We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists



185,000

200M



Our authors are among the

TOP 1% most cited scientists





WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



Qualitative Characteristics of Biodiesel Obtained from Sunflower Oil

Estelvina Rodríguez Portillo, Araceli Amaya Chávez, Arturo Colín Cruz and Rubí Romero Romero

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/59673

1. Introduction

This chapter presents the results of analysis parameters of biodiesel produced from sunflower oil in Paraguay. The analysis was prepared according to the requirements of quality demanded by the Paraguayan standard methods for this purpose, based on parameters of the American Society for Testing and Materials (ASTM) and European Norms (EN). It was found that the biodiesel produced in this country comply with international standards.

The ASTM defines biodiesel as a monoalkyl ester of long chain fatty acids derived from vegetable oils, seeds, or animal fats. Biodiesel is obtained from vegetable oil or animal fat, has significant environmental benefits such as being nontoxic, having less emission, and being biodegradable [1, 2]. Biodiesel is currently defined in the European Union in the technical regulation (European Norms) EN 14214 or in the USA in ASTM 6751-02 [3]. The most common is that the esters, which are part of the composition of biodiesel, were methyl, so they are called fatty acid methyl ester (FAME).

Biodiesel characteristics as a fuel vary depending on its composition, and the fuel used to be stringently monitored to avoid adverse impacts on the environment and engines. A very important consideration in the efficiency of combustion is the ignition delay in the combustion, which is influenced by the ratio of compression adopted, which in turn is related to the kind and quality of fuel used. The physicochemical properties of the biodiesel may vary depending on the source from which the mixture of fatty acids was obtained, from the transesterification and separation efficiency process. Factors such as hydrocarbon chain length, branching, and degree of saturation influence their composition; hence, quality control is important to guaranty the combustion efficiency and to lower atmospheric emissions [4, 5].



© 2015 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In the specific case of biofuel, some physicochemical properties have great influence in the ignition, combustion, and contaminant formation when a diesel engine is used.

As a result, the evaluation of these kinds of properties has great relevance because it practically defines the fuel's usefulness. Therefore, these papers focus on the chemical properties, reviews according to the standardized quality requirements, and test methods for biodiesel that are mentioned in the Paraguayan and International regulation.

1.1. Biodiesel production processes and quality

The world production of biodiesel between 1993 and 2003 increased to an impressive annual rate of 28.5%, from 38 to 467 million gallons, while bioethanol production increased to an annual rate of 6.7% in the same period, reaching 5.770 million gallons in the year 2003 [6]. In the USA, the annual production of biodiesel was approximately 570 million liters in 2004 (80% from soy, 19% from animal fat, and 1% from other crops). From 1999 to 2001, the car fleet that used biofuel increased to a 100%. Due to the increasing environmental concerns related to the emissions of fuel-derived atmospheric pollutants, alternative sources of energy have been receiving greater attention.

One of the things that have permitted the growth of biodiesel market is the establishment of quality regulations, trying to homogenize the production as well as the soy subsidy.

The European Union is the world leader in biodiesel production and consumption. In the year 2004, it produced around 2.2 billion liters, and the three main countries that produce this energy-giving fuel are Germany (1.4 million tons), France (1.35 million tons), and Italy (0.32 million tons). Two factors have permitted the European Union to become the production leaders; the first has to do with a Common Agricultural Policy (CAP), which is oriented to a policy of crop of the European Union members, where the subsidy to grain, oil seed, and protein crop producers was promoted so they could dedicate 10% of their lands to produce input to obtain biodiesel.

The second factor would be the high fuel taxes that have established direct subsidy for biofuel from a partial or total tax exempt. In the year 2004, 90% of fuel taxes ware exempt by the European Parliament; in Germany, 100% of taxes were exempt.

The biodiesel in Paraguay is manufactured by the transesterification of vegetable oils, in this case, sunflower oil (*Helianthus annuus*) in presence of a catalyst. The main component of vegetable oils and animal fats are triacylglycerols (TAGs). TAGs react with long three chain fatty acids and alcohol (mostly methanol), with a 6:1 ratio, to produce a mix of fatty acid methyl esters (biodiesel), and glycerol is the bioproduct. Thus, biodiesel production depends on the origin of oil used, the transesterification process, and the distribution and storage (Figure 1).

The replacement of gasoline with biodiesel does not require any engine modification, except for the combined change of natural rubber gasket (in old models) and fuel filters after using biodiesel (used diesel cars). This will apply if it is good-quality biodiesel.

The quality of biodiesel can be described in two groups: (1) the general physicochemical properties, for example, density, viscosity, flash point, % sulfur, Conradson carbon residue, %

Qualitative Characteristics of Biodiesel Obtained from Sunflower Oil 273 http://dx.doi.org/10.5772/59673

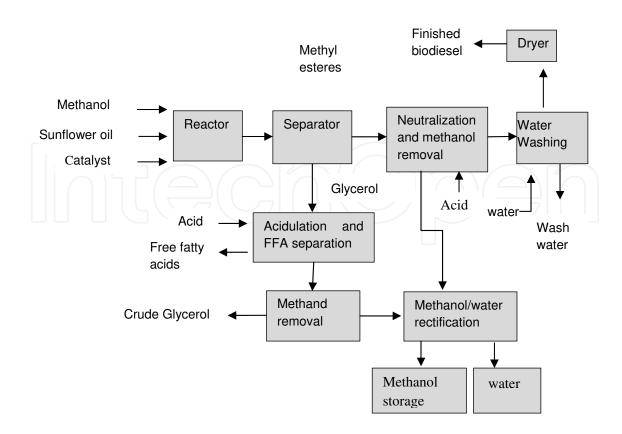


Figure 1. Schematic process flow for biodiesel production.

sulfate, ketonic number, and acid number, and (2) the composition and purity of fatty esters such as methanol, free glycerol, total glycerol, water, and esters contents, among others (Table 1) [7]. The evaluation of biodiesel quality is achieved through the determination of the chemical composition and physical properties of fuel [7]. In fact, some contaminants and other minor components are the major issues in the quality of biodiesel.

| Quality factors | Indicator | |
|--------------------------|----------------------------------|--|
| Oil source | Acidity | |
| | Phosphorus content | |
| | Oxidation stability | |
| | Iodine index | |
| Production process | Water content, impurities, waxes | |
| | Esterification | |
| | Stages of separation | |
| | Distillation | |
| Distribution and storage | Oxidation stability | |
| | Water content | |

Table 1. Quality factors of biodiesel.

As to normative reference, the International Standard Organization (ISO), the American Society for Testing and Materials (ASTM), and the European Norms (EN) have been applied in several countries for biodiesel quality control. The International Standard Organization (ISO) has developed quality standards for oil and products derived from them. Most of the other specifications for biodiesel are based on these standards. While the reference norm is comprehensive, the most representative of it is being adapted by several countries, especially the EU and the set by the ASTM.

The American Society for Testing and Materials (ASTM) describes different tests to ensure the correct function of the fuel. These specifications define the properties and the main checkpoints for the feasible use of biodiesel in the market, cited in the ASTM D 6751 guide, where most of the requirements demanded by the producer countries are based. This international organization of standardization has recently announced the publication of four rules regarding biodiesel, including the mentioned D 6751, which are as follows [8]:

- **a.** The norm ASTM D975-08a (specification for diesel fuel oil) is applied to diesel engines for transportation, with an inspection that allows mixing 5%.
- **b.** The norm ASTM D396-08b (specification for fuel oil) is referred to use of domestic heat and boilers. It has an inspection that also allows mixing 5% of biodiesel for the mentioned effects.
- **c.** The norm ASTM D7467-08 (specification for diesel fuel oil with a mix of biodiesel B6 to 20) is a completely new specification because it includes mixtures of fuel finished between 6% (B6) and 20% (20%) for engines used for transportation.
- **d.** The norm ASTM D 6751-08 (specification of biodiesel for mixture B100 destined to medium distilled fuel) is used to control the quality of pure biodiesel (B100) before mixing it with regular diesel, and it has an inspection that includes a requirement to control minor compounds through a new cold filtration test.

Nowadays, the use of 100% biodiesel is unknown since the mixture of 5–20% has been applied gradually. This is a way to ensure the correct operation of automotive machines.

According to ASTM, engine and car manufacturers, pipeline companies, biodiesel producers, and oil companies will use this group of specifications to prepare fuel for quality control, engine design, bidding processes, and acquisition contract.

The rule UNE EN 14214:2003 of the European Community specifies the requirements and the assay methods of the FAMES that are marketed and provided for use, such as the following:

- **a.** Automotive fuel in diesel engines (100% biodiesel)
- **b.** Mixture with diesel (rule EN 590)

This norm has the special feature of including the iodine value, which is not included in the ASTM since they generally use colza oil in biodiesel manufacturing in that continent. The maximum acceptable value is IV = 115, which would exclude other oils like soy and its esters because these exceed the limits [9].

Obviously pointing out once more that the properties are dependent from the raw material that is used; that way, it roughly had parameter deviation. With regard to the current state of biodiesel production technology, it can be said that is already tested, relatively mature, in dissemination period, capable of taking advantage of different raw material, and that it has reached market level in several countries. Currently, most of the biodiesel is produced by methanolysis in basic medium [10].

The challenge for any country or region consists in the implementation of processes based on native raw material, which should be optimized to obtain a low production cost biodiesel that would make it competitive but fulfilling the international specifications of quality in order to be used as a diesel engine. These parameters are of great importance since the characteristics have a major impact on the diesel engine behavior, as well as on the contaminant emission when it is used, and in securing storage and transporting conditions among others. Therefore, to know the mechanic and environmental efficiency, some indicators such as water presence, acid index, methanol content, triglycerides, etc., are of great importance. Impurities such as glycerides, glycerol, free fatty acids, and catalyzed waste bring adverse consequences to the engine performance, for example, soot deposits in the injectors. The mass calorific power of biodiesel is 13% lower than diesel and around 8% per volume unit; however, it is not exactly revealed in the loss of power because biodiesel has a slightly higher density than diesel [11]. In Paraguay (study field of this paper), the legislation NP 16 018 05 is the one that specifies the quality requirements of the produced biodiesel, and it corresponds with the American Union ASTM norm and the European Union EN (Table 2). In this legislation, the requirements and trial methods for pure biodiesel (B100) applied in diesel engines are established.

The values that overpass the limits marked by the norm would lead to engine problems as mentioned before. However, those are highly dependent on the raw material. Therefore, the main challenge when evaluating the quality is to improve the regularity and homogeneity of the raw material supply and to optimize the production process in order to standardize the final product. Despite its many advantages, it also has many problems. One of them comes from its better solvent capacity than the regular diesel, so the existent residues are dissolved and sent through the fuel line being able to clog the filters [12]. Another item is a less energetic capacity, approximately 5% less, although it is not that notorious in practice because it is compensated with the higher ketone index, which produces a more complete combustion with less compression. Certain hypotheses suggest that more combustion deposits are produced and that the cold starting of engines is degraded, but there are no records of it. Another difficulty is referred to the storage logistic area since it is degradable in a relatively short time. Therefore, an exact planning of its production and expedition is necessary, for which the quality parameters are essential.

Some potential problems of the net biodiesel-operated engine or with high-level mixtures as well as bad quality are as follows [12]:

- a. Clogging and filter obstruction
- **b.** Nozzle and injection hole block, ducts and passages, and draining of the fuel feeding system blockade

| Requirement | Unit | Limits | | Trial method ¹ |
|-------------------------------------|---------|-------------------------------|------|---------------------------|
| Minimum | Maximum | | | |
| Ester content ² | % (m/m) | 96.5 | | EN 14103 |
| Density at 20°C | g/mL | Report | | ASTM D 1298//ASTM D 7042 |
| | | | | ISO 3675 // ISO 12185 |
| Viscosity at 40°C ³ | mm²/s | 3 | 6.5 | ASTM D 445 |
| | | | | ISO 3104 |
| | | | | IRAM-IAP A 6597 |
| Flash point | °C | 100 | | ASTM D 93//ISO/CD 3679 |
| Sulfur content | mg/kg | 79 | 10 | ASTM D 5453 |
| Carbon residue | g/100 g | | 0.3 | ASTM D 189 |
| | | | | ASTM D 4530 |
| | | | | ISO 10370 |
| Cetane number | | Report ⁴ | | ASTM D 613 |
| | | - | | ISO 5165 |
| Sulfated ash | % (m/m) | 0.05 | | ASTM D 874 |
| | | | | ISO 3987 |
| Water content | % (m/m) | 0.080 ISO 12937 | | ISO 12937 |
| Silt content | ppm | 24 ASTM D 2276 | | ASTM D 2276 |
| Copper foil corrosion | | 1 ASTM D 130 | | ASTM D 130 |
| (3 h at 50°C) | | | | ISO 2160 |
| Oxidation stability at 110°Chours 6 | | 6 | | En 14112 |
| Acid index | mg | | 0.8 | ASTM D 664 |
| | KOH/g | | | IRAM 6558 |
| | | | | EN 14104 |
| Total glycerin content ⁵ | % (m/m) | | 0.25 | EN 14105//ASTM D 6584 (B) |
| Free glycerin ⁵ | % (m/m) | .) 0.02 | | EN 14105//EN 14106 (C) |
| | | | | ASTM D 6584 |
| Free methanol or ethanol | % (m/m) | 0.2 EN 14110 | | |
| content ⁶ | | | | |
| Alkaline metal (Na + K) | mg/kg | | 5 | EN 14538 |
| Phosphorus content | mg/kg | g/kg 10 ASTM D 4951//EN 14107 | | |
| Cloud point ⁷ | °C | Report | | ASTM D 2500 |

¹ The one contained in the first term four each essay is the discrepancy method.

² Includes carbon 17.

³ The determination of biodiesel viscosity can be done through the Saybolt viscosimeter to be converted later to mm²/s according to what is indicated in the table (ASTM D 2161).

⁴ The used raw material must be specified.

⁵ The methodology indicated in B and C attachments is informative, and it can be applied in the industries as an alternative method but not as a reference until the publication of it as a Paraguayan norm.

⁶ If the flash point is equal or more than 130°, it will not be necessary to analyze this item.

⁷ The cloud point must be reported.

Table 2. Quality requirements in the Paraguayan norm and trial methods.

- c. Increase of the injection pressure with an excessive pressure drop
- d. Stuck and broken piston rings
- e. Formation of deposits on the injectors, pistons, and piston slot
- f. Clogging of the fuel pump because of high viscosities
- g. Lack of fuel feeding to the engine (power drop) because of high viscosities
- h. Accelerated wear of valves, needles, and injection puma pistons and of the injectors

Between the causes attributable to the biodiesel properties, we can find the deposit production due to excess metal that causes ash formation and ash abrasion, sediment formation through polymerization, or crystallization of heavy molecules or crystallization and jellification at low temperatures. In addition, it also causes acid, aldehyde and ketone oxidation, polymerization and degradation, ester hydrolysis with free acid formation, water accumulation, microbial growth and associated iodine formation, and low fuel volatility [13].

1.2. Raw material and quality of biodiesel

The most important biodiesel production to ensure trouble-free operation of diesel engines aspects is complete reaction, removal of glycerin, removal of catalyst, removal of alcohol, and absence of free fatty acids. If any of these aspects are not adequately able to meet specifications, different types of problems arise in the motor, such as excessive formation of soaps, injection deposit formation, corrosion, etc. Other aspects, such as the removal of methanol, are important from the standpoint of safe operation of the fuel. Biodiesel production from various raw materials is technically and economically feasible, including projects in small scale. This opens an opportunity for a large number of small and medium enterprises who wish to produce their own fuel by providing a wide range of possible raw materials.

The vegetable oil used in the production of biodiesel can be obtained from various oil seeds. These species differ in their agronomic characteristics, and relative to the oil content in the composition of grain and fatty acid profile.

The main characteristics of the raw materials used in the manufacture of biodiesel that have the greatest influence on its quality are as follows:

a. Oil content: The oil content is an important feature that can influence the choice and use of a raw material for the production of biodiesel from vegetable oil. Sunflower, rapeseed, jatropha, castor, and groundnut are the sources that have higher oil content in grain, a variation of 40–64% oil. Soybean, palm, and cotton have low oil level at around 15–25%. Associated with this feature, the oil production per hectare and the production cycle of each commodity must also be considered [14]. For crops of sunflower, rapeseed, and peanut oil, content in grain and oil yield per hectare are similar. The less output of oil per hectare is presented for growing cotton.

The inclusion of nonfood raw materials in the production of biodiesel is seen as an important ally, but that does not compete with the raw materials used in food.

- **b.** Fatty acid composition: The variable composition profile and fatty acid content of the raw materials presented interferes with features and quality of biodiesel. The content of saturated and unsaturated fatty acids is highly variable among commodities. Palm oil has the highest content of saturated fatty acids (51.5%), while castor oil has a lower content (1.6%). Rapeseed oil has 6.5% saturated fatty acids, while soybean oil, sunflower, and groundnut have values between 11.7% and 17.8% [14].
- **c.** Influence of the composition and acid ester content fatty raw materials on the properties of biodiesel: The composition and the content of fatty acid esters directly influence the properties of biodiesel, and consequently the quality and performance as fuel. Ester formed during transesterification with the alcohol has the same profile of fatty acids of vegetable oil source as the process transesterification does not affect the fatty acid composition [15].
- **d.** Oxidative stability: This refers to the relative resistance to physical changes and produced by chemical interaction with the environment during storage of a liquid fuel. The composition of esters of fatty acids, the size of chain, and the presence of unsaturation directly affect the oxidative stability. Vegetable oils contain natural antioxidants, tocopherols being the most common. Antioxidants are highly reactive with free radicals to form stable compounds and, therefore, do not contribute to the oxidative process [16]. The biodiesel produced from raw materials rich in saturated and monounsaturated fatty acids has better oxidation resistance.
- e. Low temperature properties: A major problem associated with the use of biodiesel is their low resistance to low temperatures and can be indicated by parameters such as cloud point, pour point, and filter plugging point at low temperature. At lower temperatures, the formation of crystal nucleation wax solids and the temperature decrease cause the crystals to increase in size. Saturated fatty compounds have higher melting points than the unsaturated. Therefore, the biodiesel produced from vegetable fats and oils with significant amounts of unsaturated fatty compounds should be lower for the cloud and pour points values, contrary have lower oxidative stability [16].The biodiesel from soybean, sunflower, rapeseed, jatropha, peanut, and cotton are the best low temperature properties. While palm biodiesel has a high point of obstruction cold filter. The castor biodiesel shows good oxidative stability and good low temperature properties, which contradicts what was observed for the other oilseeds.

With so many differences between raw materials and fatty acid profile, what we see is that each raw material has one or more desirable properties for biodiesel quality. Then it is necessary to examine what is the best raw material for biodiesel production. Choosing any of the raw materials must meet the standards and needs of each country, without competing with food availability. In countries with sufficient availability of grains, oilseeds may represent an alternative for diversification and promotion of agricultural industries. The high oil content of sunflower seeds produces a high-protein cake, and the crop shows good adaptability with respect to soil and temperature, making this oilseed a good alternative for biodiesel. The production of biodiesel from sunflower involves simple procedures resulting in high-quality fuel, which offsets the higher market values

For sustainable development, the promotion of biofuel previous study should be done on food demand in each country. Currently, poverty is an important factor to consider owing the food security, much more than the use of land for the production of sunflower or the labor employed. The increase in biofuel production may cause problems on agricultural priority, that is, food crops, which could obstruct the availability of raw materials. In addition, the negative environmental impacts change native vegetation for farmland. It is necessary to perform the environmental impact assessment of the biodiesel production, but there are not sufficient data available [17]. For countries like Paraguay that do not have oil, it may represent an important alternative economic development. The level of competition between energy crops and food and fodder production would depend on the progress with regard to yields, efficiency of livestock feed, and conversion technologies for bioenergy.

The status of biofuel production and the possible implications for food production and security should be analyzed since the choice of feedstock depends on local availability, cultivation, relative prices, and government incentives for specific production.

A study of local realities and skills at the time of the creation of regulatory frameworks and the use of techniques such as crop planting interspersed would enable the production of both biofuel feedstock and food production.

2. Materials and methods

The biodiesel used for the study come from three national companies that use the sunflower oil species *Eliantus annus* and transesterification process with methanol, which are unloaded at the PETROPAR S.A. (Petróleos Paraguayos S. A, Villa Elisa plant), in a common reservoir of approximately 3000 L of capacity. Then the samples are taken from these tanks corresponding to pure biodiesel (B100). The sample conditions such as irreplaceability, minimum quantity, instable, or other conditions as in situ essay are considered as eliminatory criteria in the technique and method selection.

The sampling procedure was made according to the ASTM D 4057-95 norm (Reapproved 2000), Standard Practice for Manual Sampling of Petroleum and Petroleum Products.

Ten weekly samples of 2.5 L were taken from the surface in full tank (bottom sample), 10 cm away from the bottom in half tank, or 10 cm from the output level in tanks with reservoirs that were not filled.

The determination of biodiesel quality was performed through analysis, and the protocols followed are standardized in an international level and set by norms that value some properties (Table 3). Ten analysis and ten different samples were performed using the ASTM and EN methods, within the requirements of quality established by the Paraguayan norm NP 16 018 05 (Table 2).

| Method | Determination | Available equipment | | | |
|---------------|--|--|--|--|--|
| EN 14103- | Fatty and oily derivatives. Fatty acid metallic ester Gas chromatographer Headspace Shimadzu | | | | |
| 2003 | (FAME)-determination of linoleic acid ester | 2010, with AOC 5000 (autoinjector) | | | |
| | content | | | | |
| ASTM D 1298 | 1. Standard practice for density, relative density | 1. Hydrometer | | | |
| ASTM D 4052 | (specific gravity), by hydrometer method (ASTM | 2. Digital densimeter DE 40 | | | |
| | D1928). | | | | |
| | 2. Standard test method for density and relative | | | | |
| | density meter | | | | |
| ASTM D 455 | Standard test method for cinematic viscosity of | Precision kinematic viscosity bath- | | | |
| | transparent and opaque liquids (calculation of | Model "S" | | | |
| | dynamic viscosity) | | | | |
| ASTM D 189 | Standard test method for Conradson carbon | Device for determination of Conradson | | | |
| | residue | carbon | | | |
| ASTM D 93 | Standard test methods for flash point by Pensky- | Pensky-Martens closed cup flash tester | | | |
| | Martens closed cup tester | | | | |
| ASTM D 4928 | Standard test method for water by coulometric | Karl Fisher moisture titrator MKC-501 | | | |
| | Karl Fisher titration (water only) | | | | |
| ASTM D 130 | Standard test method for the detection of copper | Copper corrosion bath, copper corrosion test | | | |
| | corrosion (3 h at 50°C) | bomb | | | |
| UNE EN 141104 | Acid index-volumetric method | TAN titration and burette. Brand: Metrohm, | | | |
| | | Model 664 | | | |
| EN 14105:2003 | Total glycerin content | Gas chromatographer Headspace Shimadzu | | | |
| | | 2010, with AOC 5000 (autoinjector) | | | |
| EN 14110:2003 | Free methanol and ethanol content | Gas chromatographer Headspace Shimadzu | | | |
| | | 2010, with AOC 5000 (autoinjector) | | | |
| ASTM D2500 | Cloud point | GB/T3535 GB/T6986 | | | |
| | | | | | |

Table 3. Results obtained, trial methods, and equipment used.

3. Results and discussion

The obtained results in this investigation are presented, described, and discussed in this section.

The obtained results were averaged and grouped in a table comparing the established limits for each characteristic, with their previous statistic analysis based on the Statistical Package for the Social Sciences (SPSS) version 16.0.

In Figures 2 and 3, the observation clouds and the lineal adjustment obtained in those variables that present more lineal dependence are exposed. A correlation between viscosity and density, acid, and glycerin was found.

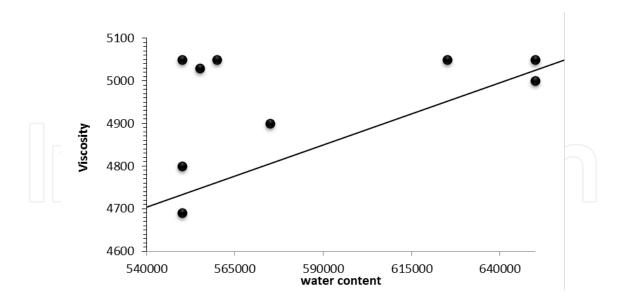


Figure 2. Water content–viscosity correlation in the biodiesel of sunflower oil.

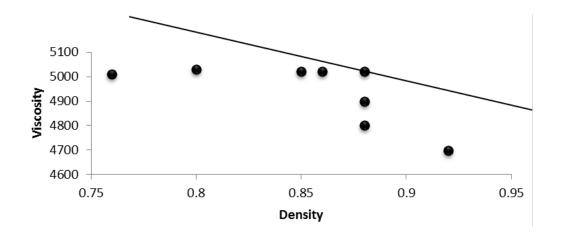


Figure 3. Density–viscosity correlation in the biodiesel of sunflower oil.

It can roughly be said that a functional dependence between the observations exists, but not the line type; therefore, the correlation is too small.

Excess water in the biodiesel causes the following:

- a. Hydrolysis reactions (appearance of free fatty acids)
- **b.** In the engine, the undissolved water can give corrosion problems
- c. Bacteriological growths (clogged filters)
- **d.** Trace of H₂SO₄

As for the viscosity, the parameter determines a minimum viscosity in which no power was lost through the injection pump and the injector outlet. The maximum value allowed is limited by considerations related to engine design, size, and characteristics of injection system. Viscosity is a very important parameter in the fuel, as it directly affects the atomization process. Fuels with high viscosity tend to form larger droplets on injection and cause poor fuel atomization, encourage the formation of engine deposits, and cause the need for more energy to pump the fuel.

The density of the fuel defines the mass of fuel injected into the combustion chamber. This is because the meters of fuel injection pumps are designed to measure the fuel volume and not mass; denser fuel contains more mass for same amount of volume.

To protect the performance and durability of combustion equipment, the standard sets limits for impurities remaining in the biodiesel production process. These standards include methanol, glycerin (a by-product), and unconverted or partially converted raw materials, and sodium and potassium may be used with caustic soda to catalyze the transesterification reaction.

Methanol is one of the reactants used to produce biodiesel. To bring the reaction to completion, usually it uses a 4:1 excess methanol so that the methanol can be removed from the product. Methanol over 0.2 wt% is incompatible with some elastomers and metals in automotive fuel systems (Figure 4).

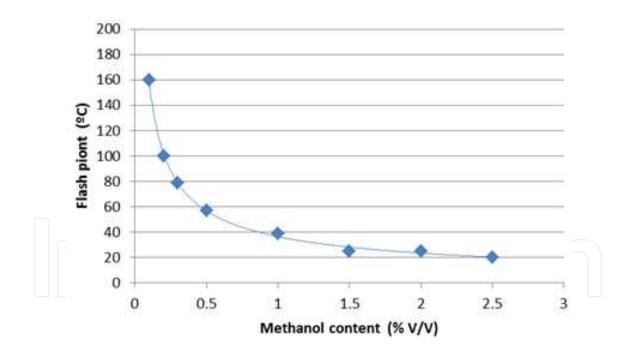


Figure 4. Relationship between flash point and methanol content.

Table 4 presents the biodiesel characteristics, and it is compared to the limits established by the norm. The values of the measured properties respond to parameters of international quality. Basically, the use of this biodiesel does not require any modification in the vehicle engine and ensures less contaminant emission when it is used as a result of the characteristics obtained in the results (Table 4).

| Characteristics/unit | Average value obtained | Limits |
|--|------------------------|--------------------------------|
| Content of linoleic acid methyl ester (%) | 97.5 | Min. 96.5% |
| Density (g/mL) | 0.8700 at 20°C | Report |
| Kinetic viscosity (mm²/S) | 5.03 | Maximum 6.5 mm ² /S |
| Carbonaceous wastes (g/100 g) | 0.06 | 0.3 g/100 g |
| Flash point (°C) | 176 | Min. 100°C |
| Water content (%m/m) | 0.0553 | Maximum 0.080%m/m |
| Copper corrosion (A, B, C) | 1 A (3 h at 50°C) | 1 A |
| Acid—volumetric method (mg KOH/g) | 0.7 | Max 0.8 mg KOH/g |
| Total glycerin (%) | 0.22 | Max 0.25% |
| Content of methanol or methanol free (%) | 0.004 | Max 0.2% |
| Cloud point (°C) | 19 | Report |

Source: Compilation based on results obtained in the laboratory of the Department of Quality Control.

Table 4. Comparison of the average values obtained from the fuel quality parameters determination with the limits established in the norm.

About the presence of linoleic acid as a quality indicator of the oil used in the process of transesterification, the presence of this acid was found, with a minimum of 96.5% as C18:2. This is considered "ideal" by the established standards for this purpose.

The relative density is useful for the load data in the vehicle where the fuel is going to be used and also for the combustion efficiency [18]. Taking into account that the specific gravity range of the oily products used as fuel goes from 0.700 to 1.050 g/mL [18] in relation to the reported density in this case, it can be considered as optimum. The kinetic viscosity expressed in 5.03 mm²/s indicates the property to resist changes in fluency with the temperature changes, so it is very interesting to consider an effective lubrication since it is closely related to temperature and defines the utility of fuel under different temperature ranges [12].

On the other hand, the carbon residue is presented between 0.06 g per each 100 g of biodiesel; therefore, it is less unlikely to form carbon residue deposits. The flash point at 176°C decreases the possibility of storage accidents as well as the tendency to vaporize in room temperature. This is also related to the quantity of emissions to the atmosphere [13].

The water in 553 ppm is inside the considered normal limits, so it does not stop being considerable in the biodiesel use since it could present chemical processes such as hydrolysis, corrosion problems, and bacterial growth [19].

Moreover, considering that corrosion is a very important factor in the utility of the whole fuel, in relation to the quality of biodiesel produced in Paraguay, the results indicate that they corrode steel to 1A (classification number of assigned 1–4 based on a comparison with the ASTM Copper Strip Corrosion Standards), which is considered the maximum allowed limit. This will probably reveal some sulfur presence, a consequence of an inadequate refining, as well as the emission of this type of contaminants in the use of biodiesel, although not in a considerable scale.

The presence of acid components could be the result of some additive components such as inhibitor agents and detergents or as degradation product formed during its use and storage [20]. Mainly, the degradation products contribute to a raise in the acidity number, which leads to the tendency to fuel corrosion on the metallic surface and increase of the degradation velocity. The acid number of crude sunflower oil was 2.8 mg KOH/g, and the moisture content and volatile matter were each 0.04%. The triacyl glycerides (TAGs) found in this oil contained 3.6% palmitic acid, 3.2% stearic acid, 78.8% oleic acid (18:1), 12.5% linoleic acid (18:2), 0.1% linoleic acid (18:3), 0.3% arachidic acid, 0.9% behenic acid, and 0.4% lignoceric acid as their main fatty acid components. The sunflower seeds used were of the high oleic acid type, as can be seen from the fatty acid composition.

The total glycerin quantity indicates a probable incomplete reaction because these are oil remains without reacting, and this could produce crystallization and deposits. However, this parameter was observed still within the limits.

On the other hand, the low presence of free methanol indicates that it was successfully removed during its process. This also influences in the increase of the flashpoint and the low possibility of corroding elements of the engine because of this factor.

As to the cloud point, fog or turbidity is seen in the sample at 19°C, indicating the starting of its own crystallization when it is under continuous cooling. This parameter is also within the allowed ranges.

4. Conclusion and recommendations

From the obtained results, can be specifically concluded that biodiesel fulfills the parameters of quality demanded by the international market, presenting itself as available alternative to replace oil. Ergo, elaborated with material from sunflower with a methanolysis process, it presents some characteristics that are suitable for its use in transportation with diesel vehicles as well as safe storage conditions. However, the manufacturing and reaction conditions to determine a more complete evaluation as well as the technology behavior against changes the raw material in order to ensure a stable product is still missing.

Therefore, it is presented as a valid potion to diverse the energetic matrix and to replace the fossil originated fuel contributing to the reduction of carbon emission to the atmosphere coming from the transportation.

It would be interesting to complement the investigation checking the environmental raw material production, as well as transportation and industrialization to ensure the sustainable production. A diversification of biodiesel feedstock, a detailed revision of the environmental and social impact, is necessary. Although major changes are not yet visible on the land with the increased production of biofuels, it is recommended to be implemented in public policies to support family farming and crop diversification in the production areas to avoid the risk of extensive monocultures.

Author details

Estelvina Rodríguez Portillo^{1*}, Araceli Amaya Chávez^{2*}, Arturo Colín Cruz² and Rubí Romero Romero²

*Address all correspondence to: aamayac@uaemex.mx

1 Research Department, Faculty of Science and Technology, National University of Itapúa, Encarnación, Paraguay

2 Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colon Esq. Tollocan, Toluca, Mexico

References

- Encinar JM, Gonzalez JF, Rodríguez JJ, Tejedor A. Biodiesel fuels from vegetable oils: transesterification of *Cynara cardunculus* L. oils with ethanol. Energy Fuels 2002;16:443–50.
- [2] Ma F, Hanna M.A. Biodiesel production: a review. Bioresour Technol 1999;70:1–15.
- [3] Narayanan D, Zhang Y, Mannan MS. Engineering for sustainable development (ESD) in bio-diesel production. Process Saf Environ Protect 2007;85:349–359.
- [4] García J, García J. Biocarburantes líquidos: Biodiesel y bioetanol. Informe de vigilancia tecnológica—CITME. Editorial Elecé Industria Gráfica, Madrid, España. 2006.
- [5] Saraf S, Thomas B. Influence of feedstock and process chemistry on biodiesel quality. Process Saf Environ Protect 2007;85:360–365.
- [6] Vargas M. Biodiesel. CONAE (Consejo Nacional de Ahorro Energético, Argentina). Buenos Aires. 2007.
- [7] Monteiro M, Pepe AA, Morais L, Ferreira AG. Critical review on analytical methods for biodiesel characterization. Talanta 07/2008;77(2):593–605.

- [8] American Society for Testing and Materials (ASTM). Web page www.astm.org.consulted in November 2009.
- [9] Centro Multidisciplinar de Innovación y Tecnología. Caracterización de Biodiesel. Biodiesel en Sustitución del Gasoil-Biodiesel de Calidad. Publicaciones Técnicas. CE-MITEC-Navarra- España. 2007.
- [10] Komers K, Stloukal R, Machek J, Skopal F. Biodiesel from rapeseed oil, methanol and KOH. 3. Analysis of composition of actual mixture. Eur J Lipid Sci Technol 2001;103:363–71.
- [11] Agudelo SJR, Benjumea R, Gómez ME, Pérez BJF. Biodiesel. Una revisión del desempeño mecánico y ambiental. Ingeniería & Desarrollo. Universidad del Norte. Medellín-Colombia 2003;13:1–14.
- [12] Canakci M, Sanli H. Biodiesel production from various feedstocks and their effects on the fuel properties. J Ind Microbiol Biotechnol 2008;35(5):431–441. doi: 10.1007/ s10295-008-0337-6.
- [13] Landa, Itziar. Caracterización de biodiesel principales parámetros de calidad. CEMI-TEC, Navarra, España. 2006.
- [14] Park JY, Kim DK, Lee JP, Park SC, Kim YJ, Lee JS. Blending effects of biodiesels on oxidation stability and low temperature flow properties. Bioresour Technol 2008;99(5):1196–1203. doi: 10.1016/j.biortech.2007.02.017.
- [15] Sharma Y, Singh B, Upadhyay S. Advancements in development and characterization of biodiesel: a review. Fuel 2008;87(12):2355–2373. doi: 10.1016/j. fuel.2008.01.014.
- [16] Ramos M. J., Fernández C. M, Casas A., Rodríguez L., & Pérez Á. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresour Technol 2009;100(1):261–268. doi: 10.1016/j.biortech. 2008.06.039.
- [17] Universiteit Utrecht. Copernicus Institute of Sustainable Development. Energy and Resource. Potential indirect land use change (ILUC). Available online: http:// www.uu.nl/en/research/copernicus-institute-of-sustainabledevelopment/ research/ energy-and-resources/potential-indirect-land-use-change-iluc
- [18] INTN (Instituto Nacional de Tecnología y Normalización). Normas Paraguayas. Legislación alimentaria y Resoluciones MERCOSUR internalizadas. INTN Asunción, Paraguay. 2008.
- [19] Proc Kenneth RL, McCormick KK, Chandler B, Buchhler B. Operating Experience and Teardown Analysis for Engines Operated on Biodiesel Blends (B20), NREL/ CP-540-38509, 2005-01-3641.
- [20] IDIADA Automotive Technology. Technical Report: Comparison of vehicle emissions at European Union annual average temperatures from E0 and E5 petrol. PEP-SOL, YPF, Abengoa Bioenergía, CEPSA, Ebro Puleva. 2003.