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# Corrosion Properties of Biodiesel and Petroleum Diesel on Copper, Aluminium and Stainless Steel

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## Abstract
As the drive in research and investment in biodiesel production from non-edible sources increases, there is also increased concern in its associated challenges like the corrosion potentials on different metals. Due to the challenges caused by corrosion, it is therefore necessary to carry out a thorough evaluation of the corrosion potential of identified bio-diesel sources. This work examined the corrosion potentials of biodiesel from soapnut and rape seed oil compared with commercial petroleum diesel using metals such as copper, aluminum, and stainless steel by the non-electrochemical weight loss method. The result shows that biodiesel produced from soapnut seed oil is more corrosive than biodiesel produced from rapeseed oil. The metals corroded with variable degrees as they were immersed in the different biodiesels at room temperature for 7 weeks (1176hours). The corrosion rates of copper, aluminum, and stainless were found to be 0.0003155, 0.0000869, and 0.0000147 mm/year respectively for biodiesel from soapnut seed oil, and 0.0002319, 0.0000773, and 0.0000147 mm/year respectively for biodiesel from rapeseed oil. However, the corrosion rates of the same metals immersed in petroleum diesel were relatively lower (0.0000835, 0.0000316 and 0.0000074 respectively) under the same conditions. The corrosive effect of biodiesel on copper was found to be more pronounced than on aluminum and stainless steel.

**Key words**: **Corrosion properties, soapnut, rape seed, biodiesel**

## 1. Introduction

As the world gradually transits from total dependence on fossil based fuels to biofuels or a blend of both at an economical and equipment safe proportion, there are concerns about the reliability of fuel from bio-sources particularly biodiesel. Some among these fears include overall cost, yield, availability of raw material and its corrosion behavior on metals. However, of particular concern in this study is the corrosion behavior of biodiesel from two (2) non-edible sources, that is, soap nut seed oil and rapeseed oil on some metals.

Over the years, corrosion has proven to be one of the most prominent challenges in the

industrial world particularly in the oil and gas industry. It is a naturally occurring phenomenon generally defined as the deterioration of metal surfaces caused by their reaction with the surrounding environmental conditions (Anonymous, 2019).It can cause damage to metals and their alloys with great economic consequences in terms of repair, outright replacement, product and financial losses, and in extreme cases may cause structural failure (Fazal et al., 2011; Raview and Uhlig, 2011).This can occur in different forms like crevice and galvanic corrosion (Rashidi et al, 2007).

It is true that serious and wide range of researches have been carried out in the evaluation of the biodiesel yield potential of several non – edible plant sources, Adebayo et al. (2011), Alemayehu and Amanu, (2014) Murugesan et al, (2009). However, it is important that the corrosion properties of biodiesel from these different bio-sources be investigated so as to ascertain biodiesel sources that can give low corrosion potential and if possible, rank these biodiesel in terms of their corrosion properties so as to guide prospective investors. This information is yet not available for biodiesel from soapnut seed oil and rapeseed oil in open literature.

Consequently, this study investigated the corrosion properties of biodiesel from non-edible soapnut seed oil and rapeseed oil already identified as biodiesel sources using methanol as a base catalyst in trans-esterification reaction using metals such as copper, aluminum, and stainless steel. This was done by a non-electrochemical metal immersion test involving weight loss measurement, and then results obtained compared with that from commercial petroleum diesel. The reason for choosing these metals in the investigation is due to their broad range of applications in transport and storage of biodiesel and in the manufacturing of automobile engine parts (Elaheh, 2011). The significance of this study is that it will present a detailed comparison of the corrosion properties of biodiesel from the two chosen sources against diesel from petroleum source on the different metals which could serve as a baseline for material selection.

## 2. Materials and Methods

The petroleum based diesel used for this study was gotten from a local fuel station in Warri, Delta State. Its properties are shown in Table 1.

**Table 1: Fuel properties of the petroleum based diesel**

| Petroleum Based Diesel | Properties |
|---|---|
| specific gravity at 25°C | 826.2 kg/m$^3$ |
| total sulphur | 0.0017wt% |
| viscosity at 40°C | 2.5cSt |
| cloud point | -20°C |
| cetane number | 49.2 |
| flash point | 59°C |
| pour point | -2°C |
| freezing point | -11°C |
| density at 25°C | 825kg/m$^3$ |
| The American Petroleum Institute, API gravity | 39.7 |

### *2.1 Seed Preparation and Diesel Production*

The outer shells of the seeds (obtained from local market in Effurun) were removed manually and then sun dried for one week. Thereafter the seeds were oven dried (CarboliteGero Oven, Laboratory High Temperature - LHT) at 120°C for 3 hours to ensure that moisture was properly removed in line with procedure of Adebayo et al, (2011). At this temperature and drying time, the seeds were not over heated and so that the oil containing cells were not de-natured.

A mechanical screw press was used to extract the oil from the prepared seeds. In line with Adebayo et al (2011), 1000 g of the prepared seeds was weighed using Scout Pro, Ohaus, London weighing balance and pretreated by steaming the prepared seeds for 15 minutes before putting the pretreated seeds into the mechanical engine driven screw press and crushed until the oil starts to flow from the crushed seeds. The screw press is a simple automated mechanical device used by oil mills for extraction of oils from seeds.

The extracted oil was allowed to settle for particle sedimentation and subsequent filtration. In accordance with Noureddini and Zhu (1998), Murugesan et al, (2009) and Romano and Sorichetti, (2011), the extracted oil was then heated mildly using the Grant JB series model water bath for 30 minutes and again allowed to sediment and then decanted after settling. The bottoms that contained impurities were further filtered using Whatman 42 filter paper to collect the oil still left in the container. Sedimentation and filtration of raw oil is a very slow process that was why heat was applied to accelerate the process.

The biodiesel was produced using the base catalyzed transesterification reaction in line with Umar, R and Farooq, A (2008); Ehsan, MD and Tofajjal, MD (2015). 250 ml of oil was poured into a 500 ml Pyrex conical flask and heated to a temperature of 54.4 $^{o}$C (130 $^{o}$F) using a hot plate with a magnetic stirrer. A solution of potassium methoxide was prepared in a 250ml Pyrex beaker using 1.75 g of KOH pellet and 50ml of anhydrous methanol. The solution was properly stirred using a Pyrex electronic stirrer model 300 until the KOH pellet completely dissolved in the methanol. The potassium methoxide solution was then poured into the heated oil at 54.4$^{o}$C (130 $^{o}$F) and stirred vigorously for 30 minutes using a magnetic stirrer, the mixture was left to settle for 24 hours in a separating funnel (see Plate 1). After settling (Plate 2), the lower layer which is the glycerol was separated first from the separating funnel and put into a separate beaker, while the upper layer which is the biodiesel was then transferred into a separate beaker.

Base catalyzed transesterification reaction is preferred over acid catalyzed transesterification reaction for the production of biodiesel because it provides better conversion rates and higher yield of biodiesel (Nur, S and Talha, S, 2016; Shemelis, NG and Jorge MM, 2017).

### *2.2 Purification of the Produced Biodiesel Samples*

The residual catalyst (KOH), methanol, soap, and glycerol were removed by successive rinsing of the produced biodiesel samples (Plate 1A) with equal volume of warm distilled water. According to Adebayo et al, (2011), the residual water was separated and removed from the biodiesel by using a separating funnel (Plate 1A), and then heating the remaining mixture of biodiesel and water above 100$^{o}$C using the DAIHAN-brand® programmable Tube Furnace.

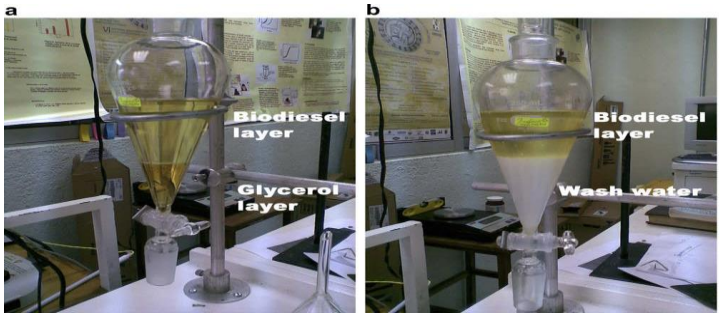

**Figure 1: Plate 1(A and B) Separating Wash Water from Biodiesel after Washing**

### *2.3 Determination of Corrosion Rate by Weight Loss Method*

Corrosion characteristics of copper, aluminum, and stainless steel in both produced biodiesel and petroleum diesel samples were investigated using the non-electrochemical metal immersion test. This involves weight loss measurement at room temperature for a period of 7 week. The coupons were made by machining and grinding a round bar to get a rectangular shape of depth 2 mm diameter. It was drilled near the edge of the specimen for suspending the specimen into the diesel environments. Before immersion, the coupons were polished with an abrasive brush, washed and degreased with acetone before and after exposing the test coupons to the diesel samples. The weight of each coupon before and after immersion was measured by a weight balance using Contech high precision balance, CAC-1502. Two duplicate coupons were also immersed in each sample. For each coupon, weight loss was measured by subtracting the final weight (obtained after exposure) from its initial weight (before exposure). At the end of the test, corrosion property was investigated by measurement of corrosion rate (m

m/year) using the equations below

;

$$\text{Corrosion rate (mm/year)} = \frac{\text{Weight Lo} \times \text{ 24hrs } \times 365 \text{ days}}{\text{Density of the Metal Coupon } \left(\frac{g}{cm^3}\right) \times \text{ Exposure Time(hr) } \times \text{ Exposed Surface Area } (cm^2)}$$

$$= \frac{W\ x\ 24\ x\ 365}{D\ x\ T\ x\ A} \qquad (1)$$

Where W is the weight loss (g), D is the density of the metal coupon (g/cm$^3$), A is the exposed surface area (cm$^2$), and T is the exposure time (hour). (Enzhu, 2012; Kuang et al, 2010).

### *2.4 Determination of Density, Specific Gravity and API Gravity (ASTM D 941)*

Pycnometer used was a cleaned and dried stoppered bottle of 50 $cm^3$ capacity. Weighed ($W_0$) and then filled with the oil stoppered and reweighed to give ($W_1$). The oil was substituted with distilled water after washing and drying the bottle and weighed to give ($W_2$). Density was estimated as:

$$\rho_{oil} = \frac{W_1 - W_0}{V} \quad @ \quad 25^oC \tag{2}$$

Where V = volume of sample used
The expression for specific gravity (S.G) is:

$$S.G = \frac{W_1 - W_0}{W_2 - W_0} or \frac{\rho_{oil}}{\rho_{water}} \quad @\ 25^oC \tag{3}$$

Where;
$W_0$ = weight of dry empty density bottle;
$W_1$ = weight of density bottle + oil;
$W_2$ = weight of density bottle + distilled water.
API Gravity was estimated from specific gravity as follows:

$$API \cdot Gravity = \frac{141.5}{S.G} - 131.5 \tag{4}$$

### *2.5 Determination of Flash Point (ASTM D93)*

The flash point of biodiesel was determined using Pensky Martens Closed Cup method. The cup was filled with the sample up to the 75 ml mark and placed in the tester. The machine was then set to heat at about $5^oC$/min with simultaneous stirring until a rise in temperature was observed. Small open flame was maintained from an external supply of petroleum gas. Periodically, the cup would be opened and flame exposed closely to the surface of the heated oil. When the flash temperature is reached, the surface of the oil would ignite. The temperature at once was noted and recorded as flash point temperature.

### *2.6 Determination of Kinematic Viscosity (ASTM D445)*

Ostwald viscometer used in this experiment was thoroughly washed and completely dried before use. The sample whose temperature was determined with a thermometer was filled into the viscometer to the appropriate mark using a long pipette to minimize wetting the tube above the mark. This was done from one end while the other end was tightly closed. The closed end was then opened with simultaneous timing, and the time of flow of sample to the next mark was recorded. The kinematic viscosity ratio was calculated by dividing the time taken with the liquid under examination by the time taken by distilled water for the meniscus to fall from initial mark to the final mark. Kinematic viscosity was estimated

according to Poiseuille's law from the equation:

$$\eta_l = \frac{n_w \rho_l t_l}{\rho_w t_w} \quad (\text{mm/s}^2) \quad (5)$$

Where:
$\eta_l$ = kinematic viscosity of the liquid sample
$\eta_w$ = absolute kinematic viscosity of water
$\rho_l$ = density of the liquid sample
$\rho_w$ = density of water
$t_l$ = time of flow of liquid sample
$t_w$ = time of flow of water

### 2.7 Determination of Acid Number (ASTM D664)

Exactly 0.1N KOH solution was prepared by dissolving 5.61g KOH (pellet) with 1000ml distilled water. Furthermore, a mixture of 99.7% pure ethanol and 98% pure benzene in a ratio of 1:1 by volume was prepared by mixing 50 ml benzene and 50 ml of ethanol. About 1g of the oil was weighed and dissolved in the mixture of ethanol and benzene. The solution was titrated with 0.1N KOH solution in presence of 2 drops of phenolphthalein as indicator until the end point with the appearance of a pale permanent pink. The titre volume of 0.1 N KOH (V) was noted. The total acidity (acid number) was calculated using the following equation

$$AV = \frac{MW \times N \times V}{W} \quad (6)$$

Where:

MW = Molecular weight of potassium hydroxide (56.1g).

N= Normality of potassium hydroxide solution (0.1 N).

V= Volume of potassium hydroxide solution used in titration.

W = Weight of oil sample.

### 2.8 Determination of Free Fatty Acid (FFA)

The FFA is gotten from the acid value using the equation below;

$$\%FFA = \frac{AV}{2} \quad (7)$$

## 3. Results and Discussion

The set of Tables below (Table 1-3) shows the results for percentage yield of oil and biodiesel as well as the critical properties of the produced biodiesels as obtained from this study.

**Table 2: Percentage Yield of the Extracted Oil from the Various Seeds**

| S/No. | Seed | Weight of Seed Extracted (g) | Weight of Oil Recovered (g) | Percentage Yield (%) |
|---|---|---|---|---|
| 1. | Soapnut Seed | 1000 | 384 | 38.4 |
| 2. | Rapeseed | 1000 | 556 | 55.6 |

**Table 3: Percentage Yield of Biodiesel from the Various Seed Oil**

| S/No. | Seed | Volume of Oil Used in Making Biodiesel (mL) | Volume of Biodiesel Recovered (mL) | Percentage Yield of Biodiesel (%) |
|---|---|---|---|---|
| 1. | Soapnut Seed | 250 | 132.1 | 52.84 |
| 2. | Rapeseed | 250 | 184.2 | 73.68 |

**Table 4: Properties of the Produced Biodiesel Samples**

| S/No. | Properties | Biodiesel (Soapnut Seed oil) | Biodiesel (Rapeseed Oil) |
|---|---|---|---|
| 1. | Viscosity ($mm^2/s$ @$40^oC$) | 5.44 | 4.19 |
| 2. | Density @ $25^oC$ ($Kg/m^3$) | 869 | 847 |
| 3. | Flash Point ($^oC$) | 116 | 98 |
| 4. | Free Fatty Acid ($^o/_o$FFA) | 0.0216 | 0.0165 |
| 5. | Total Acid Number (TAN) (mgKOH/g) | 0.0432 | 0.0330 |

Tables 2 to 4 shows the oil yield, biodiesel production and the properties of biodiesel produced from soapnut and rapeseed. Rapeseed gave a better oil yield which also translated to a better biodiesel yield compared to what was obtained from soapnut. This suggests that rapeseed's potential as biodiesel source is relatively higher than for soapnut. The result of the fuel property for the produced biodiesel samples (i.e. kinematic viscosity, density, flash point) are in line with the ASTM standard (Alemayehu and Amanu, 2014). It shows that biodiesel produced from soapnut seed oil have a higher value of kinematic viscosity (5.44 $mm^2/s$ @ 40 $^oC$) when compared to biodiesel produced from rapeseed oil (4.19 $mm^2/s$ @ 40 $^oC$) and same goes for the density, flash point, free fatty acid (FFA) and total acid number (TAN). The values of the kinematic viscosity,

density, FFA and TAN obtained are all within the specified limits for diesel and at such can be used for diesel engines. The flash point value obtained for rapeseed is observed to be slightly lower compared to the ASTM standard (110 -150 $^{o}$C). This could be due to the number of times the biodiesel sample was washed with warm water. At least washing three times or more is hereby recommended.

Figure 2 to 5 highlights the rates of corrosion of copper, aluminum and stainless steel using biodiesels from soapnut seed oil, rapeseed oil compared to biodiesel from petroleum.

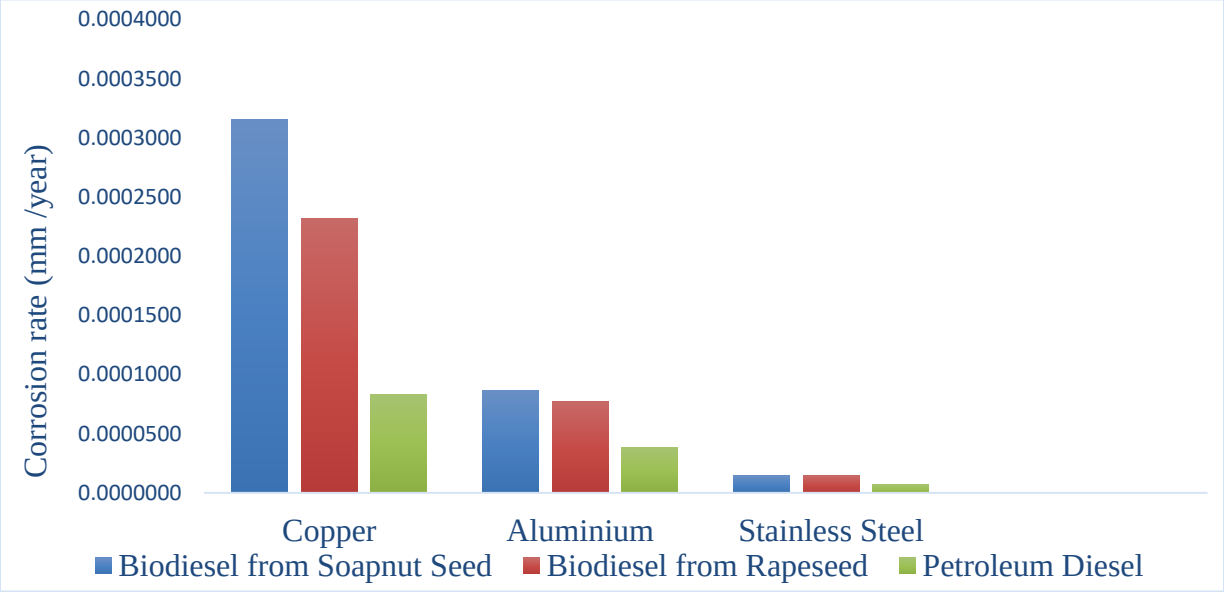


**Figure 2: Variations of Corrosion Rates in Biodiesel and Petro-Diesel**

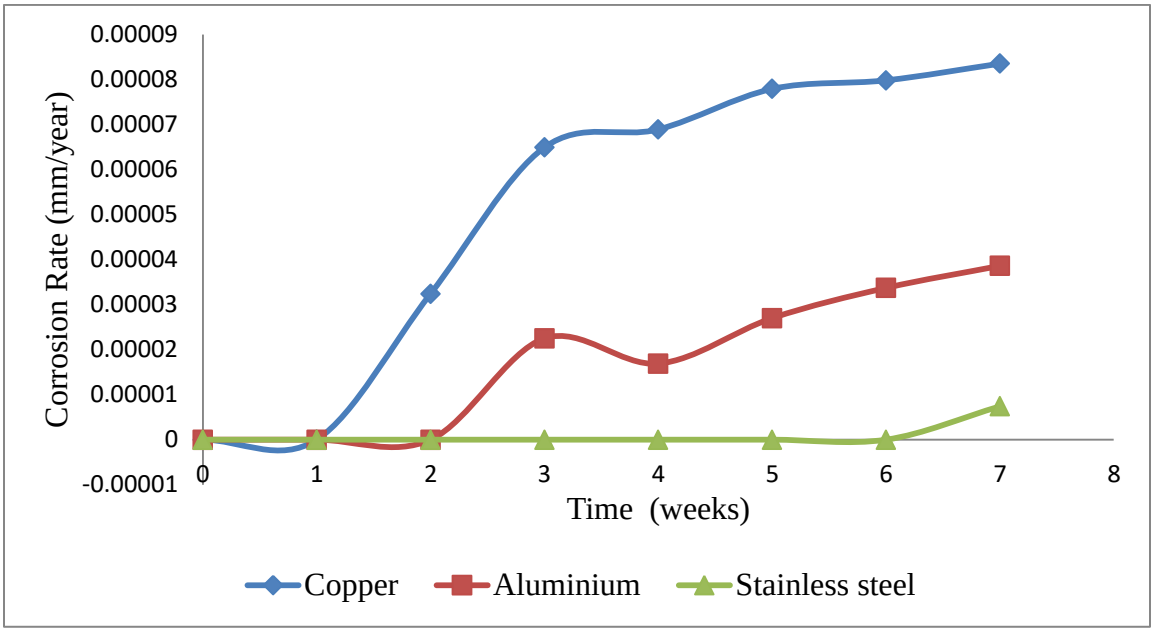


**Figure 3: Variation of Corrosion Rate of Copper, Aluminium, and Stainless Steel in Soapnut Biodiesel**

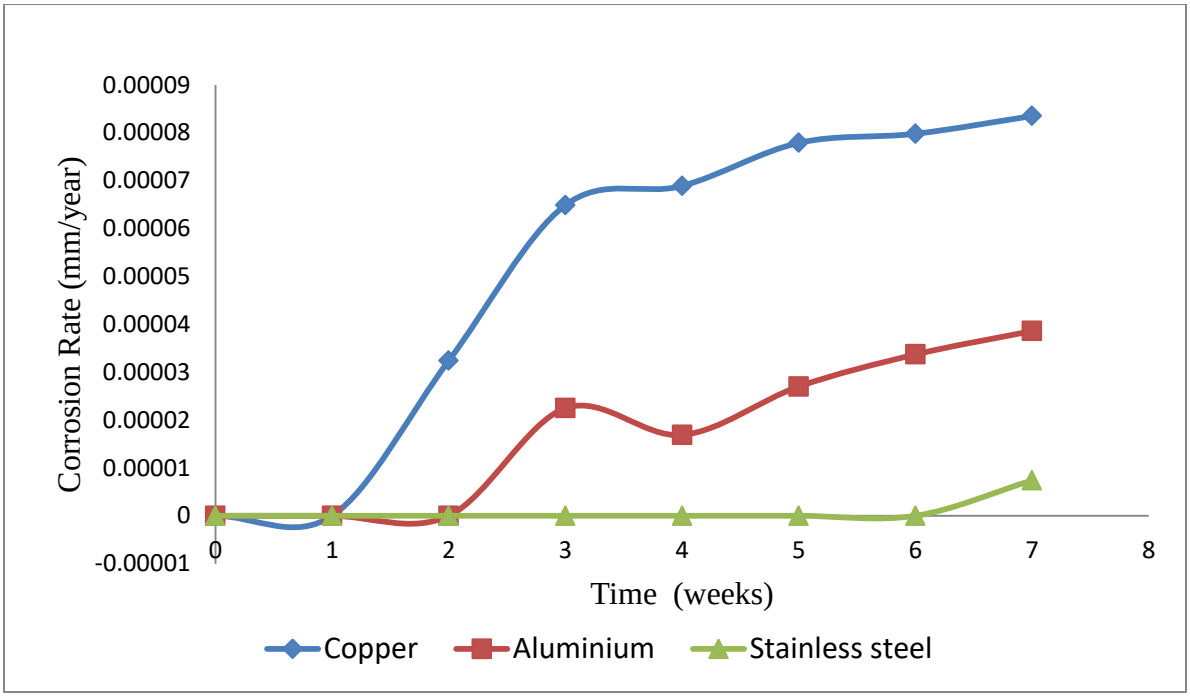


**Figure 4: Corrosion Rate of Copper, Aluminium, and Stainless Steel in Rapeseed Biodiesel**

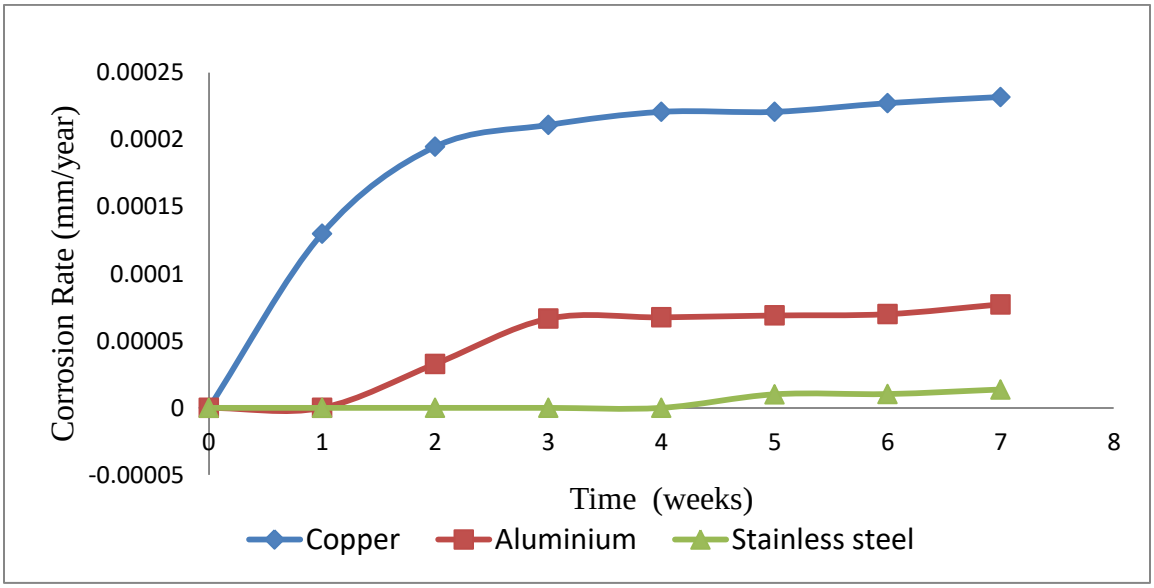


**Figure 5: Corrosion Rate of Copper, Aluminium, and Stainless Steel in Commercial Petroleum Diesel**

The corrosion properties of the produced biodiesel samples are one of the most important preconditions of biodiesel when used as engine fuel. The corrosion effects of biodiesel from rapeseed oil, soapnut seed oil, and petroleum diesel were determined by calculating their corrosion rates on the different metals used (i.e. copper, aluminium, and stainless steel) using the non-electrochemical process which involve weight loss measurements through metal immersion test. Figure 2 to 5 show that the corrosion rate of copper in all the environments was more severe than those of aluminum and stainless steel. The result obtained shows that the corrosion rate of copper is 0.0003155mm/year for biodiesel from soapnut seed oil, 0.0002319mm/year for biodiesel from rapeseed oil, and 0.0000835mm/year for commercial petroleum diesel, the corrosion rate of aluminum is 0.0000869mm/year for biodiesel from soapnut seed oil, 0.0000773mm/year for biodiesel from rapeseed oil, and 0.0000386mm/year for commercial petroleum diesel, while the corrosion rate of stainless steel is 0.0000147mm/year for biodiesel from soapnut seed oil, 0.0000147mm/year for biodiesel from rapeseed oil, and 0.0000074mm/year for commercial petroleum diesel, respectively.

Figure 2 to 5 also show that the corrosion effects of the produced biodiesel samples and petroleum diesel on aluminum was relatively minor, while the corrosion effects

of the produced biodiesel samples and petroleum diesel on stainless steel was very insignificant. These corrosion effects of the biodiesel samples on the metals were caused basically by the oxidation of the biodiesel samples leading to the creation of metal oxides. The corrosion rate of copper was higher owing to its higher oxidation rate, while aluminum and stainless steel had lower corrosion rates as a result of their lower oxidation rate. (Enzhu et al, 2019).

The results obtained also show that biodiesel from soapnut seed oil corrodes more than biodiesel from rapeseed oil, while petroleum diesel corroded the least when compared to the produced biodiesel samples in line with the works of Savita et al, (2007). Also the corrosion effect of the produced biodiesel samples and commercial petroleum diesel on copper was more severe than on aluminum and stainless steel.

## Conclusion

The corrosion rate of copper in all the samples was more severe than those of aluminum and stainless steel. The results obtained shows that biodiesel from soapnut seed oil can corrode more than biodiesel from rapeseed oil, while petroleum diesel corrodes the least when compared to the produced biodiesel samples.

In the light of the above, it is also recommended that more bio-sources be studied for their corrosion properties. This will help in the development of a corrosion behavioral ranking for biodiesel and their sources as well as creation of corrosion behavioral index for biodiesel applications.

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