



## SYNTHESIS OF BIODIESEL FROM SWEET ALMOND OIL BY HOMOGENEOUS CATALYSIS

Alida Samara Gomes da Silva<sup>1</sup>, Maria Lidiane da Silva Souza<sup>2</sup>, Lidiane Silva de Araújo<sup>3</sup> and José Carlos Oliveira Santos<sup>4</sup>

### ABSTRACT

The main objective of the present study was the production of biolubricants from a renewable source, sweet almond oil. For this, transesterification reactions were carried out with methanol and ethanol, aiming to obtain the respective esters, and later, epoxidation reactions for the production of biolubricants. The specific objectives included the synthesis and physicochemical characterization of the compounds obtained at each stage of the process. The physicochemical analyses allowed the evaluation of the properties of the products obtained, such as viscosity, acid index, density and ester content.

**Keywords:** Biolubricating, Sweet almond oil, Transesterification, Epoxidation, Physicochemical characterization.

### INTRODUCTION

There are many reasons to replace the frequent use of fossil fuels with safer alternatives, as the negative impact of these resources on society contributes to various environmental problems, such as the greenhouse effect, global climate change, ocean acidification, and the depletion of the ozone layer. These impacts result from increased levels of carbon dioxide (CO<sub>2</sub>) and other by-products from the burning of fossil fuels (Ishola et al., 2013). Biofuel, produced from biomass, has emerged as a unique alternative to replace liquid fossil fuels. Through the use of biomass, conventional fuels, such as gasoline, diesel, and LPG, began to be partially replaced by renewable fuels, such as bioethanol, biodiesel, and biogas. The increase in oil prices and the growing concern about the emission of polluting gases have driven the search for alternative energy sources that can replace fossil fuels in a sustainable way (Demirbas, 2009; Rashid; Anwar, 2008). Within this context, biofuels, especially biodiesel, stand out as a renewable, biodegradable option with

---

<sup>1</sup>Federal University of Campina Grande - Paraíba

<sup>2</sup>Federal University of Campina Grande - Paraíba

<sup>3</sup>Federal University of Campina Grande - Paraíba

<sup>4</sup>Federal University of Campina Grande - Paraíba



lower carbon emissions compared to conventional diesel (Takase et al., 2015; Knothe; Ruckenstein; Arana, 2021). Biodiesel is defined as a mixture of fatty acid esters produced by the transesterification of vegetable oils or animal fats with short-chain alcohols (Metha; Vidya Sagar; Naidu, 2006).

The production of biodiesel with conventional oils, such as palm, sunflower, rapeseed and soybean, is widespread (Balat and Balat, 2008; Demirbas, 2007). However, the use of these oils for energy purposes can affect their economic value and availability for food consumption (Rashid et al., 2008). As an alternative, researchers have investigated the use of inedible oils, waste cooking oils, and other less common sources for biodiesel production (Balat and Balat, 2008; Ofoefule et al., 2013; Bamgboye and Oniya, 2012). Biomass sources have become increasingly attractive due to the problems associated with fossil fuels, especially due to the increase in pollutant emissions resulting from their combustion. According to experts, the oil and gas reserves currently available should only be sufficient for a few decades. In order to meet the growing energy demand and reduce dependence on oil reserves, alternative fuels such as biodiesel and bioethanol have been consolidated among the promising technologies. In this way, biodiesel is positioned as a viable choice for use in compression ignition engines (CIEs).

Biodiesel is a fuel composed mostly of monoalkyl esters, derived from vegetable oils or animal fats, through a chemical process called transesterification. This process aims to reduce the natural high viscosity of these oils and fats, which can be 10 to 17 times higher than that of petroleum diesel, making them unsuitable for direct use in engines. In transesterification, the oil or fat is transformed into fatty acid esters, which results in a fuel with a viscosity similar to that of petrodiesel, allowing its efficient use in diesel engines. The reaction is catalyzed, often with simple alcohols (such as methanol or ethanol) that contain 1 to 4 carbon atoms, which favors the production of esters with properties suitable for applications in internal combustion engines. Transesterification is the essential chemical process in the production of biodiesel, in which triglycerides, which are the original esters present in oils and fats, react with a simple alcohol, such as methanol, transforming into fatty acid esters (biodiesel itself) and releasing glycerin as a byproduct. This method aims to convert vegetable oils and animal fats into lighter, lower-viscosity esters suitable for use in diesel engines. This is a widely studied reaction, with several studies and publications addressing its feasibility for alternative biomass-based fuels. Many studies show that the choice of raw materials, such as residual or inedible vegetable oils, is essential to make the process economically viable, as it reduces costs and minimizes environmental impacts. In addition, renewable biomass is constantly considered a promising alternative as a source of



oils for the production of biodiesel, allowing the development of sustainable fuels with a lower carbon footprint.

The sweet almond tree (*Prunus amygdalus "dulcis"*), belonging to the subfamily Prunoideae and the family Rosaceae, is widely known for the high lipid content of its seeds, which contain approximately 51% oils, as well as proteins, carbohydrates and fiber (Agunbiade; Olanlokun, 2006). This family also includes fruits such as apples, pears, apricots, cherries, peaches, and plums, distributed among the subfamilies Pomoideae, Prunoideae, and Rosoideae. There are two main varieties of almonds, the bitter (*Prunus amygdalus "amara"*), usually used for flavoring purposes, and the sweet (*Prunus amygdalus "dulcis"*), commonly used in culinary preparations and oil extraction (Agunbiade; Olanlokun, 2006). The choice of oil for biodiesel production is also a factor of great relevance, and sweet almond oil, widely available and rich in essential fatty acids, has significant potential for biodiesel synthesis. Recent studies indicate that the composition of fatty acids, as well as the oxidative stability of biodiesel derived from vegetable oils such as almonds, contributes to the development of biofuels with better performance and lower environmental impact (Chhem; THEE; Wong, 2023; Knothe; Mathews; Carlson, 2021). Thus, this study seeks to explore the synthesis of biodiesel from sweet almond oil, using homogeneous catalysis, highlighting the parameters of efficiency and quality of the final product. Considering the high availability of sweet almonds, particularly low-cost ones, it is feasible to use them as an alternative source for biodiesel production, thus reducing the dependence on conventional oils for food use, such as palm and peanut oil. The present work, therefore, aims to investigate the use of sweet almond oil as a potential raw material for the synthesis of biodiesel, contributing to the diversification of renewable sources and helping to mitigate the impacts of the use of traditional cooking oils in the production of biofuels.

## METHODOLOGY

Sweet almond oil was purchased in local commerce and produced by a Brazilian industry. The refined oil did not require prior treatment before the reactions it was subjected to. The laboratory research was carried out by three scholarship students of the Chemistry Tutorial Teaching Program (PET-Chemistry) under the guidance of the program's tutor, in the Environmental Chemistry and Biofuels laboratory.

For the biodiesel and biolubricant extraction process, the following procedures were performed: transesterification and epoxidation.

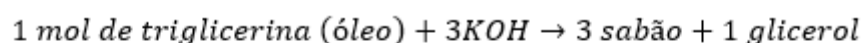


To obtain the methyl or ethyl esters, initially a calculation of the molar mass of sweet almond oil was performed based on its saponification index. In which 1.0 g of the sample was added to a 250 mL Erlenmeyer to be weighed and 25 mL of alcoholic potash was added. This Erlenmeyer was connected to a ball condenser and gently heated for 1 hour so that the sample is completely saponified. Then, a few drops of phenolphthalein were added to the Erlenmeyer diet and titrated with a 0.5M HCl solution until the pink color disappeared. We repeated the same procedure without the presence of samples to determine the blank. The saponification index can be calculated using the following equation:

$$\text{índice de Saponificação} = \frac{(B - A) * N * 56,1}{w}$$

Where A is the volume of the 0.5 M HCl solution used in the titration of the sample (mL); B is the volume of the 0.5M HCl solution used in the titration of the blank (mL); N is the normality of the HCl solution and W is the mass of the sample (g).

Thus, we obtained the molar mass of the oil from the saponification index, with the following calculation:



$$X \text{ ————— } 3 * (56,1 \text{ g/mol}^{-1})$$

$$1\text{g} \text{ ————— } \text{Índice de Saponificação}$$

With the knowledge of this mass, the amounts of alcohol (methanol or ethanol) and catalyst (KOH) necessary to carry out the reaction were calculated.

The transesterification reaction was performed adopting an oil/alcohol molar ratio equal to 1:6 and 0.7% catalyst (oil/catalyst), maintaining the temperature at approximately 45°C for 1 hour, because temperatures higher than the boiling temperature of alcohol can accelerate the saponification of glycerides by the alkaline catalyst before complete alcoholization.

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



Next, the ethyl ester (biodiesel) was washed with distilled water and 0.01M hydrochloric acid solution. Three washes were made with distilled water, then removed from the phase of the esters (glycerol residues and soaps) and two washes with 0.01M HCl solution (neutralize the esters). Phenolphthalein was used to verify the efficiency of acid washing.

After washing, anhydrous magnesium sulfate was added to remove the water that was still present in the ester, using a rotary evaporator. The same procedures were performed for the methyl route.

To identify the Peroxide index, a 250mL Erlenmeyer with a ground cap was used to weigh 3 g of the sample and add 30 mL of acetic acid:chloroform solution 3:2 (v/v) and mixed with light agitation. We add 0.5 mL of 10% KI solution and let it stand for 1 minute timed. After that, 30 mL of distilled water and 0.5 mL of 1% starch solution were added. Titration was performed with a 0.01 N sodium thiosulfate solution with constant agitation until the blue color disappeared. The peroxide index can be calculated using the following equation:

$$\text{índice de Peróxido} = \frac{(A - B) * N}{W}$$

Where A is the volume of thiosulfate used in the titration of the sample (mL); B is the volume of thiosulfate used in white titration (mL); N is the normality of the  $\text{Na}_2\text{S}_2\text{O}_2$  solution and W is the mass of the sample (g).

For the Acidity Index we use a 250 mL Erlenmeyer Sylvester Index, 3:3 g of sample will be weighed and 22 mL of the neutralized solvent mixture will be added (11 mL of toluene + 11 mL of isopropyl alcohol). The sample was well dissolved in the solvent mixture. 3 drops of phenolphthalein indicator were added and titrated with KOH 0.1 N until it could obtain a permanent pink stain for 30 seconds. The same procedure was repeated without the presence of samples in order to determine the blank type. To calculate the acidity index we use the following equation:

$$\text{Índice de Acidez} = \frac{(A - B) * N * 56,1}{W}$$



Where A is the volume of the 0.1N KOH solution used in the titration of the 9mL sample); B is the volume of the 0.1n Koh solution used in the titration of the blank (mL); N is the normality of the KOH solution and W is the mass of the sample (g).

For the iodine index, a 250mL Erlenmeyer was used, 0.25g of sample was weighed, followed by 10mL of chloroform and 24 mL of Wijs' solution (rotating the erlenmeyer to maintain half contact with the sample). Then, the vial was stored in a dark place at a temperature of 25°, for 30 minutes in which they were timed. After this time, we add 10 mL of 10% potassium iodide solution, 100 mL of distilled water and titrate with 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  solution, mix vigorously. When the brown stain was fading, 1mL of starch indicator solution was added and titrated until the dark stain completely disappeared. The same procedure was performed to determine the blank type, but without the presence of the sample. To calculate iodine content can be calculated using the following equation:

$$\text{Índice de Iodo} = \frac{12,6 * N * (A - B)}{W}$$

where N is the normality of the sodium thiosulfate solution; A is the volume of the 0.1N  $\text{Na}_2\text{S}_2\text{O}_3$  solution used in the titration of the sample (mL) and W is the mass of the sample (g).

For the soap index, we used a 250 mL Erlenmeyer Erlenmeyer Mouse test, so that 5 g of the sample was weighed, then 0.25 mL of deionized water was added and we stirred vigorously. After stirring, a solution containing 0.05g of the bromophenol indicator and 25 mL of neutralized acetone was prepared. In the Erlenmeyer containing the sample, 25 mL of this newly prepared solution was added, due to the presence of soap, a phase separation occurred and the upper layer with a bluish-green color. Then, the mixture was titrated with a standardized 0.01 N hydrochloric acid solution until it turned from bluish green to yellowish. The same procedure was performed to determine the blank ballot, but without the presence of the sample. To calculate the soap content we made the following calculation:

$$\text{Teor de Sabão} = \frac{(A - B) * N * 304,4}{W}$$



Where A is the volume of HCl solution used during sample titration (ml); B is the volume of HCl solution used in white titration (mL); N is the normality of the HCl solution and W is the mass of the sample (G).

After that, we calculate the relative density. In which we used a 25 mL pycnometer that was previously weighed and in it we added approximately 25 mL of distilled water, and then weighed it. We added approximately 25 mL of the sample that was also weighed. The density calculation was made according to the expression:

$$dx = \frac{m_x}{m_{\text{agua}}}$$

Where the relative density of the sample is the mass of the sample is the mass of the water.

On the same day that we calculated the relative density, we also made the ash content with the help of an oven at 105°C, we let the porcelain capsule dry for an hour. After this period, after this period, we transfer it to the desiccator to cool down. With the capsule empty, it was weighed and then added approximately 3 g of sample. The plate with the sample was taken to the muffle furnace at 550°C. After this period it was placed in the desiccator to cool, the capsule with the sample was weighed. The ash content can be calculated by means of one of the following equations:

$$\%Cinzas = \left[ \frac{(C - B)}{A} \right] * 100$$

Where A is the mass of the sample; B is the porcelain capsule plus sample after the muffle; C is the porcelain capsule plus sample before the muffle

This whole procedure took us about 5 hours to complete the experiment.

The moisture and volatile content was carried out with the help of a 105°C oven, in which we placed a Petri dish to dry for one hour. After this period, it was placed in the desiccator to cool down. Then the empty plate was weighed and added about 3g of sample. The sample plate was taken to the greenhouse at 105° C for one hour. With this period it was placed in the desiccator to cool down. So the sample plate was weighed. The volatile moisture content can be calculated using the following equation:





$$\%Umidade e Voláteis = \left[ \frac{(C - B)}{A} \right] * 100$$

Where A is the mass of the sample; B equals plate plus sample after greenhouse; C is equal to plate plus sample before the kiln.

## RESULTS AND DISCUSSIONS

The sweet almond oil used in this study was purchased in local commerce and produced by a Brazilian industry. The results that were obtained through the physicochemical characteristics of sweet almond oil are presented in Table 01, being compared to the compliances provided for by ANVISA's Normative Instruction No. 87, of March 2021, which defines the quality standards for oils of vegetable origin.

According to the results presented in Table 01, the appearance of sweet almond oil was within the standard required by ANVISA, presenting a clear yellow color, free of impurities. As for the moisture and volatile content, the value obtained was 0.09%, within the allowed limit of up to 0.1%. According to Giwa and Ogunbona (2014), the high amount of water present in oils in general produces negative effects, consuming the catalyst and reducing its effectiveness, increasing soap production. The ash content was 0.02%; however, ANVISA does not establish a specific standard for this parameter. This parameter indicates the amount of inorganic residue present in the sample after burning the organic matter in the muffle furnace at high temperatures. The density is within the parameter established by the regulatory body. This analysis provides information on the amount of material per unit volume.

For density, sweet almond oil obtained a value of 0.956 g/cm<sup>3</sup>, exceeding the standard range of 0.915 to 0.925 g/cm<sup>3</sup>. The acid value was 0.34 mg KOH/g of oil, within the maximum allowed limit of 0.6 mg KOH/g. According to MACHADO (2006) the acidity index can be considered one of the most important parameters of quality control of vegetable oils and fats, since it denotes the state of conservation of the oils. In the case of the iodine index, the value recorded was 118.7 g I<sub>2</sub>/100 g of oil, slightly higher than the standard range, which is 96 to 115 g I<sub>2</sub>/100 g of oil. The iodine index measures the degree of unsaturation of the oil, since each double bond of a fatty acid can bind to two halogen atoms, specifically iodine (Silva, 2007). The soap content was 0.121 ppm, well below the limit of 10 ppm, which indicates a low presence of unwanted soaps, favoring the quality of the oil.





The saponification index is used to determine the exact amount of alkali to be used in the production of soap from different oils and fats, it presented a value of 166.6, within the required standard of 189 to 195. The peroxide index was 0.018 meq/kg, well below the limit of 10 meq/kg, which points to a low oxidation of the oil. Other properties, such as the molar mass of 1010 g/mol and the kinematic viscosity at 40°C of 63.2 mm<sup>2</sup>/s, have also been proven, although ANVISA has not established standard values for these parameters.

Regarding the transesterification reaction, it was performed with an oil/alcohol molar ratio of 1:6 and 0.7% catalyst (in relation to oil), maintaining the temperature at approximately 45°C for one hour. The process was conducted by two routes: Ethyl and Metallica. In the Ethyl route, the use of anhydrous alcohol was adopted to minimize the formation of soaps, since the presence of water can cause parallel saponification reactions that consume the catalyst and reduce the efficiency of transesterification.

The results showed that the biodiesel obtained by the ethyl route achieved a yield of 92% and the one obtained by the methyl route obtained a yield of 88%, both are within the expected quality standards. Table 2 presents the values referring to the physicochemical parameters of the esters of sweet almond oil (biodiesel).

According to Resolution No. 45/2014 of the National Agency of Petroleum and Biofuels (ANP), which establishes the physicochemical parameters for biodiesel. From table 02, it can be observed that the methyl and ethyl esters of sweet almond oil have a clear yellow color, according to the visual standard of "clear and free of impurities" required. They have a moisture and volatile content of 0.04% and 0.07%, respectively, values above the expected limit of 0.02%. The ash content was 0.006% for the methyl ester and 0.014% for the ethyl ester, both below the maximum value of 0.02%, with the methyl ester exhibiting a lower ash content. Regarding density, the methyl ester presented 0.937 g/cm<sup>3</sup>, while the ethyl ester registered 0.949 g/cm<sup>3</sup>, both higher than the standard range of 0.850 to 0.900 g/cm<sup>3</sup>.

Regarding the acidity index, both esters were within the maximum limit of 0.5 mg KOH/g of oil: the methyl ester presented 0.34 mg KOH/g, while the ethyl ester presented 0.17 mg KOH/g. In the iodine index, the values recorded were 108.7 g I<sub>2</sub>/100g oil for the methyl ester and 113.4 g I<sub>2</sub>/100 g oil for the ethyl ester; The ANP does not indicate a value for this index, it is presented as "annotate". For soap content, the methyl ester presented 0.426 ppm and the ethyl ester 0.500 ppm; the ANP does not specify a standard limit for this parameter. Regarding the saponification index, the values were 121.7 mg KOH/g oil for methyl and 110.0 mg KOH/g oil for ethyl, for which the ANP also does not establish a specific limit. Regarding the peroxide index, the values collected were 0.005 meq/kg for the



methyl ester and 0.015 meq/kg for the ethyl ester; Again, the ANP has not defined a standard value for this index. Finally, the kinematic viscosity values at 40°C were 4.75 mm<sup>2</sup>/s for the methyl ester and 4.63 mm<sup>2</sup>/s for the ethyl ester, both within the allowed range of 3.0 to 6.0 mm<sup>2</sup>/s.

## **FINAL CONSIDERATIONS**

Through this research, it can be concluded that sweet almond oil, through homogeneous catalysis, indicates that this raw material has physical and chemical characteristics suitable for the production of biodiesel. The results obtained show that the biodiesel derived from sweet almond oil meets the established quality standards, especially in relation to oxidative stability, low soap formation and physicochemical properties compatible with the regulatory requirements. In addition, the use of sweet almond oil as a source for biodiesel is a sustainable and economically viable alternative, considering its high availability and the potential to reduce dependence on cooking and conventional oils in the production of biofuels. The use of renewable sources such as this contributes significantly to the development of fuels with low environmental impact, in line with contemporary energy and environmental needs. Therefore, this study not only reinforces the technical feasibility of biodiesel from sweet almond oil, but also paves the way for new research that explores other alternative feedstocks, aiming at expanding renewable options for the production of sustainable biofuels.

## **ACKNOWLEDGMENTS**

The authors thank the MEC/FNDE for the financial support for the development of the project linked to the PET/Chemistry of UFCG





## REFERENCES

1. Agunbiade, F. O., & Olanlokun, J. O. (2012). Propriedades do combustível de biocombustível de bucha vegetal (*Luffa cylindrica* L.) misturado com diesel. *African Journal of Environmental Science and Technology*, 6\*(11), 346–352. <https://www.ajol.info/index.php/ajest/article/view/88647>
2. Balat, M., & Balat, H. (2010). A critical review of biodiesel as a vehicular fuel. *Energy Conversion and Management*, 49\*(10), 2727–2741.
3. Brasil. Agência Nacional do Petróleo, Gás Natural e Biocombustíveis. (2014). *\*Resolução ANP Nº 45 de 25/08/2014\**. Diário Oficial da União, Seção 1.
4. Brasil. Ministério da Agricultura, Pecuária e Abastecimento. (2006). *\*Instrução Normativa No 49 de 22 de dezembro de 2006\**. Diário Oficial da União, Seção 1.
5. Brasil. Ministério da Saúde. Agência Nacional de Vigilância Sanitária. (2021). *\*Instrução Normativa No 87 de 15 de Março de 2021\**. Diário Oficial da União, Edição 51, Seção 1, 261.
6. Chhem, S., Ti, T. L., & Wong, W. Y. (2023). Properties and performance of biodiesel produced from different feedstocks: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 161\*.
7. Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, 50\*(1), 14–34.
8. Giwa, S., & Ogunbona, C. (2014). Sweet almond (*Prunus amygdalus* "dulcis") seeds as a potential feedstock for Nigerian Biodiesel Automotive Project. *Revista Ambiente & Água*, 9\*(1), 37–48. <https://doi.org/10.4136/ambi-agua.1272>
9. Knothe, G., Mathews, S., & Carlson, K. D. (2021). The history of vegetable oils as fuels: Transesterification of vegetable oils and biodiesel. *Fuel*, 287\*.
10. Leung, D. Y. C., & Guo, Y. (2006). Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Processing Technology*, 87\*(10), 883–890. <https://www.sciencedirect.com/science/article/abs/pii/S0301421507001516?via%3Di%3Dhub>
11. Machado, G. C., Chaves, J. B. P., & Antoniassi, R. (2006). Composição em ácidos graxos e caracterização física e química de óleos hidrogenados de coco babaçu. *Revista Ceres*, 53\*(308), 463–470.
12. Silva, A. F., Fleck, E., Mello, M. I. S., & Reis, M. F. P. (2007). Reciclagem - óleos de fritura. In *\*Anais: Mostra de trabalhos / projetos dos técnicos de nível superior da prefeitura de Porto Alegre\**. Porto Alegre, RS.
13. Takase, M., & et al. (2015). Biodiesel production from waste cooking oil: A sustainable approach. *Renewable and Sustainable Energy Reviews*, 47\*, 1–13.