Experimental Investigation on Tribological Characteristics of Biodegradable Refrigeration Oil using Pin on Disc Tribometer

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Abstract. The present study addresses the issue of the tribological behaviour of cylinder liner and piston ring material of a hermetically sealed reciprocating compressor of Vapour Compression Refrigeration system under the influence of pentaerythritol ester based biodegradable refrigeration oil and compare with synthetic refrigeration oil (Polyol ester - ISO 68 grade) using the pin on disc tribometer. Synthesis of pentaerythritol ester based biodegradable refrigeration oil for household domestic refrigeration compressors was carried out via successive transesterification of rapeseed oil. The biodegradable refrigeration oil was blended equally with synthetic refrigeration oil to formulate the best biolubricant. Further Energy Dispersive X-ray (EDX) technique was adopted for the chemical characterisation of the pin material surfaces. The wear behaviour of the tested pin materials were evaluated using scanning electron microscope. The results show that under same investigational conditions 50% blend of pentaerythritol ester biodegradable refrigeration oil (PBRO 50) with synthetic refrigeration oil demonstrated superior friction reduction performance and inferior wear reduction performance as compared to synthetic refrigeration oil.

1. Introduction

The compressors are considered to be an influential component of vapour compression refrigeration system. The major cause of loss of energy in a hermetically sealed reciprocating refrigeration compressor is due to friction and wear, which should be minimised by lubrication. A secured and sustainable operation of the vapour compression refrigeration system has accomplished by the lubrication system. The compressors consume approximately 80% of the whole power consumption of the vapour compression refrigeration system. The energy conservation is becoming an indispensable factor in the aspect of environmental and global issue. Thus the coefficient of performance escalation of the vapour compression refrigeration system can be enacted by the reduction in the compression work, which in turn reduces the energy consumption. The environmental concerns give great significance of using bio-based lubricants for the commercial purpose which leads to the major transformational growth in the lubrication market [1]. The main limitations of vegetable oil are its poor low temperature behaviour, oxidation and thermal stability and gumming effect [2,3]. Menkiti et al [4] prepared the polyl ester from sesame seed oil as biodegradable base stock through chemical transesterification of sesame methyl ester with trimethylolpropane (TMP) using calcium hydroxide catalyst. They found that temperature and mole ratio have the major effects on the synthesis of transesterification process. Journal bearing tribological
behaviour specifically for automobile utilization under the impact of a synthetic lubricant such as SAE20W40 and biolubricant from rapeseed oil (CMRO) dispersed with TiO$_2$, WS$_2$ and CuO nano particles utilized concerning illustration anti-wear additives analysed by Baskar et al [5]. They concluded that maximal friction coefficient and wear was settling up in concern with biolubricant (CMRO) than the synthetic lubricant, while the addition of nano CuO to biolubricant (CMRO) reduce the friction coefficient by 27 % and wear by about 47 % as compared with a synthetic lubricant. Habibullah et al [6] evaluated tribological characteristics of Calophyllum inophyllum (CI) based trimethylolpropane (TMP) ester as biodegradable lubricant using four ball tribometer and describe the resemblances with commercial lubricant and paraffin mineral oil on energy saving aspects. The outcomes illustrate that biodegradable lubricant had the improved friction behaviour with lower energy consumption. However, surface morphology analysis shows that CI TMP ester comprise higher wear match up to paraffin mineral oil and lower wear to commercial lubricant.

Zulkifli et al [7] conducted a detailed investigation to access the wear prevention characteristics of palm oil based TMP ester as engine lubricant through a four-ball tribo tester for various lubrication regimes. They observed that 30% reduction of friction coefficient and higher amount of load (220 kg) carrying capacity in inclusion of 3% of palm oil based TMP ester with commercial lubricant for boundary lubrications, 50% reduction of friction coefficient in inclusion of 7% of palm oil based TMP ester with conventional commercial lubricant for hydrodynamic lubrication, thus suggested that can be a surrogate as automotive engine lubricant. Nuraliza and Syahrullai [8] examined the friction and wear aspects of double fractionated palm oil (DFPO) as biolubricant using pin-on-disk tribo-tester under loads of 50N and 100N, with rotating speeds of 1-5m/s for testing time of 3600 sec and referred with hydraulic oil and SAE 40 engine oil. On the view of coefficient of friction, wear and rise in sliding speed on whole process time, the DFPO lubricant demonstrated most excellent performance, can be suggested as a base lubricant for mechanical applications.

A lot of research works are conceded using bio lubricant as replacement to synthetic lubricant for engine oil application. Likewise, plenty of investigation work is focused on the performance enhancement of vapour compression refrigeration system by using synthetic lubricant with nano particle additive. Conversely, lesser studies have been carried out with bio lubricant as refrigeration oil. From the literature, it is identified that currently no refrigeration oil is available in the market with vegetable oil as base oil for the formulation of refrigeration oil. The present study formulated the bio degradable refrigeration oil from rapeseed oil using successive transesterification with pentaerythritol through chemical modification to perceive the lubrication characteristics appropriateness as refrigeration oil for domestic compressors. Moreover, tribological behaviour of the bio degradable refrigeration oil has been accessed using pin-on-disc tribometer for examining the compatibility for using as refrigeration oil.

2. Experimental

2.1 Materials
The raw rapeseed oils were collected from the local vendor. Methanol%, NaOH, Pentaerythritol, Paratoluene sulphonic acid and xylene were purchased from Ganesh Enterprises, Kanchipuram.

2.2. Synthesis of pentaerythritol ester based Biodegradable Refrigeration oil
Rapeseed oil of 1 litre was placed in the 5 litre double necked round bottom flask. Potassium Hydroxide of 16g and methanol of 200 ml was added to the contents and were mixed by means of a stirrer and it was maintained at atmospheric temperature. The stirrer was kept at a stirring speed of 300 rpm and temperature is then raised slowly to 80- 85°C by keeping the setup as shown in Fig. 1 and maintained at same temperature. The raw rapeseed oil and mixture of methanol and potassium hydroxide are mixed, heated and stirred for 2 hours. The product of the reaction was cooled and decanted to effect a separation of the methyl ester from water phase. The obtained methyl ester is
mixed with three times of water and then heated up to 100°C to remove the presence of methanol. The blend preparation of pentaerythritol ester and ISO 68 was carried out in batch type glass reactor consisting of a three necked round bottom flask of 2 litre capacity. A motor driven speed regulator stirrer inserted in the reactor through the central neck while the other neck was used for inserting thermometer. The third neck is used for dropping the raw materials into the reactor via dropping funnel. The reactor was heated by an electric heating mantle having an arrangement for accurate control of the temperature within ±1°C of the desired temperature.

2.3. Lubricant blend sample preparation
The blend preparation of biodegradable refrigeration oil of 500 ml and synthetic refrigeration oil of 500 ml was carried out in batch type glass reactor consisting of a three necked round bottom flask of 2 liters capacity. A motor driven speed regulator stirrer inserted in the reactor through the central neck while the other neck was used for inserting thermometer. The third neck is used for dropping the raw materials into the reactor via dropping funnel. The reactor was heated by an electric heating mantle having an arrangement for accurate control of the temperature within ±1°C of the desired temperature. Further the contents were well mixed and were performed at a stirring speed of 300 rpm. The temperature is then raised slowly to 55-60°C and finally blend was obtained after the completion of 60 minutes. Table.1 shows the percentages of lubricant blend in each sample.

| Lubricant | Biodegradable Refrigeration Oil | Synthetic Refrigeration Oil |
|-----------|--------------------------------|-----------------------------|
| POE 68    | 0                              | 100                         |
| PBRO100   | 100                            | 0                           |
| PBRO50    | 50                             | 50                          |

2.4. Tribological investigation
The pin on disc tribometer [supplied by DUCOM Instruments, TR-20LE-PHM400] was used to confirm the compatibility between the formulated biodegradable refrigeration oil and synthetic refrigeration oil and cylinder liner-piston ring tribo pair materials. The tribological tests were conducted as per ASTM G99 standards. A photographic view of the pin on disc tribometer is illustrated in Fig1. The compressor cylinder liner was taken as the disc material SAE J431 grade grey cast iron heat treated hardened up to 60HRC and piston ring material of the compressor as FG 150 grey cast iron of hardness 210 BHN.

Fig.1 Pin on disc tribometer
Based on the load applied the pin is pressed against the disc. All the test section components collet, pin, disc, tube, oil tub were cleaned thoroughly using acetone. The pin will be stationary, whereas the disc will be rotating in the bottom. The sliding distance and rotational speed of the disc can be set according to the requirement as 1000m and 1200 rpm. The load of 10 kg that is to be applied is done using the lever mechanism on the pin. The combination of the rotating motion and the normal load produces frictional force indicated by a digital meter connected to the tribometer. Scanning Electron Microscope (SEM) was used to evaluate the wear characteristics of the pin surfaces under high magnification (500X).

The specific wear rate was calculated by using the following equation:

\[
\text{specific wear rate} = \frac{\text{volume loss}}{\text{applied load} \times \text{sliding distance}}
\]

\[
\text{volume loss} = \frac{\text{weight loss} \times 1000}{7.2}
\]

\[
\text{sliding distance} = \frac{\pi \times D \times N}{60000}
\]

Where,

D=track diameter
N=speed of disc in rpm
Density of the material= 7.2 kg/m³

3. Results and Discussion
3.1 Thermo-physical properties of Biodegradable Refrigeration oil

The viscosity of the bio degradable refrigeration oil and blend PBRO50 at 100º C was 11cSt and 9.16cSt. The higher viscosity index (VI) tends to the lesser change in lubricant viscosity with respect to change in temperature. Table 2 shows the thermo physical properties of synthetic refrigeration oil, bio degradable refrigeration oil and blends. The viscosity index of the bio degradable refrigeration oil is superior to the synthetic refrigeration oil for the reason due to chemical nature and higher molecular weight. The pour point is the lowest temperature of the lubricant that remains in a fluid state. The lower pour point is the critical feature of the lubricant under cold working conditions. The pour point of bio degradable refrigeration oil and blend PBRO50 were -15ºC and -7ºC. The lower pour point of the bio degradable refrigeration oil is because of complex chain formation and branched oils [9]. The total acid number (TAN) is to determine the quantity of degradation of the lubrication oil. The TAN value of bio degradable refrigeration oil and PBRO50 were 1.2 mg KOH/g and 0.79 mg KOH/g respectively. The higher TAN value for bio degradable refrigeration oil indicates the moisture contamination of the vegetable oil.

| Test parameters | Test method | Units | POE 68 | PBRO100 | PBRO50 |
|-----------------|-------------|-------|--------|---------|--------|
| Viscosity at 40ºC | ASTM D445   | cSt   | 68     | 67      | 55.3   |
| Viscosity at 100ºC | ASTM D445   | cSt   | 9.3    | 11      | 9.16   |
| Viscosity index | ASTM D445   |       | 114    | 156     | 147    |
| Flash point     | ASTM D92    | ºC    | 220    | 242     | 220    |
| Pour point      | ASTM D97    | ºC    | -39    | -5      | -7     |
| Total Acid Number | ASTM D974  | mgkoh/g | 0.30  | 1.2     | 0.79   |
3.2. Tribological investigation of biodegradable refrigeration oil

3.2.1 Friction Behaviour

The tribological studies clearly show the assessment of the lubrication characteristics of the biodegradable refrigeration oil from the base stocks of rapeseed oil.

![Graphs of Coefficient of Friction, Friction Force, and Wear](image)

Fig.2 (a) (b) (c) Variation in the Coefficient of Friction, Friction Force and Wear with respect to sliding distance
Fig. 2 (a) (b) and (c) show the variation in the coefficient of friction, friction forces and wear with respect to sliding distance for different percentages of biodegradable refrigeration oil at constant load of 10 kg. The magnitude level (µ value lies between 0.001 and 0.2) of the COF demonstrates that boundary lubrication abrasion take place in the abrasion zone. The biodegradable refrigeration oil has a lower coefficient of friction when correlated with synthetic refrigeration oil. The results reveal that the coefficient of friction of bio degradable refrigeration oil (PBRO100) was noticeably 23% and PBRO50 was 10% lower than that of synthetic lubricant. The pointed out reduced friction coefficient is owing to the presence of higher polar functional groups of carboxylic acids and ester and functions as a protective agent on pin/disc that decreases the direct contact of rubbing surface[10].Free fatty acids in vegetable oils permit monolayer film formation on the surface that offers sliding surfaces prevention of direct metal to metal contact and preservation the surface from damage. In the examination of frictional force, the mean value for bio degradable refrigeration oil was 4.8 N was smaller than the average frictional force of the synthetic lubricant. The results depicts that the friction force of bio degradable refrigeration oil (PBRO100) was noticeably 22% and PBRO50 was 9% lower than that of synthetic lubricant shown in Fig.2(b).

3.2.2 Effect of biodegradable refrigeration oil on surface roughness

Surface roughness is a term relates to wear resistance and coefficient of friction of mating surfaces. The lower surface roughness value indicates that the surface is smoother, easier for the materials slide together and the material loss is at the lowest. The value of surface roughness of the pin and disk lubricated with PBRO50 was lowest. However, the value of surface roughness for PBRO100 was higher when compared to the synthetic refrigeration oil (POE 68). According to the concept of adhesive theory, at first the tougher asperities adhere mutually and the plastic shearing of the junction produced will remove the softer asperities leaving them sticking to the hard surface. Therefore, the wear will be augmented as long as rubbing action between the disc and the pin [8].

Table 3. Surface Roughness of POE 68, PBRO100 and PBRO50

| Lubricant | Load (kg) | Duration (min) | Initial Weight of pin (gm) | Final Weight of pin (gm) | Roughness on raw material Surface (μm) | Roughness on tested Surface (μm) | Specific Wear Rate (mm³/N-m) |
|-----------|-----------|----------------|-----------------------------|--------------------------|----------------------------------------|-------------------------------|-----------------------------|
| POE 68    | 10        | 60             | 16.7738                     | 16.7100                  | 0.27                                   | 0.45                          | 7.990×10⁻⁶                 |
| PBRO100   | 10        | 60             | 17.0676                     | 16.9990                  | 0.39                                   | 0.75                          | 8.591×10⁻⁶                 |
| PBRO50    | 10        | 60             | 16.8785                     | 16.8140                  | 0.37                                   | 0.54                          | 8.078×10⁻⁶                 |

3.3 Wear Behaviour

Fig.3 shows the surface morphology of the pin surface under the influence of the synthetic refrigeration oil, biodegradable refrigeration oil and PBRO50 blend. Scanning Electron Microscope (SEM) was used to evaluate the wear characteristics of the pin surfaces under high magnification (500X). The abrasive and adhesive type of wear mechanism was observed on the boundary lubrication regime. From the Fig. 3 (a), it is clear that the synthetic refrigeration acquire smooth surface with superior wear behaviour because of improved surface adsorption rate on metal surface. The abrasive lines on the wear surface on the pin lubricated with biodegradable refrigeration oil are confirmation of abrasive wear action as shown in Fig.3 (b). This will originate the shearing of physical bonding and chemical bonding due to aggressive mechanical shearing and straight metal-to-metal [11, 12]. The higher surface fatigue, deep furrows and wear delamination found in the case of bio degradable refrigeration oil.
The PBRO50 exhibit the superior tribological properties in terms of wear when evaluate the biodegradable refrigeration oil shown in Fig. 3 (c). This owes to that the fact; synthetic refrigeration oil was prepared with anti wear, anti-detergent and anti-foam agents. Further, the addition of anti-wear additives like Zinc dialkyl-dithiophosphate will increase the characteristics related to the wear behaviour.

3.4 Elemental Analysis

The intend of the elemental investigation by using a Energy Dispersive X-Ray Spectroscopy is to observe the amount of metals containing in the surfaces of the pin material lubricated with the synthetic refrigeration oil, biodegradable refrigeration oil and their blends. Fig. 4(a-c) depicts the SEM images of the abrasion surfaces lubricated by synthetic refrigeration oil, biodegradable refrigeration oil and their blends with the consequent EDS analysis. From Fig. 4(a, b), it can be found the worn surface lubricated by synthetic refrigeration oil have micro voids and pits, meanwhile the surface lubricated by biodegradable refrigeration oil was smoothest and no sharp furrows were present on the wear surfaces. The elevated abrasive wear and intensive scratches have found in synthetic refrigeration oil. The acids and oxides developed during oxidation reduces and produce the negative effect in lubricity [13]. The C element content on the metal surface for biodegradable refrigeration oil is 19.74wt% on the EDX examination was due to the reason of main component present in the steel ball material undergoes carbonizations on lubrication and the ferrous content were increased to 63.54% because of material loss in the ball surface as shown in the Fig 4(b). The result from the PBRO50 indicates that the superior anti-wear and friction reduction properties which were confirmed by the SEM and EDS investigation.
Fig. 4 Scanning Electron Microscopy (SEM) images and corresponding (EDX) spectra of the pin worn surface
(a) POE 68  (b) PBRO100 (c) PBRO50
The rubbing exterior of PBRO50 enclose even surfaces and the content of C element was 25.16 wt%, which was 33% higher than biodegradable refrigeration oil shown in Fig 5 (c). The higher percentage of oxygen in the PBRO50 suggests that more oxide layer is retained on the surface in reducing the metal to metal contact. The higher percentage of oxygen in the SBO specimen than the PO counterpart suggests that more oxide layer is retained on the surface in reducing the metal to metal contact thus lower mass loss is produced in the SBO specimen. A similar reason could be applied to the specimen lubricated with MO in which a higher oxygen element is detected, suggesting that more oxide layer exists in preventing the metal to metal contact found by Mayank Anand et al [14]. Table 4 illustrates the summary of SEM/EDX analysis results of the elements present in the pin material surface. These results demonstrate that PBRO50 blend forming a greater continuous protective film layer and to prevent the abrasion surfaces from direct contact and improve the tribological performance of the lubricant.

| Lubricant | Weight percentages (%) |
|-----------|------------------------|
|           | C   | O    | Na | Al | Si | Ca | Fe |
| POE 68    | 18.55 | 8.20 | 0.48 | 0.78 | 0.76 | 1.11 | 70.12 |
| PBRO100   | 28.00 | 9.22 | 0.43 | 0.30 | 0.48 | 0.64 | 60.93 |
| PBRO50    | 25.75 | 13.53 | 0.37 | 0.50 | 0.69 | 1.27 | 57.89 |

4. Conclusions

In this study the tribological performance of biodegradable refrigeration oil in the lubricating contact pair FG 150 grey cast iron sliding against SAE J431 grade grey cast iron was investigated and following conclusions can be deduced from the experiment results.

- The biodegradable refrigeration oil (PBRO100) and blend PBRO50 exhibited good physicochemical properties and could be favorably used as lubricant feedstock in refrigeration applications.
- The results from the tribological study reveal that the coefficient of friction of bio degradable refrigeration oil (PBRO100) was noticeably 23% and PBRO50 was 10% lower than that of synthetic lubricant.
- The surface roughness of the pin and disk lubricated with PBRO50 was lowest and found to be 0.54.
- The higher surface fatigue, deep furrows and wear delamination found in the case of bio degradable refrigeration oil. The PBRO50 exhibit the superior tribological properties in terms of wear when evaluate the biodegradable refrigeration oil.
- From the elemental analysis, Fe and Al were increased due to the loss of material from the pin and the disc, other element like Si, Ca and Na were decreased by oxidizing and other chemical interaction. The higher percentage of oxygen in the PBRO suggests that more oxide layer is retained on the surface in reducing the metal to metal contact.

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