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Using shrimp shells as based catalysts for FAME production from palm oil feedstock

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Abstract

In this study, waste shrimp shells from industry were used as a heterogeneous bio-based catalyst for trans-esterification reaction of fresh palm oil. CaO was prepared from shrimp shells calcination. Surface area, phase composition, and basicity of the calcined shrimp shell catalysts were studied using N_2 adsorption (BET), X-ray diffraction (XRD), and CO_2 temperature-programmed-desorption (CO_2-TPD), respectively. The influence of shrimp shells calcination temperature and operation condition, methanol to palm oil ratio on trans-esterification reaction, were investigated. Five hours trans-esterification was carried out at 65°C using different shrimp shell at four different calcination temperature: 700, 750, 800 and 850°C with 9:1 methanol to palm oil ratio to determine the suitable calcined catalyst with the highest FAME yield. Methanol to palm oil ratios were varied from 6:1, 9:1, 12:1 and 15:1 with the selected catalyst. According to the results, the highest basic strength of mixed CaO and hydroxy-apatite phases were received by 800°C calcined shrimp shell catalyst, with the highest FAME yield of 87.54% under the optimum condition reaction: 65°C reaction temperature, 5 h reaction time, 9 wt% catalyst loading, and 9:1 methanol to palm oil ratio.

1. Introduction

Nowadays, many researchers have attempted to develop renewable and sustainable energy. Biodiesel is an alternative energy from natural resource which has been widely studied and developed for many years. In general, palm oil is applied as biodiesel feedstock because it includes highly content of organic compound triglycerides, leading to high FAME yield in trans-esterification. Calcium oxide (CaO) is a conventional heterogenous catalyst in trans-esterification, synthesized from calcium carbonate ($CaCO_3$) through calcination step at high temperature. Among various studies related to biodiesel issue, developing waste household such as crustacean shells as based catalyst for preparation of biodiesel has been highlighted currently. Boro *et al.* (2011) [1] developed calcium oxide catalyst obtained from the waste shells of Turbonilla in trans-esterification with mustard oil. Girish *et al.* (2013) [2] researched on calcium oxide catalyst obtained from natural white bivalve clamshells with excess waste frying oil (WFO). Rezaei *et al.* (2013) [3] focused on calcium oxide from waste mussel shells collected from Persian Gulf in trans-esterification. Lee and colleagues (2015) [4] studied calcium oxide catalyst obtain from waste obtuse horn shells. Mijan and coworkers (2015) [5] used waste clamshells with refined palm oil as a feedstock. In case of shrimp shells, it was stated in research carried out by Gedda and coworkers (2015). They prepared calcium oxide in nano-plate form by treating dried shrimp shell powder with hydrochloric acid and sodium bicarbonate solution. However, their research aimed to study different application, the antimicrobial effect [6]. According to the fact that there have been thousands of tons per year disposal shrimp shells from seafood industry after separating chitin for other industries, this research attempted to increase added value of waste shrimp shells prior to disposal and focusing on the catalytic performance shrimp shells in trans-esterification. Consequently, biodiesel from fresh palm oil was synthesized via a trans-esterification and catalyzed by shrimp shells as environmentally friendly catalysts instead of commercial CaO. The aims of this research were to study the influence of major factors on FAME yield such as shrimp shells calcination temperature and MeOH to oil ratio. Additionally, the catalysts characterizations were also performed after calcination step in order to test catalysts properties.

2. Experimental

2.1 Materials and chemicals

10 kg of waste Litopenaeous vannamei shrimp shell (white leg shrimp), residues during food production industry received from Thai Union Group PCL Company, Thailand were used to prepared based-catalysts further. 99.99% methanol and pure palm oil were employed as reactants in trans-esterification reaction. Sodium hydroxide was bought from Sigma Aldrich Co., Ltd. and applied for de-proteinization process. Commercial calcium oxide was bought from Sigma Aldrich Co., Ltd. and used to compare the catalytic performance in trans-esterification.

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2.2 Methodology

2.2.1 Catalyst preparation

Shrimp shells were washed with deionized water to remove impurities. Then, the de-proteinization step was carried out with 1 M sodium hydroxide aqueous solution at the temperature of 100°C for an hour. These treated-shrimp shells were washed and dried in the oven. The clean and dry treated-shrimp shells were finely crushed using a blender and sieved to reduce the size to be less than 250 µm. After that, the shrimp shells were calcined in the furnace at four different temperature (700°C, 750°C, 800°C, and 850°C) for 5 h before applied in the trans-esterification.

2.2.2 XRD (X-Ray diffraction spectrometer)

The phase composition of each shrimp shell catalyst was identified using X-ray diffraction instrument (Bruker AXS Model D8 Discover) which was equipped with Cu-K_α radiation (1.5418 Å), an accelerating voltage of 40 kV and 40 mA, over the Bragg angle 2-theta with the range of 10° to 90°, and step size of 0.0229° at ambient conditions.

2.2.3 N_2 adsorption-desorption (BET)

For BET analytical technique, the powder of the shrimp shell CaO catalysts was pretreated in a helium gas flow rate of 40 $ml \cdot min^{-1}$ at 180°C for 3 h. After cooling down, the weight of the shrimp shell CaO catalysts was measured and installed in the adsorption section. Sample pots were dipped in the dewar containing the liquid nitrogen to measure and collect the data.

2.2.4 Scanning electron microscopy (SEM)

SEM images of calcined shrimp shell powder at 750°C and 800°C were taken at 20 kV and 30 kx magnification to observe the surface characteristic and pore structure.

2.2.5 Temperature-programmed desorption (CO_2-TPD)

CO_2-TPD of shrimp shell powder at four different calcination temperature were carried out using chemisorption analyzer with CO_2 as an investigation molecule and He as a carrier gas. The basic strength was tested by Hammett indicator method.

2.2.6 Trans-esterification reaction

Trans-esterification was carried out in three-neck glass flask connecting with a condenser to condense methanol on the vapor phase. Methanol was mixed with the fresh palm oil at four different MeOH to palm oil molar ratios, which were 6:1, 9:1, 12:1 and 15:1. Approximately 250 mL of mixture was highly vigorously stirred with 9 wt% loading of calcined shrimp shell catalysts to promote mass transfer at 65°C. After 5 h trans-esterification reaction, the product was collected and 30 min centrifuged for catalysts removal. The product mixture was then put aside for about 2 days with opened lit. It was dried in an oven to remove excess methanol. To measure FAME yield, GC-FID (Gas Chromatography-Flame Ionization Detector) was employed with MXT-Wax column at the dimension of 30 m, 0.53 mm internal diameter, 1 µm particle size and hydrogen carrier gas. The oven temperature was programmed from 160°C to 240°C at the ramping rate of 2°C per min and then hold for 20 min. The detector temperature was set to 240°C with constant H_2 pressure at linear velocity of 40 $cm \cdot s^{-1}$. The injection volume was equal to 0.1 µL on column. FAME C-mix C4-C24 (Sigma-Aldrich, analytical standard) was applied as a standard chemical in GC-FID product characterization (measurement of % FAME yield). Finally, %FAME yield was calculated based on calibration curve of FAME standard, respectively.

3. Results and discussion

3.1 Phase composition analysis

From Figure 1, XRD patterns plot of the catalyst structure of the calcined shrimp shell catalysts demonstrated that it mostly contains CaO as a major composition with some hydroxyapatite and calcium hydroxide phases. The main characteristic peaks of 700°C calcined shrimp shell catalyst at 32.20°, 37.38°, 53.86°, 64.14°, 67.37°, and 79.65° are ascribed to CaO [7]. Since there is merely small peak of $CaCO_3$ at 39.5° [8] in XRD results, it can be quoted that the rest of $CaCO_3$ mostly converted to CaO phase at higher temperature calcination with longer calcination period [9]. However, the reflection peaks 10.9°, 26.2°, 31.9°, 32.98°, 46.72°, and 49.44° are the characteristic peaks of hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$) [10] and the reflection peaks 18.2°, 28.8°, 34.1°, 47.1°, 50.89° are the characteristic peaks of $Ca(OH)_2$ [11].

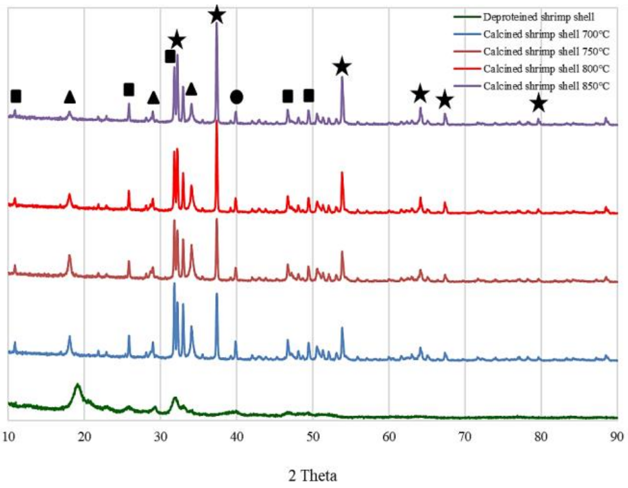

Figure 1. XRD patterns of shrimp shell catalysts using different calcination temperature,★,■,▲,●, represented CaO, ($Ca_{10}(PO_4)_6OH_2$), $Ca(OH)_2$, $CaCO_3$, respectively.

3.2 Basicity determination

For CO_2-TPD, CO_2 adsorbed amount per unit surface area, µmol $CO_2 \cdot g^{-1}$ stands for the basic sites, while peak temperature in degree Celsius represents measure the basic strength. The CO_2-TPD results in Table 1 were in agreement with the fact that the basicity of calcined shrimp shell catalysts plays a major role in trans-esterification reaction [12]. However, the calcined shrimp shell catalysts still possess fewer basic sites than commercial CaO due to the presence of hydroxyapatite phases. As seen in Figure 2, 800°C calcined shrimp shell catalyst shows the strongest basic strength with higher basic strength than commercial CaO (peak temperature at 638°C). However, the basic site of 700°C calcined shrimp shell catalyst is stronger than others since it consists of some $Ca(OH)_2$ phase which would be detrimental to trans-esterification because of less active phase when compared with pure CaO [13].

3.3 Analysis of surface area and pore structure

Table 2 shows specific surface area, mean pore, average volume of the calcined shrimp shells at different calcination temperature for 5 h measured by BET analytical instrument. The results indicate that when the calcination temperature increased, the catalysts have larger mean pore dimeter, though smaller surface area. According to Table 2, the largest surface area is established with 700°C calcined shrimp shells which could be referred to the results of X-ray diffraction as the composition includes the mixture phase of $Ca(OH)_2$ and hydroxyapatite. Since, pure hydroxyapatite phase possessing the large surface area which was equal to 59.41 $m^2 \cdot g^{-1}$ in other research [14], it would be the key cause of the largest surface area of 700°C calcined shrimp shell catalyst. While in case of 850°C calcined shrimp shells, the lower surface area is owing to particle growth and forming heterogenous aggregates of catalyst particles at higher calcination temperature, explained by Ostward ripening process [8,15]. Larger pore size appears when increase calcination temperature by linkage small pore together but leading to lower pore volume, corresponding with the other former research [16,17]. These results are in agreement with SEM images at 30 kx magnification in Figure 2. When comparing Figure 2(c) with Figure 2(a) and 2(b), at 850°C calcined shrimp shells have the most agglomerated as observing the chunk of particles and increasing of pore diameter.

Average pore size of each catalyst is also presented in Table 2, it can be observed that the calcined shrimp shell catalysts possess mesoporous type (based on IUPAC system definition) [18] when compared with average pore size of commercial CaO. The pore size for 750°C calcined shrimp shells and 800°C calcined shrimp shells were 6.60 nm and 7.17 nm, respectively. This showed that the trend as the pore size of the calcined shrimp shell catalysts would increase when the calcination temperature increase [8].

In Figure 3, BET adsorption isotherm of 800°C calcined shrimp shells show the hysteresis loop belonging to mixture of type A and type E, reflecting the morphology of tabular pores open at both ends and bottle pores [18]. The wide cylindrical pore characteristic of 800°C calcined shrimp shells leads to high performance in the trans-esterification reaction corresponding with another previous research [19]. The adsorption isotherms from IUPAC classification of the prepared catalysts exhibits the typical IV isotherm that is the characteristic of mesoporous materials [18].

Table 1. Basic sites and basic strength of shrimp shell catalysts using different calcination temperature.

Calcination temperature (°C)	**Basic strength (°C)**	**Basic site ($\mu mol\ CO_2 \cdot g^{-1}$)**
700	626.3	572.97
750	622.8	410.63
800	638.1	392.66
850	613.4	300.43
Commercial CaO	615.0	1,593.70

Table 2. BET results of the calcined shrimp shell catalysts using different calcination temperature.

Calcination temperature (°C)	**Surface area ($m^2 \cdot g^{-1}$)**	**Mean pore diameter (nm)**	**Average pore volume ($cm^3 \cdot g^{-1}$)**
700	7.85	5.41	1.89
750	5.36	6.60	1.23
800	4.57	7.17	1.14
850	4.13	7.66	1.02
Commercial CaO	5.26	11.38	1.21

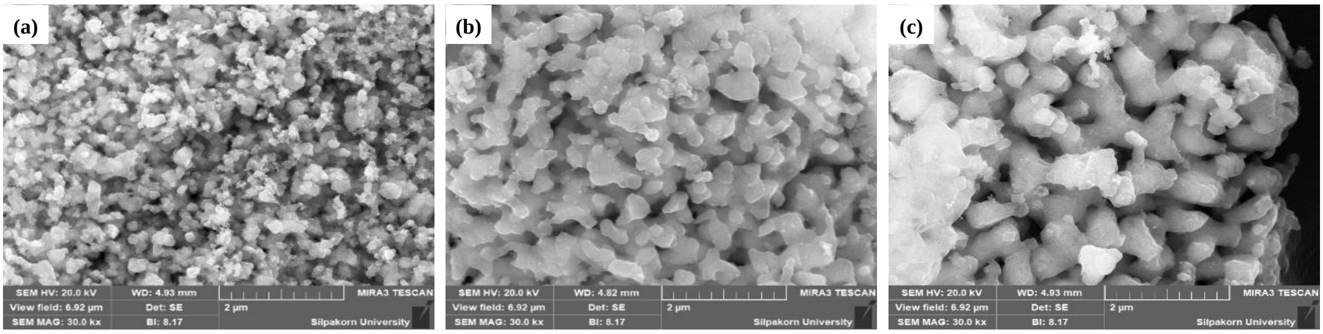

Figure 2. SEM images with 30 kX magnification of calcined shrimp shell at (a) 750°C, (b) 800°C, and (c) 850°C.

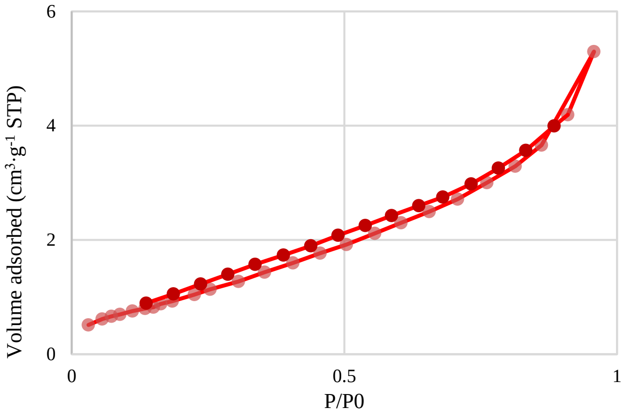

Figure 3. BET adsorption isotherm of 800°C calcined shrimp shells.

3.4 Results of trans-esterification reaction

3.4.1 Effect of calcination temperature of shrimp shells

CaO was appeared in shrimp shells after 5 h calcination at different temperature (700°C, 750°C, 800°C, and 850°C). The results of XRD indicate that purity of CaO was obtained at high calcination temperature as 850°C. From the previous section, BET results indicate that the calcination temperature was increased, the catalyst has larger mean pore dimeter, though smaller surface area. The calcined shrimp shell catalysts had better reactivity when the calcination temperature increased, relating to the catalyst characterizations results and previous research [19]. When consider the phase composition, the calcined shrimp shell catalysts consist of calcium oxide, hydroxyapatite and calcium hydroxide. Though the presence of hydroxyapatite phase in the calcined shrimp shell catalysts diminishes catalytic performance in trans-esterification when compared with CaO due to its medium basic strength [14], it enlarges surface area which can also function as a great support [20]. However, in case of $Ca(OH)_2$, it has a low surface area and blocks the pores of the catalyst and declines catalyst reactivity [13]. As discussed previously, FAME yield exhibited a gradually increasing tendency as the calcination temperature increased, shown in Figure 4. However, a further increase in the calcination temperature might decrease the obtained FAME yield due to an agglomeration of chunk particles and decrease in active sites, already observed in BET results [8]. Trans-esterification reaction favors the high base-catalyst as relating to CO_2-TPD of the calcined shrimp shells at difference temperature results in the previous section [12]. It was found that 800°C calcined shrimp shell catalyst has stronger basicity than other calcined catalysts (according to Table 1) serving as high performance catalysts in trans-esterification with 87.54% FAME yield at 9:1 methanol to palm oil molar ratio, 9 wt% catalyst loading, and 5 h reaction time. Meanwhile, 700°C calcined shrimp shells with highest basic sites brought about only 48.6% FAME yield because it includes some $Ca(OH)_2$ phases which were less active phase in trans-esterification [13]. Therefore, it can be assumed from BET and CO_2-TPD results in the previous sections that basicity superior impacts on trans-esterification than surface area which is on alongside with the other researches [12,21].

3.4.2 Effect of methanol to palm oil molar ratio

Owing to the reversible transformation of the trans-esterification reaction, abundant methanol should be used to drive the reaction forwards [20]. In Figure 5, when the methanol to palm oil molar ratio increased from 6:1 to 15:1, FAME yield of 800°C calcined shrimp shell catalyst gradually increased until the optimum values. The approximate methanol to palm oil ratio is equal to 9:1 for 800°C calcined shrimp shell catalysts. The further increase in the methanol to palm oil molar ratio beyond 9:1 resulted in a decrease of FAME yield. Generally, adding too much oil amount leads to possibility of increase water solubility, enhances calcium hydroxide formation which deactivates CaO [22]. In case of palm oil feedstock, the maximum FAME yield occurs at methanol to oil ratio equal to 12:1 [23,24]. However, in this research, the optimum methanol to oil molar ratio is found to be minimized than other previous research with palm oil feedstock [23,24], resulting in lessen required methanol amount.

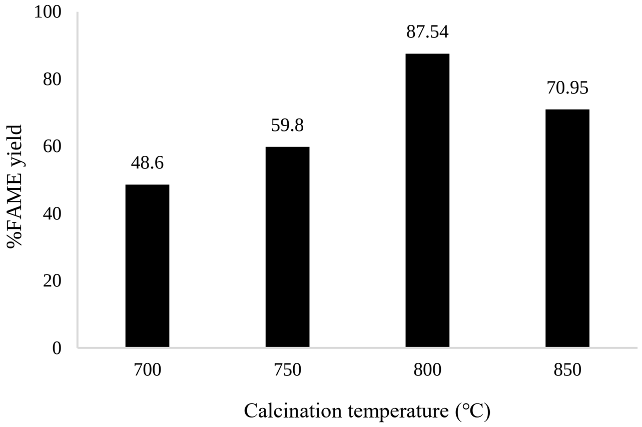

Figure 4. %FAME yield using shrimp shell catalysts at different calcination temperature.

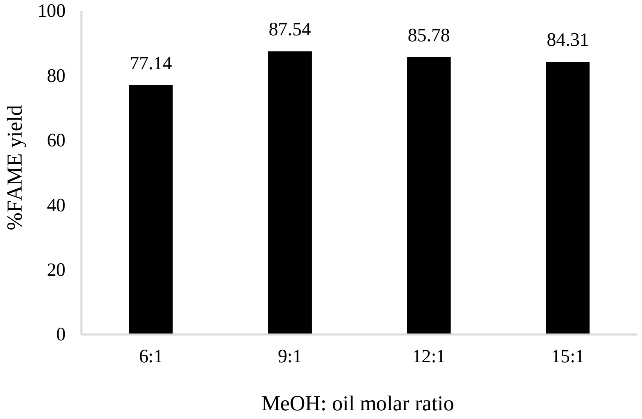

Figure 5. %FAME yield using 800°C calcined shrimp shell catalysts with different methanol to palm oil molar ratios.

Table 3. Comparison of %yield or %conversion with the different optimum transesterification conditions applied in different types of shells.

Type of shell	Calcination temperature (°C)	Optimum trans-esterification conditions			Yield (Y%) or Conversion (C%)
		Methanol to oil ratio	Catalyst loading (wt%)	Reaction time (h)	
Shrimp	800	9:1	9	5	87.54 Y%
Egg [25]	900	6:1	4	3	75.85 Y%
Mussel [3]	1,050	24:1	12	8	94.10 Y%
Obtuse horn [4]	800	12:1	5	6	86.75 C%
Clam [5]	900	9:1	1	2	98 C%

Table 3 compares the catalytic efficiency of calcined shrimp shell with other shell types [3-5,25], the optimum transesterification conditions and calcination temperature for achieving the highest %FAME yield or the highest %triglyceride conversion are different. Eggshell provided 75.85% yield with the lowest methanol to oil ratio when compared to others. It can be noticed that in case of mussel shell, it requires higher calcination temperature with longer reaction time than other shells. In this research, biodiesel product from shrimp shell in this research can be as high as 87.54%yield with requires less methanol to oil ratio and shorter reaction time than that from obtuse horn shell. Though clamshell obtains the highest %conversion of triglyceride (%yield data was not available) with the lowest catalyst loading and least reaction time, it needs higher calcination temperature than shrimp shell.

4. Conclusions

The waste shrimp shells were successfully used as a heterogeneous based-catalyst for the trans-esterification reaction of fresh palm oil to biodiesel product and serve as a comparative potential catalyst with commercial CaO. Among different catalysts preparation and various MeOH to oil molar ratios with 5 h reaction time, at 65°C reaction temperature, and 9 wt% catalyst loading, the maximum %FAME yield was achieved 87.54% with 800°C calcined shrimp shell catalysts and 9:1 methanol to palm oil molar ratio. However, this %FAME yield was still less than that of commercial CaO. The significant finding of this research is that 800°C calcined shrimp shell catalysts provide the determined %FAME yield with 9:1 MeOH to oil ratio, demanding less methanol when compared among diverse trans-esterification researches from identical feedstock.

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