EVALUATION OF KARANJA OIL (PONGAMIA PINNATA) AS A NOVEL BASE OIL FOR BIO-DEGRADABLE LUBRICANTS WITH NANO ZNO AS ANTI-WEAR ADDITIVE.

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ABSTRACT: : *The major objective of this paper is to experimentally investigate the tribological properties of karanja oil (pongammiapinnata) with nanoZnO as anti-wear additive. Nano ZnO additive in different concentrations ranging from 0 to 3 wt. % in karanja oil was tested for various base oil properties and the results were compared with SAE 30 oil. The viscosity @40 oC of the karanja oil showed an increasing trend up to 2 wt. % additive, and thereafter decreasing trend. Both coefficient of friction and wear scar diameter showed optimum values at 2 wt. % concentration. These values were comparable to that of commercial SAE 30 oil. The SEM images of the worn out surfaces indicated marked improvement in the wear behavior of karanja oil when nanoZnO additive was added. In comparison to the commercial SAE 30 oil cold flow properties of karanja oil were inferior.*

Key Words: *Coefficient of friction; Karanja oil; Nano ZnO additive; Viscosity index; Wear scar diameter.*

1. Introduction

Being precursors to mineral oil based lubricants; vegetable oils are getting a renewed interest as an alternative base stock for lubricants in view of environmental concerns and future depletion fossil oils. Many oil companies including Shell, ExxonMobil, and BP have vegetable oil based lubricants in their product line. Most of these lubricants are made from vegetable oils, such as soybean, corn, and rapeseed (canola). In such formulations, mineral oil is replaced with vegetable oils as base stock, which is typically 90% of a lubricant.

Fatty acids in vegetable oils naturally provide better lubricity than mineral oils as their polar molecules adsorb to metal surfaces better than mineral oil molecules. Notable drawbacks of vegetable oils are poor oxidation stability and cold flow properties. Like conventional lubricants, vegetable oil based lubricants need additives to improve tribological properties and corrosion resistance, depress pour point, resist hydrolysis, and inhibit microbial growth.

Large scale conversion of edible oils for industrial use has led to wide spread concerns regarding feedstock availability and cost, land use changes, and fuel/oil vs. food/feed competition [1]. One of the solutions to these concerns can be using non-edible feedstocks. Karanja oil (Pogammiapinnata) is a non-edible oil extracted from the seeds of Pogammiapinnata tree which is widely available in south east Asia. The oil is yellowish orange to brown in color and has a disagreeable smell and bitter taste. Karanja oil contains ~ 52 % monounsaturated (oleic) and ~20 % polyunsaturated (linoleic) fatty acids. Other major fatty acids in karanja oil are; palmitic acid (C16:0), stearic acid (C18:0), arachidic acid (C20:0), behenic acid (C22:0), lignoceric acid (C24:0) and erucic acid (C22:1) [2, 3]. Since fatty acid content vary slightly with geographic regions and seasons, the fatty acid profile of karanja oil was confirmed with GCMS (Make- Agilent, Model 6890N, 5975(MS)). The presence of erucic acid and the toxic flavonoids like karanjin, pongapin, and pongaglabrin, render the oil inedible according to WHO recommendations [3]. These flavonoids render natural antimicrobial and pest repellant properties to karanja oil.

The properties of vegetable oils depend heavily on their fatty acid profile. Saturated and mono unsaturated fatty acid contents provide better oxidative stability [4-6] to vegetable oils. Higher percentage of saturated fatty acids leads to poor cold flow properties. As the degree of unsaturation increases pour point decreases. Viscosity indices of predominantly saturated oils are better compared to poly-unsaturated oils [7, 8]. Saturated and monounsaturated oils show better friction and wear properties compared to polyunsaturated oils [9]. Higher content of long chain saturated fatty acids is shown to have better tribological properties [10, 11]. High monounsaturated content (about 52 %) and the presence of saturated fatty acids especially the long chain fatty acids (C20:0, C22:0, and C24:0) in karanja oil is likely to provide good friction and wear characteristics. High percentage of unsaturated fatty acid content (about 72 %) is good for cold flow properties. However, the presence of saturated fatty acids may adversely affect the cold flow behavior. The presence of polyunsaturated fatty acids (~20%) may have an adverse effect on the oxidative stability.

Unmodified vegetable oils are seldom used as industrial lubricants.They are modified by means of; 1) appropriate additives, 2) chemical modification, 3) genetic modification, and 4) a combination of the above three methods [12, 13]. Nano particles as lubricant additive got the attention of researchers in recent decades because of its anti-wear and extreme pressure properties. Numerous studies on nano particles as oil additives are reported [14, 15]. Rapoport et al. [14] reported that WS2 particles of typically 100 nm diameter reduced wear of self-mated steel approximately a factor of 2 for loads below 400 N and by factor of 10 above this threshold. They also observed decrease in friction by 40% when nano particles were added. Hernadez et al. [15] reported anti-wear behavior of CuO, ZnO and ZrO2 nano particle suspension in a polyalphaolifin. The authors observed all nano particle suspension exhibited reductions in friction and wear compared to the base oil. They also reported that the suspensions with 0.5 % of ZnO and ZrO2 had the best tribological behavior even at low deposition level on the wear surface. Several studies were conducted on the tribological characteristics of nano particle added vegetable oils [16, 17], Pingyu Zhang et al. [16] investigated tribological properties of Langmuir–Blodgett (LB) films. They found that the LB films of fatty acids and surface-modified MoS2 nanoparticles decrease the friction coefficient of a glass/steel frictional pair. Redice et al. [17] studied the effect of alumina nanoparticle suspended in an aqueous acetate buffer solution on the tribo-corrosion behavior of a 316L steel/alumina sliding contact using a reciprocating wear test rig with an electrochemical cell. They observed that the addition of 10 % volume of alumina nanoparticle to an acetate buffer solution was able to reduce the coefficient of friction by a factor of 2 and the stainless steel wear by a factor of 10.

Few studies have been reported on the behavior of nanoZnO additive on the anti-wear characteristics of karanja oil [18, 19]. Being a nonedible oil, karanja oil is a good candidate as base oil for bio-degradable lubricants. Hence, in this paper attempts were made to investigate the suitability of karanja oil, with different concentrations of nanoZnO additive, as an industrial lubricant. Various lubrication tests were conducted for different concentration of nanoZnO in karanja oil to ascertain its efficacy as a base oil for bio-degradable lubricant. For comparison, the same tests were conducted on a commercial oil of comparable viscosity grade (SAE30) and the results are reported.

2. Experiments

2.1 Materials

Karanja oil (cold pressed and double filtered) was procured from local market (Kochi, India). Nano ZnO particles were procured from Zigma Aldrich, Bangalore. Material properties of nanoZnO as per the supplier specification are shown in Table 1. ZnOnano particle is dispersed in karanja oil in different concentrations of 0.5, 1, 1.5, 2, 2.5 and 3 wt. %. The mixture is mechanically stirred for 20 minutes followed by ultra-sonication for 20 minutes before each test. SAE 30 oil was purchased from the outlet of Indian Oil Corporation, Kochi, Kerala.

Table 1. Properties of nanoZno (Zigma, Aldrich, Bangalore).

Material/Properties	Morphology	Purity (%)	Size (nm)	Melting Point(°C)
ZnO Nano Particle	Nearly Spherical	99.5	20	1975

2.2 Measurement of viscosity

The viscosity analysis was conducted using BROOKFIELD LVDV2T Extra viscometer conforming to ASTM D 2983-09 standard.

2.3 Physical and Chemical properties

The physical and chemical properties of karanja with nanoZnO and mineral oil were determined by the methods shown in parentheses; a) specific gravity (ASTM D1217), b) flash point (ASTM D92), c) fire point (ASTM D92), d) iodine value (AOCS method Ja 14-9), e) saponification value (AOCS method Cd 3-25) and f) acid value (AOCS method Cd 3d-63). GCMS analysis was carried out for karanja oil in order to confirm fatty acid profile.

2.4 Thermal and Oxidative Stability

Thermal and Oxidative stabilities of karanja and the SAE 30 oil were investigated by TGA/DTA analysis [5] using Perkin Elmer Instruments, Waltham, MA, USA. For thermal stability analysis the samples were heated from ambient to ~800 ºC temperature at a constant heating rate of 10 ºC/min with nitrogen as purge gas at a flow rate of 100 mL/min. For oxidative stability tests oxygen was used as the purge gas at a flow rate of 100 mL/min. In either case about 10 mg of sample was heated in platinum pans. Graphs are plotted with normalized data as sample weights vary slightly from sample to sample.

2.5 Cold Flow Property

The cold flow behavior of karanja oil was analyzed by ASTM D97 standard and also using Differential Scanning Calorimeter (DSC) [7]. DSC experiments were carried out on Mettler Toledo DSC 822e. In DSC experiments, about 10 mg of oil is heated to 50 ºC and maintained at that temperature for 10 min for homogenization and dissolution of any waxy material which may act as accidental seed for crystallization. The sample is then rapidly cooled to -50 ºC followed by heating to 50 ºC at the rate of 10 ºC/min. In DSC experiments heat flow (in W/g) from and into the sample are recorded accurately. Exothermic (solidification) and endothermic (melting) activities appear as peaks and valleys in the DSC thermograms (heat flow vs temperature). These peaks and valleys and the corresponding temperatures are used to study the cold flow behavior of oils. The test was repeated for additivizedkaranja oil and the SAE 30 oil for comparison.

2.6 Tribological Tests

The toxicity of the oil samples were estimated by disk diffusion technique. A petri dish containing an agar medium was spread plated with bacterial culture containing *Pseudomonas aeruginosa* (24 hours old). Three pits of 5 mm diameter and 2 mm depth was carved on every agar plate for holding the sample, gram positive and gram negative control solutions. Gram positive strain was taken as silver nitrate solution and gram negative was taken as demineralized water. The silver nitrate solution being highly toxic to the bacterial growth result in a large clear zone after incubation compared with demineralized water which is passive towards bacterial growth. Hence by comparing the diameter of the clear zone produced by sample solution with that of the silver nitrate solution, toxicity can be assessed.

3. RESULTS AND DISCUSSION

3.1 Effect of nanoZnO Additive on the Viscosity of Karanja oil

The effect of different concentrations of nanoZnO addition on the viscosity of karanja oil is shown in Fig. 1. It is observed that, as the concentration of the additive increases, the viscosity of karanja oil also increases up to a maximum value of 54 cP corresponding to 2 wt. % and then decreases. Many experimental studies reported in the literature show similar results [20]. Decrease in viscosity with increasing wt. % of the additive beyond the maximum value is attributed to agglomeration of nano particles. Viscosity with different concentrations of the additive in karanja oil versus temperature graph is shown in Fig. 2. Additivizedkaranja oil shows higher viscosity consistently up to 100°C compared to pure oil. Fig. 3 shows viscosity indices of karanja oil with different concentrations of the additive. At 2 wt. % karanja oil ZnOnano fluid has a viscosity index of 146. Further increase in concentration of the additive decreases the viscosity index of the oil additive mixture.

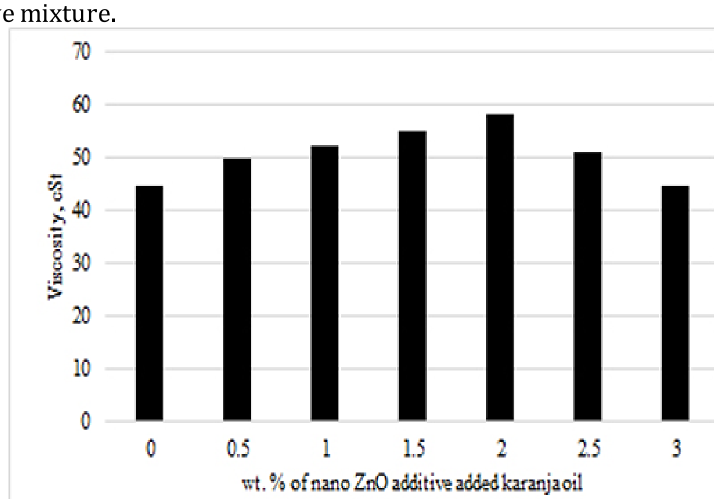

Figure 1. Viscosity verses different wt. % of nanoZnO additive added karanja oil.

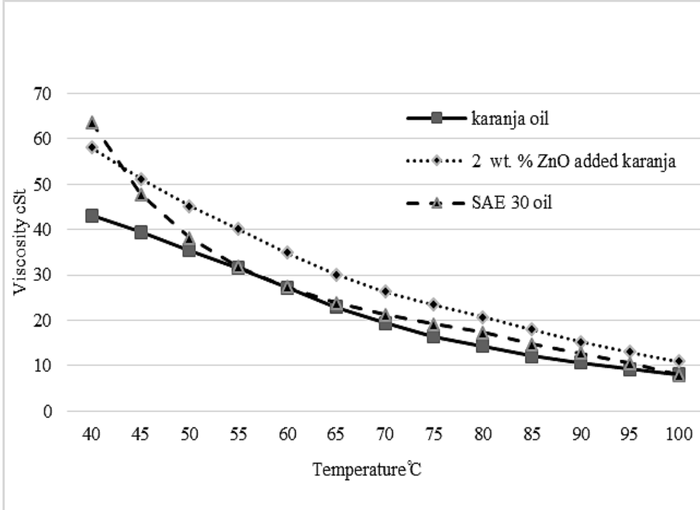

Figure 2. Viscosity verses temperature for different oils

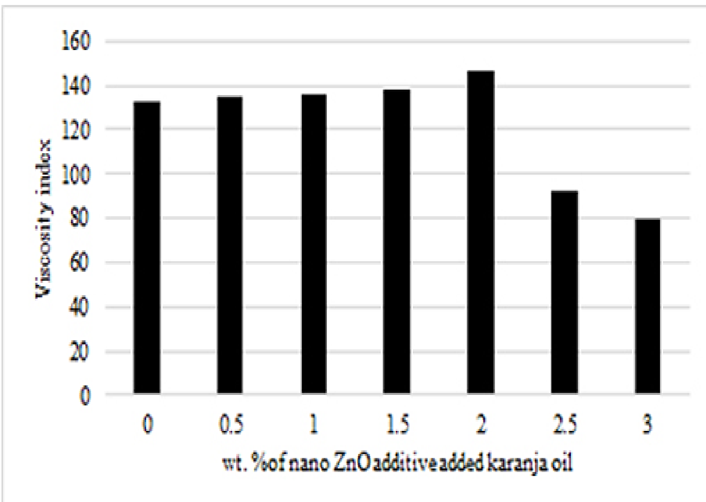

Figure 3.Viscosity index verses different wt. % of nanoZnO additive added karanja oil.

3.2 Physicochemical Properties of Karanja and SAE30 oil

Table 2 lists some of the physical properties of karanja oil and SAE 30 oil which has relevance to their use as lubricants. Table 3 lists some of the important chemical properties of karanja oil which have bearing on its use as lubricant base stock.

Table 2. Physical properties of karanja oil and mineral oils

Name of the oil	Fire Point (^{o} c)	Flash Point (^{o} c)	Pour Point (^{o} c)	Cloud Point (^{o} c)
SAE 30 oil	250	230	-6	-3
Karanja oil	262	240	4	7

Table 3. Chemical properties of karanja oil

Name of oil	Saponification value (mgKOHg⁻1)	Acid value (mgKOHg⁻1)	Iodine value (mgl g⁻1)
karanja oil	186	5.9	77

Thermal and oxidative stabilities of vegetable oils are functions of their fatty acid content. TGA can be used to compare the thermal and oxidative properties of different oils. TGA thermograms under nitrogen environment give an idea of the thermal degradation of oils. Fig. 4 shows TGA thermograms of Karanja oil and SAE 30 oil under nitrogen environment. It can be seen from the graph that the onset of thermal degradation for both oils starts around 250 °C. Weight loss in the case of karanja oil in the temperature range of 250 °C to ~500 °C is lower compared to SAE 30 oil. This may be due to the presence of long chain unsaturated fatty acid content in karanja oil.

TGA thermograms under oxygen environment gives information about the oxidative behavior of oils tested. Fig. 5 shows the TGA thermograms of karanja oil and SAE 30 oil under oxygen environment. Onset of degradation and weight loss for both oils starts about 230 °C but proceeds rapidly as the temperature increases when compared to degradation under nitrogen environment. SAE 30 oil almost completely degrades (90%) before it reaches 400°C whereas Karanja oil degrades by 90% at about 450 °C. Under oxygen environment, unsaturation in fatty acid chains causes formation of hydroperoxides by the reaction with oxygen [5,8]. The thermogram of SAE 30 oil is smooth and continuous indicating continuous degradation due to lack of unsaturated hydrocarbon content. Thermogram of karanja oil is bumpy indication weight gain by the formation of hydroperoxides and their degradation [8].

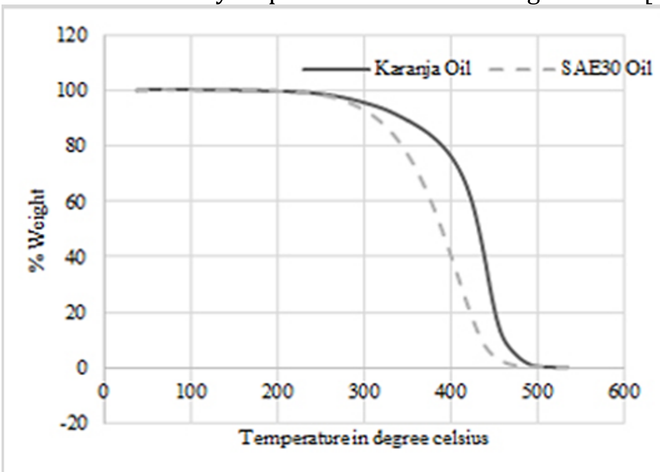

Figure 4. TGA analysis under nitrogen environment conducted for karanja and mineral oils

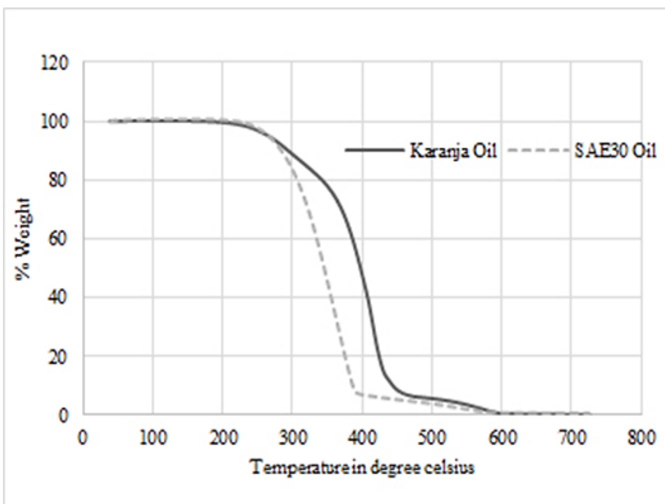

Figure 5. TGA analysis under oxygen environment conducted for karanja and mineral oil.

3.4 Cold flow behavior of karanja oil

Pour points of lubricants are traditionally determined by ASTM D97 method. Vegetable oils are triglyceride esters of different fatty acids and hence do not have a definite solidification/meting point. Moreover, they exhibit polymorphism by crystallizing into different polymorphic forms depending on cooling rate [7]. Hence, in the case of vegetable oils, pour point as determined by ASTM D97 method gives only a rough indication of cold flow behavior. DSC thermograms capture thermal activities (exothermic and endothermic heat flows) during crystallization and melting. Previous studies [7, 21] show that DSC thermograms in heating are not dependent on heating rate and hence give reproducible and reliable results. Figure 7 shows DSC thermogram (heating) of karanja oil obtained as per the method explained in experimental section (section 2.4).

The pour point obtained by ASTM D97 method was 4 °C. The DSC thermogram shows a broad peak from ~-21 °C to 19 °C. As the oil is cooled the high meting components (triglyceride esters with saturated fatty acids like C18:0, C20:0, C22:0 and C24:0) start solidifying at high temperatures and entraps the low melting components leading to formation of gels (congelation). As cooling continues the oil ceases to flow due to congelation. Previous studies show that the congelation occurs around the maximum point of the first exothermic peak [7, 21]. In the present DSC two peaks merges into one broad peak which joins at ~4°C. Hence, we can take the pour point value to be 4 °C [7].

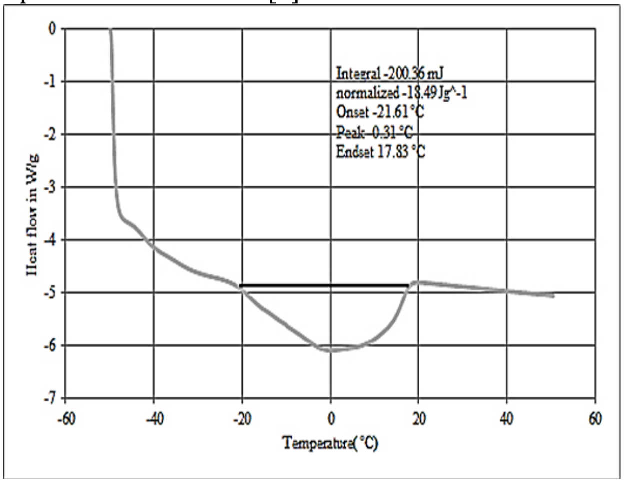

Figure 6. DSC thermogram of karanja oil.

3.5 Effect nanoZnO Concentration on the Friction and Wear Characteristics of Karanja oil

Figure 7 shows the histogram of coefficient of friction (COF) for different concentration of nanoZnO additive obtained from the four ball tribological test conducted as per ASTM D4172. As the concentration of the additive increases from 0 to 2 wt. % COF decreases from 0.055 to 0.033. Further increase in the additive concentration leads to higher COF. The initial decrease in the COF corresponds to the increase in viscosity of the oil as additive concentration increases. The COF reaches a minimum value corresponding to the maximum value of viscosity at 2% wt. additive concentration and then increases as the viscosity decreases. The initial decrease in the COF can be attributed to the combined effect of the increase in viscosity and the rolling and sliding action of the nanoZnO particles entrapped between the interacting surfaces [22]. At higher concentrations, agglomeration of additive particles leads to decreased viscosity and increased rubbing.

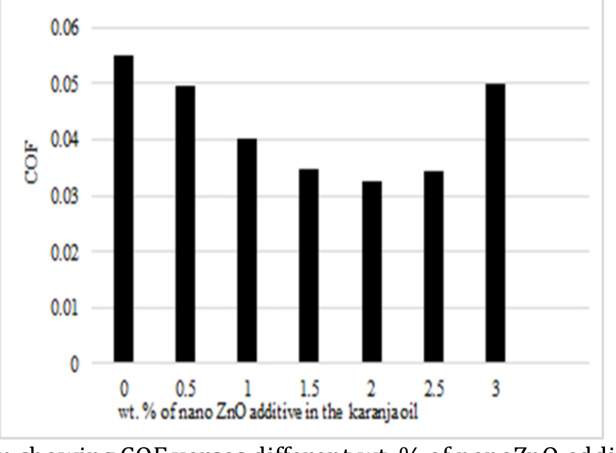

Figure 7. Histogram showing COF verses different wt. % of nanoZnO additive in karanja oil

Figure 8 shows the histogram of WSD for different concentration of nanoZnO additive. Wear scar diameters (WSD) show a similar trend as seen in the case of COF. WSD decreases from 463μm to 408 μm as the additive concentration increases from 0 to 2 wt. %. With further increase in the additive concentration, WSD increases to 447 μm at 3 wt. % additive concentration. The reasons attributed to the change in COF may be attributed to the change in WSD as well [23].

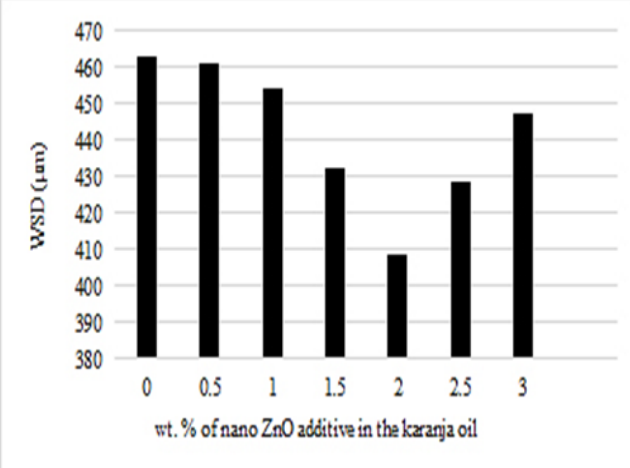

Figure 8. Histogram showing WSD verses different wt. % of nanoZnO additive

The tribological tests reveal that both COF and WSD are at their minimum at 2 wt. % additive concentration and hence 2 wt. % concentrations can be considered as the optimum concentration. Table 3 shows the values of COF and WSD for additivizedkaranja oil (2 wt. %) and SAE 30 oil, used for comparison. From the values of COF and WSD of karanja oil additive combination and SAE30 oil, it can be seen that the former clearly outperform the latter.

Table 4. Cof and wsd values of additivizedkaranja and sae 30 oils.

Oil/Properties	COF	WSD (µm)
Karanja oil	0.055	463
Karanjaoil+Additive (2 wt. %)	0.033	408
SAE 30 oil	0.048	501

Figures 9 (a) and (b) shows the SEM images of the wear surfaces of the steel balls used in the four ball tribological tests with pure karanja oil and karanja oil with 2 wt. % additive. SEM image of the wear surface with karanja oil shows deeper grooves with ragged edges and a scuffed appearance whereas the image of the wear surface with additivizedkaranja oil (with 2 wt. % nanoZnO) has shallower grooves with a smooth appearance indicating better anti wear performance

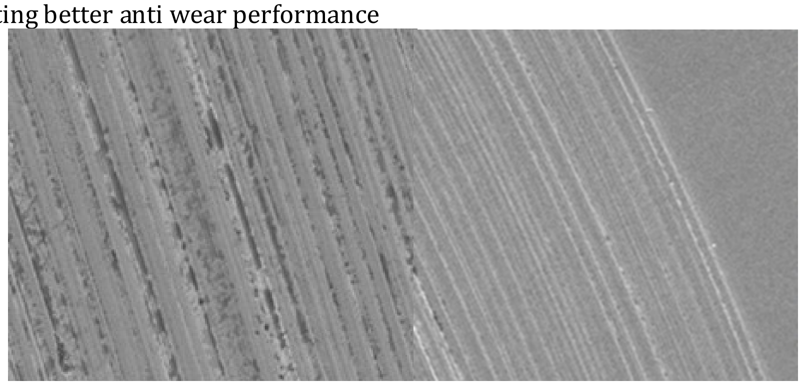

Figure 9. SEM micrograph (x 1,000) of the worn out surfaces of the steel ball in the case of (a) pure karanja oil and (b) 2 wt.% nanoZnO additive added karanja oil conducted with a load of 392 N rotating at 1200 rpm for 1 hour.

4. Conclusions

The aim of the investigation was to study the effect of wt. % of nanoZnO additive addition on the physical, chemical and tribological characteristics of karanja oil. The important conclusions drawn out of the study are as follows.

1. Addition of nanoZnO in karanja oil improved both its viscosity and viscosity index. Viscosity index of karanja oil showed an increase from 136 to 146 with an additive concentration of 2 wt. %.
2. Thermal, oxidative and cold flow properties are basically bulk oil properties and hence evaluated without additive. Thermal and oxidative behavior of karanja oil as evidenced by TGA was better than that of the SAE 30 oil. Pour point for karanja oil was much higher than the SAE 30 oil.

3. Tribological properties of karanja oil, measured in terms of coefficient of friction (COF) and wear scar diameter, showed marked improvement with the addition of 2 wt. % nanoZnO. Comparison of the SEM images of wear surfaces confirmed the improvement in tribological properties with nanoZnO additive.

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