

Article

Studying the Tribological Properties of Coffee Oil-Loaded Water-Based Green Lubricant

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Featured Application: The investigated additives for water-based lubricating fluids could be used in applications where aqueous lubricants are employed. These could be hydraulic or metal-working applications.

Abstract: Lubrication is the primary solution to reduce friction and wear. However, conventional lubricants cause pollution when not properly disposed of or due to accidental leaks. Therefore, environmentally friendly lubricating fluids are welcome in any application where they can meet the performance requirements. This study suggests using coffee oil produced from spent coffee grounds to improve the lubricity of water-based lubricating fluid. Bis(2-hydroxyethyl)ammonium oleate protic ionic liquid facilitates the dispersion of coffee oil in water. Kinematic viscosity, wettability, corrosion prevention, and lubricity tests were performed to evaluate the tribological properties provided by these additives. It was observed that a higher amount of coffee oil could be dispersed with the introduction of a higher amount of protic ionic liquid. In this study, ten wt.% of coffee oil was successfully dispersed using one wt.% of protic ionic liquid. Introducing additives increased dispersions' viscosity, improved wettability, provided protection against corrosion, and reduced wear and friction. It was proposed that polar molecules of protic ionic liquid were responsible for most of the improvement, while coffee oil contributed by increasing viscosity. Further studies could be directed toward determining rational concentration to meet each particular application's requirements.

Keywords: coffee oil; protic ionic liquid; additive; lubricant; friction; wear; environmentally friendly



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1. Introduction

According to EU legislation, environmentally friendly lubricants must be nontoxic, biodegradable, and contain a specific amount of renewable raw materials. Using renewable raw materials saves fossil resources and could reduce production costs if cost-efficient alternatives are available. Regarding lubricants, vegetable oils and animal fats are the most common choices. Recently, nonedible and waste alternatives have been preferred [1,2].

As a base lubricating fluid, water is a low-cost and environmentally friendly alternative. In addition, it has an excellent cooling capacity, which is very important in many applications. However, water has poor lubricity and a high freezing temperature. These issues can be addressed by applying additives [3,4]. In most cases, vegetable oil, glycerol, or polyethylene glycol is added to increase fluids' viscosity and reduce freezing temperature. In addition, emulsifiers, corrosion inhibitors, and antiwear additives are required to fulfil the requirements of particular applications [4–6].

Both glycerol and polyethylene glycol have good solubility in water. Therefore, any dilution ratio could be chosen. In most cases, 50:50 wt.% is selected for investigations [7–10].

These mixtures are further modified using various additives to improve their properties. For example, Zheng et al. [8] used protic ionic liquids as additives in glycerol aqueous solution. The additive-loaded samples showed enhanced lubricity. This was ascribed to its adsorption layer and tribo-film formation. Carrion et al. [11] reported nanodiamonds which, in combination with ammonium palmitate ionic liquid, enhanced the lubricity of water. It was observed that these additives could reduce wear rates by more than two orders of magnitude with respect to additive-free water.

Vegetable oils can also be blended in water. An oil-in-water lubricating mixture is typical for producing water-based lubricating fluids used in metalworking applications. However, vegetable oils are not soluble in water, and a certain amount of emulsifier is required for dispersion [5,12]. Usually, one to twenty wt.% of oil in water is applied. Gajrani et al. [5] formulated green cutting fluid using a six wt.% of raw coconut oil in water. Moreover, emulsifiers, corrosion inhibitors, and other additives were applied. The investigated formulation outperformed commercial alternatives in the lubrication of a tool–workpiece friction pair. However, the authors note that different applications may require individual formulation.

Coffee grounds are coffee brewing waste. About 25 million tons of coffee grounds are generated annually. Coffee grounds contain various organic compounds such as oil, fatty acids, lignocellulose, and polysaccharides. This oil is unsuitable for food. Therefore, it could be an attractive raw material for producing lubricants and fuels [13,14]. Grace et al. [15] investigated coffee oil as a base fluid and used two phosphonium ionic liquids to enhance its tribological properties. It was observed that ionic liquids could improve friction and wear reduction ability.

To our knowledge, coffee oil has never been tested as an additive in water-based lubricating fluids. Therefore, this study investigates the tribological properties of water-based green lubricating fluid formulated using coffee oil and protic ionic liquid. The wettability, corrosion prevention ability, and lubricity employing friction and wear were investigated. The proposed lubricating fluid contains more than 99 wt.% of renewable raw materials. Therefore, it is expected to be readily biodegradable.

2. Materials and Methods

2.1. Materials

The spent coffee grounds were gathered from local coffee stores which use filter coffee machines to produce coffee. The protic ionic liquid bis(2-hydroxyethyl)ammonium oleate was synthesised in our lab according to the methodology described in our previous study [16]. All the solvents and reagents were of chromatographic or analytical grade and obtained from Fisher Chemical, Germany. The deionised water was used as a base fluid in this study.

2.2. Physicochemical Properties of Extracted Coffee Oil and Investigated Lubricating Samples

The extracted coffee oil's acidity and acid value were determined according to the standard test method EN ISO 660 [17]. The oil yield was determined according to EN ISO 659 test methods [18].

The kinematic viscosity and density of investigated lubricating samples were determined using Anton Paar Stabinger viscometer SVM 3000. Four measurements were performed for each sample. Thermo Scientific Orion apparatus was employed to measure pH value. Contact angle/wettability measurements were performed on the polished steel surface using the Kruss DSA 30 apparatus. The steel surface was cleaned with n-heptane before each measurement. The ambient conditions were as follows: temperature of 22 °C, HR humidity of 40%. A 10 µL droplet of the investigated sample was placed on the prepared steel surfaces during the test. The contact angle between the droplet and the surface was measured immediately and after 60 s. Three repetitions were carried out for each sample.

2.3. Analysis of Fatty Acid Composition

The fatty acid composition was analysed according to the requirements of ISO 5508 and ISO 5509 standard test methods [19,20]. This analysis employed a gas chromatograph Perkin Elmer Clarus 500 (GC/FID) operating with a split/splitless injector and ZEBRON ZB-FAME (30 × 0.2 mm × 0.25 µm) capillary column. The pressure of the gas carrier (hydrogen) was kept constant at 90 kPa, split—1:100. The following chromatograph temperature program was used: initial temperature, 100 °C; the temperature of the included sample was maintained for 2 min, and then increased up to 240 °C at a rate of 3 °C/min. After reaching the set temperature value, it was maintained for 5 min. The temperature of the detector was kept constant at 285 °C.

2.4. Extraction and Analysis of Coffee Oil

The coffee oil (CO) was extracted from the collected spent coffee grounds. First, the obtained coffee grounds were dried to constant mass at 40 °C in a Binder dryer. Then, the dry coffee grounds (50 ± 5 g) were placed in a filter paper tube, and the extraction was carried out in a Soxhlet apparatus using hexane solvent. A 24 h extraction duration was chosen to obtain the maximum yield of coffee oil. After the extraction, the solvent was removed using the IKA RV 06-ML 1-B vacuum rotary distiller. The resulting coffee oil was collected in a glass container, sealed, and stored in a refrigerator (+4 °C) for further investigation.

Table 1 summarises the properties of extracted coffee oil, comparing it with the results published by other researchers. The yield of extracted coffee oil was 11 wt.% of the dry coffee grounds. This result was similar to that reported by Lourith et al. [21] (12.70%) and Phimsen et al. [22] (10–13%). The difference in coffee grounds' moisture, particle size, brewing method, and coffee bean type could affect the extraction yield.

Table 1. Acidity and yield of extracted coffee oil and their comparison with the results obtained by other researchers.

Properties	This Study	Uddin et al. [14]	Lourith et al. [21]	Phimsen et al. [22]
Acid value, mg KOH/g	61.94 ± 0.23	15.42	35.62 ± 0.30	12.20
Acidity, %	31.14 ± 0.42			6.14
Oil yield, % (dry wt.)	11 ± 0.25		12.70 ± 0.18	10–13

The acid number is a property of the oil, directly indicating its quality. The acid number corresponds to the amount of free fatty acids in the oil and is defined as the KOH required to neutralise the free fatty acids present in the oil. The acidity of extracted coffee oil was 31.14%, corresponding to 61.94 mg KOH/g acid number. This result is much higher than that observed in coffee oils analysed in other studies, i.e., 5–1.7 times higher [14,21,22]. The higher acid number is probably the result of direct contact between grounded coffee beans and hot water during the coffee production process.

The fatty acid composition depends on the type of coffee beans. Therefore, the properties and performances also will vary from type to type. The fatty acid composition observed in the extracted coffee oil is presented in Table 2. It was found that investigated coffee oil is mainly composed of saturated fatty acids. As a result, the extracted CO possess a high pour point of 25 °C. The CO mainly contains palmitic (C16:0) 37.26% and linoleic (C18:2) 36.59% fatty acids. In addition, oleic (C18:1) 9.26% and stearic (C18:0) 8.79% acids were found. Table 2 also summarises CO composition results published by other researchers.

Table 2. Fatty acid composition of extracted coffee oil and its comparison with the results obtained by other researchers.

Fatty Acid Composition	This Study	Uddin et al. [14]	Lourith et al. [21]	Phimsen et al. [22]
Saturated fatty acids (%):	51.83	37.61	43.03	86.01
Butyric acid (C4:0)	0.04 ± 0.0009			
Caproic acid (C6:0)	0.07 ± 0.01			
Caprylic acid (C8:0)	0.18 ± 0.05			0.09
Capric acid (C10:0)	0.24 ± 0.07			0.01
Undecylic acid (C11:0)	0.04 ± 0.0002			
Lauric acid (C12:0)	0.00			0.02
Tridecanoic acid (C13:0)	0.67 ± 0.15			
Myristic acid (C14:0)	0.07 ± 0.13	3.82		0.18
Pentadecanoic acid (C15:0)	0.03 ± 0.015			
Palmitic acid (C16:0)	37.26 ± 1.78	19.00	35.39	65.07
Margaric acid (C17:0)	0.14 ± 0.045			0.11
Stearic acid (C18:0)	8.79 ± 0.26	6.73	7.64	13.00
Arachidic acid (C20:0)	3.26 ± 0.026	2.96		5.47
Heneicosylic acid (C21:0)	0.1 ± 0.033			
Behenic acid (C22:0)	0.8 ± 0.05			1.35
Tricosylic acid (C23:0)	0.12 ± 0.0013	5.11		0.19
Lignoceric acid (C24:0)	0.02 ± 0.001			0.52
Unsaturated fatty acids, %:	48.17	62.27	45.63	13.99
Monounsaturated fatty acids, %:	10.19	33.56	9.78	8.98
Myristoleic acid (C14:1 cis-9)	0.14 ± 0.05	20.00		
Palmitoleic acid (C16:1 cis-9)	0.04 ± 0.003			
Oleic acid (C18:1)	9.26 ± 0.58	9.27	9.78	8.69
Paullinic acid (C20:1)	0.33 ± 0.006			0.29
Erucic acid (C22:1)	0.07 ± 0.002			
Nervonic acid (C24:1)	0.35 ± 0.025	4.29		
Polyunsaturated fatty acids, %:	37.98	28.71	35.85	5.01
Linoleic acid (C18:2)	36.59 ± 1.95	28.71	35.85	4.72
Linolenic acid (C18:3)	1.15 ± 0.045			0.04
Eicosadienoic acid (C20:2)	0.03 ± 0.0001			
Dihomo-gamma-linolenic acid (C20:3 8,11,14)	0.03 ± 0.0002			0.15
Arachidonic acid (C20:4)	0.02 ± 0.005			0.10
Eicosapentaenoic acid (C20:5)	0.11 ± 0.0047			
Brassic acid (C22:2)	0.02 ± 0.001			
Docosahexaenoic acid (C22:6)	0.02 ± 0.0033			

Values in bold represent groups of fatty acids and their amount in each group.

It was found that the coffee oil composition can vary in broad intervals. The coffee oil extracted in this study has a composition similar to that observed by Lourith et al. [21]. However, Uddin et al. [14] presented results showing a much higher amount of unsaturated fatty acids, while the results obtained by Phimsen et al. [22] show the opposite—a very high amount of saturated fatty acids.

2.5. Preparation of Lubricating Samples

It was observed that bis(2-hydroxyethyl)ammonium oleate protic ionic liquid could facilitate the dispersion of coffee oil in water. The dispersions were carried out in the following way. A 50 mL conical glass flask containing appropriate amounts of deionised water, coffee oil, and PIL was immersed in an ultrasonic bath, heated to the temperature of 45 °C, and sonicated for 15 min. Further sonication did not result in better oil dispersion. While the amount of coffee oil dispersed in water was determined by the amount of PIL, several possible concentrations were investigated. Table 3 presents the composition of investigated lubricating samples and their abbreviations used throughout the manuscript.

Table 3. Composition of investigated lubricating samples and their abbreviations.

Lubricating Sample	Coffee Oil wt. %	Protic Ionic Liquid wt. %	Water
W + CO2.5 + PIL0.25	2.5	0.25	Balance
W + CO2.5 + PIL1	2.5	1	
W + CO5 + PIL0.25	5	0.25	
W + CO5 + PIL1	5	1	
W + CO10 + PIL0.25	10	0.25	
W + CO10 + PIL1	10	1	

The dispersion of coffee oil in water is strongly related to PIL concentration: more PIL could better disperse the oil. Figure 1 presents the appearance of prepared lubricating samples. The dispersions are light yellow, with increased saturation when the amount of additive increased. Clearly, 0.25 wt.% PIL is insufficient to disperse coffee oil, and a top layer of lower-density oil is formed. However, there was an exception when applying five wt.% of coffee oil. There was no distinguishable layer, but some oil-in-water droplets were observed. This phenomenon could be related to dispersions' viscosity and optimal counterpart ratio. The dispersions with one wt.% of PIL were much more homogeneous. Further studies could be directed toward finding the optimal ratio of counterparts to obtain homogeneous dispersions and stability.

**Figure 1.** The visual appearance of investigated lubricating samples observed half an hour after the preparation.

2.6. Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was used to analyse coffee oil and lubricating sample having the highest amount of additive, namely, ten wt.% of coffee oil and one wt.% of protic ionic liquid. JASCO FT/IR-4X spectrometer was used for FTIR analysis. The scan range was set to $4000\text{--}400\text{ cm}^{-1}$, with an accumulation of 50 measurements and a resolution of 4 cm^{-1} .

The obtained FTIR spectra are presented in Figure 2. The highest intensity peaks in the coffee oil spectra were observed at 2919 cm^{-1} and 2850 cm^{-1} . The $2940\text{--}2820\text{ cm}^{-1}$ interval is related to the symmetric and asymmetric CH bond stretching of CH_2 and CH_3 groups. The symmetric and asymmetric stretching of CH_2 is related to the presence of lipids [23]. Due to dilution with water, these peaks are of low intensity in the spectra of the lubricating sample. The peak at 1745 cm^{-1} is attributed to aliphatic ester (triglyceride) groups and is also associated with the carbonyl ($\text{C}=\text{O}$) vibration, which is assigned to various functional groups, including aliphatic and aromatic acids, aldehydes, ketones, and lactones, which impart different aromas of coffee [24]. In the FTIR spectra of the lubricating sample, the most intense peak was observed at a wavelength of 3421 cm^{-1} . This peak is related to the H-O-H stretching of adsorbed water. Moreover, the peak at 1630 cm^{-1} is characteristic of carbonyl ($\text{C}=\text{O}$) stretching vibrations and may be related to the H-O-H bending of water. The range of peaks in both spectra between 1400 and 900 cm^{-1} is commonly referred to as the fingerprint region because it contains many characteristic single peaks assigned to specific functional groups. These groups are C-H, C-O, C-N, and P-O bonds [25].

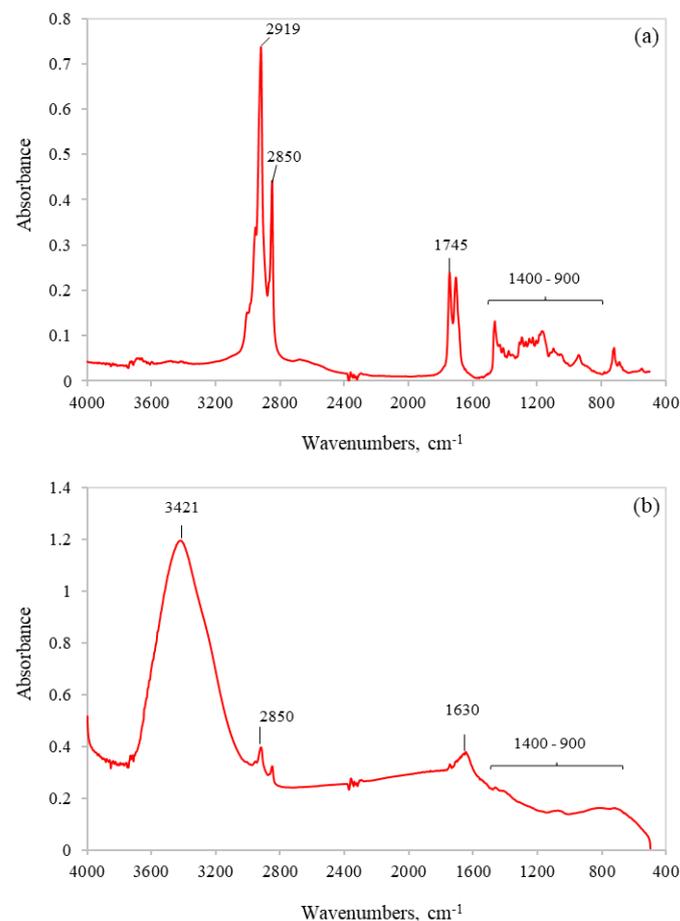


Figure 2. UV-Vis spectra of coffee oil (a) and a lubricating sample with ten wt.% of CO and one wt.% of PIL (b).

2.7. Rust Prevention Study

The cast iron chip corrosion test characterised the investigated samples' rust prevention ability. First, the cast iron chips were evenly distributed on white filter paper. The filter paper was placed in ϕ 100 mm Petri dish. Next, 5 mL of investigated lubricating sample was poured into a Petri dish to submerge filter paper. The covered Petri dish was stored for 24 h at room temperature. After this period, the filter paper and chips were removed and washed with tap water. Finally, images of corrosion spots were captured with a Nikon D90 DSLR camera and compared. The samples possessing better rust prevention showed fewer rust spots on filter paper. At least two repetitions were carried out for each sample.

2.8. Tribological Properties

The lubricity of investigated samples was investigated using a ball-on-plate reciprocating tribometer. During this test, a 6 mm diameter ball (bearing steel E-52100; hardness: 750–800 HV30; surface roughness: 0.05 μm) was rubbed against the plate (bearing steel: E-52100, 190–200 HV30, 0.02 μm). A 15 Hz reciprocation frequency, 1 mm stroke length, 4 N load, 30 °C test temperature, and 30 min test duration were chosen. Before the experiments, all parts with contact with the lubricating sample were washed in an ultrasonic bath in toluene and acetone. The coefficient of friction (CoF) variation with time was continuously recorded. At least two repetitions were carried out for each lubricating sample.

The lubricity was evaluated regarding the wear scar on the ball, wear trace on the plate, and coefficient of friction. The diameter of the wear scar on the ball (WSD) was measured using Nikon ECLIPSE MA 100 optical microscope. The wear trace on the plate was measured using a stylus profilometer Mahr GD-25.

3. Results and Discussions

3.1. Physicochemical Properties of Investigated Lubricating Samples

The viscosity of lubricating fluid plays an essential role in its lubricity. The higher viscosity-possessing lubricants can separate interacting surfaces at lower speeds. Moreover, they can withstand higher loads. However, the lubricant's viscosity must fit the need of the particular application. The kinematic viscosities of investigated samples at two different temperatures are shown in Figure 3. As could be expected, the lubricating fluid's viscosity increased with an increasing amount of coffee oil. However, with increased test temperature, the viscosity sharply decreased, and the impact of coffee oil on viscosity diminished. The reason for such behaviour is that the viscosity of coffee oil, containing saturated fatty acids, varies with temperature [26–28].

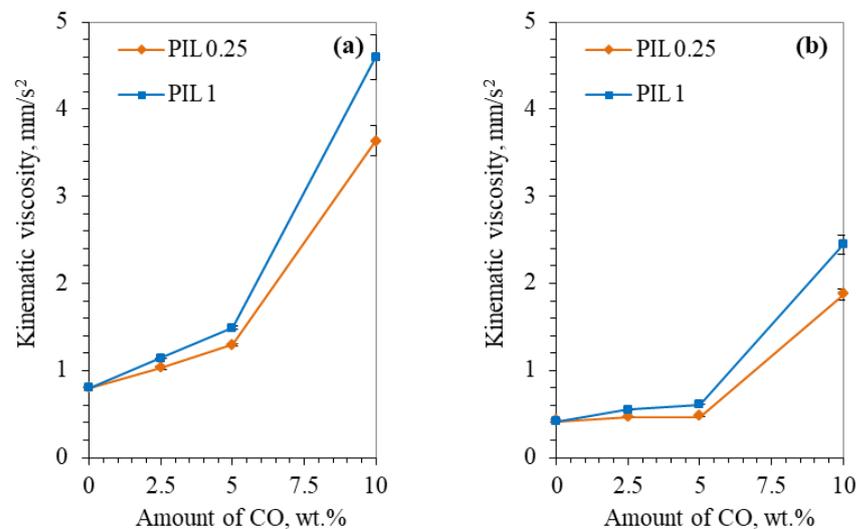


Figure 3. Kinematic viscosity as a function of the amount of coffee oil in investigated lubricating samples at the temperatures of 30 °C (a) and 70 °C (b).

Despite the low concentration, the amount of PIL also influences viscosity. Interestingly, the amount of PIL has a greater effect when the concentration of coffee oil increases. For instance, when the lubricating sample contained 2.5 wt.% CO, the viscosity difference between the two PIL concentrations was only 0.11 mm/s². When the amount of CO increased to 10 wt.%, the above-mentioned difference became 0.97 mm/s². The higher concentration of PIL may disperse more coffee oil, while at a low concentration, droplets of coffee oil remain in the dispersion and do not increase the viscosity.

The density of investigated samples plotted against temperature is shown in Figure 4. An increased amount of coffee oil decreased density, while the amount of PIL had almost no effect. However, the increment in density due to coffee oil was marginal compared to that of temperature. The density was almost linearly dependent on the temperature within the investigated temperature interval.

The acidity of the lubricating fluids could result in metal surface corrosion. Therefore, in most cases, it is kept slightly base. This study investigated samples with pH ranging between 8 and 9 (Table 4). Due to a high acid number, coffee oil increased the acidity of the lubricating sample. At the same time, PIL makes it alkaline.

The wettability of investigated samples, expressed in contact angle, is presented in Figure 5. The better wettability-possessing lubricants can more easily penetrate the interface and spread on the interacting surfaces. Therefore, wettability is vital in mixed and boundary lubrication regimes, which occur during reciprocation.

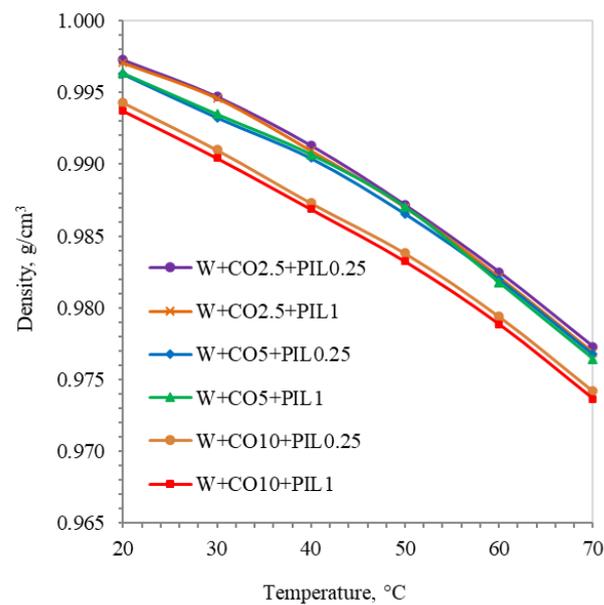


Figure 4. The density of investigated lubricating samples as a function of test temperature.

Table 4. pH values of investigated lubricating samples.

Lubricating Sample	pH
W + CO2.5 + PIL0.25	8.62 ± 0.026
W + CO2.5 + PIL1	8.78 ± 0.046
W + CO5 + PIL0.25	8.26 ± 0.022
W + CO5 + PIL1	8.53 ± 0.034
W + CO10 + PIL0.25	8.02 ± 0.017
W + CO10 + PIL1	8.52 ± 0.011

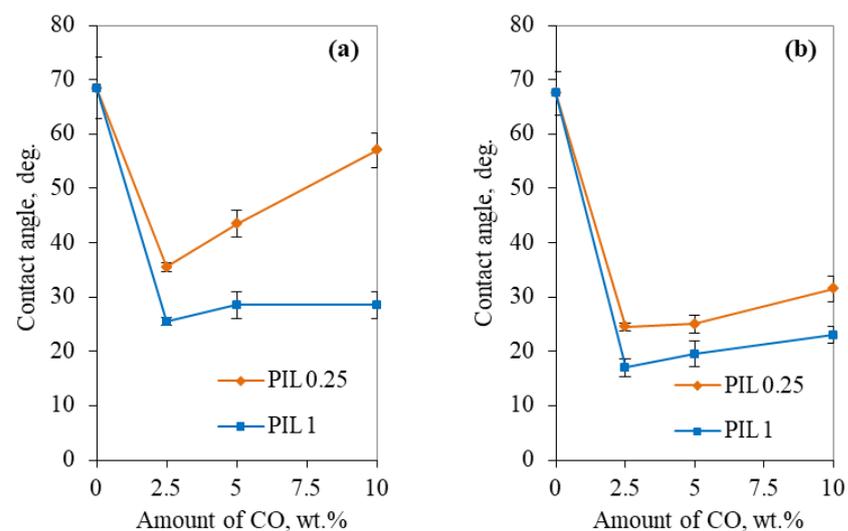


Figure 5. Contact angle as a function of the amount of coffee oil measured immediately (a) and after 60 s (b).

In the present case, additives improved the wettability of the base fluid, and most of the additive-loaded lubricating samples showed a reduced contact angle. The contact angles measured immediately and after 60 s are different. Time is required to spread the lubricant's droplet on the surface. According to the observed results, polar molecules of PIL governed wettability. Therefore, a higher number of PIL-containing samples showed a

lesser contact angle. Interestingly, the coffee oil diminished the positive effect of PIL. This was particularly evident in 0.25 wt.% PIL-containing samples when the immediate contact angle was analysed.

3.2. Corrosion Prevention Characteristics

In the presence of water, steel surfaces tend to corrode instantly. Therefore, eliminating corrosion is an advantage of water-based lubricating fluids. Generally, corrosion inhibitors are applied to improve protection against corrosion [5,12]. In the present study, bis(2-hydroxyethyl)ammonium oleate protic ionic liquid acted as a corrosion inhibitor. Figure 6 shows corroded filter paper observed after the chip corrosion test. The additive-free water caused corrosion of all the cast iron chips. The corrosion pattern changed with the introduction of coffee oil and PIL additives. However, 0.25 wt.% of PIL was not enough to eliminate corrosion. Samples loaded with one wt.% of PIL showed substantially less corrosion. It must be noted that a higher amount of coffee oil diminishes the corrosion protection effect. Using five wt.% of coffee oil resulted in the appearance of a few corrosion spots. The further increase in coffee oil resulted in even more corrosion spots.

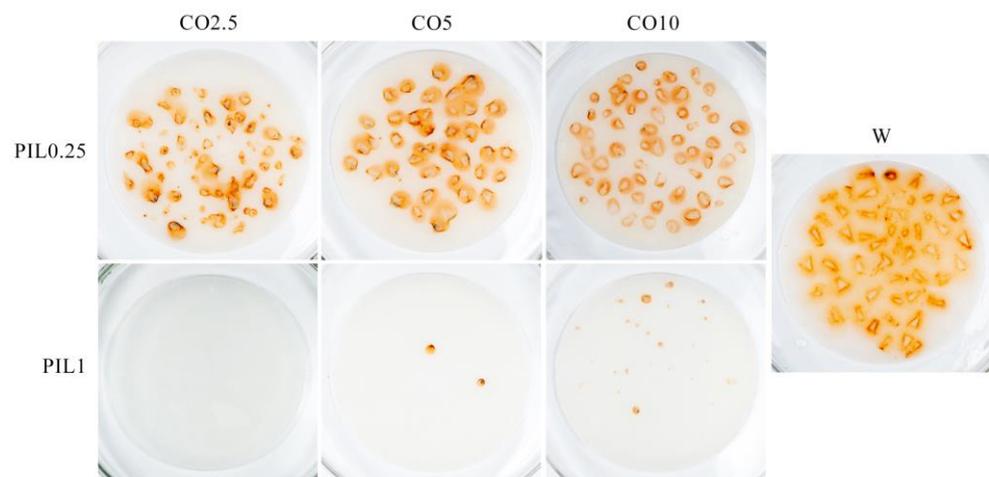


Figure 6. Corroded filter paper observed after cast iron chip corrosion test when several CO and PIL concentrations were investigated.

Polar molecules of PIL adsorb on the chip surfaces, preventing its contact with oxygen. At higher PIL concentrations, more polar molecules are available. Therefore, better corrosion protection is achieved. The increased amount of coffee oil leads to a higher pH value, thus, a more acidic medium. Moreover, the free fatty acids in coffee oil will compete with the PIL molecules on the chip surface, resulting in a less dense adsorbed layer.

3.3. Friction and Wear Reduction Ability

The energy required to keep surfaces in relative motion is directly proportional to frictional losses. The mean coefficients of friction observed in these experiments are presented in Figure 7. It was expected that lubrication with additive-free water would result in an extremely high coefficient of friction, e.g., exceeding 0.35. However, the friction was significantly reduced when introducing coffee oil and protic ionic liquid additives. Interestingly, the amounts of the particular additive had a marginal effect on the mean coefficient of friction. Generally, introducing investigated additives reduced friction by 6.6 times; this reached the value of 0.051 in the case of W + CO10 + PIL1.

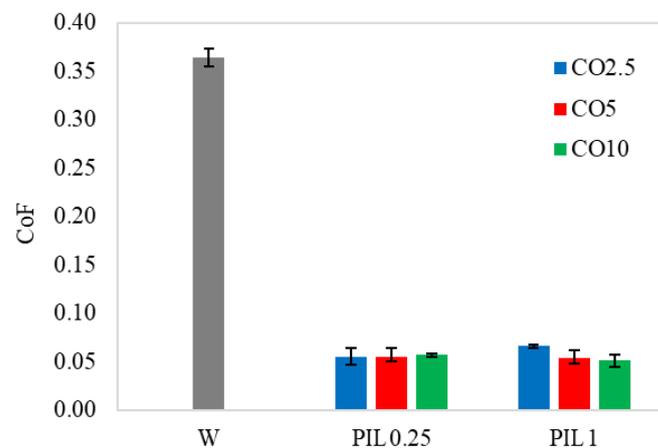


Figure 7. Mean values of the coefficient of friction observed in tribo-test.

The variations of the coefficient of friction during the tribo-tests are presented in Figure 8. With an increased amount of coffee oil, the coefficient of friction became more stable. Moreover, samples with 2.5 and 5% of coffee oil possess running-in periods at the onset of the test. The duration of this period varied from 10 to 20 min. An increased amount of coffee oil, up to 10%, resulted in less varied friction. Moreover, the running-in period was not discerned in these cases. The explanation for this could be the higher viscosity of the lubricating sample. Lubricating samples containing 10% coffee oil have considerably higher kinematic viscosity (Figure 3). The formation of surfaces separating layers is more likely to occur when higher-viscosity lubricants are used. Therefore, friction was lower and more stable when more coffee oil was blended with water.

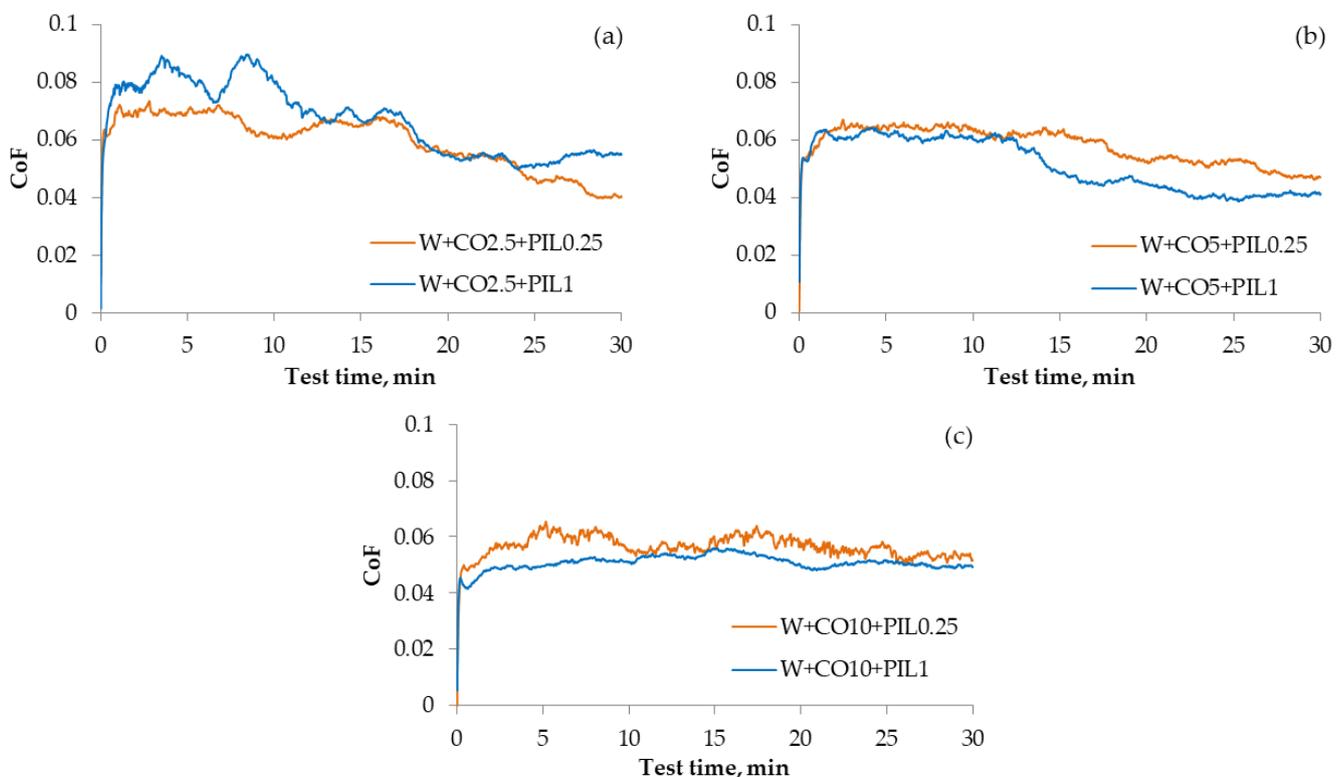


Figure 8. Variation of the coefficient of friction recorded during the tribo-test when lubricating samples having 2.5% (a), 5% (b), and 10% (c) of coffee oil where investigated.

The second additive counterpart, protic ionic liquid, also influences friction. In the cases of a higher amount of coffee oil, a higher amount of protic ionic liquid resulted in

lower and more stable friction. The higher amount of protic ionic liquid increased viscosity, thus increasing lubricity of the lubricating samples. On the other hand, a higher amount of protic ionic liquid resulted in better oil dispersion. The homogenous dispersion provides better lubrication. The higher protic ionic liquid will also result in a better-adsorbed layer. In our previous study, we found that an increased amount of protic ionic liquid could increase friction and wear [29]. The tribo-corrosion was assigned responsibility for this. In the present case, the higher amount of protic ionic liquid combined with 2.5% of the coffee oil resulted in higher, unstable friction. Fortunately, the coefficient of friction stabilised after the running-in period.

The longevity of lubricated mechanisms depends on the lubricants' ability to reduce wear. Similar to friction, wear reduction is achieved by separating interacting surfaces. The surface separation in the boundary lubrication regime could be implemented by forming adsorption or chemisorption layers, metal soaps, and friction polymers [30–32]. At higher sliding speeds, mixed lubrication takes place. In this regime, the viscosity of the lubricant determines surface separation. In the case of reciprocation, boundary lubrication occurs at the ends of the wear trace, while a mixed lubrication regime could be expected in the middle of the wear trace.

The lubrication ability of investigated lubricating samples, expressed as wear, is presented in Figure 9. Figure 9a represents the wear scar diameter on the ball, while Figure 9b represents the wear volume. The WSD is easy to measure value, but it could not evaluate the wear on the plate. Therefore, wear volume is more comprehensive and representative of lubricity. In the present case, both inspected indicators showed a positive effect from investigated additives. However, the positive effect was more evident when comparing wear volume.

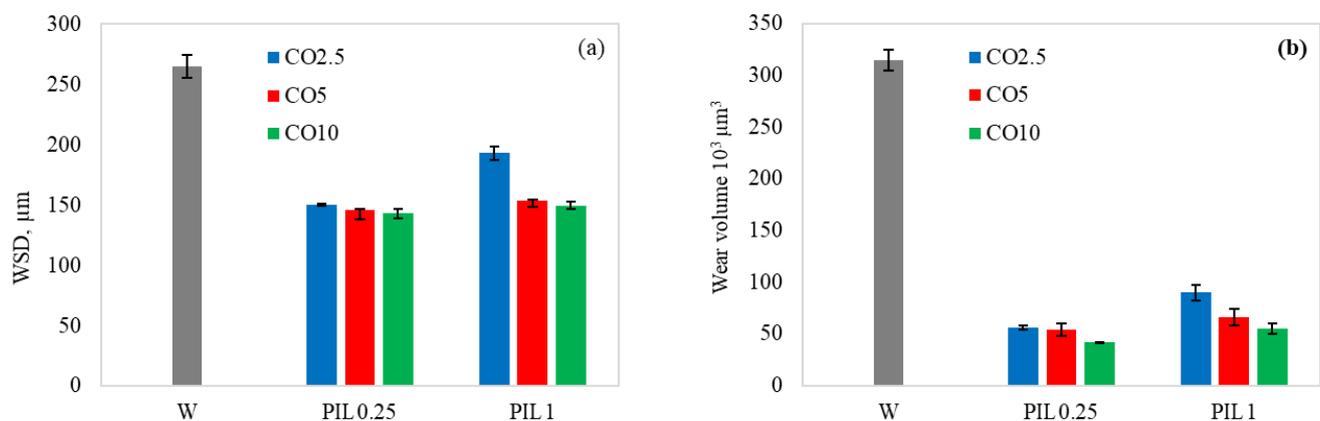


Figure 9. Wear scar diameter (a) and wear volume (b) observed after the tribo-tests.

Better wear improvement was achieved using a lower amount of 0.25 wt.% of PIL. The wear was also reduced when the amount of coffee oil was increased. The lowest wear was observed using a W + CO10 + PIL0.25 lubricating sample. In this case, a wear reduction of 7.5 times was reached. Similar to friction, the W + CO2.5 + PIL1 sample possessed the highest wear among investigated additive-loaded lubricating samples.

The cross-section profiles of wear traces on the plate measured perpendicular to the sliding direction confirm the above-presented friction and wear results (Figure 10). The lubricating sample with the deepest wear trace, and possessing the highest wear and CoF, was W + CO2.5 + PIL1. It also has a considerable amount of pushed-out material on both sides. The lower wear-possessing samples have little to no pushed-out material. The pushed-out material is formed due to surface plastic deformation, likely to occur when high wear is observed.

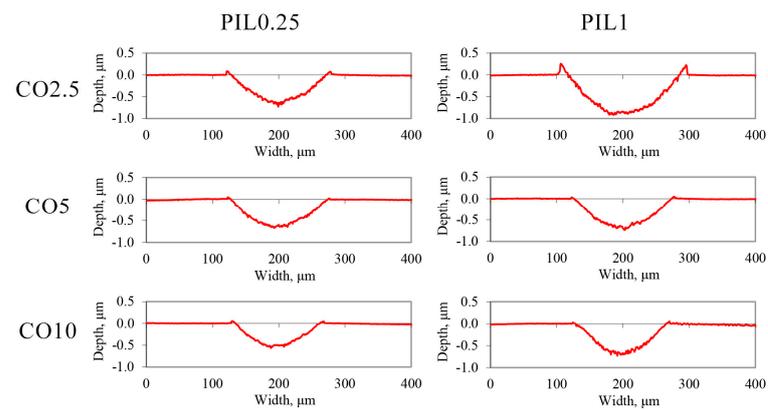


Figure 10. The cross-section profiles of the wear traces on the plate observed after tribo-test.

3.4. Analysis of the Worn Surfaces

The optical microscope images of the wear scars on the ball and segments of wear traces on the plate observed after tribo-tests are presented in Figure 11.

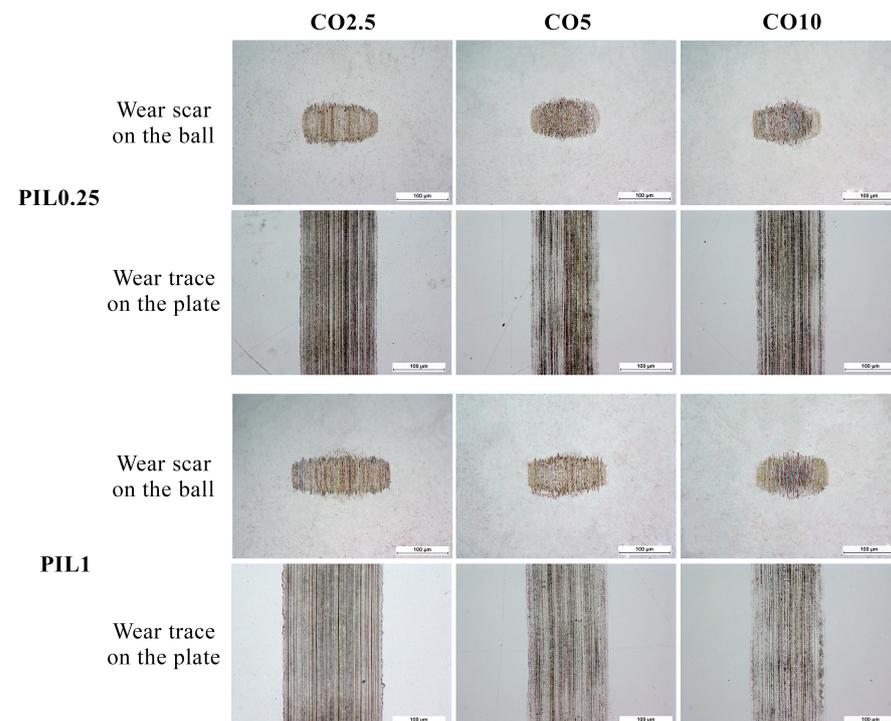


Figure 11. Wear scars on the balls and segments of wear traces on the plates observed after the tribo-test when lubricating with different CO and PIL concentrations.

Although the wear volume and depth of the wear trace differed among additive-loaded samples, the appearance of their worn surface was similar. In all the cases, the wear trace on the plate underwent slight abrasion, which was also evident in the profiles (Figure 10). The pushed-out material is apparent in the case of W + CO2.5 + PIL1. Moreover, this particular wear trace has a slightly different appearance. Namely, more plastic deformation-caused scratches could be observed. Relatively high wear, surface deformation, and low CoF could be indicators of tribo-corrosion [33].

On the other hand, the ball surfaces underwent only marginal wear. As a result, slight polishing occurred on the hard ball surface. The wear scar formed during lubrication with the W + CO2.5 + PIL1 sample was wider, but the appearance was similar.

4. Conclusions

In this study, green lubricating fluid was formulated using coffee oil from spent coffee grounds and protic ionic liquid bis(2-hydroxyethyl)ammonium oleate as additives in the water-based lubricating fluid. In order to evaluate the potential of this lubricant, physicochemical and tribological properties were investigated. As a result, the following conclusions could be reached:

- The extracted coffee oil comprises almost equal amounts of saturated and unsaturated fatty acids. Moreover, it has a high acid number which could result from the coffee preparation process. As an additive, coffee oil increases fluids' viscosity.
- Protic ionic liquid facilitated the dispersion of coffee oil into the water. With the introduction of one wt.% of PIL, ten wt.% of coffee oil was dispersed. Moreover, PIL was found to be responsible for improved wettability and corrosion prevention ability.
- With the introduction of investigated additives, the lubricity of water could be significantly improved. The adsorption layer and viscosity were assigned responsibility for this.

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