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Obtaining a biodegradable lubricant by ethylic epoxidation of sunflower oil

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ABSTRACT
Lubricating oils, derived from petroleum, play a crucial role in the industrial landscape, aiming to reduce wear resulting from friction between metal parts. Predominantly, mineral lubricants are the most widespread commercial choice globally, representing an intricate composition of paraffinic, olefinic, naphthenic and aromatic hydrocarbons, containing between 20 and 50 carbon atoms. This complex mixture results from the combination of two main components: the base oil, extracted in the oil refining process, and chemical additives, responsible for altering, preserving and intensifying the product's physical and chemical properties. Although they exhibit greater stability to oxidation and a more affordable cost compared to other lubricants, mineral lubricants also stand out for their low biodegradability, as well as releasing toxic materials into the environment (Karmakar et al., 2017).

Keywords: Biodegradable lubricant, Lubricating oils, Sunflower oil.

INTRODUCTION

Lubricating oils, derived from petroleum, play a crucial role in the industrial landscape, aiming to reduce wear resulting from friction between metal parts. Predominantly, mineral lubricants constitute the most widespread commercial choice globally, representing an intricate composition of paraffinic, olefinic, naphthenic and aromatic hydrocarbons, containing between 20 and 50 carbon atoms. This complex mixture results from the combination of two main components: the base oil, extracted in the petroleum refining process, and the chemical additives, responsible for altering, preserving and intensifying the physical and chemical properties of the product. Although they exhibit greater oxidation stability and a more affordable cost compared to other lubricants, mineral lubricants also stand out for their low biodegradability, in addition to releasing toxic materials into the environment (Karmakar et al., 2017).

With the end of the period of use recommended by the manufacturer, lubricants gradually lose their qualities due to the decomposition of their components, transforming into waste considered dangerous, popularly known as "burnt oil" (an imprecise name and to be avoided). In addition to the inherent danger of being a by-product of petroleum, used or contaminated lubricating oil carries with it an additional burden of toxicity, since the degradation of its components results in the emission of toxic

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gases, such as dioxins, organic acids, ketones and polycyclic hydrocarbons. aromatics (APROMAC, 2005).

Both harmful to the health of those who come into direct contact with the waste and to the environment when dispersed, used or contaminated lubricating oil causes significant damage, affecting not only human beings, but also fauna and flora, especially when combined with other pollutants. common in urbanized areas (APROMAC, 2005). Furthermore, just one liter of this oil has the potential to contaminate up to a million liters of water, covering an area equivalent to one thousand square meters with a thin film that obstructs the passage of air and light, compromising the respiration and photosynthesis of organisms. alive (Lubes in focus, 2011).

Despite clear regulations that require this material to be forwarded for re-refining through authorized collectors, malicious or ill-informed individuals opt for other means of disposal, putting not only their own health at risk, but also that of the community, committing acts illicit activities by improperly disposing of this waste. However, amid growing environmental concerns arising from increased pollution, more sustainable and environmentally friendly alternatives are increasingly being explored by researchers, aiming to replace products of mineral origin that have caused serious damage to the ecosystem and human health.

In this context, vegetable-based lubricants emerge as a promising alternative to replacing mineral lubricants, standing out for their greater biodegradability and their ecologically favorable nature. Biodegradable lubricants can be classified, depending on their chemical composition, into two groups: organic and synthetic. Organic ones are derived from vegetable or animal fats, while synthetic ones use organic lubricants as raw materials, resulting in biodegradable lubricants with improved chemical and physical properties. In this sense, synthetic processes involving esters, alcohols, polyalcohols, polyglycols, perfluoroalkyl ethers and other compounds are capable of integrating a natural lubricant, giving synthetic biodegradable formulations oxidative, wear resistance and lubrication properties superior to those observed in mineral lubricants (Santos , 2011). Thus, this research, faced with environmental problems, focused on the synthesis (transesterification and epoxidation) of a renewable biolubricant, using sunflower oil as its raw material, free from chemical additives that modify viscosity or inhibit corrosion.

GOAL

The objective of this research is to obtain a biolubricant from sunflower oil, through transesterification and ethyl epoxidation reactions.

METHODOLOGY

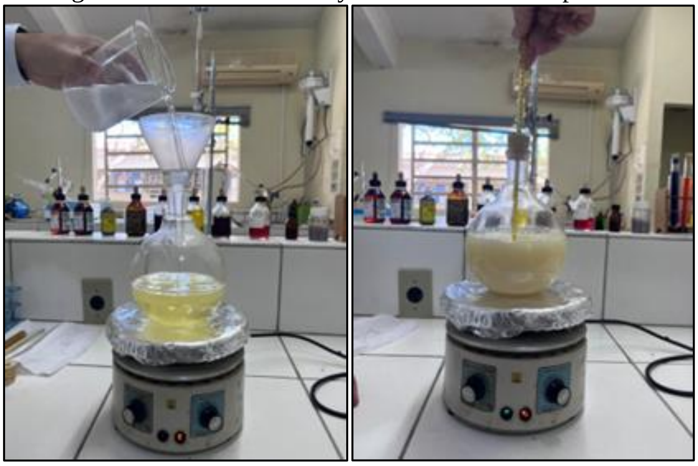
MATERIALS

Sunflower oil was purchased locally and produced by a Brazilian industry. Refined oil does not require prior treatment before the reactions to which it has been subjected.

BIODIESEL AND BIOLUBRICANT EXTRACTION PROCEDURE

To obtain the ethyl ester, initially the molar mass of sunflower oil was calculated based on its saponification index. With the knowledge of this mass, the amounts of alcohol (ethanol) and catalyst (KOH) necessary to carry out the reaction were calculated. The transesterification reaction was carried out adopting an oil/alcohol molar ratio equal to 1:6 and 0.7% catalyst (oil/catalyst) (PELANDA, 2009), maintaining the temperature at approximately 45°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).

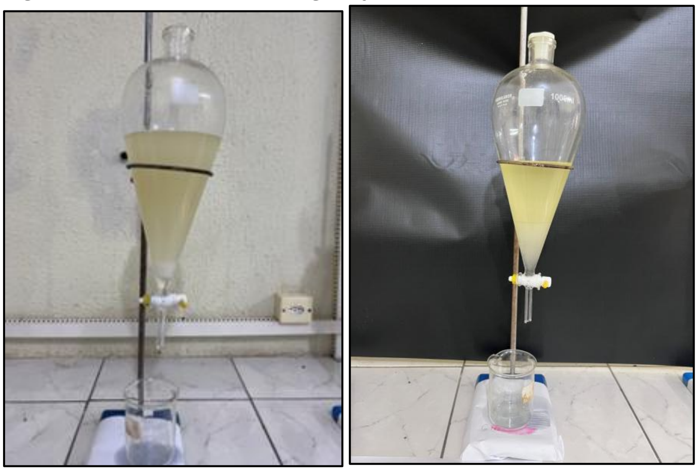
Figure 1. Sunflower oil ethyl transesterification process.



Source: Research data, 2023.

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

Figure 2. Process of decanting ethyl biodiesel from sunflower oil.



Source: Research data, 2023.

After the waiting time, the lower phase was removed and stored in a specific container. Then, the ethyl ester (biodiesel) was washed with distilled water and 0.01M hydrochloric acid solution. Three washes were carried out with distilled water (removing glycerol and soap residues from the ester phase) and two washes with 0.01M HCl solution (neutralizing the ester). To verify the efficiency of acid washing, phenolphthalein was used.

Figure 3. Washing process for sunflower oil ethyl biodiesel.

Source: Research data, 2023.

After washing, anhydrous magnesium sulfate was added to remove any water that was still present in the ester. Then, in order to remove the ethanol that could still be present in the ester, a rotary evaporator was used. In the epoxidation process of sunflower oil esters, in a 250 mL round bottom flask, 100 g of ethyl ester obtained from sunflower oil were added, and drop by drop, 140 mL of 15% commercial peracetic acid. The mixture was stirred and heated to 45°C. As the reaction is exothermic, a water and ice bath was used for 1 hour to control the temperature. The reaction was carried out using a molar ratio of 1:1.1 ester/peracetic acid.

Figure 4. Epoxidation process of methyl biodiesel from sunflower oil.

Source: Research data, 2023.

After completion of the reaction, the mixture was transferred to a separation funnel, where the lower phase, corresponding to acetic acid, was removed, and the upper phase was washed twice with 50 mL of 10% sodium bicarbonate until the particles were completely detached. bubbles due to the neutralization reaction. In order to remove residual water, anhydrous magnesium sulfate was added to an Erlenmeyer flask containing epoxide (biolubricant) obtained from sunflower oil, stirring vigorously for 5 minutes and then remaining at rest for 30 minutes (NUNES et al., 2008). To remove magnesium sulfate, vacuum filtration was performed.

Figure 5. Decantation process of sunflower oil methyl biolubricant.

Source: Research data, 2023.

DESCRIPTION

Sunflower oil was characterized by acidity index (AOCS Cd 3d-63), iodine index (AOCS Cd 1-25), saponification index (AOCS Cd 3b-76), soap content (AOCS Cc 17-95) , peroxide index (AOCS Cd 8-53), viscosity, relative density, ash content and moisture and volatile content (AOCS Da2a-48).

The procedures adopted to characterize ethyl ester (biodiesel) obtained after transesterification were the same as those used to characterize sunflower oil.

Sunflower oil ethyl ester epoxide (biolubricant) was characterized using iodine index (AOCS Cd 1-25), acidity index (AOCS Cd 3d-63), saponification index (AOCS Cd 3b-76), soap content (AOCS Cc 17-95), peroxide value (AOCS Cd 8-53), hydroxyl (AOCS Cd 13-60), oxygen oxirane (AOCS D Cd 9-57), relative density, ash content, content of moisture and volatiles (AOCS Da-2a-48).

All characterizations described above were performed according to the techniques described by Wu et al. (2000) and were performed in triplicates.

DEVELOPMENT

Sunflower oil was purchased locally and produced by a Brazilian industry. The results that were obtained through the physical-chemical characteristics of refined sunflower oil are presented in Table 1.

Table 1. Physicochemical parameters of sunflower oil.

Parameters	**Oil**	**Anvisa Standards [1, 2]**
Aspect	Clear yellow	Clear and free from impurities
Moisture and Volatiles (%)	0.09	≤ 0.1
Ash (%)	0.099	---
Density (g/ cm^3)	0.915	0.915 - 0.925
Acid value (mg KOH/g oil)	0.335	≤ 0.6
Iodine index (g I_2 /100g oil)	110	96 - 115
Soap content (ppm of sodium oleate)	0.061	≤ 10
Saponification index (mg KOH/g oil)	191	189 - 195
Peroxide index (meq/Kg)	0.004	≤ 10
Molar mass (g/mol)	881	---
Kinematic Viscosity at 40 ^{o}C (mm ^{2} /s)	31.27	---

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

Through Normative Instruction No. 49, of December 22, 2006, from ANVISA (National Health Surveillance Agency), we can see that, among the results described in Table 1, the appearance of sunflower oil is within the standards allowed by ANVISA, obtaining a clear yellow color. The moisture and volatile content is also within the stipulated range. The moisture content indicates the amount of water present in the sample and thus allows the formation of soap (Marchetti, 2005). ANVISA establishes a value for moisture and volatiles (%), as being ≤ 0.1, thus, we can see that the value obtained from sunflower oil remains low. The ash content, in turn, is high compared to Araújo et al. (2009). ANVISA does not establish a reference value for the analysis of ash content. This content shows the amount of inorganic residue present in the sample after burning the organic matter in the muffle at high temperatures. The relative density is within what is permitted by the regulatory body. This analysis parameter informs the amount of material that is contained per unit of volume. The acid value complies with regulatory agency standards. This index allows checking the state of conservation of the oil, highlighting its purity, nature, quality, type of processing and conservation conditions (Ribeiro; Seravalli, 2004; Costa et. al., 2006 apud Pelanda, 2009) . The iodine index remains within the standards established by ANVISA. The iodine index evaluates the degree of unsaturation of the oil, since each double bond of a fatty acid can incorporate two halogen atoms, in this case iodine (Silva, 2007). The soap content is within the limits expected by ANVISA parameters, which establishes a value ≤ 10, considering that the sample analyzed had a content equal to (0.061), thus highlighting the alkalinity of the sample. The saponification index indicates the amount of alkali that will be needed to saponify a given quantity of oil. The aforementioned sample analyzed using the saponification index remains within the provisions of legislation. The peroxide index established in the analyzes was 0.004 meq/kg. The amount established by ANVISA is a maximum of 10 meq/kg. Therefore, the peroxide value is within acceptable limits. The molar mass obtained was 881 g/mol. The high kinematic viscosity of the oil indicates that the triglyceride molecules present in the oil hinder its fluidity, in turn, the value obtained from the analysis of sunflower oil was 31.27 (mm2/s). It is worth mentioning that the regulatory agency's standards do not stipulate a value for this analysis.

The synthesis of ethyl biodiesel by transesterification of sunflower oil obtained a yield of 73% of ethyl ester. Thus demonstrating an acceptable performance. Table 2 shows the values referring to the physicochemical parameters of sunflower oil ethyl esters (biodiesel).

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

Parameters	Oil esters	Standards
Aspect	Clear light yellow	Clear and free from impurities
Moisture and Volatiles (%)	0.025	0.02
Ash (%)	0.011	0.02
Density (g/ cm^3)	0.938	0.850-0.900
Acid value (mg KOH/g oil)	0.471	≤ 0.5
Iodine index (g I_2/100g oil)	121.3	Note
Soap content (ppm of sodium oleate)	2,546	-----
Saponification Index (mg KOH/g oil)	275	-----
Peroxide Index (meq/Kg)	0.024	-----
Kinematic Viscosity at 40 ^{o}C (mm^2/s)	-----	3.0 – 6.0

Source: Research Data, 2023; [1] BRAZIL, 2014

Based on Resolution No. 45/2014 of the National Petroleum and Biofuels Agency (ANP), the appearance of the analyzed ethyl ester complies with the legislation, presenting a clear yellow color. On the other hand, the moisture and volatile content of the ethyl ester is beyond what is acceptable by the legislative body, this is due to the possible presence of water in the reagents used. The ash content established by legislation is 0.02%, the one obtained in the sample analysis yielded a percentage of 0.04%, showing that it is outside the standard stipulated by the ANP. The result obtained by determining the density of the analyzed ethyl ester was 0.935g/cm3, demonstrating that it does not comply with the ANP parameters. The acid value remains within standards, reaching a value of 0.47 mg KOH/g oil. According to Oliveira (2021), high acidity levels may indicate the presence of water, thus affecting combustion and may even damage engine parts. Although the legislation does not define a maximum value for the soap content, when analyzed it was found to be in the range of 2.09 ppm of sodium oleate, compared to the soap content of sunflower oil, this is high. The saponification index demonstrated values of 255.9 mg KOH/g oil, the legislation does not have a defined maximum index in this regard. The same occurs with the peroxide index, this does not have a value defined in legislation. The analyzes carried out for the peroxide index showed a value of 0.029 meq/Kg. The iodine index data obtained was 110 g I2 /100g oil, comparing them with the same parameter analyzed for commercial sunflower oil, this remained high, indicating that there was no decrease in the number of unsaturations during the transesterification process.

The epoxidation reaction using sunflower oil ethyl ester in the presence of peracetic acid favored obtaining a biolubricant, whose yield from this process was 97%, indicating an efficient process. The physicochemical characterizations of sunflower oil epoxides are listed in Table 3 below.

Table 3. Physicochemical parameters of sunflower oil epoxides (biolubricant).

Parameters	**Epoxide**
Aspect	Clear light yellow
Moisture (%)	0.38
Ash (%)	0.49
Density (g/ cm^3)	0.963
Acid value (mg KOH/g oil)	2,915
Iodine index (g I_2 /100g oil)	39.8
Soap content (ppm of sodium oleate)	0.360
Saponification Index (mg KOH/g oil)	299
Peroxide Index (meq/Kg)	0.021
Hydroxyl Index	9.91
Oxirane oxygen	10.66

Source: Research Data, 2023.

The legislation does not provide anything regarding the maximum values for the parameters analyzed for ethyl epoxides of vegetable origin. The data obtained through the analysis of the physical-chemical parameters of sunflower oil ethyl epoxides (biolubricant) shows us the moisture and volatile values, which obtained a percentage of 0.1%, compared to that of ethyl ester, which can be If you then notice a significant increase, the humidity can lead to product inefficiency, as it can cause damage to parts. The high moisture and volatile content contributed to the significant increase in the saponification index, which, in turn, presented a value of 258.7mg KOH/g oil. The ash analysis obtained a percentage of 0.09%, relating it to the analyzes carried out on ethyl ester, indicating that the presence of inorganic compounds increased. The relative density was 0.959 g/cm3, compared to commercial sunflower oil and ethyl ester, it reached high values. The density will tend to be lower if the molecular weight of the triglycerides is lower, however, the higher the degree of establishment, the denser the oil will be (Carvalho, 2016). The acidity value is 1.982 mg KOH/g oil, if we take the acidity value of ethyl ester as a basis, it is possible to notice an increase in this value. The iodine index reached a value of 30.0 g I2/100g oil, which, when compared to ethyl ester, remained low, demonstrating that epoxidation reduced the number of unsaturations. The soap content increased by 0.37 ppm of sodium oleate, compared to that of the raw material, however, compared to ethyl ester, this value remained low. The peroxide index obtained 0.013 meq/Kg, relating this value with that obtained from ethyl ester, it is clear that the peroxide index of ethyl epoxide has low values, so ethyl epoxide may present less rancid characteristics than ethyl ester . The hydroxyl index value was 7.65 mg KOH/g oil, compared to the values found by Macedo et al. (2021), the index obtained in that analysis was lower. The hydroxyl number was used to determine the occurrence of hydrolysis of the oxirane ring. These hydroxyl index values reveal the existence of hydroxyls in the epoxide, being associated with an increase in the concentration of peracetic acid used in the reaction process. The data found in the oxirane oxygen analysis was 10.8%. According to Baltacioglu and Balkose (1999), the value of the oxirane oxygen index must be low, however, greater than 6.7%. Therefore, the epoxidation reaction was successful, even though hydrolysis reactions occurred.

FINAL CONSIDERATIONS

The biolubricant synthesis in question revealed, through its analyses, that several properties are aligned with the regulations of regulatory bodies, thus demonstrating a vast potential for use in multiple sectors, including industry and agriculture. However, it is essential to carry out additional studies to fully understand the characteristics of the biolubricant produced. Through the ethyl epoxidation process of sunflower oil, the biolubricant showed promise for the manufacture of renewable and ecological lubricants. The use of sunflower oil as a basic input appears as an effective option to replace conventional oils used in the production of mineral lubricants, therefore contributing to reducing dependence on fossil resources and reducing the emission of atmospheric pollutants. However, the need for further investigations is highlighted with the aim of improving chemical reaction processes, aiming to obtain biodegradable lubricants that effectively and economically meet market demands.

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