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Comparison on the corrosion rates of copper, zinc and brass in *Pongamia* and *Jatropha* biodiesels

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Corrosion is one of the most important topics very relevant to the biodiesel compatibility issue. The corrosive effects of biodiesel are mainly caused by the presence of water and free fatty acids. In the present investigation, the compatibility of biodiesels from *Pongamia*, *Jatropha* and their different blends (5%, 10% and 20%) with diesel on copper, zinc and brass has been studied by mass loss method for a period of 100 h. Though the studied metals in *pongamia, jatropha* and diesel blends behave in different magnitude, the least corrosion rate is observe in commercial diesel when compare to biodiesels in all the metals. The effect of temperature on the corrosivity of biodiesels and their blends with diesel has been investigated by linear polarization resistance method. The changes in surface morphology and corrosion products on the biodiesels expose metal surfaces examined by optical microscope and X-ray diffraction. Copper and brass coupons in JBD show only base metal peaks and intense carbonate peak in zinc which prove the least corrosivity of JBD in studied metals.

Keywords: Corrosion, Pongamia, Jatropha, Biodiesel

Most of the biodiesel produced is mainly dependent on edible oil sources[1-4]. The cost of crop oil accounts for the large percent in direct biodiesel production cost which includes capital costs and returns. Besides, the availability of oil crop is limited. Therefore, it is necessary to find a new feed stock available for biodiesel production, which does not drain on the edible vegetable oil supply[5,6]. With no competing food uses, the attention is focused on *Pongamia pinnata* biodiesel (PBD) and *Jatropha curcus* biodiesel (JBD)[7-9]. Because of its chemical structure, biodiesel can be very sensitive to oxidative and thermal degradation[10]. Oxidation can lead to the formation of corrosive acids and deposits that may cause increased wear in automotive engine parts. Oxidative stability of biodiesel is highly related with fatty acid composition, storage condition, materials of the container, water and metal content.

Biodiesel does not exhibit long-term compatibility with certain soft metals such as copper, brass, bronze, lead, tin and zinc. These metals may accelerate the oxidation process of biodiesel creating fuel insolubles or gels and salts[11]. The physical and chemical changes for metals could lead to malfunction, leakage or even failure of individual components in the system. Sizeable amount of work has been carried out worldwide concerning compatibility of metals with various biodiesels[12-16]. Corrosive nature of biodiesels under wide spectrum of compositional and operating variables is particularly important and needed in order to confidently use biodiesels without corrosion problems. Hence, the present study is aimed to investigate and compare the corrosion behaviour of copper, zinc and brass in PBD, JBD and their commercial diesel (CD) blends under static condition.

Experimental Section

Materials

Pongamia and *Jatropha* biodiesels were procured from a dealer at Coimbatore, Tamilnadu, India. The physicochemical characteristics of PBD and JBD were examined as per American standard for Testing materials (ASTM D6751) and presented elsewhere[17]. Commercially available metal sheets machined into coupons of area 33.9 cm^2 (ASTM G184) were used for the entire study. The composition, density and equivalent weight 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).

Static mass loss method

As per ASTM G1, the 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. Then the specimens were cleaned with respective solution as per ASTM G1-90 and reweighed. The loss in mass was determined. From the mass loss, the corrosion rates were calculated and average results from three specimens were reported in Mils per year (mpy). The formula to calculate the corrosion rate is given elsewhere[18]. Conductivity of an electrolyte is one of the important parameters to understand the corrosion process. The rate of corrosion is influenced considerably by the conductivity of the electrolyte. Hence the conductivity of test media was measured using a conductivity meter (Equiptronics EQ-660A) before and after exposure of coupons.

Linear polarization resistance method

To understand the effect of temperature on the corrosivity of biodiesels, the experiments were carried out at different temperatures for biodiesels and their blends with CD by polarization resistance method. Linear polarization resistance (LPR) method is one of the electrochemical techniques to support sensitive to low corrosion rates, short experimental duration and well established theoretical understanding. A computer controlled commercial potentiostat (Solartron 1280B) was used with the software package of CORWARE @ for polarization studies. The electrochemical cell was a glass beaker containing the aerated unstirred test solution with a platinum counter electrode, a saturated calomel reference electrode and the metal specimen of same composition as in the mass loss method (with an exposed area of 1 cm^2) as the working electrode. The linear polarization measurements were carried out within the potential range of – 0.02 V to + 0.02 V (scan rate 0.1667 mV/s) with respect to open circuit potential. The corrosion rate was measured every hour for 24 h at different temperature (30°C±2, 50°C±2 and 70°C±2) to understand the effect of temperature on the corrosivity of PBD and JBD. From the polarization resistance (Rp) values, the corrosion rates were calculated (ASTM G3).

Table 1 — Composition, density and equivalent weight of the materials

Element	% Composition		
	Copper	Zinc	Brass
Zn	5.12	99.61	39.6
Al	0.002	0.034	<0.010
Sn	0.0008	-	0.011
Pb	0.006	0.161	<0.001
Si	0.01	-	0.004
Ni	0.004	0.13	0.010
Fe	0.036	-	0.037
Mn	0.0007	0.024	<0.002
P	0.001	-	<0.001
S	0.034	-	<0.005
Bi	0.001	0.027	<0.001
Sb	0.005	0.01	0.011
As	0.002	-	<0.001
Co	-	-	<0.010
Ag	0.004	-	-
Mg	0.00009	-	-
Cu	94.77	-	60.32
Density (g/cm^3)	8.96	7.14	8.75
Equivalent Weight	31.77	32.6	31.91

Surface analysis

To validate the results of mass loss studies, the optical micrographs of the polished metal samples and coupons exposed to CD, PBD and JBD, were characterized by inverted metallurgical microscope KOZO optics model XJM 404T. Corrosion products on the biodiesel exposed metal surface were also examined by using X-ray diffraction (XRD). The XRD patterns of the corroded samples were recorded by using a diffractometer (Model: XPERT-PRO) with a Cu Kα radiation operated at 45 kV/30 mA.

Results and Discussion

Corrosion rate measurements

The behaviour of studied metals (copper, zinc and brass) in PBD and JBD and their diesel blends are presented in Table 2. The measured corrosion rates of

Table 2 — Mean corrosion rates of tested metals in PBD, JBD and CD blends

Medium	Mean corrosion rates (mpy)					
	PBD			JBD		
	Copper	Zinc	Brass	Copper	Zinc	Brass
B100	0.93 ± 0.10	19.09 ± 0.84	0.38 ± 0.05	0.44 ± 0.08	0.16 ± 0.03	0.40 ± 0.16
CD	0.28 ± 0.04	0.13 ± 0.10	0.14 ±0.01	0.28 ± 0.04	0.13 ± 0.10	0.14 ± 0.19
B5	0.45 ± 0.02	1.18 ± 0.03	0.94 ± 0.02	0.37 ± 0.07	0.17 ± 0.05	0.55 ± 0.08
B10	0.65 ± 0.05	1.87 ± 0.03	1.31 ± 0.04	0.41 ± 0.03	0.17 ± 0.08	0.87 ± 0.31
B20	1.05 ± 0.23	3.41 ± 0.06	1.01 ± 0.14	0.41 ± 0.04	0.18 ± 0.02	0.91 ± 0.38

the metals were very low except zinc in PBD, the dissimilar behaviour was observed for the metals studied in the biodiesels, commercial diesel and their blends. Hence 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 > Copper> Brass for PBD and Copper > Brass > Zinc for JBD.

Though the studied metals in PBD, JBD and CD blends behave in different magnitude, the least corrosion rate was observed in commercial diesel when compared to B100 in all the metals. Reviews suggested that biodiesel was more corrosive than petro diesel due the presence of higher concentration of unsaturated acid components. Presence of free fatty acid, more oxygen moieties and water content, impurities remaining after processing and bearing more acid compounds due to higher oxidation seem to increase the corrosiveness of biodiesel as compared to diesel fuel[19-21].

Donnel *et al.*, 2015 suggested that zinc materials are more suitable for storage and transportation of biodiesels because the degradation of the biodiesel would be less in zinc materials compared to copper materials[22]. Present investigation shows that the corrosion rate of zinc in PBD is twenty times higher than that of copper. Hence, it is important to verify the impact of the alternative fuels on the corrosion of various metals with different biodiesels. The higher corrosive nature of pongamia biodiesel may be attributed due to the presence of significant amounts of esters of oleic, linoleic, linolenic acids are present[23] and the trend of increasing stability was linolenic < linoleic < oleic. These esters may effortlessly be oxidized to methyl linoleate and methyl linolenate. These are directly involved in the formation of decomposed compounds such as acids, aldehydes, esters, ketones, peroxides, alcohols and polymeric species, which not only affect the biodiesel properties but also can cause problems to engine operation.

Conductivity measurements

The variation in the conductivity of the biodiesels (PBD and JBD) and their blends in the presence of copper, zinc and brass are pictorially represented in Tables 3 and 4 respectively. The conductivities of the various test solutions (B100, CD, B5, B10 and B20) after exposure of metals were slightly higher than that before, indicating that there is an increase of ionic content in the solutions. This increased ionic content may either due to corrosion of the metals in biodiesels or due to the absorption of moisture by biodiesels or due to oxidation of biodiesels in the presence of metals. Increase in conductivity after immersion of the metal coupons in various test solution than before, immersion for pongamia oil and jatropha biodiesel have been reported in earlier publications[9,24].

Effect of temperature

The corrosion rates of studied metals as determined by LPR method at different temperatures for PBD-CD

Table 3 — Variation of conductivity - PBD and CD blends in the presence of copper, zinc and brass

Medium	Mean conductance ($\mu\Omega^{-1}$)					
	Copper		Zinc		Brass	
	Before	After	Before	After	Before	After
B100	0.21	0.23	0.21	0.25	0.18	0.21
CD	0.21	0.22	0.22	0.24	0.20	0.22
B5	0.20	0.21	0.18	0.22	0.19	0.21
B10	0.20	0.21	0.17	0.21	0.20	0.21
B20	0.20	0.21	0.17	0.23	0.19	0.21

Table 4 — Variation of conductivity - JBD and CD blends in the presence of copper, zinc and brass

Medium	Mean conductance ($\mu\Omega^{-1}$)					
	Copper		Zinc		Brass	
	Before	After	Before	After	Before	After
B100	0.21	0.22	0.21	0.22	0.18	0.22
CD	0.21	0.21	0.22	0.23	0.19	0.21
B5	0.20	0.22	0.18	0.20	0.19	0.22
B10	0.20	0.21	0.17	0.20	0.20	0.22
B20	0.20	0.21	0.17	0.21	0.19	0.22

and JBD-CD blends are presented in Tables 5 and 6. In the present investigation, studies carried out from 30°C to 70°C to depict storage tank and pipeline condition. This proves the fact that increase in temperature increases the corrosion rate because of the accelerated electrochemical and chemical reactions as evident from the table. This increase may be due to the rapid formation and dissolution of corrosion products which also lead to more deposition of metal particles in the biodiesels. This will also lead to more deterioration of materials used in engine in the presence of biodiesel at elevated temperatures, thereby reduces engine performance and efficiency. Similar results have been attributed during the investigation on the compatibility of groundnut biodiesel with copper[22].

Surface morphology – Optical microscopy

The photo micrographs of polished copper, zinc and brass coupons and samples immersed in biodiesels are presented in Fig. 1. Visual observation of the low magnification photomicrographs (40×) reveals that the polished samples are associated with polishing scratches which may be due to the physical abrasion of the samples with emery paper. The coupons exposed to PBD and JBD showed little damage to the metal surfaces with occasional pitting, which confirms the compatibility of the selected metals with both the biodiesels with the exception of zinc in PBD. Visibly, the zinc sample in PBD was covered with dark deposits which showed the presence of corrosion product and confirms the highest corrosion rate (19.09). Probable mechanism for coupons exposed to PBD and JBD and the corrosion product formed on the metal surfaces were discussed in the following section.

Corrosion product analysis – X-ray diffraction

The XRD patterns of the copper coupons immersed in PBD and JBD for 100 h are given in Fig. 2.

It is observed that with metallic copper, a small amount of CuO, $Cu(OH)_2$ and $CuCO_3$ are formed on the copper coupons immersed in PBD whereas only Cu base metal peaks are found on coupons immersed in JBD. On comparison with PBD and JBD, corrosion products are visible in PBD which confirms the higher corrosion rates of PBD (0.93) than JBD (0.44). Corrosion product formed on the copper samples immersed in palm biodiesel at different time intervals and expected reactions have been reported[25]. Corrosion products formed on the coupon immersed in PBD are oxides, carbonates and hydroxides of copper. The presence of oxygen, copper can lead to the formation of cuprous oxide (Cu_2O) by reaction. But Cu_2O is unstable and rapidly it turns to the stable species, CuO. The presence of dissolved water, CO^2, $RCOO^-$ etc. in biodiesel causes the formation of carbonate and hydroxyl based copper compounds.

The formation of different compounds on zinc coupons immersed in PBD and JBD for 100 h were also investigated by XRD and their X-ray diffractograms have been presented in Fig. 3. It is

Table 5 — Mean corrosion rates of tested metals in PBD and CD blends at different temperatures by LPR method

Medium	Mean corrosion rate (mpy)								
	Copper			Brass			Zinc		
	30°C	50°C	70°C	30°C	50°C	70°C	30°C	50°C	70°C
B100	0.094	0.416	0.712	0.006	0.039	0.124	1.112	2.198	3.137
CD	0.093	0.188	0.347	0.014	0.112	0.695	0.411	0.579	4.327
B5	0.064	0.270	0.413	0.003	0.394	0.438	0.070	0.376	3.113
B10	0.370	0.506	0.867	0.008	0.374	0.448	0.063	0.292	3.832
B20	0.010	0.240	0.355	0.008	0.394	1.115	0.482	0.803	5.172

Table 6 — Mean corrosion rates of tested metals in JBD and CD blends at different temperatures by LPR method

Medium	Mean corrosion rate (mpy)								
	Copper			Brass			Zinc		
	30°C	50°C	70°C	30°C	50°C	70°C	30°C	50°C	70°C
B100	0.160	0.396	0.549	0.031	0.135	0.386	0.224	1.061	2.158
CD	0.093	0.188	0.347	0.014	0.112	0.695	0.411	0.579	4.327
B5	0.026	0.058	0.506	0.089	0.209	0.334	0.676	0.679	4.523
B10	0.256	0.303	0.495	0.009	0.130	0.744	0.301	1.137	4.323
B20	0.073	0.396	0.460	0.066	0.093	0.196	0.811	0.859	4.319

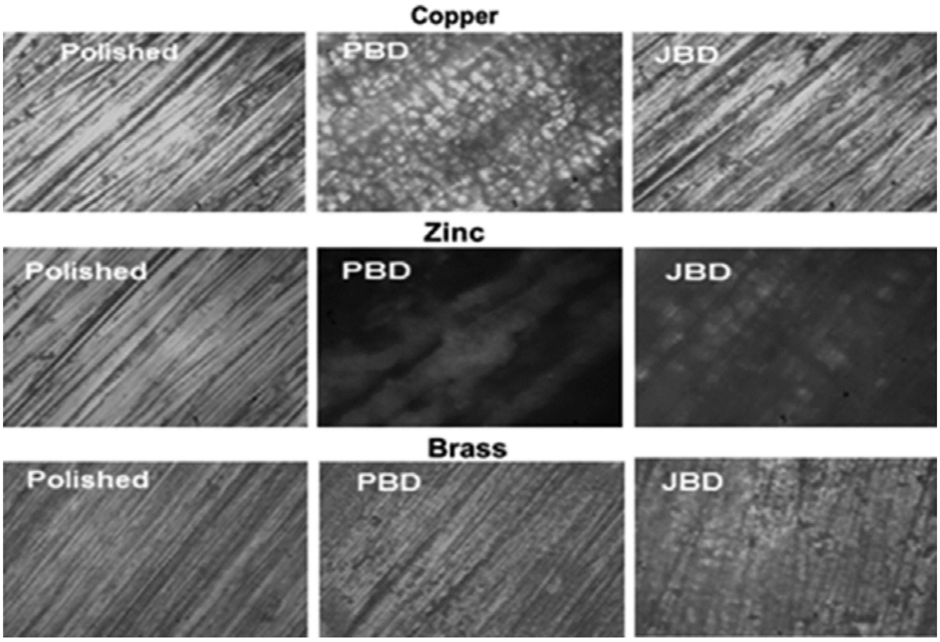

Fig. 1 — Optical micrographs (40×) of studied metals in biodiesels

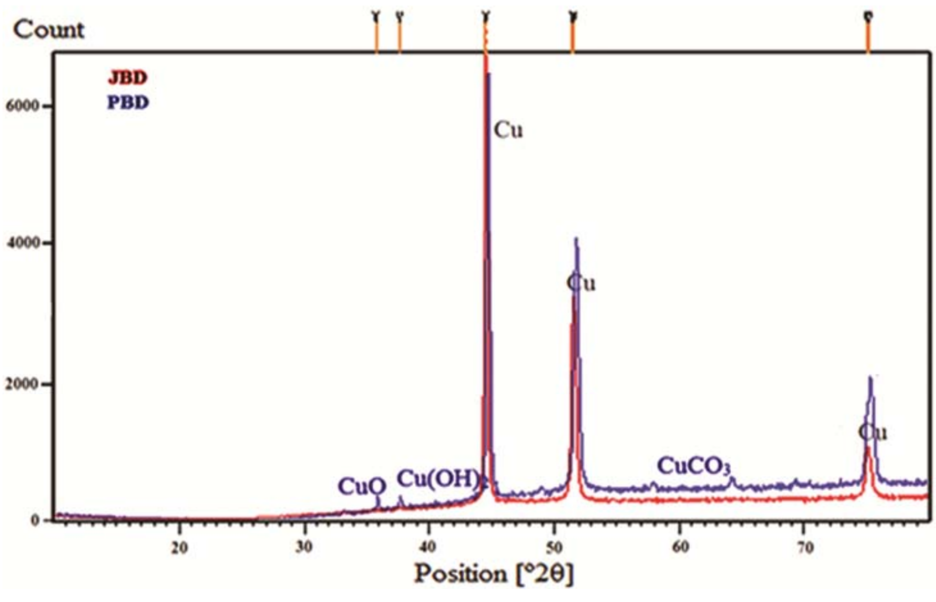

Fig. 2 — XRD pattern of copper coupons immersed in PBD and JBD for 100 h

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. The negligible corrosion rate of zinc in JBD has been proved by XRD where an only less intense ZnO peak is observed with base metal peaks. High resistance of zinc in JBD may be due to the formation of insoluble $ZnCO_3$ film on the metal surface which protects the metal from further attack. The possible reactions occur on the zinc when exposed to *Pongamia* biodiesel are as follows.

$$2\,Zn + 2\,H_2O + O_2 \rightarrow 2\,Zn(OH)_2 \quad \ldots (1)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad \ldots(2)$$

$$Zn^{2+} + 2\,RCOO^- \rightarrow ZnCO_3 + R\text{-}R + CO \quad \ldots(3)$$

$$ZnO + CO_2 \rightarrow ZnCO_3 \quad \ldots(4)$$

Figure 4 shows the X-ray diffractograms of brass coupons immersed in PBD and JBD for 100 h. Brass consists of copper and zinc which may be responsible for the passivity of brass during short exposures. Least corrosion rates of brass in PBD (0.44 mpy) and in JBD (0.38 mpy) have proven by XRD analysis which shows only metallic copper and zinc peaks. This may be due to ionization-redeposition mechanism where brass loses its zinc to corrosive media and copper appears on the brass surface in the form of a fine grained porous[26].

Further investigations are required to understand the proper reaction mechanism of the studied metals in PBD and JBD biodiesels and to identify the compositional changes of biodiesels before and after immersion of the metal coupons.

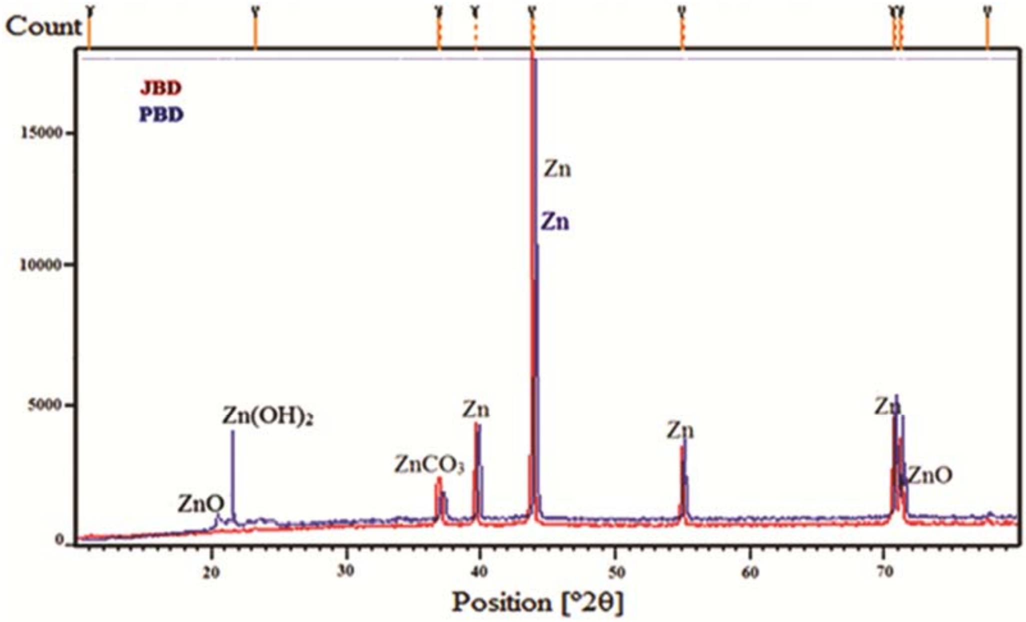

Fig. 3 — XRD pattern of zinc coupons immersed in PBD and JBD for 100 h

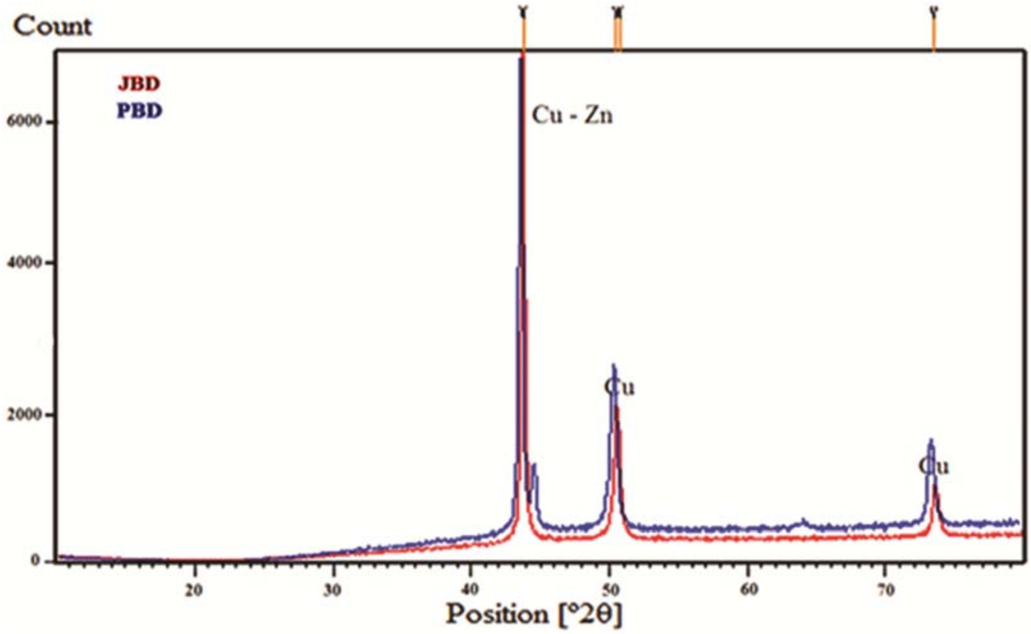

Fig. 4 — XRD pattern of brass coupons immersed in PBD and JBD for 100 h

Conclusion

- *Pongamia pinnata* and *Jatropha curcus* biodiesels adhered to most of the fuel properties as per ASTM D6751 standard indicating that PBD and JBD are acceptable as a substitute for petrodiesel fuel for diesel engines.
- The order of corrosion for the studied metals in the biodiesels, commercial diesel and their blends was found to be Zinc > Copper > Brass for PBD and Copper > Brass > Zinc for JBD.
- Though the studied metals in PBD, JBD and CD blends behave in different magnitude, the least corrosion rate was observed in commercial diesel when compared to B100 in all the metals.
- The direct correlation between conductance and corrosion has been established through the increased conductivity of the various test media after exposure of the metal coupons in them.
- The linear polarization measurements at different temperatures showed that the corrosion rate of all the studied metals increases with increase in temperature.
- The surface morphology of the corroded metal surfaces was documented from the optical micrographs and confirms the highest corrosion rate of zinc in PBD.
- The corrosion products identified by XRD on copper and zinc surfaces immersed in PBD are composed of oxides, carbonates and hydroxides due to the presence of dissolved O_2, H_2O, CO_2 and $RCOO^-$ in biodiesel.
- Copper and brass coupons in JBD showed only base metal peaks and intense carbonate peak in zinc prove the least corrosivity of JBD. The formation of insoluble $ZnCO_3$ film on the metal surface protects the metal from further attack.

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