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Corrosion of magnesium and aluminum in palm biodiesel: A comparative evaluation
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1. Introduction

Recently automotive industries are paying much attention to the problems related to fuel consumption and weight reduction. Therefore automobile researchers are now showing much interest for the light-weight metals. Use of light metal can improve the engine performance as well as reduce the energy consumption\cite{1}. At present, light-weight non-ferrous metals such as Al, Mg are being increasingly used to replace the heavy-weight cast iron blocks\cite{2}. Many automotive applications are also focusing on thermal sprayed aluminum liners, metal–matrix composite in place of heavy metals\cite{1–3}. Adaption of light materials resulted in the reduction of fuel consumption and at the same time provided better engine performance. The reported improvement in fuel consumption varies widely from 1.0 to 8.2% for every 10% reduction in vehicle weight\cite{4,5}. Many of the engine components which are made from aluminum (piston, piston ring, cylinder, transmission etc.)\cite{3} and magnesium (valve covers, cylinder head covers, housing, intake manifolds etc.)\cite{6} come in contact with fuel. Study on the compatibility of these light-weight components with the newly adapted and promising alternative fuel, biodiesel is a big issue to consider. This is because biodiesel is more corrosive compared to conventional petroleum diesel\cite{7,8}.

There are very limited number of studies reported on the corrosion of light-weight metals such as aluminum and magnesium in biodiesel. Corrosion study on aluminum piston in different biodiesels such as Jatropha Curcas, Karanja, Mahua and Salvador was carried out by Kaul et al.\cite{9}. They found that aluminum piston was more susceptible to corrosion in J. Curcas and Salvadora biodiesel as compared to other biodiesel and diesel. Diaz-Ballote et al.\cite{10} investigate the electrochemical corrosion behavior of aluminum exposed to various biodiesels at different stages of the washing process. It was reported that the corrosion characteristics of aluminum in biodiesel contaminated with alkalis are similar to the corrosion behavior of aluminum in aqueous solutions. In a couple of studies\cite{11,12}, it has been reported that aluminum is more resistant to corrosion in palm biodiesel as compared to other non-ferrous metals such as copper and brass. As a light-weight metal, magnesium is being considered as a competitor of aluminum in automotive applications. Magnesium is approximately 35% lighter than aluminum and yet it exhibits similar level of strength. A literature search on the fundamental corrosion study of magnesium in biodiesel has shown the scarcity of publications in this field. Therefore, there is a need to study the corrosion of magnesium in biodiesel and to gain comparative data on the corrosion of these light-weight metals, aluminum and magnesium. The aim of the
The present work is to compare the corrosion characteristics of aluminum and magnesium in palm biodiesel. Although both aluminum and magnesium are likely to be used in alloy form in automobile, commercially pure aluminum and magnesium are investigated in this work. The use of commercially pure form of both metals are expected to lead a basic understanding of the corrosion characteristics of those metals in biodiesel by avoiding complication imposed by alloying elements. Results obtained in the study will form a basic for further understanding of corrosion of perspective alloys in the future.

2. Material and methods

2.1. Materials and characteristics

The palm biodiesel used in this work was supplied by Mission Biotechnologies Sdn Bhd, Malaysia. The analysis report given by the supplier showed 98.8% ester content. Main impurities were free glycerol (~0.01%), monoglyceride (~0.75%), diglyceride (~0.12%), triglyceride (~0.05%), glycerol (~0.23%), water (~275 ppm) and contamination (~2.71 ppm). The acid value of the investigated biodiesel was ~0.27 mg KOH/g. All specifications were within the limit given by EN 14214 standards. The Al alloy 5086 contains 95% Al, 3.86% Mg, 0.53% Fe, 0.99% Mn and 0.03% Si, while the pure Mg sample contains 99.9% Mg, 0.01% Al, 0.04% Fe, 0.78 ppm Cr and 0.002 ppm Zn.

2.2. Experimental setup

Samples for immersion tests were prepared as follows. Aluminum and magnesium coupons of 8 mm diameter and 2 mm thickness were prepared from respective rods by WEDM (wire electrical discharge machining). Each of the coupons was then ground mechanically by using abrasive paper from grade 600 to 2000. Two beakers for two different metal samples (e.g. Al and Mg) were filled with 2 L of biodiesel (B100) each. Static immersion test was conducted by holding the coupon with silk string to allow maximum surface exposure. Before immersion, the coupons were degreased with acetone and weighted in an electronic balance with ±0.01 mg accuracy. The prepared aluminum and magnesium coupons were then hung separately in two separate beakers. Each beaker was covered by a watch glass to prevent foreign particles from entering.

Six coupons of same metal were immersed in the same beaker. The tests were carried out at room temperature (25–27°C) for 720 and 1440 h. Upon immersion test for 720 h, three coupons and 50 ml of biodiesel were taken out from each beaker. The rest three coupons of each metal were kept immersed till 1440 h. Sediments that formed on 720 h and 1440 h biodiesel exposed magnesium surface were collected for compositional analysis. Upon completion of immersion test, all the coupons were cleaned by brushing with soft toothbrush in deionized water to remove the corrosion products. Those were then degreased with acetone. Average weight loss of three coupons at each condition (e.g. 720 and 1440 h exposure) was recorded for the measurement of corrosion rate.

2.3. Corrosion analysis

The surface morphologies and chemical states of the corroded surface were examined by SEM (scanning electron microscope) and XRD (X-ray diffraction machine). The XRD analysis was performed using a diffractometer with a Cu Kα radiation of wavelength of 1.5406 Å operated at 45 kV/30 mA. At incident angle 1.0, the samples were step-scanned from position 30 to 90 with a step size of 0.1 and a step time of 1 s. The changes in acidity of the biodiesel were analyzed by TAN (total acid number) analyzer as per ASTM D664. The sediments formed on the samples were characterized by FTIR (Fourier transform infrared spectroscopy). The sediments were first mixed with KBr powder and then compressed into pellet for FTIR analysis. The FTIR analysis was conducted within the wavelength of 400–4000 cm⁻¹, with a resolution of 8.0 cm⁻¹. Quantitative metal corrosion was analyzed by measuring the corrosion rate according to the following Eq. (1). It is noted that the results obtained from the measurement of corrosion rate and total acid number (TAN) have been analyzed by error bars with standard deviation.

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\text{Corrosion rate (mpy)} = \frac{534w}{dAt}
\]

where corrosion rate, mpy stands for milli-inch per year; w: weight loss in mg; d: density in g/cm³; A: area of sample in square inch; and t: exposed time in h.

3. Results and discussion

Fig. 1 shows the corrosion rate of aluminum and magnesium upon exposure in biodiesel for 720 h and 1440 h at room temperature. Corrosion rates for pure aluminum at 720 h and 1440 h are 0.1230 mpy and 0.0257 mpy respectively. Corrosion rates of magnesium are much higher which are 3.091 mpy at 720 h and 2.6563 mpy at 1440 h.

It is seen that the corrosion rate of both magnesium and aluminum decrease with the increase of immersion period. Fazal et al. [12] also observed that corrosion of aluminum slightly decreases with immersion time. It is clear from Fig. 1 that magnesium exhibits higher corrosion rate compared to aluminum. This could be attributed to the higher reactivity of magnesium with biodiesel. It is noted that magnesium is less noble compared to aluminum in the galvanic series.

Fig. 2 shows the appearances of aluminum and magnesium coupons after the immersion test for 720 h and 1440 h. There is a big difference between the appearances of the two metals. Upon exposure to biodiesel, magnesium coupon is seen to be covered by gel-like mass, while the aluminum surface remained clean. This gel-like mass is yellowish in color and highly sticky in nature. It behaves like a gum and is not easy to remove by rubbing. The extent of gum formation is higher at longer immersion time. Formation of such type of sediment and gum may cause engine performance problem including fuel filter plugging [13]. Further
investigations were carried out on the sediment which will be discussed later.

Coupons upon exposure in biodiesel were then cleaned with soft toothbrush in deionized water and then degreased by acetone. The SEM micrographs of aluminum and magnesium before and after exposure in biodiesel are shown in Fig. 3. At 1000X magnification, the grinding lines on the as-received coupons are clearly seen in both metals. It is observed that upon 1440 h exposure, the surface of aluminum did not undergo any significant change. The grinding lines are still clearly visible as before. However, the surface morphology of the magnesium coupon changed significantly. Corrosion attack degraded the metal surface. Round pits of around 5 μm diameter are visible on the surface. Corrosion attack appears to be rather uniform.

Fig. 4 shows the XRD analysis on the surface of aluminum and magnesium after immersion test for 1440 h. XRD analysis was carried out with 1.0 incident angle, position from 30° to 90° and step size of 0.1. Both aluminum and magnesium do not show the formation of oxides. The XRD results do not reveal the existence of any metal compounds. This suggests that any corrosion product that might have formed on the surface of both Mg and Al are not thick enough to be detected by the XRD technique. It has been seen earlier that the corrosion rate of both metals decreases slightly with the immersion time. This indicates the possibility of the formation of some sort of protective layers on the metals. However, this layer appears to be too thin to be detected by XRD. Further investigations by surface analytical technique have been planned for the future study.

After the immersion test, the biodiesel sample was characterized by TAN analyzer. The results are shown in Fig. 5. According to ASTM D6657, the limit for TAN value of biodiesel is 0.5 mg KOH/g. The as-received biodiesel falls within this limit which is 0.27 mg KOH/g. However, upon exposure to aluminum and magnesium for 1440 h at room temperature, the TAN value increases significantly to 0.92 mg KOH/g and 0.87 mg KOH/g respectively.

The increase of TAN value indicates that the biodiesel has been degraded [14]. The degradation of biodiesel could be attributed to the oxidation of its unsaturated components in the presence of metal surface. The oxidation process leads to formation of acids, ketones, aldehydes, lactones, alkylfurans etc. [15]. Mg and Al exposed biodiesels show almost similar values of TAN number although the corrosion rates of these metals differ significantly. This suggests that there is no strong correlation between TAN number and corrosion rate.

Fig. 6a and b shows the FTIR spectrum of the sediment that forms on magnesium coupon upon exposure to B100. The sediments were mixed with KBr first and then compressed into pellet for its characterization by FTIR. The main features that found in the FTIR spectrum of sediments are shown in Table 1. The new peaks found in the FTIR spectrum are located at 3750 cm⁻¹ and
Full text is available at :