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Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials

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ABSTRACT

Corrosive characteristics of biodiesel are important for long term durability of engine parts. The present study aims to compare the corrosion behavior of aluminum, copper and stainless steel in both petroleum diesel and palm biodiesel. Immersion tests in biodiesel (B100) and diesel (B0) were carried out at 80 °C for 1200 h. At the end of the test, corrosion characteristic was investigated by weight loss measurements and changes on the exposed metal surface. Surface morphology was examined by optical microscope and scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDS). Fuels were analyzed by using TAN analyzer, FTIR, GCMS and ICP in order to investigate the acid concentration, oxidation level with water content, compositional characteristics and presence of metal species respectively. Results show that the extent of corrosion and change in fuel properties upon exposure to metals are more in biodiesel than that in diesel. Copper and aluminum were susceptible to attack by biodiesel whereas stainless steel was not.
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1. Introduction

As a result of increasing environmental concern and diminishing petroleum reserves, there is a growing trend to substitute biodiesel for conventional diesel fuel. As an alternative fuel, though biodiesel have some technical advantages over diesel fuel, the former appears to be more corrosive than diesel. The corrosive nature of biodiesel can be more aggravated if free water and free fatty acid are present in it. As compared to diesel, biodiesel is more prone to absorb water which tends to condense on metal surface and may cause enhanced corrosion. Beside this, auto-oxidation of biodiesel can also enhance its corrosive characteristics and degradation of fuel properties.

There are only few studies available in the literature related to corrosion of different metals in biodiesel [1–5]. Most of these studies find corrosiveness of different biodiesel other than palm biodiesel. Kaul et al. [1] investigated the corrosiveness of different biodiesel (i.e. Jatropha curcas, Karanja, Mahua and Salvadora) as compared to that of diesel fuel. They found that biodiesel from Jatropha curcas and Salvadora were more aggressive for both ferrous and non-ferrous metal. Geller et al. [2] have reported that as compared to ferrous alloys, copper alloys are more prone to be attracted by corrosion into fat based biodiesel. In an another study, pitting corrosion was found on the bronze sintered filters integrated oil nozzle after 10 h operation with biodiesel at 70 °C [3]. Such effectiveness was also reported even for lower biodiesel (2%) blend [4]. Maleque et al. [6] and Haseeb et al. [7] found that wear rate in biodiesel was relatively increased due to its oxidative and corrosive nature. It has been suggested that copper, aluminum, zinc, brass and bronze are not compatible with biodiesel [8,9]. Besides, these metals even in small concentration exposed into biodiesel have been reported as catalyst to oxidize biodiesel [10,11]. According to Sarin et al. [10], during oxidation process, the fatty acid methyl ester usually forms a radical next to double bond and then quickly bond with the oxygen from air. After 25 h oxidation of rapeseed oil methyl ester at 200 °C, Niczke et al. [12] found different types of volatile products like acids, aldehydes, ketones, lactones, alkylofurances etc. According to Tsuchiya et al. [4], oxidation of biodiesel reconverts esters into different mono-carboxylic 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 [13,14].

Concerns arises from the fact that biodiesel degrades through auto-oxidation, moisture absorption, attack by microorganisms etc. during storage or use. These may give rise to potential problems such as interaction with metal surfaces and at the same time, degradation of fuel properties. Fuel degradation due to metal contact can also be different from metal to metal. What makes the situation more complicated is the fact that under the exposure of different metals into biodiesel, dissolved oxygen may aggravate its corrosive nature in different level. 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, changes in structural features of biodiesel component etc). Irrespective of such effects, a limited but definite role

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is usually attributed to characterize the corrosion behavior of different metals into fuel.

The present study aims to investigate the corrosion behavior of copper, aluminum, stainless steel in diesel and palm biodiesel, and in turn to evaluate their influence in degradation of fuel properties. The cause behind choosing these metals for investigation can be attributed to their broad range of usages in manufacturing automobile components. In automobile fuel system, the common parts made from aluminum are piston (100%), engine block (19%), cylinder head (70%) etc. [15]. Similarly, the metals used for manufacturing pump, injector, bearing are copper or its alloys [3,16]. Many components like nozzle, fuel filter, valve bodies, and pump ring are made from stainless steel [3,17]. All these parts from different materials come into contact with fuel and seem to undergo chemical interactions and thereby degrade fuel properties too. In a previous study [18], copper was found to be affected by pitting corrosion at 60 °C. In the present study, a higher temperature (80 °C) is used to investigate its effect on pit formation on copper as well as on other ferrous and non-ferrous metals. Results obtained are expected to help in understanding the corrosion of fuel system parts in biodiesel while its inlet temperature is 80 °C [19,20].

2. Experimental

The palm biodiesel used in this study was supplied by Weshchem Technology Sdn Bhd, Malaysia. The analysis report provided by the supplier is summarized elsewhere [18]. Corrosion characteristic of copper (99.99%), aluminum (99% commercially pure) and 316 stainless steel (18% Cr, 11% Ni, 2% Mn, 1% Si and 0.08% C) in both diesel and palm biodiesel was investigated by immersion test at 80 °C for 1200 h. During the test, fuels were continuously stirred by the magnetic stirrer at speed 250 rpm. The test coupons of copper (17.2 mm diameter × 2 mm thickness), aluminum (22.6 mm diameter × 2 mm thickness) and stainless steel (16 mm diameter × 2 mm thickness) were made from round bar 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 to 1200), then washed and degreased with acetone. These were then dipped into 10% sulfuric acid at room temperature for several minutes followed by washing in deionized water. Similarly 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 exposing the test coupons into different test fuels weight was measured by a balance with four decimal accuracy. Two duplicate coupons were immersed in each test fuel. For each coupon, weight loss was measured by subtracting the final weight (obtained after exposure) from its initial weight (before exposure). At the end of the test, corrosion behavior was investigated by measurement of corrosion rate and changes in surface morphology. The average weight loss measured from duplicate test coupons was then converted into corrosion rate (mpy) using Eq (1) [21].

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

where corrosion rate "mpy" stands for mils (0.001 inch) per year, 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).

Changes in surface morphology were characterized by optical microscope (OM) and scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDS). Fuels were analyzed by using gas chromatography mass spectroscopy (GCMS), Fourier transform infrared spectroscopy (FTIR), and inductively-couple plasma (ICP) in order to investigate the changes in fuel composition, oxidation level with water content and presence of metal species respectively. Degradation of fuel properties were investigated by measuring total acid number (TAN), density and viscosity.

3. Results and discussions

3.1. Comparative corrosion rate

Fig. 1 shows the comparative corrosion rate for stainless steel, aluminum and copper upon exposure into diesel and biodiesel at 80 °C for 600 h and 1200 h. It is observed that the corrosion rate of copper in biodiesel increases with increasing time, while for aluminum, it slightly decreases. The corrosion rate of both copper and aluminum in biodiesel is much higher than that in diesel fuel. Stainless steel shows no significant corrosion even in biodiesel.

Presence of free fatty acid, more oxygen moieties and water content, impurities remaining after processing seem to increase the corrosiveness of biodiesel as compared to diesel fuel. Kaul et al. [1] suggested that biodiesel was more corrosive due the presence of higher concentration of unsaturated acid components. They have also reported that the increasing of TAN number after test duration indicates oxidation of biodiesel due to contact with metal samples. This is in good agreement with the results obtained by Tsuchiya et al. [4] where it has been reported that oxidation of biodiesel increases TAN number and water content and thereby becomes more corrosive. As shown in Fig. 1(b), the obtained corrosion rates at 80 °C in palm biodiesel for copper, aluminum and stainless steel are 0.586, 0.202

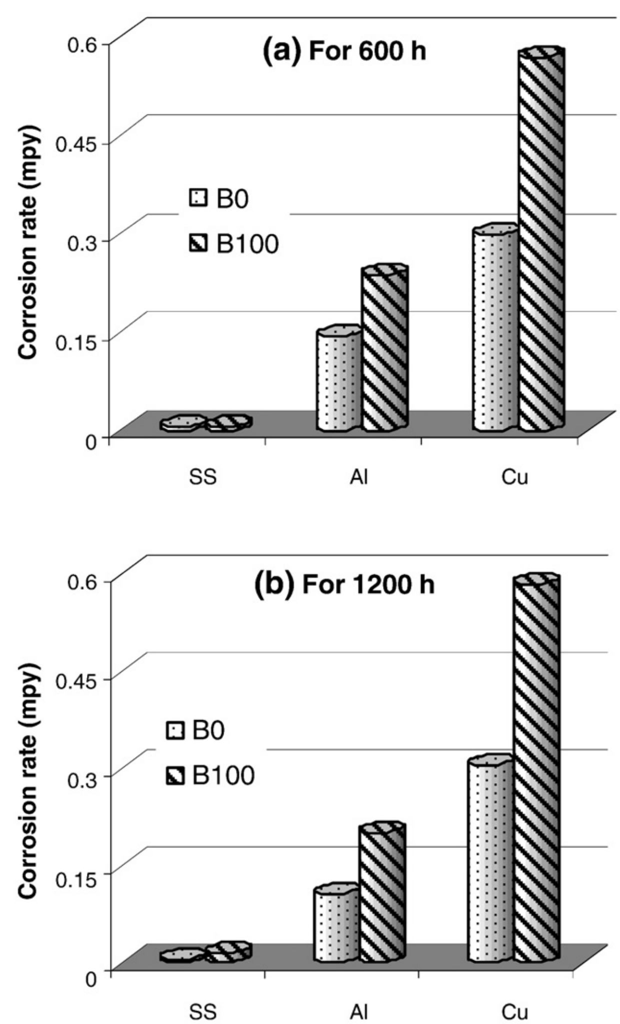

Fig. 1. Corrosion rate of stainless steel, aluminum and copper in diesel and biodiesel after immersion for (a) 600 h and (b) 1200 h at 80 °C.

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