Abstract: In this study, the thermo-oxidative stability and tribological behavior of bio-based lubricant samples synthesized from castor oil using isoamyl alcohol were evaluated. Initially, the compositional and physicochemical properties of the obtained samples were assessed using the $^1$H NMR, FTIR and ASTM methods. Oxidative stability of the samples was evaluated using the Rancimat method at 110 $^\circ$C under air flow. The final biolubricant sample (BL2), obtained after esterification, epoxidation and oxirane rings opening reactions, presented an oxidation stability time (OST) of 14.3 h. The thermal stability was also evaluated by thermogravimetry (TG) from the mass variations under inert and oxidative atmospheres. BL2 showed higher thermal stability compared to the other samples, demonstrating higher decomposition temperatures in both inert (339.04 $^\circ$C) and oxidative (338.47 $^\circ$C) atmospheres, for a mass loss of 50%. The tribological properties of the samples were evaluated using a four-ball tribometer configuration. The BL1 and BL2 samples exhibited lower friction coefficients than the mineral oil sample (MOS) by 21.5% and 43.1%, respectively. Regarding wear, the observed wear scar diameter (WSD) was also lower in BL1 and BL2 compared to MOS by 5.2% and 40.4%, respectively. The results of the tribological evaluation suggest that both samples (BL1 and BL2) have promising potential for applications in lubricating machines.

Keywords: bio-based lubricant; thermal stability; tribology

1. Introduction

The global demand for lubricants keeps increasing alongside the concern about the environmental hazards associated with non-sustainable petrochemicals. Lubricants are used primarily to reduce friction between surfaces and increase the lifespan of machinery [1]. Typical lubricants consist of mineral or synthetic oils that contain mainly paraffinic, naphthenic and aromatic (to a lesser extent) hydrocarbons [2]. As occurs during the extraction and refining of petroleum-derived products, spilling during transportation and improper disposal of lubricants may lead to soil contamination and groundwater pollution [3,4]. Therefore, economic and ecological factors require renewable lubricant base oils with higher biodegradability and lower toxicity to satisfy growing performance standards and increasingly stringent environmental regulations [5,6].

Brazil’s green market has a wide variety of potential oilseeds for biofuel production [7]. An interesting alternative to conventional lubricants is the use of fatty acids to obtain the so-called biolubricants. The opportunities presented by using several vegetable oils and alcohols may be favorable when designing special products with desired physicochemical properties [8]. Bio-based oils have most of the properties required for lubricants such as high viscosity indices, low volatility, good lubricity and improved compatibility with
additives molecules [9,10]. Despite the advantageous aspects of biolubricants, vegetable oils usually present poor thermo-oxidative stability, deposit-forming tendencies and hydrolytic instability [11]. Edible vegetable oil feedstocks show limitations in their industrial applications, so that non-edible plant oils are potential biolubricant source options [12].

Castor oil (Ricinus communis) is an attractive feedstock for bio-based fuels and lubricants production [13–16]. This vegetable oil has high ricinoleic acid content (approximately 90% wt.). Ricinoleic acid is a multifunctional compound that is used as a chemical precursor in different synthesis routes [17–20]. The hydroxyl group in the ricinoleic acid molecule has a noticeable effect on the physicochemical properties of castor oil [21]. Also, chemical modifications on the ricinoleic acid molecule, such as esterification, epoxidation and hydrogenation, may improve some properties of products [22]. However, few studies have reported understanding the impact of chemical modifications of castor oil fatty acids on their stability and tribological behavior.

Chemically modified bio-based oils can be used for several applications ranging from pour point depressants to boundary lubricants [23–25]. Some bio-based lubricants may have special properties, which reduce friction and prevent direct metal-to-metal contact through a thin film [26]. Polar functional groups attached to long carbon chains enable the oil molecules to cling to metal surfaces while sliding over themselves [11,18]. Thus, the antiwear/antifriction tribofilm acts as a protective layer for moving surfaces, which is essential in machining processes.

Nowadays, environmentally friendly lubricants are emphasized due to their renewability, biodegradability and sustainability. However, variations in chemical composition of vegetable oils make it challenging to achieve a final utilization for their oleochemicals [27,28]. Continuously, research studies have focused on surpassing the shortcomings of bio-based lubricants while improving their stability and applicability [29–32]. High-quality bio-based lubricants with higher performance are a feasible reality and a relevant option to mitigate environmental impacts.

In this study, the thermo-oxidative stability and tribological behavior of bio-based lubricants, synthesized using isoamyl alcohol, were evaluated. The esterification reaction between castor oil fatty acids and isoamyl alcohol was followed by epoxidation and epoxide ring-opening reactions, using the same alcohol as the nucleophilic agent. The main chemical and physicochemical properties of the samples were measured. The thermo-oxidative stability and tribological properties of the intermediate and final obtained samples were evaluated.

2. Materials and Methods
2.1. Materials

In this study, Castor Oil Fatty Acids (COFA, 80 to 90% wt. of ricinoleic acid) were provided by Miracema-Nuodex (Campinas, Brazil). A commercial mineral oil sample (MOS), used as reference, was provided by Petrobras (Brazil). The physicochemical properties of COFA and MOS samples are shown in Table 1. Toluene (>99% wt.), p-toluenesulfonic acid (>99.7% wt.), sodium bicarbonate (>99.7% wt.), sodium chloride (>99% wt.), hydrogen peroxide (30% wt.), formic acid (95% wt.) and anhydrous sodium sulfate (>99% wt.) were purchased from Sigma-Aldrich (St. Louis, USA). Isoamyl alcohol (3-methyl-1-butanol, >98% wt.) was purchased from Neon (Brazil). Nitrogen gas (99.999% vol.) was supplied by White Martins Praxair (Fortaleza, Brazil). All chemicals were used as received, without further treatment.
Table 1. Physicochemical properties of the Castor Oil Fatty Acids (COFA) and mineral oil sample (MOS).

<table>
<thead>
<tr>
<th>Property</th>
<th>COFA</th>
<th>MOS</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 20 °C, g/cm³</td>
<td>0.9393</td>
<td>0.9017</td>
<td>ASTM D7042</td>
</tr>
<tr>
<td>Kin. viscosity at 40 °C, cSt</td>
<td>173.18</td>
<td>20.38</td>
<td>ASTM D7042</td>
</tr>
<tr>
<td>Kin. viscosity at 100 °C, cSt</td>
<td>16.938</td>
<td>3.590</td>
<td>ASTM D7042</td>
</tr>
<tr>
<td>Viscosity index (VI)</td>
<td>104</td>
<td>13</td>
<td>ASTM D2270</td>
</tr>
<tr>
<td>Acid value, mg KOH/g</td>
<td>116.56</td>
<td>0.01</td>
<td>AOCS CD 3d-63</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>−42</td>
<td>−33</td>
<td>ASTM D97</td>
</tr>
<tr>
<td>Flash point, °C</td>
<td>216</td>
<td>160</td>
<td>ASTM D92</td>
</tr>
</tbody>
</table>

2.2. Synthesis Procedures

The synthesis procedures are summarized in Figure 1, with Castor Oil Fatty Acids (COFA) represented by the ricinoleic acid molecule (major component). A COFA sample of 250 g (0.838 mol) was added to isoamyl alcohol (COFA/alcohol molar ratio 1:3) in a round-bottom flask. The esterification reaction was carried out in the presence of p-toluenesulfonic acid (5% wt. PTSA/COFA), which was used as the catalyst. The reaction mixture was stirred and refluxed at 90 °C for 6 h under inert atmosphere. After the reaction was over, the mixture was left to cool down at room temperature. In a separating funnel, the esterification products were washed with saturated NaHCO₃ solution and distilled water until they reached a neutral pH. The washing process was repeated several times to neutralize the acidic catalyst, to break water-in-oil emulsions and to remove some impurities. Then, the organic phase was dried using anhydrous sodium sulfate and taken to a vacuum distiller to evaporate traces of alcohol and water at 90 °C for 40 min, thus obtaining BL1.

![Figure 1](image-url)  
Figure 1. Scheme of the chemical routes used for the synthesis of biolubricants from Castor Oil Fatty Acids (COFA). BL1 is the product of the esterification reaction and BL2 is the product of the oxirane ring-opening reaction.

A sample of 70 g (0.19 mol) of BL1 was then mixed with a solution containing 8.4 mL (0.19 mol) of CH₂O₂ (formic acid) and 50 mL of toluene in a flat-bottomed flask. Subsequently, 51.3 mL (0.76 mol) of a hydrogen peroxide (with a molar ratio BL1:CH₂O₂:H₂O₂ of 1:1:4) was slowly added to the reaction mixture. The reaction was then carried out at room temperature and under stirring at 900 rpm for 24 h, after which the reaction mixture was transferred to a separatory funnel. The upper phase was neutralized with NaHCO₃ solution (5% wt.), washed with distilled water and dried with anhydrous Na₂SO₄. The toluene was removed using a rotary evaporator under reduced pressure at 90 °C for 40 min.

For the oxirane ring opening reaction of the epoxidized sample, isoamyl alcohol was used as nucleophilic agent, with a molar ratio of 1:3 epoxidized ester/alcohol and 5% wt. of catalyst (PTSA/epoxidized ester). The experiment was carried out in a glass reactor at 70 °C for 4 h under reflux and stirring at 900 rpm. The catalyst was removed by washing with NaHCO₃ (5% wt.) and distilled water, until it reached pH 7. The sample was dried.
with anhydrous sodium sulfate and distilled in a Kugelrohr system (0.03 mbar) at 90 °C to remove isoamyl alcohol, and thus a sample of BL2 was obtained.

2.3. ¹H NMR and FTIR Measurements

The proton nuclear magnetic resonance (¹H NMR) spectra were collected using a DRX-500 spectrometer (Bruker, Billerica, MA, USA) operating at 500 MHz. Chloroform-d (CDCl₃ 99.8%) was utilized as solvent in the characterization and quantification of the samples.

Fourier-transform infrared spectroscopy (FTIR) was assessed on all samples using a Shimadzu IRTracer-100 instrument (Shimadzu, Quioto, Japan) to ascertain the occurrence of the reactions. The scanning range was between 4000 and 400 cm⁻¹ with a spectral resolution of 4 cm⁻¹ [33,34].

2.4. Physicochemical Characterization

The density and kinematic viscosity values were obtained using a SVM 3000 Stabinger Viscometer (Anton Paar, Graz, Austria) [35,36]. The Viscosity Index (VI), which evaluates the influence of temperature on viscosity, was determined using the ASTM D2270 method [37].

The acid value (AV) of the samples was determined via acid-base titration, according to the AOCS Cd 3d-63 procedure. A 2.5 g sample was added to 50 mL of ethanol (previously neutralized) and titrated with potassium hydroxide solution (0.1 N) using phenolphthalein 1% as the indicator. The AV indicates the mass of potassium hydroxide in milligrams required to neutralize 1 g of free fatty acids in the sample test.

The pour point (PP) was measured using a CPP 5Gs instrument (ISL, Carpiquet, France) according to ASTM D97 [38]. The test tube was filled with the sample to the 45 mL mark. The sample was cooled down and checked at regular intervals (3 °C) to observe its flow properties. In essence, the pour point is the temperature at which the sample stops flowing.

2.5. Oxidative Stability

A Rancimat (Metrohm, Herisau, Switzerland) was used to carry out the oxidative stability tests according to a method adapted from EN 14112, a standard practice for biodiesel. Samples of 3.0 ± 0.1 g were settled in the reaction vessel and then subjected to a temperature of 110 °C at a constant filtered atmospheric air flow rate of 10 L/h as external oxidation accelerators. As the oxidation reactions proceeded, the volatile products, mainly carboxylic acids, were carried to the measurement vessel. The presence of the oxidation reaction products continuously increased the water conductivity. Then, the water conductivity vs. time was monitored until it reached a value of 200 µS/cm. At this time, the oxidative stability time (OST) was obtained for each sample. This approach is similar to others reported elsewhere [23,39].

2.6. Thermal Stability

A Thermal Gravimetric Analyzer (TGA) Model DTG-60 (Shimadzu, Japan) was used to monitor the weight changes of the samples, while the derivative of a TG curve (DTG) evaluated the rate of weight loss during heating versus temperature. Samples of 10.0 mg were placed in an aluminum crucible and exposed to inert and oxidative atmospheres (40 mL/min). The temperature range for this TGA analysis extended from 30 °C to 700 °C at a constant heating rate of 10 °C/min.

2.7. Tribological Evaluation

The four-ball experiments were carried out using a DHR-3 rheometer (TA Instruments, New Castle, DE, USA) [40]. The experimental conditions were modified from ASTM D4172 [41] within the limits of the DHR-3 rheometer. The tribological tests were conducted at a sliding velocity of 0.46 m/s, a temperature of 75 °C, a load force of 55 N and for a
duration of 1 h (Figure 2). The balls’ material is a chrome steel alloy (AISI52100, 64 HRC), with a diameter of 12.7 mm and surface roughness of 0.015 μm. Before the experiments, acetone was used to clean the balls, which were then dried under room conditions. An optical microscope (Zeiss, Germany) with 100× zoom was used to study the morphology and measure the wear scar diameter (WSD). Samples of COFA and MOS were used as reference for a tribological comparison with synthesized samples.

![Four-ball tribological test setup](image)

**Figure 2.** Four-ball tribological test setup (sliding speed to 0.46 m/s, temperature to 75 °C, load force to 55 N and 1 h).

**3. Results and Discussion**

**3.1. Physicochemical Characterization**

The properties of the synthesized samples are shown in Table 2. The density at 20 °C values did not change significantly, which implies minor modifications in the mass/volume ratio of the samples. On the other hand, the kinematic viscosity of the samples showed notable changes. Kinematic viscosity has a close relationship with intermolecular interactions. In other words, samples with a high number of hydrogen bonds are more resistant to flow [20,42]. The viscosity index of BL1 showed the highest value, indicating the lowest variation in viscosity at different temperatures [19]. In addition, the pour point is another physicochemical property that shows a notable result. The BL2 sample showed the lowest pour point value; this result may be explained by the length of the branched carbon chain, since as the carbon chain length increases, the pour point value lowers [1].

**Table 2. Physicochemical properties of BL1 and BL2 samples.**

<table>
<thead>
<tr>
<th>Method</th>
<th>BL1</th>
<th>BL2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 20 °C, g/cm³</td>
<td>0.9080</td>
<td>0.9437</td>
</tr>
<tr>
<td>Kin. viscosity at 40 °C, cSt</td>
<td>28.23</td>
<td>96.92</td>
</tr>
<tr>
<td>Kin. viscosity at 100 °C, cSt</td>
<td>5.215</td>
<td>10.286</td>
</tr>
<tr>
<td>Viscosity index (VI)</td>
<td>116</td>
<td>85</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>–27</td>
<td>–45</td>
</tr>
<tr>
<td>Acid value, mg KOH/g</td>
<td>9.58</td>
<td>5.61</td>
</tr>
</tbody>
</table>

Beyond the fact that a decrease in the acidity means there will be less risk of surface corrosion, the acid value is an important property for confirming the esterification reaction, since the acid value decreased from 116.56 mg KOH/g in (see Table 1) to 9.58 mg KOH/g in BL1. Indeed, some authors reported the use of acid value to determine the conversion of the esterification reaction [20,23,39]. For samples obtained after epoxidation and oxirane rings reactions, the acid value of BL2 sample was lower, indicating that the reaction steps are favorable to the improvement of this property.
3.2. Chemical Characterization

The FTIR spectra of COFA, BL1, Epoxide and BL2 samples are shown in Figure 3. In all samples, sharp bands may be observed at 2924 cm\(^{-1}\) and 2854 cm\(^{-1}\), corresponding to the stretching vibrations of -CH\(_3\) and -CH\(_2\) [31]. The band at 1710 cm\(^{-1}\) in the COFA sample is due to the carbonyl group (C=O) of fatty acids [8]. After esterification, this peak shifts to approximately 1741 cm\(^{-1}\), corresponding to the stretching vibration of the carbonyl ester bond, confirming the formation of the ester structure in BL1 [43,44]. Additionally, it is possible to observe the C-O stretching vibration at 1175 cm\(^{-1}\) in the BL1 sample, which was not present in COFA [45].

![FTIR spectra of the COFA, BL1, EPOXIDE and BL2 samples.](image)

COFA and BL1 samples have peaks at 3007 cm\(^{-1}\) related to the band corresponding to the =CH stretch [42]. The absence of this peak in the epoxidized sample indicates the elimination of the double bond through the epoxidation reaction. Additionally, when comparing the epoxidized and the BL2 samples, it is observed that the peaks at 825 cm\(^{-1}\) and 1246 cm\(^{-1}\), which are associated with the formation of epoxy groups, disappear, confirming the oxirane ring opening reaction. In the BL2 sample, there is a peak at 1737 cm\(^{-1}\) corresponding to carbonyl elongation (C=O) and the peaks at 1174 cm\(^{-1}\) and 1246 cm\(^{-1}\) are related to the stretching vibration in the C-O band in the ester [46,47].

The results obtained in the FTIR spectra demonstrate the success of the chemical modifications performed, which is corroborated by the \(^1\)H NMR spectra (Figure 4). In the COFA sample, the peak (I) is attributed to the double bonds present in its chemical structure [48], while the peak (II) corresponds to the hydrogen atoms of the methyl group [49]. The peaks (III) and (IV) indicate the hydrogen atoms attached to the sp\(^3\) carbon (=CH\(_2\)) [49,50].

As for the BL1 sample, the appearance of the peak (V), which is associated with the hydrogen atom attached to the carbon close to the sp\(^3\) oxygen of the ester group (RCOOR'), confirms the esterification reaction [8,51]. In the epoxidized sample, the absence of the peak (VI), related to the double bonds and the appearance of the peak (VII), characteristic of the formation of the epoxy ring, indicate the success of the epoxidation reaction [52,53]. Likewise, the absence of peak (VII) in sample BL2 and the presence of peak (VIII), relating to hydrogen atoms of hydroxyl carbon [39,53], confirm the reaction of ring-opening epoxy.
3.3. Thermal-Oxidative Stability

The oxidative stability time for each sample, measured in hours and using a criterion of reaching a conductivity of 200 μS/cm, was 12.89 ± 0.57 h for BL1 and 14.29 ± 0.16 h for BL2. The improvement in the stability of BL2 compared to BL1 may be attributed to the removal of unsaturation through the epoxidation reaction, as well as to the increased degree of branching in the chemical structure of BL2 through the opening of oxirane rings, as previously reported [54–56]. This improvement in the stability of the final product through chemical modifications makes its application more viable, considering that one of the main limitations in the direct use of vegetable oils as bio-based lubricants is their low oxidative stability [39,57].

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves in inert and oxidative atmospheres were used to evaluate the thermal stability of the COFA, BL1 and BL2 samples. The TG (a) and DTG (b) curves of the samples in inert atmosphere are presented in Figure 5. The profiles of the curves for all samples exhibited similar trends composed of more than one event, indicating that analogous thermal mechanisms are involved in the degradation processes.

Figure 4. 1H NMR spectra of the COFA, BL1, EPOXIDE and BL2.

Figure 5. TG (a) and DTG (b) curves samples COFA, BL1 and BL2 in inert atmosphere.
Establishing the temperature at which the samples exhibit a 5% loss in their mass as the onset temperature of thermal decomposition (\(T_{\text{onset}}\)) [58], the values for the COFA, BL1 and BL2 samples were 229.30 °C, 219.27 °C and 195.03 °C, respectively. The decrease in the initial temperature of BL1 and BL2 may be attributed to residual solvent/alcohol, which could not be fully removed during distillation [59]. Nevertheless, all samples exhibited \(T_{\text{onset}}\) values above or very close to 200 °C, indicating good thermal stability [26].

According to the DTG of the COFA sample, the most significant thermal event occurs between 230 °C and 300 °C and is associated with the decomposition of the fatty acids, consistent with the usually reported range of 150 to 350 °C [42,43]. The initial mass loss observed in BL2 at temperatures below 200 °C was attributed to volatile components present in the sample [26]. In the BL1 and BL2 samples, the main thermal events observed between 250 and 450 °C are attributed to the evaporation and decomposition of hydrocarbons, as previously reported [34]. The second-largest thermal event observed in BL2, around 480 to 525 °C, may suggest the onset of the combustion phenomenon, as previously reported in Bezerra et al. [47], for a babassu oil biolubricant sample in the temperature range of 330 °C to 550 °C.

The temperatures associated with 10%, 20%, 50% and 90% mass loss of the samples are described in Table 3. Comparing samples BL1 and BL2, it is possible to observe that BL2 exhibits greater thermal stability, which can be explained by its chemical structure, as it contains more hydroxyl groups and a higher degree of branching compared to BL1, as reported in previous studies [11,60]. When comparing BL2 with other samples under identical conditions (50% mass loss), it was observed that its result slightly exceeded the value reported in a previous study [57] for the trimethylolpropane ester of Karanja oil (\textit{Milletta pinnata}), which was 312.53 °C. BL2 also exhibited a temperature higher than that of the 14 biolubricant samples derived from amino acid-based ionic liquids studied by Zhu et al. [61], which ranged between 174.8 °C and 236.1 °C. However, BL2 exhibited a lower temperature than that reported in the study by Jiang et al. [62] for the 5W-40 motor oil and the ionic liquid (1-vinyl-3-ethylimidazolium tetrafluoroborate), which for a 50% decomposition reached 359 °C and 402 °C, respectively.

Table 3. Decomposition temperatures and weight losses of the samples estimated from the thermogravimetric curves in inert atmosphere.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(T_{\text{onset}})</th>
<th>10%</th>
<th>20%</th>
<th>50%</th>
<th>90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>COFA</td>
<td>229.30</td>
<td>244.75</td>
<td>260.34</td>
<td>290.65</td>
<td>356.65</td>
</tr>
<tr>
<td>BL1</td>
<td>219.27</td>
<td>238.62</td>
<td>256.95</td>
<td>287.93</td>
<td>354.50</td>
</tr>
<tr>
<td>BL2</td>
<td>195.03</td>
<td>229.53</td>
<td>269.38</td>
<td>339.04</td>
<td>455.04</td>
</tr>
</tbody>
</table>

The TG (a) and DTG (b) curves of the samples in an oxidative atmosphere are shown in Figure 6, in which the DTG results corroborate the observations of the TG curves. Similarly, to DTG in an inert atmosphere, it is possible to observe multiple thermal events in all samples, indicating the presence of different thermo-oxidative processes involved.

Using the same criterion that \(T_{\text{onset}}\) is the temperature at which the sample exhibits a 5% mass loss, the values for the COFA, BL1 and BL2 samples were 236.14 °C, 223.72 °C, and 187.62 °C, respectively. It may be seen that samples COFA and BL1 exhibited high thermal stability up to 200 °C, while BL2 remained thermally stable up to around 190 °C. The mass losses observed in all samples between approximately 200–350 °C are associated with the degradation of ester bonds or double bonds present in their chemical structures, while mass losses above 350 °C suggest the complete degradation of previously generated oxidized fragments [63].
Table 4. The decomposition temperatures and weight losses of the samples deduced from thermogravimetric curve in air atmospheric.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T&lt;sub&gt;onset&lt;/sub&gt;</th>
<th>10%</th>
<th>20%</th>
<th>50%</th>
<th>90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>COFA</td>
<td>236.14</td>
<td>259.59</td>
<td>292.49</td>
<td>344.97</td>
<td>437.86</td>
</tr>
<tr>
<td>BL1</td>
<td>223.72</td>
<td>239.68</td>
<td>257.83</td>
<td>291.98</td>
<td>447.31</td>
</tr>
<tr>
<td>BL2</td>
<td>187.62</td>
<td>226.36</td>
<td>267.23</td>
<td>338.47</td>
<td>459.09</td>
</tr>
</tbody>
</table>

3.4. Tribological Results

The results obtained in the tribological tests for the obtained samples of bio-based lubricants and MOS are shown in Figure 7.

BL1 and BL2 exhibited lower friction coefficients and WSD than MOS throughout the tribological test. The presence of the polar region characterized by functional groups in the bio-based lubricant molecules enhances the adhesion to the spheres, and for this reason, the biologically sourced samples show lower FC compared to MOS, which is predominantly a non-polar molecule [8,26]. However, the friction curve of BL1 (Figure 7a) fluctuated throughout the test, indicating a type D friction trace behavior, where the lubricant is less efficient at resisting shear forces and, consequently, less capable of reducing wear between samples of biolubricants [67–69]. Other reported studies [8,70] obtained equivalent results for bio-based lubricants synthesized via an esterification reaction using 2-ethylhexanol. This lower wear reduction efficiency in BL1 can be explained by the fact that the esterification reaction converted the carboxylic functional group into an alcohol group.
Among the functional groups present in studied samples, carboxylic acid is the strongest polar group, which generates strong adhesion to the metallic surface of the spheres and excellent anti-wear properties. Therefore, the substitution of carboxylic acid with the alcohol group reduced the polarity and anti-wear efficiency of the BL1 molecule. Chan et al. [11] and Salimon et al. [71] also observed a correlation between the increase in polar functional groups in the structure of biolubricants and the improvement of lubrication, due to their intermolecular interactions with sliding surfaces. Salih et al. [72] observed the same behavior in their study of different biolubricant samples subjected to the four-ball test. In their study, the COF results ranged from 0.14 to 0.75, and the WSD sizes ranged from ca. 0.33 to 1.14 mm.

The BL2 sample exhibited the lowest FC (Figure 7a,b) among all the samples studied and an equivalent WSD (Figure 7c) to COFA. This behavior suggests that the introduction of ether-type branches (two hydroxyl functional groups and one alcohol group) improved the adhesion of the polar region to the metallic surface of the spheres while maintaining good anti-wear capacity due to the strong intermolecular interactions induced by hydrogen bonding. The insertion of branches around the polar region of a biolubricant molecule may help to protect the molecule from physical and chemical interactions due to steric hindrance [11]. Additionally, observations made by Quinchia et al. [73] in their analysis of High Oleic Sunflower Oil, Soybean Oil and Castor Oil samples suggest that castor oil tends to form a more resistant lubricating film. This improved performance may be partially attributed to its higher viscosity and the hydrogen bonds of the hydroxyl groups in its molecular structure. Qi et al. [74] also investigated the effects of carbon chain length and the number of hydroxyl groups on the lubrication performance of alcohols (such as methanol, n-propanol, n-hexanol and n-octanol), observing that with an increasing number of hydroxyl groups there is a decrease in the wear rate.

The morphologies of the worn surfaces are presented in Table 5. It is possible to observe aspects related to abrasion and adhesion wear, which is characterized by grooves in the direction of application [26,75–77]. The bio-based samples exhibit smoother surface aspects when compared to the MOS-lubricated surface, which appears rougher. This is because surfaces lubricated with bio-based lubricants form a mono- or multi-molecular structure that improves with the polar groups, inhibiting metal-to-metal contact between the balls. As a result, the surfaces exhibit smoother metal-to-metal contact compared to those observed for MOS [26,76,78].
Table 5. Wear morphology of balls after tribological tests using the biolubricants (BL1 and BL2) and comparison with COFA and MOS.

<table>
<thead>
<tr>
<th>Ball</th>
<th>COFA</th>
<th>BL1</th>
<th>BL2</th>
<th>MOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st ball</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>140.71 µm</td>
<td>247.56 µm</td>
<td>159.36 µm</td>
<td>261.34 µm</td>
</tr>
<tr>
<td>2nd ball</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>142.75 µm</td>
<td>253.46 µm</td>
<td>160.35 µm</td>
<td>269.48 µm</td>
</tr>
<tr>
<td>3rd ball</td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>138.58 µm</td>
<td>252.16 µm</td>
<td>153.92 µm</td>
<td>263.43 µm</td>
</tr>
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</table>

4. Conclusions

Samples of biolubricants derived from FACO and isoamyl alcohol were obtained through chemical modifications, presenting interesting lubrication properties. The confirmation of the occurrence of these reactions was established using spectroscopic analysis techniques such as FTIR and H3NMR. The samples were characterized to assess a variety of properties, including thermo-oxidative, physicochemical and tribological characteristics. The oxidative stability of the final biolubricant (BL2) was above 14 h when using the Rancimat technique at 110 °C. Comparing thermal mass loss, sample BL2 showed greater thermal stability than the biological base COFA and the intermediate product BL1 for both inert and oxidative atmospheres. The onset temperature of thermal decomposition (5% mass loss), in oxidative atmosphere, was 187 °C for the BL2 sample. Moreover, the pour point of the samples ranged from −27 °C to −45 °C, with the most desirable value obtained for the final product. The results revealed that the BL1 and BL2 samples exhibited a lower friction coefficient compared to the commercial oil, with the latter sample standing out as the top performer. Furthermore, the analysis of the wear scar diameter (WSD) indicated that the BL2 and COFA samples yielded similar results, suggesting excellent adhesion to the material’s surface. In particular, sample BL2 recorded a friction coefficient of 0.037, emphasizing its excellent performance with a WSD of 158 µm. Notably, the BL2 sample demonstrated particularly promising results in terms of thermo-oxidative properties. Its low pour point allows for effective lubrication even in extremely cold conditions, ensuring the proper operation of machinery and equipment. Consequently, it may be applied across a wide temperature range without compromising its properties, while also demonstrating an effective capacity to form a lubricating film that conforms to observed tribological tests, reducing friction coefficients and material wear.

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

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