<mark>Eclética</mark> Química Journal

| Vol. 45 | n. 2 | 2020 |

Study of the properties of lubricating oils obtained from biodiesel

Andreza de Faria Alves Cruz⁺, Raquel Moreira Maduro de Carvalho[®], Fábio Celso de Oliveira[®]

Centro Universitário de Viçosa (Univiçosa), 3815 Maria de Paula Santana Av, Viçosa, Minas Gerais, Brazil.

⁺Corresponding author: Andreza de Faria Alves Cruz, Phone: +55 31 9 9558-1602 email address: andrezafalvesc@gmail.com

ARTICLE INFO

Article history: Received: April 26, 2019 Accepted: December 18, 2019 Published: April 1, 2020

- Keywords: 1. biodiesel 2. engines 3. vegetable oils 4. performance 5. lubricants
- 6. transesterification

ABSTRACT: In this work, nine different biodiesels were obtained by transesterification reaction with three types of vegetable oils and three variant alcohols. The objective was to analyze them physicochemically before and after they went to the engine, to know if they had the necessary properties to act as lubricants. Subsequently, the same biodiesels were analyzed in the engine in order to observe the behavior of their dynamic viscosities, to evaluate if they were similar or superior to commercial lubricants. It was





possible to note that all biodiesel produced are within the National Agency for Petroleum, Natural Gas and Biofuels (ANP) legislation and presented as potential lubricants, due to the kinematic viscosity behavior when compared before and after the engine. These results made them possible replacements for commercial lubricants, besides having greater advantages for the engine and the environment. However, although coconut oil-derived biodiesel has good yields, it is not promising because, at temperatures below 25 °C tends to solidify, causing short, medium- and long-term engine parts wear.

1. Introduction

In the last 10 years, the world's energy consumption grew by 2.5%. Oil has been steadily falling, but it is still considered the largest primary source of used energy, although the energy consumption from renewable sources is growing. China has been reducing its energy consumption over the years, but it is still considered the most energy consuming country in the world, importing about 58% of oil. Following on the list of the world's largest energy consumers, there are the United States, India, Germany and Brazil. Brazil is expected to grow 2.2% by the year 2040, with emphasis on renewable energies (4.5%)¹.

It has now become clear that the world's perceptions about renewable energy have changed a lot and are now seen as an outlet to address some needs such as improving energy security, reducing impacts on health and the environment, mitigating greenhouse gas emissions, improving opportunities in the area of education, creation of new labor poles and poverty reduction².

Biodiesel appears as an alternative, since its main application is fuels, because it is free of aromatic compounds and sulfur, an important characteristic in the environmental sector; besides being more economically viable for stimulating agricultural production, reducing importation of oil from other countries. It can be obtained through a mixture of different esters resulting from the



esterification reaction of fatty acids or transesterification of glycerides³.

Several raw materials are used in the production of biodiesel, such as vegetable oils, animal fats and used frying oil. According to the National Petroleum Agency⁴, biodiesel produced in Brazil comes from soybean oil (76.4%), animal fat (19.8%), cotton oil (2.2%) and other vegetable oils (1.6%).

In addition to using biodiesel as fuel, it can also be used as lubricant. When it acts as a lubricant, it performs much better than commercial lubricants, due to its high lubricating power, higher viscosity and less wear on the engine parts⁵.

For the development of a lubricant, specified physicochemical properties must be obtained, such as viscosity, resistance to corrosion, total acidity index, pour point, chemiluminescence, among others. In the case of biolubricant esters which are derived from organic esters, hydrolytic, oxidative and thermal stabilities must be obtained⁶.

The lubricating oil used in the engine must meet all lubrication needs in the different tribological pairs found in the engine⁷. Thus, it can be stated that the ignition quality of the fuel, the types of hydrocarbons present in the fuel and the presence of impurities or additives in it affect the performance of the engine lubricating oil.

In this study, the synthesis of biodiesel from vegetable oils was proposed, as well as the analyses of their physicochemical properties to act as lubricants, evaluating the kinematic viscosity before and after the sample in the engine to verify if the performance of biodiesel as a lubricant is similar to or higher than commercial lubricants.

2. Experimental

2.1. Production of biodiesel

For the transesterification reactions, the methodology described by Geris *et al.*⁸ was used, which initially consisted of the preparation of an intermediate through the mixture of potassium hydroxide and varying alcohols, such as methanol, ethanol and isopropyl alcohol, under heating at 45 °C and constant stirring until complete dissolution of the solid. Later, the intermediate was mixed with the oils, which were also varied in the reaction as: being coconut oil, castor oil and rice oil. They were commercially purchased, and the reaction were carried out at 45 °C for 10 min. Afterwards, the biodiesel was elaborated, pouring

the previous mixture and separating it through a separation funnel, isolating the biodiesel and the glycerin, and the excesses of base and alcohol. The biodiesel was treated with distilled water at 70 °C, followed by aqueous solution of hydrochloric acid 0.5% v/v until it reached neutral pH. Finally, moisture was withdrawn with anhydrous magnesium sulfate under constant stirring for 15 min.

Thus, nine combinations of reactions were performed: coconut oil and methyl alcohol, castor oil and methyl alcohol, rice oil and methyl alcohol, coconut oil and ethyl alcohol, castor oil and ethyl alcohol, rice and ethyl alcohol, coconut oil and isopropyl alcohol, castor oil and isopropyl alcohol and rice oil and isopropyl alcohol.

2.2. Biodiesel yield

Regarding the mass yield of biodiesel produced through the basic transesterification process, the quantity of biodiesel obtained from the ratio of 1:6 with the highest amount of oleic acid was accounted for. Yield was evaluated from the alcohol and vegetable oil used in the reaction.

All reactions were performed in triplicate, as approximately 500 mL were required for further use in the engine.

2.3. Validation of the lubrication property of the lubricants in the internal combustion engine by the kinematic viscosity analysis

The samples were assayed in a seven-stroke gasoline four-stroke engine, Manual Start - NMG70, at Univiçosa Physics Laboratory. Initially, it was necessary to use 500 mL of commercial fuel to start the engine. Subsequently, each sample was for 3 nonconsecutive h in the motor.

For the engine to run, 500 mL of each synthesized biodiesel were used, according to routes previously described in the methodology. It is important to note that when below this amount, the motor does not run to rotate the sample.

2.4. Physicochemical characterization of biodiesel

All the biodiesel obtained were characterized by pH, specific mass, total acidity index, moisture content, kinematic viscosity, plus metal detection tests and infrared. All analyzes were performed in triplicate, except for the viscosity that was performed five times.

2.4.1. Appearance and color

In order to characterize the biodiesel in relation to aspect and color, a preliminary analysis was carried out looking for the presence of visual impurities, such as suspended materials, sediments or any turbidity in the sample, which may be due to the presence of water. In the absence of any of these contaminants, biodiesel was classified as clear and free of impurities, according to NBR 14954 ⁹.

2.4.2. pH

The pH was measured with a pHmeter, which can present values ranging from 0 to 14, indicating acidity, neutrality or basicity of the medium. For biodiesel, the pH must be 7, that is neutral¹⁰.

2.4.3. Specific mass

To determine the specific mass, a 25 mL glass pycnometer was used. First the empty pycnometer was weighed and written down to its mass. Then it was filled with distilled water, weighed and its mass was noted. Subsequently, the clean and dry pycnometer was filled with biodiesel, being again weighed with its mass noted, according to NBR 7148/14065¹¹. The specific mass was calculated with Eq. 1:

$$\rho = \frac{m}{v} \tag{1}$$

2.4.4. Total acidity index

To calculate the acid number, it was necessary to measure a mass of approximately 10 g of biodiesel in a 125 mL Erlenmeyer flask. A mixture of ethyl alcohol and ethyl ether in the ratio of 2:1 by volume was prepared. Subsequently, 25 mL of this mixture was added to the Erlenmeyer flask along with 3 drops of phenolphthalein. Titration of the solution was then carried out with 0.02 mol L⁻¹ sodium hydroxide, and the blank was titrated, that is, 25 mL of the mixture of ethyl ether and ethyl alcohol together with 3 drops of phenolphthalein without the presence of biodiesel, according to NBR 14448 ¹². The calculation of the acid number is performed by Eq. 2:

$$Ia = \frac{(V_{spent} - V_{blank \ reaction})xfx5.61}{m_{oil}}$$
(2)¹²

2.4.5. Moisture content

To determine the moisture content of the biodiesel, a greenhouse, in which a mass of approximately 20 g of biodiesel was placed in the crucible free of moisture, was used and then weighed.

The sample was then placed in an oven, with temperature at 100 °C for 24 h. After this time, the sample was cooled in a desiccator and the sample was weighed again until the value remained constant, thus obtaining the moisture content by the difference between the initial and final masses, through Eq. 3, according to ASTMD 6304 ¹³.

Moisture content =
$$P_i - P_f$$
 (3)¹³

 P_i is the initial weight of the crucible with biodiesel and P_f is the final weight of the crucible with biodiesel.

2.4.6. Kinematic viscosity

The kinematic viscosity was determined with the aid of a pipette, adding 15 mL of sample to the viscometer through the ventilation tube, and waited 5-10 min to equilibrate the liquid temperature to 25 °C. With the aid of the pipettor fitted to the capillary tube, the fluid was suctioned up to above the upper measurement mark, according to NBR 10441⁴. The kinematic viscosity can be calculated by Eq. 4:

$$v = \mathbf{K} \mathbf{x} \mathbf{t} \tag{4}^{11}$$

Where v is the kinematic viscosity of the sample (in mm² s⁻¹), K is the viscometer constant calculated for a known fluid (in mm² s⁻²) and t is the average of the time the sample took to move from the measurement mark top to bottom.

2.4.8. Qualitative test for metal detection

For the qualitative test of metal detection, electromagnetic magnets were used. The magnets were approximated to the biodiesel samples. In case of attraction, it indicates the presence of metals and if nothing happens, absence⁸.

2.4.9. Infrared

The spectra were collected in the Perkin-Elmer FT-IR 1000 spectrophotometer in the range of 4000 to 200 cm⁻¹ in the Department of Chemistry – UFV and were made in ATR.

3. Results and Discussion

3.1. Characterization of biodiesel

The biodiesel characterization was carried out from the results of some parameters, through which the quality of the biodiesel produced can be evaluated. The quality has a direct relation with the operation and the life of an engine, so it was possible to ascertain the quality of the biodiesel produced.

According to *National Agency* for *Petroleum*, Natural Gas and Biofuels regulation 25/2014 ⁴, in order to the product obtained to be considered a biodiesel, it must comply with some rules such as: be clear and free of impurities; have neutral pH; have density, total acidity index, moisture content and kinematic viscosity within the established limits.

Tables 1, 2 and 3 present the methodologies used in each parameter, the results obtained by the analysis of coconut, castor and rice biodiesel, respectively, following the limits established by the Brazilian legislation⁴.

Table 1. Results obtained for acidity index tests (mg KOH g^{-1}), relative density (kg m^{-3}), moisture content (mg k g^{-1}), followed by the Brazilian legislation⁴.

Parameters Methodology adopted		BCOM	BCOE	BCOI	NPA Resolution, 2004
Aspect	NBR 14954	Clean and free of impurities			
Specific mass	NBR 7148/14065	868.432 ± 0.002	867.012 ± 0.005	872.476 ± 0.003	850 to 900
Specific relative mass	-	0.835 ± 0.002	0.794 ± 0.005	0.780 ± 0.003	-
Acidity Index level	NBR 14448	0.090 ± 0.008	0.059 ± 0.008	0.042 ± 0.007	<0.5
Moisture content	ASTMD 6304	197.000 ± 0.003	189.09 ± 0.02	190.73 ± 0.03	<200.0

BCOM - Biodiesel coconut oil with methanol; **BCOE** - Biodiesel coconut oil with ethanol; **BCOI** - Biodiesel coconut oil with isopropanol; **BCAOM** - Biodiesel castor oil with methanol; **BCAOE** - Biodiesel castor oil with ethanol; **BCAOI** - Biodiesel castor oil with isopropanol; **BROM** - Biodiesel rice oil with methanol; **BROE** - Biodiesel rice oil with ethanol; **BROI** - Biodiesel rice oil with isopropanol.

For biodiesel produced from methanol, all are classified as clear and free of impurity, as specified by Brazilian legislation.⁴, since they have no impurities or turbidity, so biodiesel is within the cited specification.

The specific mass values obtained at 20 °C for all biodiesel are within the limits of 850 to 900 kg m⁻³ established by NBR 7148/14065⁴. The values were within the range required by the Brazilian legislation⁴, which indicates high purity of the products obtained.

Considering that Resolution n° 255, dated November 15, 2003, indicates that the maximum limit of acidity index is 0.50 mg KOH g^{-1} of oil, so the values observed in Tab. 1 are within the allowed values, which is a good result, since an acidity index above the allowed one leads to the

aging of the lubricant and it wears the parts of the motor in the long term.

For the analysis of the moisture content, Eq. 3 was used, according to methodology. It can be observed that all values obtained for biodiesel from methanol, in Tab. 1, were within the limit of 0.5 mg kg⁻¹ required by the Brazilian legislation⁴, which is important since the water content above the allowance impairs the property of the lubricant and oxidizes the engine parts over time.

The relative specific mass is given by the specific mass of the biodiesel in relation to the specific mass of the water, both obtained experimentally. Even though a limit is not specified⁴, as the specific masses were within the limit, consequently, the relative specific masses are too.

Parameters Methodology adopted		BCAOM BCAOE		BCAOI	NPA Resolution, 2004
Aspect	NBR 14954	Clean and free of impurities			
Specific mass	NBR 7148/14065	869.352 ± 0.002	898.540 ± 0.003	861.676 ± 0.002	850 a 900
Specific relative mass	-	0.853 ± 0.002	0.833 ± 0.003	0.628 ± 0.002	-
Acidity Index level	NBR 14448	0.045 ± 0.006	0.20 ± 0.02	0.070 ± 0.005	<0.5
Moisture content	ASTMD 6304	189.08 ± 0.02	190.76 ± 0.02	189.09 ± 0.02	<200.0

Table 2. Results obtained for acidity index tests (mg KOH g^{-1}), relative density (kg m⁻³), moisture content (mg kg⁻¹), followed by the Brazilian legislation⁴.

BCAOM - Biodiesel castor oil with methanol; **BCAOE** - Biodiesel castor oil with ethanol; **BCAOI** - Biodiesel castor oil with isopropanol.

In Tab. 2, it can be observed that all the biodiesels obtained through the castor oil were also clear and free of impurities.

The specific masses were within the range of 850 to 900 kg m⁻³, indicating high purity of these products obtained by the transesterification reaction. In addition, the specific mass of a biodiesel is directly linked to the molecular structure of its molecules. The longer the carbon chain of the ester, the greater its specific mass, but the value will decrease the higher the numbers of unsaturated bonds present in the molecule. The presence of impurities may also influence the specific mass. As observed, ethanol has a higher

carbon chain than methanol, so its specific mass is higher. In contrast, isopropanol has branching; consequently, there is a decrease in its specific mass, as stated by Lace *et al.*¹⁴.

The acidity index was also within the Brazilian legislation⁴ limit, being less than 0.5 mg KOH g^{-1} , with very low standard deviations, which corresponds to the accuracy of the triplicate analyzes.

Regarding the moisture content, the values obtained were lower than 200 mg kg⁻¹, indicating that all biodiesel obtained from castor oil are within the limits of the Brazilian legislation⁴.

Table 3. Results obtained for acidity ind	x tests (mg KOH g ⁻¹), relative de	ensity (kg m ⁻³), moisture content (mg
kg ⁻¹), followed by standard legislation ⁴ .		

Parameters	Methodology adopted	BROM	BROE	BROI	NPA Resolution 2004
Aspect	NBR 14954	Clean and free of impurities			
Specific mass	NBR 7148/14065	871.412 ± 0.014	876.768 ± 0.018	866.012 ± 0.021	850 to 900
Specific relative mass	-	0.83 ± 0.03	0.84 ± 0.04	0.82 ± 0.02	-
Acidity Index level	NBR 14448	0.034 ± 0.003	0.059 ± 0.002	0.037 ± 0.005	<0.5
Moisture content	ASTMD 6304	178.11 ± 0.03	178.92 ± 0.03	198.52 ± 0.03	<200.0

BROM - Biodiesel rice oil with methanol; **BROE** - Biodiesel rice oil with ethanol; **BROI** - Biodiesel rice oil with isopropanol.

Through Tab. 3, it was possible to observe that all the biodiesels obtained with isopropanol were clear and free of impurities.

For the specific mass, the values were within the limit of 850 to 900 kg m⁻³ according to the legislation⁴, indicating the high purity of these

obtained biodiesels. In the same way, the ethanol has greater carbonic chain than the methanol, therefore, greater specific mass; while the isopropanol has branching, then it has a lower specific mass, according to Lace *et al.*¹⁴.

The acidity index was also within the limit of 0.5 mg KOH g⁻¹, presenting low values, which is a good sign since it does not indicate wear of the engine parts.

Regarding the moisture content, the values were within the limit of 200 mg kg⁻¹ of the Brazilian legislation⁴. It is very important that the analyzes of moisture content are within the limit described by the National Agency for Petroleum, Natural Gas and Biofuels, since, according to Lace *et al.*¹⁴, water promotes the hydrolysis of biodiesel resulting in free fatty acids, contributing to the proliferation of microorganisms, equipment corrosion and deposition of sediments. In addition, the presence of water contributes to the increase in acidity, which is not desired.

3.2. Biodiesel yield

The yield calculation was useful to verify which vegetable oil and alcohol had the best yield in obtaining biodiesel, that is, how much was converted from reagent (vegetable oil) to product (biodiesel).

Tables 4, 5 and 6 below indicate these yields:

Table 4. Yield for biodiesel derived from coconut oil.

% biodiesel	BCOM	BCOI	BCOE
Reaction 1	60	60	58
Reaction 2	75	66	63
Reaction 3	89	70	55

Some studies by Nascimento, Vasconcelos and Azevedo¹⁵ show a technique of microwave optimization, leading to a yield of approximately 100%.

The biodiesel obtained by means of coconut oil with isopropanol presented values higher than expected, although there are no comparisons with the literature. However, according to Geris *et al.*⁸, isopropanol is not as viable for transesterification reaction due to its higher carbon chain and greater branching when compared to the other alcohols used.

Regarding biodiesel derived from coconut oil with isopropanol, the values were within the expected range, as described by Shimada *et al.*¹⁶, from 45 to 80%, a little lower than methanol due to its higher carbon chain, less toxic than it.

Geris *et al.*⁸ showed that biodiesel obtained from methanol yields between 58 and 89%, due to the lower carbon chain that facilitates the

transesterification reaction; followed by ethyl alcohol in yields between 55 and 75%, being even less toxic. The higher the carbon chains and the ramifications, the lower the yields of biodiesel due to the greater difficulty of reacting. In relation to coconut oil, for Dias, Ferraz e Almeida¹⁷ the yields with methanol are around 60 to 90%, while with ethanol, for Shimada *et al.*¹⁶, they vary between 45 and 80%.

Table 5. Yield values for biodiesel derived from castor oil.

% biodiesel	BCAOM	BCAOI	BCAOE
Reaction 1	65	45	56
Reaction 2	87	47	51
Reaction 3	93	74	64

Table 5 shows that the biodiesel obtained through castor oil with methanol presented good yields, according to the range of 60 to 96% specified by Dias, Ferraz e Almeida¹⁷.

For biodiesel derived from castor oil with isopropanol, it is believed that the values were low as expected by the chemical explanation regarding the amount of carbonic chain and branching, as explained by Geris *et al.*⁸.

The biodiesel obtained by means of castor oil with ethanol presented yield between the limit expected by Dias, Ferraz e Almeida¹⁷, from 40 to 75%. As shown in Tab. 4, yields of biodiesel obtained from coconut oil by methanol were considered as expected, since according to Dias, Ferraz e Almeida¹⁷, a yield of 60 to 90% for biodiesel from coconut oil from methanol.

Table 6. Yield values for biodiesel derived from rice oil.

% biodiesel	BROM	BROI	BROE
Reaction 1	83	46	54
Reaction 2	71	53	66
Reaction 3	81	64	96

Table 6 shows that biodiesel obtained from rice oil with methanol presented high values, as expected by Charoenchaitrakool and Thienmethangkoon¹⁸, from 70 to 95%.

The biodiesel obtained through the rice oil with isopropanol presented low yields, but already expected according to the chemical explanation of the carbon chain, as suggested by Geris *et al.*⁸.

For the biodiesel obtained by means of the rice oil with ethanol, the yields were within the expected, with highlight to the 3^{rd} reaction with

yield of 96%, higher than expected by the limit of 50 to 80% of Charoenchaitrakool and Thienmethangkoon¹⁸.

In relation to the performance of biodiesel in the engine, the yield does not directly influence. However, good yields are feasible because of the amount of 500 mL needed for the lubricant to run on the engine. A low yield means having to perform a greater amount of reaction to achieve what is required for the internal combustion engine, making the process more expensive and exhausting.

3.3. Validation of the lubrication property of the lubricants in the internal combustion engine by the kinematic viscosity analysis

It was observed that the engine maintained the correct operating temperature, since a laser thermometer was used to carry out the temperature measurements during operation, so that there was no overheating of the engine components. Also, no smoke or anomaly was observed during or after the tests.

Kinematic viscosity analyzes are listed in Tab. 7, 8 and 9, both before and after each sample for 3 h. The analyses were performed in quintuplicate and the results were given by the mean.

Analyzes before the engine will be called BE and after engine AE.

Table 7. Kinematic viscosit	v results in	biodiesel	derived	from	coconut	oil
-----------------------------	--------------	-----------	---------	------	---------	-----

Kinematic viscosity (mm ² s ⁻¹)	BOCM (BE)	BOCI (BE)	BOCE (BE)	BOCM (AE)	BOCI (AE)	BOCE (AE)
Average	2.600 ± 0.002	5.980 ± 0.004	6.000 ± 0.007	6.400 ± 0.004	-	6.500 ± 0.008

In Tab. 7, it was possible to observe that the biodiesel obtained through coconut oil before the engine showed satisfactory results, within the range of 3.0 to 6.0 mm² s⁻¹ of the NBR⁴. Only the biodiesel obtained from coconut oil with methanol showed below-expected value, which is detrimental since lubricant that has low viscosity

may not sufficiently protect engine parts, increasing parts wear, causing more friction and oxidizing faster, as explained by Farias *et al.*⁵. The viscosity values after the engine increased, but not excessively, which was expected due to the oxidation of the biodiesel in the engine.

Table 8. Result of kinematic viscosity in biodiesel derived from castor oil.

Kinematic viscosity (mm ² s ⁻¹)	BCAOM (BE)	BCAOI (BE)	BCAOE (BE)	BCAOM (AE)	BCAOI (AE)	BCAOE (AE)
Average	6.01 ± 0.01	5.80 ± 0.01	6.200 ± 0.003	11.10 ± 0.01	-	22.60 ± 0.02

From Tab. 8, it was possible to observe that the biodiesel obtained through castor oil was within the limits of standard legislation⁴, except for biodiesel from castor oil with ethanol, which presented a value above the limit of 6.0 mm² s⁻¹. A viscosity above the limit is detrimental because some parts of the engine do not receive the necessary flux to

form the lubricating film, which can result in more wear, accelerating the oxidation and shortening the life of the equipment, as explained by Farias *et al.*⁵. Regarding the biodiesel analyzed after the engine, the kinematic viscosity values increased, but not excessively, as expected.

Table 9 . Kinematic viscosit	v analy	vsis ir	hindiese	l derived	from	rice	oil
Lable 7. Exhibiting viscosit	y anar	y 51 5 11	i bibuicse	i uciivcu	nom	ncc	on.

Kinematic viscosity (mm ² s ⁻¹)	BROM (BE)	BROI (BE)	BROE (BE)	BROM (AE)	BROI (AE)	BROE (AE)
Average	6.10 ± 0.01	3.60 ± 0.01	8.90 ± 0.02	5.14 ± 0.01	10.12 ± 0.01	-

From Tab. 9, it was possible to observe that the biodiesel derived from rice oil were within the limits of the Brazilian legislation⁴, except for the rice oil with ethanol that presented divergent values, well above the expected, being considered a lubricant able to wear the parts of the engine and

cause oxidation in a shorter time. After the engine, the results are also as expected, with kinematic viscosity increasing.

Biodiesel from coconut oil with isopropanol, castor oil with isopropanol, and rice with ethanol were not analyzed in the engine because of their low reaction yields, making it impossible to produce more due to the quantity of reagents available.

3.4. Qualitative test for the detection of metals

The metal detection test analyses are listed in Tabs. 10, 11 and 12 below. They were performed in triplicate and the results were given by the average.

Table 10. Analysis of the presence of metals in biodiesel derived from coconut oil.

Presence or absence of metals	восм	BOCI	BOCE	
Average	Absent	Absent	Absent	

Table 11. Analysis of the presence of metals in biodiesel derived from castor oil.

Presence or absence of metals	BORM	BORI	BORE	
Average	Absent	Absent	Absent	

Table 12. Analysis of the presence of metals in biodiesel derived from rice oil.

Presence or absence of metals	BOAM	BOAI	BOAE	
Average	Absent	Absent	Absent	

The results obtained in Tabs. 10, 11 and 12 were satisfactory since the presence of metals could impair engine performance⁵. It is important to point out that this is a qualitative analysis. To be sure, it is necessary to carry out more restricted analyses, such as atomic absorption.

3.5. Infrared

The major bands for biodiesel are given in Tab. 13.

	Table 13.	The main	infrared	bands for	the	biodiesel	obtained.
--	-----------	----------	----------	-----------	-----	-----------	-----------

Compounds	ν C-H _{alif.} (cm ⁻¹)	ν C=O (cm ⁻¹)	νC-O (cm ⁻¹)
BOCM	2853	1740	1495
BOCI	2853	1664	1395
BOCE	2853	-	1435
BORM	2854	1685	1451
BORI	2853	-	1453
BORE	2853	1654	1451
BOAM	2853	-	1454
BOAI	2854	1667	1460
BOAE	2853	1668	1462

From the analysis of the infrared spectra, it was possible to observe in all biodiesel the presence of bands characteristic of carbonyls (C=O), aliphatic C-H and C-O ester. According to Barbosa¹⁹, a band in the range of 1650 to 1750 cm⁻¹ indicates axial deformation of the carbonyl C=O bond. In addition, the presence of bands between 2853 and 2854 cm⁻¹ indicates an aliphatic C-H band; and in the range of 1390 to 1500 cm⁻¹ correspond to ester C-O.

In this case, the characteristic bands of aliphatic C-H and C=O of carbonyl correspond to the starting vegetable oil, whereas the band referring to the ester C-O bond indicates the formation of the desired product, biodiesel. In this way, the infrared appears as another way of confirming that the product (biodiesel) was obtained through the starting vegetable oil. In the absence of the ester C-O band, there would be no conversion of triacylglyceride to ester, having only the starting vegetable oil, not biodiesel.

This can be observed in Fig. 1. The other spectra are not shown, since the three characteristic bands, which are the bands to emphasize in the work, are the same for all biodiesels, only occurring displacements due to the alcohol of departure of the reaction.



Figure 1. BOCM Infrared spectrum

4. Conclusions

Nine esters (biodiesels) were synthesized from transesterification reactions, varying the vegetable oils and the starting alcohols. These biodiesels were characterized by physicochemical analyses in order to confirm their formation and the characteristic properties of biodiesel, meeting the requirements of the National Agency for Petroleum, Natural Gas and Biofuels.

The biodiesel obtained also had its kinematic viscosity analyzed before and after the engine, demonstrating a similar profile to commercial engine lubricants, being good substituents.

Although biodiesel produced from coconut oil has good reaction yields, it is not intended to act as lubricants in the engine as it tends to solidify at temperatures below 25 °C and can cause engine parts to wear with particle adhesion in suspension.

Biodiesel derived from isopropyl alcohol is not economically viable to produce lubricants because of the poor performance to obtain it, and many reactions are necessary to obtain the necessary lubricant for the engine.

However, it was observed that the majority of biodiesel obtained have promising results to act as substituents of commercial lubricants, which fill a gap in the scientific literature.

5. Acknowledgments

To Univiçosa – Faculty of Sciences and Technology of Viçosa, for the scholarship of undergraduate research.

6. References

[1] Manieniyan, V., Senthilkumar, R., Sivaprakasam, S., Comparative wear analysis in a di diesel engine using diesel and biodiesel, International Journal of Modern Trends in Engineering and Research 2 (1) (2015) 119-124.

[2] Stepien, Z., Urzedowska, W., Czerwinski, J., Research on engine lube oil deterioration and emissions of diesel engines with biofuels (RME), Energy and Power 4 (1) (2014) 32-49. https://doi.org/10.4271/2011-01-1302.

[3] Oliveira, D. M. de, Ongaratto, D. P., Fontoura, L. A. M., Naciuk, F. F., Santos, V. O. B. dos, Kunz, J. D., Marques, M. V., Souza, A. O. de, Pereira, C. M. P. de, Samios, D., Transesterification double step process for biodiesel preparation and its chromatographic characterization: oils and fats in practical organic chemistry, Química Nova 36 (5) (2013) 734-737. https://doi.org/10.1590/S0100-40422013000500021.

[4] ANP. National Agency of Petroleum, Natural Gas and Biofuels. ANP Resolution 45 (2014). http://legislacao.anp.gov.br/?path=legislacao-anp/resolanp/2014/agosto&item=ranp-45--2014.

[5] Farias, A. M., Santana, J. S., Oliveira Filho, M. F., Santana, J. S., Barbosa, C. R. F., Medeiros, J. T. N., Os combustíveis verdes do brasil - avaliação da lubricidade do biodiesel B5 e óleos de mamona e coco, Holos 3 (27) (2011) 3-17. https://doi.org/10.15628/holos.2011.453.

[6] Wagner, H., Luther, R., Mang, T., Lubricant base fluids based on Renewable Raw Materials. Their Catalytic Manufacture and Modification, Applied Catalysis A: General 221 (1-2) (2001) 429-442. https://doi.org/10.1016/S0926-860X(01)00891-2.

[7] Caines, A. J., Haycock, R. F., Automotive Lubricants Reference Book, SAE International and Professional Engineering Publishing, Pennsylvania, 2rd ed., 2004, ch1.

[8] Geris, R., Santos, N. A. C. dos, Amaral, B. A., Maia, I. S. de, Castro, V. D., Carvalho, J. M., Soybean biodiesel - transesterification reaction to practical classes of organic chemistry, Química Nova 30 (5) (2007) 1369-1373. https://doi.org/10.1590/S0100-40422007000500053.

[9] Lôbo, I. P., Ferreira, S. L. C., Cruz, R. S. da, Biodiesel: quality parameters and analytical methods, Química Nova 32 (6) (2009) 1596-1608. https://doi.org/10.1590/S0100-40422009000600044.

[10] Soares, B. G., Souza, N. A., Pires, D. X., Organic Chemistry: Theory and Techniques of Preparation, Purification and Identification of Organic Compounds, Guanabara, Rio de Janeiro, 1988, ch.1.

[11] Machado, G. C., Chaves, J. B. P., Antoniassi, R., Composição em ácidos graxos e caracterização física e química de óleos hidrogenados de coco babaçu/ physical and chemical characterization and fatty acid composition of babassu oil, Revista Ceres 53 (308) (2006) 463-466.

[12] Costa Neto, P. R., Rossi, L. F. S., Zagonel, G. F., Ramos, L. P., Production of alternative biofuel to diesel oil through the transesterification of soybean oil used in frying, Química Nova 23 (4) (2000) 531-537. https://doi.org/10.1590/S0100-40422000000400017.

[13] Oliveira, R. S., Borges, M. F., Vieira, A. T., Henrique, M. A., Ribeiro, E. A. M., Bezerra, F. A., Portela, F. M., Pereira, N. R., Assunção, R. M. N., Ruggiero, R., Adsorption of biodiesel contaminants by surface modified bagasse fibers, Química Nova 41 (2) (2018) 121-128. https://doi.org/10.21577/0100-4042.20170164.

[14] Lace, V. O., Fraga, I. M., Fernandez, J. R. C., Gonçalves, C. R., Obtaining of methyl biodiesel through transesterification through basic catalysis of coconut oil (Cocos Nucifera L), Eclética Química Journal 39 (1) (2014) 192-199. https://doi.org/10.26850/1678-4618eqj.v39.1.2014.p192-199.

[15] Nascimento, U. M., Vasconcelos, A. C. S., Azevedo, E. B., Silva, F. C., Optimization of biodiesel production from babassu coconut oil with microwave heating, Eclética Química Journal 34 (4) (2009) 37-48.

https://doi.org/10.26850/1678-4618eqj.v39.4.2009.p37-48.

[16] Shimada, Y., Watanabe, Y., Sugihara, A., Tominaga, Y., Enzymatic alcoholysis for biodiesel fuel production and application of the Reaction to oil processing, Journal of Molecular Catalysis B: Enzymatic 17 (3-5) (2002) 133-142. https://doi.org/10.1016/S1381-1177(02)00020-6.

[17] Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Comparison of the performance of differente homogeneus álcali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality, Fuel 87 (17-18) (2008) 3572-3578. https://doi.org/10.1016/j.fuel.2008.06.014.

[18] Charoenchaitrakool, M., Thienmethangkoon, J., Statistical optimization for biodiesel production from waste frying oil through two-step catalyzed process/ Fuel Processing Technology 92 (1) (2011) 112-118. https://doi.org/10.1016/j.fuproc.2010.09.012.

[19] Barbosa, L. C. A., Espectroscopia infravermelha na caracterização de compostos orgânicos, Editora UFV, Viçosa, 2013.