

The development of fly ash-supported CaO derived from mollusk shell of *Anadara granosa* and *Paphia undulata* as heterogeneous CaO catalyst in biodiesel synthesis

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Abstract The aim of this study was to develop fly ash-supported CaO catalyst derived from waste mollusk shell of *Anadara granosa* and *Paphia undulata* for transesterification of palm oil to yield biodiesel. The active precursor Ca(OH)₂ of the catalyst has been developed from calcination of waste mollusk shell, while the mesoporous has been prepared using the wet impregnation method. The results demonstrated that the mollusk shell-derived catalyst could gain the yield of biodiesel of 92 and 94 % for *A. granosa* shell and *P. undulata* shell, respectively. The obtained yield was comparable with the yield of biodiesel gained from CaO catalyst derived from reagent grade CaCO₃ (yield = 94 %). The optimum condition was achieved at catalyst loading of 6 %, reaction temperature of 60 °C and reaction time of 2 h. The reusability study showed that the developed catalysts exhibited higher recycle degree characteristic indicated by 50 % yield reduction after three reuse cycles.

Keywords Biodiesel · Palm oil · Heterogeneous catalyst · Mollusk shells · Fly ash

Introduction

Due to the limited sources of fossil oil, biodiesel has been extensively studied as one of alternative fuels [1]. Biodiesel is composed of mono-alkyl esters of long-chain fatty acids

derived from vegetable oils or animal fats [2]. The use of biodiesel will also support the environment sustainability due to its advantages as being biodegradable, renewable, has non-toxic properties [3].

Biodiesel is conventionally produced from esterification of edible or non-edible oils with homogenous acid or base catalysts [4]. Although homogeneous catalysts can provide high catalytic activity, however, some drawbacks have been reported, such as difficulty in recovery, high losses of product, and also production of toxic water [5]. Therefore, the heterogeneous catalysts have been introduced to overcome these drawbacks. The heterogeneous catalyst can be easily recovered from the reaction mixture, making that the heterogeneous catalyst is economically and environmentally preferable against the homogeneous catalyst [6]. Several heterogeneous catalysts have been utilized in the biodiesel production, for example, Al₂O₃, ZnO, MgO, hydrotalcites, CaO–MoO₃–SBA-15, CaO–SiO₂, and CaO–CeO₂ [7–12]. Among these heterogeneous catalysts, calcium oxide (CaO)-based catalysts have drawn great interest due to their high activities and low cost of preparation [8]. The source of CaO can be either generated by decomposition of reagent grade CaCO₃ at high temperatures or derived from natural resources, such as egg shells [11], snail shell [13], mud crab shell [14], and mussel shell [15]. To increase the activity, a heterogeneous catalyst requires support materials containing SiO₂ or Al₂O₃. One of the potential sources of support materials is fly ash. Fly ash is solid waste of coal combustion which mainly contains of inorganic oxides, such as SiO₂ (41–55 %) and Al₂O₃ (20–25 %) [16]. The presence of large amounts of SiO₂ and Al₂O₃ has prompted the use of fly ash as a support for catalytically active oxides and metals [17].

However, only a few studies have been focused on the utilization of biological resource of CaO impregnated to fly

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ash. One effort has been reported by Chakraborty et al. [2] who developed a heterogenous CaO catalyst derived from egg shells impregnated in fly ash for transesterification of soybean oil. Since waste shells of *Anadara granosa* and *Paphia undulata* are very abundant in Indonesia, and the shells also contain high CaO contents (>93 %); therefore, the use of these waste shells as heterogenous CaO catalyst is still important subject to be explored. Therefore, the objective of this work was to develop heterogeneous CaO catalyst derived from the waste shells of mollusk *A. granosa* and *P. undulata* and to utilize the catalyst for esterification of palm oil into biodiesel. The CaO catalyst will be impregnated in fly ash, and the activity will be compared with CaO-based reagent grade CaCO₃.

Materials and methods

Materials

Palm oil and mollusk (*A. granosa* and *P. undulata*) shells were obtained from local market in Semarang, Indonesia. The free fatty acid (FFA) content of the palm oil was 0.16 %. Coal fly ash was collected from Paiton power plant, Indonesia. Methanol and reagent grade CaCO₃ were purchased from Merck.

Catalyst preparation

Prior to preparation, the mollusk shells were cleaned from its impurities. The shells were then dried in an oven at 110 °C for 6 h and were crushed and ground to fine powder then sieved at 100 μm. The fine powder of shell and reagent grade CaCO₃ was calcined at 800 °C for 3 h to generate CaO. Coal fly ash was dried in an oven at 105 °C for 10 h. The fly ash-supported CaO catalyst was prepared according to the wet impregnation method [18] which was also described in the previous paper [19].

Catalyst characterizations

To determine the crystallinity nature of fly ash-supported CaO catalysts, X-ray diffraction (XRD) patterns for supported catalysts samples were analyzed using Cu-Kα procedure. The analysis was performed at 2θ angle ranging from 10° to 90° at a scanning speed of 2° min⁻¹. The surface morphology of the developed catalysts was determined using scanning electron microscope (SEM), while crystalline size of catalyst was calculated from the XRD data using Scherrer's formula [20]

$$D = \frac{K\lambda}{\beta \cos(2\theta)} \quad (1)$$

This equation was developed to calculate the nano crystallite size (*D*) by XRD radiation of wavelength λ (nm) from measuring full width at half maximum of peaks (β) in radian located at any 2θ in the pattern. The Scherrer constant (*K*) = 0.9 as the crystal was to be more spherical shapes.

The properties of catalyst were revealed by FTIR spectroscopy on a Win Bomem 1000 instrument in the region of 4000–400 cm⁻¹. Before the recordings, the catalyst samples were exposed to phenol vapors to investigate the basic nature of surface sites, and afterward exposed to vacuum to remove any physically adsorbed vapors. The EDS elemental composition [particularly the calcium (Ca) concentration] was semi-quantitatively expressed in terms of weight percentages using Oxford Instruments INCA 400. In addition, X-ray diffraction (XRD) was also utilized as a quantitative determination of the CaO concentration within the catalysts.

Transesterification process

Methanolysis of refined palm oil was conducted in a 500-mL round bottom flask which was equipped with a reflux condenser and a magnetic stirrer. About 35 mL of palm oil was added into the bottom flask with amount of catalysts of 2–10 % and at constant methanol to oil mole ratio (12:1). The mixture was then stirred for a few minutes to make uniformly mixed oil-catalyst slurry and heated at 70 °C for 2 h. The catalyst was separated from its mixture using a vacuum pump. The mixture of product, methanol, and glycerol was separated in a funnel, and the excess methanol was recovered using a rotary evaporator. The biodiesel product was characterized using gas chromatography (GC).

Reusability cycle was tested through transesterification condition of 6 % catalyst, methanol:oil mole ratios = 12:1, reaction temperature of 60 °C, 2-h reaction time, and 700-rpm stirring speed. After each cycle, the spent catalyst was regenerated using methanol washing and dried in an oven at 110 °C for 12 h.

Gas chromatography analysis

The biodiesel product was analyzed by GC according to European Standard EN 14103:2011. The analysis was carried out using a GC Agilent 7890 Series with a flame ionization detector (FID). The column was HP-INNOWax with dimensions of 30 m × 0.25 mm × 0.25 μm, and helium was used as the carrier gas. The split/splitless inlet temperature was at 250 °C, split flow 100 mL min⁻¹, column temperature at 60 °C for 2 min, 10 °C min⁻¹ to 200 °C, 5 °C min⁻¹ to 240 °C, and hold 240 °C for 7 min.



The detector temperature was at 250 °C. Biodiesel was analyzed by injecting 1 μL of sample into GC, and the total ester content was calculated using the integrated peak areas of the methyl ester identified in the samples.

Biodiesel physicochemical properties determination

The measured properties of biodiesel were: (1) kinematic viscosity according to ASTM D 445; (2) density measured according to ASTM D 1298 method; and (3) cetane number (CN) calculated according to a multiple linear regression developed by Piloto-Rodriguez et al. [21] as function of the methyl ester composition found in biodiesel.

$$\begin{aligned} \text{CN} = & 56.16 + 0.07 \text{La} + 0.1M + 0.15P - 0.05 \text{Pt} \\ & + 0.23S - 0.03O - 0.19 \text{Li} - 0.31 \text{Ln} \\ & + 0.08 \text{Ei} + 0.18 \text{Er} - 0.1 \text{Ot}, \end{aligned} \quad (2)$$

where the independent variables represent the FAME composition found in biodiesel: La is the % of lauric, M is myristic, P is palmitic, Pt is palmitoleic, S is stearic, O is oleic, Li is Linoleic, Ln is linolenic, Ei is eicosanoic, Er is eruric, and Ot is the sum of the other FAMES found.

Result and discussion

X-ray diffraction (XRD)

X-ray diffraction analysis has been identified by matching the data with Joint Committee for Powder Diffraction Standard (JCPDS). The characterization of Paiton coal fly ash showed that SiO_2 is in the crystalline phase at $2\theta = 21.0^\circ$; 26.7° ; 35.8° , while Al_2O_3 is in amorphous phase. These compounds are oxide material which can be generally used as a catalyst support (Fig. 1). The presence of dicalcium silicate (Ca_2SiO_4) crystalline phase was observed at $2\theta = 34^\circ$ in the catalysts (Table 1). The formation of dicalcium silicate was due to the formation of dicalcium silicate hydrate ($\text{Ca}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$) through reaction between silica (SiO_2) and CaO in the presence of water during the wet impregnation preparation process [2]

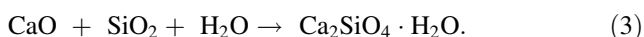


Table 1 also shows the CaO content in the fly ash and catalysts. It shows that CaCO_3 has the highest CaO contents followed by *A. granosa* and *P. undulata* shells.

Scanning electron microscopy (SEM)

Figure 2 shows SEM images of the fly ash-supported CaO catalyst. The fly ash-supported CaO catalyst derived from CaCO_3 grade demonstrates a relatively smaller morphology

size of particles compared with *P. undulata* and *A. granosa*, which also subsequently increases its surface area. The fly ash-supported CaO catalyst derived from CaCO_3 had the size distribution less than 30 μm . The fly ash-supported CaO catalyst derived from *P. undulata* shell produces molecular size less than 75 μm , while *A. granosa* shell produces molecular size less than 85 μm . SEM image also shows the structure agglomeration, because the metal oxide formed by heat treatment [2].

FTIR studies

The FTIR spectra of fly ash-supported CaO catalysts are shown in Fig. 3. This technique was employed to characterize the surface absorbed species, such as carbonates and hydroxides of CaO supported on the fly ash. The absorption bands at 1419, 774, and 670 cm^{-1} were actually CO_3^{2-} ions. The appearance of this adsorption band with similar intensity for all the three catalysts may be attributed to the basic carbonates generated by the adsorption of gaseous CO_2 from atmosphere onto catalysts [12]. The adsorption band at 953 cm^{-1} was Si–O–Ca bond from Ca_2SiO_4 that generated from reaction of CaO and SiO_2 . The FTIR band at 3644 cm^{-1} was ascribed to the stretching vibrations of surface hydroxyl groups (Ca–OH) and physisorbed moisture. The surface carbonate and hydroxyl species existed due to the catalyst exposure to the air. The FTIR results clearly showed the tendency of CaO to react with moisture and CO_2 in air.

Transesterification

The amount of catalyst used in the transesterification is shown in Fig. 4. For all heterogeneous catalyst types, the increase in catalyst amount also increases the yield of biodiesel and higher than the yield obtained by the homogenous catalyst (NaOH). This is due to the increase in the active site in the catalysts. The largest yield was shown at the amount of catalyst of 6 %, and afterward, the yield decreases. It is because of the emulsions formation that increases the viscosity of the mixture, which causes difficulty in mixing the reactants, catalysts, and products [22, 23].

Comparison of the use of resources CaO on the fly ash-supported CaO catalysts can be seen in Table 1. The experiment also showed that the mollusk shell-based catalysts are highly very active to catalyze the transesterification of palm oil. All fly ash-supported CaO catalysts produced yields more than 75 % after 2 h of reaction. The fly ash-supported CaO catalyst derived from CaCO_3 and *P. undulata* could gain biodiesel yield up to 94 %, while CaO catalyst derived from *A. granosa* achieved 92 % yield.

Fig. 1 XRD pattern *a* coal fly ash [Al_2O_3 (star) CaO (filled upward triangle) Ca_2SiO_4 (filled circle) Fe_2O_3 (filled downward triangle) SiO_2 (filled square)], *b* fly ash-supported CaO (*Paphia undulata*), *c* fly ash-supported CaO (*Anadara granosa*), and *d* fly ash-supported CaO (CaCO_3)

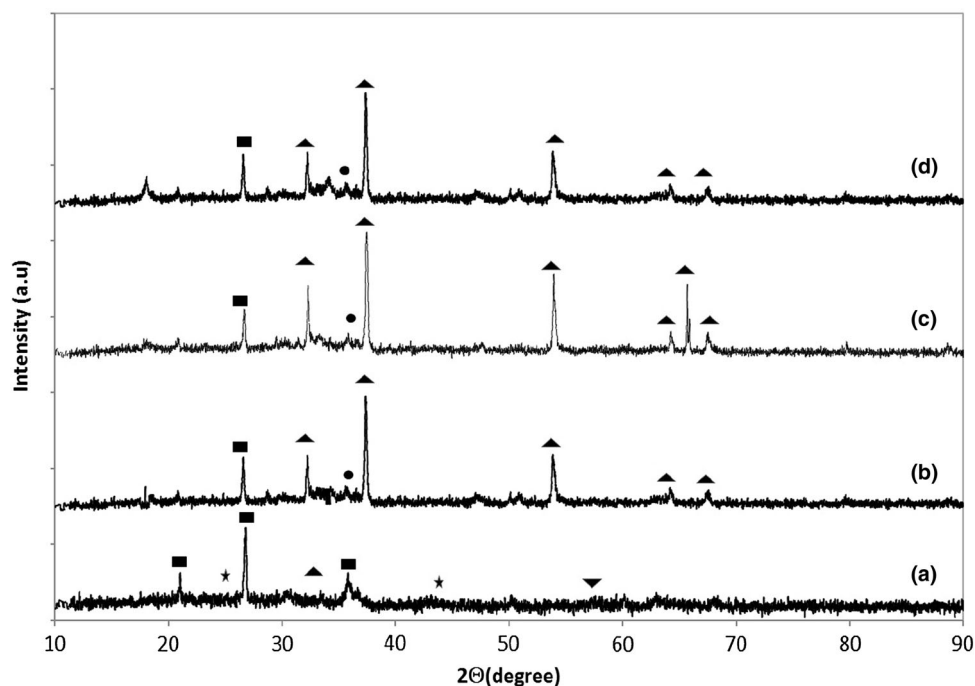


Table 1 The result of XRD diffraction and CaO concentration of each component used in the experiment

Compounds	2θ						CaO concentration (%)
	$\text{Ca}(\text{OH})_2$	SiO_2	CaO	Al_2O_3	Ca_2SiO_4	Fe_2O_3	
Coal fly ash	–	21.05; 26.80; 35.85	32.28	25.64; 43.14	–	57.58	1.43
Fly ash-supported CaO (CaCO_3 grade)	18.07	20.94; 26.63	32.24; 37.39; 53.88; 64.19; 67.41	–	34.10	–	57.31
Fly ash-supported CaO (<i>Anadara granosa</i>)	18.08	20.88; 26.69	32.27; 37.43; 53.92; 64.20; 67.44	–	34.20	–	42.98
Fly ash-supported CaO (<i>Paphia undulata</i>)	18.15	20.88; 26.65	32.26; 37.40; 53.90; 64.17; 67.42	–	34.09	–	42.88

The numbers indicate 2θ values (peak) of compounds detected by XRD analysis

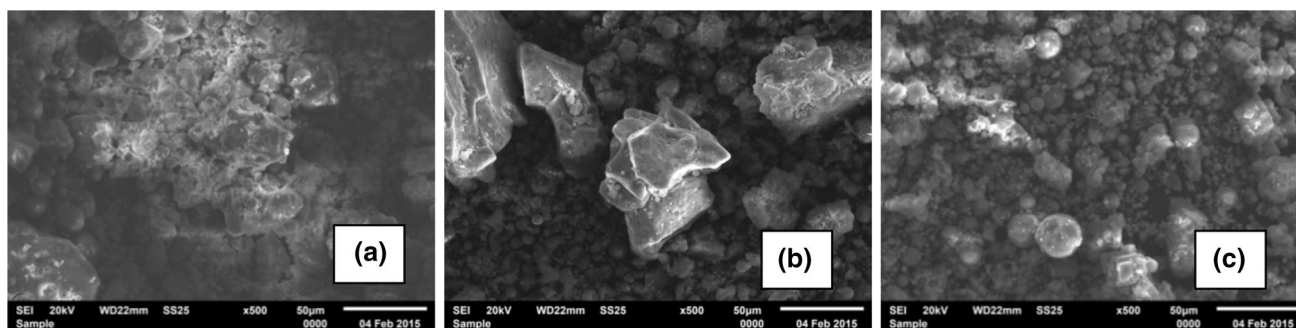


Fig. 2 SEM images fly ash-supported CaO . *a* *Paphia undulata*. *b* *Anadara granosa*. *c* CaCO_3

It also shows that the particle size has contribution in the transesterification, especially affecting the catalyst activity. The order of size of particles produced in this research is

the fly ash-supported CaO catalyst (*A. granosa*) > fly ash-supported CaO catalyst (*P. undulata*) > fly ash-supported CaO catalyst (CaCO_3). The use of heterogeneous catalysts

Fig. 3 FTIR spectra of fly ash-supported CaO catalysts: *a* fly ash-supported CaO (CaCO_3); *b* fly ash-supported CaO (*Anadara granosa*); *c* fly ash-supported CaO (*Paphia undulata*); and *d* coal fly ash

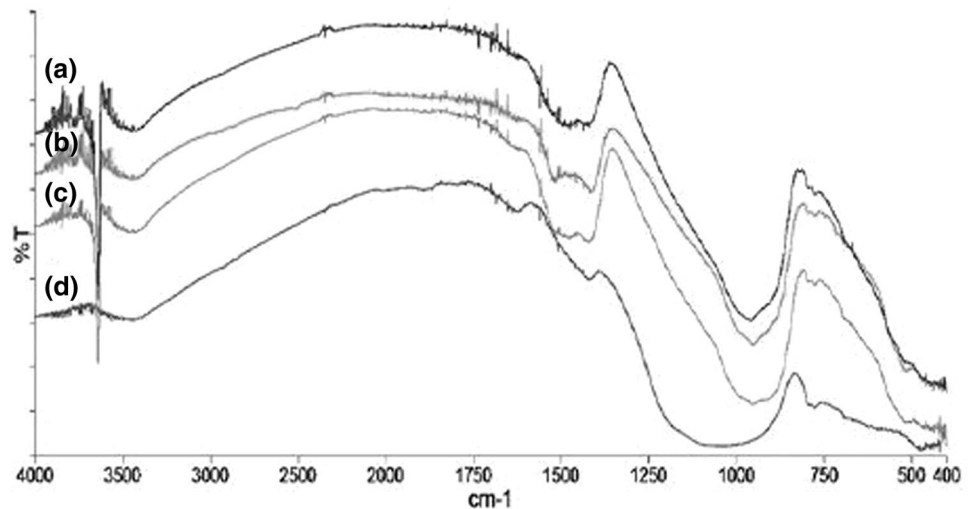
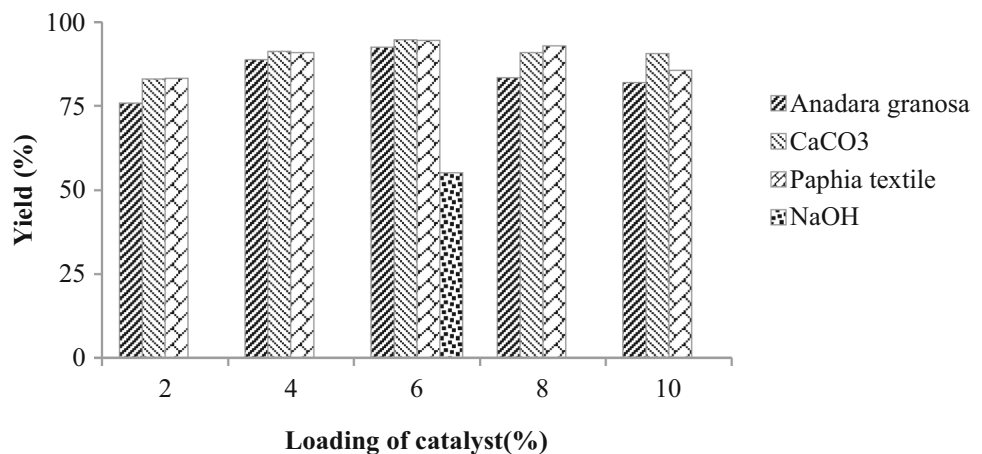


Fig. 4 The biodiesel yield obtained from different experiments at the variation of catalyst loading and type of catalyst. The NaOH catalyst represented the esterification using homogenous base catalyst



is influenced by the size of catalyst particles [11]. A small particle size of the catalyst has a large surface area and, therefore, producing greater yield. In addition, the heterogeneous fly ash-supported CaO catalyst also forms dicalcium silicate (Ca_2SiO_4) which increases the activity of the catalyst.

Biodiesel products

Characterization of biodiesel was conducted using a gas chromatography (GC) Agilent based on method EN14103:2011 [24]. The run time of 30 min were used in accordance with the method of EN14103:2011. It was found that the highest content in the biodiesel was methyl oleic and methyl palmitic, while other components were found in small quantities (Table 2).

The density and viscosity of the obtained biodiesel have already fulfilled the ASTM standard. According to ASTM D-1298, a standard density of biodiesel from 0.82 to 0.90 g cm^{-3} and a viscosity of 2.0–5.0 cSt [25]. From the

results, the biodiesel has the density ranges from 0.87 to 0.89 g cm^{-3} with a viscosity of 3.85–4.43 cSt. The predicted cetane number (Eq. 2) was less than 60.0, indicating that the produced biodiesel was very suitable for engine performance. This cetane number was mainly affected by high composition of methyl oleate (9) and methyl palmitate (C16:0) with contents of 58.44 and 37.17 %, respectively (Table 3).

As compared with other sources of heterogeneous catalyst, this study showed comparable finding with respect to biodiesel yield (Table 4). Biodiesel yield obtained from catalyst egg shells, snail shells, and *Meretrix venus* only achieved 92 % [11], which was higher than shrimp shell and horn shell (<90 %) [23, 26]. These results indicated that the mollusk shells of *A. granosa* and *P. undulata* have great potential for improving yield biodiesel.

Reusability study

Figure 5 shows that the yield of biodiesel dropped to 53.76, 40.23, and 46.76 % for spent catalysts derived from

Table 2 The physico-chemical properties of biodiesel produced by various types of catalyst

No.	Catalyst	Catalyst loading (%)	Yield (%)	Density (g cm ⁻³)	Viscosity (cSt)	CN
1	Fly ash-supported CaO (CaCO ₃ grade)	2	83.12 ± 0.65	0.88	3.91	59.96
2		4	91.32 ± 0.73	0.88	4.21	59.90
3		6	94.71 ± 1.54	0.87	4.35	59.92
4		8	90.98 ± 1.68	0.87	3.92	59.81
5		10	90.68 ± 0.92	0.88	0.06	59.96
6	Fly ash-supported CaO (<i>Anadara granosa</i>)	2	75.85 ± 1.93	0.89	4.28	59.93
7		4	88.76 ± 1.72	0.89	4.43	59.88
8		6	92.50 ± 1.25	0.89	4.28	59.87
9		8	83.48 ± 0.82	0.89	4.28	60.07
10		10	81.96 ± 0.62	0.89	4.14	55.76
11	Fly ash-supported CaO (<i>Paphia undulata</i>)	2	83.32 ± 0.43	0.89	3.85	59.80
12		4	90.92 ± 1.24	0.89	4.06	59.84
13		6	94.53 ± 1.15	0.88	4.13	59.73
14		8	92.92 ± 0.92	0.87	3.85	59.88
15		10	85.66 ± 1.63	0.87	3.99	59.92
16	Homogenous catalyst (NaOH)	6	55.22 ± 2.15	0.89	4.86	59.63

Table 3 Composition of fatty acid methyl ester (FAME) in the produced biodiesel

No.	Compounds	% weight
1	Methyl myristate (C14:0)	0.98
2	Methyl palmitate (C16:0)	37.17
3	Methyl stearate (C18:0)	0.50
4	Methyl oleate (9) (C18:1)	58.44
5	Methyl oleate (10) (C18:1)	2.19
6	Methyl linoleate (C18:2)	0.63

CaCO₃, *A. granosa*, and *P. undulata* after the third cycles. The results indicated a slight catalyst deactivation because of the leaching of the CaO active species into the reaction medium [27]. The decrease in CaO contents are shown in Table 5.

The dissolution of CaO into alcoholic phase also causes the deactivation of active sites, and thus, it leads concentration of CaO decrease. Moreover, CaO will also dissolve in products, such as glycerol and biodiesel, and therefore reducing the amount of CaO in the catalyst. The decrease in yield could also be attributed to catalyst deterioration

Table 4 Biodiesel yield from various catalyst sources

Source of catalyst	Condition	FAME yield	References
Egg	Temperature = 60 °C, methanol/oil molar ratio = 18:1, catalyst amount = 10 wt %, reaction time = 100 min	92	[11]
Golden apple snail	Temperature = 60 °C, methanol/oil molar ratio = 18:1, catalyst amount = 10 wt %, reaction time = 100 min	92	[11]
<i>Meretrix venus</i>	Temperature = 60 °C, methanol/oil molar ratio = 18:1, catalyst amount = 10 wt %, reaction time = 100 min	85	[11]
Obtuse horn shell	Temperature = 60 °C, methanol/oil molar ratio = 12:1, catalyst amount = 5 wt %, reaction time = 6 h	88	[23]
Shrimp shell	Temperature = 65 °C, methanol/oil molar ratio = 9:1, catalyst amount = 2.5 wt %, reaction time = 3 h	89	[26]
<i>Anadara granosa</i>	Catalyst amount = 6 wt %, methanol/oil molar ratio = 12:1, temperature = 60 °C, reaction time = 120 min	92	This study
<i>Paphia undulata</i>	Catalyst amount = 6 wt %, methanol/oil molar ratio = 12:1, temperature = 60 °C, reaction time = 120 min	94	This study

due to poisoning by glycerol and soap present in reaction mixture. The presence of calcium glyceroxide in the spent catalyst could possibly be a factor for its reduced reusability. Calcium glyceroxide is formed through the reaction of CaO and glycerol [28].

Figure 6 shows the FTIR analysis of the catalyst after the second recycles. The CaO-based catalyst derived from calcined *P. undulata*, *A. granosa* shells, and CaCO₃ shows

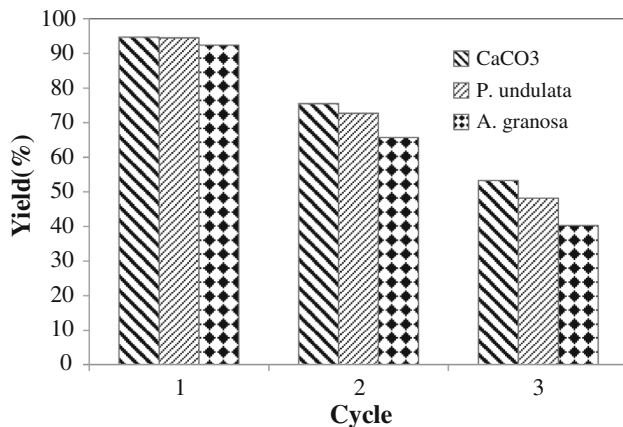
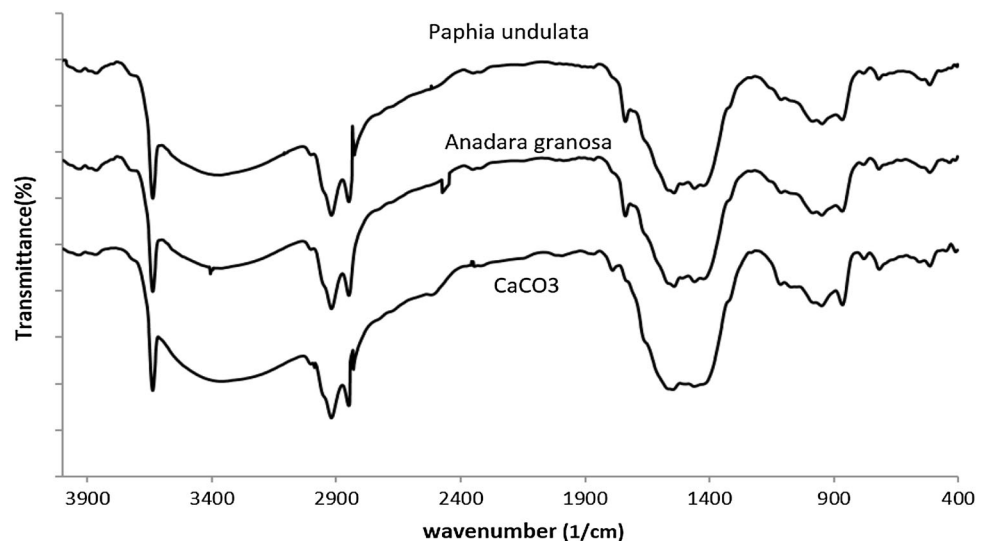


Fig. 5 Biodiesel yield during esterification after the first and second catalyst recycles for CaO catalyst derived from CaCO₃, *Paphia undulata*, and *Anadara granosa*

Table 5 The CaO content of fresh and spent catalysts after the third cycles

Catalyst	CaO contents in fly ash catalyst (%)		
	CaCO ₃ -based CaO	<i>Paphia undulata</i> -based CaO	<i>Anadara granosa</i> -based CaO
Fresh (before used)	57.31	46.98	43.26
First cycle	34.39	30.66	26.98
Second cycle	10.54	9.31	8.23
Third cycle	7.96	6.48	5.28

Fig. 6 FTIR spectra of the second recycled catalysts



the identical FTIR patterns. The functional group in the catalyst has been detected at the wavelength of 3639.2, 3365.7, 2652.7, 1550.7, and 1463.9, while CaO was detected at 725, 877, 1430, 1785, and 2530 cm⁻¹. As compared with Fig. 3, there is difference in the peaks indicated that CaO in the catalyst reduces. At peaks of 3639.2 and 3365.7 cm⁻¹ there were vibrations of OH-bonds such as Si–OH or Ca–OH bonds, while absorption around 2652.7 cm⁻¹ suggesting that SiO₂ was generated. In addition, groups of –C–H and –CH₂– were indicated by their appearance at 1550.7 and 1463.9 cm⁻¹, respectively. These organic groups also show the vibration of –C–H and –CH₂– groups, which probably from triglyceride entrapped in the catalysts.

The XRD pattern of catalyst derived from calcined *P. undulata* and CaCO₃ is shown in Fig. 7. These diffractograms showed that both recycled catalysts have identical patterns, and CaO compound was detected at 2θ = 32, 37, 53, 64, and 67. The largest portions are detected at 2θ = 32, 37, while at 2θ = 53, 64, and 67, CaO compound is presence in small quantities. This is probably due to reaction of CaO with methanol to form calcium methoxide during esterification reaction.

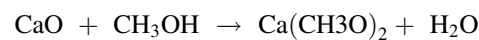
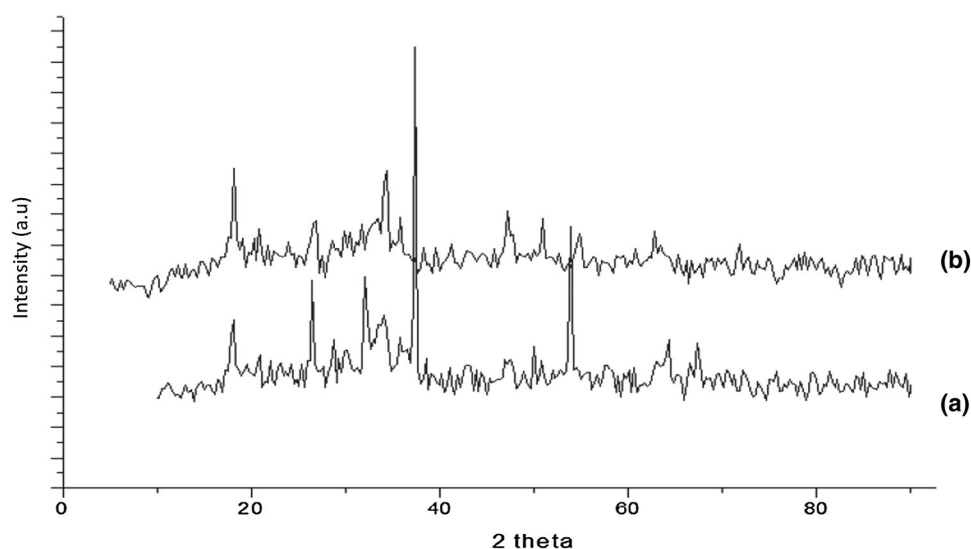


Fig. 7 Powder XRD pattern of catalysts after the second recycled. **a** CaCO₃ and **b** *Paphia undulata*



The study of the reusability revealed that the mollusk shells of *P. undulata* and *A. granosa* could be effectively utilized as low-cost-supported-based catalyst for biodiesel production.

Conclusion

This study focused on the development of heterogeneous CaO catalyst derived from mollusk shells (*A. granosa* and *P. undulata*) and CaCO₃. It was determined that transesterification conditions of 6 wt % catalyst loading, 12:1 methanol to oil mole ratio, 60 °C reaction temperature, 2 h reaction time resulted in biodiesel yield of 92 and 94 %, for CaO from *A. granosa* and *P. undulata* shells, respectively. The biodiesel physicochemical properties, including ester and linolenic acid contents, kinematic viscosity, density, and cetane number, were within the limits specified in ASTM standard. The developed catalyst could also be reused up to three consecutive cycles after regeneration. Overall, the mollusk shells have been potentially demonstrated as low-cost catalyst for transesterification applications.

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