



Article Tribological Performance of 100Cr6/8620 Steel Bearing System under Green Oil Lubrication

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Abstract: There is a great need to perform all processes and services more efficiently to reduce energy consumption and material waste. Bearing systems are present in all machines and motors, playing an important role in the reduction of energy consumption. 100Cr6 (ISO 683-17:2014) and AISI 8620 are two typical steels employed in most bearing systems. However, improving the tribological performance of these steels is still required. This study reports the analysis of green lubricants based on mixtures of vegetable oils to improve the friction and wear properties of steel bearing systems. Firstly, a method is presented to identify potential mixtures based on the excess thermodynamic properties. Then, the tribological performance of the 100Cr6/8620 steel bearing system lubricated with the selected mixtures is evaluated by the ball-on-disk method. It was found that the friction and wear behavior of the 100Cr6/8620 steel bearing system can be notably improved by the utilization of oil mixtures rather than pure green oils. The kinetic friction coefficient decreased up to 10% with the ideal mixture of castor and sesame oil, while wear was reduced up to 81% with the ideal mixture of castor and sesame oil, while wear was reduced up to 81% with the ideal mixture of the feasible manufacture of biolubricants for bearing systems.

Keywords: ISO 100Cr6 steel; AISI 8620 steel; sliding friction; bio-lubricant; oil mixture

1. Introduction

Bearings are essential components that significantly influence the efficiency of engines and machines [1,2]. These mechanical elements help to reduce energy losses and increase the durability of machines, principally by minimizing friction and wear. Therefore, to increase their efficiency, it is important to design accurate bearing systems, which involves the selection of potential materials, lubricants, and mechanical designs [2].

Steel materials are employed for many bearing applications in which high bearing loads are required. One of the most representative bearing steels is the high-carbon Cr-Mn alloy steel 100Cr6 (ISO 683-17:2014), equivalent to AISI 52100 [3]. Generally, it is used with other resistant steels, whose combination provides good tribological and mechanical performance. ISO 100Cr steel is usually employed with Ni–Cr–Mo low-alloy steel (AISI 8620) and various efforts have been made to improve the performance of this tribosystem. For example, the employment of laser treatment on AISI 52100 steel [4]; vanadium and niobium carbides protecting layers on AISI 8620, 8640, and 52100 steels [5]; and even the carburization of AISI 8620 [6] have been proposed.

Lubricants play a critical role in reducing the power losses of machines and engines. The lubricant industry is estimated to have more than ten thousand types of lubricants



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). worldwide [7], which are principally used in the automotive and industrial sectors. In bearing systems, various lubricants have been studied to improve friction and wear performance. D.-H. Hwang et al. [8] analyzed the tribological behavior of different pairs of the bearing steel 100Cr6 and commercial alumina under an additive-free mineral oil (ISO-VG100) lubricated condition. M. Sedlacek et al. [9] evaluated the tribological performance of ISO 100Cr6 under different contact conditions on a pin-on-disc tribometer with an Al_2O_3 ball counterpart. They employed pure poly-alpha-olefin (PAO) oil as a lubricant. Ulker et al. [10] studied the tribological properties of bearing boronized steels AISI 8620, 52100, and 440C against a WC-Co ball by a ball-on-disc test device under a lubricated condition with a non-specified lubricant. N. Bader et al. [11] studied the wear and friction phenomena of an ISO 100Cr6 system employing different oils with varying polymer additives. K. Milewski et al. [12] studied the tribological properties of 100Cr6 steel with and without a silicon-doped diamond-like carbon coating lubricated with an ionic liquid. Friction tests were performed on a ball-on-disc tribometer with an uncoated 100Cr6 counterpart. The largest percentage of lubricants are mineral-based due to their accessibility and low cost. However, there are several problems related to these products such as the low availability of petroleum, which decreases 3% annually [13], as well as their environmental hazards and impact on global warming [14].

To reduce the dependence on oil-derived substances, special attention has been focused on vegetable oils to be used as lubricants for different applications [15]. These oils have good quality properties emphasizing the viscosity index, high lubricity, low volatility, and a good affinity to metal surfaces due to their chemical composition [16]. However, their main drawbacks, such as their poor oxidative stability and the limited viscosity range, restrict their applications [17]. Conveniently, these specific properties can be improved by employing different lubricant additives such as anti-wear or anti-oxidation agents, or friction modifiers [18]. Nevertheless, the addition of these elements can affect their biodegradability and price. Then, as an ecofriendly alternative, the mixtures of vegetable oils offer the possibility of improving some properties due to their different chemical compositions [19].

One of the most important green lubricants is castor oil, which is a non-edible substance distinguished from other vegetable oils by its higher viscosity and oxidative stability because of the presence of 90% ricinoleic acid in its composition [20]. In addition, castor oil has also exhibited great tribological behavior without additives [21], and with some friction modifiers: zinc oxide [22], graphite [23], multiwalled carbon nanotube [23], and multilayered graphene [23]. Canola oil is the third most common edible vegetable oil produced worldwide [24]; it is composed mainly of 60% oleic acid and 20% linoleic acid. Research has shown that it has a higher viscosity index and better tribological performance than some mineral oils [25]. Furthermore, it has a higher potential to be used in the production of lubricants than other vegetable oils [26]. Sesame oil is another interesting vegetable oil that is less commonly studied but has very attractive properties for lubricating purposes. This oil is composed mainly of linoleic (44%), oleic (40%), palmitic (10%), stearic (5%), and other fatty acids in minor amounts. The main characteristics of sesame oil are superior oxidative stability, and high flashpoint and firepoint, as well as low pour point [27]. It has been observed that in pure form, sesame oil offers a better lubricity than other vegetable oils such as coconut and sunflower [27]. That behavior can be improved by the incorporation of some additives such as Cu and Al_2O_3 nanoparticles [28], paraffin [29], and polyethylene wax [29].

To our knowledge, the use of vegetable-oil-based lubricants in bearing systems is limited in the literature. Recently, the tribological response of green lubricants (castor, canola, and sesame oils) in an ISO 100Cr6/AISI 4140 steel system was studied [30]. Although all three lubricants had a notable performance, it was shown that the tribosystem exhibited the lowest friction coefficient ($\mu_{\rm k} = 0.10$) and wear rate (K = $1.8 \times 10^{-7} \text{ mm}^3/\text{Nm}$) when it was lubricated with castor oil. Nevertheless, an important limitation for the potential use of this oil is the low worldwide production of castor seed from which it is extracted. In 2020,

according to data accessed from the Food and Agriculture Organization, world production of castor seed was just 2.8% of the rapeseed production (seed from which canola oil is obtained) [31]. Whereas the worldwide production of sesame seed is three times higher than that of castor seeds and is up to 9.4% of the rapeseed production [31]. Therefore, an alternative between performance and availability could be the use of oil mixtures so that their physical properties and tribological behavior could be improved.

Based on the above, to propose green lubricant alternatives that could be employed for the improvement of the tribological characteristics of steel bearing components, this research presents the tribological evaluation of binary mixtures of castor/canola and castor/sesame oils as lubricants in the ISO 100Cr6/ AISI 8620 steel bearing system. A method through the excess molar volume and viscosity deviation properties was employed to identify the potential mixtures. Then, a tribological evaluation was performed using the ball-on-disk method.

2. Materials and Methods

2.1. Steel Materials

For the tribological tests, AISI 8620 steel disks were tested against 100Cr6 steel balls under ball-on-disk lubricated conditions. The chemical composition and mechanical properties of the employed steels are shown in Tables 1 and 2, respectively. Different techniques were employed for the chemical characterization of the steels due to the sample size required for the optical emission spectrometer.

Table 1. Chemical composition (wt.%) of bearing steels.

	С	P (max)	S (max)	Mn	Si	Cr	Мо	Ni	Fe
AISI 8620 a	0.25	0.006	0.025	0.85	0.27	0.59	0.17	0.38	Balance
ISO 100Cr6 ^b	1.05	0.025	0.025	0.3	0.3	1.5	0.1	-	Balance

^a Chemical composition obtained by PMI-MASTER smart optical emission spectrometer (Hitachi High-Tech Analytical Science, Westford, MA, USA). ^b Chemical composition obtained by Quanta 3D 200i scanning electron microscope (FEI Company, Hillsboro, OR, USA) equipped with an Oxford X-MaxN-50 energy-dispersive Xray spectrometer.

Table 2. Mechanical properties of bearing steels.

Property	ISO 100Cr6	AISI 8620
Microstructure ^a	Martensite	Martensite
Hardness (HRC) ^b	60	58
Yield strength (GPa) ^c	2	0.8
Young's Modulus (GPa) ^c	210	210
Poisson's Ratio ^c	0.3	0.3

^a Microstructure obtained by chemical etching with Nital's reagent (2%) and analyzed by optical microscope Carl Zeiss Axio Imager (Carl Zeiss, Oberkochen, Germany). ^b Converted from Vickers hardness measured in a Metrotec microhardness tester (SMVK-1000ZS, Metrotec, Lezo, Spain). ^c Standard properties from the literature.

2.2. Lubricants

For this study, canola oil (CaO), sesame oil (SO), and their blends with castor oil (CO) were studied as lubricants. Table 3 describes the principal fatty acid composition of each oil according to the literature. Nonedible castor oil was imported from India, whereas the edible canola and sesame oils were bought from the local market. All vegetable oils were used without any additional treatment other than mixing. Since vegetable oils exhibit similar properties, they can be dissolved easily. Different binary mixtures of CO/CaO and CO/SO were prepared individually by magnetic moderate stirring for 10 min at room temperature in a 600 mL borosilicate beaker. Table 4 contains the concentration of oil mixtures. The blend of these types of vegetable oils is a simple process and triglyceride mixtures cannot be separated by themselves over a long period or by simple methods.

Fatty Acid	Castor Oil	Canola Oil	Sesame Oil
Arachidic	0.25	0.57	0.57
Behenic	-	0.35	0.08
Erucic	-	0.42	-
Stearic	1.11	1.99	5.14
Gondoic	0.42	1.49	0.10
Lignoceric	-	0.16	-
Linoleic	4.82	21.19	43.46
Linolenic	0.56	9.42	0.56
Oleic	3.37	60.43	40.18
Palmitic	1.36	4.52	10.06
Palmitoleic	-	0.34	0.10
Ricinoleic	88.07	-	-

Table 3. Fatty acid composition of castor, canola, and sesame oils, data from [32].

Table 4. Volume and molar concentrations of different binary oil mixtures.

	CO/CaO M	ixture	CO/SO Mixture		
% v/v	Molar Fraction of CO in CaO, x Designat		Molar Fraction of CO in SO, <i>x</i>	Designation	
0	0.0000	CaO	0.0000	SO	
50	0.4844	CO/CaO1	0.4838	CO/SO 1	
60	0.5849	CO/CaO 2	0.5844	CO/SO 2	
70	0.6867	CO/CaO3	0.6862	CO/SO 3	
80	0.7898	CO/CaO4	0.7895	CO/SO 4	
90	0.8942	CO/CaO 5	0.8940	CO/SO 5	

2.2.1. Characterization of Lubricants

The density, dynamic viscosity, and kinematic viscosity were determined to describe the binary oil mixtures. Density was evaluated by the pycnometer method according to ASTM D 1217 [33]. A thermostatic bath (Lumistell, Celaya, Mexico) with a resolution of 0.1 °C and analytical balance Explorer Pro EP214 (Ohaus Corporation, Parsippany, NJ, USA) were used to heat and weigh the samples. The dynamic viscosity was obtained by using a rotational viscosimeter RV-DV II Pro (Brookfield, Middleboro, MA, USA) equipped with a guard leg. The torsional force was applied using RV 1–5 spindles with a combination of speeds 5–200 RPM until the minimum variation according to the supplier manual was observed. This test was performed on individual samples of 600 mL deposited in a borosilicate beaker and heated in the thermostatic bath. Figure 1 shows the setup for density and viscosity measurements of lubricants. Kinematic viscosities were calculated based on the dynamic viscosity and density at the corresponding temperatures. For each sample, the reported property values were the average of three measures.

2.2.2. Identification of Potential Binary Oil Mixtures for Tribological Tests

In engineering applications, the characterization of binary mixtures allows predicting their behavior using well-known models that can describe the interactions of substances at the chemical or physical level and thus define the scope of their applications [34]. However, such predictions may deviate from the real behavior due to the intermolecular forces that occur between the pure substances [35]. Through the excess thermodynamic properties, it is possible to obtain information on the molecular interactions between them [35]. The derivative thermodynamic properties such as excess molar volume and viscosity deviation allow analyzing the molecular interactions of the components of the solution [36]. In this investigation, to study the influence between the molecular interactions and the behavior of the binary mixtures CO/CaO and CO/SO as lubricants in mechanical systems, the excess thermodynamic properties were calculated and correlated by a Redlich–Kister-type equation [37,38]. Excess molar volume (V^E) and viscosity deviation ($\Delta \ln(\eta)$) were

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Viscosity measurements

calculated using Equation (1) and Equation (2), respectively. The correlation was made by the Redlich–Kister-type Equation (3).



Density measurements

$$V^{E} = (x_{1}M_{1} + x_{2}M_{2})/\rho - \left(\frac{x_{1}M_{1}}{\rho_{1}} + \frac{x_{2}M_{2}}{\rho_{2}}\right)$$
(1)

$$\Delta \ln(\eta) = \ln(\eta) - (x_1 \ln(\eta_1) + x_2 \ln(\eta_2))$$
(2)

$$Y = x_1 x_2 \sum_{i=0}^{n} A_i (1 - 2x_2)^i$$
(3)

In the previous equations, x is the molar fraction, M is the molar mass, ρ is the density, and η is the kinematic viscosity. The subscripts 1–2 correspond to each pure component, while the absence of them represents the properties of the binary mixture. In Equation (3), Y represents the excess molar properties and A the correlation coefficient.

2.3. Tribological Tests

AISI 8620 steel disks with a thickness of 5 mm, a diameter of 25.4 mm, and hardness of 60 HRC were manufactured by an external supplier (Grupo ETSA, Celaya, Mexico) and then polished in a wet condition with different sandpapers until a surface roughness of $0.02 \,\mu\text{m}$ in Ra was reached. ISO 100Cr6 steel balls with a diameter of 3 mm and surface roughness of 0.03 µm in Ra were purchased from Anton Paar.

The friction and wear tests between ISO 100Cr6 and AISI 8620 steel were carried out on a CSM Instrument tribometer (CSM Instruments Company, Needham, MA, USA) with a ball-on-disk configuration following the procedure of the ASTM G99 standard [39]. The tribological evaluation was performed at room temperature of 25 °C. For these tests, a normal load of 5 N, a wear radius of 2 mm, and a linear speed of 5 $\text{cm} \cdot \text{s}^{-1}$ were employed. These experiments were carried out during 1000 m of total sliding distance reaching approximately 79,000 cycles. Before the tribological tests, counterparts and tribometer accessories were sonicated for 15 min on a Branson sonicator (Branson Ultrasonics Corporation, Brookfield, CT, USA) with distilled water, and then cleaned with methanol. At the end of the experiments, the oil residues were removed from the steel counterparts with methanol and a soft cloth. The worn surfaces were analyzed by an optical microscope Leica ICC50W (Leica Camera AG, Wetzlar, Germany) with reflected light and by using a brightfield filter. In an effort to compare the performance of the green oils with that of commercial lubricants, these experiments were reproduced employing a mineral oil with a viscosity of 0.260 Pass at 25 °C; the obtained results can be found in Appendix A.

In the study, the mass loss of the ball and disk was insignificant, and it was not detected by an analytical balance. Then, for the determination of wear loss, linear measurements of the wear tracks obtained by microscopy were performed by image analysis in the LAS EZ software (3.4 DVD 272, Leica Camera AG, Wetzlar, Germany). The ball material tested with



the natural oils did not suffer significant wear (see Figure A2 in Appendix A); therefore, only the wear of the steel disks was studied. Different sections of the wear tracks were analyzed making a total of one hundred width measurements per sample and the average is presented. Figure 2 shows the configuration of the tribological studies, and a representative image of the wear track width measurements on the AISI 8620 steel tested with canola oil.



Wear track width measurement



Volume loss (V) of the steel disks was calculated according to ASTM G99 [39] by Equation (4). Then, wear rate (K) was calculated by Equation (5). In these equations, d represents the wear track width, R the wear track radius, r the radius of the ball, F the normal load, and S the total sliding distance.

$$V = \pi R d^3 / 6r \tag{4}$$

$$\mathbf{K} = \frac{V}{F \cdot S} \tag{5}$$

2.4. Lubricating Regime

The lubricating regime was associated with the lambda parameter, λ , which is a relation between the minimum film thickness and the composite surface roughness, and it is calculated according to Equation (6). In this equation, *h* is the lubricant film thickness, while R_a and R_b correspond to surface roughness of ball and disk, respectively.

$$\lambda = \frac{h}{\left(R_a^2 + R_b^2\right)^{\frac{1}{2}}}$$
(6)

In this investigation, the minimum film thickness was expected based on the Hamrock and Dowston theory for elastohydrodynamic lubrication of point contacts [40] and following the procedure utilized in [41].

3. Results

3.1. Lubricants

3.1.1. Physical Properties of Binary Oil Mixtures

The density and dynamic viscosity of the studied lubricants are shown in Figure 3. The obtained properties of pure vegetable oils are similar to those previously reported in the literature [30,42]. As expected, it can be observed in Figure 3 that the increase in temperature produced a decrement in the density and viscosity of lubricants. However, binary mixtures showed lesser variation than pure vegetable oils. It is also important to note that, in all cases, the density and viscosity of mixtures increased with the increase in castor oil concentration. At the temperature of 25 °C, the increase in density was from 2 to 4%, while the viscosity increase ranged from 88% to 398%.



Figure 3. Density and dynamic viscosity of binary oil mixtures as a function of temperature: CO/CaO (**a**,**b**) and CO/SO (**c**,**d**).

3.1.2. Identification of Potential Binary Mixtures for Tribological Tests

Figure 4 shows the excess molar volume (V^E) and viscosity deviation ($\Delta \ln(\eta)$) behavior of binary mixtures at temperatures of 25, 40, and 70 °C. In all cases, the symbols represent the experimental values obtained, while the dotted lines correspond to the values obtained after the Redlich–Kyster adjustment. The results obtained for the excess thermodynamic properties, as well as the correlation coefficients and standard deviation obtained from the adjustment, can be found in detail in Appendix B. It is observed in Figure 4a,c that the behavior of the excess molar volume presents a clear deviation from ideality. This far from ideal behavior can be attributed to the composition of the fatty acids present in the triglycerides of vegetable oils of binary mixtures.



Figure 4. Excess molar volume (V^E) and viscosity deviation ($\Delta \ln(\eta)$) of binary mixtures at different temperatures: CO/CaO (**a**,**b**) and CO/SO (**c**,**d**).

In Figure 4b,d, corresponding to the viscosity deviation, a large deviation from ideality can be observed. In the range of molar fractions from 0.5 to 1, it can be seen that there is a transition point in the behavior of the viscosity deviation. At this point, it is observed that at certain concentrations, the binary mixtures of CO/CaO and CO/SO present the behavior of ideal solutions. The transition zones are delimited by the green rectangles. In the CO/CaO mixtures, this behavior occurs between the molar concentrations of 0.4844 and 0.5849. Whereas, in the CO/SO mixtures, two transition zones were found, one located between 0.6862 and 0.7895, and the other between 0.8940 and 1.0000.

The transition zones observed in the behavior of the deviation of the viscosity are of interest due to the ordering behavior of the triglyceride molecules present in the analyzed vegetable oils. From the observations of the behavior of the excess properties, we decided to estimate the tribological properties around these transition zones in the binary mixtures of CO/CaO and CO/SO. Table 5 shows the concentrations and labels of the selected mixtures around the transition zones of the behavior of the excess properties.

Table 5. The molar concentration of binary oil mixtures next to the transition zones.

CO/CaO	Mixture	CO/SO Mixture			
Molar Fraction of CO in CaO, <i>x</i>	Designation	Molar Fraction of CO in SO, <i>x</i>	Designation		
0.4844	CO/CaO 1	0.6862	CO/SO 3		
0.5211	CO/CaO 1.5	0.7484	CO/SO 3.5		
0.5849	CO/CaO 2	0.7895	CO/SO 4		

3.2. Tribological Response of the 100Cr6/8620 Steel Bearing System Lubricated with Different Oil Mixtures

3.2.1. Friction Behavior

The kinetic friction coefficient exhibited by the 100Cr6/8620 steel bearing system lubricated with oil mixtures is shown in Figure 5. From Figure 5a it can be noted that the addition of castor oil into canola oil did not benefit the friction coefficient behavior of the steel system. The system lubricated with pure canola oil exhibited the lowest friction and the initial friction coefficient was closed to $\mu_k = 0.022$; subsequently, the friction coefficient increased gradually with sliding distance up to 100 m, after which it decreased to an asymptotic value about $\mu_k = 0.024$. The average friction coefficient value of this system was $\mu_k = 0.026$. Nevertheless, when the system was lubricated with the CO/CaO mixtures, although the friction coefficient pattern was very similar, the mean friction coefficient increased up to three times. Under the tested conditions, an influence of the concentration of castor oil on the variation of the kinetic friction coefficient was not observed, since it reached a similar value ($\mu_k = 0.084$) with the three CO/CaO mixtures.



Figure 5. Influence of CO/CaO (**a**) and CO/SO (**b**) binary oil mixtures as green lubricants in the kinetic friction coefficient (μ_k) of the 100Cr6/8620 steel system.

It can be observed in Figure 5b that the friction coefficient behavior of the steel system lubricated with sesame oil was very stable throughout the test. However, this behavior was somewhat affected by the incorporation of castor oil into sesame oil. In the system lubricated with the CO/SO 3 mixture the friction coefficient increased progressively from its initial value to a more stable value ($\mu_k = 0.092$). The lowest friction coefficient was obtained with the CO/SO 3.5 mixture, which exhibited ideal thermodynamic behavior. With this mixture, even though the friction coefficient exhibited variable behavior along with the sliding distance, it was 10% lower than that obtained with pure sesame oil. The highest friction coefficient was observed when the system was lubricated with the CO/SO 4 mixture.

3.2.2. Wear Behavior

In this study, only the AISI 8620 steel disk samples exhibited significant wear, therefore the analysis of the wear behavior was focused on this material. Figure 6 shows optical micrographs of the worn surfaces of the AISI 8620 steel samples lubricated with CaO, SO, and their binary oil mixtures. In general, in all situations, the steel suffered significant wear due to the lubricating conditions. The addition of castor oil into canola oil notably improved the wear behavior of the system reducing the wear damage and wear track width. Nevertheless, this feature was not observed on all the surfaces lubricated with the CO/SO

mixtures. Dark marks in the direction of the polished lines can be seen on all surfaces. This indicates that the wear occurred mainly in the roughness of the tribo-contact. In this type of contact, tribo-oxidation and formation of tribo-chemical films can occur due to the induced high temperatures as well as the environment [43]. However, as the sliding process continues, the size of oxide layers increases. Then, these layers can break off and be trapped or built up on surfaces. As can be observed in Figure 6, all samples exhibited this oxidative wear mechanism, only presenting variations in the intensity of wear and wear track width. In addition, some furrows and grooves characteristic of abrasive wear can be seen in most of the worn surfaces. The steel samples lubricated with CaO and CO/CaO 1 experienced greater wear in which, as can be seen, some oxidized particles were dislodged, and accumulated in layers (sample lubricated with CaO) or within the abrasive grooves (sample lubricated with CaO).



Figure 6. Worn surface analysis of AISI 8620 steel lubricated with canola oil, sesame oil, and their binary oil mixtures. Optical micrographs were taken at 500X. SD represents the direction of sliding.

Figure 7 shows the analysis in an oxidation layer zone in the AISI 8620 steel sample lubricated with canola oil as representative. Firstly, the Cr content in the two analyzed regions (dark and light areas) was very close to the content of AISI 8620 steel, which demonstrates that there were no wear traces of the counterpart. In addition, in both zones, there was a considerable amount of oxygen (mainly in the dark zone, spectrum 15), which can be related to the formation of oxides on the worn surface and corroborates the proposed mechanism.

Figure 8 shows the wear response of the AISI 8620 steel system in terms of the wear rate (K). It can be observed in Figure 8a that all three CO/CaO mixtures improved the wear resistance of the steel in comparison to the pure CaO. From these mixtures, the best wear protection was obtained with the CO/CaO 1.5 mixture as a green lubricant. With this lubricant, the wear rate was 81% lower than the one obtained with pure CaO. It is important to note that the CO/CaO 1.5 mixture was also the oil mixture with ideal thermodynamic behavior. However, it can be seen in Figure 8b that, in terms of wear, the incorporation of castor oil into sesame oil caused greater differences. The CO/SO 3 mixture as lubricant caused the highest wear of the system since the wear rate was up to one order of magnitude higher than that obtained with SO. However, it can be seen that there is a clear tendency to reduce wear with the increasing concentration of castor oil. At the highest concentration (CO/SO 4 mixture), the wear rate was up to 6% less than that obtained with pure sesame oil.



Figure 7. SEM and EDS analysis on the worn surface of AISI 8620 steel lubricated with canola oil.



Figure 8. Influence of CO/CaO (**a**) and CO/SO (**b**) binary oil mixtures as green lubricants in the wear rate (K) of the AISI 8620 steel.

3.2.3. Lubricating Regime

Table 6 shows the predicted values of central (h_c) and minimum (h_{min}) lubricant film thickness, as well as the lambda ratio (λ) for each system. It can be observed in Table 6 that pure oils produced the lowest film thickness and lambda ratio values. Favorably, an increment was observed in the lubricant film thickness and lambda ratio in all the mixtures, with the increase in castor oil content. Nevertheless, under the tested conditions, the 100Cr6/8620 steel systems lubricated with the CaO, SO, and all CO/CaO mixtures were expected to work in the boundary lubricating regime. This regime is distinguished by the existence of greater contact between the asperities; thus, higher friction and wear are usually generated. However, the systems lubricated with all the CO/SO mixtures exhibited higher lubricant film thickness and were estimated to work mainly in the mixed lubricating regime. This region is generally characterized by a thicker lubricant film that protects the surfaces, but it can still present significant friction and wear. However, these systems also presented regions where the lubricant layer was minimal and operated under boundary conditions.

Lubricant	<i>h_c</i> (nm)	λ_c	Lubricating Regime	h_{min} (nm)	λ_{min}	Lubricating Regime
CaO	13	0.35	Boundary	7	0.20	Boundary
CO/CaO1	24	0.67	Boundary	14	0.38	Boundary
CO/CaO 1.5	33	0.92	Boundary	19	0.52	Boundary
CO/CaO 2	31	0.87	Boundary	18	0.49	Boundary
SO	13	0.37	Boundary	8	0.21	Boundary
CO/SO 3	49	1.37	Mixed	27	0.76	Boundary
CO/SO 3.5	57	1.58	Mixed	31	0.87	Boundary
CO/SO 4	61	1.70	Mixed	34	0.94	Boundary

Table 6. Influence of vegetable oils as lubricants in the lambda ratio (λ) for central (h_c) and minimum (h_{min}) lubricant film thickness on the 100Cr6/8620 steel system.

4. Discussion

From the experimental data of density and viscosity, as well as the thermodynamic properties of excess, it can be observed that molecular interactions in binary mixtures of vegetable oils affect the tribological performance of the 100Cr6/8620 steel bearing system. In all the CO/CaO and CO/SO mixtures studied, an increase in both density and viscosity could be observed concerning the pure CaO and SO. This was largely because CO has a higher density and viscosity than CaO and SO. Another reason for the behavior of the thermodynamic properties in the mixtures of these vegetable oils is the high concentration of ricinoleic acid in the CO. This fatty acid has a higher molecular weight and a lesser degree of unsaturation than oleic and linoleic acids, which are the main components in CaO and SO [44].

The excess molar volumes for all mixtures, excepting some molar fraction of CO/CaO mixtures and temperatures, showed a deviation from positive ideality. This suggested that the interactions between the two oils were weaker than the intrinsic interactions of each pure oil. In addition, the viscosity deviation study showed that the oil mixtures had both positive and negative deviations from ideality. Negative values of the viscosity deviations can be interpreted as indicating that the attractive forces between molecules are stronger than the repulsion forces [45]. In the case of positive values of the viscosity deviations, they can be interpreted as indicating that the repulsive forces between the molecules are stronger than the attractive forces [45]. These forces determine the physical properties of substances, such as surface tension, density, and viscosity, among others.

That influence was later verified with the ideal mixture CO/CaO 1.5, which exhibited the lowest wear values compared to pure CaO and the other CO/CaO mixtures. This could be because it exhibited a greater thickness of the lubricating layer because of the better set of physical properties. However, due to higher variations in the excess molar volumes, the interactions of CO/CaO mixtures were lower than the interactions of the pure CaO, thus it could provide poorer friction behavior. In addition, with the ideal mixture CO/SO 3.5 a lower friction coefficient was found compared to pure SO and the other CO/SO mixtures. This, in the first instance, was due to the increase in the lubricating layer, so the system worked in the mixed regime instead of the boundary regime. Likewise, according to the properties of excess, in this region, there is a balance between the attraction and repulsion forces, which could reduce the internal friction of the oil mixture and thus the friction coefficient.

The tribological results of the present work for the 100Cr6/8620 steel bearing system exhibited low friction coefficients (between 0.026 and 0.090) and wear rate values (from 8.87×10^{-8} to 6.33×10^{-7} mm³/Nm) under lubrication with green lubricants based on CaO, SO, and their mixtures with CO. By comparing the tribological performance of this system with that of other studies it can be observed that when lubricating with one mineral oil (Appendix A), notable benefits were observed. It was noted that the friction coefficient obtained with all the proposed green lubricants was lower than that obtained with the mineral oil. Particularly, the friction coefficient obtained with canola oil was up to 73%

lower than that achieved with mineral oil (0.097). Furthermore, the wear behavior was improved by the green lubricants since the wear of the ball was completely reduced, and the wear rate of the steel disk was up to 55% lower (sample lubricated with CO/SO 4 mixture) than that obtained with the mineral oil (K = $1.96 \times 10^{-7} \text{ mm}^3/\text{Nm}$). In addition, the results of this research are also lower or similar to those reported in the literature. For example, D.-H Hwang et al. [8] found static friction coefficients between 0.1 and 0.4 for the 100Cr6/ Al₂O₃ systems lubricated with mineral oil. M. Sedlacek et al. [9] also observed friction coefficients between 0.12 and 0.16 in an ISO 100Cr6/Al₂O₃ system lubricated with a poly-alpha-olefin (PAO) oil. S Ulker et al. [10] noted friction coefficients between 0.08 and 0.14, and wear rates from 3 to 7×10^{-5} mm³/Nm for AISI 8620, 52100, and 440C steel systems against a WC-Co under a lubricated condition with a non-specified lubricant. N. Bader et al. [11] reported friction coefficients between 0.06 and 0.12 for an ISO 100Cr6 system employing different oils with varying polymer additives. As mentioned before, the selected oil mixtures of this study had high potential in the improvement of friction behavior of the 100Cr6/8620 steel bearing system, and they contribute to the sustainable tribological processes.

5. Conclusions

In this work, the tribological performance of the ISO 100Cr6/AISI 8620 steel bearing system was analyzed under green oil lubrication. Canola oil (CaO), sesame oil (SO), and their blends with castor oil (CO) were studied as biolubricants.

It was demonstrated that the analyses of the excess thermodynamic properties such as excess molar volume (V^E) and viscosity deviation ($\Delta \ln(\eta)$) can be useful to identify potential oil mixtures that could improve the friction and/or wear behavior. The analysis of the tribological performance showed that the friction coefficient and wear rate can be reduced up to 10% and 81% by using the ideal mixtures CO/SO 3.5 and CO/CaO 1.5, respectively, with respect to the pure oils.

In general, the lowest friction coefficient of the 100Cr6/8620 steel system was obtained with pure CaO ($\mu_k = 0.026$). However, the best wear behavior was observed in the system lubricated with the CO/SO 4 mixture (K = $8.87 \times 10^{-8} \text{ mm}^3/\text{Nm}$). The tribological behavior of the 100Cr6/8620 steel system lubricated with green lubricants was lower or similar to that obtained by other lubricants employed in comparable systems.

Therefore, we propose that vegetable oils and their blends have the potential to be used as green lubricants in steel bearing systems, having a strong impact on the sustainability of those systems. Additionally, vegetable oil mixtures seem to be a great alternative for the viable production of biolubricants, where the performance and availability of resources are considered.

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Appendix A

Figure A1 shows the friction and wear behavior of the ISO 100Cr6/AISI 8620 steel bearing system under mineral oil lubrication. It can be seen in Figure A1a that the friction coefficient was stable throughout the test showing a tendency to decrease with increasing sliding distance. The average friction coefficient was $\mu_k = 0.097$. Figure A1b shows the wear rate (K) of the disk and ball materials. Figure A2 shows the comparison of the worn surfaces of the ISO 100Cr6 ball tested with the mineral oil and a natural lubricant (CO/SO 4). It can be observed that with the mineral oil, the ball counterpart exhibited significant wear since the wear mark can be easily observed by light microscopy (Carl Zeiss, Oberkochen, Germany). Regarding the wear of the disk material, Figure A3 presents an optical micrograph of a region of the worn surface which exhibited furrow marks along the sliding direction, which allows determining that the main wear mechanism was abrasion.



Figure A1. Influence of mineral oil lubricant on the kinetic friction coefficient (**a**) and wear rate (**b**) of the ISO 100Cr6/AISI 8620 steel bearing system.



Figure A2. Optical micrographs of worn surfaces of the ISO 100Cr6 ball tested with the mineral oil (**a**) and a natural lubricant (CO/SO 4) (**b**).



Figure A3. Optical micrograph of worn surface of the AISI 8620 ball tested with mineral oil.

Appendix **B**

Table A1 shows the results obtained for the excess thermodynamic properties, according to those described in Section 3.1.2. The first column includes the molar concentration of castor oil present in each of the binary mixtures, and the subsequent columns correspond to the two properties evaluated at temperatures of 25, 40, and 70 °C. The validation of the Redlich–Kyster-type adjustment is shown in Tables A2 and A3 for the viscosity deviation $(\Delta \ln(\eta))$ and excess molar volume (V^E), respectively. The values of the standard deviation allow us to observe the adequate adjustment of the proposed model of five parameters of the Redlich–Kister equation to the excess thermodynamic properties of the binary mixtures of vegetable oils.

Table A1. Excess molar volume (V^E) and viscosity deviation ($\Delta \ln(\eta)$) of binary oil mixtures at 25, 40, and 70 °C.

	T = 25	T = 25 °C		T = 40 °C		°C
X ₁	V^E (cm ³ ·mol ⁻¹)	Δln(η) (Pa·s)	V ^E (cm ³ ·mol ^{−1})	∆ln(η) (Pa·s)	V ^E (cm ³ ·mol ^{−1})	Δln(η) (Pa·s)
			CO/CaO			
0.4838	2.5215	-0.5579	1.9695	-0.3648	3.3679	-0.1810
0.5844	3.4625	-0.6258	3.9392	-0.4114	6.5983	-0.2009
0.6862	1.5329	-0.6430	0.8623	-0.4327	1.6574	-0.2073
0.7895	0.4176	0.4629	1.5249	0.2930	4.4152	0.1545
0.8940	2.1331	0.4890	2.8727	0.3010	5.2860	0.1674
			CO/SO			
0.4844	-0.9146	-1.2534	-1.7141	-0.6715	-0.0036	-0.3883
0.5849	1.5635	0.8371	3.6275	0.6000	4.3914	0.3491
0.6867	-0.3564	1.0935	-0.1133	0.7981	1.3171	0.4554
0.7898	0.1205	0.4248	1.3657	0.2715	3.2708	0.1774
0.8942	2.2102	0.5019	3.1631	0.2548	4.6792	0.1986

T (°C)	A_0	A_1	A_2	A_3	A_4	σ
			CO/CaO			
25	-1.6045	12.8402	-187.9508	523.0139	-369.7274	$8.0 imes10^{-4}$
40	-1.0373	8.6436	-126.3462	350.4607	-248.0036	$3.2 imes10^{-5}$
70	-0.5168	4.2678	-61.5621	170.6758	-120.2490	$2.0 imes10^{-5}$
			CO/SO			
25	-3.3175	52.7184	-62.2430	-105.6311	148.8545	$2.2 imes 10^{-5}$
40	-1.7541	29.7662	-10.6806	-129.1024	131.7013	$1.9 imes10^{-5}$
70	-0.9962	17.6524	-10.4861	-65.6660	72.1475	$1.1 imes 10^{-5}$

Table A2. Coefficients A_i and standard deviation (σ) obtained from the Redlich–Kyster adjustment for the excess molar volume (V^E) property of the binary oil mixtures.

Table A3. Coefficients A_i and standard deviation (σ) obtained from the Redlich–Kyster adjustment for the viscosity deviation ($\Delta \ln(\eta)$) property of the binary oil mixtures.

T (°C)	A_0	A_1	A_2	A_3	A_4	σ
			CO/	CaO		
25	0.7604	119.5803	-679.1355	1094.3692	-481.0099	$1.3 imes 10^{-3}$
40	3.2769	270.4520	-1658.9135	3059.2857	-1685.2968	$3.4 imes10^{-6}$
70	8.7253	231.5880	-1472.7256	2822.0932	-1577.2949	$5.7 imes10^{-6}$
			CO/	'SO		
25	11.8867	48.0705	-223.1700	100.3162	161.3924	$1.0 imes10^{-4}$
40	13.2427	132.8593	-958.0847	1793.5566	-960.3845	$2.0 imes10^{-4}$
70	23.5513	244.7716	-1930.5180	3999.5907	-2383.2379	$3.0 imes 10^{-3}$

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