

Research Paper

Synthesis of Waste Cooking Oil Based Bioadditive Through Transesterification and Its Feasibility as Lubricity Enhancer Bioadditives For Low-Sulfur Diesel Fuel: Preliminary Investigation

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Abstract

Desulfurization of diesel fuel, which is considered to reduce pollution, causes a decrease in its lubrication power. As a result, the friction between surfaces of the engine increases, and it wears out easily. Therefore, it is necessary to increase diesel fuel lubricity through the addition of additives. Waste cooking oil modified to 2-hydroxypropyl esters has a prospect to be a lubricity-enhancing bioadditive. Polar and non-polar groups contain in 2-hydroxypropyl ester can form a bilayer on the surface of the engine that prevents friction between metal components. Synthesis of 2-hydroxypropyl esters was carried out by transesterification at 150 °C for 10 hours with a stirring speed of 500 rpm in vacuum distillation system. The mole ratio of oil to propylene glycol was adjusted to 1:7 with the loading of CaO 7% w/w oil as catalyst. The yield of the product is 88.89%. The product was identified by Gas Chromatography-Mass Spectrometry (GC-MS). The result showed that 2-hydroxypropyl palmitate and 2-hydroxypropyl oleate have dominant relative abundance with percentages of 42.46% and 57.44%, respectively. According to the molecular review as preliminary investigation, this compound has the potential to deliver better lubricity than ester-only biolubricants. Therefore, 2-hydroxypropyl ester can be proposed as an alternative bioadditive for low-sulfur diesel fuel lubricity enhancer.

Keywords: 2-hydroxypropyl esters; Bioadditive; Lubricity; Transesterification

1. Introduction

Fossil diesel fuels contain non-polar and polar groups with 75% aliphatic hydrocarbons such as alkanes and cycloalkanes, and the rest are aromatic hydrocarbons such as alkyl-benzene, styrene, thiophene, and heterocyclic compounds [1], [2]. The sulfur content of fuels is found to be carbonyl sulfide, hydrogen sulfide, dibenzothiophene, thiolane, and mercaptan derivatives such as 1-propanethiol [3]. The presence of these compounds causes large amounts of sulfur oxide (SO_x) pollutant gases and solid particles as well, which causes health problems and is harmful to the environment [4]. Therefore, it is necessary to minimize toxic gas

emissions from diesel fuel by desulfurization to obtain diesel fuel with low sulfur content. However, desulfurization causes a decrease in lubricity on the engine system because it not only removes sulfur compounds but also heteroatomic groups (oxygen and nitrogen) that play an important role in the lubrication system of the fuel [5], [6], [7]. As a result, it causes several tribological problems such as wear intensification, energy dissipation by friction, injection nozzle erosion, and corrosion. This will decrease engine life and unstable engine speed. Hence, it is necessary to increase the lubricity of diesel fuel through the addition of additives as anti-wear agents [8], [9]. Anti-wear additives are utilized to reduce friction by forming a layer on the surface



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of the fluid pad so that the two surfaces of the material in contact with each other can move more smoothly. Currently, the additives that are widely used are petroleum-based. However, petroleum-based lubricants have a bad impact on the environment because of their toxic properties and not easily degradable [10]. Therefore, it is necessary to find other alternatives that are more environmentally friendly to replace petroleum-based additives.

Recently, the investigation of vegetable oils as an alternative for petroleum-based additives in the manufacture of bioadditives has begun to attract the attention of researchers. Gul *et al.* has reported the effect of trimethylolpropane-based-cottonseed oil biolubricant blends on tribological behavior of cylinder liner-piston ring combinations [11]. Ahmad *et al.* produced biolubricant from castor oil using iron oxide nanoparticles as an additive [12]. Salimon and Salih also developed palm kernel oil as a renewable bioadditive through epoxidation reaction with trimethylolpropane polyol ester as green renewable biolubricants [13]. Vegetable oil has a prospect to be a lubricity enhancing bioadditive because it contains two main compounds, free fatty acids which belong to the carboxylic acid group and triglycerides which are ester groups [14]. Both compounds can be used as sources of polar groups, which are needed to improve the lubricity [10]. However, modification of chemical structure is required to obtain the appropriate polar group that can improve the diesel fuel lubrication system. In addition, vegetable oils are considered more environmentally friendly, easily degradable, and renewable, which has a prospect to develop as bioadditives [15], [16]. The transformation of vegetable oils into bioadditives is generally carried out through transesterification and epoxidation reactions by reactants containing polar groups, such as polyalcohols, with the addition of catalysts [13], [17]. Besides being affected by the type of vegetable oil that is used as feedstock, adding different polar groups will also obtain different performance and tribological properties. Tribological properties show interaction between surfaces of objects that move relative to each other. The field of tribology includes friction, wear, and film thickness formed in lubrication systems [5].

In this study, waste cooking oil from palm oil was used as raw material because it contains several types of free fatty acids such as myristic acid, palmitoleic acid, palmitic acid, oleic acid, and stearic acid. These free fatty acids provide polar and non-polar groups that can generate protective film on the engine surface, which can prevent friction between metal components in diesel fuel engines. The hydroxy ester group (head) is polar, and the fatty acid chain (tail) attached to the head is non-polar. These molecules interact based on the principle of "like dissolves like". The polar head (hydroxy ester) will interact by chemisorption with the polar metal surface. Meanwhile, the non-polar fatty acid chain will interact with the other non-polar fatty acid chain through van der Waals forces. The interacting molecules will form a barrier layer on the metal surface, preventing direct friction between the metal surfaces, thereby minimizing friction [18], [19]. Moreover, instead of using edible oil as feedstock for bioadditives synthesis, the utilization of waste cooking oil will avoid competition with the food industry sector. In Indonesia, the average consumption of palm cooking oil in 2022 reached 16.6 million tons [20]. The high consumption of cooking oil leads to a considerable accumulation of waste cooking oil. Unfortunately, waste cooking oil has not been utilized optimally and ends up being thrown away. In fact, waste cooking oil is harmful for environments because it causing pollution to water and soil. Besides, the utilization of waste cooking oil is also expected to increase its economic value.

Several studies on the synthesis of bioadditives using waste cooking oil as feedstock have been reported. Bashiri *et al.* has modified the chemical structure of waste cooking oil from sunflower for the production of bioadditives through epoxidation reactions. In this study, synthesis was carried out through epoxidation and hydroxylation to produce modified triester biolubricant [15]. In contrast to Hussein *et al.* who investigated the experimental and process simulation of biolubricant production from waste cooking oil through transesterification. This study uses the transesterification method with ethylene glycol and excess moles of FAME reactants to obtain dioleoyl ethylene glycol ester [21]. Negi *et al.* also investigated the potential valorization of used cooking oil into novel biolubricating grease

through chemical modification and its performance evaluation. In this study, FAME was transesterified with excess 2-ethylhexanol to obtain biolubricant ethylhexyl esters (EHEs). The WSD value of EHEs was 0.762 mm with minimal oxidative corrosion compared to MAK150 mineral oil [22].

According to the reported publications, previous research focused more on the synthesis of ester-only biolubricants. Meanwhile, the current study aims to produce hydroxy ester-based bioadditives from waste cooking oil containing excess propylene glycol through transesterification. This study will look further into the effect of the presence of hydroxy groups in bioadditives. This assessment is intended to serve as a preliminary investigation into whether 2-hydroxypropyl ester has the feasibility to provide better lubricity properties than ester-only biolubricants by considering the molecular aspect and chemical interaction.

2. Experimental Method

2.1. Materials

Waste cooking oil collected from local food traders in the Keputih area, Surabaya was used as raw materials in this study. Other components were used are KOH p.a (Merck), 1,2-propanediol (propylene glycol) p.a (Merck), CaO p.a (Merck), methanol p.a (Merck), dichloromethane ACS Reagent (Merck), 2-propanol p.a (Sigma Aldrich), *n*-hexane p.a (Merck) phenolphthalein indicator 1%, anhydrous Na₂SO₄ (Merck), coarse filter paper, Whatman filter paper No. 42 (GE Healthcare), parafilm (Bemis™), aluminum foil (Klin Pak), Thin Layer Chromatography (TLC) plate silica gel F254 20×20 cm aluminum (Merck) celite 545 (Merck), Seasand (Merck).

2.2. Waste Cooking Oil Pre-treatment

Waste cooking oil was filtered with filter paper to remove solid impurities. The filtered waste cooking oil was added with distilled water and left overnight to bind the water contained in the waste cooking oil and then extracted using a separate funnel. The waste cooking oil that has been separated from water is dried by adding anhydrous sodium sulfate and then filtered with Whatman 42 filter paper.

2.3. Measurement of Free Fatty Acid Levels

Waste cooking oil that has gone through the pretreatment process was measured for free fatty acid content (%FFA) by the acid-base titration method according to Suzihaque *et al.* [23]. The acid number calculation is determined by equation (1), if the acid number is <4 mg KOH/g oil or %FFA <2% then transesterification can be done. However, if the acid number is >4 mg KOH/g oil, esterification needs to be done first Eq. (1).

2.4. Preparation of Waste cooking oil Methyl Ester (WCOME)

Synthesis of 2-hydroxypropyl esters bioadditive consists of two stages: transesterification of waste cooking oil into WCOME (1) and transesterification of WCOME into 2-hydroxypropyl esters bioadditive (2), as shown in Figure 1. Synthesis of WCOME was carried out based on the method of Hussein *et al.* [21]. Molar ratio of waste cooking oil to methanol was adjusted to 1:6 M with the of KOH 1% w/w oil as catalyst. The reaction was run in reflux system at 65 °C for 165 minutes with stirring speed of 500 rpm. Once the reaction is complete, the mixture is poured into a separate funnel and left

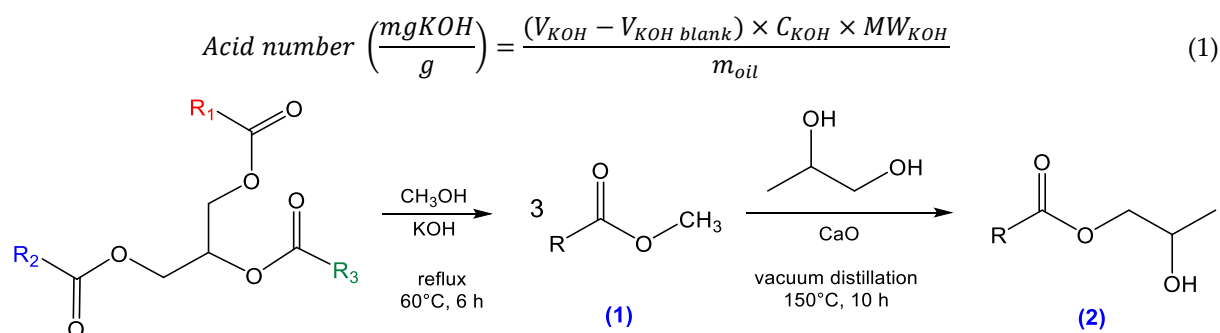


Figure 1. Proposed synthesis pathway of 2-hydroxypropyl esters

overnight to separate the glycerol by-products. The lower layer containing glycerol was separated, and the upper layer consisting of methyl ester (WCOME) was washed with distilled water until the pH is 7. It aims to bind the remaining glycerol and catalyst. WCOME was dried with anhydrous sodium sulfate and then filtered. After the post-treatment process, the mass of WCOME and glycerol was measured using an analytical balance. The mass of WCOME obtained was 355.2224 g and the mass of glycerol was 45.0024 g. The acid number of the WCOME obtained was measured.

2.5. Synthesis of Bioadditive 2-Hydroxypropyl Esters

Synthesis of 2-hydroxypropyl esters was carried out based on a method referring to the research of Joshi *et al.* [24] and Zetra *et al.* [25] with slight modifications in stoichiometry. Mole ratio of oil to propylene glycol was adjusted to 1:7 with the loading of CaO 7% w/w oil as catalyst. Propylene glycol moles are made in excess to avoid the formation of diester products. The synthesis process is run at 150 °C for 10 h, stirring rate of 500 rpm in a vacuum distillation system with a vacuum pressure of 2 mbar. After the reaction is complete, the catalyst was removed with a column containing celite 545 and seasand as a filtering agent to separate fine CaO solids. The product was separated from the remaining reactants by adding 30 ml of ethyl acetate. The remaining ethyl acetate was evaporated using a vacuum rotary evaporator at 60 °C.

2.6. Compound Identification and Analysis

Spectral analysis was performed to determine the functional groups of WCOME and 2-hydroxypropyl esters using Fourier Transform Infrared spectroscopy Shimadzu FTIR. The fatty acid composition of methyl ester from waste cooking oil was identified with Gas Chromatography-Mass Spectrometry (GC-MS) Agilent GCMSD 5975C using an HP-5MS capillary column with a film size of 60 m x 250 µm x 0.33 µm. The injection used a split method with a ratio of 54 and helium (He) as the carrier gas. The oven operating conditions were started at 70 °C and held for 5 minutes. The temperature was increased to 300 °C at a rate of 5 °C/minute and held for 19 minutes. The GC-MS result data was further analyzed using MSDA software from

Agilent. Furthermore, the composition of the 2-hydroxypropyl esters bioadditive was analyzed with a Shimadzu GC-MS QP 2010 instrument, column type RTX5-MS. The operating conditions were started at 70 °C and held for 5 minutes. The temperature was raised to 200 °C at a rate of 10 °C/minute and held for 5 minutes. The temperature was further increased to 305 °C at a rate of 4 °C/minute and held for 15 minutes. The result data was further analyzed using Shimadzu postrun analysis software.

3. Results and Discussion

3.1. Acid Value Analysis

The measurement of acid number intend to determine the level of free fatty acids in the oil as well as determining the next stage of the reaction that needs to be carried out [26], [27]. The higher acid number showed the higher free fatty acid content in the raw material, which results in soap as by-products (saponification) and reduces the yield of the main product if the transesterification reaction is directly carried out [28]. This can be prevented by converting free fatty acids (carboxylic acid groups) into esters through the Fischer esterification reaction by reacting raw materials and alcohol with an acid catalyst, so that the acid value decreases [29]. However, if the fatty acid content (%FFA) in the oil is less than 2%, esterification is not necessary, so transesterification can be carried out directly. In this study, the free fatty acid levels of feedstocks were measured and the results were obtained, which can be seen in Figure 2.

According to Figure 2, there is a significant decrease of acid number in waste cooking oil before treatment (11.85 mg KOH/g) and after treatment (3.5 mg KOH/g). The high acid number of waste cooking oil before treatment is due to the high water content that triggers the hydrolysis reaction. As a result, the oil has a high percentage of free fatty acids [30]. Meanwhile, the decrease of WCOME acid number is caused by carboxylic groups in fatty acids undergoing saponification reactions by base catalysts when transesterification reaction takes place. However, the formation of soap does not significantly affect the yield of WCOME products because the free fatty acid (%FFA) content in waste cooking oil before transesterification is already quite low (1.75%) [23].

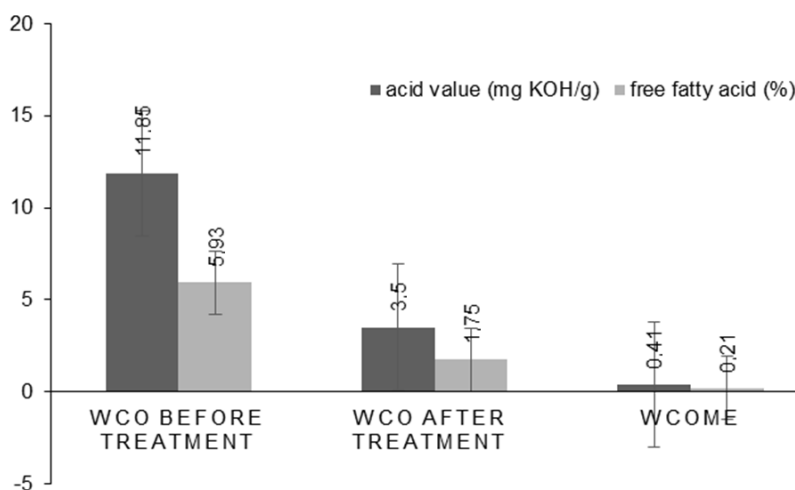


Figure 2. Result of acid value analysis. WCO: waste cooking oil

3.2. Confirmation of Product Formation by Spectral Analysis

The WCOME product and bioadditive 2-hydroxypropyl esters were confirmed through spectra analysis with FTIR, as shown in **Figure 3**. The results of the FTIR spectra analysis showed that the 2-hydroxypropyl esters contained an O-H stretching group indicated by the wave number 3347 cm^{-1} . Other groups present in WCOME and 2-hydroxypropyl esters, such as =C-H stretching at 3005 cm^{-1} , -C-H stretching at 2926 and 2855 cm^{-1} , C=O at 1738 cm^{-1} , and C-O at 1179 cm^{-1} . Based on the analysis, it is known that the methyl ester group in WCOME was successfully modified into 2-hydroxypropyl esters, which is indicated by the presence of O-H stretching shown by wave number 3347 cm^{-1} in the spectra of 2-hydroxypropyl esters, which is absent in the spectra of WCOME.

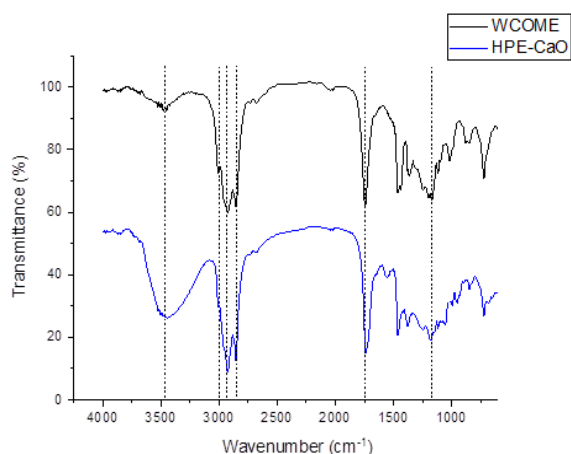


Figure 3. FTIR spectral analysis of WCOME and 2-hydroxypropyl esters (HPE-CaO)

3.3. Analysis of WCOME Fatty Acid Composition

Transesterification of waste cooking oil into WCOME obtain yield of 85.39%. It were analyzed by TLC and GC-MS. The results of TLC analysis in **Figure 4** show that waste cooking oil as a starting material contains triglycerides and free fatty acids. After transesterification, methyl esters products (WCOME) were formed and free fatty acids still present with low concentrations, this was indicated by a decrease in the intensity of stains in WCOME products. According to its R_f , WCOME has the largest R_f compared to triglycerides and free fatty acids. Some literature states that triglycerides have a lower polarity. This is due to the composition of three fatty acid chains with long hydrocarbons dominates the molecule's overall polarity and limited polar functional groups, resulting in molecules that are largely nonpolar [31], [32]. Interestingly, the TLC test result

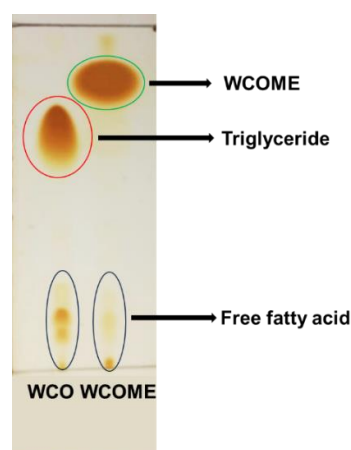


Figure 4. TLC analysis of waste cooking oil and WCOME

of WCO after post-treatment (less water content) when compared to WCOME showed spots with a lower Rf. This indicates that based on the TLC test results and its Rf value, WCO containing triglycerides is more polar than WCOME, which has a higher Rf. This phenomenon is likely caused by the type of oil used. WCO and fresh vegetable oil have different properties. WCO contains a fairly high water content. Even after treatment, the water content in WCO may still be present, although in very small amounts, which will increase its polarity. Meanwhile, fresh vegetable oil has not been contaminated by water. As a result, its nonpolar properties are still maintained. This can be proven by comparing the TLC test of fatty acid methyl ester (FAME) and fresh vegetable oil. Free fatty acids have the highest level of polarity because they contain carboxylic groups consisting of carbonyl and hydroxy, which make it difficult for stains to migrate because they are retained by a stationary phase that is polar [33].

The composition of fatty acids used as raw materials in the synthesis of bioadditives can be known through the identification results of GC-MS of waste cooking oil in the form of methyl ester presented in Figure 5. The chromatogram peaks are identified based on the mass spectral pattern, with a base peak of m/z 74 indicating a methyl ester fragment based on McLafferty's rearrangement rules [34].

According to the identification results in Figure 5, it is known that methyl palmitate and methyl

oleate have the most dominant relative abundance with percentages of 34.73% and 57.12%, respectively, with total saturated and unsaturated fatty acid of 42.27% and 57.73%, respectively. Some of the other fatty acid components contained in WCOME have a fairly low relative abundance, as shown in Table 1. The determination of the composition of WCOME fatty acids intends to estimate the molecular weight of waste cooking oil that is used in stoichiometry calculations of bioadditive 2-hydroxypropyl esters synthesis.

3.4. Product Analysis of 2-Hydroxypropyl Esters Bioadditive

Synthesis of bioadditive 2-hydroxypropyl esters has the same principle as the synthesis of WCOME but is carried out in a vacuum distillation system that aims to separate the methanol as by-products. The methyl ester group in WCOME is converted into another ester form with base catalyst so that the main product is produced in the form of 2-hydroxypropyl esters with a yield of 88.89%.

This reaction uses a base catalyst to deprotonate methanol to create a stronger nucleophile (methoxide ion). The methoxide ion, as the nucleophile, has a lone pair of electrons on the O atom. This lone pair is the HOMO (Highest Occupied Molecular Orbital), which has the highest energy orbital and contains electrons that can be donated. The carbonyl carbon in the triglyceride substrate acts as an electrophile because it has an empty antibonding π^* orbital.

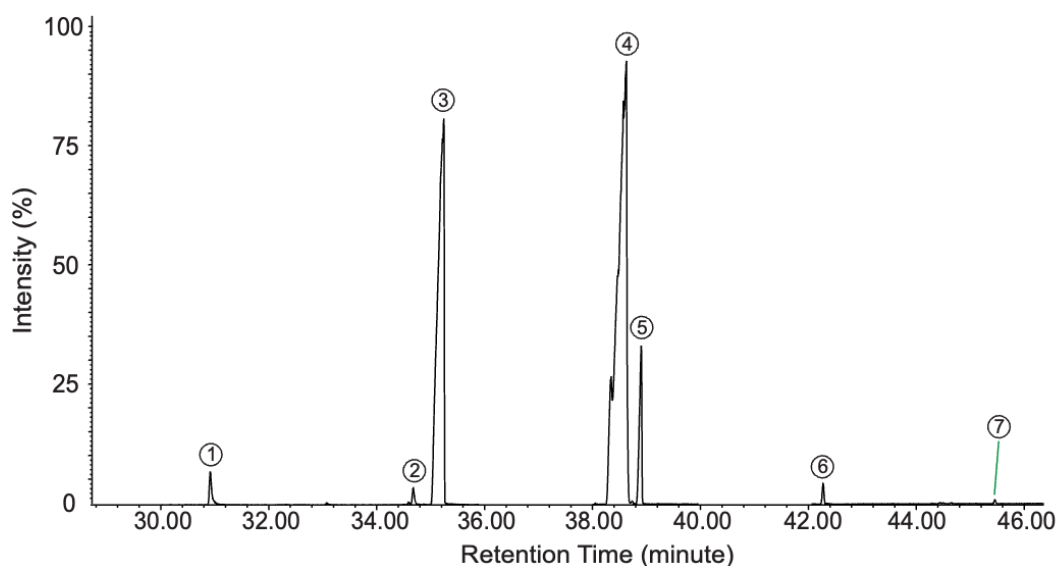


Figure 5. GC-MS chromatogram of WCOME

Table 1. Fatty acid composition of produce WCOME

Peak	Retention Time (minute)	Compound	Molecular Formula	Fatty Acid Chain	Base peak (m/z)	Molecular Weight	Relative Abundance (%)
1	30.919	Myristic acid methyl ester	C ₁₅ H ₃₀ O ₂	C14:0	74	242	1.38
2	34.680	Palmitoleic acid methyl ester	C ₁₇ H ₃₂ O ₂	C16:1	74	268	0.61
3	35.245	Palmitic acid methyl ester	C ₁₇ H ₃₄ O ₂	C16:0	74	270	34.73
4	38.574	Oleic acid methyl ester	C ₁₉ H ₃₆ O ₂	C18:1	55	296	57.12
5	38.904	Stearic acid methyl ester	C ₁₉ H ₃₆ O ₂	C18:0	74	298	5.38
6	42.275	Arachidic acid methyl ester	C ₂₁ H ₄₀ O ₂	C20:0	74	326	0.57
7	45.447	Behenic acid methyl ester	C ₂₃ H ₄₆ O ₂	C22:0	74	354	0.21

This empty orbital is called the LUMO (Lowest Unoccupied Molecular Orbital) because the electron density on the carbonyl carbon is attracted by the electronegative O carbonyl, giving the carbonyl carbon a partial positive charge and readily accepting electrons. Consequently, electron transfer occurs from the HOMO (the lone pair on the O⁻ nucleophile) to the LUMO (the antibonding π^* on C=O). This electron transfer causes the electrons to resonate upward to the O carbonyl, leaving the O negatively charged and forming a tetrahedral intermediate. The electrons then descend again, releasing the alkoxy group (-O-CH₂-) from the triglyceride. This mechanism also applies to the synthesis of 2-hydroxypropyl esters [35], [36]. Proposed mechanism of 2-hydroxypropyl esters shown in Figure 6.

Reactions are controlled by TLC analysis every 2 hours. The results of the TLC analysis in Figure 7 show that the WCOME stain fades and disappears on the tenth hour reaction. This indicates that WCOME has been completely reacted to form a 2-hydroxypropyl esters product, which is represented by two stains that appear on the TLC plate.

Based on the results of the TLC analysis, the two stains are 2-hydroxypropyl esters derived from palmitic and oleic fatty acid chains. This is evidenced by the results of GC-MS identification in Figure 8, which is shown by the high relative abundance of peaks 2 and 3.

The chromatogram peak of WCOME and 2-hydroxypropyl bioadditive was identified based

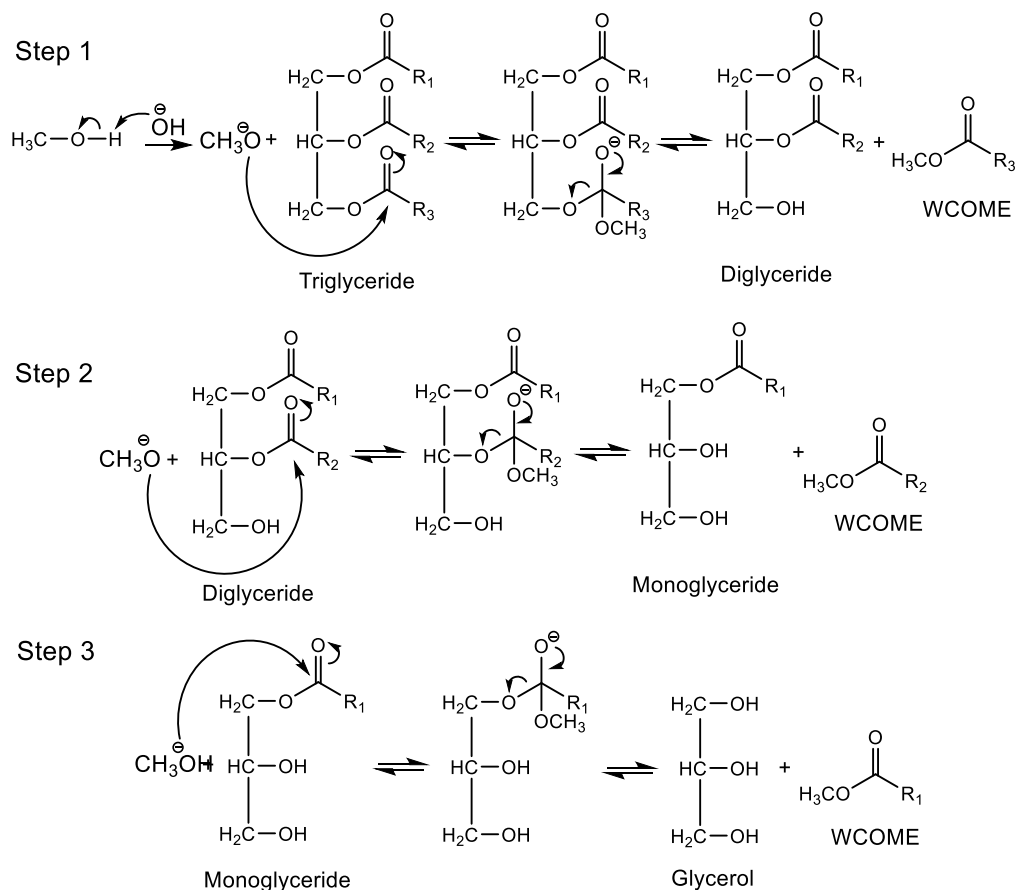
on the mass spectrum pattern with a base peak m/z 74 that indicates ⁺CH₂COOCH₃ (Figure 9c) fragment as a result of fragmentation of methyl ester compounds. Meanwhile, base peak of m/z 118 indicates 2-hydroxypropyl esters fragment (Figure 9d) according to McLafferty rearrangement rules as shown in Figure 9. In WCOME and 2-HPE fragmentation, the bonds between the ester groups and their surrounding atoms are relatively weak due to differences in electronegativity. As a result, the less stable moiety breaks first, producing more stable fragments, which are recorded as m/z that representing the resulting fragment ions. McLafferty rearrangement occurs because there is an oxygen atom on the carbonyl (electronegative and partially negatively charged) and an H γ atom, which causes the aliphatic chain to form a stable 6-membered ring conformation. This formation allows for an intramolecular H-shift with the O carbonyl due to their close position. The carbonyl oxygen after ionization will produce a cation radical that is very deficient in electrons. In this condition, carbonyl oxygen is a good H acceptor. The presence of H γ transfer will stabilize the charge on the carbonyl oxygen by forming an O-H bond [37]. With the shift of H γ to oxygen, a π bond (C=C) is formed at the γ - β position to form a stable fragment in the form of a conjugated enol or oxonium ion with the fragment ion represented by m/z 74 for WCOME (Figure 9a) and m/z 118 for 2-HPE (Figure 9b).

According to the result of GC-MS identification in Figure 8, bioadditive products were dominated by 2-hydroxypropyl palmitate

and 2-hydroxypropyl oleate compounds with relative abundance percentages of 42.46% and 57.44%, respectively (Table 2), with total saturated and unsaturated fatty acids of 42.47% and 57.53%, respectively. Interestingly, some other fatty acid components, such as palmitoleate, margarate, and arachidate are not identified in the bioadditive product. Similarly, stearate has a significant decrease in relative abundance. This is thought to

be due to the heating process during the transesterification reaction, which requires high temperatures for a long time. As a result, some compounds that previously had very low relative abundance are absent or became difficult to identify. In addition, the heating process also causes the reduction of double bonds on the fatty acid chain due to their unstable properties [38], [39].

Synthesis of WCOME



Synthesis of bioadditive 2-hydroxypropyl ester

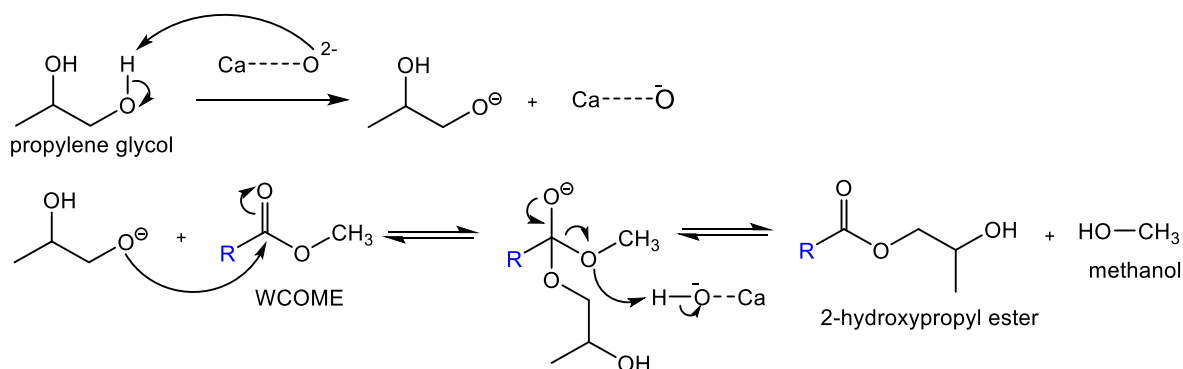


Figure 6. Proposed mechanism of synthesis 2-hydroxypropyl ester

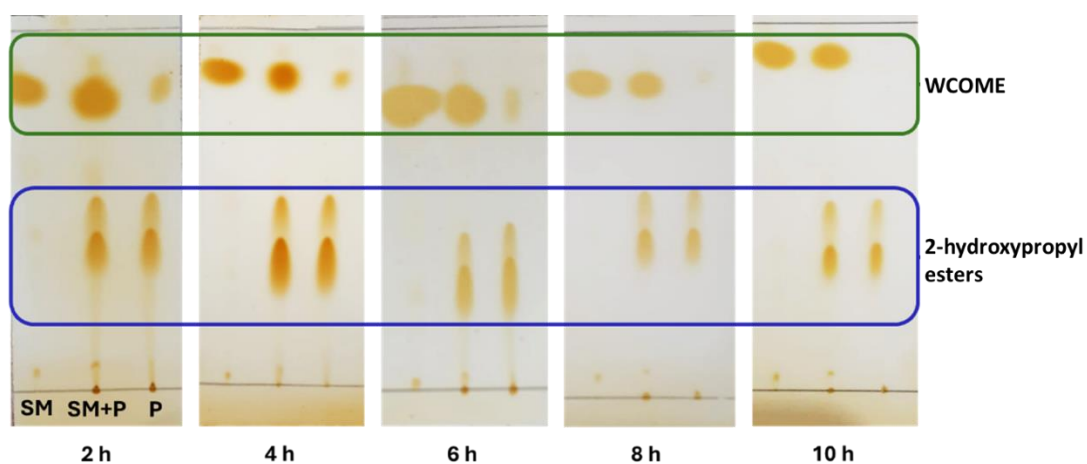


Figure 7. TLC analysis to control reaction. SM: starting material, P: product

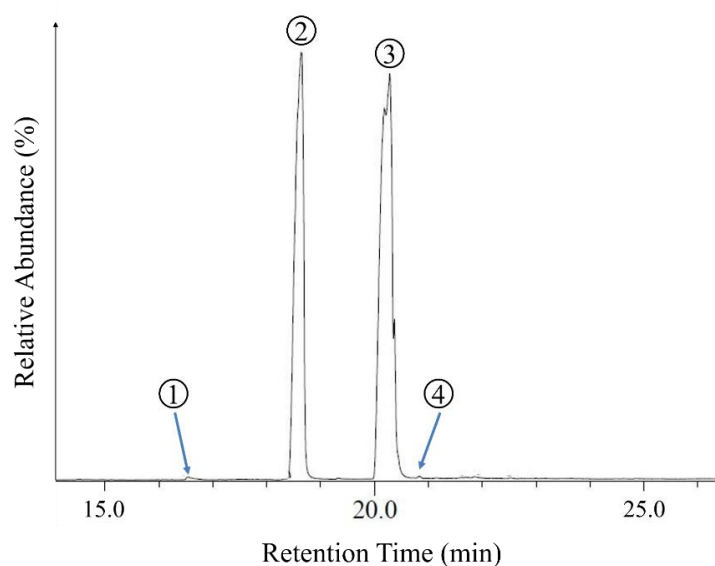


Figure 8. GC-MS chromatogram of bioadditives 2-hydroxypropyl esters

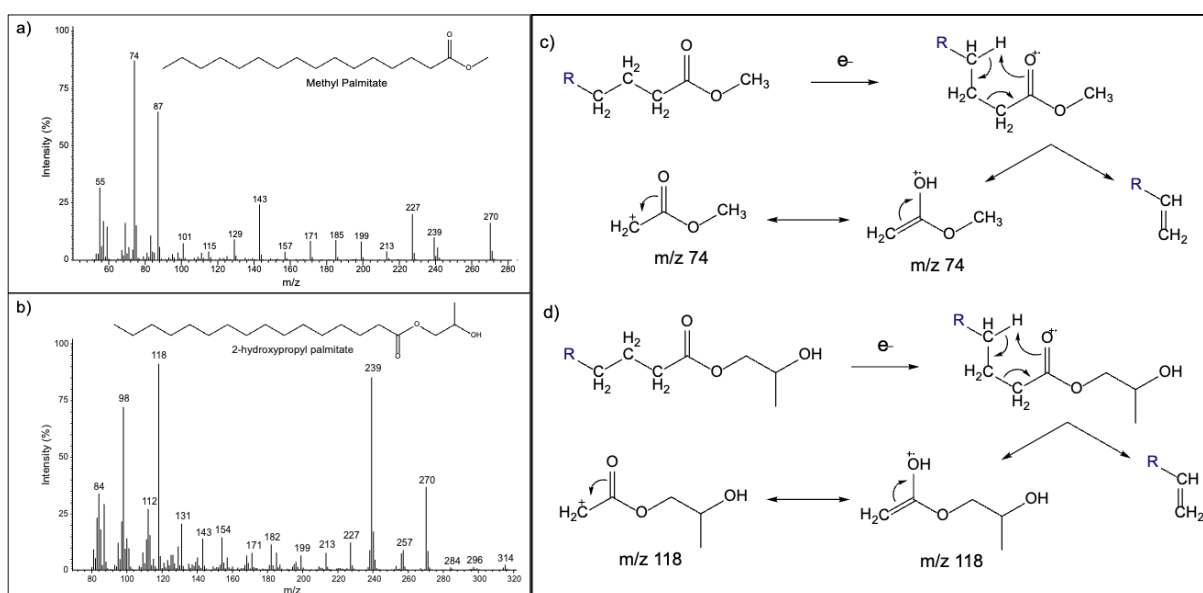


Figure 9. Mass spectrum of methyl palmitate (a) and 2-hydroxypropyl palmitate (b); and fragmentation of WCOME (c) and 2-hydroxypropyl esters (d)

Table 2. The obtained compounds of produce bioadditive

Peak	Retention Time (minute)	Compound	Fatty Acid Chain	Chemical Formula	Molecular Weight	Base Peak (m/z)	Relative Abundance (%)
1	16.540	2-hydroxypropyl myristate	C14:0	C ₁₇ H ₃₄ O ₃	286	98	0.09
2	18.639	2-hydroxypropyl palmitate	C16:0	C ₁₉ H ₃₈ O ₃	314	118	42.46
3	20.284	2-hydroxypropyl oleate	C18:1	C ₂₁ H ₄₀ O ₃	340	118	57.44
4	23.006	2-hydroxypropyl stearate	C18:0	C ₂₃ H ₄₂ O ₃	342	118	0.01

3.5. Prospect of 2-Hydroxypropyl Esters as Bioadditive for Low-Sulfur Diesel Fuel

The performance of fuel bioadditives is assessed based on their lubricity and tribological properties. The parameters measured include friction coefficient, wear scar diameter (WSD), and film thickness [40]. Proper feedstock and polyalcohol selection is critical for achieving good lubricity performance. From the molecular aspect, the waste cooking oil used in this study contains unsaturated fatty acids, which are more dominant than saturated fatty acids. The presence of predominantly saturated fatty acids will result in a decrease in the cold flow properties of low-sulfur diesel fuel after the addition of bioadditives. Conversely, the presence of predominantly unsaturated fatty acids in bioadditives will result in better cold flow performance in low-sulfur diesel fuel after the addition of bioadditives. Low-sulfur diesel fuel itself already has good cold flow properties, but these will be improved by adding bioadditives with predominantly unsaturated fatty acids [41]. However, unsaturated fatty acids are easily oxidized, causing short-term damage to the lubrication layer [42]. In this case, the abundance of saturated fatty acids in the 2-hydroxypropyl ester bioadditive is 42.46%, indicating that unsaturated fatty acids do not dominate the total composition. This condition reduces the chance of a chain reaction of auto-oxidation that can spread rapidly in mixtures with high unsaturated fatty acid content. Saturated fatty acids act as a "balancer" that minimize the oxidative vulnerability of unsaturated fatty acids, thereby helping to balance the overall properties of the fuel. This will result in a good lubrication system. Saturated fatty acids, such as myristic acid, palmitic acid, and stearic acid, have straight long-

chain molecules that generate a uniform and stable bilayer [43]. While unsaturated fatty acids such as oleic acid have double bonds that are naturally *cis*, which cause the fatty acid chains to become bent, resulting in a steric effect. In addition, the presence of C=C in oleic acid also indirectly lowers the adsorption energy because the *cis* C=C creates a bend that prevents the chains from aligning neatly with their neighbors. As a result, the adsorption energy distribution is uneven because some chains near the surface are lifted, which causing more flexible but less strong and instable layer [44], [45]. In addition, saturated fatty acids are not easily oxidized, so they do not damage the lubrication layer. However, saturated fatty acids have poor coldflow properties that cause the fuel to solidify easily [41], [46]. The type of alcohol that is used to modify fatty acids in the carboxylic group is also significant. There are several types of alcohols, such as monohydroxy, dihydroxy, and polyhydroxy. However, they all have very different viscosity properties. More hydroxy groups in a compound will increase the viscosity. This will effect the homogeneity of bioadditives mixed into diesel fuel [47]. In this study, propylene glycol was used as a reactant to provide polar groups. Propylene glycol contains two hydroxy groups and one carbon as a branch. The presence of two hydroxy groups can form a monoester with the remaining one hydroxy group, which can strengthen the chemical interaction with the iron metal surface [18], [44].

The synthesis of bioadditives has been widely reported in previous studies. Various types of raw materials are used such as, edible oils like soybean oil, peanut oil, and palm oil to non-edible oils like castor oil and jatropha oil. The polyalcohols used in several studies that have been reported are also quite diverse, with varying levels of lubricity.

Such research has been done about the use of WCOME and 2-ethyl-1-hexanol as starting materials and obtained bioadditives with a WSD of 0.15 mm and a coefficient of friction of 0.528 [24]. Another study used nyamplung oil and glycerol as starting materials and obtained a WSD value of 0.21 mm with a better friction coefficient of 0.051 and a film thickness of 86% [48]. Research by Zetra *et al.* regarding the lubrication performance of ethylene glycol ester from soybean oil as a lubricity-enhancing bioadditive for low-sulfur diesel fuel shows it has a friction coefficient of 0.057 and wear scar diameter of 0.154 mm [25]. Borugadda and Goud also modified the chemical structure of epoxidized waste cooking oil through 2-hydroxylation and hexanoylation and obtained more optimal results for hexanoylation products with a friction coefficient of 0.08, wear scar diameter of 0.232 mm, and film thickness of 0.15 mm [49]. The lubricity

performance of those bioadditives is compared with low-sulfur diesel fuel as shown in Figure 10.

In this study, the bioadditive 2-hydroxypropyl esters has a polar component containing hydroxy ester group and non-polar component containing alkyl chain derived from the fatty acid chain of waste cooking oil. According to its polarity properties, the hydroxy esters part can interact better with metal surfaces by chemisorption than ester-only biolubricant. On the other hand, the fatty acid alkyl chain will interact with other alkyl chain trough Van der Waals force to form a bilayer as illustrated in Figure 11. This bilayer serves as a barrier layer between the engine surfaces, which is expected to improve tribological properties such as minimizing direct contact between metal surfaces and reducing friction so that it can decrease the wear scars and tear on the engine surface [18], [25], [50].

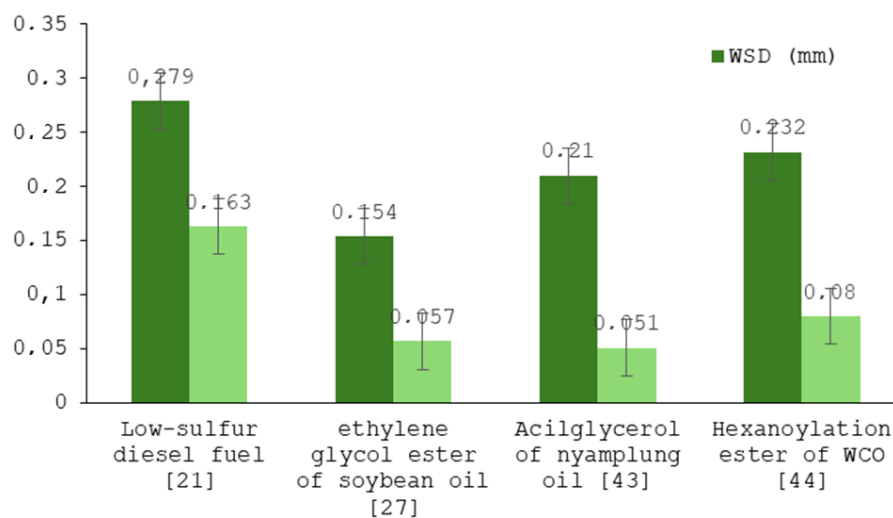


Figure 10. Comparison of various bioadditives lubricity performance

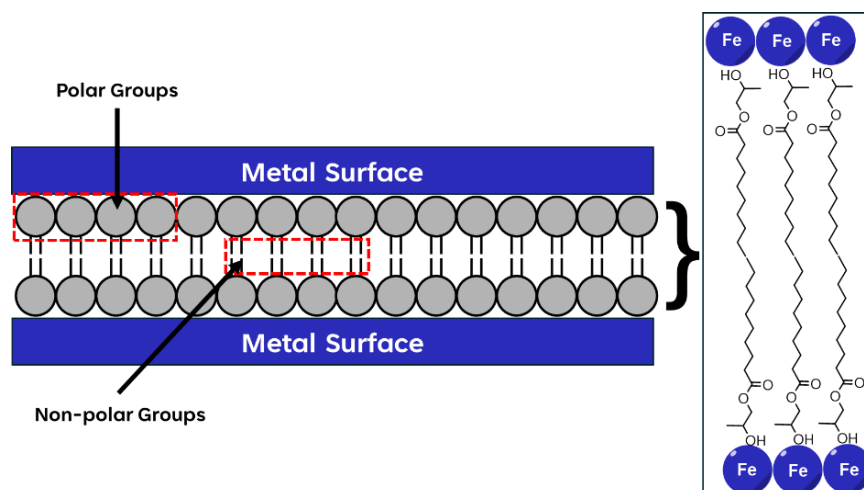


Figure 11. Proposed lubricating mechanism of 2-hydroxypropyl esters on metal surface

4. Conclusion

In this study, 2-hydroxypropyl ester was synthesized and investigated as a possibility for hydroxy-ester-based lubricity-enhancing bioadditives from a molecular perspective. The results showed that the bioadditive was primarily composed of 2-hydroxypropyl oleate and 2-hydroxypropyl palmitate, with a nearly balanced composition. According to tribological aspects, the presence of unsaturated fatty acids from 2-hydroxypropyl oleate can improve the cold flow properties of fuel. The presence of saturated fatty acids in 2-hydroxypropyl palmitate, which contains a straight fatty acid chain, can improve lubricity by creating a uniform boundary layer. A uniform boundary layer forms a stable bilayer, establishing a barrier between metal surfaces to prevent direct friction. The presence of the OH group on the ester as part of the "head" in the bioadditive is expected to provide better chemisorption interactions with the metal surface compared to ester-only based biolubricants. Based on its molecular analysis and possible chemical interactions, 2-hydroxypropyl ester has the potential to deliver better lubricity qualities than ester-only biolubricants. Furthermore, using waste cooking oil as a raw material is expected to increase its economic value while minimizing the amount of liquid waste generated. This study suggests that the potential of 2-hydroxypropyl ester from waste cooking oil as a lubricity-enhancing bioadditive should be investigated further by analyzing its application in low-sulfur diesel fuel engines.

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Author's Declaration

Authors' contributions and responsibilities

Yulfi Zetra: Validation, methodology, supervision, writing review, and editing. Rizka Berliana Putri: conceptualization, methodology, writing original draft, and writing review and

editing. Talitha Fitra Firdhausya: conceptualization and methodology. Yunita Alfiyati Firdausa: conceptualization and methodology. R.Y. Perry Burhan: Validation, methodology, supervision.

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Availability of data and materials

All data are available from the authors.

Competing interests

The authors declare no competing interest.

Additional information

No additional information from the authors.

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