The effect of free fatty acids on the tribological properties of karanja oil

J Joshy¹, Naveen and D Mahipal
Department of Mechanical Engineering, Government Engineering College Thrissur, Kerala, India
¹Email: mahipalrit@gmail.com

Abstract. Research is being carried extensively on vegetable-based lubricants to provide a suitable replacement against toxic and non-biodegradable petroleum-based lubricants. In this work, tribological properties of free fatty acids in non-edible karanja seed oil are evaluated. Free fatty acids namely palmitic acid, stearic acid, and oleic acid were added at 1%, 2%, 3%, and 5% by weight of the base oil. A four ball tribotester was utilized to study the friction and wear properties of different samples. These additives provided both anti-wear and anti-friction properties. Palmitic acid, stearic acid, and oleic acid reduced wear by 34.39%, 28.82%, and 13.12% respectively. Further, the coefficient of friction was reduced by 27.51%, 30.15%, and 44.97% respectively. The wear scar region was analyzed using optical microscopy. Flash temperature parameter (FTP) for different additives was calculated and found that at lower additive concentrations, stearic acid had a better FTP but at 5%wt., palmitic acid had the best FTP. Energy consumed during the test was calculated for different additive concentrations and oleic acid additive had the lowest energy consumption.

1. Introduction
Lubricants are those materials which are used to reduce friction [1, 2]. Majority of the lubricants being used fall into the category of petroleum-based lubricants but are non-renewable and unsafe to nature [3]. Due to the rising concern against environmental pollution and depleting petroleum sources, the need to introduce bio-lubricants is very crucial. Vegetable oils, on the other hand, possess high viscosity index, high flash point, good metal adherence, high lubricity, lower volatility, and higher biodegradability. The long hydrocarbon chains of fatty acid in vegetable oils makes them polar in nature and also enables strong interaction with the metal surfaces during boundary lubrication applications [4-7]. The effectiveness of lubricating oils highly depends upon the chemical composition as well as the presence of additives present in the oil. Vegetable oil consists of triglycerides to which long fatty acid chains are connected. The presence of unsaturation and the type of fatty acid chains determines the properties of vegetable oils [8]. Apart from the fatty acid chains that are bounded by a glycerol molecule, free fatty acids that are not part of the triglyceride structure are also present in vegetable oils [9]. Attempts have been made to obtain the relationship between the fatty acid composition of vegetable oils and their lubrication properties [5, 10]. It is reported that vegetable oils that contain a lower degree of unsaturation show better frictional properties when compared with that having high unsaturation levels [15]. Vegetable oils have been modified chemically and studied to improve properties such as oxidation stability, low-temperature properties, extreme pressure properties, etc. [12-14].
Karanja (pongamia pinnata) oil (KO) which is largely available in southern Asia is extracted from non-edible pongamia seeds and provides a viable option as a lubricant [16, 17, 18]. Karanja oil along with its chemically modified forms is used as a lubricant and biofuel [19-21]. In this work, karanja oil is studied for its tribological properties with and without the use of fatty acid additives namely palmitic acid (C16:0), stearic acid (C18:0), and oleic acid (C18:1).

2. Methodology

2.1. Materials

KO was procured from the local market and the fatty acid composition obtained using gas chromatography-mass spectrometry is shown in Table 1. Some of the physical properties of the additives used are listed in Table 2. 1%, 2%, 3%, and 5% by weight of base oil are selected on an empirical basis. Before adding the additives free fatty acid contents in the oil were removed by treating with methanol under an acid catalyst [23].

Table 1. Fatty acid composition of KO

| Sl. No. | Fatty acid        | Composition % |
|---------|-------------------|---------------|
| 1       | Oleic acid        | 47.97         |
| 2       | Linoleic acid     | 21.64         |
| 3       | Palmitic acid     | 10.75         |
| 4       | Stearic acid      | 7.29          |
| 5       | Docosenoic acid   | 3.75          |
| 6       | Eicosenoic acid   | 1.60          |
| 7       | Tetrasenoic acid  | 1.34          |
| 8       | Others            | 5.6           |

Table 2. Physical properties of additives [22]

| Sl. No. | Property                        | Palmitic acid (C16:0) | Stearic acid (C18:0) | Oleic acid (C18:1) |
|---------|---------------------------------|-----------------------|----------------------|-------------------|
| 1       | Dynamic viscosity at 100 °C (cP) | 4.13                  | 5.08                 | 4.03              |
| 2       | Melting point (°C)              | 64                    | 70                   | 14                |
| 3       | Density (kg/m³)                 | 853                   | 941                  | 895               |
| 4       | Molecular weight (g/mol)        | 256.42                | 284.48               | 382.47            |
| 5       | Molecular formula               | C_{16}H_{32}O_{2}     | C_{18}H_{36}O_{2}    | C_{18}H_{34}O_{2} |

2.2. Measurement of wear scar diameter and coefficient of friction

Wear scar diameter (WSD) and the coefficient of friction of lubricating oils is analyzed using a four-ball tribotester. Ducom four ball tester with WINDUCOM software was used to obtain the average CoF values. Chromium steel EN-31 grade balls were used for the tests. ASTM D4172 B is used as the standard for the test. Ducom image acquisition system is used to analyze the scar area and measure the wear scar diameter (WSD). Frictional torque measured using a transducer in the tribo tester is used to find the coefficient of friction ($\mu$) and is calculated using the equation,

$$\mu = \frac{T\sqrt{6}}{3Wr}$$ (1)
Where μ- CoF; W- applied load in kg; T- frictional torque in kg-mm; r- horizontal distance from the centre of the contact surface of the lower balls to the axis of rotation, which is 3.67 mm. [25].

2.3. Flash temperature parameter (FTP)
FTP was introduced in 1957 by T.B Lane to evaluate the possibility of lubricant breakdown during operation [24]. FTP is a mathematical number that indicates the minimum temperature at which a lubricant can vaporize and lead to asperity contact. Frictional heat generated at the contact area causes localized heat zones which raise the temperature of the surrounding lubricant. It is given by,

\[
FTP = \frac{W}{d^{1.4}}
\]

(2)

Where W is load in kg and d is WSD in mm.

2.4. Energy consumption in four ball testing
Energy consumed during the four-ball test is given by,

\[
\text{Thermal energy (TE)} = \frac{\mu Wg r}{1000}
\]

(3)

Where, \(\mu\)-Coefficient of friction, W-applied load (kg), g-gravitational acceleration (m/s\(^2\)), and r-horizontal distance from the centre of the contact surface on the lower balls to the axis of rotation (mm) and is found to be 3.67 mm. eq. 3 is derived by Habibullah et al. using the conservation of energy equation to analyze the energy consumption in a four ball-tester [26].

3. Results and discussion

3.1. Wear
In a four ball tribotester the rotating upper ball is supported by three stationary balls in the ball pot and a load of 40 kgf is applied as per ASTM D4172 B standard. After rotating the ball for a period of 3600 seconds, the balls are removed and the wear scar induced on the bottom balls is analyzed using Ducom optical stereo microscope (along with ‘Ducom scar view’ software). The WSD induced on the three balls are averaged and are represented in Table 3.

| Weight percentage % | Palmitic acid | Stearic acid | Oleic acid |
|---------------------|--------------|--------------|------------|
| 0                   | 760.75       | 760.75       | 760.75     |
| 1                   | 610.02       | 559.86       | 752.83     |
| 2                   | 610.7        | 542.5        | 757.65     |
| 3                   | 589.62       | 542          | 750.42     |
| 5                   | 499.1        | 541.5        | 660.92     |

It can be seen from Figure 1 that the oleic acid additive showed the least reduction in WSD and stearic acid was the most effective. The addition of saturated fatty acids improves boundary lubrication. This is attributed to two main reasons a) absence of unsaturation which provides instability and site for chemical reactions and b) the presence of double bond can weaken the intermolecular forces and also create a steric hindrance which prevents the close packing of molecules.
This is why oleic acid showed the least reduction in WSD when compared to other samples. With the increase in chain length the intermolecular forces of attraction increase and aids stronger tribo-film formation. This may be the reason why stearic acid (C18:0) showed better anti-wear properties than palmitic acid (C16:0), however, this is still debated among researchers [9].

![Figure 1. Variation of WSD for different oil samples](image)

**3.2. Friction**

The values of CoF obtained for different lubricants in four ball test are displayed in Table 3. From Figure 1 it can be seen that all combinations of additives gave lower CoF values when compared to the base KO. The highest reduction in CoF value is obtained for KO + 3% oleic acid. During boundary lubrication conditions the fatty acids are proposed to act as boundary additives forming a protective film of acid with the metal surfaces. This is why all additive combinations showed a positive effect of reducing the CoF [27, 28]. The addition of free fatty acid which is already present has little effect as the only improvement is to eliminate the need to remove the fatty acid from the triglyceride backbone.

**Table 4. CoF values for various fatty acid additive combinations**

| Weight percentage % | Palmitic acid | Stearic acid | Oleic acid |
|---------------------|--------------|--------------|------------|
| 0                   | 0.0796       | 0.0796       | 0.0796     |
| 1                   | 0.0681       | 0.0665       | 0.0689     |
| 2                   | 0.0599       | 0.0556       | 0.0499     |
| 3                   | 0.0577       | 0.0618       | 0.0438     |
| 5                   | 0.0644       | 0.062        | 0.0573     |
The physisorbed layer formed due to oleic acid produced the lowest CoF, however, it is reported that at higher loads due to the presence of unsaturation i.e. double bonds produced higher CoF values [29].

From Figure 2 it can also be noted that with the increase in additive content beyond 3%, 2%, and 3% for palmitic acid, stearic acid, and oleic acid respectively, the values of CoF increases.

### 3.3. Flash temperature parameter (FTP) and Energy consumption

FTP should have a higher value for better performance. Higher FTP also means stable film formation to prevent friction and wear. It also represents the temperature below which a lubricant film functions without breakdown. From eq. 2, it can be seen that FTP is directly proportional to the load applied. For constant load conditions, it is inversely proportional to the WSD. The graph showing the variation of FTP is shown in Figure 3. Lower energy consumption means lower CoF (eq. 3). KO+3% oleic acid affords the lowest energy curve compared to others tested under a similar procedure. This is depicted in Figure 4.
3.4 Wear scar morphology

All the wear scar images consist of shallow grooves which indicate mild abrasive wear. This is because the physisorbed layer gets desorbed due to higher shear forces and surface temperatures at the contact and this leads to asperity contacts [1]. It can also be seen that saturated fatty acid additives like palmitic acid and stearic acid reduced wear significantly compared to unsaturated oleic acid.
4. Conclusion

Karanja oil, being a vegetable oil is an environmentally friendly replacement option against commercial mineral oils. The fatty acid additives were tested for their wear and friction characteristics in this study. Even though the biodegradability of vegetable oils necessitates frequent oil changes during operation it can be compensated by protecting the ecosystem. In this study:

- The wear and friction of karanja oil are analyzed using a four-ball tester and fatty acid additives were used to reduce WSD and CoF.
- Compared to base oil, oleic acid additive gave the lowest CoF of 0.0499 with a reduction of 37.31%, followed by stearic acid and the least reduction by palmitic acid.
- At lower additive concentrations stearic acid gave the best anti-wear results, followed by palmitic acid. When unsaturated oleic acid was used as an additive, the reduction in WSD was the lowest.
- At lower additive concentrations, KO additivated with stearic acid showed a high FTP, but at 5% wt. of palmitic acid in KO, showed the highest FTP value.
- In terms of energy consumption, KO additivated with oleic acid showed the best performance compared to other additives.

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