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Research Paper

Synthesis and Characterization of Diesel Lubricity Enhancer through Transesterification Reaction of Palm Oil with 1,2-Ethanediol

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Abstract

Desulphurization of diesel fuel is necessary to be done to reduce sulphur content in the air. However, the desulphurization process will reduce the lubrication properties of diesel fuel. In order to overcome the problem, it needs bioadditive to improve the lubricity. Lubricity of diesel fuel can be improved by the subsistence of chemical compound that is hydroxy ethyl esther (HEE). HEE is synthesized through the transesterification reaction of palm oil (triglycerides) and 1,2 ethanediol at 150 °C for 5 hours and K_2CO_3 catalyst as well. The conversion of TG into the products is 72.90%. The characterization using Gas Chromatography-Mass Spectrometry (GC-MS) indicates that the chemical compound in synthesis products comprise free fatty acids, hydroxy ethyl esters and by-products. The obtained products can be used as bioadditives to improve the lubricity of diesel fuel.

Keywords: Palm oil; Bioadditive; Lubricity Enhancer; Transesterification.

Abstrak

Desulfurisasi bahan bakar diesel perlu dilakukan untuk mengurangi kandungan sulfur di udara. Namun, proses desulfurisasi akan mengurangi sifat pelumasan bahan bakar diesel. Untuk mengatasi hal tersebut diperlukan bioaditif untuk memperbaiki pelumasan. Pelumasan diesel dapat ditingkatkan dengan adanya senyawa kimianya yaitu hidroksi etil ester (HEE). HEE disintesis melalui reaksi transesterifikasi minyak sawit (trigliserida) dan 1,2 etanadiol pada suhu 150 °C selama 5 jam serta katalis K_2CO_3. Konversi TG menjadi produk sebesar 72,90%. Karakterisasi menggunakan Gas Chromatography-Mass Spectrometry (GC-MS) menunjukkan bahwa senyawa kimia dalam produk sintesis terdiri dari asam lemak bebas, hidroksi etil ester dan produk samping. Produk yang diperoleh dapat digunakan sebagai bioaditif untuk meningkatkan pelumasan solar.

Kata-kata kunci: *Minyak sawit; Bioadditive; Lubricity Enhancer; Transesterifikasi.*

1. Introduction

The high sulfur content of diesel fuel can cause problems for the environment, where the combustion products of this fuel can produce dangerous oxides gas which can cause acid rain [1]–[3]. Therefore, the sulfur content in diesel fuel must be reduced through a desulfurization process [4]. However, the desulphurization process of diesel fuel has a negative impact, namely decreasing the lubricity ability of the fuel, due to the loss of compounds that are essential for its lubricity ability, such as polyaromatic and polar compounds [5]. The low lubricity properties of diesel fuel can speed up the wear and tear on vehicle engines [6]. The solution that can be applied to overcome this problem is by adding a substance to diesel fuel, which can increase its lubricity ability [7].

Several researchers have previously reported on the compounds that can be used as lubricity improver additives. The lubricity improver additives can be obtained from chemical compounds which have carboxylic acids, amides, alcohols, ether, and esters groups [8]. Among that

several groups of compounds, additives from ester group have more advantages, such as low cost and eco-friendly, because they can be obtained from vegetable oil as raw materials [9]-[10].

The ester additive compound can be made through transesterification reactions of vegetable oils and alcohols to produce Fatty Acid Alkyl Ester (FAAE) compounds. This reaction also requires additional catalysts in it, where the catalysts that are commonly used are alkaline catalysts, such as NaOH and KOH. However, the major problem with using these two catalysts is the amount of soap formed, which can complicate the purification process [11]. Another catalyst that can be used is the potassium carbonate catalyst. The transesterification reaction using this catalyst can produce high esters with a small amount of soap [12].

The lubrication properties of FAAE compounds depend on the fatty acid composition of vegetable oils. Several researchers have previously reported that the longer the hydrocarbon chain and the greater the number of unsaturated bonds of FAAE compounds can provide better lubrication properties [8],[13]. Vegetable oil, which has a dominant proportion of unsaturated fatty acids, is good for use as raw material for making lubricity-enhancing additives. Palm oil contains unsaturated fatty acids such as C16: 1 (0.4%), C18: 1 (40-45%), and C18: 2 (8-10%) [14].

Synthesis of FAAE compounds is generally carried out using simple monohydroxy alcohol compounds, such as methanol and ethanol [15]. FAAE can also be made through the transesterification reaction of polyhydroxy alcohol compounds, such as 1,2-ethanediol to produce a product as a 2-hydroxyethyl ester compound, as shown in **Figure 1**. The presence of the hydroxy group of this compound is believed can provide better lubricity capabilities thanmethyl ester or ethyl ester products. This is referred to the research conducted by Sukjit [16] where the more polar the functional group of a lubricity additive will increase its lubricity ability, in the following order: COOH > CHO > OH > $COOCH_3$ > C = O > C-O-C [13],[16]. However, there is still no information reported regarding the application of 2-hydroxyethyl ester compounds as additives to increase the lubricity of low sulfur diesel fuel.

This study aims to synthesize a lubricant-enhancing bio additive compound 2-hydroxyethyl ester through transesterification of palm oil and 1,2-ethanediol using potassium carbonate as the catalyst. The use of a potassium carbonate catalyst in this study is expected to reduce the soap formed during the transesterification process. Modification of ester groups into hydroxyalkyl ester groups through the use of 1,2-ethanediol compounds in this study is expected to increase the lubricity properties of these ester compounds. The synthesized bioadditive products were monitored using Thin Layer Chromatography (TLC) and characterized using Gas Chromatography coupled by Mass Spectrometer (GC-MS).

2. Method

2.1. Chemicals

Methanol and potassium hydroxide (KOH) were purchased from Merck for materials of Synthesis of Fatty Acid Methyl Ester (FAME). Synthesis of Hydroxy Ethyl Ester (HEE) was used 1,2-ethanediol, potassium carbonate, hydrochloric acid (37%), sodium sulphate anhydrous, ethyl

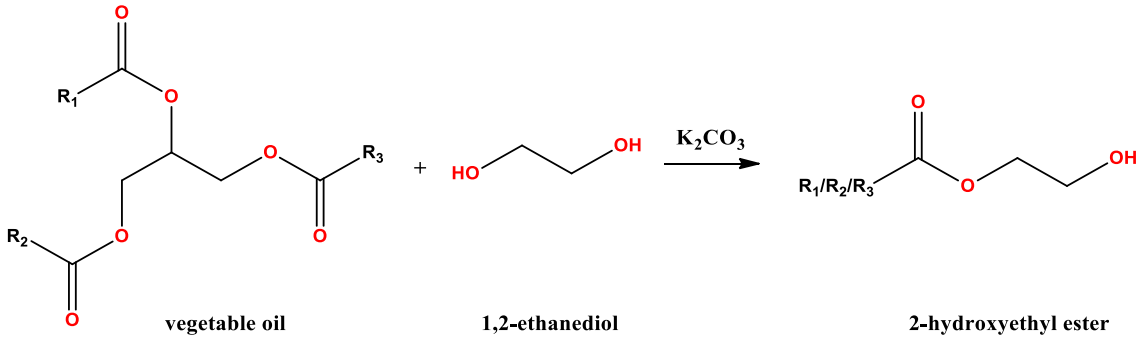

Figure 1. Transesterification reaction of vegetable oil and 1,2-ethanediol using K_2CO_3 to produce 2-hydroxyethyl ester [12].

acetate was from Merck, filter paper Whatman, palm oil and aquadest were purchased commercially. n-Hexane solvent, ethyl acetate, TLC Silica gel 60 F_{254} were from Merck.

2.2. *Fatty Acid Methyl Ester (FAME) synthesis*

The fatty acid compositions of palm oil were determined by GC-MS analysis. First, palm oil has to be changed to its Fatty Acid Methyl Ester (FAME) form through a transesterification reaction. The transesterification method is adapted from Rashid [15]. The transesterification reaction was carried out using simple reflux methods. Palm oil in the 3-necked flask was heated to the set temperature at 60 °C on a magnetic stirrer-heater. Methanol was prepared with a molar ratio of palm oil: methanol (1:6) and KOH as a catalyst (1% mass of palm oil). KOH and methanol were stirred well to prepare methanolic solutions and added into the 3-necked flask. The reaction time was set for 2 hours. The mixture was cooled to room temperature, thus forming two organic layer was separated, then evaporated using a rotary evaporator at temperature 80 °C. The product was washed with aquadest and the organic layer was dried with sodium sulfate anhydrous, followed by filtrating. The product was characterized by GC-MS.

2.3. *Hydroxy Ethyl Ester (HEE) synthesis*

This method is adapted from Rezende [12] and Costa [17]. Palm oil and 1,2 ethanediol with a molar ratio (1:10) and K_2CO_3 8% mol of palm oil were prepared for transesterification reaction using simple reflux methods. Palm oil was poured in the 3-necked flask equipped with a thermometer and a magnetic stirrer, connected with a reflux condenser. Palm oil was heated to 150 °C using a magnetic stirrer-heater with the stirring speed was set at 500 rpm. Catalyst and 1,2-ethanediol were added and the reaction time was set for 5 hours. Then, the mixture product was neutralized with 10% sulphuric acid solutions. This mixture was added to the separating funnel, extracting with ethyl acetate (4x5 mL) and the organic layer was washed with aquadest 70 °C. The organic layer was dried with sodium sulfate anhydrous and then filtrated, followed by evaporating using a rotary evaporator to remove the excess solvent. The synthesis product was monitored by TLC and the chemical compounds of the product were characterized by GC-MS.

2.4. *Instrumental analysis*

The qualitative analysis of the FAME product is using GC-MS 2010 Plus instrument equipped with a Stabilwax-MS with a length of 30 m, an internal diameter of 0.25 mm and a film thickness of 0.25μm. The temperature column was set at 100 °C with an injection temperature of 250 °C. The initial oven temperature was programmed at 100 °C (hold for 4 min.) and increased to 240 °C for 15 min. with a rate of 3 °C/min., following by raised until 250 °C for 2.33 min. with a rate of 10 °C /min. FAME product was prepared by diluted 0.1 mL with 1 mL of n-hexane and 1μL of the mixture was injected into GC column.

The qualitative analysis of the HEE product was carried out by using gas chromatography with a mass spectroscopy detector (GC-MS QP-2020 NX). Rtx-5MS was used as a capillary column with a length of 30 m, an internal diameter of 0.25 mm, and a film thickness of 0.25μm. The initial temperature was set at 70 °C, then increased to 200 °C for 5 min with a rate 10 °C /min, following by raised up until 305 °C for 20 min with a rate of 4 °C /min. HEE product was prepared by diluted 0.1 mL with 1 mL of n-hexane and 1μL of the mixture was injected into the GC column.

2.5. *TLC analysis*

Monitoring HEE product was carried out using TLC analysis and a SiO_2 gel 60 F_{254} TLC plate were used as a stationary phase with n-hexane: ethyl acetate (2:1, v/v) as the mobile phase.

3. Results and Discussion

3.1. *Result*

3.1.1. *Synthesis and characterization of FAME*

FAME as a synthesis product was analyzed by GC-MS. Chromatogram profile from GC-MS analysis was showed in **Figure 2**.

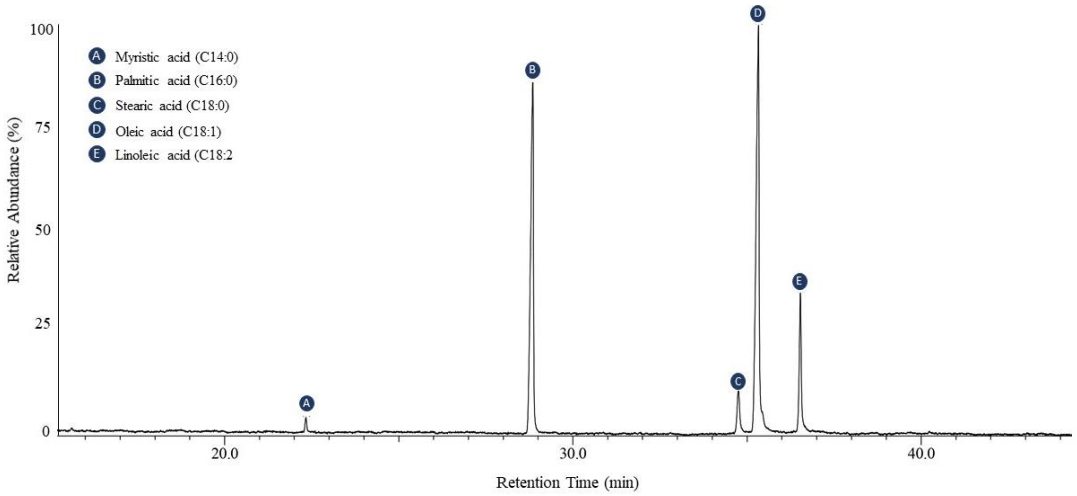

Figure 2. Chromatogram profile of FAME

3.1.2. *Monitoring HEE product by TLC analysis*

HEE as a product synthesis was monitored by TLC and the result was showed in **Figure 3**.

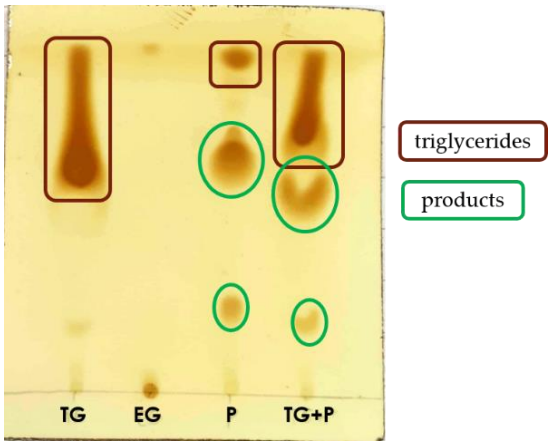

Figure 3. TLC analysis of HEE product

3.1.3. *Characterization of HEE product by GC-MS*

The chromatogram has been given from GC-MS Analysis was shown in **Figure 4** and chemical compounds of HEE product were presented in **Table 2**.

3.2. *Discussion*

3.2.1. *Synthesis and characterization of FAME product with GC-MS*

The fatty acid composition of palm oil was carried out by transesterification reaction, and the product synthesis was characterized using GC-MS analysis. GC-MS analysis was needed to determine the composition of fatty acid in the palm oil. The main composition of fatty acid in the product is palmitic acid, oleic acid, and linoleic acid. This result is similar to a previous study by Shahbazi [18], De and Boxi [19], and Marlina [20]. Shahbazi [18] was reported the fatty acid composition from transesterification palm oil with methanol using KOH catalyst. The main fatty acid composition of the product can be seen as follows: myristic acid (C14:0) is 1.0%, palmitic acid (C16:0) is 42.54%, stearic acid (C18:0) is 4.39%, oleic acid (C18:1) is 39.83%, and linoleic acid (C18:2) is 11.60%. De and Boxi [19] using TiO_2 catalyst to carry out transesterification reaction with methanol. The main composition of FAME product is palmitic acid 35.19%, oleic acid 28.47%, and linoleic acid 7.76%. Marlina [20] also reported the main fatty acid content of crude palm oil with a chemical composition of palmitic acid 40-47%, stearic acid 3-6%, oleic acid 36-44%, and linoleic acid 6-12%. The fatty acid content of this synthesis product has been given in **Table 1**.

Table 1. Fatty acid composition of palm oil

Peak	Relative Concentration (%)	Fatty Acid
A	0.9	Myristic acid (C14:0)
B	37.87	Palmitic acid (C16:0)
C	4.25	Stearic acid (C18:0)
D	45.89	Oleic acid (C18:1)
E	11.09	Linoleic acid (C18:2)

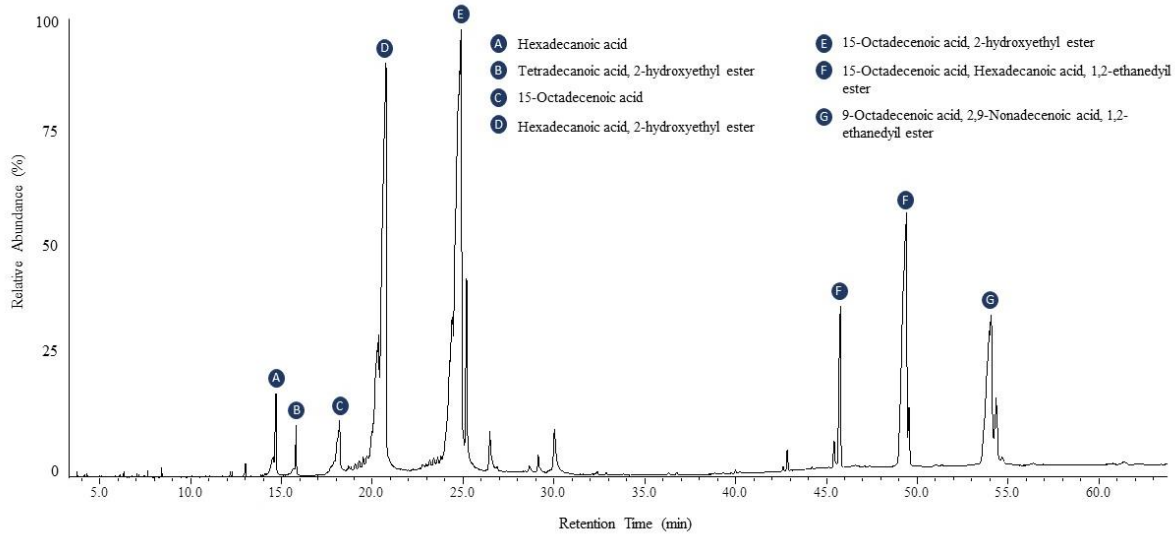

Figure 4. Chromatogram of HEE product

3.2.2. *Synthesis and monitoring HEE product by TLC analysis*

The product from this synthesis method is 14,58 grams from the transesterification process 20 grams of palm oil. This result indicates that the conversion of palm oil into the products is 72,90%. **Figure 3** shows the result of monitoring product synthesis by TLC analysis. According to this analysis, the HEE product was successfully formed because of minimum nodes of TG in P and also formed new nodes in P which have a different position with triglycerides (TG) and 1,2-ethanediol as raw materials. The difference spots in P were affected by the TLC plate and the polarity of the eluent. Because the TLC plate was polar and the eluent was semi-polar, the product which consists of HEE will more difficult to migrate than TG which contains some nonpolar compounds [21].

3.2.3. *Characterization HEE product using GC-MS analysis*

The products which have been predicted from TLC analysis were confirmed by the characterization using GC-MS to determine the chemical compounds of the product. This characterization was based on the peak which has been given in the chromatogram [21]. Figure 4 shows that four main component peaks with a high relative concentration (peak D, E, F, G) than the other peaks. Identification of the chemical structure based on the analysis of its mass spectrum from each peak shows that two peaks (D and E) are HEE compounds that have potency as a diesel lubricity enhancer. Besides, there is consist of two peaks (F and G) as a by-product of this synthesis.

The determination of the compound structure of each peak in the chromatograms has been analyzed based on the mass spectrum. The peak with a retention time of 19.2 minutes has–mass fragmentation patterns with m/z 43, 57, 104 (100%), 117, 239, and 257. The peak with m/z 104 was thought to be HEE, derived from Mc Lafferty rearrangement, as follows **Figure 5**.

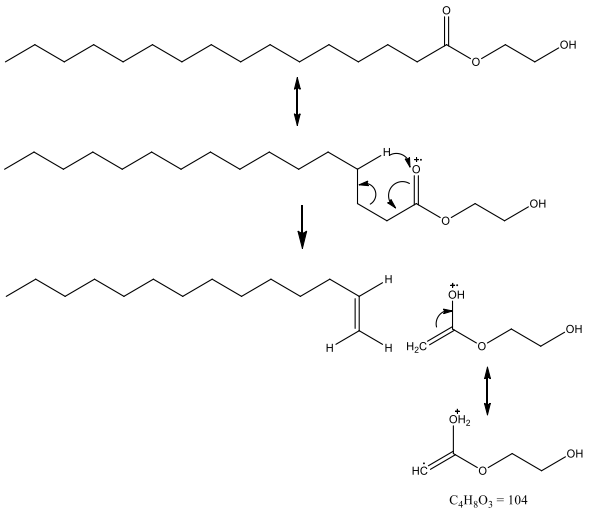

Figure 5. Mc Lafferty rearrangement

Based on mass spectrum analysis, the compound structure which has a high-intensity peak and high percent concentration is hexadecanoic acid, 2-hydroxyethyl ester (peak D), and 15-octadecenoic acid, 2-hydroxyethyl ester (peak E). This result is corresponding with the

main fatty acid of palm oil, consist of palmitic acid (C16:0) and oleic acid (C18:1), which is a major component of palm oil as shown in **Table 1**. This result is similar to previous research by Rezende [12], who reported the main composition of additive products from linoleic oils is 2-hydroxyethyl linoleate with a relative concentration of 54%. Besides, the by-product peaks were identified as 15-octadecenoic acid, hexadecanoic acid, 1,2-ethanediyl ester, and 9-octadecenoic acid, 2,9-nonadecenoic acid, 1,2-ethanediyl ester. This product is commonly named 1,2-ethanediol di-esters. According to a previous study by Attia [22], these compounds are environment-friendly and have the potency to be a bio-additives lubricity enhancer. The chemical compounds of the product can be seen in **Table 2**.

This synthesized hydroxyethyl ester has an unsaturated fatty acid structure on its tail and a hydroxyl (OH) functional group on its head. The hydroxyl group in this ester compound can increase the polarity of the bioadditive compound. The more polar the functional group of a lubricity additive compound, the better its lubrication ability. This compound can interact on the metal substrate through its functional groups, so that the more polar the functional group of a compound, the stronger it will be adsorbed on the surface of the metal being lubricated [16].

4. Conclusion

The HEE compound was successfully synthesized through a transesterification reaction between palm oil and 1,2-ethanediol using K_2CO_3 as a base catalyst. The conversion of triglycerides into the products is 72.90%. The main composition of this product is hexadecanoic acid, 2-hydroxyethyl ester (HEE) and 15-octadecenoic acid, 2-hydroxyethyl ester (HEE) with a identified by-product as a 1,2-ethanediol diesters. The main composition of HEE product has a hydroxy group (OH), so this product has a potency to be better as a diesel lubricity enhancer than biodiesel.

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Author's Declaration

Authors' contributions and responsibilities

The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

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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.

Table 2. The Chemical compound of HEE product

Peak	rt (min)	Relative Concentration (%)	Compound Name
A	14.5	1.41	Hexadecanoic Acid
B	15.7	0.41	Tetradecanoic acid, 2-hydroxyethyl ester
C	18.1	1.42	15-Octadecenoic acid
D	19.2	24.66	Hexadecanoic acid, 2-hydroxyethyl ester
E	22.7	41.88	15-Octadecenoic acid, 2-hydroxyethyl ester
F	45.7	17.88	15-Octadecenoic acid, Hexadecanoic acid, 1,2-ethanedyil ester
G	54.0	12.34	9-Octadecenoic acid, 2,9-Nonadecenoic acid, 1,2-ethanediyl ester

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