lubricants

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Curbing Petrochemical Lubricants by Plant-Based Chemicals: A Reliable Opportunity to Align with Sustainable Development Goals

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Abstract: The use of plant-based lubricants is a sustainable alternative to petrochemical lubricants. Their main advantages include proven tribological performance, higher biodegradability in the environment, and the absence of health hazards when inhaled, ingested, or in contact with the skin. In this study, nine best-selling commercial lubricants were purchased and compared with two proposed sustainable alternatives derived from plant-based resources. The alternative wet lubricant that was developed demonstrated superior tribological performance compared to the selected commercial lubricants. Meanwhile, the alternative dry lubricant exhibited a greater load capacity and high wear resistance in the presence of micrometric Al_2O_3 particles at 20 N. The results indicated that a proper formulation of plant-based resources in lubricants can achieve the same or even better functional performance than conventional lubricants, which are currently classified as hazardous under European regulations.

Keywords: plant-based lubricant; standard development goals; hazard classification; tribology

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1. Introduction

Lubricants are essential for the smooth operation of machinery across various industries. For many years, petrochemical-based lubricants have been the standard in sectors such as automotive, aerospace, and manufacturing. However, these lubricants have been linked to negative environmental impacts, public health concerns, and food safety issues [1–3]. For example, the production, use, and disposal of petrochemical lubricants contribute to greenhouse gas emissions and the depletion of non-renewable resources [4]. Additionally, their use has been associated with the contamination of food products during processing and packaging, as well as adverse health effects in exposed individuals [1,2]. As a result, the need for more sustainable and safer alternatives has driven interest in exploring plant-based lubricants [5–7].

White mineral oil is one of the petrochemical lubricants commonly used in mechanisms despite being classified as hazardous by the European Chemicals Agency (ECHA, echa.europa.eu fully operational by 1 June 2024). Similarly, the classification provided by companies to ECHA in REACH registrations for mineral oils, petrochemical distillates, and

derived extracts identifies these substances as potentially fatal if swallowed and enter the airways, capable of causing organ damage through prolonged or repeated exposure, and are suspected of impairing fertility or harming the unborn child. Additionally, mineral oil hydrocarbons (MOH) are complex mixtures that include a wide range of chemical substances derived from petroleum distillation. Among these, groups such as saturated MOH (MOSH) and aromatic MOH (MOAH) are being closely evaluated due to their potential migration into food and subsequent health implications [8].

With the current 2020–2030 agenda in mind, which aligns with the United Nations' Sustainable Development Goals (SDGs) adopted in 2015, there is increasing interest in identifying alternative lubricants that are more sustainable while maintaining the necessary properties for efficient machinery operation [7]. One promising alternative is plant-based lubricants, which have demonstrated a more environmentally friendly and safer option compared to their petrochemical counterparts.

Plant-based lubricants are derived from natural oils and fats, which are renewable resources and biodegradable [9]. These lubricants have demonstrated promising performance in reducing friction, minimizing wear, and extending the lifespan of machinery. For example, oils from soybeans, sunflower, palm, and coconut, among other plant derivatives, have been used as base oils to formulate plant-based lubricants for sustainable machining operations [7]. Furthermore, blends of plant oils, often combined with additives such as antioxidants, friction modifiers, and viscosity improvers, have been developed to enhance their performance [6]. In terms of environmental impact, plant-based lubricants are less toxic and produce fewer emissions compared to their petrochemical counterparts, primarily due to the absence of NOx during combustion. Additionally, they pose minimal risk of food contamination, making them particularly suitable as food-grade lubricants for machinery in the food industry [10].

There is no doubt that the potential of plant-based lubricants for use in various industries has been increasingly recognized in recent years, offering more sustainable and safer alternatives to petrochemical lubricants. As the demand for greener alternatives continues to grow, the development of effective plant-based lubricants presents significant opportunities for innovation, paving the way for sustainable industrial practices that reduce ecological footprints while maintaining the performance standards essential for modern machinery.

Recent advancements in the formulation of natural lubricants have focused on optimizing their compositions to achieve performance characteristics comparable to those of petroleum-based products. Key formulations often utilize triglycerides derived from vegetable oils, such as soybean oil, castor oil, palm oil, rapeseed oil, and others, which serve as base oils due to their favorable lubrication properties [11]. To enhance performance, these base oils can be chemically modified through processes such as esterification, transesterification, or the addition of specific additives, including anti-wear agents, antioxidants, and viscosity improvers [12].

Being aware that tons of lubricants composed of hazardous petrochemicals are entering the market and being used by both professionals and private users, it is crucial to highlight the tribological analogs derived from sustainable plant-based resources. Petrochemicals pose significant risks to both users and the environment, making the development of sustainable alternatives increasingly important.

The lubricants evaluated in this study are designed to enhance the mechanical performance of manual and automatic machines by reducing friction and wear of contacting components, thus minimizing energy losses, system heat, and noise under both dry and wet conditions.

This research manuscript aims to demonstrate the superior tribological performance of formulated plant-based lubricants compared to top-selling petrochemical-based lubricants. The goal is to provide evidence that sustainable alternatives are not only feasible but also beneficial for machinery performance, environmental protection, public health, and future generations.

Tribological studies were conducted using a ball-on-disc configuration to evaluate the suitability of these lubricants in mechanical working points with cyclic and/or linear contact at room temperatures. This study focuses on non-engine applications such as chains, sprockets, bearing rollers, cables, and similar components used in sports vehicles, gardening machinery, nautical equipment, carpentry tools, corrosion protection systems, food processing machines, and aeromodelling, among other external applications.

2. Materials and Methods

2.1. Lubricants

Table 1 presents five wet lubricants (L1–L5) purchased from commercial shops. These lubricants are considered top sellers in the mechanical market, primarily for external applications. Additionally, one wet lubricant, listed as L6 (Tick Verde), was developed and studied as an alternative to conventional lubricants (L1–L5) in terms of tribological performance. Wet lubricants are typically selected for wet applications or use in enclosed environments, as they generally offer longer operating times when not exposed to air or dust.

Table 2 presents four dry lubricants (L7–L10), also purchased from commercial shops and that are considered top sellers in the mechanical market, primarily for external applications. Additionally, one dry lubricant, L11, was developed and studied as an alternative to the petrochemical lubricants listed (L7–L10). Dry lubricants are typically chosen for external mechanisms that do not come into contact with water or polar solvents, as they generally offer longer operating times when not exposed to moisture.

The lubricants included in this study represent a selection of the most widely available products for external mechanisms in the Castellón region, Spain.

2.2. Tribological Tests & Operating Parameters

The tribological performance was evaluated using a Plint and Partners tribometer bench with a ball-on-disc configuration (TE79/P), following the ASTM G-99 standard [13]. This setup simulates a critical case due to the Hertzian pressures developed on the contact surface. For each lubricant, an aliquot of 10 mL was collected and tested. The lubricant mixture was directly applied to the contact area of the friction pairs at a rate of 10 drops per minute.

Wear tests were performed using 1 g of micrometric Al_2O_3 (ALO-101 PLAXAIR, ALO 325 mesh) dispersed in 10 mL of lubricant. The Al_2O_3 particles had a hardness of 1900 HV, an irregular morphology, and an average size of 45 µm, as shown in Figure 1, in order to simulate the debris particles.

The wear volume of the ball, V (mm^3), and the wear rate, K ($mm^3/N{\cdot}m$), were calculated using the following Equations (1) and (2):

$$V = \frac{1}{3}\cdot\pi\cdot a^2\cdot(3R - a) \quad (1)$$

$$K = \frac{V}{w\cdot L} \quad (2)$$

where a is the contact radius (mm), R is the ball radius (mm), W is the normal load (N), and L is the total sliding distance. The tribological parameters are summarized in Table 3.

Table 1. Wet lubricants, chemical composition of main active substances, and hazard statement code and classification.

Lubricant	Brand	CAS Number Active Substance	Substance Name	Hazard Statement Codes	Hazard Classification	Active Matter Composition	Physical Aspect
L1	Joe's	9003-29-6	Butene, homopolymer	H304, H315	Asp. Tox. 1 Skin Irrit. 2	Mineral oil hydrocarbons	liquid
L2	Podium PB 3000G	8042-47-5	White mineral oil (petroleum)	H304	Asp. Tox. 1	Mineral oil hydrocarbons, synthetic polymer additive	liquid
L3	WD-40	68814-87-9	Distillates (petroleum)	H226, H304, H332, H373, H411	Flam. Liq. 3 Asp. Tox. 1 Acute Tox. 4 STOT RE 2 Aquatic Chronic 2	Petroleum-based oil, mineral oil hydrocarbons	liquid
		8042-47-5	White mineral oil (petroleum)	H304	Asp. Tox. 1		
		112-34-5	2-(2-butoxyethoxy) ethanol	H319	Eye Irrit. 2		
L4	Finish Line	72623-86-0	Lubricating oils (petroleum)	H304, H350	Asp. Tox. 1 Carc. 1B	Petroleum-based oil	liquid
		80939-62-4	Amines, C11-14-branched alkyl, monohexyl and dihexyl phosphates	H315, H319, H411	Skin Irrit. 2 Eye Irrit. 2 Aquatic Chronic 2		
		115-86-6	Triphenyl phosphate	H400, H410	Aquatic Acute 1 Aquatic Chronic 1 Under assessment as Endocrine Disrupting	Petroleum-based oil, ceramic, phosphates	O/W emulsion
L5	Datacol	64742-48-9	Naphtha (petroleum), hydrotreated heavy	H304, H340, H350	Asp. Tox. 1 Muta. 1B Carc. 1B	Mineral oil hydrocarbons	liquid spray
		64742-49-0	Naphtha (petroleum), hydrotreated light	H304, H340, H350	Asp. Tox. 1 Muta. 1B Carc. 1B		
L6	Candidate (Tick verde)	64706-27-0	Glycerides (Plants)	-	-	Plant-based glycerides	liquid
		67701-26-2	Glycerides, C12-18 (Plants)	-	-	Plant-based glycerides	liquid

Table 2. Dry lubricants, chemical composition of main active substances, and hazard statement code and classification.

Lubricant	Brand	CAS Number Active Substances	Substance Name	Hazard Statement Codes	Hazard Classification	Active Matter Composition	Physical Aspect
L7	Wax Lube	9002-84-0	Polytetrafluoroethylene	-	-	Petroleum-derived nanomaterials—PTFE, ceramic, graphite	O/W emulsion
		7782-42-5	Graphite	-	-		
L8	Finish Line	426260-76-6	Heptane, branched, cyclic and linear	H225, H304, H315, H336, H411	Flam. Liq. 2 Asp. Tox. 1 Skin Irrit. 2 STOT SE 3 Aquatic Chronic 2	Petroleum-derived hydrocarbons, ceramic, phosphates	O/W emulsion
		200-661-7	2-propanol	H225, H319, H336,	Flam. Liq. 2 Eye Irrit. 2 STOT SE 3		
		80939-62-4	Amines, C11-14-branched alkyl, monohexyl and dihexyl phosphates	H315, H319, H411	Skin Irrit. 2 Eye Irrit. 2 Aquatic Chronic 2		
		115-86-6	Triphenyl phosphate	H400, H410	Aquatic Acute 1 Aquatic Chronic1 Under assessment as Endocrine Disrupting		
L9	X-Sauce	68441-17-8	Ethene, homopolymer, oxidized	-	-	Petroleum-derived hydrocarbons, Petroleum-derived nanomaterials—PTFE	O/W emulsion
		9002-84-0	Polytetrafluoroethylene	-	-		
L10	Squirt	68441-17-8	Ethene, homopolymer, oxidized	-	-	Paraffin and hydrocarbon waxes	O/W emulsion
		9083-41-4, 8002-74-2	Paraffin wax	-	-		
L11	Candidate (Tick verde)	95912-86-0	Fatty acids, C8-10, C12-18-alkyl esters	-	-	Plant-based alkyl esters and glycerides	liquid
		64706-27-0	Glycerides (Plants)	-	-		
		68952-94-3	Fatty acids, alkali salts	-	-		

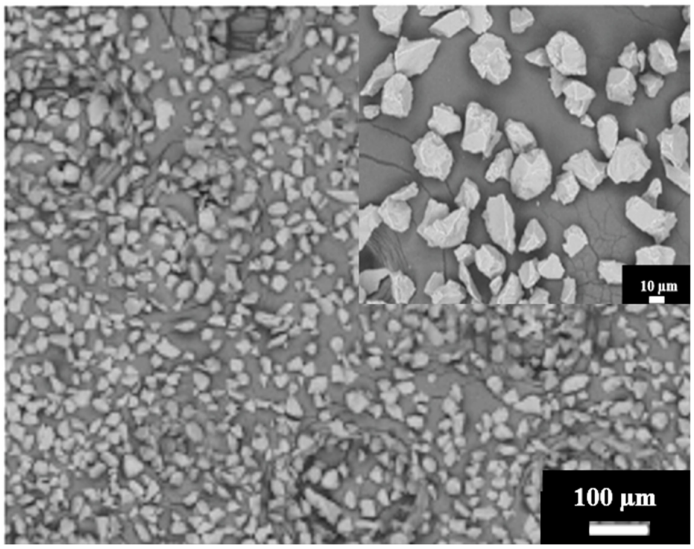


Figure 1. SEM micrograph of the morphology of micrometric Al_2O_3.

Table 3. Experimental parameters during the tribological process.

Parameters	Values Friction Test	Values Wear Test
Load (N)	6, 15 and 20	20
Slip radius (mm)	40	40
Sliding velocity (m/s)	0.16	0.16
Sliding time (s)	1800	625
Distance (m)	288	100
Temperature (°C)	20	20
Relative humidity (%)	52	52

The contact topography of the worn surface after the wear tests was analyzed using a stereo magnifier (Intralux 4000-1, Elmhurst, IL, USA), a scanning electron microscope (SEM; JOEL 7001 F EDX-WDX, Oxford, UK), and energy dispersive spectroscopy (EDX). The average values, with a deviation of 5%, were calculated based on three tests for each type of lubricant.

The friction pair consists of a 10 mm diameter GCr15 ball with the following chemical composition (wt%): 0.95–1.05 C, 0.15–0.35 Si, 0.2–0.4 Mn, 1.3–1.65 Cr, ≤0.3 Ni, ≤0.027 P, ≤0.25 Cu, ≤0.02 S, and ≤0.1 Mo. The counterpart disc used for the tribological ball-on-disc test was made of hardened and tempered F-5220 steel (100 mm in diameter and 5 mm thick), which is in compliance with A68a (01). Its chemical composition (wt%) is as follows: 0.97 C, 1.1 Mn, 0.6 Cr, 0.6 W, 0.1 V, 0.25 Si, 0.035 P, and 0.035 S. This configuration was selected to minimize the effect on the disc and focus the investigation on the wear behavior of the ball. The mechanical characteristics of the materials are detailed in Table 4.

Table 4. Mechanical characteristics of the ball–disc frictional pair.

Bearing Pair	Initial R_a (µm)	HV (200_{gf})	E (Gpa)	Poison Coefficient (υ)
Ball GCr15	0.97	820	208	0.3
Disc F-5220	1.85	930	190	0.3

Tribological tests were initially conducted on commercial wet lubricants (L1–L5) and dry lubricants (L7–L10) to identify the best functional benchmarks. Friction tests were performed at room temperature using the ball-on-disc system. The average friction coefficient values were obtained for the applied loads of 6 N, 15 N, and 20 N over a total sliding distance of 100 m.

After evaluating the initial tests, the tribological studies focused on the best-performing lubricants (L3 and L4 for wet lubricants, and L9 and L10 for dry lubricants), and these were compared with the plant-based candidates, L6 (wet) and L11 (dry).

2.3. Viscosity Analysis

The viscosity of the alternative lubricants was analyzed at 25, 40, and 100 °C by conducting tests under steady-state conditions using a Bohlin CVO-120 rheometer (Malvern Instruments Ltd., Malvern, UK) equipped with a double-gap (DG 40/50) device composed of two concentric cylinders, specifically designed for low-viscosity suspensions. The viscosity index (VI) of the developed plant-based lubricants was determined in accordance with the ASTM D2270-10 standard [14].

2.4. Calculation of Hertzian Pressure

The Hertzian contact was analyzed to estimate the maximum stresses produced in the ball-on-disc system during lubricant tribology experiments. The tribological system is illustrated in Figure 2. The contact radius, a (mm), can be calculated using Equation (3), where W is the applied load (N), R is the ball radius (mm), and E is the equivalent Young's modulus (GPa) of the friction pair:

$$a = \sqrt[3]{\frac{3WR}{2E'}} \tag{3}$$

$$\frac{1}{E'} = \frac{1}{2}\left[\frac{1-v_1^2}{E_1} + \frac{1+v_2^2}{E_2}\right] \tag{4}$$

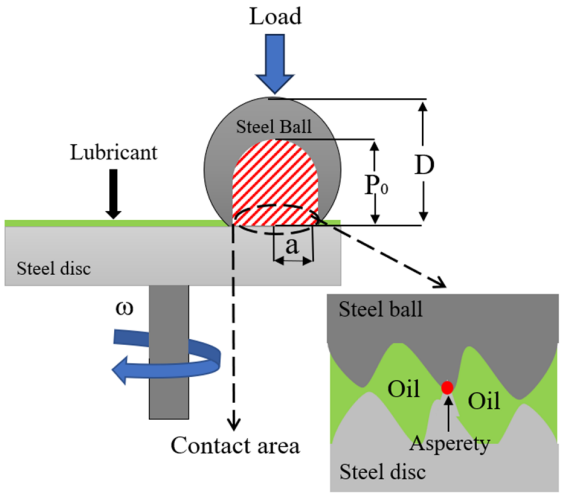


Figure 2. Model tribological system ball-on-disc.

The maximum apparent Hertzian pressure P_0 (Mpa) can be calculated from Equation (4) [15,16]:

$$P_0 = \frac{3W}{2\pi a^2} \tag{5}$$

Using this equation, the maximum apparent Hertzian pressures developed in the friction tests are calculated as 517, 702, and 773 Mpa.

3. Results and Discussion

3.1. Lubricant Composition and Surrounding Implications

Tables 1 and 2 list the chemical compositions of the petrochemical lubricants most commonly used in mechanical systems by industry (wet lubricants in Table 1, from L1

to L5, and dry lubricants in Table 2, from L7 to L10), alongside more sustainable and environmentally friendly alternatives to petrochemical-based lubricants (L6 and L11). The hazard classifications are detailed in the tables using codes for the active substances, which indicate the levels of irritation, toxicity, and carcinogenicity associated with each substance.

In terms of public health, the risk of skin and/or eye irritation must be considered before using chemical substances. More sensitive and dangerous risks are associated with lubricants (L1 to L5), such as fatality if swallowed and entering the airways (H304), potential cancer-causing properties (H350), or the risk of genetic defects (H340). These classifications are primarily linked to petrochemical derivatives, where MOS (mineral oils) are predominant, along with other active substances such as butene, white mineral oil, petroleum distilled fractions, and Triphenyl Phosphate (TPP).

TPP, as an aromatic petrochemical plasticizer additive, is commonly used due to its load-carrying capacity and anti-wear properties. However, its toxicity to the aquatic environment and organisms should not be overlooked, as it is classified under the H400 risk series by the ECHA. Toxicity studies are being conducted to determine its potential health effects, particularly in lubricants (L4 and L8) (Tables 1 and 2).

The environment is also negatively impacted by synthetics and petrochemicals, such as those selected and listed in Tables 1 and 2, due to their poor compatibility and biodegradability. The use of hazardous lubricants presents risks to both the environment and public health, including soil and waterway contamination, as well as harm to workers handling these substances [3].

Singh et al. (2017) discussed, and this work supports, that vegetable oil-based lubricants are biodegradable and renewable, offering viable solutions for obtaining renewable and eco-friendly alternatives due to environmental concerns [4].

Studies have shown that plant-based lubricants can offer comparable or even superior performance properties to petrochemical-based lubricants [6,17,18]. For example, Ortega et al. (2023) reviewed the use of vegetable oil-based lubricants and cutting fluids, finding that they exhibit excellent lubricating properties, as well as high resistance to oxidation and thermal degradation [8]. Similarly, Quinchia et al. (2023) conducted research on plant-based lubricants, demonstrating their promising friction and wear performance for industrial applications [6].

Regarding the application conditions, the wet lubricant concept appears to be the "closest to ideal" when water or humidity is present, as it helps keep the mechanism lubricated. This refers to non-water-soluble lubricants based on wet formulations (Table 1). In contrast, dry lubricants have water-amenable compositions, are soluble in polar solvents, and can be easily lost when water enters the mechanism.

Selecting the proper lubricant based on the working conditions is crucial. Wet lubricants are ideal for rainy days, marine environments, and water-contacted mechanisms, while dry lubricants are the better choice in dry conditions, environments without groundwater contact, or in dirty and rusty surroundings. Thanks to these characteristics, dry lubricants are also generally "easier to clean" than wet lubricants.

3.2. Plant Lubricants Aligned with the Standard Development Goals

Although there is still a lack of overall awareness about the risks of petrochemicals in the industry, recent years have seen growing interest in developing more sustainable and environmentally friendly lubricants that are free from hazardous substances [4]. Since the start of the 2030 Agenda, new research lines have been launched to develop lubricants free of hazardous substances, aligning with, among other things, the Sustainable Development Goals (SDGs, un.org.) and ensuring they remain competitive and mechanically

efficient [11,12]. The lubricants proposed in this manuscript (L6 and L11) are fully aligned with the SDGs.

Chemicals and lubricants derived from green and blue resources have been studied as reliable, sustainable, and clean alternatives for industry (SDG 9: Sustainable Industrialization and Fostering Innovation). The use of plant-based lubricants can contribute to SDG 12 (Responsible Consumption and Production), SDG 13 (Climate Action), and SDG 14 (Life Below Water), as they reduce the use of non-renewable resources, mitigate climate change, and protect aquatic ecosystems.

Plant-based lubricants are derived from renewable and biodegradable resources such as vegetable oils and fats. These resources are abundant and readily available, and their use in lubricants reduces dependence on non-renewable and depleting resources like petroleum and mineral oils. Furthermore, the production and use of plant-based lubricants result in lower greenhouse gas emissions and smaller carbon footprints compared to traditional lubricants. Additionally, the tribology research discussed in Section 3.4 provides evidence of their suitability for use in sustainable industries.

Regarding SDG 14, the use of plant-based lubricants supports the protection and conservation of marine ecosystems. Traditional petrochemical and synthetic lubricants pollute aquatic environments and pose risks to aquatic organisms [19]. In contrast, plant-based lubricants are non-toxic, readily biodegradable, and do not accumulate in the environment, making them safer for aquatic ecosystems [4].

3.3. Viscosity

As illustrated in Figure 3, as the temperature increases from 25 °C to 40 °C and then to 100 °C, the viscosity of the lubricants decreases for both L6 and L11. The higher viscosity values observed for L6 compared to L11 are primarily associated with its higher lipophilic profile, which includes longer-chain glycerides derived from plant oils (C12–C18). These glycerides also have a higher content of monounsaturated esters (>60%) and polar organic groups (-COOH and -OH).

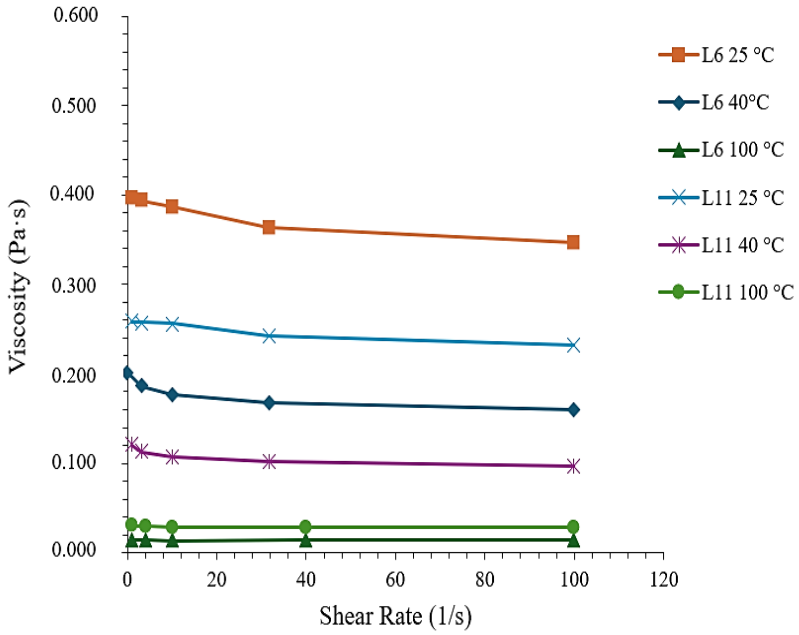


Figure 3. Apparent viscosity–shear rate curves for L6 (wet) and L11 (dry) at 25, 40, and 100 °C.

On the other hand, the dry lubricant (L11) contains potassium salts derived from linear C8–C18 and C18 unsaturated plant-based glycerides (50%) dissolved in a polar solvent with -OH groups. It is important to note that neither ethanol nor methanol has been included in the formulation.

Table 5 shows the different viscosity values at various temperatures for the plant-based lubricants (L6 and L11), as well as the VI value calculated according to ASTM D2270-10 and the density at 25 °C. The VI of lubricant L6 is 93.7, with its viscosity reduced by up to 96% in relation to temperature. In contrast, lubricant L11 has a VI of 363.1, with its viscosity reduced by up to 79% as the temperature increases. This means that the lubricant with the higher VI exhibits better viscosity behavior with temperature.

Table 5. The viscosity and density of lubricants developed from plant-based resources.

Lubricant	Viscosity 25 °C (Pa.s)	Viscosity 40 °C (Pa.s)	Viscosity 100 °C (Pa.s)	VI	Density 25 °C (g/mL)
L6	0.377	0.177	0.015	93.7	0.950
L11	0.138	0.087	0.029	363.1	1.028

Thanks to their compositions with long chains and polar groups, lubricants easily form physical and chemical adsorption films on metal surfaces, providing beneficial effects in reducing friction and wear. Reeves et al. concluded that natural oils with high percentages of monounsaturated fatty acids are optimal for ensuring superior thermal-oxidative stability in both ambient and high-temperature environments. However, the higher the degree of unsaturation, the lower the viscosity at room temperature, revealing that oils with higher amounts of monounsaturated fatty acids exhibit superior friction and wear properties [17]. As stated by Shah et al. (2021), bio-lubricants not only have a high viscosity index (VI) but also offer a reliable range of physicochemical and performance advantages, such as low toxicity, high lubricity, high load-carrying capacity, excellent anti-wear characteristics, low evaporation losses, and rapid biodegradability [20].

3.4. Tribology Tests

3.4.1. Friction Analysis

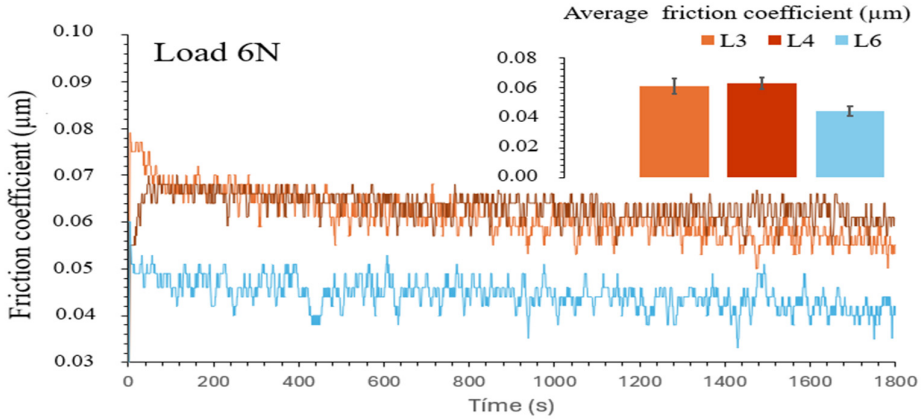
Preliminary tests were conducted at room temperature using the ball-on-disc system to select the best functional benchmarks for the tribological tests (Tables 1 and 2). The lowest coefficients of friction were observed for lubricants L3 and L4 (wet conditions) and L9 and L10 (dry conditions), as shown in Figures S1 and S2 in the Supplementary Information. L3 and L4 were identified as the best wet lubricants, while L9 and L10 were the best dry lubricants from the list.

The benchmark lubricants from the preliminary study were then studied and compared to L6 and L11 to determine whether the tribology of these alternative lubricants is at a competitive performance level, thus confirming their potential as a reliable market trend. Targeted friction tests were conducted using the ball-on-disc system under laboratory conditions with different maximum Hertzian pressures applied (517, 702, and 773 MPa). The bearing pair consists of a GCr15 steel ball and an oil-hardened, tempered F-5220 steel disc.

The experimental evolution of the friction coefficient for the wet lubricants is shown in Figure 4. At a Hertzian pressure of 517 MPa, the friction coefficient value for lubricant L6 was 0.044 ± 0.003, while for L3 and L4, these values were 0.061 ± 0.005 and 0.063 ± 0.004, respectively (Figure 4a). After applying a higher Hertzian pressure of 702 MPa (Figure 4b), the friction coefficient values slightly increased, reaching mean values of 0.075 ± 0.0048 for L3 and 0.086 ± 0.0042 for L4, while L6 maintained a lower friction coefficient of 0.064 ± 0.003. Finally, applying a maximum Hertzian pressure of 773 MPa (Figure 4c),

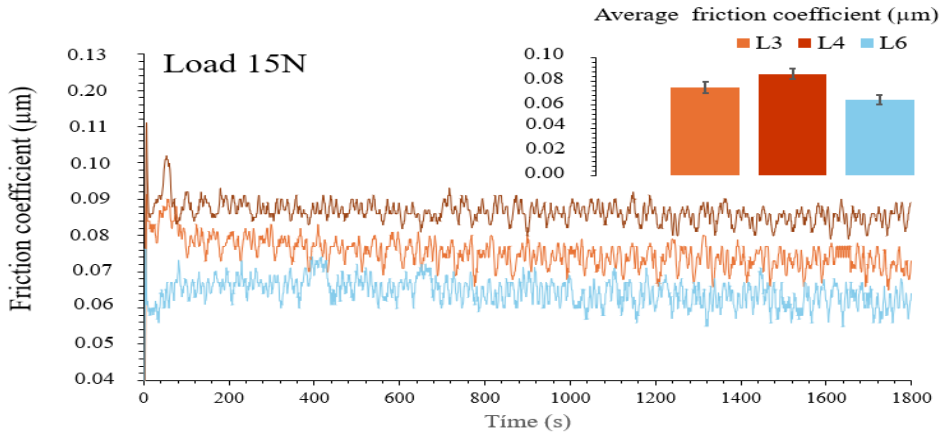
the mean friction coefficient values for lubricants L3 and L4 were 0.105 ± 0.012 and 0.084 ± 0.005, respectively, while L6 reached a mean friction coefficient of 0.066 ± 0.002. As the pressure increased, L3 lost its load-carrying capacity during the transition from the mixed lubrication regime (0.002 ± 0.1) to the boundary lubrication regime (>0.1) [21], showing a high dispersion of friction values over time. In contrast, L6 exhibited a higher load-carrying capacity throughout the range of applied loads, with low dispersion of the friction values over time. This was due to the formation of a more stable lubrication film, which effectively isolated the two surfaces of the ball–disc friction pair. This can be attributed to its high viscosity, resulting from its formulation based on longer-chain plant esters (C12–C18) derived from a high content of monounsaturated fatty acids (>60%) and polar organic groups (-COOH and -OH).

The commercial petrochemical lubricant (L10) exhibits high stability and continuity of the lubrication film across Hertzian pressures between 517 MPa and 702 MPa, with average friction coefficient values of 0.024 ± 0.002 and 0.041 ± 0.005, respectively. The commercial lubricant (L10) can reduce the friction coefficient by 2.5 to 2.7 times compared to the commercial lubricant (L9) and the plant-based lubricant formulated (L11), as shown in Figure 5a,b. When the pressure increases to 773 MPa (Figure 5c), the plant-based lubricant (L11) demonstrates a higher load capacity, stability, and continuity in the lubrication film. It reduces the friction coefficient by up to 5.1% between the transition from 15 to 20 N applied load (702 and 773 MPa), reaching an average friction coefficient of 0.055 ± 0.003. This lubricant can increase the separation between the two surfaces in contact in the ball–disc friction pair, thus reducing intermetallic contact between asperities. The friction coefficient of lubricant L10 is 0.058 ± 0.005, showing less stability in the lubrication film compared to L11, as evidenced by its higher deviation in friction values over time. Furthermore, the lubrication film breaks during the transition from the 15 to 20 N applied load, increasing intermetallic contact between the asperities of the two friction surfaces, resulting in a 41% increase in the friction coefficient. The average friction coefficient for the commercial lubricant L9 is 0.073 ± 0.006, which is more unstable due to its high fluctuation in friction values over time; though, the friction coefficient during the transition from 15 to 20 N remains nearly the same.

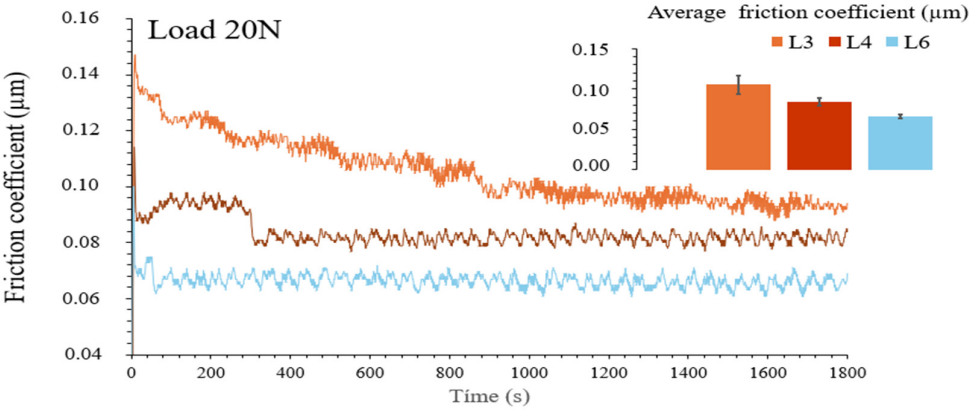


(**a**)

Figure 4. *Cont.*



(**b**)



(**c**)

Figure 4. Variations in the coefficient of friction during ambient conditions of the test with various loads: (**a**) 6 N, (**b**) 15 N, and (**c**) 20 N, for commercial lubricants (L3–L4) and alternative natural lubricant L6 during 1800 s.

3.4.2. Study of Frictional Energy Losses

The calculation of the dissipation of frictional energy losses caused by the frictional pair interaction of the different tested lubricants can be determined using the following expression [22]:

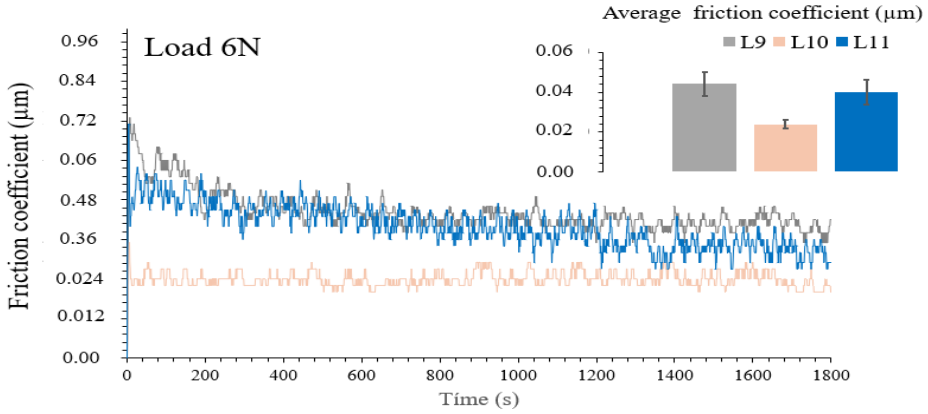
$$E = F_n \cdot v \int \mu \, dt \tag{6}$$

where F_n is the applied normal force (6, 15, and 20 N), v is the linear sliding velocity (0.07 m/s), and μ is the average kinetic friction coefficient during the sliding time of 1800 s. The tangential force F_t is a function of the friction coefficient with respect to the applied normal force:

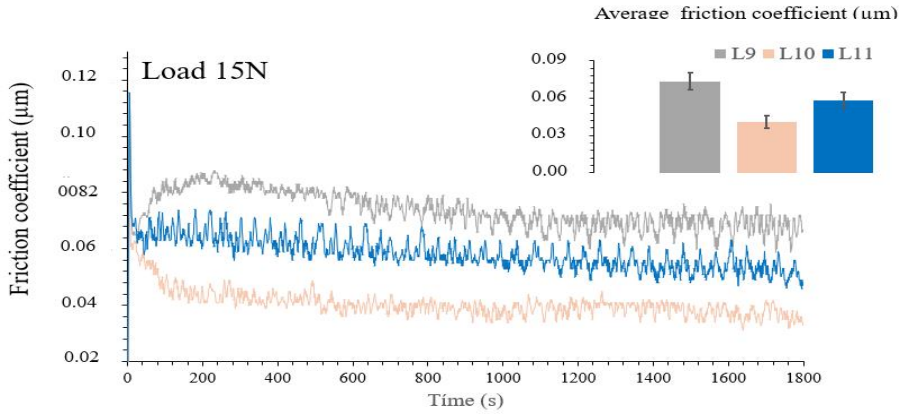
$$F_t = \mu \cdot F_n \tag{7}$$

The friction coefficient is a function of the applied normal force according to the following expression:

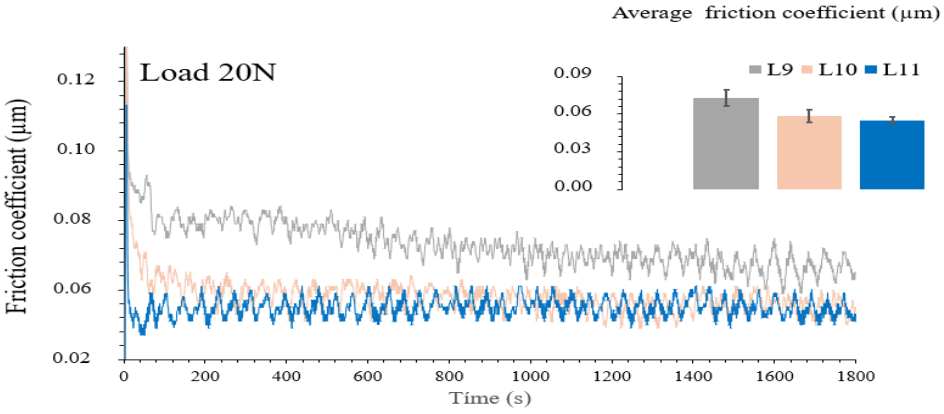
$$F_t = \int \mu \, f(F_n) \, dF_n \tag{8}$$



(**a**)



(**b**)



(**c**)

Figure 5. Variations in the coefficient of friction during ambient conditions of the test with various loads: (**a**) 6 N, (**b**) 15 N, and (**c**) 20 N, for commercial lubricants (L9–L10) and alternative natural lubricant (L11) during 1800 s.

Thus, the calculation of the frictional energy losses of the frictional pair in lubricated media can be expressed as follows:

$$E = \int \mu \, f(F_n) \, dF_n \cdot v \int dt \tag{9}$$

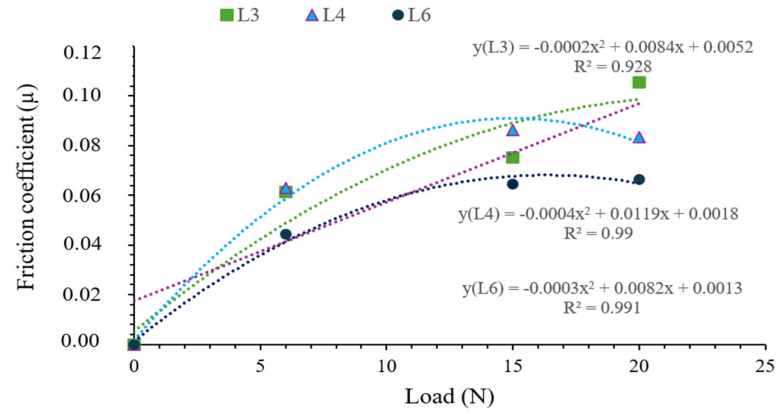
As shown by the correlation coefficients (R^2), the dependence of the coefficient of friction on the applied load can be assumed to be true (Figure 5). Thus, the generic model is of the polynomial type of degree 2 according to the following expression:

$$\mu\, f(F_n) = -aF_n^2 + bF_n + c \tag{10}$$

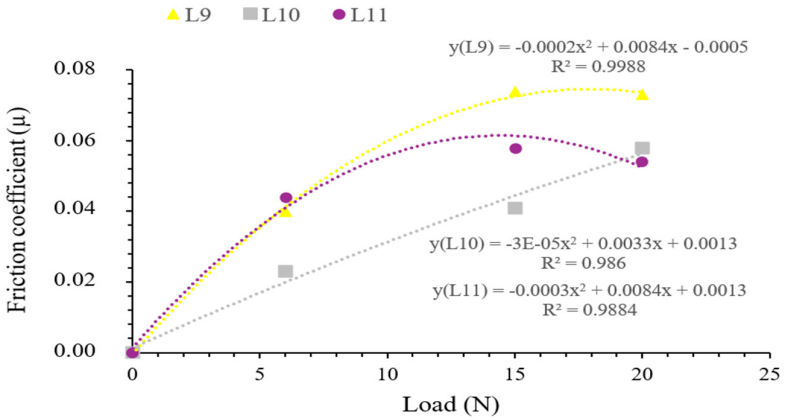
Therefore, the calculation of the frictional energy losses in lubricated media could be calculated by Equation (10), where a, b, and c are constants resulting from the friction coefficient with respect to the applied normal force:

$$E = (-a\frac{F_n^3}{3} + b\frac{F_n^2}{2} + cF_n)\cdot v\cdot t \tag{11}$$

The experimental values for a, b, and c, following the previously defined polynomial model, are listed in Figure 6. Equation (11) enables the calculation of the different frictional energy losses resulting from the tribological tests for each lubricant. The relationship between the friction coefficient and the applied load, used to calculate the frictional energy losses for each lubricant, is illustrated in Figure 6. The values for the wet lubricants (L3, L4, and L6) are shown in Figure 6a.



(**a**)



(**b**)

Figure 6. Correlation between coefficient of friction and applied load: (**a**) lubricants in wet conditions (L3, L4, and L6) and (**b**) lubricants in dry conditions (L9, L10, and L11).

L6 exhibits lower frictional energy losses across the entire range of applied normal loads compared to the benchmarks (L3 and L4). Both L4 and L6 demonstrate high load-carrying capacities during the transition between 15 and 20 N [23], reaching asymptotic

friction values. In the case of L4, the critical pressure capable of breaking the lubrication film is observed at a Hertzian pressure of 702 MPa (15 N), which leads to increased frictional energy losses.

The energy losses due to friction for L3 and L4 are 945.5 J and 1020.1 J, respectively, while for the plant-based lubricant L6, the value is significantly lower at 654.7 J. It is worth highlighting that, with the L6 lubricant, energy losses are reduced by 44.4% and 55.8% compared to L3 and L4, respectively.

The values of frictional energy loss for dry lubricants L9, L10, and L11 (Figure 6b) were calculated using the polynomial correlation between the friction coefficient and the normal force (Equation (10)). The frictional energy losses for the petrochemical lubricants L9 and L10 are 859.3 J and 458.1 J, respectively, while the alternative lubricant L11 shows a value of 684.9 J. This represents an energy saving of approximately 25% compared to L9.

For L10, this lubricant exhibits lower energy losses compared to L9 and slightly lower losses than L11 across the entire range of applied Hertzian pressures

In the transition from 442 MPa to 481 MPa, the friction at maximum Hertzian pressure (15 N and 20 N) results in an energy loss for L10 as the lubrication film breaks. This leads to an increase in the friction coefficient and energy losses of up to 62.75 J. In contrast, the plant-based lubricant (L11) remains stable under high applied pressures, with minimal variations in frictional energy losses, reaching up to 70.31 J during the transition from 15 to 20 N of the applied load.

This behavior may be attributed to the high concentration of potassium salts derived from the composition of long-chain fatty acids (Table 2), which effectively isolate the two surfaces of the friction pair (ball-on-disc).

3.5. Wear Study

The ball-on-disc system, combined with the higher abrasive wear mechanism of micrometric Al_2O_3 at a normal force of 20 N, has been considered the ideal condition for the wear tests. Figures 7 and 8 show the topographies of the worn surfaces in the ball contact zone after experimental wear over a sliding distance of 100 m for each type of lubricant: L3, L4, and L6 for wet lubricants, and L9, L10, and L11 for dry lubricants.

The resulting wear rates for L3 and L4 are 3.18E-5 and 3.32E-5 cm3/Nm, respectively, with the radii of the worn surfaces being 0.94 mm and 0.95 mm. Wear resistance in the presence of micrometric Al_2O_3 dispersed in the lubricant is similar for L3 and L4, with only slight differences in the wear rate (Figure 7a,b).

In contrast, for the plant-based lubricant L6, the study reveals greater stability and continuity of the lubricating film in the presence of micrometric Al_2O_3 particles dispersed in the lubricant. These particles effectively isolate the two contact surfaces (Figure 7c), reducing the average wear rate by up to 63.75% compared to L3 and L4.

The wear rate and radius of the worn surface for L9 are 6.21×10^{-5} cm^3/Nm and 1.12 mm, respectively, while for L10, the wear rate and radius of the worn track are 5.96 cm^3/Nm and 1.11 mm (Figure 8a,b). In the case of L11, the wear rate is 2.95×10^{-5} cm^3/Nm, and the radius of the worn surface is 0.93 mm (Figure 8c).

Based on this experiment, it can be demonstrated that L11 offers greater resistance to wear in the presence of hard abrasive particles such as micrometric Al_2O_3 dispersed in the lubricant. The potassium salts of long-chain fatty acids and the higher viscosity of L11 are effective in isolating the two contact surfaces under high applied Hertzian pressures (773 MPa).

The use of L11 can reduce the wear rate in severe working conditions (high pressures and the presence of Al_2O_3 particles) by up to 47.5% compared to commercial petrochemical-

based lubricants, positioning it as a viable alternative to those currently available on the market.

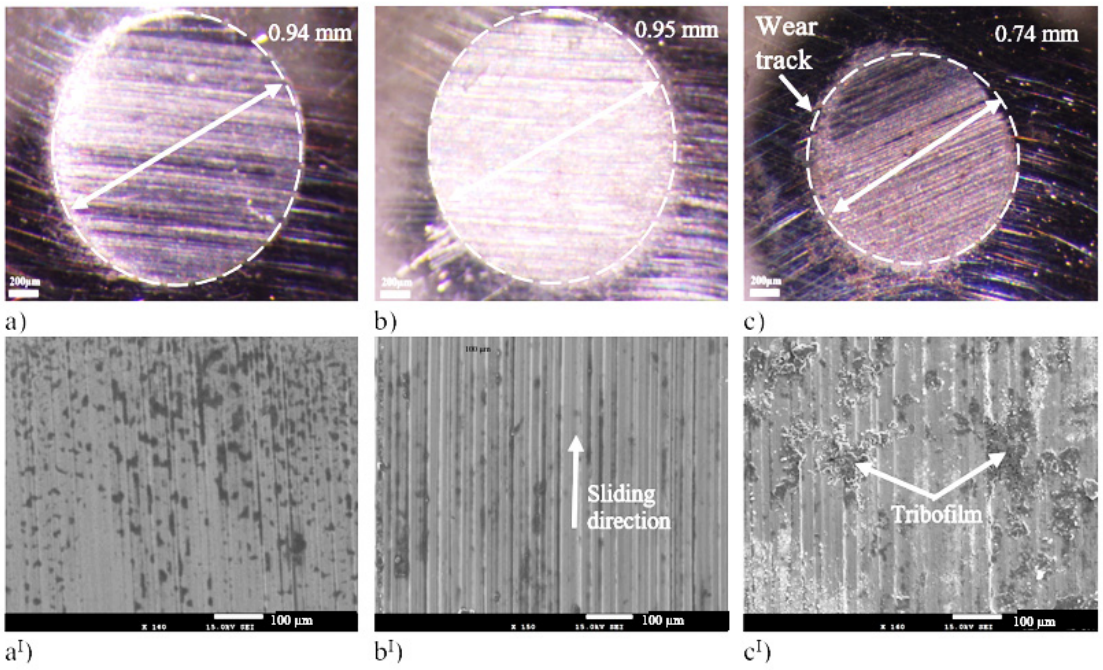


Figure 7. Optical (2×) and SEM zoom magnifier images of the worn ball surface after tribological tests in lubricated media in the presence of micrometric Al_2O_3 debris from dry lubricants after 100 m distance: (**a**,**a^{I}**) L3, (**b**,**b^{I}**) L4, and (**c**,**c^{I}**) L6.

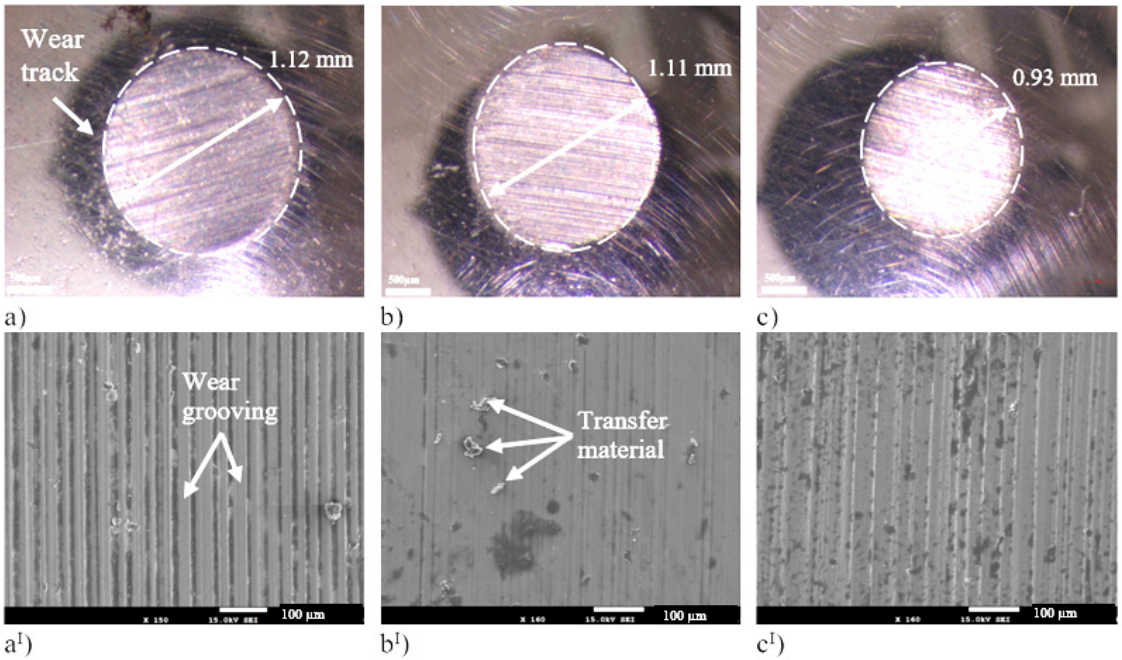


Figure 8. The Optical (1.25×) and SEM zoom magnifier images of the worn ball surface after tribological tests in lubricated media in the presence of micrometric Al_2O_3 debris from dry lubricants after 100 m distance: (**a**,**a^{I}**) L9, (**b**,**b^{I}**) L10, and (**c**,**c^{I}**) L11.

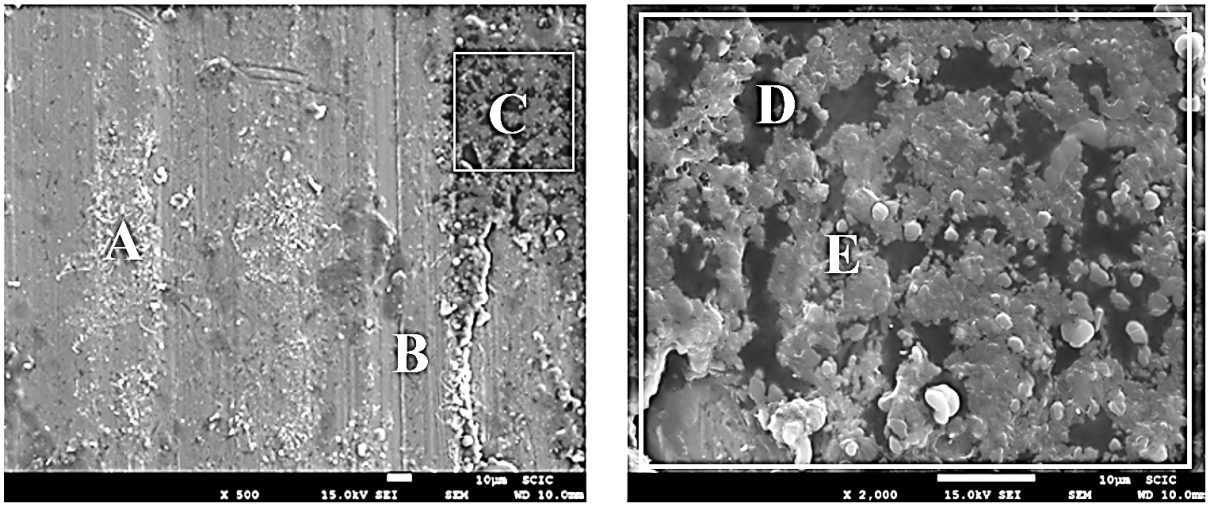
The use of Al_2O_3 particles trapped between moving surfaces allows them to rotate, roll, and slide across the space between the interacting surfaces. The predominant wear mechanisms vary depending on the particle size. Smaller Al_2O_3 particles create indentations and micro-deformations due to high-speed collisions, while larger particles cause

plowing. Micron-sized Al_2O_3 particles carried by the lubricants can easily pass through the dynamic clearance between friction surfaces. Abrasive particles with acute angles penetrate the coating surface, depending on factors such as the applied load, mechanical properties, shape, dimensions, and sliding velocity of the contacting surfaces [24].

These Al_2O_3 particles can induce abrasive wear mechanisms such as micro-sandblasting and micro-cutting. The penetration of a sliding abrasive particle into a metallic surface results in micro-sandblasting or micro-cutting, depending on the angle of attack [25]. Sliding hard particles on softer metallic materials primarily causes elastic-plastic deformations as a function of the angle of attack. These deformations occur around the particles and ahead of their motion. In both scenarios, no material is removed from the friction surfaces; however, particles with higher angles of attack can shift the wear mechanism from micro-sanding to micro-cutting [26].

Alternative plant-based lubricants have demonstrated the ability to reduce friction between the ball-on-disc friction pair and enhance wear resistance in abrasive environments under severe working conditions (high pressure and low speed). This is achieved by combining plant fatty acids, alkali salts of mineral origin, plant-derived alkyl esters, and long-chain glycerides with unsaturated bonds, as studied in this research, with L6 and L11. These formulations, along with the presence of polar groups, enable the creation of a physical–chemical adsorption film on the ball–disc friction surfaces. This film effectively bonds the two contact surfaces, providing greater stability and continuity to the lubrication film.

In Figure 9a, the presence of a tribofilm from the plant-based lubricant (L6) can be observed at point C on the damaged contact surface of the ball. Figure 9b provides a detailed view of the tribofilm morphology, where points D and E were analyzed using the EDX technique. This analysis identified the presence of the following elements: O, C, Fe, and Al.



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

Figure 9. SEM micrograph and EDX map of steel ball wear scar against F-5220 steel disc using plant-based lubricant (L6): (**a**) location of tribofilm formation and (**b**) tribofilm detail.

The formation of a tribofilm on the ball's contact surface can partially isolate the two contact surfaces of the bearing pair, reducing intermetallic contact and consequently decreasing the wear rate. Table 6 presents the results obtained from the point-specific EDX analysis conducted on different areas of the ball's contact surface.

Table 6. Semi-quantitative EDX analysis at different points of the ball-wear track using the plant-based formulated lubricant (L6).

Point	Elements Wt (%)			
	Fe	C	O	Al
A	35.56	13.42	51.02	(-)
B	42.32	10.53	46.67	0.49
C	7.95	24.12	67.80	0.13
D	8.37	24.02	67.70	(-)
E	19.47	19.52	60.77	0.14

As shown in Figure 10, abrasive wear is the primary wear mechanism, with varying degrees of severity, depending on each lubricant's ability to isolate the two friction surfaces. The accompanying sub-mechanisms in the wear process are a combination of micro-sanding and micro-cutting, with different levels of deterioration.

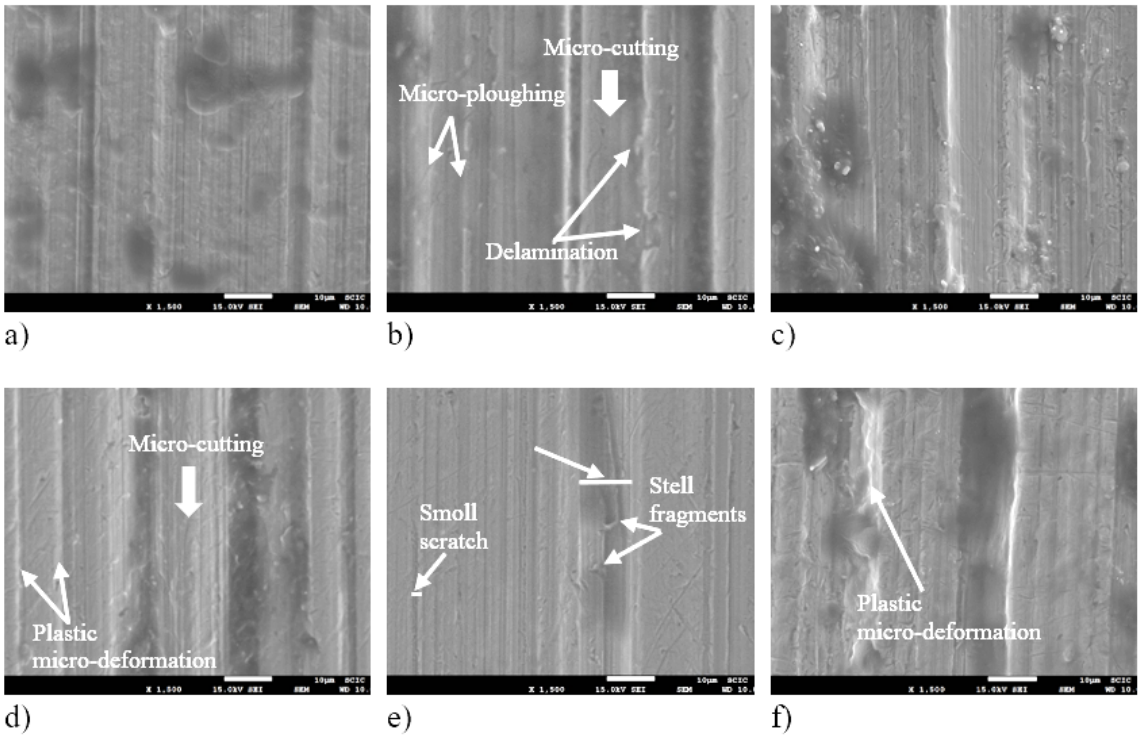


Figure 10. SEM micrographs of wear track of the steel ball of the different lubricants tested: (**a**) L3, (**b**) L4, (**c**) L6, (**d**) L9, (**e**) L10, and (**f**) L11.

As illustrated in Figure 10b,d, commercial lubricants (L4 and L9) exhibit severe micro-sanding on the ball's contact surface, accompanied by less pronounced micro-sanding. Additionally, L9 displays localized areas of delamination on the ball's contact surface.

In the case of lubricants (L3 and L10), the micro-sanding and micro-cutting sub-mechanisms are less pronounced, as observed in Figure 10a,e. For plant-based lubricants, the ball's contact surface shows zones with varying degrees of deformation, characterized by a combination of less severe micro-sanding and micro-cutting compared to commercial petrochemical lubricants (Figure 10c,f).

4. Conclusions

Plant-based lubricants have proven to be a reliable alternative to petrochemical lubricants due to their use of sustainable plant-derived resources, demonstrated performance

at room temperatures, environmental suitability, and absence of negative public health impacts, aligning perfectly with the SDGs.

The plant-based lubricant formulated for wet environmental conditions (L6) shows greater stability and continuity of the lubrication film across the full range of applied Hertzian pressures, reducing frictional energy losses by up to 44.4% and 55.8%, respectively.

The lubricant formulated for dry conditions (L11) exhibits a higher load-carrying capacity. The data indicate that plant-based lubricants can provide the same or even better functional performance compared to conventional lubricants, which are currently classified as hazardous under European Regulations.

The wear rate in the presence of micrometer-sized Al_2O_3 particles in commercial petrochemical lubricants, both in wet (L3 and L4) and dry (L9 and L10) conditions, did not show significant differences. In contrast, the natural-origin lubricants (L6 and L11) reduced the wear rate by up to 63.73% and 47.5%, respectively, compared to the commercial petrochemical lubricants.

It is crucial to emphasize the importance of continuing to work on the reformulation of plant-based lubricants to enhance their characteristics and performance in various industrial applications while ensuring safety for human health in their handling, environmental respect, and overall sustainability.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/lubricants13020071/s1. Figures S1 and S2 to show the tribology tests for benchmarks.

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