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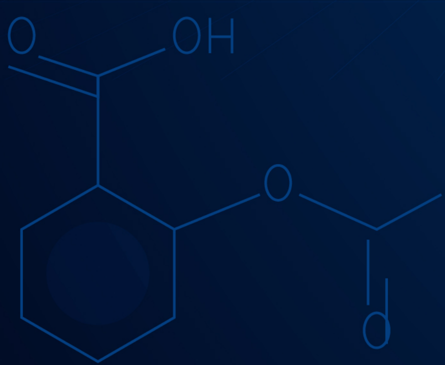

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Influence of Nano Copper Oxide Addition on the Thermal, Rheological and Tribological Properties of Locally Sourced Avocado Oil Based Nanofluids

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ABSTRACT

The goal of this study is to turn waste into value by producing lubricant from abandoned avocado fruits, as the globe looks for more environmentally friendly and sustainable lubricants than those derived from fossil fuels. In response to the growing need for high-performance, environmentally friendly products, we created a lubricant enriched with copper oxide nanoparticles (nCuO) using avocado oil as the foundation. The nano copper oxide was elucidated using XRD. To find out how these nanoparticles impact the oil's viscosity, thermal stability, and other important characteristics, we introduced trace amounts of nCuO at concentrations of 0.4 wt%, 0.8 wt%, and 1.2 wt% in our studies. The nanofluids underwent 3.5 hours of ultrasonication at 75°C. The formulation with 0.8 weight percent nCuO proved to be the most effective, with a higher flash point of 220°C and viscosities of 7.5 cSt at 40°C and 2.7 cSt at 100°C, all of which satisfied the ASTM D445 standards. Furthermore, as compared to pure avocado oil, the ideal formulation demonstrated a 13.6% decrease in the coefficient of friction (COF) and a 16.9% decrease in wear rate. Good low-temperature performance was indicated by the pour point of -1°C and the cloud point of 15°C, respectively. According to the thermal conductivity measurements, the oil's capacity for heat transport was improved by the addition of nCuO. These results imply that avocado oil-based nanofluids, especially those containing 0.8 weight percent nCuO, have great potential as high-performing, environmentally friendly substitutes for lubricating light-duty engines and other industrial uses.

INTRODUCTION

Rising awareness of environmental sustainability and dwindling fossil fuel reserves have driven a worldwide movement towards eco-friendly alternatives across various industries. The lubricant sector, in particular, faces mounting pressure to lessen its dependence on petroleum-based products due to their non-biodegradable nature and harmful impact on the environment. Conventional lubricants made from petroleum not only damage ecosystems but also accelerate the depletion of finite resources. To address these issues, bio-based lubricants especially those sourced from vegetable oils are increasingly recognized as promising substitutes. Avocado oil, known for its high viscosity index, outstanding thermal stability, and abundant fatty acid content, has gained attention as potential base oil for bio-lubricants. Its natural attributes make it ideal for uses that demand consistent lubrication at diverse temperatures. Nevertheless, similar to other vegetable oils, avocado oil struggles to meet the demanding performance standards of industrial applications especially in wear resistance, friction reduction and oxidative stability which have impeded the broader adoption of bio-lubricants in sectors with rigorous performance criteria. Nanotechnology presents a promising solution to these challenges. Integrating nanoparticles like nano copper oxide (CuO) into bio-lubricants has been proven to significantly improve their tribological properties. With its high surface area and distinct physical characteristics, Nano CuO enhances anti-wear and anti-friction qualities while offering excellent thermal conductivity.

These improvements position nano CuO as an excellent additive for enhancing the performance of lubricants derived from avocado oil, potentially closing the gap between environmental sustainability and industrial efficiency. Although the outlook is promising, there is limited comprehensive research on avocado oil-based lubricants formulated with nano CuO additives. Current studies mostly address either the base properties of avocado oil or the overall impact of nanoparticles on lubricant performance, which leaves a significant gap in understanding this unique combination fully. This study aims to fill that gap by developing an eco-friendly and high-performance lubricant using avocado oil as its base combined with nano CuO additives. By employing systematic formulation, thorough characterization, and extensive performance testing methods, our research seeks to advance sustainable lubricant technologies while providing a viable alternative to conventional options that align with both environmental and industrial standards.

Traditional petroleum-based lubricants, though effective, present considerable environmental challenges due to their non-biodegradability and the emission of harmful byproducts. With Nigeria being a signatory to the Paris Accord and international environmental regulations becoming stricter alongside increasing demand for

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sustainable industrial practices globally, reducing reliance on fossil fuel-based products has become crucial. This shift necessitates finding eco-friendly alternatives. However, bio-based lubricants made from vegetable oils often fail to meet performance requirements in heavy-duty or high-temperature applications, which hinder their widespread use. Large quantities of avocado fruit are being transported from Gembu in the Sardauna Local Government Area of Taraba State to other regions, especially Jalingo, the state capital. However, due to long travel distances and a lack of specialized transportation methods, many avocados spoil before reaching their destination markets. This results in waste that needs disposal and underscores an urgent need to transform this wasted produce into valuable products. Avocado oil is known for its high thermal stability and viscosity index which make it promising base oil for bio-lubricants. Nevertheless, its natural properties do not yet match up with the superior performance offered by synthetic lubricants alone. Advances in nanotechnology have shown that adding nano copper oxide (CuO) additives could significantly boost anti-wear qualities while reducing friction and enhancing thermal stability when used within avocado-based oils as lubricants. Despite these possibilities, there remains insufficient research on formulating such improved lubricant solutions featuring enhanced characteristics through nano scale CuO integration marking out crucial gaps needing bridging toward establishing sustainable high-efficiency lubrication standards systematically vetted via appropriate testing methodologies under various conditions.

In their study, Shafi *et al.* (2018), investigated the tribological performance of copper (Cu) nanoparticles mixed with avocado oil as a lubricant. They used a Pin-on-Disc tribometer to evaluate both the lubricating capabilities of pure avocado oil and the enhanced effectiveness when Cu nanoparticles were added. Stribeck curves were plotted for both base oil and oils containing Cu nanoparticles at concentrations of 0.5 wt. % and 1 wt%. The worn surfaces on aluminum alloy 6061 pins were examined using scanning electron microscopy (SEM). Their findings revealed that incorporating Cu nanoparticles reduced friction and wear noticeably. A minimum coefficient of friction was observed at a concentration level of 1 wt%, while specific wear rate reached its lowest point at the concentration of 0.5 wt%. This enhancement in overall tribological properties was attributed to the film-forming ability offered by adding these particles to bootstrap those advantages over ordinary base oils.

In another study by Guzman *et al.* (2018), they explored the tribological properties of copper nanoparticles. They incorporated these particles at concentrations of 0.3 wt% and 3.0 wt% into both mineral oil and synthetic ester base oils. The team utilized a pin-on-disk tribometer to measure the coefficients of friction (COF). From their investigations into friction and wear, they arrived at several conclusions: (1) they discovered that copper nanoparticles are unsuitable for use in synthetic ester base oil. The addition of these particles increased wear by 7.5 times, and there was no change observed in the friction behavior. (2) Incorporating copper nanoparticles into mineral base oil significantly decreased friction and wear. At a concentration of 0.3 wt% of copper nanoparticles, the reduction in wear was observed to be as much as 64%. Ultimately, they concluded that while copper nanoparticles are effective in mineral base oils, they do not perform well in synthetic base oils.

Akl *et al.* (2018) had examined the tribological properties of engine lubricants enhanced with nano-copper oxide as an additive. They incorporated copper oxide nanoparticles into Mobil 1 SAE15W-40SF engine oil at a concentration of 0.1% by weight. Two new engines were utilized for testing over a period of 1000 hours; one was supplemented with the nanolubricant while the other used standard lubricant. Periodic sampling resulted in twelve samples from each engine to assess wear particles using ASTM-D6595 spectrometry standards. Further analysis on selected oil samples employed Laser Net Fines Analyzer tests, revealing improved friction characteristics through decreased wear rates when nano-additives were applied. Specifically, reductions in aluminum, iron, and chromium wear particles were observed at rates of 48%, 11.5%, and 42%, respectively alongside average declines in specific types: cutting wear reduced by around 39%, severe sliding wear by approximately 36%, and fatigue wear by about 60%. Additionally, a notable decrease in engine temperature was achieved.

In their study, Rajaganapathy *et al.* (2021) investigated the tribological properties of vegetable oil enhanced with nanoparticles using a pin-on-disc tribometer. They utilized palm and brassica oils in their experiments, incorporating copper oxide (CuO) and titanium oxide (TiO2) nanoparticles as additives at weight percentages of 0.1% and 0.5%. The findings revealed that palm oil containing a lubricant sample with 0.5% CuO exhibited a significant reduction in both coefficient of friction and wear compared to other lubricant samples tested. Additionally, the viscosity and thermal conductivity properties increased as nanoparticle concentrations were raised within these vegetable oils.

MATERIALS AND METHOD

Materials

The materials used to carry out this research safely are listed below:

- Waste Avocado fruit.
- Copper acetate
- Sodium hydroxide
- Oleic acid
- Ethanol
- Phosphoric acid
- Water
- Potassium Hydroxide
- Sodium Hydroxide

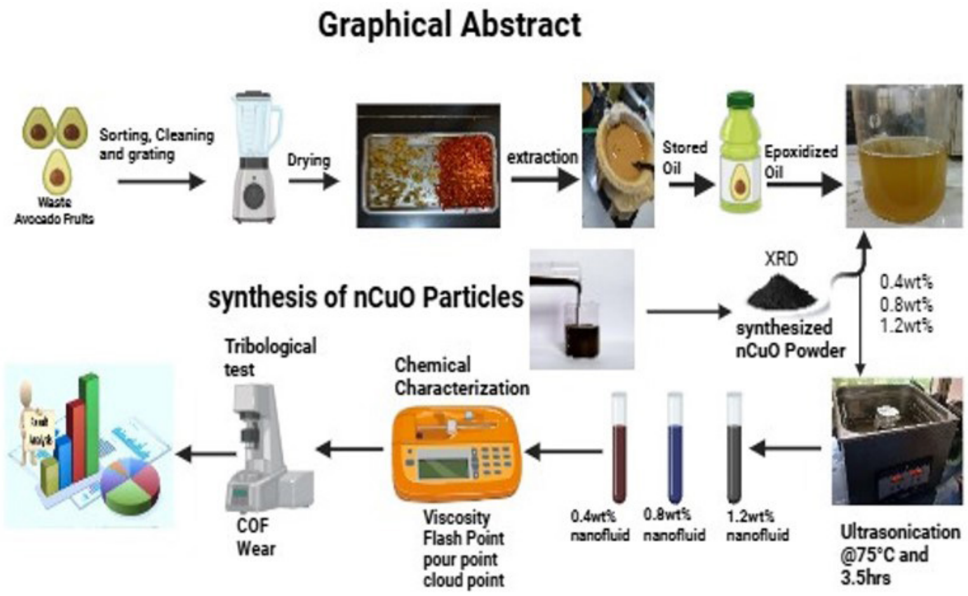

Figure 1: Graphical Abstract

Method

Preparation of Base Oil

Waste avocado fruits were collected from Gembu and Jalingo. They fruits were cleaned, with the stones separated from the skins. The pulp was placed in a blender and bitten until it becomes thick paste. The paste was then thin spread onto a tray to ensure a wider surface area. The tray was lodge into an oven initially set at the temperature of 45^{0}C and held for 5-6hrs until it turns dark green. The dark green paste was transferred in small batch onto thin cheesecloth, while applying pressure, the oil is extracted slowly into a cleaned container. This procedure was repeated until 1000cm^3 of avocado oil was obtained. Finally, the extracted oil is transferred into plastic bottle and labeled AvoOil for storage. This process is painstaking and the oil yield is small as compared to the industrial process.

Purification of Base Oil

Determination of the Acid Value

A digital balance was used to weigh 1.11g of base oil, while another measurement recorded 0.56g of KOH, which was then dissolved in 100ml of water to create a 0.1 molar solution. This KOH solution was titrated against the oil until the endpoint indicated by the oil turning pink was reached at a volume of 2.7 ml, determining what is known as either the acid value or neutralization number.

Determination of % Total Fatty Acid

The %TFA was obtained from equation 1 below,

%TFA= (Total Fatty Acid)/2 (1)

Preparation of Copper Oxide Nanoparticles

An aqueous solution containing 0.02 mol of copper acetate was prepared in a round-bottom flask. To this, 1 ml of glacial acetic acid was added and the mixture heated to 100°C with constant stirring using magnetic stirrer. Subsequently, 0.4 g NaOH was gradually introduced into the warmed solution until its pH reaches neutral (pH = 7), resulting in a copious formation of black precipitate. This precipitate was then subjected to centrifugation and washed four times using deionized water before being air-dried for up to one day. To enhance surface functionality, CuO nanoparticles were modified by adsorbing oleic acid as a carboxylate onto their surfaces; this chemical modification facilitates superior integration within blends acting as solid-liquid suspensions ultimately fostering strong intermolecular forces at interfacial zones according Van Der Waals theory by minimizing molecular agglomerations. This was achieved by dispersing 5g of nanoparticle into a preheated 100ml of ethanol at 60^{0}C. The solution was then stirred for 15 minutes to attain even dispersion, and then 0.25 ml oleic acid was added and stirred for 2h. The solution was centrifuged to separate the ethanol-oleic acid mixture. The resulting nanoparticles were oven dried at 80 ^{0}C to remove the excess surfactant as adopted from (Oparanti *et al.*, 2021).

Bio NanoLubricant Preparation (BNnL)

The nano-lubricant was formulated into one sample by dispersing the treated CuO nanoparticles (NP) into the purified avocado fruit oil in weight percentages from 0.4 wt. % and stirred. The dispersion of nanoparticles in the base oil was done by ultra-sonication for 3.5h, at fixed interval of 30 minutes throughout the process. The sonication was conducted at 59 Hz frequency, 100% power, and temperature of 75 ^{0}C. The precipitates at the bottom of the beaker were checked to make sure that the dispersion process is going in accordance with the protocols by (Lawal *et al.*, 2023). After the sonication, the blend was vacuum dried for 24hrs to exclude the effect of gas bubbles and moisture generated during the process. The Biolubricant produced was stored into a bottle and labeled AvonCuO4.

Evaluation of Chemical Properties

XRD of Nano Copper Oxide

The phase composition of the nano copper oxide powders were investigated through data that were collected on X-ray powder diffraction (XRD) patterns machine (Rigaku Miniflex diffractometer operating a copper tube at λ=1.5418A, which was generated at a voltage of 40 KV and a current of 30 mA.

Viscosity Measurement

Kinematic viscosity at 40°C and 100°C was measured using a Brookfield DV-II+ Pro Viscometer following ASTM D445. Viscosity index was calculated based on the measured values.

Cloud Point and Pour Point Measurement

The cloud point and pour point were determined using ASTM D2500 and ASTM D97, respectively.

Cloud Point

Visual observation of wax formation while cooling the nanofluid.

Pour Point

The lowest temperature at which the nanofluid remained flowable.

Flash Point Measurement

Flash point was measured using the Pensky-Martens closed-cup apparatus according to ASTM D93.

Tribological Test

The pin-on-disk Anton Paar tribometer, which measures friction and wear with extreme precision under controlled loading circumstances, was chosen to evaluate the tribological characteristics of the nanofluids. The test was devised to assess the impact on wear behavior and friction of varying quantities of copper oxide (CuO) nanoparticles distributed in avocado oil.

Friction and Wear Measurements

During the tribological test, the following properties were measured:

Coefficient of Friction (COF)

The COF was continuously recorded using the Anton Paar tribometer's high-resolution friction force sensor (0.06 mN resolution), which accurately captured small variations in frictional forces throughout the test.

Wear Scar Diameter

After each test, the wear scar on the stationary balls was measured using optical microscopy. This allowed for an estimation of the wear resistance of the nanofluids.

RESULTS AND DISCUSSION

XRD pattern of the nCuO particles

From figure 2 below, the crystalline planes of nano copper oxide, or nano CuO, are generally represented by discrete peaks in the X-ray diffraction (XRD) pattern. The peaks at 2θ values of 36° and 39° in a nano CuO XRD pattern are particularly interesting to examine because they can reveal information about the sample's phase composition and crystal structure. Prominent peaks at 36° and 39° usually suggest that monoclinic CuO makes up the majority of the sample's composition. The lack of further prominent peaks may indicate phase purity, which would indicate the presence of none or very little other copper oxides (such as Cu2O or metallic copper).

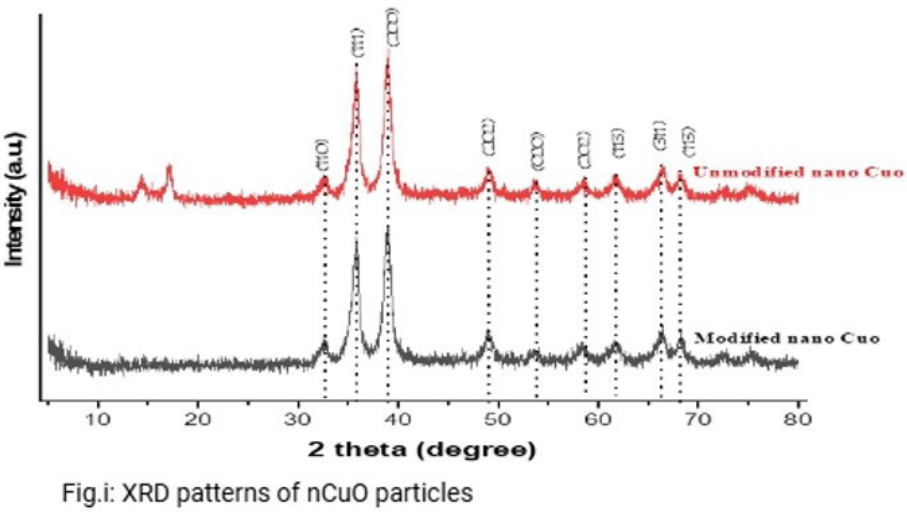

Figure 2: XRD patterns of nCuO particles

The size of the CuO nanoparticles can be inferred from the peak broadening. Larger crystallites are indicated by sharper peaks, and smaller nanocrystallites are indicated by broader peaks. The degree of crystallinity can be inferred from the relative intensities of these peaks in relation to other peaks in the XRD pattern. Relative to the background noise, high-intensity peaks indicate well-ordered crystal formations.

Kinematic Viscosity

The kinematic viscosity of the nanofluids was measured at both 40°C and 100°C for three different concentrations of nCuO: 0.4 wt%, 0.8 wt%, and 1.2 wt%. The results are summarized in Table 1 and illustrated in Figure 3.

Table 1: Viscosity of nCuO nanofluid at different concentrations

Conc. (wt%)	Viscosity @40°C	Viscosity @100°C
0.4	6.2	2.1
0.8	7.5	2.7
1.2	8.9	3.5

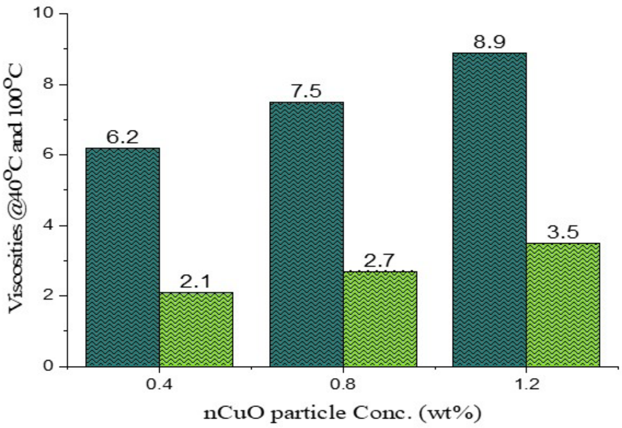

Figure 3: Viscosities of nCuO particles at different Conc

Figure 3 illustrates a steady rise in viscosity with increasing nCuO concentration. At 40°C, the viscosity rose to 8.9 cSt at 1.2 wt% from 6.2 cSt at 0.4 wt%. Likewise, across the same concentration range, the viscosity at 100°C increased from 2.1 cSt to 3.5 cSt. These findings support the notion that the presence of nanoparticles, particularly at greater concentrations, increases fluid resistance to flow. These viscosity values are within permissible bounds for lubricants, per ASTM D445, particularly for industrial applications where temperature control is crucial. Ali *et al.* (2015) showed a similar trend in which the addition of metal oxide nanoparticles raised the viscosity.

Cloud and Pour Point

The cloud and pour points of the nanofluids were measured to assess the low-temperature performance of the fluids. Table 2 and Figure 4 summarize the results.

Table 2: Cloud and Pour Points of nCuO Nanofluids

Conc. (wt %)	Cloud Point in °C	Pour Point in °C
0.4	15	-1
0.8	13	-3
1.2	11	-4

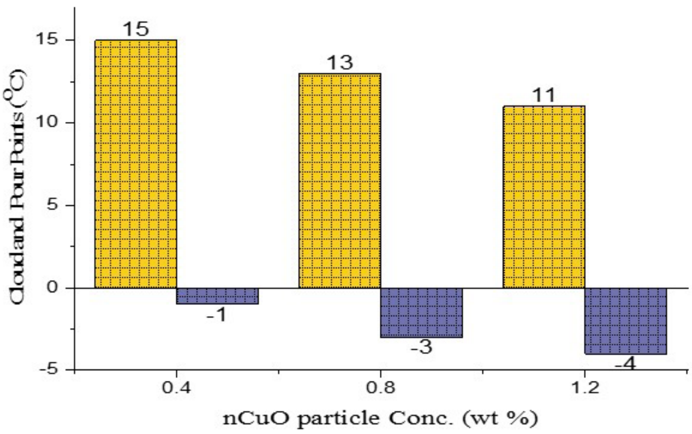

Figure 4: Cloud and Pour Points of nCuO Nanofluids

Figure 4 illustrates how cloud and pour points gradually decrease as nCuO concentration rises. The cloud point was 15°C at 0.4 weight percent and 11°C at 1.2 weight percent. The pour point also dropped, going from -1°C at 0.4 wt% to -4°C at 1.2 wt%. These decreases imply that raising the nCuO concentration improves the fluid's low-temperature performance and increases its suitability for cold situations. The observed pour points satisfy ASTM D97 specifications for hydraulic fluids and industrial lubricants that must continue to function at lower temperatures. The findings of Sedighi *et al.* (2014), who found that metal oxide nanoparticles decreased the pour point of oil-based fluids, are likewise consistent with this trend.

Flash Point

The flash point is an important safety measure for fluids that operate at elevated temperatures. Table 3 and Figure 5 summarize the results of the flash point measurements for the nanofluids.

Table 3: Flash Points of nCuO Nanofluids

Conc. (wt %)	Flash Point (oC)
0.4	217
0.8	224
1.2	231

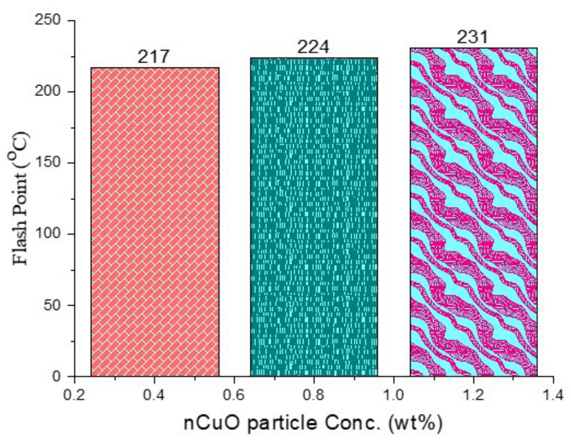

Figure 5: Flash Points of nCuO Nanofluids

The flash point rose as the concentration of nCuO increased, as Figure 5 above illustrates. From 217°C at 0.4 wt% to 231°C at 1.2 wt%, the flash point increased. This increase in flash point suggests that as nanoparticle concentration rises, so does the nanofluid's thermal stability. For industrial applications, like engine oils or heat transfer fluids, that need stability at higher operating temperatures, these values are acceptable, under ASTM D93, which describes the closed-cup test procedure for flash point determination. Vajjha and Das (2009) observed a similar trend, with metal oxide nanoparticles improving base oils' thermal stability.

Tribological Properties

Table 4: Tribological properties of Nanofluid

Sample	COF	Wear Scar Diameter (mm)
Pure Avocado Oil	0.096	0.45
0.4wt% nCuO Nanofluid	0.081	0.38
0.8wt% nCuO Nanofluid	0.073	0.32
1.2wt% nCuO Nanofluid	0.078	0.35

The friction coefficient is marginally lower at 0.4 weight percent nCuO than base oil, indicating a minimal degree of lubrication enhancement. More nanoparticles suspended in the base fluid at 0.8 weight percent cause the friction coefficient to further decrease, improving boundary lubrication. Because of an even thicker coating of protective nanoparticles that lessens direct metal-to-metal contact, the friction coefficient for the 1.2 weight percent sample is at its lowest. This decrease is in line with earlier research (Li *et al.*, 2015), which demonstrates that friction in nanofluids is much reduced at increasing nanoparticle concentrations.

It is clear from the data that tribological performance improves with increasing nCuO concentration. The wear scar diameter, wear rate, and lowered frictions are all well-balanced in the 0.8 weight percent sample. The 1.2 weight percent sample, on the other hand, had the lowest wear rate, friction coefficient, and wear scar diameter, offering the best overall performance. When taking into account both tribological and economic factors, 0.8 weight percent may be the best option because it offers significant improvement without the higher costs and possible handling complications associated with a higher concentration of nanoparticles, even though 1.2 weight percent offers superior tribological performance.

CONCLUSION

The potential of avocado oil-based nanofluids augmented with nano copper oxide (nCuO) as a workable substitute for traditional lubricants is well demonstrated by this study. The viscosity, tribological performance, and thermal stability of the lubricant were all markedly enhanced by the addition of nCuO at an ideal concentration of 0.8 weight percent. According to the findings, the improved formulation significantly reduced the coefficient of friction and wear rate when compared to pure avocado oil, in addition to showing a higher flash point and excellent viscosity characteristics. These results demonstrate how well nano additives work to improve the performance of bio-lubricants, which qualifies them for use in high-performance lubrication applications. The combination of the advanced qualities of nCuO with avocado oil, a renewable and biodegradable resource, is in line with the growing need in a variety of industrial sectors for environmentally friendly lubricants.

Additionally, this work opens the door for future studies into the stability and long-term performance of avocado oil-based nanofluids and advances our knowledge of the synergistic impacts of nanotechnology on bio-lubricants. In summary, this research highlights the significance of creative methods for improving environmentally friendly lubrication technology, encouraging a change in the lubricant sector toward more environmentally friendly options.

Recommendations

i. It is recommended to explore additional concentrations of nCuO beyond 0.8 wt% to identify any potential enhancements in lubrication performance and thermal stability. This may help determine the optimal concentration for specific applications.

ii. Conduct long-term stability and aging studies of avocado oil-based nanofluids to evaluate their performance over extended periods. This will help ascertain their viability for real-world applications and identify any degradation issues that may arise.

iii. Implement field tests in various mechanical systems, such as light-duty engines and industrial machinery, to assess the performance of the optimized nanofluids under operational conditions. This will provide insights into their practical effectiveness and durability.

iv. Investigate the environmental impact of using avocado oil-based nanofluids in comparison to conventional lubricants. This assessment should include studies on biodegradability and toxicity to ensure that these formulations align with sustainability goals.

v. Consider investigating other bio-based oils as potential base fluids for nanofluid formulations. This could expand the range of sustainable lubricant options available and enhance the understanding of how different oils interact with nano additives.

vi. Encourage collaboration with industry stakeholders to facilitate the adoption of advanced bio-lubricants. This partnership can foster innovation and support the development of new technologies that enhance the performance and sustainability of lubricants.

vii. Educational Outreach: Promote awareness and education on the benefits of using bio-lubricants, particularly those enhanced with nanotechnology, within both the industrial sector and academic circles. This will help drive interest and investment in sustainable lubricant solutions.

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