The effect of corrosion inhibitor on corrosion of automotive materials in Biodegradable engine oil

R.Ellappan[1*], S.Arumugam[1]**

[1]Department of Mechanical Engineering, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Kanchipuram - 631561, Tamilnadu, India.

*ellsraaj@gmail.com, **aru_amace@yahoo.co.in

Abstract - Bio-degradability is one of the major issue in the disposal of used synthetic engine lubricants, by considering this the development of vegetable based engine lubricants shows more attention, the corrosion of engine parts owing to its usage under bio-lubricant environment can be suspected due to its hygroscopic nature. This work aims to analyse the effect of blend of poly-ethylene glycol and benzotriazole as corrosion inhibitor on ferrous and non-ferrous metals in chemically modified rapeseed oil based bio- degradable engine oil as per ASTM D6594. Scanning Electron Microscope (SEM) analysis shows that the pitting corrosion over the surfaces of lead and copper is found more comparatively with other metals in the bio lubricant environment without corrosion inhibitor, the metals immersed in the bio-lubricant with inhibitor provides the protective oxide film layer over the metallic surfaces restrict the corrosion rate.

1. Introduction

Development of alternate fuels to alter the place of fossil fuel due to the higher consumption rate leads to search suitable substitute fuels [1]. Similarly focus towards eco-friendly bio-lubricant from canola oil is renewable and bio-degradable and nontoxic , therefore it can be considered as a replacement for synthetic lubricants [2]. Bio lubricants meet out the tribological properties compared with commercially available synthetic lubricants [3]. Arumugam et al., reveals that the bio-diesel contaminated bio lubricant shows better performance in terms of wear and frictional force and friction, over mineral lubricant under similar operating conditions [4]. Bio-diesel reacts with metals resulting in corrosion due to hygroscopic nature and oxygen moieties present in bio diesel [5]. Metal samples were prepared and cleaned as per ASTM standard G01 [6]. A test rig was developed as per ASTM D6594, to conduct   laboratory corrosion test at high temperature environment for synthetic lubricant [7].

Katherine et al., reported that the effect of synthetic lubricant under high temperature environment suspected to corrosion over ferrous and non-ferrous metals [8]. Haseeb et al., concluded that the copper bronze shows higher corrosion among non ferrous metals [9]. Singh et al., describes about the cause for the corrosion is due to the auto oxidation and moisture presence in vegetable oils [10]. Fazal et al., express that the static immersion test on bio-diesel at 800c for 1200 hours, the copper and aluminium are susceptible to corrosion [11]. Haseeb et al., justifies that the increasing TAN number in oil leads to corrosion [12]. Krazan et al., investigated tribological properties of formulated rapeseed oil and compared with synthetic oil [13]. Arumugam et al., reported that rapeseed based bio-lubricant is very much comparable with synthetic lubricants in all respects [14]. Arumugam et al., concluded that bio-lubricants are more corrosive than synthetic lubricants by conducting on test as per ASTM D6594 [17]. Fazal, et al., and Matjaz Finsger et al., justifies that the effect of corrosion inhibitors like TBA, BTA over cast iron and low carbon steel on corrosion in palm biodiesel, shows better performance in reading the acidity of the bio diesel and creates protective layer over the metal surface which prevents the corrosion [15,16].

2. Materials and methods

2.1 Selection of materials and preparation of sample
Material selection is the key parameter to predict the corrosion probability on both ferrous and non-ferrous material which is used in diesel engines are cylinder liner and journal bearing. Ferrous metals such as CI and Mild steel and nonferrous metals such as copper, tin, lead and zinc were considered for testing. Metal samples of CI, mild steel and copper were cut from round bars and rest of Tin, lead and zinc samples has been copper from sheet.

All samples were polished by using 600 – 1200 grade silicon carbide emery sheets. Before immersion the specimen were cleaned to remove oiliness with acetone followed by ultrasonic cleanic in an absolute ethanol bath as per ASTM G1 STD [6]

2.2 Selection of corrosion inhibitors

2.2.1 Ferrous Metal and Its Inhibitor (Tert Butyl amine)
Fazal et al. [15] investigated the effects off TBA as inhibitor on cast iron and low carbon steel in palm biodiesel (B100) and concluded TBA exhibits best inhibition properties. At 300 K inhibitor efficiency at 250 ppm is 86.5% for cast iron and 86.71% for low carbon steel. At concentration of 100ppm the inhibitor efficiency is 47% for both cast iron and low carbon steel. The high inhibitor efficiency could be attributed to the dominant physical adsorption of N-containing compound which creates protective layer over the metal surface which prevents corrosion. The protective coating compounds indicates it is form of $Fe(NO_3)_3.9H_2O$. Figure 1 shows the structure of $Fe(NO_3)_3.9H_2O$.

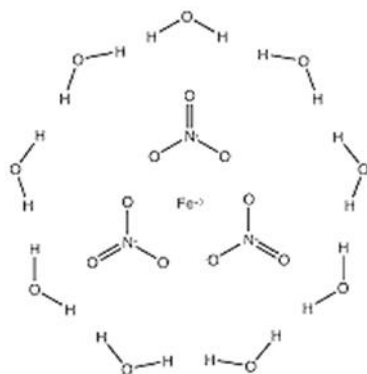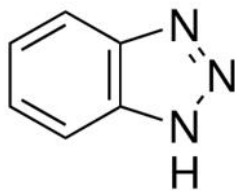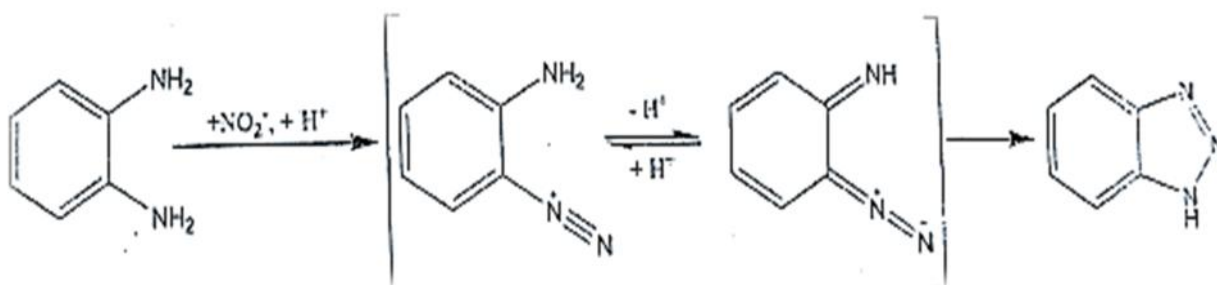**Figure 1** Structure of $Fe(NO_3)_3.9H_2O$

The leading and prominent group for corrosion inhibition is amine group. A peak of N-containing compound $Fe(NO3)_3.9H_2O$ at around 40 degree is formed on the metal surface may help from an N-rich layer which contributes in reducing corrosion attack. The adsorption molecules on metal surface via hetero cyclic moiety N atoms exhibits a stronger interaction compared with that via other hetero atoms. A nearly uniform region enriched with N and probably composed of $Fe(NO3)3.9H2O$ is observed via XRD the main constituents within the layer are N , which proves the assumption of TBA adsorption on LCS surface forms protective layer to prevent further interaction between the metal and the bio diesel. The thickness of compound $Fe(NO3)3.9H2O$ on CI and LCS are found out to be 19.97 μm and 7.78 μm respectively.
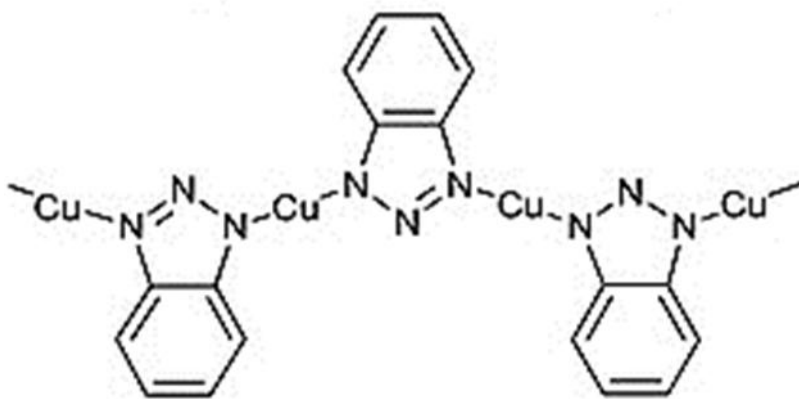
2.2.2 Non-Ferrous Metal and Its Inhibitor (Benzotriazole)
It is a heterocyclic organic compound produced by reaction of ortho-phenylenediamine with sodium and acetic acid giving a white powder at room temperature. It is sufficiently soluble in water solutions and used as corrosion inhibitor. Figure 2 (a, b, c) shows the structure of Benzotriazozle, Structure of BTAH and Cu-BTA complex chemisorbed on the Cu surface.

Figure 2 (a) Structure of Benzotriazole

Figure 2 (b) Structure of BTAH

BTAH on reaction with Cu in 10% H_2SO_4 solutions under dynamic conditions and at low flow rate (Reynolds no. < 500) there is maximum IE at 10mM.For a medium of 3% NaCl and (3-5.3) pH limit 20mM concentration of BTAH the H_2 and air punged test gives an effectiveness of (63-95%).

Naphthatriazole is the one of the best inhibitors used for Corrosion of non-ferrous metals. The advantage is that effectiveness increases when compared to BTAH. But it is very expensive.

Figure 2 (c) Cu-BTA complex chemisorbed on the Cu surface

Protective coating is the film or multilayer and not monolayer formed by adsorption or chemisorption due to gas molecules present nearer to cu atoms. The above diagram denotes the co-ordination of (C-N) atoms where the lone pair of electron (N) is at the center. In the (N-H) bond the removal of H atom is replaced to form a C-BTA structure as shown. It's known as polymeric chain. The thickness of the film is around (50 A0) and the concentration increased if time of immersion is high. If the film is thin then effectiveness of BTAH is high. The film formed because of adsorption of BTAH on the surface of Cu.

2.3 High temperature corrosion bench test (HTCBT)

Fig 3 (a-c). Shows Laboratory test set up, as per ASTM D 6594 corrosion test was conducted about 160 hours at 1350c. [7] The samples immersed in both the lubricant with and without inhibitor were cleaned .the corrosion products on the metal surfaces were removed by dipping the metal coupons about twice for 5 – 10 sec in 10 – 15 % Hydrochloric acid with Clarke solution. The table 1 shows the corrosion rate of the bio-degradable engine oil with and without inhibitor. Metal samples were then cleaned by acetone and dried and instantly weighed in weigh balance with 5 decimal accuracy to find out the weight loss for evaluating corrosion rate. Rapeseed based bio lubricant with 10% diluted rapeseed methyl ester as immersion medium. Table 1 shows the values of corrosion rates.
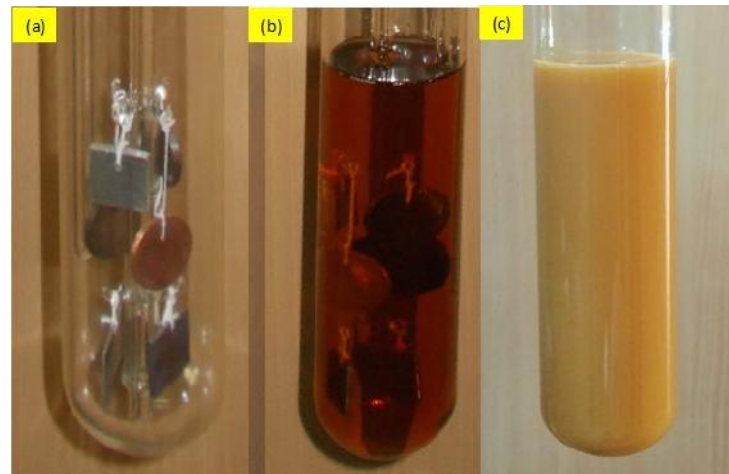

Figure 3 photographic view of a) Test samples b) Samples immersed in without inhibitor c) Samples immersed in with inhibitor

2.4 Corrosion Rate

The rate of corrosion is the speed at which any metal deteriorates in a specific environment. Degradation of metals was investigated by measurement of corrosion rate. It is expressed in mpy (mils per year). The corrosion rate can be calculated using the equation given below,

$$\text{Corrosion rate (mpy)} = \frac{w \times 534}{D \times t \times A}$$

Where,

w – Weight loss in the metal in mg

D – Density of the metal in g/cm^3

A – Exposed surface area of the metal in $inch^2$

T – Time of exposure of the metal in lubricant in h = 168h

Table 1 Corrosion rate

S.no	Metal	Density at 20˚C (g/cm³)	Bio Lubricant Without Inhibitor		Bio Lubricant With Inhibitor	
			Weight lost (mg)	Corrosion rate (mpy)	Weight lost (mg)	Corrosion rate (mpy)
1	Cast Iron	7.272	3.04	0.9415	0.2	0.0531
2	Mild Steel	7.833	3.58	1.16	0.5	0.1447
3	Copper	8.954	4.03	1.27	2.31	0.4127
4	Zinc	7.144	3.04	0.9584	1.1	0.3739
5	Tin	7.304	2.05	0.6249	1.37	0.35074
6	Lead	11.393	5.02	7.171	3.95	0.98145

3. Result and Discussion

3.1 Visual examinations for the specimens used in the corrosion studies
The Figure 4 (a-c) demonstrates the specimens of the test samples before and after testing with and without inhibitor.
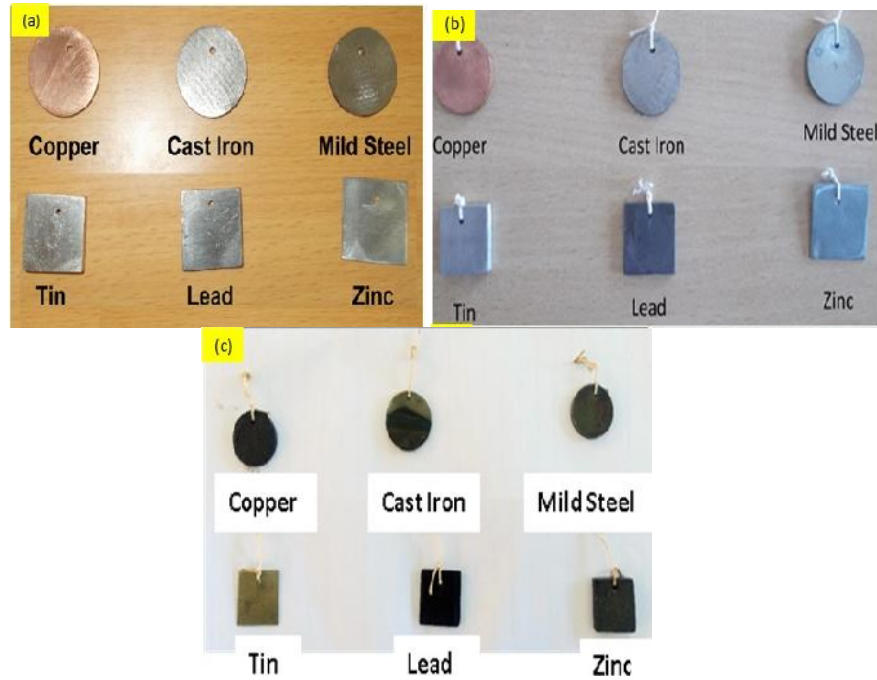

Figure 4 photographic view of a) Specimens before testing b) Specimens after testing in bio lubricant with inhibitor c) Specimens after testing in bio lubricant without inhibitor

3.2 Investigation of Surface Morphology Using SEM
 Scanning Electron Microscopy (SEM) is a method for high-resolution imaging of surfaces. It is preferred for getting the information about qualitative differences in the surfaces before and after testing in bio and reference lubricants. The SEM images of different metals before and after testing in bio and reference lubricants are shown and discussed below. The figure 5 (a-i) shows the SEM images of different material used in this investigation.

3.3 Cast Iron
The SEM images taken for Cast iron shows no noticeable amount of corrosion even though some deposits can be seen in case specimen is exposed to bio lubricant with or without inhibitor. Hence it can be said that pitting corrosion may have started to take place in the specimens.
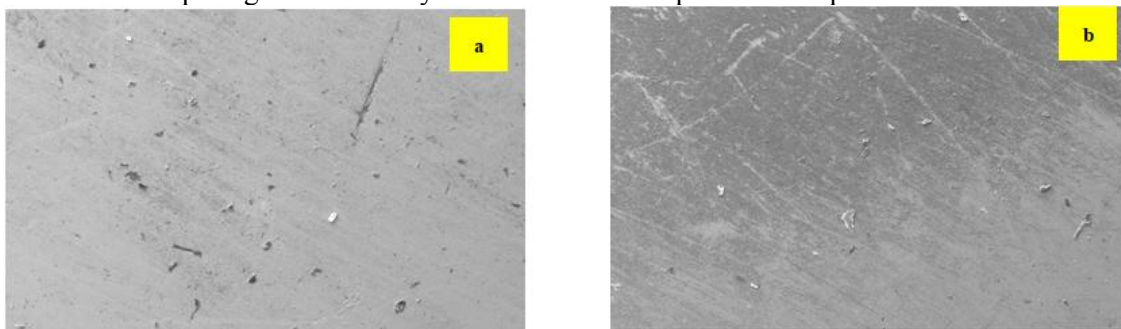

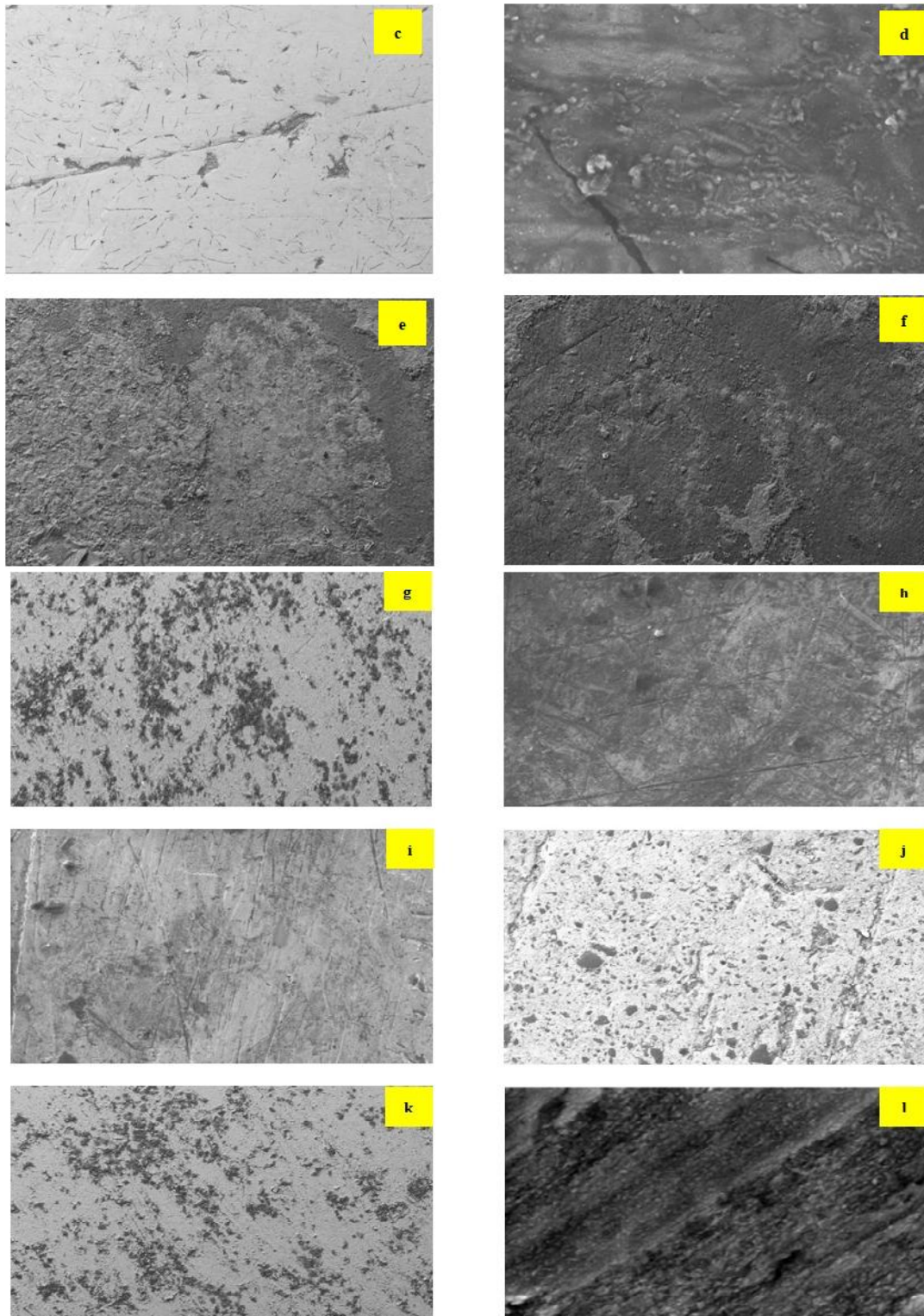**Figure 5** SEM images of (a) CI with inhibitor (b) CI without inhibitor

Figure 5 SEM images of (a) CI with inhibitor (b) CI without inhibitor (c) Mild steel with inhibitor (d) Mild steel without inhibitor (e) Copper with inhibitor (f) Copper without inhibitor (g) Zinc with inhibitor (h) Zinc without inhibitor (i) Tin with inhibitor (j) Tin without inhibitor (k) Lead with inhibitor (l) Lead without inhibitor

3.4 Mild Steel
There no noticeable amount of corrosion is found on mild steel except some white dots, which are non-metallic deposits in case specimen exposed to bio lubricant with inhibitor and some shaded regions which may denote compounds formed out of corrosion on specimen exposed to bio lubricant without lubricant.

3.5 Copper
In case of copper exposed to bio lubricant with inhibitor number of pits can be found throughout the surface which shows that pitting corrosion has taken place. Whereas the specimen exposed to bio lubricant without inhibitor is not corroded as much as the one exposed to bio lubricant with inhibitor but it also shows some very small pits which may be the starting of pitting corrosion.

3.6 Zinc
Zinc specimen exposed to bio lubricant with inhibitor shows some deposits over the surface which may later lead to corrosion and the specimen exposed to without inhibitor has white spots that indicates non-metallic deposits throughout the surface. Otherwise there is no noticeable amount of corrosion is found.

3.7 Tin
Tin exposed to both bio lubricants doesn't show any noticeable corrosion. It can be justified with the help of corrosion rate calculation in which tin shows least corrosion rate for both bio lubricants.

3.8 Lead
Among all the specimens Lead shows the maximum corrosion effect specifically on the specimen exposed to bio lubricant without inhibitor. Very large pits and debris are found over the specimen exposed to bio oil. Similarly specimen exposed to reference oil also shows number of small pits through the surface but no debris found. From the SEM images it can be clearly said that the corrosion is more in case of all specimens which are exposed to bio lubricant as compared to the specimens exposed to synthetic lubricants. In specimens exposed to bio oil deposits are found frequently over the surface. The highest corrosion is found on lead followed by copper exposed to bio lubricant. There was no noticeable corrosion in case other specimens. Tin is the least corroded metal among all other.

The density of the each metal at 20˚C is taken from the Heat transfer data book and the weight loss is calculated from the weight of the specimens measured before and after testing, which is converted into corrosion rate by substituting the values in the above equation and the results are tabulated in Table From the above table 1 it can be found that for the specimens tested in bio lubricant without inhibitor, the corrosion rate increases in the order given below,

$$Pb > Cu > MS > Zn > CI > Sn$$

Whereas for the specimens tested in bio lubricant with inhibitor, the corrosion rate increases in the order given below,

$$Pb > Cu > Zn > Sn > MS > CI$$

4. CONCLUSIONS
The degradation of different metals which comprises in the engine lubrication system was investigated with High Temperature Corrosion Bench Test Rig. The following points has been concluded from the above study,
- All analysis carried on specimens and oils as well as corrosion rate calculations and properties measured before and after testing prove that the bio lubricant without inhibitor is more corrosive than the bio lubricant with inhibitor in majority of cases.

- Upon exposure to different metals the corrosivity of the lubricants increases. Among the metals tested Lead, Copper and Tin are more prone to corrosion.
- Ferrous compounds such as Cast Iron and Mild Steel doesn't show significant corrosion as compared to other metals.
- Cast iron is found to be more resistant to the corrosion in case of exposure to both bio and synthetic lubricants.
- Further investigation has to be done in order to understand the corrosion mechanism and different types of corrosion taking place.
- Suitable additives can be added to reduce the corrosion effect on the metals. The corrosion inhibitor, mixture of PEG 400 and Benzotriazole shows a downfall in corrosion rates for Cast iron, Mild steel, Zinc and Lead, however the corrosion rate for Tin and Copper have increased.

5. REFERENCES

[1] Singh. B, John Korstad, Y.C. Sharma, 2012 *Renewable and Sustainable Energy Reviews 16*, 3401–3408.
[2] Rajesh V. Sharma, Ajay K. Dalai, 2013,Applied *Catalysis B: Environmental*, Volumes 142–143, 604-614.
[3] I.M. Atadashi, M.K. Aroua, A. Abdul Aziz 2012, *A review, Renewable and Sustainable Energy Reviews*, Volume 14, Issue 7,1999-2008.
[4] Krzan B, Vizintin J 2003, *Tribology International*,36 (11): 827-833.
[5] Arumugam, S., and G. Sriram,2012 ,*Tribology Transactions* 55.4: 438-445.
[6] ASTM G:1.*Standard Practice for Preparing, Cleaning, and Evaluation Corrosion Test Specimens*
[7] ASTM D: 6594. *Standard Test Method for Evaluation of Corrosiveness of Diesel Engine Oil at 135°C.*
[8] Katherine M. Richard 2010, *SAE International Journal of Fuels Lubr*. 2(2):66-71.
[9] Haseeb. A.S.M.A, H.H. Masjuki, L.J. Ann, M.A. Fazal 2010, *Fuel processing Technology* 91, 329-334.
[10] Singh. B, John Korstad, Y.C. Sharma, 2012, *Renewable and Sustainable Energy Reviews* 16, 3401–3408.
[11] Fazal. M.A, A.S.M.A. Haseeb, H.H. Masjuki, 2012, *Energy* 40, 2012; 76 – 83.
[12] Haseeb. A.S.M.A, H.H. Masjuki, L.J. Ann, M.A. Fazal, 2010, *Fuel processing Technology* 91, 329-334.
[13] Krzan B, Vizintin J.2003, *Tribology International*. 36 (11): 827-833.
[14] S. Arumugam, G. Sriram, R. Ellappan, 2014, *Energy*, 72, , 618-627.
[15] Fazal, M.A.AU - Sazzad, B.S.AU - Haseeb, A.S.M.A.AU - Masjuki, H.H.Jo, 2016 *Energy Conversion and Management*, 122- 290 - 297.
[16] Matjaz Finsgar, Ingrid Milosev, 2010,*Corrosion Science,* 52, 9, 2737-2749.
[17] S. Arumugam, R. Ellappan, S. Sangavi, G. Sriram and P. Ramakrishna. 2018, *Arab J Sci Eng* 43: 1345.