The effect of KOH concentration and calcination temperature on the cement clinker catalyst activity in the transesterification of off-grade palm oil into biodiesel

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Abstract. Cement clinker has been researched and has shown good performance as a heterogeneous catalyst in the biodiesel production process. The purpose of this study was to synthesize and characterize a cement clinker/KOH catalyst, to determine the effect of KOH concentration and calcination temperature on biodiesel yield. The catalysts were prepared by impregnation-calcination in the various KOH concentrations of 5, 10 and 15% and the calcination temperature of 500, 600 and 700 °C. The transesterification process was carried out for 3 hours with a mole ratio of oil: methanol of 4:1, reaction temperature of 65 °C, catalyst concentration of 6% wt oil, and stirring of 400 rpm. The results showed that the catalyst with the KOH concentration of 15% and the calcination temperature of 700 °C had the best performance with a biodiesel yield of 88.82%. The catalyst has a surface area of 9.622 m²/g, basicity of H_2O > 12.2 and a crystalline phase of 3CaO·SiO₂, K₂CO₃, Ca(OH)₂, and K₂O. From the research, it is known that calcination temperature and KOH concentration in the impregnation process are directly proportional to the biodiesel yield.

1. Introduction
The US Energy Information Administration (2019) predicted that world energy consumption will increase by 28% from 2015 to 2040, where 77% of energy source used is fossil fuels. This is a problem because this source is a non-renewable one that can experience scarcity. Therefore, the replacements, renewable fuels, are developed. There are some renewable energies developed by several country in the world, that are hydro, wind, solar [1], geothermal [2–8], and biodiesel [9,10]. Biodiesel is a renewable fuel that made from vegetable oils that contain a lot of fatty acids [11,12]. To obtain biodiesel, the vegetable oils are transesterified to produce FAME (Fatty Acid Methyl Ester) or biodiesel and glycerol.
Riau is rich in diversity of natural resources for vegetable oil production. Based on data from the Directorate General of Plantation, Ministry of Agriculture of the Republic of Indonesia (2018) [13], this province has the largest oil palm plantations in Indonesia with CPO as the main product. Off-grade palm oil is the rest of the CPO mill's grading which tends to be unsuitable for processing into CPO. To improve the use and economic value, several researchers have tried to convert this product to biodiesel and succeed to obtain biodiesel yield from 70% up to 90% [10,14–16]. These studies prove that off grade palm oil is potential and suitable as a raw material for biodiesel production.

There are several parameters that affect the transesterification process in biodiesel production, namely temperature, reactant mole ratio, reaction time, stirring and catalyst. The catalyst is the most important one because it affects the reaction speed and yield. There are two types of catalysts in the transesterification, that are heterogeneous catalysts and homogeneous catalysts. The Heterogeneous catalysts have the advantages than homogeneous one because it is non-corrosive, environmentally friendly, simple waste handling, and easy to separate [17].

CaO are one of the popular heterogeneous catalyst used in transesterification because it have high activity, strong alkaline, light reaction conditions, long catalyst life, and low cost [17]. CaO is usually derived from limestone, calcium carbonate, and calcium hydroxide. Recent research even extracted CaO from eggshells waste [18]. Cement clinker is limestone that has undergone a pre-calcination process [19] have successfully used cement clinker impregnated with methanol as a catalyst to convert rubber seed oil into biodiesel. It reported to have better stability and recyclability than other solid base metal catalysts. [20] have succeed to support cement clinker with KOH in biodiesel production from soybean oil produced 84.25% yield [21] reported that cement clinker impregnated with KOH by wet-calcination impregnation method for transesterification of used cooking oil produced a very high biodiesel yield of 96.8%.

Recently, [22] have applied cement clinker catalyst without even impregnation to convert off grade palm oil into biodiesel. Even so, the biodiesel yield is relatively high up to 84.26%. In this study, the catalyst was developed from cement clinker impregnated with KOH and applied in biodiesel production from off grade palm oil. The performance of the catalyst also studied on different KOH concentrations and calcination temperatures.

2. Materials and methods

The materials used in this study were cement clinker obtained from PT Semen Padang, KOH, aquadest, off-grade palm fruits obtained from PTPN V, H₂SO₄, methanol, and hammet indicators obtained from PT. Bratachem. The tools used were spindle hydraulic press, condenser, three neck boiling flask, thermometer, magnetic stirrer and heating mantle.

2.1. Raw material preparation

The research began with washing the oil palm fruit, then steaming it for 120 minutes to soften the fruit. Furthermore, palm oil extraction is carried out using a spindle hydraulic press. The oil obtained was then analyzed for its FFA and water content.

2.2. Preparation of cement clinker/KOH catalyst

The cement clinker was dried at 105 °C for 2 hours. Then it was crushed and sieved with a 100 mesh sieve. The powder obtained was impregnated by KOH with a concentration of 5, 10 and 15% weight. The Impregnation is carried out by dropping the KOH solution into the cement clinker while stirring until it forms a paste. The mixture was then allowed to stand for 24 hours and dried at 110 °C. The catalysts product was calcined at the temperature variation of 500, 600, and 700 °C for 5 hours.

2.3. Study of the catalytic performance on transesterification process
150 grams of extracted off grade palm oil was put into the esterification reactor which was equipped with a stirrer and condenser. The reactor was heated until the temperature reached 60 °C. After that, 1% wt H$_2$SO$_4$ and methanol (methanol: oil molar ratio of 12: 1) were added. The reaction was carried out for 1 hour with a stirring speed of 400 rpm. The esterification product resulted was separated in a separating funnel. The lower layer was taken for FFA analysis purpose and for the transesterification stage [14].

The oil from esterification was heated at 65 °C and fed to the transesterification reactor which contains a mixture of methanol (methanol: oil molar ratio of 10: 1) and 6% weight -b oil cement clinker/KOH catalyst. The reaction was carried out for 3 hours with a stirring speed of 400 rpm. The product obtained was cooled and separated to obtain crude biodiesel (glycerol), remaining methanol and catalyst. Crude biodiesel is purified by washing with distilled water until the pH is neutral. Then the biodiesel is heated in the oven at 105 °C for 60 minutes to evaporate the residual methanol from the reaction and water [14].

2.4. Characterization of catalyst and biodiesel
The crystalline phase, basicity and the specific surface area of the catalyst were analyzed by X-Ray Diffraction (XRD), Hammet Indicators, and Brunauer-Emmet-Teller (BET) methods, respectively. The characteristics of biodiesel also tested that included the acid number, flash point, cetane number, and viscosity (kinematic viscosity). The biodiesel composition was analyzed using GC-MS.

3. Result and discussion
3.1. Off-grade palm extraction
The extracted off-grade palm oil was characterized its properties of density, viscosity, water content and free fatty acid content tests. The characteristics of off-grade palm oil (Table 1) showed the high water content. The water can hydrolyze the oil to make FFA [23]. In addition, the catalytic activity on transesterification will decrease because the water will react with the catalyst [24] and can also cause the soap forming [25]. So that, water must be removed by heating. To reduce FFA levels on the extracted oil, the esterification reaction was carried out before transesterification one, so that the FFA was decrease from 9.28% to 1.38 [26].

| Parameters       | Off grade palm oil | CPO Standard SNI 01-2901-2006 |
|------------------|--------------------|-------------------------------|
| Colour           | Orange             | Yellow                        |
| Density 40°C (kg/m$^3$) | 892.11             | -                             |
| Viskosity 40°C (mm$^2$/s)   | 29.47              | -                             |
| Water content (%)     | 3.5                | Max 0.5                       |
| FFA (%)               | 9.28               | Max 0.5                       |

3.2. Catalyst characterization used XRD analysis
To determine the effect of calcination temperature and KOH concentration on the crystalline phase of the catalyst, the XRD patterns were compared between those different treatment, that are 700 °C with 5%, 500 °C with 5%, 700 °C with 15%, and 500 °C with 15%. All XRD pattern showed the crystalline phases contained 3CaO.SiO$_2$, K$_2$CO$_3$, Ca(OH)$_2$, and K$_2$O (Figure 1). The highest peak is 3CaO.SiO$_2$ which is the main composition of cement. Ca(OH)$_2$ was formed through water absorption by CaO from the air during impregnation process or at the catalyst on the free space. The reaction of Ca(OH)$_2$ formation followed equation 1

\[ \text{CaO + H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \]  (1)
Figure 1. XRD diffractograms of cement clinker/KOH catalyst at different calcination temperature and KOH concentration of (a) 700 °C with 5%, (b) 500 °C with 5%, (c) 700 °C with 15%, and (d) 500 °C with 15%.

In addition, there is no KOH peak appeared on the diffractogram, but K₂CO₃ and K₂O peaks were observed. This proves that all KOH has been converted to K₂CO₃ and K₂O. According to [27], at 300 °C, KOH will convert into K₂O, H₂O, O₂, and K₂CO₃. At 400 °C, K₂O will begin to change to K₂CO₃. At temperatures of ≥700 °C, K₂CO₃ is converted back into K₂O. K₂CO₃ has alkaline-lowering properties while K₂O is alkalizing. Therefore, K₂O is more expected than K₂CO₃[25]. The reaction for the formation of K₂O and K₂CO₃ can be seen in the following equation:

\[
\begin{align*}
2\text{KOH} & \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} \quad (2) \\
2\text{KOH} + \text{CO}_2 & \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \quad (3) \\
\text{K}_2\text{O} + \text{CO}_2 & \rightarrow \text{K}_2\text{CO}_3 \quad (4)
\end{align*}
\]

3.3. Brunauer-Emmet-Teller (BET) and basic strenght
The catalyst that gave the highest biodiesel yield, Cement clinker/KOH catalyst under calcination temperature of 700 °C and KOH concentration of 15%, was analyzed by BET. The result showed that the surface area of the catalyst was 9.622 m²/g. This value is even smaller than non-activated Cement Clinker and calcined Cement clinker catalysts that the surface area of 21.746 m²/g and 25.497 m²/g [22], respectively. The reduced surface area may happen during impregnation process that caused catalyst pore closure [25].

The cement clinker/KOH catalysts that were made in various KOH concentration (5%, 10% and 15%) and calcination temperature (500 °C, 600 °C, and 700 °C) were tested the basic strength. The results showed that the catalyst alkalinity ranged from H > 9.3 - 12.2. The basicity of the catalyst increases with increasing KOH concentration. The Catalysts that have basicity of H > 9.3 are the strong catalysts in the transesterification reaction [28].
3.4. Biodiesel yield and characterization
The effect of KOH concentration and calcination temperature on biodiesel yield can be seen in Figure 2. The highest yield of 88.82% produced by catalyst that prepared by the calcination temperature at 700 °C and a KOH concentration of 15%. The result showed that calcination temperature was directly proportional to biodiesel yield. The higher the calcination temperature, the more crystals formed [29]. In addition, the more K₂O is also formed. The more high temperatures, K₂CO₃ is converted to K₂O that increase the basicity, so that the catalytic activity was also increased [25].

![Figure 2](image)

**Figure 2.** The effect of calcination temperature and KOH concentrations on biodiesel yield.

As the same as the calcination temperature, the KOH concentration was also directly proportional to the biodiesel yield. The higher KOH concentration, the more the alkalinity increased. So that, the catalyst activity also increased [29]. In contrast with the calcination temperature, too high a KOH concentration reduced the catalytic activity. At this condition, KOH can dissolve the cement clinker, thereby reducing the active site number of the catalyst [30]. In this study, the increase of the KOH concentration still increased the biodiesel yield. This showed that the KOH concentration has not passed the optimum concentration in the synthesis of cement clinker/KOH catalyst.

To determine the effect of activation and impregnation to the catalytic activity, the biodiesel yield produced by calcined-impregnated catalyst, calcined catalyst and non-activated catalyst were compared (Figure 3). The result showed that the use calcined-impregnated catalysts produced the highest biodiesel yield, followed by calcined catalyst and non-activated catalyst. The calcination caused the loss of moisture (water content) and CO₂ which is still absorbed in cement clinker [31]. The calcination also opened pores and formed the crystals phase which increased the surface area [29]. So that, the catalytic activity on transesterification reaction also increased.

![Figure 3](image)

**Figure 3.** Biodiesel yield by using the various cement clinker catalyst treatments Calcination-Impregnation; (B) Calcination; (C) Without Activation.
Although the calcination increased the surface area, not all catalyst surfaces played a role in the transesterification process, but only the active side played one. Therefore, the basicity has a greater influence than the surface area. The KOH impregnation caused the increase in the catalyst active site numbers and catalyst alkalinity [32]. The KOH impregnation followed by the calcination caused the generation of active $\text{K}_2\text{O}$ and $\text{K}_2\text{CO}_3$ phases and formed the crystals. This condition stabilized the catalyst and increased the surface area of the catalyst. Therefore, the impregnation-calcination catalyst showed a good catalyst performance in the transesterification process.

Table 2. Characteristic of the obtained biodiesel.

| Characteristic         | Result | SNI 7182:2015 |
|------------------------|--------|---------------|
| Density (kg/m$^3$)     | 863.21 | 850-890       |
| Kinematic viscosity (mm$^2$/s) | 5.2   | 0.3-6.0       |
| Acid number            | 0.29   | Maks 0.5      |
| Cetane number          | 52     | Min 51        |
| Flash point            | 125    | Min 100       |

Figure 4. The GC chromatogram of the obtained biodiesel using cement clinker/KOH-700-15%.

Based on biodiesel characteristic (Table 2), the biodiesel made has met SNI standards. The Biodiesel density that is in range of standard indicates that the biodiesel will completely combust, so that it reduced the emissions and engine wear. Flash point values that are above the minimum standard indicates that biodiesel is safe for storage and transportation. The acid number below the maximum standard indicates that biodiesel is not corrosive. The viscosity that is in range of standard indicates that biodiesel has low effect to injection equipment on machines [33].

To determine the composition in biodiesel, a GC-MS test was performed. The results (Figure 4) showed that there were 2 highest peaks, namely methyl palmitate and methyl oleate with the level in the composition of 51.9% and 43.48%, respectively. This showed that the biodiesel has a high level of purity.

4. Conclusion
The best cement clinker/KOH catalyst is the catalyst that impregnated with 15% KOH and calcined at the temperature of 700 °C with the biodiesel yield of 88.82%. The catalyst has an alkaline value of $\geq 12.2$, the surface area of 9.622 $\text{m}^2$/g and the crystalline phase of $3\text{CaO} \cdot \text{SiO}_2$, $\text{K}_2\text{CO}_3$, $\text{K}_2\text{O}$, $\text{Ca(OH)}_2$. The biodiesel yield was directly proportional to the increase in calcination temperature and KOH concentration.
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