Corrosivity of *Pongamia pinnatta* biodiesel on zinc and its alloy - a comparison

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Abstract: Biodiesel has been widely put to use all over the world on account of global warming prevention and reduction of fossil fuel consumption. Oxidation of biodiesel is determined by the degree of unsaturation in the fatty acid alkyl ester chain, water content and environmental factors such as temperature, nature of storage container and air exposure during storage. The corrosivity of biodiesel on metals is higher than diesel due to their distinct chemical characteristics. Some metals have a catalytic effect on the biodiesel oxidation process which causes severe corrosion during long-term storage. Higher concentrations of biodiesels may begin to create problems more rapidly with zinc, tin, brass and bronze. Hence the present study is aimed to investigate the corrosivity of *Pongamia pinnata* biodiesel (PBD) and its blends with commercial diesel on zinc and brass by mass loss method. Zinc was found to be highly corroded than brass in PBD. The surface morphology and the elemental composition of the corrosion products were determined by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). Corrosion products on the PBD exposed metals were also examined by X-ray diffraction (XRD).

Keywords: biodiesel; brass; corrosivity; diesel; *Pongamia pinnata*; zinc.

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1 Introduction

Biodiesel is a fast-developing alternate and renewable source of fuel for transportation, became the corner stone of our energy security strategy. Concern 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 corrosion of metals and degradation of fuel properties (Tsuchiya et al., 2006; Karavalakis, Stournas and Karonis, 2010; Knothe, 2005). The presence of impurities and water increases the corrosion tendency of biodiesel (Fazal, Haseeb and Masjuki, 2010; Fazal, Haseeb and Masjuki, 2011; Geller et al., 2008; Kaul et al., 2007; Meenakshi et al., 2013). Fuel degradation due to metal contact can also be different from metal to metal

(Anisha, Meenakshi and Shyamala, 2011; Fazal, Haseeb and Masjuki, 2012; Haseeb et al., 2010).

Various metals are used to handle biodiesel during the storage, transportation, combustion and automobile operational conditions. Regardless of how well the infrastructure is maintained, biodiesel may be contaminated with water at various stages. Increase in free water content may promote microbial growth and corrode fuel system components (Klofutar and Golob, 2007). Under the exposure of different metals into biodiesel, dissolved oxygen may aggravate its corrosive nature in different levels. Biodiesel has chemical characteristics that are distinct from that of petroleum diesel. It is therefore expected that they will interact with materials differently. The research findings available in this field indicate that biodiesel is more corrosive than diesel (Haseeb et al., 2011; Sgroi et al., 2005).

The currently used indicators of corrosiveness of biodiesel the copper strip corrosion and TAN value that are prescribed by different standards (ASTM D 6751 and EN 14214) are not effective enough. Clearly at present, there is a serious lack of scientific data on the corrosion of automotive metals and alloys in biodiesel based on which confident decisions could be made. The corrosive nature of biodiesel under the wide spectrum of compositional, environmental and operating variables should be investigated. The present study focused on the corrosivity of *Pongamia pinnata* biodiesel and its commercial diesel blends on zinc and brass.

2 Materials and methods

Pongamia biodiesel was procured from a dealer at Coimbatore, Tamilnadu. The physicochemical characteristics of PBD was examined as per ASTM D6751 and presented elsewhere (Meenakshi et al., 2013). Commercially available metal sheets machined into coupons of area 33.9 cm^2 (ASTM G184) were used for the entire study.

The elemental compositions of the studied metals are presented in Table 1. The different test media used for the study were B100 (100% biodiesel), B20 (20% biodiesel + 80% commercial diesel), B10 (10% biodiesel + 90% commercial diesel), B5 (5% biodiesel + 95% commercial diesel) and CD (100% commercial diesel).

Table 1 Elemental composition of the materials

	Elements (% composition)										
Metal	*Zn*	*Al*	*Sn*	*Pb*	*Si*	*Ni*	*Fe*	*Mn*	*Bi*	*Sb*	*Cu*
Zinc	99.61	0.034	-	0.161	-	0.13	-	0.024	-	0.01	-
Brass	39.6	-	0.011	-	0.004	0.01	0.037	-	-	0.011	60.32

As per ASTM G1the metal coupons were immersed in triplicate in various test media for a period of 100 h. Specimens were removed after the set intervals of time and wiped with trichloroethylene for the removal of the excess fuel. They were cleaned and reweighed. The loss in mass was determined and from the mass loss the corrosion rates were calculated and the average results from three specimens are reported. The following formula has been used to calculate the corrosion rate in mils per year (mpy).

$$\text{Corrosion rate}\left(\text{mpy}\right)=\frac{3.45\times10^{6}\times\text{Mass loss}\left(\text{grams}\right)}{\text{Density}\left(\text{g/cm}^{3}\right)\times\text{Area}\left(\text{cm}^{2}\right)\times\text{Time}\left(\text{hours}\right)}$$

The conductivity was measured using a conductivity meter (Equiptronics EQ-660A) before and after exposure of coupons. The surface morphology of the polished metal samples, coupons exposed to CD and PBD were characterised by SEM. The elemental composition of the corrosion products were determined by EDS model JEOL, JSM-6390 Scanning Electron microscope equipped with a light element energy dispersive X-ray detector. Corrosion products on the biodiesel exposed metal surface were also examined by XRD. The XRD patterns of the corroded coupons immersed in PBD were recorded by using a diffractometer (Model: XPERT-PRO) with a Cu Kα radiation operated at 45 kV/30 mA.

3 Results and discussion

The corrosion rates of zinc and brass in PBD and its diesel blends and conductivity measurements of various test media before and after immersion of the metals coupons are presented in Table 2. Though the studied metals in PBD and CD blends behave in different magnitudes, the least corrosion rate was observed in commercial diesel when compared to PBD. As compared to diesel, biodiesel is more prone to absorb water and may cause enhanced corrosion. Besides this, auto-oxidation of biodiesel can also enhance its corrosive characteristics and degradation of fuel properties. In comparison of studied metals, zinc (19.09 mpy) was found to be highly corroded than brass (0.38 mpy) in B100. The higher degradation of zinc surface when in contact with pongamia biodiesel is probably related to its fatty acid components, auto-oxidation by-products (acids, esters, aldehydes, ketones, and lactones), water content, oxygen moieties and presence of other contaminants. The measured corrosion rates of the metals were very low in various test media except zinc in PBD. The dissimilar behaviour was observed for the metals studied in PBD, commercial diesel and its blends. Hence the most repeated trend has been taken to find the order of metal corrosion in B100 and CD blends. It is well evident from Table 2 that the order of metal corrosion was found to be Zinc > Brass.

Table 2 Mean corrosion rates of tested metals and conductance in PBD and CD blends

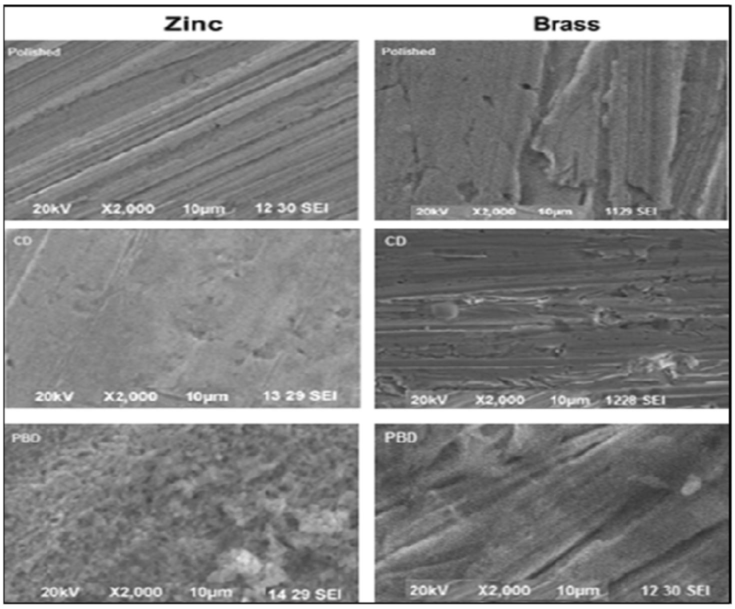
	Mean corrosion rates (mpy)		*Conductance (μ℧)*			
			Before immersion		*After immersion*	
Medium	*Zinc*	*Brass*	*Zinc*	*Brass*	*Zinc*	*Brass*
B100	19.09	0.38	0.21	0.08	0.25	0.21
CD	0.13	0.14	0.19	0.32	0.21	0.37
B5	1.18	0.94	0.18	0.30	0.21	0.34
B10	1.87	1.31	0.19	0.43	0.21	0.47
B20	3.41	1.01	0.19	0.42	0.21	0.49

The variation in the conductivity of the biodiesel and its blends in the presence of zinc and brass are tabulated in (Table 2). The conductivities of the various test solutions (B100, CD, B5, B10 and B20) after exposure of metals were found to be higher than that before, indicating that there is an increase of ionic content in the solutions. This increased ionic content may either be due to corrosion of the metals in biodiesel or due to the absorption of moisture by biodiesel or due to oxidation of biodiesel in the presence of metals.

SEM micrographs of polished zinc and brass coupons and the coupons exposed to CD and PBD were taken for further investigations.

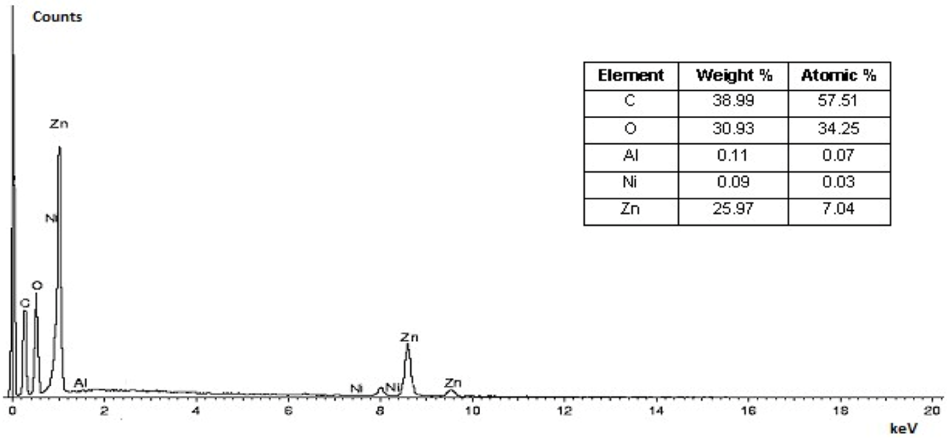
After 100h immersion, the coupons were cleaned and SEM micrographs were taken for further investigations (Figure 1). The polished samples were associated with polishing scratches which may be due to the physical abrasion of the samples with emery paper. The coupons exposed to CD and brass coupon immersed in PBD showed neat metal surfaces with occasional pitting, which proves the compatibility of the selected metals in CD and brass in PBD. Zinc sample in PBD was covered with dark deposits which showed the presence of corrosion product and confirms the highest corrosion rate (19.09). The elemental analysis of the zinc and brass coupons immersed PBD are given in Figures 2 and 3. Though the exposed coupons were cleaned before the elemental analysis, it shows the presence of oxygen, carbon with base metals. The obtained EDS results reveal that the concentration of oxygen higher in zinc than in brass. The presence of higher oxygen suggests greater concentration of oxygenated zinc compounds adherent to the metal surface confirms the highest corrosion rate of zinc in PBD.

Figure 1 SEM micrographs of polished samples and coupons immersed in CD and PBD



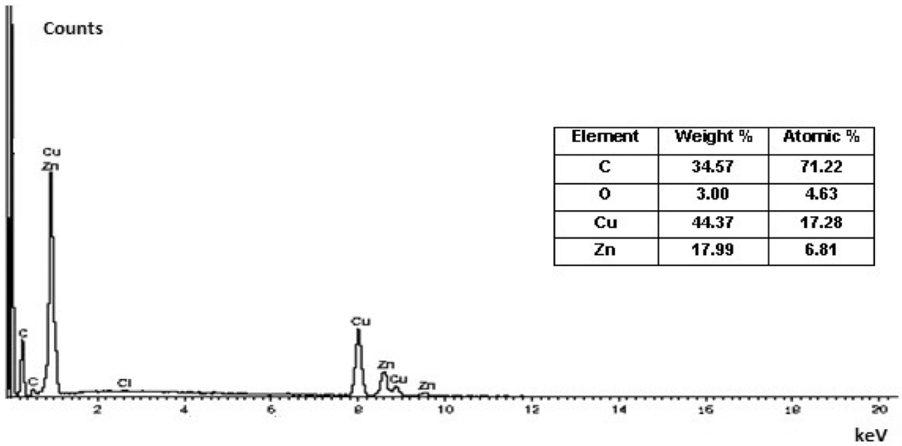
The formation of different compounds on zinc and brass coupons immersed in PBD for 100 h were also investigated by XRD and their X-ray diffractograms have been presented in Figures 4 and 5. It is observed that the compounds like ZnO, $Zn(OH)_2$, $ZnCO_3$ are formed on the coupon immersed in PBD. Formation of these compounds may be due to the presence of dissolved O_2, H_2O, CO_2 and $RCOO^-$ in biodiesel. Least corrosion rates of brass in PBD (0.44 mpy) has been proven by XRD analysis which shows only metallic copper and zinc peaks.

Figure 2 EDS spectra for elemental analysis of zinc coupon exposed to PBD



Element	Weight %	Atomic %
C	38.99	57.51
O	30.93	34.25
Al	0.11	0.07
Ni	0.09	0.03
Zn	25.97	7.04

Figure 3 EDS spectra for elemental analysis of brass coupon exposed to PBD



Element	Weight %	Atomic %
C	34.57	71.22
O	3.00	4.63
Cu	44.37	17.28
Zn	17.99	6.81

Figure 4 XRD pattern of zinc sample immersed in PBD (see online version for colours)

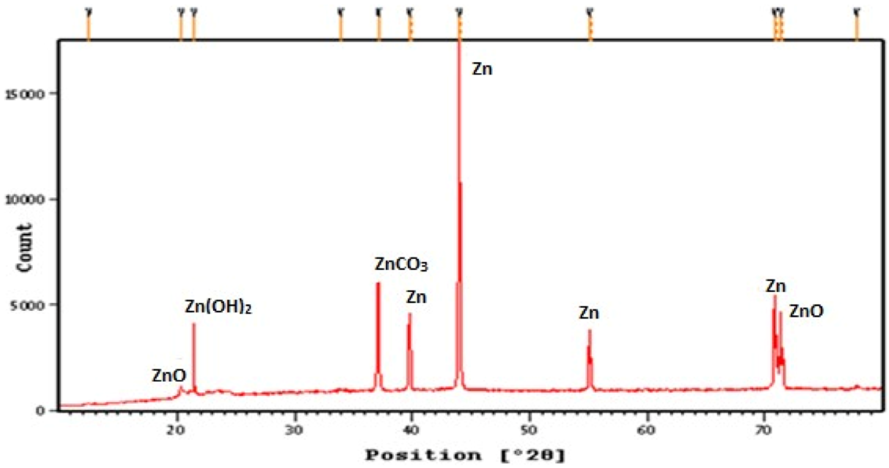
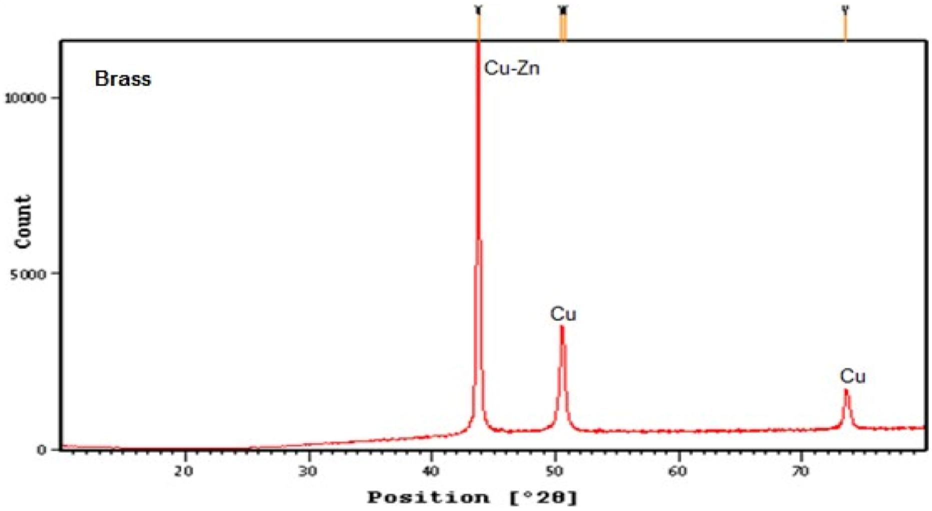


Figure 5 XRD pattern of brass sample immersed in PBD (see online version for colours)



4 Conclusion

- The order of corrosion rate for studied metals in PBD was found to be zinc > brass.
- The influence of the biodiesel blends (B5, B10, B20 and CD) on metal corrosion was negligible and validates the acceptable blending (20%) with commercial diesel.
- The least corrosion rate of brass in PBD under storage condition has also been supported by SEM/EDS analyses.
- The corrosion product identified on zinc surface by XRD is composed of ZnO, $ZnCO_3$, $Zn(OH)_2$ whereas brass surface was showed only by base metal peaks which confirms the least corrosion rate of brass in PBD.

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