RESEARCH ARTICLE

# Lubricity Performance of Ethylene Glycol Ester from Soybean Oil as a Lubricity Enhancer Bio-Additive for Low-Sulfur Diesel Fuel

**Yulfi Zetra[a]\*, Rhiby Ainur Basit Hariyanto[a], R. Arizal Firmansyah[b], R. Y. Perry Burhan[a], Pusparatu[c]**

[a]Department of Chemistry, Faculty of Science and Data Analitics, Institut Teknologi Sepuluh Nopember, Kampus Keputih, Surabaya 60111, Indonesia; [b]Department of Chemistry Education, Faculty of Science and Technology, Universitas Islam Negeri Walisongo, Semarang 50185, Indonesia; [c]Departement of Oil and Processing Engineering, Politiknik Energi dan Mineral Akamigas, Jl. Gajah Mada No.38, Cepu, Blora, 58315, Indonesia

Abstract The present study aims to show the tribological properties of soybean oil's ethylene glycol ester (SOEGE) and its effect on low-sulfur diesel fuel lubrication. The SOEGE or 2-hydroxyethyl ester was synthesized by a transesterification reaction of soybean oil and ethylene glycol with a potassium carbonate catalyst. The product was characterized using Gas Chromatography-Mass Spectrometry (GC-MS). Then, the lubricity of commercial diesel fuel (Pertadex) and SOEGE were tested alone using the High-Frequency Reciprocating Rig (HFRR) machine. Its mixture form with various product doses in Pertadex (0.2, 0.4, 0.6, 0.8, and 1% v/v) was also tested with the same apparatus. This study showed that the product's coefficient of friction and Wear Scar Diameters (WSD) were 0.057 and 154.4 m, respectively. This value is lower than Pertadex and Fatty Acids Methyl Ester (FAME) of Soybean oil from the literature. Furthermore, adding products into Pertadex can reduce the coefficient of friction and WSD of Pertadex. The Pertadex coefficient of friction was reduced from 0.161 to 0.135 after the addition of 0.8% product. At a concentration of 1% product, WSD Pertadex was successfully reduced by 39.42%. These phenomena imply that ester ethylene glycol has an excellent lubricating effect on low-sulfur diesel. This work's findings open opportunities for other researchers to develop alternative lubricating bio-additives for low-sulfur diesel through the in-depth study of tribochemistry or tribosurface.

**Keywords**: Bio-additive, low-sulfur diesel, lubrication, ethylene glycol ester.

## Introduction

Combustion of diesel fuel, which contains much sulfur, produces air pollutant gas such as $SO_2$, which can be harmful to the environment and health [1]. For this reason, governments worldwide provide regulations about a minimum level of sulfur content in diesel fuel [2]. Through the Ministry of Energy and Mineral Resources, Indonesia provides a policy that the sulfur content in diesel fuel may range from 500 ppm to 50 ppm.

A well-known method for reducing sulfur content in diesel fuel is hydrodesulfurization [3]. However, this process can diminish some of the natural lubricating agents in diesel fuel, such as polyaromatic, oxygen and nitrogen compounds [4], [5]. The loss of some of these natural lubricating agents can cause a decrease in the lubricating properties of the diesel fuel, then it continues to the emergence of friction and wear on the components of the diesel engine. Furthermore, it shortens the lifetime of the diesel engine [6], [7]. Therefore, the researchers suggest adding additives to diesel fuel to improve its lubricating properties and protects certain engine parts from friction and wear such as the fuel injection pump and injector [8]–[11].

Several previous studies have a general tendency to use industrial waste, agricultural waste, and biomass as raw materials for the synthesis of more valuable materials. Hence, the sustainable and environmentally friendly aspects are achieved [12]–[14]. One of the valuable alternative lubricity enhancer additives is ester compounds derived from vegetable oil, because it is renewable, biodegradable and it has great lubricity properties [15]. However, the use of vegetable oil as an additive has problems because it has a very high viscosity and low volatility. Therefore, it can cause the incomplete combustion of diesel fuel [16].

Transesterification of vegetable oils with alcohol compounds can transform triglyceride molecules of vegetable oils into simpler fatty acid alkyl esters and is recognized to reduce viscosity, overcome volatility problems of vegetable oils and increase lubricity at the same time [17]. This fatty acid alkyl ester compound has a carboxyl group at the head and a long chain hydrocarbon at the tail, making this compound has good lubricity properties [18]. Fatty acid alkyl esters derived from vegetable oil are well known to have similar characteristics to petrodiesel fuel, making them suitable for use as a lubricant-enhancing additive for petrodiesel fuel [19].

Costa *et al.* [20] revealed that ethylene glycol esters could be used as bio-additives to enhance low-sulfur diesel lubrication. This ester is synthesized through the transesterification of soybean oil and ethylene glycol. However, the lubricating properties of the ethylene glycol ester were not reported. This lubrication property is essential to be investigated further because it is beneficial for developing alternative bio-additives to improve the lubrication of low-sulfur diesel.

Based on the ethylene glycol ester structure, the presence of a hydroxy group on its head is thought to increase the polarity of the ester. It consequently leads to an increase in the adsorption between the head part of the ester and the metal surface. Meanwhile, long-chain unsaturated fatty acids of this compound strengthen the intermolecular interaction of the ethylene glycol ester. It can imply the stability of the film formed. Finally, we hypothesize that the polarity increase of the head part of ester and its constituent fatty acids improves the lubrication of the ethylene glycol ester. To prove this hypothesis, we used soybean oil as the raw material in this study because it contains high unsaturated fatty acids. Then, we transesterified soybean oil using ethylene glycol. Several studies support this hypothesis. Knothe [21] stated that fatty acids methyl ester (FAME) might be modified to obtain better lubrication properties. Sukjit *et al.* [22] reported that increasing the polarity of the head of the ester improved the lubricating properties of bio-additives significantly.

Therefore, this study aims to demonstrate the lubrication properties based on the coefficient of friction and wear scar diameter (WSD) parameters of ethylene glycol esters derived from soybean oil and their effect on the lubrication commercial low-sulfur diesel. The results of this work as a future fundamental idea for the synthesis of bio-based additives to improve the lubrication of low-sulfur diesel can be considered. This paper also suggests a more in-depth tribological study in the future. SOEGE applied research after optimized reaction can be considered for diesel engine pumps and injectors.

## Materials and Methods

The soybean oil used in this study was got from the local market. Another materials used in this study such as: Potassium carbonate: for analysis EMSURE ACS,ISO,Reag. Ph Eur. CAS No. 584-08-7, EC Number 209-529-3. Ethylene glycol: for analysis EMSURE Reag. Ph Eur,Reag. USP. CAS 107-21-1, EC Number 203-473-3. Ethyl acetate: for analysis EMSURE Reag. Ph Eur,Reag. USP. CAS 141-78-6, EC Number 205-500-4. Hydrochloric acid 37 %: for analysis EMSURE Reag. Ph Eur,Reag. USP. CAS 7647-01-0, EC Number 231-595-70. n-hexane: for analysis EMSURE" ACS. CAS 110-54-3, EC Number 203-777-6. Anhydrous sodium sulfate: for analysis EMSURE Reag. Ph Eur,Reag. USP. CAS 7757-82-6 EC 231-820-9. This study's low-sulfur diesel fuel is commercial diesel fuel, namely Pertadex (Pertamina DEX) which is produced by Pertamina Oil Company in Indonesia, with sulfur content below 500 ppm.

### Soybean Oil Characterization

Characterization of the oil used includes analysis of the acid number, determination of fatty acid composition and soybean oil molecular weight. The acid number analysis was carried out by the titration method, while the determination of the fatty acid composition of the oil was carried out by the gas chromatography-mass spectrometry (GCMS) method in which the vegetable oil was converted to fatty acid methyl ester (FAME) form first. The procedures for acid number analysis, FAME preparation and GC-MS preparation are described in the following sections.

## Acid Value Analysis

The procedure for analyzing the acid value (AV) of soybean oil in this study was adapted from the research conducted by Zhang *et al.* [23]. First, 20 grams of soybean oil and 50 mL of isopropanol were poured into a 250 mL Erlenmeyer flask. A volume of 0.8 mL 1% phenolphthalein indicator was added into the mixture and the flask was shaken for 10 seconds. Next, the titration was carried out with 0.1M of KOH solution drop by drop through the burette while rattling the flask. Titration was stopped after reaching the titration endpoint, indicated with a stable pink color persisting for at least 30s. The titration was carried out three times to ensure precision. In the same way, a blank titration was performed. The AV was calculated according to Eq.1

$$AV = \frac{(A-B) \times C \times 56,1}{M} \text{ (mg KOH) g}^{-1} \tag{1}$$

A = Volume of KOH required for sample titration (mL)
B = Volume of KOH required for blank titration (mL)
C = Molarity of KOH solution (M)
M = Mass of oil used (g)

## Preparation of FAME Soybean Oil

The fatty acid composition of soybean oil is expressed as the fatty acid methyl ester composition. The conversion of triglycerides from soybean oil into fatty acid methyl ester was carried out by transesterifying soybean oil and methanol with a molar ratio (1:6) and 1% potassium hydroxide (m/m to oil) catalyst. The reaction was carried out at atmospheric pressure at 60 °C and constant magnetic stirring at 500 rpm for 120 minutes [20].

The compound composition of soybean oil methyl ester was determined by GC-MS analysis. The interpretation of the analysis results is based on the Wiley 9 database and the mass fragmentation study [24]. Determination of the fatty acid composition serves in determining the molecular weight of soybean oil, which will be used as raw material for the preparation of ethylene glycol ester. The average molecular weight of soybean oil was calculated according to Eq. 2 based on the corresponding FAME composition [25].

$$MW_s = \sum MW_t \times C_{FAME} \tag{2}$$

Where $MW_s$ is the molecular weight of soybean oil, $MW_t$ is the molecular weight of triglycerides from fatty acid methyl esters and $C_{FAME}$ is the molecular composition of FAME's soybean oil (%).

## Determination of FAME's Composition

The chromatographic analysis was applied to define the composition of the FAMEs of soybean oil. The GC analysis was implemented using Shimadzu Gas Chromatograph-QP 2010 SE. A mass spectrometer detector was used and its interface temperature was 250 °C, injection temperature was 250 °C. The column used was an Rtx-5 MS with specification (30 m/ 0.25 mm/0.25 μm) and the column temperature was set at 100 °C (4 min) and then was increased to 240 °C at a rate of 3 °C/min and held for 15 min. The final temperature was set at 250 °C (rate: 10 °C/min) and a final isothermal period of 4.33 min.

## Preparation of SOEGE or 2-hydroxyethyl ester

Soybean oil's ethylene glycol ester (SOEGE) in this study was made using a simple reflux method by adopting the method of Costa *et al.* [20] with some modification. The molar ratio of soybean oil and ethylene glycol was 1:10. The two raw materials were refluxed for 5 hours at 150 °C with a stirring rate was 500 rpm. The catalyst used was potassium carbonate with a catalyst percentage of 7% (% mole of oil). After 5 hours, the reaction was stopped by adding hydrochloric acid until the pH was neutral. Extracting the organic phase from the aqueous phase is carried out by adding ethyl acetate in a separating funnel. After that, the obtained organic phase was washed with distilled water (3x30 mL) and decanted. The organic phase is dried by adding anhydrous sodium sulfate. After filtering, the remaining ethyl acetate was evaporated using a rotary evaporator at a temperature of 60 °C.

## Determination of SOEGE Composition

The compositional analysis of the 2-hydroxyethyl ester was gained using a QP 2020 NX Gas Chromatography coupled with a Mass Spectrum detector. The specification of the column used was the capillary column Rtx-5 MS with a film thickness of 0.25 mm, column length 30.0 m and an inner diameter of 0.25 μm. The product was diluted with n-hexane solvent and 1 μL of the diluted sample was injected with a split injection mode and a split ratio of 10 and an injection temperature of 290 °C.

The carrier gas used was helium. The interface temperature was set at 300 °C. The analysis was carried out with a scanning mode starting from m/z 28 to 1000. The oven temperature was initially set at 70 °C and increased to 200 °C with a temperature rise rate of 10 °C/min. After being held for 5 minutes, the oven temperature was increased to 305 °C at a rate of 4 °C/min, then held for 20 minutes.

## Lubricity Study: Determination of Wear Scar Diameter, Friction Coefficient and Film Thickness

Pertadex diesel fuel, SOEGE were tested for their lubricity and the mixture of the two with various concentrations of additives, specifically 0.2%; 0.4%; 0.6%; 0.8%; and 1%. A high-frequency reciprocating rig (HFRR) instrument (PCS Instrument D-1731) was used to evaluate the fuel lubricity of each test sample according to ASTM D-6079 standard method. This HFRR method generates data outputs in the form of WSD values (µm), coefficient of friction and film thickness (%). The test was carried out in duplicate under the same conditions and operators. Both results were always ensured to be less than the repeatability method (50 µm) with uncertainties was ± 5µm. The measurement process can be observed through computer software.

The HFRR method in this experiment was as follows. Two mL of sample (Pertadex/SOEGE/blending) was placed in the HFRR test reservoir throughout the test. The fuel temperature was stabilized at 60 °C. After that, the vibrator arm that holds the test ball from rotating is loaded with a mass of 200 g and lowered until it touches the test disk that has been submerged in the fuel. Test ball specification (Grade 28 per ISO 3290) of SAE-AMS 6440 steel, with a diameter of 6.00 mm, having a Rockwell hardness "C" scale (HRC) number of 58–66. Test disk specification, 10 mm disk of SAE-AMS 6440 steel machined from the annealed rod, having a Vickers hardness "HV 30", by specification E92, a scale number of 10-210, turned, lapped, and polished to a surface finish of less than 0,02 µm $R_a$. The steel ball oscillates at a fixed frequency of 50 Hz. After 75 minutes, the test ball was removed from the vibrator's arm and cleaned. The spots (wear scars) that form on the surface of the ball are measured using an optical microscope, with digital camera (PCS Instrument) capable of 100x magnification, installed and calibrated according to manufacturer instructions, capable of capturing a crisp image of the wear scar. Camera system resolution should be a minimum of 2048 x 1536 pixels. The measurement system should allow horizontal and vertical measurement devices or cursors to be positioned at the wear scar boundaries with an accuracy of 1 micron.

The WSD on the steel ball was calculated from the average WSD on the X-axis and Y-axis. The smaller of WSD value suggests the better the lubrication ability of the sample. The allowed limit of WSD of diesel fuel is 460 µm refer to the ASTM D-975.

In addition to WSD, the lubricity of Pertadex, SOEGE and blending of the two, are also correlated with the coefficient of friction. Once a metal surface moves on top of another, there is opposite to the movement and the force that opposes that motion is called friction. If the friction is relative to the load, then the coefficient of friction (µ) can be calculated by dividing the friction force with the applied load as shown in Eq. 3 [17]. A compound with a high friction coefficient value indicates that the compound has inadequate lubrication ability.

$$\mu = F/P \tag{3}$$
F = friction force (Newtons)
P = The applied load (Newtons).

Film thickness (%) can be obtained based on the electrical resistance during the test (75 min) between the steel ball and the steel disc. The film 0% indicates that there is no diesel or specimen between the steel ball and the plate when contact occurs. A film thickness of up to 100% means that the steel ball and the plate are separated by thin film of the specimen.

## Results and Discussion

SOEGE compounds were synthesized through ethylene glycolysis to produce ester compounds containing a hydroxy group at the head moiety. The presence of a hydroxy group is expected to increase the polarity of the ester and have an impact on increasing the lubrication of diesel fuel.

### Oil Characterization

Oil characterization was employed based on acid value and fatty acids composition parameters. The acid value of vegetable oil indicates the amount of free fatty acids in the vegetable oil [26].

Determination of the acid number of soybean oil is essential because transesterifying vegetable oil with a high acid value (over 2 mg KOH/gram vegetable oil) using an alkaline catalyst produces a large amount of soap. It complicates the purification process [27]. In this study, due to the low acid value of soybean oil (0.87 mg KOH/ gram vegetable oil), soybean oil was transesterified directly without pretreatment.

In this study, the soybean oil's fatty acids composition was characterized by GC-MS, Wiley 9 database and analysis of fragmentation pattern. In addition, the results were compared with the fatty acid composition of soybean oil reported by other researchers. It is presented in Table 1.

**Table 1.** Comparison of fatty acid methyl esters composition derived from soybean oil

| FAME composition | Relative Abundance (%) | | | |
|---|---|---|---|---|
| | Costa *et al.* [20] | Panchal *et al.* [28] | Li *et al.* [29] | This research |
| C14:0 | - | - | - | 0.09 |
| C16:0 | 11.6 | 9.0 | 11.08 | 11.26 |
| C18:0 | 4.1 | 4.75 | 3.90 | 4.83 |
| C18:1 | 22.1 | 25.5 | 24.21 | 25.73 |
| C18:2 | 58.5 | 47.4 | 53.14 | 50.39 |
| C18:3 | 2.5 | 4.9 | 5.35 | 6.85 |
| C20:0 | - | - | - | 0.41 |
| C20:1 | - | - | 0.50 | - |
| C22:0 | - | - | 0.94 | 0.34 |
| ∑ Saturated | 14.94 | 13.75 | 15.92 | 16.93 |
| ∑ Unsaturated | 85.05 | 77.8 | 83.2 | 82.97 |
| Others | 0.01 | 8.45 | 0.88 | 0.01 |

Based on Table 1, it is known that the soybean oil sample contains high unsaturated fatty acids (oleic acid, linoleic acid, and linolenic acid = 82.97%). In comparison, saturated fatty acids are 16.93%. It consists of myristic acid, palmitic acid, stearic acid, eicosanoic acid and docosanoic acid. This work's predominance of unsaturated fatty acids over saturated fatty acids like other studies. The high oleic and linoleic acids in soybean oil have the potential to produce good product lubrication properties. Then, the obtained fatty acids composition was used to calculate the molecular weight of soybean oil as shown in Table 2 and stoichiometric calculations to prepare ethylene glycol ester.

**Table 2.** Molecular weight profile of soybean oil

| Triglyceride derived from FAME | $C_{FAME}$ (%) | $MW_t$ | $MW_t * C_{FAME}$ |
|---|---|---|---|
| C14:0 | 0.09 | 723.13 | 0.65 |
| C16:0 | 11.26 | 807.29 | 90.90 |
| C17:0 | 0.10 | 849.37 | 0.85 |
| C18:0 | 4.83 | 891.45 | 43.06 |

| Triglyceride derived from FAME | $C_{FAME}$ (%) | $MW_t$ | $MW_t * C_{FAME}$ |
|---|---|---|---|
| C18:1 | 25.73 | 885.45 | 227.83 |
| C18:2 | 50.39 | 879.45 | 443.16 |
| C18:3 | 6.85 | 873.45 | 59.83 |
| C20:0 | 0.41 | 975.61 | 4.00 |
| C22:0 | 0.34 | 1059.78 | 3.60 |
| **Molecular mass of soybean oil** | | | 873.88 |

### Synthesis and Characterization of SOEGE

Synthesis of ethylene glycol ester was carried out using the reflux method. The transesterification progress of soybean oil with ethylene glycol was monitored using Thin Layer Chromatography (TLC). It is shown in Figure 1.
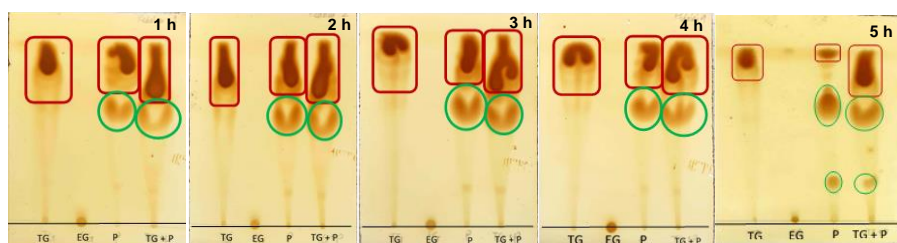


**Figure 1.** Monitoring result of transesterification progress between soybean oil and ethylene glycol using TLC. TG = Triglyceride, EG = Ethylene Glycol, P = Product. Red square = Triglyceride spot, green cycle = Product Spot

Figure 1 demonstrates that longer time of reaction, the product spots tend thicker than triglyceride spots. The reaction was stopped after achieving 5 hours because the products have been formed enough. If the reaction run more than 5 hours, it allowed unsaturated fatty acids contained in soybean oil can be oxidized [30].

The obtained chromatogram of the product is shown in Figure 2. The esters were identified based on Wiley 9 mass spectrum database and fixed by fragmentation study refer to Maulidiyah *et al.* [24]. Molecular ion $[M]^+$ and base peak ion are characteristic of each compound, as presented in Table 3. Based on the data in Table 3, it is known that the result of test is in 95.54% of mono and diester ethylene glycol ester.
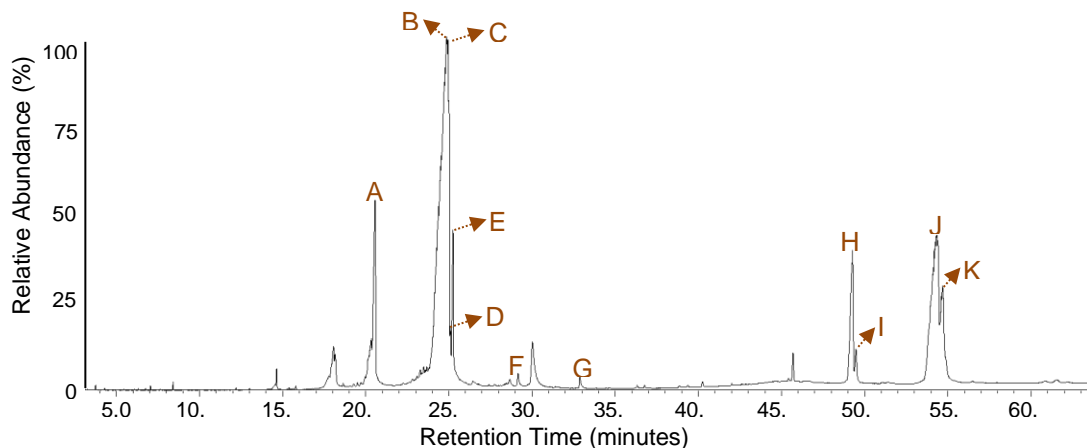


**Figure 2.** Chromatogram of Ethylene Glycol Ester

**Table 3.** The results of GCMS analysis of SOEGE

| Peak | Ethylene Glycol Ester Composition | % Area | Ion [M]$^+$ (m/z) | Base peak ion (m/z) |
|------|-----------------------------------|--------|------------------|---------------------|
| A | Ethylene glycol monopalmitate | 20.14 | 300 | 104 |
| B | Ethylene glycol monolinoleate | 21.30 | 324 | 67 |
| C | Ethylene glycol monooleate | 15.33 | 326 | 55 |
| D | Ethylene glycol monolinolenate | 2.02 | 322 | 55 |
| E | Ethylene glycol monostearate | 17.06 | 328 | 104 |
| F | Ethylene glycol monoeicosanoate | 1.39 | 356 | 98 |
| G | Ethylene glycol monodocosanoate | 0.76 | 384 | 98 |
| H | Ethylene glycol diester (C16:0 and C18:2) | 5.61 | 562 | 283 |
| I | Ethylene glycol diester (C16:0 and C18:3) | 2.53 | 560 | 283 |
| J | Ethylene glycol diester (C18:1 and C18:3) | 2.38 | 586 | 309 |
| K | Ethylene glycol diester (C18:3 and C18:2) | 7.02 | 584 | 311 |

The esters identified in this work are formed by the following presumed reaction mechanism. The $K_2CO_3$ catalyst takes the hydroxyl group's protons of alcohol to produce alkoxide nucleophiles. This alkoxide attacks the C atom of the carbonyl on triglyceride produce ethylene glycol monoester (the primary product). Then, the reaction continues to form glycerol (by-product), as shown in Figure 3.
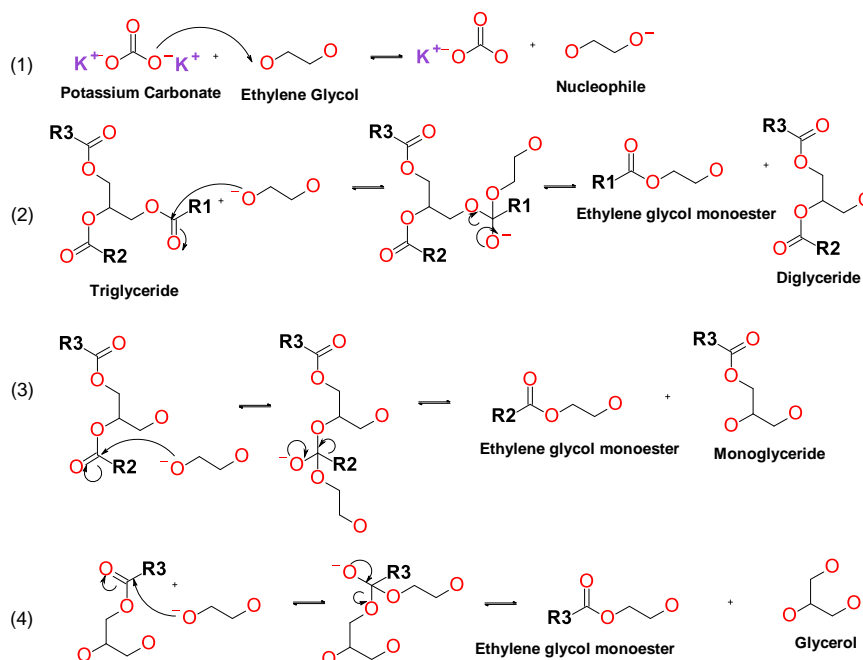


**Figure 3.** Proposed reaction mechanism for formation process of ethylene glycol monoester

The formation process of the ethylene glycol diester is like the formation of the ethylene glycol monoester. The excess of the $K_2CO_3$ catalyst takes a proton from the ethylene glycol monoester to form an alkoxide anion from the ethylene glycol monoester. Furthermore, these alkoxides attack the carbon of carbonyl on the monoglyceride molecule, producing ethylene glycol diester, as shown in Figure 4.
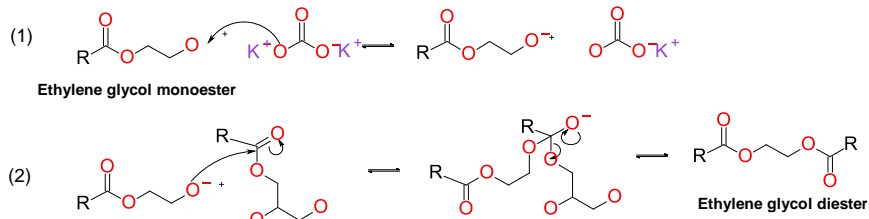
**Figure 4.** Proposed reaction mechanism for the formation of ethylene glycol diester

Ethylene glycol monoester in this work was more dominant than ethylene glycol diester. Hence, it is thought to be the main causes of the lubricating properties of SOEGE and its mixture with diesel fuel. Based on their structure, ethylene glycol monoester has a polar group at the head and a non-polar group at the tail. This structure allows the compound to minimize contact between the two metal surfaces.

## Wear Scar Diameter Analysis

The results of the HFRR analysis showed that the WSD of Pertadex and SOEGE were 279 μm and 154.4 μm, respectively (Figure 5). The lubricity of Pertadex is quite good. However, the SOEGE has a much better lubricating than Pertadex diesel fuel, so it is expected that when both are mixed, SOEGE can reduce the wear scar diameter of Pertadex.
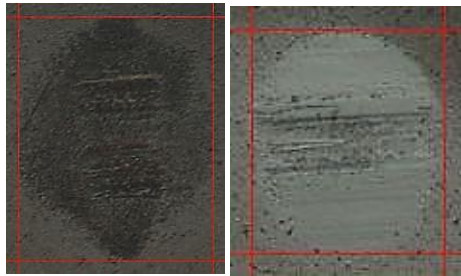


**Figure 5.** Wear scar images of Pertadex (a) and SOEGE (b)

The lubrication of the mixture form between Pertadex and SOEGE was also measured in this work. The effect of the addition of SOEGE on the WSD value of Pertadex is displayed in Figure 6. The test results show that SOEGE successfully reduces the WSD value of Pertadex below a dose of 1%. The best reduction is achieved by adding SOEGE at a concentration of 1%, from 279 μm to 169 μm. Adding more than 1% will reduce the value of WSD and friction coefficient (better lubrication but it is not too significant). It is due to increasing the concentration of additives, increasing the thickness of the protective film, and allowing the stability of the protective film to increase as well. It will have an impact on improving the lubrication properties of diesel fuel [17]. However, a concentration of more than 1% is not an economical choice [32].
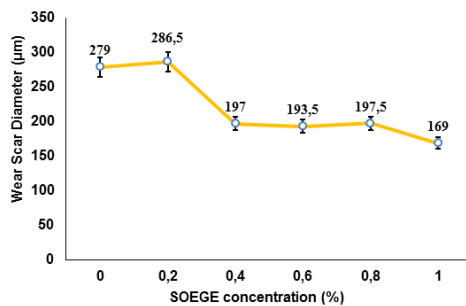


**Figure 6.** Effect of the addition of SOEGE with various concentrations on the lubricity of Pertadex

The excellence of SOEGE lubricity can also be seen from its comparison with published bio-additives. Lubricity of SOEGE shows better than published bio-additives, as shown in Figure 7. However, Glycerol monooleate (GMO) has a smaller WSD value than SOEGE's. It is due to the two polar groups (hydroxyl) in the "head" moiety of GMO, which strengthen the chemisorption with the metal surface [33]. It is due to the two polar groups (hydroxyl) in the "head" moiety of GMO, which strengthen the chemisorption with the metal surface. In contrast, SOEGE has one polar group (hydroxyl) in the "head" moiety of ethylene glycol monoester (as the main component).Therefore, GMO's lubricity is better than SOEGE's.
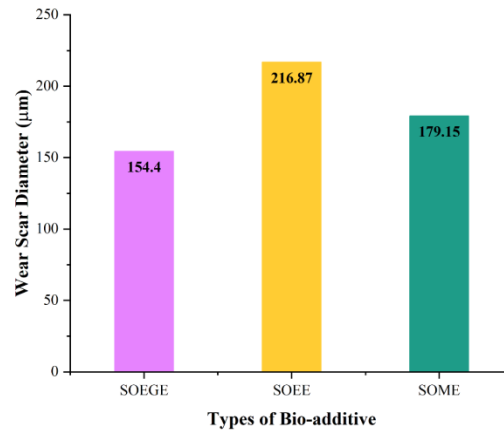


**Figure 7.** Wear scar diameter comparison from several ester bio-additive. SOEGE (this research), SOEE = Soybean Oil Ethyl Ester [34], SOME = Soybean Oil Methyl Ester [29]

## Coefficient of Friction Analysis

The coefficient of friction value supports the excellent lubricating properties of ethylene glycol esters from soybean oil, as shown in Figure 8. SOEGE has a smaller friction coefficient than Pertadex diesel fuel, indicating that this additive has better lubricity than Pertadex. The friction coefficient data from a blend of Pertadex and SOEGE with various concentrations also support the excellent lubricating properties of the SOEGE, as shown in Figure 8.
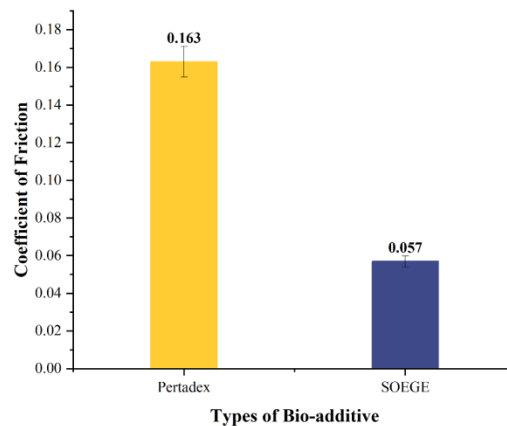


**Figure 8.** Friction coefficient of pertadex and SOEGE

As shown in Figure 9, increasing the SOEGE concentration generally decreases the friction coefficient of Pertadex. The best decrease in the Pertadex coefficient of friction occurred with the addition of 0.8% ethylene glycol ester, from 0.163 to 0.14.
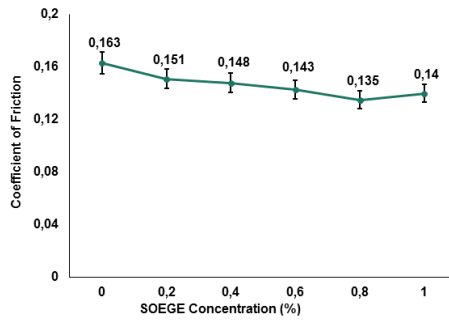
**Figure 9.** Effect of SOEGE concentration vs friction coefficient

A good lubrication-enhancing agent can be seen from the stability of the protective film in reducing friction in a certain period. The protective film is the compound molecules that are arranged parallel to each other so that the polar parts of molecules bond with the metal atoms on the metal surface that are in contact with each other and the non-polar moieties move away from the metal surface [35]. As shown in Figure 10 (a-b), we observe more friction in pure Pertadex during the test. It is visible in the first 10 minutes of the test (blue line). This higher friction caused more significant damage to the protective film of pure Pertadex compared with the protective film of Pertadex have added 0.8% SOEGE (green line). This condition means that the addition of SOEGE improves the lubrication of Pertadex. Although the temperature in this work was relatively constant (60 °C), the phenomenon of film thickness due to the addition of 0.8% SOEGE can be predicted to be relatively stable when the metal materials in contact have different heat capacities or thermal conductivity [36].
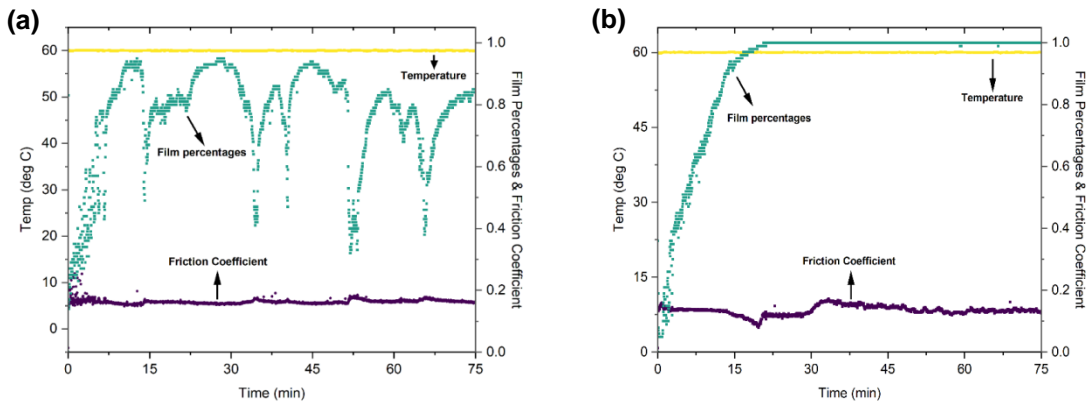


**Figure 10.** Graph of friction coefficient and film percentage of: (a) Pertadex diesel fuel; (b) Mixture of Pertadex and 0.8% of SOEGE

The comparison of SOEGE's coefficient of friction and published bio-additives also supports that SOEGE has excellent lubricating properties except for ethyl esters of castor oil as presented in Table 4. This reason is that the different vegetable oil used. Prasad *et al.* [17] used castor oil as a reactant, which is dominant in the content of ricinoleic acid (C18:1 OH). The hydroxy group in the "tail" moiety is believed to have a significant impact on its lubricity.

Based on the experimental data above and compared to other bio-additives, we suspect that the ethylene glycol monoester is the main contributor to the lubrication properties. Furthermore, the hydroxyl groups on the ethylene glycol monoester increase its polarity and chemisorption with the metal surface. This is supported by the findings of Sukjit *et al.* [22] and Zulfattah *et al.* [37] The role of polar groups in reducing wear by SOEGE is suspected to be similar to that of aromatic polyamide-imide (PAI) and pyrophosphate [38], [39]. They have polar groups that allow form chemisorption with the metal surface.

In the insulation film, the SOEGE monoesters play a vital role in its lubricity. The film is formed by adsorption of the polar group in the "head" moiety onto the metal surface through chemisorption or physical adsorption. Meanwhile, the long-chain tails of these compounds are aligned directionally to

form a film by the van der Waals interaction and dipole interaction between molecules. The stability of film depends on the carbon chain length and the number of double bonds in the tail. Increasing the carbon chain's length and the number of double bonds can increase the van der Waals and electrostatic interactions. It causes cohesiveness between additive molecules to be higher. This phenomenon supports the stability of the protective film. Hence, it provides better lubricating properties [40]. However, it needs to be proven in the future through in-depth research on tribosurface or based on a tribochemical point of view to clearly understand the lubrication mechanism of SOEGE and the major and minor components of SOEGE play a role in improving the lubricity of low-sulfur diesel.

Based on the data in Figure 6, it can be said that increasing the concentration of SOEGE causes a decrease in the value of WSD (good lubrication). It indicates that increasing the concentration of SOEGE can increase the thickness of the protective film, as the trend was reported by Prasad *et al.* [17] study. This situation can reduce friction and wear between metal surfaces contact.

## Conclusions

The coefficient of friction and WSD of the SOEGE or 2-hydroxyethyl ester were 0.057 and 154.4 μm. These parameters' value is lower than the standard ASTM D-975, reference diesel and FAME of soybean oil (literature review). The 1% ethylene glycol ester concentration gave the best lubricating effect on reference diesel (WSD = 169.0 μm). It may be due to ethylene glycol esters, especially ethylene glycol oleate. A hydroxy group on the oleate head of ethylene glycol is responsible for the lubrication properties. This study shows that ethylene glycol esters from soybean oil can be proposed as a lubrication bio-additive for low-sulfur diesel. However, this research needs to be improved to obtain more products by adequately adjusting the reaction conditions and substitution of ethylene glycol with other safer solvent. Furthermore, further studies can apply to non-edible oils such as castor oil and other non-edible oils, which have excellent prospects of being developed for industrial scale. The paper also suggests more in-depth tribology or tribochemistry studies in the future. It acquires comprehensive knowledge, such as SOEGE's lubrication mechanism and the major and minor components of SOEGE's contribution to improving the lubrication of low-sulfur diesel. SOEGE applied research after optimized reaction can be considered for diesel engine pumps and injectors.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

## Acknowledgment

## References

[1]   S. Agarwal, V. K. Chhibber, and A. K. Bhatnagar. (2013). Tribological behavior of diesel fuels and the effect of anti-wear additives. *Fuel, 106*, 21-29. Doi: 10.1016/J.FUEL.2012.10.060.

[2]   Z. Hu, L. Zhang, and Y. Li. (2017). Investigation of tall oil fatty acid as antiwear agent to improve the lubricity of ultra-low sulfur diesels.*Tribol. Int.*, 114(January), 57-64. Doi: 10.1016/j.triboint.2017.04.016.

[3]   M. A. Hazrat, M. G. Rasul, and M. M. K. Khan. (2015). Lubricity Improvement of the ultra-low sulfur diesel fuel with the biodiesel. *Energy Procedia*, *75*, 111-117. Doi: 10.1016/j.egypro.2015.07.619.

[4]   V. S. Mello, E. R. Do Vale Souza, M. V. De Araújo Oliveira, and S. M. Alves. 2014. Effect of desulfurization of diesel and its blends with biodiesel on metallic contact. *Mater. Res.*, *17*, 82-88. Doi: 10.1590/1516-1439.222313.

[5]   S. M. Reddy, N. Sharma, N. Gupta, and A. K. Agarwal. (2018). Effect of non-edible oil and its biodiesel on wear of fuel injection equipment components of a genset engine, *Fuel*, *222*(May), 841-851. Doi: 10.1016/j.fuel.2018.02.132.

[6]   M. A. Mujtaba *et al.* (2021). Effect of palm-sesame biodiesel fuels with alcoholic and nanoparticle additives on tribological characteristics of lubricating oil by four ball tribo-tester. *Alexandria Eng. J.*, *60*(5), 4537-4546. Doi: 10.1016/j.aej.2021.03.017.

[7]   D. X. Peng. (2017). Biodiesel improves lubricity of low-sulfur petro-diesels. *Chem. Technol. Fuels Oils*,

*52*(6), 699-703. Doi: 10.1007/s10553-017-0762-1.

[8]   G. Anastopoulos, E. Lois, A. Serdari, F. Zanikos, S. Stournas, and S. Kalligeros. (2001). Lubrication properties of low-sulfur diesel fuels in the presence of specific types of fatty acid derivatives, *15*(12), 106-112. Doi: 10.1021/ef990232n.

[9]   R. H. Barbour, D. J. Rickeard, and N. G. Elliott. (2000). Understanding diesel lubricity. *SAE Tech. Pap.*, *724*, 1-13. Doi: 10.4271/2000-01-1918.

[10]  B. Hornby, G. Cuckston, R. Caprotti, and I. More. (2013). Pushing the boundaries of the HFRR: Impact of increased test severity on wear, *SAE Tech. Pap.*, 11. Doi: 10.4271/2013-01-2688.

[11]  Bhatia, S.C. (2014). *Advanced Renewable Energy Systems, (Part 1 and 2)*. WPI Publishing. https://doi.org/10.1201/b18242.

[12]  N. Soltani, A. Bahrami, M. I. Pech-Canul, and L. A. González. (2015). Review on the physicochemical treatments of rice husk for production of advanced materials. *Chem. Eng. J.*, *264*, 899-935. Doi: 10.1016/j.cej.2014.11.056.

[13]  A. Bahrami, N. Soltani, M. I. Pech-Canul, and C. A. Gutiérrez. (2016). Development of metal-matrix composites from industrial/agricultural waste materials and their derivatives. *Crit. Rev. Environ. Sci. Technol.*, *46*(2), 143-207. Doi: 10.1080/10643389.2015.1077067.

[14]  A. Bahrami, G. Schierning, and K. Nielsch. (2020). Waste Recycling in thermoelectric materials. *Adv. Energy Mater.*, *10*(19). Doi: 10.1002/aenm.201904159.

[15]  M. Gul, H. H. Masjuki, M. A. Kalam, N. W. M. Zulkifli, and M. A. Mujtaba. (2020). A review: role of fatty acids composition in characterizing potential feedstock for sustainable green lubricants by advance transesterification process and its global as well as pakistani prospective. *Bioenergy Res.*, 13(1). Doi: 10.1007/s12155-019-10040-7.

[16]  G. Karmakar, P. Ghosh, and B. K. Sharma. (2017). Chemically modifying vegetable oils to prepare green lubricants. *Lubricants*, 5(4), 1-17. Doi: 10.3390/lubricants5040044.

[17]  L. Prasad, L. M. Das, and S. N. Naik. (2012). 'Effect of castor oil, methyl and ethyl esters as lubricity enhancer for low lubricity diesel fuel (LLDF). *Energy and Fuels*, *26*(8), 5307-5315. Doi: 10.1021/ef300845v.

[18]  J. Joshy, Naveen, and D. Mahipal. (2021). The effect of free fatty acids on the tribological properties of karanja oil. *IOP Conf. Ser. Mater. Sci. Eng.*, *1114*(1), 012053. Doi: 10.1088/1757-899x/1114/1/012053.

[19]  D.-X. Peng. (2016). Room temperature tribological performance of biodiesel (soybean oil). *Ind. Lubr. Tribol.*, *68*(6), 617-623.

[20]  K. P. Costa *et al.* (2018). Synthesis and evaluation of biocide and cetane number improver additives for biodiesel from chemical changes in triacylglycerides. *J. Braz. Chem. Soc.*, *29*(12), 2605-2615. Doi: 10.21577/0103-5053.20180140.

[21]  G. Knothe. (2009). Improving biodiesel fuel properties by modifying fatty ester composition. *Energy Environ. Sci.*, *2*(7), 759-766. Doi: 10.1039/b903941d.

[22]  E. Sukjit, P. Poapongsakorn, K. D. Dearn, M. Lapuerta, and J. Sánchez-Valdepeñas. (2017). Investigation of the lubrication properties and tribological mechanisms of oxygenated compounds. *Wear*, 376-377, 83-842. Doi: 10.1016/j.wear.2017.02.007.

[23]  J. Zhang, M. Lu, F. Ren, G. Knothe, and Q. Tu. (2019). A greener alternative titration method for measuring acid values of fats, oils, and grease. *JAOCS, J. Am. Oil Chem. Soc.*, *96*(10), 1083-1091. Doi: 10.1002/aocs.12281.

[24]  Maulidiyah, M. Nurdin, F. Fatma, M. Natsir, and D. Wibowo. (2017). Characterization of methyl ester compound of biodiesel from industrial liquid waste of crude palm oil processing. *Anal. Chem. Res.*, *12*, 1-9. Doi: 10.1016/j.ancr.2017.01.002.

[25]  A. Sánchez, R. Maceiras, A. Cancela, and M. Rodríguez. (2012). Influence of n-hexane on in Situ transesterification of marine macroalgae. *Energies*, *5*(2), 243-257. Doi: 10.3390/en5020243.

[26]  A. J. Dijkstra. (2015). *Vegetable Oils: Composition and Analysis*, (1st ed.). Elsevier Ltd. Doi: 10.1016/B978-0-12-384947-2.00708-X.

[27]  M. C. Hsiao, P. H. Liao, N. V. Lan, and S. S. Hou. (2021). Enhancement of biodiesel production from high-acid-value waste cooking oil via a microwave reactor using a homogeneous alkaline catalyst, *Energies*, *14*(2), 1-11. Doi: 10.3390/en14020437.

[28]  B. Panchal, Q. Shenjun, T. Chang, S. Yuzhuang, W. Jinxi, and B. Kai. (2019). Production of methyl esters from fried soybean oil using dimethyl carbonate with hydrobromic acid. *Energy Reports*, *5*, 1463-1469. Doi: 10.1016/j.egyr.2019.10.007.

[29]  F. Li, Z. Liu, Z. Ni, and H. Wang. (2019). Effect of biodiesel components on its lubrication performance. *J. Mater. Res. Technol.*, *8*(5), 3681-3687. Doi: 10.1016/j.jmrt.2019.06.011.

[30]  M. S. N. Awang *et al.* (2021). Effect of addition of palm oil biodiesel in waste plastic oil on diesel engine performance, emission, and lubricity, *6*(33), 21655-21675. Doi: 10.1021/acsomega.1c03073.

[31]  L. Aisyah, C. S. Wibowo, S. A. Bethari, D. Ufidian, and R. Anggarani. (2018). Monoglyceride contents in biodiesel from various plants oil and the effect to low temperature properties. *IOP Conf. Ser. Mater. Sci. Eng.*, *316*(1). Doi: 10.1088/1757-899X/316/1/012023.

[32]  G. Knothe and K. R. Steidley. (2005), Lubricity of components of biodiesel and petrodiesel. The origin of biodiesel lubricity. *Energy and Fuels*, *19*(3), 1192-1200. Doi: 10.1021/ef049684c.

[33]  B. M. Fry, M. Y. Chui, G. Moody, and J. S. S. Wong. (2020). Interactions between organic friction modifier additives.*Tribol. Int.*, *151*(May),106438. Doi: 10.1016/j.triboint.2020.106438.

[34]  M. Lapuerta, J. Sánchez-Valdepeñas, D. Bolonio, and E. Sukjit. (2016). Effect of fatty acid composition of methyl and ethyl esters on the lubricity at different humidities. *Fuel*, *184*, 202-210. Doi: 10.1016/j.fuel.2016.07.019.

[35]  P. Y. Hsieh and T. J. Bruno. (2015). A perspective on the origin of lubricity in petroleum distillate motor fuels', *Fuel Process. Technol.*, *129*, 52-60. Doi: 10.1016/j.fuproc.2014.08.012.

[36]  M. Kaneta, K. Matsuda, and H. Nishikawa. (2022). Effects of Thermal Properties of Contact Materials and Slide-Roll Ratio in Elastohydrodynamic Lubrication. *J. Tribol.*, 144(6), 1-10. Doi: 10.1115/1.4053095.

[37]    Z. M. Zulfattah *et al.* (2021). Friction and wear performance of oleate-based esters with two-, three-, and four-branched molecular structure in pure form and mixture. *J. Tribol.*, *143*(1), 1-10. Doi: 10.1115/1.4047584.

[38]    B. Sun *et al.* (2022). Synthesis and evaluation of alkyl methacrylate-norbornene anhydride copolymers with various pendants as pour point depressants for soybean biodiesel-diesel blends. *Fuel*, *317*, 123542. Doi: 10.1016/j.fuel.2022.123542.

[39]    Y. Chen, X. Wang, Z. Han, A. Sinyukov, A. Clearfield, and H. Liang. (2022). Amphiphilic zirconium phosphate nanoparticles as tribo-catalytic additives of multi- performance lubricants, *J. Tribol.*, 144(7), 1-9. Doi: 10.1115/1.4053352.

[40]    D. Mei, S. Dai, T. Chen, H. Wang, and Y. Yuan. (2020). Absorption of fuel containing esters on iron surface based on molecular simulation and its effects on lubricity. *Energy Sources, Part A Recover. Util. Environ. Eff.*, 1-12. Doi: 10.1080/15567036.2020.1783395.