Corrosion Behavior of Ferritic Stainless Steel in Locally Prepared Biodiesel Media

Feyisayo V. Adams, *Member, IAENG,* Anuoluwapo T. Bankole, O'Donnell P. Sylvester, Ayodeji O. Apata, Ifeoma V. Joseph and Onoyivwe M. Ama

Abstract— **A study on the influence of biodiesel prepared from fresh and used oils on the corrosion behavior of ferritic stainless steel was investigated. Esterification process was employed in this work to reduce the free fatty acids present in these samples and further trans-esterified to produce biodiesel. The properties of produced samples of biodiesel such as American Petroleum Institute (API), viscosity, flash point, acid value, cloud point, and pour point were investigated and compared. The cloud points, pour points and flash points of the samples of biodiesel from vegetable oil were lower compared to those obtained from corn oil samples. The analysis of the results show that the acid values of biodiesel from corn oils were lower than those of vegetable oils, while the biodiesel samples from fresh corn oil exhibited lowest viscosity at both lower and higher temperatures. The API gravity values for all the samples studied were 33.11, 34.97, 33.22, and 33.88 for biodiesel from fresh corn oil, waste corn oil, fresh vegetable oil and waste vegetable oil, respectively. The corrosion study was investigated by immersion technique at 30 °C and 60°C for 30 days. At 60°C, the biodiesel produced from used vegetable oil was more corrosive compared to other biodiesel samples. However, at 30°C, fresh vegetable oil was most corrosive. The results obtained also show that ion diffusion controlled the oxidation steps during the corrosion process.**

Index Terms— **Biodiesel, characterization, corrosion, stainless steel**

I. Introduction

Some metals corrode easily while others have higher corrosion resistance. Examples of metals that have a high corrosion resistance are stainless steels, silver, gold etc., while those with low corrosion resistance include: iron, aluminum, magnesium etc [1]. High temperatures foster corrosion and increased corrosion rates. Rate of corrosion also depends on the amount of chemical or electrochemical energy stored in the metal. Stainless steel is an alloy and it is composed of iron, carbon and chromium. It is a metal that is of great importance to various manufacturing and production industries. Stainless steel possesses a metal film, an oxide film that avoids contact of biodiesel from the metal. Fusion of metallic elements such as; chromium, nickel, and molybdenum, increases the corrosion resistance, hardness, and strength during the production of stainless steel. The most common US grades of stainless steel are: 304-austenitic, 316-Austenitic (chromium-nickel stainless class), 409, 410 martensitic, 430 ferritic (plain chromium stainless category) [2].

Hu et al. [3] carried out a comparison of the corrosion rates of various metals in rapeseed biodiesel using immersion technique at 43 °C for 60 days. The results showed that copper and carbon steel, were as resistant to corrosion as aluminum and stainless steel. Also, Kaul et al. [4], reported on the corrosiveness of biodiesel obtained from different precursors, which include; *Jatropha curcas*, Karanja, *Madhuca indica* and Salvadora oils. The study was carried out through stationary dipping using metallic (aluminum alloy) piston for 300 days at a temperature of about 15 to 40°C. The authors observed that the corrosion rates of the samples tested varied depending on the chemical composition and properties of each producing oil feed. Salvadora was observed to have the highest corrosion rate value compared to the other oil samples tested. This was due to the high sulphur content which Salvadora possessed. While Haseeb et al. [5], executed the afore mentioned experiment with tokens of copper and leaded bronze in palm biodiesel at room temperature for 840 hours and at 60 °C for 2640 hours, the corrosion rates for copper and bronze were relatively higher at the 60°C.

The presence of alloying elements in metals is proven to increase the corrosion resistance of metals. Similarly, Fazal et al. [1] observed that copper showed highest corrosion rates in a study that was carried out using copper, brass, aluminum, cast iron at room temperature (25-27 °C) for 120 days in palm biodiesel. This was confirmed by Geller et al. [6] who stated that copper alloys are more prone to corrosion in biodiesel than ferrous alloys. Other methods employed to test for corrosion of metals in biodiesel include electrochemical process, which involves an estimation and characterization of extent of corrosion in a metal sample. It is used to determine corrosion and passivation rates, anodic and cathodic protection [5]. Immersion of metal coupons is done in biodiesel mixed with acids. These acids are acids that were formed during biodiesel oxidation. The presence of these acids accelerates the effect of corrosion on the metal.

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F. V. Adams is with the American University of Nigeria, Yola, Nigeria (corresponding author phone: +2348028024519; e-mail:feyikayo@gmail.com).

A.T. Bankole is with the American University of Nigeria, Yola, Nigeria (e-mail: anuoluwapo.baankole@aun.edu.ng).

O. P. Syvester is with the American University of Nigeria, Yola, Nigeria (e-mail: odonnell.sylvester@aun.edu.ng).

A. O. Apata is with the Federal Polytechnic, Ida, Kogi state, Nigeria (toyinben.toyinben@gmail.com)

I. V. Joseph is with the American University of Nigeria, Yola, Nigeria (ifeoma.joseph@aun.edu.ng)

O. M. Ama is with DST/CSIR National Center for Nano-structured Materials, Council for Scientific and Industrial Research, Pretoria, South Africa (e-mail: onoyivwe4real@gmail.com)

This present study is aimed at studying the corrosion resistance of ferritic stainless steel in biodiesel made from fresh and used corn oil as well as fresh and used vegetable oil.

II. MATERIALS AND METHODS

A. Materials

The feed stocks used for this research were fresh and used corn and vegetable oil. These products were obtained from Jimeta market and the cafeteria of the American University of Nigeria, respectively; both locations are in Yola, Nigeria. The apparatus used to set up the esterification and trans-esterification processes included; a round-bottom flask, heating mantle, thermometer, a reflux condenser and magnetic stirrer. Other materials used in this project included stopwatch, weighing balance, viscometer for measuring the viscosities of fluids, test tubes, water bath, and ferritic stainless steel (Type 440) coupons obtained from Jimeta market, Yola, Nigeria. The elemental composition of the stainless steel as supplied by the manufacturer is shown in Table 1. The reagents used were 99.5% ethanol, 99.5% methanol, potassium hydroxide and 32% sulphuric acid.

B. Methods

The esterification of the used oil samples (250 ml) was carried out using 75 ml ethanol and 1.25 g of 32% sulfuric acid before the trans-esterification step. A magnetic stirrer was placed in the round bottom flask containing the oil sample and the latter was fitted with a reflux condenser to avoid any leakage of ethanol during the esterification process through evaporation at boiling point. The oil samples were heated to about 60^{o}C for 20 minutes, while sulphuric acid and ethanol were mixed in a 100 ml beaker with a magnetic stirrer. This whole process was carried out in a fume cupboard. The mixture was immediately poured in a separating funnel and left for 24 hours to totally separate after which it was subjected to trans-esterification process.

In order to produce biodiesel, the feed (samples obtained from the esterification process) was heated to 60^{o}C and 2% weight of the oil sample was derived to account for the measurement of finely ground anhydrous potassium hydroxide (KOH). Methanol (99% purity) (90 ml) was mixed with 5 g KOH. The methoxide solution was added to the 300 ml warmed oil, while stirring continually for 30 minutes. The mixture was then centrifuged to speed the separation of the biodiesel from the glycol. This was done for 60 minutes after the trans-esterification reaction was initiated. After 60 minutes of rigorous stirring and constant flow of water to the reflux condenser from a tap, the mixture was poured into a separating funnel and left for 24 hours for total separation. After 24 hours, the lower product, which is known as glycerol was removed, while the top product is biodiesel. The biodiesel was washed with warm water (50^{o}C) about 4 times before it was placed in a dryer at room temperature for 24 hours to remove moisture. The percentage yield of the prepared biodiesel sample was determined using Equation (1), to evaluate the production efficiency of biodiesel produced from the oil samples [7].

TABLE I
ELEMENTAL COMPOSITION OF TYPE 440 FERRITIC STAINLESS STEEL

Elements	Compositions
Cr	18.0
C	0.12
Mn	1.00
P	0.04
Si	0.70
S	0.03
Fe	Balance

$$\%yield = \frac{vol_p}{vol._u} \times 100 \tag{1}$$

Where vol.$_p$ is the volume of biodiesel produced and vol.$_u$ is the volume of the oil used.

The mass and volume of the biodiesel were measured and recorded, also, the mass and volume of water was also measured and recorded. Hence, the specific and API gravity values were calculated using the formulae in Equations (2) and (3) respectively [7].

$$S.G = \frac{\rho_b}{\rho_w} \tag{2}$$

Where S.G is specific gravity, ρ_b is the density of biodiesel and ρ_w is the density of water.

$$API = \frac{141.5}{S.G} - 131.5 \tag{3}$$

The corrosion potential behavior of ferritic stainless steel was studied in these samples of biodiesel. These samples included biodiesel produced from fresh corn oil, used corn oil, fresh vegetable oil and used vegetable oil. Stainless steel coupons of dimensions 2 cm by 1cm were weighed and the values were recorded before they were inserted in test tubes containing each biodiesel sample. The test tubes were then immersed in water baths at room temperature and 60^{o}C. The corrosion study was set-up and left at respective temperatures for a period of thirty days and the change in weight was observed at an interval of five days. The weight of the stainless steel in each biodiesel sample was measured after being washed with ethanol and the values were recorded. These values were used to calculate the rate of corrosion using Equation (4).

$$C.R = \frac{87.6W}{\rho At} \tag{4}$$

C.R is the corrosion rate in mm/yr, W is weight loss (mg), A is surface area of coupon (cm^2), t is time (hr) and ρ is density in g/cm^3.

III. RESULTS AND DISCUSSION

A. Percentage Yield of Biodiesel

The percentage yield of all the biodiesel samples is shown in Fig. 1. It can be seen that the overall average value for the produced biodiesel was 60.08%. It can also be seen that used vegetable oil had the highest percentage yield (78%) which can be attributed to a successful esterification process, which reduced the amount of free fatty acids present in the oil before the production of biodiesel. Fresh corn oil had a comparatively high percentage yield of 67% which could be as a result of the sample being a virgin feedstock. On the other hand, samples obtained from used corn oil and fresh vegetable oil had a low percentage yield compared to the average value obtained for the percentage yield. This could possibly be as a result of an incomplete esterification process as well as waste during washing.

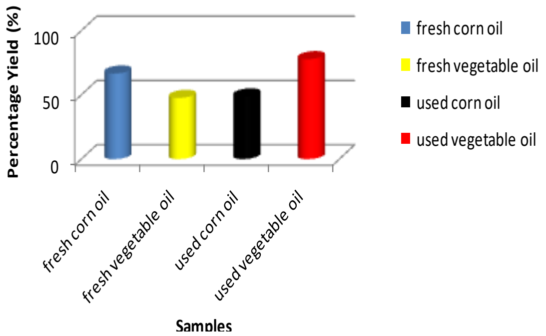

Fig.1. Percentage yield for all biodiesel samples

A. Properties of Biodiesel

The viscosity of diesel has to be high enough to supply adequate lubrication for the engine parts and low enough to flow at operational temperature [8]. Fuel filter and injection system in engines can be plugged by high viscosity. It can be seen that the viscosities of feed were relatively higher (Fig. 2), thus, the trans-esterification of the oils resulted in a less viscous fuels that could function more appropriately compared to the feed [9].

It was also observed that the biodiesel sample from the used vegetable oil was the most viscous compared to the other three samples. This is because the used vegetable oil feedstock was very dense before it was trans-esterified to produce biodiesel. Comparing both biodiesel samples as a pair, biodiesel samples produced from vegetable oil was more viscous than biodiesel samples obtained from corn oil.

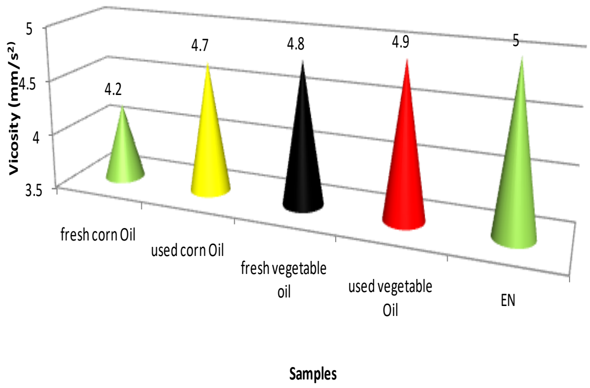

Fig. 2. Viscosity for all samples

In this study, there was no ash content in each 10.0 ml of sample subjected to 700°C temperature for 15 minutes. The cloud and pour points (Table 2) recorded for each biodiesel sample prepared in this study conformed to the European Standard for biodiesels, EN 14214. It was observed that all biodiesels obtained from fresh feed stock had relatively higher cloud points and pour points compared to those obtained from waste feed stock. This trend could be attributed to the presence of more free fatty acids present in the waste feed stock as compared to fresh feed stock.

The density values of all the four biodiesel samples conformed to the standard diesel fuel density criteria as shown in Table 2. The specific gravity for all samples also met the specific gravity of standard diesel. Therefore it can be stated with reasonable accuracy that all samples of biodiesel prepared have close similarities of specific gravity as that of the standard biodiesel.

TABLE 2
PROPERTIES OF THE BIODIESEL SAMPLES

Sample	Cloud point (°C)	Pour point (°C)	Density (Kg/m^3)	Specific gravity	API gravity
Fresh corn oil	-9	-6	855	0.857	33.11
Used corn oil	-8	-5	848	0.850	34.97
Fresh vegetable oil	-13	-9	857	0.859	33.22
Used vegetable oil	-9	-8	853	0.855	33.88

The API gravity of all biodiesel samples in this study are greater than the API gravity of a standard diesel fuel thus, it can be inferred that the biodiesels produced were of good quality. According to the European Standards, EN 14214 [10], the allowable value to measure for acidity is <0.5 mg KOH/g, which is usually 0.1% of the biodiesel's weight. In this study, the recorded acid values of each biodiesel sample conformed to the European Standards and biodiesel obtained from waste vegetable oil possessed the highest acid value.

TABLE 3
ACID VALUES AND FLASH POINTS OF BIODIESELS

Sample	Flash point (°C)	Acid values (mg KOH/g)
Fresh corn oil	115	0.1122
Used corn oil	135	0.1132
Fresh vegetable oil	111	0.1653
Used vegetable oil	114	0.1683

The flash point values of the biodiesel samples show that the biodiesel sample from used corn oil possessed the highest flash point. This means that at 135°C, this biodiesel would ignite when in contact with an ignition source. The biodiesel sample obtained from fresh vegetable oil shows the least flash point, which implies that the biodiesel sample obtained from fresh vegetable oil, would ignite at a lower temperature than the biodiesel sample obtained from used corn oil. A low flash point value is attributed to the presence of alcohol residue in the process [10]. Comparing the fresh and used biodiesel products, it can be seen that the biodiesel samples obtained from used feed stocks possess higher flash point than those obtained from fresh feed stock.

B. Effect of Temperature on the Corrosiveness of Biodiesel

According to Singh et al. [11], an increase in temperature directly increases the corrosiveness of biodiesels. This is due to the fact that at high temperature, the amount of free fatty acids increases and the chemical properties of the biodiesel are altered. All biodiesel samples showed an increase in the rate of corrosion at elevated temperature of 60°C. At 30°C, biodiesel samples from fresh vegetable oil showed increase in weight with time while result shows that stainless steel exhibited loss in weight thus, high corrosion rate in the biodiesel obtained from the used vegetable oil. This behavior is in contrary to the behavior of stainless in biodiesels made from fresh and used corn oil. Generally, biodiesels produced from used vegetable oil show highest corrosive attack, while biodiesel from used corn oil exhibit the least corrosiveness. At lower temperature, biodiesel from fresh vegetable oil was more corrosive than biodiesel from fresh corn oil, but at the higher temperature, the reverse is the case.

C. Effect of Composition of Oil on the Corrosiveness of Biodiesel

Each feedstock used for the production of various samples of biodiesel in this study had different chemical properties and composition. Both used oil samples were trans-esterified to reduce the amount of free fatty acids present in each sample, but used vegetable oil exhibits a composition of fatty methyl esters which makes it more aggressive than other biodiesel sample. Pinzi *et al.* [12] reported that the composition of alkyl esters present in biodiesel influence the oxidation rate of a metal that is exposed to it. Methyl esters of fatty acids often form a radical which rapidly links with oxygen in the air during the oxidation process of biodiesel [13]. This forms volatile products such as aldehydes, lactones, ketones [14], formic, propionic, acetic, and caproic acids [14]. These volatile products can increase the aggression and degradation properties of biodiesel [1].

D. Effect of Acid Value on the Corrosiveness of Biodiesel

A change in the acid value of biodiesel is one of the different factors that may be involved in the corrosion ability in biodiesel. Other factors include the presence of metal species, increase in water content, the presence of oxidation products, and changes in the structural characteristics of the biodiesel [15]. All biodiesel samples produced in this study had acid values below the European standard (>0.5). It was reported that metals act as catalysts for biodiesel oxidation. Thus, the acid number of biodiesel increases proportionally with the corrosion rate for various metals [16]. From this study, it was noticed that the acidity of each biodiesel sample was directly proportional to their rate of corrosion at elevated temperature (Tables 3 and 4). The biodiesel samples produced from the fresh and used vegetable oil possessed high acid values, thus, the stainless steel immersed in these samples show high rate of corrosion. However, stainless steel immersed in biodiesel samples produced from fresh and used corn oil which possessed a lower acid values had a lower rate of corrosion. At 30°C, it can be seen from Table 4 that biodiesel produced from fresh feed stock (corn and vegetable oils) were more corrosive than those produced from used feed stock. However, at elevated temperature, the reverse is the case. This could be attributed to the higher flash points of biodiesels from used oil samples.

F. Effect of Cloud and Pour Points on the Corrosiveness of Biodiesel

It was observed that the lower the cloud and pour points, the more corrosive the media. At 30°C, the stainless steel exhibits high rate of corrosion in biodiesels from used and fresh vegetable oils (Table 4). This resulted from the lower value of cloud and pour points of the biodiesels. The biodiesel sample from fresh vegetable oil possessed the least cloud point value and the highest rate of corrosion was observed in it as compared to the other biodiesel samples. It can also be seen that at 60°C, an alteration of chemical properties caused biodiesel from fresh vegetable oil to be less corrosive compared to waste vegetable oil.

IV. CONCLUSIONS

Stainless steels possess a considerably higher resistance to corrosion. However, the stainless steel used showed some corrosiveness in the biodiesel produced. From the corrosion studies carried out, at 60°C, biodiesel made from used vegetable oil was most corrosive followed by the one from fresh vegetable oil, then fresh corn oil and the biodiesel sample that was least corrosive was made from waste corn oil. At 30°C, biodiesel obtained from the fresh vegetable oil was most corrosive compared to the other three samples. It was also proven that the corrosiveness of a biodiesel sample depends on temperature, composition, acid value, cloud and pour point of the biodiesel samples.

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TABLE 4
OXIDATION RATE PARAMETERS AND CORROSION RATES OF STAINLESS STEEL IN VARIOUS BIODIESEL SAMPLES AT VARYING TEMPERATURE

Temperature (^oC)	Samples	Corrosion rate (mm/yr)
30	Fresh corn oil	3.19E-6
	Used corn oil	2.50E-6
	Fresh vegetable oil	4.10E-6
	Used vegetable oil	4.03E-6
60	Fresh corn oil	3.75E-6
	Used corn oil	Weight gained
	Fresh vegetable oil	5.00E-6
	Used vegetable oil	5.56E-6

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