Research Article

# Two-Step Reaction for Biodiesel Synthesized from a High-Free Fatty Acid Crude Palm Kernel Oil

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## Abstract
Biodiesel was synthesized through a two-step reaction using crude palm kernel oil with high-free fatty acids (FFAs) and methanol. The two-step reaction involves esterification and transesterification. Esterification was carried out with a variation of $H_2SO_4$ (10%, 15%, and 20% w/v) at 65 °C for 120 min. Esterification produced fatty acid methyl ester (FAME) with an ester content of 67.56%. FAME was used as feedstock for transesterification. Transesterification was carried out with variations in reaction time (120, 180, and 240 min) at 65 °C in addition to NaOH 0.5% (w/w). Transesterification produced biodiesel, glycerol, and soap (side product). Biodiesel was separated using decantation and washing with warm distilled water at 40 °C. The optimum biodiesel was obtained at 180 min with 96.59% ester content. The characteristics of the optimum biodiesel were an FFAs of 0.2 mg KOH/g, iodine value of 20.12 g $I_2$/100 g, density of 0.86 g/mL, kinematic viscosity of 2.51 $mm^2$/s water content of 0.031%, ash content of 0.02%, cetane number of 60.8, flash point of 120 °C. Biodiesel has strong band spectra for C-H on 2,922.70 $cm^{-1}$, C=O on 1,739.38 $cm^{-1}$, C-$H_2$ on 1,460.25 $cm^{-1}$, C-O on 1,197.29 $cm^{-1}$, and O-H on 3,425.10 $cm^{-1}$. In conclusion, a two-step reaction is an effective method to synthesize biodiesel using CPKO with high FFAs as feedstock.

**Keywords**: Biodiesel, Crude palm kernel oil, Esterification, Free fatty acid, Transesterification

## 1 Introduction

The dwindling of petrochemical supplies must be efficiently managed to meet the needs of human life [1]. Many efforts have been made by the government to develop petroleum substitutes for various oil sources, both vegetables [2], [3] and animal [4], such as soybean, corn oil, coconut oil [5], [6], *Aegle marmelos* oil [7], [8], [9], palm oil [10], [11], sheep oil fat [12]. Due to its advantages, biodiesel is becoming more attractive in production [13]. Biodiesel is a renewable biomass energy consisting of a mixture of mono-alkyl esters of medium-long chain fatty acids [14]. Biodiesel must contain ≥ 96.5% ester content to qualify as a high-quality product and can be used as a biofuel or fuel blend [15].

Biodiesel exhibits several advantages over other biofuel products. Biodiesel is a biodegradable compound and non-toxic [16], the production is shorter and easier than petrochemical [11]. Biodiesel

has a shallow sulfur content because it is derived from plant sources and has a much lower sulfur content than fossil fuels [17]. The sulfur content of biodiesel is 0.005% (50 ppm) [15], [18]–[20], while the sulfur content of fossil diesel is 0.1–0.5% (1000–5000 ppm) [21]–[23]. Biodiesel contains more than 10–11% $O_2$ [24], which increases the complete combustion rate of the fuel and reduces the production of pollutants such as total hydrocarbon content (THC), carbon monoxide (CO), and particulate matter (PM) [25]. Biodiesel is regarded as a foremost substitute [3] due to its analogous physical and chemical characteristics to conventional petrochemical diesel fuels [26]. Biodiesel can be used as a direct substitute fuel without any engine modification [8], [27], [28].

Biodiesel is synthesized through esterification or transesterification reactions [29]. Esterification is carried out by reacting fatty acids with methanol at a temperature of 60–75 °C using acid compounds as catalysts [30], such as HCl, $H_2SO_4$, and $CH_3COOH$. Transesterification is carried out by reacting triglycerides and methanol using base catalysts [31], namely NaOH, KOH, and CaO. Since fatty acids are widely used in food, cosmetics, and pharmaceutical industries, and their price is higher than triglycerides [32], transesterification reactions are more desirable for large-scale biodiesel production [33], [34]. Although biodiesel has potential as a new energy source, its development has challenges, certain socio-economic and technological factors limit the large-scale deployment and commercialization of biodiesel. The economic factors of biodiesel production are highly dependent on feedstock prices. Almost 70–95% of total biodiesel production costs are feedstock costs [16], [35]. Production of biodiesel uses three main kinds of triglycerides as feedstock, these include; 1) edible oils, 2) non-edible oils, and 3) extract of microalgae. The production of microalgae on an industrial scale is very expensive, thus non-edible and edible oils have been dominantly considered [36]. Based on the above discussion, triglycerides from vegetable oils, especially palm oil are a potential feedstock for biodiesel production due to their availability.

Palm oil industries are the biggest economic drivers in Southeast Asian countries, such as Indonesia, Malaysia, India and Thailand [37], which account for more than 85% of the global oil palm production. Palm oil industries produce 45,741,845 tons of crude palm oil (CPO) an increase of 2–5% per year [38]. Almost half of CPO is consumed for food, especially cooking oil, margarine, and shortening. The use of CPO as raw material for biodiesel can disrupt food stability. One method of achieving energy sustainability is to utilize non-edible triglycerides in biodiesel production. Crude palm kernel oil (CPKO) is a good example of non-edible palm oil [10]. CPKO is a by-product of the palm oil industry. During the processing process, the flesh of the oil palm fruit is pressed to obtain CPO [39]. Meanwhile, palm kernel is a by-product of the industry. Palm kernel is mechanically pressed to produce CPKO [40]. Each palm oil production process obtains about 45–48% of palm kernel. The substantial CPKO production capacity ensures a reliable supply of raw materials for expanding the biodiesel industry. CPKO is pale yellow, has a low melting point, is non-oxidizable, and is high in saturated fatty acids [41]. CPKO contains 2.48% of capric acid (C8), 2.42% of caprylic acid (C10), 59.83% of lauric acid (C12), and 12.68% of myristic acid (C14) [42]. Based on quantitative analysis, CPKO has a high FFAs of 5.46 mg KOH/g. Industries usually reject it because it is an off-grade quality. This induces CPKO to be more cost-effective than other triglyceride sources [43]. The utilization of CPKO is a solution for feedstock price while increasing its economic value, which has been considered a by-product of the palm oil industry. Feedstocks for biodiesel production should not contain $\geq 1\%$ FFAs to prevent uncontrolled saponification (side product in the form of soap) reactions between base catalysts and FFAs [35]. This side product reduces the quality of the biodiesel that is produced. Because CPKO has a high FFA, it is cheaper than other triglyceride sources. The high FFA in CPKO can be overcome by a two-step reaction and the guaranteed availability makes it attractive for large-scale production.

Previous studies have synthesized biodiesels from various triglycerides: soybean oil [44], sunflower oil [45], linseed oil [46], and corn oil [47]. However, its development towards an industrial scale is difficult due to the high price of feedstocks and their limited production capacity. Therefore, its development to an industrial scale using these is still under consideration. CPKO with high FFAs is a new feedstock for biodiesel synthesis. Developing the biodiesel industry from low-quality and cheaper renewable resources is challenging.

The synthesis of biodiesel through two-step reactions has been developed. Previous research by [44], conducted a two-step reaction for the production of ethyl esters from several triglycerides using NaOH, KOH, (transesterification), and p-toluene sulfonic acid

(esterification) as catalysts followed by a washing process using water-saturated with $CO_2$, and produced an ester content of 92.3%. A similar study by [48], used coconut oil as a source of triglycerides and reduced free fatty acids by 96.5%. Another research synthesized biodiesel from a fatty acid distillate of rice bran oil with a (supercritical-hydrolysis) system and produced an ester content of 93.01% [49]. The previous studies used a toxic group of acid catalysts and required complicated purification. Biodiesel produced from previous studies did not meet ASTM D6751 standards, especially for ester content ($\geq$ 96.5%). This research aims to produce biodiesel with high ester content through a two-stage reaction (esterification-transesterification) using CPKO with high FFA as raw material. The catalysts used were $H_2SO_4$ for esterification and NaOH for transesterification, which were known to have excellent catalytic activity for biodiesel production [50]–[52]. This research has an important urgency in solving the problem of biodiesel feedstock that can be produced from non-edible oil, by utilizing CPKO, which is by-products of the palm oil industry that have low economic value, simple biodiesel purification and effective waste treatment [53]. It is feasible to be developed on an industrial scale.

## 2   Material and Methods

### 2.1   *Material*

CPKO was sourced from PTPN IV, a palm oil processing plant in the Pabatu region, North Sumatra Province, Indonesia. CPKO was stored at a temperature of $\leq$ 27 °C to FFAs avoid increasing the FFAs during the study. The increase in FFAs is due to hydrolysis reactions by natural enzymes present in CPKO. Other reagents i.e. methanol, $H_2SO_4$, and NaOH were analytical grade. The characteristics of CPKO used in the study [54], are shown in Table 1.

**Table 1**: Characteristics of crude palm kernel oil from North Sumatera Province, Indonesia.

| Properties | Result |
|---|---|
| Free Fatty Acids (mg KOH/g) | 5.46 |
| Saponification value (mg KOH/g) | 248.78 |
| Water content (%) | 0.15 |
| Impurities (%) | 0.04 |
| Viscosity (mm²/s) | 31.94 |
| Density (g/mL) | 0.91 |

### 2.2   *Biodiesel Synthesis*

#### 2.2.1   *Step-1: Esterification*

The experiment was conducted in a 500 mL flat-bottomed glass reactor, equipped with a heater and magnetic stirrer, a circular water condenser, and a thermocouple. A total of 150 g CPKO and 65 mL methanol were reacted with adding $H_2SO_4$ as an acid catalyst. The reaction lasted for 120 min, with a stirrer rotation of 450 rpm. The reaction temperature was maintained constant at 65 °C. The addition of $H_2SO_4$ was carried out when the reaction temperature reached 65 °C. The acid catalyst of $H_2SO_4$ was slowly added to avoid exothermal reaction conditions. After 120 min, the fatty acid methyl ester (FAME) was obtained on the top layer and the bottom layer was $H_2O$ (by-product) mixed with $H_2SO_4$. FAME was separated from the reaction mixture by the decantation method. During the reaction, sampling was conducted every 15 min for FFA analysis. The concentration of $H_2SO_4$ varied from 10%, 15%, and 20% (w/v) based on the initial amount of CPKO. Gas chromatography (GC) was used to analyze FAME to determine the ester content. FAME with the highest ester content is used as feedstock in step-2 (transesterification).

#### 2.2.2   *Step-2: Transesterification*

A total of 150 g FAME (from esterification) was reacted with a 65 mL methoxide solution. The methoxide solution was prepared from 65 mL of methanol and 0.5% (w/w) of NaOH as a base catalyst (based on the initial amount of FAME). The reaction temperature was maintained constant at 65 °C using a circular water condenser and thermocouple. With a stirrer rotation of 400 rpm. After the reaction time was completed, crude biodiesel, crude glycerol, and a small amount of soap were obtained. The crude biodiesel was in the upper layer and crude glycerol was in the lower layer, which was separated by decantation. During the reaction, FFAs were measured every 15 min. The reaction time was varied for 120, 180, and 240 min.

#### 2.2.3   *Purification of Biodiesel*

The crude biodiesel from the transesterification step continued to the purification. The crude biodiesel is washed with 40 °C distilled water 3–4 times (until the washing water is clear). The washing aims to separate the NaOH catalyst (in the form of soap) remaining in

the biodiesel. The biodiesel was evaporated at 105 °C to evaporate the washing water residue from the washing stage. Next, the product was analyzed to determine the ester content in the biodiesel using gas chromatography.

### 2.2.4 Determination of ester content in biodiesel

0.05 g sample of biodiesel was prepared, added with 100 mL of trycaprin and 100 mL of n-methyl-n-trimethylsilyltriflouro acetamide (MSTFA), and then homogenized. Then, 1 mL tetrahydrofuran (THF) was add and vortex for 1 min, then let it stand for 10 min in a dark room. After that, 2.5 mL of n-heptane was added, then vortexed the sample for 1 min. The top layer (supernatant) was injected into a gas chromatograph (GC) 2010 Plus, Shimadzu Corp, Kyoto-Japan with a C8-C22 standard fatty acid methyl ester mixture obtained from Sigma Aldrich. An open-tube fused silica column coated with SP 2340 (60 m x 0.25 mm) was used. The column was heated to 120–185 °C with a temperature increase of 3 °C.min$^{-1}$. The injector and detector were set at 240 °C. Helium (He) was used as carrier gas at a flow rate of 0.8 mL.min$^{-1}$, with nitrogen ($N_2$) at 30 mL.min$^{-1}$ [55].

### 2.2.5 Characterization of biodiesel

Characteristics of biodiesel include free fatty acid, iodine value, water content, density, viscosity, ash content, cetane number, and flash point [4]. The main functional groups of the biodiesel were analyzed using a spectrophotometer-FTIR Prestige IR21 Shimadzu. Spectra were collected in the infrared region range of 400 to 4,000 cm$^{-1}$ [56]. CPKO was used as a comparison, to identify the functional groups formed after the esterification and transesterification reactions were completed.
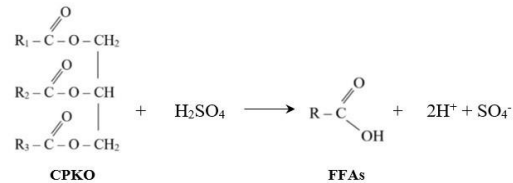
## 3 Result and Discussion

### 3.1 Step-1: Effect of $H_2SO_4$ concentration on FFAs reduction in esterification

CPKO was reacted with methanol by adding $H_2SO_4$ as an acid catalyst. The reaction was carried out at 65 °C for 120 min, based on the boiling point of methanol. The reactivity of $H_2SO_4$ acid is higher than other inorganic acids because it has $2H^+$ ions. As a catalyst, $H_2SO_4$ plays an important part in accelerating the esterification reaction. In the beginning, $H_2SO_4$ hydrolyses CPKO into FFAs before converting to FAME. The following is the mechanism of the esterification reaction.
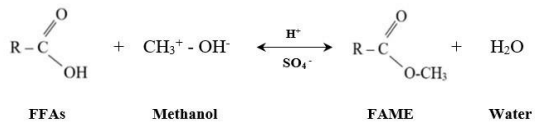


**Figure 1**: Mechanism of esterification between CPKO with high FFAs and methanol using $H_2SO_4$.

The use of $H_2SO_4$ is known to increase the collision speed of methanol and fatty acid molecules with each other. This collision speed can be measured quantitatively through a decrease in FFAs. The decrease in FFAs linearly indicates the amount of fatty acids converted to alkyl esters. The quantity of $H_2SO_4$ used affects the FFA content during the reaction. In the production of biodiesel, FFAs demonstrate the presence of carboxylic acid that is unbound from the triglyceride molecule. The presence of FFAs can interfere with the transesterification reaction thus reducing the characteristics of biodiesel. High FFAs will form soap in the transesterification reaction. Esterification is the initial pre-treatment to reduce FFAs of CPKO, before proceeding to transesterification reaction.

The esterification reaction is an equilibrium reaction. The reaction is slow, therefore excess methanol is needed to push the reaction to completion. According to the stoichiometry of the reaction, 1 mole of methanol is required to convert 1 mole of triglyceride into FAME (Figure 1). The use of excess methanol is essential for the activity of $H_2SO_4$ to bind the water formed during the esterification reaction. The equilibrium limit due to the reversibility of the reaction can be driven to the right of the reaction [57]. Therefore, at the end of the esterification reaction, a homogeneous mixture of $H_2SO_4$ and water is obtained. The esterification focuses on the effect of $H_2SO_4$ concentration on FFA reduction, as shown below.
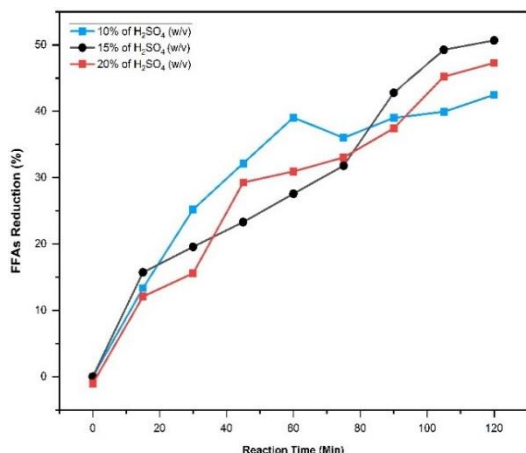
**Figure 2**: Effect of $H_2SO_4$ concentration on free fatty acids reduction during esterification reaction.

Based on the analysis results (Figure 2), it is known that the decrease in FFAs is influenced by the concentration of $H_2SO_4$ added in the esterification reaction. The concentration of $H_2SO_4$ used affects the hydrolysis reaction rate of CPKO into fatty acids and glycerol, and then fatty acids are converted into FAME [58]. The same research results reported, that the use of $H_2SO_4$ as a catalyst in the esterification reaction facilitates the reaction toward to direction [59], and reduces FFAs so that high ester content is obtained [60].

The highest FFA reduction was achieved at a concentration of $H_2SO_4$ 15% (w/v), and the lowest FFA reduction was respectively at $H_2SO_4$ concentrations at 20% and 10%. The use of $H_2SO_4$ concentration above 15% (w/v), has driven the reaction towards the reactants. This was identified by lower FFA reduction at a concentration of $H_2SO_4$ 20% (w/v), compared to a concentration of $H_2SO_4$ 15% (w/v). An excess of $H_2SO_4$ concentration leads to a slow reduction in FFAs, due to two factors: 1) the formation of dimethyl sulfate as a result of the reaction between $H_2SO_4$ and methanol ($2CH_3OH + H_2SO_4 \rightarrow (CH_3O)_2SO_2 + 2H_2O$) [61]; 2) the hydrolysis reaction between CPKO and water (which is combined with $H_2SO_4$) increases FFAs and glycerol. The FFAs and glycerol become more difficult to separate as the rate of transesterification and saponification is hindered by the high concentration of acid catalyst [62].

Excess sulfuric acid and NaOH can give rise to a neutralization reaction, so the reactivity of NaOH decreases in catalyzing the transesterification reaction. Furthermore, the reaction between excess $H_2SO_4$ and organic compounds also results in a change in the color of the reaction mixture, which becomes darker (brownish-green). The color of the final biodiesel produced is also darker, even though it has passed the purification stage. The transesterification reaction is carried out in stages after esterification is complete. It is only used FAME with optimum ester content as feedstock. The following is the GC chromatogram of FAME to determine the ester content successfully converted from CPKO.
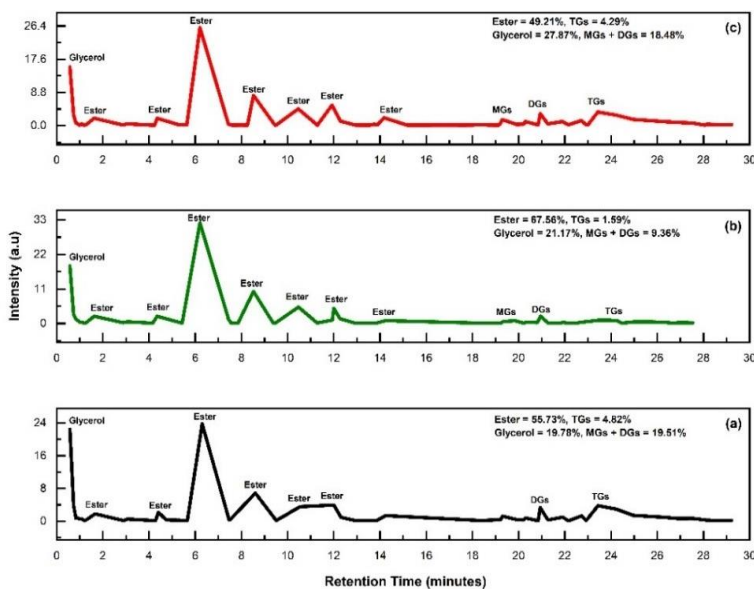


**Figure 3**: GC chromatogram of FAME at different concentrations of $H_2SO_4$. (a) 10% w/v, (b) 15% w/v, (c) 20% w/v.

The GC chromatogram (Figure 3) demonstrates that the ester content is significantly influenced by the concentration of $H_2SO_4$ used in the esterification reaction. At a concentration of $H_2SO_4$ 10% (w/v), the ester content was 49.21%. While at a concentration of $H_2SO_4$ 20% (w/v), the ester content was 55.73% after 120 min reaction time. Following the results of the qualitative analysis, which indicated that the lowest FFAs reduction was achieved at a concentration of $H_2SO_4$ 15% (w/v), the optimum ester content was attained under these reaction conditions with a value of 67.56%. FAME from CPKO contains medium-long chain mono-glycerides (MGs) and di-glycerides (DGs), which are not commonly found in other products.

The result of the gas chromatography (GC) analysis indicated that the retention times ($t_R$) for the mono-myristate = 15.18 min, mono-palmitate $t_R$ = 17.29 min, mono-stearate $t_R$ = 18.37 min, mono-oleic $t_R$ = 19.12 min, and mono-linoleic esters $t_R$ = 20.20 min [63]. The FAME also exhibited a high glycerol content, which was detected at 0.57–0.87 min [64]. According to the stoichiometry of the esterification reaction, $H_2O$ is generated as a by-product. The presence of $H_2O$ in the reaction mixture results in the hydrolysis of CPKO, which produces fatty acids and glycerol. Therefore, the higher the concentration of $H_2SO_4$ used, the higher the c of glycerol produced. In the esterification reaction, triglycerides are hydrolyzed into fatty acids in an acidic system before being converted into methyl esters. The greater the number of $H_2SO_4$ molecules that bind water, the greater the chance of hydrolysis reactions [49].

Many biodiesel industries perform esterification reactions using $H_2SO_4$ as an acid catalyst to reduce FFA from low-quality triglycerides. $H_2SO_4$ is regarded as a more reactive form of strong acid than other analogous compounds. Despite its classification as hazardous and toxic waste, $H_2SO_4$ is relatively straightforward to handle compared to other chemical wastes. Following the esterification reaction, the industry frequently performs a transesterification reaction. Transesterification typically involves the use of base catalysts, such as NaOH, KOH, CaO, and $CaCO_3$. In practice, industries often utilize the base-containing waste stream from the transesterification reaction to neutralize the acid-containing waste from the esterification stage. This approach facilitates subsequent waste treatment before the waste is returned to the environment [53].

## 3.2 Step-2: Effect of reaction time on FFAs reduction in transesterification.

The transesterification process involves the conversion of triglycerides into an ester and glycerol in the presence of methanol and NaOH as a catalyst, as illustrated in Figure 4 below. In this study, transesterification aims to enhance the probability of obtaining a higher ester content. FAME was reacted with methanol as an acyl donor at 65 °C by adding NaOH 0.5% (w/w). Formation of methoxide ions (methanol and NaOH), being the breaking agent of carbonyl bonds into alkyl esters, which improves the chemical reaction kinetics during the transesterification process [65]. Previous studies have reported that the NaOH concentration to produce optimum esters is 0.5–1.5% (w/w) [66]. The ratio of CPKO: methanol used was 1:10 (mole) for all experiments. Methanol has one carbon bond, which makes it more stable than medium or long-chain alcohols. The polarity of methanol is higher than other alcohols. It is easily reacted with triglycerides converted to biodiesel. Three molecules of methanol are needed for one molecule of triglycerides to obtain an equilibrium reaction, following the following mechanism to convert one triglyceride molecule.
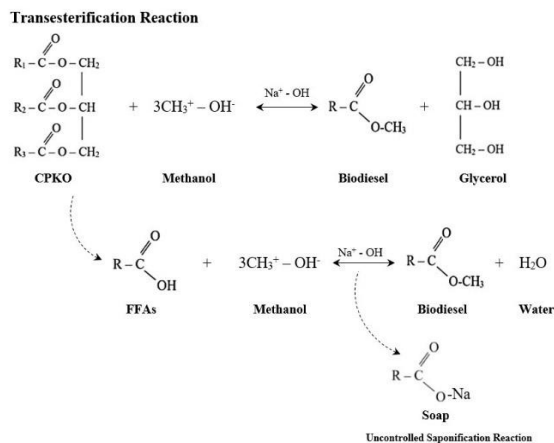


**Figure 4**: Mechanism of transesterification between CPKO with high free fatty acid and methanol using NaOH as base catalyst.

Besides biodiesel and crude glycerol as a by-product, a small amount of soap is also obtained. The reaction mixture was easily separated into two layers when the reaction was complete. The biodiesel is in the first layer, and the glycerol is in the second layer. This is due to the difference in density between

biodiesel and crude glycerol [67]. Biodiesel has a density of 0.5 g/mL and glycerol of 1.26 g/mL. At this stage, biodiesel still contains soap and is purified in the purification. Soap usually comes from an uncontrolled saponification reaction between FFAs and NaOH. Even in small amounts, soap will always appear [68]. FFAs are an internal factor derived from the feedstock. Although the internal factors are hard to control, pre-treatment can overcome them. The $H_2SO_4$ catalyst ratio and reaction time are external factors that affect the product characteristics. External factors are easier to control than internal factors. The effect of reaction time for transesterification is shown in Figure 5 below.
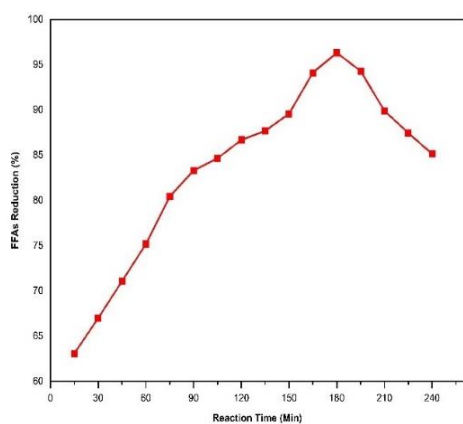


**Figure 5**: Effect of time reaction on free fatty acids reduction during transesterification reaction.

An increase in the reaction time provides a greater opportunity for collisions between reactant particles to occur. The longer the contact between the reactant particles, the higher the FFA reduction. This is applicable when the equilibrium reaction is reached within the reaction time range. The concentration of reactants and products is present in equal concentration. In this condition, the quantity of reactants and products no longer changes, so the increase in reaction time does not affect the decrease in FFAs. The reaction temperature influences the selection of the reaction time at 120, 180, and 240 min. It is necessary to utilize longer reaction times when employing temperatures below 65 °C to facilitate the conversion of fatty acids into esters.

Based on Figure 5 shows that the percentage reduction of FFAs increased consistently from the beginning of the transesterification reaction, regardless of the different reaction time treatments. The initial FFAs of FAME was 60.4%. After the

reaction had been running for 15 min, there was a decrease in FFAs to 56.87%. As with the esterification reaction, the decrease in FFAs is linear to the amount of fatty acids in CPKO that are hydrolyzed and converted into esters [5].

The decrease in FFAs from biodiesels initially increased until it reached an optimum value and then began to decrease. The decrease in FFAs occurred throughout the reaction time range of 120–180 min. When the reaction time was extended to 240 min, the decline in FFAs decelerated and tended toward stationary equilibrium [69]. FFA analysis at 210 min indicated higher FFAs than that observed at 180 min. This suggests that the equilibrium has driven from the products towards the reactants. It is characterized by a lower decrease in FFAs compared to the 180-minute reaction time. This indicates that the reaction equilibrium has occurred at 180 min with a percentage decrease in FFAs of 96.34% (initial FFAs of CPKO at 5.46 mg KOH/g). In this condition, increasing the reaction time cannot increase the ester content. The CPKO has gradually converted, with the formation of 2 layers, as shown in Figure 6, below.
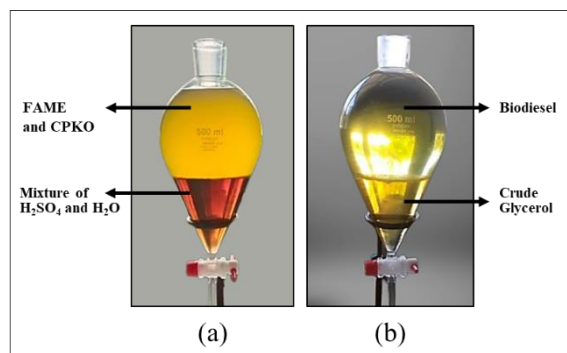


**Figure 6**: Separation process. (a) FAME from esterification, (b) biodiesel from transesterification.

The chemical reaction of transesterification involves the progressive conversion of triglycerides into DGs, then MGs, and finally glycerol. This molecular transformation results in a major decrease in the viscosity of CPKO [70]. The fatty acid chains in CPKO are gradually hydrolyzed before being converted into ester compounds. DGs and MGs molecules form after cleavage of one to two fatty acid acyl chains of triglycerides. When one to two fatty acid acyl chains of triglycerides are cleaved, DGs and MGs molecules are formed. After the third fatty acid acyl chain is cleaved, the fatty acid binds to a methyl group to form a biodiesel. Transesterification occurs

under excess methanol concentration conditions, with CPKO acting as the limiting reactant. This approach increases the conversion of reactants in a relatively short reaction. Triglycerides are derived from three hydroxyl groups of glycerol attached to fatty acids. Therefore, transesterification uses at least three moles of methanol for each mole of triglyceride (Figure 4).

The results of the GC analysis were in agreement with the FFAs analysis. The GC chromatogram (Figure 7) shows that the reaction time affects the ester content. At a reaction time of 120 min, the ester content was 84.91%, unreacted CPKO detected as TGs was 1.21%, MGs was 2.57% and glycerol was 8.87%. In this treatment, a higher glycerol content was obtained compared to the other reaction time treatments. This glycerol is bound to the biodiesel and is difficult to separate by decantation and purification. On the other hand, the use of 180 min of reaction time is known to increase the ester content. The highest

ester peak was detected under these reaction conditions, which was detected at $t_R$ = 6.08 min. The ester content reached an optimum of 96.59%. The quantity of TGs was 0.35%, glycerol 0.64%, and mono-diglycerides (MGDs) was 2.02% (MGs = 1.16%, DGs = 0.86%). The opposite was observed at a reaction time of up to 240 min, which showed a decrease in ester content. This treatment gave an ester content of 79.01%, TGs of 3.07%, glycerol of 4.37%, and MGDs was 13.36% (MGs = 2.47%, DGs = 10.89%). This confirms that the use of a reaction time greater than 180 min causes a reversible reaction. Ester compounds react with glycerol to form glycerol esters which interfere with the transesterification reaction and increase the FFAs. In each experiment, glycerol was the first compound detected at $t_R$ = 0.96 minutes. Ester compounds started to be detected at $t_R$ = ± 1.05–14.01 min, followed by MGs, DGs, and TGs detected at $t_R$ = 16.78 min, $t_R$ = 21.17 min, and $t_R$ = 25.24 min, respectively.
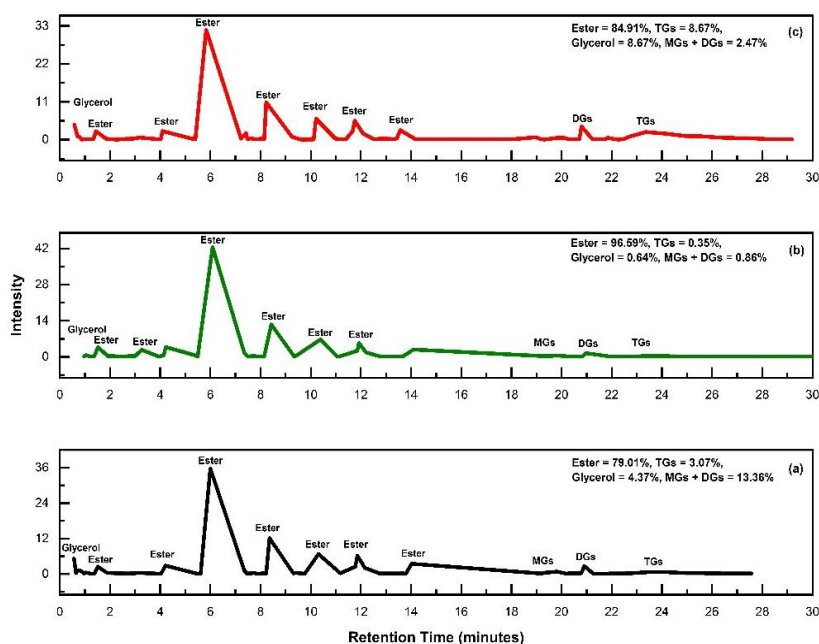


**Figure 7**: GC chromatogram of biodiesel from CPKO at different time reactions. (a) 120 min, (b) 180 min, (c) 240 min.

Glycerol has a higher polarity than biodiesels, MGs, DGs, and TGs, so it is more easily fragmented than other compounds, and it is detected as the first peak at the GC chromatogram [71]. MGs and DGs compounds always appear in the synthesis of biodiesels from triglycerides because they are intermediates formed during transesterification. The formation of MGs and DGs can be an indicator of the

reaction speed in biodiesel synthesis. Total MGs and DGs in commercial biodiesel should not exceed 0.8%, as it can reduce the quality of biodiesel [15], [49]. Based on the results, the synthesis of biodiesel through a two-stage reaction has reduced 96.34% of FFAs and converted it into ester compounds, with total MGs and DGs 0.86%. The MGs and DGs content slightly exceeded the limit set by ASTM D6751 of 0.4–0.8%

for B100 (biodiesel 100%) applied directly as fuel [15], [72]. Several studies have reported that high MGs have a negative impact on the use of biodiesel in low-temperature, as biodiesel causes deposits in diesel engines [73]–[75]. However, this requirement is lowered when biodiesel is used as a blended fuel with fossil fuels. The proposed upper limits for MG content in substitution biodiesel are B30 (0.42–0.62%), B20 (0.51–0.62%), and B10 (0.33–0.51%), respectively [76]. It helps to reduce the use of fossil fuels whose availability is increasingly limited [77].

### 3.3 *Product purification*

Purification is carried out to obtain pure biodiesel. The biodiesel is washed using distilled water (50 °C) to remove residual NaOH catalyst (in the form of soap) or other impurities [78]. Soap must be removed, as it increases the viscosity of the biodiesel and hinders glycerol separation [79]. The washing step is done repeatedly until the washing water does not contain soap (the washing water has been clear). To remove bound water or water from the remaining washing, evaporation is carried out at a temperature of 110 ºC using a vacuum rotary evaporator with a pressure of 420 mmHg. The evaporation of water is very important to protect biodiesel from molecule breakdown. This is due to oxidation or hydrolysis reactions during the study. During storage, $Na_2SO_4$ was added to the biodiesel to absorb the bound water that could not be removed through the evaporation process.

Previous research has demonstrated that washing biodiesels using warm distilled water is more effective than washing with ethanol or HCl [44]. This procedure allows for the removal of soap without the formation of FFAs. In this study, the biodiesel synthesized from CPKO has good characteristics. It has a clear bright yellow color because CPKO contains a small quantity of carotene. In contrast, biodiesel derived from CPO has a reddish-orange color because it contains higher carotene than CPKO. The resulting biodiesel from this study does not form fatty solids at room temperature or below, despite the high saturated fatty acid content of CPKO. Saturated fatty acids consist of capric, caprylic, lauric, and myristic acids which have several carbon chains from 8 to 12 (medium). This indicates that the saturated fatty acids have been completely converted into biodiesels, which is reinforced by the low FFAs of 0.2 mg KOH/g in biodiesel. In step-2 (transesterification), the ester content of the biodiesel is determined using GC analysis after the purification is completed.

### 3.4 *Characteristics of biodiesel*

Today, biodiesel is employed in a biofuel mixture in B30, B20, and B10 forms. Several organizations have established standards for the physical and chemical properties of biodiesel, including ASTM D6751 [15] and SNI 7182:2015 [80]. The objective is to ensure that biodiesel produced from different sources of fatty acids and triglycerides (vegetables or animals) has similar characteristics. Therefore, when it is used as a fuel or blended fuel in a diesel engine, the biodiesel will have the same performance characteristics. The characteristics of biodiesel synthesized from CPKO through a two-step reaction are shown in Table 2.

**Table 2**: Physical and chemical characteristics of biodiesel.

| Properties | Biodiesel (synthesis) | ASTM D6751 |
|---|---|---|
| FFA (mg KOH/g) | 0.2 | 0.5 |
| Iodine value (g $I_2$/100) | 20.12 | - |
| Density (g/mL) | 0.86 | 0.87–0.9 |
| Kinematic viscosity ($mm^2$/s) | 2.51 | 1.9–6 |
| Water content (%) | 0.031 | - |
| Ash content (%) | 0.02 | 0.02 |
| Cetana number | 60.8 | $\geq 47$ |
| Flash point | 120 | 100 |

#### 3.4.1 *Free fatty acid*

The FFAs are the number of milligrams of KOH required to neutralize FFAs in 1 g of triglycerides. A high FFA indicates that many fatty acids in CPKO are not converted into biodiesel. The results showed that the biodiesel had a low FFAs of 0.2 mg KOH/g (FFAs max = 0.5 mg KOH/g).

#### 3.4.2 *Iodine value*

The iodine value expresses the number of grams of iodine absorbed in 1 g of triglyceride. This parameter indicates the degree of unsaturation of a compound. The amount of iodine bound then shows the number of double bonds the biodiesel has (unsaturated fatty acid). The higher the iodine value, the more unstable the biodiesel, as double bonds are unstable and thus easily broken. The optimum biodiesel has a low iodine value of 20.12 g $I_2$/100 g (max 115 g $I_2$/100) [80].

#### 3.4.3 *Density*

Density is the ratio of the mass of a compound to its volume. Density is one of the most important physical characteristics and is often used to identify a compound.

The density of CPKO is 0.91 g/mL, and the density of biodiesel is 0.86 g/mL. According to ASTM D6751, the density of biodiesel at 0.85–0.89 g/mL [15].

### 3.4.4 Kinematic viscosity

CPKO has a high viscosity of 31.94 mm$^2$/s. After conversion to biodiesel, the viscosity decreased to 2.51 mm$^2$/s. Esterification and transesterification reactions can reduce the viscosity of CPKO. Viscosity and density are closely related to the viscosity of a liquid and indicate the shear ability of a fluid over the surface of another fluid. Thus, a fluid with a lower viscosity has the opportunity to mix more easily with other fluids. The ASTM D6751 defines 2.3–6.0 mm$^2$/s for kinematic viscosity.

### 3.4.5 Water content

Water content is the amount of water bound in the methine ester. Water content is one of the factors that affect enzymatic reactions in further synthesis. Therefore, the water content of the biodiesel must be minimal. Although the lipase enzyme needs water for its metabolism, there is a limit to the water content that can be tolerated by the lipase enzyme. The water content of biodiesel is 0.031%, while the initial CPKO water content is 0.148%.

### 3.4.6 Ash content

Ash content is the residual inorganic material from the combustion or complete oxidation of organic material components. Measuring ash content provides valuable information about the quality of the biodiesel. High ash content in materials can cause air pollution because many inorganic and organic particles remain after the combustion process is complete. CPKO has a very low impurities content of 0.04% and therefore does not influence the ash content. The analysis results confirm that the biodiesel synthesized from CPKO has an ash content of 0.02% and meets the ASTM D6751.

### 3.4.7 Cetane number

The characteristics of biodiesels are sufficiently similar to those of biofuels that they can be employed as substitutes for petroleum diesel. All fossil fuels are classified according to their cetane number [81]. Cetane number (CN) is a parameter used to measure the ease with a compound, which ignites in a combustion chamber. In general, the higher the CN, the faster it ignites and produces more power. The CN of biodiesel has met the ASTM D6751 standard of 60.8. The CN was determined using the following Equation (1) [82]:

$$CN = 46.3 + \left(\frac{5.458}{SV}\right) - 0.225 \text{ x IV} \qquad (1)$$

The saponification value (SV) for biodiesel was 298.12 mg KOH/g, which is higher than CPKO. This confirms that the FFAs, MGs, DGs, and TGs in the sample of biodiesel were very low.

### 3.4.8 Flash Point

The flash point is the lowest temperature at which the biodiesel can ignite for the first time, without continuing to burn [83]. The optimum flash point of biodiesel is 120 °C (min 100 °C).

Based on the analysis of physical and chemical characteristics that have been carried out, biodiesel has met ASTM D6751 and SNI 7128:2015 for use as B30, B20, and B10 fuels.

### 3.5 Functional group

The physical and chemical characteristics of the biodiesel produced were supported through functional group analysis, to accurately detect the structure of biodiesel synthesis from CPKO. The infrared spectra of biodiesel and CPKO are compared, and shown in Figure 8. The strong band at 1,739.38 cm$^{-1}$ is typical for the C=O carbonyl group. The characteristic bands of esters appear in the strong absorption region, detected at 1,197.29 cm$^{-1}$, 1,168.37 cm$^{-1}$, and 1,113.69 cm$^{-1}$. A broad stretching vibration of the alkene group (-CH$_2$)$_n$ was detected at 728.36 cm$^{-1}$. This alkene group is derived from unsaturated fatty acids converted to biodiesel. The bending vibration of the C-H$_3$ group detected at 1,460.25 cm$^{-1}$ is dedicated to methyl groups derived from methanol. While the C-H$_2$ group was detected at 1,362.66 cm$^{-1}$, and the C-C group was detected at 876.86 cm$^{-1}$. These three peaks originate from the stretching of the O-CH$_3$ methyl group which proves the presence of fatty acid-derived biodiesels [84]. The sharp and strong peaks of C-H absorption were at 2,922.70 cm$^{-1}$, and 2,853.76 cm$^{-1}$, which came from saturated fatty acids that converted to biodiesels. Meanwhile, vibrations of the C-O-C group were detected at 1,029.49 cm$^{-1}$. This spectrum is in the fingerprint region, a definitive characteristic of palm oil-derived products [85].

The FTIR results matched those of the GC analysis, confirming the presence of MGs and DGs compounds at 2.02% and the presence of the C-O-C group. The peak absorption region of 3,425.10 cm⁻¹ is usually associated with the O-H band which is thought to be derived from unconverted FFAs and bound glycerol contained in the biodiesel [14]. Similar results have been reported in an earlier study on the production of biodiesel from palm oil sludge using alum and KOH as a catalyst [66]; preparation of fatty acid esters from medium and long-chain fatty acids for bio-plasticizers [86], and synthesis of FAME sulfonate from ketapang seed oil and methanol through transesterification reaction for 4.5 h of reaction time [87]. The functional groups of biodiesels have similarities with CPKO because it is synthesized directly from CPKO. The typical characteristics of CPKO are still attached to the final product. CPKO does not have an O-H group because it is a non-polar compound.

The main functional groups of CPKO are C-H, C=O, C-O, C-$H_2$, and C-$H_3$, and (C-$H_2$)n was detected with strong bands derived from saturated and unsaturated fatty acids. This characterizes that CPKO consists of a mixture of fatty acids. These functional groups appear in biodiesel which confirms the characteristics of the derived product. Meanwhile, C-O-C and C-C groups do not appear in CPKO. These two groups are the distinguishing indicators between CPKO and biodiesel. The C-O-C and C-C functional groups appear at wave numbers 1,000–400 cm⁻¹. In this wave number range, all organic compounds have unique absorbance as their characteristic, including biodiesel. The following is a tabulation of the biodiesel and CPKO spectra bands in Table 3.

**Table 3**: Wave number of biodiesel and CPKO.

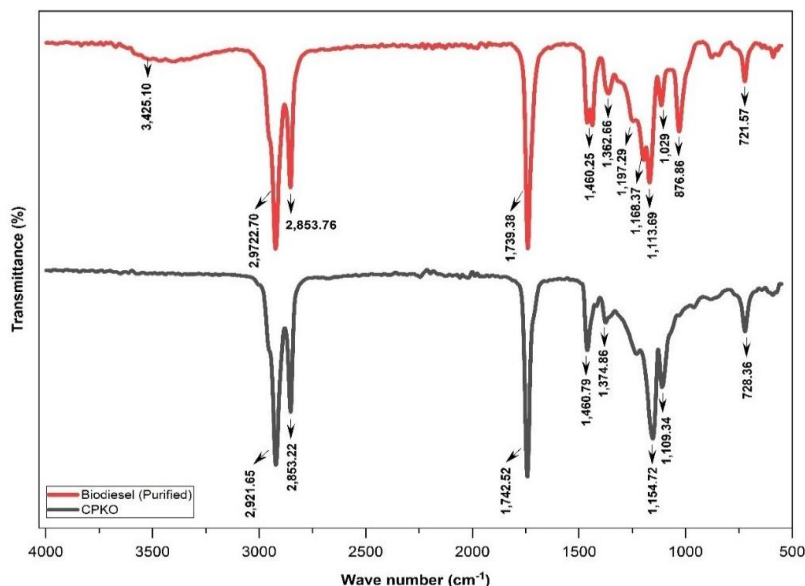| Functional Group | Wave Number (cm⁻¹) | |
|---|---|---|
| | **Biodiesel** | **CPKO** |
| C – H | 2,922.70 | 2,921.65 |
| | 2,853,76 | 2,853.22 |
| C = O | 1,739.38 | 1,742.52 |
| C – O | 1,197.29 | 1,154.72 |
| | 1,168.37 | 1,109.34 |
| | 1,113.69 | |
| C – $H_2$ | 1,460.25 | 1,460.79 |
| C – $H_3$ | 1,362.66 | 1,374.86 |
| C – O – C | 1,029 | - |
| C – C | 876.86 | - |
| (C – $H_2$)ₙ | 721.57 | 728.36 |
| O – H | 3,425.10 | - |



**Figure 8**: Comparison of infrared wavelength spectra. (a) CPKO, (b) Biodiesel (Purified).

## 4 Conclusions

The experiments successfully synthesized biodiesel from CPKO, which has a high FFAs of 5.46 mg KOH/g, through a two-step reaction. The optimum biodiesel with an ester content of 96.59% was obtained under the following reaction conditions: Step 1: Esterification ($H_2SO_4$ 15% w/v, temperature at 65 °C, reaction time at 120 min), Step 2: Transesterification (NaOH 0.5% (w/w), temperature at 65 °C, reaction

time at 180 min). In the esterification reaction, the utilization of $H_2SO_4$ concentration greatly affects the decrease in FFAs. The use of $H_2SO_4$ concentration at 10% (w/v) decreased FFA by 42.5%, while $H_2SO_4$ concentration at 20% (w/v) gave a decrease in FFA by 50.7%. The concentration of $H_2SO_4$ affects the rate of esterification reaction, so the acid catalyst must be applied at the correct concentration to reduce FFA optimally. While in the transesterification reaction, the reaction time above 180 min causes a reversible reaction, because almost all FAME and fatty acids have been converted into biodiesel. at this condition, increasing the reaction time is no longer beneficial to increase the ester content. Based on physical and chemical property analyses, the biodiesel produced by the two-step reaction has been shown to meet the standards set out in ASTM D6751. The physical and chemical properties of biodiesels have been shown to fulfill the standards in ASTM D6751 and SNI 7128:2015. This has been confirmed through spectrophotometer-FTIR analysis, which has revealed the presence of the main functional groups, including C-H, C=O, C-O, C-$H_2$, C-$H_3$, C-O-C, (C-$H_2$)n, C-C and O-H. The carbonyl C-O group and the C=O ester group show high wave number intensity and sharp peaks, which indicates that biodiesel has a high ester content.

## Acknowledgments

## Author Contributions

E.K.: writing – review & editing, writing – original draft, methodology, data curation, conceptualization; R.R.: writing – review & editing, validation, supervision, resources, methodology, data curation, conceptualization; M.D.S.: writing– review & editing, validation, supervision, resources, data curation, conceptualization. D.D.: writing –review & editing, validation, supervision, resources, data curation, conceptualization.

## Conflict of interest

The authors declare no conflict of interest.

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