Impact of Biodiesel on the Corrosion of Zinc and Copper Strips

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Abstract— The rates of corrosion of zinc and copper materials at room temperature, 40°C and 60°C in biodiesels obtained from olive, groundnut and soya oils were studied. The study showed that copper materials have a higher corrosion rate in the biodiesels studied compared to zinc materials. The corrosion rate of zinc materials increased with increase in temperature of the biodiesels over a period of time.

Index Terms— Corrosion, Biodiesels, Copper, Weight loss, Zinc

1 Introduction

Biodiesels refer to lower alkyl esters of long-chain fatty acids which are synthesized either by transesterification of vegetable oils with lower alcohols or by the esterification of free fatty acids with lower alcohols [1]. Extensive studies on biodiesels are on-going to explore product yield maximization and cost reduction. Biodiesel is advantageous because it is biodegradable, renewable and non-toxic. It is also known to have a higher cetane number than normal fossil fuels. Other advantages of biodiesels include its little or no carbon dioxide emission to the atmosphere during production and use. It is also reported to have good fuel properties; high flash point and good lubricity [2]. Different inedible oil sources are being studied as viable feedstocks for biodiesel production while the search for effective heterogeneous catalysts are growing fields in the study of biodiesels. With the growing interest in biodiesel production, proper handling and transportation means are necessary to ensure effective engine performance of the fuel.

Copper is widely used in many industrial fields due to its excellent electrical and thermal properties, good mechanical workability and its ability to form good alloys. It is a component of materials used in transporting and storing different fuels. It is found to be resistant towards atmospheric pressure and many chemicals however, in aggressive media; it undergoes corrosion easily [3], [4], [5], [6], [7].Corrosion disintegrates materials as it reacts with them when they make contact. Corrosion of materials result in the formation of scales and other products which have negative effects on heat transfer and cause a decrease in the heating efficiency of the equipment. This necessitates periodic de-scaling and cleaning in hydrochloric acid solution which are increased costs [8], [9], [10]. However, the extent of corrosion varies for metal ions depending on oxidation potentials and other prevailing conditions in the fuel.

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Biodiesel handling guidelines however, reported that copper, brass, bronze, lead, tin and zinc which are the materials used for the production and transportation of biodiesels are corroded by biodiesel [3]. Corrosive characteristics are vital for long-term durability of pipelines and storage tanks. The presence of metal contaminants can trigger undesirable reactions leading to instability and degradation of the biodiesel [3]. The level of corrosion in biodiesel is specified by the copper strip corrosion test and determined by American Society for Testing and Materials (ASTM) [11]. It involves immersing a polished copper strip in a specified volume of biodiesel for a known period of time and temperature. The copper strip is then removed, washed and the color of the strip is assessed following the ASTM standard. This test however, is limited as it measures the level of corrosion that will occur when copper is present as a metal. The corrosion in biodiesel fuels is due to the chemical composition of the biodiesel which has unsaturated molecules that easily undergo oxidation.

The unsaturated acids in biodiesel make the fuel susceptible to oxidation. This oxidation could be supported by the presence of metals in the biodiesel and significantly increase sediment formation. The corrosive nature of biodiesels under wide variety of compositional and operating conditions should be investigated to obtain data for confident utilization of biodiesels. Copper and its alloys are more prone to corrosion in biofuels compared to ferrous alloys [4] and data on the corrosion of other zinc coated materials is little. Therefore, the corrosion behavior of copper and zinc coated material in three biodiesels (olive oil biodiesel, groundnut oil biodiesel and soya oil biodiesel) has been studied under static conditions. The study intends to investigate the rate of corrosion of the metals in different biodiesel samples.

2 Materials and Methods

2.1 Sample collection and Preparation

The copper and zinc sheets used were machined into 27 rectangular sheets with average lengths of 2.5 cm and average width 1.3 cm. The metal strips were cleaned and stored for use. Olive oil, groundnut oil and soya oil biodiesels used were prepared in the research laboratory of the American University of Nigeria using the method described in [12]. Table 1

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shows the kinematic viscosities of the biodiesels used.

Table 1: Comparison of the Kinematic Viscosities of biodiesels to ASTM standard

Samples	ASTM Standard	Olive-Biodiesel	Groundnut-Biodiesel	Soya-Biodisel
Viscosity@ 40°C (mm^2/sec)	1.9-6.0	4.85	5.34	3.90

2.2 Weight Loss Studies

The static immersion method involved weighing the samples before and after immersion in 50 mL of the biodiesel samples. The study was conducted at room temperature, 40°C and 60°C. The metals strips were taken out weekly, cleaned and reweighed. The loss in mass was determined and average results from three specimens per oil sample were reported. The corrosion rate was determined using the values obtained from the weight loss and Equation 1 illustrated below [9].

$$Rate\left(\frac{\mu m}{yr}\right) = K\frac{m_i - m_f}{A\rho T}$$

Where K = 87.6 $mcm^{-2}hyr^{-1}$, m_i = initial mass, m_f = final mass, A = area of metal, ρ = density of metal and T = time in hours

2.3 UV/Vis Spectrometry

The Helios zeta UV/Vis Spectrophotometer was used to test the composition of the biodiesels before and after exposure of the metals in the biodiesels. This was to determine the dissolution of copper and zinc deposits in the oil after the corrosion tests.

3 RESULTS AND DISCUSSION

3.1 Corrosion rate of zinc in biodiesels

The mean corrosion rates for zinc are illustrated in Table 2. From the data, it is generally observed that there is an increase in the corrosion rate with increase in temperature. This shows that as the engine of a machine heats up, or when a zinc or copper material comes in contact with the studied biodiesels at elevated temperatures, there is a tendency that these materials will corrode. This will lead to the degradation of the biodiesel and lower engine or machine performance. A comparison of the corrosion rates of zinc materials in the three biodiesel samples shows that zinc corrodes more in olive oil biodiesel at all the temperatures studied. Soya oil biodiesel corrodes zinc materials less than olive oil biodiesel but more than groundnut oil biodiesel. Thus, the rate of corrosion of zinc for the three biodiesels can be illustrated as olive > soya > groundnut biodiesel at room temperature, 40 and 60°C.

The corrosivenesss of olive, groundnut and soya oil biodiesels were due to the presence of free fatty acids. Olive oil has 75% oleic acid as a major component while soya oil has 52.18% linoleic acid and 23.27% Oleic acid [4]. The higher percentage of oleic acid in olive oil could be responsible for the higher corrosion rate observed for olive oil biodiesel.

Table 2: Mean corrosion rate of zinc in different biodiesels at room temperature, 40 and 60°C

Media	Condition	Mean Corrosion Rate (μm/yr)
Groundnut-oil biodiesel	Room Temp. 40°C 60°C	2.784 7.305 8.832
Soya oil biodiesel	Room Temp. 40°C 60°C	4.646 6.866 8.416
Olive oil biodiesel	Room Temp. 40°C 60°C	7.447 7.584 28.395

3.2 Corrosion rate of Copper in biodiesel

Table 3 below shows the mean corrosion rates for copper in the three biodiesels studied. For groundnut oil biodiesel, the corrosion rate increases as the temperature increases which shows that an increase in the temperature of the oil will lead to more deposition of copper particles in the oil. This will also lead to more deterioration of the oil at higher temperatures. Soya oil biodiesel however, shows a decrease in the mean corrosion rates as the temperature increases. The corrosion rate is higher at room temperature and decreases at 40°C and it is lowest when the temperature is increased to 60°C. The decrease could be attributed to the interaction between the copper material and the properties of the oil that could result in the formation of passive oxides of Cu on the copper strip instead of the degradation of the copper material by the biodiesel. Olive oil biodiesel shows an increase in the corrosion rate from room temperature to 40°C. However, when the temperature increased to 60°C, the corrosion rate was observed to decrease. A possible reason for this behavior could also be attributed to the interaction between the copper and the olive oil biodiesel.

Table 3: Mean corrosion rate of Copper in different biodiesels at room temperature, 40 and 60°C

Media	Condition	Mean Corrosion Rate (μm/yr)
Groundnut oil biodiesel	Room Temp. 40°C 60°C	18.028 23.469 25.465
Soya oil biodiesel	Room Temp. 40°C 60°C	25.490 24.859 12.254

Olive oil biodiesel	Room Temp.	71.564
	40°C	88.341
	60°C	81.434

The copper materials have higher values of corrosion rate compared to the zinc materials which implies that copper corrodes more than zinc in biodiesel. Copper materials corrode more in different biodiesel samples compared to zinc coated materials at room temperature, 40 and 60°C. Thus, zinc materials are more suitable for storage and transportation of biodiesels because the degradation of the oil would be less in zinc materials compared to copper materials.

3.3 IDENTIFICATION OF METALS DISSOLUTE IN BIODIESEL

UV/Vis Spectroscopy identified the presence of copper and zinc deposits in the biodiesel samples after the period of study. This was seen as copper solution and zinc solution were tested and compared to the biodiesel samples after the study period. It was observed that absorption of both control and samples occurred at the same wavelength. This illustrates that there was sediment formation and metal contact which could lead to fuel degradation based on the metal found in the biodiesel samples. The concentrations were observed to be higher at higher temperatures of 40 and 60°C.

4 CONCLUSION

The corrosion of materials is a serious problem in the storage and transportation of various fuels. The application of biodiesel as an alternative to fossil fuels have been widely explored because the fuel is biodegradable, non-toxic, has lower emissions and very efficient. However, the storage and transportation of biodiesel can be affected by the medium used since the presence of free fatty acids in various oils can lead to the deposition of metallic materials in the oil. This will lead to the contamination of the oil as well as reduce engine performance and efficiency. This study showed that biodiesel samples from groundnut oil, soya oil and olive oil can lead to the corrosion of copper and zinc plated materials in static conditions over a period of time. However, the rate of corrosion varies for different biodiesels studied and the copper and zinc materials. Zinc was observed to corrode more in olive oil biodiesel followed by soya oil biodiesel and groundnut oil biodiesel was the least corrosive. However, for copper, olive oil biodiesel has greater corrosion rates followed by groundnut oil biodiesel and the least was soya oil biodiesel which the corrosion rate was observed to be decreasing with increase in the temperature. Generally, copper materials have a higher corrosion rate in the biodiesels studied compared to zinc materials. The corrosion rates could be attributed to the percentage of FFAs in the samples as well as the composition of the parent oil. Further studies would explore measures of reducing the rate of corrosion in the oil samples as well as identification of measures to extract deposit sediments in the biodiesel.

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