Transesterification of Crude Palm Oil (CPO) to Biodiesel Using Heterogeneous Catalyst K-CaO from Anadara Granosa Synthesized by Sol Gel Method

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Abstract. This study aimed to synthesize biodiesel from CPO using heterogeneous K-CaO catalyst from blood cockle (anadara granosa) shells. The catalyst was synthesized by sol gel method with variation calcination temperatures of 700, 800 and 900°C. The catalyst was characterized using X Rays Diffraction (XRD) and X-Ray fluorescence (XRF). The XRD results showed the presence of mineral lime, portlandite and calcite. Based on the XRF results that K-CaO heterogeneous catalyst contained 96,538% of calcium oxide (CaO). Biodiesel was synthesized by transesterification reaction with variations in time conditions (1, 2, 3 and 4 hours) and reaction temperature (50, 55, 60 and 65°C). The maximum biodiesel yield of transesterification reaction using heterogeneous K-CaO catalyst from blood cockle shell (anadara granosa) was 92,648% using catalyst calcination at a temperature of 700 °C and the optimum reaction time was 2 hours using 3% (w/w) catalyst, mol ratio of oil: methanol 1:6, stirring speed of 500 rpm and reaction temperature of 60 °C.

1. Introduction

The main energy source comes from fossil fuels which become the world's energy needs by 90%. Excessive use of fossil fuels will produce greenhouse gas emissions and global warming. Experts estimate that availability of fossil fuel sources will be exhausted by 2050 [1]. Biodiesel is a renewable alternative energy source that environmentally friendly, non-toxic and has low gas emissions when used for combustion. Biodiesel (fatty acid alkyl esters) was produced from the transesterification reaction of triglycerides or oils with short chain alcohols, usually using methanol. The oil obtained comes from vegetable oil or animal fats [2].

Riau has an area of oil palm plantations of 1.013.887 (ha) with a production volume of 4.715.000 (Tons) and a productivity of 5.105 (kg per ha) [3]. Based on this data, crude palm oil (CPO) has the potential to be developed as a raw material for biodiesel production. Biodiesel can be produced through transesterification reaction between triglycerides with methanol to methyl esters and glycerol with the help of a catalyst [4]. In the industrial process, the transesterification reaction uses homogeneous base catalyst such as KOH. The use of homogeneous catalysts has several disadvantages, such as the catalyst of the product was quite complicated. Homogeneous catalysts when used for synthesis biodiesel with oil containing high free fatty acids (FFA) will cause saponification and hence reduced the biodiesel yield and making it more difficult to purify. The CPO containing high free fatty acids was likely to cause soap when it was directly used.
Alternatives to overcome these problems was to use heterogeneous catalysts [5]. Heterogeneous calcium oxide (CaO) based catalyst for the synthesis of biodiesel have been widely used because CaO was relatively inexpensive, easy to obtain, not corrosive, environmentally friendly and high enough alkalinity [1]. The synthesis biodiesel using CaO catalyst derived from blood cockle calcined at 900°C was done and the maximum biodiesel yield obtained was 87.17% under 3 hours reaction conditions, 3% of catalyst weight, molar ratio of oil : methanol of 1:6 and reaction temperature of 60°C [5]. Although the yield of biodiesel was quite high, however, its purity was still low. To obtain better biodiesel results, researcher used two stages of reaction, esterification using an acid catalyst and transesterification using a CaO based catalyst [6].

Several researchers modified CaO catalyst for synthesize of biodiesel as done by Oko and Feri using catalyst CaO of shells and used egg shell impregnated KOH with raw materials castor oil and obtained the biodiesel yield was 96.07% [7]. Potassium hydroxide that support was chosen as a catalyst for strong base groups including alkalis. Alkalinity of alkaline oxides is stronger than alkaline earth oxides and transition oxides. KOH is used as a heterogeneous catalyst by impregnation to increase catalyst activity [8].

Degirmenbasi, et all [9] synthesized biodiesel using raw materials canola oil. The results of yield biodiesel was 97.67% using catalyst K2CO3/CaO. The catalyst impregnated K2CO3 on catalyst CaO [9]. The aimed of this research was synthesis biodiesel carried with one step reaction (transesterification) using CaO heterogeneous bases catalyst from blood cockle shell (anadara granosa) and modified with KOH by sol gel method. The sol gel method was one of the most frequently used methods in preparing metal oxide materials to form nano sizes. Nano-sized catalysts are very well used in biodiesel synthesis because of their high surface area, there by increasing the catalytic activity of catalyst [10].

2. Methodology

2.1 Instrumentation and materials
The instrumentation used in this research was analytical balance (Mettler Toledo AL204), oven (Heraeus Instrument D-63456), desiccator, furnace (Naberthemb type L31R), crucible, mortar, hotplate stirrer (RSH-IDR ), magnetic stirrer (spin bar), three-neck flask, condenser, thermometer, separating funnel, Ostwald viscometer, pycnometer, Cleveland flash point tester and other glassware. The materials used wee Crude palm oil (CPO), blood cockle (anadara granosa), isopropyl alcohol (IPA), phenolphthalein indicator, KOH 0.1 N, potassium hydrogen phthalate, acetone, HCl 0.5 N, CCl4, reagent wjs, KI, Na2S2O3, and starch solution.

2.2 Procedure

2.2.1. Synthesis and characterization of CaO heterogeneous base catalyst
The blood cockle shell (CKD) was soaked using vinegar (acetic acid 2%) for 30 minutes. After that, blood cockle shell washed using akaudes to clean and ovened for 24 hours. The shell was drying, pounded and crushed using mortar martyrs. Then sifed through 200 mesh. Powder of CKD was obtained for sol gel using KOH and ethylene glycol with ratio KOH: CKD: C2H6O2 of 1: 6: 12. Mixture of compounds and was stirring for 10 minutes at 300 rpm. Mixed results obtained settled for 5 hours. After the mixture was formed the gel, then filtered and washed using aquadm. The catalyst obtained was calcined by variation time of calcination at temperatures of 700, 800 and 900°C for 3 hours. The catalyst obtained in the form of catalyst was name code K-CaO-700, K-CaO-800 and K-CalCao-900.

2.2.2. Biodiesel synthesis
50 g CPO was heated at 105 ± 5°C and stirred using magnetic stirrer for 30 minutes. After heating, the CPO was cooled to temperature of 50°C. In a three neck flask, mixedtured of 3% catalyst (before use, the catalyst was heated at 105°C for at least 10 minutes) and 11.91 g of methanol (mole ratio of oil: methanol 1:6) was refluxed for 1 hour. CPO (temperature 50°C) was added to the catalyst-methanol
mixture and stirred for 3 hours at stirring speed of 500 rpm of 60°C. After 3 hours, the mixture was put into glass beaker and left overnight to separated the catalyst. Once separated, the results of biodiesel are filtered using ordinary filter paper to obtain crude biodiesel. Repetition was done for the variation of reaction time 1, 2, 3 and 4 hours and the reaction temperature variations of 50, 55, 60 and 65°C.

3. Results and Discussion

3.1 Catalyst Characterization

Characterization of mineral content and chemical composition of CaO catalyst from blood cockle shell modified with KOH using sol gel method, each analyzed using X-ray diffraction (XRD) and x-ray flrnce (XRF) compared to the JCPDS (Join Committee Powder standard Difraction Structure) by Markgraf and Reeder [11]. The XRD data from heterogeneous catalyst is shown in Figure 1.

![Figure 1](image-url)  
**Figure 1.** XRD patterns of CaO heterogeneous bases catalyst

The XRD pattern on the heterogeneous catalyst K-CaO-900 showed the presence of lime (CaO), portlandite (Ca(OH)₂) and calcite (CaCO₃) peaks found in 2 theta of 17.9497° (portlandite) 33.9709° (calcite) ; 37.3205° (lime) and 64.1704° (lime). Characterization of heterogeneous catalyst K-CaO-800 showed the same mineral in 2 theta of 37.3167° (lime) 43.1371° (calcite) 50.7915°(portlandite). Characterization of heterogeneous catalyst K-CaO-700 showed in 2 theta of 29.3706°; (calcite) 57.4077° (portlandite) and 65.6208° (lime). Blood cockle shell contain lots of CaCO₃ which when decomposed above 700, 800 and 900°C can produce CaO. Furthermore, the analysis of chemical composition using XRF is shown (Table 1), it can be seen that the main content of the heterogeneous catalyst from these blood cockle shell was CaO. The blood cockle was calcined temperature 900°C for 10 hours obtained percentage CaO of 99.09% [12].
Table 1. XRF results of K-CaO heterogeneous bases catalyst from blood cockle shell (*anadara granosa*)

| Elements      | Concentrations (%) | K-CaO-700 | K-CaO-800 | K-CaO-900 |
|---------------|--------------------|-----------|-----------|-----------|
| CaO           |                    | 96,538    | 93,612    | 94,982    |
| K₂O           |                    | 2,195     | 2,448     | 2,198     |
| MnO           |                    | 0,011     | 0,010     | 0,010     |
| SrO           |                    | 0,314     | 0,312     | 0,253     |
| Ag₂O          |                    | 0,321     | 0,417     | 0,536     |
| In₂O₃         |                    | 0,578     | 1,031     | 1,097     |
| BaO           |                    | 0,007     | 0,006     | -         |
| TiO₂          |                    | 0,003     | 0,002     | -         |
| Fe₂O₃         |                    | 0,008     | 0,034     | 0,009     |

3.2 The effect of reaction condition on biodiesel yield

Biodiesel synthesis in this study was carried out through the transesterification reaction under 3% catalyst weight conditions, 1: 6 mole ratio of oil: methanol, stirring speed of 500 rpm and variation time used was 1, 2, 3 and 4 hours. The maximum biodiesel yield of transesterification reaction using heterogeneous K-CaO catalyst from blood cockle during 2 hour reaction of 92.66486% (*Figure 2.*) using K-CaO-700, K-CaO-800 and K-CaO-900 catalysts.

![Figure 2. The effect of reaction time on biodiesel yield](image)

The increase in reaction time causes an increase in longer contact between reactants so that the particles more frequently interact and biodiesel yield increases. However, the longer of reaction time used biodiesel results will be reduced because the transesterification reaction occurs which is a reversible reaction. Biodiesel yield decreases during 3 hour reaction. Biodiesel synthesis using heterogeneous catalysts requires a long time to obtain optimum results. However, it is usually a short time for a transesterification reaction using a homogeneous catalyst, but this research proves that heterogeneous catalysts produce biodiesel in a short time [13]. Homogeneous base catalyst, KOH is used for biodiesel synthesis with a yield of 87% at a reaction temperature of 50 °C, catalyst weight of 0.075%, mol ratio oil: methanol of 1: 6 and reaction time of 5 hours [14]. Biodiesel synthesis using CaO from blood cockle shell without KOH using CPO with a reaction temperature of 60°C, catalyst
weight 4%, mol ratio of oil: methanol 1: 6 produced biodiesel yield of 77.89% with the optimum reaction time of 3 hours [5].

Biodiesel synthesis was also carried out with variations of reaction temperature at 50, 55, 60 and 65°C using the optimum reaction time that has been obtained 2 hours, 1: 6 mole ratio of oil: methanol and stirring speed of 500 rpm. The maximum biodiesel yield of transesterification reaction using heterogeneous K-CaO catalyst from blood cockle shell (anadara granosa) was 92.648% using reaction temperature of 60°C (Figure 3).

Figure 3. The effect of reaction temperature on biodiesel yield

According to Farooq and Ramli [15], transesterification reactions are endothermic which react faster at high temperatures, because the higher the temperature will cause the movement of molecules faster or the kinetic energy of the reagent molecules was greater so that collisions between reagent molecules also increase. However, there is a decrease in the results of biodiesel at a temperature temperature of 65°C reaction. That is because, if the temperature used was high and exceeds the normal boiling point of methanol, it can induced evaporation or loss of methanol. CaO was synthesized of 900 °C calcined blood cockle obtained yield of 77.89% using CPO raw material under conditions of reaction time 3 hours, catalyst weight 4%, mol ratio (oil: methanol) 1: 6, and the optimum reaction temperature 60 °C [5].

4. Conclusion
Biodiesel was successfully synthesized through transesterification reaction using CPO raw materials and the K-CaO catalyst that was synthesized by sol gel method. The K-CaO-700, K-CaO-800 and K-CaO-900 catalyst were characterized using XRD and XRF. XRD results show the presence of mineral lime, portlandite and calcite. Based on the results of XRF characterization the CaO content in heterogeneous catalyst was 96.538%. The maximum biodiesel yield in the transesterification reaction using CaO catalyst from blood cockle shell (anadara granosa) was 92.648% with K-CaO-700 catalyst under 2 hour of reaction time, 3% of catalyst weight, molar ratio (oil: methanol) 1: 6, and the stirring speed of 500 rpm at a reaction temperature of 60°C.

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