Evaluation of lubricant properties of vegetable oils as base oil for industrial lubricant

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Abstract. The possible insufficiency of oil resources in the future and the poor bio-degradability of mineral oil based lubricant resulted in the need of bio lubricant. Bio-based products are typically produced from vegetable oils. For the present study rice bran oil [RBO], jatropha oil [JO] and karanja oil [KO] are selected as the base oils for the industrial lubricant. Friction and wear characteristics are evaluated on four ball tester and the initial findings show that wear scar of RBO is lowest, this is because of the presence of natural anti-oxidants like gamma oryzanol. The coefficient of friction and wear of all the oils were evaluated as per ASTM D5183 and ASTM D 4172 respectively. Viscosity of the oils are tested on Brookfield rheometer and KO is having high viscosity when compared to other two oils but the change in viscosity with temperature is low for both RBO and JO. Chemical properties of the oils are conducted as per IS: 548 (Part 1) –1964. The iodine value for KO is less when compared to RBO and JO. Less iodine value is required to impart better oxidation stability. Thermogravimetric analysis showed that RBO is stable till 320 °C and KO, JO started degrading at 200 °C. The thermal properties of all the oils are measured and RBO has shown better properties at wide range of temperatures. The disadvantages of vegetable oils like oxidative stability need to be improved by adding additives and by chemical modifications.

1. Introduction
Growing environmental considerations and the regulations to reduce contamination and pollution will further propel the need for renewable and biodegradable lubricants. Most of the lubricants in the market are petroleum based, they became prominent because of their superior quality at low price [1]. The major concern by using mineral oil based lubricants is they are non-renewable and non-biodegradable. Because of these reasons an alternate environmentally friendly lubricants gained prominence. Most of the advantages and properties possessed by vegetable oils like biodegradability [2], good lubricating properties, high thermal stability [3], less toxicity, high viscosity and high flash point [4] are making them a potential alternate to be a good lubricant. The major disadvantages with the vegetable oils are poor low temperature behaviour and low oxidative stability which can be improved by modifying the oils chemically and mix with additives [5]. Oxidative stability of vegetable oils can be improved by chemically modifying the vegetable oils by transesterification or epoxidation [6].

Molecules of vegetable oils consists of glycerol part and fatty acid part. The structure of vegetable oils determines several properties to be a good lubricant. Stearic acid as additive in sunflower oil is useful in reducing the wear and coefficient of friction [7]. Coconut oil under oxidative environment has shown better oxidative stability and high pour point when compared to the other vegetable oils considered in the study [8]. Smaller percentages of linoleic acid in soybean oil resulted in having low abrasion rate and coefficient of friction [9]. The natural anti-oxidant resulted in the low wear scar of rice
bran oil compared with other vegetable oils [10]. Jatropha curcas L. oil (JCL) has the lowest followed by raw rapeseed oil (RME), Hydro treated Vegetable oil (HVO). JCL has shown low COF which is attributed to high amount of stearic acid [11]. Cutting fluids based on Palm Kernal Oil and Cotton Seed Oil showed better results when compared with commercial cutting fluids [12]. Avocado oil was shown low friction and wear when compared with other selected oils under research like canola (rapeseed), peanut, safflower, corn, olive, sesame, and soybean oils [13].

The monounsaturated acid that is found in the vegetable Oils called oleic acid is thermally stable than polyunsaturated fatty acids and shows good lubricating properties therefore it is highly desirable. Rice bran oil [RBO], karanja oil [KO] and Jatropha oils [JO] are having high percentages of oleic acid which is the major property to be a good lubricant. Karanja and Jatropha trees are grown in India, they are non-edible and drought-resistant plants with faster growth rate. Rice bran oil, which is grown much in countries like India, Korea, China, Japan, and Indonesia is used as edible oil. India is the second largest country producing rice in the world which helps in the growth of Indian economy if used for industrial purpose. There is not much research done on this oils yet hence for the present work this oils are considered.

The aim of the current study is to evaluate the physico-chemical, thermal, oxidative and tribological properties of RBO, KO and JO and study the feasibility of using them as base oil for industrial lubricant.

2. Materials and methods

The RBO, KO and JO are purchased from the market and preliminary tests like fatty acid composition, tribological, physico-chemical, thermal and oxidative properties were evaluated

2.1. Materials

The bran of the rice is squeezed and rice bran oil is extracted. The refined RBO was purchased from Kalady Rice Mill Consortium Pvt.Ltd, Kerala. Both KO and JO are extracted from the seeds.

2.2. Fatty acid composition

The fatty acid composition is very important in deciding the lubricating properties, oxidative stability and several other properties of oils. The fatty acid composition of the selected three vegetable oils was evaluated as per IS548 by Gas chromatography (GC).

2.3. Tribological properties

As per ASTMD 5183 standard the coefficient of friction for RBO, KO and JO was evaluated by using Four Ball Tester as shown in figure 1. The tests were carried out for 60 min at 75°C with 600 rpm. Chrome alloy steel balls with 12.7 mm diameter were used for the experiments. A rotating steel ball is pressed against three steel balls which are firmly held together and immersed in lubricant under test. All the parameters such as test load, duration, temperature and rotational speed will be set before starting the test. The wear scar diameter on the bottom three balls is evaluated by using optical microscope as shown in figure 2.
2.4. Physico-chemical properties

The viscosity of RBO, KO and JO are evaluated by using Brookfield Rheometer as per standards and the equipment is shown in figure 3.

The chemical properties which indirectly explains the lubricating properties like acid number and iodine number were evaluated based on IS: 548 (Part 1) –1964. Acid number is defined as the measure of free fatty acids present in the oil. The amount of unsaturated bonds present in the oil is called as iodine number. The acid value is determined by chemical methods. Firstly, weigh 20 ± 0.1 grams of oil sample in a conical flask. Add 50 ml of methanol to the oil in the conical flask and drop 1 ml of the phenolphthalein indicator solution to the mixture in the conical flask. Then titrate the mixture against the potassium hydroxide in the burette. The break point is the point at which the colour of the mixture in the conical flask turns pink colour. Acid value \( V \times 10^\frac{N \times 56.1}{W} \), where \( V \) = volume of titrate sample, \( N \) = Normality of alkali solution (KOH), \( W \) = Weight of the sample.

The iodine number indicates the amount of unsaturated bonds present in the sample. The material is treated, in carbon tetrachloride medium, with a known excess of iodine monochloride solution in glacial acetic acid (Wijs solution). The excess of iodine monochloride is treated with potassium iodide and the liberated iodine estimated by titration with sodium thiosulphate solution.

Iodine value \( = \frac{12.66N(B–S)}{W} \), where \( B \) = Volume in ml of standard sodium thiosulphate solution required for the blank, \( S \) = volume in ml of standard sodium thiosulphate solution required for the sample, \( N \) = normality of the standard sodium thiosulphate solution, and \( W \) = weight in g of the material taken for the test.

2.5. Thermal properties

The flash point is the temperature at which the oil catches spark and gives out smoke whereas the fire point indicates the temperature at which the oil catches fire. Both of them gives the safe operating temperature of the oil. The flash point and fire point were estimated by Cleveland open cup equipment as per ASTM D92. The pour point is the temperature at which oil loses its flow ability and is evaluated by physical technique. The thermal degradation of the three oils are measured by using thermogravimetric analysis with an operating range of 0˚C – 500˚C.

2.6. Oxidative stability

The vegetable oils are having low oxidative stability because of the presence of poly unsaturated acids like linoleic and linolenic acids present. Hot Oil Oxidation Test (HOOT) as per American Oil Chemists Society (AOCSCD-12-57) was followed for evaluating the oxidative stability of the selected oils. The experiment is conducted in a dark oven with air vent at 100˚C for 30 h.
3. Results and discussions
The fatty acid composition of RBO, JO and KO are shown in Table 1. It is clear that all the three oils are having higher percentages of oleic acid which is responsible for imparting good lubricating properties. Hence the selected oils can be potential alternate for mineral oil based lubricants.

Table 1. Fatty acid composition of rice bran oil, karanja oil and jatropha oil

| Fatty acids | Rice bran oil % | Karanja oil % | Jatropha oil % |
|-------------|----------------|--------------|---------------|
| C18:0       | 2.12           | 7.2          | 6.8           |
| C18:1       | 41.26          | 50.40        | 40.1          |
| C18:2       | 32.63          | 15.54        | 33.9          |
| C18:3       | 0.84           | 1.3          | 0.12          |

The viscosity of the oils under study is evaluated at different temperatures and are tabulated and shown in Table 2. From figure 5 it is clear that KO is having high viscosity when compared to other two oils but the change in viscosity with temperature is low for both RBO and JO. This helps in using the oils at wide range of temperatures. The thermogravimetric analysis (TGA) for the selected oils is shown in figure 6. RBO is stable up to a temperature of 320˚C. The mass degradation starts from 320 ˚C to 440 ˚C. Both JO and KO is stable till 200 ˚C. The rapid mass degradation of KO starts at 380 ˚C whereas rapid degradation of JO starts at 320 ˚C.

Table 2. Viscosity values of RBO, JO and KO

| Temperature (˚C) | Viscosity (cp) |
|-----------------|----------------|
|                 | Rice Bran Oil  | Jatropha Oil  | Karanja Oil  |
| 40              | 35.26          | 30.141        | 38.995       |
| 50              | 22.34          | 21.893        | 26.863       |
| 60              | 16.5           | 16.547        | 19.697       |
| 70              | 12.62          | 12.801        | 14.577       |
| 80              | 9.798          | 10.053        | 11.246       |

The coefficient of friction (COF) and wear scar diameter of the selected oils are evaluated by using four ball tester and are tabulated and shown in Table 3. Gamma oryzanol which is the natural anti-oxidant present in the RBO resulted in low wear scar. However the friction coefficient of RBO is high compared to the other oils.

Table 3. Coefficient of friction and wear scar diameter of RBO, KO and JO

| Name of the oil  | Coefficient of Friction | Wear Scar (mm) |
|-----------------|-------------------------|----------------|
| Rice Bran Oil   | 0.0898                  | 0.547          |
| Karanja Oil     | 0.0624                  | 0.584          |
| Jatropha Oil    | 0.0673                  | 0.571          |
The chemical properties of the selected oils are evaluated and tabulated in Table 4. The less amount of free fatty acids present in the RBO resulted in the low acid value. The iodine value indicates the presence of unsaturated fatty acids present in the oil. Among the 3 vegetable oils selected karanja has the lowest iodine value which indicates good oxidative stability.

| Name of the oil   | Acid Value | Iodine Value |
|------------------|------------|--------------|
| Rice Bran Oil    | 0.66       | 93.033       |
| Karanja Oil      | 5.02       | 75.207       |
| Jatropha Oil     | 19.5       | 91.833       |

The thermal properties of the selected oils are evaluated and tabulated in Table 5. The fire point of RBO is higher than KO and JO which implies its ability to work at higher temperatures. The pour point of RBO is lower than KO and JO which makes it able to flow at lower temperatures. The higher fire point and lowest pour point of RBO is due to the presence of unsaturated fatty acids present in it. It is clear that RBO can be worked at wide range of temperatures than JO and KO.

| Name of the oil    | Flash Point (˚C) | Fire Point (˚C) | Cloud Point (˚C) | Pour Point (˚C) |
|--------------------|------------------|-----------------|------------------|-----------------|
| Rice Bran Oil      | 312              | 326             | -5               | -8              |
| Karanja Oil        | 225              | 232             | 2                | -6              |
| Jatropha Oil       | 240              | 252             | -6.5             | -7.5            |

The hot oil oxidation test is conducted on all the selected oils and results are tabulated and shown in Table 6. The change in the acid value of RBO before and after heating is 1.24 whereas the change in acid value for KO and JO are 0.925 and 1.655 respectively. The increase in the acid value of JO due to heating indicates that JO has a very low oxidative stability and hence any type of chemical modifications are very much required for JO.

| Name of the oil | Acid value at different heating hours |
|-----------------|---------------------------------------|
| Rice Bran oil   | 0.66 1.11 1.22 1.45 1.68 1.9066       |
| Karanja oil     | 5.02 5.12 5.5620 5.6717 5.805 5.945   |
| Jatropha oil    | 19.5 20.18 20.4999 20.685 20.95 21.155 |

4. Conclusions
The lubricant properties of RBO, KO and JO are evaluated and the results were compared with each other. The following conclusions were made from this work:

i. The tribological properties of the oils were evaluated and coefficient of friction for KO is lowest than RBO and JO whereas wear scar of RBO is less when compared to the other selected oils.

ii. Among all the selected oils KO has a higher viscosity at 40˚C and 80 ˚C than that of RBO and JO.

iii. The acid value of RBO is lower than that of JO and KO and the iodine value of KO is lower than that of RBO and JO.

iv. The fire point of RBO is higher than that of KO and JO and the pour point of RBO is lesser than that of KO and JO.

v. KO is showing better oxidative stability than RBO and JO.
vi. RBO is stable till 320 °C whereas JO and KO started degrading after 200 °C

From the feasibility study it is clear that the selected oils are suitable as base oil for industrial lubricants. However chemical modifications may be required for JO and RBO to improve their oxidative stability.

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