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An Experimental–Numerical Study on Oxidation Inhibition of SiO_2 Nanoparticles in Biolubricants for Internal Combustion Engines

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Abstract

Modern agriculture depends heavily on machinery to maximize operational efficiency and, consequently, profitability, but the wear-and-tear on the mechanical components of machinery due to ageing can lead to reduced efficiency, more downtime, and higher maintenance expenses, thus raising the operative costs. These problems have been addressed by the use of specific lubricant additives for machinery; however, additives have known disadvantages, such as compatibility restrictions and environmental concerns, which represent critical issues especially in case of possible dispersion in the environment. Modern industry is always looking for techniques and solutions to increase efficiency and productivity, and this study investigates the possible advantages of employing nanotechnology in lubricant formulations. Amongst all possible substances, SiO_2 nanoparticles are increasingly promising as lubricant additives due to their unique properties, which include heat resistance, high levels of stability, and good biocompatibility. Moreover, biolubricants, derived from renewable sources, offer an environmentally friendly alternative to conventional lubricants. This article contributes to the field of agricultural technology by demonstrating the potential of SiO_2 nanoparticles in formulations of biolubricants thought to be used in agricultural machines. Key degradation parameters, including density, viscosity, total acid number (TAN), total base number (TBN), oxidation, and elemental composition, were systematically analysed. The results showed that SiO_2 nanoparticles mitigate viscosity loss and density increase, optimize TAN and TBN, reduce oxidation of the biolubricants by up to 17.7% at 1.00 wt% SiO_2, and stabilize elemental composition during ageing. Nanoparticles remained uniformly dispersed without sedimentation for over 30 days. This provides insights that can prevent machinery performance degradation over time, reduce lubricant changes, and suggest a more sustainable and environmentally friendly lubrication solution, thus promoting more sustainable industry.

Keywords: farm machinery; lubricant additives; SiO_2 nanoparticles; biocompatibility; biolubricants; sustainable industry; oxidation

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1. Introduction

In modern agriculture, the efficiency and reliability of machinery are crucial for maintaining high field yields and profitability. However, the mechanical parts of these machines will eventually wear out from long-term usage. This leads to lower productivity, more

downtime, and further expensive maintenance [1,2]. To prevent these problems, conventional lubricants and their additives have been used, but they frequently have serious disadvantages, like compatibility restrictions [3] and environmental concerns. Given the potential that lubricants could leak into the environment, thus contaminating ecosystems, water, and soil, this is extremely concerning [4]. The machinery industry sector is constantly looking for novel and innovative methods to increase machinery production and efficiency while reducing its negative environmental effects in order to overcome these challenges. Using nanoparticles in lubricant compositions is one potential remedy [5,6]. Recent review papers published between 2022 and 2025 have confirmed that metal–oxide nanoparticles such as SiO_2, TiO_2, and Al_2O_3 can significantly improve friction reduction, thermal stability, and oxidation resistance in conventional lubricants and biolubricants, highlighting their growing importance in sustainable lubrication research [7–9].

Notably, SiO_2 (silicon dioxide) nanoparticles have become very successful lubricant additives because of their unique characteristics, which include strong biocompatibility [10], heat resistance and high levels of stability [11]. SiO_2 nanoparticles are additionally non-toxic and environmentally friendly [12], and these features make them an outstanding choice for use in machinery industries where lubricant leaks are potentially extremely hazardous.

"Biolubricants", i.e., lubricants coming from renewable sources [13], are an attractive solution to address these issues as well [14]. In the event of spills or leaks, biolubricants have less of an adverse effect on the environment and are more biodegradable than conventional lubricants [15,16]. They are a more environmentally friendly [17] and sustainable solution because they are usually made from vegetable or animal fats [18]. In machinery settings, where lubricant leakage can pose serious threats to the ecosystem, it is imperative to minimize negative environmental effects while reducing dependency on fossil fuels through the use of biolubricants [19]. Given the aforementioned premises, the absolutely most promising solution lies in the joint exploitation of these two substances, i.e., in having a biolubricant with nanoparticles added, as done in the present study.

Recent studies have also emphasized that improving the oxidation resistance and long-term thermal stability of vegetable-oil-based lubricants remains a major challenge, motivating the use of nanoparticle additives to enhance ageing resistance [20–22].

Indeed, Cortes et al. [5] investigated the rheological and tribological properties of sunflower oil enhanced with SiO_2 and TiO_2 nanoparticles. They found that the addition of these nanoparticles significantly reduced the coefficient of friction by up to 93.7% and lowered wear volume loss by up to 74.1% compared to the base oil. Their study suggests that nanoparticle-enhanced sunflower oil could serve as an effective biodegradable lubricant. Singh et al. [23] explored the use of the oil obtained from Balanites aegyptiaca L. (desert date) as an eco-friendly lubricant alternative to synthetic oils. Their study demonstrated that adding up to 0.6 vol% SiO_2 nanoparticles to the oil significantly reduced the coefficient of friction and wear rate, enhancing the oil's tribological performance. The findings suggest that this biolubricant blend could effectively replace mineral oils while addressing environmental concerns. Nik Roselina et al. [24] investigated the effect of TiO_2 nanoparticles on the viscosity of renewable palm oil lubricant. Their study revealed that adding 0.50 wt% and 1.00 wt% TiO_2 nanoparticles increased the viscosity index, making it comparable to SAE 0W20 grade lubricants. This indicates that TiO_2-enhanced palm oil could serve as an effective biolubricant with improved performance. Ahmad et al. [25] devised a method for producing biolubricant from castor oil by incorporating Fe_3O_4 nanoparticles and ethylene glycol ($C_2H_6O_2$) through transesterification. Optimal operational parameters were determined, resulting in a 94% yield after two hours at 160 °C. Artificial neural networks (ANNs) were utilized to predict biolubricant yield, demonstrating a linear correlation with key parameters. The tribological evaluation revealed that the produced biolubricant exhibited

a significantly reduced friction coefficient and wear of lubricated components compared to what was observed with raw castor seed oil and other biolubricant samples, particularly with the addition of 0.50 wt% Fe_3O_4 nanoparticles. Navada et al. [26] explored eco-friendly lubricants by blending Pongamia oil (*Millettia pinnata* L.) with neem oil (*Azadirachta indica* A. Juss.) and adding SiO_2 nanoparticles. The results showed a significant reduction in the average coefficient of friction by 8.69% with SiO_2 nanoparticles, extending the lubrication regime of Pongamia oil. Additionally, antioxidant properties were assessed using DPPH (2,2-diphenyl-1-picrylhydrazy) analysis, revealing a maximum free radical scavenging activity of 74.38% at the highest nanoparticle concentration. Singh et al. [27] explored the tribological properties of epoxidized Madhuca indica oil (*Madhuca longifolia* J. Konig) with SiO_2 nanoparticles. They found that the addition of nanoparticles improved viscosity and reduced friction and wear, which was particularly notable at 0.80 wt% nanoparticle concentration.

This study investigates the potential advantages of using SiO_2 nanoparticles in biolubricants under specific ageing conditions, a combination not extensively explored in previous studies. Biolubricants, derived from renewable sources, offer an environmentally friendly alternative to traditional lubricants. When combined with SiO_2 nanoparticles, they can provide enhanced performance and reduced environmental impact. By analysing key degradation parameters such as density, viscosity, total base number (TBN), total acid number (TAN), oxidation, and elemental composition, this research aims at providing a comprehensive understanding of the impact of SiO_2 nanoparticles on the performance and longevity of biolubricants. The experimental procedures involved evaluating the stability of the so-formed "nanobiolubricants", followed by subjecting the nanoparticles to artificial thermal ageing. The base biolubricant chosen for this study, prepared with various nanoparticles, underwent a degradation process in a hot-air oven. The degradation assessment and the impact analysis of the SiO_2 nanoparticles were evaluated through systematic chemical analyses and regression modelling. Accordingly, the present study focuses on the ageing behaviour of SiO_2-based nanobiolubricants under accelerated thermal ageing conditions (220 °C for 240 h), with systematic chemical analysis and regression modelling.

Despite the growing interest in nanoparticle-enhanced biolubricants, most previous studies have mainly focused on tribological or rheological performance, while systematic investigations on lubricant ageing remain limited. It should be noted that the present study specifically focuses on the chemical and oxidative stability of the biolubricant. Tribological performance is undoubtedly important for practical lubricant applications; however, the primary objective of this work was first to determine whether SiO_2 nanoparticles could improve oxidation resistance and ageing stability, since oxidative degradation directly affects viscosity retention, acidity increase, deposit formation, additive depletion, and ultimately lubricant service life. Although the tribological performance of SiO_2 nanoparticles has been widely reported in previous studies, it is beyond the scope of this work and therefore represents a limitation of the present study, although it should be investigated in future research in conjunction with the observed chemical stability improvements.

The novelty of the present work lies in the following:

- Investigating the chemical ageing behaviour of SiO_2-enhanced biolubricants, an aspect rarely addressed in previous studies compared with tribological performance.
- Developing an accelerated thermal ageing protocol (220 °C for 240 h) for SiO_2-based nanobiolubricants.
- Providing an integrated evaluation of key degradation indicators (density, viscosity, TAN, TBN, oxidation, and elemental composition).
- Comparing fresh biolubricant, aged base oil, and nanoparticle-modified biolubricants within the same experimental framework.

- Applying regression modelling to quantify the influence of SiO_2 concentration on lubricant degradation trends.

Overall, this work clarifies the role of SiO_2 nanoparticles in improving the stability and durability of environmentally sustainable biolubricants.

2. Materials and Methods

2.1. Nanoparticles and Formulation of Nanobiolubricants

The biolubricant (bio engine oil according to EN 16807) utilized in this study is PLANTO MOT SAE 10W40, obtained from Fuchs Lubricants Germany GmbH (Mannheim, Germany) [28]. According to the manufacturer, this lubricant contains more than 25% renewable raw materials as determined by ASTM D6866, thereby fulfilling the EN 16807 requirement for classification as a biolubricant. Table 1 provides the technical properties for this biolubricant. SiO_2 nanoparticles, characterized by specific dimensions and coated with KH570 Silane coupling agent (3-Methacryloxypropyltrimethoxysilane, $C_{10}H_{20}O_5Si$), were acquired from Nanografi Inc. (Ankara, Turkey) [29]. The main properties of these nanoparticles are presented in Table 2. The KH570-Silane-coated nanoparticles' elemental composition is primarily SiO_2, at 95.9 wt%. About 3–4 wt% of the material is covered with the KH570 coating. Iron (Fe) is present at 0.032 wt%, calcium (Ca) at 0.056 wt%, magnesium (Mg) at 0.0085 wt%, and sulfur (S) at 0.025 wt%.

Table 1. Properties of biolubricant (PLANTO MOT SAE 10W40).

Property	Unit	Value	Method
Kinematic viscosity at 40 °C	$[mm^2 \cdot s^{-1}]$	87	ASTM D445-24 [30]
Kinematic viscosity at 100 °C	$[mm^2 \cdot s^{-1}]$	13.7	ASTM D445-24 [30]
Viscosity index	[−]	160	ISO 2909:2002 [31]
Density at 15 °C	$[g \cdot cm^{-3}]$	0.8719	ASTM D4052-22 [32]
TBN	$[mg(KOH) \cdot g^{-1}]$	9.7	ASTM D4739-17 [33]
TAN	$[mg(KOH) \cdot g^{-1}]$	1.7	ASTM D664-18e2 [34]

Table 2. Technical properties of SiO_2 nanoparticles.

Technical Property	Unit	Value/Appearance
Purity	%	95.9+
Colour	[−]	white
Particle shape	[−]	amorphous
Average particle size	[nm]	18–35
Specific surface area	$[m^2 \cdot g^{-1}]$	150–550
Bulk density	$[g \cdot cm^{-3}]$	<0.1
True density	$[g \cdot cm^{-3}]$	2.2

When dealing with these nanoparticles, personnel utilized goggles, respirators, and latex gloves, among other appropriate personal safety equipment (PPE). To prevent and minimize exposure to nano hazards, the safety protocol specified in the material safety data sheet supplied by the manufacturer was followed.

The nanobiolubricants in this study were formulated using a two-step technique, illustrated in Figure 1:

1. Initially, SiO_2 nanoparticles were precisely measured to the desired mass and then introduced into the biolubricant samples at varying concentrations (0.25, 0.50, 0.75, and 1.00 wt%). These concentrations were selected using recommendations from the literature that provide the most effective ranges of SiO_2 nanoparticles in lubricants [5,35].

To achieve optimal stability and uniformity, the samples were subjected to magnetic stirring for 1.5 h at a speed of 1500 rpm under controlled temperature conditions to prevent agglomeration.

2. Following this, the samples underwent homogenization using an ultrasonic cleaner (VWR USC 600 THD, VWR International, Malaysia), which operates at a frequency of 45 kHz and with a power output of 120 W. This process, lasting 2.5 h, involved transmitting ultrasonic waves through water to break down nanoparticle agglomerates into smaller sizes. To ensure consistent conditions during sonication, the frequency, water temperature, and water volume were kept constant.

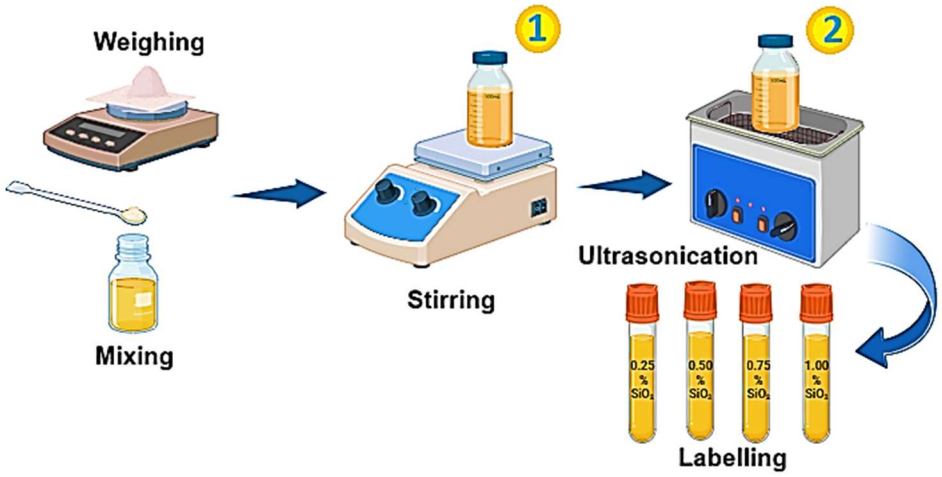


Figure 1. Two-step preparation technique for nanobiolubricants.

After the homogenization process, the nanobiolubricants were carefully poured into 10 mL glass test tubes for stability assessment.

2.2. Experimental Procedures

The physicochemical properties of the biolubricant and nanobiolubricants, including density, kinematic viscosity, viscosity index, TAN, TBN, oxidation, and elemental composition, were determined using standardized analytical methods prior to and after artificial ageing. The stability of the nanoparticles' dispersion was first evaluated through sedimentation photography [36]. The dispersion of nanoparticles was observed by visual inspection as a qualitative screening approach immediately after preparation, acknowledging that SiO_2 nanoparticles are intrinsically colourless when dispersed in oil. This preliminary qualitative observation was used to assess macroscopic dispersion behaviour prior to further stability evaluation in nanobiolubricants. The stability was assessed through qualitative visual inspection aimed at detecting macroscopic sedimentation or phase separation over time. This method involved leaving the samples undisturbed and observing any visible signs of particles settling at the bottom of the test tubes. Nanobiolubricant samples at four concentrations (0.25, 0.50, 0.75, and 1.00 wt%) were then left undisturbed for 30 days and examined. It should be noted that visual inspection has limitations in detecting nanoscale aggregation; alternative techniques such as dynamic light scattering (DLS), UV-Vis spectroscopy, centrifugation with particle quantification, or electron microscopy (TEM/SEM) could provide more sensitive and quantitative assessments. Visual inspection was chosen in this study because even slight macroscopic sedimentation could block valve pistons or promote rapid localized wear, which may be more critical than general lubricant ageing. Future studies could combine visual inspection with these more sensitive techniques to achieve a comprehensive evaluation of sedimentation behaviour.

Following this, the nanoparticles were subjected to artificial thermal ageing to examine their effects over time. Regarding this procedure, both the base biolubricant, PLANTO MOT SAE 10W40, and all the prepared nanobiolubricants were exposed to a degradation process. They were heated in a hot-air oven (TCF 120 PLUS by TC Farmer Co., Canandaigua, NY, USA; https://www.tcfarmer.com/) at 220 °C (493.15 K) for 240 h. The selected temperature and time were not based on a standardized method but, rather, were determined through preliminary trials aimed at identifying a condition where noticeable oxidative degradation could occur. Initial tests at 90 °C and 150 °C for up to 240 h showed minimal changes in degradation markers. Therefore, 220 °C for 240 h was chosen as the lowest temperature at which significant oxidation and ageing effects were clearly observed [37,38]. This threshold also aligned with thermal stability limits found in the literature [39,40], while still remaining below the 250 °C boundary beyond which irreversible breakdown typically occurs [41]. To maintain a uniform temperature and ensure proper air circulation, the oven's internal ventilation was on to grant better temperature homogeneity throughout the ageing period. The nanobiolubricant samples were placed in open 100 mL bottles without lids for the experiments. To assess the degradation of nanobiolubricants and analyse the impact of the SiO_2 nanoparticles as an additive, the methods and instruments outlined in Table 3 were employed. The selected analytical techniques and standardized test methods ensured reliable determination of the physicochemical properties relevant to lubricant degradation assessment.

Table 3. Techniques and equipment used for evaluating degradation and analysing nanoparticle effects.

Measured Parameter	Used Instrument	Manufacturer, Model	Precision
Density Viscosity 40–100 °C Viscosity Index	Viscometer	Anton Paar (Graz, Austria), SVM 3001	on Density = 0.0001 [g·cm^{-3}] on Viscosity = 0.001 [mm^2·s^{-1}]
IR Nitration Oxidation	FT-IR Spectrometer	PerkinElmer, Spectrum 100	0.1 [au·cm^{-1}]
TBN TAN	Titrator	Mettler Toledo (Greifensee, Switzerland), T50	on TBN = 0.01 [mg(KOH)·g^{-1}] on TAN = 0.001 [mg(KOH)·g^{-1}]
Metals Wear Elements (Fe, Cr…) Pollution Elements (Si,…) Additive Elements (Ca,…)	ICP-OES	PerkinElmer, OPTIMA 8000	1 [ppm]

FTIR analysis was conducted using a PerkinElmer Spectrum 100 FTIR spectrometer (PerkinElmer Inc., Waltham, MA, USA). The spectra were recorded in the range of 4000–500 cm^{-1} with a cell path length of 0.1 cm. The oxidation index was calculated by integrating the absorbance area of the carbonyl band in the 1710–1740 cm^{-1} region after baseline correction. These values were automatically computed using Spectrum OilExpress v. 4.0 software (PerkinElmer, Inc., Waltham, MA, USA).

2.3. Data Analysis

To statistically evaluate the influence of SiO_2 nanoparticles on the ageing behaviour of the biolubricant, the experimental data were processed using linear regression analysis. Regression modelling was employed to describe how the independent variable, namely SiO_2 concentration (0.25–1.00 wt%), affected the measured response variables (density, viscosity, TAN, TBN, oxidation, and elemental concentrations) and, in particular, state if the relation between the measured response variables is increasing or decreasing as the

nanoparticle concentration increases (i.e., if the angular coefficient of the regression line is positive or negative). The 0.00 wt% SiO_2 sample was treated as a baseline reference and excluded from the regression analysis.

Since only one factor was varied, and the experimental trends were monotonic, linear models were found to best represent the data. The regression equations were all expressed in the following general form (explicit linear equation):

$$y(x) = a_0 + a_1 \cdot (x - 0.25)$$

where y(x) is a generic inquired response variable, a_0 is the intercept, corresponding to the reference condition at 0.25 wt% SiO_2 (minimum tested concentration), and a_1 is the slope describing the effect of SiO_2 concentration. The coefficient of determination (R^2) was used to assess the quality of each fit.

All regression equations are expressed relative to the baseline concentration of 0.25 wt% SiO_2, which was chosen as the experimental starting point.

This approach allowed for a clear quantification of the influence of SiO_2 nanoparticles on the degradation parameters, providing straightforward mathematical models to approximate the observed ageing behaviour.

All measurements were performed under identical and controlled experimental conditions using calibrated instruments. Due to experimental constraints, replicate measurements were not available for all parameters, and the reported values therefore represent single-point measurements. This aspect is acknowledged as a limitation of the present study.

3. Results and Discussion

3.1. Visual Evaluation of Nanoparticle Sedimentation

These observations were made following the visual inspection procedure described in Section 2.2. No macroscopic phase separation was observed during or at the end of this period. Figure 2a illustrates the samples after 30 days, while Figure 2b depicts that even after tilting the laboratory glass, only a minimal amount of material was observed at the bottom, indicating slight macroscopic sedimentation.

(**a**) (**b**)

Figure 2. Visual evaluation: (**a**) nanobiolubricant samples after 30 days; (**b**) minimal sedimentation observed after tilting the laboratory glass.

3.2. Analysis of Nanobiolubricants' Degradation Due to Artificial Ageing: Viscosity, Density, TAN, TBN

The degradation of the nanobiolubricants after 240 h at 220 °C was analysed to assess the influence of SiO_2 nanoparticles on the biolubricant stability. The measured parameters

included density, viscosity, TBN, TAN, oxidation, and elemental composition, with the fresh biolubricant without nanoparticles (0.00 wt% SiO_2) used as a reference baseline. In addition, an aged base biolubricant sample (0.00 wt% SiO_2), subjected to the same artificial ageing procedure, was included for direct comparison.

The resulting regression equations are as follows (in all of them, x is the SiO_2 nanoparticle concentration in wt%):

$$\text{Density } [\text{g}\cdot\text{cm}^{-3}] = 0.8779 + (-0.0009) \cdot (x - 0.25) \ (R^2 = 0.97) \quad (1)$$

$$\text{Viscosity at } 40\ ^\circ\text{C } [\text{mm}^2\cdot\text{s}^{-1}] = 81.70 + (-4.40) \cdot (x - 0.25) \ (R^2 = 0.99) \quad (2)$$

$$\text{Viscosity at } 100\ ^\circ\text{C } [\text{mm}^2\cdot\text{s}^{-1}] = 12.60 + (-0.40) \cdot (x - 0.25) \ (R^2 = 1.00) \quad (3)$$

$$\text{Viscosity Index} = 153.00 \text{ (constant, not significantly affected by x)} \quad (4)$$

In the reference fresh biolubricant, the density was 0.8719 $g\cdot cm^{-3}$, the kinematic viscosity values were 87.0 $mm^2\cdot s^{-1}$ (40 °C) and 13.7 $mm^2\cdot s^{-1}$ (100 °C), and the viscosity index was 160. After ageing without nanoparticles (base aged sample, 0.00 wt% SiO_2), significant degradation occurred. Density increased to 0.8766 $g\cdot cm^{-3}$, and viscosity decreased to 79.2 $mm^2\cdot s^{-1}$ (40 °C) and 12.4 $mm^2\cdot s^{-1}$ (100 °C), while the viscosity index slightly decreased to 154. The incorporation of SiO_2 nanoparticles mitigated these degradation effects, however present, as indicated by the recorded modifications to the observed properties.

This behaviour can be explained in terms of the thermo-oxidative stability of the biolubricant. During high-temperature ageing, oxidation reactions and molecular rearrangements typically lead to an increase in density due to the formation of higher-molecular-weight compounds and more compact molecular structures. The presence of SiO_2 nanoparticles can influence these processes by modifying heat transfer and intermolecular interactions within the lubricant matrix, thereby partially limiting structural changes induced by thermal degradation.

Similar considerations on the relationship between molecular structure, thermal stability, and physicochemical properties have been reported in the literature. For instance, Moreira et al. [42] showed that biolubricants with improved thermo-oxidative stability exhibit more controlled variations in density, kinematic viscosity, and viscosity index under elevated temperatures. This supports the interpretation that both formulation chemistry and additives, such as nanoparticles, play a key role in stabilizing lubricant properties during thermal ageing.

Density increased for all aged samples compared to the fresh biolubricant, with the best stability observed at 1.00 wt% (0.8772 $g\cdot cm^{-3}$). At 0.25 wt%, viscosity retention was best preserved (81.8 $mm^2\cdot s^{-1}$ at 40 °C, 12.6 $mm^2\cdot s^{-1}$ at 100 °C), though the viscosity index remained nearly constant (153–154). Figure 3 presents the regression plots for density and viscosity, highlighting the statistical relationship between SiO_2 concentration and ageing responses. The viscosity index exhibited only minor variations (153–154) across the investigated SiO_2 concentrations. The slightly higher value observed at 0.75 wt% is attributed to the sensitivity of the ISO 2909 viscosity index calculation to small variations and rounding in kinematic viscosity values, rather than to a systematic concentration-dependent effect. Therefore, the viscosity index is reported directly in the text rather than through a graphical representation.

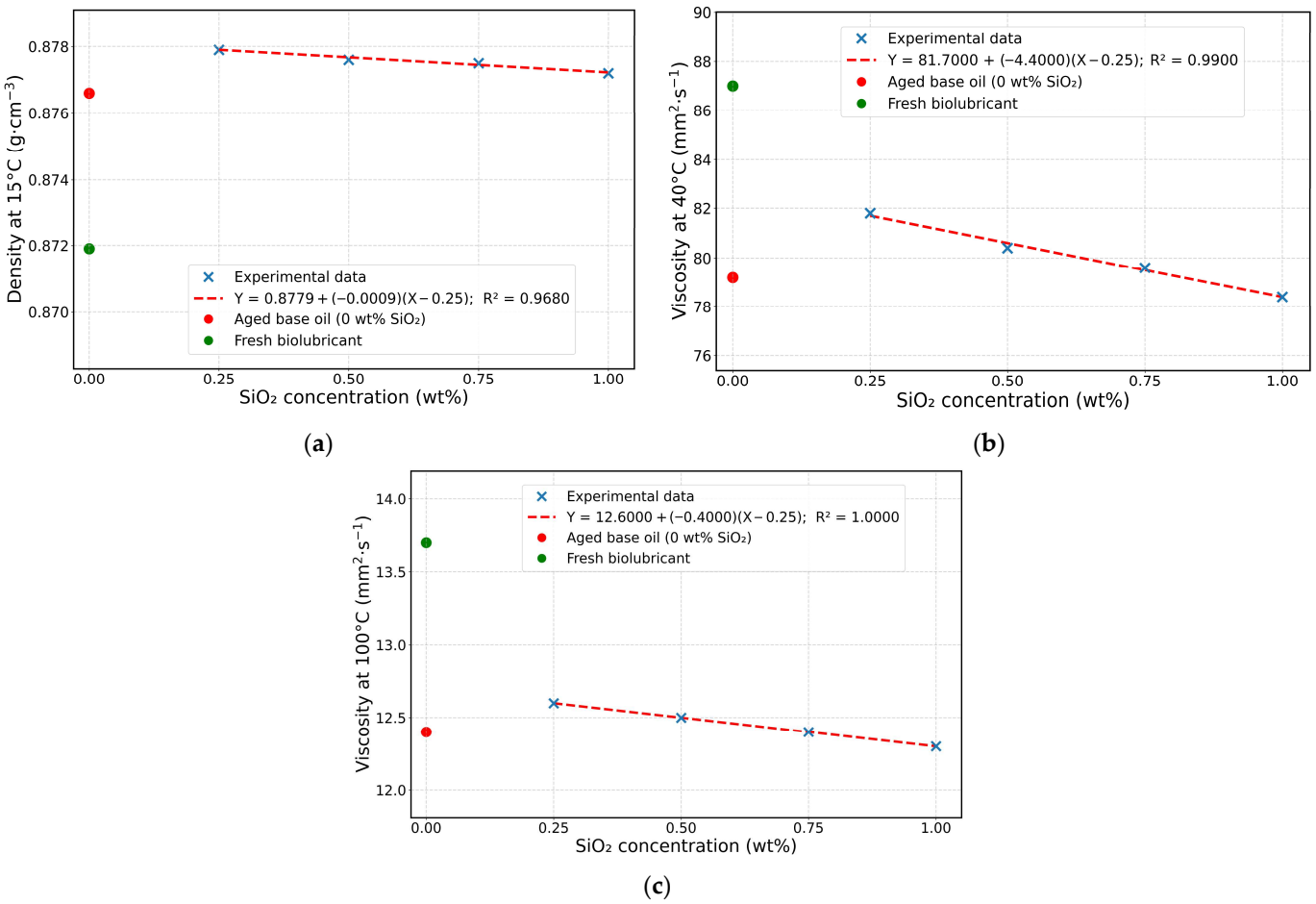


Figure 3. Regression plots of (**a**) density at 15 °C; (**b**) kinematic viscosity at 40 °C; (**c**) kinematic viscosity at 100 °C.

The total acid number (TAN) increased significantly from 1.7 mg(KOH)·g^{-1} in fresh oil to approximately 3.5–3.4 mg(KOH)·g^{-1} in aged samples, indicating sensible acid formation due to ageing. The total base number (TBN), which measures the alkaline reserve, decreased from 9.7 mg(KOH)·g^{-1} in fresh oil to around 6.9–7.2 mg(KOH)·g^{-1} in aged samples, showing depletion of additives over time. Notably, at 1.00 wt% SiO_2, the TAN value (3.4 mg(KOH)·g^{-1}) was the lowest while the TBN value (7.2 mg(KOH)·g^{-1}) was the highest, confirming that this concentration provided the most favourable ageing performance. The regression plots for TAN and TBN are displayed in Figure 4, emphasizing the statistical connection between ageing responses and SiO_2 concentration. The resulting regression equations are as follows:

$$\text{TAN [mg(KOH)·g}^{-1}\text{]} = 3.59 + (-0.24) \cdot (x - 0.25)\ (R^2 = 0.90) \quad (5)$$

$$\text{TBN [mg(KOH)·g}^{-1}\text{]} = 6.95 + (0.40) \cdot (x - 0.25)\ (R^2 = 0.83) \quad (6)$$

3.3. Elemental Analysis of Nanobiolubricants Degraded Due to Artificial Ageing

Elemental analysis was performed to monitor the variations in key additive and contaminant elements in the biolubricant samples after artificial ageing in the presence of SiO_2 nanoparticles. The measured elements included calcium, magnesium, zinc, phosphorus, and boron (typical detergent, dispersant, and antiwear additives), together with trace levels of sodium and silicon. Molybdenum was also analysed due to its role in friction-modifying additives. To statistically validate these observations, linear regression analysis was per-

formed using SiO_2 concentration (0.25–1.00 wt%) as the independent factor. The resulting regression equations are as follows:

$$\text{Silicium [ppm]} = 222.4000 + (753.6000) \cdot (x - 0.25)\ (R^2 = 0.99) \quad (7)$$

$$\text{Sodium [ppm]} = 9.1000 + (26.4000) \cdot (x - 0.25)\ (R^2 = 0.98) \quad (8)$$

$$\text{Calcium [ppm]} = 1838.5000 + (-124.0000) \cdot (x - 0.25)\ (R^2 = 0.92) \quad (9)$$

$$\text{Magnesium [ppm]} = 373.9000 \text{ (constant, not significantly affected by x)} \quad (10)$$

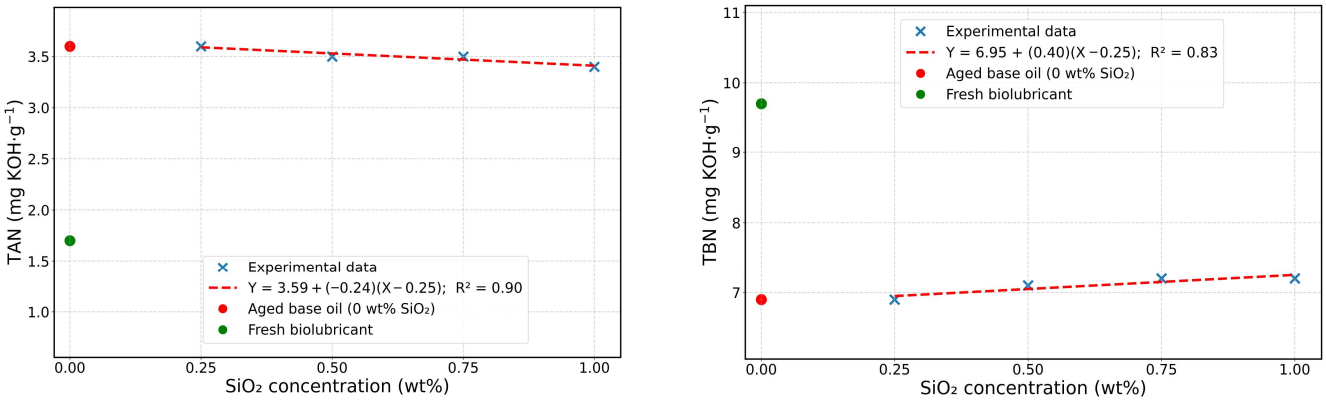
$$\text{Zinc [ppm]} = 752.8000 + (-14.8000) \cdot (x - 0.25)\ (R^2 = 0.45) \quad (11)$$

$$\text{Phosphorus [ppm]} = 668.5000 + (-58.0000) \cdot (x - 0.25)\ (R^2 = 0.96) \quad (12)$$

$$\text{Boron [ppm]} = 450.4000 + (-74.4000) \cdot (x - 0.25)\ (R^2 = 0.97) \quad (13)$$

$$\text{Molybdenum [ppm]} = 77.7000 + (-5.2000) \cdot (x - 0.25)\ (R^2 = 0.96) \quad (14)$$

The regression plots for elemental concentrations are presented in Figure 5, showing the relationships between SiO_2 concentration and each of the measured elements (Si, Na, Ca, Mg, Zn, P, B, and Mo). Each plot includes both the experimental data and the corresponding linear regression model, with the regression equation and coefficient of determination (R^2) displayed in the legend.



(**a**) (**b**)

Figure 4. Regression plots of: (**a**) the total acid number (TAN); (**b**) the total base number (TBN).

Silicon exhibited a strong positive correlation with nanoparticle concentration ($R^2 = 0.99$), reflecting the expected increase in elemental Si due to stable nanoparticle dispersion in the lubricant matrix.

Sodium also increased consistently with higher SiO_2 concentrations ($R^2 = 0.98$), which may be attributed to contamination effects or interactions between sodium-containing residues and nanoparticle surfaces.

In contrast, calcium, phosphorus, boron, and molybdenum showed pronounced decreases with increasing nanoparticle content, with R^2 values above 0.90, confirming significant depletion of detergent, dispersant, and friction-modifying additives during thermal ageing. Zinc displayed only a moderate reduction ($R^2 = 0.45$), suggesting that its depletion was not strongly influenced by nanoparticle addition but rather by general oxidative degradation mechanisms. This behaviour can be attributed to the thermal decomposition of zinc dialkyldithiophosphate (ZDDP)-type antiwear additives, which are known to undergo partial consumption during high-temperature ageing regardless of nanoparticle presence. The relatively low R^2 value indicates that zinc depletion is governed by multiple

concurrent mechanisms, including oxidative degradation and additive transformation, rather than a direct interaction with SiO_2 nanoparticles.

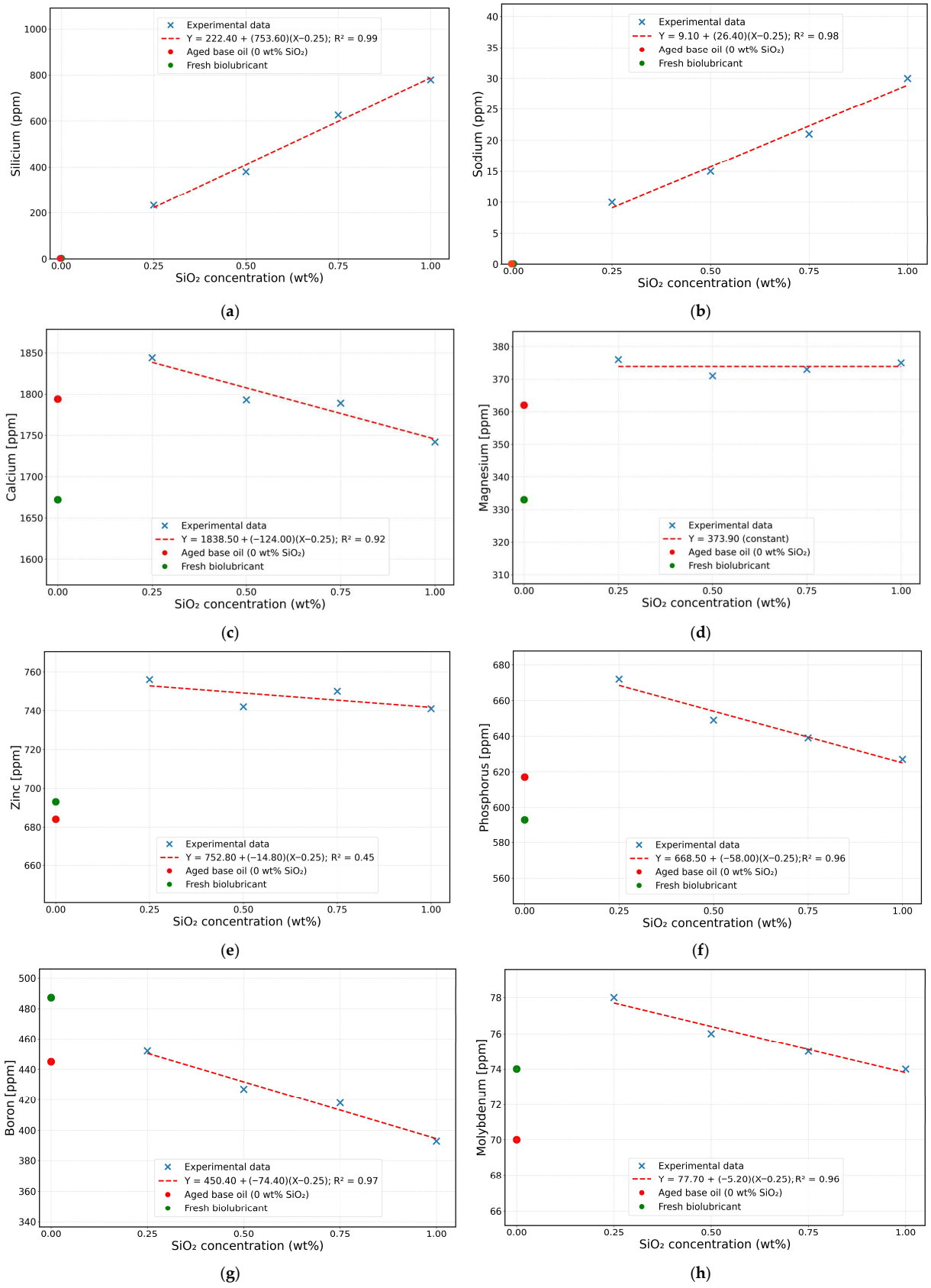


Figure 5. Regression plots of: (**a**) silicium [ppm]; (**b**) sodium [ppm]; (**c**) calcium [ppm] (**d**) magnesium [ppm]; (**e**) zinc [ppm]; (**f**) phosphorus [ppm]; (**g**) boron [ppm]; (**h**) molybdenum [ppm].

Magnesium remained practically constant across all samples (373.8 ± 2.5 ppm, $R^2 \approx 0.00$), indicating negligible dependence on SiO_2 concentration and confirming that this element did not participate in degradation or additive depletion reactions. This stability is consistent with the role of magnesium-based detergents (e.g., magnesium sulfonates), which are typically present in overbased and thermally stable forms. These additives are less prone to depletion during thermal ageing and do not readily interact with inert SiO_2 nanoparticles, resulting in minimal variation across the investigated concentration range.

All elemental results for nanoparticle-containing samples were evaluated relative to the aged base biolubricant (0.00 wt% SiO_2), which served as the reference condition.

3.4. Analysis of Nanobiolubricants' Degradation Due to Artificial Ageing: Oxidation

The effects of SiO_2 nanoparticles on oxidation are noteworthy. In the aged biolubricant without nanoparticles, the oxidation level, obtained from the FTIR spectra [15,43,44], reached 27.0 au·cm^{-1}. In contrast, the addition of nanoparticles reduced the oxidation values to 25.7–22.2 au·cm^{-1}, corresponding to a 17.7% reduction at the highest nanoparticle concentration (1.00 wt%). To statistically validate this effect, linear regression analysis was carried out with SiO_2 concentration (0.25–1.00 wt%) as the independent factor. Because the trends were monotonic, linear models provided the best description of the data (Figure 6). Representative FTIR spectra of fresh and aged PLANTO MOT SAE 10W40 samples with different SiO_2 concentrations are provided in Figure 7, showing a decrease in the carbonyl peak intensity (~1739 cm^{-1}) with increasing nanoparticle content.

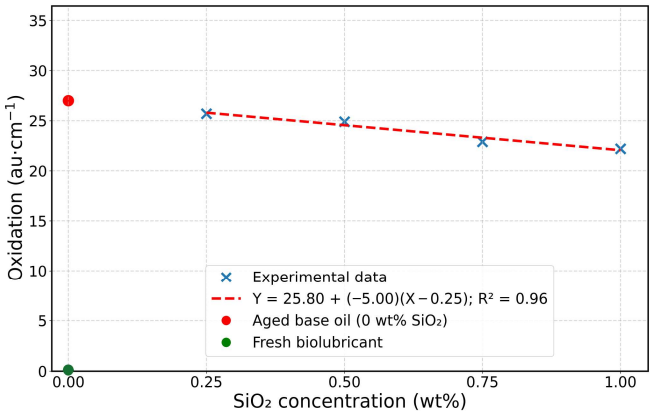


Figure 6. Regression plots of oxidation.

All oxidation results for nanoparticle-containing samples were evaluated relative to the aged base biolubricant (0.00 wt% SiO_2), which served as the reference condition.

$$\text{Oxidation [au·cm}^{-1}\text{]} = 25.80 + (-5.00) \cdot (x - 0.25)\ (R^2 = 0.96) \quad (15)$$

By looking at the angular coefficient of the regression equation, it is possible to state that, while maintaining a constant thermal load, the oxidation level decreases by approximately 5.00 au·cm^{-1} for every unit increase in SiO_2 content (wt.%). Furthermore, this negative coefficient clearly shows the protective function of SiO_2 nanoparticles against oxidation, as oxidation levels decline with increasing SiO_2 concentration. Within the studied range (0.25–1.00 wt%), the model therefore confirms that nanoparticle addition significantly mitigates oxidation. This FTIR-derived reduction in oxidation is consistent with the improved viscosity retention and lower TAN values observed in the aged nanobiolubricants, further supporting the protective role of SiO_2 nanoparticles against thermo-oxidative degradation.

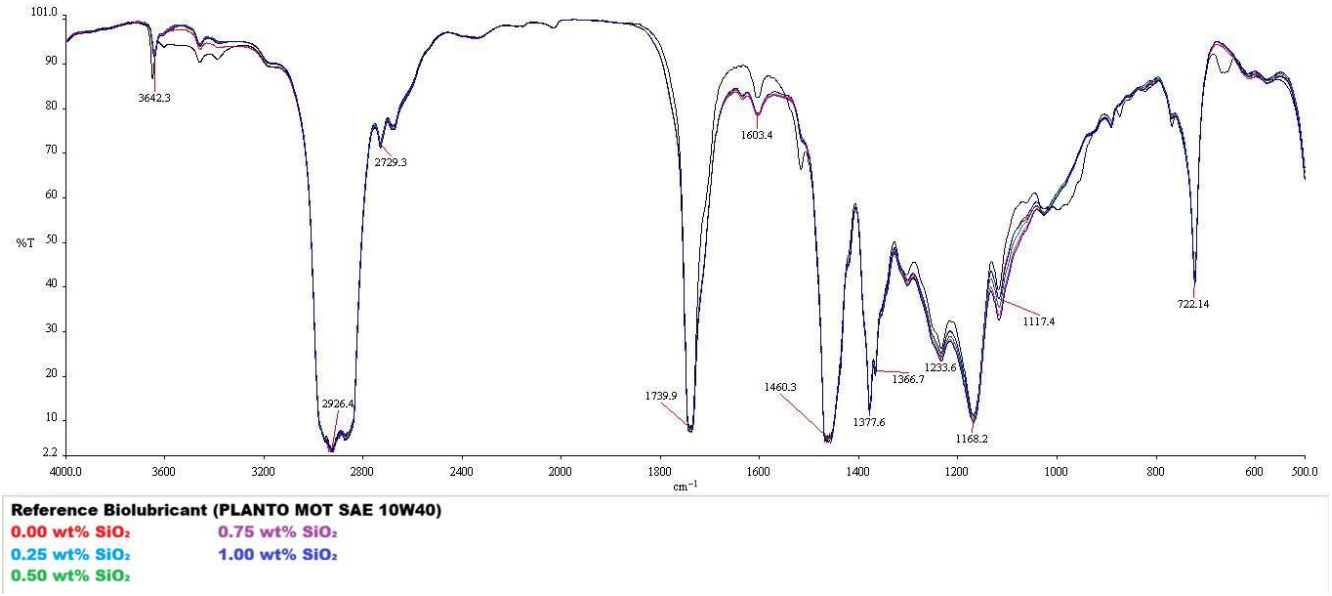


Figure 7. FTIR spectra of aged PLANTO MOT SAE 10W40 nanobiolubricants with different SiO_2 concentrations.

4. Conclusions

Research on SiO_2 nanoparticles' potential as additives to biolubricants for internal combustion engines has resulted in promising outcomes. The artificial ageing experiments conducted at 220 °C for 240 h reported in this study provided valuable insights into the role of SiO_2 nanoparticles in the degradation behaviour of a commercial biolubricant, representative of this type of interesting lubricant. Linear regression analysis on data concerning many physicochemical and chemical properties of the lubricant confirmed that the addition of nanoparticles has a significant influence. Density, viscosity, TAN, TBN, oxidation, and elemental concentrations were systematically evaluated, with regression models demonstrating monotonic trends and high statistical significance in most cases. The results revealed the following:

- Viscosity and density: Incorporation of SiO_2 nanoparticles mitigated the viscosity loss and density increase observed in the aged base biolubricant. Viscosity retention was best at 0.25 wt% SiO_2, while density stability was achieved at 1.00 wt%.
- TAN and TBN: The most favourable balance was found at 1.00 wt% SiO_2, where TAN reached its lowest value (3.4 mg(KOH)·g^{-1}) and TBN its highest value (7.2 mg(KOH)·g^{-1}), indicating improved resistance to acid formation and preservation of the alkaline reserve.
- Oxidation: A clear protective effect was observed, with oxidation levels decreasing by up to 17.7% at 1.00 wt% SiO_2 compared with the aged base biolubricant. The linear model indicated a constant reduction of approximately 5.00 au·cm^{-1} per unit increase in SiO_2 concentration.
- Elemental analysis: While silicon and sodium increased with nanoparticle concentration, reflecting dispersion stability and minor contamination effects, additive elements such as calcium, phosphorus, boron, and molybdenum decreased markedly, confirming progressive depletion during ageing. Zinc exhibited only a moderate decline, and magnesium remained nearly constant.

Furthermore, throughout the period of 30 days, there was no visible sedimentation and the nanoparticles remained in a stable dispersion within the biolubricant. In order to

maintain consistent biolubricant performance and avoid clogging or damage to machinery components, this stability is essential.

Overall, the use of SiO_2 nanoparticles in biolubricants presents a viable approach to enhancing the performance and sustainability of lubricants. By reducing the frequency of lubricant changes and improving operational efficiency, these nanotechnology-based additives offer a pathway to more sustainable machinery practices.

Future research should explore the long-term performance of SiO_2 nanoparticle-enhanced biolubricants under real engine operating conditions, including cyclic thermal and mechanical stresses. In addition, further investigations are needed to better characterize nanoparticle dispersion and stability using advanced techniques such as dynamic light scattering (DLS) or electron microscopy. The evaluation of different types of nanoparticles, surface functionalizations, and concentration ranges could provide further insights into optimizing formulation performance. Moreover, future studies should assess tribological behaviour (e.g., friction and wear reduction) and conduct comprehensive environmental impact analyses, including biodegradability and potential nanoparticle release. These aspects are essential to fully validate the applicability of nanobiolubricants for sustainable industrial use.

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