

Preparation of Heterogeneous CaO Catalysts for Biodiesel Production

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Abstract. The objective of this research was to develop heterogeneous catalysts from three CaO sources for biodiesel synthesis. The CaO catalyst were prepared from limestone, calcium hydroxide and calcium carbonate with thermal processing in a muffle furnace at 900°C. The results showed that CaO catalyst from limestone has better characteristic than catalyst from Calcium Hydroxide and Calcium Carbonate. From morphology testing, the CaO catalyst derived from limestone formed a crystal, while The X-ray diffraction analysis showed that the amount of CaO contained in limestone was the highest among the others. The yield of biodiesel obtained from the experiment was 89.98% for the catalyst from limestone; 85.15% for the catalyst Ca (OH)₂; and 78.71% for CaCO₃ catalyst.

1. Introduction

Catalyst is a substance that enables a chemical reaction to proceed at a usually faster rate. Commonly, catalyst was developed in homogenous or heterogenous phases. In biodiesel production, the homogenous catalyst generally use acid and base catalysts such as sulphuric acid, sodium hydroxide (NaOH) and potassium hydroxide (KOH). The sulphuric acid is used in esterification reaction in which free fatty acid (FFA) is reacted to methanol. The sodium hydroxide and potassium hydroxide are mostly used in transesterification reaction where triglyceride is reacted with methanol[1,2]. The disadvantages of utilization of homogeneous catalysts in biodiesel production are saponification reaction [1] and regeneration issue after the transesterification process is completed as well as producing toxic wastewater[3] and corrosive in reactor[4]. Hence, the heterogeneous base catalysts was introduced to overcome these problems[5].

The heterogeneous catalysts which have been widely used include KI/KIO₃/H-zeolite[6], calcium hydroxide (CaO)[7-12], zirconia[13-14] and zinc oxide[15]. To saving cost of biodiesel production, the catalyst must be economically feasible. One option is by developing catalyst from natural resources such as bone, waste and natural rock like limestone. Limestone can be found as a raw material for cement production. Limestone contains a calcium carbonate and calcium hydroxide / Ca(OH)₂[16]. If the calcium carbonate (CaCO₃) and Ca(OH)₂ were calcined in high temperature, then they will decompose to CaO which is the main source of heterogeneous catalyst. CaO is a strong basic oxide which has high catalytic activity [12]. The objective of this research was to prepare CaO catalyst from multi resources of CaO, like limestone, Ca(OH)₂ and CaCO₃.



2. Methods

2.1. Material

Limestone was obtained from local material store. Methanol has industrial specification and sulphuric acid, calcium hydroxide and calcium carbonate were obtained from Merck Ltd. Palm oil was used as feedstock in performance testing and it was purchased from local market. Palm oil must has FFA content under 0.5%. Pretreatment for reducing of FFA was done by using esterification reaction. The esterification reaction was carried out in a three-neck bottle reactor equipped with a condenser and a thermometer. A 800 ml cooking oil was mixed with 10 ml sulphuric acid and methanol by mole ratio to FFA 40:1, which all of the material had already been heated to 60°C. The reactor was placed in a water bath and heated on a hotplate. The agitating speed was kept at 600 rpm to ensure the efficient mixing. The reaction kept going for 2 hours. FFA contents was analyzed by using acidi-alkalimetry.

2.2. Catalyst preparation

The limestone were washed by deionized water to remove dust and impurities, and then dried overnight in an oven at 105°C. The acquired limestone as well as commercial CaCO_3 were crushed and sieved, and then calcined at 900°C for 1 ½ h. The same process was carried out for calcium carbonate and calcium hydroxide.

2.3. Catalyst characteristic

The catalyst product was analyzed of characterization consist of morphology and crystallite. The analysis crystallography was used x-ray diffractometer, XRD-7000S model Shimadzu brand with X-ray tube target Cu, voltage 30 kV, current 30 mA, and $\text{K}\alpha$ radiation. XRD data was analyzed with PCXRD software. Morphology of catalyst was analyzed with JEOL PC Scanning Electron Microscope (PCSEM) model JSM-6510LA with magnification x5000. The analysis process was conducted in Center of Research and Service Diponegoro University (CORES DU).

2.4 Catalytic testing for biodiesel production

The transesterification reaction was carried out in a batch reactor equipped with a propeller. The reactions were performed using Branson (USA) ultrasonic processor (42 kHz) with a full power of 200 W. 100 ml of cooking oil filled into reactor and require in ultrasonic reactor. Methanol was added with mole ratio methanol to oil 9:1 and catalyst loading 2.6 wt%. The transesterification reaction has been done for 40 minute and CaO catalyst was separated by filtration. The filtrate was deposited until the glycerol (lower layer) and the methyl ester (upper layer) separate. FAME product was analyzed with Gas chromatography (GCMS) for composition of methyl ester[17].

3. Result and discussions

3.1 Characterization of CaO catalysts

The results SEM analysis was presented in Figure 1. Figure 1a is a result of SEM of limestone before calcination. The surface is still amorphous because there are many impurities contents. Limestone contains Ca(OH)_2 and CaCO_3 while limestone looks fragile. After calcination process the limestone convert to CaO and carbon dioxide and water gases. Figure 1 b) is a CaO catalyst after calcination of limestone so called as CaO catalyst 01. This catalyst has formed crystal on it's surface and hence will act as an active site and speeding up the reaction time. Figure 1c) is the catalyst of Ca $(\text{OH})_2$ after calcination so called as CaO catalyst 02. The surface of the particles is similar to Figure 1 b) which has formed crystal on its surface. While Figure 1 d) is the catalyst of the raw material Ca(CO)_3 so called as CaO catalyst 03 The surface of CaO catalys 03 has particles that looks different compared to the other catalyst. It could be concluded that no crystal was formed on its surface. This could be caused because the calcination process is not perfectly ocured. Thus, the formation of crystals of CaO

catalyst of limestone and $\text{Ca}(\text{OH})_2$ is better than $\text{Ca}(\text{CO})_3$ because morphologically it has already formed crystals on its surface.

Calcination temperature of 900°C is chosen because at these temperatures, will be produced an optimized CaO and it will be indicated by how much H_2O and CO_2 evaporates, the surface area formed, and the catalyst activity[11].

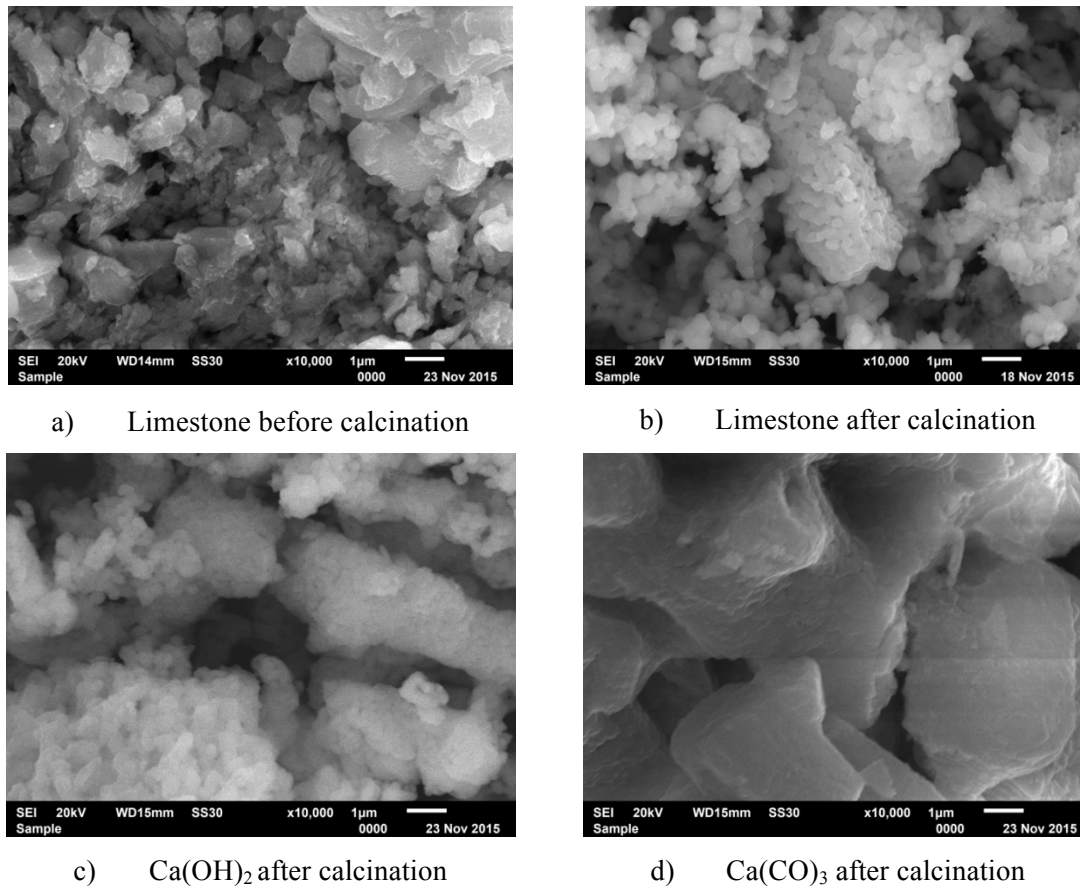


Figure 1. The result of SEM Analysis with x10.000 magnifications.

The graphics shown in Figure 2 are based on the XRD analysis. CaO catalyst 01 has higher intensity than the other substances. XRD pattern of limestone was different with CaO catalysts. Limestone was contained of CaCO_3 and $\text{Ca}(\text{OH})_2$ as identified in 2 theta 29; 34, 48 and 52. CaO catalyst 02 was also identified at peaks of 2 theta 29, 34, 48 and 52. CaO catalyst 02 was CaO catalyst that prepared from $\text{Ca}(\text{OH})_2$. It shows that calcium hydroxide can not be decomposed to calcium oxide and water vapor at 900°C during 1,5 hours. CaO catalyst 03 has the same peaks as CaO catalyst 01, but intensity CaO catalyst 03 is more less than intensity CaO catalyst 01.

The results of XRD analysis was presented in Table 1. Table 1 shows that limestone was contained $\text{Ca}(\text{OH})_2$, CaCO_3 , and $\text{Cr}_{0.5}\text{Li}_2\text{O}_3\text{Sb}_{0.5}$. CaO catalyst 01 was contained CaO and small amount of CaD_2O_2 . CaO catalyst 02 was contained CaO and few $\text{Ca}(\text{OH})_2$ remaining. CaO catalyst 03 was contained mostly CaCO_3 , and a few of $\text{Ca}(\text{OH})_2$ and CaO . This shows that calcination processing of limestone was better than calcination of $\text{Ca}(\text{OH})_2$ and CaCO_3 . $\text{Ca}(\text{OH})_2$ substance contains of hydrogen bond so the energy for decomposition of $\text{Ca}(\text{OH})_2$ is more than energy for decomposition CaCO_3 . Therefore $\text{Ca}(\text{OH})_2$ is still detected in XRD analysis.

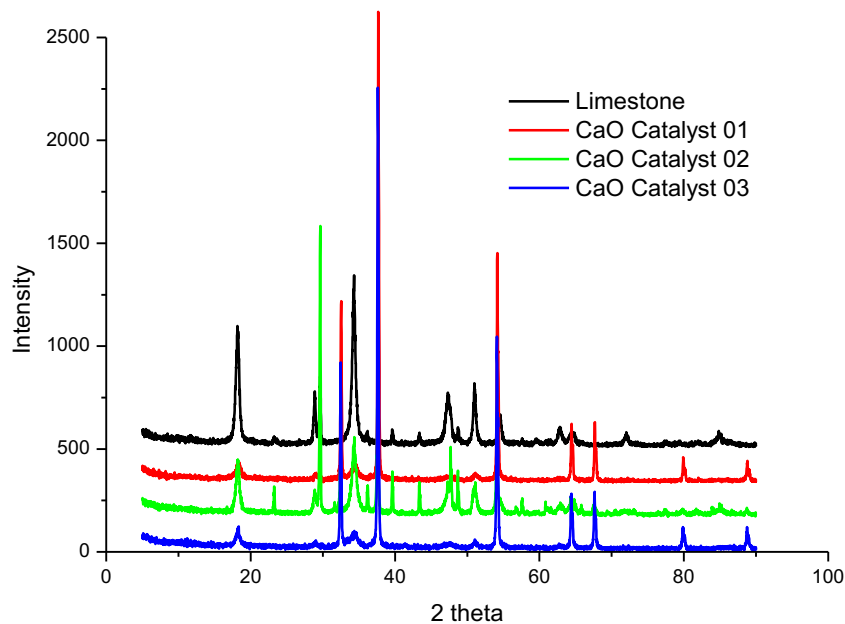


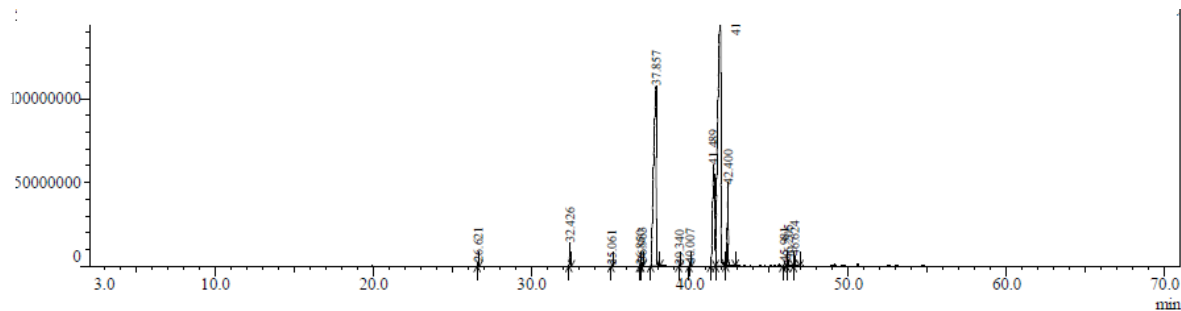
Figure 2. XRD pattern of limestone and CaO catalyst

Table 1. composition of the CaO catalyst and limestone.

Material	Compound	Formula	Composition (%)
Limestone	Portlandite	$\text{Ca}(\text{OH})_2$	78,7
	Calcium Carbonate	CaCO_3	13,2
		$\text{Cr}_{0,5}\text{Li}_2\text{O}_3\text{Sb}_{0,5}$	8
CaO catalyst 01	Calcium oxide	CaO	88,1
		CaD_2O_2	11,9
CaO catalyst 02	Portlandite	$\text{Ca}(\text{OH})_2$	19,4
	Calcium Oxide	CaO	80,6
	Calcum carbonate	CaCO_3	37,7
CaO catalyst 03	Calcium Oxide	CaO	18
	Portlandite	$\text{Ca}(\text{OH})_2$	44,2

3.2 Catalytic testing for biodiesel production

Biodiesel from catalytic testing was analyzed by using Gas Chromatography Mass Spectrophotometry (GCMS) (Figure 3) Figure 3 shows typical methyl ester in a biodiesel product. Dodecanoic acid methyl ester was detected in a retention time (RT) of 26.62 minute, tetradecanoic acid methyl ester was detected in a RT of 32.43 minute, pentadenoic acid methyl ester was detected in a RT of 35.06 minute. All atty acid methyl ester (FAME) compounds found in the Chromatography is listed in Table 2 The largest compound found in FAME is 9-Octadecenoic acid methyl ester followed by hexadecanoic acid methyl ester and 9,12-Octadecadienoic acid methyl ester.

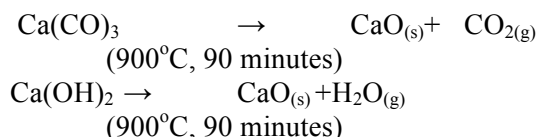
**Figure 3.** Chromatograph of biodiesel product**Table 2.** Types of FAME in biodiesel product

Retention time (minute)	Compound	Composition (%)
26.62	Dodecanoic acid methyl ester	0.17
32.43	Tetradecanoic acid methyl ester	1.02
35.06	Pentadecanoic acid methyl ester	0.03
36.85	9-Hexadecenoic acid methyl ester	0.21
37.86	Hexadecanoic acid methyl ester	29.66
39.34	Cis-10 Heptadecenoic acid methyl ester	0.03
40.01	Heptadecanoic acid methyl ester	0.09
41.49	9-12 Octadecadienoic acid methyl ester	14.43
41.92	9-Octadecenoic acid methyl ester	47.79
42.40	Octadecanoic acid methyl ester	5.50
45.98	Cis 10-heptadecenoic acid methyl ester	0.22
46.21	Octadecanoic acid 9,10 dihydroxy methyl ester	0.35
46.62	Eicosanoic acid methyl ester	0.50

The yield of biodiesel was calculated by using Eq 1

$$\text{Yield FAME} = \frac{\text{Mass of FAME}}{\text{Mass of Triglyceride}} \times 100 \quad (1)$$

The calculated yield was shown in Figure 4. The best catalyst performance was shown at experiment with CaO catalyst 01 produces a yield of 89.98%. Yield of FAME by using CaO catalyst 02 was 78.71% and CaO catalyst 03 yield of FAME 85.15%. In this study, the compound serves as the catalyst is a compound CaO based on following reaction:



The three raw materials after calcination contains different amount of CaO. Based on XRD analysis and Table 1, CaO content of each raw material is 88.1% for limestone, 80.6% for $\text{Ca}(\text{OH})_2$, 18% for CaCO_3/CaO . The higher CaO contents give higher yield due to more catalytic activity in the [12]. $\text{Ca}(\text{OH})_2$ shall be used in liquid phase so that it can act as catalyst in transesterification reaction.

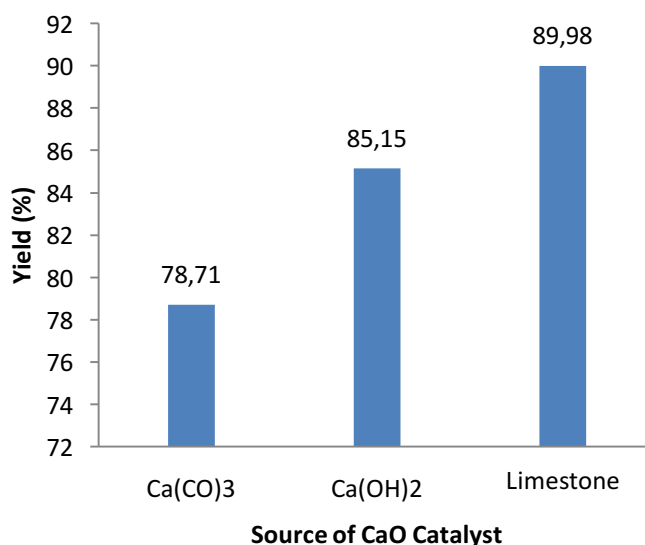


Figure 4. Yield amount of Methyl Ester produced by each different catalyst.

4. Conclusion

In summary, CaO catalyst has been prepared from limestone, calcium carbonate and calcium hydroxide by using calcination process. CaO catalyst prepared from limestone, give higher performance than other CaO catalysts from calcium hydroxide and calcium carbonate.

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