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Activation of Cement Clinker as Catalysts for Transesterification Reaction of Palm Oil Off Grade to Biodiesel

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Abstract

Calcium oxide (CaO) is a heterogeneous solid base which is generally used as a catalyst in making biodiesel. It is mainly obtained from cement clinker and activated through calcination method. The purpose of this study was to determine the effect of using cement clinker catalyst on the yield of the biodiesel. A batch reactor with a condenser was used in making the biodiesel under favorable conditions such as calcination temperatures of 700 °C, 750 °C and 800 °C, calcination time of 5, 6 and 7 hours, and catalyst concentration of 1%-w, 2%-w, and 3%-w oil. The analysis involved X-Ray Diffraction (XRD) and Brunauer-Emmett-Teller (BET) for catalysts and Gas Chromatography-Mass Spectrometry (GC-MS) for biodiesel. The catalyst calcination temperature determined the optimum conditions. From this study, the conditions necessary for transesterification reaction include the mole ratio of methanol/oil of 6 to 1, the temperature of 70 °C for 2 hours and 700 °C for 5 hours, and catalyst dosage of 2% by weight. Under these conditions, the yield of the biodiesel was 84.26%. Additionally, at the calcination temperature of 800 °C for 7 hours and catalyst dosage of 3% by weight, the yield of the biodiesel was 76.84%. CaO, SiO_2, $2CaO.SiO_2$ and $3CaO.SiO_2$ were found in the catalyst through XRD analysis. The specific surface areas of the catalyst were 25,497 m^2/g (700 °C/5 hours) and 35,879 m^2/g (800 °C/7 hours) through BET analysis. According to the GC-MS analysis, the main components of the biodiesel include methyl palmitate, methyl oleate, and methyl stearate.

Keywords: biodiesel, CaO, catalysts, cement clinker, transesterification.

1. Introduction

Petroleum is a non-renewable energy source, though it takes millions of years to convert its raw materials into fuel. Fatty acid methyl ester (FAME), commonly referred to as biodiesel, is a substitute fuel with much potential. It is a mixture of fuel with cleaner combustion compared to diesel (Helwani et al., 2018).

Generally, biodiesel is produced through transesterification reactions using a homogeneous base catalyst. The choice of the catalyst is based on the fact that it has a high catalytic activity and biodiesel conversion in relatively short reaction time (± 1 hour) (Hu et al., 2011). However, the use of the catalyst has some disadvantages. For instance, it cannot be reused or regenerated, difficult to separate from the product, and requires more equipment for separation and purification, increasing the production costs (Marinkovic et al., 2016).

Calcium oxide (CaO) is among the basic heterogeneous catalysts used in transesterification of vegetable oils and is used as an alternative to homogeneous catalytic agents. Clinker is a source of CaO which might be used in this regard. Cement clinker, also called *calcinated raw meal,* is produced from the combustion of raw meal in cement production. It contains 66.61% CaO, 21.92% SiO_2, 6.33% Al_2O_3, 4.00% Fe_2O_3, and 2.56% is constituted by other components, thus showing properties suitable for catalyst synthesis (Gimbun et al., 2013). Additionally, the clinker is given a pre-treatment in the form of a simple activation using a calcination method to eliminate CO_2 compounds and moisture and increase the composition of CaO in it (Hussain et al., 2016).

Nowadays, several studies are conducted to examine heterogeneous base catalysts in making biodiesel since it is easily separated, has a high selectivity, and contains little waste.

Hussain et al. (2016) examined the effect of CaO catalysts from activated clinkers on rubber seed oil in biodiesel production. The optimum catalyst condition was at 6%-w clinker with a calcination temperature of 700 °C for 5 hours in the furnace. The transesterification process uses Microwave-Assisted Extraction (MAE) method with operating conditions of a 5 to 1 oil methanol molar ratio, a reaction temperature of 60 °C, and a time of 1 hour. With these conditions, a biodiesel yield of 53.60% is produced. The acquisition of conversion is 96.8%, while the main composition of biodiesel from GC-MS analysis is 45.1% methyl vaccenate, 43.2% methyl linolelaidic, 7.7% methyl palmitate, and 3.9% methyl stearate. Moreover, the catalyst surface area was analyzed using the BET method. The surface area obtained before catalyst activation was 2.9 m^2 / g and 59.5 m^2 / g after activation. According to Niju et al. (2014), the higher surface area and alkalinity affect catalyst activity and increase the biodiesel yield.

The high availability of clinker in the cement industry and the large amount of CaO content in the clinker makes clinker suitable as a solid catalyst for the transesterification process in biodiesel production, so it is expected that the use of clinker as a CaO catalyst can increase biodiesel yield.

2. Methodology

2.1. Tools and Materials

The main tools used in this study include (1) hydraulic press spindles, (2) 100/200 mesh sieves, (3) ovens and furnaces, (4) 500 ml three-neck rounded flasks as batch reactors equipped with condensers (Figure 1), (5) hot plate / heating mantle and magnetic stirrer, (6) thermometer and (7) Oswald viscometer.

Furthermore, other ingredients were used, including (1) off-grade palm oil in the Riau University environment (2) cement clinker, (3) aquades, (4) methanol p.a, (5) concentrated H_2SO_4, and (6) technical ethanol, and (7) KOH.

2.2. Raw Material Preparation

Off-grade palm fruit is extracted through the artisanal method. The first step involves washing the fruit to remove dirt such as sand and fruit crowns. Furthermore, the fruit is steamed in a boiler for 120 minutes to soften it. Once the steaming process is complete, the fruit is pressed using a hydraulic press spindle. The extraction results are then put into a separating funnel to form two layers of oil and water. The oil obtained is analyzed to determine the levels of ALB and water.

2.3. Preparation of Cement Clinker Solid Catalysts

The cement clinker catalyst is prepared through the calcination method. It is first mashed to ensure the particles pass through the 100 mesh sieve but held at the 200 one. Furthermore, the cement clinker catalyst was calcined in the furnace at temperature variations of 700 °C, 750 °C and 800 °C for 5, 6, and 7 hours, respectively. The catalysts obtained were then assessed using XRD analysis and the BET method. Also, the uncalcined cement clinker catalyst was prepared as a control.

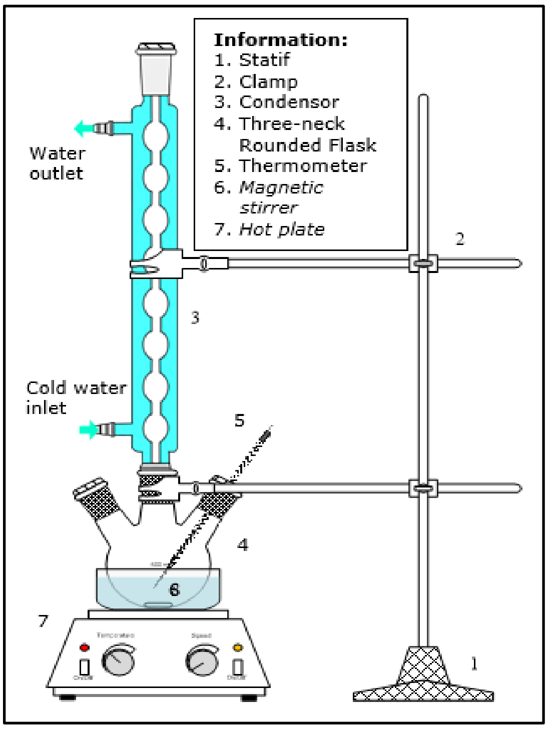

Figure 1. Series of biodiesel making process tools

2.4. Esterification Reaction

The esterification reaction was carried out since the *off-grade* palm oil has ALB levels of more than 2%. Oil from the extraction of *off-grade* palm fruit is weighed to 150 g and put into an esterification reactor with stirrers and condensers. The process is carried out in batch and placed on a heater to maintain the reaction temperature. Once the temperature reaches 60 °C, the methanol reagent with a mole ratio of methanol to the oil of 12:1 and a 1% -w H_2SO_4 catalyst is added. The reaction lasts for 1 hour with a stirring speed of 400 rpm. The mixture is separated using a separating funnel. The top layer which is mainly H_2SO_4 and methanol from the rest of the reaction is separated from the bottom part, and then transesterification reaction takes place. However, the ALB levels are first analyzed prior to transesterification of the lower layer.

2.5. Transesterification Reaction

The lower layer in the separation of the product resulting from the esterification reaction is put into a transesterification reactor with a condenser of 50 grams and heated on a hot plate to a reaction temperature of 70 °C. Afterward, methanol reagent is added with a mole ratio of methanol to oil 6:1 and the cement clinker catalyst with a concentration of 1% -w, 2% -w and 3% -w oil. The reaction lasted for 2 hours with a stirring speed of 400 rpm using a magnetic stirrer.

The initial reaction time is calculated after the catalyst and reactants are fed into the reactor. Once the reaction is complete, the mixture is cooled, and the catalyst is separated from the solution using a magnet. The above steps are repeated for the catalyst prepared previously with the temperature and time of dehydration varied. The solution is separated and refined to obtain biodiesel according to the established standards.

3. Result and Discussion

3.1. Off Grade Palm Oil Extraction

Off-grade palm raw material is steamed to soften the fruit mesocarp and deactivate the lipase enzyme to prevent an increase in free fatty acid (ALB) levels in oil (Budiawan et al., 2013). The characteristics of off-grade palm oil are shown in Table 1.

The *off-grade* palm oil has high water content and ALB levels. The high water content decreases the catalyst in the reaction by reacting with it (Ulfayana and Helwani, 2014). Additionally, the high water content in oil leads to hydrolysis, which is one of the causes of ALB formation (Pahan, 2012). To reduce high ALB levels, the esterification process is carried out first to ensure the oil ALB level meets the requirements of the transesterification process, which is <2% (Helwani et al., 2018).

3.2. Activation and Characterization of Cement Clinker Catalysts

The use of CaO catalyst/iron powder in the transesterification process of *off-grade* palm oil to biodiesel affect the quality, amount of product, and reaction process conditions. CaO content in cement clinker is 65.15% and it is the primary and most crucial component in the transesterification process. The catalyst thermal activation is carried out again to remove *moisture* and CO_2 absorbed in the clinker (Hussain, 2016). With the thermal treatment, the catalyst pore structure is more open, increasing its surface area.

3.2.1. Characterization of Cement Clinker Catalysts using X-Ray Diffraction (XRD)

The XRD pattern of the cement clinker without calcination should be used as a control and then compared with the trend of the catalyst activated based on the temperature variations of 700 °C, 750 °C and temperatures of 800 °C for 5, 6 and 7 hours, respectively.

The XRD pattern in the uncalcined clinker cement catalyst samples used as catalyst control had the components of CaO, SiO_2, $2CaO.SiO_2$ and $3CaO.SiO_2$ (Figure 2). Furthermore, the XRD pattern of activated cement clinker catalyst using variations in calcination temperature of 700 °C, 750 °C and 800 °C and time of 5, 6 and 7 hours respectively has a peak which tends to be the same as the control sample. With increase in temperature and calcination time, the intensity of $2CaO.SiO_2$ enlarges (Figure 3, 4 and 5 respectively).

Table 1. Characteristics of *off grade* palm oil

No	Characteristic	Unit	Extraction Results	Standard of CPO SNI 01-2901-2006
1	Color		Reddish orange	Reddish orange
2	Density (40 °C)	kg/m^3	892.11	-
3	Viscosity (40 °C)	mm^2/s	29.47	-
4	Water content	%	3.5	Max 0.5
5	Free fatty acid levels	%	6.24	Max 0.5

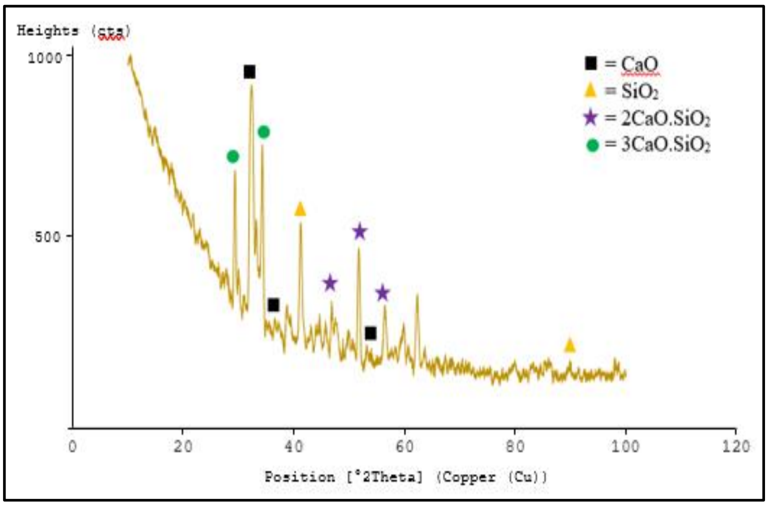

Figure 2. Catalyst XRD pattern without calcination

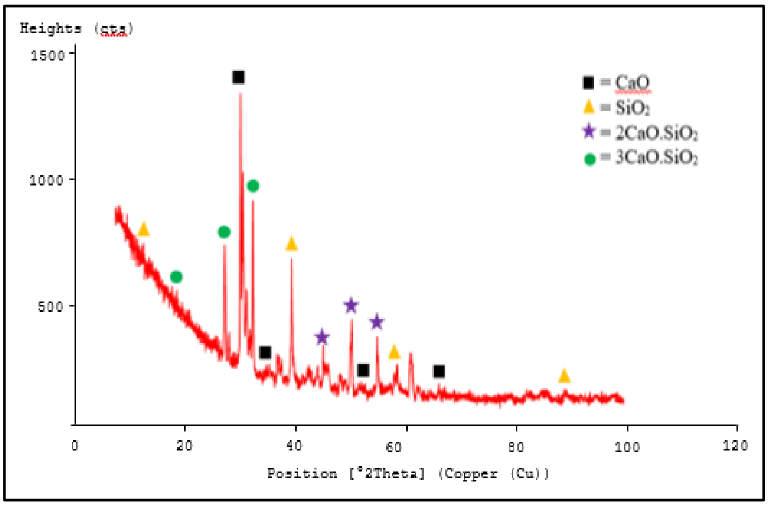

Figure 3. Catalyst XRD pattern after calcination at 700 °c for 7 hours

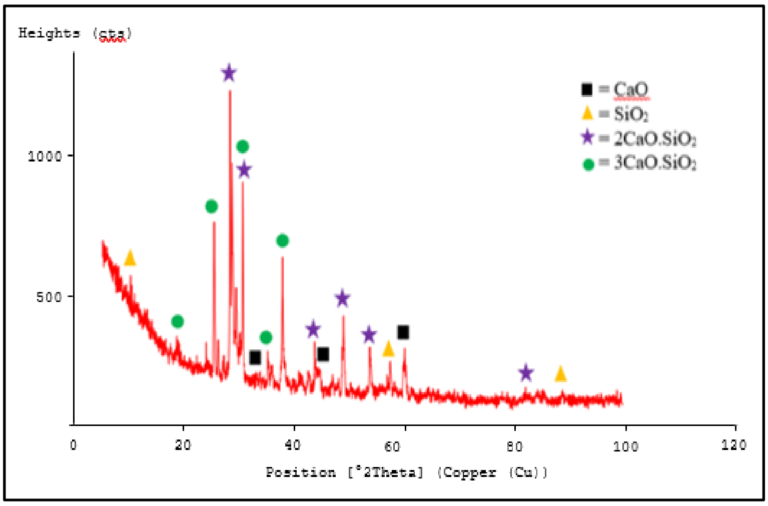

Figure 4. Catalyst XRD pattern after calcination at 750 °c for 7 hours

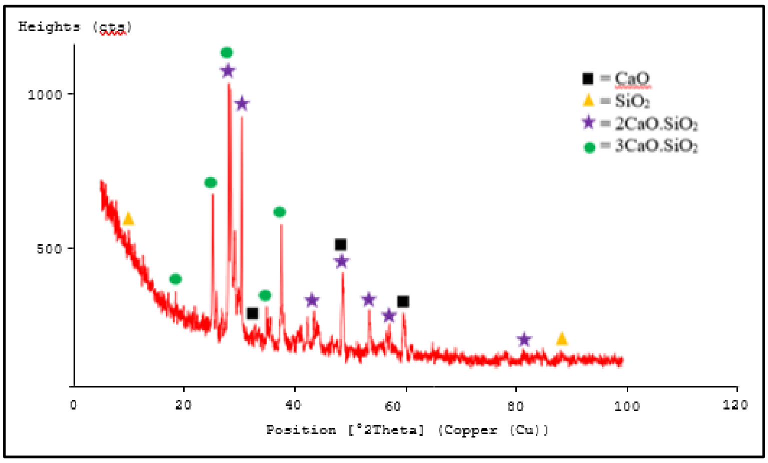

Figure 5. Catalyst XRD pattern after calcination at 800 °c for 7 hours

Basically, a calcination temperature of 800 ° C for 7 hours makes SiO_2 more reactive with CaO compounds to form a new product in the form of $2CaO.SiO_2$ (Putra et al., 2018). The reaction for the formation of $2CaO.SiO_2$ and $3CaO.SiO_2$, as follows :

$$2CaO + SiO_2 \longrightarrow 2CaO.SiO_2 \quad (1)$$
$$2CaO.SiO_2 + CaO \longrightarrow 3CaO.SiO_2 \quad (2)$$

3.2.2. Characterization of Cement Clinker Catalysts using Brunaeur-Emmet-Teller (BET) Surface Area

Based on the BET surface area test results, the surface area of the activated clinker is greater than the catalyst not activated. From Table 2, the largest surface area of the activated cement clinker catalyst was obtained at a calcination temperature of 800 °C for 7 hours which amounted to 35,879 m^2 /g. On the other hand, the surface area of the unused catalyst clinker is 21,746 m^2 /g. This is consistent with the research of Hussain et al. (2016) ie, the surface area of the activated cement clinker is higher than the catalyst which has not been activated.

Table 2. Comparison of BET surface area for cement clinker catalysts

Catalyst	Condition	Surface area (m^2/g)
Cement Clinker	Without Activation	21.746
	Activation T = 700 °C	25.497
	Activation T = 750 °C	n/a
	Activation T = 800 °C	35.879

An increase in the surface area of the clinker after thermal activation indicates the calcination method is effective in enlarging the pores on the surface of the clinker. It later affects clinker performance in accelerating the process of making biodiesel. With the thermal treatment, the catalyst pore structure is more open, and as a result, its surface area also increase (Niju et al., 2014).

3.3. *Yield* and Characteristics of Biodiesel

3.3.1. Biodiesel Yield

To determine the effect of variations in catalyst concentration and calcination temperature on the activity of the cement clinker indicating the amount of biodiesel yield produced, all catalysts were tested under the same conditions, including methanol to oil mole ratio 6:1, reaction time 2 hours and temperature of 70 °C reaction. The yield of the biodiesel is shown in Figure 6 and Figure 7.

The biodiesel concentration at 3% had the highest yield of 83.66% using a cement clinker catalyst calcined for 5 hours at a temperature of 700 ° C.

The yield of biodiesel using a calcined catalyst for 6 and 7 hours at a temperature of 700 °C had a decrease in yield. According to Tang et al. (2012), a further increase in the temperature and calcination time of the catalyst causes the active component of the catalyst to be lost. As a result, a catalyst agglomeration occurs, leading to a decrease in the yield of biodiesel, as well as the uneven distribution of active sites, preventing it from reacting adequately.

Table 3. Characteristics of biodiesel research result with SNI standards

No	Characteristics	Unit	Biodiesel Research Results	SNI Standards 7182:2015
1	Density	kg/m^3	884.75 – 887.34	850-890
2	Kinematic Viscosity	mm^2/s	5.15 – 5.16	2.3-6,0
3	Flash Point	°C	134	Min. 100
4	Acid Number	mg-KOH/g	0.350 – 0.409	Max. 0.5

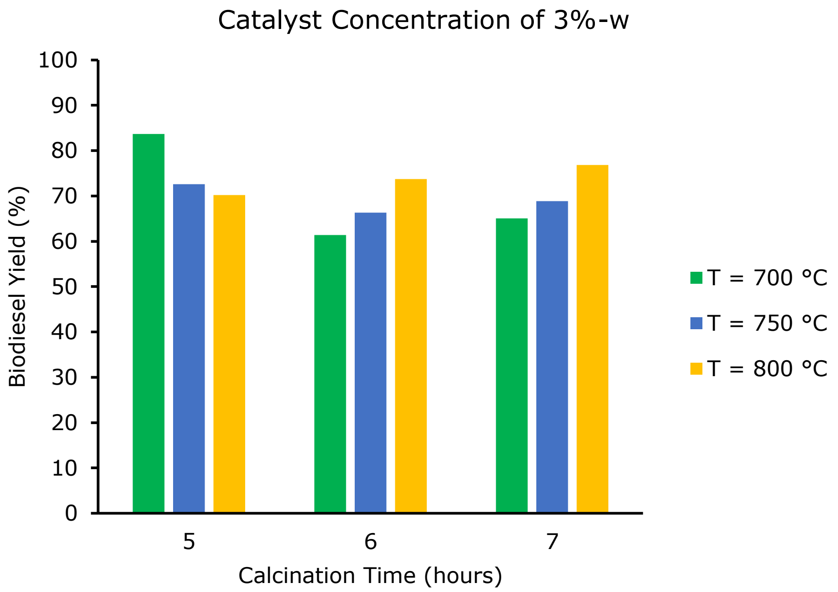

Figure 6. The Effect of calcination temperature and time on catalyst concentration of 3% on biodiesel yield

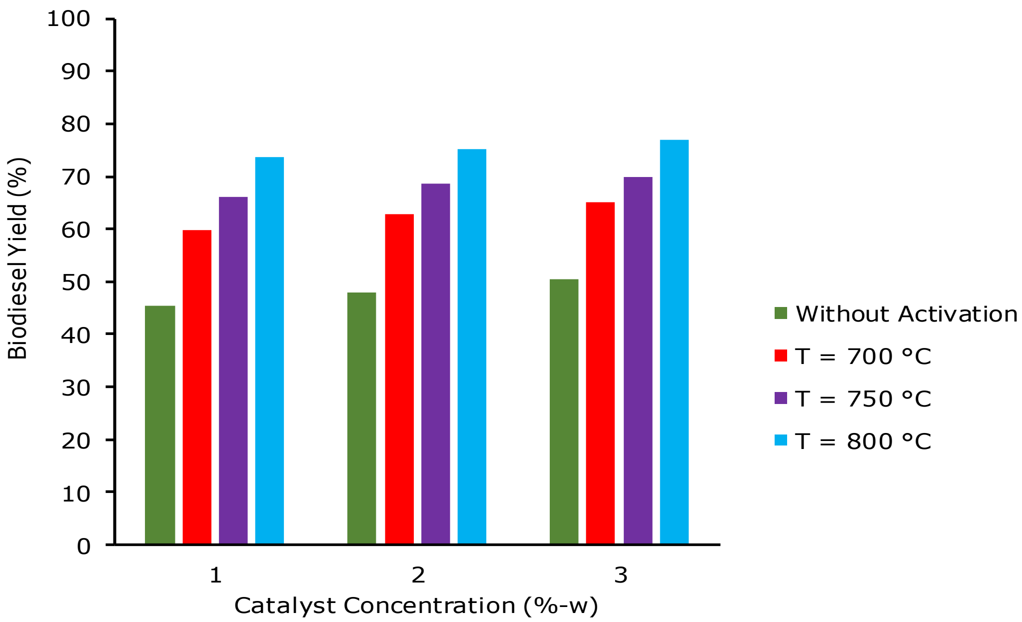

Figure 7. Effect of calcination temperature and catalyst concentration on biodiesel yield

From Figure 6, the optimum conditions for the cement clinker catalyst at a concentration of 3% -w were calcined at 800 °C with a biodiesel yield of 76.84%.

An increase in calcination temperature has a significant effect on the catalytic activity and influences biodiesel yield. With the increase in calcination temperature, the catalyst gradually becomes stable as its surface area also increases (Tang et al., 2012). From these two variable comparisons, the cement clinker catalyst stability is obtained at temperatures above 700 °C. This is consistent with Wei et al. (2009) research which stated that to obtain an appropriate cement clinker catalyst performance, the calcination temperature used should be above 700 ° C.

3.3.2. Biodiesel Characteristics

It is essential to determine the characteristics of the biodiesel produced to ensure it meets the quality standards set and that it is used according to the needs of Indonesians. The characteristics tested were density, kinemwitatic viscosity, acid number, and flashpoint, as shown in Table 3.

Table 3 shows that the characteristics of biodiesel are in line with SNI 7182: 2015 standards. The density and viscosity of biodiesel affect the engine's combustion and the injection systems

The flashpoint, according to the standard, indicates the biodiesel is safe for transportation and storage. The standard acid number shows the biodiesel is not corrosive. Based on the results of GC-MS analysis, the largest composition of methyl esters is methyl palmitate at 49.07% and methyl oleate at 44.43%, while the smallest composition is methyl laurate of 0.11%.

4. Conclusions

Solid cement clinker catalyst has the potential to be activated and used in the transesterification process of making biodiesel from low-quality *off-grade* palm oil. Additionally, the cement clinker catalyst has a surface area of 35,879 m^2/g, and the XRD analysis results show that the catalyst has a peak of CaO, SiO_2, $2CaO.SiO_2$ and $3CaO.SiO_2$. The main composition of biodiesel from GC-MS analysis results include methyl palmitate, methyl oleate, and methyl stearate.

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