

Modified CaO Catalyst from Golden Snail Shell (*Pomacea canaliculata*) for Transesterification Reaction of Used Cooking Oil

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Abstract: Calcium oxide (CaO) shows catalytic activity because its strength, low solubility in methanol, and excessive. It can be found in golden snail shell (*Pomacea canaliculata*). The CaO/fly ash catalyst was applied in transesterification reaction of used cooking oil. There were three catalysts obtained, which were golden snail shell calcined (CK), 75% golden snail shell calcined modified by 25% fly ash (CKFA), and by 25% fly ash leached (CKFAL). Result showed that after the golden snail shell was calcined at 900 °C, it produced 93.94% Ca-(OH)₂. Modified CaO catalyst from golden snail shell and fly ash were active to convert used cooking oil become biodiesel.

Keywords: catalyst, fly ash, leaching, golden snail shell, trans-esterification reaction.

INTRODUCTION

Biodiesel is a methyl ester made from vegetable or animal oils by trans-esterification process (Knothe, 2000). Biodiesel has been selected as an alternative fuel because it is renewable, biodegradable, non-toxic, and its physical and chemical similarity to conventional diesel fuel (Basumatary, 2013; Lotero et al., 2005). Besides, the use of biodiesel as a fuel can decrease pollutants such as CO₂, SO₂, CO, and HC gas (Anonymous, 2012; Endalew, Kiros, & Zanzi, 2011; Huang, Zhou, & Lin, 2012).

Vegetable oil has a big potency as a biodiesel. The main contents of vegetable oils are triacylglycerol which has three esters or fatty acid chains (acyl functional group) attached on glycerol functional group (Endalew et al., 2011; Issariyakul & Dalai, 2014). Used cooking oil is waste material derived from palm oil. The used cooking oil is an easy to get materials in reducing the cost of biodiesel production. The high free fatty acids (FFA) content in used cooking oil was reduced through the esterification reaction using acid catalyst (usually sulfuric acid, hydrochloric acid, and sulfonic acid) (Moecke et al., 2016; Ullah, Bustam, & Man, 2015).

Biodiesel is produced through the trans-esterification reaction of used cooking oil with low FFA levels (Kolyaei, Zahedi, Nasef, & Azarpour, 2016). This reaction needs catalyst to accelerate the conversion of triglycerides (oil) and alcohol into alkyl esters (biodiesel) and glycerol. Homogeneous based catalysts (e.g. NaOH, KOH, and alkoxides) were commonly used but caused the saponification reaction (Semwal, Arora, Badoni, & Tuli, 2011). Therefore, many studies related to heterogeneous catalyst preparation for biodiesel production. Heterogeneous catalysts have several advantages: less toxic, non-corrosive, environmentally friendly, easily to be separated and re-useable. Heterogeneous metal oxide

catalysts were often used in the biodiesel conversion process because its availability in nature such as CaO (Lee, Bennett, Manayil, & Wilson, 2014; Olutoye, Suleiman, & Yusuff, 2016; Saadon, Mohd Yusof, Razali, Mat Yashim, & Roslan, 2015; Santos et al., 2015; Semwal et al., 2011).

CaO catalyst from natural materials such as limestone has better performance than catalyst from Calcium Hydroxide and Calcium Carbonate in converting biodiesel from palm oil. Biodiesel yield obtained by using CaO from limestone, $\text{Ca}(\text{OH})_2$, and CaCO_3 were 89.98%, 85.15%, and 78.71% sequentially (Widayat, Satriadi, Syaiful, Khaibar, & Almakhi, 2017). Besides, the CaO source is not only from natural material but also from food material waste such as crab shell, egg shell, fish bone, and golden snail shell.

The use of golden snail shells as catalysts of trans-esterification reactions has been investigated by Ong et al. (Ong et al., 2014). The study stated that golden snail shells have the potential as a catalyst for biodiesel production. Prastyo, et al. used the golden snail shells to convert palm oil and maximum biodiesel yield obtained was 94.43% (Prasetyo, Margaretha, Ayucitra, & Ismadji, 2011).

Golden snail shell contains calcium carbonate, which was converted through the calcination process to gain CaO (Nopriansyah, Baehaki, & Nopianti, 2016; Prasetyo et al., 2011). The catalytic activities of CaO catalyst could be increased by adding supporting material. This study used fly ash as CaO catalyst support. Fly ash is a by-product of coal combustion consisting of micro particulates. The high amount of SiO_2 and Al_2O_3 in fly ash is an affordable catalyst support material (Chakraborty, Bepari, & Banerjee, 2010; Jain, Khatri, & Rani, 2011). According to Jain et al. reported dispersion of fly ash on CaO catalyst increases catalytic activity due to increase the base strength (OH content) catalyst. Enggawati and Ediati modified the CaO catalyst from egg shell with fly ash to catalyze transesterification reaction of Nyamplung oil (Enggawati & Ediati, 2013). Furthermore, Rodiah and Ediati synthesized CaO catalysts from dolomite modified with leaching and non-leaching fly ash. The study reported that CaO catalyst supported by fly ash was able to convert refined palm oil to biodiesel (Rodiah & Ediati, 2015).

This research investigate the synthesis of catalysts from golden snail shells (*Pomacea canaliculata*) modified with fly ash to convert used cooking oil into biodiesel. Fly ash is treated differently to observe the catalyst activity.

RESEARCH METHOD

Materials and Tools

The tools used in this study such as beaker glass, porcelain dish, measuring glass, filter paper, dropping pipette, magnetic stirrer, mortar agate, analytical balance, oven, muffle furnace, glass funnel, triple neck flask, condenser. X-Ray Diffractometer is used to characterize the catalysts.

Golden snail shells were collected from Pelajau village, Banyuasin, South Sumatera. The fly ash was obtained from PT. Bukit Asam Persero (Tbk) Tanjung Enim, South Sumatera. Then, the used cooking oil was collected from street vendors around campus of UIN Raden Fatah Palembang and methanol p.a and n-hexane p.a. were purchased from Merck and aquades.

Procedure

Preparation of Catalysts

Preparation of golden snail shell

Golden snail shells were washed using clean water, and then crushed. The shells were dried for 24 hours at 110°C, then calcined at 900°C for 2 hours. The calcined golden snail shells were mashed with agate to get powder.

Preparation of Fly Ash

Fly ash washed using hot water at beaker glass while stirring for 30 minutes, this procedure was repeated 3 times. The deposited mixture was filtered, then dried at 100°C for 24 hours. The powder obtained is called FA.

The fly ash was leached with a 10% hydrochloric acid solution (25:1 (mL /g), while stirring at 80°C for 1 hour. The precipitate was washed with distilled water for about 3 times then filtered. The precipitate was dried at 100°C for 24 hours. The powder obtained was fly ash leaching (FAL).

Preparation of golden snail shell catalyst/fly ash

Two beaker glass which contained of 75% (m/m) of calcined snail shells were added 200 mL aquadest for each and stirred until homogeneous. Then, the first beaker glass added by 25% (m/m) FA, and the other added by 25% FAL. The mixtures stirred at 70°C, pH 12.1 for 4 hours then left for 24 hours. The precipitate obtained was dried for 20 hours at 100°C, then calcined at 800°C for 2 hours.

Characterization of Catalysts

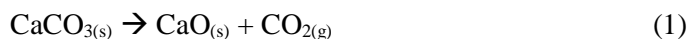
The crystal structure of catalysts was confirmed by Philips X-pert XRD Powder Diffractometer using CuK α radiation with an angle range of $2\theta = 20-100^\circ$ at scanning speed of 1°/min.

Transesterification Reaction

The transesterification reaction was carried out in a 250 mL three neck flask equipped with a condenser and magnetic stirrer. The reaction conditions were 3% of the catalyst (by weight of oil), 1:30 of the ratio oil: methanol (m/m), at 65 °C for 2 hours with the mixing speed of 1200 rpm. The biodiesel obtained was added n-hexane to dissolve main product. n-Hexane was separated from the product using rotary evaporator. Biodiesel obtained was analyzed by Gas Chromatography to determine biodiesel yield.

RESULT AND DISCUSSION

CaO from golden snail shells was gained after calcinating at 900°C for 2 hours. The Calcination process serves to activate the catalyst because during calcination at high temperatures, the carbonate group decomposes to CaO (Eqs. 1) which plays an important role in trans-esterification reactions (Aransiola, Ojumu, Oyekola, Madzimbamuto, & Ikhu-Omoregbe, 2014; Ilgen, 2011; Shajaratun Nur et al., 2014). Etuk et al. reported that the main content in golden snail shell ash was 61.95% of CaO.

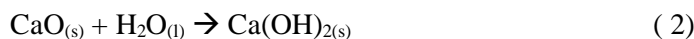


This study produced three types of catalysts with different compositions, see Table 1.

The catalysts were re-calcined to reactivate the CaO catalyst which had been changed to Ca(OH)₂ after being dissolved into water in the preparation process (Eqs 2). ~~Reactions that occur according to the following equation 2.~~ The presence of Ca(OH)₂ was confirmed by an X-Ray Diffraction (XRD) spectrophotometer (Table 2).

Tabel 1. The composition of the catalyst synthesized

No	Composition (% mass)			Name of catalyst
	FA	FAL	CK	
1			100	CK
2	25		75	CFA
3		25	75	CFAL



In this study, fly ash was used as a source of SiO₂ which was dispersed on CaO catalyst from golden snail shells. The presence of SiO₂ on the surface of the CaO catalyst affects the content of Ca(OH)₂. This is caused by the reaction between Ca(OH)₂ and SiO₂, thereby reducing the levels of Ca(OH)₂ on each catalyst.

Dispersion of SiO₂ (fly ash) on CaO (dolomite) influenced catalyst crystallinity. CaO was initially crystalline, but after adding SiO₂ to the surface of CaO, the catalyst crystallinity decreased. SiO₂ dispersion from fly ash on CaO from dolomite causes the catalyst to be amorphous (Rodiah & Ediati, 2015). The catalyst phase was confirmed by an XRD spectrophotometer.

The diffractogram of calcined golden snail shell (CK) is shown in Figure 1. Diffractogram of CK catalyst showed peaks that appeared at $2\theta = 28.64^\circ$; 34.13° ; 47.26° ; 50.99° ; and 54.44° which was the peak of CaO. Then new peak appeared at $2\theta = 17.95^\circ$ and 47.26° showed the presence of Ca(OH)₂. This peak shows the occurrence of hydration during activation of the catalyst (Prasetyo et al., 2011).

Tabel 2. The content of Ca(OH)₂ on the prepared catalyst

No	Catalyst	Ca(OH) ₂ (%)
1	CK	93,94
2	CKFA	67,22
3	CKFAL	68,06

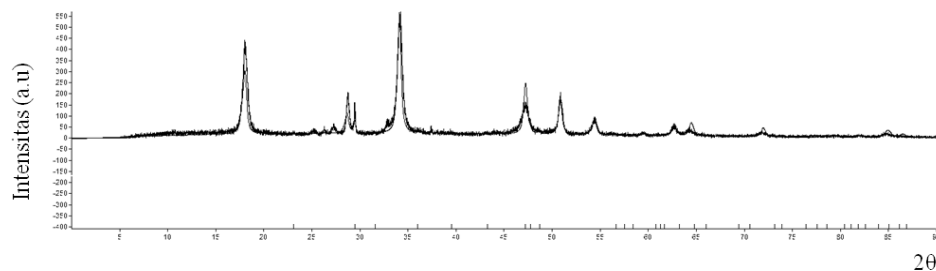


Figure 1. The diffractogram of CK catalyst

Rodiah and Ediati reported that CaO peaks from calcined dolomite appeared at $2\theta = 28.88^\circ$; 34.15° ; 47.32° ; 51.02° ; and 54.54° (Rodiah & Ediati, 2015). Meanwhile, Prasetyo et al. reported that golden snail shells calcined had peak at $2\theta = 32.1^\circ$; 37.3° ; 53.9° for the CaO phase and at $2\theta = 17.9^\circ$; 28.6° ; 34.1° ; 46.9° ; and 50.7° phase of $\text{Ca}(\text{OH})_2$ (Prasetyo et al., 2011). CK catalyst diffractogram did not show the appearance of the characteristic peak of CaCO_3 , which means that CaCO_3 was fully converted into CaO and $\text{Ca}(\text{OH})_2$ in the calcination process.

Figure 2 is a comparison of the diffraction patterns of the three catalysts, namely CK, CKFAL, and CKFA. There were several peaks appears such as CaO peaks from golden snail shells, and quartz peaks (SiO_2), mulit ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), and hematite (Fe_2O_3) were from fly ash. Peak at $2\theta = 28.78^\circ$; 34.06° ; 47.33° ; 50.85° ; and 53.9° was the peak of CaO on CKFAL catalyst whereas in CKFA catalyst, the characteristics of CaO appeared at $2\theta = 28.71^\circ$; 34.13° ; 47.26° ; 50.79° ; and 53.9° .

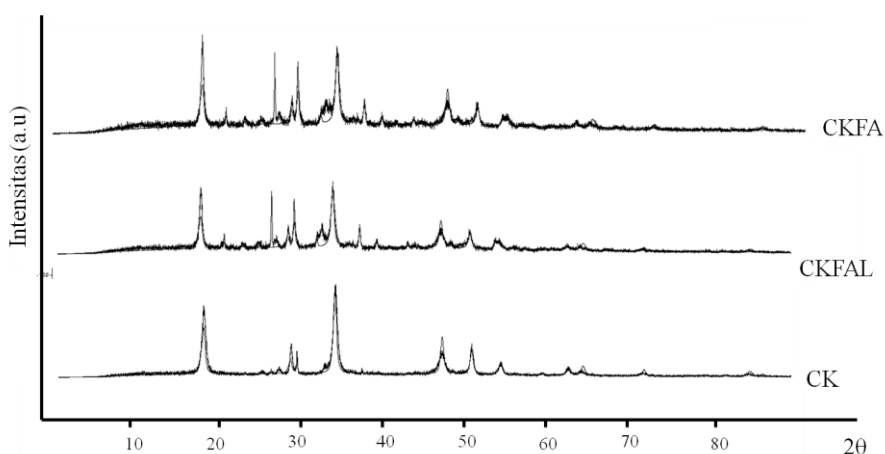


Figure 2. The diffractogram of CK, CKFAL, and CKFA catalyst

In addition, the new peaks at $2\theta = 29.45^\circ$; 32.84° ; and 29.39° were the peak of mulit ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) from each CKFAL and CKFA catalyst respectively. Then peak at $2\theta =$

20.92°; 26.61°; 39,54°; and $2\theta = 20.92^\circ; 26.75^\circ; 39.41^\circ$; is characteristic of quartz peaks (SiO_2) from CKFAL and CKFA catalysts respectively. The peak of Ca_2SiO_2 had the highest intensity, It indicated the high of SiO_2 in the CKFAL catalyst due to leaching treatment, thus more dicalcium silicate hydrate was formed (see Eqs 3).



After the calcination process, the water content in the dicalcium silicate hydrate evaporated and obtained dicalcium silicate. Dicalcium silicate has a Si-O-H bond which was expected to increase the basicity of the catalyst (Chakraborty et al., 2010).

The used cooking oil in this study contained 0.63% FFA which was classified as low level, so that it can be directly used in the trans-esterification reaction without going through esterification. In this study, the trans-esterification reaction was catalyzed by three catalysts: CK, CKFA, and CKFAL. The mass of biodiesel from the reaction with CK, CKFA, and CKFAL catalysts was 20.43 grams, 18.62 grams and 19.89 grams, respectively (See Table 3).

Table 3. Biodiesel mass after evaporating

No.	Catalyst	Mass of used cooking oil	Biodiesel mass
		(g)	(g)
1	CK	15,0111	20,4309
2	CKFA	15,0126	18,6241
3	CKFAL	15,0059	19,8990

From these results indicate that the CK catalyst showed better activity compared to other catalysts in this research. Dispersion of fly ash on CaO catalyst affected catalyst activity. Catalysts dispersed with leaching fly ash had better activity than catalysts dispersed with non-leaching fly ash. This can be caused by the active site of the catalyst being higher after diluting of fly ash in acid solution. Leaching process aimed to dissolve of metal impurities which covered the active site of the catalyst. The more active sites of the catalyst base, the higher of the catalyst activity. Thus the conversion of biodiesel increased because the transesterification reaction depends on the number of active sites of the base (Ilgen, 2011).

On the other hands, CK catalysts were more active than CKFA and CKFAL catalysts. According to Rodiah and Ediati, dispersion of fly ash on the surface of CaO can cover the active side of the catalyst, thereby causing a decrease in catalytic activity (Rodiah & Ediati, 2015). Therefore, the main key to increasing the modified catalytic activity of CaO was to maintain the CaO side during the modification process. However, the difference between the mass of biodiesel generated from the use of CK catalysts (20.4309 grams) and CKFAL (19.8990 grams) was quite small. This showed that leaching fly ash can be used as CaO catalyst support from a potential golden snail shell. In addition, the density of biodiesel (Table 4) with the use of CKFAL catalyst were closer to the characteristics of biodiesel

according to the biodiesel quality requirements (BSN, 2012), that the density of biodiesel allowed is between 850 - 890 Kg / m³ or 0,85 - 0.89 g/cm³.

Table 4. Density of biodiesel observed

No.	Catalysts	Density (g/cm ³)
1.	CK	0,8090
2.	CKFA	0,9158
3.	CKFAL	0,8295

CONCLUSIONS

In this study the CK, CKFA, and CKFAL catalysts were successfully prepared which were used to catalyze the trans-esterification reaction of used cooking oil into biodiesel. The CK catalyst produces a higher mass than the reaction catalyzed by the CKFA and CKFAL catalysts. But the mass of biodiesel obtained from catalysis with CKFAL and CK catalysts did not have a significant difference. Biodiesel density obtained from the reaction catalyzed by CKFAL was close to the standard biodiesel density which was 0.8295 g/cm³.

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