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Obtaining a biodegradable lubricant by ethylic epoxidation of cotton oil for application in civil construction

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ABSTRACT
Considering the unbridled exploitation and dependence on oil reserves, the search for alternative energy sources to replace fossil fuels has become urgent. Practices that advocate the use of renewable fuels aim to achieve a positive relationship between the costs and benefits obtained by replacing fossil fuels, reducing pollution and its consequences. Thus, there is a need to promote the exchange of polluting energy matrices for correct and environmentally beneficial energy matrices as an alternative to harmonizing economic and environmental benefits (EREDA, 2004).

Keywords: Biodegradable lubricant, Cottonseed oil, Construction.

INTRODUCTION

Considering rampant exploration and dependence on oil reserves, the search for alternative energy sources to replace fossil fuels has become urgent. Practices that advocate the use of renewable fuels aim to achieve a positive relationship between the costs and benefits obtained from replacing fossil fuels, reducing pollution and its consequences. Therefore, there is a need to promote the exchange of polluting energy matrices for correct and environmentally beneficial energy matrices as an alternative to harmonizing economic and environmental benefits (EREDA, 2004).

The search for renewable sources of alternative energy to obtain fuels has been growing around the world, mainly due to environmental concerns related to raw materials. Among the possibilities that could lead to a reduction in the use of petroleum derivatives is the use of biodiesel and vegetable oil-based biolubricants.

Conventional mineral lubricants are gradually being replaced by biolubricants based on vegetable oils. Coming from renewable resources, such as plant seeds, vegetable oils promote a series of environmental benefits, including mitigating impacts on biodiversity and reducing greenhouse gas emissions. These oils exhibit similar lubricating properties to mineral oils, making them suitable for many industrial and automotive applications.

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In Brazil, cotton production stands out, mainly in the Cerrado regions, where the climatic characteristics are favorable for the cultivation of the plant. Brazil is the third largest cotton exporter in the world (SEVERINO et al., 2019). Cotton fibers can be used in the textile industry, and the seeds can be used to extract oil, used as raw material for the production of biodiesel and biolubricants.

The production of biodiesel from cotton oil, a renewable and less polluting source of energy, will enable large and small national producers to make maximum use of cotton, without diverting from their main production line, the textile industry (PUTTI et al., 2012).

Biolubricants derived from vegetable oils or other biological sources constitute a class of sustainable lubricants, recognized for their environmental benefits and satisfactory performance. However, challenges such as thermal and oxidative stability are still faced, with a view to improving the viability and widespread use of this product.

Procedures such as transesterification and epoxidation are often used to synthesize biodiesel (ethyl ester) and biolubricant (epoxides), respectively, from cottonseed oil. Biodiesel and biolubricant produced from cottonseed oil offer a clean, renewable alternative to fossil fuels.

GOAL

The objective of this research is to obtain a biolubricant from cottonseed oil, through transesterification and ethyl epoxidation reactions, with a view to its use in civil construction.

METHODOLOGY

The cottonseed oil used in the procedure is a vegetable oil refined from cottonseeds and purchased from a local store. The samples were subjected to transesterification and epoxidation treatments.

OBTAINING PROCEDURES

Transesterification

To obtain ethyl esters, the molar mass of cottonseed oil was initially calculated based on its saponification index. Knowing the molar mass, the amounts of alcohol (ethanol) and catalyst (KOH) necessary to carry out the reaction were calculated. Thus, transesterification was carried out using an oil/alcohol molar ratio equal to 1:6 and 0.7% catalyst (oil/catalyst), maintaining the temperature at approximately 45 º C for 1 h (DANTAS et al. , 2021).

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. 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. Subsequently, five washes were carried out with distilled water (removing glycerol and soap residues from the ester phase) and two washes with 0.01M HCl solution (neutralize the esters). To verify the efficiency of acid washing, phenolphthalein was used. After washing, anhydrous magnesium sulfate was added to remove any water that was still present in the esters. Then, in order to remove the ethanol that could still be present in the ester, a rotary evaporator was used.

Epoxidation

The reaction was carried out adopting a molar ratio of 1:1.1 ester/peracetic acid. In a 250 mL round bottom flask, 100 g of ethyl ester obtained from cottonseed oil were added, and, drop by drop, 140 mL of 15% commercial peracetic acid. The mixture was stirred and heated to 45 ^{o}C in an ice water bath for 1 hour. 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 (biolubricant) was washed twice with 50 mL of 10% sodium bicarbonate. until the bubbles completely detach 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 cottonseed oil, stirring vigorously for 5 minutes and then remaining at rest for 30 minutes (DANTAS et al. ., 2021). To remove magnesium sulfate, vacuum filtration will be performed.

Physicochemical Characterization

Cottonseed oil was characterized by acidity index (AOCS Cd3d-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), relative density, ash content, moisture and volatile content (AOCS Da-2a-48), dynamic viscosity. Cottonseed oil ethyl ester epoxide was further characterized by hydroxyl index (AOCS Cd 13-60) and oxirane oxygen (AOCS D Cd 9-57).

All characterizations described previously were carried out according to the techniques described by (FARIAS et al., 2021) and carried out in triplicates.

DEVELOPMENT

Cottonseed oil was characterized using the physicochemical parameters listed in table 1.

Table 1. Physicochemical parameters of cottonseed oil.

Parameters	Oil	Anvisa Standards [1, 2]
Aspect	Clear yellow	Clear and free from impurities
Moisture and Volatiles (%)	0.09	≤ 0.1
Ash (%)	0.03	---
Density (g/ cm^3)	0.916	0.919 - 0.925
Acid value (mg KOH/g oil)	0.056	≤ 0.6
Iodine index (g I_2/100g oil)	102.1	96 – 115
Soap content (ppm of sodium oleate)	0.09	≤ 10
Saponification index (mg KOH/g oil)	41.7	189 – 195
Peroxide index (meq/Kg)	0.007	≤ 10
Approximate molar mass (g/mol)	856	---
Kinematic Viscosity at 40 °C (mm^2/s)	38.52	---

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

The appearance of the oil used is in accordance with that established by ANVISA, as well as the moisture and volatile content, where a value of 0.09% was obtained, lower than the value established by ANVISA, this value is important as it indicates the amount of water present in the oil, demonstrating the non-existence of contamination.

The ash content presented a value of 0.03%, the same as that obtained by Ramos (2023). When comparing to studies where other types of oil were used, we find that cottonseed oil has a lower ash content than the 0.05% residual soybean oil obtained by Macedo et. al (2021), by Cruz (2022) for refined soybean oil 0.06%, and by Macedo (2021) for castor oil 0.05%.

The density (0.916 g/cm^3) for the oil is below the range delimited by ANVISA from 0.919 to 0.925 g/cm^3, but equal to that obtained by Ramos (2023. The acidity index reached the value of 0.056 mg KOH/ g oil, meeting the standards established by legislation and below the index obtained by Ramos (2023). The acidity index determines the oil's conservation status, quality and purity.

The iodine index indicates the degree of unsaturation of an acid, which can influence the density of the oil, causing variations. For cottonseed oil, a value of 102.1 g I_2/100 g of oil was obtained, within the range defined by ANVISA. The result is corroborated by the value obtained by Ramos (2023).

The saponification index of cottonseed oil reached 41.7 mg KOH/g oil, a value lower than that determined by legislation. This value, however, is higher than that obtained by Ramos (2023) who obtained 24.6 mg KOH/g oil.

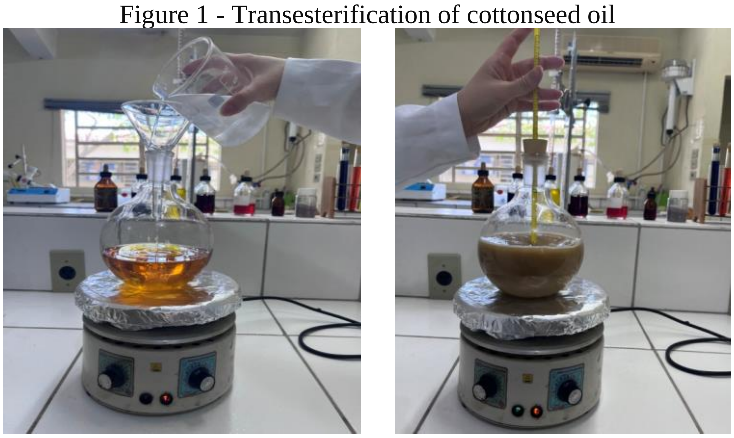
The peroxide index, according to legislation, must be ≤ 10 meq/Kg. Therefore, the value obtained for cottonseed oil is within the established range, since a value of 0.007 meq/kg was obtained. The molar mass of the oil was 856 g/mol and the kinematic viscosity reached a value of 38.52 mm^2/s.

Having carried out the characterization of cottonseed oil, transesterification was carried out to obtain ethyl ester from cottonseed oil (biodiesel). The transesterification reaction is reversible, where a triglyceride is subjected to react with a short-chain alcohol, commonly ethanol or methanol, under acid or basic catalysis (Cruz, 2022).

In the procedure, a 1:6 oil/alcohol ratio was adopted, with a view to increasing the yield of alkyl ester, obtaining glycerol as a by-product, under catalysis at 0.7% catalyst/oil. Ethanol and basic catalysis with KOH were used.

The transesterification reaction illustrated in figure 1, presented a yield of 80%, which can be explained by the use of ethanol, a longer chain alcohol, when compared to methanol, which allowed a yield of 97% in the work of Ramos (2023).

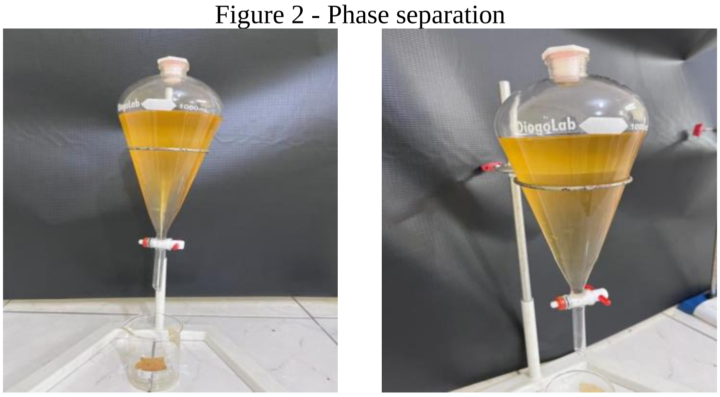
Figure 1 - Transesterification of cottonseed oil



Source: Own Authorship

After the transesterification reaction, the reaction mixture was transferred to a separation funnel where the phase containing glycerol (by-product), soaps and excess base and alcohol was removed, as illustrated in figure 2.

Figure 2 - Phase separation



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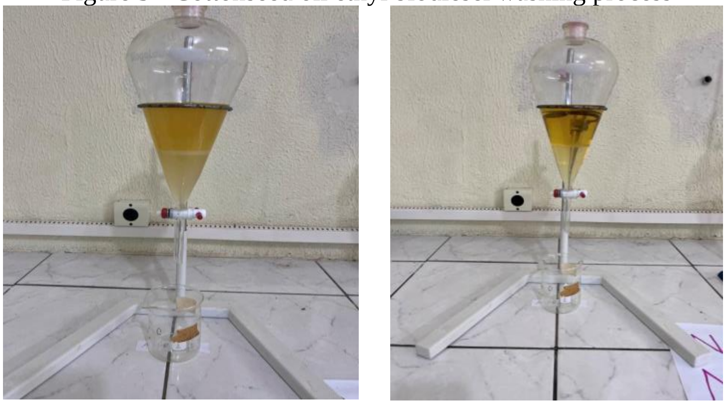
After the period of decantation and separation of the mixture phases, the ethyl ester (biodiesel) was washed to ensure the removal of impurities still present, figure 3.

Figure 3 - Cottonseed oil ethyl biodiesel washing process



Source: Own Authorship

After the purification process of the cottonseed oil ethyl ester was completed, the physicochemical characterization was carried out, obtaining the results listed in table 2.

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

Parameters	Oil esters	[1] Standards
Aspect	Clear yellow	Clear and free from impurities
Moisture and Volatiles (%)	0.016	0.02
Ash (%)	0.05	0.02
Density (g/ ^{cm3})	0.939	0.850-0.900
Acid value (mg KOH/g oil)	0.047	≤ 0.5
Iodine index (g I_2/100g oil)	102.9	Note
Soap content (ppm of sodium oleate)	0.54	---
Saponification Index (mg KOH/g oil)	222.1	---
Peroxide Index (meq/Kg)	0.03	---
Kinematic Viscosity at 40 ^oC (mm ^{2}/s)	---	3.0 – 6.0

Source: Research Data, 2023; BRAZIL, 2014.

Resolution No. 45/2014 of the National Petroleum and Biofuels Agency (ANP), establishes that the moisture and volatile content must respect the standard of 0.02%, therefore, the ethyl ester obtained is within the standards, presenting a content of 0.016%, a result similar to that obtained by Ramos (2023), 0.019%.

With regard to ash content, the ethyl ester obtained is above the standard established by the ANP, having a content of 0.05% ash. This content is important especially when the objective is to use it in automobile engines.

Cottonseed oil ethyl ester (0.939 g/cm ^{3}) presented a density above the standard established by the ANP. This density value suggests the presence of a long alkyl ester chain. The result is above that obtained by Ramos (2023) for cottonseed oil methyl ester (0.870 g/cm ^{3}). Suggesting a possible interference of the alcohol used in the density of the ester obtained.

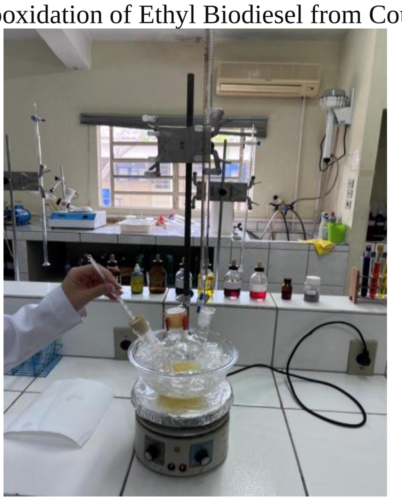
The acid value for cottonseed oil ethyl ester (0.047 mg KOH/g oil) is within the standard established by the ANP. Indicating excellent conservation status of the ester under analysis. For the iodine value of the ethyl ester, a value of 102.9 g I_2/100 g oil was reached, suggesting the presence of a degree of unsaturation that is not so excessive. The value achieved is higher than that obtained by Ramos (2023) for cottonseed oil methyl ester 91.7 g I_2/100 g oil. The iodine index indicates the product's ability to resist oxidation.

The saponification index for the ethyl ester reached a value of 222.1 mg KOH/g oil. When compared to the value obtained for cottonseed oil, ethyl ester showed an increase in the saponification index, indicating a reduction in unsaponifiable impurities in the transesterification process. The high value obtained for the saponification index suggests an interference in the yield of the transesterification reaction, possibly being a consequence of the use of basic catalysis with KOH, as basic catalysts promote a higher level of saponification in the process, due to the catalyst reacting with fatty acids. free from oil, leading to soap formation.

The cotton oil biolubricant was obtained through the epoxidation reaction of ethyl esters obtained in the transesterification reaction, following the process illustrated in figures 4-6.

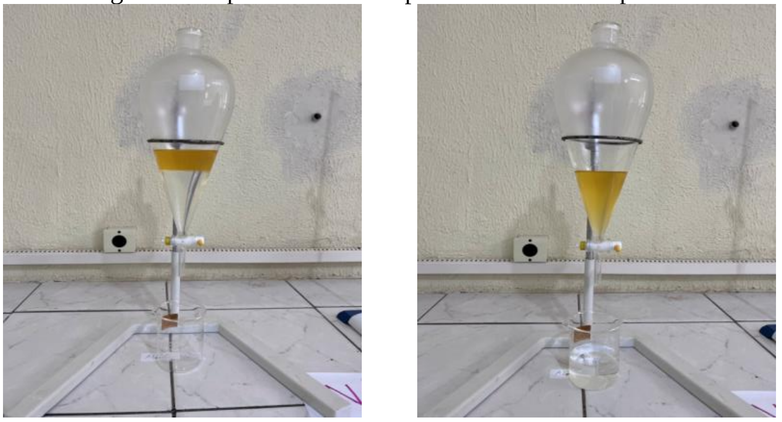
Epoxidation is the reaction of an unsaturated compound with a peracid, characterized by the addition of an oxygen to the double bond present in lubricating esters, producing an epoxide ring. It is possible to obtain these epoxides through esters, fatty acids or triglycerides. The epoxidation reaction is widely applied in the oleochemical industry to obtain biodegradable lubricants with greater thermal stability.

Figure 4 - Epoxidation of Ethyl Biodiesel from Cottonseed Oil



Source: Own Authorship

Figure 5 - Separation of the Epoxide/Acetic Acid phases



Source: Own Authorship

Figure 6 - Washing the Cottonseed Oil Ethyl Ester Epoxide

Source: Own Authorship

The epoxidation of ethyl esters from cottonseed oil, using 15% peracetic acid, made it possible to obtain biolubricants, with a yield of 97.0%.

The epoxides (biolubricants) obtained by the epoxidation process of cottonseed oil ethyl esters were subjected to physicochemical characterization (table 3) and the results were compared with the literature.

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

Parameters	Epoxide
Aspect	Clear yellow
Moisture (%)	1.72
Ash (%)	0.037
Density (g/ cm^3)	0.959
Acid value (mg KOH/g oil)	0.248
Iodine index (g I_2 /100g oil)	32.6
Soap content (ppm of sodium oleate)	0.12
Saponification Index (mg KOH/g oil)	277.7
Peroxide Index (meq/Kg)	0.02
Hydroxyl index (mg KOH/g oil)	8.33
Oxirane oxygen (%)	11.02
Kinematic Viscosity at 40 ^oC (mm ^{2} /s)	---

Source: Research Data, 2023.

The moisture content for cotton oil ethyl ester epoxide reached a value of 1.72%, higher when compared to that obtained by Ramos (2023) for cotton oil methyl ester epoxide 1.48%. This content is important for the applicability of the biolubricant, since greater humidity can cause damage to car parts, and also when thinking about its application in civil construction, as this type of use requires a material capable of reducing humidity in the surfaces where the biolubricant is applied.

The epoxide had an ash content of 0.037%, a result that is in agreement with that presented by Ramos (2023) for the ash content of cotton methyl ester epoxide (0.032%). The ash content indicates the presence of organic and inorganic, non-combustible material after burning the biolubricant. The density obtained for the epoxide was 0.959 g/cm^3, higher than that presented by Ramos (2023) for cotton oil methyl ester epoxide 0.895 g/cm^3.

The acidity value for cotton ethyl ester epoxide was 0.248 mg KOH/g oil, which is lower than the acidity value obtained by Ramos (2023) for cotton methyl ester epoxide 0.982 mg KOH/g oil. The lower the acidity index, the greater the efficiency of the biolubricant in preserving the material, equipment or surface where the epoxide is applied, mitigating the corrosion process.

For cottonseed oil ethyl ester epoxide, the iodine index obtained was 32.6 g I_2 /100 g oil, a value lower than that obtained by Ramos (2023) for cottonseed oil methyl ester epoxide. The reduction in the iodine value of epoxide when compared to ethyl ester indicates the efficiency of the epoxidation reaction in breaking double bonds in fatty acids.

The saponification index obtained for ethyl ester epoxide was higher than that presented by Ramos (2023) for methyl ester epoxide. The value was also higher when compared to that obtained for cottonseed oil ethyl ester. This index reveals the amount of high and low molecular weight fatty acids.

The soap content obtained for ethyl ester epoxide was 0.12 ppm of sodium oleate, a value lower than that obtained by Macedo et al. (2023) for methyl epoxide from canola oil. The soap content indicates the presence of traces of oil that ended up reacting with the base.

The peroxide index obtained for ethyl ester epoxide from cottonseed oil was 0.02 meq/kg, higher than that obtained by Macedo et.al (2023) for methyl epoxide from canola oil. The peroxide index is associated with the rancidity of the material.

The hydroxyl index reached a value of 8.33 mg KOH/g oil, lower than those obtained by Cruz (2022) for ethyl epoxide from residual soybean oil (18.9 mg KOH/g oil) and for ethyl epoxide of commercial soybean oil (19.8 mg KOH/g oil).

The value of 11.02% oxirane oxygen was obtained for the ethyl ester epoxide. This value exceeds that obtained by Cruz (2022) for the biolubricant from residual oil, which was 6.7%. And the result presented here is lower than that obtained by Cruz (2022) for the biolubricant in commercial oil, which was 11.6%. The value obtained here indicates the success in carrying out the epoxidation reaction, despite some hydrolysis reactions having occurred.

FINAL CONSIDERATIONS

The transesterification reaction obtained a good yield of 80%, as did the epoxidation reaction where the yield was 97%. The results obtained for the physical-chemical parameters of biodiesel and biolubricant are in agreement when compared to the standards established by legislation and when compared with the literature.

According to the physicochemical characterization carried out, cottonseed oil ethyl ester epoxide has potential use as a biodegradable biolubricant in the automotive industry and also in construction, although it is still necessary to carry out specific feasibility tests for this application.

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