*lubricants*

MDPI

*Article*

# Halloysite Reinforced Natural Esters for Energy Applications

**Jose Jaime Taha-Tijerina [1,*], Karla Aviña [2], Victoria Padilla-Gainza [3] and Aditya Akundi [1]**

[1] Department of Informatics and Engineering Systems, The University of Texas Rio Grande Valley, Brownsville, TX 78520, USA
[2] Engineering Department, Universidad de Monterrey, Av. Ignacio Morones Prieto 4500 Pte., San Pedro Garza García 66238, Mexico
[3] Department of Mechanical Engineering, The University of Texas Rio Grande Valley, 1201 West University Drive, Edinburg, TX 78530, USA
* Correspondence: jose.taha@utrgv.edu

**Abstract:** Recently, environmentally friendly and sustainable materials are being developed, searching for biocompatible and efficient materials which could be incorporated into diverse industries and fields. Natural esters are investigated and have emerged as eco-friendly high-performance alternatives to mineral fluids. This research shows the evaluations on thermal transport and tribological properties of halloysite nanotubular structures (HNS) reinforcing natural ester lubricant at various filler fractions (0.01, 0.05, and 0.10 wt.%). Nanolubricant tribotestings were evaluated under two configurations, block-on-ring, and 4-balls, to obtain the coefficient of friction (COF) and wear scar diameter (WSD), respectively. Results indicated improvements, even at merely 0.01 wt.% HNS concentration, where COF and WSD were reduced by ~66% and 8%, respectively, when compared to pure natural ester. The maximum significant improvement was observed for the 0.05 wt.% concentration, which resulted in a reduction of 87% in COF and 37% in WSD. Thermal conductivity was analyzed under a temperature scan from room temperature up to 70 °C (343 K). Results indicate that thermal conductivity is improved as the HNS concentration and testing temperature are increased. Results revealed improvements for the nanolubricants in the range of 8–16% at 50 °C (323 K) and reached a maximum of 30% at 70 °C (343 K). Therefore, this research suggests that natural ester/HNS lubricants might be used in industrial applications as green lubricants.

**Keywords:** natural ester; halloysite; energy; wear; thermal conductivity

check for updates

**Citation:** Taha-Tijerina, J.J.; Aviña, K.; Padilla-Gainza, V.; Akundi, A. Halloysite Reinforced Natural Esters for Energy Applications. *Lubricants* **2023**, *11*, 65. https://doi.org/10.3390/lubricants11020065

Received: 19 January 2023
Revised: 2 February 2023
Accepted: 3 February 2023
Published: 5 February 2023

**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

## 1. Introduction

For more than a century, the primary source of energy has been fossil fuels. Petroleum-based fluids are used as lubricants and coolants in electronic or electrical equipment, machinery, transportation fields, and power transmission systems, among others [1–5]. Research and industrial focus are on critical challenges to reduce pollution and mitigate global warming and climate change, among others [6]. Due to their poor biodegradability, eco-toxicity, and extremely likely carcinogenic characteristics, these materials exhibit environmental concerns [7,8].

Among the diverse drawbacks to be resolved about these materials are how to properly dispose of them and how to hinder products from impacting negatively on both health and the environment [9–11]. Additionally, due to the forthcoming scarcity of petroleum reserves and the rise in lubricant disposal costs, among other factors, the importance of incorporating and applying renewable energies has grown significantly [12–14]. Consequently, interest in natural lubricants has increased recently.

Technology is moving forward very fast with high efficiency, miniaturization, and novel equipment requirements and developments. The increasing demand for higher-performance of conventional fluids and lubricants has been crucial for diverse industrial manufacturing processes. Energy applications such as power transmission systems, transportation vehicles, and battery subsystems require materials which would be lighter but

with much higher mechanical properties, which require higher processing loadings, need a hefty lubrication regime due to higher wear and friction among base substrates and tooling.

Recently, several investigations have been performed by scientists and industry to find sustainable and eco-friendly alternatives [15–19]. The usage of these materials has been emerging and is more common in certain environmentally-sensitive fields [1–4,20–22]. Natural esters serve as an alternative solution against petroleum-based lubricants due to their non-toxic attributes and specific characteristics as renewable and eco-friendly. Furthermore, these fluids have been proven to diminish hydrocarbon and $CO_2$ emission levels [23], which is why their application in diverse systems and subsystems has recently increased in the industry [24]. Natural esters also possess excellent lubricity [25,26], high thermal conductivity [27,28], compatibility with additives, relatively low production costs [29], biodegradability, and high fire and flash points [30,31], comparable to mineral lubricants and fluids [26,32–34]. In general, these materials are defined as fatty acids, which contain an extended aliphatic chain in addition to the ester function, which determines the mechanical and chemical characteristics of the lubricants [35]. Unsaturated can display less viscous performance but are more susceptible to oxidation [35,36], leading to an increase in viscosity and degradation, therefore affecting the tribological, thermal, and other characteristics of the lubricant [37].

Regardless of all the excellent attributes of natural esters, the application of stand-alone material had hit their tribological and thermal transport limit. Advancements in science and nanotechnology provide the potential to enhance the performance of fluids and lubricants reinforced by nanostructures additives. Since the mid-1990s, the exploration of the incorporation of myriad solid ultrafine particles within conventional fluids and lubricants has been investigated [38]. These nanostructures possess superb characteristics compared to base fluids and lubricants, and when they are homogenously dispersed or formulated within conventional materials, there is a significant enhancement in their properties.

Lubricants play a paramount role in reducing the wear and friction of mechanical pairs or contacts as well as in internal components and mechanisms of machinery and devices. The most significant enhancements and advantages of applying nanoparticles as reinforcement are the reduction of coefficient of friction (COF) and wear. Therefore, reducing machining cutting forces and power consumption [39]. One more key feature is the improvement of surface roughness or finishing of processed components and products, having a significant impact on quality and secondary processing. An additional benefit for tools and components of machinery by applying nanoreinforced fluids and lubricants is that they also work as thermal dissipators of the heat generated by material interactions or mechanisms working in contact [40–43].

For instance, Rapoport et al. results demonstrated that $WS_2$ nanostructures reduced the COF of paraffin lubricant by 30% [44]. Kumar et al. [45] investigated natural oil blends (sunflower oil:rice bran oil) reinforced with CuO nanostructures as an additive, and it was observed that at 0.04 vol.% of nanoparticles resulted in the greatest improvements of 6% and 10% in WSD and COF, respectively when compared to conventional material. Omrani et al. [46] studied vegetable oil with the addition of nano-graphene by sliding contact, observing improvements in COF of ~84%. Karthikeyan et al. [47] performed pin-on-disk evaluations for olive- and castor-oil-based nanolubricants reinforced with 0.7 wt.% of molybdenum disulfide ($MoS_2$). A wear reduction of 21% and 37% for these vegetable nanolubricants, respectively. Potential uses for nanomaterials in the automotive industry with natural-based lubricants from bio-lubricants and nanostructures as additives were found by Yadav et al. [48]. Important wear scar and COF reductions in vegetable nanolubricants were also observed by Lim et al. [49], Gupta et al. [50], and Taha et al. [51]

The importance of thermal management as heat transport in industrial and energy segments is a key topic to work on with the aid of nanofluids. Since base fluids and lubricants have very limited thermal conductivity, researchers endeavor to strengthen this characteristic by incorporating diverse types, morphologies, and concentrations of nanostructures into conventional materials and have shown good enhancements. Nevertheless, a

crucial aspect that must be addressed to preserve their thermophysical characteristics after production for an extended period is the stabilization of nanofluids and nanolubricants.

Jacob et al. [52] investigated the thermal conductivity of a natural ester (soybean lubricant) by adding $Al_2O_3$ nanostructures. They observed an enhancement of 6.3% and 10.3% at 0.04 wt.% and 0.1 wt% filler fraction, respectively. Karthikeyan et al. [47] studied $MoS_2$ nanostructure effects on vegetable lubricants (olive and castor oils). Both exhibited an improvement of 28% and 21%, respectively, at 0.7 wt% filler fraction. Farade et al. [53] developed cottonseed nanofluids with graphene oxide (GO) nanosheets at diverse concentrations varying from 0.01 wt.% to 0.05 wt.%. Thermal conductivity was improved at each level of filler fraction, and the value increased up to 36.4% at 0.05 wt.%. In another research on 2D nanostructures, Taha et al. [28] evaluated hexagonal boron nitride (h-BN), $MoS_2$, and their combination in a natural ester media. In their study, the improvement was increased with the nanostructure's filler fraction. The greatest improvement was at 323 K. It was shown that the incorporation of 2D nanomaterials enhanced the thermal transport performance in the 20% to 32% range. Similarly, Khan et al. [54] reported positive effects on the thermal transport behavior of $TiO_2$ and GO nanostructures within natural and synthetic ester lubricants.

Halloysite nanotubular structures (HNS) possess high modulus (140 GPa), allowing a high loading resistance under extreme pressure conditions [55]. These nanostructures are emerging as natural biocompatible minerals [56,57], readily available worldwide [58], with low-cost (about USD 3000 per ton) [59,60], corrosion protection [61,62], non-toxic and non-conductor resource as alternative "green" nanoreinforcement to improve tribological and thermal transport properties of conventional fluids and lubricants. They have been employed as mechanical reinforcing of polymer matrices and composites [63–65], improving tribological performance and other characteristics. Nevertheless, HNS has proven beneficial in characteristics of diverse systems and media as reinforcement; scarcity of research coupled with natural esters and lubricants has not been deeply explored.

For instance, for tribological studies, Ahmed et al. [66] studied the characteristics of castor oil by incorporating HNS. They were able to observe maximum reductions of 21.3% in wear scar diameter (WSD) and 28.2% in COF at 1 wt.% reinforcement. Qin et al. [67] investigated the effects of halloysite employing a ball-on-disk tribometer. Interesting results were shown where halloysite-containing lubricant exhibited good friction reduction of 34%, primarily attributed to a tribofilm formation of the nanostructures and also to the halloysite rolling role in the contact surface of the specimens [68]. In a similar work on pongamia lubricant, Suresha et al. [69] observed a wear and friction reduction of 10% and 14%, respectively, with the addition of 1.5 wt.% of HNS.

On the thermal aspect, Alberola et al. [70] evaluated the thermophysical behavior of halloysite nanofluids, showing a thermal conductivity increase of 8% for the 5 vol.% nanofluids at 80 °C. Similarly, Ba et al. [71] explored the effects on the thermal transport performance of halloysite nanofluids, where an increase of 18% for 1.5 vol.% was observed compared to the conventional fluid. In another investigation, Ba et al. [72] analyzed the pool boiling heat transport behavior of nano halloysite / deionized water (DI) fluids. Their findings revealed that increasing the reinforcement filler fraction leads to improved thermal performance. At 0.05 vol.% nanofluid, a greater improvement of ~6% at moderate heat flux (HF) was achieved, indicating that HNS is a promising material for applications that entail heat transfer performance.

In this work, the tribological behavior of HNS reinforcing natural ester lubricant at various filler fractions (by weight) is evaluated. Temperature-dependent measurements over ranges up to 70 °C (343 K) were also analyzed.

## 2. Materials and Methods

Natural ester—Envirotemp® FR3™ (Cargill Industrial Specialties—Minneapolis, MN, USA) (Table 1) served as base material to develop various nanolubricants reinforced with hollow rod-shaped HNS (Sigma-Aldrich Co., St. Louis, MO, USA. CAS #: 1332-58-7)

(Table 1) at various filler fractions: 0.01, 0.05, and 0.10 wt.%. Scanning electron microscopy (Carl Zeiss, Sigma VP, NY, USA) was employed to examine the size and morphology of HNS (Figure 1). From SEM images, it can be observed a tubular rod-type shape of the HNS. The measured lengths of these nanostructures have a maximum of 589 nm and 120 nm as a minimum. Average length was 302 nm with a standard deviation of 83 nm. The average measured diameter was 61 nm ± 18 nm, where the minimum and maximum diameters were 28 nm and 96 nm, respectively.

**Table 1.** Material characteristics.

| **Materials** | **Properties and Characteristics** | |
|---|---|---|
| **Conventional Lubricant** | **Density (20 °C)** | **Kinetic Viscosity ($mm^2/s$)** |
| Natural ester | 0.92 $g/cm^3$ | 190 @ 0 °C; 32–34 @ 40 °C; 7.7–8.3 @ 100 °C |
| **Nanostructures** | **Properties** | |
| Halloysite (HNS) | Chemical formula: $H_4Al_2O_9Si_2$. $2H_2O$<br>Specific gravity: 2.57 $g/cm^3$<br>Molecular weight: 294.19 g/mol<br>Size–Length: 302 nm ± 83 nm; Diameter: 61 nm ± 18 nm | |

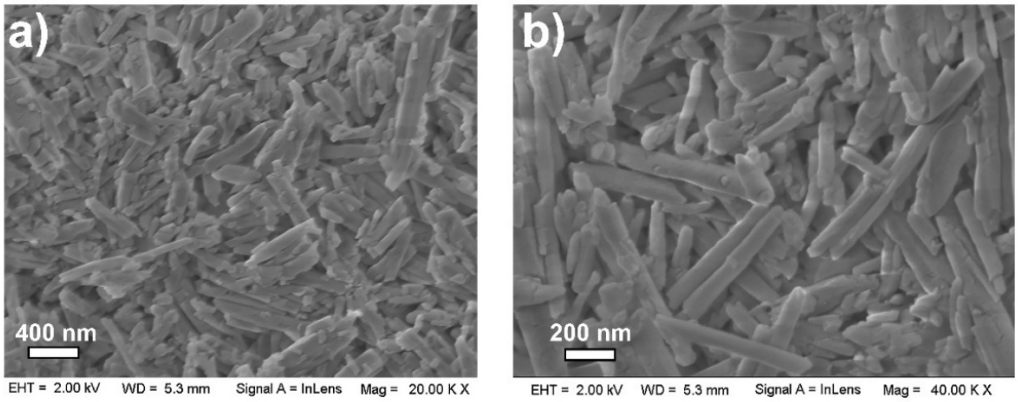


**Figure 1.** HNS morphology at (**a**) 20 KX, and (**b**) 40 KX magnifications.

Table 1 depicts the general properties and characteristics of the natural ester, nanostructures, and specimens for the tribological tests.

*Nanolubricants Preparation*

Homogeneous nanolubricants were prepared by a two-step methodology dispersing HNS within the natural ester lubricant. For each set of nanolubricants 42 mL glass containers were prepared at 0.01, 0.05, and 0.10 wt.%. Water bath ultrasonication (Branson ultrasonic homogenizer model 5510—Danbury, CT, USA, 40 kHz) was used for extensive time (8 h). According to the following methodology, a constant temperature (24 °C) was kept in the sonicator water bath to prevent the nanostructures from clumping together, causing fast sedimentation. All glass vials specimens were kept on a shelf for about 15 days without significant particle sedimentation (Supplementary Materials). Preliminary sonication of each sample for 15 min was performed before the experimental testing.

## 3. Experimental Details

### *3.1. Tribological Evaluations*

For tribological measurements, COF and WSD were analyzed with a tribotester in a four-ball configuration based on the ASTM D 4172 methodology. This tribosystem employs three fixed steel balls on a cylindrical container (fluid cup) and one more on top of them (Figure 2), applying a load P = 40 kgf (392 N). A temperature of 75 °C was employed for the

evaluated nanolubricants; the upper ball rotates at a specific rotational speed n = 1200 rpm during 1200 s. An AISI 52100 steel is used for the ball's material (60 HRC and 12.7 mm in diameter). This tribotester configuration is widely applied to determine the wear properties of lubricating fluids and oils in sliding metal-metal applications. The anti-wear performance of nanolubricants was tested with the block-on-ring configuration at room temperature (24 °C), 3000 N load, 200 rpms, and time of 1200 s. The evaluated nanolubricants were deposited in a fluid pool, allowing constant lubrication while the test ring was rotating. For these evaluations, the blocks used were AISI 1018 steel with 79 HRB hardness, and the rings were AISI D2 tool steel with 61 HRC hardness. To obtain statistically significant results, four replicas were measured for each set of nanolubricants. Worn scars of steel components were analyzed by a 3D surface profiler microscope measurement system (Keyence Corp Precision, Itasca, IL, USA) and a TescanVega 3SB Scanning Electron Microscope (SEM).

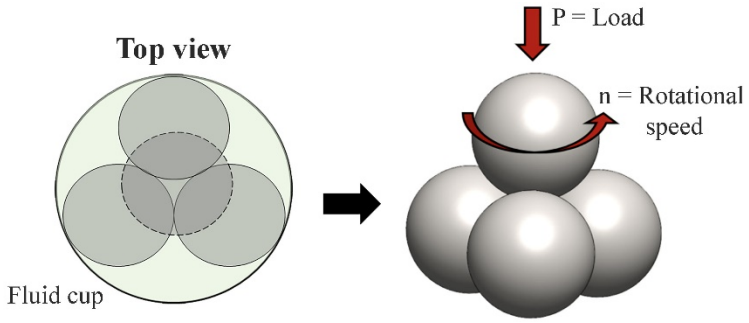


**Figure 2.** Schematic of tribotesting four-balls setup.

### *3.2. Thermal Conductivity Evaluations*

Thermal conductivity evaluations of HNS nanolubricants were evaluated with a TEMPOS thermal analyzer device and KS-3 sensor probe (METER GROUP, Inc., Pullman, WA, USA) following the transient hot-wire (THW) methodology. A temperature-dependence scan up to 70 °C (343 K) was performed. Before thermal measurements, 20 min ultrasonication was applied to the samples. Above room temperature evaluations, before measurements, each set of specimens was maintained at least 12 min in thermal equilibrium. This procedure promotes the preparation of stable homogeneous nanolubricants, which are then evaluated. The obtained thermal conductivity values were compared with the conventional natural ester ($k_0$). The effective thermal conductivity of the nanolubricants is $k_{eff}$. For each set of specimens, at least six measurements were obtained, reporting the average values with error bars as standard deviation.

## 4. Results and Discussion

### *4.1. Tribological Performance*

The tribological behavior of natural ester lubricant was analyzed with reinforcement of HNS. Figure 3 depicts COF curves recorded during block-on-ring evaluations being consistent with the testing conditions for all the samples. The tribotests were performed under lubrication with natural ester and HNS nanolubricants. It was observed that the addition of diverse filler fractions of HNS resulted in a profound effect of friction reduction during the tribological evaluations.

The initial measured COF for evaluated lubricants was in the vicinity of 0.085. After the first minutes of testing, the HNS nanolubricants showed a significant decrease in COF. Lower COF represents less energy loss caused by contact pairs friction. At merely 0.01 wt.% concentration, it was observed a COF value of 0.075, with maximum improvement for 0.05 wt.% of 0.029. As can be observed, after the complete run of experiments, the HNS nanolubricants showed superb behavior, reaching the greatest improvement of 87% at 0.05 wt.%, compared to pure lubricant.

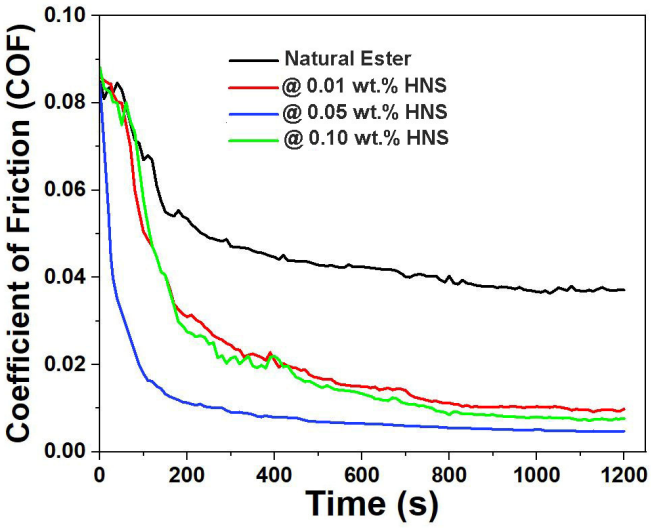


**Figure 3.** Block-on-ring evaluation for HNS nanolubricants showing COF versus time.

Figure 4 shows the average COF values for nanolubricants. COF was reduced from 0.042 for the natural ester to 0.015 with 0.01 wt.% HNS. The best improvement was observed at 0.05 wt.% concentration, where COF is 0.006. It is also shown an increase in these properties at higher filler fractions because, at higher concentrations and increasing temperature, nanostructures tend to agglomerate, decreasing the lubrication performance [73,74]. The lower improvement was shown at 0.10 wt.% filler fraction; this can be attributed to a higher concentration of nanostructure agglomeration. Nanostructures deposit in the surface depressions; hence, as smaller the size of the nanostructures, the more likely to creep into those gaps, minimizing contact and friction is mend to reduce the roughness and also to withstand higher loads [39]. Previous research of sunflower and soybean nanolubricants with $SiO_2$ displayed a reduction in the COF of 10% and 26% in comparison. [34].

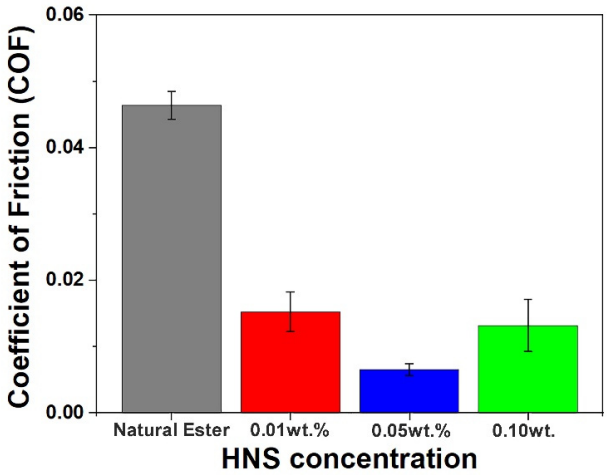


**Figure 4.** Average COF results for natural ester reinforced with HNS nanostructures.

Figure 5 depicts SEM of the scars of worn steel balls for conventional natural ester and HNS nanolubricants at various filler fractions. The average diameters of the three bottom steel balls were used to calculate the WSD, as shown in Table 2. When HNS were incorporated into natural ester, 188 μm scar diameter was measured, showing a decrease of 8.29%, with the highest reduction of 37.56% (128 μm) at 0.05 wt.%. The highest concentration, 0.10 wt.% of HNS, showed a reduction of 28.29%. This minor decrease in the lubrication properties for higher nanostructure filler fraction could be attributed to the tendency of agglomeration of nanostructures, as was also observed in the COF evaluations.

In accordance with Wu et al. [75], the experimental temperature has a direct impact on the lubricating mechanisms; higher evaluation temperatures result in a decrease in viscosity, which could affect the formation of the lubricant tribofilm between contact surfaces.

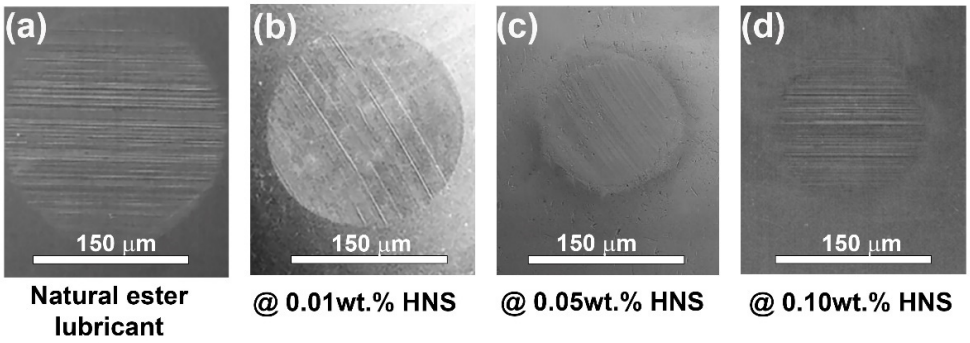


**Figure 5.** SEM of steel ball wear for: (**a**) natural ester, and (**b**–**d**) HNS nanolubricants.

**Table 2.** WSD of HNS nanolubricants by ASTM D5183.

| Lubricant | WSD (μm) (Reduction %) |
|---|---|
| Natural ester | 205 |
| @ 0.01 wt.% HNS | 188 (8.29%) |
| @ 0.05 wt.% HNS | 128 (37.56%) |
| @ 0.10 wt.% HNS | 147 (28.29%) |

For anti-wear conditions, tribological mechanisms for HNS play a paramount role in the lubricant characteristics and properties. It must be mentioned that the characteristics and performance of the lubricant are significantly influenced by these nanostructures. The size and morphology of HNS have considerable effects on the properties and characteristics of conventional lubricants, such as have been observed with other rod-type structures such as single/multi-wall carbon nanotubes (CNTs). These peculiar structures act by rolling and sliding under transversal sliding forces action, playing a bearing-like function among contact components and pairs in friction, changing the sliding friction into rolling friction and enhancing the anti-wear characteristics of the material. According to Zhang et al. [76], friction reduction is not promoted by the action of the nanorods themselves working as molecular bearings. Instead, a vortex structure is developed during the friction process, causing the rolling friction behavior. In this case, HNS has a load-bearing mechanism that promotes the reduction of wear and lowers COF [77,78]. Additionally, the smoothing and mending effects of nanostructures after being deposited on contact areas (COF reduction [39]) and the rolling-sliding effect by rod-type nanostructures (decreasing WSD [79,80]) could affect the tribological performance.

### *4.2. Thermal Performance*

The Brownian motion of nanostructures within a fluid or lubricant is mostly governed by the nanofluid thermal transport properties (thermal conductivity). Shafi et al. [81] described how the Brownian motion of nanostructures enhances the thermal transport behavior of a fluid or lubricant; first, nanostructures collide and create a solid- -solid conduction mode of heat transfer (percolation channel formation). Then, thermal conductivity is enhanced by a convective heat transfer mode.

Figure 6 depicts the temperature-scanning evaluations for the thermal conductivity of HNS nanolubricants at various concentrations. The natural ester did not exhibit significant affectation in thermal conductivity (only a 2.4% increase) as the temperature was raised up to 70 °C (343 K), compared to room temperature. Moreover, the nanolubricant's thermal performance was observed to be gradually enhanced with the HNS concentration increase.

Furthermore, as the filler fraction of nanofluids is increased and the testing temperature is also elevated, the thermal conductivity improves, indicating the contribution of the thermal transport characteristics. For instance, it can be observed that at room temperature, a slight increase in thermal conductivity is shown for nanolubricants, achieving a maximum of 4% at 0.10 wt.%. Elevating the test temperature to 50 °C (323 K) showed enhancements of 8, 11, and 16% for 0.01, 0.05, and 0.10 wt.%, respectively, compared to conventional natural ester. The maximum evaluated temperature of 70 °C (343 K) showed a maximum enhancement of 30% at 0.10 wt.%. It is important to mention that as the testing temperature is elevated, there is more deviation from the data obtained. This is mainly due to the properties of the lubricant and its interaction with the nanostructures.

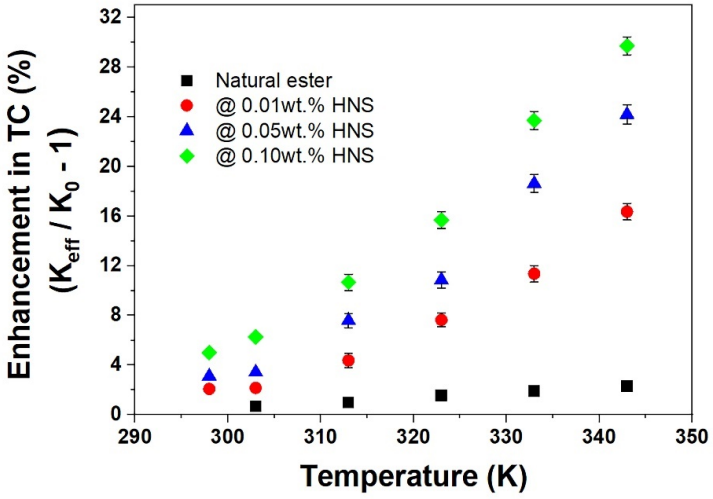


**Figure 6.** Temperature-dependence evaluation for thermal conductivity.

According to Guo et al. [82], it is suggested that due to the small quantity of concentration of nanostructures, the improvement in thermal conductivity is triggered by molecular interactions between the natural ester and the HNS. Additionally, the percolation mechanism, as well as the liquid layering interface at the nanostructures—lubricant also promotes this enhancement [51,83,84]. The lubricant molecules interacting with the nanotubular particles are prone to form a systematic layered structure around the nanostructures, which is associated with improved lubricant thermal transport [81].

## 5. Conclusions

The lubrication and thermal transport performance of natural ester lubricant reinforced with HNS were broadly addressed in this research. In general, HNS nanolubricants resulted in a significant decrease in COF and WSD. Even at merely 0.01 wt.% concentration of HNS, results showed a ~66% and 8% reduction, respectively, when compared to natural ester. The maximum enhancement was shown for the 0.05 wt.% filler fraction, resulting in a reduction of 87% in COF and 37% in WSD. Results indicate that at higher HNS concentration (0.10 wt.%), a minor impact was observed, which could be attributed to the tendency of agglomeration of nanostructures. The morphology and size of HNS promote the anti-wear behavior of the nanolubricants, as load bearing and rolling-sliding mechanism of the nanostructures, as well as the contribution from the smoothing and mending effects in the contact areas, reduce WSD and COF.

Nanolubricants have a good effect on thermal conductivity as well. A temperature scanning evaluation was performed. At room temperature, reinforcing HNS has a slight impact on thermal conductivity, but as the temperature is elevated, the effect is more significant. For instance, at 50 °C (323 K), thermal conductivity measurements resulted in enhancements of 8%, 11%, and 16% for 0.01, 0.05, and 0.10 wt.%, respectively, compared to conventional natural ester. Achieving the greatest improvement of 30% with 0.01 wt.%

HNS concentration at 70 °C (343 K). This behavior, additionally from the Brownian motion effect on the natural ester, is attributed to the percolation mechanism as well as the liquid layering interface contributing to the enhancement in thermal transport characteristics.

A key driver is increasing environmental awareness of novel scientific and technological developments. HNS has been demonstrated to be a good eco-friendly alternative to petroleum-based fluids, mainly in sensitive industrial fields where these materials have the potential to succeed.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/lubricants11020065/s1. Figure S1. Observation of nanostructure's sedimentation after 15 days on the shelf.

**Author Contributions:** J.J.T.-T. contributed to the conceptualization, project administration, methodology, literature research, measuring campaign, data analysis, data interpretation, validation, formal analysis, resources, investigation, figures, study design, supervision, and writing—original. K.A. contributed to the measuring campaign methodology, resources, validation, formal analysis, investigation and writing—original. V.P.-G. contributed to the measuring campaign, data interpretation and investigation. A.A. contributed to the investigation, literature research and formal analysis. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** Authors acknowledge Cargill Industrial Specialties, The University of Texas Rio Grande Valley and Karen Lozano for their support given in this research.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Wong, K.V.; De Leon, O. Applications of Nanofluids: Current and Future. *Adv. Mech. Eng.* **2010**, *2*, 519659. [CrossRef]
2. Salehirad, M.; Nikje, M.M.A. Properties of Modified Hexagonal Boron Nitride as Stable Nanofluids for Thermal Management Applications. *Russ. J. Appl. Chem.* **2019**, *92*, 78–86. [CrossRef]
3. Fofana, I. 50 years in the development of insulating liquids. *IEEE Electr. Insul. Mag.* **2013**, *29*, 13–25. [CrossRef]
4. Taha-Tijerina, J.; Narayanan, T.N.; Gao, G.; Rohde, M.; Tsentalovich, D.A.; Pasquali, M.; Ajayan, P.M. Electrically insulating thermal nano-oils using 2D fillers. *ACS Nano* **2012**, *6*, 1214–1220. [CrossRef]
5. Contreras, J.E.; Rodriguez, E.A.; Taha-Tijerina, J. Chapter 39: Recent Trends of Nanomaterials for High-Voltage Applications. In *Handbook of Nanomaterials for Industrial Applications*; Elsevier: Amsterdam, The Netherlands, 2018; pp. 724–738.
6. Abas, N.; Kalair, A.; Khan, N. Review of fossil fuels and future energy technologies. *Futures* **2015**, *69*, 31–49. [CrossRef]
7. Madanhire, I.; Mbohwa, C.; Madanhire, I.; Mbohwa, C. Development of Biodegradable Lubricants. In *Mitigating Environmental Impact of Petroleum Lubricants*; Springer: Berlin/Heidelberg, Germany, 2016; pp. 85–101.
8. Nowak, P.; Kucharska, K.; Kamiński, M. Ecological and health effects of lubricant oils emitted into the environment. *Int. J. Environ. Res. Public Health* **2019**, *16*, 3002. [CrossRef]
9. Krolczyk, G.M.; Maruda, R.W.; Krolczyk, J.B.; Wojciechowski, S.; Mia, M.; Nieslony, P. Ecological trends in machining as a key factor in sustainable production—A review. *J. Clean. Prod.* **2019**, *218*, 601–615. [CrossRef]
10. Benedicto, E.; Carou, D.; Rubio, E.M. Technical, Economic and Environmental Review of the Lubrication/Cooling Systems used in Machining Processes. *Procedia Eng.* **2017**, *184*, 99–116. [CrossRef]
11. Taha-Tijerina, J.; Narayanan, T.N.; Avali, S.; Ajayan, P.M. 2D Structures-based Energy Management Nanofluids. In Proceedings of the ASME 2012 International Mechanical Engineering Congress & Exposition (IMECE 2012), Houston, TX, USA, 9–15 November 2012; p. 87890.
12. Liu, R. The challenges and opportunities of nanofluids. In Proceedings of the 2019 2nd International Conference on Electrical Materials and Power Equipment (ICEMPE), Guangzhou, China, 7–10 April 2019; pp. 110–114.
13. Sharma, P.; Said, Z.; Kumar, A.; Nizetic, S.; Pandey, A.; Hoang, A.T.; Huang, Z.; Afzal, A.; Li, C.; Le, A.T.; et al. Recent Advances in Machine Learning Research for Nanofluid-Based Heat Transfer in Renewable Energy System. *Energy Fuels* **2022**, *36*, 6626–6658. [CrossRef]
14. Rafiq, M.; Lv, Y.Z.; Zhou, Y.; Ma, K.B.; Wang, W.; Li, C.R. Use of vegetable oils as transformer oils-A review. *Renew. Sustain. Energy Rev.* **2015**, *52*, 308–324. [CrossRef]
15. Kumar, S.; Vo, D.-V.N.; Selvaraju, N.; Ramalingam, S.; Sikdar, S.; Rahman, H. Synergistic Study of Solid Lubricant Nano-Additives Incorporated in canola oil for Enhancing Energy Efficiency and Sustainability. *Sustainability* **2022**, *14*, 290.

16. Fernández-Silva, S.D.; García-Morales, M.; Ruffel, C.; Delgado, M.A. Influence of the Nanoclay Concentration and Oil Viscosity on the Rheological and Tribological Properties of Nanoclay-Based Ecolubricants. *Lubricants* **2021**, *9*, 8. [CrossRef]
17. Narayanan, G.A.A.; Babu, R.; Vasanthakumari, R. Studies on Halloysite Nanotubes (HNT) Natural Rubber Nanocomposites for Mechanical Thermal and Wear Properties. *Int. J. Eng. Res. Technol.* **2016**, *5*, 152–156.
18. Ahmed Abdalglil Mustafa, W.; Dassenoy, F.; Sarno, M.; Senatore, A. A review on potentials and challenges of nanolubricants as promising lubricants for electric vehicles. *Lubr. Sci.* **2022**, *34*, 1–29. [CrossRef]
19. Kadirgama, G.; Kamarulzaman, M.K.; Ramasamy, D.; Kadirgama, K.; Hisham, S. Classification of Lubricants Base Oils for Nanolubricants Applications—A Review. In *ICMER 2021: Technological Advancement in Mechanical and Automotive Engineering*; Ismail, M.Y., Mohd Sani, M.S., Kumarasamy, S., Hamidi, M.A., Shaari, M.S., Eds.; Lecture Notes in Mechanical Engineering; Springer: Singapore, 2023; pp. 205–213.
20. Huang, Z.; Li, J.; Yao, W.; Wang, F.; Wan, F.; Tan, Y. Electrical and thermal properties of insulating oil-based nanofluids: A comprehensive overview. *IET Nanodielectr.* **2019**, *2*, 27–40. [CrossRef]
21. Taha-Tijerina, J.J. Thermal transport and Challenges on Nanofluids Performance. In *Microfluidics and Nanofluidics*, 1st ed.; Kandelousi, M.S., Ed.; IntechOpen: Rijeka, Croatia, 2018; pp. 215–256.
22. Nagendramma, P.; Kaul, S. Development of ecofriendly/biodegradable lubricants: An overview. *Renew. Sustain. Energy Rev.* **2012**, *16*, 764–774. [CrossRef]
23. Pawar, R.V.; Hulwan, D.B.; Mandale, M.B. Recent advancements in synthesis, rheological characterization, and tribological performance of vegetable oil-based lubricants enhanced with nanoparticles for sustainable lubrication. *J. Clean. Prod.* **2022**, *378*, 134454. [CrossRef]
24. Ab Ghani, S.; Muhamad, N.A.; Noorden, Z.A.; Zainuddin, H.; Abu Bakar, N.; Talib, M.A. Methods for improving the workability of natural ester insulating oils in power transformer applications: A review. *Electr. Power Syst. Res.* **2018**, *163*, 655–667. [CrossRef]
25. Thampi, A.D.; Prasanth, M.A.; Anandu, A.P.; Sneha, E.; Sasidharan, B.; Rani, S. The effect of nanoparticle additives on the tribological properties of various lubricating oils—Review. *Mater. Today Proc.* **2021**, *47*, 4919–4924. [CrossRef]
26. Kazeem, R.A.; Fadare, D.A.; Ikumapayi, O.M.; Adediran, A.A.; Aliyu, S.J.; Akinlabi, S.A. Advances in the Application of Vegetable-Oil-Based Cutting Fluids to Sustainable Machining Operation: A Review. *Lubricants* **2022**, *10*, 69. [CrossRef]
27. Dombek, G.; Nadolny, Z.; Marcinkowska, A. Thermal properties of natural ester and low viscosity natural ester in the aspect of the reliable operation of the transformer cooling system. *Eksploat. Niezawodn. Maint. Reliab.* **2019**, *21*, 384–391. [CrossRef]
28. Taha-Tijerina, J.; Ribeiro, H.; Aviña, K.; Martínez, J.M.; Godoy, A.P.; Cremonezzi, J.M. Thermal Conductivity Performance of 2D h-BN/MoS2/-Hybrid Nanostructures Used on Natural and Synthetic Esters. *Nanomaterials* **2020**, *10*, 1160. [CrossRef] [PubMed]
29. Zainal, N.A.; Zulkifli, N.W.M.; Gulzar, M.; Masjuki, H.H. A review on the chemistry, production, and technological potential of bio-based lubricants. *Renew. Sustain. Energy Rev.* **2018**, *82*, 80–102. [CrossRef]
30. Zhang, C.; Yang, Z.; Lu, Z.; Wang, X.; Jia, L.; Wang, J.; Gao, Q.; Li, L.; Zhou, C.; Chen, G.; et al. Synthesis and tribological properties of bio-inspired green dopamine oil soluble additive. *Tribol. Int.* **2022**, *174*, 107697. [CrossRef]
31. Durango-Giraldo, G.; Zapata-Hernandez, C.; Santa, J.F.; Buitrago-Sierra, R. Palm oil as a biolubricant: Literature review of processing parameters and tribological performance. *J. Ind. Eng. Chem.* **2022**, *107*, 31–44. [CrossRef]
32. Abdalla, H.S.; Patel, S. The performance and oxidation stability of sustainable metalworking fluid derived from vegetable extracts. *Proc. Inst. Mech. Eng. Part B J. Eng. Manuf.* **2006**, *220*, 2027–2040. [CrossRef]
33. Petlyuk, A.M.; Adams, R.J. Oxidation stability and tribological behavior of vegetable oil hydraulic fluids. *Tribol. Trans.* **2004**, *47*, 182–187. [CrossRef]
34. Taha-Tijerina, J.; Aviña, K.; Diabb, J.M. Tribological and Thermal Transport Performance of $SiO_2$-Based Natural Lubricants. *Lubricants* **2019**, *7*, 71. [CrossRef]
35. Eberhardt, R.; Muhr, H.M.; Lick, W.; Baumann, F.; Pukel, G. Comparison of alternative insulating fluids. In Proceedings of the Annual Report Conference on Electrical Insulation and Dielectric Phenomena, Quebec, QC, Canada, 26–29 October 2008; IEEE: Piscataway, NJ, USA, 2008; pp. 591–593.
36. Fox, N.J.; Stachowiak, G.W. Vegetable oil-based lubricants—A review of oxidation. *Tribol. Int.* **2007**, *40*, 1035–1046. [CrossRef]
37. IEEE Power Engineering Society. *C57.147-2018—IEEE Guide for Acceptance and Maintenance of Natural Ester Insulating Liquid in Transformers*; IEEE: Piscataway, NJ, USA, 2018.
38. Choi, S.U.S.; Eastman, J.A. Enhancing thermal conductivity of fluids with nanoparticles. In *Developments and Applications of Non-Newtonian Flows*; ASME: New York, NY, USA, 1995; Volume 231, pp. 99–105.
39. Li, H.; Zhang, Y.; Li, C.; Zhou, Z.; Nie, X.; Chen, Y.; Cao, H.; Liu, B.; Zhang, N.; Said, Z.; et al. Extreme pressure and antiwear additives for lubricant: Academic insights and perspectives. *Int. J. Adv. Manuf. Technol.* **2022**, *120*, 1–27. [CrossRef]
40. Sharma, A.K.; Tiwari, A.K.; Dixit, A.R. Progress of Nanofluid Application in Machining: A Review. *Mater. Manuf. Process.* **2015**, *30*, 813–828. [CrossRef]
41. Ben Said, L.; Kolsi, L.; Ghachem, K.; Almeshaal, M.; Maatki, C. Application of nanofluids as cutting fluids in machining operations: A brief review. *Appl. Nanosci.* **2021**, 1–32. [CrossRef]
42. Kishawy, H.A.; Hegab, H.; Deiab, I.; Eltaggaz, A. Sustainability assessment during machining Ti-6Al-4V with nano-additives-based minimum quantity lubrication. *J. Manuf. Mater. Process.* **2019**, *3*, 61. [CrossRef]
43. Kadirgama, K. A comprehensive review on the application of nanofluids in the machining process. *Int. J. Adv. Manuf. Technol.* **2021**, *115*, 2669–2681. [CrossRef]

44. Rapoport, L.; Leshchinsky, V.; Lapsker, I.; Volovik, Y.; Nepomnyashchy, O.; Lvovsky, M. tribological properties of $WS_2$ nanoparticles under mixed lubrication. *Wear* **2003**, *255*, 785–793. [CrossRef]
45. Sunil Kumar, D.; Garg, H.C.; Kumar, G. Tribological analysis of blended vegetable oils containing CuO nanoparticles as an additive. *Mater. Today Proc.* **2022**, *51*, 1259–1265. [CrossRef]
46. Omrani, E.; Siddaiah, A.; Moghadam, A.D.; Garg, U.; Rohatgi, P.; Menezes, P.L. Ball Milled Graphene Nano Additives for Enhancing Sliding Contact in Vegetable Oil. *Nanomaterials* **2021**, *11*, 610. [CrossRef]
47. Karthikeyan, K.M.B.; Vijayanand, J.; Arun, K.; Rao, V.S. Thermophysical and wear properties of eco-friendly nano lubricants. *Mater. Today Proc.* **2021**, *39*, 285–291. [CrossRef]
48. Yadav, A.; Singh, Y.; Negi, P. A review on the characterization of bio based lubricants from vegetable oils and role of nanoparticles as additives. *Mater. Today Proc.* **2021**, *46*, 10513–10517. [CrossRef]
49. Lim, S.K.; Azmi, W.H.; Jamaludin, A.S.; Yusoff, A.R.; Lim, S.K.; Azmi, W.H. Characteristics of Hybrid Nanolubricants for MQL Cooling Lubrication Machining Application. *Lubricants* **2022**, *10*, 350. [CrossRef]
50. Gupta, H.S.; Sehgal, R.; Wani, M.F. Tribological characterization of eco-friendly bio-based mahua and flaxseed oil through nanoparticles. *Biomass Convers. Biorefin.* **2022**, 1–13. [CrossRef]
51. Taha-Tijerina, J.; Shaji, S.; Sharma Kanakkillam, S.; Mendivil Palma, M.I.; Aviña, K. Tribological and Thermal Transport of Ag-Vegetable Nanofluids Prepared by Laser Ablation. *Appl. Sci.* **2020**, *10*, 1779. [CrossRef]
52. Jacob, J.; Preetha, P.; Sindhu, T.K. Stability analysis and characterization of natural ester nanofluids for transformers. *IEEE Trans. Dielectr. Electr. Insul.* **2020**, *27*, 1715–1723. [CrossRef]
53. Farade, R.A.; Wahab, N.I.A.; Mansour, D.E.A.; Azis, N.B.; Jasni, J.B.; Soudagar, M.E.M. Development of Graphene Oxide-Based Nonedible Cottonseed Nanofluids for Power Transformers. *Materials* **2020**, *13*, 2569. [CrossRef] [PubMed]
54. Khan, S.A.; Tariq, M.; Khan, A.A.; Alamri, B.; Mihet-Popa, L. Assessment of Thermophysical Performance of Ester-Based Nanofluids for Enhanced Insulation Cooling in Transformers. *Electronics* **2022**, *11*, 376. [CrossRef]
55. Lecouvet, B.; Horion, J.; D'Haese, C.; Bailly, C.; Nysten, B. Elastic modulus of halloysite nanotubes. *Nanotechnology* **2013**, *24*, 105704. [CrossRef] [PubMed]
56. Yuan, P.; Tan, D.; Annabi-Bergaya, F. Properties and applications of halloysite nanotubes: Recent research advances and future prospects. *Appl. Clay Sci.* **2015**, *112–113*, 75–93. [CrossRef]
57. Yang, S.; Li, S.; Yin, X.; Wang, L.; Chen, D.; Zhou, Y.; Wang, H. Preparation and characterization of non-solvent halloysite nanotubes nanofluids. *Appl. Clay Sci.* **2016**, *126*, 215–222. [CrossRef]
58. Joussein, E.; Petit, S.; Churchman, J.; Theng, B.; Righi, D.; Delvaux, B. Halloysite clay minerals—A review. *Clay Miner.* **2005**, *40*, 383–426. [CrossRef]
59. Lv, Y.; Sun, X.; Yan, S.; Xiong, S.; Wang, L.; Wang, H. Solvent-free halloysite nanotubes nanofluids based polyacrylonitrile fibrous membranes for protective and breathable textiles. *Compos. Commun.* **2022**, *33*, 101211. [CrossRef]
60. Massaro, M.; Noto, R.; Riela, S. Past, Present and Future Perspectives on Halloysite Clay Minerals. *Molecules* **2020**, *25*, 4863. [CrossRef]
61. Udoh, I.I.; Shi, H.; Daniel, E.F.; Li, J.; Gu, S.; Liu, F. Active anticorrosion and self-healing coatings: A review with focus on multi-action smart coating strategies. *J. Mater. Sci. Technol.* **2022**, *116*, 224–237. [CrossRef]
62. Massaro, M.; Noto, R.; Riela, S. Halloysite Nanotubes: Smart Nanomaterials in Catalysis. *J. Catal.* **2022**, *12*, 149. [CrossRef]
63. Paul, A.; Augustine, R.; Hasan, A.; Zahid, A.A.; Thomas, S.; Agatemor, C. Halloysite nanotube and chitosan polymer composites: Physicochemical and drug delivery properties. *J. Drug Deliv. Sci. Technol.* **2022**, *72*, 103380. [CrossRef]
64. Same, S.; Nakhjavani, S.A.; Samee, G.; Navidi, G.; Jahanbani, Y.; Davaran, S. Halloysite clay nanotube in regenerative medicine for tissue and wound healing. *Ceram. Int.* **2022**, *48*, 31065–31079. [CrossRef]
65. Liao, J.; Wang, H.; Liu, N.; Yang, H. Functionally modified halloysite nanotubes for personalized bioapplications. *Adv. Colloid Interface Sci.* **2023**, *311*, 102812. [CrossRef] [PubMed]
66. Ahmed, M.S.; Nair, K.P.; Tirth, V.; Elkhaleefa, A.; Rehan, M. Tribological evaluation of date seed oil and castor oil blends with halloysite nanotube additives as environment friendly bio-lubricants. *Biomass Convers. Biorefin.* **2021**, 1–10. [CrossRef]
67. Qin, Y.; Wu, M.; Yang, Y.; Yang, Y.; Yang, G. Enhanced ability of halloysite nanotubes to form multilayer nanocrystalline tribofilms by thermal activation. *Tribol. Int.* **2022**, *174*, 107718. [CrossRef]
68. Yuan, Q.; Yang, Y.; Yang, Y.; Wu, M.; Yang, G. Formation mechanism of wear-resistant composite film by Span 80-decorated halloysite nanotubes. *Ceram. Int.* **2022**, *48*, 23897–23907.
69. Suresha, B.; Hemanth, G.; Rakesh, A.; Adarsh, K.M. Tribological behaviour of pongamia oil as lubricant with and without halloysite nanotubes using four-ball tester. *AIP Conf. Proc.* **2019**, *2128*, 030011.
70. Alberola, J.A.; Mondragón, R.; Juliá, J.E.; Hernández, L.; Cabedo, L. Characterization of halloysite-water nanofluid for heat transfer applications. *Appl. Clay Sci.* **2014**, *99*, 54–61. [CrossRef]
71. Ba, T.; Alkurdi, A.Q.; Lukács, I.E.; Molnár, J.; Wongwises, S.; Gróf, G. A Novel Experimental Study on the Rheological Properties and Thermal Conductivity of Halloysite Nanofluids. *Nanomaterials* **2020**, *10*, 1834.
72. Ba, T.; Baqer, A.; Saad Kamel, M.; Gróf, G.; Odhiambo, V.O.; Wongwises, S. Experimental Study of Halloysite Nanofluids in Pool Boiling Heat Transfer. *Molecules* **2022**, *27*, 729.
73. Guimarey, M.J.G.; Liñeira del Río, J.M.; Fernández, J. Improvement of the lubrication performance of an ester base oil with coated ferrite nanoadditives for different material pairs. *J. Mol. Liq.* **2022**, *350*, 118550. [CrossRef]

74. Chen, Y.; Renner, P.; Liang, H. Dispersion of Nanoparticles in Lubricating Oil: A Critical Review. *Lubricants* **2019**, *7*, 7. [CrossRef]
75. Wu, P.R.; Liu, Z.; Cheng, Z.L. Growth of $MoS_2$ Nanotubes Templated by Halloysite Nanotubes for the Reduction of Friction in Oil. *ACS Omega* **2018**, *3*, 15002–15008. [CrossRef]
76. Zhang, Z.; Yu, G.; Geng, Z.; Tian, P.; Ren, K.; Wu, W.; Gong, Z. Ultra low friction of conductive carbon nanotube films and their structural evolution during sliding. *Diam. Relat. Mater.* **2021**, *120*, 108617. [CrossRef]
77. Wang, B.; Qiu, F.; Barber, G.C.; Zou, Q.; Wang, J.; Guo, S. Role of nano-sized materials as lubricant additives in friction and wear reduction: A review. *Wear* **2022**, *490–491*, 204206. [CrossRef]
78. Gara, L.; Zou, Q. Friction and Wear Characteristics of Water-Based ZnO and $Al_2O_3$ Nanofluids. *Tribol. Trans.* **2012**, *55*, 345–350. [CrossRef]
79. Wu, Y.Y.; Tsui, W.C.; Liu, T.C. Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. *Wear* **2007**, *262*, 819–825. [CrossRef]
80. Azman, N.F.; Samion, S. Dispersion Stability and Lubrication Mechanism of Nanolubricants: A Review. *Int. J. Precis. Eng. Manuf. Technol.* **2019**, *6*, 393–414. [CrossRef]
81. Shafi, W.K.; Charoo, M.S. An overall review on the tribological, thermal and rheological properties of nanolubricants. *Tribol. Mater. Surf. Interfaces* **2020**, *15*, 20–54. [CrossRef]
82. Guo, W.; Li, G.; Zheng, Y.; Dong, C. Measurement of the thermal conductivity of $SiO_2$ nanofluids with an optimized transient hot wire method. *Thermochim. Acta* **2018**, *661*, 84–97. [CrossRef]
83. Taha-Tijerina, J.; Aviña, K.; Martínez, J.M.; Arquieta-Guillén, P.Y.; González-Escobedo, M. Carbon Nanotori Structures for Thermal Transport Applications on Lubricants. *Nanomaterials* **2021**, *11*, 1158. [CrossRef] [PubMed]
84. Taha-Tijerina, J.; Cadena-de la Peña, N.; Cue-Sampedro, R.; Rivera-Solorio, C. Thermo-physical evaluation of dielectric mineral oil-based nitride and oxide nanofluids for thermal transport applications. *J. Therm. Sci. Technol.* **2019**, *14*, JTST0007. [CrossRef]


**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.