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STUDY OF THE OXIDATION OF AUTOMOTIVE LUBRICANTS CONTAMINATED WITH BIODIESEL AND BLENDS

Maria Thereza dos Santos Silva
Salete Martins Alves
salete.martins@gmail.com

Raíssa Maradja Kadydja Silva
raissa.mk@hotmail.com

Ranaildo Gomes da Silva
Universidade Federal do Rio Grande do Norte, Department of Mechanical Engineering, Natal, RN, Brazil.
ranaildobandeira@gmail.com

Abstract. *The use of biodiesel as a fuel can cause wear to the internal parts of the engine because it comes in contact with lubricating oil and causes an increase in the rate of oxidation of the lubricant, thus causing it to not perform its function. There is great use of biodiesel in the world, but the effects of this fuel on the performance of lubricating oil must be investigated. This study investigated the presence of biodiesel in the condition of lubricating oil, monitoring the contact time. Methyl soybean biodiesel samples (B100) and diesel biodiesel blends (B10 and B20) were used as contaminant for 15W40 oil lubricant, the percentage of contamination was 1% and 2%. Oxidative stability was measured by the acid index, differential scanning calorimetry (DSC) and confirmed by infrared spectroscopy (FT-IR) technique. The acidity index increased proportionally with the proportion of the presence of the contaminant. The DSC curves showed oxidation peaks and the spectra indicated low intensity signals and bands, but showed the presence of carbonyl and alkanes, oxidation products. However, lubricants contaminated with biodiesel in small quantities and exposed to natural environmental conditions have small signs of oxidative degradation, resulting in a shorter service life.*

Keywords: *Lubricant, Contamination, Biodiesel, Blends, Oxidation.*

1. INTRODUCTION

Amid concerns about environmental and energy issues, several countries have opted for using biodiesel as fuel replacing diesel, because of their similarity in physical properties. Its use in Brazil is already a reality, and it can be found diluted in commercial diesel in 8% by volume. There are laws that guarantee that each year this percentage increases (Law nº 13.263/2016). However, there are few studies that show the effects caused by their use as fuel in the engines' operation.

Biodiesel is an ester and has different chemical properties than diesel. Biodiesel can contaminate the lubricant oil during engine operation, where the fuel reaches the crankcase due to small leaks in the rings (Gulzar *et al.*, 2016). However, the fuel may remain in contact with the lubricating oil for a long period, causing deterioration of the lubricant, reducing its ability to lubricate.

Biodiesel has the ability to oxidize, therefore its contact with the lubricating oil causes auto-oxidation in the lubricant, and this is due to the presence of double bonds in the fatty acid chains, so the allylic carbons present a greater susceptibility to oxidation (Knothe *et al.*, 2006). This oxidation has a mechanism that goes through three stages, starting with the formation of free radicals in the allylic carbon, then these radicals react with the oxygen forming peroxides and with the hydrogens forming hydroperoxides, in this way new free radicals arise, increasing the mass of the acids and end up reacting with each other.

Some works were carried out to study the effect of the biodiesel presence in the lubricat oil. Agarwal, (2007) removed the lubricating oil from the engine and found a perceptual of biodiesel, and these oil were oxidized. Therefore, due to the oxidation suffered by the lubricating oil, it believes that there were chemical interactions with the biodiesel. Shanta *et al.* (2011) analyzed the effect of this dilution and verified the reduction of the anti-wear protection layer, even in the presence of small quantities of biodiesel. Gulzar *et al.* (2016) proved that the acceptable mixture should be lower to 20% biodiesel diluted in the fuel, since above the additives of the lubricants are depleted and no longer perform their protection function.

However, this work investigates the effects of oxidation of lubricants, due to biodiesel contamination in function of contact time and biodiesel percentage. This study intends to understand by chemical analysis the oxidation level of lubricant oil contaminated with the biodiesel and its blends.

2. EXPERIMENTAL PROCEDURE

In this study, the commercial mineral oil SAE 15W40 was used, three biodiesel-diesel blends were used to contaminate the lubricant in the percentages of 1% and 2% of contaminants. To obtain the three blends it was necessary to synthesize the biodiesel, being obtained through this transesterification reaction (Silva *et al.,* 2013). However the reagents were chosen, taking into account the conditions used in the Brazilian reality. The procedure started with the preparation of a potassium methoxide solution, the potassium hydroxide (KOH) being dissolved in methanol under stirring and controlling the temperature at 45°C. Thereafter, the soybean oil (feedstock) was added under agitation and controlled temperature, the process remained for about 50 minutes and at the end complete phase separation was obtained by decantation, about 12 hours. After its production, Biodiesel was neutralized, washed and purified.

The blends were prepared with diesel (S 10) purchased at gas stations and the biodiesel synthesized, the biodiesel percentage was of 10% (B 10), 20% (B 20) and 100 % (B100). It is known that in commercial diesel, in Brazil, there is already 7% biodiesel, so it was necessary to calculate the exact amount of biodiesel to be added, to arrive at the correct percentages of the blends.

The choice of SAE 15W40 mineral commercial lubricating oil was achieved through its wide use in domestic combustion vehicles in Brazil. This mineral oil was contaminated with 1% and 2%, this percentage was based on Kimura (2010), with B10, B20 and B100. The samples of contaminated lubricants were named as follows: LP: Pure Lubricant; L 10-1: Lubricant with 1% Biodiesel contamination B10; L 10-2: Lubricant with 2% Biodiesel contamination B 10; L 20-1: Lubricant with 1% B 20 Biodiesel contamination; L 20-2: Lubricant with 2% B 20 Biodiesel contamination; L 100-1: Lubricant with 1% B 100 Biodiesel contamination; L 100-2: Lubricant with 2% B 100 Biodiesel contamination.

The acidity value of the samples was measured immediately after being contaminated and after six months, following the ASTM D-664 standard. The amount of 7 g of each sample was weighed, 75 ml of the ether-alcohol solution (2:1) and three drops of phenolphthalein were added, then used to titrate a solution of 0,1 M sodium hydroxide (NaOH) to obtain a pink coloration. From the volume of NaOH spent in the titration, it was possible to have enough information to solve the calculation in obtaining the acid number.

The samples were analyzed by Fourier Transform Infrared (FT-IR) spectroscopy in order to understand the behavior of the organic functional groups present in lubricant, and the changes in the chemical composition over time. It was necessary 0,4 mL of each sample and was taken to the BRUKER spectrometer cuvette, model FT-IR VERTEX 70. These results were obtained by spectra in the range of 400-4000 cm^{-1} with 4 cm^{-1} resolution, measured in absorbance.

To understand the oxidative stability of the contaminated samples, it was used thermal analysis through Differential Exploration Calorimetry (DSC). The samples were aged at room temperature analyzed after 3 and 6 months. The DSC curves were obtained in simultaneous calorimeter, whose manufacturer is the TA Instruments and model SDTQ 600. The tests were carried out following the purge gas flow rate of 50 mL/min and the heating rate of 10 °C/min, with a final temperature of 700 °C. Only 7 mg of the sample was used in alumina crucibles under an atmosphere of Nitrogen.

3. RESULTS AND DISCUSSION

The effect of biodiesel contamination on lubricant oil was analyzed by acidity index, FTIR spectroscopy, and DSC curves, in order to identify the level of oxidation. Table 1 shows the results of acidity index, it is possible to compare the acid test results of biodiesel-contaminated lubricants after being contaminated and after six months.

The results showed that the lubricant after the contamination showed an acidity index within the standards, but after six months of contamination, the index increases to the limits established by the ANP of 0.05 mg KOH / g. The contact with biodiesel increases the acidity index and is proven according to the results, but the increase of acidity did not have a direct relation with the level of contamination, nevertheless showed that the presence of biodiesel increases acidity in contact by time. However, when the acidity rate is high, it causes a low alkalinity reserve, allowing a longer lubricating life (Gulzar et al., 2016).

Table 1. Results of the acidity test of biodiesel contaminated lubricants.

Contamination		Acidity Index (zero days of Contamination) (mg KOH/g)	Acidity Index (six months of Contamination) (mg KOH/g)	Increased Acidity (%)
B 10	1%	0,017	0,052	35
	2%	0,012	0,051	39

B 20	1%	0,015	0,051	36
	2%	0,015	0,052	37
B 100	1%	0,015	0,052	37
	2%	0,019	0,053	34

Figure 1 shows Fourier Transform Infrared (FT-IR) spectra of the various biodiesel contaminated lubricant samples, from which they were monitored as a function of time, for comparison of the structural changes of the lubricants.

By analyzing the absorption spectra it was possible to verify the typical functional groups of the lubricant oil and especially the appearance of signs with the time after the contamination. Comparing the spectra's (Fig. 1a and 1b), it observed that there were no significant differences in the time of contamination and after six months, but there were slight displacements of the signals with peaks and bands of absorption with light intensity. These detachments appeared in the region of 1171 to 1740 cm^{-1}, showing formations of products of oxidation reactions.

In 1740 cm^{-1} there is a peak of axial deformation of carbonates (C=O), products of degradation of the oil, so it is possible to note that this peak is precisely in the sample of contaminant B 100, confirming that the higher biodiesel concentration promote the oxidation process. This oxidation is due to the biodiesel presence that increases acidity, favoring the degradation of antioxidants present in the lubricating oil composition (Gulzar *et al.*, 2016). In the region of 1171 to 1207 cm^{-1} the absorptions indicate a widening in the band referring to the alkanes group, which indicates initial stages of degradation of the lubricant oils (Natarajan and Yaakob, 2007).

The spectra revealed oxidation products from the contamination of the lubricant, so the samples of contaminant B 100, which contains higher biodiesel content, showed higher signal intensity, in which it allows the oxidation of the lubricant to be verified. However the signs were not so intense, it can still be concluded that after six months of the contamination there are oxidation products in the initial stage.

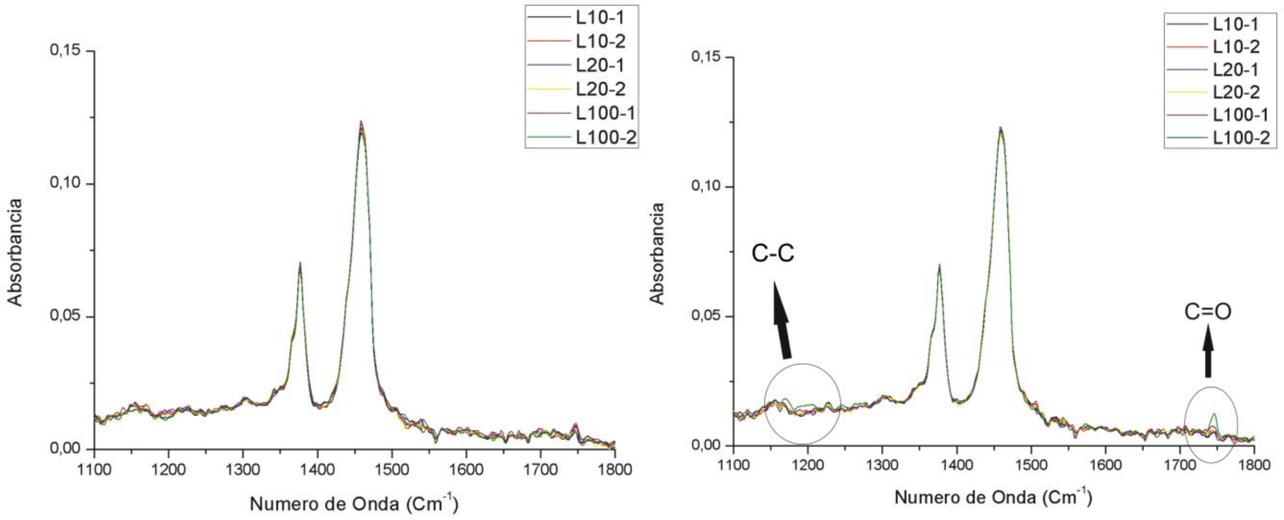

Figure 1. FT-IR Spectra of biodiesel contaminated lubricants. a) After the contamination; b) After six months of contamination.

The samples were also monitored through the energy variations, in order to observe changes in their chemical reactions over time (Figure 2). The DSC curves showed that the contaminated lubricants had a decrease in their oxidative stability, even subjecting the samples to an atmosphere of nitrogen occurred to the oxidation, due to the decomposition of the air in the atmosphere, referring to the processes of combustion of hydrocarbons (Santos *et al.*, 2004). Therefore, in the middle of an atmosphere of nitrogen, it was possible to verify that the samples oxidize.

In the Fig. 2a after three months of contamination it is possible to observe that all samples tend to have in the first exothermic transition, however, L20-1 presented only one endothermic transition, L100-1 and L20-2 had a first endothermic transition and second exotherm. The samples L10-1, L10-2, L100-2 presented the first exothermic transition stage linked to sample oxidation and a second endothermic transition being product volatilization. In the Fig. 2b after six months of contamination it is observed in all the samples that in the first exothermic transition turned to the oxidation of the product, a second endothermic transition and a third exotherm due to the combustion. The oxidation indicated by DSC curves corresponds to different phases of oxidation mechanism.

A three-month analysis is compared as propagation and branching steps, in which there is an increase of oxidation with the intense peaks, especially in the samples that have exothermic transmissions. After six months for an observation of a finishing phase, where the hydroperoxides do not remain more stable, then a lower oxidation peak and a rapid decomposition are obtained.

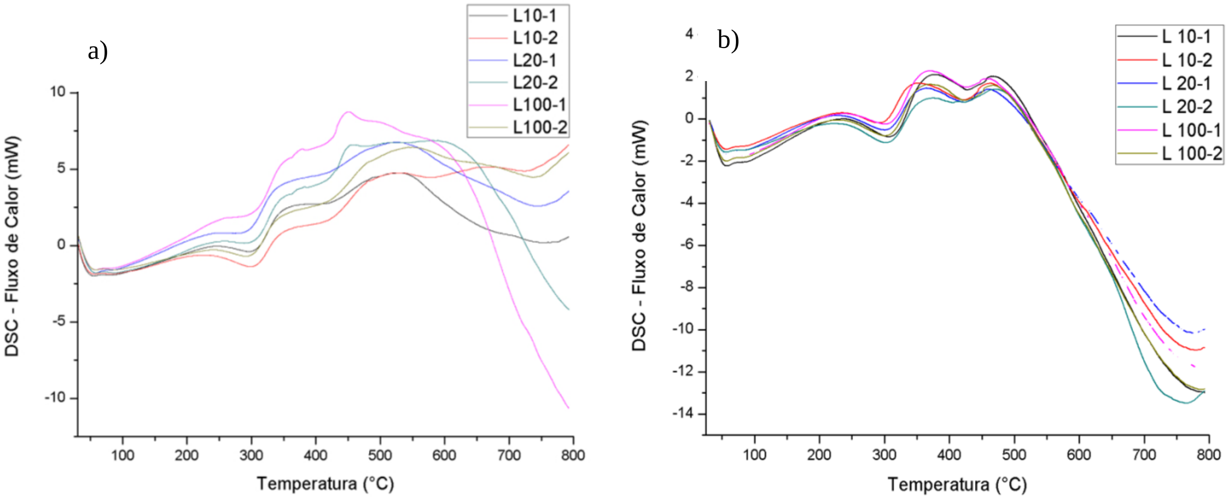

Figure 2. DSC Curves of Biodiesel Contaminated Lubricants. a) After three months of the contamination; b) After six months of contamination.

For the oxidizing lubricant it is necessary to condition it at high temperatures and to add metallic particles, in this way the oxidation process is accelerated, and both act as catalysts accelerating the degradation of the lubricants (Lopes and Carvalho, 2007). However, even with the presence of additives in its composition and small percentages of biodiesel, after exposure under natural conditions presented oxidative degradation, which was verified through this study.

4. CONCLUSIONS

This study presented results that characterize the oxidative stability of the mineral lubricant oil contaminated with biodiesel and blends in small percentages. It was possible through these analyzes to trace the behavior of these lubricants when they are in contact with the biodiesel. From the acidity index of the contaminated lubricants, it was possible to verify that the rate proportionally increased the presence of biodiesel. Regarding the chemical analysis, the FTIR spectra presented peaks and bands of low intensity, but showed the presence of carbonyl and alkanes, products of oxidation. The curves of DSC showed oxidation peaks that describes the phases of the oxidation mechanism. According to results, the presence of biodiesel as contaminant accelerate the oxidation process. It was not observed a linearity in the oxidation as to the percentage of contamination, but the contamination increased with the presence of biodiesel. Therefore, lubricants contaminated with in small amounts of biodiesel and its blends and exposed to natural environmental conditions showed signs of oxidative degradation. This results in a shorter useful life, in other others, the presence of biodiesel in lubricating oils accelerates its degradation and consequently decreases the oxidative stability over time.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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