Effect of SiC nanoparticles on the tribological properties of rice bran oil-based lubricant

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Abstract. The environmental impact of petroleum products has forced the industry to search for alternative bio-products. Vegetable oils can be considered as an alternative to these petroleum products due to the high viscosity index and excellent boundary lubrication properties. In this work, rice bran oil (RBO) is selected as a base-stock for developing bio-lubricants. The silicon carbide (SiC) nanoparticles were added to RBO in different proportions (0.01 to 0.05 wt. %). The tribological properties were evaluated for different samples using a standard four-ball tribo-tester. The weight percentage of SiC in RBO was optimised based on the tribological results. The optimum concentration of SiC nanoparticles in RBO was found to be 0.03 wt. %. The experimental study also evaluated the tribological properties of chemically modified RBO (MRBO) with 0.03% SiC nanoparticles. It was noted that the tribological properties are better for MRBO with 0.03% SiC nanoparticles.

1. Introduction

Lubricants are introduced between two moving contact surfaces to minimize wear and friction. Lubricants are extensively used in all manufacturing and automobile industries to lubricate their machines. Kline and the company reported that about 38,000,000 tonnes of lubricants were used in the global world during the year 2005 and it was mentioned that the usage will increase by 1.2 to 1.8 % over the next decade[1]. According to Loredana et al., 85% of lubricants utilized globally are petroleum derivatives. They reported that the extensive use of mineral oil-based lubricants will cause environmental problems due to the inherent toxicity of mineral oils[2]. Few studies indicated that approximately eighty percent of the workers exposed to lubricants are facing skin cancer, cough, occupational asthma, etc. To get over these hurdles, researchers are currently searching to find out alternatives to petroleum-based lubricants. Many researchers are trying to formulate lubricants from various vegetable oils available globally. Vegetable oils are biodegradability [3], possess excellent lubricating characteristics and high thermal stability [4]. These vegetable oils have high viscosity and high flash points and they are considered to be less toxicity. These reasons make vegetable oil a potential alternative to be a good lubricant. One of the major issues with vegetable oils is their poor oxidative stability[5]. Common vegetable oils like soya bean oil, rapeseed oil, jatropha oil, coconut oil, etc are already used for formulating bio-lubricants. Very few works have been conducted on Rice bran oil (RBO) as industrial lubricant and biodiesel.

The RBO is mostly used in Asian countries like India, China, Indonesia, Japan, etc. as cooking oil. It is extracted from the husk of the rice and India is the second-largest producer of rice. So, RBO is easily available in the local market. RBO has more oxidative stability than other available vegetable
oils, this is due to the presence of natural antioxidants such as gamma oryzanol RBO[6]. Oxidation stability of vegetable oil can be boosted through chemical modification such as epoxidation, transesterification and hydrogenation. Epoxidation of vegetable oil is a reaction in which C-C double bonds react with highly reactive oxygen to form an epoxy ring. Epoxidation is controlled by reaction variables such as the volume of reactants and products, selected catalysts, temperature, stirring speed, etc.

Okieimen et al.[7] reported that acetic acid will act as an oxygen carrier whereas hydrogen peroxide will act as an oxidizing agent. Their quantities have a favourable effect on the formation of oxiranes. Since epoxidation is a two-phase reaction, stirring speed is a critical parameter for epoxide formation. It was noted that at 1500 rpm, stirring speed does not affect epoxide conversion. Petrovic et al. [8] have studied and reported that temperature is a crucial parameter that decides the duration and conversion rate of epoxide formation. According to their studies at higher temperature (80°C) acetic acid provides better results while at a lower temperature (40 to 60°C) formic acid gives better yield. Goud et al.[9] also reported that the optimal oxirane conversion took place at intermediate temperature (55 to 65°C) with minimal reaction time. Dinda et al.[10] reported that developing peracetic acid in situ along with sulphuric acid as a catalyst will increase the epoxide yield. Campanella et al.[11] also reported that formic acid formed after epoxidation negatively affects the epoxide amount and moderate temperature (60°C) is good for better yield. Recently Thampi et al.[12] had investigated the tribological characteristics of chemically modified RBO and the results indicated that the evaluated lubricant properties improved after chemically modifying RBO.

The base stock properties can be further improved by adding additives such as nanoparticles. It was observed that the usage of nanoparticles has drastically improved the performance of the lubricants. The lubricant properties such as coefficient of friction (COF), load-carrying capacity, viscosity, wear scar diameter (WSD) and pressure properties have improved significantly[13]. Singh et al. has chemically treated Moringa oleifera oil with neopentylglycol. The SiC nanoparticles in different proportions were added to the chemically modified oil. It was observed that the physico-chemical properties of the lubricant improved at 0.5% Sic concentration. The viscosity increment was noted to be maximum at 100°C temperature and 1.0% nanoparticles concentration[14]. The main reason for considering SiC nanoparticles as lubricant additive is because of its excellent properties of homogeneity and they also provide harness to the surface[15]. Sriharsha et al. studied the load-carrying capacity and pressure distribution of the lubricants added with nanodiamonds and SiC nanoparticles. It was observed that both the evaluated properties of the lubricants added with nanoparticles were better when compared with that of the base lubricant[16].

2. Materials and methods

2.1. Materials used
RBO which is used as a base oil in this work was purchased from Kalady Rice Millers Consortium Pvt. Ltd., Kerala, and the fatty acid profile was evaluated by Gas chromatography analysis. The additive used in this work is SiC nanoparticles with 30-50nm particle size. It was purchased from Ultrananotech Pvt. Ltd, Karnataka. The chemicals such as glacial acetic acid, hydrogen peroxide solution were purchased from Qualigens Fine Chemicals, and acids such as butanoic acid, sulphuric acid were purchased from Sigma Aldrich Co.

2.2. Formulation of bio-lubricant
The lubricant characteristics of RBO can be improved by two different methods i.e. chemical modification and addition of nanoparticles. The MRBO was formulated by initially reacting to RBO with per-acetic acid. This per-acetic acid was formed in-situ by the combination of glacial acetic acid and 30% aqueous hydrogen peroxide solution in the presence of sulphuric acid as a catalyst. Then the product obtained was reacted with butanoic acid for ring-opening. The MRBO is finally water-washed and using a separating funnel the water is removed, followed by that the final product is heated along
with the application of vacuum. The steps followed for chemical modification of RBO is mentioned in our previous work [17]. The nano-lubricant samples were prepared by mixing unmodified silicon carbide nanoparticles with RBO at different concentrations (0.01wt.% to 0.05wt.%) using an ultrasonicator for 20 minutes. The stability of samples with SiC nanoparticles was analysed by the visual inspection method. The optimum concentration of SiC nanoparticles in RBO was observed experimentally by tribological evaluation. Then the optimum concentration of SiC nanoparticles was also added to the MRBO sample.

2.3. Evaluation of Tribological properties
The tribological properties such as COF and WSD were evaluated using a DUCOM four-ball tribometer. The wear and friction characteristics were determined as per ASTM D 4172. The test conditions are shown in Table 1. The material of the test ball was AISI 52100 steel with 12.7 mm diameter. Three balls are placed in a stationary ball pot and the fourth ball which is attached to a spindle with a collet is made to rotate against them. The ball pot and test balls were cleaned properly using acetone before and after each test run.

![Table 1: Test Condition during the tribological analysis](image)

| Parameters                  | Fixed Value |
|-----------------------------|-------------|
| Spindle rotation speed (rpm)| 1200        |
| Applied Load (N)            | 392         |
| Temperature (°C)            | 75          |
| Test Duration (s)           | 3600        |

3. Results and discussions
The amount of SiC nanoparticle concentration was optimized based on the COF and WSD results. Table 2 shows the tribological results obtained after adding different Weight % of SiC nanoparticles in RBO.

![Table 2: Tribological results obtained for different SiC concentration](image)

| Weight % of SiC nanoparticle | WSD (µm) | COF     |
|------------------------------|----------|---------|
| 0                            | 575 ± 13 | 0.090 ± 0.002 |
| 0.01                         | 562 ± 8  | 0.082 ± 0.004 |
| 0.02                         | 548 ± 10 | 0.074 ± 0.003 |
| 0.03                         | 542 ± 11 | 0.076 ± 0.002 |
| 0.04                         | 588 ± 12 | 0.078 ± 0.003 |
| 0.05                         | 612 ± 14 | 0.079 ± 0.004 |

From Table 2, the optimum SiC concentration in RBO was noted to be 0.03%. The COF value for all the samples with SiC nanoparticles was noted to be lower than that of pure RBO. The WSD and COF value of RBO with 0.03% SiC nanoparticles was found to be better than that of pure RBO.

The evaluated fatty acid profile of RBO was noted to be oleic acid (43.5%), linoleic acid (32.84%), palmitic acid (20.13%), stearic acid (2.54%), arachidic acid (0.88%), and linolenic acid (0.08%). It was...
observed that fatty acids like oleic acids, etc. are used by researchers to prevent the agglomeration of nanoparticles. The main reason for using unmodified nanoparticles as an additive in this work was due to the presence of these fatty acid contents in RBO. It was noted that the presence of unsaturated fatty acids which contain double bond will lead to the failure of lubricant films. To make RBO more suitable for lubrication purposes, the chemical modification of RBO was performed. The WSD and COF results of RBO, MRBO and both samples with optimum SiC concentration are shown in Figure 1.

From Figure 1, it was noted that the WSD and COF values of RBO have improved by adding the optimum concentration of SiC and chemical modification. The tribological results obtained for MRBO improved when compared with that of RBO because of the thick tribo-film formed between the contact surfaces. The addition of SiC nanoparticles to MRBO has reduced the WSD value but a slight increase in COF value was observed when compared to MRBO. The effective change in fatty acid contents after the chemical modification process may have slightly affected the dispersion of nanoparticles in MRBO, this may be the reason for such an increase in COF value of MRBO after adding SiC nanoparticles. The presence of nanoparticles in samples provides a rolling effect which helps in the effective lubrication by converting sliding friction between contacts to rolling friction. The WSD and COF value was noted to be lowest for the MRBO sample with 0.03% SiC (i.e., 481µm) and MRBO sample (i.e., 0.053) respectively.

The experimental results indicated that the chemical modification of RBO has provided effective lubrication due to the presence of a long molecular chain. Whereas, the rolling phenomenon takes place after the addition of nano-particle into these oil samples but when the nano-particle concentration increases after an optimum value, agglomeration starts to occur which will result in the abrasion of the surface.

4. Conclusions
This work focused to study the effect of Silicon Carbide nanoparticles on the tribological characteristics of RBO. The tribological evaluation of chemically modified RBO with optimum SiC concentration is also conducted in this work. Based on the observations, the following conclusions are noted:

- The optimum concentration of SiC in RBO is noted to be 0.03 wt. %.
- The COF and WSD values of MRBO are noted to be better than that of pure RBO due to the effective tribo-film formed by chemical modification.
- The WSD of RBO and MRBO after adding 0.03wt.% SiC nanoparticles have improved due to the rolling mechanism. Thus SiC nanoparticles are noted to be an effective anti-wear additive.
The WSD value is noted to be lowest for the MRBO sample with 0.03% SiC. Whereas, the COF value is noted to be lowest for the MRBO sample. Thus it is suggested that while using vegetable oils for lubrication purposes, chemical modification of vegetable oils needs to be considered.

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