

Application of Eggshell Wastes as a Heterogeneous Catalyst for Biodiesel Production

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Abstract The duck and chicken eggshell wastes were applied as raw materials for the preparation of heterogeneous catalyst in biodiesel production. Prior to use, the calcium carbonate (CaCO_3) content in the waste shell was converted to calcium oxide (CaO) by calcining at 600-900°C for 4h. The physicochemical properties of the solid oxide catalyst were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and the Brunauer-Emmett-Teller (BET) method. The catalytic activity of the catalyst in transesterification of palm oil with methanol was evaluated, and the fuel properties of obtained biodiesel were measured. The effect of reaction time, reaction temperature, methanol/oil molar ratio, catalyst loading, and reusability of catalyst was also investigated. Eggshell waste is a bioresource for the production of heterogeneous base catalyst that can be successfully utilized for the synthesis of biodiesel with high purity.

Keywords: *biodiesel, eggshell wastes, heterogeneous catalyst, calcium oxide, transesterification*

1. Introduction

Because of the energy and global warming crisis, development of renewable energy has been focused worldwide [1]. Biodiesel is one of the most potential alternative energy since it is renewable and environmental friendly. Biodiesel is produced by transesterification of vegetable oils or animal fats with methanol to produce fatty acid methyl ester (FAME) and glycerol as a by-product [2]. Transesterification can be catalyzed by an acid, base, or enzymes [3]. Heterogeneous catalysts have the advantage that separation and regeneration of the catalyst is easy and cheap [4]. Heterogeneous basic catalysts include alkaline earth metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and hydrotalcites [5,6].

Eggshells are comprised of a network of protein fibers, associated with crystals of calcium carbonate (CaCO_3), magnesium carbonate (MgCO_3) and calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), and also of organic substances and water. CaCO_3 , the major constituent of the eggshell (96%), is an amorphous crystal that occurs naturally in the form of calcite (hexagonal crystal) [7]. Using eggshell wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced the heterogeneous catalysts with high cost effectiveness. In fact, the agricultural and food industries are the large private sectors in Thailand [8]. Development of value-added by-products from waste is of great interest as eggs are part of daily meal in most of the countries. Investigations related to the utilization of the eggshell waste as a renewable

catalyst was taken up by many scientists in different work [9,10,11].

Recently, the application of natural calcium sources from waste materials has been considered as a new trend for biodiesel production [12]. In this work, we have carried out transesterification using the duck and chicken eggshell wastes as inexpensive and environment-friendly catalyst. The objective was to optimize the process for biodiesel production from palm oil using CaO catalyst. The effects of reaction time, reaction temperature, methanol/oil molar ratio, catalyst loading, and reusability of catalyst were systematically investigated.

2. Experimental

2.1. Materials

Palm oil was purchased from Morakot Industries Public Company Limited, Thailand. The density and molecular weight of the oil were measured to be 0.868g/cm³ and 851.06 g/mole, respectively. The duck and chicken eggshells were collected as wastes from university cafeterias. The eggshell was rinsed with water to remove dust and impurities, and was then dried in an oven. All chemicals were analytical-grade reagents (Merck, >99% purity) and were used as received.

2.2. Preparation and Characterization of Eggshell Waste-Derived Catalyst

CaO catalyst was prepared by calcination method. The dried eggshell waste (100-200 mesh) was calcined at 600-900°C in air atmosphere with a heating rate of 10°C/min

for 4h [12]. The product was obtained as white powder. All calcined samples were kept in the close vessel to avoid the reaction with carbon dioxide (CO₂) and humidity in air before used. Figure 1 illustrated the preparation process of eggshell waste-derived catalyst.



Figure 1. Preparation of CaO catalyst derived from eggshell waste

The X-ray diffraction (XRD) characterization of the CaO catalyst was performed on a Rigaku (MiniFlex II, England) based generator X-ray diffractometer using CuK α radiation over a 2 θ range from 20° to 80° with a step size of 0.04° at a scanning speed of 3°/min. The elemental chemical compositions of the samples were analyzed by X-ray fluorescence spectroscopy (XRF - Oxford, ED-2000, England) under energy dispersive mode for precise measurement of both light and heavy elements. The microstructures of the calcined eggshells were observed by a scanning electron microscope (SEM). The SEM images of the representative sample were obtained from a Camscan-MX 2000 (England) equipped with an energy dispersive spectroscope (EDS). To evaluate the surface area, mean pore diameter and pore volume, adsorption-desorption of nitrogen (N₂) at 77K was carried out by a Quantachrome Instrument (Autosorb-1 Model No. ASIMP.VP4, USA). Before taking adsorption data, degassing at 120°C and a residual pressure of 300 μ m Hg for 24h was performed using the degas port. The surface area was calculated using the Brunauer-Emmett-Teller (BET) equation and the mean pore diameter and pore volume was obtained by applying the Barret-Joyner-Halenda (BJH) method on the desorption branch [13].

2.3. Catalytic Testing

The production of biodiesel from palm oil and methanol was carried out in a 500mL glass reactor equipped with condenser and mechanical stirrer at atmospheric pressure. The effects of reaction time (1 to 5h), reaction temperature

(50 to 70°C), methanol/oil molar ratio (6 to 18), catalyst loading (10 to 30wt.%), and reusability of catalyst (1 to 4 times) on the conversion to FAME were studied. After a certain period of time, a known amount of sample was taken out from the reactor for analysis. All experiments were repeated 3 times and the standard deviation was never higher than 7% for any point.

Composition of the FAME was analyzed with gas chromatograph-mass spectrometry (GC-MS QP2010 Plus, Shimadzu Corporation, Japan) equipped with a flame ionization detector (FID) and a capillary column 30m \times 0.32mm \times 0.25 μ m (DB-WAX, Carbowax 20M). Yield of biodiesel was calculated by Equation (1).

$$Yield(\%) = \frac{m_i A_b}{A_i m_b} \times 100 \quad (1)$$

Where m_i is the mass of internal standard added to the sample, A_i is the peak area of internal standard, m_b is the mass of the biodiesel sample and A_b is the peak area of the biodiesel sample [14,15]. The physical and chemical properties of FAME including kinematic viscosity, density, flash point, cloud point, pour point, acid value and water content were analyzed according to ASTM methods [16].

3. Results and Discussion

3.1. Catalyst Characterization

The thermal treatment resulted in a change in the XRD pattern, caused by the removal of CO₂ from the starting material (Figure 2). The diffraction patterns of the samples heated at temperatures <800°C were characteristic of CaCO₃, while samples calcined at temperatures >800°C displayed diffraction reflections characteristic of CaO. Samples calcined at 800°C contain CaCO₃ as the major phase and CaO as a minor phase [11]. The major component of the calcined waste at 900°C for 4h was CaO species (Figure 3). The result reveals sharp XRD reflections with (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) orientations, implying that the calcined material was well crystallized during the heat treatment process [12].

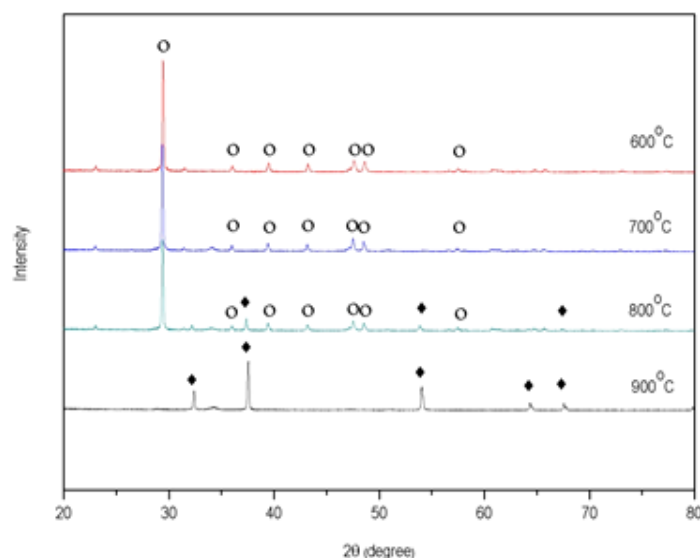


Figure 2. XRD patterns of the materials obtained by calcining duck eggshell waste in the range of 600-900 °C (Symbols: \circ CaCO₃, \blacklozenge CaO)

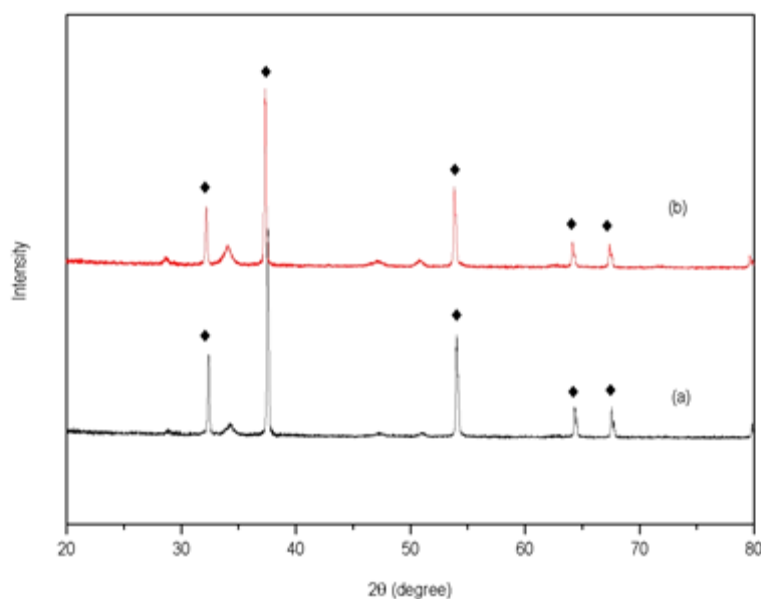


Figure 3. XRD patterns of the materials obtained by calcining (a) chicken, and (b) duck eggshell waste at 900°C (Symbols: ♦ CaO)

Table 1. Chemical compositions of eggshell waste-derived catalyst

Oxide	Concentration (wt.%)	
	Duck eggshell	Chicken eggshell
Na ₂ O	-	0.144
MgO	-	1.159
P ₂ O ₅	0.602	0.351
SO ₃	0.443	0.195
CaO	98.925	98.124
SrO	0.03	0.026

The chemical compositions of the catalyst are presented in Table 1. The major mineralogical component is CaO. The duck and chicken eggshell waste-derived catalysts

have concentration of CaO 98.93 and 98.12 wt.%, respectively.

The morphology of the eggshell waste-derived catalyst was investigated by SEM as shown in Figure 4 (5000× magnification). According to the SEM images, the calcined eggshell waste typically comprises irregular shape of particles. In other words, there were various sizes and shapes of particles [12]. The smaller size of the grains and aggregates could provide higher specific surface areas. The size of the particle should directly respond to the surface area. Additionally, the wave-like surface of the calcined eggshell which was not found over other samples might also promote the specific surface area [1].

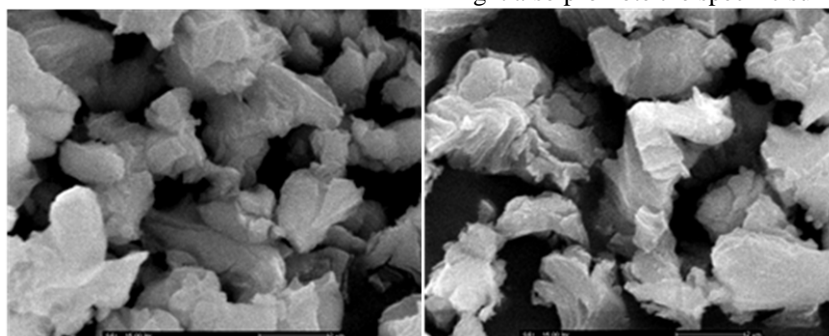


Figure 4. SEM images of the materials obtained by calcining (a) duck, and (b) chicken eggshell waste at 900°C

The physical properties of the catalyst are summarized in Table 2. The chicken eggshell waste-derived catalyst had a large surface area (136.10m²/g) and pore volume (0.12cm³/g), and presented a uniform pore size. The duck eggshell waste-derived catalyst presents lower values for surface area (128.50m²/g) and pore volume (0.10cm³/g) related to chicken eggshell. It can be seen that the catalyst resulted in a strong increase in the active sites [17]. This assumption is supported by the SEM images of catalyst.

Table 2. The physical properties of eggshell waste-derived catalyst

Physical property	Material	
	Duck eggshell	Chicken eggshell
Surface area (m ² /g)	128.50	136.10
Pore volume (cm ³ /g)	0.10	0.12
Mean pore diameter (Å ^o)	34.08	34.12

3.2. Optimization of Transesterification Over Eggshell Waste-Derived Catalyst

The effect of reaction time on the conversion of palm oil to FAME was investigated. Reaction time is one of the key parameters during the transesterification carried out in glass reactor. Figure 5 shows a gradual increase in the yield with time from 1 to 5h with a catalyst amount of 20 wt.% relative to oil and a methanol/oil molar ratio of 9:1. The maximum yield of 92.92 and 94.49% were obtained in 4h at 60°C for duck and chicken eggshell waste, respectively. In the initial stages of the transesterification reaction, production of methyl esters was rapid, and the rate diminished and finally reached equilibrium [15,18] in about 4h. This can be explained by that transesterification

reaction between oil and alcohol is reversible, when the reaction time is long enough [19].

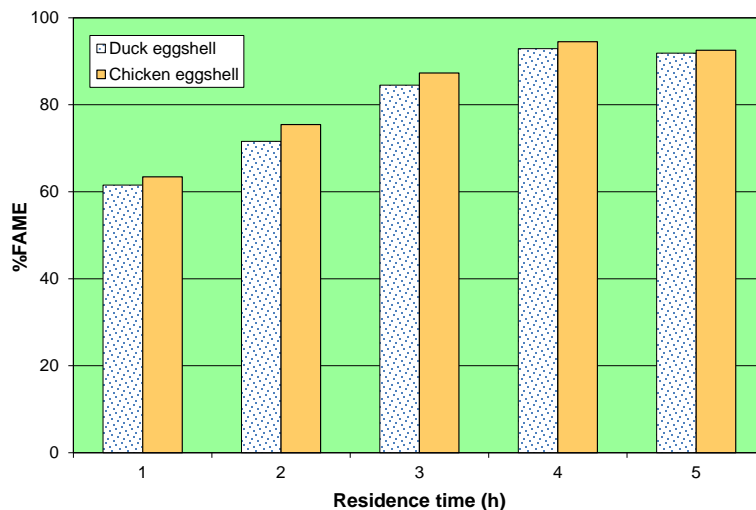


Figure 5. Effect of reaction time on % yield of FAME

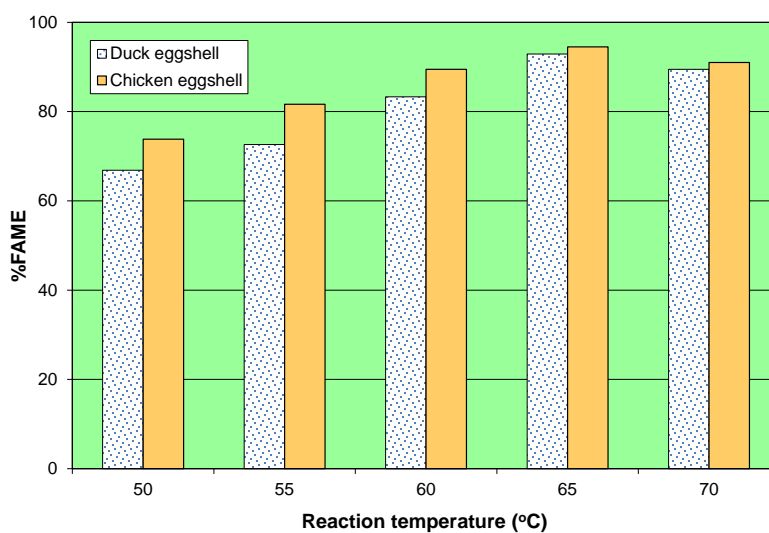


Figure 6. Effect of reaction temperature on % yield of FAME

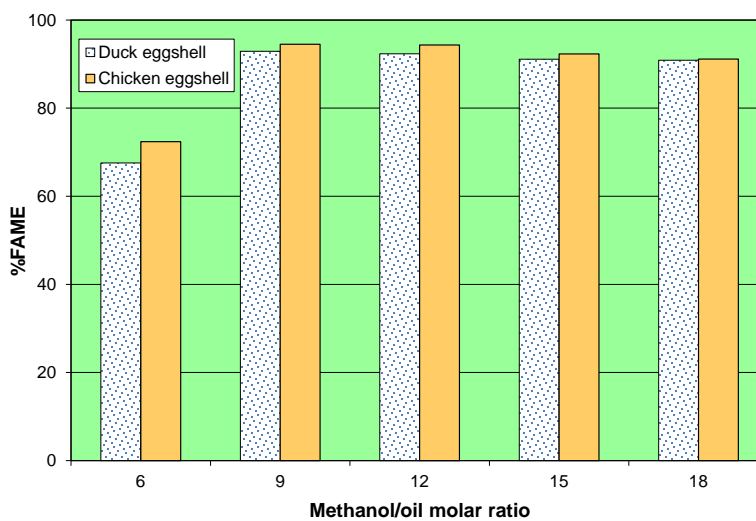


Figure 7. Effect of methanol/oil molar ratio on % yield of FAME

Figure 6 shows that an increase in reaction temperature led to higher yields. At the beginning of reaction, yield of FAME was increased because reactant contacted fresh

catalyst. Then the yields decreased due to slightly deactivated but stabilized catalyst, and the conversions reached steady state at all temperatures [17]. At 65°C, the

reaction yield was highest (92.92 and 94.49% for duck and chicken eggshell waste, respectively). When the reaction was carried out at 65°C, which is above the boiling point of methanol, the solvent vaporized and remained in the vapor phase in the reactor causing a reduction in the methanol in the reaction media [3,20].

The FAME content increased significantly when the methanol/oil molar ratio was changed from 6 to 18 (Figure 7). The high amount of methanol promoted the formation of methoxy species on the CaO surface, leading to a shift in the equilibrium in the forward direction, thus increasing the rate of conversion up to 92.92 and 94.49% for duck and chicken eggshell waste, respectively. However, further increases in the methanol/oil molar ratio, did not promote the reaction. It is understood that the glycerol would largely dissolve in excessive methanol and subsequently inhibit the reaction of methanol to the

reactants and catalyst, thus interfering with the separation of glycerin, which in turn lowers the conversion by shifting the equilibrium in the reverse direction [21]. Therefore, the optimum molar ratio of methanol to oil was 9, which is more than the practical methanol to oil molar ratio for homogeneous transesterification of 6 [22].

The effects of catalyst mass were studied by varying the amount of catalyst loaded into the reactor in respect to the mass of oil used in the reaction. Figure 8 shows the yield of methyl ester using different weight percentages of catalyst. The rate of reaction increases with the mass of catalyst up to a maximum of 20 wt.% and then decreases with any higher loadings. The loadings of 25 and 30 wt.% created catalyst accumulation on the wall of the glass reactor, possibly contributing to diffusional problems during reaction and, therefore, lowering the activity [23].

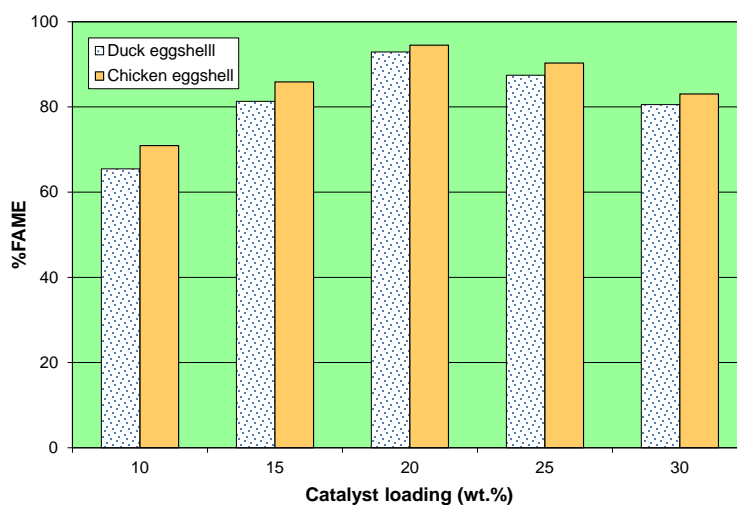


Figure 8. Effect of catalyst loading on %yield of FAME

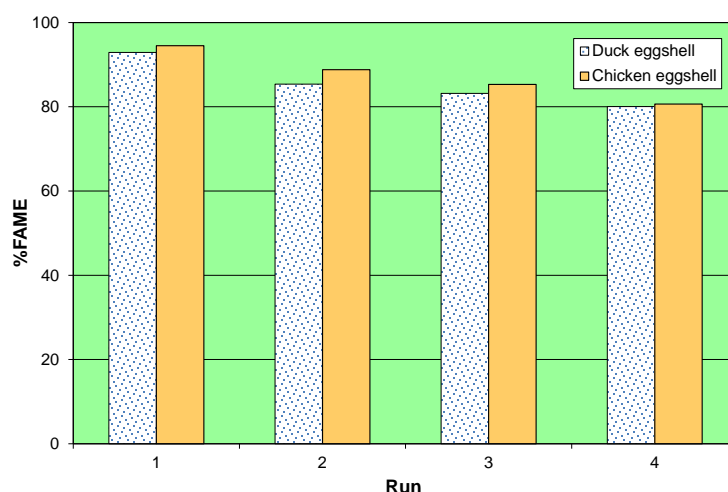


Figure 9. Effect of reusability of catalyst on %yield of FAME

Reusability of CaO catalyst in the transesterification of palm oil under the optimum condition in the glass reactor was studied (Figure 9). After each run, the used catalyst was taken out from the reactor and dried for reutilization. The catalytic activity remains 80% of the fresh catalyst when the catalyst is employed for the fourth time. It was calculated based on the conversion of oil to FAME under the optimum condition. The decay in catalyst activity

could be due to the leaching of active sites to the reaction media. Leaching of the active phase to the alcoholic phase can be attributed to the bond breaking and formation of Ca^{2+} and CH_3O^- [23]. As shown in Table 2, the catalytic activity is within the range reported by other researchers [12, 22, 24-26]. This heterogeneous catalyst showed high stability and reusability for transesterification with small loss of its catalytic activity during reaction. Small loss of

the catalyst is an important factor for good catalyst reusability [14].

Table 3. The reusability comparison between waste-derived catalysts

Waste-derived catalysts	Run	Catalytic activity	Reference
Duck eggshell	4	80.06	This work
Chicken eggshell	4	80.66	This work
Industrial eggshell	5	76.76	[12]
Animal bone	5	83.70	[22]
Mussel shell	5	59.10	[24]
<i>Turbonilla striatula</i>	3	50.00	[25]
<i>Anadara granosa</i>	3	97.80	[26]

The fuel properties of methyl ester obtained in this work are summarized in Table 4. It can be seen that most of its properties are in the range of fuel properties as described in the latest standards for biodiesel [27].

Table 4. The fuel properties of eggshell waste-derived catalyst

Fuel property	Material		ASTM D6751-02
	Duck eggshell	Chicken eggshell	
Kinematic viscosity @ 40 °C (mm ² /s)	4.6	4.5	1.9-6.0
Density @ 80°C (g/cm ³)	0.880	0.878	0.870-0.900
Flash point (°C)	164	165	130 min
Cloud point (°C)	11	12	-3 to 12
Pour point (°C)	7	8	Report
Acid value (mg KOH/g oil)	0.64	0.48	0.80 max
Water content (%)	0.03	0.02	0.05 max

4. Conclusion

Using cost-effective and environment-friendly catalysts is particularly useful for the production of biodiesel. The eggshell wastes are used as the catalyst for this process. This catalyst contains CaCO₃ which is converted to CaO after calcination at temperatures 900°C for 4h. The optimum conditions, which yielded a conversion of palm oil of nearly 92 and 94% for duck and chicken eggshell waste-derived catalyst, were reaction time 4h, reaction temperature 65°C, methanol/oil molar ratio 9, and catalyst loading 20 wt.% with pressure 1 atm in glass reactor. The experimental results show that CaO catalyst had excellent activity and stability during transesterification. The catalyst was used for 4 times and apparent low activity loss was observed. The fuel properties of the biodiesel so obtained meet all biodiesel standards. As a solid catalyst, CaO can decrease the cost of biodiesel and the steps of purification. It has potential for industrial application in the transesterification of palm oil to FAME.

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