Synthesis and characterization of biolubricant obtained by methyl epoxidation of sunflower oil

Síntese e caracterização de biolubrificanteobtido pela epoxidação metílica doóleodegirassol

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ABSTRACT
One of the issues present in the determinations of the National Solid Waste Policy concerns the disposal of vegetable oil from frying generated in homes and commercial establishments. In Brazil, it is estimated that three billion liters of edible vegetable oil are produced per year. Of this total, only 2.5% is reused for some purpose, while the rest is improperly disposed of by the population and industries, in soils, water bodies, sewage system, or even incinerated (ABIOVE, 2012).According to Folha do Amapá (2007), a safer way to dispose of waste vegetable oil is to deliver it to a collection point, for later reuse in the manufacture of biodiesel or soap.

Keywords: Biolubricant, Sunflower oil, Methyl.

RESUMO
Uma das questões presentes nas determinações da Política Nacional de Resíduos Sólidos, diz respeito ao descarte do óleo vegetal de frituras gerado nas residências e estabelecimentoscomerciais. No Brasil estima-se a produção de três bilhões de litros de óleo vegetal comestível porano. Deste total, apenas 2,5% é reutilizado para alguma finalidade, enquanto que orestanteéindevidamente descartado, pela população e indústrias, nos solos, corpos d’água, rede deesgotos,ou ainda, incinerados (ABIOVE, 2012). Segundo a Folha do Amapá (2007), uma forma mais segurade descarte de óleo vegetal residual é a entrega deste em um posto de coleta, para posteriorreutilização na fabricação de biodiesel ou sabão.

Palavras-chave: Biolubrificante, Óleo de girassol, Metílica.

1 INTRODUCTION

One of the issues present in the determinations of the National Solid Waste Policy concerns the disposal of vegetable oil from frying generated in homes and commercial establishments. In Brazil, it is estimated that three billion liters of edible vegetable oil are produced per year. Of this total, only 2.5% is reused for some purpose, while the rest is improperly disposed of by the population and industries, in soils, water bodies, sewage system, or even incinerated (ABIOVE, 2012).According to Folha do Amapá (2007), a safer way to dispose of waste vegetable oil is to deliver it to a collection point, for later reuse in the manufacture of biodiesel or soap.

Energy sources are essential to human life, as they provide a higher quality of life. According to Ramos et al. (2017), about 80% of the energy generated in the world comes from fossil fuels, such as coal, oil and natural gas. This fact has triggered a serious environmental problem, mainly because the use of fossil fuels releases a high amount of polluting gases, such as carbon monoxide, which contribute, for example, to the intensification of the greenhouse effect, gradually increasing global warming.

The rapid depletion of fossil fuel reserves, extraction, transportation and industrial processes of oil transformation are responsible for various environmental damages (EREDA, 2004). Thus, at present, reconciling experimental teaching activities with sustainable practices has become an alternative to the environmental problems faced.

In addition to their high calorific value, vegetable oils have qualities that distinguish them as sustainable fuels: the absence of sulphur in their chemical composition; the fact that their industrial production does not generate substances harmful to the environment and, also, the fact that they are made from vegetable crops that consume carbon dioxide from the atmosphere during photosynthesis (PIANOVSKI JÚNIOR, 2002). Despite being favorable from an energy point of view, the direct use of vegetable oils in diesel engines is very problematic, hence the need to use vegetable oils in diesel engines need for its use after processes. Studies show that its direct combustion leads to carbonization of parts, resistance to ejection in the pistons, dilution of the crankcase oil, contamination of the lubricant, among other problems (RINALDI et al., 2007).

The disposal of large quantities of cooking oil continues to be done in an inappropriate manner, causing serious environmental problems such as water contamination, increased expenditure on sewage treatment, etc. One way to avoid this is to raise public awareness and encourage recycling. Waste oil, whether from restaurants, industries or homes, can be used in soap making, biodiesel production and other biodegradable products, such as biolubricants. Thus, this research work was developed with the objective of synthesizing biofuels from sunflower oil used in frying and comparing its properties with the biofuel obtained with commercial sunflower oil, aiming to minimize impacts to the different ecosystems. Through the theme involving fuels, biofuels and renewable energies, it can be suggested to use this research as a proposal that provides students with problem situations. This whole context motivated the search for experimentation methodologies in the teaching of Chemistry and its implications in the chemical and social formation of these students.

2 OBJECTIVE

To obtain biolubricants, to reduce environmental impacts using renewable raw material, sunflower oil through transesterification and methyl epoxidation reactions and to make its physicochemical characterization.

3 METHODOLOGY

The refined sunflower oil was an oil produced by Brazilian industry and purchased in local commerce and the residual soybean oil was purchased in a university restaurant located in the Center of Education and Health (Campus Cuité) of the Federal University of Campina Grande. The samples were collected, purified and submitted to transesterification and epoxidation processes. To obtain methyl or ethyl esters, initially the molar mass of sunflower oil will be calculated from its saponification index. With the knowledge of this mass will be calculated the amounts of alcohol (methanol) and catalyst (KOH) needed to perform the reaction. The transesterification reaction will be carried out adopting an oil/alcohol molar ratio equal to 1:6 and 0.7% catalyst (oil/catalyst) (PELANDA, 2009), maintaining the temperature of the oil. At approximately 45o C for 1 h, because temperatures higher than the boiling temperature of alcohol can accelerate the saponification of glycerides by the alkaline catalyst before complete alcoholysis (FERRARI et al., 2005).

Figure 1. Methyl transesterification process of sunflower oil.

Source: Survey data, 2023.

After the transesterification reaction, the reaction mixture was transferred to a separatory funnel allowing the separation of the phases: upper containing the methyl ester and lower composed of glycerol, soaps, excess base and alcohol.

Figure 2: Decantation process of methyl biodiesel from sunflower oil.

Source: Survey data, 2023.

After the waiting time, the lower phase was removed and stored in an appropriate container. Then, the methyl ester (biodiesel) was washed with distilled water and 0.01M hydrochloric acid solution. Three washes were made with distilled water (removing glycerol residues and soaps from the ester phase) and two washes with 0.01M HCl solution (neutralizing the ester). Phenolphthalein was used to check the efficiency of the acid wash.

Figure 3: Washing process of methyl biodiesel from sunflower oil.

Source: Survey data, 2023.

After washing, anhydrous magnesium sulfate was added to remove any water still present in the ester. Then, in order to remove any ethanol that might still be present in the ester, a rotary evaporator was used.

In a 250 mL round-bottomed flask, 100 g of the methyl ester obtained from sunflower oil will be added, and drop by drop, 140 mL of 15% commercial peracetic acid. The mixture will be stirred and heated at 45o C in a water and ice bath for 1 hour. The reaction will be carried out using the molar ratio of 1:1.1 ester/peracetic acid.

Figure 4 - Sunflower oil epoxidation process.

Figure 5: Decantation process of sunflower oil methyl biolubricant.

Source: Survey data, 2023.

After completion of the reaction, the mixture will be transferred to a separatory funnel, where the lower phase, corresponding to acetic acid, will be removed and the upper phase will be washed twice with 50 mL of 10% sodium bicarbonate until the total detachment of bubbles due to the neutralization reaction. In order to remove the residual water, anhydrous magnesium sulphate will be added to a liquid. erlenmeyer flask containing the epoxide (biolubricant) obtained from sunflower oil, shaking vigorously for 5 minutes and then keeping at rest for 30 minutes (NUNES et al., 2008). To remove the magnesium sulfate, a vacuum filtration will be performed.

Figure 6. Washing process of sunflower oil methyl biolubricant.

Source: Survey data, 2023.

The sunflower oil will be characterized by acidity index (AOCS Cd 3d-63), saponification index (AOCS Cd 3b-76), soap content (AOCS Cc 17-95), peroxide index (AOCS Cd 8-53), relative density, ash content. The procedures adopted to characterize the methyl ester obtained after transesterification will be the same as those used to characterize sunflower oil. The epoxide of methyl and ethyl esters of sunflower oil will be characterized by means of peroxide index (AOCS Cd 8-53), relative density, ash content. All characterizations described above will be performed according to the techniques described by Wu et al. (2000) and will be done in triplicates.

3.1 ACIDITY INDEX (AOCS CD3D-63)

In a 250 mL erlenmeyer flask, 10 g of sample will be weighed and 62 mL of the neutralized solvent mixture (31 mL toluene + 31 mL isopropyl alcohol) will be added. The sample must be well dissolved in the solvent mixture. To facilitate this process, it can be heated a little. 2 to 3 drops of phenolphthalein indicator will be added and titrated with 0.1N KOH until a neutral color is obtained.

Permanent pink coloration for 30 seconds. The same procedure will be repeated without the presence of sample to determine the blank. The acidity index can be calculated using the following equation:

$$\text{Acidity Index} = (A - B) \,.\, N \,.\, 56{,}1 / W$$

where A: volume of the 0.1N KOH solution used in the titration of the sample (mL); B: volume of the 0.1N KOH solution used in the titration of the blank (mL); N: normality of the KOH solution; W: mass of the sample (g)].

3.2 SOAP CONTENT (AOCS CC 17-95)

In a 250 mL erlenmeyer flask, 10 g of sample will be weighed, 0.25 mL of deionized water will be added and shaken vigorously. Then, a solution containing 0.1 g of bromophenol indicator and 50 mL of neutralized acetone will be prepared. It will be added in the erlenmeyer flask containing the sample, 50 mL of this newly prepared solution and if there is soap, a phase separation occurs and the upper layer will have a bluish green color. Then, the mixture will be titrated with a standardized 0.01N hydrochloric acid solution until the blue-green color turns to yellow. The same procedure will be repeated without the presence of sample to determine the blank. The soap content can be calculated using the equation:

$$\text{Soap content} = (A - B) \,.\, N \,.\, 304{,}4 / W$$

where: A: volume of the HCl solution used in the titration of the sample(mL); B: volume of the HCl solution used in the titration of the blank(mL); N: normality of the HCl solution; W: mass of the sample(g).

3.3 SAPONIFICATION INDEX (AOCS CD 3B-76)

1.0 g of the sample will be weighed into a 250 mL conical flask and 25 mL of alcoholic potash will be added. This flask will be connected to a ball condenser and the set will be heated gently for 1 hour so that the sample is completely saponified. Then a few drops of phenolphthalein will be added to the flask and titrated with 0.5M HCl solution until the pink color disappears. The same procedure will be repeated without the presence of sample to determine the blank. The saponification index can be calculated using the following equation:

$$\text{Saponification index} = (B - A) \cdot N \cdot 56{,}1 / W$$

where: A: volume of the 0.5M HCl solution used in the titration of the sample (mL); B: volume of the 0.5M HCl solution used in the titration of the blank (mL); N: normality of the HCl solution; W: mass of the sample (g). From the saponification index, the molar mass of the oil can be calculated.

3.4 PEROXIDE INDEX (AOCS CD 8-53)

Weigh 3 g of the sample into a 250 mL ground-glass conical flask and add 30 mL of 3:2 (v/v) acetic acid:chloroform solution and mix with gentle stirring. Add 0.5 mL of 10% KI solution and leave to stand for 1 minute. Add 30 mL of distilled water and 0.5 mL of 1% starch solution. Titrate with 0.01 N sodium thiosulfate solution with constant stirring until the blue color disappears. The peroxide value can be calculated using the following equation:

$$\text{Peroxide value} = (A - B) \cdot N / W$$

where: A: volume of thiosulfate used in the titration of the sample (mL); B: volume of thiosulfate used in the titration of the blank (mL); N: normality of the Na2S2O3 solution; W: mass of the sample (g). 6 Relative Density In a previously weighed 5mL pycnometer, approximately 5 mL of distilled water will be added and weighed. Then approximately 5 mL of the sample will be added and weighed.

4 DEVELOPMENT

Through the results obtained for sunflower oil, it was possible to observe that the raw material used was unfit for human consumption, due to its inadequate acidity index, but would be suitable for reuse both for biodiesel, soaps and others.

Table 1. Physicochemical parameters of sunflower oil.

Parameters	Oil	Anvisa Standards1, 2
Aspect	Yellow clear	Clear and free from impurities
Ash (%)	0,099	---
Density (g/cm)^3	0,915	0,915 - 0,925
Acidity index (mg KOH/g oil)	0,335	≤ 0,6
Soap content (ppm sodium oleate)	0,061	≤ 10
Saponification index (mg KOH/g oil)	191	189 - 195
Peroxide value (meq/Kg)	0,004	≤ 10

The transesterification reaction provided a yield of 98% for the methyl biodiesel obtained from sunflower oil. Thus demonstrating its good yield.Based on the Normative Instruction No. 49, of December 22, 2006, of ANVISA (National Health Surveillance Agency). It can thus be seen that, among the data obtained in Table 1, the appearance of sunflower oil is within the ANVISA standards, obtaining a clear yellow color. The relative density of the sample shows the amount of material that is contained per unit volume, this will assist in the characterization of the substances. Given the parameters of ANVISA, it is noted that the relative density of the sample analyzed is within the standard imposed by it. The acidity index has a characteristic that allows us to show, thus, the state of conservation in which the oil is, as well as, it is associated with the purity, nature, quality, type of processing and conservation conditions of the same (RIBEIRO; SERAVALLI, 2004; COSTA et. al., 2006 apud PELANDA, 2009). The values expressed in table 1, reveals that the acidity index of the oil analyzed is within the standard, according to ANVISA regulations, which directs the acidity index (mg KOH/g oil), as being ≤ 0,6. The ash content established by the legislation is 0.020%, when comparing with the analyzes made of the ash content of the sample, it is noted that the methyl ester of corn oil is within the acceptable, obtaining a percentage of 0.099%.The soap content is within the limits expected by the parameters of ANVISA, which establishes a value ≤ 10, considering that the analyzed sample obtained a content equal to (0.0), thus highlighting the alkalinity of the sample. The saponification index remains within the provisions of the legislation. The saponification index is an important parameter, which aims to indicate the amount of alkali that will be needed to saponify a given amount of oil. The peroxide index established in the analysis was 0.004 meq/Kg. The one established by ANVISA is a maximum of 10 meq/kg. Therefore, this parameter is within the acceptable range. The molar mass obtained was 881 g/mol.

Table 2. Physicochemical parameters of sunflower oil methyl esters (biodiesel).

Parameters	**Oil esters**	**ANP1 Standards**
Aspect	Light yellow clear	Clear and unbiased of impurities
Density ($g/cm3$)	0,863	0,850-0,900
Acidity index (mg KOH/g oil)	0,112	≤ 0,5

Source: Survey data, 2023;1 BRAZIL, 2014.

According to the ANP standards, it was observed in Table 2 that the density, the methyl ester of sunflower oil presented the density according to the ANP (BRASIL, 2014). The higher the degree of instauration, the denser the oil and the lower the molecular weight of the triglycerides, the lower the density (CARVALHO, 2017).

The epoxidation reaction provided in 95.0% yield for the methyl biolubricant from sunflower oil. The methyl epoxides (biolubricants) obtained from sunflower oil by the epoxidation process of its methyl esters were characterized by their physicochemical properties and the results were compared with the literature. In view of Resolution No. 45/2014 of the National Petroleum and Biofuels Agency (ANP), the aspect of the methyl ester analyzed is in accordance with the legislation. On the other hand, if compared with refined sunflower oil, the result obtained by determining the density of the analyzed methyl ester was 0.863 g/cm3 , showing itself within the parameters of the ANP. The acidity index, in turn, remains within the standards, reaching a value of 0.112 mg KOH/g oil. The soap content is 1.338 ppm of sodium oleate, and although the legislation has not defined the maximum value of the soap content, this is related to Escorsim et al. (2014). The saponification index showed values of 310 mg KOH/g oil, the legislation does not have a maximum index defined in this regard, but if correlated with the saponification index of corn oil, it is high. The same occurs with the peroxide index, which does not have a defined value in the legislation. And in the analyzes made the peroxide index obtained a value of 0.021 meq/Kg. The reaction process of epoxidation using the methyl ester of sunflower oil in the presence of peracetic acid, favored the obtaining of the epoxide of methyl ester of corn oil (biolubricant). The yield of this process was 95%, which indicates the efficiency of the procedure. The physicochemical characterizations of the sunflower oil epoxide are listed in the table below.

Table 3. Physicochemical parameters of sunflower oil methyl epoxide (biolubricant).

Parameters	Epoxide
Aspect	Clear yellowish white
Ash (%)	0,1
Density (g/cm)³	0,888
Acidity index (mg KOH/g oil)	2,228
Soap content (ppm sodium oleate)	2,889
Saponification index (mg KOH/g oil)	291
Peroxide value (meq/Kg)	0,012

Source: Survey data, 2023

Although the legislation does not inform anything about the maximum values for such parameters of methyl epoxides. The data obtained from the physicochemical parameters of methyl epoxides of sunflower oil (biolubricant). The relative density obtained 0.888g/cm3, if compared to refined sunflower oil, it reached low values. If the molecular weight of triglycerides is lower, the density will tend to be lower, on the other hand, the higher the degree of instauration, the denser the oil will be (CARVALHO, 2016). The acidity index is 2.228 mg KOH/g oil, if we take as a basis the acidity index of the methyl ester, it is possible to perceive an increase in this index. The data obtained for the analysis of ashes were 0.1%, relating it to the analyzes made of the methyl ester, indicates that the presence of inorganic compounds remained the same.The soap content is found with 2.889 ppm of sodium oleate, if compared with that of the raw material, it is high. The peroxide index obtained 0.012 meq/Kg, relating this value with that of the methyl ester, it is noticed that the index of the methyl epoxide is low, so the methyl epoxide can present less rancid characteristics than the methyl ester.If we compare the peroxide indexes of the methyl esters of used oil with that of commercial oil with its biolubricants, it is verified that the biolubricant presents the highest peroxide index. Peroxides are the first to form in oil deterioration, so the biolubricant of used soybean oil is likely to deteriorate faster than the biolubricant of commercial soybean oil (PEREIRA, 2022).

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5 FINAL CONSIDERATIONS

This research focuses on the reuse of raw materials aiming to benefit both the environment and the advancement of research in this area, including green chemistry, which seeks to minimize environmental impacts. The results obtained indicated that the raw materials used are suitable for the production of biodiesel and biolubricant. The transesterification and epoxidation reactions demonstrated efficiency, presenting a good yield. In addition, the products obtained met most of the physicochemical properties established by the applicable legislation. This means that the raw materials tested are

The results show promising results for the production of biodiesel and biolubricant, since the final products have adequate characteristics in terms of quality and meet the standards established by the regulatory authorities. These results indicate a significant advance in the field of reuse of raw materials and in the search for more sustainable solutions, since the use of renewable sources for the production of fuels and lubricants can reduce dependence on fossil resources and contribute to the mitigation of environmental impacts caused by these industries.

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