Fuel 92 (2012) 239–244

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Biodiesel production over Ca-based solid catalysts derived from industrial wastes

N. Viriya-empikul [a], P. Krasae [b], W. Nualpaeng [a], B. Yoosuk [b], K. Faungnawakij [a,*]

[a] *National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), 111 Thailand Science Park, Pahonyothin Rd., Klong Laung, Pathumthani 12120, Thailand*

[b] *National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency, 114 Thailand Science Park, Pahonyothin Rd., Klong Laung, Pathumthani 12120, Thailand*

ARTICLE INFO

Article history:
Received 29 March 2011
Received in revised form 27 June 2011
Accepted 12 July 2011
Available online 23 July 2011

Keywords:
Transesterification
Heterogeneous catalyst
Egg and mollusk shells
CO_2 poisoning
Basicity

ABSTRACT

The solid oxide catalysts derived from the industrial waste shells of egg, golden apple snail, and meretrix venus were used as biodiesel production catalysts. Their catalytic activity in transesterification of palm olein oils and their physicochemical properties (by TG/DTA, EDX, SEM, N_2 sorption, CO_2-TPD, and XRD) were systematically investigated. The waste materials calcined in air with optimum conditions (temperature of 800 °C, time of 2–4 h) transformed calcium species in the shells into active CaO catalysts. The activity of the catalysts was in line with the basic amount of the strong base sites, surface area, and crystalline phase in the catalysts. All catalysts derived from egg and mollusk shells at 800 °C provided high activity (>90% fatty acid methyl ester (FAME) in 2 h). These abundant wastes showed good potential to be used as biodiesel production catalysts.

1. Introduction

Because of the energy and global warming crisis, development of renewable energies, for example, H_2 energy [1], solar energy [2], and biodiesel [3–6], have been focused worldwide. Biodiesel, long-chain fatty acid alkyl ester is one of the interesting alternative fuels which can be produced from renewable sources and provides complete combustion with less gaseous pollutant emission [7]. Biodiesel is produced conventionally via transesterification of vegetable oils using homogeneous catalysts, e.g. NaOH, KOH, and $NaOCH_3$ [6,8]. The homogeneous catalytic process however, provides some disadvantages, such as, a huge production of wastewater from washing process of catalyst residues and nonreusability of the catalysts [9]. Although the transesterification in supercritical methanol can be a solution to these problems, the technology requires high temperatures (350–400 °C) and pressures (10–25 MPa) and therefore the high capital cost. Alternatively, the heterogeneous catalyst has been developed to defeat the problems [7,10,11]. The heterogeneous catalytic process overcomes the homogeneous one since the solid catalysts can be easily recovered and potentially be reusable. Additionally, a neutralization step producing wastewater would be eliminated. The heterogeneous process can be operated at the similar conditions used for the homogeneous one or at the moderate temperatures (<250 °C) and pressures (<10 MPa). Thus the operating cost would be minimized and this would result in the low-cost biodiesel [12,13].

The wastes from agricultural and food industries are produced several tonnes a day in Thailand. Some kinds of wastes such as eggshells and mollusk shells were highly potential to be used as biodiesel production catalysts [5,13,14]. In fact, a number of heterogeneous catalysts, for example, CaO [15,16], MgO [17,18], SrO [19], Zeolite [20,21], Al_2O_3 [11,16,22], ZnO [22], TiO_2 [11,17], ZrO [11], and hydrotalcites [23–25] have been employed in the transesterification process. Among these catalysts, the alkaline earth metal oxides (e.g. MgO, CaO, and SrO) have the high activity for using in the typical process (at low temperature and under atmospheric pressure condition). Among the alkaline earth metal oxides, CaO is close on the environmental material. Generally, $Ca(NO_3)_2$, $CaCO_3$, or $Ca(OH)_2$ is the raw material to produce CaO catalysts [26]. As alternative way to synthesize CaO catalyst, there are several natural calcium sources from wastes, such as eggshell, mollusk shell, and bone. Not only eliminating a waste management cost, but also the catalysts with high cost effectiveness can be simultaneously achieved for biodiesel industry. The prize of biodiesel is anticipated to be competitive with petroleum fuels. Recently, Nakatani et al. [5] examined transesterification of soybean oil catalyzed by combusted oyster shell at 700 °C, and found that it is active for biodiesel production. Wei et al. [13] reported that calcination of eggshell above 700 °C could produce CaO catalyst for biodiesel production. However, the catalytic behaviors during the reaction as well as the catalyst characteristics were not clearly demonstrated. Boey et al. [27] proposed a waste mud crab shell as a catalyst to be efficiently

---

* Corresponding author. Tel.: +66 2 564 7100x6638; fax: +66 2 564 6981.
E-mail address: kajornsak@nanotec.or.th (K. Faungnawakij).

0016-2361/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2011.07.013

used or co-used for biodiesel production. The study of varying waste shells, such as mollusk shells and eggshell, was reported by Viriya-empikul et al. (2010) [14]. The works revealed that the waste shell-derived catalysts were active for catalyzing transesterification. Further study on the characteristics of the catalysts and the catalytic activity together with the optimization of the catalyst preparation and the reaction conditions would be essentially useful for realizing this approach.

In this research, the catalytic activity of meretrix venus shell was investigated by various parameters, for example, molar ratio of methanol/oil, calcination time and calcination temperature of catalysts. Furthermore, the catalyst sources, such as, two types of waste mollusk shells, golden apple snail shell and meretrix venus shell, and waste eggshell, were compared by biodiesel production activity. The waste shell-derived catalysts were characterized by thermo-gravimetric/differential thermal analyzer (TG/DTA), X-ray diffraction (XRD), energy dispersive X-ray fluorescence (EDXRF) spectroscopy, scanning electron microscope (SEM), nitrogen sorption and CO_2 temperature-programmed desorption, and were tested in transesterification to produce biodiesel from palm olein oil. The characteristics of the catalysts derived from those wastes and their catalytic activity were investigated.

2. Experimental

2.1. Materials and catalyst preparation

Palm olein oil was purchased from Morakot Industries PCL., Thailand. Compositions of fatty acid in palm olein oil are given in Table 1. The analytical reagent grade methanol (Fluka) was used in the transesterification reaction. Waste mollusk shell and eggshell were transformed to CaO catalyst by thermal synthesis. The raw materials (waste shells) were calcined at designated temperature (700–1000 °C) and time (0.5–8 h). All catalysts were kept in the close vessel to avoid the reaction with CO_2 and humidity in air before used.

Table 1
Fatty acid composition of palm olein oil.

Fatty acid	Composition (wt.%)
C12:0	0.4
C14:0	0.8
C16:0	37.4
C16:1	0.2
C18:0	3.6
C18:1	45.8
C18:2	11.1
C18:3	0.3
C20:0	0.3
C20:1	0.1

2.2. Material characterization

The waste shells were analyzed by thermo-gravimetric/differential thermal analyzer (TGA/SDTA 851^e, Mettler Toledo, Switzerland) under air flow condition with a heating rate of 10 °C min^{-1} to find out thermal transition of the samples. The crystalline phases of calcined samples were analyzed by X-ray diffraction (JDX-3530, JEOL, Japan) using an X-ray tube with Cu kα radiation source and accelerated at 30 mA and 40 kV. The elemental chemical compositions of the samples were determined by EDX (EDX-720, Shimadzu, Japan) under vacuum mode for precise measurement of both light and heavy elements. The calcined samples were characterized by scanning electron microscope (S-3400, HITACHI, Japan) and nitrogen adsorption (BELSORP-max, BEL, Japan) to find out their morphology and BET (Brunauer–Emmett–Teller) surface area (S_{BET}), respectively. Temperature programmed desorption using CO_2 as a probe molecule (CO_2-TPD) was used to study basic properties of the catalysts. Prior to CO_2 adsorption, a sample (0.3 g) was pretreated under a helium flow at 300 °C for 30 min. Then, the temperature was decreased to room temperature, and a flow of pure CO_2 (30 mL min^{-1}) was subsequently introduced to the samples for 90 min. The system was flushed with He for 60 min. The CO_2-TPD was carried out under a helium flow at a flow rate of 30 mL min^{-1}. The temperature was increased from 40 to 800 °C with a heating rate of 10 °C min^{-1}, and held at the final temperature for 60 min. The CO_2 desorption was monitored by an online mass spectroscopy coupled with a thermal conductivity detector (TCD). In addition, TPD measurement without CO_2 adsorption step was carried out over fresh calcined samples to determine the CO_2/steam poisoning during the catalyst preparation process.

2.3. Transesterification reaction procedure

The transesterification was carried out in a batch reactor. The palm olein oil (50 cm^3) in a 500 cm^3 round-bottom flask equipped with a reflux condenser was stirred at 60 °C. A mixture of methanol (MeOH) and catalyst preheated at 60 °C was added to the oil. Then the transesterification reaction was conducted under conditions of various MeOH to oil ratios (9:1, 12:1, 15:1, and 18:1) and catalyst amount of 10 wt.% for the required reaction times. To finish the reaction, the catalyst was separated from biodiesel product by centrifugation, and then excessive amount of methanol was evaporated before analysis of %FAME (Fatty Acid Methyl Ester). Note that the error of %FAME, which was ±2.0 wt.%, was observed by replica experiments.

Table 2
Physicochemical properties and catalytic activity of waste shell-derived catalysts calcined at 800 °C for 4 h.

Catalyst source	S_{BET}[a] (m^2 g^{-1})	Total pore volume[a] (cm^3 g^{-1} × 10^{-2})	%Ca[b]	Basic site[c] (μmol g^{-1})				Basic site density[d] (μmol m^{-2})	%FAME[e] at reaction time	
				Weak (<400 °C)	Medium (400–550 °C)	Strong (>550 °C)	Total		1 h	2 h
Meretrix venus shell	0.9	0.5	98.6	–	42	113	155	172.2	74.0	92.3
Golden apple snail shell	0.9	0.5	99.0	–	54	133	187	207.8	85.5	93.2
Eggshell	1.1	0.5	99.2	10	23	161	194	176.4	93.1	94.1

[a] Determined by N_2 adsorption analysis.
[b] Determined by EDX analysis.
[c] CO_2-TPD.
[d] Basic density = total basic site/S_{BET}.
[e] Transesterification conditions: temperature = 60 °C, methanol/oil molar ratio = 18:1, catalyst amount = 10 wt.%.

2.4. Determination of %FAME

The compositions of biodiesel were determined by a gas chromatograph (GC-2010, Shimadzu) equipped with capillary column, DB-WAX (30 m × 0.15 mm) and a flame ionization detector. Methylheptadecanoate was used as internal standard for quantification, according to EN14103 standard method. The biodiesel content was represented in term of %FAME as a function of time.

3. Results and discussion

3.1. Preliminary experimental works

In this research, three raw materials were used to synthesize the solid catalysts and their physical and catalytic properties were then investigated. In Table 2, the result of elemental chemical compositions, basicity, and BET surface area (S_{BET}) were obtained by EDX, CO_2-TPD, and nitrogen adsorption, respectively. The result of thermal transition, crystalline phase, and morphology of samples are sequentially shown in Figs. 1–3. In Fig. 1, the eggshell and mollusk shells were analyzed by TG/DTA to find out the suitable calcination temperature to produce the calcium oxide catalyst from the shells. Only one dominant step of weight loss (ca. 50%) was found over all samples at the temperature range of 700–850 °C. Above 850 °C, the weight of the sample kept almost constant, while the peak maxima in the DTG curves was around 810–830 °C. The eggshells and mollusk shells generally contain $CaCO_3$ as a main Ca-based component. The high temperature range above 700 °C is required to transform $CaCO_3$ to CaO which could be confirmed by the TG and DTG curves. In the viewpoint of preparation time and energy consumption, the temperature of 800 °C was selected as a suitable calcination temperature to produce CaO catalysts from the waste shells. Nakatani et al. [5] reported that the transformation of oyster shell composed of $CaCO_3$ to CaO required the combustion temperature at 700 °C or above. Further report from Wei et al. [13] also described that the temperature of eggshell transformation was above 800 °C. Generally, the required calcination temperature to transform $CaCO_3$ to CaO is ca. 800 °C. Thus, in this research, raw materials were calcined at 800 °C under air atmosphere for 4 h to obtain the biodiesel production catalysts, unless otherwise stated.

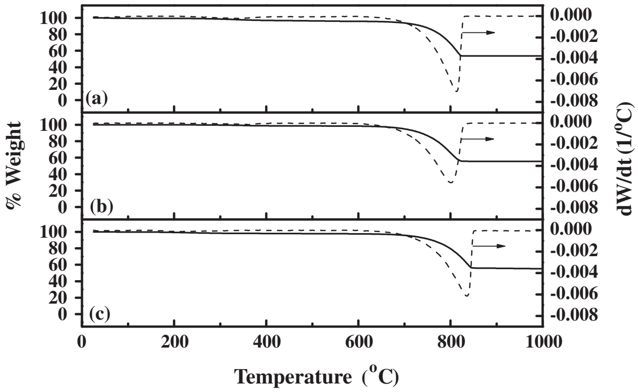


Fig. 1. TG and DTG curves for (a) eggshell, (b) golden apple snail shell, and (c) meretrix venus shell.

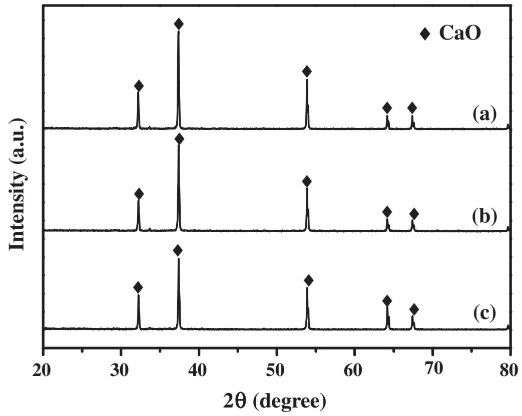


Fig. 2. XRD patterns of (a) eggshell, (b) golden apple snail shell, and (c) meretrix venus shell calcined at 800 °C for 4 h.

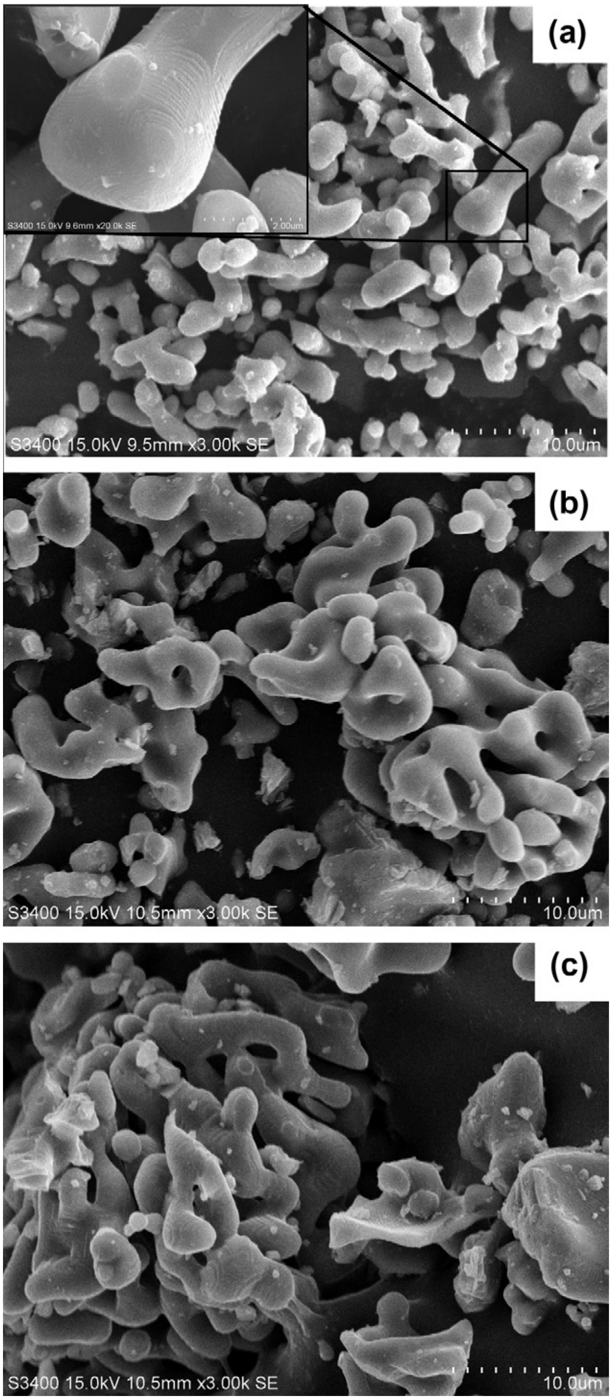


Fig. 3. SEM images of (a) eggshell, (b) golden apple snail shell, and (c) meretrix venus shell calcined at 800 °C 4 h.

XRD patterns of the shell-derived catalyst samples calcined at 800 °C for 4 h are demonstrated in Fig. 2. The catalyst samples showed clear and sharp peaks, identical for all samples. These peaks match a crystalline phase of CaO. This result confirmed that the condition to synthesize CaO from the shells was acceptable.

Furthermore, Table 2 shows S_{BET} of the catalysts, including eggshell = 1.1 $m^2\ g^{-1}$, golden apple snail shell = 0.9 $m^2\ g^{-1}$, and meretrix venus shell = 0.9 $m^2\ g^{-1}$. The eggshell-derived sample exhibited a slight higher surface area than the mollusk shell-derived ones. The different value of S_{BET} of each catalyst could be describable by SEM observation as shown in Fig. 3. In Fig. 3a, the calcined eggshell was rod-like particles and some of them bonded together as aggregates. The calcined golden apple snail shell and meretrix venus shell showed similar particle morphology with the calcined eggshell. However, the aggregates with larger size were also observed (Fig. 3b and c). The particle size of calcined eggshell ranged from 1 to 10 μm, while that of both calcined mollusk shells (golden apple snail and meretrix venus), which were observed as clusters of particles agglomerated from small particles, ranged up to several tens of microns. The smaller size of the grains and aggregates could provide higher specific surface areas. Since all samples are considered to be less-porous or even nonporous, 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. The Ca contents in the catalyst samples were all above 98%.

The basic property of the catalysts which should be expected from CaO species is considered a key factor yielding biodiesel. CO_2-TPD characteristics over all samples are shown in Fig. 4. It can be seen that all catalysts provided basic functions. The desorption curve over eggshell showed a very small shoulder from temperature of 250 to 550 °C which is considered as a weak/medium base. The desorption curve sharply increased and peaked at ca. 700 °C. For golden apple snail and meretrix venus shells, two distinctive peaks were observed in the temperature range of 400–550 °C and 550–750 °C, which were considered the medium strength and the strong one, respectively.

The catalytic property of CaO catalysts derived from eggshell, golden apple snail shell, and meretrix venus shell were elucidated to be active in heterogeneous transesterification for biodiesel production as summarized in Table 2. At the reaction time of 1 h, the descending order of the catalytic activity in term of %FAME over the shell-derived catalysts was as follows: eggshell (93%) > golden apple snail shell (86%) > meretrix venus shell (74%). All catalysts provided %FAME greater than 90% at reaction time of 2 h. Among the three raw materials, the catalyst synthesized from eggshell showed the highest surface area with smallest particle size, which is in line with the highest %FAME. According to CO_2-TPD results, the derived eggshell provided strongly basic sites (>550 °C) with a basic amount of 161 $\mu mol\ g^{-1}$, while its total basic amount is 194 $\mu mol\ g^{-1}$. The golden apple snail and meretrix venus showed similar desorption behaviors; they possessed two major functions of medium (54 and 42 $\mu mol\ g^{-1}$ (400–550 °C), respectively) and strong (133 and 113 $\mu mol\ g^{-1}$ (>550 °C), respectively) base sites. The experimental results suggested that the basic amount of the strongly basic sites strongly corresponded to the activity of the catalysts; namely the higher basic amount brought about the higher biodiesel yield. Although apple snail and meretrix have also medium base sites, they seem to be less effective to the reaction as compared with the strong ones. The ascending order of basic site density was as follows: meretrix venus (172 $\mu mol\ m^{-2}$) < egg (176 $\mu mol\ m^{-2}$) < golden apple snail (208 $\mu mol\ m^{-2}$). It should be noted that partial CO_2 poisoning over all fresh catalyst samples occurred during the preparation process, as a result shown in Fig. 4 (dotted lines). The poisoning majorly proceeded on the strong base sites (550–700 °C). The basic sites poisoned over catalysts derived from eggshell, golden apple snail shell, and meretrix venus shell were, respectively, 15, 17 and 19 $\mu mol\ g^{-1}$, which were less than 10% of their total basic sites. These results are consistent with XRD analysis, suggesting that $CaCO_3$ and $Ca(OH)_2$ formation are very minor. It was reported that the strong base sites (CO_2 desorbed above 700 °C) actively catalyzed transesterification, when compared with weak-to-medium base sites [28,29]. The present work clearly showed the potential use of waste-derived catalysts for biodiesel production. These wastes could stand for abundant resources of low-cost catalysts which could bring about the low-cost biodiesel.

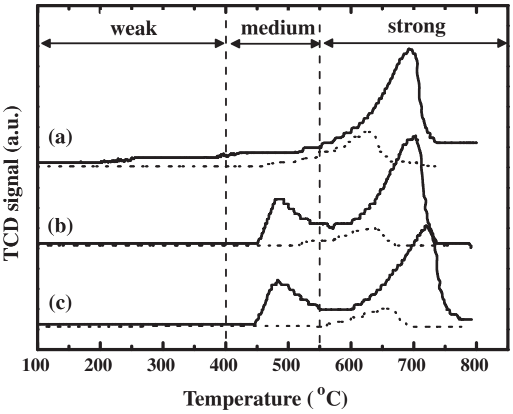
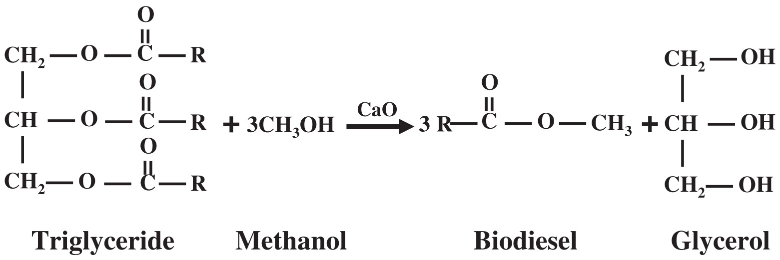


Fig. 4. CO_2 desorption curves from CO_2-TPD over (a) eggshell, (b) golden apple snail shell, and (c) meretrix venus shell catalysts calcined at 800 °C 4 h. Dotted lines represent CO_2 desorption from CO_2 poisoning during preparation step.

3.2. Effect of methanol/oil ratio

The biodiesel production by transesterification reaction is expressed in Eq. (1). By the transesterification in heterogeneous process, the palm olein oil or triglyceride is mixed with methanol and catalyzed by alkaline earth oxide; CaO in this case. Such triglyceride is catalyzed to di- and mono-glyceride, subsequently, while biodiesel (or fatty acid methyl ester) is produced simultaneously during the conversion of triglyceride as well. When the reaction is completed, biodiesel and glycerol co-exist in the process as reaction products. Regarding the catalytic reaction mechanism in the transesterification, calcium methoxide species, $Ca(CH_3O)_2$, was reported to form on the surface of CaO catalyst and enhanced the reaction between palm oil and methanol [30,31]. The basic sites in CaO can be ascribed to the presence of the Ca^{2+}–O^{2-} ion pair, when oxygen anions of low coordination number are considered to be responsible for catalyzing transesterification.



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R \\ CH-O-\overset{O}{\overset{\|}{C}}-R \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R \end{array} + 3CH_3OH \xrightarrow{CaO} 3\,R-\overset{O}{\overset{\|}{C}}-O-CH_3 + \begin{array}{l} CH_2-OH \\ CH-OH \\ CH_2-OH \end{array} \tag{1}$$

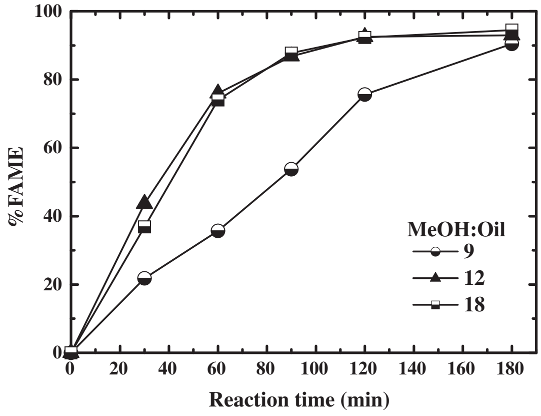


Fig. 5. Reaction time-dependence of FAME yield obtained in transesterification over meretrix venus shell-derived catalyst calcined at 800 °C for 4 h with various methanol/oil molar ratios (MeOH:oil). Transesterification conditions: temperature = 60 °C, catalyst amount = 10 wt.%.

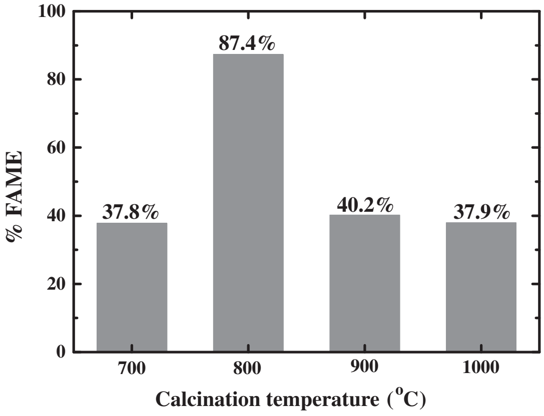


Fig. 6. %FAME obtained in transesterification over meretrix venus shell-derived catalysts calcined at interest temperature for 4 h. Transesterification conditions: temperature = 60 °C, methanol/oil molar ratio = 15:1, catalyst amount = 10 wt.% for 2 h.

Fig. 5 shows the effect of methanol/oil molar ratios on %FAME obtained in transesterification over meretrix venus shell-derived catalyst. By increasing the methanol/oil ratio from 9 to 12, the FAME content increased significantly in the entire range of reaction time studied. The higher amount of methanol would promote the formation of methoxy species on CaO surface, and should also shift the reaction equilibrium to the forward direction, resulting in enhanced FAME yield. However, further increase in methanol/oil ratio up to 18 did not promote the reaction. In a typical case, the increase in the methanol:oil ratios would enhance the FAME yield. However, it was considered that the high methanol content (beyond the ratio of 9 or 12 depending on the system [32,33]) favorably induced the reversible reaction of transesterification of high biodiesel yield. Since the transesterification is a base-catalyzed reaction of a reversible nature, it is likely that the reverse transesterification occurs between the methyl ester product and glycerol, forming monoglycerides and diglycerides that behave molecularly like a co-solvent, and homogenize the products. This might cause FAME yield to decrease or to be inhibited at a high methanol:oil ratio. Teng et al. [33] investigated that increase in the molar ratio made the lower relative concentration of soybean causing the lower reaction rate and changing the reaction equilibrium. Additionally, increasing the ratio above 12 also makes the methanol recovery process complicated, and raises its cost. The difficulty of separating of methyl esters and glycerol was observed at a high methanol:oil ratio. This might be because methanol has a polar hydroxyl group that can act as an emulsifier causing emulsification. Therefore, in the present study the optimum MeOH:oil molar ratio was 12:1 over the catalyst. The ratio was two times higher than that generally used in homogeneous transesterification having the MeOH:oil ratio of 6:1.

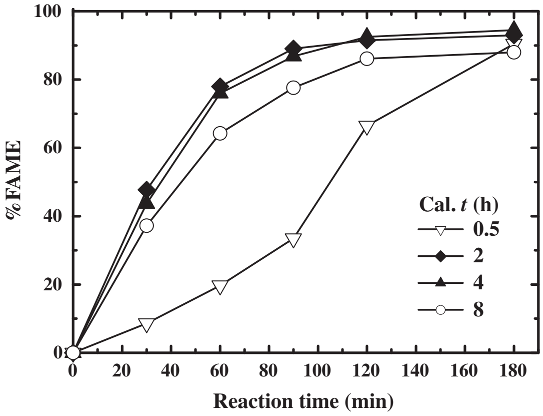


Fig. 7. Reaction time-dependence of %FAME obtained in transesterification over meretrix venus shell-derived catalyst calcined at 800 °C with various calcination times (Cal. *t*). Transesterification conditions: temperature = 60 °C, methanol/oil molar ratio = 12:1 catalyst amount = 10 wt.%.

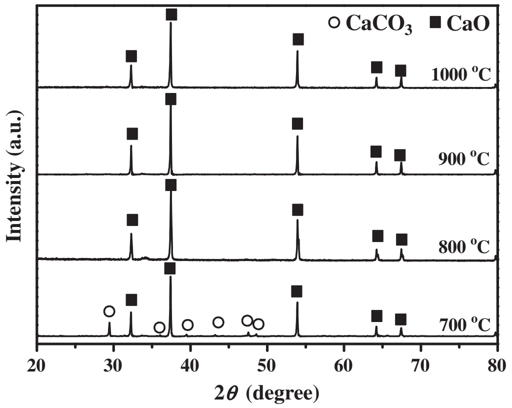


Fig. 8. XRD patterns of meretrix venus shell calcined at 700, 800, 900, and 1000 °C for 4 h.

3.3. Effect of calcination temperature and time

The meretrix venus shell-derived catalyst was used to investigate the effects of catalyst synthesis parameters such as temperature (700–1000 °C) and time (0.5–8 h) of calcination. Fig. 6 shows the %FAME obtained from transesterification catalyzed by meretrix venus shell-derived catalysts calcined at varied temperatures. As a result, the %FAME significantly increased from 38 to 87 %FAME when the calcination temperature increased from 700 to 800 °C. In contrast, when the calcination temperature was elevated to 900 and 1000 °C, the %FAME dramatically decreased to ca. 40 and 38%, respectively. Analogously, Wei et al. [13] reported that the highest biodiesel yield was obtained by the eggshell catalyst calcined at 800 °C. Fig. 7 demonstrates the reaction time-dependence of %FAME obtained in transesterification over meretrix venus shell-derived catalyst with various calcination times (Cal. *t*) of 0.5–8 h at calcination temperature of 800 °C. It can be clearly seen that calcining the sample for 0.5 h was not sufficient enough to give the active catalyst for the reaction. With this short calcination time, the calcined sample was a mixture of black and white powders, suggesting the incomplete transformation. The samples calcined for 2–4 h exhibited comparable activity throughout the reaction course. However, further increase in calcination time inversely suppressed the catalytic activity of the catalyst.

XRD, N_2 adsorption, and SEM analyses were employed to elucidate the catalyst characteristics after varied calcination conditions. XRD patterns of the catalysts calcined at varied temperatures are shown in Fig. 8. As a result, the catalyst samples calcined from 800 to 1000 °C showed clear and sharp peaks of a crystalline phase of CaO. In contrast, the calcined catalyst at 700 °C exhibited the mixed crystalline phases between CaO and $CaCO_3$. The low %FAME obtained over the catalyst calcined at 700 °C was attributed to the incomplete formation of CaO as suggested by XRD results, although the S_{BET} of the catalyst (1.6 $m^2\ g^{-1}$) was higher than that calcined at 800 °C (0.8 $m^2\ g^{-1}$). The inhibited activity of the catalysts calcined at 900 and 1000 °C could be describable to the decrease of S_{BET} to 0.2 $m^2\ g^{-1}$ due to the severe sintering of the catalyst particles as observed by SEM (*Fig. S1*), though the formation of CaO phase was completed. In addition, the prolonged treatment process would bring about the sintering of the catalyst and therefore the lowering of the surface area. The shrinkage of the catalyst grains would eventually suppress the active sites for the reaction. The optimum calcination temperature and time were 800 °C and 2–4 h, respectively, over the catalyst in the present study. This condition would be optimum for other waste shells since the thermal analysis (TG) showed almost identical behaviors.

4. Conclusions

The biodiesel production in heterogeneous transesterification could be achieved by all CaO catalysts derived from eggshell, golden apple snail shell, and meretrix venus shell. The descending order of the catalytic activity over the shell-derived catalysts (sequenced as eggshell, 94.1 %FAME > golden apple snail shell, 93.2 %FAME > meretrix venus shell, 92.3 %FAME) was attributed to the decrease of specific surface areas and basic amount of the strong base sites. The optimum calcination temperature and time were 800 °C and 2–4 h, respectively. The shorter time and lower temperature caused the incomplete formation of active Ca-based catalysts, while the longer time and higher temperature caused the severe sintering of catalyst particles, resulting in suppressed biodiesel yields. These industrial wastes could stand for promising resources of low-cost catalysts which could bring about the low-cost biodiesel.

Acknowledgments

Authors acknowledged the Cluster and Program Management Office, NSTDA, for financial support to the project, Development of Acid/Base-Bifunctional Nanocomposite Catalysts for Biodiesel Production by Heterogeneous Transesterification.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fuel.2011.07.013.

References

[1] Faungnawakij K, Kikuchi R, Shimoda N, Fukunaga T, Eguchi K. Effect of thermal treatment on activity and durability of $CuFe_2O_4$–Al_2O_3 composite catalysts for steam reforming of dimethyl ether. Angew Chem Int Ed 2008;120:9454–7.

[2] Bach U, Lupo D, Comte P, Moser JE, Weissortel F, Salbeck J, et al. Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies. Nature 1998;395:583–5.

[3] Ferella F, Celso DGM, Michelis DI, Stanisci V, Vegliò F. Optimization of the transesterification reaction in biodiesel production. Fuel 2010;89:36–42.

[4] Pinto AC, Guarieiro LLN, Rezende MJC, Ribeiro NM, Torres EA, Lopes WA, et al. Biodiesel: an overview. J Brazil Chem Soc 2005;16:1313–30.

[5] Nakatani N, Takamori H, Takeda K, Sakugawa H. Transesterification of soybean oil using combusted oyster shell waste as a catalyst. Bioresource Technol 2009;100:1510–3.

[6] Asakuma Y, Maeda K, Kuramochi H, Fukui K. Theoretical study of the transesterification of triglycerides to biodiesel fuel. Fuel 2009;88:786–91.

[7] Helwani Z, Othman MR, Aziz N, Kim J, Fernando WJN. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review. Appl Catal A: Gen 2009;363:1–10.

[8] Sivakumar P, Anbarasu K, Renganathan S. Bio-diesel production by alkali catalyzed transesterification of dairy waste scum. Fuel 2011;90:147–51.

[9] Macleod CS, Harvey AP, Lee AF, Wilson K. Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. Chem Eng J 2008;135:63–70.

[10] Vasudevan PT, Briggs M. Biodiesel production-current state of the art and challenges. J Ind Microbiol Biot 2008;35:421–30.

[11] McNeff CV, McNeff LC, Yan B, Nowlan DT, Rasmussen M, Gyberg AE, et al. A continuous catalytic system for biodiesel production. Appl Catal A: Gen 2008;343:39–48.

[12] Kawashima A, Matsubara K, Honda K. Development of heterogeneous base catalysts for biodiesel production. Bioresource Technol 2008;99:3439–43.

[13] Wei Z, Xu C, Li B. Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresource Technol 2009;100:2883–5.

[14] Viriya-empikul N, Krasae P, Puttasawat B, Yoosuk B, Chollacoop N, Faungnawakij K. Waste shells of mollusk and egg as biodiesel production catalysts. Bioresource Technol 2010;101:3765–7.

[15] Liu X, He H, Wang Y, Zhu S, Piao X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. Fuel 2008;87:216–21.

[16] Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalysts for biodiesel production: a review. Appl Catal A: Gen 2009;366:154–9.

[17] Serio MD, Cozzolino M, Giordano M, Tesser R, Patrono P, Santacesaria E. From homogeneous to heterogeneous catalysts in biodiesel production. Ind Eng Chem Res 2007;46:6379–84.

[18] Wang Y, Zhang F, Xu S, Yang L, Li D, David EG, et al. Preparation of macrospherical magnesia-rich magnesium aluminate spinel catalysts for methanolysis of soybean oil. Chem Eng Sci 2008;63:4306–12.

[19] Liu X, He H, Wang Y, Zhu S. Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. Catal Commun 2007;8:1107–11.

[20] Macario A, Giordano G, Onida B, Cocina D, Tagarelli A, Giuffrè MA. Biodiesel production process by homogeneous/heterogeneous catalytic system using an acid–base catalyst. Appl Catal A: Gen 2010;378:160–8.

[21] Kotwal MS, Niphadkar PS, Deshpande SS, Bokade VV, Joshi PN. Transesterification of sunflower oil catalyzed by fly ash-based solid catalysts. Fuel 2009;88:1773–8.

[22] Pugnet V, Maury S, Coupard V, Dandeu A, Quoineaud AA, Bonneau JL, et al. Stability, activity and selectivity study of a zinc aluminate heterogeneous catalyst for the transesterification of vegetable oil in batch reactor. Appl Catal A: Gen 2010;374:71–8.

[23] Zeng H-Y, Feng Z, Deng X, Li Y-Q. Activation of Mg–Al hydrotalcite catalysts for transesterification of rape oil. Fuel 2008;87:3071–6.

[24] Liu Y, Lotero E, Goodwin Jr JG, Mo X. Transesterification of poultry fat with methanol using Mg–Al hydrotalcite derived catalysts. Appl Catal A: Gen 2007;331:138–48.

[25] Trakarnpruk W, Porntangjitlikit S. Palm oil biodiesel synthesized with potassium loaded calcined hydrotalcite and effect of biodiesel blend on elastomer properties. Renew Energy 2008;33:1558–63.

[26] Cho YB, Seo G, Chang DR. Transesterification of tributyrin with methanol over calcium oxide catalysts prepared from various precursors. Fuel Process Technol 2009;90:1252–8.

[27] Boey PL, Maniam GP, Hamid SA. Biodiesel production via transesterification of palm olein using waste mudcrab (*Scylla serrata*) shell as a heterogeneous catalyst. Bioresource Technol 2009;100:6362–8.

[28] Take JI, Kikuchi N, Yoneda Y. Base-strength distribution studies of solid-base surfaces. J Catal 1971;21:164–70.

[29] Yoosuk B, Udomsap P, Puttasawat B. Hydration–dehydration technique for property and activity improvement of calcined natural dolomite in heterogeneous biodiesel production: structural transformation aspect. Appl Catal A: Gen 2011;395:87–94.

[30] Gryglewicz S. Rapeseed oil methyl esters preparation using heterogeneous catalysts. Bioresource Technol 1999;70:249–53.

[31] Reddy CRV, Oshel R, Verkade JG. Room-temperature conversion of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides. Energy Fuel 2006;20:1310–4.

[32] Kim H-J, Kang B-S, Kim M-J, Park YM, Kim D-K, Lee J-S, et al. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catal Today 2004;93–95:315–20.

[33] Teng G, Gao L, Xiao G, Liu H. Transesterification of soybean oil to biodiesel over heterogeneous solid base catalyst. Energy Fuel 2009;23:4630–4.