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Research Article

Preparation and Characterization of *Anadara Granosa* Shells and $CaCO_3$ as Heterogeneous Catalyst for Biodiesel Production

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Abstract

Nowadays, the use of homogenous catalyst has been gradually reduced for its operational reason. The homogenous catalyst leads in difficulty of separation after the process completed and the life cycle is shorter. Therefore, most of researches are introducing heterogeneous catalyst for its substitution. This research was aimed to evaluate the use of shell of *Anadara granosa* and $CaCO_3$ as source of CaO based catalyst through impregnation method. The preparation of the catalyst was started by decomposition of shells and $CaCO_3$ at temperature of 800 °C for 3 hours, followed by impregnation at 70 °C for 4 hours and then calcined at 800 °C for 2 hours. The $CaCO_3$ based catalyst gained high yield of biodiesel (94%) as compared to *Anadara granoasa* based catalyst (92%). The reusability study showed that these catalysts could be used until three times recycle with 40-60% yield of biodiesel. The CaO contents of catalyst decreased up to 90% after three times recycles.

Keywords: Anadara granosa; heterogeneous catalyst; biodiesel; CaO

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1. Introduction

Currently the world's attention has drawn to search new energy sources since the resource of fossil energy has limitation of its availability. In fact, 85% of the world's energy is still supplied by fossil fuels [1]. Renewable energy is expected to overcome the energy fossil limitation issues. One of the energy alternatives is biodiesel and the use of biodiesel is expected to reduce dependence on fossil fuels. Biodiesel has several advantages, i.e. biodegradable, non-toxic, and does not produce greenhouse gas emissions. Burning biodiesel does not produce sulfur, carbon dioxide (CO_2), carbon monoxide (CO), and nitrogen oxides (NOx) [2].

However, when it is compared to petroleum diesel, biodiesel production costs are still relatively high. Some attempts have been conducted to reduce the production cost of biodiesel, one of them by using a heterogeneous catalyst. Commonly, biodiesel production uses homogeneous base or acid catalysts such as NaOH, KOH, and H_2SO_4 which have several problems such as catalyst separation and product purification. Therefore, heterogeneous catalysts were introduced to overcome these problems. As the heterogeneous catalyst is in differ-

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ent phase with the product, then it is relatively easier for product purification. Therefore, the use of this catalyst will also reduce the production cost, reusable, eco- and environmentally friendly [3].

The problem of the use of heterogeneous catalysts relies on the diffusion mechanism because there are three-phases of reactants. This problem can be overcame by using promoter or support catalyst which can increase the catalyst surface area and improve the reaction with triglyceride molecule. The advantage of using promoter/support is the increasing life time of the catalyst and thermal stability [3]. Fly ash has been widely used as promoter for this heterogeneous catalyst. The CaO catalyst is the common heterogeneous catalyst which can be generated from the decomposition of $CaCO_3$ or from calcined mollusk shells at high temperatures. With content of $CaCO_3$ of 95-98%, mollusk shells are highly potential as a heterogeneous catalyst [4]. The use of mollusk shells as catalyst has been investigated and proven to be an effective replacement of $CaCO_3$. Viriyaempikul *et al*. [5] have synthesized biodiesel with a catalyst of mollusk and egg shells and showed that the shell based catalyst is very effective for biodiesel synthesis.

One of mollusk shells is *Anadara granosa* and its availability is very abundant in Indonesia. The large amount of waste of *Anadara granosa* has not been optimally used. This paper investigates the use of *Anadara granosa* as source of CaO catalyst and will be impregnated with fly ash as promoter. The use of support/promoter on CaO is expected to increase the surface area on the catalyst. The content of SiO_2 and Al_2O_3 in the fly ash is a high potential as a catalyst support [6].

2. Materials and Methods

2.1. Materials

In this research, palm oil (Indofood), $CaCO_3$ (99%, Merck) and methanol (95%, Merck) were used as raw materials. The fly ash was provided by PT. Paiton, East Java and *Anadara granosa* shells were obtained from local market in Semarang.

2.2. Catalyst preparation and characterization

Mollusk shell (*Anadara granosa*) were collected from local market at Semarang. The shell were cleaned to remove impurities and then were dried in an oven at 110 ^oC for 6 h. The shell were crushed and ground to fine powder then sieve at 100 µm. The fine powder of shell and $CaCO_3$ were calcined at 800 ^oC for 3 h to generate CaO. Coal fly ash were dried in an oven at 105 ^oC for 10 h. The fly ash supported CaO catalyst was prepared according to wet impregnation method [7]. In order to prepare 45 wt% CaO loaded catalyst, 13.5 g of calcined shell or $CaCO_3$ powder were added to 200 ml of water to prepare aqueous solution of $Ca(OH)_2$, then added 16.5 g of dried fly ash and mix using magnetic stirrer under total reflux for 4 h at 70 ^oC. The solution was aged for 18 h. Excess water was removed using hot air oven at 105 ^oC for 12 h and calcined at 800 ^oC for 2 h.

In order to determine the crystalline nature of fly ash supported CaO catalysts, X-ray diffraction (XRD) patterns for supported catalysts samples were analyzed using Cu-Kα. The analysis was performed at 2θ angle ranging from 10^o to 90^o at a scanning speed of 2^o min^{-1}. The surface morphology of the developed catalysts was determined using scanning electron microscope (SEM).

2.3. Transesterification reaction and biodiesel analysis

The transesterification of palm oil was carried out in a 500 mL round bottom flask which was equipped with a magnetic stirrer and reflux condenser. At one side-neck was inserted with a thermometer while another side used for sampling. For all experiments, 31 g of palm oil was added to the bottom flask with catalyst loading of 2.6, and 10% while the methanol:oil mole ratio was set constant at 12:1. The mixture was then stirred for few minutes to make uniformly mixed oil-catalyst slurry and heated to 70 ^oC for 2 h.

Once the reaction was completed, the CaO catalyst was filtered out from the mixture by using a vacuum pump. The sample was separated by centrifugation at 3000 rpm for 25 min. This step formed two phases i.e. Fatty acid methyl ester (FAME) phase and glycerol phase. For purification, the glycerol was removed by using a separating funnel and the methanol in the FAME phase was evaporated in a rotary evaporator. The yield obtained from the reaction was calculated by using Equation 1. The product was analyzed for its density and viscosity.

$$Yield\,(\%) = \frac{W_{biodiesel}}{W_{oil}} x100\% \qquad (1)$$

2.4. The Catalyst Reusability

Just after the first cycle of transesterification, the recovered catalysts were evaluated with methanol washing and followed by recalcination procedures. After the completion of reaction in the first cycle the spent catalyst was separated from the mixture by filtration and washed with methanol to remove glycerol from the catalyst surface. The catalyst then was dried in the oven (65 ^{o}C for 3 h) before recalcination at 800 ^{o}C for 2 h. A total of 3 esterification cycles were carried out to study the catalyst reusability. The determination of the CaO and Ca concentrations of the catalyst after each regeneration method and each transesterification cycle was carried out using XRD method.

3. Results and Discussion

3.1. Characterization of fly ash supported CaO catalyst

Figure 1 shows XRD pattern of fly ash supported CaO. The CaO loading ratio was 45 % and the catalyst calcination CaO/fly ash at temperature of 800 ^{o}C. The XRD analysis of the catalyst CaO/fly ash from several sources CaO showed the same diffraction pattern and CaO crystals is dominate. The diffractogram also show that SiO_2 is the main composition of coal fly ash. The XRD patterns of catalyst also shows that CaO peaks was observed at 2θ of 32^{o}, 37^{o}, 53^{o}, 64^{o} and 67^{o}. At 2θ of 34^{o} indicated the presence Ca_2SiO_4 formed by dehydration due to calcination at 800 ^{o}C. This compound ($Ca_2SiO_4.H_2O$) produced by the pozollanic reaction between CaO and SiO_2 in the presence of water molecules.

Figure 2 shows the SEM image of the catalyst CaO/fly ash and it shows irregular particles. The molecular size of the catalyst CaO/fly ash was not more than 100 µm. In contrast, the CaO catalyst derived from $CaCO_3$ has smaller distribution molecular sizes (3-30 µm), while the size of CaO derived from *Anadara granosa* was in the range of 3 to 67.67 µm. The SEM images also showed the presence of agglomeration structure. Agglomeration is a metal oxide that formed by the heat treatment [8].

3.2. Transesterification and characterization of FAME

The esterification process of palm oil was performed at 60°±2°C for 120 minutes with mole ratio methanol of palm oil (12:1) and stirring of 700 rpm. Excessive use of methanol was to drive the reaction toward the product. The catalyst was varied between 2-10% to determine the optimum catalyst loading for this transesterification of palm oil.

The use of shells as a source of CaO for CaO/fly ash catalyst on biodiesel showed that the catalyst was active to catalyze the trans-

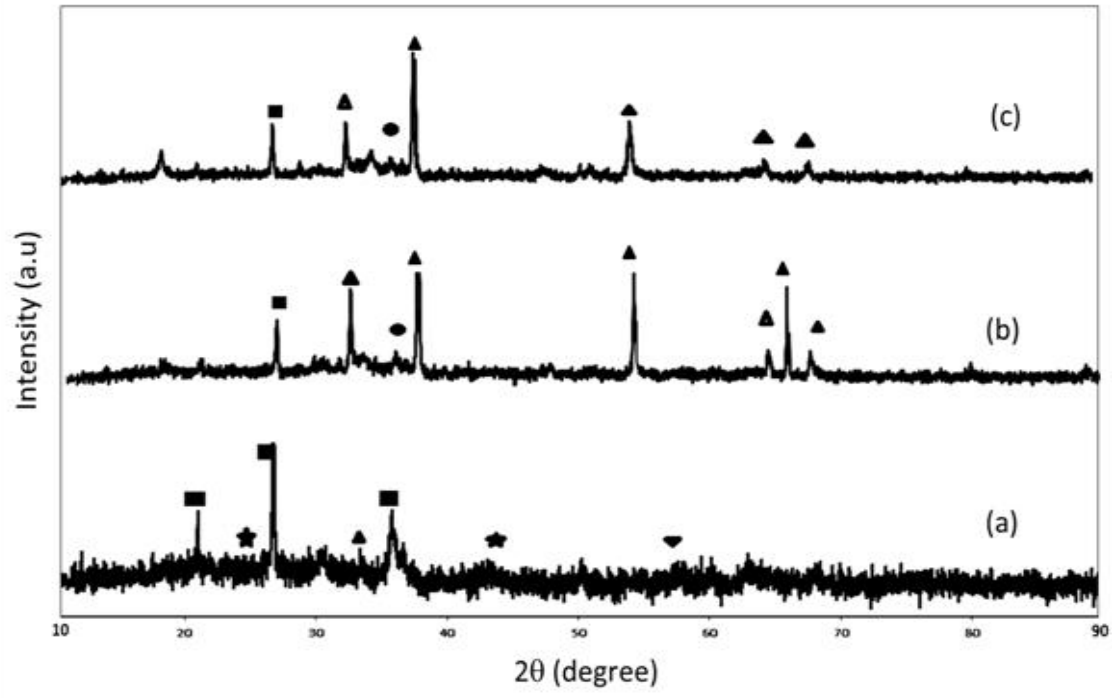


Figure 1. XRD patterns of catalysts (a) coal fly ash (b) Fly ash supported CaO (*Anadara granosa*) (c) Fly ash supported CaO ($CaCO_3$) [SiO_2 (■) CaO, (▲) Al_2O_3 (★) Ca_2SiO_4 (●) Fe_2O_3 (▼)]

esterification of palm oil and methanol. All CaO/fly ash based catalysts could gain yield more than 75% after 2 hours of reaction. The yield of biodiesel produced by using CaO catalyst from $CaCO_3$ (94.71%) was higher than the one produced by *Anadara granosa* which was 92.5% at catalyst loading of 6%.

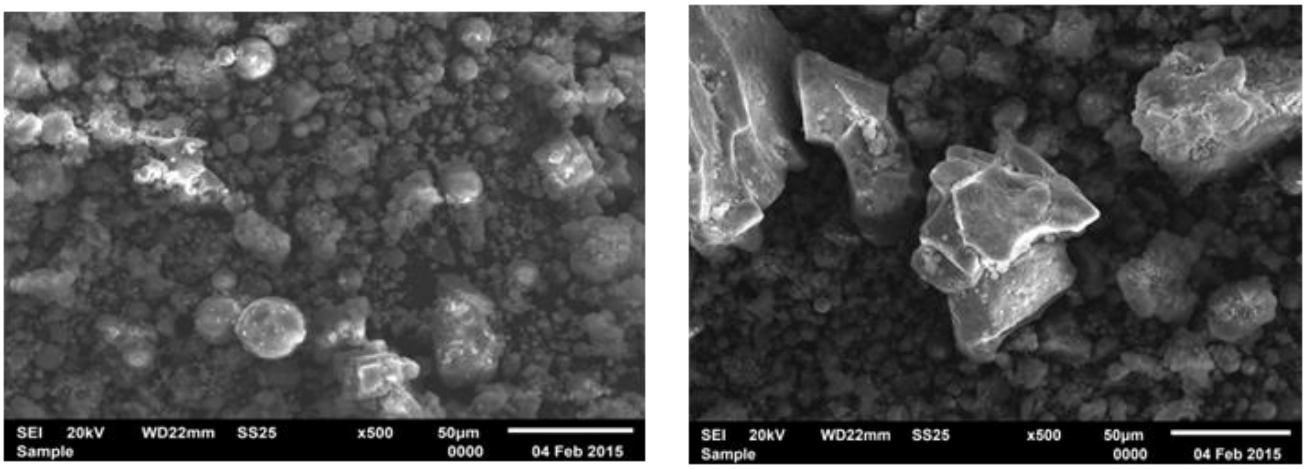
The analysis of viscosity and density of biodiesel obtained from experiment was already fulfilled the SNI and ASTM standards. The density and viscosity of biodiesel obtained by 2-10% catalyst loading of CaO based $CaCO_3$ were in the range of 0.87-088 g/cm^3 and 3.91-4.35 cSt, respectively, whereas, for CaO based *Anadara granosa* was 0.89 g/cm^3 and 4.14-4.28 cSt, respectively (Table 1).

3.3. Reusability Cycle

Reusability cycle was tested under esterification reaction condition of 6% catalyst loading, methanol:oil mole ratio of 12:1, reaction temperature of 60 ^oC, reaction time of 2 h and stirring speed of 700 rpm. After each cycle, the spent catalyst was regenerated using methanol washing and dried in an oven at 110 ^oC for 12 h.

Figure 3 shows that the yield of biodiesel dropped to 56.76 % and 43.26 % after three times uses of catalyst derived from $CaCO_3$ and *Anadara granosa*, respectively. The result indicates slight catalyst deactivation because the leaching of the CaO active species into the reaction media [8]. This also supported by Ho *et al.* [7] who evaluated the use of heterogeneous catalyst on palm oil esterification and obtained 39 % of yield after fourth cycle and no biodiesel produced after that cycle.

The decrease of CaO contents after 3rd cycles are depicted in Table 2. Dissolution of CaO to alcoholic phase also caused the deactivation of active sites; it made concentration of CaO decrease. The decrease in yield could be attributed to catalyst deterioration due to poisoning by glycerol and soap present in reaction mixture [9]. The presence of calcium glyceroxide in spent catalyst could possibly be a factor in its reduced reusability. Calcium glyceroxide was probably formed due to mixture of CaO and glycerol [10].



(a) (b)

Figure 2. SEM images of fly ash supported CaO (a) $CaCO_3$ (b) *Anadara granosa*

Table 1. The properties of biodiesel as function of catalyst loading and type of catalyst

Catalyst	Catalyst loading (%)	Yield (%)	Density (g/cm^3)	Viscosity (cSt)
Fly ash supported CaO ($CaCO_3$ pure)	2	83.12	0.88	3.91
	6	94.71	0.87	4.35
	10	90.68	0.88	4.06
Fly ash supported CaO (*Anadara granosa*)	2	75.85	0.89	4.28
	6	92.50	0.89	4.28
	10	81.96	0.89	4.14

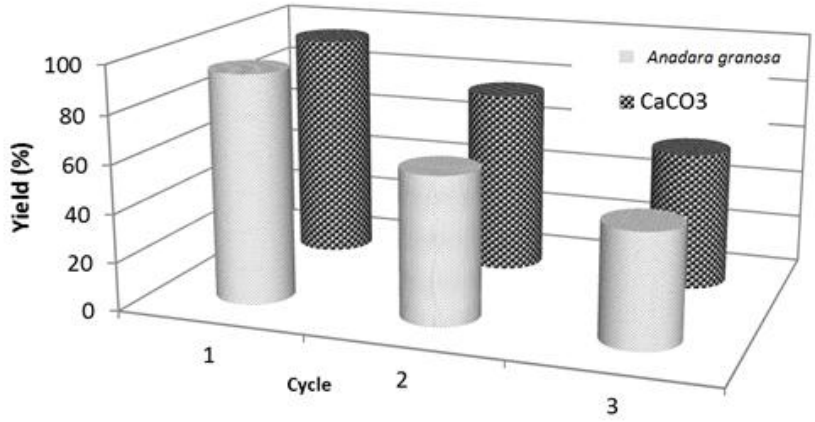


Figure 3. Biodiesel yield in the reusability study for *Anadara granosa* and $CaCO_3$

Table 2. CaO concentration of fresh and recycled catalysts

Catalyst	CaO contents in fly ash catalyst (%)	
	$CaCO_3$ based CaO	*Anadara granosa* based CaO
Fresh (before used)	57.31	43.26
1st cycle	34.39	26.98
2nd cycle	10.54	8.23
3rd cycle	7.96	5.28

4. Conclusions

Heterogeneous catalysts of fly ash supported CaO (derived from *Anadara granosa* shell and $CaCO_3$ grade) was effective for transesterification of palm oil to biodiesel. The waste of mollusk shell can be considered as alternative as low-cost catalysts for biodiesel production. The yield of biodiesel obtained by CaO based *Anadara granosa* was 92% and the physical properties of biodiesel fulfilled the ASTM standards. The catalyst derived from *Anadara granossa* could be used up to 3rd cycle with 40% yield of biodiesel. The CaO contents decreased significantly after 3rd cycles at 85-90% due to formation of calcium glyceroxide as result of mixture of CaO and glycerol.

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