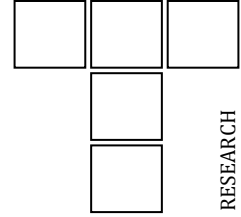


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Investigation of Tribological Properties of Mahua Oil Mixed with Zinc Oxide Nanoparticles

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ABSTRACT

In today's paradigm petroleum and petro-based chemical products are being extracted and consumed at a substantial rate, proving to be hazardous and detrimental to the earth. Bio based resources are environmentally friendly, energy efficient, economical, and proved to be an alternative to the present mineral oils. This paper documents the research on naturally available mahua seed oil for bio-lubrication, its flash point and fire point, tribological properties namely coefficient of friction and wear scar diameter have been modified by the addition of zinc oxide (ZnO) nanoparticles in different concentrations by weight percentage (0.25, 0.50, 0.75, and 1.0). four-ball tester was used according to ASTM-D-4172 standards (60 min under 40 kg running at 1200 rpm). Probe ultrasonicator was used for particle dispersion. It was found that 0.75 wt. % loading of ZnO in mahua oil resulted in a 57.14% drop of coefficient of friction, but a slight increase in the wear scar diameter of 30.60% was observed.

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1. INTRODUCTION

The urgent need for alternatives to synthetic oils has led to various experimentations on different non-edible bio-oils. A detailed literature survey showed very little research on the utilization of mahua oil as lubricant in contrast to its potential to be an effective alternative. The flash and fire point of pure mahua oil have been noted to be higher than the other bio-oils and were comparable with synthetic oils available in present day market [1]. Mahua is a tropical tree mainly cultivated in regions of South Asia for its non-edible flowers and oil seeds. This plant is

known for its resistance to harsh environments and can be grown in almost any terrain and crop fields. It yields between 35% to 45% of oil. In India potential mahua oil production could be up to 60 million Tons per year [2]. It is to be noted that pure bio-oils have poor oxidative stability and thermal resistance [3,4]. Sulfide and phosphide ions are present in synthetic oils; these ions help a lot in reducing wear scar diameter because of their repulsive action on the surfaces leading to the development of a thin protective film on the contact interfaces [5]. However, bio-oils do not contain these hydroxyl ions, hence an additive containing such ions are

a preferable choice for blending with bio-oils. Experiments conducted by Luo et al. [6] revealed that alumina (Al_2O_3) has a hexagonal close-packed crystal structure, having excellent hardness, heat resistive and wear resistive properties. Addition of Al_2O_3 resulted in a drop of nearly 17.61% coefficient of friction (COF). Similarly, Asrul et al. [7] have proved that tribological properties of base oils could be enhanced with increasing concentrations of copper oxide (CuO). Jason et al. have found out that addition of zinc oxide (ZnO) nano-additive to mineral based oils exhibited excellent friction and wear properties, but on addition to vegetable oils were not beneficial for wear reduction [8]. ZnO nanoparticles exhibit promising tribological performance when used as additives in lubrication systems owing to its high colloidal stability and tendency to smoothen the shearing surfaces as seen in Sarkar et al. research [9]. A trend similar to such metal oxides can be expected from this research.

The literature survey has suggested that mahua oil is readily available in major parts of the world, with India being a key supplier. mahua oil is recognized as possible substitute for decreasing petroleum fuels. According to the literature, traditional lubricants have proven to be unsatisfactory in harsh working environments. Information on the impact of nano-additives in bio-lubricants, along with ineffective reactions to bio-lubricants' underperformance by adding nano-additive are currently study gaps. The research gaps require an optimal mix of nano-additives with lubricants for considerable improvement in efficacy. Apart than that, there have been few investigations into the effects of mixing ZnO nanoparticles with mahua oil in the available experimental data. This research intends to evaluate the feasibility of generating biolubricant from mahua oil, as well as the increase in mahua oil performance by adding ZnO nanoparticles, as measured by flash point, fire point, coefficient of friction, and wear scar diameter.

2. EXPERIMENTAL

2.1 Materials

Mahua seeds were collected from naturally cultivated trees in Bannur district, Karnataka. The crude oil was extracted at National

Institute of Engineering, Centre for Renewable Energy and Sustainable Technology (NIE-CREST, Mysore, Karnataka). Zinc Oxide (ZnO) nanoparticles were purchased from AdNano Technologies Pvt. Ltd. India. The specifications of ZnO are, surface area $110 \text{ m}^2\text{g}^{-1}$, the ZnO considered had particle size in the range of 30-80 nm and was spherical in structure. Table 1 details the other specifications of the chosen nano additive. Figure 1 shows the scanning electron micrographs of ZnO [10].

Table 1. Specifications of ZnO nanoparticles.

ZnO Nanoparticle	Specifications
Purity	99.9%
Average particle size	30-80 nm
Surface area	$100\text{-}120 \text{ m}^2/\text{g}$
Molecular weight	81.408 g/mol
Hardness	424 HV
Melting point	$1,975^\circ\text{C}$
Bulk density	$0.6 \text{ g}/\text{cm}^3$
Physical form	Powder
Morphology	Spherical
Colour	Milky white
CAS number	1314-13-2

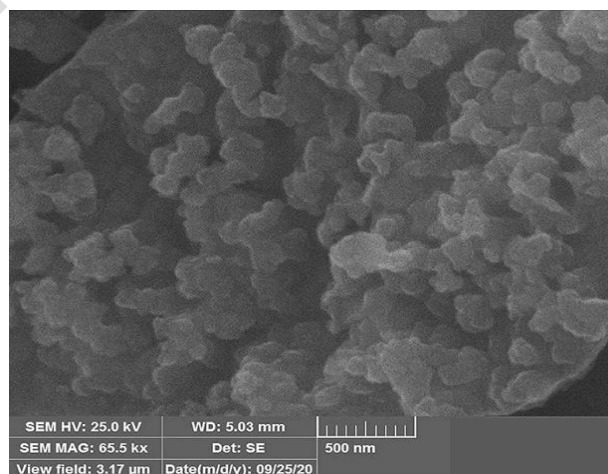


Fig. 1. SEM Microstructure of ZnO (500 nm scale) taken from product data sheet.

2.2 Mahua oil preparation

The mahua oil from the collected seeds was mechanically extracted using cold press method. The obtained oil was then filtered under two stages. Coarse filtering process involved 300-micron filter and the Fine

filtering process used a 20-micron filter. The density of the oil is 0.92 g/cm³ and the kinematic viscosity fell in the range of 35 – 40 cSt at 40 °C as measured in the Saybolt’s viscometer. In this research mahua oil (OMO) was mixed with ZnO nano-additives using a probe ultrasonicator. Zinc oxide was blended with mahua oil in the concentrations 0.25 wt.% (0.25MO), 0.5 wt.% (0.5MO), 0.75 wt.% (0.75MO), and 1 wt.% (1MO) [11-13]. Out of the various methods for dispersion, the authors found that ultrasonication was the most efficient technique [14-16], wherein sound energy is applied to agitate the particles. It generates alternating low pressure and high-pressure waves which helps in uniform distribution of Nano-additives in the base oil.



Fig. 2. Probe ultrasonicator used for particle dispersion.

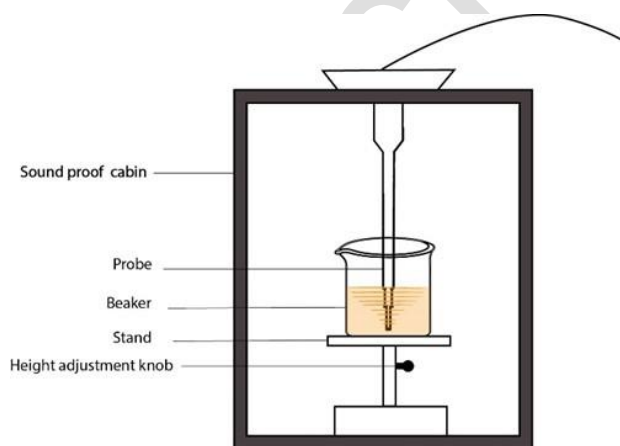


Fig. 3. Schematic representation of ultrasonication process.

Figure 2. shows the probe ultrasonicator used for particle dispersion and Figure 3. illustrates it’s working. The frequencies of sound wave usually used are greater than 20 KHz. For this research a probe ultrasonicator was used at 22

KHz for a duration of 20 minutes at a constant temperature of 75 °C for all test samples. Figure 4 illustrates the flow process of the research work, and Table 2 shows the combination and designation of the oil samples.

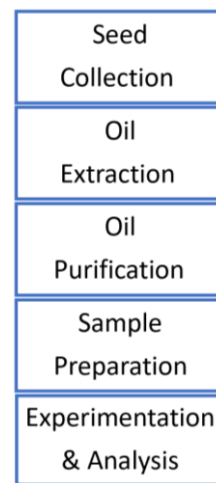


Fig. 4. Research flow chart.

Table 2. mahua oil – ZnO blend designations.

Mahua oil (wt.%)	ZnO (wt.%)	Designation
100.00	0.00	OMO
99.75	0.25	0.25MO
99.50	0.50	0.5MO
99.25	0.75	0.75MO
99.00	1.00	1MO

2.3 Test procedure

Flash point and fire point of the prepared oil samples were obtained from the Pensky Martens closed cup tester [17,18]. The tribological investigation of the test samples was performed on Four-Ball Tester manufactured by Magnum Engineers, Bangalore. Figure 5 and 6 shows the four-ball tester equipment. 12.7 mm diameter 100Cr6 chromium steel balls from SKF of hardness 58-67 HRC and surface roughness of 0.03µm were used [20]. The research was conducted on a load of 40 kg (392.27 N) running at 1200 rpm for 60 minutes maintained at 75 °C as per the ASTM D-4172 standards [19]. Each of the test samples were tested thrice for determination of COF and wear rate and the mean average value was chosen. The coefficient of friction was determined using the computer software and wear scar diameter was detected via optical microscopy and measured by constructing 3-point circle around the wear.



Fig. 5. Lubricant test rig.

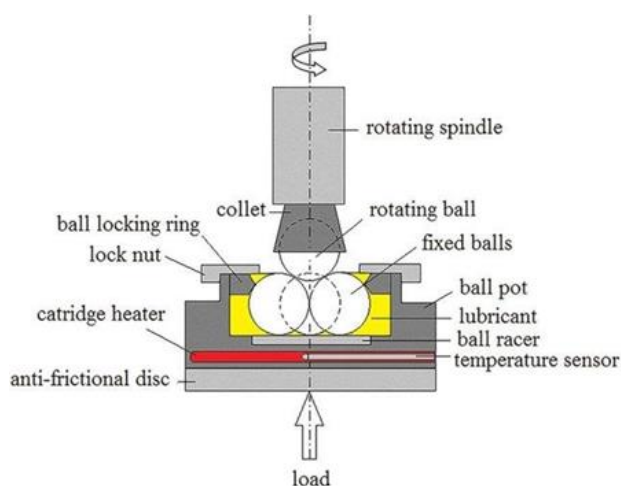


Fig. 6. Schematic diagram of the working of the four-ball tester.

3. RESULTS AND DISCUSSION

3.1 Effects on flash and fire point

The effect on the flash point and fire point of mahua oil on addition of ZnO was analyzed and compared with that of 0MO. The flash and fire points for each test sample were measured three times and the average was chosen to avoid experimental errors. It was found that with the increase in nanoparticle concentration the flash point increased proportionally as tabulated in Table 3. The reason being, with increase in particle size, the volatility of the lubricant decreases [21,22]. Also, at higher concentrations of ZnO, the bio-oil is unable to give off sufficient vapors required to generate a burnable mixture with air. The findings in

Table 3 show that there is a rise in the fire point when ZnO nanoparticles are present. This rise ranges from 238 °C for the basic mahua oil to 245 °C for samples with 0.25, 0.5, 0.75, and 1 wt.% MO.

Table 3. Flash point and fire point of test samples.

Test Sample	Flash point (°C)	Fire Point (°C)
0MO	224	238
0.25MO	226	239
0.5MO	230	242
0.75MO	233	243
1MO	233	245

3.2 Effects on friction coefficient

On testing the bio-oil blend in the four-ball tester under ASTM-D4172 standards and analysing the results in the software, figure 7 and 8 have been plotted. It was established that the COF for 0MO was 0.042. A slight hike of 26.19% COF was attained in 0.25MO whereas a substantial drop of 23.80% and 57.14% was observed in 0.5MO and 0.75MO respectively. The trend was similar to the results achieved by Battez et al. [23]. However, at higher concentration (1MO) the COF had risen by 42.85%. Thus, it was comprehended that 0.75MO was the optimal concentration and could be used for application purposes. The drop in COF at 0.5MO and 0.75MO was congruent to Peng et al. [24]. As described in Table 1. the ZnO nanoparticles chosen for experimentation are spherical in nature. This enables the conversion of sliding friction into rolling friction at the mating surfaces, also known as ball bearing effect. A defensive film is created on the steel balls facilitating the drop in COF [25,26]. Additionally, the ease of penetration of the particles in between the rubbing surfaces is enhanced with the small size of ZnO. The authors speculate that at higher concentrations, nanoparticles tend to agglomerate, forming larger clusters. These clusters might not disperse uniformly in the mixture, leading to regions with higher nanoparticle concentrations. This can create uneven distribution and interaction patterns, potentially affecting the friction behavior. However, to substantiate these claims, techniques like spectroscopy and microscopy would have to be included. This becomes the scope for future research on this work.

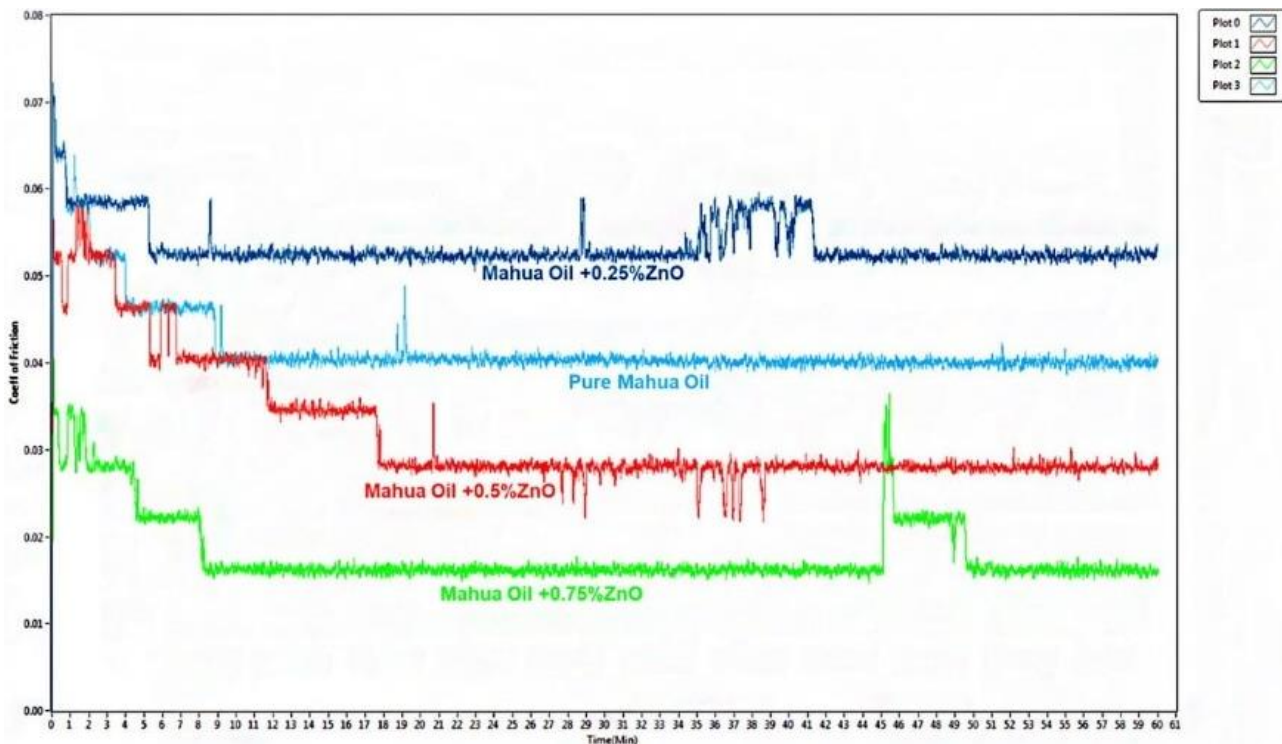


Fig. 7. Shows variation of coefficient of friction for different compositions of mahua oil.

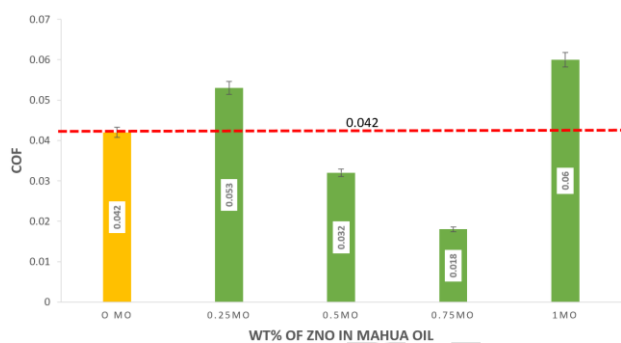


Fig. 8. Comparison of coefficient of friction for various concentrations with pure mahua oil.

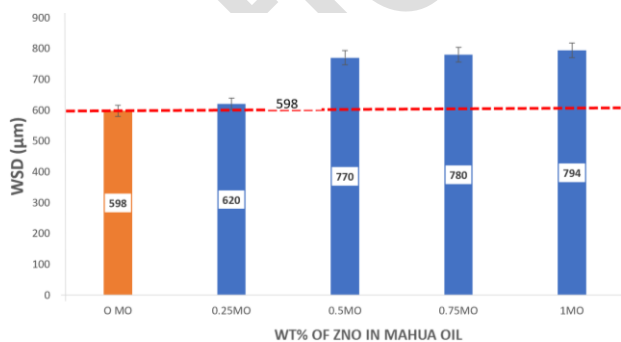
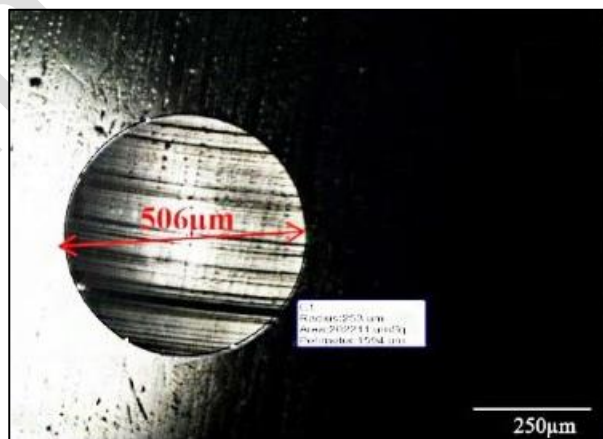


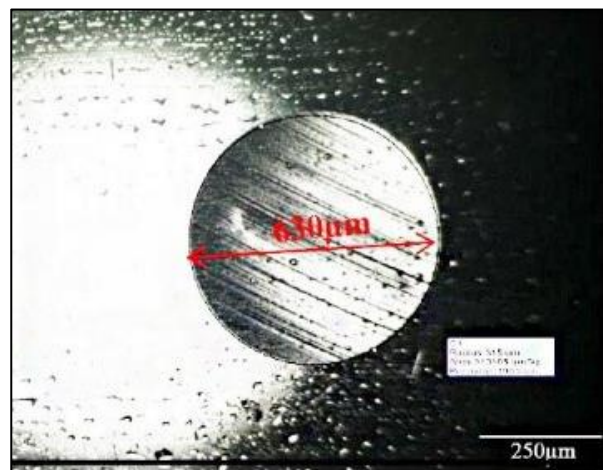
Fig. 9. Comparison of wear scar diameter for various concentrations with pure mahua oil.

3.2 Effects on wear scar diameter

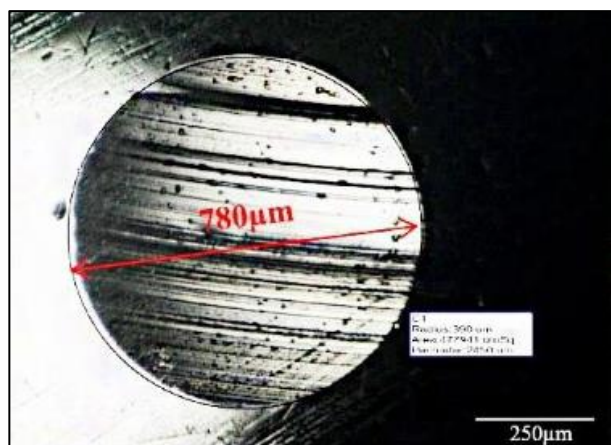
It was found that while the average wear scar diameter for 0MO was 598 µm, it increased with increase in concentration of nanoparticles.



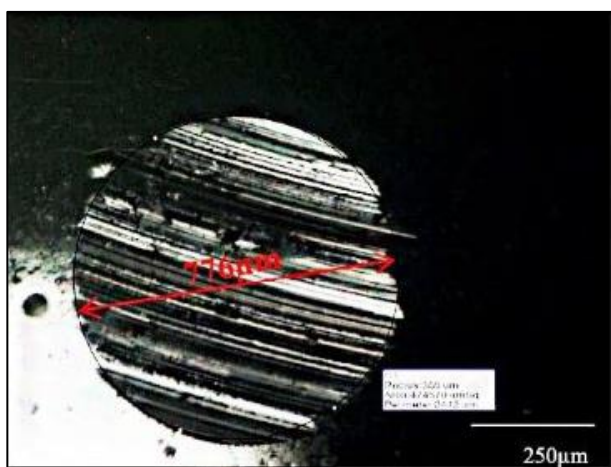
(a)



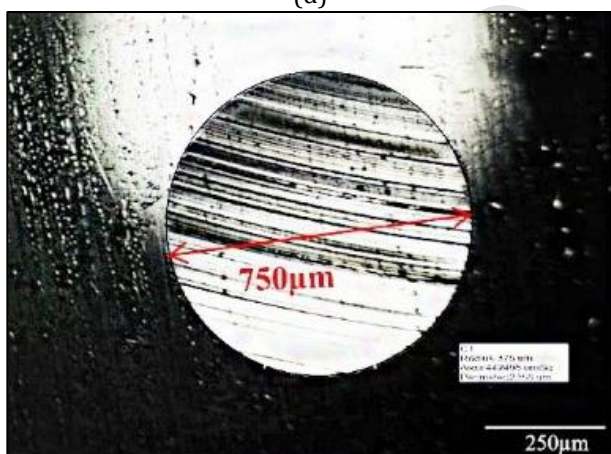
(b)



(c)



(d)



(e)

Fig. 10. Optical micrographs (250 μm scale) showing wear scar diameter: (a) 0MO, (b) 0.25MO, (c) 0.5MO, (d) 0.75MO and (e) 1MO.

The results have been compared with 0MO in figure 7. An increment of 3.67% in the wear was observed for 0.25MO. An average WSD of 770 μm i.e., 28.67% increase was obtained for 0.5MO. Furthermore, a hike of 30.60% was attained for 0.75MO and for 1MO the average WSD was 794 μm resulting in

32.77% increase in the wear scar of the chromium balls. The achieved results were in testimony to Alves et al. [27] who achieved similar results for ZnO blended in vegetable oils. It can thus be established that ZnO was detrimental for wear reduction due to the small size of ZnO and are in par with the claims made by Battez et al. [28]. Figure 10. shows the microscopic images capturing WSD for 0MO, 0.25MO, 0.5MO, 0.75MO and 1MO. This abrasive nature of ZnO is consequential of its small size and a relatively higher hardness.

4. CONCLUSION

The purpose of this research is to create a niche for advancement in future research and use of alternatives to presently used mineral oils. This research presents an overview on the preparation investigation and evaluation of the tribological properties of mahua oil mixed with ZnO nanoparticles at various concentrations. It can thus be concluded from the results attained that:

1. With increase in concentration of ZnO, an increment in flash point was observed. At optimum concentration of 0.75MO, the flash point rose to 233 $^{\circ}\text{C}$. The achieved flash points are comparable with that of synthetic engine oils.
2. The minimum COF was obtained for 0.75MO, making it the optimum concentration by weight, thus proving ZnO to be excellent at reducing friction between the mating surfaces. Minute fluctuations in load during experimentation led to variations in the COF.
3. The wear on the steel balls at different concentrations (0MO-1MO) were observed using an optical microscope. It was found that ZnO is not beneficial for wear reduction.

The scope of future research lies in gaining an understanding changes in the oil's structure on addition of ZnO and other nano-additives by employing techniques such as surface analysis, microscopy, and spectroscopy to investigate the changes. In addition, to assess the applicability of the mahua oil with ZnO nano-additives, researchers might explore how this lubricant performs under extreme conditions such as high temperatures, high pressures, and different loadings. This can help determine its suitability for industrial and automotive applications.

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