Synthesis of 2-Hydroxyethyl Esters from Castor Oil as Lubrication Bio-Additive Candidates for Low-Sulfur Fossil Diesel

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Abstract: *The present work aims to study the synthesis of 2-hydroxyethyl esters from castor oil and its lubrication properties, promising as a lubrication bio-additive in low sulfur diesel fuel. This compound has been successfully synthesized from castor oil and ethylene glycol. The oil to ethylene glycol molar ratio was adjusted to 1:10, and the catalyst loading was used at 9% mole oil. Then, the mixture was refluxed for 5 h. The product components were characterized using GC-MS. The standard ASTM method was used to study the kinematic viscosity and lubrication. The product was dominated by 2-hydroxyethyl esters (94.16%), di-ester (1.12%), and cyclic ester (1.92%). The analysis of friction coefficient and wear scar diameter (WSD) using High-Frequency Reciprocating Rig (HFRR) shows the coefficient of friction and WSD of the product better than reference diesel fuel. From the results of this study, the 2-hydroxyethyl ester of castor oil, especially 2-hydroxyethyl ricinoleate, is the main responsible for the lubricating properties. Thus, 2-hydroxyethyl esters of castor oil can be proposed as an alternative bio-additive to improve the lubrication of low-sulfur fossil diesel fuels.*

Keywords: *2-hydroxyethyl ester; castor oil; lubrication; bio-additive; diesel*

INTRODUCTION

Fossil diesel still becomes a consumer choice because diesel engines have a higher efficiency than gasoline engines [1-2]. It was estimated that the demand for diesel from fossils has continued to increase [3-4]. However, fossil diesel's sulfur content causes air pollution and acid rain [5-6]. Therefore, a policy has been made to regulate allowed sulfur content in 10 to 500 ppm [7-8]. One strategy to meet this regulation is by applying the hydrodesulfurization method. Nevertheless, this method causes the compounds as natural lubricants to disappear [9-11], decreasing the lubricating properties of fossil diesel. Thus, lubrication enhancing additives are essential.

The fatty acids methyl ester (FAME) or fatty acids ethyl ester (FAEE) or biodiesel have been considered bio-additive with good lubricating properties. Adding biodiesel with a small concentration (less than 1%) into fossil diesel could improve its lubricity. Adding 1% methyl ester from rapeseed oil reduced 13% of diesel's wear scar diameter (WSD) [12]. The addition of 0.2 and 0.5 wt.% methyl ester of used oil caused the WSD values to decrease to 432 and 368 μm, respectively [13]. Addition of methyl ester in diesel was 0.1, 0.5, 1, 2, 5, and 10 wt.% from castor oil reduced the WSD from 581 to 299 μm [14]. Prasad et al. [15] reported that a mixture of 0.2 and 0.4% v of ethyl ester from castor oil into diesel decreased the WSD value to 320 and 186 μm, respectively.

Methyl or ethyl ester is generally prepared via transesterification of triglyceride or fatty acids using monohydroxy alcohol. Similar to this reaction principle, another ester can also be prepared by applying polyalcohols, such as ethylene glycol, to form the 2-hydroxyethyl esters [16-17]. Another study reported that low monoglycerides in FAME significantly contribute to FAME lubrication properties. It is due to hydroxy groups at head moiety [18-19]. However, it is challenging to synthesize FAME with a particular monoglyceride concentration [19]. Monoglyceride synthesis takes a long time, and special reactors [20-22] cannot be applied industrially [23]. Therefore, we synthesized esters whose structure is similar to monoglycerides by a simple reflux method, which did not require a long time, and tested their lubricity properties. The compound has a hydroxyl group at the head moiety (2-hydroxyethyl ester), which can be a bio-additive to improve the lubrication of low sulfur diesel. The 2-hydroxyethyl ester is vital as a starting point for other researchers in developing lubricity enhancer bio-additives for diesel in the future. So far, other researchers have not reported the lubricating properties of the 2-hydroxyethyl ester from non-edible oils.

Not many researchers have reported the synthesis of 2-hydroxyethyl esters from renewable feedstocks throughout our search. Rezende et al. [17] have reported the synthesis of 2-hydroxyethyl esters from cottonseed and sunflower oil. Nosal et al. [24] studied that fatty acids were esterified to 2-hydroxyethyl esters. Like other renewable raw materials, castor oil has the potential to be modified into 2-hydroxyethyl esters. Ricinoleic acid's high content (80–90% w/w) and its uniqueness in castor oil inspired researchers to develop bio-additives for lubrication of low sulfur diesel. The hydroxy group in ricinoleic acid improved the lubricating properties of low-sulfur diesel after adding methyl ricinoleate. Hence, the viscosity of methyl ricinoleate is higher than methyl esters of other fatty acids such as methyl stearate and methyl oleate. This increase in viscosity provides an advantage in lubricity behavior [25].

The basic principle in synthesizing the 2-hydroxyethyl ester is similar to the synthesis of FAME or FAEE [26]. The vegetable oil can be transesterified with the desired alcohol, and the base or fatty acid esterified with the desired alcohol and acid catalyst. However, the alcohol used in this work is ethylene glycol. This alcohol provides one hydroxy group in the resulting 2-hydroxyethyl ester structure or a structure similar to FAEE with the addition of one hydroxy group. The structure is analogous to monoglycerides which have two hydroxy groups. Adding one hydroxy group to the 2-hydroxyethyl ester is expected to strengthen the interaction with the metal surface, similar to the function of the two hydroxy groups on the monoglyceride [27]. As a result, this produces a protective film that minimizes direct contact between metal surfaces. The strength of this protective layer is also supported by the fatty acids contained in vegetable oil [28].

Therefore, this paper aims to discuss the synthesis of 2-hydroxyethyl esters from castor oil and its lubricity properties. Interestingly, the product in this work demonstrated good lubrication properties. It can be proposed as a potential bio-additive for improving the lubricity of low-sulfur fossil diesel.

■ EXPERIMENTAL SECTION

Materials

The castor oil in this study is commercial refined castor oil in Indonesia. The utilized fossil diesel was the leading diesel commercialized in Indonesia, containing 300 ppm sulfur. Meanwhile, sulfuric acid (H_2SO_4) was obtained from SMART Lab Indonesia, and other chemicals were obtained from Sigma-Aldrich (EMSURE for analysis grade): ethylene glycol, potassium carbonate (K_2CO_3) that was heated before being used, ethyl acetate, potassium hydroxide (KOH), and sodium sulfate anhydrous (Na_2SO_4). All those chemicals were used without any purification.

Instrumentation

The instruments used in this work were GC-MS QP 2010 Shimadzu with the RTX5-MS column. The lubricity properties analyzed by HFRR with test ball specifications: SAE-AMS 6440 steel, diameter 6.00 mm, Rockwell "C" (HRC) scale hardness rating 58–66 (Class

28 per ISO 3290). Test disc specifications: SAE-AMS steel 10 mm disc 6440, which machined from annealed rods, Vickers solidity HV 30, in line with E92, scale number 10-210, rotated, stacked, and polished to obtain a surface of less than 0.02.

Procedure

Determination of fatty acids derived from castor oil

Methanol was used in this work because it is more reactive than ethylene glycol. The methoxide ion is more easily formed than the ethylene glycoxide ion. In addition, the methoxide ion is smaller than the ethylene glycoxide ion. Hence the methoxide ion more easily attacks the carbonyl carbon of the triglyceride [29]. The castor oil and methanolic KOH as base catalysts were preheated. The molar ratio of oil to methanol is 1:6, castor oil, 20 g and methanol, 4.1556 g and the base catalyst loading was used 1 wt.% of oil. Then, the oil and catalyst were mixed under reflux at 60 °C for 2 h. The mixture was left in a separation funnel overnight. The glycerol, methanol, and water occupied the lower layer. In the next step, this layer was discarded. The methyl ester in the upper layer was evaporated to eliminate the solvent and dried using Na_2SO_4 [30].

The purified methyl ester of refined castor oil was characterized using GC-MS with a capillary column comprised of 5% diphenyl and 95% dimethyl polysiloxane with a thickness of 0.25 mm, column length of 30.0 m, and an inner diameter of 0.25 µm. The injection temperature was adjusted to 250 °C. The split ratio mode was 138.7, with the flow rate of Helium gas being 1.16/min. The oven was programmed at 100 °C as the initial temperature for 4 min. Then, this temperature was raised to 240 °C at 3°C/min for 15 min. This temperature was raised to 250 °C again with 10 °C/min and maintained for 4 min.

Quantitative data from the characterized methyl esters were then used to calculate the molecular weight of castor oil according to Eq. (1) [31]. The obtained molecular weight of the castor oil was to synthesize 2-hydroxyethyl ester.

$$P_c = \sum (P_i \cdot Y_i) \quad (1)$$

P_c is the molecular weight of castor oil, P_i is the molecular weight of FAME in castor oil, and Y_i is the percentage of FAME in castor oil.

Synthesis of 2-hydroxyethyl esters

The 2-hydroxyethyl esters compound from castor oil was synthesized without optimizing the reactant molar ratio, reaction time, reaction temperature, and catalyst loading parameters. The synthesis of the 2-hydroxyethyl ester procedure refers to Jiang et al. [16] with a slight modification in reaction time, temperature, and loading catalyst until form a product based on thin-layer chromatography (TLC) spots. The molar ratio of oil to ethylene glycol was adjusted to 1:10: castor oil, 20 g, and ethylene glycol, 13.4176 g. The castor oil was heated at 150 °C by reflux in this study. Then, ethylene glycol and K_2CO_3 as catalysts were added to that system. This condition was maintained for 5 h. Next, the mixture was neutralized until pH 7, transferred to a separating funnel, and left overnight until two layers were formed. As a result, esters were in the top layer, and glycerol at the bottom was discarded. Furthermore, the top layer was washed with hot water until the water layer was clear. The Na_2SO_4 was used to eliminate water in the mixture. Finally, the excess solvent was removed by a rotary evaporator [16].

Characterization of 2-hydroxyethyl esters

Transesterified products were checked through the TLC. The eluent used in this study was *n*-hexane and ethyl acetate (2:1). Spot of product observed in iodine chamber. Furthermore, the profile of the transesterified product was analyzed by GC-MS. The oven was programmed at 70 °C and ramped to 200 °C at 10 °C/min (hold time was 5 min). The temperature was ramped again to 305 °C at 4 °C/min (hold time was 15 min).

Kinematic viscosity and lubrication properties measurement of the product

The kinematic viscosity or fluidity property was measured by kinematic viscometer followed ASTM D445 procedure at 40 °C. This apparatus was chosen to measure based on the time for a volume to flow under gravity. The lubrication testing of the transesterified product was performed using the HFRR apparatus referring to ASTM D6079. The measurement condition was maintained at 2 mL of sample volume, 200 g of loading mass, the testing duration of 75 min, and the temperature at 60 °C.

■ RESULTS AND DISCUSSION

Fatty Acids Profile Derived from Castor Oil

The fatty acids in castor oil are determined using a methanolysis reaction. The profile of fatty acids as their methyl esters and other published research can be seen in Table 1. Each of these methyl esters was identified by comparing each mass spectrum with the Wiley 9 database and analyzing the fragmentation pattern of each spectrum. Table 1 shows that the fatty acids of castor oil in this study are similar to other published reports. The castor oil is dominated by unsaturated fatty acids, especially methyl ricinoleate. It potentially has a good effect on the lubricity to low sulfur diesel [32]. The obtained methyl ester of castor oil was used to calculate the molecular weight of castor oil and synthesis of 2-hydroxyethyl ester, as shown in Table 2.

The fatty acid composition in castor oil was determined based on the optimum reaction conditions suggested by Rashid et al. [30]. This investigation provides a brief description of the types of fatty acids in the feedstock. However, compared with previous studies, the fatty acid composition in this study did not differ much (Table 1). The percentage of fatty acids in the feedstock helps estimate the molecular weight of castor oil. This information is helpful in stoichiometric calculations for the preparation of 2-hydroxyethyl esters (Table 2).

Characterization of 2-Hydroxyethyl Esters

TLC was carried out to know whether 2-hydroxyethyl ester formed. Fig. 1 also demonstrated that the triglycerides had reduced and formed the product. Furthermore, detailed chemicals of the product were analyzed by GC-MS.

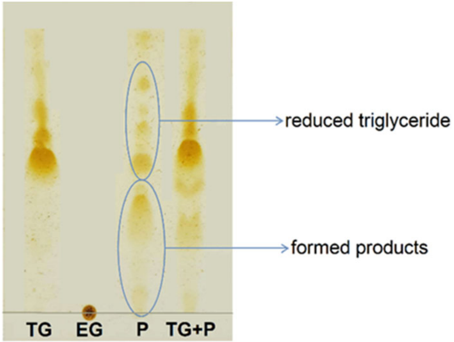

Fig 1. TLC spots of product synthesis. TG = triglyceride; EG = ethylene glycol; P = product

Table 1. Yield methyl ester of this study compared to another published research (%)

Yield GC-MS (%) of fatty acids methyl ester										
Palmitate (C16:0)	Palmitoleate (C16:1)	Stearate (C18:0)	Oleate (C18:1)	Linoleate (C18:2)	Linolenate (C18:3)	Ricinoleate (C18:1 OH)	∑ saturated methyl ester	∑ unsaturated methyl ester	Others	Ref.
1.30	-	1.31	3.57	4.52	0.41	88.89	2.61	97.39	2.61	This study
1.10	-	1.30	3.60	4.40	0.7	88.80	2.4	97.5	2.5	[34]
1.09	-	0.94	3.70	4.44	-	89.93	2.03	98.07	1.93	[35]
1.96	-	2.06	5.46	6.15	-	84.26	4.02	95.87	4.13	[36]
-	0.72	0.64	2.82	3.74	-	90.85	0.64	98.13	1.87	[37]
-	1.08	0.91	2.93	3.48	0.32	91.06	0.91	98.87	1.13	[38]

Table 2. Percentage of methyl ester and molecular weight of castor oil

FAME in castor oil	P_i (g/mol)	Y_i (%)	$P_c = \Sigma (P_i . Y_i)$
Palmitate	807.29	1.30	10.49
Stearate	891.45	1.31	11.68
Oleate	885.45	3.57	31.61
Linoleate	879.45	4.52	39.75
Linolenate	873.45	0.41	3.58
Ricinoleate	902.45	88.89	802.19
			899.31

The obtained compounds are summarized in Table 3. This result was obtained from the percentage of the peak chromatogram. Similar to the FAME of castor oil (Table 2), 2-hydroxyethyl ricinoleate dominates 2-hydroxyethyl esters. The reaction mechanism for forming the proposed 2-hydroxyethyl ester shown in Fig. 2 is analogous to the transesterification of triglycerides with alcohols using a base catalyst [26]. In the first step, carbonate anions attack ethylene glycol protons to form ethylene glycoxide anions as the nucleophile. Second step, carbonyl carbon of triglyceride is attacked by ethylene glycol nucleophile to form 2-hydroxyethyl ester and di-glyceride. The third and fourth step is similar to the second step. The ethylene glycol anion attacks the carbonyl carbon of di-and mono-glyceride to form mono-glyceride and glycerol, respectively, beside 2-hydroxyethyl ester.

According to Table 3, obtained product is also containing a di-ester. It may be due to the proton of the hydroxy group on the 2-hydroxyethyl ester allowing is attacked by the carbonate anion. In the next step, the anion of 2-hydroxyethyl ester attacks 2-hydroxyethyl

Table 3. The obtained product profile of castor oil

tR* (min)	Molecular ion (m/z)	Base peak (m/z)	Transesterified product	Yield GC-MS (%)
16.32	280	98	Cyclic ester	1.92
20.29	300	104	2-HE# palmitate	1.94
24.44	324	67	2-HE linoleate	6.33
24.53	326	55	2-HE oleate	5.93
25.02	328	104	2-HE stearate	2.21
29.41	342	55	2-HE ricinoleate	77.75
48.88	560	55	di-ester	1.12

*tR = retention time; #HE = hydroxyethyl

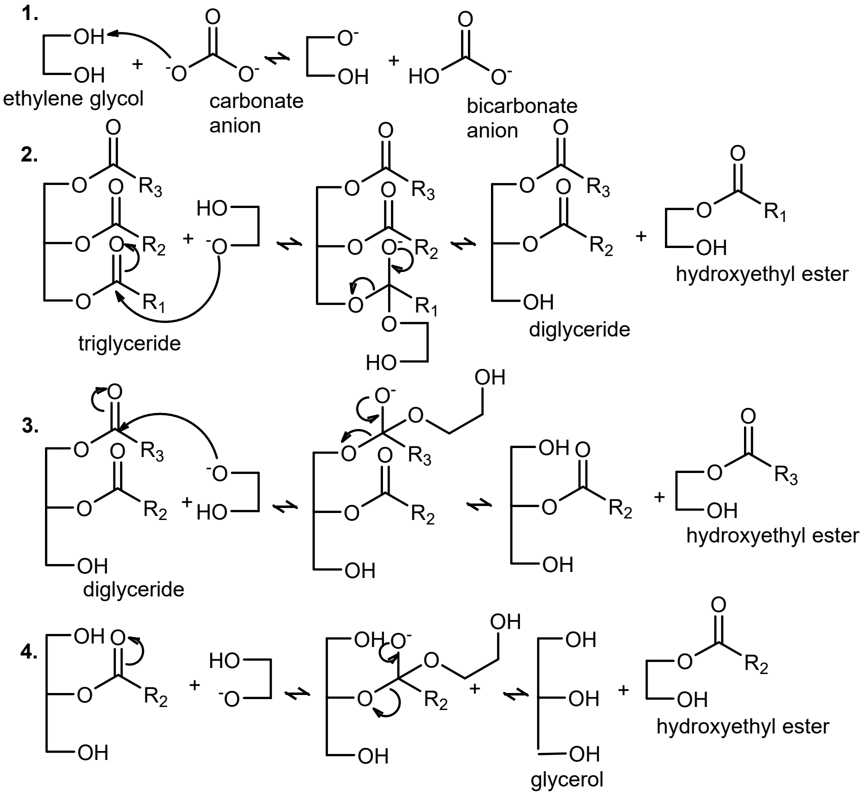

Fig 2. Proposed reaction mechanism of 2-hydroxyethyl esters formation

ester's carbonyl carbon. As a result, di-ester and ethylene glycol are produced, as shown in Fig. 3. The reaction mechanism for the formation of the di-ester, as in Fig. 3, is analogous to the di-esterification of ethylene glycol [38-39].

In this study, a cyclic ester was also identified. It may be derived from the intramolecular esterification of ricinoleic acid (Fig. 4). The reaction mechanism is generally a nucleophilic addition reaction to the carbonyl group [40]. The carbonate anion reacts with ethylene glycol to produce carbonic acid. Furthermore, ricinoleic acid in castor oil captures protons from carbonic acid. The carbon on the ricinoleic acid carbonyl becomes electrophilic. It causes cyclization to form cyclic ester.

Kinematic Viscosity and Lubrication Properties of the Product

Kinematic viscosity and lubricity are vital properties of low-sulfur fossil diesel lubrication additives. The kinematic viscosity of the product in this study and low-sulfur fossil diesel can be seen in Table 4. The synthesized product is much more viscous (51.86 mm^2/s) than the reference diesel fuel (3.39 mm^2/s). Based on this information, the lubricating properties of the product are better than reference diesel fuel. Generally, better kinematic viscosity can lead to better lubrication [15,41].

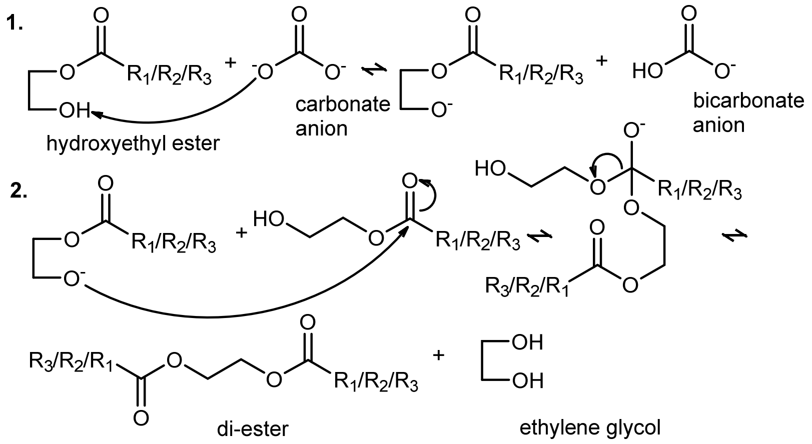

Fig 3. Proposed reaction mechanism of di-ester formation

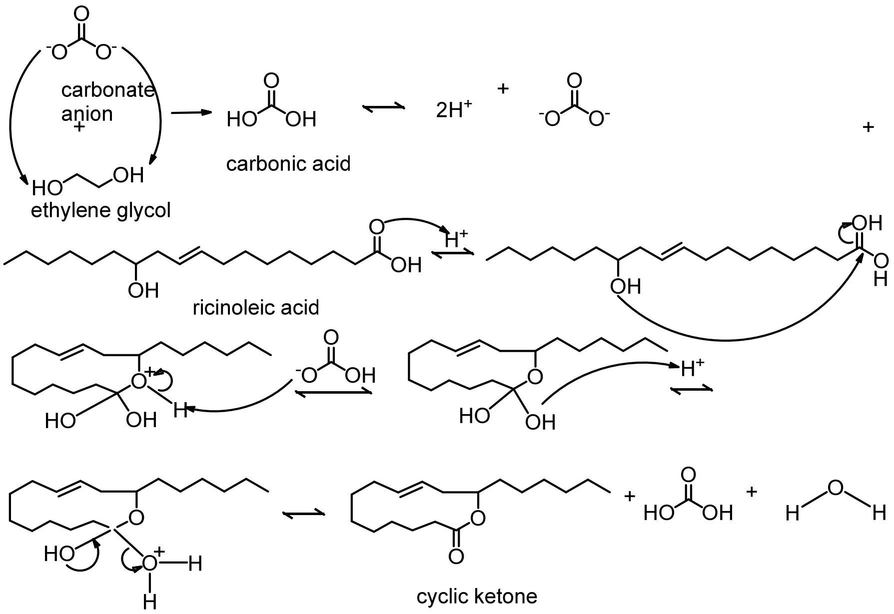

Fig 4. Proposed intramolecular esterification of ricinoleic acid

Table 4. Kinematic viscosity and lubrication properties of the transesterified product and low-sulfur fossil diesel

Properties	Unit	Testing method	Product of this study	Low-sulfur fossil diesel
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	51.86	3.39
Lubricity		ASTM D6079		
- WSD average	µm		198.5	279
- Coefficient of friction average	-		0.083	0.163
- Film thickness				
	%		75	77

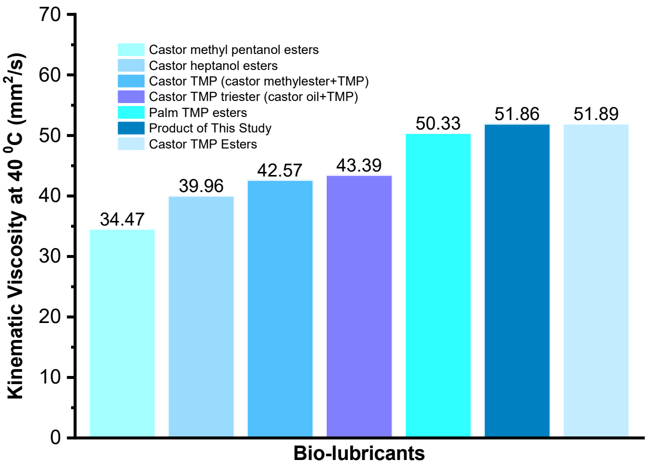

Fig 5. Comparison of kinematic viscosity between the product of this study and bio-lubricants. **A–E** (meet ISO viscosity grade 46); **F–G** (meet ISO viscosity grade 32). Reference of **B** [42]; **C** [43]; **D** [43]; **E** [42]; **F** [44]; **G** [44]. TMP = trimethyl propane

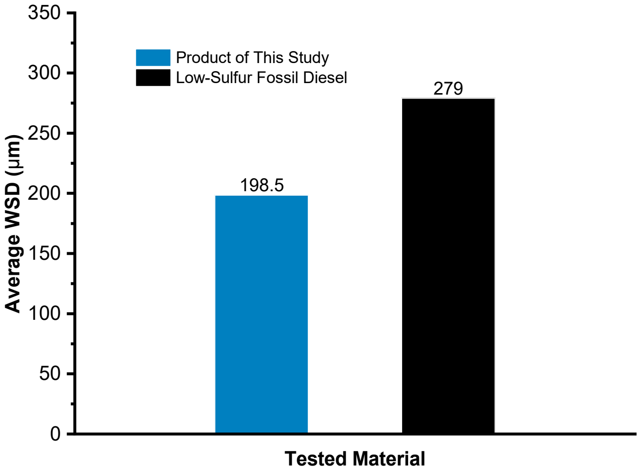

Fig 6. WSD value of product of this study (blue) and low-sulfur fossil diesel (black)

The kinematic viscosity in this work is similar to bio-lubricants 34–51 mm^2/s, as reported by Heikal et al. [42] McNutt et al. [43], and Encinar et al. [44] (Fig. 5). The kinematic viscosity of the product of this work met ISO Viscosity Grade 46.

From Fig. 6, it is known that the WSD value of the product in this study is below EN 590 (460 µm) and ASTM D975 (520 µm) limit. It is lower than the fossil diesel reference. This circumstance is caused by the ester and cyclic ester content in the product (Table 3), although the cyclic ester has a minor contribution to lubrication [45].

Based on obtained WSD value, the 2-hydroxyethyl esters are suspected to be the main contributors to lubrication, especially 2-hydroxyethyl ricinoleate (as shown in Table 3, 77.75%). This data is supported by film thickness data displayed in Fig. 7. The black line demonstrates that the lubrication film fluctuates in the fossil fuel during the test. Lubrication film is created and destroyed repeatedly. The destruction of the lubrication film is more severe in fossil diesel than in the product of this study (blue line). As a result, the WSD value of the product of this study is lower than fossil diesel. Based on this evidence, the head and tail polarity of 2-hydroxyethyl ricinoleate are responsible for the product's lubrication.

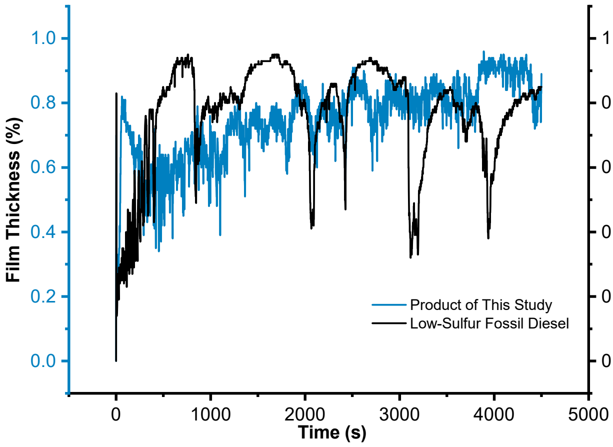

Fig 7. Graphic of film thickness: product in this study (blue) and low-sulfur fossil diesel (black)

It was similar to Canoira et al. [46] and Prasad et al. [15] that lubrication film formation related directly to methyl ricinoleate as the major component. Fig. 8 indicates that the friction coefficient of low-sulfur fossil diesel high-fluctuates at the beginning of the measurement (black). It means more friction occurred for low-sulfur fossil diesel than for the product in this study (blue). As a result, the friction coefficient value of low-sulfur diesel is higher than the product of this work.

We observe that the product's lubrication film and friction coefficient during testing are relatively more stable than fossil diesel. This phenomenon shows that utilizing ethylene glycol has successfully enhanced the polarity of ester. It also indicates that besides FAME or FAEE, the 2-hydroxyethyl ester can be a potential alternative bio-additive for lubricity enhancement of low-sulfur fossil diesel. This fact is supported by Sukjit et al. [45]. Knothe and Steidley [18] reported that the functional group polarity impacted the lubrication properties. The increasing functional group polarity causes lubrication properties enhancement significantly.

Analysis of the WSD value of this study compared to castor oil ethyl ester from the published article can be seen in Fig. 9. Although our product has a hydroxyl group on the alkyl ester, we notice a difference between the WSD value in this research and the ethyl ester of castor oil reported by Prasad et al. [15] and Yusoff et al. [29]. Some reasons may explain this phenomenon. First, the FFA content in our raw material was not decreased. The presence of FFA may react with part of carbonate ions to form soap. Consequently, it reduces hydroxyethyl esters yield (including 2-hydroxyethyl ricinoleate). It is analogous to the influence of FFA in the FAME synthesis [47]. The second reason is due to applying wet catalysts in this research. The presence of water content in K_2CO_3 may encourage hydrolysis and saponification reactions. It also decreased hydroxyethyl ester yield, and it is similar to the water content effect on the FAME synthesis [48]. Besides that, monoglyceride content significantly affects lubrication improvement. In this study, monoglyceride was not detected in the product. Hence, it diminishes lubrication [18-19,49].

For the reasons mentioned above, our product quality allows being boosted. The product can be a candidate bio-additive to improve low-sulfur fossil diesel lubrication.

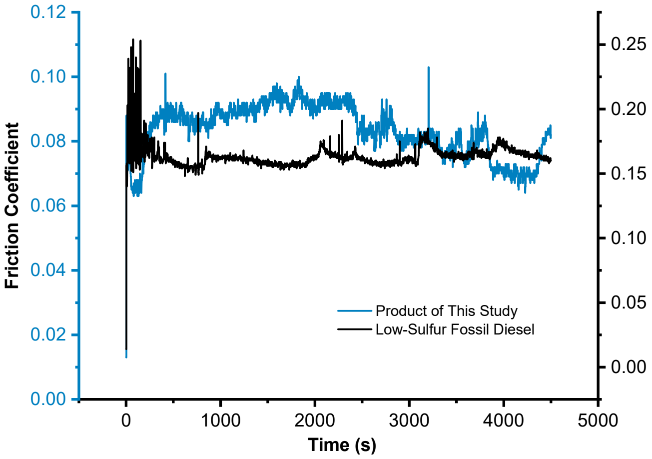

Fig 8. Graphic friction coefficient: product in this study (blue) and low-sulfur fossil diesel (black)

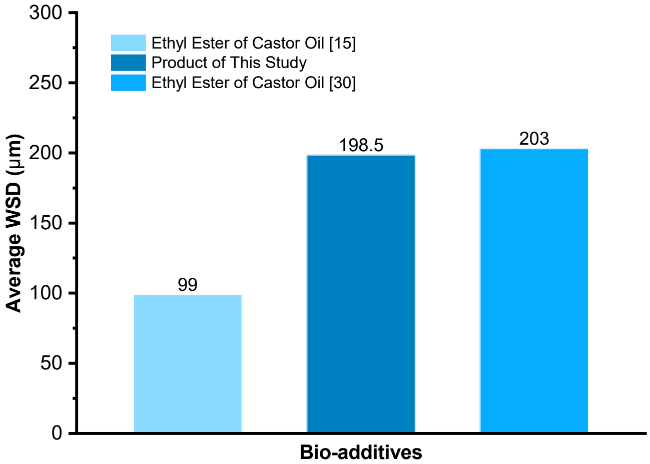

Fig 9. Comparison of WSD value between bio-additive this study and others. WSD value of other ethyl ester = 99 µm [15], 203 µm [29]

Possibility of Lubrication Mechanism of 2-Hydroxyethyl Ester from Castor Oil

The lubrication mechanism of the product may be explained by the compound majority contained in the mixture, similar to Loehlè et al. [50-51]. As shown in Fig. 10, among fatty acid chains, 2-hydroxyethyl ricinoleate occurred Van der Waals forces, hydrogen bonding, and physisorption on the metal surface. Oxygen moieties of hydroxyl group or carbonyl group bound to iron or iron oxide of a metal surface (chemisorption). The presence of

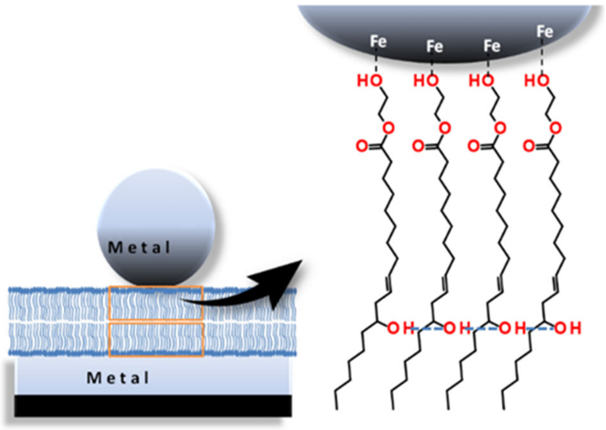

Fig 10. Possibility proposed lubrication mechanism of 2-hydroxyethyl ricinoleate

these sorptions generated and kept the boundary lubrication film. It prevents direct contact with metal surfaces, thereby dwindling friction and wear. The hydroxyl group at the alkyl chain played a vital role in the lubrication of the product of this study. This hypothesis agrees with the findings reported previously [18, 45].

■ CONCLUSION

The castor oil was successfully transesterified by ethylene glycol, and the fossil diesel fuel used as a reference in the lubrication comparison is low-sulfur commercial diesel fuel. Based on the measurement results, ethylene glycolysis products' kinematic viscosity and lubricity properties are better than low-sulfur fossil diesel. Although the film thickness of fossil diesel is slightly larger than that of the synthetic product, the stability of the protective layer of fossil diesel is worse than the product of this study. Good tribological behavior of the product of ethylene glycolysis due to the chemical contained in it, the compounds were 2-hydroxyethyl esters (94.16%), lactone (1.92%), and di-ester (1.12%). The central lubrication contributor was 2-hydroxyethyl ricinoleate. The kinematic viscosity and lubricity of the product were 51.86 mm^2/s and 198.5 µm, respectively. It met ISO viscosity grade 46 and lubricity below EN 590 or ASTM D975 limit. It has proven that the product in this study deserves to be proposed as a bio-additive to enhance low-sulfur diesel lubrication derived from the desulfurization process at the refinery. However, it is necessary to carry out further research on this subject, such as strategies to obtain the maximum 2-hydroxyethyl ester yield. The tribological effect of adding bio-additive to fossil diesel also needs to be attempted. Other studies can also be performed by comparing the tribological properties of 2-hydroxyethyl ester and ethyl ester of the same castor oil. Thus, the results of this study encourage other researchers to develop alternative bio-additives for fossil diesel lubricity enhancers.

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■ AUTHOR CONTRIBUTIONS

Arizal Firmansyah: conceptualization, writing-original draft, and writing-review & editing. R. Y. Perry Burhan: conceptualization, methodology, supervision, writing-review & editing. Yulfi Zetra: validation, methodology, supervision, writing-review & editing. Didik Prasetyoko: validation, methodology, supervision, writing-review & editing. Novesar Jamarun: proofreading. All authors agreed to the final version of this manuscript.

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