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Synthesis and characterization of biolubricants by ethyl epoxidation of corn oil

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ABSTRACT

Lubricating oils are derived from petroleum and widely used in the industrial sector, in order to reduce wear caused by friction of metal parts. Currently, mineral lubricants are commercially the most widely used worldwide, they are a complex mixture of paraffinic, olefinic, naphthenic and aromatic hydrocarbons of 20 to 50 carbon atoms. These are products of the union of two main components: chemical additives and base oil. The base oil is extracted from the petroleum refining process and the chemical additive is used to modify, preserve and intensify the physical and chemical characteristics of the product. They have greater oxidation stability and are cheaper than other types of lubricants. However, mineral lubricants have poor biodegradability and release toxic materials into the environment (Karmakar et al., 2017).

Keywords: Lubricating oils, Biolubricants, Corn oil.

INTRODUCTION

Lubricating oils are derived from petroleum and widely used in the industrial sector, in order to reduce wear caused by friction of metal parts. Currently, mineral lubricants are commercially the most widely used worldwide, they are a complex mixture of paraffinic, olefinic, naphthenic and aromatic hydrocarbons of 20 to 50 carbon atoms. These are products of the union of two main components: chemical additives and base oil. The base oil is extracted from the petroleum refining process and the chemical additive is used to modify, preserve and intensify the physical and chemical characteristics of the product. They have greater oxidation stability and are cheaper than other types of lubricants. However, mineral lubricants have poor biodegradability and release toxic materials into the environment (Karmakar et al., 2017).

At the end of the period of use of lubricants recommended by the manufacturer, they tend to lose certain qualities, due to the decomposition of their components, making them unsuitable for the use for which they were intended, becoming considered hazardous waste, popularly known as "burnt oil" (a name that is not correct and should be avoided). Thus, in addition to having a certain degree of danger because it is a product derived from petroleum, used or contaminated lubricating oil has an additional load of

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toxicity, since its components, when degraded, generate toxic gases such as dioxins, organic acids, ketones and polycyclic aromatic hydrocarbons (APROMAC, 2005).

As well as causing damage to the health of people who have direct contact with the waste, used or contaminated lubricating oil, when dispersed in the environment, causes great damage, affecting many people, fauna and flora, especially when associated with other pollutants common in more urbanized areas (APROMAC, 2005). In addition, one liter of this lubricating oil has the capacity to contaminate one million liters of water, covering the equivalent of a thousand square meters, with a thin layer that prevents the passage of air and light, preventing the respiration and photosynthesis of living organisms (Lubes em foco, 2011). Although the Legislation clearly determines that all this material must be sent for re-refining through authorized collectors, ill-intentioned or ill-informed people choose other destinations for the waste, putting their health and that of the community at risk, committing illegal acts, improperly disposing of this waste. However, with concerns related to the environment due to increased pollution, more sustainable and more ecological alternatives have been increasingly studied by researchers, in order to replace products of mineral origin that, through their burning or improper disposal, have been causing serious damage to the ecosystem and human health.

As a result, vegetable-based lubricants are increasingly being studied as a viable alternative to replace mineral lubricants, as they have greater biodegradability and are environmentally friendly. Biodegradable lubricants are classified, according to their chemical composition, into two groups: organic and synthetic lubricants. Organic oils are produced from vegetable or animal fats, while synthetics use organic lubricants as raw materials, so as to create biodegradable lubricants with better chemical and physical properties. In this bias, synthetic processes involving esters, alcohols, polyalcohols, polyglycols, perfluoroalkyl ethers and others are capable of integrating a natural lubricant, making a synthetic biodegradable lubricant exhibit oxidative, wear resistance and lubrication properties, even better than those observed in mineral lubricants (Santos, 2011). Thus, this research, in view of environmental problems, focused on the synthesis (transesterification and epoxidation) of a renewable biolubricant, having corn oil as raw material, free of chemical additives that modify viscosity or inhibit corrosion.

OBJECTIVE

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

METHODOLOGY

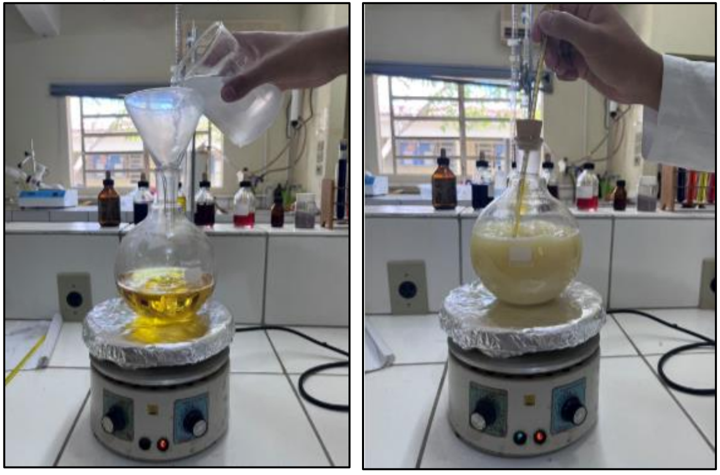
MATERIALS

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

BIODIESEL AND BIOLUBRICANT EXTRACTION PROCEDURE

To obtain the ethyl ester, initially a calculation of the molar mass of corn oil was made 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 performed by adopting an oil/alcohol molar ratio equal to 1:6 and 0.7% of 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 alcoholization (FERRARI et al., 2005).

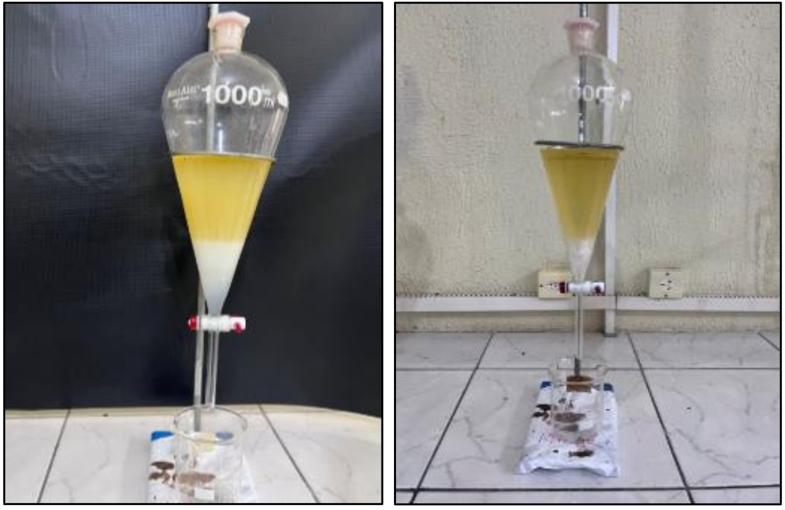
Figure 1. Ethyl transesterification process of corn oil.



Source: Survey data, 2023.

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.

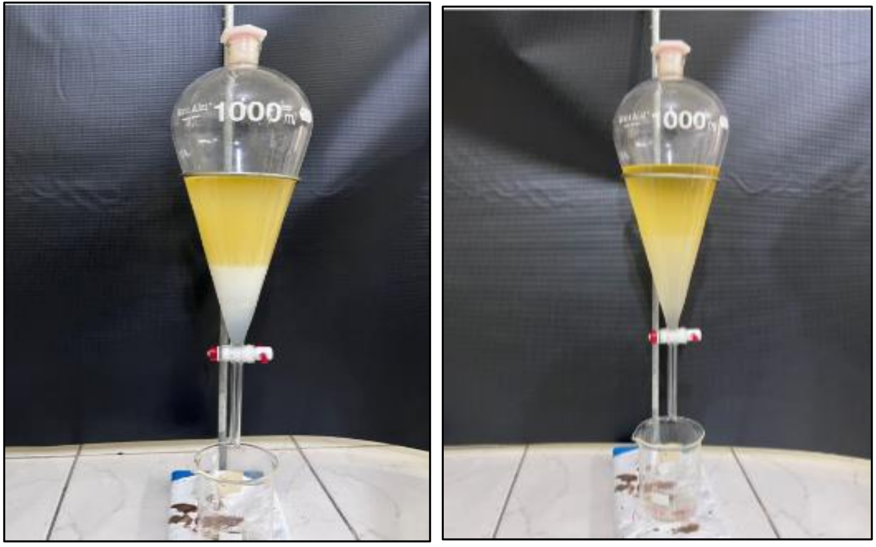
Figure 2. Decanting process of ethyl biodiesel from corn oil.



Source: Survey data, 2023.

After the waiting time, the lower stage was removed and stored in a suitable container. Next, the ethyl 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). To verify the efficiency of acid washing, phenolphthalein was used.

Figure 3. Washing process of ethyl biodiesel from corn oil.

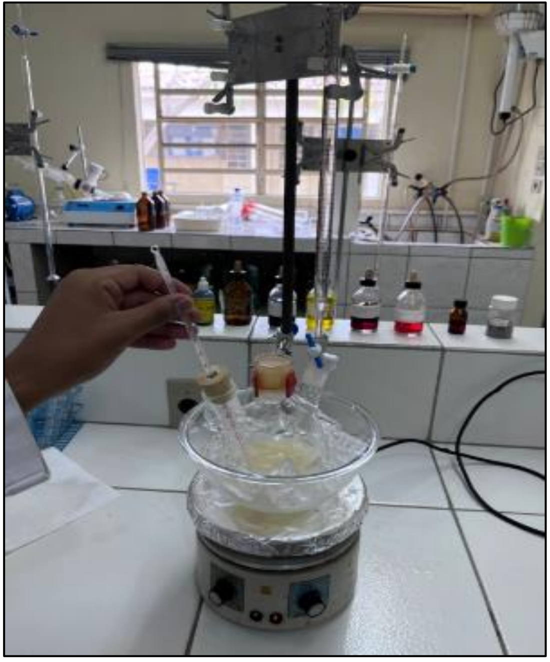


Source: Survey data, 2023.

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

In the process of epoxidation of the corn oil esters, in a 250 mL round-bottomed flask, 100 g of the ethyl ester obtained from corn oil were added, and 140 mL of 15% commercial peracetic acid dropped. The mixture was under agitation and heating to 45°C, as the reaction is exothermic, a bath of water and ice was used for 1 hour to control the temperature. The reaction was performed using a molar ratio of 1:1.1 ester/peracetic acid.

Figure 4. Epoxidation process of ethyl biodiesel from corn oil.



Source: Survey data, 2023.

After the end 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 bubbles were completely released due to the neutralization reaction. In order to remove the residual water, anhydrous magnesium sulfate was added to an erlenmeyer containing the epoxide (biolubricant) obtained from corn oil, stirring vigorously for 5 minutes and then remaining for 30 minutes (NUNES et al., 2008). To remove the magnesium sulfate, a vacuum filtration was performed.

Figure 5. Decantation process of ethyl biolubricant from corn oil.

Source: Survey data, 2023.

CHARACTERIZATION

Corn 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 used to characterize corn oil.

The ethyl ester epoxide of corn oil (biolubricating) was characterized by iodine (AOCS Cd 1-25), acid value (AOCS Cd 3d-63), saponification index (AOCS Cd 3b-76), soap content (AOCS Cc 17-95), peroxide index (AOCS Cd 8-53), hydroxyl (AOCS Cd 13-60), oxirane oxygen (AOCS D Cd 9-57), relative density, ash content, 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

Corn oil was purchased in local commerce and produced by a Brazilian industry. The results obtained through the physicochemical characteristics of refined corn oil are presented in Table 1.

Table 1. Physicochemical parameters of corn oil.

Parameters	**Oil**	**Anvisa Standards1, 2**
Aspect	Clear yellow	Clean and isento of impurities
Moisture and Volatiles (%)	0,034	≤ 0.1
Ash(%)	0,029	---
Density (g/cm3)	0,916	0,915 - 0,925
Acid value (mg KOH/g oil)	0,220	≤ 0.6
Índice de iodo (g I2/100g óleo)	107	96 - 115

Soap content (ppm sodium oleate)	0,0	≤ 10
Saponification index (mg KOH/g oil)	190	189 - 195
- Peroxide index (meq/kg)	0,009	≤ 10
Approximate molar mass (g/mol)	886	---
Kinematic Viscosity at 40 ^{oC} (mm2/s)	33,64	---

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

Through Normative Instruction No. 49, of December 22, 2006, of ANVISA (National Health Surveillance Agency), we can see that, among the results described in Table 1, the appearance of corn oil is within the standards allowed by ANVISA, obtaining a clear yellow color. The moisture and volatile content is also within the stipulated. 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, so we can see that the value obtained from corn oil remains low. The ash content, in turn, is high when 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 furnace at high temperatures. The relative density is within the limits allowed by the regulatory body. This analysis parameter informs the amount of material that is contained per unit volume. The acidity index complies with the standards of the regulatory agency. This index allows the verification of the state of conservation of the oil, evidencing 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 the ANVISA parameters, 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 indicates the amount of alkali that will be needed to saponify a given amount of oil. This sample, analyzed through the saponification index, remains within the provisions of the legislation. The peroxide index established in the analyses was 0.009 meq/kg. The peroxide index established by ANVISA is a maximum of 10 meq/kg. Therefore, the peroxide index is within the acceptable range. The molar mass obtained was 886 g/mol. The high kinematic viscosity of the oil is indicative that the triglyceride molecules present in the oil hinder its fluidity, in turn, the value obtained from the analysis of the corn oil was 33.64(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 corn oil obtained a yield of 84% of ethyl ester. Thus demonstrating an acceptable income. Table 2 shows the values referring to the physicochemical parameters of corn oil ethyl esters (biodiesel).

Table 2. Physicochemical parameters of ethyl esters of corn oil (biodiesel).

Parameters	**Oil esters**	**ANP1 Standards**
Aspect	Yellow clear	Clean and isento of impurities
Moisture and Volatiles (%)	0,07	0,02
Ash(%)	0,04	0,02
Density (g/cm3)	0,935	0,850-0,900
Acid value (mg KOH/g oil)	0,47	≤ 0.5
Índice de iodo (g I2/100g óleo)	110	Jot
Soap content (ppm sodium oleate)	2,09	-----
Saponification Index (mg KOH/g oil)	255,9	-----
- Peroxide Index (meq/kg)	0,029	-----

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

Based on Resolution No. 45/2014 of the National Agency of Petroleum and Biofuels (ANP), the aspect of the ethyl ester analyzed is in accordance with the legislation, presenting a clear yellow color. On the other hand, the moisture and volatile content of the ethyl ester is outside the acceptable by the legislative body, this is due to the possible presence of water in the reagents used. The ash content established by the legislation is 0.02%, which was obtained in the analysis of the sample, 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 ethyl ester analyzed was 0.935g/cm3, demonstrating that it was not in accordance with the ANP parameters. The acidity index remains within the standards, reaching a value of 0.47 mg KOH/g oil. According to Oliveira (2021), high acidity levels can indicate the presence of water, thus affecting combustion and can also damage engine parts. Although the legislation does not define a maximum value for the soap content, when analyzed it was found in the range of 2.09 ppm of sodium oleate, if compared to the soap content of corn oil, it is high. The saponification index showed 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, which does not have a value defined in the legislation. The analyses made for the peroxide index showed a value of 0.029 meq/Kg. The data of the iodine index obtained was 110 g I_2 /100g oil, comparing them with the same parameter analyzed for commercial corn oil, which remained high, indicating that there was no decrease in the number of unsaturations during the transesterification process.

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

Table 3. Physicochemical parameters of ethyl epoxides from corn oil (biolubricant).

Parameters	**Epoxide**
Aspect	Clear yellow
Humidity (%)	0,1
Ash(%)	0,09
Density (g/cm3)	0,959

Acid value (mg KOH/g oil)	1,982
Índice de iodo (g I2/100g óleo)	30,0
Soap content (ppm sodium oleate)	0,37
Saponification Index (mg KOH/g oil)	258,7
- Peroxide Index (meq/kg)	0,013
Hydroxyl Index	7,65
Oxirane oxygen	10,8

Source: Survey Data, 2023.

The legislation does not inform anything about the maximum values referring to the parameters analyzed for ethyl epoxides of vegetable origin. The data obtained through the analysis of the physicochemical parameters of the ethyl epoxides of corn oil (biolubricating), shows us the values of moisture and volatiles that obtained a percentage of 0.1%, compared to that of the ethyl ester, it can then be perceived a significant increase, the humidity can lead to inefficiency of the product, since it can cause damage to parts. The high moisture content and volatiles contribute 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 analyses made of the ethyl ester, indicating that the presence of inorganic compounds increased. The relative density obtained 0.959 g/cm3, if compared to commercial corn 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 index is 1.982 mg KOH/g oil, if we take the acidity index of the ethyl ester as a basis, it is possible to notice an increase in this index. The iodine index achieved a value of 30.0 g I2/100g oil, which compared to the ethyl ester, remained low, demonstrating that epoxidation decreased 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 the ethyl ester, this value remained low. The peroxide index obtained 0.013 meq/Kg, relating this value with that obtained from the ethyl ester, it is noticed that the peroxide index of the ethyl epoxide is with low values, so the ethyl epoxide may present less rancid characteristics than the ethyl ester. The value of the hydroxyl index was 7.65 mg KOH/g oil, compared to the values found by Macedo et al. (2021), the index obtained in the aforementioned analysis was lower. The hydroxyl index was used to determine the occurrence of hydrolysis of the oxirane ring. These hydroxyl index values reveal the existence of hydroxyl in the epoxide, being associated with an increase in the concentration of peracetic acid used in the reaction process. The data found in the analysis of oxirane oxygen was 10.8%. According to Baltacioglu and Balkose (1999), the value of the oxirane oxygen index should be low, however, higher than 6.7%. Thus, we have that the epoxidation reaction was successful, even though hydrolysis reactions occurred.

FINAL CONSIDERATIONS

The aforementioned synthesis of the biolubricant found in its characterizations that many of its properties are in accordance with the legislative agencies, evidencing a potential for application in several areas, related to industry and agriculture, however, the relevance of more analyzes to determine all the properties of the product obtained is highlighted. Thus, the biolubricant by ethyl epoxidation of corn oil showed great potential for the production of renewable and sustainable lubricants. The use of corn oil as a raw material proves to be a viable alternative to replace base oils used to produce mineral lubricants, thus demonstrating its contribution to reducing dependence on finite fossil resources and reducing emissions of polluting gases. However, further studies are needed to optimize chemical reaction processes, to obtain biodegradable lubricants that better meet market demands, with lower cost and excellent efficiency.

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