SYNTHESIS OF BIOFUELS BY TRANSESTERIFICATION OF GRAPE SEED OIL

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INTRODUCTION

The search for sustainability has become increasingly frequent in society, proving to be a more effective way to reduce inorganic waste on the planet, promoting a healthier and less polluting standard of living for terrestrial life. With this in mind, one of the main changes that human beings are trying to acquire is the search for replacing fossil fuels with more renewable energy sources that are less harmful to the planet. As a result, a search for materials that could promote this change began, and among them Biofuels emerged, proving to be a viable alternative for reducing pollution on the planet because it consists of the reuse of biodegradable materials that arise from organic materials.

According to (ROCKEMBACH et. al 2014), the benefits that biofuels can provide range from economic to sustainable, as they have proven to be more effective for the development of cleaner and less harmful energy, one of the benefits that can also be mentioned is the incentive within agricultural communities, considering that most biofuels are derived from organic materials, such as vegetable oils. According to the author, it is mentioned that biofuels are a mixture of fatty esters and is usually obtained by the transesterification reaction of triglycerides with short-chain alcohols and catalyst.

As previously stated, Biofuels arise through organic materials that are reused, and one of the main ones are vegetable oils and according to (RIZZI et al. 2010) the technological perspective on the production of biodiesel based on vegetable oils does not show the useful life of the equipment that is used, since scientists have assumed that oils can, For example, corroding the pistons can disrupt the mechanical process. But in any case, this means proved to be more efficient and more appropriate for sustainable development.

A vegetable oil that proved to have great potential to develop a Biodiesel was the oil derived from the grape seed. According to (OLIVEIRA, 2010), grapes are one of the fruits with the highest production in the world, with more than 67 million tons per year, cultivated mainly in the *Vitis vinifera* variety, which is the most used for wine production. From this extraction for wine production, grape pomace represents an important by-product of the wine industry, basically composed of seeds, skins and stems. As said, one of these by-products is the seed, from which the oil can be extracted from it.

Grape seed oil has stood out in the pharmaceutical, cosmetic and food industries, for having a good restoration of barrier function, intense hydration and antioxidant action. In addition to not being toxic to the body, it has a pleasant flavor and can be used in culinary preparations. With this in mind, this work was prepared with the aim of synthesizing a biofuel from grape seed oil, so that it is less harmful to the environment, without containing synthetic additives, viscosity modifiers, corrosion inhibitors and the high presence of heavy metals, so that it can promote a more sustainable and less harmful source of energy for the environment.

METHODOLOGY

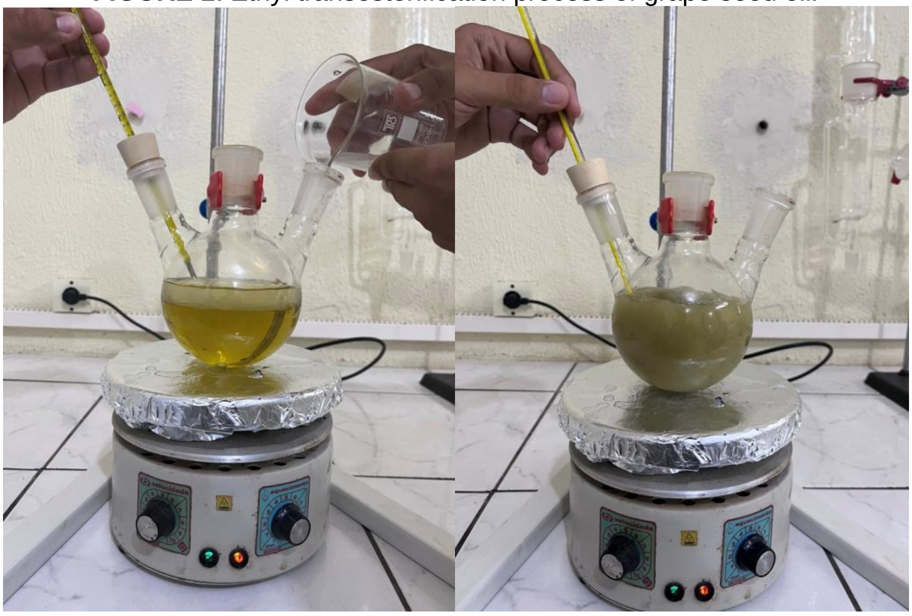
MATERIALS

Grape seed oil was purchased in local commerce and produced in the Brazilian industry. The refined oil does not need prior treatment before the reactions to which it has been subjected.

SYNTHESIS OF ETHYL BIODIESEL BY TRANSESTERIFICATION OF GRAPE SEED OIL

To obtain the ethyl ester (biodiesel), initially a calculation of the molar mass of grape seed oil was made from the saponification index. With the knowledge of this mass, it was possible to calculate the amounts of alcohol (ethanol) and catalyst (KOH) necessary to carry out the reaction. The transesterification reaction was performed adopting an oil/alcohol molar ratio = 1:6 and 0.7% catalyst (oil/catalyst), maintaining the temperature at approximately 45°C for 1 h.

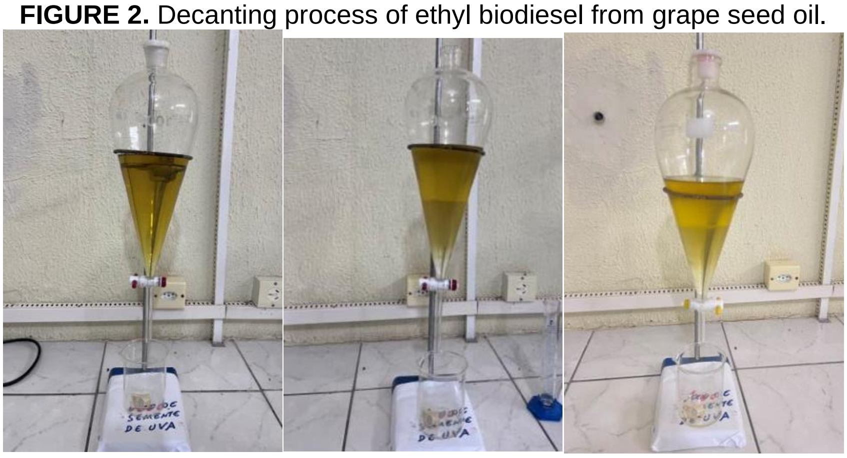
FIGURE 1. Ethyl transesterification process of grape seed oil.



Source: Survey data, 2024.

After the transesterification reaction, the reaction mixture was transferred to a separation funnel allowing the separation of the phases: upper containing ethyl ester and lower composed of glycerol, soaps, excess base and alcohol, after the waiting time the lower phase was removed and stored in an appropriate container.

FIGURE 2. Decanting process of ethyl biodiesel from grape seed oil.



Source: Survey data, 2024.

Next, the ethyl ester (biodiesel) was washed with distilled water and 0.01M hydrochloric acid solution. Three washes with distilled water and two washes with 0.01M HCl solution will be performed. After washing, anhydrous magnesium sulfate was added to remove the water that is still in the ester.

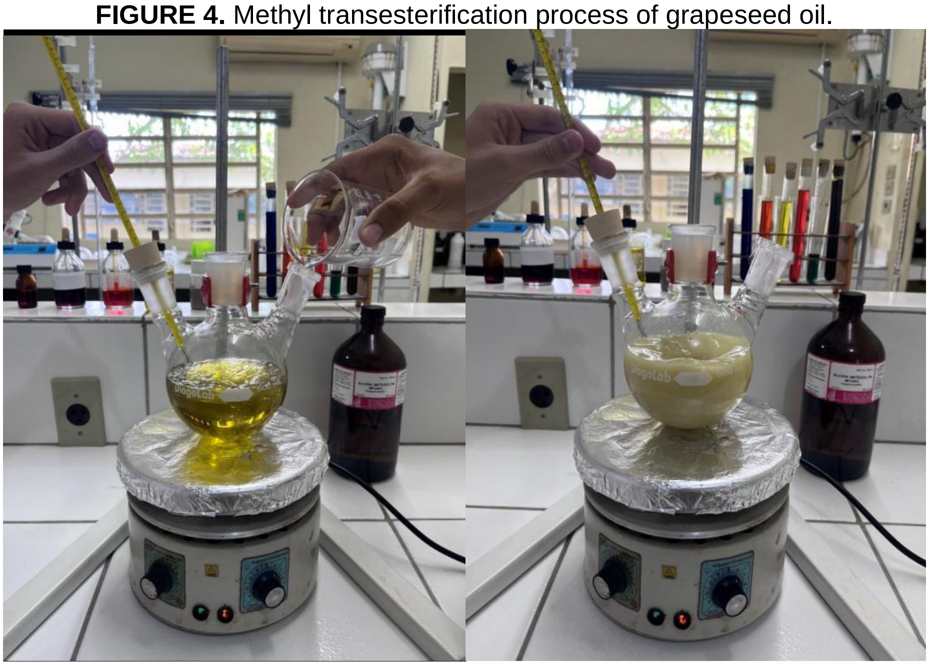
FIGURE 3. Washing process of ethyl biodiesel from grape seed oil.

Source: Survey data, 2024.

The same procedure was performed for the metallic route as shown in Figures 4, 5 and 6.

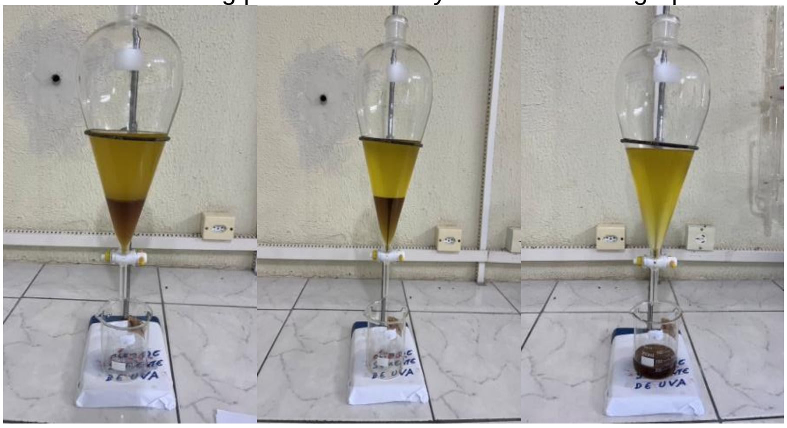
SYNTHESIS OF METHYL BIODIESEL BY TRANSESTERIFICATION OF GRAPESEED OIL

FIGURE 4. Methyl transesterification process of grapeseed oil.



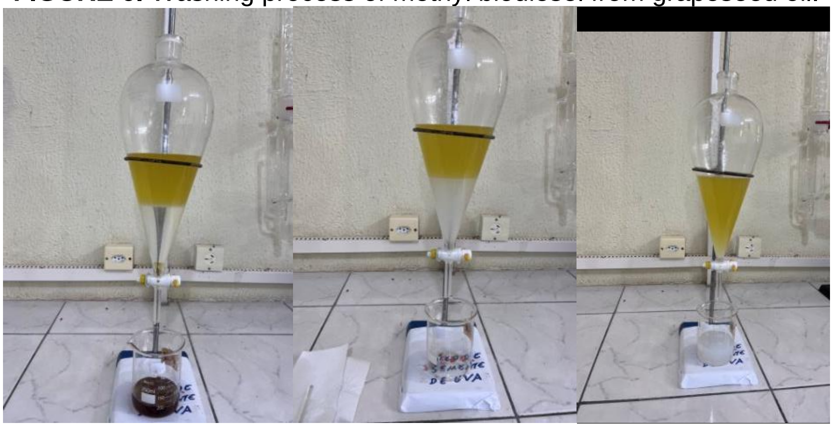
Source: Survey data, 2024.

FIGURE 5. Decanting process of methyl biodiesel from grape seed oil.



Source: Survey data, 2024.

FIGURE 6. Washing process of methyl biodiesel from grapeseed oil.



Source: Survey data, 2024.

PHYSICOCHEMICAL CHARACTERIZATION

The characterization of grape seed oil was made by means of the acidity index (AOCS Cd3d-63), iodine index (AOCS Cd 1-25), saponification index (AOCS Cd3b-76), soap content (AOCS Cc 17-95), peroxide index (AOCS Cd 8-53), relative density, ash content, moisture content and volatiles (AOCS Da-2a-48)Dynamic viscosity.

The procedures adopted to characterize the ethyl ester (biodiesel) after transesterification were the same as those used to characterize grape seed oil (WU et al., 2000). The epoxide of ethyl ester of grape seed oil was characterized by the indices of iodine (AOCS Cd 1-25), peroxide index (AOCS Cd 8-53), idroxyl (AOCS Cd 13-60) and oxirane oxygen (AOCS D Cd 9-57), relative density, ash content, viscosity, moisture content and volatiles (AOCS Da-2a-48). All the characterizations described above were performed according to the techniques described by Wu et al.(2000) and were performed in triplicates.

DEVELOPMENT

In view of the results obtained, we can analyze the physicochemical parameters of grape seed oil comparing with the standards established by Anvisa and the National

Petroleum Agency. The evaluation included essential characteristics, such as appearance, moisture content, density, acidity index, and other important parameters to determine the quality and stability of the oil, shown in tables 1 and 2.

Table 1. Physicochemical parameters of grape seed oil.

Parameters	Oil	Anvisa Standards1, 2
element.**Aspect**	yellow clear	clear and unbiased of impurities
Moisture and Volatiles (%)	0,18	≤ 0.1
Ash(%)	0,027	---
Density (g/cm3)	0,957	0,915 - 0,925
Acid value (mg KOH/g oil)	0,337	≤ 0.6
Iodine content (I2 g/100g oil)	140,5	96 - 115
Soap content (ppm sodium oleate)	0,121	≤ 10
Saponification index (mg KOH/g oil)	193,4	189 - 195
Peroxide Index (meq/Kg)	0,169	≤ 10
Approximate molar mass (g/mol)	633	---
Kinematic Viscosity at 40oC (mm2/s)	15,78	---

Source: Survey Data, 2023; [1]BRAZIL, 2021; [2]BRAZIL, 2006.

The results of table 1 of the grape seed oil parameters show that the oil has good compliance with most standards, especially in relation to acidity, where the acidity value is within the limit allowed by Anvisa which is ≤ 0.6 (mg KOH/g oil), which indicates that the oil has low levels of free acids, an important feature to prevent corrosion and degradation of the product. The saponification index also has a good yield within the range specified by Anvisa of 189-195 (mg KOH/g oil), which indicates that the oil has an adequate composition of fatty acids for the production of soap and other derived products, and peroxide index being within the limits recommended by Anvisa.

However, it has a high moisture content and a non-standard iodine content, which could impact the oxidative stability of the oil. The soap content is satisfactory, and the density and viscosity indicate that the oil may have unique properties, slightly different from conventional standards.

Comparing data with Anvisa's is essential to ensure the compliance of products and services with established safety and efficacy standards. This ensures that what is offered to the public and companies is the safety and stability of the product, increasing the credibility of studies and facilitating informed decision-making. In addition, it promotes continuous quality monitoring and protection of public health.

The transesterification reaction using grape seed oil with methanol and ethanol in the presence of potassium hydroxide provided a mixture of methyl and ethyl esters (biodiesel). The yields obtained were 96% for the methyl route and 92% for the ethyl route, which indicates a good efficiency of the process. The esters obtained were characterized according to their physicochemical properties listed in Table 2.

Table 2. Physicochemical parameters of grape seed oil esters (biodiesel).

Parameters	Methyl esters	Ethyl esters	ANP1 Standards
Aspect	Yellow clear	Yellow clear	Clear and exempt from Impurities
Moisture and Volatiles (%)	0,25	0,16	0,02
Ash(%)	0,02	0,03	0,02
Density (g/cm3)	0,937	0,946	0,850-0,900
Acid value (mg KOH/g oil)	0,170	0,339	≤ 0.5
Iodine content (I2 g/100g oil)	117,7	119,4	-----
Soap content (ppm sodium oleate)	0,670	0,791	-----
Saponification Index (mg KOH/g oil)	121,4	115,2	-----
Peroxide Index (meq/Kg)	0,03	0,09	-----
Kinematic Viscosity at 40oC (mm2/s)	5,30	5,79	3.0–6.0 bnm,;

Source: Survey Data, 2023; [1]BRAZIL, 2014.

In these parameters, it can be observed according to Rockenbach, C. T. et al (2014.) that the viscosity of an oil increases proportionally with the length of the fatty acid chain of triglycerides and decreases when unsaturations increase. A product with high viscosity can cause deposition of residues on the internal parts of the engine. Thus, the determination of viscosity is characterized as an important indicator of the quality of biodiesel.

The acidity index is a very important determination, as it serves both to provide data that evaluate the state of conservation of the oil, and to inform about the quality of the product, since acidity values are within the parameter estimated by the National Petroleum Agency of ≤ 0.5 (mg KOH/g oil). It is also worth noting that the ash content of methyl esters is within the established ANP parameter of 0.02 (%). On the other hand, we see that ethyl esters are 0.1% above what Anvisa determines, being 0.03%. For the other parameters, they are out or the ANP does not have a defined standard. In view of this lack of additional data, there is a need to compare the results obtained with other bibliographies that are consistent with the characterization of the biodiesel mentioned.

With this in mind, when analyzing the results described in the soap content, we can analyze and compare with the parameters of the tests carried out by Rockembach (2010) where a biodiesel based on grape seed oil was synthesized by means of ultrasound and its results were somewhat high when compared to those obtained in this research, having a value of 185.10 while in biodiesel synthesized through the two routes, both methyl and ethyl are respectively 121.4 and 115.2. The value presented by the author was very high compared to the analyses made, this may have occurred due to the use of alternative methods for its synthesis.

In view of this, there is a need to compare these data with the values dated by the ANP, as it is related to the continuous improvement of inspection, thanking the report's suggestions and recognizing that they will improve the identification of discrepancies in oil development and production activities in Brazil (Rodrigues, 2022). The knowledge of these data is of paramount importance, as it is an agency responsible for the treatment of fuels and their treatment and having these results equivalent to those established by the institution can demonstrate that the oil has a great potential to become an effective energy source.

FINAL CONSIDERATIONS

Considering the importance of the energy issue, due to the fact that fossil fuels are the main pollutant of the environment, there is a need to create sustainable energy alternatives, and grape seed oil can be used as an alternative source of energy and biofuel. In this work, a perspective of how biofuel technology can be used, providing sustainable alternatives, was shown.

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