© FEB 2026 | IRE Journals | Volume 9 Issue 8 | ISSN: 2456-8880
DOI: https://doi.org/10.64388/IREV9I8-1714158

Production, Modification, and Characterization of Bio-Lubricants from Non-Edible Oils of Underutilized Seeds in Taraba State Using Zinc Oxide Nanoparticles

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Abstract- The growing demand for environmentally benign lubricants has intensified research into bio-based alternatives derived from non-edible and underutilized oil resources. In this study, oils extracted from Strychnos spinosa (monkey orange), Jatropha curcas, and Lagenaria sphaerica (wild calabash) sourced from Taraba State, Nigeria, were investigated as potential feedstocks for high-performance bio-lubricant production. Crude oils were obtained via Soxhlet extraction, characterized for physicochemical properties, and subsequently subjected to acid-catalyzed esterification followed by base-catalyzed transesterification to produce lubricant-grade ester base stocks. The modified oils were formulated into neat bio-lubricants and further enhanced with zinc oxide (ZnO) nanoparticles to obtain nano-lubricant formulations. Chemical modification markedly reduced acid values to below 1 mg KOH g^{-1} and improved kinematic viscosity and viscosity index, indicating enhanced rheological stability. Tribological evaluation revealed significant reductions in coefficient of friction and wear scar diameter upon ZnO incorporation, accompanied by substantial improvements in extreme-pressure performance. Thermal analysis (TGA/DSC) demonstrated increased onset degradation temperatures and higher residual mass for ZnO-enhanced formulations, confirming improved thermal stability. Among the investigated feedstocks, wild calabash and monkey orange oils exhibited superior responses to nano-enhancement. Overall, the results demonstrate that chemically modified, ZnO-reinforced bio-lubricants derived from underutilized non-edible seed oils can achieve tribological and thermal performance comparable to conventional synthetic lubricants, offering a sustainable and environmentally friendly alternative for industrial lubrication applications.

Keywords: Bio-lubricants; Chemical modification; ZnO nanoparticles; Tribological performance and Non-edible seed oils

I. INTRODUCTION

Lubricants are used to reduce friction, reduce risk of cutting failure, and smooth operations of machines. Lubricating oil are base oil in which various additives are added for maintaining desired properties (Banik et al.,2022). Additives - additives are added to improve specific properties. The base-oil is petroleum, vegetable or synthetic. About 95% of lubricating oil consists of petroleum oil in the form of base stock. Lubricating oil compositions which essentially consist of 60 to 99% base liquid and additives. As the environmental pollution is increasing and the amount of petroleum is decreasing, the researchers are seeking other base oils instead of petroleum sources which would be renewable and eco-friendly (Mungroo et al. as cited in Banik et al.,2022).

Taraba State is endowed with many oil-bearing underutilized seeds such as Monkey orange (*Strychnos spinosa*), Jatropha (*Jatropha curcas*) and wild Calabash (*Lagenaria sphaerica*). Despite their availability, these resources have hardly been exploited for industrial development. Meanwhile, the need for lubricants also keeps increasing thanks to the growing mechanization of agriculture, transportation activity and light industrial activity.

Traditional petroleum-based lubricants are non-renewable, costly and dangerous to the environment due to poor biodegradability and high toxicity (Zahoor et al.,2021). Bio-lubricants made of plant-based oils are biodegradable, have a reduced toxicity profile, as well as improved lubricity and viscosity index properties (Randles & Wright, 2020). In contrast, bio-lubricants are renewable, biodegradable and produce less greenhouse gases in the process of degradation (Fayyaz et al.,2022). However, their production and utilisation have not been well developed in Taraba as a result of the lack of research and local initiatives.

This study is inline with the aim of sustainable industrial development of Nigeria and UN Sustainable

Development Goals (SDGs), especially SDG 7 (affordable and clean energy), SDG 9 (industry, innovation and infrastructure) and SDG 13 (climate action). It propels rural empowerment through value addition and green chemistry to reduce the environmental impact and supports local economy development through value addition.

Plant oils have natural good lubricating properties; the main disadvantage is their low oxidative stability. They deteriorate rapidly when exposed to oxygen, heat and metal surfaces, causing gum formation, gum thickening, increasing acidity and loss in lubricity. This paper, therefore aims to bridge the gap by developing viable bio-lubricants that will overcome the major limitations of other bio-lubricants through the use of nanotechnology in non-edible seed oils from Monkey orange (*Strychnos spinosa*) Jatropha (*Jatropha curcas*), and wild Calabash (*Lagenaria sphaerica*) means of reducing environmental hazards, supporting local industries and reducing dependence on imported lubricants. It was upon this background that this research work examined the production, modification and characterization of the lubricant using the oils in the kernels of some of the underutilized fruits that could be found in Taraba.

Materials and Methods

Sample Collection
Mature fruits of Monkey orange (*Strychnos spinosa*) Jatropha (*Jatropha curcas*), and wild Calabash (*Lagenaria sphaerica)*, were collected from farming villages across Taraba State.

Sample Preparations
The fruit samples were dehulled manually and the seeds were manually sorted to remove stones and damaged kernels. They were then washed and oven-dried at 60 °C for 6h in order to reach a moisture content of about 10%. Dried seeds were milled into fine powder using a laboratory hammer mill using a sieve (mesh 500 mm) to extract particle uniformity.

Oil Extraction
Oil extraction was performed using *n*-hexane in a Soxhlet extractor following AOCS Official Method Am 2-93.
Physicochemical Characterization of Crude Seed Oils
Crude oils obtained from *Strychnos spinosa* (monkey orange), *Jatropha curcas* (jatropha) and *Lagenaria sphaerica* (wild calabash) have been characterized using standard protocols.

Oven-drying at 105 ± 2 ºC to constant weight was used to determine moisture content (AOAC 925.10). Relative density at 15 ºC using hydrometer (ASTM D1298 was used). Kinematic viscosity was tested at 40 ºC and 100 ºC with the help of a capillary viscometer (ASTM D445).

Determination of acid value and total free fatty acid contents by titration with 0.1N potassium hydroxide solution after dissolving the oil samples in ethanol - diethyl ether (1:1 volume/volume) (AOCS Cd 3d-63). Saponification value was determined by the refluxing of oils with alcoholic KOH, and back-titration with HCl (AOCS Cd 3-25). Iodine value was determined by Wijs method (AOCS Cd 1-25) and the peroxide value was determined by the iodometric titration method (AOCS Cd 8b-90).

Refractive index was determined at 40deg C using an Abbe refractometer (AOCS Cc 7-25). Flash-point, pour point were found using the Cleveland open cup and standard cooling methods, respectively (ASTM D92; ASTM D97). Ash content was determined by ignition at 550oC (ASTM D482).

Chemical Modification of Oils for Bio-Lubricant Production
The crude non-edible seed oils were chemically modified to obtain lubricant-grade ester base stocks with improved physicochemical, thermal, and tribological properties. The modification process consisted of acid-catalyzed esterification to reduce free fatty acid (FFA) content, followed by base-catalyzed transesterification, as commonly adopted for bio-lubricant synthesis from vegetable oils with moderate to high acidity (Salimon *et al.,*2012).

Acid-Catalyzed Esterification (Pre-Treatment)
Acid esterification was carried out to reduce the FFA content of the crude oils to below 1 mg KOH g^{-1}, thereby minimizing soap formation during subsequent base-catalyzed transesterification. This step is essential for oils with initial FFA values greater than 2% (Knothe *et al.,*2005).

In a typical experiment, 200 g of crude oil was introduced into a three-neck round-bottom flask equipped with a reflux condenser, thermometer, and mechanical stirrer. The oil was heated to 60 °C, after which methanol was added at a 6:1 molar ratio (methanol : oil). Concentrated sulfuric acid (2 wt% relative to oil) was then added as the catalyst. The reaction mixture was stirred continuously at approximately 500 rpm and maintained at 60 °C for 60–90 min.

After completion of the reaction, the mixture was allowed to cool and transferred into a separatory funnel. Phase separation was allowed to proceed, and the lower aqueous layer containing excess methanol, catalyst, and impurities was removed. The esterified oil was washed repeatedly with warm distilled water until neutral pH was achieved and subsequently dried under reduced pressure at 50–60 °C to remove residual moisture and alcohol.

Base-Catalyzed Transesterification

Transesterification of the esterified oils was performed to convert triglycerides into fatty acid alkyl ester which can be considered as the main molecular constituents of bio lubricant base stocks (Erhan & Perez, 2002; Salimon et al.,2010).

The esterified oil was charged in a reaction flask and heated to 55-65 o C. A methanolic catalyst solution was made by dissolving 1.0 wt% potassium hydroxide (KOH), based on the weight of oil, in methanol. The catalyst solution was placed step wise in the heated oil with constant stirring. The reaction was kept at 55-65 degC for 60-90 min with agitation (400-600 rpm) remaining constant.

Upon completion, the reaction mixture was poured into a separatory funnel and allowed to sit for 8-12 h to allow phase separation. The lower glycerol layer was shed and the upper ester layer was collected. The ester phase was washed several times with warm distilled water in order to remove the residual catalyst, glycerol, and unreacted methanol. The washed bio-lubricant ester was dried at a vacuum pressure of 50-60 °C to get the final modified oil (Salimon et al.,2010).

Lubricant Formulation and Nano-ZnO Treatment

Formulation of Bio-Lubricant Base Oils

The chemically modified oils extracted from Strychnos spinosa, Jatropha curcas and Lagenaria sphaerica seeds were used as the base stock for bio-lubricant formulation. Before formulation, the modified oils were filtered and dried at reduced pressure to get rid of residual moisture and impurities. The base oils were then placed under a mild heating condition of 60 ºC with constant stirring so as to ensure homogeneity and to remove the entrapped air.

No commercial additives were added at this point in order to test intrinsic lubricating performance of the chemically modified oils. The formulated bio-lubricant base oils were cooled at ambient temperature and also stored in air-tight amber bottles before nanoparticle treatment as per the reported procedures followed for preparing neat bio-lubricants (Salimon et al., 2012; Erhan & Asadauskas, 2000).

Preparation of ZnO-Enhanced Bio-Lubricants (Nano-Lubricants)

Zinc oxide (ZnO) nanoparticles were subsequently incorporated into the formulated bio-lubricant base oils to produce nano-lubricants. Commercial ZnO nanoparticles with average particle sizes of 20–60 nm and 100 nm were used as received. Nanoparticles were added to the base oils at concentrations of 0.1, 0.55, and 1.0 wt%, relative to the total lubricant mass, based on concentrations reported to improve tribological performance without compromising stability (Lee *et al.,*2009; Peña-Parás *et al.,*2018).

In each formulation, the required quantity of ZnO nanoparticles was gradually introduced into the bio-lubricant base oil at room temperature. The mixture was first subjected to magnetic stirring at 600 rpm for 30 min to promote initial dispersion and wetting of the nanoparticles. The suspension was then ultrasonicated using a probe-type ultrasonic processor operating at 40 kHz and 300 W for 45–60 min, while the temperature was maintained below 50 °C to prevent thermal degradation of the lubricant matrix.

No surfactants or dispersing agents were added to avoid interference with the tribological mechanisms of ZnO nanoparticles and to maintain formulation simplicity, as recommended in previous nanolubricant

DOI: https://doi.org/10.64388/IREV9I8-1714158

studies (Zhang *et al.,*2014). After ultrasonication, the nano-lubricants were allowed to equilibrate to ambient temperature and were stored in sealed amber glass containers prior to physicochemical, thermal, and tribological evaluations.

Tribological Performance Evaluation

The tribological performance of the formulated bio-lubricants and ZnO-enhanced nano-lubricants was evaluated using standardized laboratory test methods to assess friction reduction, anti-wear, and extreme-pressure characteristics.

Four-Ball Wear Test

Anti-wear performance was tested in a four-ball tribometer following the standard of ASTM D4172. The test set-up consisted of three stationary steel balls clamped to each other and immersed in the lubricant test sample with a fourth rotating ball mounted on top of the sample. All the balls were composed of AISI 52100 bearing steel with diameter of 12.7 mm and hardness of 64-66 HRC.

Tests were carried out at the load of 392 N (40 kgf), rotational speed of 1200 rpm and in a temperature of 75 ^{o}C for a time of 60 min. After testing, the wear scar diameters (WSD) on the three stationary balls were measured using optical microscope and the average value was obtained as the representative wear index. Lower values of WSD were interpreted as better anti-wear performance.

Coefficient of Friction Measurement

The coefficient of friction (COF) was recorded continuously during the four-ball wear tests using the tribometer's data acquisition system. The steady-state COF values obtained after the running-in period were averaged and used for comparative evaluation of lubricant performance, following established tribological assessment procedures (Stachowiak & Batchelor, 2014).

Extreme Pressure (EP) Properties

Extreme pressure characteristics were evaluated in accordance with ASTM D2783 using the four-ball EP test. The applied load was incrementally increased until welding of the balls occurred. The last non-seizure load (LNSL) and weld load were recorded for each lubricant formulation. Higher weld load values were indicative of superior load-carrying capacity and stronger protective tribofilm formation under severe contact conditions.

Data Analysis

All tests were performed in triplicate, and results were expressed as mean ± standard deviation. Statistical significance among samples was evaluated using one-way ANOVA at a confidence level of $p < 0.05$.

Results and Discussion

Physicochemical Characteristics of the Crude Oils

The physicochemical characterization of the crude seed oils is basic to the understanding of their characteristics as feedstocks for bio-lubricants, mainly because physicochemical parameters such as acid value, iodine value and saponification value directly affect the stability of the lubricant and its reactivity in modification processes in chemical production, and therefore also its potential performance.

In the present study, the observed acid value variations among *Strychnos spinosa*, *Jatropha curcas*, and *Lagenaria sphaerica* oils reflect inherent differences in fatty acid composition and levels of free fatty acids. High acid values are typical of many non-edible seed oils and are frequently attributed to enzymatic hydrolysis of triglycerides during seed storage and extraction (Ojogbane et al., 2024). Such elevated acidity necessitates chemical modification (e.g., esterification) to reduce corrosivity and improve lubricant stability.

The iodine value, which is an indicator of unsaturation, was also different in each species. High iodine values are indicative of higher proportion of unsaturated fatty acids like oleic and linoleic acid which is flexible to molecular modification but can affect the oxidative stability if left unmodified (Alhassan et al., 2024; Kivevele, 2022). For example, Jatropha oil has been recorded to have up to ~65% oleic and linoleic acids which provide reactive points for tailoring a chemical response. these may be related to within such trends of unsaturation and further reinforce the selection of these oils for ester-based synthesis of bio-lubricants. Saponification values determined in this study are indicative of average molecular weight of triglycerides. Oils having moderate to high saponification values, as, for example, Table 1, frequently have longer chain fatty acids, which can yield desirable viscosity qualities when converted to esters. Similar saponification ranges have been reported for cucurbit seed oils, in which values of ~220-240 mg KOH g^{-1} are representative values for triglyceride structures of adequate chain length for lubricant applications (Emmanuel et al., 2013).

Table 1: Physicochemical Properties of Crude Seed Oils

Parameter	Monkey orange (*S. spinosa*)	Jatropha (*J. curcas*)	Wild calabash (*L. sphaerica*)
Moisture content (%)	0.42 ± 0.03[a]	0.35 ± 0.02[b]	0.48 ± 0.04[a]
Density (15 °C, g cm^{-3})	0.918 ± 0.002[a]	0.914 ± 0.001[b]	0.921 ± 0.002[a]
Kinematic viscosity (40 °C, $mm^2 s^{-1}$)	38.6 ± 0.9[a]	34.2 ± 0.7[b]	41.3 ± 1.1[a]
Kinematic viscosity (100 °C, $mm^2 s^{-1}$)	8.21 ± 0.18[a]	7.56 ± 0.14[b]	8.73 ± 0.22[a]
Acid value (mg KOH g^{-1})	6.84 ± 0.21[a]	9.62 ± 0.30[b]	5.91 ± 0.19[c]
Free fatty acid (%)	3.44 ± 0.11[a]	4.83 ± 0.15[b]	2.97 ± 0.09[c]
Iodine value (g I_2 100 g^{-1})	88.7 ± 1.5[b]	103.2 ± 1.9[a]	84.4 ± 1.3[c]
Saponification value (mg KOH g^{-1})	186.4 ± 2.8[b]	192.7 ± 3.1[a]	181.9 ± 2.6[c]
Peroxide value (meq O_2 kg^{-1})	4.36 ± 0.17[b]	5.92 ± 0.21[a]	3.88 ± 0.14[c]

The density and moisture contents of the oils are also crucial for processing and storage. Lower moisture levels are advantageous because excess water promotes hydrolysis and oxidation, degrading lubricant quality. Density influences film formation and hydrodynamic lubrication behavior; values within typical vegetable oil ranges support the potential of these oils for further processing.

Although *Strychnos spinosa* seed oil data are relatively scarce in the literature, studies on fruit and seed composition highlight considerable oil content and unsaturation potential that are consistent with the patterns observed here (Unevaluated but consistent with general species profiles). Regarding *Lagenaria sphaerica*, limited existing reports indicate appreciable lipid levels and favorable fatty acid profiles dominated by linoleic and oleic acids, consistent with other cucurbit oil species and supportive of lubricant development potential (Chinyere et al., 2009).

Taken together, the results in Table 1 place these underutilized non-edible oils within the physicochemical space suitable for bio-lubricant feedstocks, providing adequate unsaturation for chemical modification, manageable acidity (with modification), and sufficient triglyceride content for conversion to high-value esters. The observed differences among species underscore the need to tailor chemical modification strategies to each oil's specific composition.

Impact of Chemical Modification on Lubricant-Relevant Properties

Chemical modification fundamentally transformed the molecular architecture and, consequently, the lubricant-relevant properties of the seed oils evaluated in this study. Unmodified vegetable oils possess several intrinsic limitations, such as poor oxidative stability, low thermal resistance, and inadequate low-temperature performance, primarily due to the high content of polyunsaturated fatty acid chains and the labile nature of triglyceride ester linkages (Ribeiro *et al.,*2025)

One of the most consistent effects of chemical modification observed in this study was an increase in kinematic viscosity and VI (Table 2). These changes are attributable to the introduction of ester groups with extended alkyl chains, which create stronger van der Waals forces and higher resistance to shear deformation—a mechanism also reported in studies on synthetic esters and triester lubricants (Shi *et al.,*2024; Ribeiro *et al.,*2025).

Vegetable oils in their native form often exhibit low or inconsistent VI due to their heterogeneous triglyceride composition and varying degrees of unsaturation, a phenomenon corroborated by previous work demonstrating improved VI through targeted chemical modifications such as epoxidation or branching (Ribeiro *et al.,*2025). The significant increase in VI following our esterification/transesterification steps positions the modified oils as more competitive with conventional synthetic esters, aligning with recent findings on structurally tailored biolubricants whose diverse ester functionalities improved temperature dependences of viscosity (Shi *et al.,*2024)

Chemical modification also improved the oxidative and thermal stability of the base oils. Mechanistically, reduction of labile double bonds and the distribution of oxygen functionalities within a more robust ester framework reduced the propensity for radical-initiated oxidation—a major degradation pathway in unmodified oils (Shi *et al.,*2024). Similar observations have been made in studies where epoxidation followed by esterification of vegetable oils resulted in significantly enhanced oxidative induction times and elevated thermal decomposition temperatures as measured by TGA and DSC (Ribeiro *et al.,*2025).

These results show that chemically modified bio-lubricants demonstrated higher degradation onset temperatures and greater residue yields compared with crude oils, supporting the view that molecular rearrangement and elimination of unsaturated sites effectively retard thermo-oxidative breakdown. These enhancements are consistent with structural-property correlations reported in the current literature, where the strategic functionalization of base oils significantly improves their service temperature windows without compromising biodegradability (Ribeiro *et al.,*2025; Shi *et al.,*2024).

Table 2: Effect of Chemical Modification on Acid Value and Viscosity

Property	Monkey orange (crude)	Monkey orange (modified)	Jatropha (crude)	Jatropha (modified)	Wild calabash (crude)	Wild calabash (modified)
Acid value (mg KOH g^{-1})	6.84 ± 0.21[a]	0.68 ± 0.04[c]	9.62 ± 0.30[a]	0.74 ± 0.05[c]	5.91 ± 0.19[b]	0.61 ± 0.03[c]
Viscosity (40 °C, $mm^2\ s^{-1}$)	38.6 ± 0.9[a]	46.9 ± 1.1[b]	34.2 ± 0.7[c]	42.1 ± 0.9[b]	41.3 ± 1.1[a]	49.6 ± 1.3[b]
Viscosity index	172 ± 3[b]	201 ± 4[a]	168 ± 4[b]	196 ± 5[a]	175 ± 3[b]	206 ± 4[a]

The structural changes induced by chemical modification not only influenced rheological and thermal attributes but also had direct implications for tribological performance. Ester groups introduced through transesterification are more polar and adsorb more strongly onto metal surfaces than native triglycerides, enhancing boundary film formation (Shi *et al.,*2024). Adsorption strength is a key determinant of anti-wear performance, with stronger surface interactions promoting more durable interfacial films that resist shear and reduce metal–metal contact. This mechanism aligns with recent advancements showing that chemically functionalized bio-lubricants exhibit improved wear resistance compared to their unmodified counterparts (Adeoti *et al.,*2024).

These results confirm that chemical modification acts as a molecular engineering step, transforming triglyceride-rich oils into temperature-stable ester base stocks suitable for high-performance lubrication.

Tribological Performance and Role of ZnO Nanoparticles

The tribological data (Table 3) demonstrate that ZnO nanoparticles significantly enhanced the anti-wear and friction-reducing properties of all bio-lubricants. The reduction in wear scar diameter by up to 34% and the corresponding decrease in coefficient of friction are statistically significant ($p < 0.05$) and comparable to improvements reported for ZnO-, CuO-, and TiO_2-based nanolubricants (Lee *et al.,*2009; Wu *et al.,*2017; Peña-Parás *et al.,*2018).

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DOI: https://doi.org/10.64388/IREV9I8-1714158

Table 3: Tribological Performance of Neat and ZnO-Enhanced Bio-Lubricants

Parameter	MO	MO + ZnO	J	J + ZnO	WC	WC + ZnO
Coefficient of friction (COF)	0.092 ± 0.004[a]	0.061 ± 0.003[c]	0.104 ± 0.005[a]	0.069 ± 0.004[b]	0.089 ± 0.004[a]	0.058 ± 0.003[c]
Wear scar diameter (mm)	0.62 ± 0.03[a]	0.41 ± 0.02[c]	0.68 ± 0.04[a]	0.45 ± 0.02[b]	0.60 ± 0.03[a]	0.38 ± 0.02[c]

MO = Monkey orange; J = Jatropha; WC = Wild calabash

Previous studies have attributed such improvements to a combination of rolling, mending, and tribofilm formation mechanisms (Zhang *et al.,*2014). In ester-based lubricants, the polar ester groups enhance adsorption onto steel surfaces, facilitating nanoparticle retention within the contact interface. This synergistic interaction between ester molecules and ZnO nanoparticles likely explains why even highly unsaturated wild calabash oil exhibited pronounced wear reduction upon nano-enhancement.

Comparable reductions in wear scar diameter (25–40%) have been reported for ZnO-enhanced vegetable oil lubricants under ASTM D4172 conditions, placing the present results well within the range of established nanolubricant performance (Peña-Parás *et al.,*2018; Hwang *et al.,*2011).

Extreme Pressure Performance and Boundary Film Strength

The extreme pressure (EP) properties reported in Table 4 reveal that both the chemically modified base oils and their ZnO-enhanced counterparts exhibit significant load-bearing capabilities, a key indicator of lubricant efficacy under severe contact stresses. Notably, the addition of ZnO nanoparticles resulted in substantial increases in both the last non-seizure load (LNSL) and weld load, indicating enhanced boundary film integrity and load-sharing capability relative to neat formulations.

These enhancements align with recent findings that metal oxide nanoparticles (including ZnO) can significantly improve EP performance through synergistic tribochemical film formation and mechanical reinforcement (Asadi *et al.,*2023; Liu *et al.,*2024). Under elevated contact pressures, ZnO nanoparticles reportedly undergo localized deformation and tribochemical interaction with iron surfaces, contributing to the formation of a zinc-rich tribofilm that resists adhesive wear and delays seizure (Liu *et al.,*2024). This mechanism is consistent with theoretical models of nanoparticle-mediated boundary lubrication, wherein hard inclusions at asperity junctions absorb shear energy and distribute load more evenly across the contact interface (Zhang *et al.,*2022). Across the three oil matrices evaluated, wild calabash and monkey orange oils exhibited more pronounced improvements in EP metrics with ZnO addition compared with Jatropha. This may be interpreted through the lens of fatty acid composition and ester structure, which influence the strength and continuity of the adsorption layer prior to nanoparticle reinforcement (Ribeiro *et al.,*2025). Highly unsaturated matrices can provide weaker intrinsic boundary films, making nanoparticle reinforcement comparatively more impactful in improving load-bearing capacity. In contrast, Jatropha's more balanced unsaturation and moderate polarity likely generated stronger base boundary films, which were further enhanced by ZnO but to a lesser relative degree.

Table 4: Extreme Pressure (EP) Properties of Bio-Lubricants

EP parameter	Monkey orange (crude)	Monkey orange + ZnO	Jatropha (crude)	Jatropha + ZnO	Wild calabash (crude)	Wild calabash + ZnO
LNSL (N)	784 ± 28[b]	981 ± 34[a]	686 ± 25[c]	882 ± 30[b]	812 ± 27[b]	1008 ± 36[a]
Weld load (N)	1568 ± 52[b]	1960 ± 61[a]	1372 ± 48[c]	1764 ± 55[b]	1617 ± 50[b]	2016 ± 64[a]

LNSL = last non-seizure load

Importantly, the observed weld load values for ZnO-enhanced formulations approach those reported for commercially formulated extreme-pressure additives (e.g., sulfur–phosphorus organometallics) used in industrial gear oils (Wang *et al.,*2023). Achieving comparable EP performance without traditional sulfur/halogen chemistries underscores the viability of environmentally acceptable bio-nanolubricants for high-stress applications, a key research priority in sustainable tribology (Bhushan & Li, 2021).

Thermal Stability Enhancement by ZnO Nanoparticles

The thermal stability profiles presented in Table 5 indicate that both the chemically modified bio-lubricants and their nano-enhanced formulations possess significantly enhanced thermal resistance relative to unmodified vegetable oil base stocks. Thermal stability is a critical performance attribute, particularly for applications involving sustained high temperatures (e.g., gearboxes, manufacturing equipment) where lubricant degradation can lead to viscosity breakdown, oxidation products formation, and deposit generation.

For the base modified oils, onset degradation temperatures in the range of ~298–320 °C are consistent with recent reports for chemically tailored bio-lubricants where esterification reduces labile moieties and lowers the concentration of easily oxidizable double bonds (Shi *et al.,*2024; Ribeiro *et al.,*2025). Structural modification via esterification/transesterification mitigates primary oxidation pathways by eliminating free fatty acids and reorganizing the fatty acid chains into more thermally robust esters, which aligns with mechanistic insights from advanced thermal analysis of biobased esters (Yang *et al.,*2023).

The incorporation of ZnO nanoparticles further shifted both onset degradation and maximum degradation temperatures upward by ~30–35 °C. This thermal augmentation is consistent with recent experimental observations that metal oxide nanoparticles can act as thermal stabilizers in lubricant matrices by altering heat transfer dynamics and restricting molecular diffusion, thereby delaying the onset of volatilization and chain scission (Kumar & Singh, 2024; Qian *et al.,*2022). ZnO's high intrinsic thermal conductivity may facilitate improved dissipation of localized heat under thermal stress, reducing hotspots that initiate decomposition.

Table 5: Thermal Stability Parameters of Modified and Nano-Lubricants

Thermal parameter	Monkey orange (modified)	Monkey orange + ZnO	Jatropha (modified)	Jatropha + ZnO	Wild calabash (modified)	Wild calabash + ZnO
Onset degradation (°C)	312 ± 5[b]	342 ± 6[a]	298 ± 4[c]	331 ± 5[b]	320 ± 5[b]	349 ± 6[a]
Tmax (°C)	378 ± 6[b]	401 ± 7[a]	365 ± 5[c]	392 ± 6[b]	385 ± 6[b]	409 ± 7[a]
Residual mass (%)	4.2 ± 0.3[b]	7.9 ± 0.4[a]	3.6 ± 0.2[c]	6.8 ± 0.3[b]	4.9 ± 0.3[b]	8.4 ± 0.4[a]

In addition to delaying degradation onset, the increased residual mass at high temperatures for ZnO-containing samples indicates suppressed thermal cracking and reduced formation of low-molecular-weight volatiles. This effect mirrors findings in polymer nanocomposite studies where nanoparticle networks constrain polymer chain mobility and inhibit weight loss at elevated temperatures (Zhao *et al.,*2025). Translated to lubricant systems, constrained molecular motion reduces the propensity for β-scission and free radical propagation, which are key drivers of thermal degradation in ester-based oils.

From a practical standpoint, the combined tribological and thermal enhancements suggest that ZnO-enhanced bio-lubricants can maintain functional viscosity and film integrity over extended high-temperature service, addressing an enduring limitation of many vegetable oil-derived lubricants. These results support the broader literature advocating the integration of nanoadditives to expand the usable thermal window of biolubricants without resorting to synthetic harsh chemistry (Sangar *et al.,*2023; Girishkumar *et al.,*2022).

CONCLUSION

This study demonstrated that underutilized non-edible seed oils from *Strychnos spinosa*, *Jatropha curcas*, and *Lagenaria sphaerica* can be effectively converted into high-performance bio-lubricants through targeted chemical modification and ZnO nanoparticle reinforcement. Acid-catalyzed esterification followed by transesterification significantly improved lubricant-relevant physicochemical properties by reducing free fatty acid content and enhancing viscosity stability. The incorporation of ZnO nanoparticles further enhanced tribological performance, evidenced by reduced friction and wear, improved extreme-pressure characteristics, and increased thermal stability. Among the evaluated feedstocks, wild calabash and monkey orange oils exhibited superior responses to nano-enhancement. Overall, the findings confirm that chemically modified, ZnO-enhanced bio-lubricants derived from locally available non-edible oils can serve as sustainable and environmentally friendly alternatives to conventional synthetic lubricants for demanding industrial applications.

ACKNOWLEDGMENT

The author would like to profoundly appreciate Tertiary Education Trust Fund (TETFund), Nigeria for giving financial support for the research through Taraba State Polytechnic Suntai, Nigeria. Engr. Tijani Idowu Abdulfatah of Integrated Research Laboratories located in Tanke, Oke–Odo, Ilorin, Kwara State, Nigeria, is also appreciated for the analyses carried out in his laboratories.

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