48 THE EFFECT OF OXIDIZED AND NON-OXIDIZED PALM OIL METHYL ESTER (POME) ON THE STABILITY PROPERTIES DURING TIME OF STORAGE

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ABSTRACT

Intensive research on biodiesel as alternative diesel fuel in transportation sector has been done for over 20 years. However, stability of the fuel is still a problem after being stored for a long time. This problem will affect to the performance and emissions of the engine. This study has been focused on the effects of oxidized the biodiesel from Palm Oil on their stability properties based on time of storage.

***Keywords*: Palm Oil Methyl Ester, Biodiesel, Diesel Engine, Stability Properties**

1. Introduction

Nowadays, the impact of increasing fossil fuel price has driven the Malaysian government to look for other alternative renewable energy resources. The price of fossil fuel in Malaysia has been predicted to increase five cent in October 2005 [**1**]. Moreover, a statement from Malaysian Minister of Plantation Industries and Commodity who said that the commercialization of biodiesel, can be expected as a bonus toward this country, besides reducing carbon dioxide [**2**]. The above statement was also supported by the Prime Minister who has instructed all Malaysian people to pay more attention on the use of biodiesel as diesel fuel substitute.

According to the Malaysian Palm Oil Board (MPOB), the research on palm oil conversion to biodiesel or Palm Oil Methyl Ester (POME) and biodiesel utilization has been conducted for over 20 years [**3**]. However, stability of the fuel is still a problem after being stored for a long time. This problem will affect to the performance and emissions of the engine. This study has been focused on the effects of oxidized the biodiesel from Palm Oil on their stability properties based on time of storage.

2. Biodiesel Oxidation and Stability

Biodiesel from vegetable oils are generally more susceptible to oxidative attack because they are less saturated as a result of double bond in their structures. The oxidative instability of some types of biodiesel may result in fuels that have unexpected low flash point after storage.

As biodiesel are made from unsaturated oils which is exposed to oxygen, the oxygen attaches to a carbon which is immediately adjacent to those involved in the double bond (a β-Carbon). This phenomenon was known as a hydro peroxide molecule formation process which is an indicator of early steps in the oxidation process.

According to Bondioli and Folegatti [**4**], a fuel is considered unstable when it undergoes chemical changes and produce undesirable consequences such as deposits, acidity or odorless. Moreover, the number and location of the double bonds have been identified as the possibility contributing to the instability of biodiesel [**4**]. The stability of the fuel is generally affected by two parameters, which are temperature and the nature of storage [**5**]. The parameters were suspected could also influence the viscosity and Total Acid Number (TAN) of the biodiesel fuel [**6**].

The above effects on Palm Oil Methyl Ester were presented in this paper. However, the analysis was done for single treatment of storage (ambient temperature) and without the addition of additives.

3. Tested Fuel and Methodology

The analysis and the preparation of tested fuels were conducted at The Alternative Fuel and Tribology Engine Laboratory. Department of Mechanical Engineering University of Malaya. The tested fuels chosen are 100% Conventional Diesel Fuel supplied by Malaysia Petroleum Company (PETRONAS), 100% Palm Oil Methyl Ester supplied by MPOB and 20% POME blended with 80% Conventional Diesel Fuel. The blending process was done using mechanical stirrer under room temperature with stirring speed 2000rpm.

The store media chosen is glassware which has been cleaned up scrupulously by using Toluene in order to avoid any contamination such as oxidized material or trace metal. The stored samples were closed by using Aluminum foil. The storage was not exposed to the sunshine (indoor storage) and maintained at room temperature (27°C).

Oxidation of each samples were done based on AOCS Recommended Practice Cg 5-97 [**7**]. The accelerated aging factor analysis was done by placing the fuels in the temperature controlled furnace (60°C ± 1°C) for 7 days before being stored. The storage are then placed in an area where the temperature is greater than 25°C but lower than 80°C.

The storage analysis procedure was done for two types of sample which is oxidized fuels and non-oxidized fuels. All the fuels were analyzed by using Viscometer, FT-IR and TAN analyzer after stored up to 7 weeks. However, the initial test prior stored was also conducted for oxidized and non-oxidized fuels. Additionally, visual inspection for each samples were also conducted.

Full specifications of the tested fuels are presented in table 1 as follows.

Table 1 Tested fuels specification

Name	Contents	Volume
S1	100% Diesel	250ml
S2	20% POME +80% Diesel	250 ml
S3	100% POME	250 ml

Furthermore, the initial standard properties of fresh fuels are presented in Table 2.

Table 2 Basic properties of tested fuels

Properties	S1	S2	S3
Viscosity @ 40°C (cSt)	3.4	4	4.6
TAN (mg/KOH)	n/a	0.6	0.8
Water Content (%)	n/a	< 2	< 1

4. Results and Discussions

4.1 Kinematic viscosity analysis

Viscosity of the samples is measured according to ASTM D455 standard. The test was conducted at second, fourth and seventh week of storage. The trend of viscosity from the three oxidized samples versus day of storage is represented in Figure 1. The highest viscosity value is given S3 while the lowest value showed by S1. Hence, it proves that the conventional diesel is less viscous compare to POME while the fuels have been oxidized.

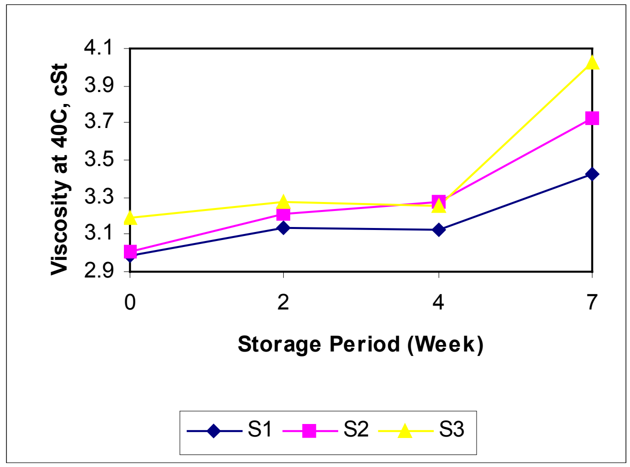

Fig.1 Viscosity Analysis at 40°C for the oxidized fuels

Figure 2 shows the viscosity trend of non-oxidized tested fuels which are stored for seven weeks. There are significant drop of viscosity after stored for 4 weeks for S1 and S3 sample. However, S2 tend to increase its viscosity gradually. The rate of increase in percent of non-oxidized fuels compared to oxidized fuels is about 14-26 percent for each sample

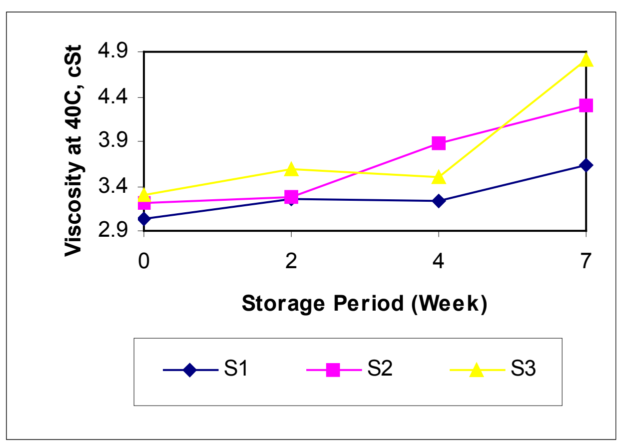

Fig.2 Viscosity Analysis at 40°C for the non-oxidized fuels

4.2 Total Acid Number (TAN) Analysis.

Total acid number (TAN) analysis was performed in order to measure the oil acidity, which is an indication of its ability to counter the corrosive effects due to oxidation. The results show an increasing trend of total acid number over the period of storage as shown in Figure 3 and 4. Initial value of all samples for TAN is obtained before the storage test. The test was conducted during the accelerated storage test, which are the second, fourth and seventh week.

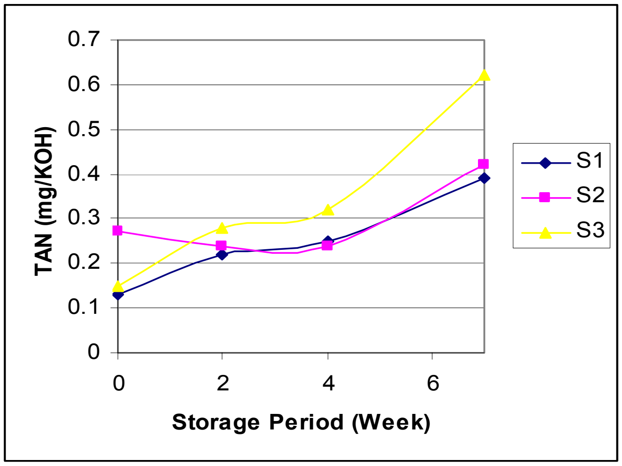

Fig. 3 TAN analyses for the non-oxidized fuels.

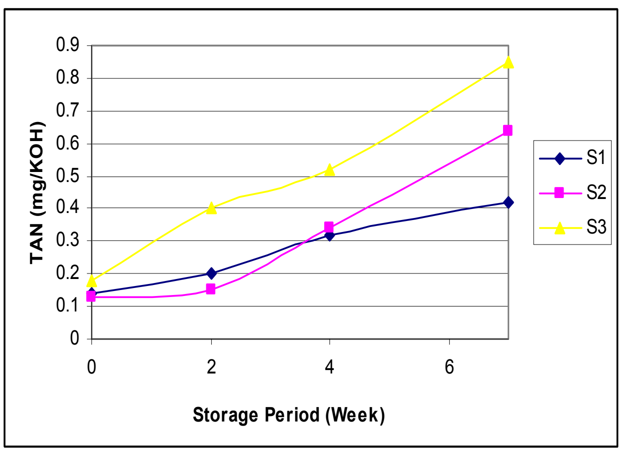

Fig. 4 TAN analyses for the oxidized fuels.

Figure 3 shows the increasing trend of TAN for non-oxidized samples. TAN was suspected to increase significantly since the fuels were store in the furnace. The changes of TAN for the oxidized samples are shows in Figure 4. The difference of TAN value between oxidized and non-oxidized samples is not much significant. However, it is shown that the time of storage has significant effect on TAN value of fuel. In addition, based on the graph for S2, it is possible to reduce the acidity number of the fuel although the fuels have been stored up to 7 weeks.

The results obtained by the test shows that POME tend to increase TAN value compared to conventional diesel during time of storage. Theoretically, in the presence of oxygen in POME (palm oil methyl ester), hydrocarbons of mineral oil react with the oxygen molecule to form carbonyl-containing products (primary oxidation products), which subsequently undergo further oxidation and finally forming carboxylic acids (secondary oxidation products) which results in increased TAN values [**6**].

4.3 FT-IR Quantitative Analysis.

The results of FT-IR quantitative analysis for oxidative degradation of blended POD are represented in Figure 5 based on percentage of composition of tested fuels.

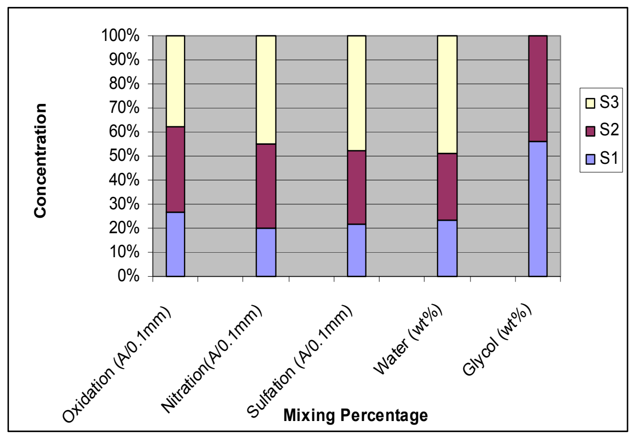

Fig.5 FT-IR quantitative analysis for tested fuels after 8 weeks storage.

Absorbance values related to the thickness of sample exposed to light are reported. The unit used is absorbance per 0.1 millimeter (A/0.1 mm), which relates directly to the peak intensities observed in the different spectrum of oxidized oil. FT-IR quantitative data indicated that an increased oxidation product is obtained from sample S3. However, soot content is not reported because the procedure is just limited to oxidation.

Sulfation, nitration, glycol and water are identified as an oxidation product. S3 give the highest result for oxidative degradation. However, the result of S3 does not show any presence of glycol. It is because the sample is not blended with diesel. Theoretically, glycol is detected if there is a presence of diesel. Highest sulfation was shown influenced by the concentration of POME in the fuel. Furthermore, S1 and S2 show the lowest composition of water content which is produced during storage test.

4.4 Physical change observation

During the storage test for oxidized fuels, the color of 100% POME (S3) and the blended fuel (S2) tend to be slightly darkened compared to the initial observation (fresh fuel). Meanwhile, a few quantity of brown dirt is been traced in both the POME samples. Theoretically, it is believed that the substance is varnish deposits and sediments that are produced by biodiesel during the oxidation process.

The situation is different for the non-oxidized fuels. The non-oxidized fuel tested tends to lose its colors after seven weeks of storage. The general hypothesis to explain this phenomenon lights around the area of stored fuels influencing the changes of color of oxidized fuels. However, 100% POME shows significant changes when mislaid the yellow intensity approximately 100% compared to initial observation.

Conclusions

The conclusions of this study can be drawn as follows.

1. The oxidation affects to degradation of physical and chemical properties and subsequently reduces the performance of oil.
2. The increase of viscosity and TAN reflect the increase of auto oxidation in the POME fuels. This shows that POME oxidizes slowly compared to conventional diesel due to the effect of natural antioxidant in the composition which delayed the oxidation process.
3. Pure POME fuel shows higher TAN value for oxidized and non-oxidized fuels. POME blended fuel also shows high TAN value which could lead to instability if the period of storage added for several weeks.
4. The duration storage, temperature of storage and presence of light have influence on the stability of the POME.
5. Finally, based on several attempts of analysis shows that POME fuel and its blends tend to oxidize rapidly in elevated temperature and long term of storage. Hence, 100% POME and POME blended fuel needs an antioxidant during period of storage in order to maintain its stability.

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