

Current Status of Biodiesel Development in Brazil

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Abstract

In recent years, the concept of producing biodiesel from renewable lipid sources has regained international attention. In Brazil, a national program was launched in 2002 to evaluate the technical, economic, and environmental competitiveness of biodiesel in relation to the commercially available diesel oil. Several research projects were initiated nationwide to investigate and/or optimize biodiesel production from renewable lipid sources and ethanol derived from sugarcane (ethyl esters). Once implemented, this program will not only decrease our dependence on petroleum derivatives but also create new market opportunities for agribusiness, opening new jobs in the countryside, improving the sustainability of our energy matrix, and helping the Brazilian government to support important actions against poverty. This article discusses the efforts to develop the Brazilian biodiesel program in the context of technical specifications as well as potential oilseed sources.

Index Entries: Renewable energy; biodiesel; ethyl esters; monoalkyl esters; alcoholysis.

Introduction

After an initial surge of interest in alternative fuels in the 1970s (sparked by the first oil crisis), many governments backed away from alternative fuel programs. However, in recent years, environmental and energy security issues have renewed interest in alternative fuels such as biodiesel, and the production of biofuels from renewable resources has regained international attention (1–5).

Biodiesel is a diesel fuel substitute that can be produced by transesterification or alcoholysis of renewable lipid sources such as vegetable oils, animal fats, and recycled cooking oils. It is typically produced by reacting these materials with methanol (methanolysis) or ethanol (ethanolysis) in

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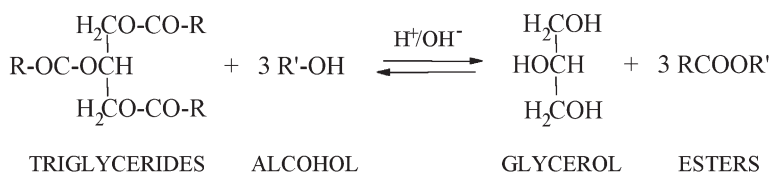


Fig. 1. Transesterification of triglycerides from vegetable oils and fats.

the presence of a catalyst to yield glycerine and monoalkyl esters (Fig. 1) (1–3). In this process, glycerine is considered a valuable coproduct that must be obtained in suitable yield and quality to meet the minimum requirements for important applications in the pharmaceutical, cosmetics, and chemical industries (2,6).

Monoalkyl esters can be made from virtually any oil-bearing material, including rapeseed, soybeans, cottonseed, peanuts, corn, olives, sesame seeds, safflower, and sunflower (2,7,8). Other tropical oiliferous materials are also amenable to transesterification, such as *Ricinus communis* (mamona), *Raphanus sativus* L. (wild turnip), *Jatropha curcas* (physic nut), *Cyperus esculentus* (tigernut), *Simmondsia chinensis* (jojoba), *Persea gratissima* (avocado), *Lupinus albus* (white tremço), and *Caryocar brasiliense* (pequi); and palm trees such as *Acrocomia aculeata* (macaúba), *Mauritia flexuosa* (buriti), *Elaeis oleifera* (dendê), *Syagrus coronata* (licuri), and *Attalea speciosa* (babaçu) (8,9). Alternatively, biodiesel can be derived from yellow grease or waste vegetable oils and fats derived from fish, potato chips, or fried chicken establishments (2,9). The manufacturing process can be totally benign, imposing no detrimental effect on the environment.

The fact that biodiesel can be produced from a large variety of renewable lipid sources is a great advantage for countries where favorable agroeconomic conditions are found, including a large availability of land for farming and processing (2). However, it is widely recognized that both soybean and sugarcane Farming are very well-established agroindustrial activities in Brazil. As a result, there has been a clear tendency to implement soybean ethyl esters as the leading model for biodiesel development in Brazil (3,8,9).

Biodiesel has a powerful ecologic appeal, and many claims support its utilization as a diesel oil substitute. In general, these include the following:

1. Biodiesel is biodegradable and harmless.
2. Biodiesel can be almost exclusively produced from renewable materials such as vegetable oils and ethanol derived from biomass.
3. Methyl esters usually contain little sulfur (about 0.001%), and this undesired component is completely absent in ethyl esters.
4. Biodiesel decreases soot emission considerably (up to 50%).
5. Biodiesel emits about the same amount of CO₂ that is absorbed during cultivation of the oilseed.

6. There are numerous social and economic advantages from its use, particularly in developing countries such as Brazil.
7. Biodiesel does not contain any of the carcinogens found in diesel oil.
8. Biodiesel represents a suitable outlet for the vegetable oil industry, serving as an important tool for market regulation.
9. Biodiesel can be used in blends or as a neat fuel.
10. Biodiesel is not considered a hazardous material because it has a flash point above 110°C.
11. Biodiesel increases engine lifetime owing to a superior lubrication capability.
12. Biodiesel can be produced with a straightforward technology, particularly in the case of methyl esters (methanolysis) (2,3,9,10).

Biodiesel generally operates in combustion-ignition engines without any critical requirement for modifications in the engine technology, particularly when used in blends containing up to 20% biodiesel (B20 blends) (6,10–12). Essentially, biodiesel maintains the payload capacity and range of diesel oil. Because modifications are not required, there is no need to replace the current fleet or change spare parts inventories, refueling stations, or skilled mechanics (10).

The use of biodiesel in conventional diesel engines also results in a substantial reduction of unburned hydrocarbons, CO₂, and particulate matter (11–13). Emissions of nitrogen oxides are either slightly reduced or slightly increased, depending on the duty cycle and the testing methods (13). The higher oxygen content of biodiesel enables a more complete combustion of the solid carbon fraction to CO₂, whereas soluble hydrocarbons are unaffected or even increased. Therefore, biodiesel is a suitable complement to the current effort to reduce the soluble carbon fraction of diesel particulate matter and to prolong engine life by decreasing the amount of carbon deposits in the inner parts of the engine.

In 1996, biodiesel was already present in more than 28 countries around the globe (10,14). The greatest development in this field was observed in Europe, with France, Germany, Italy, and Austria being the leading countries in biodiesel research and development (R&D). Nowadays, smaller production capacities are also available in many other European locations, such as Denmark, Belgium, the United Kingdom, Sweden, Spain, Portugal, and the Czech and Slovakian republics (2,10). The overall production capacity of biodiesel in Europe reached nearly 2,050,000 metric t in 2003, nearly twice as much as the amount of biodiesel produced in 2002 (14). Likewise, the total biodiesel production in the world has increased dramatically during the last few years and is expected to exceed 2,750,000 metric t in 2004.

Recently, biodiesel R&D has experienced a tremendous expansion in other regions as well, particularly in the United States, Canada, Australia, the Philippines, and Malaysia. More than 100,000 metric t/yr of biodiesel

is now being produced in North America for a variety of applications (10), whereas in South America, production is still very small. According to the Austrian Biofuels Institute (14,15), nearly 84% of the biodiesel produced worldwide is in the form of rapeseed methyl esters, even though sunflower, soybean, and palm oils have gradually increased their contribution to this net balance. Most of this biodiesel production is used in urban transportation and truck fleets, and other applications are still under development, such as in heating fuels, hydraulic oils, high-lubricity fuel additives, and dissolving agents (2,6,10).

Conversion of vegetable oils into biodiesel involves transesterification of the oil triglycerides to monoalkyl esters of the component fatty acids (10,15,16). This reaction can be catalyzed by a large variety of chemicals involving mineral acids (e.g., sulfuric acid) (17,18), alcoxides (3,9,18), Lewis bases (3), zeolites (19), metal complexes (19,20), strong ion-exchange resins (21), functionalized clays (21), intercalated lamellar double hydroxides (22), and enzymes (lipases) (18,23). Of these options, it is unquestionable that the alkaline catalysis in homogeneous media, using sodium and potassium alcoxides, still remains the most economically viable process for transesterification (2,9,10). However, technological innovations to reduce (or eliminate) the formation of soap during biodiesel production, to improve the efficiency of biodiesel purification by enhancing phase separation after washing (this is particularly important in ethanolysis), and to recover coproducts such as glycerol in a suitable condition for upgrading (2,3,9) are still in great demand.

Current Developments of Biodiesel in Brazil

In Brazil, as in many other countries, the first oil crisis of the mid-1970s led to political initiatives to allocate funds for the development of alternative motor fuels. These programs dealt with various types of raw materials and studied different conversion technologies to produce liquid fuels from renewable resources, such as ethanol from sugarcane (4) and mono-alkyl esters (biodiesel) from vegetable oils and animal fats (2,8).

The first attempt to produce biodiesel in Brazil was carried out in the mid-1940s, when both methyl and ethyl esters of cottonseed oil were demonstrated as alternative biofuels to replace petrodiesel in times of war (24). However, a national program was launched only three decades later to evaluate a variety of vegetable oils and their ester derivatives for the substitution of diesel oil (8). In general, the results obtained in biodiesel field tests were encouraging but the process economics were unfavorable. As a result, maintenance of the program could not be justified on the basis of political and/or environmental issues, and its main activities were halted immediately after the international situation was improved, with oil prices returning to reasonable market costs.

The first Brazilian patent on biofuels derived from vegetable oils was granted by the National Institute for the Intellectual Property (INPI) to a

process developed by Expedito José de Sá Parente at the Technological Center of the Federal University of Ceará (Fortaleza, CE, Brazil). This patent application was registered in 1980 and granted in 1983 (industrial patent PI 80 07957) to protect an original process for the alcoholysis of vegetable oils and the application of the resulting biofuel in both aviation (as biokerosene) and ground transportation (as biodiesel). The patent claim was also extended to the *in situ* alcoholysis of renewable lipid sources (particularly vegetable oils) and included the use of both methanol and ethanol as the transesterification agent (2).

Several other countries implemented programs for biodiesel R&D and many of these have been very successful, such as those carried out in Austria, Germany, France, the United States, and Italy (14,15). Currently, Brazil is attempting to get back to its original objectives about biodiesel, and the supporting reasons for this action are partly political and partly environmental. The overall economics of biodiesel are still very weak but discussions about sovereignty, sustainable development, public health, social justice, job availability, and many other aspects related to externalities are the political drivers (2,9). This together with technological improvements that are about to be demonstrated in preindustrial facilities make the future of biodiesel look promising as a suitable way to support many of our social activities and transportation needs without compromising the environment as much as fossil fuels.

The driving forces that are currently supporting the development of a broad biodiesel program in Brazil can be summarized as follows:

1. There is a need to reduce the amount of diesel oil imported from abroad.
2. The demand for energy (electricity) in remote areas is currently increasing.
3. New market opportunities in agribusiness could provide a clear benefit to our economy, particularly through further incentives to local (small) producers.
4. The environmental impact of energy production must be reduced, particularly within largely populated urban areas.
5. There is a continual pursuit for viable ways to improve important social issues, such as creating new jobs in the countryside, promoting a better income distribution and quality of living, and making energy available throughout the country (2,9,25).

In addition, the new legislation for diesel oil quality, particularly where sulfur content is concerned, clearly justifies the search for an environmentally friendly additive that could improve fuel properties that are lost during the process of sulfur removal.

The annual consumption of petrodiesel in Brazil approached 36 million L in 2002 and is likely to increase in the near future if the economy is to grow 3.5 to 4%, as currently announced by the federal government.

Table 1
Biodiesel Requirement for a B5 Blend with Petrodiesel Throughout Brazil

Region	Diesel consumption		Requirements for B5		
	Diesel (10 ³ L)	Fraction (%)	Biodiese (10 ³ L)	Main crop	Area (10 ³ ha)
South	7200	20	360	Soybeans	600
Southeast	15,840	44	792	Soybeans	1320
Northeast	5400	15	270	Mamona	600
North	3240	9	162	Dendê	36
Center-West	4320	12	216	Soybeans	360
Total	36,000	100	1800		2916

Considering that one of the major milestones of the National Biodiesel Program is to have B5 blends (5% biodiesel in petrodiesel) running nationwide by 2005, the Brazilian market for biodiesel will soon develop to a minimum demand of 1.8 million L/yr (26). Today, soybeans are the only oil-bearing materials that could support this national demand but with a further expansion of the current agricultural frontier. Table 1 provides a simple calculation of the main requirements for the implementation of B5 blends in the national fleet. In short, if the program is solely based on soybeans, nearly 9 million t of oilseed will be required, from which 7.2 million t of soybean meal will be produced, adding up to a total revenue of US\$1.85 billion and to the creation of 234,000 jobs (26). For a country that is continually fighting against its level of poverty and social injustice, biodiesel seems to be a more than reasonable option if oriented to local producers and small co-ops that could directly benefit from the growth of this new market for oil-bearing materials. However, soybeans are not likely to be the best option for small-scale production units because their oil content is much lower than that of other potential feedstocks; conversion to biodiesel usually requires degumming; and, being a powerful commodity, their price and availability are closely controlled by the international market. Therefore, other (cheaper) raw materials are being examined for biodiesel production in different regions of the country (2).

The Brazilian biodiesel program was created by the Ministry of Science and Technology (Decree #702) in October 30, 2002. The program was initially conceived to be an integrated effort, organized through a national network and oriented to the development of technologies for the production, industrialization, and use of biodiesel and biodiesel blends. The aim of this program was to develop biodiesel technologies throughout the country and to implement a series of fleet trials using biodiesel blends, in order to set up the scene for replacing as much as 5% of the national consumption of petrodiesel by 2005, 10% by 2010, and 20% by 2020 (25). Currently, a working group, formed by a consortium of 12 ministries and

their technical staff, is responsible for defining the main goals and milestones of the program. In this scenario, the federal government itself acts as the stakeholder through programs supported by national funding agencies such as the National Council for Research and Development, CNPq (www.cnpq.br), and Financing Agency for Studies and Projects, FINEP (www.finep.gov.br).

Ever since its creation, the national biodiesel program has been considered strategic for the Brazilian economy because nearly 10% of the national diesel consumption is imported from abroad. Nevertheless, the cost of producing ethyl esters is still beyond the cost of producing diesel oil, and efforts are being made to improve biodiesel competitiveness through the search for cheaper renewable lipid sources, better process engineering, and the development of new catalyst for transesterification. In addition, the possibility of partially alleviating biodiesel producers from taxes that apply to several steps of the oilseed life cycle has also been considered to help the economics of the process (2,9).

Designing such a large biodiesel program is a rather difficult task because many variables are involved. Each and every stage has to be evaluated in all of its complexity and decisions have to be made on a very solid technical basis in order to maintain the desired focus on the main objectives of the program. Some of these decisions include what is to be defined as biodiesel; whether use will be based on blends or restricted to the neat fuel; what the potential raw materials to be exploited nationwide are; what the industrial scale that has to be pursued (this includes the strategic location of industrial facilities) is; which market destinations are available for coproducts; what the actual demand of the end users is; which specifications are to be accepted as the national biodiesel standard; and, finally, whether the establishment of public policies and regulatory issues could provide further incentives to biodiesel producers.

Biodiesel Standardization

The first Brazilian specification for biodiesel was released in September 15, 2003, by the federal regulatory agency for petroleum derivatives (Agência Nacional do Petróleo [ANP]) after months of public consultation (Table 2). This specification, named ANP 255 (27), was created to support the preliminary activities of the National Biodiesel Program by ensuring good fuel properties for biodiesel blends up to B20. ANP 255 defines biodiesel as a diesel fuel substitute comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats. The same as for ASTM D 6751, no differentiation is made between biodiesel derived from methanol or ethanol, regardless of their differences in physical and chemical properties.

Defining the best (or most appropriate) biodiesel standard in Brazil is a very complicated task because exceedingly conservative parameters in the specification can be quite detrimental to the application of nonclassic

Table 2
Provisional Biodiesel Specifications in Brazil, Released September 15, 2003,
by ANP, the Federal Regulatory Agency for Petroleum Derivatives

Property	Limit	Method
Flash point (°C)	100 min.	NBR 14598; ISO/CD 3679
Water and sediments (%)	0.02 max.	D 2709
Kinematic viscosity, 40°C (mm ² /s)	ANP 310	NBR 10441; D 445; EN/ISO 3104
Sulfated ash (% [m/m])	0.02 max.	NBR 9842; D 874; ISO 3987
Sulfur (% [m/m])	0.001 max.	D 5453; EN/ISO 14596
Copper corrosion 3 h, 50°C	No. 1 max.	NBR 14359; D 130; EN/ISO 2160
Cetane number	45 min.	D 613; EN/ISO 5165
Cold filter plugging point (°C)	ANP 310	NBR 14747; D 6371
Carbon residue (% [m/m])	0.05 max.	D 4530; EN/ISO 10370
Acid number (mg KOH/g)	0.80 max.	NBR 14448; D 664; pr EN 14104
Free glycerine (% [m/m])	0.02 max.	D 6854; pr EN 14105-6
Total glycerine (% [m/m])	0.38 max.	D 6854; pr EN 14105
Distillation recovery, 95% (°C)	360 max.	D 1160
Phosphorus (mg/kg)	10 max.	D 4951; pr EN 14107
Specific gravity, 20°C (kg/m ³)	ANP 310	NBR 7148/14065; D 1298/4052
Alcohol (% [m/m])	0.50 max.	pr EN 14110
Iodine number	Take note	pr EN 14111
Monoglycerides (% [m/m])	1.00 max.	D 6584; pr EN 14105
Diglycerides (% [m/m])	0.25 max.	D 6584; pr EN 14105
Triglycerides (% [m/m])	0.25 max.	D 6584; pr EN 14105
Na + K (mg/kg)	10 max.	pr EN 14108-9
Aspect	LII	—
Oxidation stability, 110°C (h)	6 min.	pr EN 14112

oily materials for biodiesel production. For this reason, ANP 255 has been referred to as provisional, and the fine-tuning of many of its technical parameters is still an ongoing process. Owing to the great variability of raw materials and working conditions found in Brazil, many groups and decision makers strongly believe that the national specification must be somewhat different from those developed in the United States and Europe. However, some of the most critical parameters of the specification, such as viscosity and total glycerine content, cannot be made more flexible without the establishment of a series of long-term field tests whereby no harmful effects are clearly demonstrated on engine performance and durability. Otherwise, the general acceptance of this product can be severely compromised, together with the credibility of the national program.

Because the provisional ANP 255 specification restricts field tests to private fleets using B20 or less, it is clear that biodiesel blends shall never exceed the critical limits established by the engine technology used to date. These limits are expressed in the national specification for petroleum

diesel (ANP 310), and biodiesel blends, regardless of their actual biodiesel content (B2 up to B20), will have to comply with technical specifications such as those established in ANP 310 for kinematic viscosity, flash point, cold filter plugging point, and specific gravity.

In Brazil, many raw materials have been assessed and/or proposed for biodiesel production, because different regions of the country have different social and/or geopolitical interests, offering different weather and soil conditions for the extensive cultivation of oil-bearing materials. In general, it is correct to say that biodiesel can be produced from a large variety of renewable lipid sources. However, choosing the best feedstock will depend on both agronomic and technological attributes. Agronomic attributes include the productivity per unit area, the oil content and composition of the feedstock, the nutritional value of the oil cake, and the availability of reasonable agronomic data to establish large plantations with an adequate plant cycle and a favorable territorial adaptation. On the other hand, technological attributes are also critical and include the content of polyunsaturated fatty acids (influence oxidation stability) and saturated fatty acids (influence cold flow properties), the technology required for oil extraction, the presence of extraneous compounds in crude oil, the fuel properties of the biodiesel so derived, and whether there are other valuable coproducts in the oilseed that could help the economics (2,9,26).

Most of the official methods listed and recommended by ANP 255 are based on either ASTM or EN/ISO standard methods and, in some cases, either one would be considered acceptable to indicate biodiesel quality (27). Only seven parameters have a corresponding Brazilian standard procedure (NBR standards), developed and/or proposed by the Brazilian Association of Technical Methods (Associação Brasileira de Normas Técnicas). These are flash point (NBR 14598), kinematic viscosity (NBR 10441), copper corrosion (NBR 14359), sulfated ash (NBR 9842), acid number (NBR 14448), cold filter plugging point (NBR 14747), and specific gravity (NBR 7148 and NBR 14065).

In general, ANP 255 has most if not all parameters found in ASTM D 6751, together with seven other parameters listed in EN 14214. Of the parameters based on EN 14214 and ASTM D 6751, only the total glycerol content is proposed to be different and equivalent to plus 50% of the maximum tolerance found in ASTM D 6751 (27). It is not clear whether this decision was made on a solid technical basis, but it is probable that the greater flexibility found in this parameter is somewhat related to the general expectation that raw materials such as castor oil are less amenable to alcoholysis than other materials such as soybean or rapeseed oil.

One interesting observation about ANP 255 is that the iodine number is only required to be reported. This is another clear attempt to avoid ruling out some of the most promising feedstocks available in Brazil for biodiesel production. It is reasonable to assume that if a short range of

iodine number is officially established as part of the specification, several vegetable oils would be immediately ruled out, regardless of whether they are suitable alternatives to produce a good-quality biodiesel. On the other hand, the iodine number can be indirectly used to assess oxidation stability, but there are other ways to evaluate this important parameter, such as the European standard method pr EN 14112. This, together with the evidence that ANP 255 defines biodiesel as to be used in blends, justified the use of iodine number just as "to be reported," thus avoiding situations such as that of the European standard, which is clearly restrictive to biodiesel made of rapeseed oil and, to a certain extent, sunflower oil.

Another important consideration about ANP 255 is that many of the official methods listed in the specification are not appropriate for analyzing ethyl esters. For instance, the gas chromatography (GC) method used to determine total ester content (pr EN 14103^d) does not include standards and response factors for ethyl esters. Therefore, this method cannot be used to determine total ester content in biodiesel samples other than methyl esters. In addition, both methods used to quantify unreacted glycerides (pr EN 14105 and ASTM D 6584) are also specific for methyl esters and, as such, they cannot be extended to other applications without changes in their technical content.

In general, official biodiesel specifications should be made as simple as possible because the cost of validating a commercial sample must be reasonably affordable and, therefore, not economically prohibitive for small producers. Thus, procedures that are somewhat repetitive in providing similar conclusions should be avoided. One clear example is the requirement for measuring alcohol content by GC. Table 2 indicates that pr EN 14110 is recommended by ANP as part of the specification, even though it only applies to methanol (rather than ethanol) content in biodiesel. Hence, it is reasonable to assume that ethyl esters will always comply 100% with pr EN 14110 because they would not contain methanol anyway. Therefore, the method must be adjusted for biodiesel types other than methyl esters. On the other hand, if biodiesel specifications are to be made simple, it may be possible to eliminate the requirement for alcohol content because a more general flash point specification would suffice as a general alcohol-limiting parameter.

Other comparisons involving ethyl and methyl esters would include cetane number, cold flow properties, and oxidation stability. Ethyl esters have cetane numbers slightly higher than the corresponding methyl esters (28). Therefore, it is apparently unnecessary to specify a limitation for cetane number lower than that already defined by ASTM D 613 and EN ISO 5165 for methyl esters. Whether this higher tolerance for cetane number is to be attributed in ANP 255 to the wide variety of lipid sources that are available in Brazil for biodiesel production is still a matter of debate because, there are not enough experimental data to back up this technical assumption.

Ethyl esters also have better cold flow properties and are likely to have better oxidation stability because the Rancimat/OSI method (pr EN 14112) uses material on a mass basis, not on a molar basis (29). Higher viscosities are also expected for ethyl esters owing to their inherently higher molar mass. Observations such as these may strongly interfere with the validation of an ethyl ester sample under the current specifications for biodiesel. Therefore, if a more general specification is to be accepted worldwide, the technical range of some of the most critical parameters of the specification will have to be further evaluated. Otherwise, biodiesel samples other than soybean or rapeseed methyl esters will have to be treated by a different specification, in which different methods are proposed to ensure good biodiesel quality and process control.

Future Perspectives

Biodiesel is the most immediate alternative to diesel oil, and many environmental, social, and economic benefits would readily arise from its utilization in both the transportation and energy sectors. In Brazil, there has been an increasing interest in developing such an alternative, but the economics of producing biodiesel from vegetable oils has always been negative. However, several factors indicate that changes are just around the corner. These include the severe turbulence recently observed in the international petroleum market, the recent achievements toward the production of a good-quality biodiesel from cheaper and more readily available lipid sources, and the development of new catalysts for alcoholysis. Therefore, biodiesel may soon become competitive and its use to replace diesel oil will increase steadily.

At this point in time, it is correct to say that Brazilians have come a long way in understanding the need for changes in the biodiesel specification in order to accommodate alternatives other than soybean and rapeseed methyl esters. Definitions in this regard are on great demand to help define the future of the National Biodiesel Program. However, these lively discussions about specifications must not overlook other important aspects of its sustainable development. These include the search for both agronomic and technological information on alternative raw materials available nationwide for biodiesel production, the construction of suitable demonstration plants in which the viability and competitiveness of ethyl esters could be demonstrated against the current knowledge in this field, the development of technically monitored endurance tests with ethyl esters to demonstrate engine performance and durability, and the definition of political and regulatory issues that are related to the use of biodiesel within the Brazilian energy matrix. Hence, the future of biodiesel rests with policy makers, and only a strong political support from all segments of the Brazilian society (including farmers) will possibly overcome the cost barriers that still exist.

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