Study of methyl epoxidation of cottonseed oil to obtain a biodegradable lubricant

Estudo da epoxidação metílica do óleo de algodão visando a obtenção de um lubrificante biodegradável

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1 INTRODUCTION

The consumption of energy sources has been increasing over the years, both for the industry and for the comfort and quality of life provided to humans. However, despite ensuring all comforts to humanity, non-renewable energy sources, derived from fossil fuels, can be depleted and trigger impacting environmental problems. The rapid depletion of fossil fuel reserves, the extraction, transport, and industrial processes of oil transformation are responsible for several environmental damages, such as spilling, generation of toxic waste and effluents that are difficult to degrade, contamination of groundwater by gasoline and its additives, and the accumulation of carbon dioxide in the atmosphere, intensifying the greenhouse effect (EREDA, 2004). Thus, the use of biofuels is necessary for a more sustainable environment.

These concerns followed a great interest in vegetable oils with high oleic acid content, such as biofuels and their derivatives, which would be the case for lubricants because they are renewable raw materials, thus replacing conventional mineral oils, made from petroleum (LATHI; MATTIASSON, 2007). It is known that for some types of application, mineral lubricating oils are not able to withstand the performance requirements, for example, the current automotive engine oils, which have requirements for long periods for change and high oxidative stability, and the use of synthetic bases for new engines is required by all automakers.

The inappropriate use of lubricants obtained from petroleum are major cause of environmental problems, i.e., by the inappropriate disposal causing pollution of the air, soil and consequently of the food. Therefore, lubricants based on vegetable oils have been a good alternative to optimize these negative results precisely because they are biodegradable, non-toxic, and originate from renewable sources. In addition, vegetable oils present qualities that differentiate them as sustainable fuels: the absence of sulfur in their chemical composition and the reality that their industrial production does not produce substances that are harmful to the environment (PIANOVSKI JÚNIOR, 2002).

Despite being favorable from the energy point of view, the direct use of vegetable oils in diesel engines is very problematic, hence the need for their use after processes. Studies have shown that the direct combustion of vegetable oils leads to the carbonization of parts, resistance to ejection in pistons, dilution of crankcase oil, contamination of the lubricant, among other objections (RINALDI et al., 2007). Studies found in the literature show that alternatives to improve the performance of these vegetable oils are structural modifications, such as transesterification reactions (biodiesel) and epoxidation (biolubricant).

Because of its great resistance to drought, cotton is one of the few options for cultivation in semi-arid regions, and can keep people in the countryside and generate employment and income in rural and urban areas. Cotton oil is the oldest vegetable oil produced and consumed on a large scale, besides its use in the biofuel industry (DANTAS, 2006). Cotton (Gossypium sp.) is the only domesticated species, considered in economic terms as a triune crop due to its constitution in the second economic activity in the world, and for producing fiber - its main product - that currently wears almost half of humanity, for its oil that serves for human food and for energy production (biodiesel) (BELTRÃO, 1999). The production of biolubricant from cotton seed oil aims at the use of a renewable energy source, less pollutant, that strengthens both the large and the small producer, seeking the total use of cotton, without taking away the main focus of its production, which is for the textile industry. Thus, this work aims to synthesize a renewable and biodegradable lubricant from cotton oil.

2 OBJECTIVE

Obtaining a biodegradable lubricant from cottonseed oil through transesterification and methyl epoxidation reactions.

3 METHODOLOGY

Initially the methyl transesterification of cotton oil was performed from its saponification index. From the molar mass obtained, the amounts of alcohol (methanol) and catalyst (KOH) needed to perform the reaction were determined using a molar ratio oil/alcohol equal to 1:6 and 0.7% catalyst (oil/catalyst) (PELANDA, 2009), keeping the temperature at approximately 45º C for 1 hour (FERRARI et al., 2005).

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. Then the methyl ester (biodiesel) was washed with distilled water and 0.01M hydrochloric acid solution. Subsequently three washes were made with distilled water (to remove glycerol and soap residues from the esters phase) and two washes with 0.01M HCl solution (to neutralize the esters). To check the efficiency of the acid wash, phenolphthalein was used. After the washes, anhydrous magnesium sulfate was added to remove any water that was still present in the esters. Then, in order to remove the methanol that might still be present in the ester, a rotary evaporator was used.

For the epoxidation reaction in a 250 mL round bottom flask, 100 g of the methyl ester obtained from the cottonseed oil, and drop by drop, 140 mL of 15% commercial peracetic acid were added. The mixture was stirred and heated at 45º C in a water and ice bath for 1 hour. The reaction was carried out using a molar ratio of 1:1.1 ester/peracetic acid. After the end of the reaction, the mixture was transferred to a separation funnel, where the lower phase, corresponding to the acetic acid, was removed, and the upper phase (biolubricant) was washed twice with 50 mL of 10% sodium bicarbonate until the bubbles were completely detached due to the neutralization reaction. In order to remove the residual water, anhydrous magnesium sulfate was added to an Erlenmeyer flask containing the epoxide (biolubricant) obtained from cottonseed oil, stirring vigorously for 5 minutes and then kept at rest for 30 minutes (NUNES et al., 2008). To remove the magnesium sulfate, a vacuum filtration was performed.

4 DEVELOPMENT

Table 1. Physicochemical parameters of the raw material.

Parameters	Oil	Anvisa Standards[1, 2]
Aspect	Clear yellow	Clear and free of impurities
Humidity and Volatiles (%)	0,09	≤ 0,1
Density (g/cm)[3]	0,916	0,919 - 0,925
Acid value (mg KOH/g oil)	0,166	≤ 0,6
Iodine value (g I_2 /100g oil)	102,1	96 - 115

Saponification index (mg KOH/g oil)	24,6	189 - 195
Approximate molar mass (g/mol)	856	---

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

By ANVISA's Normative Instruction No. 49/2006, the cottonseed oil presented in the moisture and volatiles parameter a value below the standards set by ANVISA, showing itself within the standard value. The moisture content and volatiles are able to indicate the amount of water present in the oil under analysis, so the value presented is suitable for the production of biodiesel.

The ash content showed a value of 0.03%, which when compared to the work of TOFANINI (2004) it was noticeable that its value was a little high compared to soybean, sunflower, corn, and rice oils. It can be seen that the density of the cottonseed oil is not within the parameters established by ANVISA, since its density should be between the values of 0.919 and 0.925 (g/cm^3). The acidity index showed a value in accordance with the standard of the legislation, through which the conservation status of the oil, that is, its purity and quality are determined.

Also by the normative resolution taken as reference previously, the iodine index should be between the values of 96 and 115, and the cottonseed oil showed a value equal to 102.2 (g I_2 /100g Oil) being in accordance with the standard normative. The saponification index established on the same path of the standard, stresses that this should be between the values of 189-195, but the vegetable oil under study showed a value equal to 24.6 (mg KOH / g Oil), so this value below the allowed may indicate the presence of long-chain triglycerides.

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

Parameters	Oil esters	ANP Standards[1]
Aspect	Clear yellow	Clear and free of impurities
Humidity and Volatiles (%)	0,019	0,02
Ash (%)	0,018	0,02
Density (g/cm)^3	0,870	0,850-0,900
Acid value (mg KOH/g oil)	0,056	≤ 0,5
Iodine value (g I_2 /100g oil)	91,7	Annotate
Saponification Index (mg KOH/g oil)	61,7	-----

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

Resolution No. 45/2014 of the National Petroleum and Biofuels Agency (ANP) establishes a standard of 0.02% of moisture and volatiles for oil esters. The biodiesel derived from cottonseed oil presented a value equal to 0.019% showing that it is within the established standards. Similarly, taking the ANP standard as a reference, the ash content showed a result of 0.018% included in the standards taken as a reference. In this sense, it is important that it is within the standards, because this is influential in the operation of automobile engines.

The density in turn showed a value of 0.870 g/cm^3 equal to the density of methyl ester from soybean oil found in the work of Botelho (2016), besides being between the ANP standard parameters. The acidity index showed a result according to the National Petroleum Agency equal to 0.056 mg KOH / g sample, moreover its value was lower than the work of Rockembach et al., (2014).

The iodine index refers to the degree of unsaturation of biodiesel, serving as an indication of the product's ability to resist oxidation and tendency to form degradation products, this parameter is relevant when you want a biodiesel that is really functional. For the methyl ester derived from cotton oil, the iodine index had a value 91.7 lower than those highlighted in the literature that could reach up to 170.04 g I_2 / 100g oil, agreeing that its degree of unsaturation were not so excessive.

The saponification index is intended to characterize the oils by the amount of basic material needed to saponify the lipids in a sample (VINEYARD; FREITAS. 2014). It is known that the lower this index, the better the biodiesel yield. This in turn obtained a lower result when compared to the work of LIMA and collaborators (2007) in which their babassu biodiesel had a saponification index equal to 233 (mg KOH / g Oil).

The yield of Biodiesel from cotton oil was 96%, this yield is higher than those found in the literature. This result could be satisfactory due to the use of the alcohol (because it is reactive), as well as the catalyst and the oil used for the production of the methyl ester. That is, from the time the methyl ester and glycerol were in the final process of decantation, they were well removed, making it possible to obtain a good yield. As well as the use of a basic catalyst, which is better employed when compared to the acid ones, because it presents a shorter reaction time besides needing less of the molar ratio (alcohol/oil). The state of the matter is taken into consideration, i.e., the closer the results are to the standard parameters, the better the reaction process will be, favoring the yield of the reaction.

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

Parameters	Epoxide	Literature Standards
Aspect	Clear yellow	Yellow
Humidity (%)	1,48	0,1

Ash (%)	0,032	0,05
Density (g/cm)[3]	0,895	0,953-0,960
Acid value (mg KOH/g oil)	0,982	7,92
Iodine value (g I_2 /100g oil)	40,3	8,73
Saponification Index (mg KOH/g oil)	60,2	178

Source: Survey Data, 2023

The moisture content showed a higher value than that determined in the work of Oliveira (2013) which was 0.1%. The humidity is interesting not to be high because it can cause problems in car parts, perhaps one of the reasons for this is inadequate storage. The ash content that expresses the inorganic, non-combustible residues resulting after the burning of the biolubricant, in turn is lower than the research of Pereira (2022) showing that there are few inorganic materials present in the epoxide. A low ash content is valid due to the abrasion these can cause to engines when at high levels.

The density is in the range of values found in the work of Cruz (2022), which ranges from 0.953 g/cm^3 for used oil and 0.960 g/cm^3 for refined oil. Regarding the acidity index to which determines the amount of KOH in milligrams needed to neutralize one gram of oil, the acidity index of the biolube was 0.982 (mg KOH/ g Oil) lower than the acidity of the epoxide found in the work of Rodrigues (2013). In this sense, acidity of a lubricant is related to the corrosion of metal surfaces, the lower its index the better in relation to the non-corrosion of the equipment.

The iodine index, responsible for measuring the degree of unsaturation of fatty acids, was compared to the work of Oliveira (2013), which showed a very high index of 40.3 (g I2/ 100g oil). The saponification index indicates the relative amount of high and low molecular weight fatty acids. The saponification parameter showed a much lower value when compared to the result obtained from the oil used by the research of Cruz (2022).

The epoxidation reaction using the cottonseed oil methyl ester in the presence of peracetic acid provided the obtaining of the cottonseed oil methyl ester epoxide (biolubricant). The epoxide derived from cottonseed oil biodiesel showed a good yield equal to 98%, this value is higher than those found in the literature.

Furthermore, it can be considered that its yield was higher than that of other authors due to the state of the initial material presenting good parameters, the biodiesel having good specifications as well as the whole process of decantation, that is, its washing and correct removal of the biolube for storage.

5 CONCLUDING REMARKS

Thus, we conclude that the work obtained good results regarding yields, both biodiesel with a yield of 96% and biolubricant with 98%. In addition, it showed good values when compared to standard parameters such as those found in the literature. For biodiesel, the content of ash, moisture and volatiles, density and acidity index. For the biolubricant, the following parameters stand out: ash, density, acidity and saponification index. The purpose of obtaining biodegradable lubricants from cottonseed oil was to reduce the various environmental damage and atmospheric pollution resulting from the great industrial need, providing well-being and quality of life without generating consequences to the environment.

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