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Pseudo-Oxidation In Lubricants Induced by FAME

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Abstrak
Aplikasi biodisel di Indonesia menjadi satu keniscayaan yang di setiap periode mengalami kenaikan persentase dari mulai B2.5, B10, B15, B20, B30 hingga B35 dan bahkan kemungkinan hingga B100. Pengaplikasian biodiesel di segala segmen seperti perkapalan, pertambangan hingga pembangkit listrik memiliki isu- isu teknis yang selalu menarik untuk dikaji oleh banyak peneliti di dunia. Dalam makalah ini dipaparkan kajian eksperimen tentang potensi terjadinya fenomena pseudo - oxidation atau oksidasi semu dalam pelumas akibat adanya kontaminasi biodiesel dalam pelumas yang kemungkinan terbaca sebagai oksidasi di pengujian FTIR. Hal tersebut dapat terjadi diakibatkan kandungan Fatty Acid Methyl Ester (FAME) dalam biodiesel dan produk oksidasi pelumas memiliki gugus C=O (carbonyl) yang identik sehingga kemungkinan wavenumber yang terdeteksi diantara FAME dan oksidasi dapat saling mempengaruhi interpretasi satu sama lain. Oleh karena itu, studi eksperimental sangat penting untuk menyederhanakan interpretasi sampel pelumas yang sedang digunakan dan berpotensi terkontaminasi biodiesel. Dengan melakukan eksperimen yang terkontrol, akan lebih mudah membedakan antara oksidasi sebenarnya dan efek pseudo-oksidasi yang disebabkan oleh kontaminasi biodiesel. Hal ini sangat krusial untuk memastikan pemantauan kondisi yang tepat serta strategi pemeliharaan yang efektif dalam berbagai aplikasi industri.

Kata kunci: *Pelumas, Biodiesel, Oksidasi, FAME, FTIR.*

Abstract
The application of biodiesel in Indonesia is a necessity that in each period experiences an increase in percentage beginning from B2.5, B10, B15, B20, B30 to B35 and even possibly up to B100. The application of biodiesel in all segments, such as shipping, mining, and power plants, has technical issues that are always interesting to be studied by many researchers in the world. This paper presents an experimental study on the potential for pseudo-oxidation phenomena in lubricants due to biodiesel contamination in lubricants, which is likely to be read as oxidation in FTIR testing. This can occur due to the Fatty Acid Methyl Ester (FAME) content in biodiesel and lubricant oxidation products having identical C=O (carbonyl) groups so that the possibility of wavenumbers detected between FAME and oxidation can influence each other's interpretation. Therefore, experimental studies are essential to simplify the interpretation of used lubricant samples that may be contaminated with biodiesel. By conducting controlled experiments, it becomes easier to distinguish between actual oxidation and the pseudo-oxidation effect caused by biodiesel contamination. This is crucial to ensure accurate condition monitoring and effective maintenance strategies in various industrial applications.

Keywords: *Lubricant, Biodiesel, Oxidation, FAME, FTIR.*

1. INTRODUCTION

Biofuel applications are one of the most promising alternative fuels and the development of its technology has been so exciting. There is almost no country in the world that does not implement (obligation) the use of biofuel (Tomo, 2015). In Indonesia, biofuel applications generally use biodiesel and there have been many studies conducted on the effects of biodiesel use on the properties and performance of engine lubricants. This research is motivated by observations of phenomena that occur in the field, namely that there are often indications of a fairly drastic decrease in viscosity in biodiesel-fueled diesel engine oil, but at the same time there is an interpretation of high oxidation that exceeds the limit with a low drain interval. This is quite out of the norm, because in theory, oxidation should increase viscosity (Fitch, 2015), but what happens in the field is the opposite. One thing that is of concern is the possibility of fuel contamination causing a decrease in viscosity, although there is a possibility that the application of biodiesel causes change in the oxidation stability of the lubricant (Kovač, et al, 2013), but in this case considering the relatively minimal drain interval of around 250 hours, there is a gap for misinterpretation. This phenomenon may occur even at operating hours below 250 hours, as fuel dilution conditions are also influenced by the overall health of the engine itself. The gap for misinterpretation refers to the possibility of misidentifying the root cause as either fuel dilution or oxidation. These two interpretations carry different consequences and root causes in machine maintenance, making it crucial to accurately diagnose the issue to implement the correct maintenance strategy.

Oxidation in mineral lubricants produces compounds including aldehyde, ketone, ester, and carboxylic acid, having a wavenumber range of 1800-1670 cm^{-1} (ASTM E2412-23a); in more specific literature, it mentions that oxidation is at wavenumbers around 1750 cm^{-1} and 1740 cm^{-1} (Wright, 2015). While FAME has wavenumber range of 1800-1692 cm^{-1} and 1327-940 cm^{-1} (ASTM D7371-14), in contrast, diesel fuel has a wavenumber range of 815-808 cm^{-1} (ASTM E2412-23a). In other literature, it is more specifically mentioned that FAME has a wavenumber of 1745 cm^{-1} (CIMAC, 2024) and 1740 cm^{-1} (Araújo, 2011).

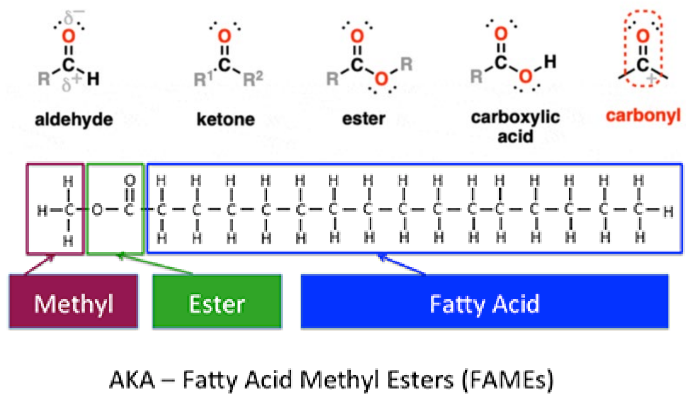

Figure 1. Structure of oxidation compounds of aldehyde, ketone, ester, carboxylic acid (Clifford. (n.d.))& FAME (Forsyth. (2010)).

In the author's perspective, the wavenumber produces a hypothesis about the potential for overlapping or masking, or interference between FTIR FAME readings and oxidation because they are in the same wavenumber range due to the identical carbonyl group (C=O) in the ester compound. While the decrease in viscosity is caused by biodiesel contamination in the lubricant during operation. The study aims to prove the effect of biodiesel FAME contamination on the confusion of oxidation interpretation in lubricant analysis. The results of this study are very important because errors in interpretation between biodiesel contamination or oxidation, result in different consequences of actions in engine maintenance activities.

Table 1. Variation of FTIR Wavenumber Reference for Oxidation Product & FAME

Component	Wavenumber (cm^{-1})	Sources
Oxidation	Oxidation A – (1800–1660)	ASTM E2412
Oxidation	Oxidation B – (1685–1725)	ASTM E2412
Oxidation	1740	Wright (2015)
Oxidation	1750	Wright (2015)
Carboxylic Acid	1725–1700	Coates (2000), Nandiyanto (2019)
Ketone	1725–1705	Coates (2000), Nandiyanto (2019)
Aldehyde	1740–1725	Coates (2000), Nandiyanto (2019)
Ester	1750–1725	Coates (2000), Nandiyanto (2019)
Biodiesel	1800–1692	ASTM D7371
Biodiesel	1327–940	ASTM D7371
FAME	1740	Araújo (2011)
FAME	1745	CIMAC (2024)

2. METHODOLOGY

A. Material

In this study, the lubricant sample used the ISO VG 46 hydraulic oil type, considering that the spectrum of hydraulic oil is simpler than engine oil. In addition, the forced oxidation process is expected to produce peak wavenumbers faster because of the simpler additive composition. Meanwhile, the biodiesel fuel sample used B35 containing 35% FAME.

B. Experimental Method

This experiment focuses on two things, including the effect of biodiesel contamination on changes in the fresh oil spectrum and the effect of biodiesel contamination on changes in the oxidized oil spectrum. This experiment was inspired by the study of Kovač et al. (2013) on the influence of biodiesel on the oxidation stability of engine oils, but with a different purpose. The stages of this experiment include:

1. Preparation of fresh oil samples
2. Preparation of contaminated fresh oil samples. Fresh oil + 1% B35, fresh oil + 2% B35, fresh oil + 3% B35, and fresh oil + 4% B35
3. FTIR, viscosity, and TAN testing
4. Preparation of oxidized oil samples (fresh oil and heating media, copper wire catalyst, and room air)
5. Monitoring conditions after heating until the oxidation peak and physical symptoms of lubricant oxidation appear for 13 days
6. FTIR, viscosity, and TAN testing of fresh oil
7. Preparation of contaminated oxidized oil includes oxidized oil + 1% B35, oxidized oil + 2% B35, oxidized oil + 3% B35, and oxidized oil + 4% B35.
8. FTIR, viscosity, and TAN testing of oxidized oil
9. Data processing includes reading FTIR interpretation numbers and processing wave spectrum data.
10. Making conclusions

The hypothesis of this experiment tests is biodiesel contamination can cause pseudo-oxidation effects in FTIR interpretation. The study begins with preparing fresh oil samples as a reference, followed by controlled contamination with 1%, 2%, 3%, and 4% B35 biodiesel. These samples undergo FTIR, viscosity, and TAN testing. Oxidized oil samples are then prepared using heat, copper wire as a catalyst, and room air, with oxidation monitored over 13 days. Once oxidation peaks, FTIR, viscosity, and TAN tests are conducted. To analyze contamination effects on oxidized oil, 1%–4% B35 biodiesel is added, followed by the same tests. Finally, FTIR spectra and wave spectrum data are analyzed to determine whether biodiesel contamination influences oxidation readings, leading to potential misinterpretations. The results provide insights into the pseudo-oxidation phenomenon and its impact on lubricant condition monitoring.

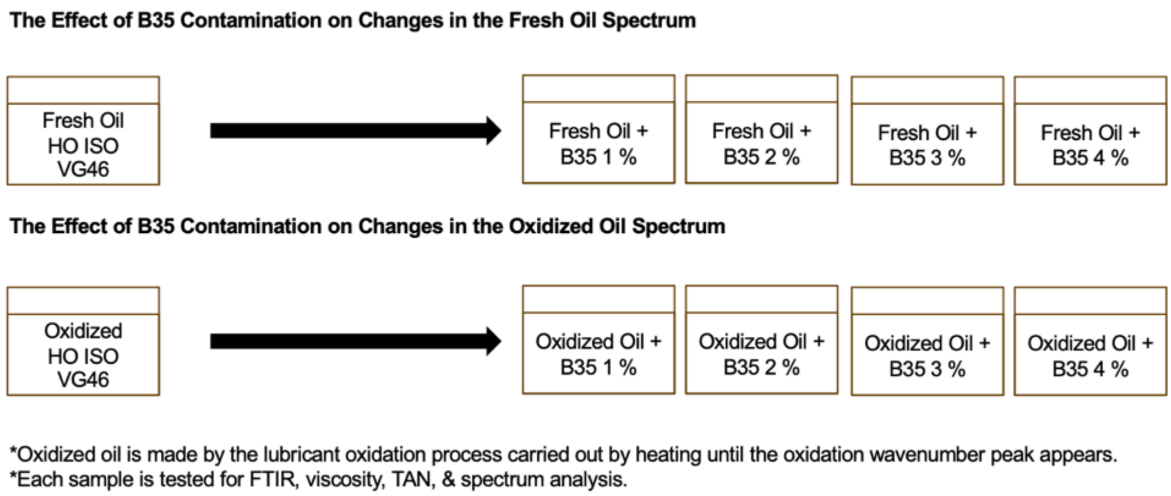

Figure 2. Hypothesis proof experiment

3. RESULTS AND DISCUSSION

A. The Effect of B35 Contamination on Fresh Oil Spectrum

Table 2. Results of the interpretation of the experiment on the effect of B35 contamination on fresh oil

Sample	RESULT								
	Soot (abs/ 0.1 mm)	Fuel (% vol)	Nitration (abs/0.1 mm)	Oxidation (abs/0.1 mm)	Sulfation (abs/0.1 mm)	Water (% vol)	TAN (mg KOH/ g)	Kinematic Viscosity 100 °C (cST)	Kinematic Viscosity 40 °C (cST)
Fresh Oil	0,00	0,00	0,00	0,00	0,00	0,00	0,509	6,996	45,1
Fresh Oil + 1% B35	0,00	0,65	0,00	0,11	0,01	0,00	0,484	6,897	43,42
Fresh Oil + 2% B35	0,00	1,04	0,00	0,22	0,02	0,00	0,480	6,748	41,71
Fresh Oil + 3% B35	0,00	1,55	0,00	0,32	0,03	0,00	0,474	6,605	40,25
Fresh Oil + 4% B35	0,00	1,80	0,00	0,43	0,05	0,00	0,465	6,486	38,85

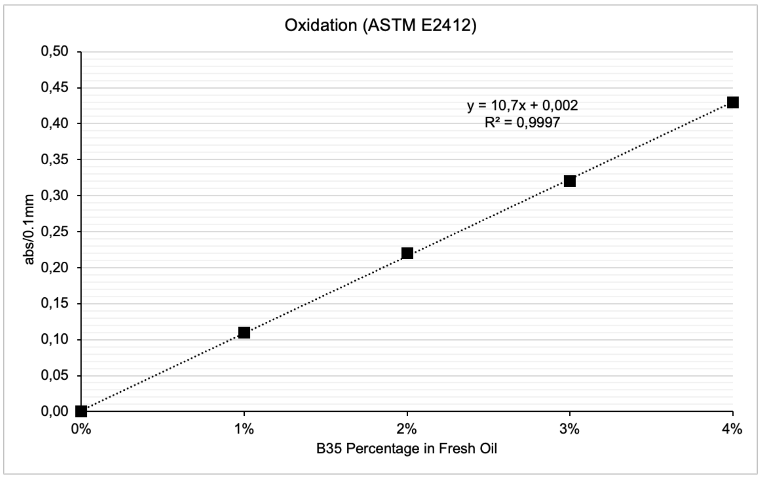

Figure 3. Graph of the effect of B35 contamination on FTIR oxidation readings

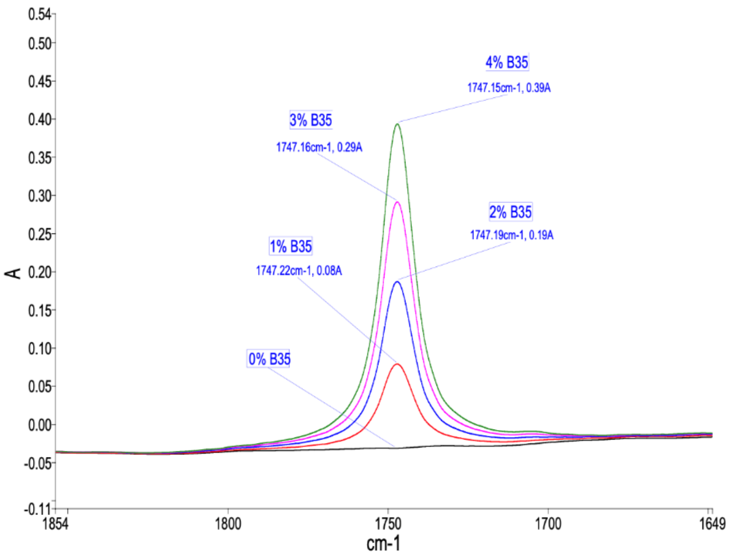

Figure 4. Visual in the spectrum range 1800 - 1670 cm-1

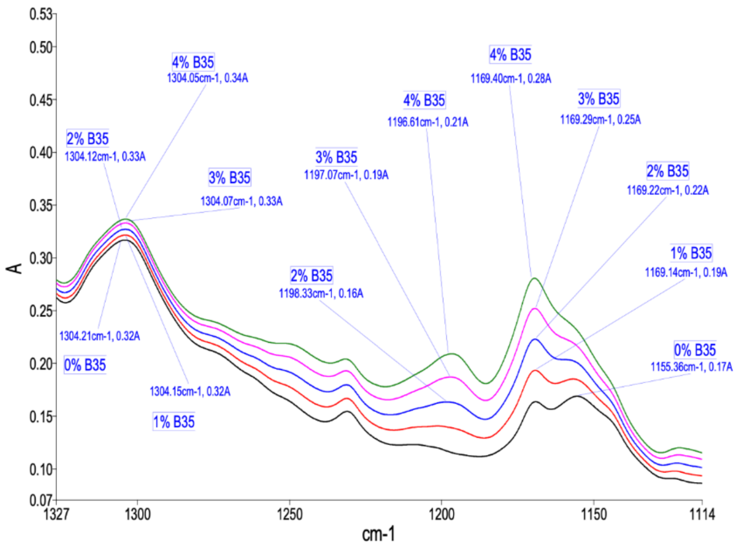

Figure 5. Visual in the spectrum range 1327 - 940 cm-1

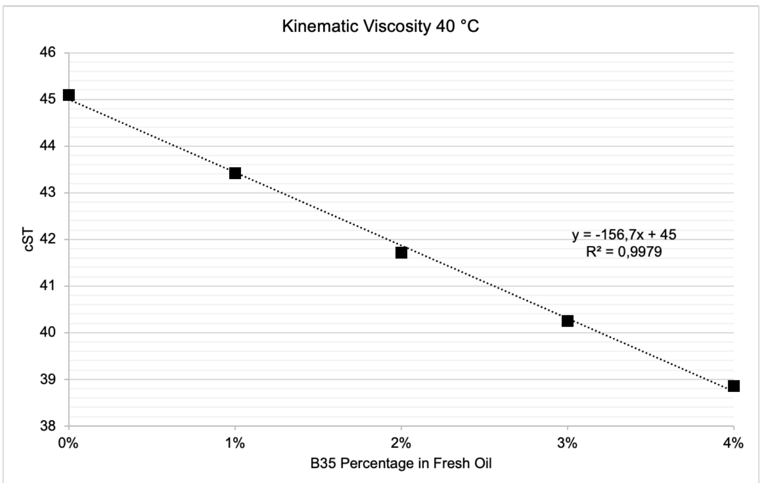

Figure 6. Graph of the effect of B35 contamination on viscosity change

The experimental results show that the higher the B35 contamination in the lubricant, the lower the kinematic viscosity. Meanwhile, the oxidation value reading increases along with the increase in B35 contamination (Table 2). These results prove the hypothesis that the occurring phenomena is likely pseudo-oxidation (not actual oxidation) because only the C=O (carbonyl) ester group of the FAME ester compound component is read as oxidation. In other parameters, TAN fresh oil appears to decrease after mixing B35, sulfation increases, and fuel dilution increases along with the increasing of B35 contamination.

Spectrum identification shows a linear increase around wavenumber 1747,1 cm^{-1}, which is a carbonyl ester group along with the increase in B35 contamination (Figure 4). The increase also occurs at wavenumbers 1304 cm^{-1}, 1197 cm^{-1}, and 1169 cm^{-1} (Figure 5). The data are in accordance with ASTM D7271-14, which states that the biodiesel spectrum is in the wavenumber spectrum of 1800-1692 cm-1 and 1327-940 cm-1. In this case, the observed wavenumber around 1747 cm^{-1} is also within the oxidation wavenumber range of 1800-1670 cm^{-1} based on ASTM E2412-23a.

B. The Effect of B35 Contamination on Change in the Oxidized Oil Spectrum

Table 3. Interpretation results of forced oxidation experiments of lubricants

Day	RESULT									
	Temp (°C)	Heating Duration (hours)	Soot (abs/ 0.1 mm)	Nitration (abs/0.1 mm)	Oxidation (abs/0.1 mm)	Sulfation (abs/0.1 mm)	Water (%vol)	Kinematic Viscosity 100 °C (cST)	Kinematic Viscosity 40 °C (cST)	TAN (mg KOH /g)
1	180–190	6	0,00	0,00	0,00	0,00	0,00	–	–	0,509
2	180–190	8	0,00	0,00	0,00	0,00	0,00	–	–	–
3	180–190	8	0,00	0,00	0,00	0,00	0,00	–	–	–
4	200–210	7	0,00	0,00	0,00	0,01	0,00	–	–	–
5	200–210	7	0,00	0,00	0,00	0,01	0,00	–	–	–
6	200–210	8	0,00	0,00	0,01	0,01	0,00	–	45,61	–
7	230–240	7	0,00	0,00	0,01	0,02	0,00	–	45,49	–
8	230–240	6	0,00	0,00	0,02	0,02	0,00	6,986	45,41	–
9	200–210	7	0,00	0,00	0,02	0,02	0,00	7,014	46,01	–
10	200–210	7	0,01	0,01	0,03	0,02	0,00	7,019	46,11	–
11	200–210	7	0,01	0,01	0,04	0,03	0,00	7,036	46,35	–
12	200–210	7	0,01	0,02	0,06	0,03	0,01	7,066	47,19	–
13	200–210	7	0,01	0,02	0,07	0,03	0,01	7,104	47,21	0,581

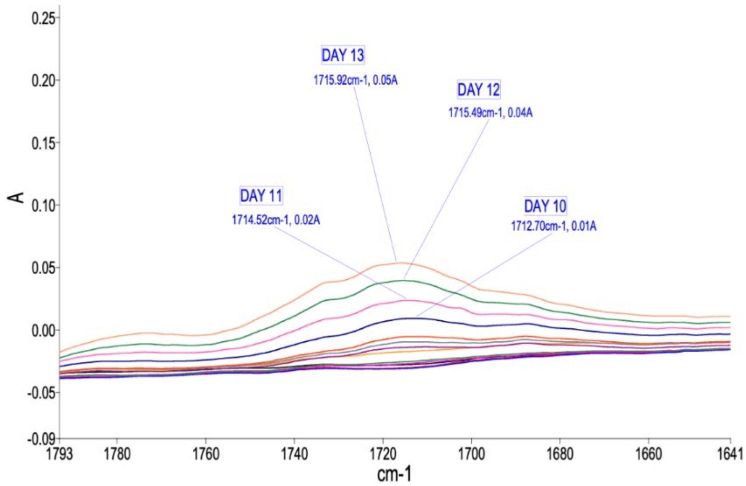

Figure 7. Peak at oxidation wavenumber (detected around 1715 cm-1) in the spectrum range 1800 - 1670 cm-1

The results of the lubricant oxidation efforts produced an increase in absorbance starting from day 6 after the heating process of 0,01 abs/0,1 mm and increasing slowly to 0,07 abs/0,1 mm on day 13 (Table 3). The spectrum reading on the FTIR, increased at around wavenumber 1715 cm^{-1} (Figure 7). According to Coates (2000), this wavenumber is likely to come from the carbonyl of the carboxylic acid type, or it could also come from ketones, both of which are types of oxidation products (Wooton, 2007). An increase also occurred in the viscosity parameter up to 2 cSt above fresh oil. In addition, there was an increase in the TAN value from 0,509 to 0,581 mgKOH/g. These results prove that the lubricant has indeed begun to oxidize.

The 13th-day sample that had undergone oxidation of 0,07 abs/0,1 mm was then contaminated with B35 with variations of 1%, 2%, 3%, and 4% to determine whether there was an effect of contamination on the oxidation value reading in the FTIR spectrum (Table 4).

Table 4. Interpretation results of B35 contamination experiments in oxidized oil

Sample	**RESULT**								
	Soot (abs/ 0.1 mm)	Fuel (% vol)	Nitration (abs/0.1 mm)	Oxidation (abs/0.1 mm)	Sulfation (abs/0.1 mm)	Water (% vol)	TAN (mg KOH/ g)	Kinematic Viscosity 100 °C (cST)	Kinematic Viscosity 40 °C (cST)
Oxidized Oil (0% B35)	0,01	0,00	0,02	0,07	0,03	0,01	0,581	7,22	47,62
Oxidized Oil + 1% B35	0,01	0,72	1,02	0,14	0,04	0,01	0,590	7,21	45,52
Oxidized Oil + 2% B35	0,01	1,01	2,02	0,24	0,05	0,01	0,620	6,81	43,93
Oxidized Oil + 3% B35	0,01	1,53	3,02	0,35	0,06	0,01	0,636	6,75	42,30
Oxidized Oil + 4% B35	0,01	1,96	4,02	0,44	0,07	0,01	0,670	6,51	42,16

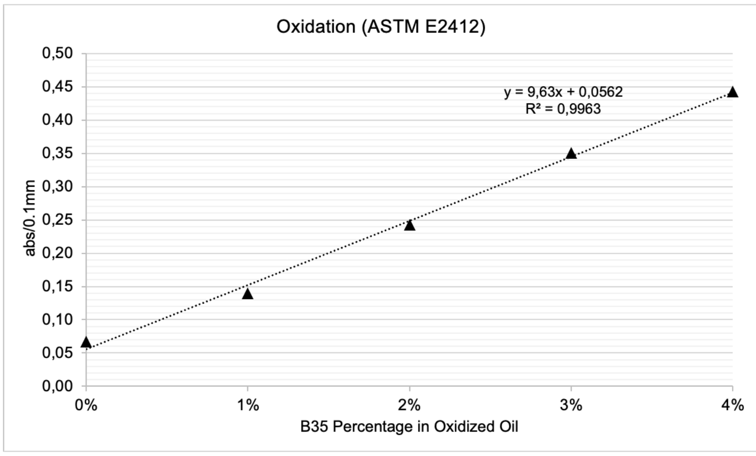

Figure 8. Graph of the effect of B35 contamination on FTIR oxidation readings

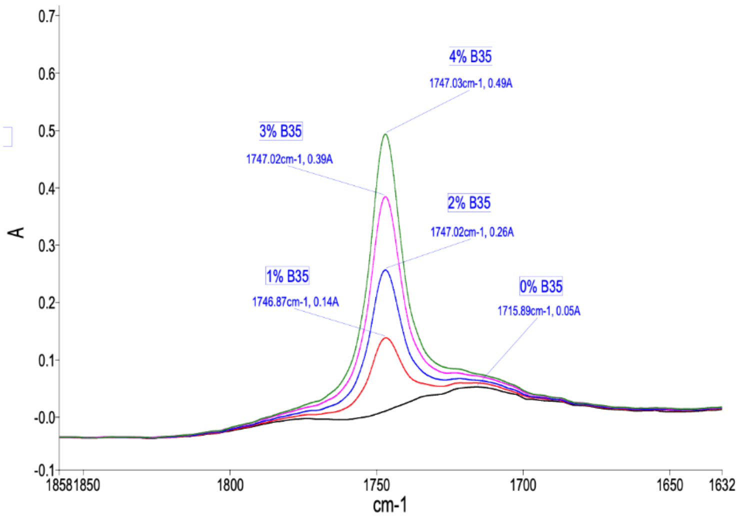

Figure 9. Peak at wavenumber in the range of 1800 -1670 cm-1 after being given B35 contamination

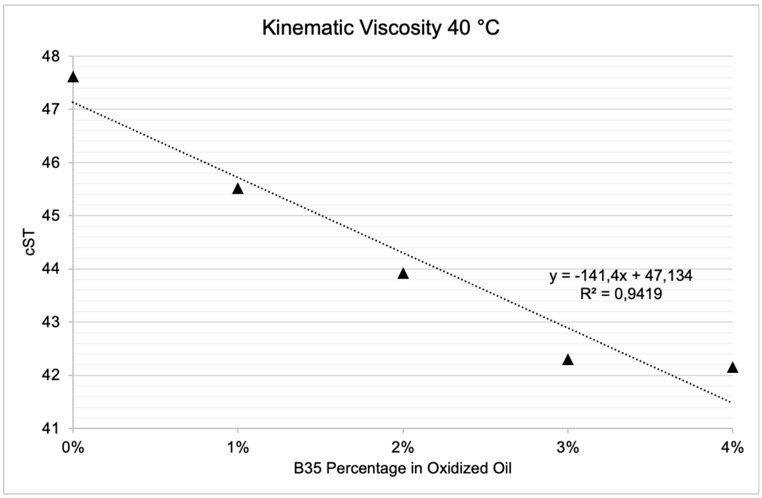

Figure 10. Graph of the effect of B35 contamination on viscosity change

The results of the B35 contamination experiment on oxidized oil showed that the oxidation value increased with a value similar to B35 contamination in fresh oil (Figure 8). The viscosity value in this experiment also showed a linear decrease with the increasing concentration of B35 contamination in oxidized oil (Figure 10). The pattern that appears is different from the TAN parameter. TAN testing showed that oxidized oil contaminated with B35 appeared to increase, compared to before being contaminated with B35. This is different from the TAN pattern shown in the fresh oil experiment (Table 2). This experiment proves the hypothesis made previously that FAME contamination in lubricants can affect the interpretation of oxidation readings in lubricants.

In the FTIR spectrum monitoring, appears to be an additional peak at the wavenumber around 1747 cm^{-1} as occurred in the fresh oil experiment (Figure 9). The emergence of the carbonyl ester peak from FAME causes the original oxidation peak around 1715 cm^{-1} to experience masking or interference so that the actual oxidation value is not readable and what is read as oxidation, is the peak that is actually the carbonyl ester of FAME.

However, although it is sufficient to answer the hypothesis of this case, according to the author, more experimental data is needed on where the peak variations in oxidation wavenumbers appear in various types of lubricants and oxidation methods so that identification can be more accurate.

4. CONCLUSION

Based on the analysis of experimental data, it can be concluded that the phenomenon of pseudo-oxidation or false oxidation is highly possible to occur during FTIR interpretation of biodiesel-fueled diesel engine used oil, if fuel dilution is present. So that to improve the quality of lubricant analysis interpretation, it needs to be done in more comprehensive analysis. In addition to affecting the FTIR oxidation reading, biodiesel contamination can also lead to a decrease in viscosity and affect the FTIR sulfation, TAN, nitration, and fuel dilution interpretation. Further research will be needed to obtain the most appropriate method so that the quality of used oil interpretation is satisfactory.

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