

Influence of Temperature on Corrosion Characteristics of Metals in Used Cooking Oil Methyl Ester

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Keywords- Used cooking oil methyl ester, copper, mild steel, aluminum, stainless steel.

Date of Submission: 16 March 2016	Date of Accepted: 25 April 2016

I. INTRODUCTION

Biodiesel is derived from the reaction of vegetable oils or animal fats and methanol or ethanol in the presence of catalysts. Chemically, biodiesel is a mixture of methyl or ethyl esters with long-chain fatty acids. Different raw materials and preparation processes can produce biodiesels with variable properties [1]. Biodiesel has been recently reported to have some merits including its gross heat of combustion, specific gravity, and kinematic viscosity comparable to conventional diesel (petrol diesel). It blends well with petrol diesel and enhances the cetane number, which decreases ignition delay times [2]. Biodiesel is known to enhance lubricity and anti-wear characteristics when blended with low-sulfur petro diesel [3]. However, since the biodiesel has free fatty acids compositions similar to the parent oils or fats with considerable amount of unsaturated fatty acids, its oxidative stability is affected, especially during its long-time period storage [4, 5]. According to Aquino et al [6], the degradation degree of biodiesel after contact with metals is not directly related to its corrosiveness, for short immersion times. The biodiesel degradation degree and corrosiveness as well as corrosion resistance presented by metals depends on a set of variables including raw material (feedstock), biodiesel purity summed to external factors like incidence of light, heat, oxygen and presence of metallic ions.

Nowadays, only diesel/biodiesel blends with low percentage in volume of biodiesel are being used in diesel cycle engines, due to some concerns that include the incompatibility of materials present in the fuel system with biodiesel [7]. The corrosive nature of biodiesel can be more aggravated if free water and free fatty acid are present in it. As compared to diesel, biodiesel is more prone to absorb water which tends to condense on metal surface and may cause enhanced corrosion. Beside this, auto-oxidation of biodiesel can also enhance its corrosive characteristics and degradation of fuel properties [8]. Fazal et al. [9] investigated the effect of temperature on the corrosion behavior of mild steel upon exposure to palm diesel. Their results showed the corrosion rate of mild steel increased with increasing temperature. Hu et al.[1] investigated corrosion behavior of metals in biodiesel from rapeseed oil and methanol at 43 °C for 60 days. The authors found out that the effects of biodiesel on the corrosion of copper and mild carbon steel were more significant than on aluminum and stainless steel. According to Hazeeb et al. [6] pure copper was more susceptible to corrosion in biodiesel as compared to leaded bronze.

Apart from a number of parameters affecting biodiesel properties, temperature has a significant effect on oxidative degradation of fuel and metal corrosion. Higher temperatures may aggravate the metal corrosion and change in fuel properties at different level. Corrosion of metal is a serious concern in automobile engines since fuel comes into contact with a lot of parts are composed of variety metals such as aluminum, copper, stainless steel and alloys. The percent of aluminum in engine parts includes piston (100%), cylinder heads (70%), and

engine blocks (19%). Pumps and injectors are composed of copper and its alloys. Parts composed of stainless steel include fuel filter, valve bodies, nozzle, and pump ring [10-12]. There is still little information available in the literature on the corrosion of metals in biodiesel, especially corrosion of metals in used cooking oil. The aim of the present study is to investigate the influence of temperature on the corrosion characteristics of metals (copper, mild steel, aluminium, and stainless steel) in used cooking oil biodiesel. Static immersion tests have been carried out at room temperature (25-30 °C), 40 °C, 60 °C, 80 °C, and 100 °C. The results obtained in this study can help in understanding the corrosion characteristics of diesel engine parts in biodiesel.

II. EXPERIMENTAL

2.1. Materials and Methods The used cooking oil methyl ester was produced from used cooking oil and methanol in the presence of potassium hydroxide as catalyst. The used cooking oil used for the production of the biodiesel used for this experiment was collected from Tantalizer eatery, Ibadan Oyo state Nigeria. The physical and chemical properties of the prepared biodiesel, commercial diesel, and diesel-biodiesel blends are presented in Table 1. The acid value was determined by titration in accordance with ASTM D 664. 5.0 g of each fuel sample was

Acid Value = $\frac{titre \ value \ (ml) x \ M x \ 56.1}{weight \ of \ oil \ (g)}$

titrated by 0.25 M potassium hydroxide with methanol. The acid value was calculated according to the formula:

blends.										
FUEL PROPERTY	UNIT	B0	B20	B40	B60	B80	B100	ASDM6751	EN14214	
Ester content	%mass						96.4 %	96.5% (min)	96.5% (min)	
Density at 15 °C	g/cm ³	0.830	0.840	0.847	0.853	0.858	0.860	NS*	0.86-0.90	
Viscosity (40°C)	mm ² /s	2.60	2.75	2.80	3.00	3.60	4.00	1.9 - 6.0	3.5 - 5.0	
Flash point	°C	65	87	100	120	130	178	130 (min)**	120 (min)**	
Cetane number		65.80	66.53	67.04	67.22	67.40	68.83	47 (min)**	51 (min)**	
Acid value	mg KOH/g	0.600	0.596	0.590	0.585	0.582	0.55	0.50 (max)***	0.50 (max)***	
Smoke point	°C	45	48	50	65	80	95	NS*	\mathbf{NS}^{*}	

 Table 1: Physical and Chemical Properties of Methyl Ester, Commercial Diesel, and diesel-Methyl Ester blends.

* Not Specified; ** Minimum; *** Maximum

2.2. Corrosion experiment and analysis

Corrosion characteristics of copper alloy (78% Cu, 17.4%), mild steel (1020), aluminium (97.43% Al) and stainless steel (SS 347) were investigated by static immersion test. The immersion test for each of the metals was carried out in B0 (100% commercial diesel), B20 (20% biodiesel and 80% commercial diesel), B40 (40% biodiesel and 60% commercial diesel), B60 (60% biodiesel and 40% commercial diesel), B80 (80% biodiesel and 20% commercial diesel), and B100 (100% biodiesel) at room temperature (25-30 °C) for 965 hours, and at 40 °C, 60 °C, 80 °C, and 100 °C for 8 hours. The blends were made on volume basis and stored in glass bottle. The surface of every specimen was polished by emery cloth, washed and degreased with acetone before immersion and allowed to dry. A hole of 2 mm was drilled near the end of each metal specimen for hanging the specimen into the test fuels. The weight of each specimen was measured before and after the immersion into the test fuels by a balance with four decimals accuracy. The length (21.5mm), width (21.5mm) and thickness (1mm) of each specimen were measured by a caliper of 0.02 mm precision. At the end of 40 days at room temperature, and 8 hours at higher temperature above room temperature, the rate at which each metal corroded was analyzed quantitatively by converting the data obtained from the weight loss into corrosion rate (mm/year) using the equation below:

Corrosion rate (mm/yr) = $\frac{(m_1 - m_2) X 24 X 365}{DAT X 1000}$

$$= \frac{8.76 X \Delta m}{DAT}$$

Where m_1 = weight before immersion (g), m_2 = weight after immersion (g), Δm = change in weight (g). That is,

 $(m_1 - m_2)$, D = density of metal (g/cm³), A = total exposed surface area of metal specimen (m²), and T = exposure time (hr).

III. RESULTS AND DISCUSSION

3.1. Influence of temperature on corrosion rate of copper-magnesium alloy

The influence of temperature on the corrosion rate of copper-magnesium alloy is presented in the Fig. 1. The corrosion rate of copper-magnesium alloy increases as the temperature increases. It was also observed that the corrosion rate of copper-magnesium alloy increases as the concentration of used cooking oil based methyl ester increases in diesel-methyl ester blends. The corrosion rates of copper-magnesium alloy in B100 fuel at room temperature and 100 °C are 0.005627 and 0.35151 mm/year respectively. It can be seen that the corrosion rate in B100 fuel at 100 °C is about 62.5 times the corrosion rate observed at room temperature. The higher corrosion rate of the fuel at higher temperature would have been occasioned by the fact that methyl ester is an oxygenated fuel which tends to be more readily available at higher temperature of the fuel. Again, strong affinity of copper for oxygen readily made copper to react with oxygen to form copper (I) oxide. Due to the fact that copper (I) oxide is which can form passive layer, which protects the surface of copper from having further contact with the test fuels, is not stable at temperature below 1200 °C, hence at temperature of 1200 °C and below, copper (I) oxide further reacts with oxygen to form copper (II) oxide which does not readily form passive layer, hence, the high corrosion rate of copper-magnesium alloy.

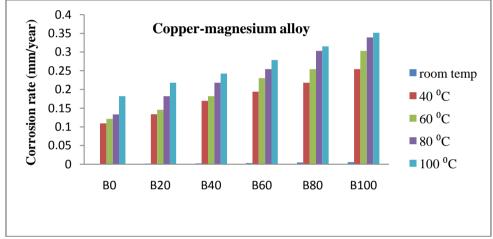


Fig. 1. Effect of temperature on corrosion rate of copper-magnesium alloy in commercial diesel, used cooking oil methyl ester and diesel-methyl ester blends

3.2. Influence of temperature on corrosion rate of mild steel

The influence of temperature on the corrosion rate of is mild steel presented in the Fig. 2. The corrosion rate of mild steel was found to increase as the temperature increases. It was also observed that the corrosion rate of mild steel increases as the concentration of used cooking oil based methyl ester increases in diesel-methyl ester blends. The corrosion rates of mild steel in B100 fuel at room temperature and 100 °C are 0.00377 and 0.12408 mm/year respectively. It can be seen that the corrosion rate of mild steel in B100 fuel at 100 °C is about 32.9 times the corrosion rate observed at room temperature. The higher corrosion rate of the fuel at higher temperature would have been occasioned by the fact that methyl ester is an oxygenated fuel which tends to be more readily available at higher temperature of the fuel. Mild steel oxidized quickly in contact with the test fuels, and the chemical reaction quickly took place leading to the formation Iron (III) oxide which has strong affinity for oxygen. Hence, the high corrosion rate of mild steel.

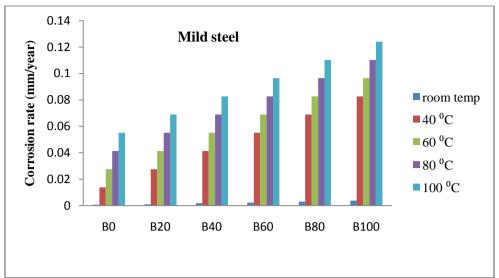


Fig. 2. Effect of temperature on corrosion rate of mild steel in commercial diesel, used cooking oil methyl ester and diesel-methyl ester blends

3.3. Influence of temperature on corrosion rate of aluminium

The influence of temperature on the corrosion rate of aluminium is presented in the Fig. 3. The corrosion rate of aluminium was also found to increase as the temperature increases. It was also observed that the corrosion rate of aluminium increases as the concentration of used cooking oil based methyl ester increases in diesel-methyl ester blends. The corrosion rates of aluminium in B100 fuel at room temperature and 100 $^{\circ}$ C are 0.003644 and 0.319652 mm/year respectively. It can be seen that the corrosion rate of aluminium in B100 fuel at 100 $^{\circ}$ C is about 87.7 times the corrosion rate observed at room temperature. The higher corrosion rate of the fuels at higher temperature would have been occasioned by the fact that methyl ester is an oxygenated fuel which tends to be more readily available at higher temperature of the fuel. Aluminium formed passive layer which protected its surface from corrosive effect of the test fuels. Hence, low corrosion rate of aluminium.

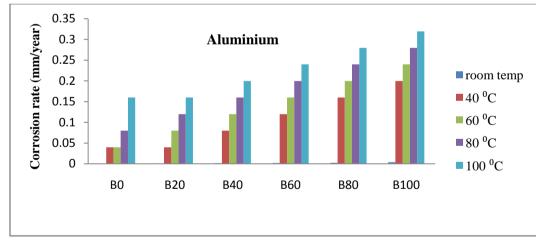


Fig. 3. Effect of temperature on corrosion rate of aluminium in commercial diesel, used cooking oil methyl ester and diesel-methyl ester blends

3.4. Influence of temperature on corrosion rate of stainless steel

The influence of temperature on the corrosion rate of is stainless steel presented in the Fig. 4. The corrosion rate of stainless steel was found to increase as the temperature increases. It was also observed that the corrosion rate of stainless steel increases as the concentration of used cooking oil based methyl ester increases in diesel-methyl ester blends. The corrosion rates of stainless steel in B100 fuel at room temperature and 100 °C are 0.000112 and 0.094817 mm/year respectively. It can be seen that the corrosion rate of stainless steel in B100 fuel at 100 °C is about 846.6 times the corrosion rate observed at room temperature. The higher corrosion rate of the fuel at higher temperature would have been occasioned by the fact that methyl ester is an oxygenated fuel which tends

to be more readily available at higher temperature of the fuel. Also, stainless steel readily forms passive layer due to the presence of high percentage of chromium and nickel.

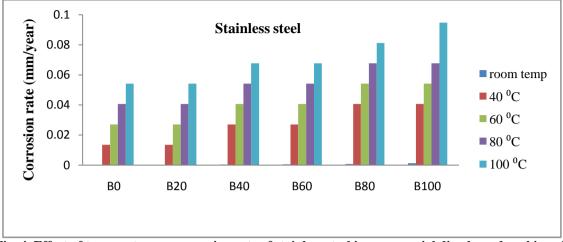


Fig. 4. Effect of temperature on corrosion rate of stainless steel in commercial diesel, used cooking oil methyl ester and diesel-methyl ester blends

IV. CONCLUSIONS

Based on the results of influence of temperature on corrosion characteristics of metals in used cooking oil methyl ester obtained in this work, it can be concluded that copper-magnesium alloy is more prone to corrosion than mild steel, aluminium and stainless steel. Also, commercial diesel is less corrosive than used cooking oil based methyl ester. Moreover, temperature influences corrosion rate as evidenced by higher corrosion rates of copper-magnesium alloy, mild steel, aluminium and stainless steel observed with increasing temperature.

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