Sustainability of additive-doped biodiesel: Analysis of its aggressiveness toward metal corrosion

M.A. Fazal a, b, *, N.R. Suhaila a, A.S.M.A. Haseeb a, Saeed Rubaiee b, c

a Department of Mechanical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
b Department of Mechanical Engineering, University of Jeddah, Saudi Arabia
c Department of Industrial Engineering, University of Jeddah, Saudi Arabia

A R T I C L E   I N F O
Article history:
Available online 1 February 2018

Keywords:
Sustainability
Copper alloys
Palm biodiesel
Corrosion
Additives

A B S T R A C T
The recent shortage of fossil fuel sources and the growing environmental concerns have considerably affected the necessity to search for alternative energy sources. The tremendous increase in energy demands in the transportation and industrial sectors has strengthened efforts to identify sustainable alternative fuel sources. In this regard, biodiesel can be considered a promising substitute for diesel. However, biodiesel is corrosive when it comes in contact with metals. The present study aims at investigating the sustainability of additive-doped biodiesel upon exposure of copper-based materials. A static immersion test was conducted at room temperature (25 °C–27 °C) for 2160 h. The metals used in the experiment were copper, leaded bronze, and phosphorous bronze. The investigated fuel was 100% palm biodiesel without and with additives (300 ppm), including tert-butylamine, benzotriazole, propyl gallate, pyrogallol, and butylated hydroxytoluene. The corrosion rate of the metals was determined at the end of the experiment via weight loss measurement. The metals were further characterized via scanning electron microscopy, energy-dispersive spectroscopy, and X-ray diffraction analysis. Results showed that the corrosion rate of copper was considerably higher than those of the other metals. X-ray diffraction analysis indicated the presence of copper carbonate and cupric oxide on the copper surface that was exposed to biodiesel. The occurrence of these compounds could be attributed to the high concentrations of carbon dioxide and oxygen in the biodiesel when additive was absent. Gas chromatography–mass spectrometry data showed that the unsaturated molecules in biodiesel could reduce the sustainability of metals upon exposure to biodiesel. However, metal surface degradation was significantly reduced in the presence of additives, in particular, benzotriazole and tert-butylamine considerably improved the sustainability of biodiesel by limiting metal surface degradation.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The use of biodiesel is becoming increasingly popular because of the depletion of fossil fuel sources and the increasing energy demands (Jakeria et al., 2014). This type of fuel is a favorable alternative to fossil fuels due to its technical advantages, which include being natural, being produced from renewable sources (Bala et al., 2017) and exhibiting properties that are similar to those of diesel (Sarave et al., 2017). Biodiesel also does not contain sulfur. Hence, its use results in low gas emissions, which significantly affect the environment. Nonetheless, the use of biodiesel has several limitations, including metal surface degradation (Fazal et al., 2013), autoxidation (Jain and Sharma, 2014), and instability of fuel properties (Pilczmann et al., 2016). The majority of engine components, such as the fuel pump, filters, bearing, and piston, are affected by contact with biodiesel (Jakeria et al., 2014).

The material compatibility of biodiesel, along with its economic, technological, social, political, and environmental aspects, is important in determining its sustainability. To assess the compatibility of biodiesel with different materials, several studies have been conducted in which automotive components are exposed to biodiesel by varying test temperature (Haseeb et al., 2010), test duration and exposed metal types (Fazal et al., 2014). Jain and Sharma (2014) reported that the oxidation stabilities of biodiesel...
and diesel blends are affected by different metal contents used to dope the fuels. Fazal et al. (2012) investigated the corrosion behavior of copper, cast iron, bronze, and aluminum in biodiesel; they found that copper exhibited a higher corrosion rate than the other tested metals. Furthermore, different metals generate diverse corrosion products. Haseeb et al. (2010) noted that copper-based metals corroded more in biodiesel when temperature was increased. Fazal et al. (2014) observed that the corrosion rate of copper was higher than that of mild steel at different immersion periods in biodiesel.

The situation becomes complicated when biodiesel is affected by other factors, such as storage conditions (Yang et al., 2013), moisture adsorption, and temperature (Aquino et al., 2012), which can accelerate its degradation (Serrano et al., 2013). Moreover, biodiesel is sensitive to oxygen because it contains 11% oxygen by weight (Balat and Balat, 2010). These negative effects contribute to engine problems; possible issues may include corrosion, filter plugging, and injector choring (Sorate and Bhole, 2015).

Additives must be used to limit fuel degradation and improve sustainability. Many studies have been conducted to investigate the effects of additives that can improve biodiesel compatibility. Mittelbach and Schober (2003) investigated the effects of several antioxidants on rapeseed oil, sunflower oil, used frying oil, and beef tallow oil to improve the oxidation stability of the investigated biodiesel. Sarin et al. (2010) observed the effects of natural and synthetic antioxidants on the oxidation stability of jatropha methyl ester. Butylated hydroxytoluene (BHT), α-tocopherol (α-T), tert-butylated phenol derivative (TBP), octylated butylated diphenyl

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Standard value</th>
<th>Tested value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (40 °C)</td>
<td>kg/m³</td>
<td>850–890</td>
<td>878</td>
</tr>
<tr>
<td>Kinetic viscosity (40 °C)</td>
<td>mm²/s</td>
<td>2.30–6.00</td>
<td>4.44</td>
</tr>
<tr>
<td>Acid value</td>
<td>mg KOH/g</td>
<td>Max 0.80</td>
<td>0.42</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>mass%</td>
<td>Max 0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>mass%</td>
<td>Max 0.24</td>
<td>0.08%</td>
</tr>
<tr>
<td>Ester alkyl content</td>
<td>mass%</td>
<td>Max 85.50</td>
<td>88.90</td>
</tr>
<tr>
<td>Iodine value</td>
<td>mass%</td>
<td>Max 115</td>
<td>89.60</td>
</tr>
<tr>
<td>Viscosity</td>
<td>mm²/s</td>
<td>—</td>
<td>52.39</td>
</tr>
</tbody>
</table>

**Table 3**: Corrosion rate and inhibitor efficiency for copper (Cu), leaded bronze (LB) and phosphorus bronze (PB) after immersion in palm biodiesel (B100) in the absence and presence of additives at room temperature for 2160 h.

<table>
<thead>
<tr>
<th></th>
<th>Corrosion Rate (μm/y)</th>
<th>Inhibitor Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>LB</td>
</tr>
<tr>
<td>B100</td>
<td>5.56</td>
<td>3.08</td>
</tr>
<tr>
<td>PG/B100</td>
<td>4.23</td>
<td>1.89</td>
</tr>
<tr>
<td>HBT/B100</td>
<td>3.03</td>
<td>1.47</td>
</tr>
<tr>
<td>PB/B100</td>
<td>2.12</td>
<td>1.17</td>
</tr>
<tr>
<td>TBA/B100</td>
<td>1.90</td>
<td>1.19</td>
</tr>
<tr>
<td>BTA/B100</td>
<td>1.72</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Inhibitor Efficiency (%) = 100 × (Corroded without additive - Corroded with additive / Corroded without additive

**Table 2**: Structural formula of different additives used in the biodiesel.

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibitor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzotriazole (BTA)</td>
<td>C₅H₇N₃</td>
<td></td>
</tr>
<tr>
<td>Tert-butylamine (TBA)</td>
<td>C₈H₁₃N</td>
<td></td>
</tr>
<tr>
<td>Antioxidant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butylated hydroxytoluene (BHT)</td>
<td>C₁₅H₁₉O₂</td>
<td></td>
</tr>
<tr>
<td>Propyl Gallate (PG)</td>
<td>C₁₉H₂₃O₃</td>
<td></td>
</tr>
<tr>
<td>Pyrogallol (PV)</td>
<td>C₁₀H₇O₃</td>
<td></td>
</tr>
</tbody>
</table>
amine (OBPA), and tert-butylhydroquinone (TBHQ) were used in their experiment. The best improvement in oxidation stability was achieved by TBHQ, followed by BHT, TBA, OBPA, and α-T.

Fazal et al. (2011a) investigated the effects of amine-based inhibitors on metal surface upon exposure to palm biodiesel; they found that tert-butylamine (TBA) was the most effective inhibitor. In contrast to the addition of n-butylamine (nBA) and TBA, the addition of ethylenediamine (EDA) caused sediments to form on the metal surface (Fazal et al., 2011a). Li et al. (1997) reported that amine-based inhibitors protect against corrosion primarily through their adsorption onto a metal surface; amine-based compounds typically serve as effective corrosion inhibitors in diesel (Rajasekar et al., 2007). However, information regarding the improvement of corrosion resistance in biodiesel remains limited. Hancsók et al. (2008) reported that a 20 ppm concentration of succinimide derivative (SID) exhibited excellent corrosion-inhibiting property in the biodiesel blends B0, B5, and B100. To characterize a metal surface exposed to biodiesel and to improve the sustainability of

Fig. 1. SEM micrographs of copper, leaded bronze, and phosphor bronze surfaces before and after exposure to biodiesel (B100) in the presence of additives at room temperature for 2160 h.
biodiesel, the present study investigates the inhibition of metal surface degradation upon exposure to palm biodiesel. The use of additives is expected to limit the degradation of metal surface.

2. Material and experiments

The palm biodiesel was supplied by Weschem Sdn Bhd and the additives were purchased from Ksciencia Sdn Bhd. A static immersion test was conducted in 100% palm biodiesel at room temperature. Table 1 presents the analysis report of this fuel as provided by the supplier. The metal coupons used were copper (99% commercial pure copper), leaded bronze (87% copper, 6% tin, 6% lead), and phosphor bronze (9.9% zinc, 2.20% tin, 1.90% iron, 0.03% phosphorus, 85.97% copper). The additives used were tert-butylammonium (TBA), benzotriazole (BTA), propyl gallate (PG), pyrogallol (PY), and butylated hydroxytoluene (BHT). Table 2 provides the structural formula of the additives used in the experiment.

A total of 500 ppm additives was mixed with the biodiesel. The test coupons were cut from round bars via machining and grinding. A 2 mm hole was drilled into the edge of each coupon for hanging. Duplicate test coupons were immersed into fuels that contained 400 ml biodiesel. Each coupon was then polished using silicon carbide papers (grade: 400 to 1200), washed with distilled water, and degreased with acetone. At the end of the test, the average weight loss for the two duplicate coupons was determined and the corrosion rate was measured using Equation (1) (Fazal et al., 2017):

\[
\text{Corrosion rate} = \frac{8.76 \times 10^9 w}{D t A}
\]

where the corrosion rate is in μm/y, w denotes the weight loss (kg), D denotes the density (g/cm³), A denotes the exposed surface area (m²), and t denotes the exposure time (h). Changes in surface morphology were characterized via scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS).

3. Results and discussion

After conducting the immersion test, the corrosion rate of the metal samples was measured from the obtained weight loss. Then, the metal surface was characterized by performing SEM/EDS and X-ray diffraction (XRD) analysis. Furthermore, the fuel was investigated via gas chromatography–mass spectrometry (GCMS) and by measuring its density. The succeeding sections provide the detailed results and discussion.

3.1. Corrosion rate and inhibitor efficiency

The corrosion rate and inhibitor efficiency of different metals in biodiesel in the absence and presence of different additives are provided in Table 3. All the tested metals exhibit a high corrosion rate in the absence of additives. The corrosion rates of the metals in B100 are as follows: copper (5.56 μm/y), leaded bronze (3.08 μm/y), phosphor bronze (1.46 μm/y). The findings of the corrosion rate measurement demonstrate the improved sustainability of phosphor bronze compared with the other tested metals. As shown in Table 3, the corrosion rate decreased to a certain level with the use of different additives. This finding suggests that the corrosion rate of metals can be reduced by using additives, thereby increasing sustainability. The corrosion inhibition efficiency levels of the additives are as follows: BTA > TBA > PY > BHT > PG.

Among the three metals investigated in palm biodiesel, copper exhibited the most severe corrosion. This result may be attributed to alloying elements such as tin, zinc, and lead, which enhance the resistance of copper alloys to corrosion. Fazal et al. (2010) reported that the corrosion rate of copper is comparatively higher than those of brass, aluminum, and cast iron. This observation indicates that copper behaves more aggressively upon exposure to palm biodiesel than its alloys. By contrast, the presence of additives reduced corrosion rate and improved stability of fuel properties. This finding may be attributed to the effectiveness of the additives used to limit

---

Fig. 2. EDS analysis of copper, leaded bronze, and phosphor bronze surfaces after exposure to biodiesel (B100) in the presence of additives at room temperature for 2160 h.

---
biodiesel degradation. This observation is in agreement with the data reported by Fazal et al. (2018) at where test was conducted for different diesel-biodiesel blends.

The corrosion rate of copper in biodiesel after exposure for 2160 h is 5.56 μm/y. Then, this rate declined to 4.23, 3.03, 2.12, 1.9, and 1.72 μm/y in the presence of PG, BHT, BY, TBA, and BTA, respectively. It was observed that BTA and TBA induced the lowest corrosion rate among all the additives. A low metal corrosion rate indicates that the metal is highly resistant to corrosion. BTA is an effective corrosion inhibitor for copper and its alloys; this additive can prevent undesirable surface reactions when metals are exposed to aqueous or organic solutions, as suggested by Finšgar and Milošev (2010). Ileri and Koçar (2013) investigated the effects of antioxidant additives on diesel engine using canola oil. The use of antioxidants improved oxidation stability and reduced the NOx emissions of biodiesel. Kivevele and Huan (2015) used PY and PG in their study on corn oil methyl ester (COME) and moringa oil methyl ester (MOME) biodiesel. PY and PG can help improve the oxidation stability of these fuels. Thus, additives must be used to limit metal corrosion (Serrano et al., 2013). Supriyono et al. (2015) confirmed that PY, PG, and BTA are effective antioxidants for biodiesel.

3.2. Coupon surface analysis

After the experiment, the coupon samples were cleaned under a light stream of distilled water and then SEM micrographs were taken. Fig. 1 shows the SEM micrographs of all the tested metals after exposure to palm biodiesel in the presence of different additives. Copper is clearly subject to more severe corrosion in palm biodiesel than leaded bronze and phosphor bronze. Several studies have suggested that copper is more prone to corrosion than other materials. Kivevele and Huan (2015) suggested that copper exerts a strong detrimental effect on MOME and COME biodiesel. Therefore, the use of copper components in biodiesel may not be a sustainable approach.

Corrosion was more severe on all the tested metals in the absence of additives than in their presence. Furthermore, no scratch is observed in Fig. 1 (a, e, and i), whereas the as-received metal surfaces in Fig. 1 (b, f, and j) show numerous scratches. Fazal et al. (2012) reported that the lack of scratches could be attributed to severe corrosion during exposure to palm biodiesel. In addition, clear pits were detected on the tested metal surfaces. Copper in B100 (a) was more severely pitted than leaded bronze (e) and phosphor bronze (i). This finding is consistent with the corrosion rate results presented in the succeeding section. Furthermore, the size and the propensity of the observed pits are significantly larger and higher than those on the surfaces with TBA and BTA.

TBA and BTA considerably prevented the formation of pits on the metal surfaces. Parook et al. (2015) found that TBA effectively prevents the corrosion of copper and copper-based alloys by creating a protective monolayer or multilayer on the surface of metals, thereby preventing further corrosion. The clear scratch depicted on the SEM image with the formation of a few pits indicates that corrosion was reduced on these surfaces.

Fazal et al. (2011a) investigated the efficiency of amine-based inhibitors, namely, EDA, nBA, and TBA, against the corrosion of cast iron in palm biodiesel. The effectiveness levels of these inhibitors are as follows: EDA > TBA > nBA. TBA also imparted no color or sediment on the metals used throughout the experiment. Li et al. (1997) reported that amine-based inhibitors protect surfaces through the adsorption of metal–nitrogen bonding via π electrons. Further study should be conducted to understand the related mechanism. BTA is an effective volatile corrosion inhibitor for the early stage of copper corrosion under adsorbed thin electrolyte layers (Chen et al., 2012). A comprehensive review by Finšgar and Milošev (2010) stated that complex protective layers are formed when copper-based alloys or brasses are immersed in a solution that contains BTA. These layers strongly inhibit copper alloys. This result is consistent with the results obtained via SEM.

3.3. Corrosion product analysis

Fig. 2 shows the EDS analysis results of different metal coupons after exposure to palm biodiesel at room temperature. Copper, carbon, and oxygen are the main components detected after exposure. Copper in B100 contains a higher concentration of oxygen than the other copper-based alloys. The increased amount of oxygen suggests that a high concentration of oxygenated compounds adheres to the metal surface. Oxygen concentration decreases in the presence of additives, which implies that the use of additives can reduce oxygen content. Accordingly, the amounts of oxygenated compounds on the coupon surface are decreased. Notably, lead content in the as-received leaded bronze is 6%. After the corrosion tests, the metal surfaces exhibit 2.1% lead in the
biodiesel and 0.4% lead in the additive-doped biodiesel. Such changes in percentage for an alloying element can be due to the presence of oxygen and carbon, among others, in the corrosion products formed on the biodiesel-exposed metal surface and the corrosion potential of that particular element.

The possible mechanism of the corrosion process can be determined based on the chemical reaction of a metal with a biodiesel.

The corrosion products formed after exposure were detected through the XRD spectra. The surface patterns of copper and copper-based alloys exposed to biodiesel in the absence and presence of 500 ppm additives are depicted in Figs. 3–5.

The XRD pattern of the copper surface (Fig. 3) mainly exhibits a metal base that is composed of copper, cupric oxide (CuO), and copper carbonate (CuCO3). The formation of a dark layer suggests
Fig. 5. XRD analysis of phosphor bronze surface exposed to biodiesel (B100) in the absence and presence of TBA and BTA.

Fig. 6. Densities of biodiesel (B100) before and after exposure to copper, leaded bronze, and phosphor bronze surfaces in the absence and presence of additives at room temperature for 2160 h.

high concentrations of CuCO₃ (green color) and CuO. However, CuCO₃ disappeared completely from the copper surface in the presence of additives (TBA and BTA). Norouzi et al. (2012) found that the exposure of copper to the atmosphere generates oxygen-rich oxide CuO/CuCO₃ films. This finding is consistent with the results obtained in the current study. The reaction can be explained by the following possible reactions (2)–(3):

\[2\text{Cu} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}_2\text{O}\]  
\[\text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuO}\]  

Cuprous oxide (Cu₂O) is unstable during the reaction and transforms rapidly into CuO (Hernández et al., 2010). Consequently, the XRD spectra cannot detect the presence of Cu₂O. An extended reaction involves the formation of carbonates, as proposed by Fazal et al. (2013). However, carbonates do not adhere to metal surfaces. Accordingly, the subsequent formation and dissolution of metal oxide increase corrosion rate. The existence of CuCO₃ with CuO can be attributed to the higher concentrations of carbon dioxide (CO₂) and oxygen (O₂). The absorption of moisture and CO₂ from the environment is assumed to increase the free oxygen and CO₂ contents of biodiesel. The possible chemical reactions are presented in reactions (4)–(5):

\[\text{Cu}_2\text{O} + 2\text{CO}_2 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuCO}_3\]  
\[\text{CuO} + \text{CO}_2 \rightarrow \text{CuCO}_3\]  

Fig. 4 shows the XRD pattern of leaded bronze after exposure to palm biodiesel with and without TBA and BTA. The major products are a metal oxide (copper) and a few oxides, including CuSn, Cu₃Sn₃, PbO, and Pb(OH)₂, after exposure to palm biodiesel with additives. This result demonstrates that the presence of additives prevents the formation of CuCO₃ and CuO. Further study should be conducted to understand the related mechanism. Zohdy et al. (2014) indicated that copper-based alloys are widely used because of their advantages, such as exhibiting moderate-to-high strength, corrosion resistance, and self-lubricating properties. The addition of lead to copper alloys improves the properties of the alloys. Zohdy et al. (2014) investigated the corrosion behavior of leaded bronze in seawater and reported that corrosion rates are dependent on alloying compositions. However, information regarding the mechanism of leaded bronze with additives in biodiesel remains limited. Further study should be conducted to clarify this mechanism. The XRD patterns of phosphor bronze mainly show the formation of CuZn and CuO (Fig. 4). The corrosion rate of phosphor bronze is comparatively lower than those of copper and leaded bronze, as shown in Table 3. Phosphor bronze alloys have high open-circuit potential values and exhibit various capabilities, such as strong wear resistance, corrosion resistance, effective machinability, and fatigue resistance (Sharma et al., 2001). The addition of tin improves the corrosion resistance and alloy strength. Phosphorus increases the wear resistance and the stiffness of alloys. The corrosion rate of phosphor bronze decreases further due to the addition of additives in biodiesel. However, the formation of compounds resulting from the use of additives is not observed.

3.4. Fuel analysis

The fuel was further characterized to determine the effects of metal contact and the additives used. The density of the fuel was measured before and after exposure to metals at room temperature. The limits of biodiesel density range are from 860 kg/m³ to 890 kg/m³ according to the ASTM D1298 standard. As shown in
Table 4

GCMS analysis (mass %) of palm biodiesel in the absence and presence of additives and metal.

<table>
<thead>
<tr>
<th>Name</th>
<th>B/(B100)</th>
<th>B/Cu</th>
<th>B/LB</th>
<th>B/PB</th>
<th>B/Cu/TBA</th>
<th>B/LB/TBA</th>
<th>B/PB/TBA</th>
<th>B/Cu/BTA</th>
<th>B/LB/BTA</th>
<th>B/PB/BTA</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl palmitate</td>
<td>45.20</td>
<td>47.17</td>
<td>48.61</td>
<td>50.56</td>
<td>35.70</td>
<td>48.52</td>
<td>48.70</td>
<td>39.15</td>
<td>47.90</td>
<td>48</td>
<td>46</td>
<td>5</td>
</tr>
<tr>
<td>Methyl oleate</td>
<td>32.50</td>
<td>25.13</td>
<td>29.65</td>
<td>29.70</td>
<td>26.35</td>
<td>27.99</td>
<td>30.31</td>
<td>27.73</td>
<td>30.11</td>
<td>29.83</td>
<td>29</td>
<td>2</td>
</tr>
<tr>
<td>Methyl stearate</td>
<td>18.40</td>
<td>8.23</td>
<td>7.80</td>
<td>8.91</td>
<td>4.95</td>
<td>9.11</td>
<td>9.68</td>
<td>5.22</td>
<td>8.49</td>
<td>9.53</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Methyl myristate</td>
<td>3.30</td>
<td>3.60</td>
<td>2.23</td>
<td>2.29</td>
<td>3.52</td>
<td>2.08</td>
<td>2.58</td>
<td>3.54</td>
<td>2.51</td>
<td>2.43</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Methyl laurate</td>
<td>1.10</td>
<td>1.37</td>
<td>0.07</td>
<td>0.07</td>
<td>2.11</td>
<td>0.06</td>
<td>1.25</td>
<td>1.97</td>
<td>0.10</td>
<td>0.05</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Methyl arachidonate</td>
<td>0.90</td>
<td>1.12</td>
<td>0.08</td>
<td>0.09</td>
<td>2.17</td>
<td>0.08</td>
<td>0.08</td>
<td>2.22</td>
<td>0.09</td>
<td>0.08</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>0.10</td>
<td>0.14</td>
<td>0.07</td>
<td>0.06</td>
<td>0.57</td>
<td>0.08</td>
<td>0.63</td>
<td>0.56</td>
<td>0.11</td>
<td>0.09</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Palmitoleate</td>
<td>0.30</td>
<td>0.42</td>
<td>0.09</td>
<td>0.10</td>
<td>1.41</td>
<td>0.05</td>
<td>0.12</td>
<td>1.39</td>
<td>0.57</td>
<td>0.06</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The density increases when palm biodiesel is exposed to copper, leaded bronze, and phosphor bronze. This phenomenon may be attributed to the high-oxidation products formed during exposure to metals. The fuel exposed to copper and copper-based alloys was analyzed for compositional changes before and after the exposure. Table 4 presents the GCMS analysis results of the palm biodiesel before and after the exposure to copper, leaded bronze, and phosphor bronze. The presented data are the mass percentages of fatty acid methyl esters that have been normalized to the weight of the biodiesel. Palm biodiesel mainly contains methyl palmitate and methyl oleate. As expected, the major component is methyl palmitate (saturated), followed by methyl oleate (mono-un saturated), based on the GCMS data presented in Table 4. The standard deviation indicates that the data are spread out and no cluster occurs around the mean. Notably, the ANOVA table decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, which is equal to 0.02 in this study, is a ratio of the between-group estimate to the within-group estimate. The F-value of the F-test is greater than or equal to 0.05; hence, no statistically significant difference is found among the means of the additives at the 5% significance level.

The concentration of methyl oleate in copper that was exposed to biodiesel is lower than those in leaded bronze and phosphor bronze that were exposed to biodiesel. Similar results were obtained by Fazal et al. (2013). This reduction can be attributed to the reactive nature of copper toward unsaturated methyl ester. Methyl oleates with a double-bond structure assist metal ions in biodiesel oxidation. Copper could function as a powerful catalyst for reducing methyl oleate content. In the current study, methyl palmitate concentration is slightly increased, whereas the concentration of unsaturated molecules, such as methyl oleate, is decreased. Such compositional changes could be attributed to chemical interaction with metal surface as well as oxidation. Ávila and Sodré (2012) reported that unsaturated ester can be easily oxidized in the presence of metals. Other minor components, including methyl linoleate, methyl stearate, palmitic acid, methyl myristate, and methyl laurate, can also be formed after exposure. Accordingly, the properties of palm biodiesel may deteriorate. The presence of additives enhances ester value, although not excessively. Further study should be conducted to clarify the effect of additives on fuel properties.

4. Additives and fuel properties

From the sustainable perspective, the considerable challenge in clean production is to be integrated into social consumption (Qian, 2009). The consumption of a product can be automatically increased when this product and its related production process are efficient, cost-effective, and reduce risks to humans and the environment. The current study shows that the presence of oxygen, CO₂, and unsaturated molecules in biodiesel causes metal corrosion. The presence of additives in biodiesel leads to excellent corrosion retardation, thereby proving that the investigated additives are suitable for making biodiesel more sustainable and competitive with petroleum diesel. Compared with pure biodiesel, additive-doped biodiesel can reduce metal surface degradation and improve fuel properties. The results obtained from this study show that the effectiveness levels of the additives in improving the sustainability of biodiesel are as follows: BTA > TBA > PY > BHT > PG.

The findings from the literature show that biodiesel is environment-friendly (Caliskan, 2017) and causes reduced emission (Qi et al., 2009). The combustion of biodiesel has been reported to have lower emissions compared with that of petroleum diesel. Such result can be attributed to the presence of oxygenated moieties in biodiesel (Agarwal and Das, 2001). Biodiesel contains 10% oxygen, whereas diesel has no oxygen content (Murillo et al., 2007). In the current study, the presence of oxygen causes the corrosion of metal and degrades fuel properties. By contrast, biodiesel with oxygen can ensure complete combustion, and reduce exhaust emissions (Fazal et al., 2011b). Tickell (1999) reported the reduction of SO₂ to 100%, soot to 60%, CO to 50%, hydrocarbons (HCs) to 50%, polyaromatic HCs (PAH) to 75%, and aromatics to 15%, compared with those in diesel. Qi et al. (2009) indicated that the emission of CO, HCs, nitrogen oxides, and smoke are decreased by an average of 27%, 27%, 5%, and 52%, respectively, under speed characteristic at a full load. The emission rate decreases further by mixing different additives, including butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), with biodiesel (Hess et al., 2005). The use of additives also minimizes brake-specific fuel consumption (BSFC) by reducing oxidation. Ryu (2010) reported that the efficiency of additives in reducing BSFC is in the following order: TBF > PG > BHA > BHT > α-tocopherol. Thus, the use of additives in biodiesel can reduce the negative effects on its life cycle and make its use more sustainable in the automobile sector.

5. Conclusions

The following conclusions can be drawn from the current study.

i. The presence of oxygenated moieties and unsaturated molecules is the major concern with regard to material sustainability in biodiesel. By contrast, the presence of oxygen in biodiesel is believed to ensure complete combustion, and reduce exhaust emissions.

ii. The presence of additives comprehensively reduced the corrosion rate of the tested metals, thereby suggesting increased material sustainability. The effectiveness levels of improving material sustainability are arranged in the following order: BTA > TBA > PY > BHT > PG.

iii. SEM/EDS characterization conducted at the end of the immersion test confirmed the presence of pitting corrosion on
the metal exposed to biodiesel. More pitting is observed on the copper surface than on the leaded bronze and phosphor bronze surfaces. The increased sustainability of the leaded bronze and phosphor bronze is attributed to alloying elements, such as tin, lead, and phosphorus.

iv. CuCo3 was observed along with the base metal (copper) and CuO upon exposure to B100. However, CuCo3 was not detected in the presence of additives. Therefore, the metals remain safe from degradation and exhibit increased sustainability.

v. The principal constituents of palm biodiesel were methyl palmitate (saturated) and methyl oleate (mono-unsaturated). The concentration of methyl palmitate changed comparatively less than that of methyl oleate. This finding can be attributed to the saturated structure, which has a low affinity to metals. Methyl oleate possesses an unsaturated structure that appears to be particularly reactive to metal and that reduces material sustainability.

vi. PG and PY exhibited better performance in density reduction compared with the other additives after exposure to the metal samples. Further studies should be conducted to investigate the effects of these additives on the environmental (e.g., economic) and economic (e.g., BSFC rate) dimensions of sustainability.

Acknowledgments

The authors would like to acknowledge the financial support provided by the Research Grant of the University of Malaya (Grant no. RG157-11AET and RF013B-13AET).

References

Fitzgir, M., Milosev, I., 2010. Inhibition of copper corrosion by 1,2,5-benzenetrazole: a review. Corrosion Sci. 52, 2737–2749.
Hernández, R.P.B., Páez, H., Sanz, M., 2005. Charact...