Electro-chemical corrosion Behavior of Vegetable oil-Based Engine oil

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Abstract. Progressive development of bio-lubricants is the need of the day for replacing petroleum-based lubricants in terms of dependency and degradation. Though the developed lubricants meeting out the properties of petroleum-based lubricants, the hygroscopic nature of the lubricants derived from vegetable oils are suspected to deteriorate the metal surfaces by corrosion. The vegetable oil-based engine oil was formulated via chemical alteration method. The mobility of ions is the key factor for electro-chemical corrosion. In this work we executed the corrosion study of engine oils on metallic coupons through electro-chemistry technique. therefore, vegetable oil-based engine oil and synthetic engine oil were tested in conductivity test using Galvanic cell. In this Galvanic cell, Tetra butyl ammonium perchlorate is used as a catalyst to enhance the mobility of ions in engine oils (electrolyte). The test coupons of ferrous and non-ferrous metal are considered as electrodes. The Tafel plot and impedance curve showed that the corrosion rate for the given current potential is not in the measurable range. Therefore, the electro-chemical corrosion study is not a suitable method to evaluate the corrosion rate of metals on viscous fluids like vegetable oil-based engine oil.

1. Introduction

Lubricants are mainly focused in the tribological aspects of contact surfaces. Subsequently, the development of vegetable oil-based bio-lubricants is the best alternate for synthetic lubricants in the aspects of degradation and sustainability. Wagner et al.[1] identified the alternative methods to improve the biodegradability of high oleic sunflower oil by chemical modification and also suggested that vegetable oil lubricants could be produced in higher volume through this route. Erhan et al. [2] reported that the total production and consumption rate of non-renewable petroleum-based lubricants must be replaced by vegetable oil-based lubricants due to their better rheological properties and bio-degradability. Arumugam et al. [3] reported the chemical modification of vegetable oil and found that the biodegradability of base stock doesn’t affect even after the chemical modifications.

Bekal et al. [4] recorded the mixture of synthetic engine oil and vegetable oil as crankcase lubricant in diesel engine fuelled with bio-diesel. They concluded that the blended engine offers better performance as compared with synthetic engine oil. Savita kaul [5] conducted the static immersion test for different metallic coupons in biodiesel environment and showed that the biodiesel induced the traces of corrosion on the metallic surfaces. Chew et al. [6] investigated the comparative corrosion study of magnesium and aluminium metals in biodiesel environment and SEM, XRD, FTIR results showed that the considerable amount of corrosion is identified in magnesium. Singh et al. [7, 8] observed the formation of new phase in the biodiesel immersed surfaces and concluded that the presence of moisture in biodiesel promoting oxidation of metals. Sergio Luiz de Assis et al. [9] studied the electrochemical corrosion behaviour of titanium alloys in hank’s solution, and the polarization curve as well as EIS (Electro chemical Impedance Spectroscopy) test results showed the formation of passive film on the surfaces to act as barriers against corrosion. Jun Qu et al. [10] suggested that the addition of ionic liquids in vegetable oils showed no indication of corrosion on cast iron surface at room temperature.
Bommersbach et al. [11] identified that the amine group inhibitor forms thick film at the interface of steel surface and surrounding fluid. This thick film prevents the oxidation of metallic ions. Wang et al. [12] analysed biodiesel corrosion behavior in sea water environment through electrochemical studies and found that the ion concentration in biodiesel exposed area is more than sea water exposed area and hence, the biodiesel protect the metal surface against corrosion. Tian et al. [13] conducted the electrochemical corrosion study of steel in oil-water emulsion and observed that the anodic dissolution of steel is inhibited by oil, therefore the lower solubility of ionic spices found in oil. Zhang et al. [14] concluded that the presence of oil in the electrolyte solution decreases the anodic dissolution of metal due to the oil phase formation. Bommau et al. [15] used the different concentrations of natural oil as corrosion inhibitor on tin plates, observed the better inhibitor efficiency at moderate temperatures. Wang et al. [16] investigated the corrosiveness and stability of oil-brine mixed solutions through electrochemical studies and found that corrosion could be retarded by the addition of oil in brine solution.

2. Materials and Methods

2.1 Test coupon selection and preparation

To study the electrochemical corrosion behaviour of lubricants, the material selection is the important parameter to correlate with the real time component interfacing surfaces which are exposed with lubricants as electrolyte in this electrochemical corrosion study. A cast-iron test coupons of size 10x10x1 mm are polished in 500-1200 grit emery papers and polished surfaces are cleaned with distilled water and chemical reagents are separately used for the further cleaning of silicon carbide abrasive deposits over ferrous and non-ferrous coupons and were prepared as per ASTM G1 standard as shown in Figure 1(a). Teflon is surrounded over the test coupon to so as to expose minimum area of contact in the electrolyte solution, to avoid the over loading in the corrosion cell as shown in Figure 1(b).

Figure 1. Metallic coupon in electrochemical corrosion study (a) before and (b) after
2.2 Conductivity analysis of lubricants

A 50 ml aliquot of the biolubricant was taken in a neutral glass beaker for the conductivity measurement. The lubricant sample was subjected to ultrasonication for ten minutes to ensure homogeneity and conductivity was measured with a high sensitivity conductivity meter with cell constant of $1\text{cm}^{-1}$ (Make: EQUIP-TRONICS; Model: EQ-667; India) and its corresponding setup is shown in Figure 2. The specific conductance of biolubricant was compared with a standard synthetic lubricant i.e., SAE20W40. For this, also the same test was repeated for synthetic lubricant.

![Figure 2](image1.png) Conductivity test set up

2.3 Experimental set up

The electro-chemical corrosion studies were done in a three-electrode corrosion cell, with different components of IC engine material as working electrodes, Saturated calomel electrode (SCE) as reference electrode and a platinum foil as counter electrode. Tetra butyl ammonium perchlorate, a catalyst was added to test lubricant to improve the ion mobilities. In this study, biolubricant and synthetic lubricants are used as electrolyte. The potentiodynamic polarization curves were recorded between +0.1 V to -0.1 V windows. Earlier to this, vegetable oil (Rapeseed oil) based biolubricant was synthesised through epoxidation, hydroxylation and esterification reaction by adopting the detailed procedure of Arumugam et al. [3]. The Figures 3(a) and 3(b) show the three-electrode galvanic cell and electro-chemical corrosion test setup.

![Figure 3](image2.png) (a) Three-electrode galvanic cell and (b) Electro-chemical corrosion test setup

3. Results and Discussion

3.1 Conductivity of lubricants

Table 1 shows the specific conductance of synthetic and biolubricant. The conductivity study shows that the biolubricant is having higher specific conductance than synthetic lubricant-SAE20W40. The specific conductance of lubricants is played a major role to accelerate corrosion in the electrochemical corrosion.
Table 1. Conductivity of lubricants

| Parameter                  | Synthetic Lubricant | Biolubricant |
|----------------------------|---------------------|--------------|
| Specific conductance (mS cm\(^{-1}\)) | 1.204              | 1.232        |

3.2 Electro-chemical corrosion analysis

A cast iron in synthetic lubricant and as well as biolubricant samples was studied via the polarization curves as depicted in Figure 4. As seen from Figure 4, there was a slight improvement in the anodic current density, and a synchronised negative shift of the corrosion potential of the cast iron material against biolubricant was detected. The ester molecules correspond to vegetable oil-based lubricant led to the establishment of a defensive corrosion scale, which resulted in diminished cast iron dissolution. The noticeable anodic dissolution increases and a negative shift in corrosion potential recommended a higher activity of the cast iron material under biolubricant atmosphere as compared with SAE20W40. The slight shift in the anodic current density of the cast iron sample, signifying a lesser formation of iron oxides over the electrode surface.

![Figure 4. Potentio dynamic polarization curve](image)

4. Conclusions

The corrosion behaviour of various engine components in presence of newly synthesized biolubricant was investigated electrochemically.

- The higher specific conductance value for biolubricant confirmed the presence of more ionic species when compared to synthetic counter-part.
- The potentio dynamic polarization studies were done to investigate the nature of corrosion.
- The results of these studies revealed that the corrosion of cast iron material vegetable oil-based biolubricant behaves almost an identical behavior with synthetic lubricant in terms of electro-chemical corrosion.
- This study further opens up an idea to execute tribo-corrosion analysis of vegetable oil-based lubricant in addition to electro-chemical corrosion analysis.

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