Influence of copper on the instability and corrosiveness of palm biodiesel and its blends: An assessment on biodiesel sustainability

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Abstract

Biodiesel is comparatively more corrosive than petroleum diesel; therefore, the issue of sustainability has become a major concern. Biodiesel is auto-oxidative in nature; thus, its fuel properties could be changed. The present study aims to investigate the sustainability of biodiesel and its different blends with diesel in terms of instability and corrosiveness upon exposure to copper. The investigated fuels are diesel, 20% biodiesel in diesel, 50% biodiesel in diesel, and pure biodiesel. Immersion tests in the absence and presence of 100 ppm tert-butylamine or butylated hydroxyanisole additive were conducted at temperatures of 25°C to 27°C for 600 and 1200 h. At the end of the tests, corrosion of copper was examined by weight loss measurement and changes on the metal surface. Metal surfaces were characterized by scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, and atomic force microscopy. Fuel was analyzed by gas chromatography-mass spectroscopy, and its properties were investigated by density meter and Rancimat method. Results show that corrosion rate of copper in biodiesel or its high percentage of blends rises with the increase in immersion time. Corrosion rate of copper in diesel and 20% diesel–biodiesel blends are similar and do not significantly change with immersion time. To improve sustainability, BHA is found to be effective in reducing biodiesel oxidation, whereas TBA reduces the metal surface degradation.

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1. Introduction

Biodiesel is gradually gaining acceptance because it is derived from renewable sources and has of environmental benefits (Chuah et al., 2017; Caliskan, 2017). Chemically, biodiesel refers to fatty acid alkyl esters that are derived from different feedstocks, such as palm, corn, rapeseed, soybean, and used fried oil. Fuel properties of biodiesel are extremely close to those of petroleum diesel. Biodiesel has a few technological advantages over petroleum diesel (Miri et al., 2017) and it also reduces emission (Aoun et al., 2016). Therefore, biodiesel appears to be a promising alternative fuel for automobile applications. However, a few concerns have arisen regarding the properties of biodiesel and its effect on engine durability. With regard to sustainability, the oxidation and corrosive character of biodiesel appear to be major concerns (Zuleta et al., 2012; Agarwal et al., 2015; Fazal et al., 2017). These critical issues might affect fuel quality and the materials that come in contact with biodiesel.

When biodiesel is oxidized, its fuel composition and properties change at different levels. The underlying principles of biodiesel oxidation have been well documented (Silva et al., 2017). When biodiesel made from unsaturated oil is exposed to oxygen, the oxygen attaches itself to the bis-allylic site that is directly adjacent to the two double bonds, thereby initiating autoxidation reactions. Through oxidation, esters of biodiesel are converted into different components, including alcohols, ketones, ethers, alkanes, organic acids, aldehydes, and oligomers (Schaich, 2005). Consequently, biodiesel properties, such as acid value, peroxide value, and viscosity increase, whereas the iodine value and the content of methyl esters decrease (Zuleta et al., 2012). These properties could be further aggravated when metals are exposed to biodiesel (Fazal et al., 2017). In addition, the changes in the chemical and physical properties of biodiesel can affect the integrity and stability of the
biodiesel are mainly caused by the presence of water and free fatty acids. The chemical composition of biodiesel changes upon exposure to metals in biodiesel. In addition, biodiesel degradation causes enhanced corrosion of metal surfaces. Upon exposure to biodiesel, the corrosion behavior of different materials, such as copper, cast iron, leaded bronze, and aluminum, stainless steel has been investigated by several researchers (Haseeb et al., 2011; Geller et al., 2008). Copper was found to be more susceptible to corrosion in biodiesel compared to aluminum and stainless steel (Fazal et al., 2010). Copper is also reported to act as a strong catalyst to oxidize biodiesel (Fazal et al., 2013). Sgroi et al. (2005) reported pitting corrosion on the nozzle of sintered bronze upon biodiesel exposure. These studies suggest that copper and copper-based alloys are

<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>B0</td>
<td>diesel</td>
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<tr>
<td>B20</td>
<td>20% biodiesel in diesel</td>
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<tr>
<td>B50</td>
<td>50% biodiesel in diesel</td>
</tr>
<tr>
<td>B100</td>
<td>100% biodiesel</td>
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<tr>
<td>FAAEs</td>
<td>fatty acid alkyl esters</td>
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<tr>
<td>TBA</td>
<td>tert-butylamine</td>
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<td>BHA</td>
<td>butylated hydroxyanisole</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>EDS</td>
<td>energy dispersive spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>GCMS</td>
<td>gas chromatography–mass spectroscopy</td>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<td>IP</td>
<td>induction period</td>
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material, thereby possibly limiting the extensive use of biodiesel. The oxidation level of biodiesel is measured by determining the induction period (IP), which corresponds to the appearance of the secondary oxidation products or low-molecular organic acids. The time that elapses until the appearance of these secondary reaction products is called oxidation stability, induction time, or IP, which characterizes the resistance of biodiesel against oxidation. Given its chemical structure, oxidation rates of biodiesel could depend on many variables, such as temperature, light, radiation intensity, and presence of different metals.

Owing to the problems that are associated with the corrosion and compatibility of automotive parts, a high percentage of biodiesel still remains unused in engines. In vehicles, the fuel remains in direct contact with different parts of the engine, such as the fuel pump, fuel injector, pistons, and piston rings (Haseeb et al., 2011). Several studies (Haseeb et al., 2011; Fazal et al., 2014) reported that biodiesel is more corrosive than diesel. The corrosive effects of

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<th>Table 1</th>
<th>Specification of Palm biodiesel.</th>
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<tr>
<td>Parameter</td>
<td>Unit</td>
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<tr>
<td>Density</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Kinetic Viscosity</td>
<td>mm²/s</td>
</tr>
<tr>
<td>Acid number</td>
<td>mg KOH/g</td>
</tr>
<tr>
<td>Free glycerin</td>
<td>wt%</td>
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<tr>
<td>Total glycerin</td>
<td>wt%</td>
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<tr>
<td>Ester content</td>
<td>wt%</td>
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<th>Table 2</th>
<th>Structural formula of different additives used in biodiesel.</th>
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<tr>
<td>Inhibitor</td>
<td>Tert-butylamine (TBA)</td>
</tr>
<tr>
<td>Anti-Oxidant</td>
<td>Butylated Hydroxy Anisole (BHA)</td>
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![Flowchart of the experimental procedure adopted in the current work.](image-url)
more susceptible to corrosion in biodiesel. Different fuel properties, including viscosity, density, total acid number, oxidation stability, and water content, change with biodiesel oxidation and become more chemically aggravated. Therefore, 100% pure biodiesel does not appear to be a sustainable fuel in automobiles. The present study aims to investigate the level of instability and corrosiveness of different biodiesel blends upon exposure to copper. The influence of different additives on the corrosion of copper will also be examined.

2. Experimental investigation

The specification of palm biodiesel used is shown in Table 1. The structural formula of the investigated additives, such as tert-butylamine (TBA) and butylated hydroxyanisole (BHA), are presented in Table 2. The experimental investigation was conducted by immersion tests, followed by the analysis of metal surface and tested fuels. Fig. 1 shows the flowchart of the experimental procedure adopted in the present work. The test coupons of copper, which are 17.2 mm in diameter and 2 mm in thickness, were made from round copper bars by machining and grinding. A 2 mm in diameter hole was drilled near the edge of each coupon. This hole helps to hang the specimen in biodiesel during the immersion test. Haseeb et al. (2010) also used a similar size of coupon for investigating the corrosion of different metals in palm biodiesel. First, test coupons were polished with silicon carbide abrasive papers of grade 400–1200. Then, the polished coupons were dipped into the alcohol for several minutes and degreased with acetone. After drying, two duplicate coupons of each metal were individually immersed into the glass beakers. Each 600 mL beaker was previously filled with 400 mL of different fuels/blends, such as diesel (B0), 20% biodiesel in diesel (B20), 50% biodiesel in diesel (B50), pure biodiesel (B100), 100 ppm TBA-doped biodiesel (B100/TBA), and 100 ppm BHA-doped biodiesel (B100/BHA). After immersion test for 600 and 1200 h at temperatures 25°C–27°C, the samples were washed in a stream of water. Before and after exposing the test coupon into different test fuels, the weights of each coupon were measured by a weighing scale with four decimal points. Similar experimental procedures were also followed by Fazal et al., (2013) to investigate the corrosion mechanism of copper in palm biodiesel. It is worth mentioning that none of these corrosion tests in biodiesel is in accordance to any particular standard method. For each tested coupon, weight loss was calculated by subtracting the final weight (after exposure) from its initial weight (before exposure). Average weight loss was obtained for the two duplicate coupons used, and corrosion rate was then measured by using Equation (1) (Fazal et al., 2013).

![Fig. 3. Photograph of exposed metal surface after exposure to different fuels for 1200 h: a) Cu in B0, b) Cu in B20, c) Cu in B50, d) Cu in B100, e) Cu in B100/TBA, f) Cu in 100/BHA.](image1)

![Fig. 4. SEM micrographs of copper (2000× magnification) before and after exposure (1200 h) in palm biodiesel at room temperature.](image2)
Corrosion rate \[ \text{Corrosion rate} = \frac{8.76 \times 10^6 w}{D t A} \] (1)

In Equation (1), the corrosion rate is in micrometer per year (\( \mu m/y \)), \( w \) is the weight loss (kg), \( D \) is the density (kg/m³), \( A \) is the exposed surface area (m²), and \( t \) is the exposure time (h). Changes in surface morphology were characterized by a digital camera and scanning electron microscopy (SEM). Elemental and compositional analysis of the corrosion products were examined by using energy dispersive spectroscopy (EDS) and X-ray diffraction pattern (XRD). The changes in composition, density, and oxidation of the fuels were examined by gas chromatography–mass spectroscopy analyzer, density meter (DMA35), and Rancimat method, respectively.

3. Results and discussion

Fig. 2 shows the corrosion rate of copper in different fuels/blends in the presence and absence of additives. Corrosiveness of different biodiesel blends is found in the following order: \( B100 > B50 > B20 > B0 \), thereby suggesting that corrosiveness of biodiesel blends rises with the increase of biodiesel concentration. Enhanced corrosion rate upon increased concentration of biodiesel could be attributed to the presence of oxygen and absorbed moisture (Jakeria et al., 2014). Fig. 2 also indicates that corrosiveness of B50 and B100 rises with the increase of metal exposure time. However, B0 and B20 did not show any significant change in copper corrosion with exposure time.

Fig. 2 uses a \( t \)-test for statistical analysis to test a hypothesis about the difference between the means of the populations from which the two specimens come. In this statistical analysis, the \( t \)-test has been constructed to determine whether the difference between the two means equals zero versus the alternative hypothesis that the difference does not equal zero. It is noted that the equal variances have been assumed in this test and therefore \( t = -0.771 \) and the computed \( P \)-value is 0.458 which is not less than 0.05. As a result, we cannot reject the null hypothesis (i.e., there is not a statistically significant difference between the means of the two specimens at the 95.0% confidence level).

Notably, the corrosion rates of copper in biodiesel fuel are approximately 6.6 and 9.8 \( \mu m/y \) for 600 h and 1200 h of exposure time, respectively. These results could be compared with the data from literature where it is reported that the corrosion rate of copper in a 2880 h test is 9.97 \( \mu m/y \) in palm biodiesel at 25–27 °C (Fazal et al., 2010), 60 days (~1440 h) test is 23.34 \( \mu m/y \) in biodiesel fuel at 43 °C (Enzhu et al., 2012), and 1200 h test is 16–18 \( \mu m/y \) in palm biodiesel at 25–27 °C (Fazal et al., 2013). The reported corrosion rates vary depending on test conditions as well as quality of biodiesel. It is worth mentioning that biodiesel is conventionally purified using water, dry washing or membrane technologies (Atadashi, 2015). Water could eliminate the remaining sodium salts and soaps formation because of their water solubility (Hayyan et al., 2010). The content of water, salt etc. in biodiesel as well as molecular components could also vary with the purification process adapted and these things might cause variation of metal corrosion even in similar test conditions. Although copper was found to be extremely aggressive in B100, its corrosion rate in B20 and B0 was...
Similar assumptions were also reported by Haseeb et al. (2010). Returns of biodiesel or its blends, a black corrosion product layer is found to be formed on the copper; whereas the original color of the coupon in diesel does not significantly change. Furthermore, the black color appears to be dark for the coupons that were exposed to high concentrations of biodiesel. Increased concentration of biodiesel is believed to be an important factor to enhance the corrosion of copper. A dark corrosion product layer on the copper surface suggests the appearance of more corrosion products after exposure. By visual inspection, the TBA additive was found to be more effective in preventing the formation of such black/dark corrosion products. Copper in TBA-doped biodiesel has a nearly similar appearance to that of diesel exposed coupon, thereby suggesting that TBA is effective to protect the copper surface from corrosion. Thus, using TBA additive has significant importance in reducing corrosion.

Fig. 3 shows the appearances of copper surfaces after exposure to diesel, palm biodiesel, and blends. Upon exposure to copper in biodiesel or its blends, a black corrosion product layer is found to be formed on the copper; whereas the original color of the coupon in diesel does not significantly change. Furthermore, the black color appears to be dark for the coupons that were exposed to high concentrations of biodiesel. Increased concentration of biodiesel is believed to be an important factor to enhance the corrosion of copper. A dark corrosion product layer on the copper surface suggests the appearance of more corrosion products after exposure. By visual inspection, the TBA additive was found to be more effective in preventing the formation of such black/dark corrosion products. Copper in TBA-doped biodiesel has a nearly similar appearance to that of diesel exposed coupon, thereby suggesting that TBA is effective to protect the copper surface from corrosion. Thus, using TBA additive has significant importance in reducing corrosion.

Fig. 4 shows the SEM micrographs of different fuel exposed copper surfaces. A few pits marked by arrows evidently formed on biodiesel exposed metal surfaces due to corrosion attack or breaking down of oxygenated compounds. Corrosion attack on biodiesel exposed copper surface is comparatively more than that in additive-doped biodiesel. A few scratches marked by arrows are evident on the as-received SEM image, but those are not found on biodiesel exposed metal surfaces. Scratches could disappear because of corrosion in biodiesel. In the presence of the TBA and BHA additives as shown in Fig. 4c and d, respectively, the rough surface is visibly reduced. A close inspection reveals that the pit density in the presence of TBA is less than that in the presence of BHA.

The EDS indicates that corrosion products of different fuel exposed copper surfaces contain mainly C, O, and Cu as shown in Fig. 5. The corrosion products of copper in B0 and B100 have slightly different compositions. Concentrations of C and O are comparatively more in B100 exposed copper than that in B0, which could be attributed to the formation of corrosion compounds inside the pits, such as oxides and carbonates, due to corrosion attacks in biodiesel. Similar assumptions were also reported by Haseeb et al. (2010). Based on the results obtained by Fazal et al. (2013), the composition of corrosion products could be different copper compounds, such as CuCO3 and Cu(OH)2. Given that TBA was added in B100, the EDS results show an increased concentration of C, thereby possibly suggesting the formation of a carbonate layer on the copper surface. The formation of carbonate-based layer on copper in biodiesel could contribute to corrosion rate reduction.

Fig. 6 shows the XRD spectra of biodiesel/diesel exposed copper surface in the absence and presence of 100 ppm additives, such as TBA or BHA. Copper in biodiesel evidently forms Cu(OH)2, CuO, and CuCO3, whereas Cu2O is only formed in diesel. Such result is in good agreement with the results reported by Fazal et al. (2013). Reactions (2)–(5) represent the possible formation mechanisms of the corrosion compounds. Biodiesel absorbs moisture from environment. In the presence of oxygen and CO2, metal surface interacts with moisture and forms different compounds. In the present study, copper upon exposure in biodiesel forms different corrosion products as shown in reactions (2)–(5). These corrosion products are loosely bonded to the metal surface. Subsequent formation and dissolution of these compounds on copper in biodiesel appear to increase the corrosion rate. Diesel exposed coupons that form lower concentrations of oxides indicate lower corrosion compared to that for biodiesel exposed coupons. The related reaction mechanism is shown in reaction (6). Notably, the formation of nitrogen-based compounds, such as Cu(NO3)2.3H2O, are only observed when biodiesel is doped with additives. This finding suggests that the nitrogen-bearing additives, such as TBA and BHA, were absorbed on the metal surface by forming nitrogen-bearing compounds. Furthermore, Fig. 6 indicates that the amount of oxide/carbonate compounds is highly reduced in TBA-doped biodiesel. High concentrations of CuCO3 are found to be formed even after BHA addition. This finding suggests that TBA is a comparatively better additive than BHA in reducing corrosion attacks on the metal surface while exposed in biodiesel.

Major corrosion compounds formed in biodiesel:

$$2Cu + O_2 + 2H_2O \rightarrow 2Cu(OH)_2$$  \hspace{1cm} (2)

$$2Cu + \frac{1}{2} O_2 \rightarrow CuO$$  \hspace{1cm} (3)

$$CuO + CO_2 + \frac{1}{2} O_2 \rightarrow 2CuCO_3$$  \hspace{1cm} (4)

$$CuO + CO_2 \rightarrow CuCO_3$$  \hspace{1cm} (5)

Major corrosion compound formed in diesel:

$$2Cu + \frac{3}{2} O_2 \rightarrow Cu_2O$$  \hspace{1cm} (6)
AFM images of biodiesel exposed copper surfaces in the absence and presence of 100 ppm TBA are shown in Fig. 7. Surface roughness is respectively found to be 243.504 nm and 186.935 nm. These results are complementary to the SEM micrographs, which are shown in Fig. 4. The sample examined in the presence of TBA shows less corrosion attack which results in less surface roughness.

Fig. 8 shows the oxidation stability of biodiesel prior to and after exposure to copper in the presence or absence of additives. The IP of as-received biodiesel is 1.2 h, and it decreased to 0.72 h while exposed to the copper surface. Naturally, biodiesel has less oxidation stability (Yaakob et al., 2014). The oxidation stability of biodiesel in the presence of TBA and copper was decreased to 0.4 h. Owing to the addition of BHA, oxidation stability reached close to the value of as-received biodiesel, whereas it further decreased for copper exposed TBA-doped biodiesel. Such result suggests that BHA is better than TBA in increasing oxidation stability. Moreover, this result is in good agreement with the results obtained from the study related to the effect of different inhibitors in reducing corrosion of cast iron in biodiesel (Fazal et al., 2011).

Table 3 shows the compositional changes of palm biodiesel before and after exposure to copper for 600 h. Methyl palmitate, oleate, and linoleate are the major components of palm biodiesel, which were slightly reduced in concentration after exposure to copper for 600 h. A few components, such as palmitic acid and C16H32O2, were newly produced; meanwhile, some components, such as methyl myristate, laurate, and 9, 10-epoxyoctadecanoate, were increased in concentration. Further studies should be conducted to understand the related mechanism of changing biodiesel composition and their effect on fuel properties.

Fig. 9 shows that the as-received biodiesel and diesel have 0.883 and 0.852 g/cm³ density, respectively. The density of copper exposed blends increases with the increase in biodiesel concentration. Copper exposed B100 shows nearly similar density to that of as-received biodiesel and is not excessively changed even after TBA or BHA addition. Although the metal exposed biodiesel exhibits increased density, these values remain within the range of 0.86 g/cc to 0.9 g/cc given by the EN14214 standard.

4. Conclusion

The following conclusions are drawn from the present study.

a. Instability of fuel properties and corrosiveness of biodiesel are found to be significant sustainable issues. Lower percentages of biodiesel blends are more sustainable than pure or higher percentages of biodiesel.

b. Corrosiveness of B20 (20% biodiesel and 80% diesel) and diesel appears to be nearly similar. Therefore, B20 is acceptable for automobile applications. Furthermore, 100% biodiesel shows
higher corrosiveness for copper compared to diesel. Hence, copper is not recommended to be used in biodiesel.

c. TBA was found to be an effective corrosion inhibitor for copper, whereas BHA showed better antioxidant properties for biodiesel. Formation of nitrogen-based compounds on biodiesel exposed copper surface might reduce the corrosion rate. Further studies should be conducted to understand the related mechanisms.

d. Methyl palmitate, oleate, and linoleate are found to be the major components of palm biodiesel, and these were slightly reduced in concentration after exposure to copper for 600 h. Densities of biodiesel and its blends before and after immersion test were found to be within the limit given by EN 14214. However, the oxidation stability of palm biodiesel upon exposure to copper was found to be extremely poor and further decreased with the TBA addition. By contrast, the IP of biodiesel was found to be increased upon BHA addition and becomes very close to that of as-received biodiesel.

Acknowledgments

The authors would like to acknowledge the financial support provided by the Institute of Research Management and Consultancy of University of Malaya (UM) under UMRG (University of Malaya Research Grant) fund Project Nos. RP013B-13AET and RG137-12AET.

References


Fig. 9. Change in density of biodiesel and its blends before and after exposure to copper in the presence and absence of additives at room temperature for 600 and 1200 h.