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Effects of Corrosion on Compression Ignition Engine Parts: A Case Study of Biodiesel Blends

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Abstract: **This paper examines the effects of corrosion on the engine parts that come in contact with a newly developed biodiesel fuel and its blend (with petro-diesel). The metals copper, aluminum, copper alloys (bronze), and elastomers caused significant levels of corrosive in biodiesel and biodiesel blend as opposed to low corrosion with petro-diesel. Specimens of stainless steel showed significant resistance to corrosion in biodiesel samples as compared to copper, aluminum, and copper alloys, but the level of corrosion was still higher than that in petro-diesel. Common methods adopted for measurement of corrosion include weight loss through static emersion tests and electrochemical techniques by electrochemical impedance spectroscopy or on Potentiostat/Galvanostat. The surfaces of the specific metal strips were analyzed by optical, scanning electron, and atomic force microscopy, revealing the nature and extent of corrosion. Fourier transform Infrared Spectroscopy revealed formation of secondary product due to degradation, and x-Ray Diffractometer revealed formation of a new phase in the metal strips exposed to biodiesel and its blend with mineral diesel. Biodiesel seemed to degrade due to auto-oxidation and presence of moisture to secondary products that enhanced the corrosion rate. The problem related to the use of non-compatible materials as engine parts for biodiesel-run vehicles is dual in nature. The engine part in contact with the fuel is corroded as a result of fuel degradation, causing the fuel to go further off-specification.**

Keywords: Corrosion, static immersion, stainless steel, aluminum, copper

INTRODUCTION

At present, biodiesel is being used regularly in automobiles as B5 blend (diesel containing 5 vol % biodiesel) in different parts of the world including Australia, Europe and America. Higher percentages of biodiesel have not been used so far due to some concerns which include compatibility of biodiesel with materials in the automotive fuel system. Corrosion is one of the topics arisen from biodiesel compatibility issues. Biodiesel becomes more corrosive if free water and free fatty acid present. Free fatty acid may exist as a consequence of incomplete trans-esterification reaction. Beside this, auto-oxidation of biodiesel can also enhance its corrosive characteristics. In automobile engine, fuel comes into contact with wide variety of engine parts including fuel pump, gaskets, fuel injector, filters, fuel liners, bearing, piston, piston rings etc. Among them, copper and its alloy based parts like fuel pump; bearing, bushing etc. are mostly affected by the fuel [1]. It has also been suggested that copper, aluminum, zinc, brass and bronze are not compatible with biodiesel [2]. Geller et al. [3] observed that copper alloys are more prone to corrosion by biodiesel as compared with ferrous alloys. Pitting corrosion was found on the bronze sintered filters integrated in the oil nozzle after 10 h of operation with biodiesel at 70^0 C [4]. Such effectiveness was also reported even for lower biodiesel (2%) blend levels [5]. Concerns arises from the fact that biodiesel degrades through oxidation, moisture absorption, attack by microorganisms etc. during storage or use and thereby becomes more corrosive. According to Tsuchiya et al. [5], oxidation of biodiesel reconverts esters into fatty acids such as formic acid, acetic acid, propionic acid, caproic acid etc which are responsible for enhanced corrosion. This process also increases the free water content. Free water is undesirable because it may promote microbial growth and corrode fuel system components [6]. According to Maleque et al. [7], Kalam and Masjuki [8], wear rate in biodiesel was relatively increased due to its oxidative and corrosive nature. What makes the situation more complicated is the fact that under the circumstances of aeration, dissolved oxygen into biodiesel can accelerate its corrosive phenomena. A full clarification of such observations is often quite complicated, as a number of different effects may be involved (changes in TAN value, increased water content, oxidation product, presence of metals species etc). Irrespective of such effects, a limited but definite role is usually attributed to characterize the corrosive behavior of metals in biodiesel. The aim of the present study is solely to evaluate the corrosion behavior of copper and leaded bronze in palm biodiesel.

MATERIAL AND METHODOLOGY

Corrosion behavior of copper (99.99% commercially pure) and leaded bronze (87% Cu, 6% Sn, 6% Pb) in palm biodiesel was investigated by static immersion test at two different temperatures. At room temperature, immersion tests in B0 (petroleum diesel), B50 (50% biodiesel in diesel) and B100 fuels were carried out for 2640 h. Similar immersion tests at 60ºC in B0, B100 and B100 (oxidized) fuels were also conducted for 840 h. The blends were made on volume basis and stored in glass bottles. B100 (oxidized) fuel was prepared from as-received B100 biodiesel by heating at 60ºC for 18 h. The test coupons of copper (17.2 mm diameter x 2 mm thickness) and leaded bronze (22.6 mm diameter x 2 mm thickness) were made from respective rod by machining and milling. For hanging with cotton thread into test fuels, each coupon was drilled by 2 mm diameter. After machining, drilling and polishing, the coupons were cleaned by detergent and then dipped into 10% sulfuric acid at room temperature for several minutes. Finally all samples were degreased by acetone. Before and after exposing the test coupons into different test fuels, weight was measured by four decimal weight measuring device. At the end of the test, corrosion behavior was investigated by corrosion rate measurements and changes in surface morphology. The obtained data from mass loss was converted into corrosion rate (mpy) using the Equation 1.

$$Corrosion\,rate(mpy) = \frac{W \times 534}{D \times T \times A} \quad .. \;.. \;.. (1)$$

Where

W is the weight loss (mg),

D is the density (g/cm^3),

A is the exposed surface area (square inch) and T is the exposure time (h).

Fuels were analyzed by using TAN (Total acid number) analyzer, Fourier transform infrared spectroscopy (FTIR), Multi-element oil analyzer (MOA) to investigate acidic concentration, oxidation level with water content and corrosive impurities respectively.

RESULTS AND DISCUSSION

The calculated corrosion rates for both metals at each temperature are shown in Figs. 1 and 2. Corrosion rates are not significantly high at room temperature, especially for leaded bronze. However, there is increasing trend of corrosion rate for both metals at each temperature with increasing the concentration of biodiesel. This demonstrates that for both metals, biodiesel causes more corrosion than that of diesel fuel.

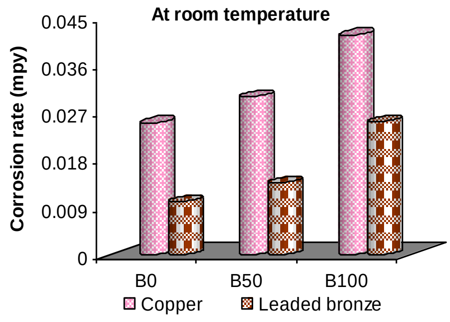


Fig. 1 Corrosion rate of copper and leaded bronze at room temperature.

In the case of 60ºC for both diesel and biodiesel, corrosion rate of each metal is much higher than that of room temperature. This may be explained from the fact that at high temperature, both copper and leaded bronze surface become comparatively more reactive than that of room temperature. This can also be attributed to condensation or dissolution of oxygen into the fuels from atmosphere. Oxidation of biodiesel can produce different types of fatty acids which can ultimately accelerate the corrosion rate. This agreement is also supported by the compared corrosion rates for both metals in B100 and B100 (oxidized) fuels (Fig. 2). The average corrosion rate of copper in 20 yr test is 0.05 mpy in an industrial atmosphere, 0.03 mpy in marine atmosphere, 0.02 in rural atmosphere which correspond to good corrosion resistance [9]. This indicates that at room temperature, copper in petroleum diesel has almost useable corrosion resistance while in biodiesel it loses its value. However, leaded bronze showed good corrosion as compared to copper.

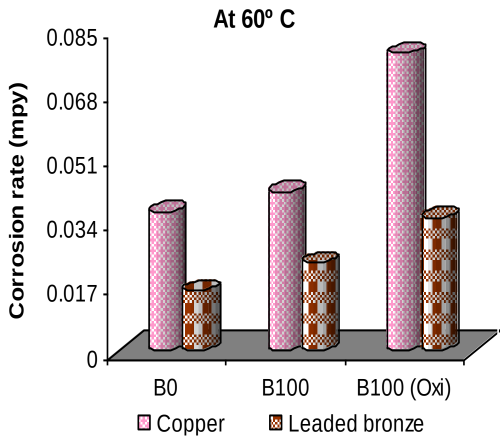
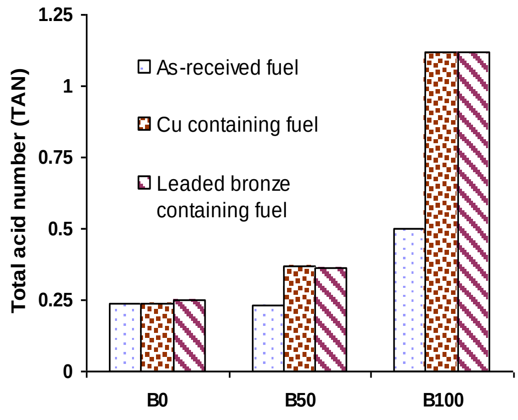


Fig. 2 Corrosion rate of copper and leaded bronze at 60º C.

The total acid numbers of the fuels were measured before and after exposure into different fuels as shown in Fig.3.

Fig. 3 Change in total acid number (TAN) after conducting immersion test



at room temperature for 2640 h.

Similarly, results of oxidation product rate and free water content obtained from FTIR analysis are shown in Figs. 4 and 5 respectively. It is noted that biodiesel containing different metals showed significant degradation, as evidenced by large increased TAN number, oxidation products as well as free water content with increasing the concentration of biodiesel in blends.

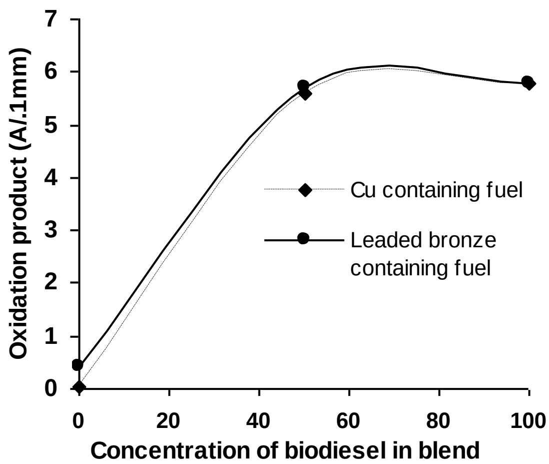


Fig. 4 Change in oxidation product with increasing concentration of biodiesel in blend during immersion test at room temperature for 2640 h.

A far more striking fact, however, is that the oxidation products as well as TAN value for metal containing both fuels, are almost similar irrespective to their respective rate of corrosiveness (Figs. 3 and 4). In other words, upon exposure, the acid number and rate of oxidation product are increased in similar trend for both metals while the corrosion rate for different metals is different. This indicates that metal itself has also its own characteristics to determine the corrosiveness of the fuel. However, it is found that for metal containing both fuels, TAN value increases with increasing the concentration of biodiesel in blends and their corresponding corrosiveness is also increased. But the increasing ratios (K1, K2) of corrosion rate and total acid number with increasing the concentration of biodiesel (K1 for B0/Cu to B50/Cu is 0.0386 and K2 for B0/Cu to B50/Cu is 0.0155) are not similar. This suggests no strong correlation between change in acid number and corrosiveness of the fuel. Similar agreement was also found by Grainawi et al. [10].

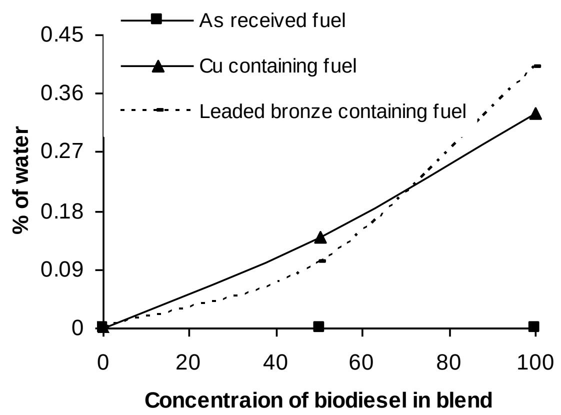


Fig. 5 Comparative water content for as received fuel and the fuels obtained after conducting immersion test at room temperature.

Water is the major ingredient to make the fuel more aggressive. From Fig. 5, it is seen that as-received both diesel and biodiesel have no water while for the copper and leaded bronze containing fuel, water content increases with the increasing concentration of biodiesel. Though as-received fuels are virtually water-free, during storage or use, it can come into contact with water. In fact, water can be condensed or dissolved into biodiesel as humidity in the air. Increasing of water with the concentration of biodiesel seems to act as the major factor to increase the corrosion rate for both copper and leaded bronze. According to Kaminski and Kurzydlowski [6], water can promote microbial growth and corrode fuel system components. Besides, water particularly at high temperature can hydrolyzed esters as well as triglycerides and thereby produce different types of fatty acids which are more corrosive [11]. Data obtained from Multi-element oil analysis (MOA) showed that the copper content in both copper and leaded bronze containing biodiesel was 5 ppm, against 0 ppm for as-received biodiesel. But copper or leaded bronze containing diesel fuel had less amount of copper. Leaded bronze containing biodiesel showed 10 ppm Zn, 4 ppm lead [Table 1]. These results indicates that Cu, Zn, Pb metals are highly reactive in biodiesel as compared to that in diesel fuel.

TABLE 1: Multi-element oil analysis (MOA) data obtained

Condition	Fuel types	Cu (ppm)	Pb (ppm)	Sn (ppm)	Zn (ppm)
As Received	B0 B100	0 0	0 0	0 0	0 0
Cu containing	B0 B100	4 5	0 0	0 0	0 0
Leaded bronze containing	B0 B100	3 5	] 0.5 4	0.5 0	3 10

The conditions of the exposed surfaces after drying can be observed in Figs. 6 and 7. These photographs show that copper forms green oxide layer on its surface at room temperature while it turns into black for 60ºC. For leaded bronze, test coupons at 60ºC are cleaner than those at room temperature.

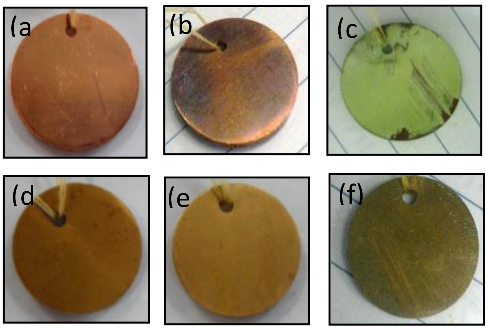


Fig. 6 Photographs of copper (a-c) and leaded bronze (d-f) specimens after conducting immersion test at room temperature in B0, B50 and B100: (a) and (d) in B0; (b) and (e) in B50; (c) and (f) in B100.

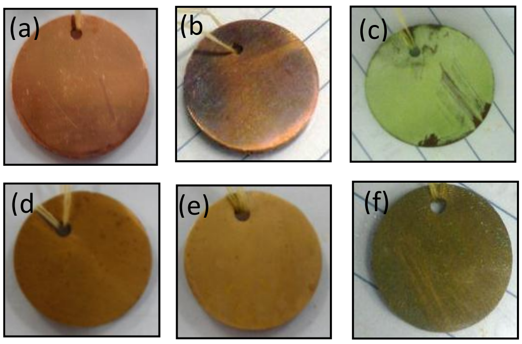


Fig. 7 Photographs of copper (a-c) and leaded bronze (d-f) specimens after conducting immersion test at 60ºC in B0, B100 (oxidized): (a) and (d) in B0; (b) and (e) in B100; (c) and (f) in B100 (Oxidized).

The photographs of the coupons show only the formation of oxide layers other than occasional surface damages. In most cases, the amount of oxides formed on the surface was slightly higher for copper in B100 and B100 (oxidized) than in other fuels. This indicates copper is more reactive in B100 or oxidized B100 fuel. According to Huang and Tsai [12], color variation is an indicator of the transformation of copper species with reaction temperature and oxygen atmospheres. At room temperature, the formed oxide layer for copper in B100 seems to be copper carbonate (CuCO3) of pale green color [Fig. 6(c)]. For similar test coupon at 60ºC, the formed oxide layer likely to be oxygen rich cupric oxide (CuO) of black color as a consequence of higher dissolved oxygen in biodiesel [Figs. 7(b) and 7(c)]. The mechanism for the formation of different oxides will be explored in future study. However, upon examining the surface of the coupons exposed to B100 or oxidized B100 fuel, it is noted that the corrosion only affects the surface and it appears to be non-uniform, no deep localized corrosion sites (pits) are observed. To further investigate the surface damage observed on the test coupons, low magnification (100X) optical micrographs were taken. Representative micrographs of each test coupon for both temperatures are shown in Figs. 7 and 8 respectively. These optical photographs do not show any severe surface damage.

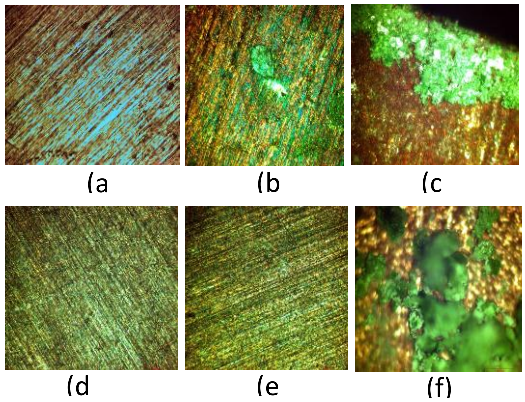


Fig. 8 Optical photographs (100X) of copper (a-c) and leaded bronze (d-f) specimens after conducting immersion test at room temperature in B0, B50 and B100: (a) and (d) in B0; (b) and (e) in B50; (c) and (f) in B100.

The optical photographs confirm the visual observations, that is, only a small amount of surface damage is presented on the test coupons, no extensive general corrosion damage or pitting are observed. However, copper in B100 at 60ºC shows few pits surrounded by black or pale green surfaces. But even these pits are very small and seem to represent as a beginner of pit formation. This suggests that at higher temperature, copper in biodiesel is subjected to pitting corrosion.

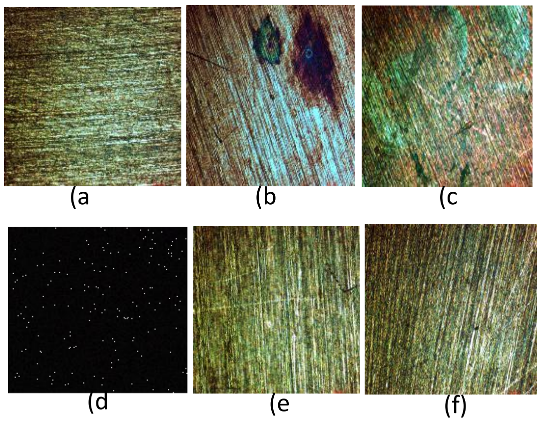


Fig. 9 Optical photographs (100X) of copper (a-c) and leaded bronze (d-f) specimens after conducting immersion test at 60ºC in B0, 100 and B100 (oxidized): (a) and (d) in B0; (b) and (e) in B100; (c) and (f) in B100 (oxidized).

CONCLUSIONS

This study suggests the following conclusions:

1. Both copper and leaded bronze in biodiesel showed higher corrosion rate than that in diesel. However, corrosion rate for leaded bronze in each fuel was lower as compared to copper.
2. Biodiesel containing copper or leaded bronze showed significant degradation, as evidenced by increased TAN number, oxidation product rate, and free water content.

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3. Free water content was increased with increasing the concentration of biodiesel and it seemed to act as a major factor to increase the corrosion rate for metals.
4. Oxidized biodiesel was more corrosive as compared to as-received biodiesel.

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