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GOLDEN APPLE CHERRY SNAIL SHELL AS CATALYST FOR HETEROGENEOUS TRANSESTERIFICATION OF BIODIESEL

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Abstract - Calcium oxide catalysts prepared from golden apple cherry snail shell (*Pomacea canaliculata*) via two steps - deproteination and calcination - were compared: the structure was characterized by XRD and XRF and morphology by SEM. In addition, the effects of reaction time, catalyst loading amount, methanol:oil molar ratio and reaction temperature on the biodiesel yield were measured. The optimum conditions for biodiesel production, 0.8 wt% catalyst loading, 12:1 methanol:oil molar ratio, 65 OC reaction and 6 h reaction time, gave a biodiesel up to 95.2%. Moreover, the catalyst demonstrated high stability, permitting reuse for up to four cycles with biodiesel yield falling by only 4%.

Keywords: Golden apple cherry snail shell; Biodiesel; Heterogeneous transesterification.

INTRODUCTION

Biodiesel is a non-petroleum-based fuel, that generally consists of fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), derived from the transesterification of triglycerides (TG) with methanol or ethanol, respectively. The complete conversion of the TG via transesterification involves three consecutive, but reversible, reaction steps, with monoglyceride (MG) and diglyceride (DG) as intermediates. The reaction sequence is:

$$TG + ROH \rightleftharpoons DG + R'COOR \quad (1)$$

$$DG + ROH \rightleftharpoons MG + R'COOR \quad (2)$$

$$MG + ROH \rightleftharpoons Glycerol + R'COOR \quad (3)$$

$$TG + 3ROH \rightleftharpoons Glycerol + 3R'COOR \quad (4)$$

Equations (1)-(3) eventually produce glycerol forming one ester molecule for each alcohol molecule consumed in each step. Equation (4) shows the overall reaction, with 1 mole of triglyceride and 3 moles of alcohol forming 3 moles of alkyl esters and 1 mole of glycerol as a by-product (Nomanbhay *et al*., 2017).

In recent years, biodiesel is becoming more attractive as a non-toxic, renewable and biodegradable fuel (Huang *et al*., 2015). The energy crisis encourages research and development of biodiesel as an alternative energy because biodiesel can fuel existing diesel engines (Imkum Putkham *et al*., 2014) and can be obtained from biological materials such as animal oil, algae, sunflower oil, sesame, bean, soybean, castor bean, jatropha curcas and used vegetable oil. Biodiesel contains various types of methyl or ethyl esters of fatty acids with C_{14}-C_{24} carbon chains. Biodiesel is clean energy that can decompose naturally and contains very little sulfur. In addition, biodiesel has a higher

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flash point than diesel so it is safer for transportation (Demirbas, 2009).

Biodiesel can be generated either with or without a catalyst . With a catalyst, animal fat or vegetable oil can be transformed into methyl- or ethyl-esters faster at lower temperatures and pressures. However, without a catalyst the reaction may require temperatures of between 250 and 400 ^{O}C and pressures between 35 and 60 MPa (Zabeti *et al*., 2009) Currently, research for biodiesel production focuses on catalytic reactions because they use lower temperatures and pressures and avoid the more complex equipment needed for catalyst-free reactions. Moreover, catalyzed processes can be more easily extended to the industrial production. Homogeneous catalysts are dissolved in the initial substance. One common example is NaOH or KOH which are cheap and readily available. Also, it activates the reaction in mild conditions, accelerating the reaction 4000-fold, compared to acid as catalyst (Lotero *et al*., 2005). For used cooking oil with more than 1 wt% free fatty acid, H_2SO_4 will accelerate the reaction (Ming Chai *et al*., 2014). If vegetable oil contains more than 6 wt% free fatty acid, Felizardo *et al*. suggested not using base for the reaction (Felizardo *et al*., 2006). However, homogeneous catalysis sometimes leads to phase separation and difficulty separating the glycerine side product and the biodiesel, so the catalyst solution is not reusable. Also, producers are responsible for wastewater purification to remove catalyst from biodiesel.

Therefore, our research employs heterogeneous or solid catalysts. In particular, calcium oxide (CaO) has been reported to lead to high biodiesel yield. It is only slightly soluble in alcohol, so it can be reused many times and there is no waste water from washing the biodiesel. (Zeljka *et al., 2016*) Moreover, CaO, synthesized from natural materials and wastes, can be used. Recent studies reported the use of CaO catalyst in biodiesel production from used vegetable oil (e.g. sunflower oil) (Veljkovia *et al*., 2009), soybean oil (Kouzu *et al*., 2008), and waste frying oil (Nair *et al*, 2012). CaO is strongly basic and leads to 93-99 % biodiesel yields. Other heterogeneous catalysts have been reported: e.g., Kim *et al*. (2004) used Na/NaOH/γ-Al_2O_3 with vegetable oil; Brito *et al*. (2007) used Zeolite Y with used vegetable oil and Serio *et al*. (2006) used magnesium oxide with soybean oil. Soetaredjo *et al*. (2011) used KOH/bentonite as a catalyst for transesterification of palm oil to biodiesel. However, some of these materials still need improvement as they show low catalytic activity, high sensitivity to moisture and are soluble in methanol. Many heterogeneous catalysts are also complicated to produce.

Among the heterogeneous catalysts, CaO has been extensively studied because it has high basicity, high transesterification activity in mild reaction conditions, is less soluble in methanol and is non-toxic (Roschat *et al*., 2016). In addition, CaO can be prepared from natural calcium carbonate ($CaCO_3$) sources such as waste eggshells (Wei *et al*., 2009), mollusk shells (Somnul *et al*., 2014), ostrich eggshells (Chen *et al*., 2014), crab shells (Correia *et al*., 2014), capiz shells (Suryaputra *et al*., 2013) and clam shells (Asikin-Mijan *et al*., 2015) which further reduces cost (Roschat *et al*., 2016). Currently, farmers in Phon-Ngam Village, Kosumpisai , Mahasarakham Province, Thailand (16.3297°N 102.9519°E) face declining rice production because the rice stalks are disturbed by pests, especially golden apple cherry snails (*Pomacea canaliculata*), which grow and reproduce quickly, and directly impact declining rice production. Some farmers may earn extra income from the snails by boiling and selling them. However, this has a negative effect in that the snail shells are waste. These shells are increasing daily and causing an increased waste problem and air polution from the smell of rotten snails. Therefore, if these shells find a use, it may reduce these problems, adding value to the shells as a source of CaO for a catalyst.

Thus, we studied the potential use of golden apple cherry snail shells as a cost-effective source of CaO as a heterogeneous catalyst for biodiesel production. Three modifications were assessed to enhance the catalytic activity and optimum reaction conditions were determined using palm oil and methanol as starting reagents.

MATERIALS AND METHODS

Materials

Palm oil was purchased from Morakot Industries Public Company Limited, Thailand. The fatty acids in palm oil were determined by gas-chromatography (GC) as 0.4% lauric acid ($C_{12:0}$), 0.8% myristic acid ($C_{14:0}$), 37.4% palmitic acid ($C_{16:0}$), 0.2% palmitoleic acid ($C_{16:1}$), 3.6% stearic acid ($C_{18:0}$), 45.8% oleic acid ($C_{18:1}$), 11.1% linoleic acid ($C_{18:2}$), 0.3% linoleic acid ($C_{18:3}$), 0.3% arachidic acid ($C_{20.0}$) and 0.1% eicosenoic acid ($C_{20:1}$) (Viriya-empikul *et al*., 2012). The golden apple cherry snails were collected from paddy fields in Phon-Ngam Village. AR methanol and sodium hydroxide were purchased from Merck Inc. Distilled water was used for solution preparation.

Catalyst Preparation

CaO from the snail shells was prepared via calcination, deproteination and a deproteination and calcination combination.

The snails were boiled at 100 ^{O}C for 1 h. The snail body was extracted and the shells were cleaned, dried by sunlight, ground and filtered out using a 2 mm aperture sieve. Three CaO catalyst preparation methods were assessed to obtain maximum CaO content:

(1) calcinations: the ground shell was calcined at 1050 ^{O}C for 2 h and labelled sample C_{1050} ,

(2) deproteination: ground shell was agitated with 4 %w/v NaOH at 60 ^{O}C for 1 h and then allowed to precipitate, the filtrate was washed with distilled water until the pH of the wash water was neutral, dried in an oven at 100 ^{O}C for 1 h, decolorized by boiling in acetone for 1 h, filtered and washed with methanol and dried at 100 ^{O}C for 1 h. The output product in white powder form was labelled C_{deprot},

(3) deproteination (as in 2) followed by calcination (as in 1): the sample prepared following method (2) was calcined at 1050 ^{O}C for 1 h and labelled $C_{deprot+1050}$.

Catalyst Characterization

Minerals in the samples were identified and their structural properties determined by X-Ray Diffraction (XRD). Diffraction spectra were captured with a Bruker D8 diffractometer with Cu-K_{α} radiation with a 30kV tube voltage at 30 mA. Morphology was observed using a Scanning Electron Microscope (SEM) (Leo 1455 VP, UK), using a 15 kV accelerating voltage. Chemical compositions were determined by X-ray fluorescence spectroscopy (XRF) using a Bruker AXS SRS 3400 spectrometer.

Catalytic Tests

Catalytic activity in the transesterification reaction was checked under various conditions. 100 g palm oil was placed in a batch reactor consisting of a flask with a condenser and a port for adding the sample, thermometer, magnetic stirrer to enhance mass transfer of immiscible reactants (oil and methanol) and a water bath to adjust the reaction temperature. All experiments were carried out under atmospheric pressure. In a typical transesterification reaction, palm oil and methanol (12:1 methanol to oil molar ratio) and 1 % by wt of catalyst were loaded into the flask. The reaction medium was heated to 65 ^{O}C while stirring at 590 rpm. After 6 h, the catalyst was separated from the reaction mixture by filtration. A rotary evaporator removed excess methanol from the reaction products. The sample was analyzed by GC-MS for FAME content. The biodiesel yield was calculated as:

$$\text{Biodiesel Yield}(\%) = \left(\frac{M_B}{M_{oil}}\right) \times 100\% \qquad (5)$$

where M_B is mass of biodiesel produced (g) and M_{oil} is mass of palm oil used (g)

Product Analysis

Biodiesel components were identified and quantified by gas chromatography-mass spectrometry using an Agilent GC-MS system: GC-model 6890N, MS-model 5973, equipped with a HP-5MS capillary column (30m, 0.25 mmID, 0.25 μm).

RESULTS AND DISCUSSION

Characterization of Catalysts

Figure 1 shows XRD spectra of samples derived from the snail shells by methods (1), (2) and (3). The figure clearly shows that CaO was generated with methods (1) and (3), evidenced by 2θ diffraction peaks at 32.24°, 37.39°, 53.88°, 64.18°, 67.40°, 79.66° and 88.50°. The diffraction pattern of CaO match those in the JCPDS database. Method (2) spectrum contained $CaCO_3$ only with 2θ peaks at 29.35° and 47.12° which meant that no $CaCO_3$ decomposed to CaO on deproteination. The shell has a very strong outer shell layer which is difficult to decompose. Figure 1, top line, marked GACSS, indicates that the snail shell mostly contained $CaCO_3$. However, method (1) - calcination at 1050 ^{O}C - and method (3) - both deproteination and calcination at 1050 ^{O}C - transformed $CaCO_3$ into CaO as the shell was mostly calcium carbonate, as shown on the top - GACSS line. After calcination at high enough temperature, $CaCO_3$ decomposed into CaO and CO_2

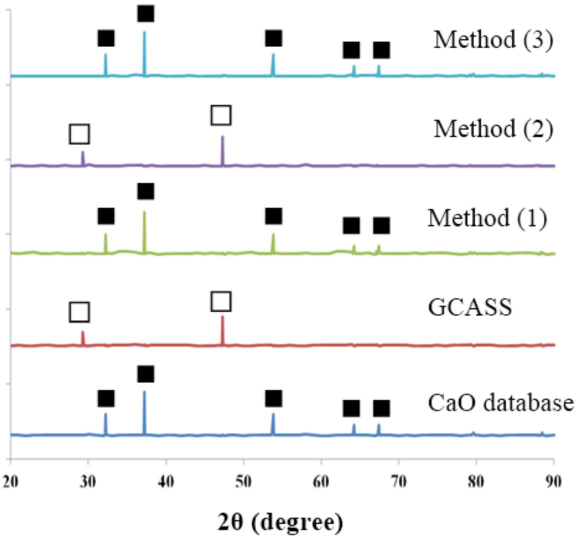


Figure 1. XRD spectra of CaO (from JCPDS database), ground snail shell and after processing by methods (1) to (3) when present: ■ as CaO and □ as $CaCO_3$.

(Boonyuen *et al.*, 2015). However, preparation by method (2) - deproteination - did not generate any CaO at the low temperature and was only able to remove protein residues from the shell. So the high calcination temperature used in methods (1) and (3) is necessary to generate CaO.

X-ray fluorescence spectra showed that the CaO prepared by deproteination combined with calcination at 1050 ^{O}C led to a slightly higher percentage of CaO than calcination alone, i.e., method (3) not only provided a higher percentage of CaO, but also removed protein from the sample (evidenced by the absence of Si and Mn oxides) making it purer - see Table 1.

SEM micrographs (Figure 2) indicated that the snail shell before calcination possessed large, flat, dense structures with dispersed tiny pores and a slightly rough surface - see Figure 2a. However, after calcination, Figure 2b, the surface was rougher with many cracks. Heat degrades organic substances in the shell and also transforms $CaCO_3$ into CaO which looks porous and brittle and more easily ground than those without calcination (Boro *et al.*, 2011). After calcination (method (1), 2b and method (3), 2d) there was a porous surface dispersed over the whole surface compared to those without calcination (2a and 2c).

Table 1. Chemical composition.

Sample	Component (% weight)			
	Na_2O	CaO	SiO_2	MnO
Method (1) (C_{1050})	0.5	98.6	0.5	0.4
Method (3) ($C_{deprot+1050}$)	0.5	99.5	-	-

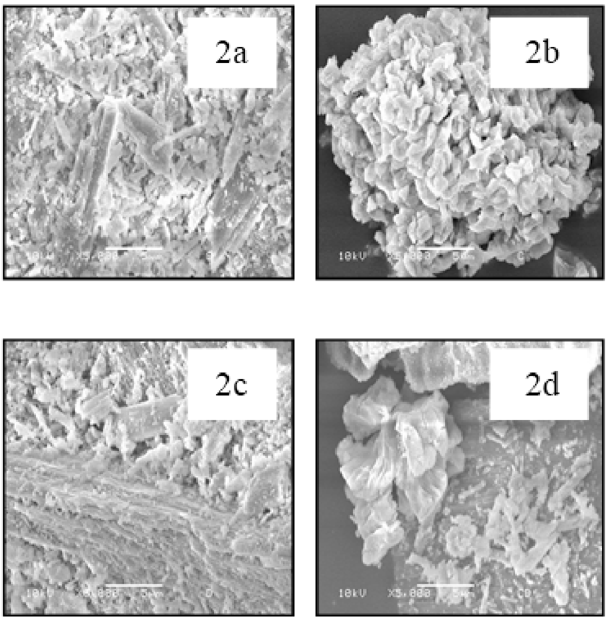


Figure 2. SEM images of (2a) original snail shell; (2b) method (1) : calcination only; (2c) method (2): deproteination only and (2d) method (3) : both deproteination and calcination.

Catalytic Activity in Transesterification

To assess catalytic activity, 100 g palm oil samples, with a methanol:oil molar ratio of 12:1; 0.8 wt% catalyst loading amount; reaction temperature 65 ^{O}C; and time 6 h**.** Figure 3 shows that method (3) led to a higher 95.2 % biodiesel yield than others with M0 (ground snail shell alone) giving 82.3%, calcination alone (M1) 90.7%, deproteination (M2) 85.6%. Therefore, the best method, deproteination and calcination combination (M3), was applied in the following experiments.

The methanol to oil molar ratio, catalyst loading, reaction temperature and reaction time exert a major influence on the biodiesel yield for transesterification of vegetable oil or animal fat. We varied one variable at a time while keeping the others constant to understand the influence of the main parameters that govern the yield and the optimal processing conditions were also investigated. This technique is widely used to optimize the reaction conditions for biodiesel synthesis. In the following experiments we varied one of the parameters in Table 2 and kept the remaining ones constant.

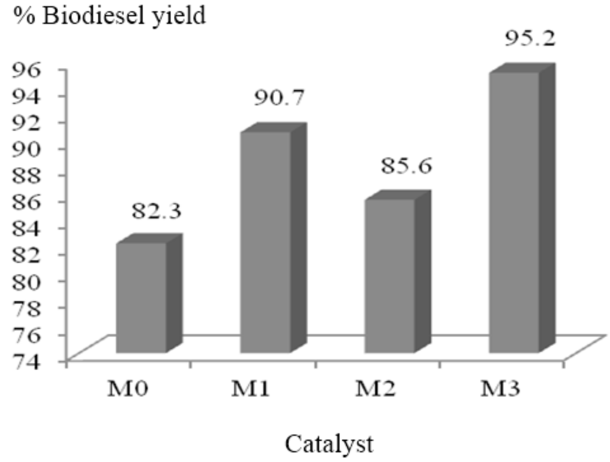


Figure 3. Transesterification activities of catalysts – see text for experimental conditions - raw ground shell (M0), calcination (M1), deproteination (M2) and deproteination and calcination combination (M3).

Table 2. Base conditions for the following experiments.

Method	3
methanol:oil	12:1molar ratio
Temperature	65^{o}C
Catalyst loading	0.8 wt%
Reaction time	6 hours

Effects of reaction time

Buasri *et al* (2013) reported palm oil biodiesel production using calcium oxide catalyst from several shells with the following yields after 6 hours: mussel 96%, cockle 93% and scallop 94%. Ismail *et al.* (2016) found that biodiesel produced from castor oil using calcium oxide prepared from mud clam shell at 3 hours yielded biodiesel at 87%. Zein *et al*. (2016) showed that biodiesel production from waste palm oil using CaO/H-ZSM-5 after 6 hours had a biodiesel yield of 95% but, at 8 hours, showed no further conversion. Therefore, we used times up to 6 hours, because past studies showed that longer reaction times would yield little or no additional conversion because only a small quantity of triglycerides remain after the reaction with methanol and equilibrium was reached, leading to the potential for reverse reactions - see equations (1) to (4) (Samart *et al*., 2009; Santana *et al*., 2012). The CaO catalyst is likely to adsorb products when the reactant concentration is too low (Taufiq-Yap *et al*., 2011). So, long reaction time allows the CaO catalyst to absorb the biodiesel and thus reduce the yield (Ismail *et al*., 2016).

Results shown in Figure 4 indicate that the biodiesel yield increased from 89.4 to 95.2% when the reaction time increased from 3 to 6 h.

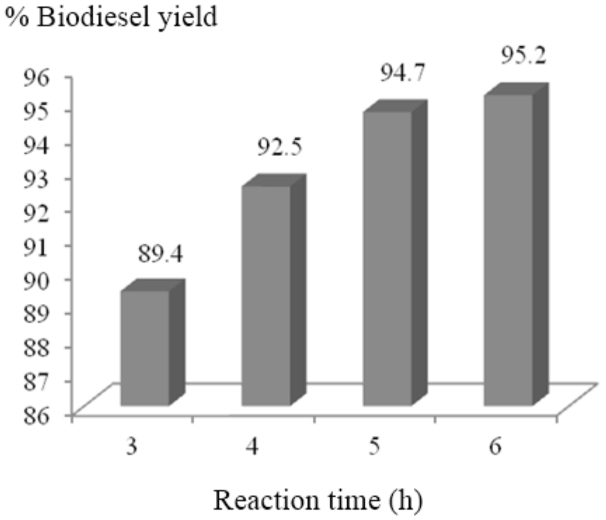


Figure 4. Yield *vs* reaction time: transesterification reaction of palm oil to biodiesel (base reaction conditions followed Table 2).

Effects of Reaction Temperature

Testing the reaction temperature using the same conditions as the previous experiment showed that 65 ^{O}C led to the maximum yield. At other temperatures the yield was approximately 9% less. The boiling point of methanol at atmospheric pressure is 64.7^{o}C, but in these circumstances the methanol cannot easily escape and the pressure will be above atmospheric, so we were able to run experiments at temperatures of 65^{o}C and higher. However, as seen in Figure 5, the yield decreased above 65^{o}C because of the rapid loss of the methanol. However, at lower temperatures, the biodiesel yield could decrease due to reduced molecular mobility. Therefore, 65 ^{O}C, the point of maximum yield, was selected as the base condition in Table 2. This is consistent with several other reports which report 65^{o}C as the optimum temperature for batch stirred and packed-bed reactors: Lengyel *et al*. (2015) for rapeseed oil using CaO; Buasri *et al*. (2013) for palm oil over CaO derived from eggshell wastes in a batch stirred tank reactor and Ketcong *et al*. (2014) for palm oil over limestone-derived CaO in a fixed-bed reactor.

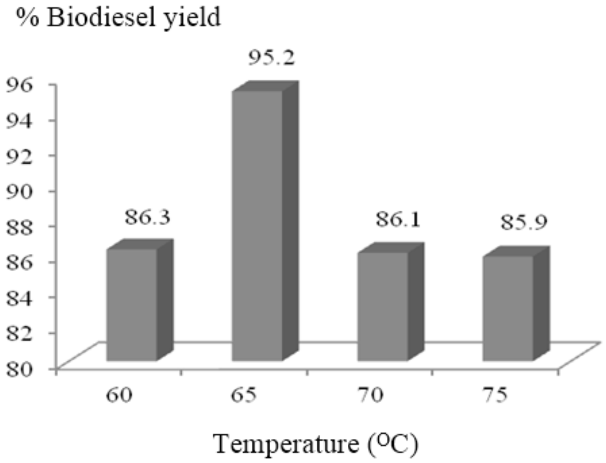


Figure 5. Yield *vs* temperature: transesterification reaction of palm oil to biodiesel (base reaction conditions followed Table 2).

Effects of Methanol to Oil Ratio

The controlled variables were the reaction at a time of 6 h**,** the catalyst loading amount at 0.8 wt% of palm oil, the reaction temperature at 65 ^{O}C and the independent variable was methanol to oil molar ratio in a range of 6:1 to 12:1. From Figure 6, the percentage of

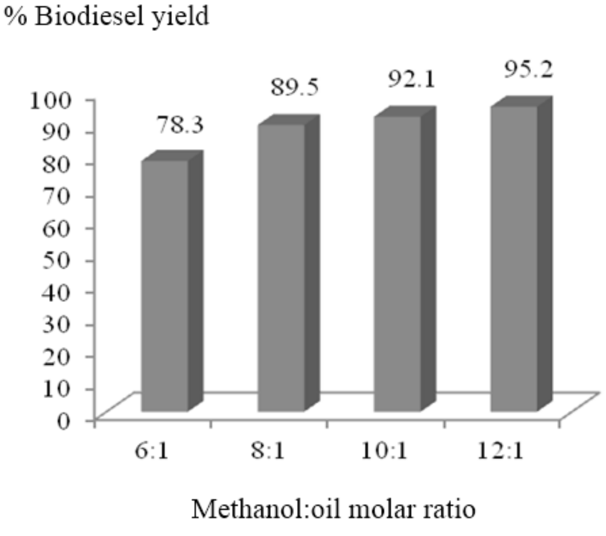


Figure 6. Yield *vs* methanol : oil molar ratio : transesterification reaction of palm oil to biodiesel (base reaction conditions followed Table 2).

biodiesel produced from the transesterification process by using method (3) catalyst showed that a methanol to oil molar ratio at 12:1 could produce the highest biodiesel yield at 95.2%. Optimum methanol:oil molar ratios were reported as 14:1 (Ismail *et al*., 2016) and 12:1 (Zein *et al*., 2016). However, excess methanol did not increase the yield and led to the undesirable result of decreasing the biodiesel concentration and increasing the downstream processing cost (Kasim and Harvey, 2011). Also, excess methanol tended to dilute reactant concentration, decreasing the contact among them and lowering conversion yield.

Effects of Catalyst Loading Amount

Catalyst loading in the range 0.6 to 4.0 wt% was assessed using 12:1 methanol:oil molar ratio, 65 ^{O}C temperature, 6 h reaction time and stirring at 590 rpm. In Figure 7, we see that the biodiesel yield peaked at 95.2% with a 0.8 wt% catalyst loading. Catalyst accumulation on the wall of the glass reactor was observed above 1 wt% catalyst loading, which reduced the exposed and active area of the catalyst during reaction and effectively lowered catalyst activity (Buasri *et al*., 2012).

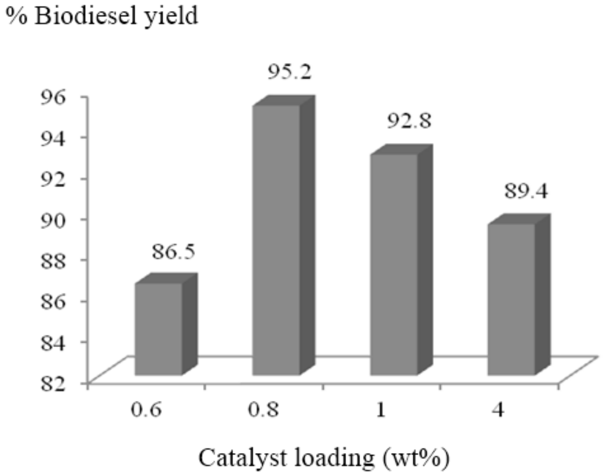


Figure 7. Yield *vs* catalyst loading: transesterification reaction of palm oil to biodiesel (base reaction conditions followed Table 2).

Reusability of Catalyst

Our reusability tests revealed that the catalytic activity of the deproteination and calcination combination catalyst remained stable upon successive reuse since the yield marginally decreased with the catalyst recycled after 4 consecutive runs. Recycling experiments were carried out under identical experimental conditions. Figure 8 shows that conversions of 95.2, 94.4, 93.5 and 90.7% were obtained for the first four cycles of methanolysis of the palm oil using a recovered deproteination and calcination combination catalyst The reduction of efficiency was due to intermediate products, such as diglyceride and monoglyceride, which blocked the holes of the catalyst (Wong *et al*., 2015). Also, water or oxygen reacted at the catalyst surface, reducing its sensitivity. However, the solid catalyst, although having decreased sensitivity, could be used to generate heat from the exothermic reaction and thus be reused.

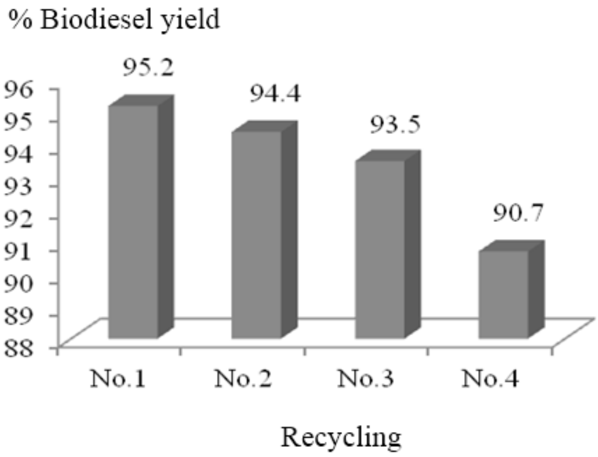
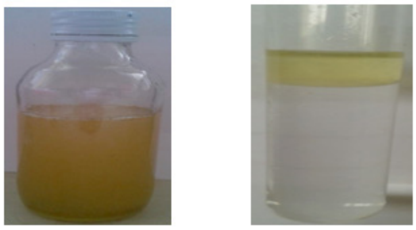


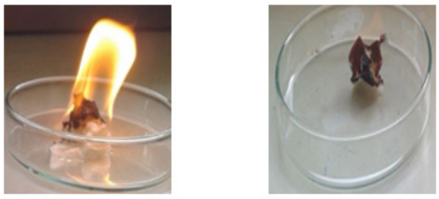
Figure 8. Yield *vs* recycling: transesterification reaction of palm oil to biodiesel (base reaction conditions followed Table 2).

Characterization of the Biodiesel Product

The synthesized products were tested for water solubility and flammability: biodiesel was yellow, insoluble and flammable whereas palm oil is not flammable, confirming that the synthesized product is consistent with biodiesel (Figure 9).



Raw Biodiesel Separated Biodiesel



Flammability biodiesel soaked in cotton – initiation complete combustion

Figure 9. Physical properties of generated biodiesel.

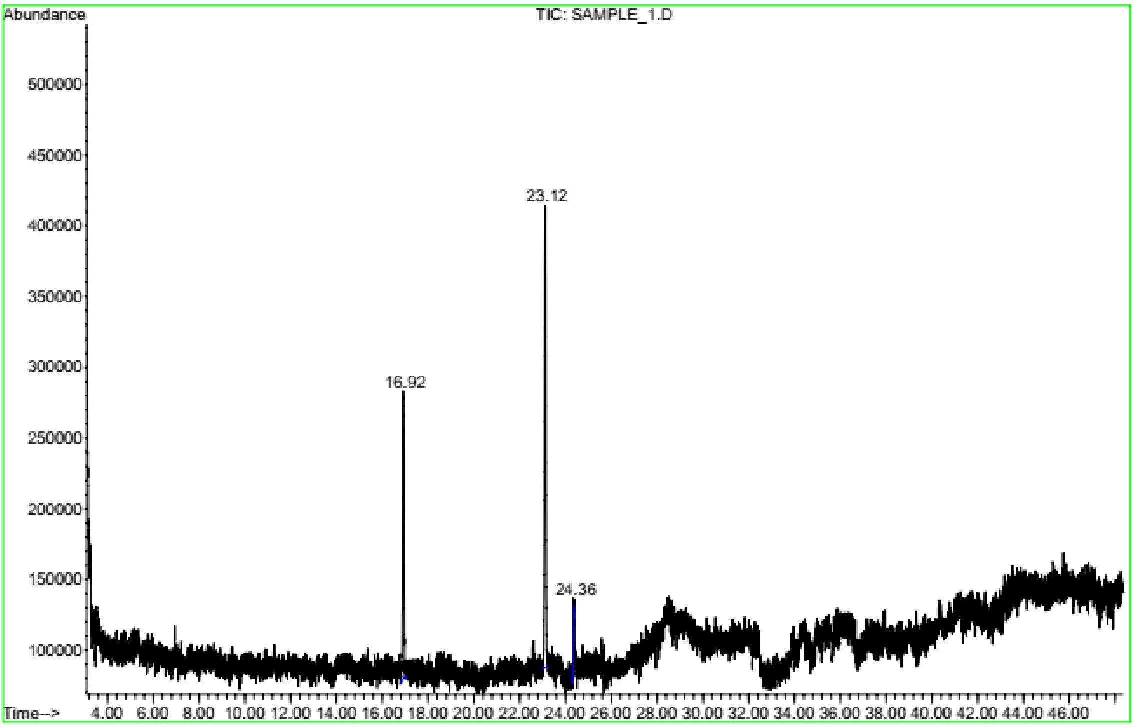


Figure 10. GC-MS peaks for biodiesel components: transesterification reaction of palm oil to biodiesel (base reaction conditions followed Table 2).

The biodiesel product components were characterized by GC-MS. Identified peaks of the fatty acid methyl esters, and quantities at different retention times are summarized in Table 3 and Figure 10. The composition of the final biodiesel product mainly consisted of 38.5% tetradecanoic acid methyl ester, 60.1% 16-octadecenoic acid methyl ester and 1.3% trans-1,4-hexadiene at retention times of 16.9, 23.1 and 24.3 respectively.

Table 3. Components of biodiesel.

Retention time, s	Composition	%FAME
16.9	Tetradecanoic acid methyl ester	38.5
23.1	16-Octadecenoic acid methyl ester	60.1
24.3	Trans-1,4-Hexadiene	1.3

CONCLUSION

We prepared calcium oxide catalysts from golden apple cherry snail shells using two steps: elimination of the protein or deproteination followed by calcination. This combination led to the highest CaO yeild - 99.5%. The optimum conditions for biodiesel production from palm oil by transesterification produced in this way was methanol : oil molar ratio 12:1, catalyst loading 0.8 wt% , 6 h reaction time, 65^{O}C reaction which led to 95.2% biodiesel yield. In addition, the catalyst could be reused 4 times with the biodiesel yield remaing above 90%.

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