Degradation of automotive materials in palm biodiesel

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Abstract

As compared to petroleum diesel, biodiesel is more corrosive for automotive materials. Studies on the characterization of corrosion products of fuel exposed automotive materials are scarce. Automotive fuel system and engine components are made from different ferrous and non-ferrous materials. The present study aims to investigate the corrosion products of different types of automotive materials such as copper, brass, aluminum and cast iron upon exposure to diesel and palm biodiesel. Changes in fuel properties due to exposure of different materials were also examined. Degradation of metal surface was characterized by digital camera, SEM/EDS and X-ray diffraction (XRD). Fuel properties were examined by measuring TAN (total acid number), density and viscosity. Among the metal investigated, copper is found to be least resistant in biodiesel and formed comparatively more corrosion products than other metals. Upon exposure of metals in biodiesel, TAN number crosses the limit given by standard while density and viscosity remain within the acceptable range of limit.

1. Introduction

Biodiesel is a sustainable alternative fuel which is rapidly getting more popularity in automobile section. It is produced from renewable sources [1] and has much potential to meet the concerns related to fossil fuel depletion and environmental degradation [1,2]. However, corrosion of automotive metals in biodiesel is one of the problems related to biodiesel compatibility issues. Studies on the corrosion of different automotive materials in diesel and biodiesel have been done by several researchers [3–5]. It becomes more corrosive during storage, transportation and utilization. It has been reported that biodiesel degrades through moisture absorption [6], oxidation [7,8] and other contaminations [9]. Haseeb et al. [4] observed that biodiesel is more corrosive for copper and bronze materials as compared to diesel. Geller et al. [3] reported that as compared to ferrous alloys, copper alloys are more prone to corrosion in fat based biodiesel. Pitting corrosion was found in bronze sintered nozzle after 10 h operation with biodiesel at 70 °C [5].

The existing data shows that biodiesel is more corrosive than diesel. Upon exposure of metals in biodiesel, the composition of biodiesel is also changed. However, such studies do not provide any information related to characterization of corrosion products on different metal surfaces upon exposure to biodiesel. Detection of corrosion products is important to understand the degradation mechanism of materials in biodiesel. In our recent study [10], we found that due to exposure of copper in palm biodiesel, the color of biodiesel was completely changed into green. The copper surface was subjected to pit corrosion but the presence of corrosion products on the biodiesel exposed copper surface was not visible. That study [10] was conducted by immersing copper in palm biodiesel at 80 °C for 1200 h under 250 rpm stirring speed. It was suspected that subsequent formation and dissolution of copper compounds which were mostly green in color could be attributed to change the color of biodiesel from colorless to green. Another study [4], which was conducted by static immersion test at room temperature, showed the presence of green copper compounds on biodiesel exposed copper surface. However, that study [4] was not devoted to characterise the corrosion products. Upon exposure to palm biodiesel at room temperature, the present study aims to investigate degradation mechanism of different automotive materials such as copper, brass, aluminium and cast iron by characterising the corrosion products. Under such condition, comparative corrosion rate for different metals and the change in fuel properties will also be investigated.

2. Materials and experiments

Palm biodiesel used in this work was supplied by Weshchem Technology Sdn Bhd, Malaysia. The analysis report provided by the supplier is summarized elsewhere [4]. Corrosion of copper (99.9%, commercially pure), brass (Cu: 58.5%, Zn: 41.5%), aluminum (99%, commercially pure), and cast iron was studied. The TAN number of biodiesel was increased from 2.2 to 7.7 within 1200 h. The density of biodiesel was found to be 0.872 kg/L.
commercially pure) and cast iron (C: 3%, Si: 1.84%, Mn: 0.82%, P: 0.098%, S: 0.089%, Fe: balance) in palm biodiesel (B100) and petroleum diesel (B0) was investigated at room temperature (25–27 °C) for 2880 h.

The test coupons of copper (22.2 mm diameter × 2 mm thickness), brass (25.4 mm diameter × 2 mm thickness), aluminium (22.6 mm diameter × 2 mm thickness) and cast iron (36 mm diameter × 2 mm thickness) were prepared from respective round bars by machining and grinding. For hanging the specimen into fuels, a hole of diameter 2 mm was drilled near the edge of the specimen. Before immersion, the coupons were treated as follows: polished with silicon carbide abrasive papers (from grade 400–1200), then washed and degreased with acetone, rinsed with deionised water and finally immersed into test solution B100 and B0. After exposure, for removing corrosion products, samples were scrubbed lightly in a stream of water with a polymer brush so as not to mechanically abrade the original surface. Before and after immersion, weight of each coupon was measured by a balance with four decimal accuracy. Two duplicate coupons were immersed in each test fuel. Used glass-beakers (600 mL each) contained 400 mL fuel and were partly covered by the watch glass during the immersion period. At the end of the test, degradation of metals was investigated by measurement of corrosion rate and changes in surface morphology. The obtained data from weight loss was converted into corrosion rate (mpy) using the equation (1) [11].

\[
\text{Corrosion rate (mpy)} = \frac{w \times 534}{D \times t \times A} 
\]

Where corrosion rate “mpy” stands for mils (0.001 inch) per year, \(w\) is the weight loss (mg), \(D\) is the density (g/cm³), \(A\) is the exposed surface area (square inch) and \(t\) is the exposure time (h).

Changes in surface morphology were investigated by HITACHI S-3400N scanning electron microscopy connected with energy dispersive X-ray analysis (SEM/EDS). Corrosion products on biodiesel exposed metal surface were examined by using X-ray diffraction (XRD). The XRD patterns of the corroded samples were recorded using a diffractometer with a Cu \(K\alpha\) radiation of wavelength of 1.5406 Å operated at 40 kV/40 mA. The samples were step-scanned in the \(2\theta\) range of 5° with a step size of 0.01 and a time step of 3s. On the other hand, changes in fuel properties were investigated by measuring TAN (total acid number) number, viscosity and density according to ASTM (American society for testing and materials) standard D664, European standard EN14214 and ASTM (D6751 and D975) respectively.

3. Results

3.1. Comparison of corrosion for different metals

Fig. 1 shows the corrosion rate of copper (Cu), brass (BS), aluminum (Al) and cast iron (CI) in diesel (B0) and palm biodiesel (B100) after immersion in diesel (B0) and biodiesel (B100) at room temperature for 2880 h.

![Fig. 1. Corrosion rate of copper (Cu), brass (BS), aluminum (Al) and cast iron (CI) after immersion in diesel (B0) and biodiesel (B100) at room temperature for 2880 h.](image)

![Fig. 2. Photographs of copper (Cu), brass (BS), aluminum (Al) and cast iron (CI) surfaces before and after exposure in diesel (B0) and palm biodiesel (B100) at room temperature for 2880 h.](image)
immersion at room temperature (25–27 °C) for 2880 h. It is seen that for each metal, biodiesel is more corrosive than diesel. Corrosion in biodiesel is found to decrease at the following order: copper (0.39278 mpy) > brass (0.209898 mpy) > aluminum (0.173055 mpy) > cast iron (0.112232 mpy).

3.2. Surface characteristics

Fig. 2 shows the appearance of different metal coupons before and after exposure to diesel and palm biodiesel. It is observed that the as-received copper, brass, aluminum and cast iron are brown, yellow, ash and grey in color respectively. After exposure to biodiesel, a green layer formed on both copper and brass, while in diesel the original color turned into reddish. Color change of aluminum surface in diesel and biodiesel is not so significant but cast iron is more likely seen to form metal compounds in both fuels. Black and reddish corrosion product layer is observed on the biodiesel exposed cast iron.

Figs. 3 and 4 respectively show the XRD pattern on of metal surfaces exposed to diesel and biodiesel. It is seen that the XRD pattern on diesel exposed copper surface indicates the presence of CuO, Cu2O, Cu(OH)2 along with base metal. Biodiesel exposed copper surface shows comparatively higher concentration of CuCO3 along with other copper compounds such as CuO, Cu2O, Cu(OH)2, CuCO3, Cu(OH)2 etc. A small amount of CuCO3 is found to be formed on biodiesel exposed brass surface while diesel exposed surface shows other than CuCO3 (Fig. 3b). These results more likely suggest that for copper and copper based alloy, copper carbonate (CuCO3) of pale green color is the dominant compound formed in biodiesel while in diesel, it is cuprite oxide (Cu2O) of red color. Aluminum does not show any compound formed on its surface exposed in diesel or biodiesel (Figs. 3c and 4c). The concentration of iron compounds (e.g. Fe2O3, FeCO3, Fe(OH)2) formed in diesel is comparatively less than that in biodiesel (Figs. 3d and 4d). For investigating the degradation of metal surfaces, these metal compounds were cleaned and then SEM pictures were taken.

After conducting XRD analysis, the fuel exposed coupons were cleaned and then further investigation was done to examine the corrosion attack on metal surfaces. Fig. 5 shows the scanning electron micrographs of different metal coupons. It is seen that corrosion attacks on diesel exposed metal surfaces are...
comparatively less than that on biodiesel exposed metal surfaces. Copper, brass and cast iron in biodiesel are subjected to higher corrosion attack followed by aluminum.

Fig. 6 shows EDS elemental analysis of diesel and biodiesel exposed different metal surfaces. It is seen that for each metal, the concentration of oxygen on biodiesel exposed metal is comparatively higher than that on diesel exposed surfaces. For instance, the concentration of oxygen on biodiesel exposed copper (Fig. 6a) surface is 8.96% which is higher than that of diesel exposed copper (Fig. 6b) surface (3.09%). This is more likely attributed to the presence of higher oxygen in biodiesel which seems to enhance the interaction with metals to form metal compounds.

3.3. Analysis of fuel

Fig. 7 shows the color of as-received and metal exposed diesel and biodiesel. It is seen that the as-received biodiesel is colorless while diesel is yellow in color. After exposure of copper, brass and cast iron, the color of biodiesels has been changed slightly from its original color. The color of diesel is also changed upon exposure of copper and brass. Such type of color change indicates the compositional change which may change the fuel properties as well.

The total acid number (TAN) of diesel and biodiesel was measured before and after exposure to different metals and is shown in Fig. 8. It is seen that TAN number for both as-received diesel (0.15 mgKOH/g) and as-received biodiesel (0.35 mgKOH/g) are below the limit (max: 0.5 mgKOH/g) given by ASTM standard. But biodiesel, after exposure to different metals at room temperature for 2880 h, crosses this limit while for diesel, no significant changes are observed. Higher TAN number is found for copper exposed biodiesel followed by brass, cast iron and aluminum exposed biodiesels.

Figs. 9 and 10 respectively show the changes in density and viscosity of diesel and biodiesel before and after exposure to metals at room temperature for 2880 h. It is noticeable that for both density and viscosity, each fuel shows their values within the limit given by specific standard.

4. Discussion

For all the metals investigated, palm biodiesel is found to be more corrosive than diesel. This result is similar to the results on the corrosion of metals in animal fat based biodiesel blends obtained by Geller et al. [3]. They reported that the corrosion rate of copper and admiral brass in fat based biodiesel blend (B80) is comparatively higher than that of grey cast iron. Increased corrosion rate of different metals in palm biodiesel as compared to that in diesel could be attributed to the presence of oxygen and
moisture absorption \[5,10\]. Compositionally, biodiesel contains 10–12 wt% oxygen while diesel contains no oxygen \[12,13\]. In the presence of oxygen, metal could easily be oxidized to different oxides and later it forms different metal compounds by further oxidation \[14\]. This is why in most cases, biodiesel exposed metal surface shows higher oxygenated species. In addition, the ester molecules of biodiesel are more hygroscopic and polar in nature \[15,16\] as compared to diesel. Such properties of biodiesel may increase the chemical affinity with metals and thereby causes enhanced corrosion of metals. XRD results show that diesel exposed copper surface contains only a small concentration of CuO, Cu_2O and Cu(OH)\(_2\) formation while biodiesel exposed copper shows much higher amount of CuCO_3 along with Cu(OH)\(_2\), Cu(OH)\(_2\).H_2O, CuCO_3.Cu(OH)\(_2\), CuO and Cu_2O. Brass forms ZnO and CuO in diesel and relatively higher concentration of CuCO_3, Cu(OH)\(_2\), ZnO, CuO and Cu_2O in biodiesel. Like copper, brass is also found to form greenish layer of CuCO_3 in biodiesel. So, it is believed that corrosion of brass is greatly influenced by its major component copper. To understand the corrosion mechanism, changes of corrosion products with exposure time should be investigated.

The possible reaction mechanisms to form the different compounds of copper are shown below (reactions (2)–(9)). As per above discussion, dissolved oxygen and absorbed moisture react with metal or metal compounds to form different other compounds.

Fig. 6. Elemental analysis (EDS) of copper (Cu), brass (BS), aluminum (Al) and cast iron (CI) surfaces upon exposure in diesel (a, c, e, g) and palm biodiesel (b, d, f, h) at room temperature for 2880 h.
It is noted that dissolved CO₂ from the atmosphere [17] or RCOO⁻ radical generated from esters (R₁ - COOR → R₁ - COO⁻ + R⁺) can also play an important role to form copper compounds.

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

\[
\text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuO} \tag{3}
\]

\[
\text{Cu}_2\text{O} + 2\text{CO}_2 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuCO}_3 \tag{4}
\]

\[
\text{CuO} + \text{CO}_2 \rightarrow \text{CuCO}_3 \tag{5}
\]

\[
2\text{Cu} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Cu}(%OH)_2 \tag{6}
\]

\[
\text{CuO} + \text{H}_2\text{O} \rightarrow \text{Cu}(%OH)_2 \tag{7}
\]

\[
\text{Cu}^{2+} + 2\text{RCOO}⁻ \rightarrow \text{CuCO}_3 + \text{R} - \text{R} + \text{CO} \tag{8}
\]

\[
2\text{Cu}(%OH)_2 + \text{CO}_2 \rightarrow 2\text{Cu}(%OH)_2\cdot\text{CuCO}_3 + \text{H}_2\text{O} \tag{9}
\]

Cast iron forms a small concentration of Fe₂O₃ and Fe(OH)₂ in diesel while relatively higher amount of FeCO₃, Fe₂O₃, Fe(OH)₂, Fe₂(OH)₂CO₃ is formed in biodiesel. The color of biodiesel exposed cast iron was changed to black-reddish rust from its original grey color. It is believed that the formation of FeCO₃, Fe₂O₃, Fe(OH)₂, Fe₂(OH)₂CO₃ causes black-reddish color of cast iron surface. Possible mechanism for the corrosion of cast iron in biodiesel is shown by the reactions (10)–(12). The first two reactions are assumed to be occurred because of the presence of water and oxygen in biodiesel. Wattyl [18], reported that iron can form red ferrous hydroxide in the presence of water and oxygen. Ferrous hydroxide then further reacts with oxygen to form hydrated ferric oxide-rust. The last reaction is believed to be due to ester component of biodiesel [19].

\[
4\text{Fe} + 4\text{H}_2\text{O} + 2\text{O}_2 \rightarrow 4\text{Fe}(%OH)_2 \tag{10}
\]

\[
4\text{Fe}(%OH)_2 + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O} \tag{11}
\]

\[
\text{Fe}^{2+} + 2\text{RCOO}⁻ \rightarrow \text{FeCO}_3 + \text{R} - \text{R} + \text{CO}_2 \tag{12}
\]
However, the XRD result for aluminium surface does not show any compound on its surface either in diesel or biodiesel. To understand the corrosion mechanism of aluminium in biodiesel, further studies should be conducted.

The aggressive corrosiveness of biodiesel is further evident in SEM micrographs of the exposed surfaces. By visual observation, SEM micrographs reveal that both size and propensities of pits resulted from corrosion attacks are comparatively higher than that on diesel exposed surfaces. Microscopic observation of as-received coupon of each metal shows some scratches on its surface. Presence of scratches on biodiesel exposed copper and brass surfaces has completely been disappeared while diesel exposed surfaces shows their existence. Disappearance of the scratches seems to be attributed to higher corrosion attack due to enhanced corrosiveness of biodiesel. Both diesel and biodiesel exposed aluminum surfaces show some scratches but cast iron shows no scratch after exposure in diesel or biodiesel. Presence of scratches on fuel exposed surface indicates lower corrosion attacks. Biodiesel exposed aluminum surface shows comparatively more corrosion attack than that on diesel exposed surface. Enhanced corrosion attack on cast iron coupon is more likely attributed to dissolution of graphite inclusions from its surface. Though the exposed surface was cleaned before taking SEM/EDS, the elemental analysis by EDS shows the presence of oxygen and carbon on fuel exposed metals, which is again comparatively higher on biodiesel exposed surface than that on diesel exposed surface. Presence of higher oxygen suggests greater concentration of oxygenated compounds adherent to the metal surface. Pit may form on the metal surface due to corrosive attack on base metal as well as due to breaking down of the oxygenated compounds.

Increased TAN indicates the increased level of oxidation of biodiesel. Due to exposure to metals, different types of monocarboxylic acids such as octanoic acid, myristic acid, palmitic acid etc. are found to form [10]. Increased TAN number of biodiesel from 0.35 to 2.5, 2.29, 1.68 and 1.69 mgKOH/g upon exposure of copper, brass, aluminum and cast iron respectively at room temperature for 2880 h could be attributed to the formation of different acid components. It is seen that due to exposure of copper or copper based alloy, TAN is increased more. Increased TAN number indicates the presence of corrosive acids which may result higher corrosion. This is in consistent with the results obtained by Kaul et al. [20]. Like the TAN number, similar trends for the change of density and viscosity were also observed but these were under the limit given by standard. The change of viscosity and density could also be attributed to the compositional change of biodiesel resulted from different materials exposure [21–23] as well as corrosion products. In conclusion, it can be said that due to exposure of metals, only increased TAN number is found to be a problem from the investigated fuel properties.

5. Conclusions

Degradation of different automotive materials in palm biodiesel was investigated by static immersion test. The following points had been concluded from the study:

1. Upon exposure to palm biodiesel, the degradation order for different metals is: copper > brass > aluminum > cast iron.
2. As compared to diesel, biodiesel exposed copper surface shows comparatively higher concentration of CuO 2 along with other copper compounds such as CuO, Cu 2 O, Cu(OH) 2 , CuO(C₂H₅OH)₂ etc. A small amount of CuO 3 is found to be formed on biodiesel exposed brass surface while diesel exposed surface shows other than CuO 3 . Further study should be conducted to understand the initiation and conversion in the formation of different corrosion products.
3. The concentration of iron compounds (e.g. Fe₂O₃, FeO, Fe(OH)₂) formed on cast iron surface exposed to diesel is comparatively less than that to biodiesel. To detect corrosion products on fuel exposed aluminum surface, further investigation should be done.
4. For each metal, degradation of surfaces exposed in palm biodiesel is comparatively higher than that in diesel. Copper metal is less resistant in biodiesel and also causes more degradation of fuel properties.
5. Upon exposure of different metals in biodiesel, only TAN number crosses the limit given by ASTM D6751 standard while changes of density and viscosity remain within the limit. Copper and copper based alloy (brass) increase TAN number comparatively more than other metals.

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