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Investigation of the Corrosion Metals in Moringa Biodiesel Fuel

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ABSTRACT

One of the many problems that engineers face is the failure of numerous automotive parts due to corrosion. This investigative project was instituted to study the immersion of different types of metal surfaces such as aluminium, mild steel and copper in Moringa non-edible biodiesel at 60˚C for 1100 hours. This project gave an insight on the corrosion performance of similar metals immersed in Moringa biodiesels. Besides that, this project had fulfilled its objective to study the elemental composition of selected corrosion spots on the surface of the metal as there were presence of aggressive pitting corrosion on unpolished metal surface than on polished surface. In additions, any colour changes of biodiesels were also recorded as proof of chemical reactions between the metal and biodiesel. The results show that copper had the highest corrosion rate followed by aluminium and lastly, by steel. Marginally changes in biodiesel colour for aluminium and steel when immersed in Moringa biodiesel but the complete opposite was seen when copper was immersed in Moringa biodiesel.

Keywords:
Corrosion; non-edible; biodiesel

1. Introduction

Nowadays, biodiesel is commonly used as fuel in engines more often than diesel due to environmental concerns and the amount of emissions it gives out. Biodiesel will one day replace petroleum diesel depending on the how much the advantages diesel has over biodiesel. However, there will still be problems that have to be taken into account when exposing biodiesel with the engine walls. The problems are such as corrosion, tribo-corrosion, instability of biodiesel properties due to exposure of metal and with some other related environmental factors as stated by Fazal *et al.,* [1].

Engineers face an obstacle when the use of costly engines parts fail due to exposure to biodiesel. The static components include fuel tank, filter, fuel pump injector housing, fuel line, exhaust system,

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and cylinder liner while the dynamic components that are prone to failure include piston, rings on the piston, inlet and exhaust valve, fuel pumps, plunger in filter, and rod that connects to a piston as collected by Haseeb *et al.,* [2]. These are made from different metals that have different percentage levels of iron in them that come in contact with fuel and engine oil as mentioned by Fazal *et al.,* [3]

Therefore, it is important for research work to be done to understand the corrosion of engine parts when in contact with biodiesel. The factors that can affect the corrosion rate are such as temperature, light, radiation intensity and presence of different metals as mentioned by Fazal *et al.,* [4]. Fazal *et al.,* [5] have added corrosion inhibitors such as tert-butylamine (TBA), butylated hydroxyanisole (BHA) and antioxidants such as pyrogallol (PY), and butylated hydro-oxy toluene (BHT) to biodiesel and observed for long hours to investigate the corrosion rate based on previous research. The objectives of this research study is to investigate the corrosion rate on different types of metals when exposed to non-edible Moringa biodiesel (MB) under the same temperature and time. Also, the project aims to study the elemental composition of corrosion spots on the polished and unpolished surface of the metals.

2. Methodology

Aluminium (Al), copper (Cu) and mild steel (St) metal coupons of diameters 38mm, thickness 3mm with a hole of 2mm diameter were polished by micro-cloth polishing. Only one side of the metals were micro-cloth polished while the other sides were left as they were. After polishing the metals, the initial weight, w_i of the metal coupons where measured using an electronic balance with an accuracy of 5 decimal places in grams. Multiple perimeter readings of the metals such as the diameter, D (mm) and height, h (mm) were measured and recorded.

Three 100 ml beakers were labelled MB Al 1, MB Cu 1 and MB St 1 respectively. Strings were then inserted through each individual metal hole and were tied to sticks. The coupons were then rinsed using an alcohol with a low water content, absolute ethanol (98.8% concentrated) and degreased with a cleaning solvent, an acetone to get rid of any unwanted residues that may contaminate the project.

After the solutions have dried on the metal, they were immersed in beakers. After this step, the beakers were placed on the hotplate set to temperature of 60˚C. After 1100 hours have been completed, the hotplate was switched off and the biodiesels were allowed to cool. The metal samples were taken out and dried on petri dishes. Pictures of both polished and unpolished metal surfaces were taken using the digital microscope. Any obvious detection of corrosions was recorded. The metal coupons were measured with a Hitachi SUI510 SEM and Bruker Quantax EDX under voltage value of 10 kV for SEM micrographs and EDS analysis. Surface characterization using the similar equipment was also reported by most of the researchers [6, 7]. Three spots were taken from each metal sample; 1 for the unpolished side and 2 for the polished side. For each spot, there is a SEM micrograph and EDS analysis each and a magnification of 100X and 2000X. The metal coupons where placed on the electronic balance 3 times each to find the average final weight, w_f.

Difference in initial and final weights were labelled as w and were used to calculate the corrosion rate using Eq. (1) where w = weight loss (mg), ρ = density (g/cm^3), A = exposed surface area (square inch) and t = exposed time (hr).

$$\text{Corrosion rate } = \frac{534 \bigtriangleup w}{\rho \times A \times t} \tag{1}$$

3. Results

3.1 Corrosion Rate for Project

To calculate the corrosion rate for metals, Table 1 holds information of the metals before and after immersion for 1100 hours.

Table 1
Characteristics and corrosion rate of metals in Moringa biodiesel

Metals	Density (g/cm^3)	Area ($inch^2$)	Change in weight, $\triangle w$ (mg)	Corrosion rate, mpy
MB Al 1	2.70	1.7521	0.53	0.0544 (2)
MB St 1	7.85	1.7401	0.51	0.0181 (3)
MB Cu 1	8.96	1.7144	-28.6	0.9045 (1)

Using the formula below, Table 1 can be constructed to calculate the corrosion rate (mpy). The ratings (1) shows the highest corrosion rate and (3) shows the lowest corrosion rate.

3.1.1 Discussion

After calculating, MB Cu 1 (0.9045) holds the highest corrosion rate followed by MB Al 1 (0.0544) and finally, MB St 1 (0.0181) has the slowest corrosion rate.

a. Copper

Copper metal in Moringa biodiesel had a corrosion rate of 0.9045 mpy. Although all the metal samples had the more or less the same diameters, their densities were different. Copper metal had the highest density and had the biggest weight change such that it gained weight instead of losing weight as seen in the cases of both aluminium metals and mild steel metals. This does not necessarily mean that it did not corrode. In fact, the additional weight could be contributed by the oxide layer that was formed when the copper metal corroded while immersed in Moringa biodiesel. Since it showed similar results when compared to aluminium and mild steel when immersed in palm oil biodiesel as reported by Fazal *et al*., it can be assumed that their copper metal either lost or gained a significant amount of weight. In the corrosion rate formula, the change in weight is directly proportional to the corrosion rate (mpy). It does not matter if the metal lost weight or gain weight in this part of the discussion because as long as there is weight change, however small, is enough evidence that corrosion took place. Corrosion rates cannot be negative because it all came down to how fast the metals surfaces react with time as explained in Chemistry LibreTexts [8].

The immersion time is proportional to the corrosion rate [9, 10]. Fazal *et al.,* [11] have mentioned that the corrosion rate will gradually decrease with time if the copper metal is immersed for more than 1200 hours. Normally, increase in weight loss which causes increase in corrosion rate will happen in 2 stages: formation of corrosion products in the form of layers on biodiesel exposed metal surface and dissolution of formed layers. In that said journal, when the copper metal was immersed for 200 to 600 hours, there seems to be an indication of subsequent formation and dissolution of corrosion products in palm biodiesel.

Dissolution of corrosion product layer after immersion of 1200 hours decreased and this caused the weight loss also decreased. Since this project had metals immersed for 1100 hours, which was slightly less than 1200 hours, it was deduced that this project's copper metal experienced almost the same chemical reactions as this journal in such a way that there was a thin layer that have already started to form on the metal surface and there were also dissolutions of those formed layers that can be found in the Moringa biodiesel. This explains the gain in weight after immersion in Moringa biodiesel.

b. Aluminium

Aluminium in Moringa biodiesel had a corrosion rate of 0.0544 mpy. This metal had the second highest corrosion rates when compared to the other metal samples. Aluminium had the lowest density (2.70 g/cm^3). In the corrosion formula, it can be seen that density is inversely proportional to corrosion rate. That could be one of the reasons why aluminium metal had higher corrosion rates than mild steel. This statement can be supported again when aluminium in Moringa had a slightly more change in weight (≈0.02 mg more) than mild steel in Moringa.

In the Galvanic series mentioned in literature review part, aluminium is less noble than mild steel, making it more susceptible to corrosion than mild steel. Besides, Chew *et al.,* [10] have also mentioned that the position of metals in the Galvanic series also affect the ability of metals to donate and receive electrons. This supports the results that aluminium has a higher corrosion rate than mild steel.

Just like copper metal, aluminium also has the ability to form an oxide layer which also acts as a protective layer that prevents corrosion and hence, reduces the rate of reaction. Thangavelu *et al.,* [11] have suggested that this metal oxide layer not only stops oxygen from contacting with the metal surface but also prevents the biodiesel from contacting them. Similar to quarantine conditions. These factors will cause a low rate of corrosion.

c. Mild steel

For mild steel metal, its density is almost 3 times more than the density of aluminium and slightly less than the density of copper. This means that even though all the metal samples were of the same diameter and thickness, the weight of the mild steel metal is almost 3 times heavier than aluminium but also slightly less than copper. Mild steel metal in Moringa biodiesel had the same weight loss as the aluminium metal in the same type of biodiesel. Just like what was mentioned in the discussion part previously for aluminium and the corrosion rate formula, a lower density will result in lower rate of corrosion. Mild steel did not exhibit such a high rate of corrosion. Fazal *et al.,* [12] used stainless steel and recorded that the metal did not show significant corrosion even in palm oil biodiesel. Through this investigative project, the same can be said for Moringa biodiesel.

Hu *et al.,* [13] had suggested that mild steel has most likely formed layers of metal oxide which prevented the metal from undergoing further oxidation and hence, reduces the corrosion rate just like in aluminium. As mentioned before, this layer of metal oxide prohibits both oxygen atoms and biodiesel from further contacting the metal surface.

In summary, this project's results showed that copper had the highest corrosion rate followed by aluminium and steel regardless of whether it was immersed in Moringa biodiesel. This is in agreement with the results obtained by Fazal *et al.,* [12] where they had also used more or less the same type of metals: stainless steel, aluminium and copper. The difference is that this project used mild steel which contains carbon as the alloy whereas stainless steel uses chromium.

3.2 Comparing this Project's Corrosion Rates with Literature Reviews.
a. Aluminium

The maximum percentage difference which was 85.19% and minimum percentage difference was 5.24% can be seen when this project was compared to studies done by Fazal *et al.,* [14] and Thangavelu *et al.,* [11] respectively.

Although this project's Al 6061 immersed in Moringa biodiesels at 60˚C, it shows a lower corrosion rate when compared to the aluminium metals immersed at a lower temperature (room temperature around 25˚C to 27˚C) in palm oil and rapeseed oil except for in Chew *et al.,* [10] and Thangavelu *et al.,* [11]. This showed a good sign because normally when comparing palm oil biodiesels with each other, the higher temperature will show a higher corrosion rate as proven by Haseeb *et al.,* [15] and Fazal *et al.,* [12].

It is well worth noting that although this project's metals were submerged for 1100 hours, the corrosion rate was slower than other journal's metals that were submerged for shorter hours and even under the same temperatures or lower. These journals are concluded by Chew *et al.,* [10], and Thangavelu *et al.,* [11]. Chew *et al.,* [10] had metals immersed for 720 hours at room temperature and Thangavelu *et al.,* [11] immersed metals for 800 hours at room temperature and 400 hours at 60˚C. This is another good sign because according to Fazal *et al.,* [9] and Chew *et al.,* [10], the longer the immersion time, the higher the corrosion rate. This project has proven that findings' limitation.

b. Mild steel

The minimum percentage difference was 33.67% and the maximum was 97.20%. Both original corrosion rates were taken from Fazal *et al.,* [12] and Hu *et al.,* [13] respectively. This project's Moringa metals has lower corrosion rate than journals that have the same temperature (60˚) and lower even though the journals' metals were immersed for shorter hours. For example, Fazal *et al.,* [16] have immersed the metals for 480 hours and 960 hours under room temperature. The corrosion rates were 0.0525 mpy and 0.0687 mpy which was higher than this project's corrosion rate. In another study carried out by Thangavelu *et al*., [11], the temperatures used were room temperature for 800 hours and 60˚C for 400 hours. That study showed corrosion rates that were faster than this project's corrosion rate. Just like the Aluminium discussion previously, this is a good sign because by using Moringa instead of palm oil and rapeseed oil biodiesel, metals will corrode in a slower rate. In additions, other researchers also added various additives such as TBA, BHT, PY and etc in biodiesel to compare the corrosion rate of metals [17].

c. Copper

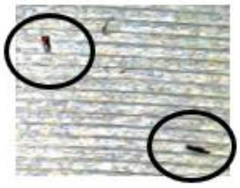
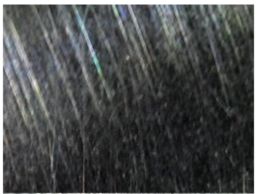
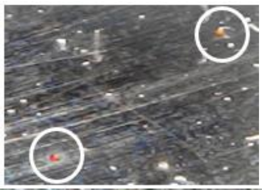
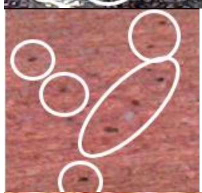
This project's copper metal immersed in Moringa biodiesel had one of the highest corrosion rates when compared to the previous journals' metals. For copper, Moringa biodiesel proved to provide a more corrosive environment to it than palm oil biodiesel. This could be due to the chemical compositions in the metals and how they react with the biodiesels.

When MB Cu 1 was compared to the metals investigated by Hu *et al.,* [13] that used rapeseed biodiesel, it had a lower corrosion rate by a small amount and hence extinguishes the thought of calculation error. This copper in Moringa biodiesel may not have a lower rate of corrosion when compared to palm oil biodiesel but it does at least have a lower rate than the copper metal immersed in rapeseed oil.

3.3 Metal Surfaces Before and After Immersion

Mild steel is an alloy which contains around 90% of iron, Fe. Based on the findings by Fazal *et al.,* [14], mild steel in this project will form small amounts of Fe_2O_3 and $Fe(OH)_2$ but high amounts of Fe_2O_3, $Fe(OH)_2$ and $Fe_2(OH)_2CO_3$. There were countless reddish spots on the surfaces that were large enough to be detected by the USB digital microscope for MB St 1. There were so many of these spots that in Table 2, majority of the surface area of MB St 1 are covered in reddish spots that can be seen by the human eye. These reddish spots are from the formation of Fe_2O_3, $Fe(OH)_2$ and $Fe_2(OH)_2CO_3$. The reactions can be simplified below. These two reactions are caused due to the presence of water and oxygen in biodiesel. Rusting, ferrous hydroxide, can happen when water and oxygen come in contact with iron metal.

Table 2
Metal surfaces before and after immersion

Metals	Before immersion	After immersion
MB Al 1 (unpolished surface)		
MB Al 1 (polished surface)		
MB St 1 (unpolished surface)		
MB St 1 (polished surface)		
MB Cu 1 (unpolished surface)		
MB Cu 1 (polished surface)		

$$4Fe + 4H_2O + 2O_2 \rightarrow 4Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3{\cdot}H_2O + 2H_2O$$

3.4 SEM and EDS Analysis

The SEM and EDS analysis for three different metals on polished surfaces are shown in Figure 1 to Figure 6.

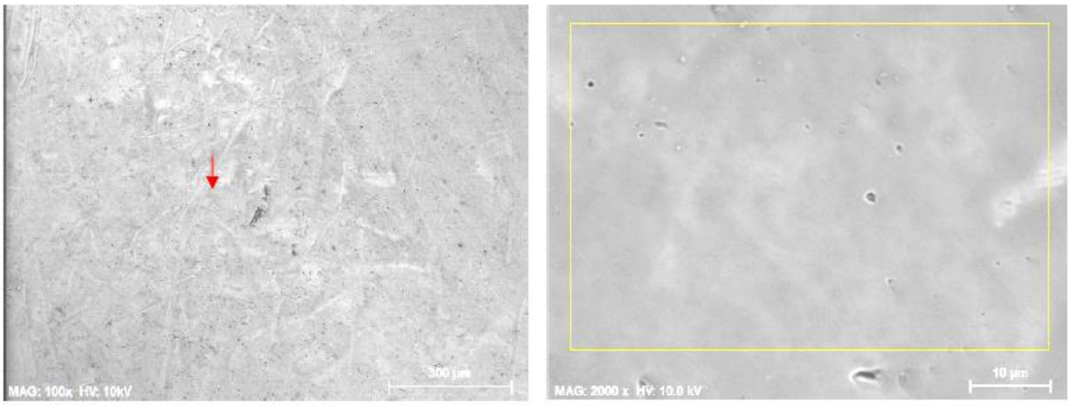


Fig. 1. SEM picture of Spot 2 (polished surface) for magnification 100X (left) and 2000X (right) of mild steel metal immersed in Moringa biodiesel for 1100 hours in 60˚C

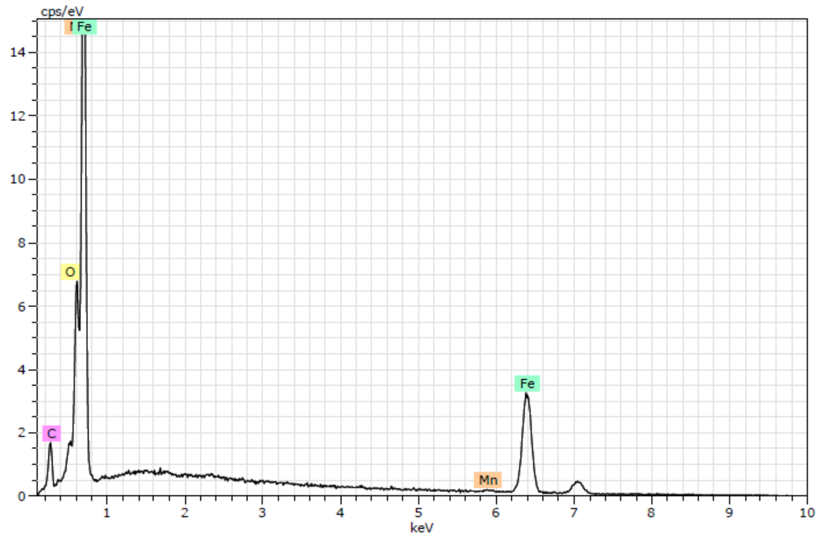


Fig. 2. EDS elemental analysis of Spot 2 (polished surface) of mild steel metal immersed in Moringa biodiesel for 1100 hours in 60˚C

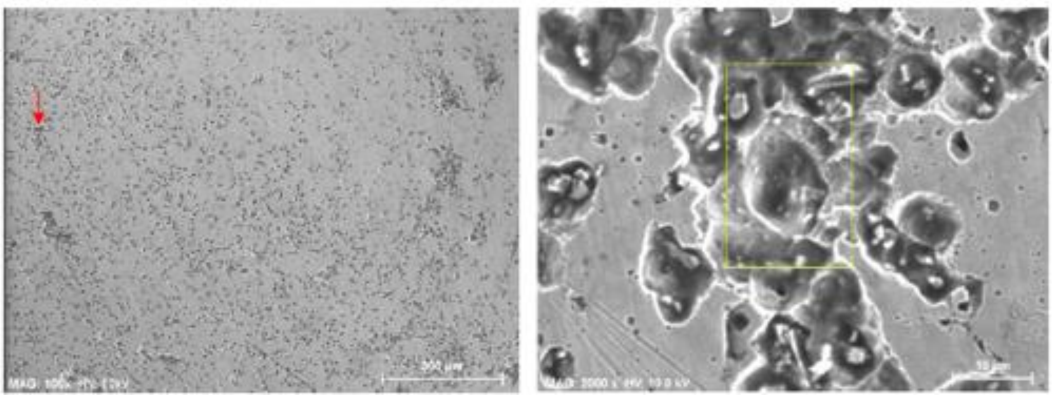


Fig. 3. SEM picture of Spot 3 (polished surface) for magnification 100X (left) and 2000X (right) of copper metal immersed in Moringa biodiesel for 1100 hours in 60˚C

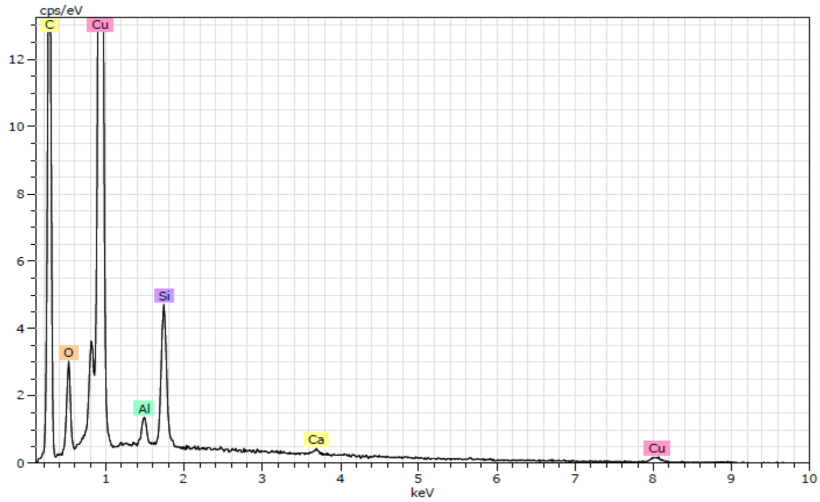


Fig. 4. EDS elemental analysis of Spot 3 (polished surface) of copper metal immersed in Moringa biodiesel for 1100 hours in 60˚C

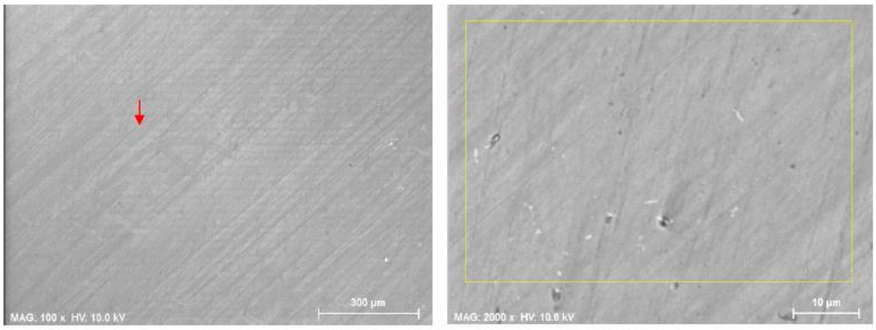


Fig. 5. SEM picture of Spot 2 (polished surface) for magnification 100X (left) and 2000X (right) of aluminium metal immersed in Moringa biodiesel for 1100 hours in 60˚C

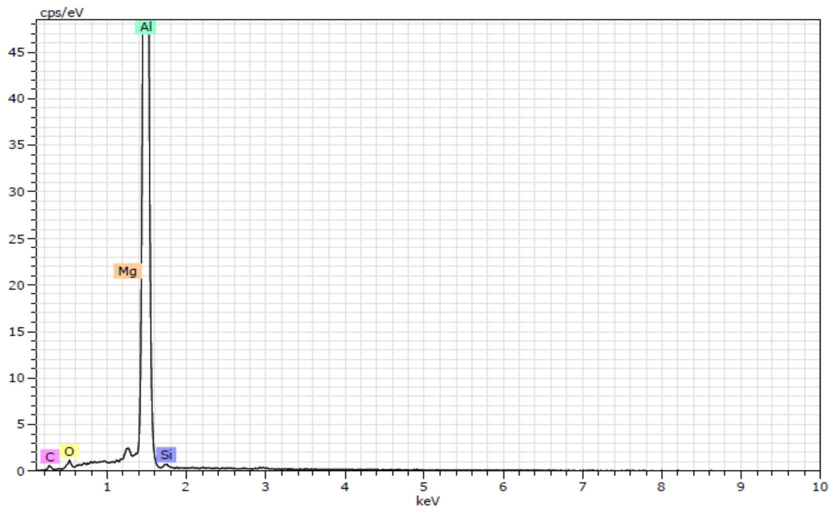


Fig. 6. EDS elemental analysis of Spot 2 (polished surface) of aluminium metal immersed in Moringa biodiesel for 1100 hours in 60˚C

MB St 1 had the lowest corrosion rate whereas MB Cu 1 had the highest corrosion rate. Based on Figure 1, 3 and 5, copper had more severe pitting corrosion than mild steel and aluminium. This can be further proven in EDS elemental analysis as shown in Figure 2, 4 and 6 when copper had higher percentage of C and O atoms than other metals.

3.3 Pictures of Biodiesel Before and After Immersion

Based on Figure 7, there wasn't much changes in biodiesel colour except for MB Cu 1. The biodiesel exposed copper should have traces of $CuCO_3$ along with Cu(OH), $Cu(OH)_2{\cdot}H_2O$, $CuCO_3{\cdot}Cu(OH)_2$, CuO and Cu_2O. This could mean that there is more change in biodiesel composition which in turn will affect the fuel properties.

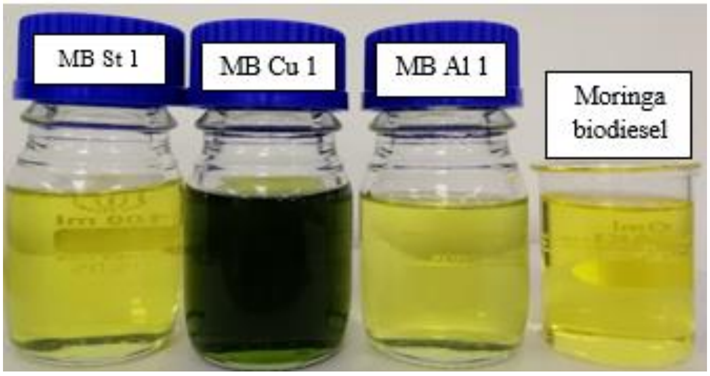


Fig. 7. MB St 1, MB Cu 1 and MB Al 1 after immersion (in bottle) and Moringa biodiesel before immersion (in beaker)

4. Conclusions

In this study, it was found that copper had the highest corrosion rate followed by aluminium and lastly, by steel. When their rate of corrosions were compared to previous journals that used palm oil, rapeseed oil and other biodiesels, it was also found aluminium and steel immersed in Moringa biodiesels showed lower corrosion rates. This is due to the formation of metal oxide layer that prevents biodiesel and oxygen atoms from coming into contact with the metal surface.

In additions, polished metal surfaces no matter the type of metal will show less pitting corrosion when compared to their unpolished counterparts. Although polished surfaces may sometimes have higher percentage of carbon and oxygen atoms than unpolished area, this corrosion spot can only be found in a few desolated parts of the metal surface. Majority of the unpolished surface will be covered with aggressive pitting corrosion.

Lastly, there is not a lot of change in biodiesel colour for aluminium and steel when immersed in Moringa biodiesel but the complete opposite was seen when copper was immersed in biodiesel. This could mean that there is more change in biodiesel composition which in turn will affect the fuel properties.

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