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Biodiesel production process catalyzed by acid-treated golden apple snail shells (*Pomacea canaliculata*)-derived CaO as a high-performance and green catalyst

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Abstract

In this study, acid-treated golden apple snail shells (*Pomacea canaliculata*)-derived calcium oxide (CaO_tr) were used as a high-performance catalyst for the transesterification of palm oil and waste cooking oil (WCO) because the golden apple snail shells were found in plenty in Thailand, and they were also the major pest of rice. The obtained final materials were calcined in air at 800 °C for 3 h referred by TGA analysis denoting as CaO_tr catalyst. All of the catalysts were characterized and tested by using several techniques including XRD, EDX, SEM, basic strength by Hammett indicator method, total basic site by TPD-CO_2, and BET specific surface area by N_2 adsorption. The results indicated that the CaO_tr had a specific surface area of 7.5544 m^2/g and it was higher than CaO_un approximately 2 times. The kinetics of the reaction followed pseudo-first-order with the rates constants of reaction (*k*) equal 1.35×10^{-2} min^{-1} for the reaction which catalyzed by acid-treated golden apple snail shells-derived CaO catalyst (CaO_tr), while un-treated golden apple snail shells-derived CaO catalyst (CaO_un) gave *k* value of 1.18×10^{-2} min^{-1}, respectively. Under the optimal of reaction conditions at catalyst loading of 5 wt. %, methanol/oil molar ratio of 12:1, reaction temperature 65 °C, and 5% v/v relative to the amount of methanol of THF as a co-solvent; more than 97% yield of biodiesel could be achieved in 150 min by using CaO_tr. The final part, biodiesel product obtained from palm oil and WCO catalyzed by CaO_tr catalyst has high quality and meets the specified standards of biofuels for the diesel engines both of the EN-14214 and ASTM-D6751 standard testing method. Thus, the utilization of the acid treatment method for enhancement of the catalytic activity of CaO catalyst from golden apple snail shells and the applied co-solvent method for increase the performance of biodiesel production was a process with a high potential in the biodiesel production for the community scale and industrial scale.

Keywords: Golden apple snail shells (*Pomacea canaliculata*), CaO, Acid-treatment, Biodiesel oil, Kinetics of reaction

1. Introduction

Generally, biodiesel oil is well known that it is one of the best choices for alternative renewable energy sources because it can be produced from various sources of plant oil and animal fat. In addition, biodiesel oil is biodegradable, non-toxicity, and environmentally friendly with showing low emission pollutant gases such as CO, CO_2, NO, NO_x and SO_x. It also can be used directly in the diesel engine with no requirement modifications engine especially agricultural engines [1-4].

Biodiesel is generally produced on an industrial scale with the use of transesterification reactions catalyzed by homogeneous catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH_3ONa) [4, 5]. Normally, the methanol (CH_3OH) is popularly applied as a reagent in the biodiesel production process via the transesterification reaction than ethanol (C_2H_5OH) due to the methanol is suitable physicochemical properties, highly active in the mild reaction conditions, and easy phase separation [6]. Although these homogeneous catalysts provide a high yield of biodiesel products under the moderate reaction conditions (low temperature and pressure) and short reaction time, it has many drawbacks including a large amount of wastewater from the cleaning process to remove the catalyst and soap in the product. It is also corrosion of the reactor and sensitive with water and free fatty acid that content in the oil as raw material to produce soap formation. These major problems have directly increased the cost of biodiesel production and the environmental crisis [6-8]. Consequently, several researchers have focused on solving the disadvantages of the homogeneous catalytic process with the use of heterogeneous catalysts for biodiesel production.

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The advantages of heterogeneous catalysts are less reactivity with free fatty acid and moisture in the oil, easy to separate from the reaction mixture, reduced the use of water for cleaning biodiesel product, and simple to reuse and recycle [7, 8]. However, the major drawback of the heterogeneous catalyst is the case of the slow reaction rate (needed to the long reaction time) and requirement a large amount of catalyst due to the problem from the reaction mixture. In the system of biodiesel production via the heterogeneous catalyzed process, it consists of a three-phase mixture namely the oil (reactants), methanol (reagent), and the catalyst [7, 9]. Hence, the solution to this problem is a great challenge to enhance the biodiesel production process. The modification of the heterogeneous catalyst is one of the attractive ways from several choices into development biodiesel production.

Alkaline earth metal oxides especially calcium oxide (CaO) is one of the most chosen to apply in the biodiesel production process because they are low cost, non-toxicity, easy to find and prepare, and can be used under mild reaction conditions and easy to reusability [7-11]. Several articles have been reported the use of egg shells and shells as raw materials for synthesis CaO as a catalyst and study the optimum reaction conditions [12]. Buasri et al. [13] has reported the application of eggshell wastes to prepare CaO as a heterogeneous catalyst for synthesis biodiesel product. They found that the calcinated eggshell at 900 °C for 4 h under the air atmosphere can be converted to CaO material and the optimum conditions to produce biodiesel product including the reaction time of 4 h, methanol to oil molar ratio of 9:1, reaction temperature of 65 °C, catalyst loading of 20 wt. % to give the yield of biodiesel approximately of 92−94%. Sai Bharadwaj et al. [14] have presented that the utilization of eggshell to generate CaO as a catalyst for biodiesel production from rubber seed oil (RSO). The results found that the conversion of RSO to biodiesel product reached a yield of 99.7% at the condition of 4 wt. % of the catalyst, 12:1 methanol to oil molar ratio, and 3 h of reaction time. Pike et al. [15] utilized eggshells as catalyst to synthesize biodiesel product at room temperature. The results indicated that the biodiesel yield was 97-98% after the reaction time of 11 h for the use of catalyst 5.8 wt. %, and 6:1 methanol to oil molar ratio.

Furthermore, the uses of several type shells as raw material to synthesize CaO catalyst for biodiesel production have been reported. Roschat et al. [3] was used the river snail shell-derived CaO catalyst to produce biodiesel oil from palm oil and waste cooking oil. The results found that the reaction condition at the temperature of 65 °C, methanol to oil molar ratio of 12:1 and catalyst amount of 3 h, gave the yield of biodiesel highly of 94-97%. Sani et al. [16] applied the waste snail shell by calcination at 800 °C for 4 h to convert $CaCO_3$ to CaO and they also reported relating to the catalytic activity of the obtained catalyst. The results displayed that the yield of biodiesel was 84.14% following reaction conditions of temperature at 60 °C, time of 3 h, and methanol to oil molar ratio of 9:1. Laskar et al. [17] found that a waste snail shell (*Pila spp.*) can be used to prepare the CaO catalyst with a calcination temperature of 900 °C for 4 h. This report was shown that the biodiesel yield of 98% was achieved following the optimized conditions of the catalyst loading of 3 wt. %, a reaction time of 7 h, methanol to oil molar ratio of 6:1, and carried out at ambient temperature (28 °C). Hangun-Balkir [18] utilized waste shells (the eggshells and lobster shells) to prepare CaO as sustainable catalysts for biodiesel production from *camelina sativa* oil. The maximum biodiesel yields were the conditions of catalyst loading amount of 1 wt. %, methanol to oil molar ratio with 12:1 and time of 3 h at 65 °C. In the previous examples, it is found that the traditional preparation of CaO as a catalyst from several shells with simple calcination is not enough to enhance catalytic activity due to the biodiesel production process still need to use a long reaction time.

Therefore, the present work emphasizes the use of the waste shells from agricultural namely golden apple snail shells (*Pomacea canaliculata*) which are found in plenty in Thailand and they are also the major pest of rice. The utilization of golden apple snail shells to prepare CaO as a catalyst for biodiesel production is interested especially the development and improvement of their catalytic activity. Consequently, the objective of this work is the preparation of a highly active CaO derived from golden apple snail shells by the acid treatment and hydrothermal method which might be a way to increase efficiency and catalytic activity. Due to the acid treatment method followed by the calcination of the raw material could be eliminated some impurity and may cause corrosion on parts of the surface of them which resulted in a larger area of the obtained catalyst. The physicochemical properties of the obtained catalyst were analyzed, characterized, and tested by several techniques such as XRD, BET surface area, SEM, EDX, TGA, Hammett indicators method and CO_2-TPD. The palm oil and waste cooking oil were used as a precursor to performing the transesterification reaction in order to examine the catalytic activity of CaO catalyst with and without acid treatment of the golden apple snail shells. Additionally, the reaction rate kinetics of this biodiesel production process was investigated by following the hypothesis of pseudo-first-order kinetic. In the final part of this work, the obtained biodiesel product was evaluated following the European Standard methods (EN14214) and American Society testing and material (ASTM) method which was the standard method for testing biodiesel oil as a bio−auto fuel. All of the data obtained from this work could be employed for applications in the biodiesel production process both on the community-scale and industrial-scale production in the future.

2. Experimental

2.1 Materials

The palm oil and waste cooking oil (denoted as WCO) were collected from the commercial sources in Thai market and the free fatty acid (FFA) content was 0.28 mg KOH/g of oil and 1.24 mg KOH/g of oil, respectively. Golden apple snail shells (*Pomacea canaliculata*) were obtained from agricultural areas in Sakon Nakhon province. The chemicals used in this work namely methanol (CH_3OH), tetrahydrofuran (C_4H_8O; THF), acetone (C_3H_6O), hydrochloric acid (HCl), sodium carbonate (Na_2CO_3), potassium hydroxide (KOH), and calcium oxide (CaO) were obtained from SIGMA and QReC™. Hammett indicators namely phenolphthalein ($C_{20}H_{14}O_4$), thymolphthalein ($C_{28}H_{30}O_4$), indigo carmine ($C_{16}H_8N_2Na_2O_8S_2$), 2,4-dinitroaniline ($C_6H_5N_3O_4$), and 4-nitroaniline ($C_6H_6N_2O$) used to test the basic strengths ($H_$value) of the catalyst were purchased from Aldrich and Fluka.

2.2 Catalyst preparation and characterization

The highly active CaO derived from golden apple snail shells (*Pomacea canaliculata*) via the acid treatment and hydrothermal method was performed by cleaning the shells with water several times and air-dried in an oven at 100 °C for 3 h. After that, the dried golden apple snail shells were crushed and sieved to be the powder. Then, the obtained powder material was brought into the process of acid treatment and the overall reactions for the acid-treated golden apple snail shells-derived CaO catalyst step can be summarized from chemical equation (1)-(3):

$$\mathrm{CaCO_{3(s)} + 2HCl_{(ag)} \longrightarrow CaCl_{(ag)} + CO_{2(g)} + H_2O_{(1)}} \tag{1}$$

$$\mathrm{CaCl_{2(ag)} + Na_2CO_{3(ag)} \longrightarrow CaCO_{3(s)} + 2NaCl_{(ag)}} \tag{2}$$

$$\mathrm{CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}} \tag{3}$$

The acid treatment process started with the direct interaction of the obtained golden apple snail shells powder ($CaCO_3$) reacted against HCl (concentration 2 molar) to produce $CaCl_2$ solution. Subsequently, the obtained $CaCl_2$ solution was reacted with Na_2CO_3 to generate $CaCO_3$ phase by sedimentation. The obtained $CaCO_3$ phase was dried in hot air oven 100 °C for 3 h. The final step for preparing the catalyst was the calcination of the obtained $CaCO_3$ material for the transformation into the highly active CaO at the temperature of 800 °C for 3 h based on TGA analysis results denoted as CaO_tr. The raw material golden apple snail shells were also calcined at the same condition to produce the CaO phase (denoted as CaO_un) for the comparison of the catalytic activity against CaO_tr.

The first process of the characterization part started with the use of thermal gravimetric analysis (a Rigaku TG/DTA 8120 thermal analyzer, Japan) to determine the thermal decomposition of the $CaCO_3$ phase obtained by acid treatment and compared with raw material golden apple snail shells. The condition of the TGA analysis consists of a heating rate of 10 °C/min under the airflow and the thermal degradation range for analysis of the sample was between room temperature to 1000 °C. All of the obtained material was identified by X–ray powder diffraction (XRD) (a Brüker D5005 X-ray diffractometer, Germany) followed parameter of the Cu Kα radiation (k = 1.5418 A) at 1600 W, 40 kV, and 40 mA, 0.02° per step, and the range of 2Θ from 20-80°. EDX-720 (Shimadzu, Japan) was applied to determine the elementals chemical composition of the sample both before and after the treatment of golden apple snail shells. Bel-sorp-mini II (Bel-Japan) was used to study surface area according to Brunauer-Emmett-Teller (BET) isotherm plot of nitrogen adsorption and desorption at the low temperature. The morphology of the treated golden apple snail shells was studied by JEOL JSM 6010LV scanning electron microscope (Shimadzu, Japan). The basic site property of the obtained material was tested by temperature programmed desorption using a probe molecule of CO_2 (CO_2-TPD method) with the Chemisorption Analyzer (Belcat B, Bel-Japan). Finally, the Hammett indicator method was used to test basic strength of the obtained CaO sample by observing the color change of all indicators namely phenolphthalein (pK_a=9.7), thymolphthalein (pK_a=9.9), indigo carmine (pK_a=12.2), 2, 4-dinitroaniline (pK_a=15) and 4-nitroaniline (pK_a=18.4) followed the method of Roschat et al., (2018).

2.3 Transesterification reaction process

The biodiesel oil was synthesized via transesterification reaction of palm oil against methanol by following the conditions consisting of 12:1 methanol to oil molar ratio, 5 wt.% of CaO catalyst and reaction temperature of 65 °C agreeable with the report of Roschat et al. [2, 3, 19] and Hangun-Balkir [18]. The reaction was carried out in a 3-necked round flask batch reactor with a size of 250 mL and equipped with a reflux condenser, magnetic stirrer, and a thermometer control. This work focused on the catalytic performance tests of CaO_tr compared with CaO_un under the same reaction condition. To monitor the reaction progress, the reaction mixture was sampled 0.5-1.0 mL every specific period of time. The excess amount of methanol in the reaction mixture was eliminated by an oven at 80 °C for 3 h before preliminary testing with the Thin-layer chromatography (TLC) method which referred from Supamathanon et al. [20] as depicted in Figure 1.

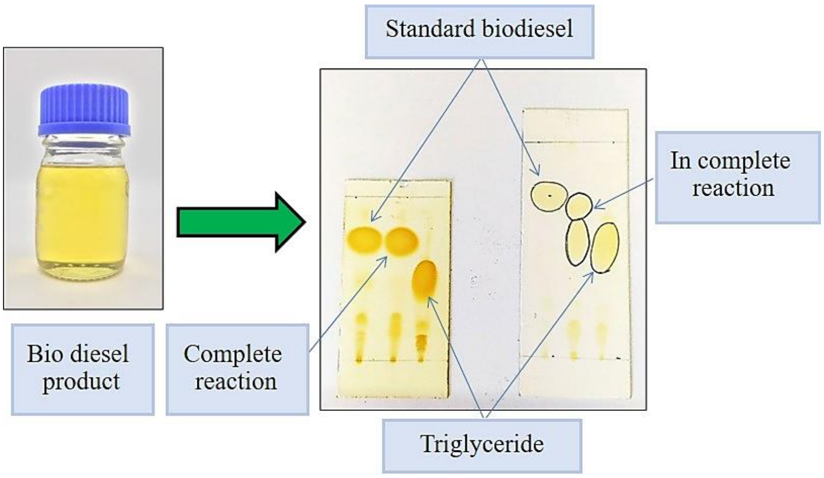

Figure 1 Monitoring the transesterification reaction progress by the thin-layer chromatography (TLC) method.

The percentage conversion of the palm oil to biodiesel product (denoted as fatty acid methyl ester; %FAME) was evaluated by proton nuclear magnetic resonance (^{1}H-NMR) using a Brüker AVANCE III HD (600 MHz) spectrometer (Brüker, Germany) and the $CDCl_3$ was employed as a solvent as shown in Figure 2. To calculate %FAME, the equation from reports of Niju et al. [7, 10] and Roschat et al. [19] was used and referred according to the Eq. (4) as following:

$$\%\ \mathrm{FAME} = \frac{2_{\mathrm{A-CH_3}}}{3_{\mathrm{A-CH_2}}} \times 100 \tag{4}$$

where %FAME is the percentage conversion of the palm oil to biodiesel product. A-CH_3 is an integration value of the methoxy protons of the methyl ester (biodiesel) moiety ($C\underline{H}_3$–OCO–) at chemical shift of 3.68 ppm. A-CH_2 is an integration value of the proton in α–carbonyl methylene protons (R–$C\underline{H}_2$–OCO–) both in triglyceride and methyl ester (biodiesel) at chemical shift of 2.31 ppm. The factors 3 and 2 were derived from the number of attached protons both of the methoxy group and α–carbonyl methylene group, respectively. It should be noted that all of the data in this study were averages from at least three measurements with a deviation within 3%.

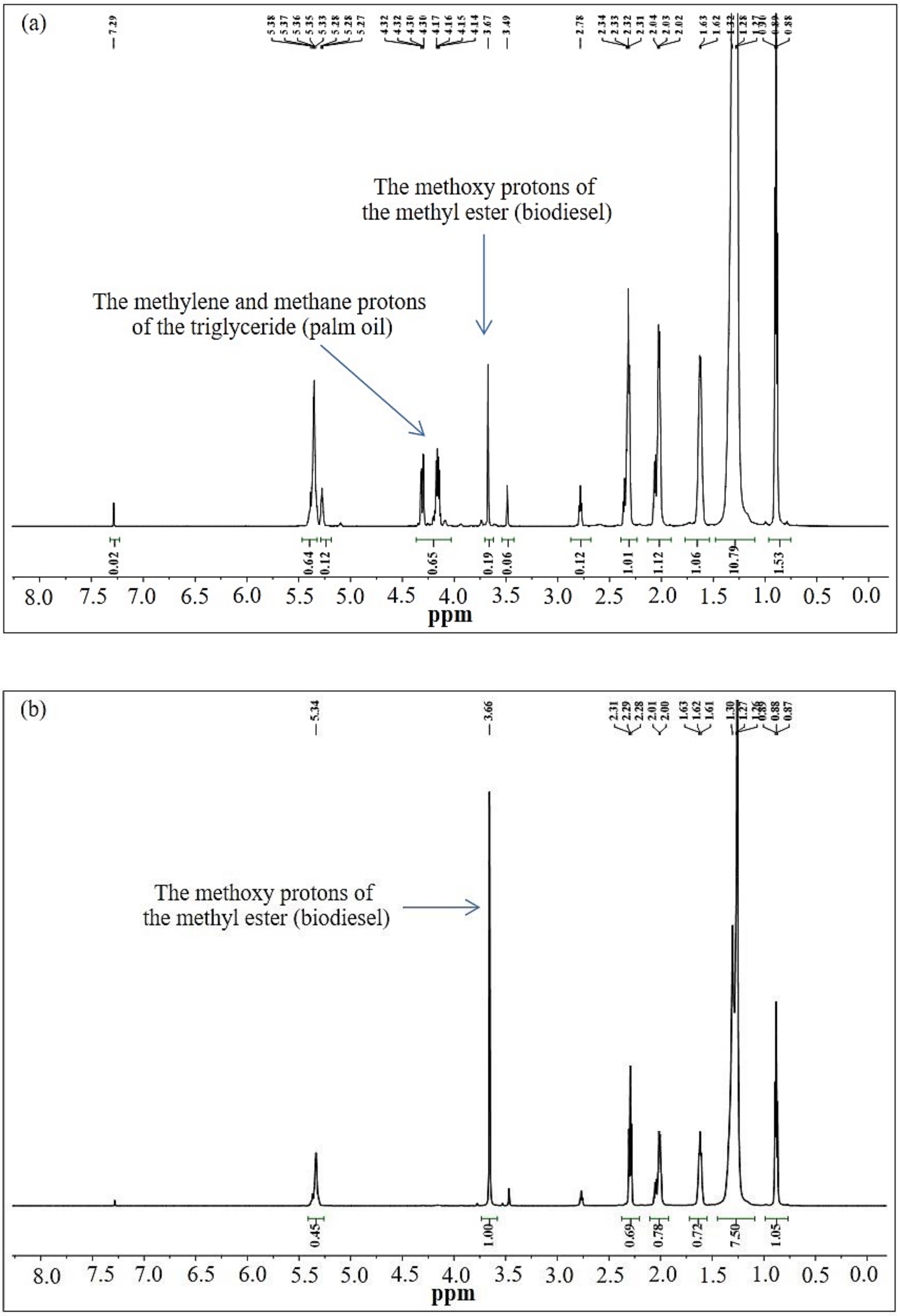

Figure 2 ^{1}H-NMR spectra of (a) incomplete reaction (triglyceride + biodiesel) and (b) complete reaction (shown only biodiesel product).

2.4 The study of reaction kinetics of the transesterification catalyzed by CaO_tr and CaO_un

The data of reaction kinetics from the transesterification of palm oil with methanol and catalyzed by CaO catalyst derived from the golden apple snail shells both with and without treatment was used to compare the catalytic activity. The calculation of reaction rate coefficient (*k*) employed the method from the report of Roschat et al. [2, 3], Muthukumaran et al. [21], Hebbar et al. [22], and Feyzi and Shahbazi [23]. In this case, the transesterification reaction is assumed to be a single step and pseudo-first order reaction which can be rearranged the equation as in the following:

$$-\ln[1 - X_{ME}] = kt \tag{5}$$

where X_{ME} is the yield of FAME (%FAME/100). *k* is the reaction rate coefficient and t is the reaction time. Consequently, the equation (5) was applied to study the reaction kinetics of the transesterification catalyzed by CaO_tr compared with CaO_un by the plot of $-\ln[1-X_{ME}]$ versus t which obtained linear graph and the slope to be a k constant.

2.5 The study of fuel properties of biodiesel product

The final process of the study in this work was the evaluated fuel properties of the final biodiesel product. The first step started by purification of the obtained biodiesel oil with the accorded method from the report of Roschat et al. [2, 3]. After the purification process, the purified biodiesel oil was evaluated and tested agreeable to ASTM D6751 and EN 14214 standard method for bio-auto fuel [24-26]. This work focused on the physicochemical property of the testing purified biodiesel oil namely methyl ester content (%FAME) by using gas chromatography (GC-2010, Shimadzu, Japan), kinematic viscosity at 40 °C, density at 15 °C, pour point, cloud point, oxidation stability, total acid number, and total contamination, respectively. All of the parameters for testing the purified biodiesel oil were performed at the Materials for Energy Research Group laboratory, the National Metal and Materials Technology Center (MTEC), the National Science and Technology Development Agency (NSTDA), Thailand.

3. Results and discussion

3.1 The catalyst preparation and characterizations

The obtained $CaCO_3$ material from the acid treatment process of golden apple snail shells (*Pomacea canaliculata*) was analyzed by thermogravimetric analysis (TGA) and compared with golden apple snail shells material as illustrated in Figure 3. The results found that a major decomposition in the range of 600-800 °C was to be the loss of CO_2 molecule from $CaCO_3$ to give CaO phase both of obtained $CaCO_3$ material from the golden apple snail shells and acid treatment process. These similar results were also explained and reported from the research of Roschat et al. [3], Lee et al. [5], and Laskar et al. [16]. Therefore, the temperature of 800 °C was suitable to select for calcination the obtained $CaCO_3$ phase from the acid treatment process and golden apple snail shells for 3 h to produce CaO_tr and CaO_un as a catalyst. Because from 800 °C onwards, the decomposition of $CaCO_3$ phase which transformed to CaO phase was complete and the weight of the sample remained constant although the temperature was higher than 800 °C. Thus, a temperature of at least 800 °C would be applied to produce CaO material from natural shells which this summary was also in agreement with the reports of Roschat et al. [3] and Laskar et al. [16].

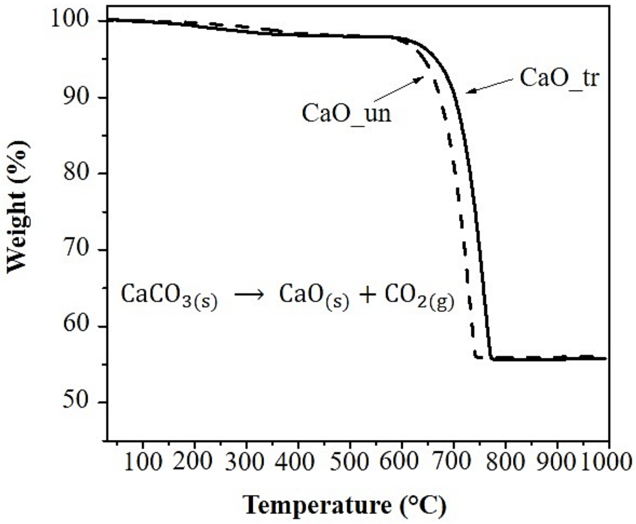

Figure 3 TGA Thermogram of the resulting material obtained from the golden apple snail shells and the acid treatment process.

Figure 4 (a) illustrated the XRD patterns of raw golden apple snail shells and golden apple snail shells after treating with acid. The results found that the raw golden apple snail shells were an orthorhombic structure of $CaCO_3$ phase, while after acid-treated it was found that the resulting materials were a rhombohedral structure. This result could be discussed that the acid treatment process changed the structure and atomic arrangement of $CaCO_3$ compounds. However, the calcination of the $CaCO_3$ phase both with and without acid treatment at 800 °C for 3 h followed by TGA data found that the obtained materials were CaO phase which was a simple cubic structure as displayed in Figure 4 (b). Furthermore, the result was also shown that the crystalline phase of CaO_tr has higher than that of CaO_un. This phenomenon was also discussed in reports of Phewphong et al. [27], and Cizer et al. [28].

The EDX spectroscopy as depicted in Figure 5 showed the element percentage of the materials both with and without the acid treatment process. The data indicated that the raw golden apple snail shells had the purity of $CaCO_3$ equal to 95.05%. On the other hand, the obtained $CaCO_3$ material after the purification process with acid treatment had a percentage of purity achieved to 100%. In this case, the acid-treated golden apple snail shells reached a high purity due to the reaction between golden apple snail shells ($CaCO_3$ phase) with HCl acid that could be extracted Ca^{2+} ion and converted it to $CaCl_2$ compound completely. After that, the $CaCl_2$ solution sedimented by the reaction with Na_2CO_3 to give purified $CaCO_3$ material. This process could eliminate other impurities and it also rearranged the structure of the resulting $CaCO_3$ according to the XRD data.

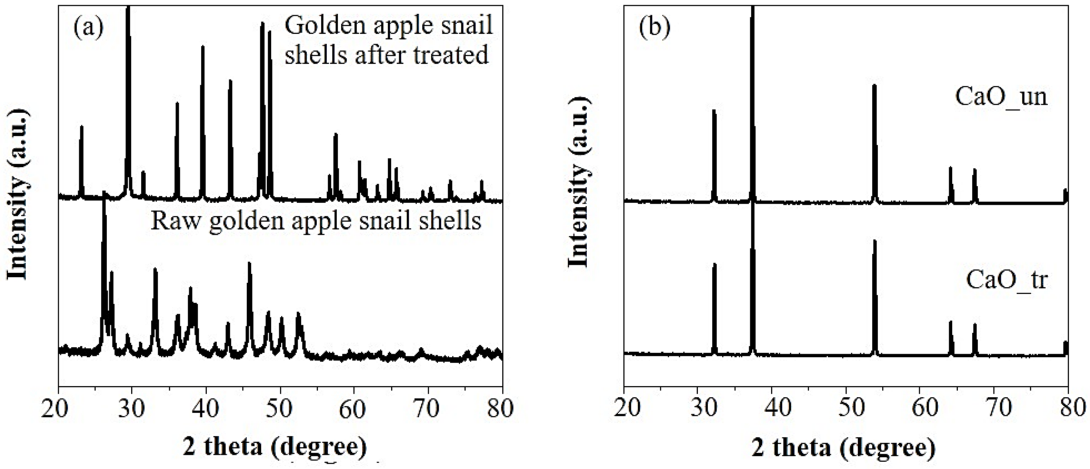

Figure 4 XRD Patterns of (a) raw golden apple snail shells and golden apple snail shells after treating them with acid and (b) resulting material after calcination process namely CaO_tr and CaO_un.

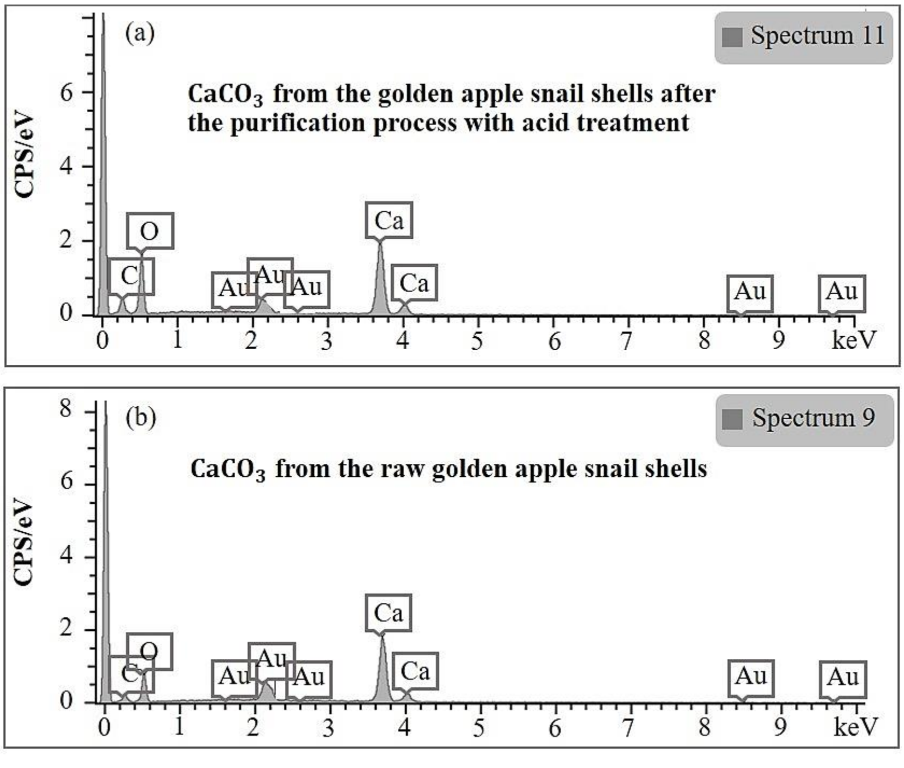

Figure 5 EDX Spectrum of $CaCO_3$ obtained from (a) the golden apple snail shells after the purification process with acid treatment and (b) the raw golden apple snail shells.

Figure 6 presented the SEM image morphology of CaO_un and CaO_tr catalyst. The CaO_tr (Figure 6(b)) displayed the image like a small sheet stacked neatly together and agglomerated spheres. Additionally, it has a porous distributing throughout the particle. When compared morphology against CaO_un as shown in Figure 6 (a), the result showed the different particle sizes distributed alternately both small and large particle sizes. Moreover, the distribution porous of CaO_un tended to be relatively less than CaO_tr. These results accorded with the specific surface area obtained by the BET isotherm as illustrated in Table 1. The CaO_un derived from calcination golden apple snail shells had a specific surface area 3.8772 m^2/g which similarly a specific surface area of CaO derived from river snail shells as the same condition process [3]. However, the specific surface area of CaO_tr obtained from the acid-treated golden apple snail shells increased to 7.5544 m^2/g and showed higher than that of CaO_un approximately 2 times. The results of the BET specific surface area data of each catalyst in this work followed the SEM image morphology in Figure 6.

Table 1 The specific surface area, total basic site, and basic strength of the catalysts.

Samples	Specific surface area (m^2/g)	Total basic site (mmol/g)	Basic strength ($H\_$ value)	%FAME^a	
				Palm oil	**WCO**
CaO_un	3.8772	4.14	$15.0 < H\_ < 18.4$	79.5	74.6
CaO_tr	7.8544	7.82	$15.0 < H\_ < 18.4$	93.2	91.0

^{a} Transesterification conditions: catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 °C and reaction time of 180 min.

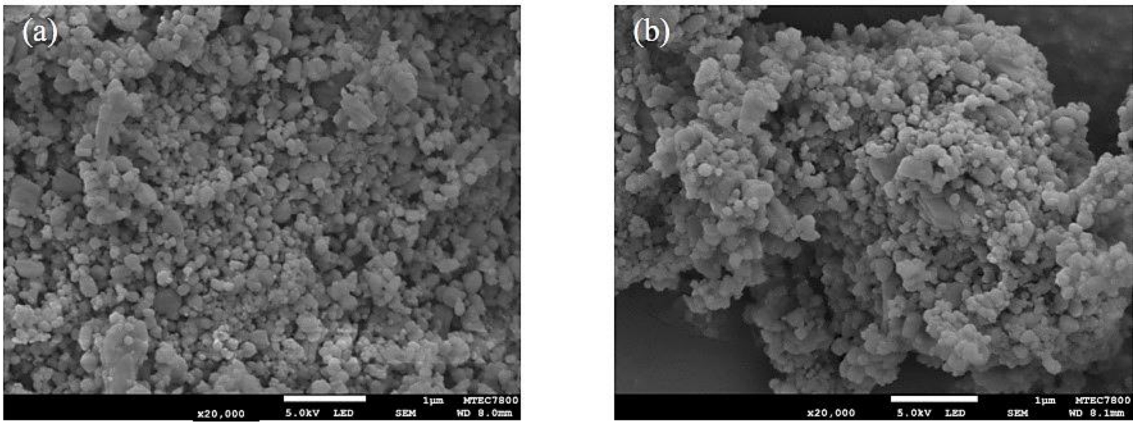

Figure 6 SEM Image of (a) the CaO_un and (b) the CaO_tr catalyst derived from golden apple snail shells.

The total basic site of all CaO catalysts in this study was evaluated by the CO_2-TPD technique and showed the results in Figure 7. The data revealed that the CaO_tr catalyst had higher total basic site than that of CaO_un almost 2 times. These results could be described that the morphology of CaO_tr catalyst had a high specific surface area due to the acid treatment method and it directly correlated with the active site [7, 10, 19]. Furthermore, all of the CaO catalysts were also tested the basic strength ($H\_$ value) by the Hammett indicator method. The $H\_$ value of all the CaO catalysts showed a strong basic strength in the range of 15.0-18.4 which could change the color of 2, 4-dinitroaniline (pKa = 15.0) indicator but could not change the color of 4–nitroaniline (pKa = 18.4).

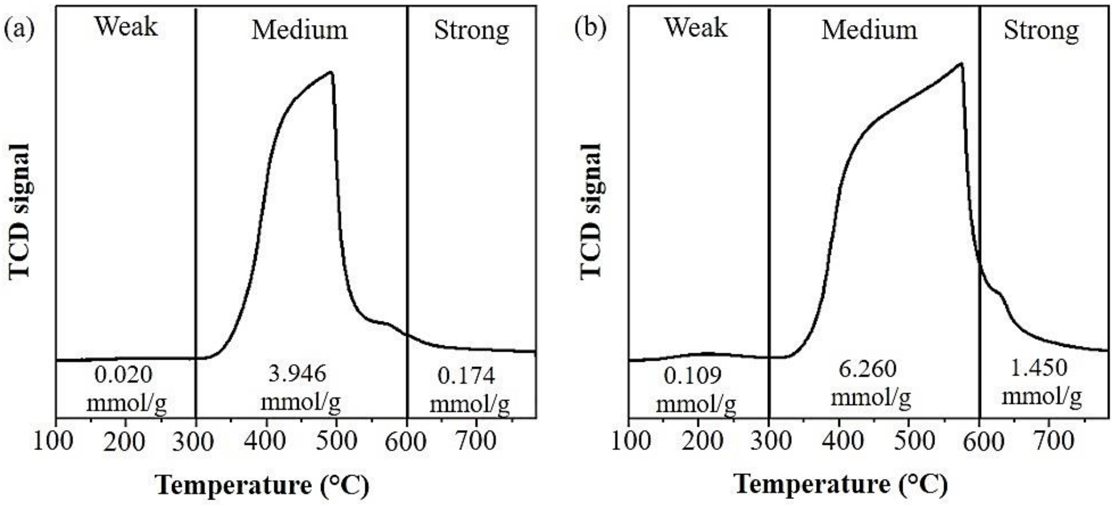

Figure 7 CO_2-TPD of (a) the CaO_un and (b) the CaO_tr catalyst obtained from golden apple snail shells.

All of the results from the preparation and characterization of the CaO_un and CaO_tr catalyst demonstrated that the acid treatment method before calcination golden apple snail shells have directly affected the morphology of both specific surface area, total basic site and basic strength of the catalysts. In this case, the CaO_tr catalyst has a larger specific surface area and higher the total basic site than that of CaO_un. Consequently, the catalyst activity of the CaO_tr catalyst was higher than that of the CaO_un on the transesterification reaction both of the palm oil and WCO to biodiesel products as also presented in Table 1. Thus, these results could confirm that the acid treatment process not only increased the purity of CaO_tr but also improved the physicochemical properties especially the catalytic activity of CaO_tr catalyst for use to the transesterification reaction process.

3.2 The reaction kinetics of the biodiesel production process catalyzed by CaO_tr and CaO_un

The reaction kinetics study of the transesterification reaction for biodiesel production is one of the important points because this data can be used to explain the reaction mechanism, design and control the reaction condition that directly affected the rate of reaction. Hence, this study focused on the comparison of the reaction kinetics catalyzed by CaO_tr and CaO_un catalyst in the transesterification reaction of palm oil to biodiesel products under the same reaction conditions. The results as demonstrated in Figure 8 (a) showed the comparison catalytic performance between CaO_tr and CaO_un catalyst in terms of the yield of biodiesel product (%FAME) versus reaction time. In the case of using the CaO_un as a catalyst, the reaction was completely at the reaction time of 300 min (5 h) with the FAME yield of higher than 90%. On the other hand, the conversion of palm to biodiesel product was completely at the reaction time only 180 min (3 h) with higher than 93% of FAME yield under the catalyzed reaction by CaO_tr. When compared of the results with the other reports found that the traditional calcination method of the natural shells for synthesis CaO catalyst gave similar results with CaO_un such as Buasri et al. [13]. They applied eggshell for use as raw material to produce CaO catalyst with the traditional calcination method and tested the catalytic activity of the obtained catalyst. From this report, the yield of biodiesel was approximate 92-94% with a reaction time of 4 h. While Pike et al. [14] reported that CaO derived from eggshells as starting material could produce the biodiesel yield around 97-98% after the reaction time was up to 11 hours. Sani et al. [15] presented the report of the use of waste snail shells to generate CaO catalyst and testing the performance of their catalyst. The result indicated that the yield of biodiesel was only 84.14% with a reaction time of 3 h. Laskar et al. [16] revealed the report involving the use of CaO catalyst obtained from waste snail shell (*Pila spp.*) in the biodiesel production process. This report displayed that the biodiesel yield was achieved of 98% under the reaction time of 7 h. All of the examples reports obviously indicated that the preparation of CaO catalyst by conventional calcination provided quite a few catalyst efficiencies compared to that of CaO_tr catalyst.

Furthermore, the evaluation of the reaction kinetics of palm oil to biodiesel production was illustrated in Figure 8 (b) which was the plot of $-\ln [1-X_{ME}]$ against t (time) and slope was equal to rate constant (*k*). The *k* value was the descriptor of the reaction speed which *k* value has a high as equal as a high rate of reaction and meaning the reaction would complete at the short reaction time. This case observed that the k value of the use CaO_tr catalyst had an equal of 1.35×10^{-2} min^{-1} which was higher than that of CaO_un catalyst (1.18×10^{-2} min^{-1}) as around 14%. Consequently, all these results of the reaction kinetics study could confirm that CaO_tr derived from the acid treatment process of golden apple snail shells has a high catalytic activity and agreeable with the results from the evaluated the catalyst characterization.

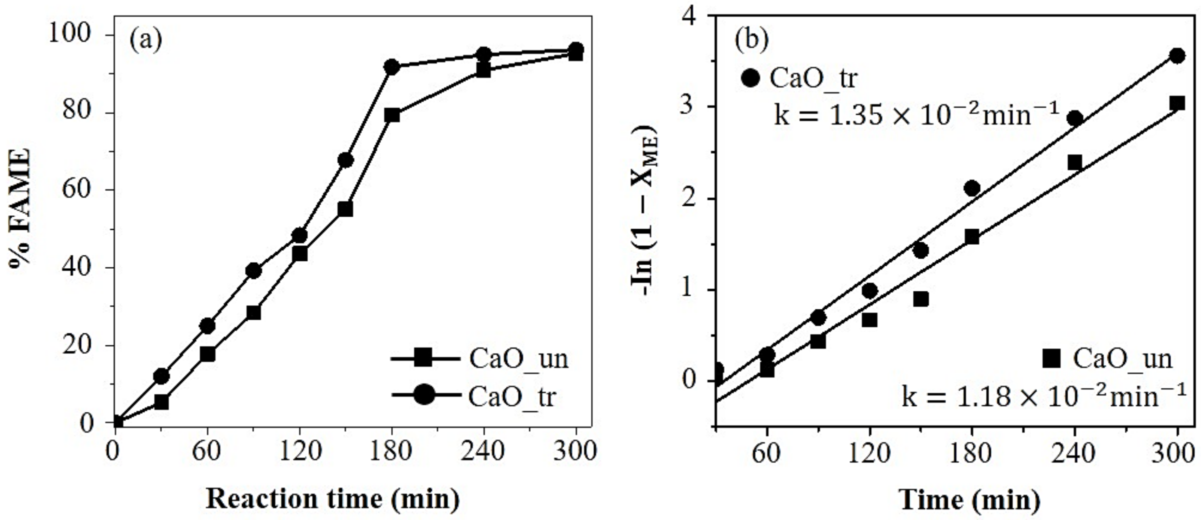

Figure 8 (a) comparison of catalytic performance between CaO_un and CaO_tr, and (b) the reaction kinetics study by plot $-\ln [1-X_{ME}]$ against t (time) and the slope was equal to rate constant (*k*) (transesterification conditions: catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, and reaction temperature of 65 °C)

3.3 The study of the decreasing in reaction time by added the co-solvent

Several reports indicated that adding a small amount of the co-solvent such as THF and acetone could improve biodiesel production by decreasing the reaction time and increasing the rate of a transesterification reaction [29-31]. The effect of co-solvent on the biodiesel production process could describe by the dissolution between triglyceride (oil) as a hydrophobic against hydrophilic methanol during the reaction mixture process which co-solvent would be as a binder [32-34].

As shown in Table 2 without a co-solvent system, the biodiesel production process gave the FAME yield which tended to be relatively low in every catalyst especially CaO_un (yield of FAME as only 78.2% at the reaction time of 180 min). While using THF and acetone as a co–solvent by adding a small amount of co-solvent (5% v/v) into methanol, the data represented not only yield of FAME has increased but the reaction time is also shorter. Focus on the use of THF as a co-solvent system, the reaction completed at around 150 min by the FAME yield higher than 93% which catalyzed with every CaO catalyst. Furthermore, the comparison of the type of co-solvent between THF and acetone revealed that the reaction trend using THF was higher than that of acetone consistent with the report of Rochat et al. [3], Tu et al. [35], and Ambat et al. [36]. Moreover, Trisupakitti et al. [37] reported that calcium oxide catalysts generated from golden apple cherry snail shells (*Pomacea canaliculata*) could provide biodiesel up to 95.2% under the optimum conditions of 0.8 wt.% catalyst loading amount, 12:1 methanol to oil molar ratio, 65 °C, and used the reaction time up to 6 h. Thus, adding a small amount of THF as a co-solvent into the biodiesel production process could improve biodiesel yield under the shorter reaction time which meant a reduction in overall production costs and was a green production process.

Transesterification conditions: catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 °C and 5% v/v of the co-solvent relative to amount of methanol. It should be noted that all of the data in this study were averages from at least three measurements with a deviation within 3%.

Table 2 The results study the effect of co-solvent on the decrease in reaction time for biodiesel production from palm oil.

Type of catalysts	Non co-solvent				THF as a co-solvent				Acetone as a co-solvent			
	%FAME at the reaction time (min)				%FAME at the reaction time (min)				%FAME at the reaction time (min)			
	90	120	150	180	90	120	150	180	90	120	150	180
CaO_un	33.8	47.3	63.0	78.2	67.9	80.1	93.2	95.7	60.9	77.6	90.7	93.8
CaO_tr	50.9	66.5	80.2	94.4	75.2	86.5	97.5	97.6	71.2	84.1	94.9	96.8
CaO[a]	43.1	55.7	72.4	83.7	73.1	84.3	95.2	96.8	69.8	83.6	91.5	96.8
CaO[b]	44.4	59.5	72.1	89.6	77.7	85.8	98.0	97.8	70.7	84.0	93.4	97.0

[a] CaO derived from egg shell (calcined at 800 °C for 3 h)

[b] CaO commercial grade

3.4 Fuel properties of biodiesel product synthesized by using CaO_tr catalyst.

The fuel properties of the final biodiesel product derived from palm oil and WCO catalyzed by CaO_tr were evaluated following the EN-14214 and ASTM-D6751 standard test method especially the major properties of biodiesel product for diesel engine namely methyl ester content, kinematic viscosity, density, acid number, copper strip corrosion, oxidation stability, carbon residue, sulfated ash, total contamination, cloud point, and pour point. The results in Table 3 presented the fatty acid methyl ester composition and methyl ester content of biodiesel product analyzed by gas chromatography (GC) technique and the percentage conversion of oil to biodiesel (biodiesel yield) both the use of palm oil and WOC as a raw material. The major fatty acid methyl ester composition of palm oil biodiesel was methyl oleate ($C_{18:1}$), methyl palmitate ($C_{16:0}$), and methyl linoleate ($C_{18:2}$), respectively. WCO biodiesel had the major fatty acid methyl ester composition including methyl oleate ($C_{18:1}$), methyl palmitate ($C_{16:0}$), methyl linoleate ($C_{18:2}$), and methyl palmitoleate ($C_{16:1}$), respectively, because this oil was processed via frying and may be resulted to contamination from the food especially the animal fats.

The percentage of methyl ester content (%FAME) was calculated following the equation from EN-14214 standard test method which used the relation between total peak areas of the methyl ester versus the peak area of methyl heptadecanoate ($C_{17:0}$) as an internal standard. In this case, %FAME of palm oil biodiesel and WCO biodiesel were higher than that of the criterion value definition of standard biodiesel fuel (>96.5%). Additionally, the yield of biodiesel product calculated by the ratio volume of biodiesel product against the volume of the oil (palm oil and WCO) as a raw material indicated that the use of palm oil as a starting material had a high percentage of yield product than the use of WCO. This phenomenon could be discussed that the WCO was contaminated of impurity such as moisture, free fatty acid, and food waste. These impurities directly affected the transesterification reaction because this reaction process could cause a competitive reaction namely a saponification reaction to generate the soap as a by-product. Similar research reports were found by Roschat et al. [2], Changmai et al. [12], and Luu et al. [33].

Table 3 The percentage of FAME composition of biodiesel product obtained from palm oil and WCO catalyzed by CaO_tr and evaluated by gas chromatography (GC) following the EN-14214 standard test method.

Peak	FAME Compound name	Composition (wt. %)[a]	
		Palm oil biodiesel	WCO biodiesel
1	Methyl laurate ($C_{12:0}$)	0.35	0.30
2	Methyl myristate ($C_{14:0}$)	0.80	0.70
3	Methyl palmitate ($C_{16:0}$)	35.50	29.35
4	Methyl palmitoleate ($C_{16:1}$)	1.50	11.60
5	Methyl stearate ($C_{18:0}$)	2.60	2.30
6	Methyl oleate ($C_{18:1}$)	46.10	36.50
7	Methyl linoleate ($C_{18:2}$)	11.00	16.55
8	Methyl linolenate ($C_{18:3}$)	1.15	1.00
9	Methyl arachidate ($C_{20:0}$)	0.50	1.20
10	Methyl eicosenoate ($C_{21:1}$)	0.50	0.50
Total peak areas of the methyl ester ($\sum A$)		36,570	35,920
Peak area of methyl heptadecanoate ($C_{17:0}$) as an internal standard (AIS)		15,770	15,650
$\%\text{FAME} = \frac{(\sum A) - (\text{AIS})}{\text{AIS}} \times \frac{\text{CIS} \times \text{VIS}}{\text{m}} \times 100$		97.69 (m = 1.35 mg)	96.66 (m = 1.34 mg)
where CIS = concentration of the methyl heptadecanoate solution (1 mg/mL) VIS = volume of the methyl heptadecanoate solution (1 mL) m = mass of the biodiesel sample (mg)			
$\text{Biodiesel yield} = \frac{\text{volume of biodiesel}}{\text{volume of oil}} \times 100$		87.5 (%v/v)	85.3 (%v/v)

[a] Transesterification conditions: catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 °C, 5% v/v of THF as a co–solvent relative to amount of methanol and reaction time of 150 min.

The fuel properties of the final biodiesel product obtained from palm oil and WCO and catalyzed by CaO_tr were evaluated at the National Metal and Materials Technology Center (MTEC)-Thailand, using the EN-14214 and ASTM-D6751 standard testing method as shown in Table 4. All of the results indicated that both palm oil and WCO biodiesel product have high-quality fuel properties, met the specified standards and, they were suitable to use any diesel-engine especially a diesel engine for agriculture such as walk-behind tractor and tractor. Therefore, all of these studies could be concluded that CaO_tr derived from golden apple snail shells has a high potential for applications as a green, low–cost, and renewable catalyst for biodiesel production in the community scale and industrial scale to self-reliance on renewable energy.

Table 4 Fuel properties of biodiesel product (FAME) derived from the different raw material and catalyzed by CaO_tr catalyst.

Fuel properties	Standard biodiesel	Palm oil biodiesel[c]	WCO biodiesel[c]
Methyl ester content (%)[a]	> 96.5	97.69	96.66
Kinematic viscosity @40°C (cSt)[a]	3.5-5.0	4.22	4.31
Density at 15 °C (kg/m^3)[a,b]	860-900	880	883
Acid number (mg KOH/g oil)[a,b]	< 0.5	0.28	0.33
Copper strip corrosion[a,b]	No. 1	No. 1	No. 1
Oxidation Stability (h)[a]	> 6	> 12	>12
Carbon residue (%w/w of oil)[a]	≤ 0.05	0.034	0.042
Sulfated ash (%w/w of oil)[a,b]	≤ 0.02	0.012	0.016
Total contamination (ppm)[a]	< 24	18.0	18.2
Flash point (°C)[a]	> 120	188	191
Cloud point (°C)[b]	report	<6	<6
Pour point (°C)[b]	report	<–5	<–5

[a] European standard (EN-14214) test method

[b] American Society for Testing and Material (ASTM-D6751) standard test method

[c] Transesterification conditions: catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 °C, 5% v/v of THF as a co-solvent relative to amount of methanol and reaction time of 150 min.

4. Conclusion

Transesterification of refined palm olein oil and WCO to biodiesel product catalyzed by CaO derived from the acid treated golden apple snail shells (*Pomacea canaliculata*) were studied. All of the characterization (TGA, XRD, SEM, and EDX) results indicated that acid-treated golden apple snail shells before the calcination process at 800 °C for 3 h was a sufficient technique to improve the purity of the obtained CaO catalyst achieved to 100% while CaO derived from un-treated golden apple snail shells has lower purity of about 95.05%. In addition, physicochemical properties namely BET specific surface area, CO_2-TPD (total basic site) and the catalytic activity of CaO_tr showed higher than CaO_un. According to the study of reaction kinetics for biodiesel production catalyzed by CaO_tr was higher than the reaction catalyzed by CaO_un which reaction time completed at 3 h and 5 h, respectively. Moreover, to apply the co-solvent method by adding a small amount of THF and acetone in the reaction mixture could increase the rate of reaction and reduce the reaction time. Additionally, the final palm oil biodiesel and WCO biodiesel product obtained from the reaction the synthesis catalyzed by CaO_tr have high qualities following standard biodiesel fuel both ASTM and EN testing methods and could be used with a diesel engine for agriculture as well. Therefore, the acid−treated golden apple snail shells before the hydrothermal process not only directly enhanced the purity, physicochemical properties, and catalytic performance of the obtained CaO catalyst but also improved the catalytic activity for the transesterification reaction of palm olein oil and WCO to be the biodiesel product. Consequently, all of the data in this research work is one of the possible ways to develop and improve the catalytic activity of economic CaO catalyst which synthesized from natural shells as a raw material for the green biodiesel production process both on the local community and industrial scale.

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