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Biodiesel Production from Crude Palm Oil Using Sulfuric Acid and K_2O Catalysts through a Two-Stage Reaction

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Abstract: This study examines biodiesel production from crude palm oil (CPO) through an esterification reaction with methanol as a solvent and transesterification reactions catalyzed by calcium oxide (K_2O). K_2O catalyst synthesized from the oil palm empty fruit bunches ash (PEFB-ash) with impregnation method and calcined at a temperature of 700 ºC. The esterification reaction results showed that the free fatty acid content decreased from 5.47% to 0.57% at 60 ºC, while the results transesterification reaction showed the highest methyl ester content of 39.33% at optimal conditions, which was K_2O catalyst amount of 3%. The GC-MS analysis results showed that as many as eleven fatty acid methyl esters were confirmed from biodiesel crude palm oil (CPO) based on their respective retention times and fragmentation patterns. The main components of the methyl ester formed include methyl hexadecanoic (17.75%), methyl 9.12-octadecadienoate (3.97%), and methyl 9-octadecenoate (12.06%). Biodiesel properties were examined using the American Society for Testing and Materials (ASTM-6751).

Keywords: crude palm oil; PEFB-ash; K_2O catalyst; transesterification; biodiesel.

1. Introduction

Energy demand continues to increase in line with industrial development and population growth in the world. Energy consumption currently depends mostly on fossil fuels like natural gas, coal, and crude oil [1–4]. Fuel needs are increasing, causing fewer crude oil inventories. This resulted in an energy crisis globally, mainly from fossil fuels, because it is non-renewable. The use of fossil fuels, on the other hand, will pollute the environment due to the release of hazardous substances such as carbon dioxide (CO_2) [5,6], hydrocarbon gases (HCs) [7], and sulfur oxides (SOx) [8]. So, we need alternative renewable energy sources but also environmentally friendly and abundant availability.

In recent years biodiesel has been reported as one of the most promising renewable fuel sources due to its environmentally friendly, non-toxic, high flash point, and biodegradable properties [9,10]. Biodiesel is produced from alga oil, animal fat, use cooking oil, vegetable oil, and alcohol (methanol and ethanol) through a transesterification reaction with the aid of a catalyst, both acid and alkaline catalysts [11–13]. Southeast Asia, particularly Indonesia, has an abundant palm oil industry and produces Crude Palm Oil (CPO) in large quantities for consumption [14–16]. During CPO is widely used for cooking oil and has not been used optimally. The CPO was selected as the raw material for biodiesel in this work because availability is abundant, economical, and environmentally friendly [17,18].

Biodiesel from CPO is a new hope to answer some of the world's energy needs. Indonesia is listed as the second-largest palm oil producer in the world after Malaysia [19]. The biodiesel production process consists of two stages: esterification with an acid catalyst in the first stage and transesterification with a base catalyst in the second stage. The esterification process aims to reduce the activation energy with the aid of an acid catalyst such as sulfuric acid (H_2SO_4) [20,21]. An acid catalyst is considered better than a base catalyst because it does not produce soap and can increase biodiesel production. Weerachanchai *et al.* [22] conducted esterification of vegetable oil palm shells using sulfuric acid (H_2SO_4) catalyst to yield higher conversions. Likewise, Ho *et al.* [23] reported that the used cooking oil esterification reaction using the H_2SO_4 catalyst could achieve high transformation quickly. On the other hand, the disadvantages of palm oil for biodiesel production are its high viscosity and low volatility. Therefore transesterification stage must transform the CPO into biodiesel.

Transesterification is the most straightforward process because of its low cost and reduced biodiesel production viscosity [24]. In the process of transesterification, triglycerides will react with alcohol to form methyl esters of fatty acids and glycerol with the aid of a catalyst. Commonly used catalysts are typically homogeneous alkaline-based catalysts such as potassium hydroxide (KOH), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH). Some literature associated with homogeneous catalysts-based biodiesel production has been carried out, including Danis *et al.* [25], Gebremariam *et al.* [26], and Hiwot *et al.* [27]. However, it should be noted that the use of homogeneous catalysts can also cause problems, such as high corrosivity, generates much waste, soap formation occurs, and the catalyst is difficult to reuse. We use heterogeneous catalysts based on oil palm empty fruit bunches ash (PEFB-ash) to avoid such problems. PEFB-ash as heterogeneous catalysts has many advantages: ease of obtaining, high activity, low catalyst cost, environmentally friendly, and non-toxic.

Today, the concept of "green chemistry" and environmentally friendly materials as a source of catalysts have attracted great attention. PEFB-ash utilization as a heterogeneous catalyst potassium oxide (K2O) source offers many advantages, including abundant availability. Palm empty fruit bunches ash is known to have high potassium levels (45-50%), causing potential as a source base. The main components contained in PEFB-ash are inorganic components such as potassium oxide. The combustion process and calcination obtain potassium oxide at moderate temperatures. Several studies related to biodiesel production by utilizing ash as a heterogeneous catalyst source have been published, including rice husk ash [28], cocoa pod husk ash [29], walnut shell ash [30], sugarcane leaf ash [31], banana peel ash [31], wheat bran ash [32], coconut husk ash [33], and oil palm empty fruit bunch ash [34]. The ash-based catalyst showed good activity and was environmentally friendly for biodiesel production.

This work focuses on utilizing crude palm oil (CPO) for biodiesel's simultaneous production through a two-stage reaction, namely the esterification and transesterification reactions. There are two crucial steps undertaken in this study. The first step is the esterification of CPO using sulfuric acid (H_2SO_4) with methanol as a solvent, and in the second step, transesterification using a heterogeneous base catalyst potassium oxide (K_2O). The K_2O catalyst is made from the ash of empty oil palm fruit bunches with the impregnation method and calcined at 700 ºC. In this study, biodiesel was characterized using Gas Chromatography-

Mass Spectrometry (GC-MS) to determine the methyl esters in biodiesel products. Furthermore, the biodiesel quality test uses the ASTM standards.

2. Materials and Methods

2.1. Material.

Palm Empty Fruit bunches ash (PEFB-ash) are taken from the palm oil mill of PT. Damai Jaya Lestari North Konawe Regency, South East Sulawesi - Indonesia. PEFB-ash was then filtered with a size of 120 mesh and calcined at 700 ºC for five hours. Curd Palm Oil (CPO), ethanol (C_2H_5OH), methanol (CH_3OH), hydrochloric acid (HCl), potassium nitrate (KNO_3), sulfuric acid (H_2SO_4), oxalic acid ($C_2H_2O_4$), nitric acid (HNO_3), chloroform ($CHCl_3$), potassium hydroxide (KOH), sodium thiosulfate ($Na_2S_2O_3$), phenolphthalein indicator, dan amylum indicator purchased from Sigma-Aldrich.

2.2. Esterification of CPO using H_2SO_4 catalyst.

150 mL of CPO was heated using a hot plate to ± 60°C. After that, added 60 mL methanol and 2 mL H_2SO_4 simultaneously, then heated and stirred using a magnetic stirrer for two hours. The mixture was centrifuged for 3 minutes at a speed of 1600 rpm. Furthermore, esterification results are separated by taking the top layer to be used in the transesterification process.

2.3. Transesterification process of treated CPO using K_2O catalyst.

100 mL of esterified oil was put into a 250 mL beaker and heated to 60 °C. Furthermore, K_2O catalyst was added up with variations of 1%, 2%, and 3%, each dissolved with 60 mL ethanol and heated for two hours within the temperature of 60 °C while stirred using a magnetic stirrer. Then, the reaction mixture was centrifuged at a speed of 1600 rpm for 3 minutes at room temperature and subjected to analysis.

2.4. Identification of biodiesel compound.

The identification of biodiesel compounds was carried out using Gas Chromatography-Mass Spectroscopy (GC-MS) QP2010S SHIMADZU.

2.5. Characterization of biodiesel produced.

Characterization of biodiesel properties was conducted using the American Society for Testing and Materials (ASTM-6751). Properties of biodiesel have been characterized physicochemically, such as total acid number, density at 40°, saponification value, kinematic viscosity at 40°C, and total cetane number.

3. Results and Discussion

3.1. Esterification and transesterification reaction.

The esterification reaction is a reaction between free fatty acids and alcohols to produce esters, as an initial reaction to the transesterification reaction to reduce free fatty acid levels. The esterification reaction results showed that the free fatty acid content decreased from 5.47% to 0.57% at 60 ºC. The mechanism esterification reaction using H_2SO_4 catalyst is shown in

Figure 1a in this study. A series of transesterification reactions were carried out for 2 hours at 60 ° C with a methanol-oil molar ratio of 3: 1 and varying amounts of catalyst. Methyl ester formation mechanism transesterification reaction using K_2O catalyst can be seen in Figure 1b.

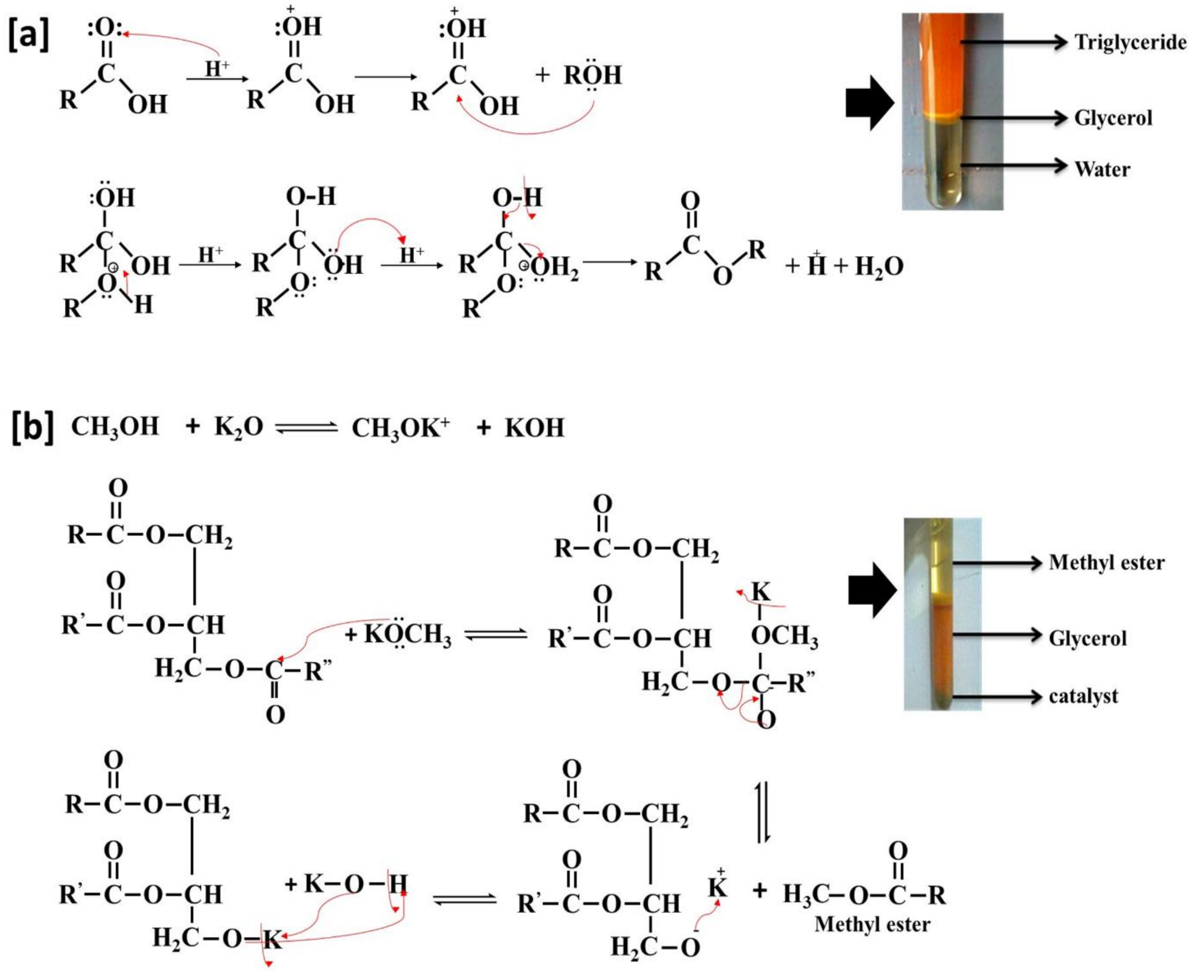

Figure 1. (**a**) Esterification reaction using H_2SO_4 catalyst; (**b**) Transesterification reaction-based K_2O catalyst.

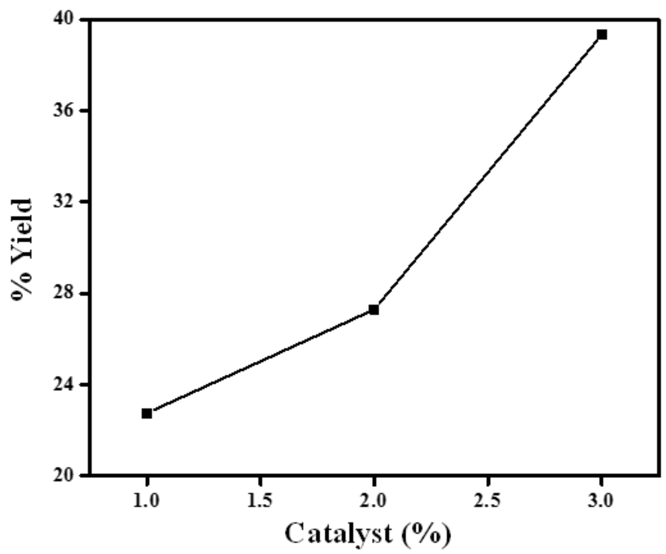

Figure 2. Influence of variation of K_2O catalyst on biodiesel yield.

The transesterification reaction of CPO was carried out using a K_2O catalyst by varying the concentration of 1%, 2%, and 3% to determine the optimum concentration of K_2O catalyst. It appears that when the amount of K_2O catalyst increases, the methyl ester content of biodiesel increases significantly. This is presumably because the increasing catalyst amount causes more contact between the reactants and catalysts K2O, thereby growing higher conversions [35,36]. Besides, the increase in the catalyst's active site during the transesterification reaction can also improve biodiesel conversion [37]. This shows that the K_2O catalyst can increase the transesterification level of crude palm oil. The maximum % yield was 39.33% using a K_2O catalyst of 3% (Figure 2). A similar thing was also found in Ho *et al.* [38] study regarding the transesterification of CPO using palm oil mill ash-based catalysts supported by calcium dioxide catalysts. The results showed that CPO increased from 56.44% to 73.23% when the catalyst increased from 2% to 4%.

3.2. GC-MS analysis.

The chemical composition of methyl ester contained in biodiesel was determined using gas chromatography-mass spectrometry (GC-MS). The profile of biodiesel GCMS results obtained in this study can be seen in Table 1. The crude palm oil component obtained is in accordance with that reported. Maulidyah *et al.* [16] and De *et al.* [39] reported that the most common fatty acids contained in Crude Palm Oil (CPO) biodiesel are methyl 9-octadecenoate, methyl hexadecanoic, and methyl 8.11-octadecadienoate. Likewise, Putra *et al.* [40] synthesized CaO/SiO_2 catalyst from eggshell waste and palm empty fruit bunch waste for biodiesel production based on cooking oil waste. Similar results were also reported in this study are shown in Table 1.

Table 1. Composition of biodiesel methyl ester from GC-MS analysis.

No	Retention Time (min)	Compounds identified	Composition (%)
1	19.21	1,2-Benzenedicarboxylate	1.11
2	19.72	Methyl hexadecanoic	17.75
3	20.06	Hexadecanoic acid	22.66
4	20.72	7-Pentadesin	3.78
5	21.34	Methyl 9.12-octadecadienoate	3.97
6	21.39	Methyl 9- octadecenoate	12.06
7	27.59	2-methyl-7-phenylindole	7.08
8	27.67	Acetamide	3.10
9	27.81	1-methyl-2- phenilindol	12.60
10	29.43	1.2.4-Benzenetricarboxylate	8.78
11	29.51	hexamethylcyclotrisiloxane	0.92

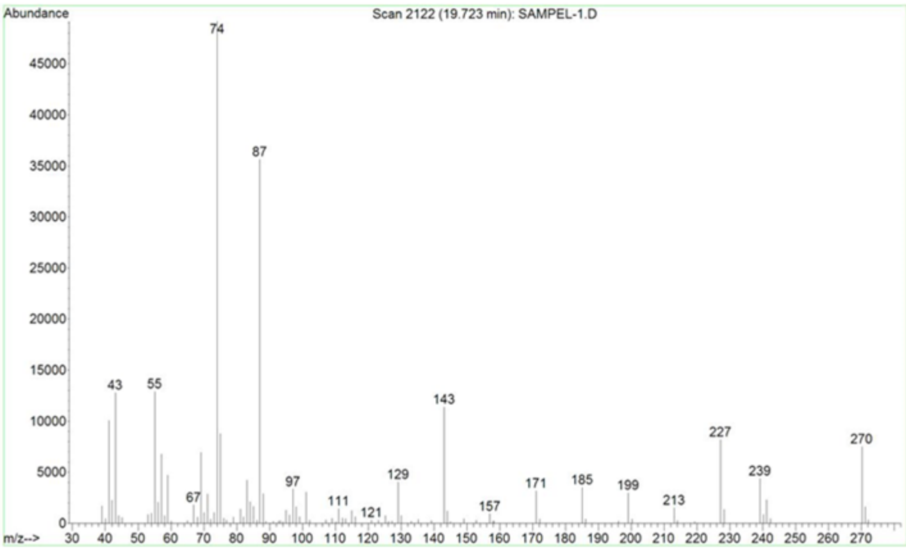

Figure 3. Mass spectrum of methyl hexadecanoic.

Based on Figure 3 shows that the basic peak from the mass spectrum of fatty acid methyl ester is seen at m/z = 74, which has a high relative abundance due to McLafferty rearrangement [41,42]. Two other peaks are m/z 239 and m/z 43, produced from the methoxy group's loss from the molecular ion and radical detachment [43]. Other peaks at m/z 87, 101, 115, 129, 143, 171, 185, 199, 227, and 239 are fragmentation patterns due to each C-C bond's breakdown and are known as the $C_nH_{2n-1}O^{2+}$ ion series, where n = 2, 3, 4, 5…. , 87, 102 m/z. This fragmentation pattern is a characteristic fragmentation pattern for compounds in a long-chain ester group [44].

3.3. Physical-chemical properties of biodesel.

The biodiesel physicochemical properties were calculated using American Society for Testing and Materials (ASTM-6751) specifications, as shown in Table 2. Physical-chemical properties were tested, including density at 40°, kinematic viscosity at 40°C, total acid number, saponification value, and total cetane number. It can be seen that biodiesel was obtained following the standards of ASTM-6751.

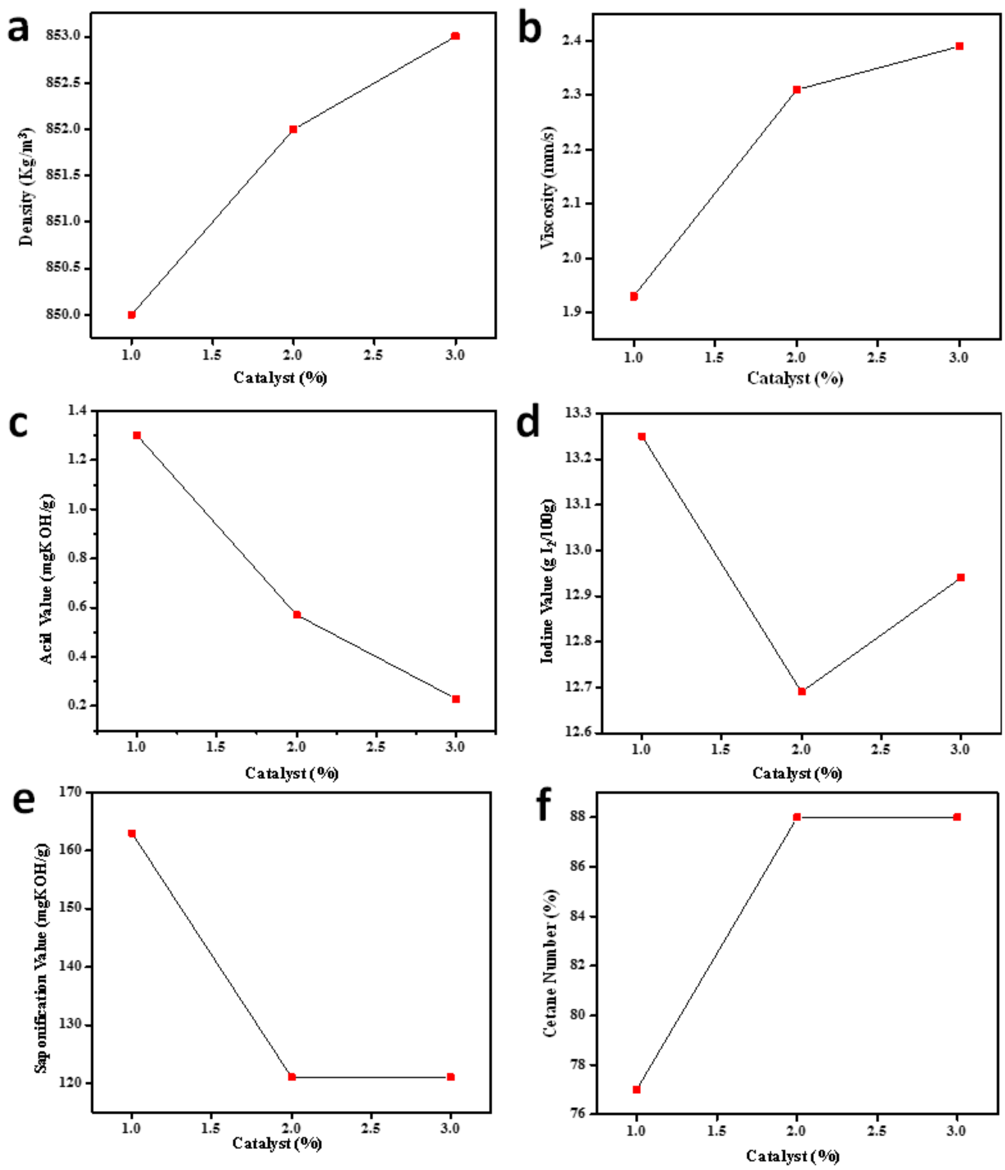

Figure 4. Physical-chemical properties of biodiesel.

Based on Figure 4a, biodiesel density increases with the addition of a K_2O catalyst. At a catalyst concentration of 3%, density increases from 850 Kg/m^3 to 853 Kg/m^3. The biodiesel's density value is generally influenced by the type of fatty acid contained in it and the purity of biodiesel made. Besides, density will also increase with a decrease in the carbon chain's length and an increase in double bonds in fatty acids [45].

Viscosity is vital for biodiesel to ensure that it meets diesel engines' operating requirements [46]. The Kinematic viscosity value obtained for each additional amount of K_2O catalyst is 2.24, 2.31, and 2.39 mm^2/s, respectively (Figure 4b, Table 2). According to Ong *et al.* [47], low kinematic viscosity value may be due to linoleic acid in CPO. This value was still in the specified range of the ASTM-6751 limit standard. The use of K_2O catalyst affects biodiesel's viscosity value because water absorption occurs by the catalyst during the transesterification reaction. Generally, viscosity is related to the fatty acid composition contained in biodiesel products. Low viscosity will result in easy oil flow, small pumpability, and good injection.

Based on Figure 2c, it can be seen that the most optimum free fatty acid conversion occurs when using a 3% K_2O catalyst which is characterized by the lowest acid number, which is around 0.23 mg KOH/g. Similar reported by Qu *et al.* [48] using crude palm oil obtained an acid number of 0.23 mg-KOH/g. According to ASTM-6751 standards, the maximum acid value for biodiesel is 0.8 mgKOH/g [49]. It shows that the increasing amount of catalysts, the more free fatty acids are converted into methyl esters. The decrease in acid number is due to free fatty acids in the oil reacting with methoxide ions to form esters during the transesterification process.

Iod numbers indicate the level of unsaturation or number of fatty acid double bonds of biodiesel. The iodine numbers obtained for each additional amount of K_2O catalyst are 13.25, 12.69, 12.94, respectively (Figure 4d, Table 2). The iodine number of biodiesel obtained is tiny, and this indicates that most of the biodiesel is composed of fatty acids with saturated hydrocarbon chains [50]. Biodiesel with a high iodine number is more easily oxidized when in contact with air.

Figure 4e and Table 2 show that crude palm oil biodiesel's saponification value using K_2O catalysts 1, 2, and 3% are 163.76 mgKOH/gram, 121.73 mgKOH/gram, and 121.75 mgKOH/gram, respectively. The saponification value obtained for each catalyst concentration still falls within the range of ASTM-6751 standards.

In general, the cetane number increases with the increase in the amount of K_2O catalyst. Figure 4f shows that K_2O catalyst with a concentration of 3% has the highest cetane number, and K_2O 1% has the lowest value, and all of these values still conform to ASTM-6751 standards. The average value of cetane number for crude palm oil biodiesel is 84.33, within the ASTM-6751 limits.

Table 2. Specifications of biodiesel from CPO compared with standard values.

Properties	**CPO biodiesel**			**ASTM-(6751)**
	(K_2O 1%)	**(K_2O 2%)**	**(K_2O 3%)**	
Density at 40°C (Kg/m^3)	850	852	853	860-900
Kinematic viscosity at 40°C (mm^2/s)	2.24	2.31	2.39	1.9-6
Acid value (mg-KOH/g)	1.3	0.57	0.23	0.5 max
Iodine value (g I_2/100 g)	13.25	12.69	12.94	120
Saponification value (mg-KOH/g)	163.76	121.73	121.75	-
Cetane number	77	88	88	47 min

4. Conclusions

This study focused on biodiesel production from CPO through an esterification reaction using an H_2SO_4 catalyst and a transesterification reaction based on a K_2O catalyst. K_2O catalyst synthesized from the oil palm empty fruit bunches ash (PEFB-ash) with impregnation method and calcined at 700 ºC. The easy preparation of K_2O catalysts and abundant availability makes the catalyst very promising in developing early processing of biodiesel production. The esterification reaction's optimal conditions are a reaction temperature of 60 ºC and a reaction time of 2 hours; this optimal condition reduces the free fatty acid content from 5.47% to 0.57%. The use of a K_2O catalyst of 3% produces methyl ester of 39.33%. The GCMS analysis confirmed eleven fatty acid methyl esters in the presence of biodiesel crude palm oil. The main components of the methyl ester formed include methyl hexadecanoic (17.75%), methyl 9.12-octadecadienoate (3.97%), and methyl 9-octadecenoate (12.06%). The biodiesel produced from CPO meets international standards (ASTM-6751).

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Conflicts of Interest

We declare that this article has no conflict of interest

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