwhile, the amount of Rice bran oil (RBO) generated during the same period was recorded at 1.5×10^6 tons, substantially lower than the global RBO production potential. RBO's high free fatty acid (FFA) concentration is seen as a significant drawback when utilized as a fuel in diesel engines, especially in cold climates, being an unfavorable characteristic due to high values of viscosity, surface tension, and density, leading to difficulty in pumping the fuel, as well as poor spraying and atomization characteristics, formation of the heterogeneous air–fuel mixture, and eventually incomplete combustion, leading to excessive increase in pollutant emission.

Given these disadvantages, the direct application of RBO in diesel engines does not appear appealing; hence, the conversion of oil into biodiesel via transesterification should be investigated [23]. Different methods have been used to produce biodiesel from RBO, including acid-catalyzed and base-catalyzed transesterification, lipase-catalyzed transesterification, and noncatalyzed methods. Base-catalyzed alcoholysis is the most advantageous because of the short reaction time and high efficiency. Generally, homogeneous base catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), are considered to have the greatest application thanks to their high activity, availability, and reasonable cost.

More efficient and energy-saving technologies in the biorefinery framework should be applied for biodiesel production from RBO to improve process yield and reduce production costs. Inexpensive, efficient, nontoxic, and reusable catalysts should be applied during biodiesel production from RBO. In addition, integrating the continuous production process with enhanced mass transfer characteristics, along with the combination of the reaction and separation phases in a single loop, can produce biodiesel with high quality and almost zero waste. Regarding the use of RBO-based biofuels, the experimental investigations published so far aim to evaluate the performance, combustion, and emission characteristics of diesel engines powered by pure RBO-based biofuels and their blends with mineral diesel.

Several experimental works have been conducted to determine the properties of blends of biodiesel [47], combustion behavior, and emission of pollutants [48]. In this context, using an experimental analysis, Lamba and Chen [47] determined the physicochemical properties of blends (B20, B40, B60, and B80) made of *Pongamia* and *Jatropha* biodiesel with EURO-III and EURO-IV high-speed diesel. The results showed that, for both *Pongamia* and *Jatropha* blends, an increase in diesel concentration resulted in a considerable decrease in viscosity and improved oxidation stability. The *Jatropha* blend showed a synergistic relationship with high-speed diesel, with the cetane index values for blends above 20% biodiesel being higher than those for pure biodiesel. The *Pongamia* blends did not show synergistic behavior regarding the cetane index values. Blends above 60% diesel exceeded the viscosity limit, while those above 40% biodiesel exceeded the density limits.

Similarly, using experimental analysis, Dordic et al. [48] evaluated the combustion properties and emissions of waste engine oil considering different blends with diesel, for the drive of a 40 kW furnace to verify the energy feasibility and environmental impacts in low-power heat generators. The results showed that a mixture of waste engine oil (WMO) blends generated higher combustion gas temperatures in the furnace than diesel, as well as higher NO, CO, and CO_2 emissions; the CO_2-to-CO ratio in the combustion gas was lower in WMO when compared to diesel. The concentrations of sulfate, sulfide, nitrate, and nitrite when in the atmosphere are harmful to the environment, and they were found in the combustion gases for all fuels tested, whereby the WMO blends generated more sulfate than diesel, but less nitrate, nitrite, and sulfite. The nitrate concentrations in all tests exceeded the allowable limits, and the nitrite concentration exceeded the limit only with diesel as fuel. Thus, it was concluded that WMO blends can be used as a replacement for diesel in low heat generators and internal combustion engines, with low fuel consumption and less environmental impact.

Determining the negative reason for the non-mass production of biodiesel is a significant factor to be addressed. In this sense, through bibliometric and regression methods, Bylan et al. [14] determined the causal relationship between environmental taxes and the increase in production and consumption of biofuels, thus describing the purpose of assessing the potential of state regulation in the development of the biofuel industry. They showed that environmental taxes have a relevant impact on the production and consumption of biofuels, that transport sector taxes have a medium-term effect, and that energy sector taxes have a more immediate impact on the increase in importance of bioenergy within a country. The study represents an analytical tool for adjusting and implementing new policies that aim to impact the energy sector with regulatory measures.

4. Biodiesel Production and Potential: Tropical Cultivars

Several countries that are entirely located in or have territories within the tropics are among the largest producers of biodiesel or those with high potential for research and dissemination of this biofuel. These are the cases of Brazil, Malaysia, Indonesia, Thailand, Bangladesh, Colombia, and, to a lesser extent, some countries on the African continent.

Countless agricultural cultivars produced in tropical climates have already been tested for biodiesel production, such as soy, sunflower, sugar cane, *Jatropha curcas*, *Moringa oleifera*, palm, corn, cotton seed, castor bean, rubber seed, and coconut. However, each of the agricultural varieties has distinct characteristics in obtaining biodiesel, differing even in the function of the types of catalysts involved in its transesterification process.

Transesterification is the process where triglycerides present in vegetable oils and branched into large molecules react with lower-molecular-weight alcohol in the presence of a strong acid or base catalyst, producing monoalkyl esters and glycerol. Because this process is reversible, excess alcohol is needed to ensure that the reaction occurs in the right direction. In its course, the triglyceride is converted first to diglyceride, and then to monoglyceride, resulting in monoalkyl esters and glycerol [49].

The catalysts are used to accelerate the biodiesel formation reaction, typically being homogeneous, heterogeneous, or enzymatic, as shown in Figure 5. Due to their importance in this process, there have been numerous studies in the literature in the last 3 years related to the most diverse methods and catalysts to obtain biodiesel from tropical cultivars.

Maposa et al. [50] analyzed the transesterification for biodiesel production from soybean oil and methanol, using $Ni_{0.5}Zn_{0.5}Fe_2O_4$ synthesized by combustion as a magnetic catalyst and using X-ray diffraction (XRD), N_2 physisorption at 77 K, Fourier-transform infrared, thermogravimetry, scanning electron microscopy (SEM), and transmission electron microscopy for analysis. They obtained a biodiesel yield of 92.1% for a methanol/soybean oil molar ratio of 9:1 and catalyst loading of 2% at 180 °C in 3 h. Furthermore, they observed that $Ni_{0.5}Zn_{0.5}Fe_2O_4$ has excellent magnetic properties, suggesting that the catalyst can be separated and reused after the reaction. Zhu et al. [51] analyzed the production of soybean oil biodiesel using CaO/Ag as a synergistic heterogeneous nanocatalyst from kinetic analysis, economic evaluation, and a search for optimization of this process. The authors found that the nanocatalyst reduced the mass transfer resistance of triglycerides during transesterification, obtaining a maximum biodiesel yield of 90.95% ± 2.56% for a molar ratio of methanol oil of 13, with CaO/Ag loading of 5% and a reaction time of 90 min at a reaction temperature of 72 °C. Wang et al. [52], achieved a maximum biodiesel conversion yield of 98.4% for a methanol-to-oil molar ratio of 10:1 mol/mol in a reaction at 100 °C and reaction time of 60 min. This was obtained in a kinetic and optimization analysis of soybean oil biodiesel production, using new tetraethylammonium ionic liquids with amino-acid-based anions as catalysts.

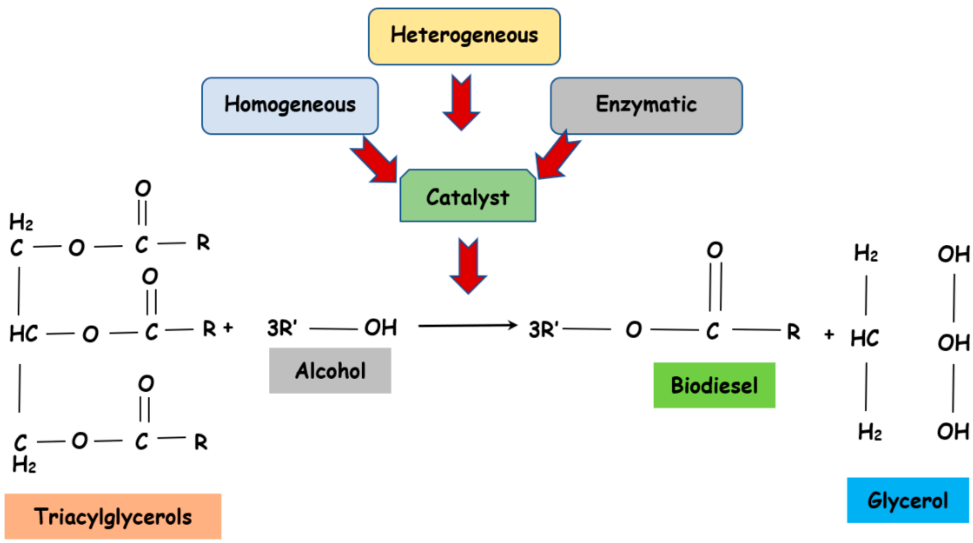


Figure 5. Catalytic routes for biodiesel production through the transesterification reaction (adapted from Baioni et al. [53]).

Dahdah et al. [54] analyzed the effect on biodiesel production from sunflower oil transesterification with different Ca–Mg–Al-based catalysts. The effect of heat treatment was studied, and the mixed oxides obtained were characterized by X-ray diffraction, N_2 adsorption–desorption, and CO_2 temperature-programmed desorption. The authors determined that the best performance as a catalyst was obtained using uncalcined Mg_4Al_2 impregnated with 40 wt.% calcium, followed by calcination at 600 °C, and the optimum biodiesel conversion of 95% occurred in a reaction time of 6 h for a molar ratio of 15:1 methanol/oil in a reaction at 60 °C. Baioni et al. [55] investigated biodiesel production from sunflower oil using basic CaO/ZSM-5 catalysts. Various combinations of these elements were prepared, calcined at 800 °C to form different catalysts, and tested in the transesterification reaction. The authors found that the most active catalyst was the CaO/ZSM-5 catalyst with a load of 35 wt.%, which gave the highest yield of fatty acid methyl ester. Marinkovic et al. [56], aiming to obtain a catalyst with better performance in the transesterification of sunflower oil and consequent higher biodiesel yield, performed the synthesis of a heterogeneous catalyst based on the support of aluminum oxide (Al_2P_3) promoted with potassium iodide (KI) as an active dopant, varying the methods used for the synthesis of the support. The authors found that the sol–gel method was the most favorable, achieving up to 99.99% maximum conversion for a molar ratio of methanol to sunflower oil of 15:1, catalyst loading of 2.5 wt.%, 600 rpm stirring rate, and 4 h of reaction.

Gutiérrez-López et al. [57], aiming to obtain more sustainable biodiesel from *Jatropha curcas* oil with lower environmental degradation capabilities, assessed the use of a heterogeneous catalyst based on $NaFeTiO_4/Fe_2O_3$–$FeTiO_3$ for transesterification. The synthesis of this material was evaluated as successful using techniques such as XRD, and SEM multivariate statistical optimization, which resulted in a maximum biodiesel conversion of 93.24% at a molar ratio of 12.47:1 methanol/oil, catalyst loading of 13.80 wt.%, and 590 rpm stirring rate. In the same context of the search for catalysts that provide less environmental degradation in the formation of biodiesel from the oil of *Jatropha curcas*, the studies presented by Sahu et al. [58] and Amesho et al. [59] should be highlighted. The first evaluated the use of K/Mg for the transesterification process. It was found that the ratio of 1:2 K/Mg was the best combination to provide biodiesel formation, with good physicochemical characteristics being found in the catalyst formed in this ratio, at a maximum of 99.5% conversion for a 10:1 mol/mol proportion of methanol/oil, in a reaction lasting 4 h at 70 °C using 6 wt.% catalyst. Meanwhile, the latter authors carried out a kinetic study of biodiesel formation using CaO-derived bioresidue as a heterogeneous catalyst via a microwave heating system. The catalyst proposed by the authors was prepared by calcination and characterized using different instrumental techniques, including Fourier-transform infrared spectroscopy (FTIR), energy-dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD), and Brunauer–Emmett–Teller (BET); in its optimized formation and at 5 wt.% loading, it allowed a yield of 91.1% biodiesel conversion in a reaction time of 3 h (microwave power of 800 W) at a temperature of 65 °C and methanol/oil molar ratio of 9:1.

Using agricultural waste, Foroutan et al. [60] evaluated the use of walnut shell/ZnO/K_2CO_3 as a catalyst for transesterification to form biodiesel from *Moringa oleifera* oil. X-ray and FTIR tests confirmed the expected potential of the compounds as catalysts. A model was made to predict the conversion into biodiesel from changes in the reaction variables, and the maximum efficiency obtained was 97.34% of its formation rate in a methanol-to-oil mol/mol ratio of 18:1, with a reaction duration of 4 h at 65 °C and a 4 wt.% catalyst. At [60], a hydroxyapatite (HAp) support derived from poultry bones with MgO/K_2CO_3 as a heterogeneous catalyst for biodiesel production from *Moringa oleifera* oil was tested. The generated catalyst was analyzed using SEM, EDX-Map, XRD, FTIR, and N_2 adsorption/desorption. The reaction parameters were varied to evaluate the impact on the biodiesel generation rate, and the maximum obtained was 99.3%.

Lopes et al. [61] evaluated the behavior of the transesterification reaction of palm fatty acid oil to form biodiesel with the use of Oxone® as the catalyst of this process. After optimization of the reaction variables, such as Oxone® concentration (%), temperature, and reaction time, it was possible to obtain a conversion rate higher than 90% with 15% Oxone® by mass at 42 °C, ethanol-to-oil molar ratio of 5:1, and a reaction period of 12 h. Ojala et al. [62], aiming to improve the transesterification of oil obtained from the dendê palm, the fruit of a tropical palm tree, applied heat treatment on chicken eggshell to improve its performance as a heterogeneous catalyst for biodiesel production. The following parameters were varied to obtain optimal biodiesel formation: calcination temperature, catalyst amount, methanol-to-oil molar ratio, and reaction time. The optimal operational parameters were 4% catalyst mass proportion, methanol-to-oil molar ratio of 10:1, reaction temperature of 50 °C, and elapsed time of 1 h, yielding a biodiesel conversion rate of 97.10%.

Regarding cottonseed oil, Malhorta et al. [63] evaluated the performance of porous silica impregnated with 5-Ma/ZnO as a solid catalyst in the transesterification process to obtain biodiesel from this raw material. The catalyst prepared underwent characterization via BET, FE-SEM, and XPS and was used in the reaction. Its optimization, equivalent to 12% by mass, in a molecular weight ratio of 24:1 methanol/oil, for a reaction temperature of 65 °C, time of 4 h, yielded a conversion level of 74%.

As for the catalysts for castor oil transesterification, Du et al. [64] proposed, synthesized, and evaluated the use of three carbon-based MgO solid bases for the production of biodiesel employing this bio-oil. The methods used to prepare the catalysts were sol–gel and calcination. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), N_2 adsorption (BET), Fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA) were used to analyze and evaluate the physicochemical properties of the generated catalysts. The best results were found using the MgO-UREA-800 catalyst, which allowed obtaining an optimum biodiesel yield of 96.5% for an ethanol-to-oil molar ratio of 12:1, catalyst loading of 6 wt.%, reaction temperature of 75 °C, and reaction time of 1 h. Khan et al. [65], aiming to increase biodiesel production using castor oil, evaluated the use of CaO nanocatalyst based on a mussel shell doped with praseodymium. The authors used different catalyst ratios (3, 5, 7, 9, and 11 wt.%), with characterization conducted using XRD, TGA, and SEM. The optimum biodiesel yield of 87.42% was obtained by 7 wt.% Pr-CaO nanocatalyst, methanol-to-oil ratio of 8:1, and reaction temperature of 65 °C.

Both Bharadwaj et al. [66] and Aryasomayajula et al. [67] searched eggshell compounds to find new catalysts for the transesterification of rubber seed oil (RSO). The first used calcium oxide from eggshells as a direct catalyst to obtain biodiesel. After characterization of the catalyst by MEV, SEM-EDS, XRD, and FTIR, a computational methodology of parameter optimization was used, as well as a prediction model, obtaining a conversion of 99.7% of biodiesel, for a ratio of 12:1 of methanol to oil in mol/mol, with 4 wt.% catalyst and a reaction time of 3 h. The second used calcined eggshell impregnated with Al_2O_3 as a heterogeneous catalyst for biodiesel formation, comparing two methodologies for the optimization of reaction parameters: response surface methodology (RSM) and artificial neural network (ANN).

Helmiyati [68] developed a heterogeneous catalyst using a MgO–Fe_3O_4 composite and cellulose biopolymer to evaluate its application in transesterification for the formation of biodiesel from coconut oil. After physicochemical characterization of the generated catalyst and optimization of the reaction, they obtained a conversion of 89.93% biodiesel in 2 h of reaction and application of 4 wt.% of the catalyst, proving that the elements used are promising for application as catalysts in the production of biodiesel from this tropical raw material. In the case of Widiarti et al. [69], the improvement of the performance of NiO/CaO/MgO from natural limestone as a catalyst for coconut oil transesterification and biodiesel formation was sought. In this process, the limestone was first converted into a catalyst via the calcination–hydration–dehydration method. Thermal decomposition at 900 °C transformed the dolomite $CaMg(CO_3)_2$ into large CaO/MgO crystals, and the size of the crystals formed was reduced by adding polyethylene glycol. Implementing the catalyst formed from this methodology caused an increase in oil conversion from 16.45% to

49.27% in biodiesel; after optimization of the reaction parameters, it was demonstrated that conversion of up to 81.76% was possible. However, introducing NiO further improved this yield, reaching up to 90%.

Other studies related to transesterification catalysts for biodiesel formation from tropical agricultural varieties are listed in Table 3.

Table 3. Summary of catalyst studies applied to tropical cultivars.

Feedstock	Catalyst Element	Alcohol/Oil Proportion	Maximum Conversion Rate	Authors
Jatropha Curcas	CaO/coal fly ash	12:1 methanol/oil	95.64%	[70]
Jatropha Curcas	NiO	15:1 methanol/oil	59.8%	[71]
Jatropha Curcas	KF-impregnated CaO	10:1 methanol/oil	97%	[72]
Jatropha Curcas	*Heteropanax fragrans* (Kesseru)	12:1 methanol/oil	97.75%	[73]
Sunflower	K_2CO_3	6:1 methanol/oil	95.3% ± 1.2%	[74]
Sunflower	K_2CO_3/talc material	6:1 methanol/oil	98.4%	[75]
Soybean	Ni/CaO–MgO	27:1 methanol/oil	97.6%	[76]
Soybean	$ZnO{\cdot}Na_2ZrO_3$	14:1 methanol/oil	97%	[77]
Moringa Oleifera	CaO and chicken eggshells	6:1 methanol/oil	86.56%	[78]
Palm	Zn/Ca	30:1 methanol/oil	83.87%	[79]
Palm	Zn–Ce/Al_2O_3	18.53:1 methanol/oil	99.44%	[80]
Cottonseed	CaO and MgO impregnated on saw dust ash	6:1 (CaO) and 8:1(MgO) methanol/oil	86% (CaO)	[81]
Castor	Carbon-doped mix metal oxide	21:1 methanol/oil	91.1%	[82]
Castor	Al_2O_3-, Al_2O_3–NiO-, and Al_2O_3–CoO-modified bentonite	15:1 ethanol/oil	98% (Al_2O_3–CoO)	[83]
Rubber seed	Potassium oxide alumina supported by (K_2O/Al_2O_3)	10:1 methanol/oil	96.9%	[84]
Rubber seed	SO_3H-MCM-	16:1 methanol/oil	84%	[85]
Rubber seed	CaO with subcritical methanol	28:1 methanol/oil	86.79%	[86]
Coconut	Rice husk silica and aluminum foil	4:1 methanol/oil	Approximately 100%	[87]

5. Biodiesel Applications in Internal Combustion Engines

In recent decades, the use of biodiesel as a source of ignition for internal combustion engines has been investigated and analyzed, emphasizing the role of placing an alternative source that allows the production of energy [4,88], while reducing environmental impacts [89], as well as enabling the use of local input in its production [90].

According to this critical survey of biodiesel and its applications in internal combustion, the main studies and research conducted and discussed are shown in summary form in Figure 6: energy, exergetic, exergoeconomic, and environmental analyses directed toward the viability of this biofuel and its relevance in driving internal combustion engines, followed by studies in pollutant emissions, aiming at the detailed analysis of ways to reduce or mitigate the number of pollutants rejected into the atmosphere, to make the use of biodiesel more competitive. Another widely researched topic is the study and determination of the adequate concentrations that may provide the best energetic and environmental performances, followed by subjects directed toward the operational and technical availability of biodiesel in engines, in terms of the mechanical wear and performance of these equipment. Lastly, a well-discussed topic is related to several modifications and adaptations in internal combustion engines to improve their performance respecting technical, financial, and mainly environmental criteria.

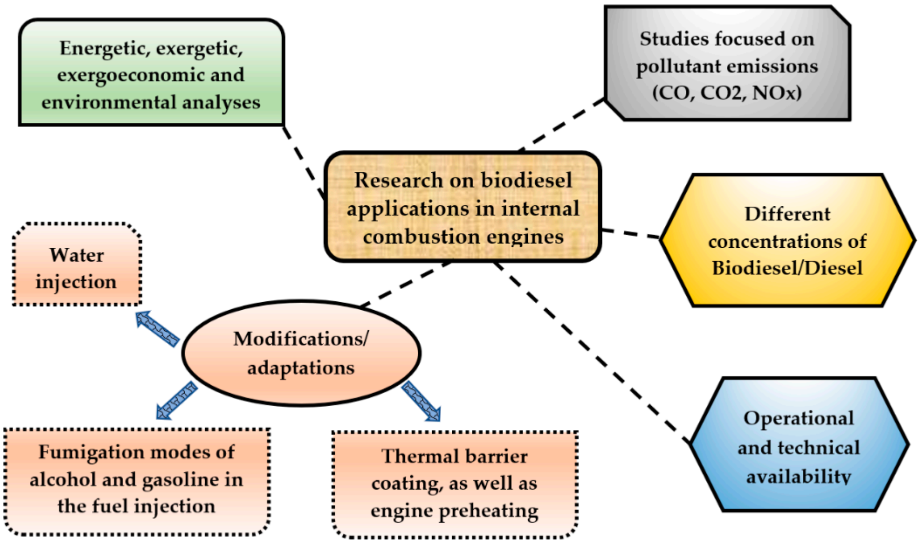


Figure 6. Leading research on biodiesel applications in internal combustion engines.

In this context, studies related to energy analysis aiming at the first and second laws of thermodynamics are relevant to verify and compare the performance of internal combustion engines using diesel and biodiesel as a drive source [91]. This type of analysis, aimed at the SPECO methodology and environmental assessment, was presented in Cavalcanti et al. [92], where an exergetic, exergoeconomic, and exergoenvironmental study was carried out to verify the performance of a stationary direct injection engine considering different biodiesel concentrations (5%, 25%, 50%, 75%, and 100%). The study was centered on life cycle analysis using Simapro software and considering the indicated Eco-indicator 99 for environmental impact. The life cycle analysis checked the effects of the different categories, considering the production of 3.36 kg of soybean diesel and 0.406 kg of glycerin. The results in terms of biodiesel concentration, cost, and environmental impact were that the engine showed the best exergetic performance (~33%) at low biodiesel concentrations (5/25%), with lower performance (~32%) at higher biodiesel concentrations (50%, 75%, and 100%) considering 27 kW load, but the variation was slightly small (<1%). In monetary terms, for lower biodiesel concentrations, the values were lower (42–73 USD/GJ) than those for pure biodiesel (94–160 USD/GJ), for the 27, 18, and 9 kW loads, leading to an exergoeconomic factor ranging from 0.355% (5% biodiesel) to 0.1613% (100% biodiesel), i.e., there was a decrease as a function of biodiesel purity. This indicates that increasing biodiesel purity led to worse financial performance conditions. However, from an environmental point of view, increasing purity leads to significantly lower environmental impacts associated with power. Therefore, the authors emphasized that the choice of the best fuel is linked to the desired objective of the system, be it exergetic, financial, or environmental performance, defining this methodology as a decision-making tool in the selection of fuels for power generation in internal combustion engines.

The importance of the combustion process using fuel blends within the thermodynamic cycle was presented by Novaes et al. [93]. This study presented a numerical model of the thermodynamic cycle of a diesel engine operating with diesel/biodiesel blends, considering the processes of compression, combustion, and expansion. The first law of thermodynamics, the equation of state, and heat transfer through the walls employing the Wiebe function were used, and the model was built on the basis of a zero-dimensional mathematical model to determine the behavior of the pressure and temperature of gases inside the cylinder as a function of the crankshaft angle. The results showed a reduction in the values of gas temperature and pressure as a function of increasing biodiesel concentration in the fuel.

The use of biodiesel in conventional engines has not been as efficient as regular diesel; thus, studies have been directed at finding alternatives that can help increase performance and significantly reduce the emission of pollutants. Khan [91] surveyed researchers highlighting several studies on modifying engine components and systems to develop a diesel engine that runs on biodiesel to improve performance, progressive combustion, and reduced emissions. Although the use of biodiesel tends to provide an alternative renewable fuel, there is the possibility of increased emission of nitrogen oxide (NO_x) in the combustion process.

Caligiuri et al. [94] conducted an experimental study in a cogeneration system to verify the influence of the use of biodiesel blend and injection time on NO_x production and the study on the energy performance of the cogeneration system. Four types of Biodiesel blends B0, B15, B30, and B100 produced from palm oil methyl-ester were used. In addition, three injection times (17.2°, 20.8°, and 12.2°), and three power loads (0.90, 2.45, and 3.90 kW) were evaluated. The tests were performed using an experimental micro-cogeneration test bench, consisting of an internal combustion engine directly coupled to a thermal energy recovery system (Figure 7). The single-cylinder type has a water-cooled compression ignition engine (Farymann 15W430) coupled to a synchronous AC generator. The thermal energy, recovered by cooling the motor from the water circuit, is passed through a heat exchanger to the external water circuit. The electrical energy output is dissipated through an absorption system (0.1–4.0 kW) using several halogen lamps. The genset manufacturer is known as "Paguro 4000", and it is frequently applied as a power generator unit on small marine vessels.

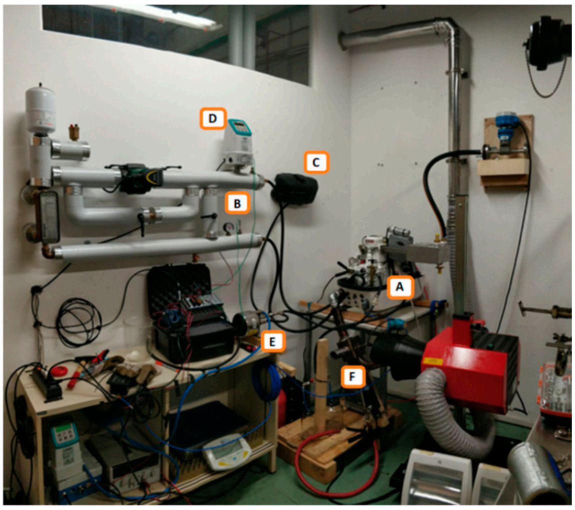


Figure 7. The test bench with its main components: (**A**) the genset; (**B**) the heat-recovery system; (**C**) the fuel tank; (**D**) the water-circuit mass flow meter; (**E**) the fuel mass flow meter; (**F**) the exhaust line [94].

From the experimental analysis of the collected data, statistically adjusted response models of the system's electrical efficiency (Equation (1)) and NOx emission (Equation (2)) were built. These equations allow describing the behavior of the electrical efficiency (%) and the NO_x emission (ppm) of the cogeneration system as a function of load (*L*), biodiesel mixture (*B*), and injection time (*IT*) of the fuel.

$$\eta_e = 1.69 + 11.98 \cdot L + 0.03 \cdot B - 1.51 \cdot L^2. \quad (1)$$

$$NO_x = -129.13 + 207.24 \cdot L + 6.29 \cdot IT - 1.29 \cdot B + 4.33 \cdot L \cdot IT - 0.14 \cdot L \cdot B - 28.86 \cdot L^2 + 0.01 \cdot B^2. \quad (2)$$

The study led to the following final considerations:

- It was observed that increasing the percentage of Biodiesel in the blend led to a significant improvement in the electrical and thermal efficiency of the cogeneration system, specifically for the blends of B30 and B100. Values of 29% and 42% electrical and thermal efficiency were achieved at full load. Through the response surface methodology (RSM) analysis, it was detected that the electrical efficiency has a greater dependence on load variation (~+15%) than the biodiesel blend (~+2.7%).

- Another important aspect was the effect of injection timing on the production of NO_x emissions, observing an average reduction of 27% when applying an early rather than a late injection strategy and 16% when compared to a standard injection strategy. In addition, this procedure allowed homogenization for the operating conditions in the power output. This positive effect is related to the thermal NO_x formation mechanism; that is, by delaying fuel injection, combustion temperatures in the cylinder and NOx emissions were reduced.
- The regression models allowed predicting the behavior of electrical efficiency and NO_x emissions with excellent accuracy, with $R^2 > 0.990$, representing a good way to predict the overall behavior of cogeneration systems using biodiesel as a driving fuel.

Different applications have been tested in internal combustion engines that use biodiesel as fuel, such as water injection, alcohol, and gasoline fumigation modes, incorporation of guide vanes, thermal barrier coating, and even preheating of the engine. Among these, a very environmentally friendly alternative is the introduction of hydrogen into the biodiesel blend, input directly into the engine, as shown by Zhang et al. [95], where an experimental and mathematical study was conducted with a diesel engine using different biodiesel blends as fuel, plus hydrogen injection for combustion. The biodiesel blends were produced from rubber seed (RSO) with concentrations from 10% to 30% and 10 L/min of constant hydrogen supplied directly to the combustion chamber through an air intake manifold. The tests were completed considering the partial and full load of the equipment (25–100%). In the mathematical part, the machine learning technique was used to build a long short-term memory (LSTM) regression model to predict the engine performance and operational characteristics, such as brake thermal efficiency and brake-specific fuel consumption, as well as the pollutant components of the combustion products.

Among the most important results, the following was shown:

- The use of this type of biodiesel with the inclusion of hydrogen increased the thermal efficiency of the brakes, in addition to reducing fuel consumption, specifically with the use of B10H (10% biodiesel with hydrogen), which allowed obtaining the maximum efficiency value of approximately 32%, a reduction of up to 6% when compared to the use of biodiesel without the addition of hydrogen.
- Another important effect of this blend was the decrease in the temperature of the combustion gases of the other blends tested (B10, B30, B30H, B50, and B50H). In the same context, there was a significant reduction in the emission of pollutants (CO_2, CO, HC, and NO_x) due to the addition of biodiesel and hydrogen blends to diesel (excess supply of oxygen molecules to the combustion chamber).
- Regarding the regression model, it was evident that the LSTM approach can be applied to predict performance and emission under partial or full load conditions. Considering the findings, the 10% biodiesel blend with 10 L/min hydrogen can be a potential alternative to diesel.

In the same context, Markov et al. [96] investigated the physicochemical properties of rapeseed oil blends with diesel and emulsified multicomponent biofuel, studying its emissions, thermal efficiency, and nozzle inner flow, and then determined if the blends can be used as a replacement for diesel in internal combustion engines. The engine used to collect the data measurements was a diesel engine D-245. Experiments were conducted using a diesel engine D-245 considering the external characteristic curve and a 13-mode test cycle, as shown in Figure 8, to determine the engine performance and emission data.

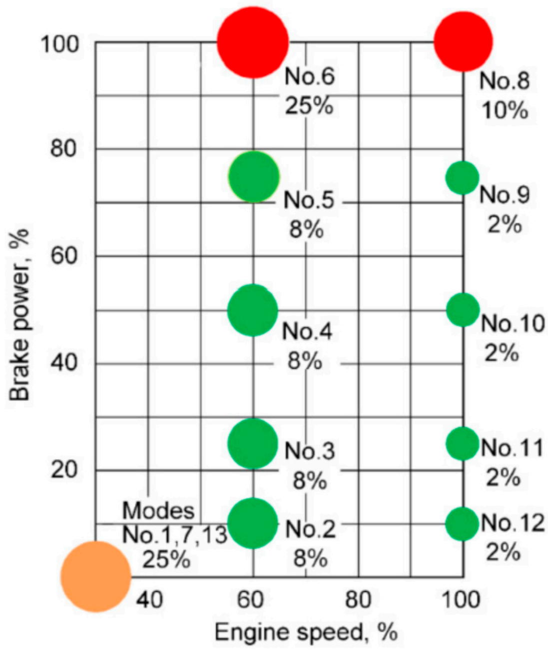


Figure 8. Operation points in the 13-mode steady-state test cycle ECE R49 for vehicle diesel engine. The percentage represents the mode time-share (weighting factor). Red circles—full load; green circles—partial load; orange circles—idle [96].

The results showed that the tested blends and emulsions could be efficiently used as fuel in transport diesel engines. The emulsions provided much better emission characteristics than the diesel, with the addition of water being much more impactful in reducing NO_x values than the rapeseed oil. Table 4 shows the results of the test performance of the engine.

Table 4. Diesel engine D-245 performance working on pure DF and DF-RO blends. Operating conditions were the external characteristic curve and 13-mode test cycle.

Engine Performance	Volume Content of RO			
	0%	20%	40%	60%
BSFC, g/kW-h	249.0/225.8	255.1/231.8	258.1/239.8	265.1/243.1
BTE	0.340/0.375	0.340/0.374	0.345/0.372	0.345/0.376
Exhaust smoke opacity, % on Hartridge scale	11.0/25.0	8.0/16.5	7.0/13.0	8.0/11.0
ABSFC over the 13 modes	247.20	254.38	259.40	272.23
ABTE over the 13 modes	0.343	0.341	0.343	0.336
IBSNOx over the 13 modes, g/kWh	7.442	7.159	7.031	6.597
IBSCO over the 13 modes, g/kWh	3.482	3.814	3.880	3.772
IBSHC over the 13 modes, g/kWh	1.519	0.965	0.949	1.075

The water also helped reduce the viscosity of the emulsified fuel, which improved fuel injection and subsequent combustion processes. Both water and rapeseed oil significantly impacted reducing exhaust smoke; thus, in conclusion, the emulsified multicomponent biofuel presented less environmental impact while maintaining similar properties to the regular Diesel.

The possibility of declining global oil supply, uncertain crude oil prices, global warming, and national energy security drive investments in alternative renewable fuels. In Nabi et al. [97], a study referring to the performance and emissions of engines using mixtures of waste tire oil with diesel and biodiesel was conducted. The authors presented the steps used in the preparation of biodiesel and tire oil, focused on physicochemical properties, engine performance, exhaust emissions, and fundamental energy and exergy parameters. They also comprehensively characterized the fuel and significant reductions in greenhouse gases (GHG) with unaltered engine noise emissions. All tests were carried out on a single-cylinder direct-injection diesel engine with natural aspiration. A list of the engine's characteristics, the measuring instruments, and their precision and uncertainty were shown. The results obtained from the tests demonstrated that the engine performance parameters, including braking power, braking torque, and average effective brake pressure, were lower for the binary and ternary mixtures than the reference diesel fuel. Such parameters were compared with simulation data performed in the commercial software Gamma Technology and showed maximum variations within the acceptable range. The thermal efficiency of the brake for the binary and ternary mixtures was almost identical, while the specific fuel consumption of the brake was higher for the same mixtures. There was a similarity between all mixtures and the reference diesel for the tests on engine noise. In addition to the engine performance parameters mentioned above, the exergy, energy, and respective fuel efficiencies were identical. Their relationship showed a straight line, indicating that exergy and energy correlate strongly. NOx emissions were higher for the mixtures than for the reference diesel. This fact can be explained by increasing engine speeds, given that there is a greater release of gross heat. CO_2 emissions for the two ternary mixtures were lower at all engine speeds than diesel. On the basis of the mentioned information, it is possible to promote waste tire pyrolysis oil as an alternative fuel for diesel engines. This is in line with alternative energy development initiatives around the world.

With the limited supply of fossil fuels, a proposal emerged to use a biodiesel/diesel mixture in internal combustion engines to reduce dependence on petroleum derivatives. However, this is still an area of study under development, already exhibiting advantages and disadvantages, such as the high viscosity of biodiesel, which results in high NO_x emissions during combustion. In Selvan et al. [98], 12 different biodiesel/diesel blends prepared by splash techniques were analyzed. The bases were four microalgae, four macroalgae, two cottonseed oils, and two *Pongamia* oils. Using the standard protocol of the Bureau of Indian Standards 1448 (2007), the following parameters were analyzed: kinematic viscosity, specific mass, API degree, flashpoint, combustion point, cetane number, aniline point, and calorific value. For performance analysis, the indicators were the emission of carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), hydrocarbons (C_xH_y), and smoke. Brake thermal efficiency (ηBT), total fuel consumption (TFC), and specific fuel consumption (SFC) were also considered. For comparison, a four-stroke, single-cylinder internal combustion engine, with a compression ratio of 18:1, and a nominal power of 3.75 kW, operating at a constant speed of 1500 rpm and connected to an electric dynamometer, was used in the tests. Among the blends, AO10D produced the best result with a cetane number of 51.20 and ηBT of 45–50% load. The combustion was complete. CO_2 (2.3%), CO (22%), NO_x (0.97%), and smoke (6.54%) emissions decreased compared to 50% load. The AO10D blend could be used as an alternative fuel for diesel engines without any physical modification.

It is important to note that several applications use diesel/biodiesel blends in internal combustion engines operating on the diesel cycle. Nevertheless, it is necessary to evaluate the operational availability of these thermal machines depending on the type of concentration, specifically, the type of biodiesel used and its operational and energy availability. In this context, Zhuravel et al. [99] conducted an experimental study on heavy vehicles and tractors operating with a blend of biodiesel to determine the availability of these equipment operating with this alternative fuel. The Kolmogorov system method was used to describe the variability of the state probabilities of a multielement system with failures and restorations. Regarding the experimental methodology, tests were conducted using 12 MTZ-80 tractors of the traction class (1.4) due to the high level of reliability (0.8–0.9), using the same initial resource of the engine fuel systems, as well as the same operating conditions at the beginning of the tests. The fuel mixture used was B70, i.e., 70% mineral fuel and 30% rapeseed oil. The most significant results achieved from the research were that the availability factor of the fuel system operating with biodiesel and without any substitution of the structured materials of the system was 0.66, whereas, with the substitution, it increased to 0.71, due to the adaptation of the systems with this type of fuel. The technical utilization coefficients without and with the replacement of materials were 0.36 and 0.40, respectively. In the same context, the time to perform technical operations for the maintenance and repair of fuel equipment decreased by approximately 10–25%. As an environmental aspect and to maintain the improvement of the availability factor, it was recommended that the structural materials of the fuel system be replaced with an inert biodiesel fuel for the harsh environment, based on carboxylic acids.

Although not a direct application with internal combustion engines, biodiesel represents an alternative for cooling lithium-ion batteries, as shown by Al Qubeissi et al. [100], where the effect of using different types of biodiesel and two conventional refrigerants (air and 3M Novec) on maintaining the proper operating temperature in hybrid vehicle batteries was compared through a CFD analysis. Four dielectric biodiesels produced from palm, karanja, *Jatropha*, and mahua oils were used. Compared to conventional coolants in these battery modules, the biodiesel fuels were shown to provide better results in terms of maintaining the lithium-ion battery (LIB) temperature within the operating range, with palm biodiesel showing the best thermal performance (a 43% reduction compared to conventional coolants), while maintaining the operating performance of the battery module.

6. Final Considerations on the Use of Biodiesel in Energy Production

Several factors have been highlighted about the use of biodiesel in electric power production, as well as in the transportation sector, such as the use of alternative fuel, reduction in pollutants in the atmosphere, encouragement of the local market through the use of local inputs for production, and modifications that improve the performance of the generation systems [27,89,101]. In this context, the literature has demonstrated the various applications of internal combustion engines to improve the performance of generation systems by injecting water into the combustion process [93], cycle changes to reduce CO and NO_x formation [102–105], strategic systems to check the availability of vehicle operation [99], and the use of intelligent methods to improve the control and operation of systems that use biodiesel or biodiesel blends to drive them [95,106].

The use of thermodynamic methods based on the second law of thermodynamics (exergy) with financial aspects (exergoeconomics) and environmental impact (exergoenvironmental and life cycles) has helped with the verification and feasibility of generation system projects [92,107], through the total and partial use of biodiesel as a source of driving energy, encouraging the use of this renewable source and replacing fossil fuels. All of these approaches have the main objective of reducing the emission of pollutants in the environment, and enabling the possibility of competing energetically with other renewable energy sources, such as solar and wind [108,109].

Many studies have shown promising results for the use of biodiesel in comparison with diesel [9,110]. In the context of engine performance, studies related to emissions and thermal efficiency have been conducted, showing good thermal results and, in some cases, an improvement in pollutant emissions [6,27,97,103]. Other studies have tested diesel and biodiesel blends, to evaluate their properties and propose replacements for the use of regular diesel [92,98,103].

To reduce the environmental impacts, studies of diesel blends and residual engine oil that would be discarded were conducted, reaching results compatible with diesel for use in internal combustion engines with low fuel consumption, which represents an advantage in terms of energy and environmental aspects when compared to fossil fuels, as well as in terms of the socioeconomic aspect, since it encourages the production of biofuel, stimulating the local economy through direct and indirect jobs [12,19,111], as well as allowing for the expansion of the energy matrix in the country [14,19].

Given what has been presented in the specialized literature on the subject, it can be seen that biodiesel and its blends with diesel can be applied as a substitute fuel for diesel [112,113], thereby reducing environmental impact and pollutant emissions [104,114].

Other studies have also shown that environmental taxes can impact the production and consumption of biofuels, having a medium-term effect on transport taxes and an immediate impact on the development of the importance of bioenergy within a country [11,12,19].

As seen from the state of the art, there is a great interest in the scientific community in biodiesel production [115]. It is vital to note, however, that production through tropical cultivars plays a relevant role in developing and disseminating biofuels, which concomitantly necessitates the scientific development of nations located in the tropics [18,116].

In this scenario, the transesterification process [7,75] for biodiesel formation is fundamental to increase its potential as an energy source, once higher conversion rates of bi-oil into biofuel, in more efficient chemical reactions, increase the viability of using the numerous cultivars developed in tropical climates [117,118], with the search for new catalysts for this reaction being a determining variable in this process [119,120].

Governments and international entities can and should create policies to encourage the use of biodiesel as an incentive source for the use of renewable energy. In Brazil, for example, since 2010, the use of at least 5% biodiesel in diesel used for transportation has been mandatory by law [121]; however, the Brazilian government recently updated this policy with the percentage of blend biodiesel in diesel being increased to 12%, effective 1 April 2023. In the subsequent years, 2024, 2025, and 2026, the increase will be 13%, 14%, and 15%, respectively [122]. The European Union has also been financially encouraging the use of renewable fuels. Promoting this type of energy can help the national energy security of each country; however, for this to happen, biofuel production must increase efficiency, which also encourages more investment in research and technological development in this area. In addition, the conflict of interest among the agricultural, food, social, and energy sectors must consider the energy, operational, and economic aspects [3]. The climate change mitigation policies must be reviewed, considering the appropriate land use, since this is essential for expanding biofuel production as an alternative source. Another critical aspect that must be discussed is that other sectors, such as recycling, must also be involved and respected to reach commercial production levels.

7. Conclusions

A critical and objective review of biodiesel, related to production as an alternative fuel for energy generation systems, and its relevance in the energy matrix was presented. The main aspects reported and confronted were the real applications in internal combustion engines, numerical and experimental studies, and equipment analysis using biodiesel as a drive source. The production of biodiesel and its importance in integrating the energy matrix of countries, specifically in tropical climates, were reviewed. In addition, the new trends and recommendations in using biodiesel as an alternative biofuel in the energy matrix of different countries and its relevance in reducing the emission of pollutants into the environment were highlighted.

The most relevant conclusions of this state-of-the-art study are as follows:

- The use of thermodynamic methods based on the first and second laws of thermodynamics (energy + exergy) with financial aspects (exergoeconomics) and the environmental impact (exergoenvironmental and life cycles) has helped with the verification of the feasibility of generation systems projects, through the total and partial use of biodiesel as a driving energy source.
- *Jatropha curcas*, sunflowers, soybean, *Moringa oleifera*, palm, cottonseed, castor, rubber seed, and coconut were tropical cultivars in which the use of various catalysts to accelerate the reaction, whether homogeneous or heterogeneous, allowed extremely high rates, varying up to values very close to 100% of conversion of their obtained oils into biodiesel.
- The reduction in environmental impacts through the blending of diesel and waste engine oil, reaching results compatible with diesel for use in internal combustion engines with low fuel consumption, provides an advantage in terms of energy and environmental aspects when compared to fossil fuels.

- The use of biodiesel represents an advantage in the socioeconomic aspect since it stimulates the production of biofuel, fostering the local economy through direct and indirect jobs for the nations that encourage this type of production.
- There is the possibility of integration and support in the energy matrix of different countries, as well as the possibility of competing and complementing, energetically, with other renewable energy sources, such as solar and wind.
- It was verified, through analyses of availability and energy, economic, and environmental feasibility, that biodiesel and its blends with diesel can be applied as a substitute fuel for diesel, thus reducing environmental impact and pollutant emissions.
- The research results can be used as a theoretical basis for new policies that aim to impact the energy sector with regulatory measures, specifically for policies that can be adopted in the South American region (Argentina, Colombia, and Brazil, among others), targeting MERCOSUR.

Considering the current state of the art of production, and applications of Biodiesel in internal combustion engines, it can be seen that there is still more research needed to understand, develop, and scale up methods and procedures to produce biodiesel and to identify the appropriate raw materials, as well as minimize pollution emissions into the environment. In this context, the recommendations for the future of biodiesel production and its applications in internal combustion engines are as follows:

- To propose adequate incentives by governments and world organizations in the search for more optimized methods and procedures in the production of biodiesel from various raw materials, as well as from the use of waste products, such as residual vegetable oils.
- Creation of incentive policies for the use of biodiesel as a source of renewable energy by governments and international entities.
- Studies related to the use of catalysts to accelerate the reactions (homogeneous or heterogeneous), allowing high conversion rates of obtained oils into biodiesel.
- Development of intelligent models for predicting energy performance using several types of biofuels, aimed at optimizing Biodiesel concentrations, and minimizing the consumption and emission of pollutants to the environment.

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