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Effect of Zinc Dialkyl Dithiophosphate (ZDDP) Additive on the Physicochemical Characteristics of Neem Oil-Based Bio-Lubricants

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Abstract

This study investigates the effects of Zinc Dialkyl Dithiophosphate (ZDDP) additive on selected physico-chemical properties of neem oil bio-lubricant. Raw neem oil transesterified into bio-lubricant ester, was prepared as a base formulation and amended with ZDDP at concentrations of 1%, 2%, and 3% (w/w). The properties evaluated included density, specific gravity, kinematic viscosity, acid value, free fatty acid (FFA) content, saponification value, pour point, cloud point, and flash point. Experimental results show that increasing ZDDP concentration slightly reduced density and specific gravity while producing a gradual increase in viscosity. Acid value and free fatty acids decreased marginally with higher ZDDP loading. Saponification value increased slightly across the additive concentrations. Cold-flow properties improved modestly, as evidenced by lowered pour and cloud points. Flash point increased with ZDDP addition, suggesting enhanced thermal safety. Overall, ZDDP positively influenced multiple physico-chemical indicators relevant to engine-oil suitability, although the specific tribological performance and wear protection require further evaluation through wear and oxidation tests.

Keywords: Neem Oil, Bio-Lubricant, ZDDP, Physico-Chemical Properties, Viscosity, Flash Point, Pour Point.

Introduction

The process of applying an oil coating or film between two objects that are moving relative to one another in order to lessen friction between them is known as lubrication (Nehal and Amal, 2013). A fluid known as lubricating oil or lubricant is necessary to reduce wear and friction between surfaces that are moving relative to one another (Nehal and Amal, 2013). Lubricant must therefore have specific goals, such as minimizing wear and power loss in order to overcome friction, lowering oxidation to prevent corrosion, acting as a shock absorber in automotive engine parts, serving as a cleaning agent in a variety of applications, and lowering heat from friction (Nehal and Amal, 2013).

High viscosity and viscosity index, thermal stability, high oxidation resistance, and corrosion avoidance are all necessary for a suitable lubricant, (Nehal and Amal, 2013). Crude oil or petroleum is the traditional source of lubrication. It is a byproduct of petroleum refining. Crude oil disposal contributes to the degradation of both the terrestrial and maritime environments, even though the applications of mineral oil are restricted due to its limited availability (Nehal and Amal, 2013). The use of petroleum-based oil in automobile engines produces emissions that are detrimental to the environment because they contain traces of metals including iron, zinc, and magnesium (Menon et al., 2023).

In order to address the issues with the use of mineral-based lubricants, research has recently focused on alternative bio-lubricants (Gul, et al. 2021). Bio-lubricants are simply and quickly biodegradable (Noreen et al., 2021). Furthermore, they don't harm people, animals, or land (Salih et al., 2011). They may be based on esters made from modified oils or oils taken from plants or animals. Jatropha seed oil, castor seed oil, soybean oil, and sunflower oil are a few common types of oil utilized in the creation of biolubricants (Cavalcanti et al., 2018; Odetoye et al., 2016; and Kumar et al., 2021).

The hunt for bio-lubricants made from renewable feedstocks as greener substitutes for petroleum-based lubricants has accelerated due to the global move toward sustainable industrial practices. Benefits of bio-oils include their high biodegradability, reduced toxicity and high viscosity indices by nature. Because of its high unsaturated fatty acid content and potential as a basic stock for lubricant formulations following suitable chemical modification, including transesterification, neem oil (Azadirachta indica) has attracted a lot of scientific interest among non-edible oils.

Despite their potential, raw bio-oils frequently show drawbacks for full-scale engine applications, such as unfavorable acidity levels, limited thermal working ranges, and poor oxidative stability. Multipurpose additives are crucial to overcoming these obstacles. In the lubricant business, zinc dialkyl dithiophosphate (ZDDP) is still one of the most used anti-wear (AW) and antioxidant additives. ZDDP works by breaking down hydroperoxides, which are precursors to oxidative deterioration, and by creating protective polyphosphate tribofilms on rubbing surfaces. Recent studies have demonstrated that ZDDP concentrations as low as 1–2%

can significantly reduce the coefficient of friction and wear scar diameter in vegetable oil blends.

Ester groups of the triacylglycerol molecule react with phosphate groups to form a protective fatty-phosphite layer during tribochemical interactions. This is a critical reaction for boundary lubrication performance. (Gomes, et al. 2025)

Polar functional groups in the triacylglycerol molecule of vegetable oils in conjunction with oil-additive-metal interactions during metal rubbing can significantly improve wear resistance.

Increasing the polar functionality of the vegetable oil structure has a positive impact on wear protection resulting from stronger adsorption on metal surfaces as well as greater lateral interaction between ester chains

Phosphorus-based molecules like phosphates and phosphites (with phosphorus oxidation states of +5 and +3, respectively) serve distinct roles: organic phosphites primarily function as friction modifiers, whereas phosphates are more effective as anti-wear additives. Under conditions of heat and pressure, these additives undergo chemical reactions that produce thin, durable layers known as tribofilms, which bond tightly to metal surfaces.

The interaction occurs because boundary lubrication in a dynamic mechanical system is primarily governed by the formation of a stable tribochemical film, where polar functional groups in the triacylglycerol molecule work in conjunction with oil-additive-metal interactions.

While the tribological mechanisms of ZDDP are well-documented, its influence on the foundational physico-chemical properties of neem oil requires detailed investigation to ensure formulations meet international standards such as ISO VG-32 or SAE 20W40. This work examines the impact of varying ZDDP concentrations on the physical and chemical markers of a neem-based bio-lubricant.

Materials and Methods

Materials

- **Base Oil:** Neem oil bio-lubricant extracted from neem seeds, which typically contain an oil content of 25–45%.
- **Additive:** Commercial grade Zinc Dialkyl Dithiophosphate (ZDDP).
- **Formulations:** Four samples were analyzed: 0% (Neem base), 1%, 2%, and 3% ZDDP by weight (w/w).

Preparation

The neem bio-lubricant was mixed with ZDDP at predetermined mass percentages. The mixes were stirred magnetically to provide a uniform mixing. The mixture was heated to 50^0C, stirred for 180minutes at a speed of 650rpm. The choice of these conditions is to ensure complete dissolution and uniform dispersion while stirring in accordance with lubricant blending standards. The same conditions were maintained for all mixes. According to earlier research,

ZDDP is easily soluble in oil and frequently needs to be heated to a moderate temperature (such as 60°C) or sonicated for the best dispersion.

Physico-Chemical Property Determination

Testing was conducted following standard procedures:

- **Density & Specific Gravity (ASTM D4052):** Measured using standard hydrometer methods or AOAC/ASTM methods.
- **Kinematic Viscosity (ASTM D445):** Determined at 40°C, a standard reference temperature for identifying ISO viscosity grades.
- **Acid Value & FFA (AOCS Official Method Ca 5a-40) :** Determined via titration; essential as raw neem oil can have initial FFA levels as high as 3.7%–4.87%.
- **Cold-Flow Properties (ASTM D97):** Cloud and pour points were determined to evaluate low-temperature fluidity.
- **Flash Point (ASTM D92):** Measured using the Cleveland Open Cup method to assess thermal safety.

Results and Discussion

Table 1. Physico-chemical properties of neem bio-lubricant with different ZDDP concentrations.

S/N	Property	Neem Base	1% ZDDP	2% ZDDP	3% ZDDP
1	Density (g/mL)	0.8628	0.8624	0.8603	0.8586
2	Specific gravity	0.8822	0.8818	0.8797	0.8779
3	Viscosity (mm²/s)	4.37	4.41	4.48	4.55
4	Acid value (mg KOH/g)	0.6732	0.6520	0.6500	0.6500
5	Free fatty acid (%)	0.3366	0.3260	0.3250	0.3250
6	Saponification value (mg KOH/g)	150.0675	152.33	154.21	154.26
7	Pour point (°C)	−13.2	−14.33	−14.36	−14.37
8	Cloud point (°C)	−9.4	−11.02	−11.07	−11.09
9	Flash point (°C)	183	184	184.4	186.2
10	Heating value (mJ/kg)	38.96	39.22	39.26	39.34

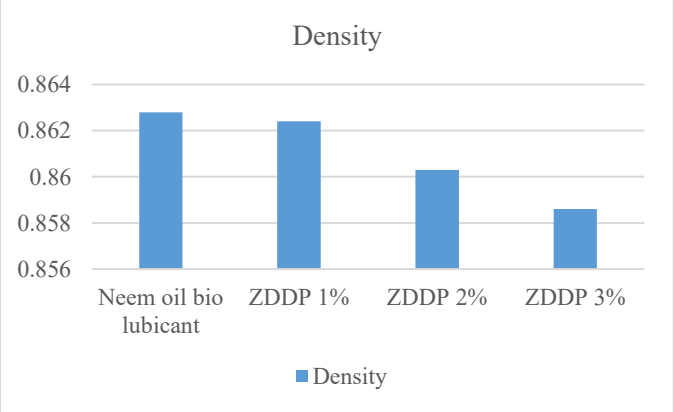


Fig 1: Density

Density and Specific Gravity

The density of the base neem bio-lubricant was 0.8628 g/mL, which is in line with values published for refined neem oils. The density dropped somewhat to 0.8586 g/mL after 3% ZDDP was added. This faint pattern implies that the molar volume of the triglyceride matrix is changed by the molecular integration of ZDDP. Although ZDDP is a dense organometallic complex in and of itself, depending on the length of the additive's alkyl chain, its dilution in vegetable oil can occasionally result in slight changes in bulk density. This pattern is in line with research on Pongamia oil lubricants, where it was found that adding ZDDP could lower bulk density by up to 2 weight percent. The slight reduction suggests that the organometallic complex modifies the molar volume of the triglyceride matrix, potentially offering minor energy efficiency gains by reducing fluid mass in circulating systems. (Salih, 2011)

Viscosity Behavior

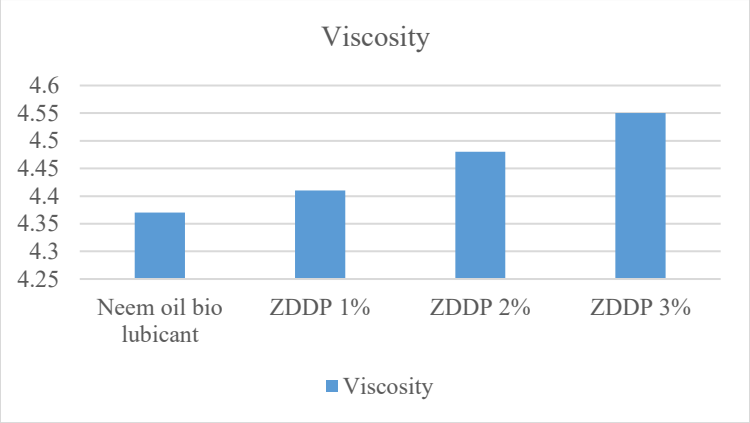


Fig 2: Viscosity

The most important factor in preserving a hydrodynamic lubrication film is viscosity. The findings indicate a steady rise from 4.37 mm²/s to 4.55 mm²/s. Studies on Karanja oil, where ZDDP was found to produce a small viscosity enhancement, substantiate this marginal improvement in viscosity upon adding ZDDP. Although vegetable oils naturally have high viscosity indices that already provide strong temperature-viscosity stability, increasing viscosity is generally advantageous for preventing film failure at higher loads. From 4.37 to 4.55 mm²/s, kinematic viscosity gradually increased. However, some research on canola oil and corn revealed a minor decrease in viscosity at 2 weight. % ZDDP, other literature indicates that higher concentrations of ZDDP can increase viscosity due to the presence of excess metal and long phosphate chain formation in the oil. The observed increase in this study supports better film formation and load-carrying capacity under mechanical stress. (Al sheik et al. 2022)

Acid Value and Free Fatty Acids (FFA)

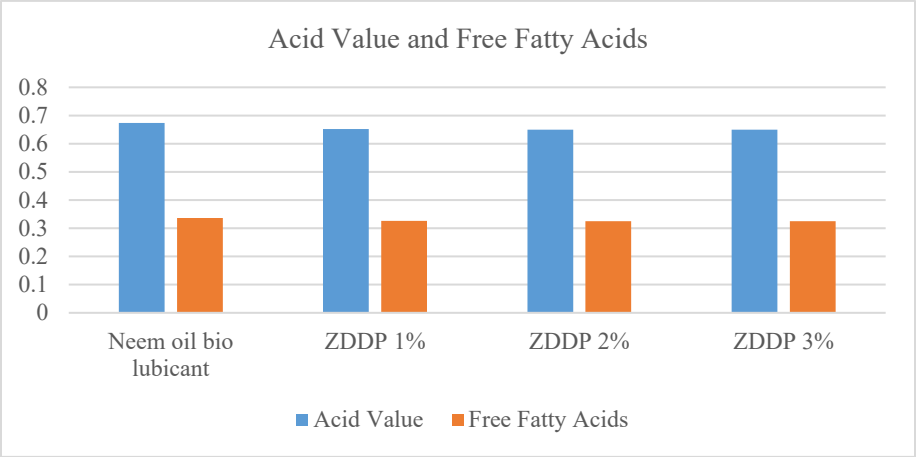


Fig 3: Acid Value and Free Fatty Acids

Since acidic components in bio-oils are principally responsible for corrosion and promoting oxidative deterioration, the decrease in acid value (0.6732 to 0.6500 mg KOH/g) is noteworthy. Precursors to organic acids are neutralized by ZDDP's secondary function as an antioxidant, more precisely as a peroxide decomposer. The amount of acid formed during oxidation is reflected in the acid value, in addition to the amount of acid that already exists. On metal surfaces, ZDDP is known to produce a zinc–polyphosphate/zinc phosphate-type tribofilm. This film minimizes oil breakdown processes, lowers wear and surface catalysis, and decreases metal-catalyzed oxidation (reduced oxidation-driven production of carboxylic acids).

Slowing oxidation results in fewer new acidic oxidation products, which lowers the acid value and consequently, the free fatty acid over time. Because of this chemical synergy, the bio-lubricant is more stable and more like refined industrial lubricants. Barnes et al. (2001).

Saponification Value

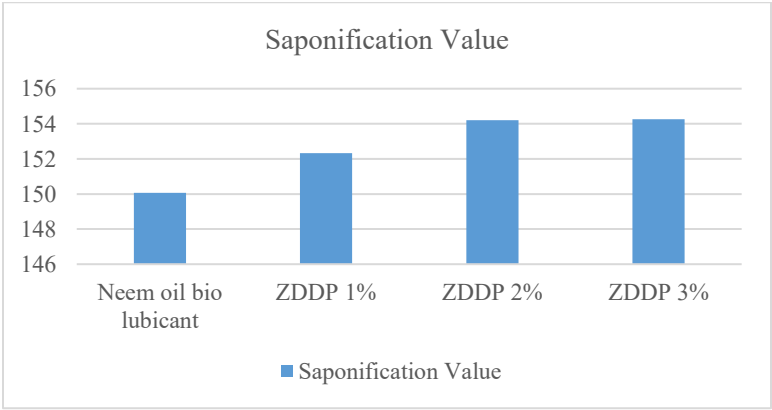


Fig 4: Saponification Values

The increase in saponification value (from 150.06 to 154.26 mg KOH/g) reflects the introduction of phosphorus and sulfur-rich species that may influence the reactive profile during titration. Saponification values are measures of the average molecular weight of fatty acids; hence, the additive concentration modifies the reactive chemical environment of the base oil. his reflects the increased complexity of the chemical profile, as ZDDP introduces sulfur and phosphorus-containing species that can influence the reactive environment during alkaline titration. (Azhari et al. 2015)

Cold flow Properties

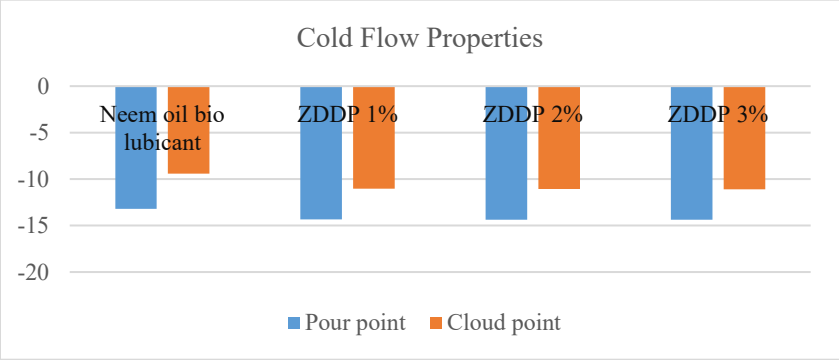


Fig 5: Cold flow properties

Because saturated fats crystallize, vegetable oils frequently have poor cold-flow performance. According to this investigation, ZDDP increased the pour point from −13.2°C to −14.37°C and the cloud point from −9.4°C to −11.09°C. This implies that ZDDP may function as a minor crystal modifier, preventing wax crystals from packing neatly and preserving fluidity at lower temperatures. The degree of fatty acid saturation usually determines the cold-flow characteristics of vegetable oils. The improvement implies that ZDDP might function as a moderate crystal modifier, preventing saturated triglycerides from crystallizing in an ordered manner and maintaining fluidity at lower temperatures. Azhari et al. (2015)

Flash Point and Thermal Safety

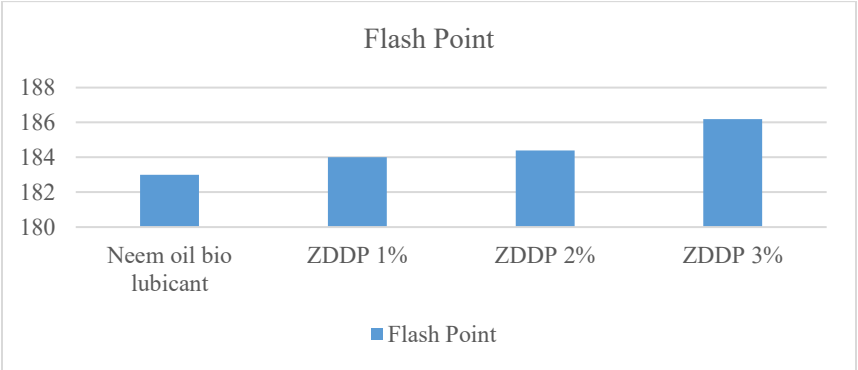


Fig 6: Flash point

The flash point increased from 183°C to 186.2°C at 3% loading. Vegetable oils naturally have higher flash points than mineral oils, which is a key safety advantage. The further increase with ZDDP indicates improved ignition resistance and reduced volatility, ensuring safer operation in high-temperature environments such as motorbike or agricultural engines. Higher flash points indicate improved ignition resistance. The addition of ZDDP enhances the thermal stability of the blend, likely by reducing the volatility of lighter components through antioxidant mechanisms that suppress early-stage thermal decomposition. (Azhari, et al. 2017).

Conclusion

ZDDP is a multipurpose modifier for neem oil bio-lubricants, as this study reveals. The formulation was improved by adding up to 3% ZDDP, which increased viscosity, decreased acidity, and improved thermal and cold-flow characteristics. These findings imply that neem oil enhanced with ZDDP may be a viable alternative to lubricants derived from petroleum. In order to measure the 21–75% reductions in wear scar diameter and friction that are commonly seen in ZDDP-enhanced bio-oils, future research should include tribological testing with four-ball testers to help compare ZDDP for performance in conditions resembling sliding/rolling point contacts (e.g., bearings, gears, cam/follower contacts depending on configuration).

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